A Modern Course in Transport Phenomena
Solutions to Exercises

David Christopher Venerus and Hans Christian Öttinger

Solutions to exercises

Exercise 1.1

The standard barrel of crude oil is 42 US gallons, that is, $42 \times 3.785\,\text{litres} = 0.159\,\text{m}^3$. The $100\,000\,\text{m}^3$ of crude oil pumped through the Trans-Alaska Pipeline per day given in Section 1.1 hence correspond to 630 000 barrels. With a current price of some 50 US dollars per barrel (mid 2016), the value of the crude oil transported through the Trans-Alaska Pipeline in a day is given by the impressive number of 31 000 000 US dollars.

Exercise 2.1

Straightforward differentiations of the probability density $p_{\alpha_t \Theta_t}(x)$ defined in (2.16) give the following results:

$$\frac{\partial}{\partial t} p_{\alpha_t \Theta_t}(x) = \left[\frac{\dot{\Theta}_t}{2\Theta_t^2}(x-\alpha_t)^2 + \frac{\dot{\alpha}_t}{\Theta_t}(x-\alpha_t) - \frac{\dot{\Theta}_t}{2\Theta_t} \right] p_{\alpha_t \Theta_t}(x) \,,$$

$$-\frac{\partial}{\partial x}[A_0(t) + A_1(t)x] p_{\alpha_t \Theta_t}(x) = \\ \left[\frac{A_1(t)}{\Theta_t}(x-\alpha_t)^2 + \frac{A_1(t)\alpha_t + A_0(t)}{\Theta_t}(x-\alpha_t) - A_1(t) \right] p_{\alpha_t \Theta_t}(x) \,,$$

and

$$\frac{1}{2}\frac{\partial^2}{\partial x^2} D_0(t) p_{\alpha_t \Theta_t}(x) = \frac{D_0(t)}{2\Theta_t^2} \left[(x-\alpha_t)^2 - \Theta_t \right] p_{\alpha_t \Theta_t}(x) \,.$$

By comparing the prefactors of $(x-\alpha_t)^2$, $x-\alpha_t$, and 1, we recover the evolution equations (2.9) and (2.10).

Exercise 2.2
According to the superposition principle, we have

$$p(t,x) = \int_{-1/2}^{1/2} p_{y\,t}(x)dy = \int_{-1/2}^{1/2} p_{0\,t}(x-y)dy = \int_{(x-1/2)/\sqrt{2t}}^{(x+1/2)/\sqrt{2t}} p_{0\,1/2}(z)dz$$
$$= \frac{1}{2}\left[\mathrm{erf}\left(\frac{x+1/2}{\sqrt{2t}}\right) - \mathrm{erf}\left(\frac{x-1/2}{\sqrt{2t}}\right)\right].$$

Exercise 2.3
In Mathematica:

```
convol[x_,sig_]=
  Integrate[(1-t)*PDF[NormalDistribution[t,sig],x],{t,0,1}]+
  Integrate[(1+t)*PDF[NormalDistribution[t,sig],x],{t,-1,0}]
Plot[{Piecewise[{{1+x,-1<x<=0},{1-x,0<x<1}},0],
  convol[x,Sqrt[.03]],convol[x,Sqrt[.3]]},{x,-2,2},
  PlotRange->{0,1},AxesLabel->{Text[Style[x,FontSize->20]],
  Text[Style[p[t,x],FontSize->20]]}]
```

Notice that Mathematica® actually gives an analytical result for the integral implied by the superposition principle in terms of error functions. The resulting curves are shown in Figure C.9.

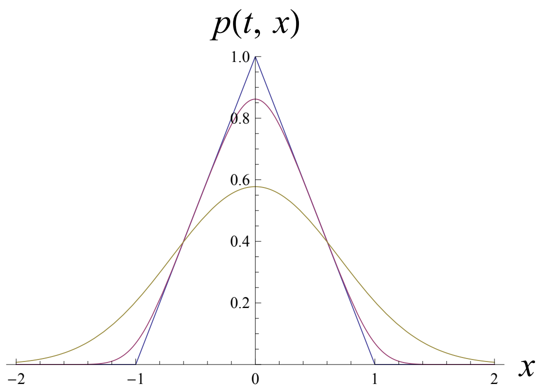

Figure C.9 Mathematica® output for the diffusion problem of Exercise 2.3.

Exercise 2.4

$$\frac{d}{dt}\left[-\int p\ln(p/p_{\mathrm{eq}})\,dx\right] = -\int\left[\frac{\partial p}{\partial t}\ln(p/p_{\mathrm{eq}}) + \frac{\partial p}{\partial t}\right]dx$$

$$= \int \ln(p/p_{\rm eq}) \, \frac{\partial J}{\partial x} \, dx = -\int J \, \frac{\partial}{\partial x} \ln(p/p_{\rm eq}) \, dx \, ,$$

where the normalization of p and the diffusion equation have been used. By inserting the expression for J given in (2.25) we obtain the desired result.

Exercise 2.5

The eigenvalue problem for pure diffusion with $D = 1$ is given by

$$-\lambda p(x) = \frac{1}{2} \frac{d^2 p(x)}{dx^2} \, ,$$

which has the solutions

$$p(x) = C_1 \sin(\sqrt{2\lambda}\, x + C_2) \, .$$

The boundary condition $p(0) = 0$ suggest $C_2 = 0$ and the boundary condition $p(1) = 0$ then selects discrete values of λ,

$$\sqrt{2\lambda_n} = n\pi \, , \qquad \lambda_n = \frac{n^2 \pi^2}{2} \, .$$

We can now write the solution as the Fourier series

$$p(t, x) = \sum_{n=1}^{\infty} c_n \sin(n\pi x) \, e^{-\lambda_n t} \, ,$$

where the coefficients c_n are determined by the initial condition at $t = 0$. By multiplying with $\sin(m\pi x)$ and integrating, we find

$$\int_0^1 \sin(m\pi x) \, dx = \sum_{n=1}^{\infty} c_n \int_0^1 \sin(m\pi x) \, \sin(n\pi x) \, dx \, ,$$

leading to the explicit expressions

$$\frac{1}{m\pi} [1 - (-1)^m] = \frac{c_m}{2} \, .$$

Note that all the coefficients c_n with even n vanish. The fraction of the substance released as a function of time is given by

$$1 - \int_0^1 p(t, x) \, dx = 1 - \sum_{n = \rm odd} \frac{8}{n^2 \pi^2} \, e^{-\lambda_n t} \, .$$

Exercise 2.6

According to the respective definitions, we have

$$\mathcal{T}\!- \exp\{\boldsymbol{M}(t_1) + \boldsymbol{M}(t_2)\} = \boldsymbol{1} + \boldsymbol{M}(t_1) + \boldsymbol{M}(t_2)$$

$$+\frac{1}{2}\,[\boldsymbol{M}(t_1)^2 + \boldsymbol{M}(t_2)^2] + \boldsymbol{M}(t_2)\cdot\boldsymbol{M}(t_1)$$
$$+\frac{1}{6}\,[\boldsymbol{M}(t_1)^3 + \boldsymbol{M}(t_2)^3] + \frac{1}{2}\,[\boldsymbol{M}(t_2)\cdot\boldsymbol{M}(t_1)^2 + \boldsymbol{M}(t_2)^2\cdot\boldsymbol{M}(t_1)] + \ldots\,,$$

and

$$\exp\{\boldsymbol{M}(t_1)+\boldsymbol{M}(t_2)\} = \mathbf{1} + \boldsymbol{M}(t_1) + \boldsymbol{M}(t_2) + \frac{1}{2}\,[\boldsymbol{M}(t_1)+\boldsymbol{M}(t_2)]^2 + \frac{1}{6}\,[\boldsymbol{M}(t_1)+\boldsymbol{M}(t_2)]^3 + \ldots\,.$$

In terms of the commutator $\boldsymbol{C} = \boldsymbol{M}(t_2)\cdot\boldsymbol{M}(t_1) - \boldsymbol{M}(t_1)\cdot\boldsymbol{M}(t_2)$, the difference can be written as

$$\mathcal{T}\!-\exp\{\boldsymbol{M}(t_1)+\boldsymbol{M}(t_2)\} - \exp\{\boldsymbol{M}(t_1)+\boldsymbol{M}(t_2)\} = \frac{1}{2}\,\boldsymbol{C}$$
$$+\,\frac{1}{6}\,[\boldsymbol{C}\cdot\boldsymbol{M}(t_1) + \boldsymbol{M}(t_2)\cdot\boldsymbol{C} + \boldsymbol{M}(t_2)\cdot\boldsymbol{M}(t_1)^2 - \boldsymbol{M}(t_1)^2\cdot\boldsymbol{M}(t_2)$$
$$+\,\boldsymbol{M}(t_2)^2\cdot\boldsymbol{M}(t_1) - \boldsymbol{M}(t_1)\cdot\boldsymbol{M}(t_2)^2] + \ldots\,.$$

Exercise 2.7

Straightforward differentiations of the probability density $p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x})$ defined in (2.39) give the following results:

$$\frac{\partial}{\partial t}p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x}) = \bigg[\frac{1}{2}(\boldsymbol{x}-\boldsymbol{\alpha}_t)\cdot\boldsymbol{\Theta}_t^{-1}\cdot\dot{\boldsymbol{\Theta}}_t\cdot\boldsymbol{\Theta}_t^{-1}\cdot(\boldsymbol{x}-\boldsymbol{\alpha}_t) + (\boldsymbol{x}-\boldsymbol{\alpha}_t)\cdot\boldsymbol{\Theta}_t^{-1}\cdot\dot{\boldsymbol{\alpha}}_t - \frac{1}{2}\,\mathrm{tr}\left(\dot{\boldsymbol{\Theta}}_t\cdot\boldsymbol{\Theta}_t^{-1}\right)\bigg]p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x})\,,$$

$$-\frac{\partial}{\partial\boldsymbol{x}}\cdot[\boldsymbol{A}_0(t)+\boldsymbol{A}_1(t)\cdot\boldsymbol{x}]\,p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x}) = \bigg[\frac{1}{2}(\boldsymbol{x}-\boldsymbol{\alpha}_t)\cdot(\boldsymbol{\Theta}_t^{-1}\boldsymbol{A}_1(t) + \boldsymbol{A}_1^T(t)\cdot\boldsymbol{\Theta}_t^{-1})\cdot(\boldsymbol{x}-\boldsymbol{\alpha}_t) + (\boldsymbol{x}-\boldsymbol{\alpha}_t)\cdot\boldsymbol{\Theta}_t^{-1}\cdot(\boldsymbol{A}_0(t)+\boldsymbol{A}_1(t)\cdot\boldsymbol{\alpha}_t) - \mathrm{tr}\boldsymbol{A}_1(t)\bigg]p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x})\,,$$

and

$$\frac{1}{2}\frac{\partial}{\partial\boldsymbol{x}}\frac{\partial}{\partial\boldsymbol{x}}:\boldsymbol{D}_0(t)\,p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x}) = \frac{1}{2}\Big[(\boldsymbol{x}-\boldsymbol{\alpha}_t)\cdot\boldsymbol{\Theta}_t^{-1}\cdot\boldsymbol{D}_0(t)\cdot\boldsymbol{\Theta}_t^{-1}\cdot(\boldsymbol{x}-\boldsymbol{\alpha}_t) - \mathrm{tr}\left(\boldsymbol{D}_0(t)\cdot\boldsymbol{\Theta}_t^{-1}\right)\Big]p_{\boldsymbol{\alpha}_t\boldsymbol{\Theta}_t}(\boldsymbol{x})\,.$$

By comparing prefactors, we obtain the following evolution equations:

$$\dot{\boldsymbol{\alpha}}_t = \boldsymbol{A}_1(t)\cdot\boldsymbol{\alpha}_t + \boldsymbol{A}_0(t)\,,$$

and

$$\dot{\boldsymbol{\Theta}}_t = \boldsymbol{A}_1(t) \cdot \boldsymbol{\Theta}_t + \boldsymbol{\Theta}_t \cdot \boldsymbol{A}_1^T(t) + \boldsymbol{D}_0(t) \,.$$

Exercise 2.8
In Mathematica®:

```
Theta={{0.4,0.3},{0.3,0.6}}
invT=Inverse[Theta]
f[x1_,x2_]:=Exp[-1/2 {x1,x2}.invT.{x1,x2}]/Sqrt[(2 Pi)^2 Det[Theta]]
Plot3D[f[x1,x2],{x1,-2,2},{x2,-2,2}]
```

The output is shown in Figure C.10.

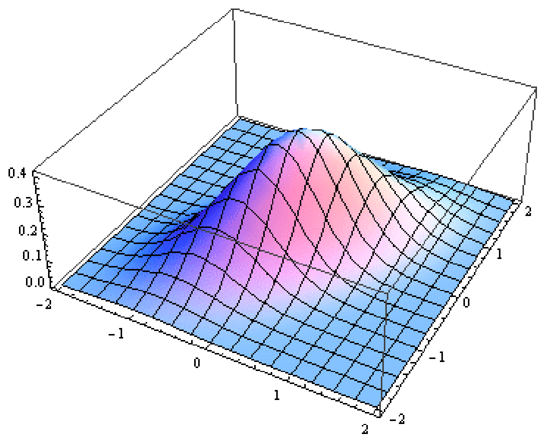

Figure C.10 Mathematica® output for the two-dimensional Gaussian of Exercise 2.8.

Exercise 2.9
The covariance matrix $\boldsymbol{\Theta}$ is symmetric and can hence be diagonalized. By a linear transformation to suitable coordinates, $\boldsymbol{\Theta}$ can hence be assumed to be diagonal. For diagonal $\boldsymbol{\Theta}$, the probability density in (2.39) indeed is the product of d one-dimensional Gaussians.

Exercise 3.1
To switch from a rectangular to a triangular initial distribution, we only need to change the stochastic initial condition. The curve for $t = 0.03$ is produced by the following MATLAB® code:

```
% Simulation parameters
```

```
NTRA=1000;NTIME=3;NHIST=100;DT=0.01;
XMIN=-1.;DX=0.05;XMAX=1.;
edges=XMIN:DX:XMAX;
centers=XMIN+DX/2:DX:XMAX-DX/2;

for K=1:NHIST
   % Generation of NTRA trajectories x
   y=random('Uniform',-1,1,[1,NTRA]); x=sign(y).*(1-sqrt(abs(y)));
   for J=1:NTIME
      x=x+random('Normal',0,sqrt(DT),[1,NTRA]);
   end
   % Collection of NHIST histograms in matrix p
   p(K,:)=histc(x,edges)/(DX*NTRA);
end

% Plot of simulation results
errorbar([centers NaN],mean(p),std(p)/sqrt(NHIST),'LineStyle','none')
```

Exercise 3.2
By integrating (3.19) over x, we obtain

$$1 - \int_0^\infty p_\mathrm{f}(t,x)\,dx = \int_0^\infty \int_0^t \frac{a(t')}{\sqrt{2\pi(t-t')}}\,\exp\left\{-\frac{1}{2}\frac{(x+t-t')^2}{t-t'}\right\} dt'dx\,.$$

For the time derivative of the left-hand side of this equation, we obtain by means of the diffusion equation

$$-\frac{d}{dt}\int_0^\infty p_\mathrm{f}(t,x) = \frac{1}{2}\frac{\partial p_\mathrm{f}(t,x)}{\partial x}\bigg|_{x=0} + p_\mathrm{f}(t,0)\,.$$

The contribution to the time derivative of the right-hand side of the above equation resulting from the upper limit of the time integration is

$$a(t)\,\lim_{\epsilon\to 0}\frac{1}{\sqrt{2\pi\epsilon}}\int_0^\infty \exp\left\{-\frac{1}{2}\frac{(x+\epsilon)^2}{\epsilon}\right\} dx = \frac{1}{2}\,a(t)\,,$$

where we can neglect the mean value $-\epsilon$ compared to the width $\sqrt{\epsilon}$ of the Gaussian distribution. For the time derivative of the Gaussian under the integral in the above equation, we can again use the diffusion equation to obtain

$$\int_0^\infty \int_0^t \frac{a(t')}{\sqrt{2\pi(t-t')}}\left(\frac{\partial}{\partial x}+\frac{1}{2}\frac{\partial^2}{\partial x^2}\right)\exp\left\{-\frac{1}{2}\frac{(x+t-t')^2}{t-t'}\right\} dt'dx = \\ -\frac{1}{2}\int_0^t \frac{a(t')}{\sqrt{2\pi(t-t')}}\,e^{-(t-t')/2}\,dt'\,.$$

By equating the time derivatives of the left- and right-hand sides, we arrive at the desired result (3.20).

Exercise 3.3

Mathematica® code for the inverse Laplace transform using the Zakian method, adapted from the implementation `Zakian.nb` by Housam Binous in the Wolfram Library Archive (`library.wolfram.com`):

```
alph={12.83767675+I 1.666063445,
   12.22613209+I 5.012718792,
   10.9343031+I 8.40967312,
   8.77643472+I 11.9218539,
   5.22545336+I 15.7295290};
K={-36902.0821+I 196990.426,
   61277.0252-I 95408.6255,
   -28916.5629+I 18169.1853,
   4655.36114-I 1.90152864,
   -118.741401-I 141.303691};
abar[s_]=Exp[1-Sqrt[1+2s]]*(Sqrt[1+2s]+1)/(Sqrt[1+2s]-1);
a[t_]=2/t Sum[Re[K[[i]]abar[alph[[i]]/t]],{i,5}];
Plot[a[t],{t,0,5},PlotRange->{0,2.5}]
```

Mathematica® code for the evaluation of (3.19):

```
p[t_,x_]:=(1/Sqrt[2Pi t]) Exp[-0.5(x-1+t)^2/t]+
   NIntegrate[(a[tp]/Sqrt[2Pi(t-tp)]) Exp[-0.5(x+t-tp)^2/(t-tp)],{tp,0,t}]
Plot[p[0.3,x],{x,0,2}]
```

Exercise 4.1

From (4.15) and (4.21) we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{3N\tilde{R}}{2U}$$

which gives (4.22a). Similarly, from (4.16) and (4.21) we have

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{N\tilde{R}}{V}$$

which gives (4.22b). Finally, from (4.17) and (4.21) we have for a single-component fluid

$$-\frac{\tilde{\mu}}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V} = \tilde{s}_0 + \tilde{R}\ln\left[\left(\frac{U}{N\tilde{u}_0}\right)^{3/2}\left(\frac{V}{N\tilde{v}_0}\right)\right] - \frac{5}{2}\tilde{R}$$

Rearranging and using previous results, we can write

$$\tilde{\mu} = -T\tilde{s}_0 - \tilde{R}T\ln\left[\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{\tilde{R}T}{p\tilde{v}_0}\right)\right] + \frac{5}{2}\tilde{R}T$$

where we have used $\tilde{u}_0 = \frac{3}{2}\tilde{R}T_0$. Collecting all terms depending on T in $\tilde{\mu}^0(T)$ leads to (4.22c).

Exercise 4.2
We first invert (4.21) to obtain

$$U(S,V,N) = N\tilde{u}_0 \Big(\frac{V}{N\tilde{v}_0}\Big)^{-2/3} \exp\Big\{\frac{2}{3}\frac{S-N\tilde{s}_0}{N\tilde{R}}\Big\}$$

as a starting point for our Legendre transformation. By differentiation with respect to S we obtain

$$T(S,V,N) = \frac{2\tilde{u}_0}{3\tilde{R}} \Big(\frac{V}{N\tilde{v}_0}\Big)^{-2/3} \exp\Big\{\frac{2}{3}\frac{S-N\tilde{s}_0}{N\tilde{R}}\Big\} ,$$

and by inversion

$$S(T,V,N) = N\tilde{s}_0 + N\tilde{R} \ln\Big[\frac{V}{N\tilde{v}_0}\Big(\frac{3\tilde{R}T}{2\tilde{u}_0}\Big)^{3/2}\Big] .$$

Now, from (4.24) the Helmholtz free energy is then given by $F(T,V,N) = U(S(T,V,N),V,N) - TS(T,V,N)$,

$$\begin{aligned} F(T,V,N) &= \frac{3}{2}N\tilde{R}T - N\tilde{s}_0 T - N\tilde{R}T \ln\Big[\frac{V}{N\tilde{v}_0}\Big(\frac{3\tilde{R}T}{2\tilde{u}_0}\Big)^{3/2}\Big] \\ &= -N\tilde{R}T \ln\Big[\frac{V}{N\tilde{v}_0}\Big(\frac{3\tilde{R}T}{2\tilde{u}_0 e}\Big)^{3/2} \exp\Big\{\frac{\tilde{s}_0}{\tilde{R}}\Big\}\Big] . \end{aligned}$$

This expression can be simplified considerably by introducing a new constant c in terms of all the other constants,

$$c = \frac{1}{\tilde{v}_0}\Big(\frac{3\tilde{R}}{2\tilde{u}_0 e}\Big)^{3/2} \exp\Big\{\frac{\tilde{s}_0}{\tilde{R}}\Big\} .$$

Exercise 4.3
By integrating $p = N\tilde{R}T/V$ we find

$$F(T,V,N) = -N\tilde{R}T \ln\Big[\frac{V}{C(T,N)}\Big] ,$$

where $C(T,N)$ represents an additive integration constant. To obtain an extensive free energy, $C(T,N)$ must be of the form $C(T,N) = N\,\tilde{C}(T)$. Equation (4.25) then leads to the entropy

$$S(T,V,N) = N\tilde{R} \ln\left[\frac{V}{N\,\tilde{C}(T)}\right] - N\tilde{R}T \frac{1}{\tilde{C}(T)}\frac{d\tilde{C}(T)}{dT} .$$

For reproducing the ideal-gas entropy (see solution to Exercise 4.2) we need to choose

$$\frac{1}{\tilde{C}(T)} = c\,T^{3/2} ,$$

where c plays the role of a further integration constant. For a suitable matching of constants, the resulting Helmholtz free energy (4.39) coincides with the solution to Exercise 4.2.

Exercise 4.4

In terms of intensive quantities we can write (4.15) as $1/T = (\partial s/\partial u)_\rho$ and (4.17) as $-\hat{\mu}/T = (\partial s/\partial \rho)_u$. Applying these to (4.56) we obtain

$$\frac{1}{T} = \frac{3}{2}\frac{k_\mathrm{B}\rho}{mu}, \qquad -\frac{\hat{\mu}}{T} = \frac{s}{\rho} + \frac{k_\mathrm{B}}{m}\left[\frac{\partial \ln R_0(\rho)}{\partial \ln \rho} - \frac{5}{2}\right].$$

Combining these using the Euler equation (4.44) gives the following equations of state:

$$u = \frac{3}{2}\frac{\rho k_\mathrm{B} T}{m}, \qquad p = \frac{\rho k_\mathrm{B} T}{m}\left[1 - \frac{\partial \ln R_0(\rho)}{\partial \ln \rho}\right],$$

which match the equations of state for an ideal gas if $R_0(\rho)$ is constant.

Exercise 4.5

Using the Maxwell relation $(\partial \hat{s}/\partial \hat{v})_{T,w_\alpha} = (\partial p/\partial T)_{\hat{v},w_\alpha}$ and definition for specific heat capacity $\hat{c}_{\hat{v}} = T(\partial \hat{s}/\partial T)_{\hat{v},w_\alpha}$ in (4.49) gives

$$d\hat{u} = \hat{c}_{\hat{v}} dT + \left[T\left(\frac{\partial p}{\partial T}\right)_{\hat{v},w_1} - p\right] d\hat{v} + \left[T\left(\frac{\partial \hat{s}}{\partial w_1}\right)_{T,\hat{v}} + (\hat{\mu}_1 - \hat{\mu}_2)\right] dw_1.$$

Focusing on the last term in square brackets, we use (4.52) and write

$$T\left(\frac{\partial \hat{s}}{\partial w_1}\right)_{T,p} = T(\hat{s}_1 - \hat{s}_2) = \hat{u}_1 - \hat{u}_2 + p(\hat{v}_1 - \hat{v}_2) - (\hat{\mu}_1 - \hat{\mu}_2),$$

which can be arranged to give

$$T\left(\frac{\partial \hat{s}}{\partial w_1}\right)_{T,p} + (\hat{\mu}_1 - \hat{\mu}_2) = (\hat{h}_1 - \hat{h}_2).$$

Now, to change the independent variables in the derivative on the left-hand side, we write

$$\left(\frac{\partial \hat{s}}{\partial w_1}\right)_{T,p} = \left(\frac{\partial \hat{s}}{\partial w_1}\right)_{T,\hat{v}} + \left(\frac{\partial \hat{s}}{\partial \hat{v}}\right)_{T,w_1}\left(\frac{\partial \hat{v}}{\partial w_1}\right)_{T,p} = \left(\frac{\partial \hat{s}}{\partial w_1}\right)_{T,\hat{v}} + \left(\frac{\partial p}{\partial T}\right)_{\hat{v},w_1}(\hat{v}_1 - \hat{v}_2),$$

where have used the Maxwell relation and (4.52) to obtain the second equality. Combining the last two results, we obtain

$$T\left(\frac{\partial \hat{s}}{\partial w_1}\right)_{T,\hat{v}} + (\hat{\mu}_1 - \hat{\mu}_2) = (\hat{h}_1 - \hat{h}_2) + T\left(\frac{\partial p}{\partial T}\right)_{\hat{v},w_1}(\hat{v}_1 - \hat{v}_2).$$

Substitution in the expression above for $d\hat{u}$ gives the result in (4.53).

Now, substituting the total differential of $\hat{s}(T, p, w_1)$ in (4.45) gives

$$d\hat{u} = T\Big(\frac{\partial \hat{s}}{\partial T}\Big)_{p,w_1} dT - pd\hat{v} + T\Big(\frac{\partial \hat{s}}{\partial p}\Big)_T dp + \Big[T\Big(\frac{\partial \hat{s}}{\partial w_1}\Big)_{T,p} + (\hat{\mu}_1 - \hat{\mu}_2)\Big] dw_1.$$

Using $\hat{c}_p = T(\partial\hat{s}/\partial T)_{p,w_\alpha}$ for the specific heat capacity at constant pressure and composition and the Maxwell relation $(\partial\hat{s}/\partial p)_{T,w_\alpha} = (\partial\hat{v}/\partial T)_{p,w_\alpha}$ we obtain

$$d\hat{u} = \hat{c}_p dT - pd\hat{v} + T\Big(\frac{\partial \hat{v}}{\partial T}\Big)_p dp + \Big[T\Big(\frac{\partial \hat{s}}{\partial w_1}\Big)_{T,p} + (\hat{\mu}_1 - \hat{\mu}_2)\Big] dw_1.$$

Replacing the terms inside the square brackets with the result found previously gives the expression in (4.57)

Exercise 4.6
The total differential of the specific Gibbs free energy for a two-component system $\hat{g} = \hat{g}(T, p, w_1)$ can be written as

$$d\hat{g} = -\hat{s}dT + \hat{v}dp + (\hat{\mu}_1 - \hat{\mu}_2)dw_1,$$

where

$$\hat{s} = -\Big(\frac{\partial \hat{g}}{\partial T}\Big)_{p,w_1}, \quad \hat{v} = \Big(\frac{\partial \hat{g}}{\partial p}\Big)_{T,w_1}, \quad \hat{\mu}_1 - \hat{\mu}_2 = \Big(\frac{\partial \hat{g}}{\partial w_1}\Big)_{T,p}.$$

Setting $\hat{a} = \hat{g}$ in (4.52) and comparing with the third expression above, we have $\hat{g}_\alpha = \hat{\mu}_\alpha$. Now, from (4.51) we can write $\hat{g}_1 = \hat{\mu}_1 = \hat{u}_1 + p\hat{v}_1 - T\hat{s}_1$ so that the total differential of $\hat{\mu}_1 = \hat{\mu}_1(T, p, w_1)$ can be written as

$$d\hat{\mu}_1 = -\hat{s}_1 dT + \hat{v}_1 dp + \Big(\frac{\partial \hat{\mu}_1}{\partial w_1}\Big)_{T,p} dw_1.$$

where

$$\hat{s}_1 = -\left(\frac{\partial \hat{\mu}_1}{\partial T}\right)_{p,w_1}, \qquad \hat{v}_1 = \left(\frac{\partial \hat{\mu}_1}{\partial p}\right)_{T,w_1}.$$

Exercise 4.7
One way to define an ideal mixture (not necessarily comprised of ideal gas components) is by the fundamental equation for the molar Gibbs free energy

$$\tilde{g}(T, p, x_\alpha) = \sum_{\alpha=1}^{k} x_\alpha \tilde{g}_\alpha^0(T, p) + \tilde{R}T \sum_{\alpha=1}^{k} x_\alpha \ln x_\alpha.$$

Now, since $\tilde{g} = \tilde{u} + p\tilde{v} - T\tilde{s}$, we can write using (4.59) the following:

$$T\tilde{s} = -\sum_{\alpha=1}^{k} x_\alpha \tilde{g}_\alpha^0 - \tilde{R}T \sum_{\alpha=1}^{k} x_\alpha \ln x_\alpha + \sum_{\alpha=1}^{k} x_\alpha \tilde{u}_\alpha^0 + p \sum_{\alpha=1}^{k} x_\alpha \tilde{v}_\alpha^0$$

$$= -\sum_{\alpha=1}^{k} x_\alpha(\tilde{g}_\alpha^0 - \tilde{u}_\alpha^0 - p\tilde{v}_\alpha^0) - \tilde{R}T\sum_{\alpha=1}^{k} x_\alpha \ln x_\alpha$$

$$= T\sum_{\alpha=1}^{k} x_\alpha \tilde{s}_\alpha^0 - \tilde{R}T\sum_{\alpha=1}^{k} x_\alpha \ln x_\alpha,$$

which gives

$$\tilde{s}(T,p,x_\alpha) = \sum_{\alpha=1}^{k} x_\alpha \tilde{s}_\alpha^0(T,p) - \tilde{R}\sum_{\alpha=1}^{k} x_\alpha \ln x_\alpha,$$

where the second term is the entropy of mixing, which is always positive. Now, since $\tilde{g} = \tilde{\mu}$ and $\tilde{g}_\alpha = \tilde{\mu}_\alpha$, we write the fundamental equation for ideal mixtures as follows:

$$\sum_{\alpha=1}^{k} x_\alpha \tilde{\mu}_\alpha = \sum_{\alpha=1}^{k} x_\alpha \tilde{\mu}_\alpha^0 + \tilde{R}T\sum_{\alpha=1}^{k} x_\alpha \ln x_\alpha = \sum_{\alpha=1}^{k} x_\alpha(\tilde{\mu}_\alpha^0 + \tilde{R}T\ln x_\alpha),$$

which gives (4.60).

Exercise 4.8
Using (4.62), the chemical potential for a non-ideal gas (I) is

$$\tilde{\mu}_\alpha^{\mathrm{I}} = \tilde{\mu}_\alpha^{0,\mathrm{ig}}(T,p) + \tilde{R}T\ln(x_\alpha^{\mathrm{I}}\bar{\phi}_\alpha p^{\mathrm{I}}).$$

Using (4.63) for a liquid (II) that is a nonideal mixture, the chemical potential is

$$\tilde{\mu}_\alpha^{\mathrm{II}} = \tilde{\mu}_\alpha^{0,\mathrm{sl}}(T,p_\alpha^{\mathrm{sat}}) + \tilde{R}T\ln(x_\alpha^{\mathrm{II}}\bar{\gamma}_\alpha),$$

Now, for $\tilde{\mu}_\alpha^{0,\mathrm{sl}}(T,p_\alpha^{\mathrm{sat}})$, we can write

$$\tilde{\mu}_\alpha^{0,\mathrm{sl}}(T,p_\alpha^{\mathrm{sat}}) = \tilde{\mu}_\alpha^{0,\mathrm{ig}}(T,p) + \tilde{R}T\ln(\bar{\phi}_\alpha^0 p_\alpha^{\mathrm{sat}}),$$

so that

$$\tilde{\mu}_\alpha^{\mathrm{II}} = \tilde{\mu}_\alpha^{0,\mathrm{ig}}(T,p) + \tilde{R}T\ln(x_\alpha^{\mathrm{II}}\bar{\gamma}_\alpha\bar{\phi}_\alpha^0 p_\alpha^{\mathrm{sat}}).$$

For a system at equilibrium, setting $\tilde{\mu}_\alpha^{\mathrm{I}} = \tilde{\mu}_\alpha^{\mathrm{II}}$ gives (4.64).

Exercise 4.9
For the case of a gas dissolved at low concentration in a liquid (II), substitution of $\mathfrak{f}_\alpha = k_{\mathrm{H},\alpha}x_\alpha$ in (4.61) gives

$$\tilde{\mu}_\alpha^{\mathrm{II}} = \tilde{\mu}_\alpha^{0,\mathrm{ig}}(T,p) + \tilde{R}T\ln(k_{\mathrm{H},\alpha}x_\alpha^{\mathrm{II}}).$$

Using the expression for $\tilde{\mu}_\alpha^{\mathrm{I}}$ from Exercise 4.8 and setting $\tilde{\mu}_\alpha^{\mathrm{I}} = \tilde{\mu}_\alpha^{\mathrm{II}}$ gives (4.65).

Exercise 4.10
By combining (4.60) and (4.70), we obtain

$$\sum_{\alpha=1}^{k} \tilde{\nu}_\alpha \ln x_\alpha = -\frac{1}{RT} \sum_{\alpha=1}^{k} \tilde{\nu}_\alpha \tilde{\mu}_\alpha^0(T,p),$$

from which we obtain (4.72) by exponentiation. By differentiation we get

$$\tilde{R}T^2 \frac{d}{dT} \ln K(T) = \sum_{\alpha=1}^{k} \tilde{\nu}_\alpha \left[\tilde{\mu}_\alpha^0(T,p) - T\frac{\partial \tilde{\mu}_\alpha^0(T,p)}{\partial T} \right].$$

A Maxwell relation implied by (4.29), together with (see Exercise 4.7)

$$\tilde{s}(T,p,x_\alpha) = \sum_{\alpha=1}^{k} x_\alpha \tilde{s}_\alpha^0(T,p) - \tilde{R} \sum_{\alpha=1}^{k} x_\alpha \ln x_\alpha,$$

leads to

$$\frac{\partial \tilde{\mu}_\alpha^0}{\partial T} = -\frac{\partial S^0}{\partial N_\alpha} = -\tilde{s}_\alpha^0,$$

so that we obtain (4.73) with $\tilde{h}_\alpha^0 = \tilde{\mu}_\alpha^0 + T\tilde{s}_\alpha^0$.

Exercise 5.1
For (i): $\boldsymbol{\nabla} \cdot \boldsymbol{u} = u'$, $\int_V \boldsymbol{\nabla} \cdot \boldsymbol{u}\, dV = u' L^3$, and

$$\begin{aligned}\int_A \boldsymbol{n} \cdot \boldsymbol{u}\, dA &= \int_0^L dx_2 \int_0^L dx_3 \left[u_1(x_1 = L, x_2, x_3) - u_1(x_1 = 0, x_2, x_3) \right] \\ &= L^2 \left[u_0 + u'L - u_0 \right] = u' L^3.\end{aligned}$$

For (ii): $\boldsymbol{\nabla} \cdot \boldsymbol{u} = 3x_2^2 + x_1$ and

$$\begin{aligned}\int_V \boldsymbol{\nabla} \cdot \boldsymbol{u}\, dV &= \int_0^2 dx_3 \int_{-1}^1 dx_2 \int_{-1}^1 dx_1\, (3x_2^2 + x_1) \\ &= \int_0^2 dx_3 \int_{-1}^1 dx_2\; 6x_2^2 = 8.\end{aligned}$$

$$\begin{aligned}\int_A \boldsymbol{n} \cdot \boldsymbol{u}\, dA &= \int_0^2 dx_3 \int_{-1}^1 dx_2 \left[u_1(x_1 = 1, x_2, x_3) - u_1(x_1 = -1, x_2, x_3) \right] \\ &\quad + \int_0^2 dx_3 \int_{-1}^1 dx_1 \left[u_2(x_1, x_2 = 1, x_3) - u_2(x_1, x_2 = -1, x_3) \right] \\ &\quad + \int_{-1}^1 dx_2 \int_{-1}^1 dx_1 \left[u_3(x_1, x_2, x_3 = 2) - u_3(x_1, x_2, x_3 = 0) \right] \\ &= 2 \int_0^2 dx_3 \int_{-1}^1 dx_1 = 8.\end{aligned}$$

Exercise 5.2
For constant u:

$$\begin{aligned}\boldsymbol{\nabla}\cdot\boldsymbol{u} &= \left(\boldsymbol{\delta}_r\frac{\partial}{\partial r}+\frac{1}{r}\boldsymbol{\delta}_\phi\frac{\partial}{\partial\phi}+\frac{1}{r\sin\phi}\boldsymbol{\delta}_\theta\frac{\partial}{\partial\theta}\right)\cdot u\,\boldsymbol{\delta}_r\\ &= \left(\frac{2}{r}+\frac{\partial}{\partial r}\right)u=\frac{2u}{r}.\end{aligned}$$

$$\int_V \boldsymbol{\nabla}\cdot\boldsymbol{u}\,dV = 4\pi\int_0^R r^2dr\frac{2u}{r}=4\pi R^2u.$$

$$\int_A \boldsymbol{n}\cdot\boldsymbol{u}\,dA=\int_A dA\,\boldsymbol{\delta}_r\cdot\boldsymbol{u}=4\pi R^2u.$$

For $u(r)$:

$$\boldsymbol{\nabla}\cdot\boldsymbol{u}=\left(\frac{2}{r}+\frac{\partial}{\partial r}\right)u(r).$$

$$\begin{aligned}\int_V \boldsymbol{\nabla}\cdot\boldsymbol{u}\,dV &= 4\pi\int_0^R r^2dr\left(\frac{2u(r)}{r}+u'(r)\right)\\ &= 4\pi\int_0^R dr\frac{d}{dr}(r^2u(r))=4\pi R^2u(R).\end{aligned}$$

$$\int_A \boldsymbol{n}\cdot\boldsymbol{u}\,dA=\int_A dA\,\boldsymbol{\delta}_r\cdot\boldsymbol{u}=4\pi R^2u(R).$$

For $u(r)=Q/r^2$, $\boldsymbol{\nabla}\cdot\boldsymbol{u}=\frac{2u(r)}{r}+u'(r)=0$, which implies that from all spherical shells the contribution is zero. Nevertheless, $\int_A\boldsymbol{n}\cdot\boldsymbol{u}\,dA=4\pi R^2u(R)=4\pi Q$. The reason is the singularity at the origin.

Exercise 5.3
The unit vector $\boldsymbol{t}=\boldsymbol{v}/v$ is tangent to a streamline with position $\boldsymbol{r}(\zeta)$ so that $\boldsymbol{t}=d\boldsymbol{r}(\zeta)/d\zeta$. Hence, we can write $\boldsymbol{v}\times\boldsymbol{t}=\boldsymbol{0}$, or

$$\sum_{i,j=1}^{3}\varepsilon_{ijk}v_i\frac{\partial x_j}{\partial\zeta}=0.$$

For $\boldsymbol{v}=v_1(x_1,x_2)\boldsymbol{\delta}_1+v_2(x_1,x_2)\boldsymbol{\delta}_2$ the above can, using (5.9), be written as

$$\frac{\partial\psi}{\partial x_2}\frac{\partial x_2}{\partial\zeta}+\frac{\partial\psi}{\partial x_1}\frac{\partial x_1}{\partial\zeta}=0,$$

or $\frac{\partial\psi}{\partial\zeta}=0$, which means the stream function ψ is constant along a streamline. Now, for $x_1=c$, an arbitrary constant, we can write $d\psi(c,x_2)=\frac{\partial\psi}{\partial x_2}dx_2=$

$\rho v_1 dx_1$, which after integration gives:

$$\psi_2 - \psi_1 = \int_{\psi_1(c,x_2)}^{\psi_2(c,x_2)} \rho v_1 dx_2$$

where ψ_1, ψ_2 are values of the stream function on adjacent streamlines. Hence, the mass flow rate (per unit width) between any two streamlines is equal to the difference between the values of the two streamlines.

Exercise 5.4
Substitution of $c_\alpha = cx_\alpha$ for c_α in (5.21) gives

$$c\Big(\frac{\partial x_\alpha}{\partial t} + \boldsymbol{v}^* \cdot \boldsymbol{\nabla} x_\alpha\Big) + x_\alpha\Big[\frac{\partial c}{\partial t} + \boldsymbol{\nabla} \cdot (c\boldsymbol{v}^*)\Big] = -\boldsymbol{\nabla} \cdot \boldsymbol{J}_{\boldsymbol{\alpha}}^* + \tilde{\nu}_\alpha \tilde{\Gamma}$$

Using (5.22) to replace terms in the square bracket gives the result in (5.23).

Exercise 5.5
We begin with the difference in reference velocities, which can be written as

$$\boldsymbol{v} - \boldsymbol{v}^* = \sum_{\beta=1}^{k} x_\beta(\boldsymbol{v} - \boldsymbol{v}_\beta) = -\sum_{\beta=1}^{k} \frac{x_\beta}{\rho_\beta}\boldsymbol{j}_\beta = -\frac{1}{c}\sum_{\beta=1}^{k} \frac{\boldsymbol{j}_\beta}{\tilde{M}_\beta},$$

which is the result in (5.24). Note that (5.13) was used for the second equality, and the third equality follows from basic relations between concentration variables: $x_\beta = c_\beta/c = \rho_\beta/c\tilde{M}_\beta$. Next, we combine (5.13) and $\tilde{M}_\alpha$ times (5.20), which gives

$$\tilde{M}_\alpha \boldsymbol{J}_\alpha^* = \boldsymbol{j}_\alpha^* = \boldsymbol{j}_\alpha + \rho_\alpha(\boldsymbol{v} - \boldsymbol{v}^*) = \boldsymbol{j}_\alpha - \frac{\rho_\alpha}{c}\sum_{\beta=1}^{k} \frac{\boldsymbol{j}_\beta}{\tilde{M}_\beta},$$

where we have used (5.24) to get the result in (5.25). For the volume-average velocity, we have

$$\rho_\alpha \boldsymbol{v}_\alpha = \rho_\alpha \boldsymbol{v}^\dagger + \boldsymbol{j}_\alpha^\dagger.$$

Multiplication by $\hat{v}_\alpha$ and summing we obtain: $\sum_{\alpha=1}^{k} \hat{v}_\alpha \boldsymbol{j}_\alpha^\dagger = \boldsymbol{0}$. Since $\boldsymbol{v}^\dagger = \sum_{\alpha=1}^{k} \rho_\alpha \hat{v}_\alpha \boldsymbol{v}_\alpha$, the difference in reference velocities can be written as

$$\boldsymbol{v} - \boldsymbol{v}^\dagger = \sum_{\beta=1}^{k} \rho_\alpha \hat{v}_\alpha(\boldsymbol{v} - \boldsymbol{v}_\beta) = -\sum_{\beta=1}^{k} \hat{v}_\beta \boldsymbol{j}_\beta,$$

which is the result in (5.27). Now, using (5.13), we can write

$$\boldsymbol{j}_\alpha^\dagger = \boldsymbol{j}_\alpha - \rho_\alpha(\boldsymbol{v} - \boldsymbol{v}^\dagger),$$

which, when combined with (5.27) gives (5.28).

In the absence of chemical reaction ($\Gamma = 0$), we write (5.11) as follows

$$\frac{\partial \rho_\alpha}{\partial t} = -\boldsymbol{\nabla} \cdot (\boldsymbol{v}^\dagger \rho_\alpha + \boldsymbol{j}_\alpha^\dagger).$$

Multiplication by $\hat{v}_\alpha$ and summing, we have

$$\frac{\partial}{\partial t} \sum_{\alpha=1}^{k} (\hat{v}_\alpha \rho_\alpha) = -\boldsymbol{\nabla} \cdot \sum_{\alpha=1}^{k} (\hat{v}_\alpha \rho_\alpha) \boldsymbol{v}^\dagger - \boldsymbol{\nabla} \cdot \sum_{\alpha=1}^{k} (\hat{v}_\alpha \boldsymbol{j}_\alpha^\dagger),$$

where, since we are considering ideal mixtures, we have taken $\hat{v}_\alpha$ to be constant. Now, since $\sum_{\alpha=1}^{k} \rho_\alpha \hat{v}_\alpha = 1$ and $\sum_{\alpha=1}^{k} \hat{v}_\alpha \boldsymbol{j}_\alpha^\dagger = \mathbf{0}$, we obtain

$$\boldsymbol{\nabla} \cdot \boldsymbol{v}^\dagger = 0.$$

Exercise 5.6

Multiplying $dN_\alpha = \sum_{j=1}^{n} \tilde{\nu}_{\alpha,j} d\xi_j$ by $\tilde{M}_\alpha$, we obtain

$$d(N_\alpha \tilde{M}_\alpha) = \sum_{j=1}^{n} \tilde{M}_\alpha \tilde{\nu}_{\alpha,j} d\xi_j$$

Summing over α, the left-hand side vanishes so that we can write

$$\tilde{M}_{q,j} = \sum_{\alpha=q_j+1}^{k} \tilde{\nu}_{\alpha,j} \tilde{M}_\alpha = -\sum_{\alpha=1}^{q_j} \tilde{\nu}_{\alpha,j} \tilde{M}_\alpha.$$

Dividing the first equation by $V dt$ and using $\tilde{\nu}_{\alpha,j} = \nu_{\alpha,j}(\tilde{M}_{q_j}/\tilde{M}_\alpha)$ gives

$$\frac{d}{dt}\Big(\frac{N_\alpha \tilde{M}_\alpha}{V}\Big) = \sum_{j=1}^{n} \tilde{M}_\alpha \tilde{\nu}_{\alpha,j} \frac{1}{V} \frac{d\xi_j}{dt} = \sum_{j=1}^{n} \nu_{\alpha,j} \tilde{M}_{q,j} \frac{1}{V} \frac{d\xi_j}{dt} = \sum_{j=1}^{n} \nu_{\alpha,j} \Gamma_j,$$

where $\Gamma_j = \tilde{M}_{q,j}/V d\xi_j/dt$. Dividing (5.29) by $\tilde{M}_\alpha$ and using (5.20) we obtain

$$\frac{\partial c_\alpha}{\partial t} = -\boldsymbol{\nabla} \cdot (\boldsymbol{v}_\alpha c_\alpha) + \sum_{j=1}^{n} \frac{\tilde{\nu}_{\alpha,j}}{\tilde{M}_{q,j}} \Gamma_j = -\boldsymbol{\nabla} \cdot (\boldsymbol{v}^* c_\alpha + \boldsymbol{J}_\alpha^*) + \sum_{j=1}^{n} \tilde{\nu}_{\alpha,j} \tilde{\Gamma}_j,$$

where $\tilde{\Gamma}_j = \Gamma_j/\tilde{M}_{q,j}$. Summing over α we obtain

$$\frac{\partial c}{\partial t} = -\boldsymbol{\nabla} \cdot (\boldsymbol{v}^* c) + \sum_{\alpha=1}^{k} \sum_{j=1}^{n} \tilde{\nu}_{\alpha,j} \tilde{\Gamma}_j.$$

Now, setting $c_\alpha = cx_\alpha$, the last two results can be used to obtain

$$c\Big(\frac{\partial x_\alpha}{\partial t} + \boldsymbol{v}^* \cdot \boldsymbol{\nabla} x_\alpha\Big) = -\boldsymbol{\nabla} \cdot \boldsymbol{J}_\alpha^* + \sum_{j=1}^{n} \Big(\tilde{\nu}_{\alpha,j} - x_\alpha \sum_{\beta=1}^{k} \tilde{\nu}_{\beta,j}\Big)\tilde{\Gamma}_j.$$

Exercise 5.7

From the mass balance (5.5) we have with the assumption of constant ρ and velocity $\boldsymbol{v} = v\boldsymbol{\delta}_z$ the following:

$$\frac{dv}{dz} = 0,$$

which implies the velocity is constant along the length of the reactor. For steady state, the species mass balance (5.14), neglecting diffusive transport, simplifies to

$$0 = -v\frac{d\rho_\alpha}{dz} + \nu_\alpha \Gamma.$$

Dividing by $\tilde{M}_\alpha$ making the substitution $\tilde{\nu}_\alpha = \nu_\alpha \tilde{M}_q / \tilde{M}_\alpha$ gives

$$v\frac{dc_\alpha}{dz} = \tilde{\nu}_\alpha \tilde{\Gamma},$$

where $\tilde{\Gamma} = \Gamma/\tilde{M}_q$. Integration from the entrance with $c_\alpha(0)$, to the exit with $c_\alpha(L)$, of the reactor having length L, gives the desired result.

Exercise 5.8

To find the vector product of $\boldsymbol{r}$ with (5.32) we write

$$\boldsymbol{r} \times \frac{\partial \boldsymbol{m}}{\partial t} = -\boldsymbol{r} \times \boldsymbol{\nabla} \cdot (\boldsymbol{v}\boldsymbol{m}) - \boldsymbol{r} \times \boldsymbol{\nabla} \cdot \boldsymbol{\pi} + \boldsymbol{r} \times \rho \boldsymbol{g}.$$

The first term on the right-hand side can be written as

$$\begin{aligned}
\boldsymbol{r} \times \boldsymbol{\nabla} \cdot (\boldsymbol{v}\boldsymbol{m}) &= \sum_{i,j,k,p=1}^{3} x_p \boldsymbol{\delta}_p \times \boldsymbol{\delta}_i \frac{\partial}{\partial x_i} \cdot v_j \boldsymbol{\delta}_j m_k \boldsymbol{\delta}_k = \sum_{j,k,p=1}^{3} x_p \boldsymbol{\delta}_p \times \frac{\partial}{\partial x_j} v_j m_k \boldsymbol{\delta}_k \\
&= \sum_{j,k,p,m=1}^{3} \varepsilon_{pkm} x_p \frac{\partial}{\partial x_j} v_j m_k \boldsymbol{\delta}_m \\
&= \sum_{j,k,p,m=1}^{3} \varepsilon_{pkm} \frac{\partial}{\partial x_j} x_p v_j m_k \boldsymbol{\delta}_m - \sum_{j,k,p,m=1}^{3} \varepsilon_{pkm} v_j m_k \frac{\partial x_p}{\partial x_j} \boldsymbol{\delta}_m \\
&= \sum_{j,k,p,m=1}^{3} \frac{\partial}{\partial x_j} v_j (\varepsilon_{pkm} x_p m_k \boldsymbol{\delta}_m) - \sum_{j,k,m=1}^{3} \varepsilon_{jkm} v_j m_k \boldsymbol{\delta}_m
\end{aligned}$$

$$= \boldsymbol{\nabla}\cdot\boldsymbol{v}(\boldsymbol{r}\times\boldsymbol{m}) - \boldsymbol{v}\times\boldsymbol{m} = \boldsymbol{\nabla}\cdot\boldsymbol{v}(\boldsymbol{r}\times\boldsymbol{m})$$

The second term on the right-hand side can be written as

$$\begin{aligned}
\boldsymbol{r}\times(\boldsymbol{\nabla}\cdot\boldsymbol{\pi}) &= \sum_{i,j,k,p=1}^{3} x_p\boldsymbol{\delta}_p\times\boldsymbol{\delta}_i\frac{\partial}{\partial x_i}\cdot\pi_{jk}\boldsymbol{\delta}_j\boldsymbol{\delta}_k = \sum_{j,k,p=1}^{3} x_p\boldsymbol{\delta}_p\times\frac{\partial}{\partial x_j}\pi_{jk}\boldsymbol{\delta}_k \\
&= \sum_{j,k,p,m=1}^{3} \varepsilon_{pkm}x_p\frac{\partial}{\partial x_j}\pi_{jk}\boldsymbol{\delta}_m \\
&= \sum_{j,k,p,m=1}^{3} \varepsilon_{pkm}\frac{\partial}{\partial x_j}x_p\pi_{jk}\boldsymbol{\delta}_m - \sum_{j,k,p,m=1}^{3} \varepsilon_{pkm}\pi_{jk}\frac{\partial x_p}{\partial x_j}\boldsymbol{\delta}_m \\
&= \sum_{j,k,p,m=1}^{3} \frac{\partial}{\partial x_j}\varepsilon_{pkm}x_p\pi^T_{kj}\boldsymbol{\delta}_m - \sum_{j,k,m=1}^{3} \varepsilon_{jkm}\pi_{jk}\boldsymbol{\delta}_m \\
&= \sum_{j,k,p,m=1}^{3} \frac{\partial}{\partial x_j}(\varepsilon_{pkj}x_p\pi^T_{km})^T\boldsymbol{\delta}_m + \sum_{j,k,m=1}^{3} \varepsilon_{mkj}\pi_{jk}\boldsymbol{\delta}_m \\
&= \boldsymbol{\nabla}\cdot(\boldsymbol{r}\times\boldsymbol{\pi}^T)^T + \boldsymbol{\varepsilon}:\boldsymbol{\pi}
\end{aligned}$$

Combining the above results, and recognizing that $\boldsymbol{r}$ is independent of time, gives desired result. For the source term we write

$$\begin{aligned}
\boldsymbol{\varepsilon}:\boldsymbol{\pi} &= \sum_{i,j,k,p,m=1}^{3} \varepsilon_{ijk}\boldsymbol{\delta}_i\boldsymbol{\delta}_j\boldsymbol{\delta}_k : \pi_{mp}\boldsymbol{\delta}_m\boldsymbol{\delta}_p = \sum_{i,j,k=1}^{3} \varepsilon_{ijk}\pi_{kj}\boldsymbol{\delta}_i \\
&= \sum_{i,j=1}^{3} (\varepsilon_{ij1}\pi_{1j} + \varepsilon_{ij2}\pi_{2j} + \varepsilon_{ij3}\pi_{3j})\boldsymbol{\delta}_i \\
&= \varepsilon_{321}(\pi_{12}-\pi_{21})\boldsymbol{\delta}_3 + \varepsilon_{231}(\pi_{13}-\pi_{31})\boldsymbol{\delta}_2 + \varepsilon_{132}(\pi_{23}-\pi_{32})\boldsymbol{\delta}_1,
\end{aligned}$$

which vanishes only if $\pi_{ij} = \pi_{ji}$, or the pressure tensor is symmetric $\boldsymbol{\pi}^T = \boldsymbol{\pi}$.

Exercise 5.9

To show the velocity gradient $\boldsymbol{\nabla v}$ is symmetric, we must find its relation to the vorticity $\boldsymbol{w}$. We begin by computing $\boldsymbol{\varepsilon}\cdot\boldsymbol{w}$,

$$\begin{aligned}
\boldsymbol{\varepsilon}\cdot\boldsymbol{w} &= \sum_{i,j,k,p=1}^{3} \varepsilon_{ijk}\boldsymbol{\delta}_i\boldsymbol{\delta}_j\boldsymbol{\delta}_k\cdot w_p\boldsymbol{\delta}_p = \sum_{i,j,k,m,n,p=1}^{3} \varepsilon_{ijk}\boldsymbol{\delta}_i\boldsymbol{\delta}_j\boldsymbol{\delta}_k\cdot\varepsilon_{mnp}\frac{\partial v_n}{\partial x_m}\boldsymbol{\delta}_p \\
&= \sum_{i,j,k=1}^{3} \boldsymbol{\delta}_i\boldsymbol{\delta}_j\varepsilon_{ijk}\varepsilon_{mnk}\frac{\partial v_n}{\partial x_m} = \sum_{i,j,k=1}^{3} \boldsymbol{\delta}_i\boldsymbol{\delta}_j(\delta_{im}\delta_{jn} - \delta_{in}\delta_{jm})\frac{\partial v_n}{\partial x_m}
\end{aligned}$$

$$= \sum_{i,j,k=1}^{3} \boldsymbol{\delta}_i \boldsymbol{\delta}_j \Big(\frac{\partial v_j}{\partial x_i} - \frac{\partial v_i}{\partial x_j} \Big) = \boldsymbol{\nabla v} - \boldsymbol{\nabla v}^T$$

where the second equality in the second line follows from a well known identity between the permuation symbol and Kronecker delta. Since $\boldsymbol{w} = \mathbf{0}$ for an irrotational flow, the velocity gradient is symmetric.

We use the identity $\boldsymbol{\nabla} \times \boldsymbol{\nabla} a = \mathbf{0}$, which holds for arbitrary scalar a. For irrotational flow $\boldsymbol{w} = \boldsymbol{\nabla} \times \boldsymbol{v} = \mathbf{0}$, so that can write $\boldsymbol{v} = -\boldsymbol{\nabla}\Phi$, which when substituted in (5.36), gives (5.44).

Now, for the two-dimensional flow $\boldsymbol{v} = v_1(x_1, x_2)\boldsymbol{\delta}_1 + v_2(x_1, x_2)\boldsymbol{\delta}_2$, we can write $\boldsymbol{v} = -\boldsymbol{\nabla}\Phi$ as follows:

$$v_1 = -\frac{\partial \Phi}{\partial x_1}, \qquad v_2 = -\frac{\partial \Phi}{\partial x_2}.$$

Combining these with (5.9) setting $\rho = 1$ gives the following:

$$\frac{\partial \Phi}{\partial x_1} = -\frac{\partial \psi}{\partial x_2}, \qquad \frac{\partial \Phi}{\partial x_2} = \frac{\partial \psi}{\partial x_1},$$

known as the Cauchy-Riemann equations. Hence, the stream function $\psi(x_1, x_2)$ and velocity potential $\Phi(x_1, x_2)$ are orthogonal.

Exercise 5.10
Using the identity in (5.45), we write the steady-state form of (5.40) as follows:

$$\boldsymbol{\nabla}\mathcal{P} = -\rho \Big[\frac{1}{2} \boldsymbol{\nabla} v^2 - \boldsymbol{v} \times (\boldsymbol{\nabla} \times \boldsymbol{v}) \Big] = -\rho \boldsymbol{\nabla} \Big(\frac{1}{2} v^2 \Big),$$

where the second equality follows since $\boldsymbol{\nabla} \times \boldsymbol{v} = \mathbf{0}$. Using (5.41) and rearranging terms taking ρ to be constant gives (5.46).

Exercise 5.11
Since $\boldsymbol{v} = -\boldsymbol{\nabla}\Phi$, we can write

$$v_r = -\frac{\partial \Phi}{\partial r}, \qquad v_\theta = -\frac{1}{r} \frac{\partial \Phi}{\partial \theta},$$

so that $\Phi(r, \theta)$ is governed by (5.44), which takes the form

$$\frac{1}{r} \frac{\partial}{\partial r} \Big(r \frac{\partial \Phi}{\partial r} \Big) + \frac{1}{r^2} \frac{\partial^2 \Phi}{\partial \theta^2} = 0.$$

For an impermeable cylinder $v_r(R, \theta) = 0$, which leads to the boundary condition $\partial \Phi / \partial r(R, \theta) = 0$. Since $\boldsymbol{v}(\infty, \theta) = V \boldsymbol{\delta}_1 = V \cos\theta \boldsymbol{\delta}_r - V \sin\theta \boldsymbol{\delta}_\theta$, which leads to the boundary condition $\Phi(\infty, \theta) = Vr\cos\theta$. Substitution of $\Phi = f(r)\cos\theta$ in the equation above leads to

$$\frac{1}{r}\frac{d}{dr}\Big(r\frac{df}{dr}\Big) - \frac{f}{r^2} = 0,$$

which is solved subject to

$$\frac{df}{dr}(R) = 0, \qquad f(\infty) = -Vr.$$

Writing $f(r)$ as a power series, we find using the boundary conditions $f(r) = VR(R/r + r/R)$, so that the velocity potential is

$$\Phi = VR\cos\theta\Big(\frac{R}{r} + \frac{r}{R}\Big).$$

Hence, the velocity field is given by

$$v_r = V\cos\theta\Big[1 - \Big(\frac{R}{r}\Big)^2\Big] = \frac{1}{r}\frac{\partial\psi}{\partial\theta}, \qquad v_\theta = -V\sin\theta\Big[1 + \Big(\frac{R}{r}\Big)^2\Big] = -\frac{\partial\psi}{\partial r},$$

where the second equalities give the relation to the stream function. Integration with the condition $\psi(R, \theta) = 0$ gives

$$\psi = VR\sin\theta\Big[\Big(\frac{r}{R}\Big) - \Big(\frac{R}{r}\Big)\Big].$$

The velocity potential and stream function are plotted in Figure C.11. To find the pressure field, we use (5.46), which implies $\mathcal{P} + \rho/2v^2$ is equal to a constant. Setting $\mathcal{P}(\infty, \theta) = 0$, where $v(\infty, \theta) = V$, we have

$$\mathcal{P} = \frac{1}{2}\rho V^2\Big[1 - \Big(\frac{v}{V}\Big)^2\Big] = \frac{1}{2}\rho V^2\Big(\frac{R}{r}\Big)^2\Big[2 - 4\sin^2\theta - \Big(\frac{R}{r}\Big)^2\Big].$$

Note that pressures at the front and back of the cylinder cylinder are equal $\mathcal{P}(R, 0) = \mathcal{P}(R, \pi)$.

Exercise 5.12

The scalar product of velocity $\boldsymbol{v}$ with the momentum balance (5.32) gives:

$$\boldsymbol{v}\cdot\frac{\partial \boldsymbol{m}}{\partial t} = -\boldsymbol{v}\cdot\boldsymbol{\nabla}\cdot(\boldsymbol{vm}) - \boldsymbol{v}\cdot(\boldsymbol{\nabla}\cdot\boldsymbol{\pi}) + \boldsymbol{v}\cdot\rho\boldsymbol{g}.$$

We evaluate the above term-by-term:

$$\boldsymbol{v}\cdot\frac{\partial \boldsymbol{m}}{\partial t} = \boldsymbol{v}\cdot\frac{\partial}{\partial t}(\rho\boldsymbol{v}) = \sum_{i,j=1}^{3} v_i\boldsymbol{\delta}_i\cdot\frac{\partial}{\partial t}(\rho v_j\boldsymbol{\delta}_j) = \sum_{i=1}^{3} v_i\frac{\partial}{\partial t}(\rho v_i) = \frac{1}{2}\frac{\partial}{\partial t}(\rho v^2)$$

$$\boldsymbol{v}\cdot\boldsymbol{\nabla}\cdot(\boldsymbol{vm}) = \sum_{i,j=1}^{3} v_i\boldsymbol{\delta}_i\cdot\boldsymbol{\nabla}\cdot(\rho v_j\boldsymbol{\delta}_j\boldsymbol{v}) = \sum_{i} v_i\boldsymbol{\nabla}(\rho v_i\boldsymbol{v}) = \frac{1}{2}\boldsymbol{\nabla}\cdot(\rho v^2\boldsymbol{v})$$

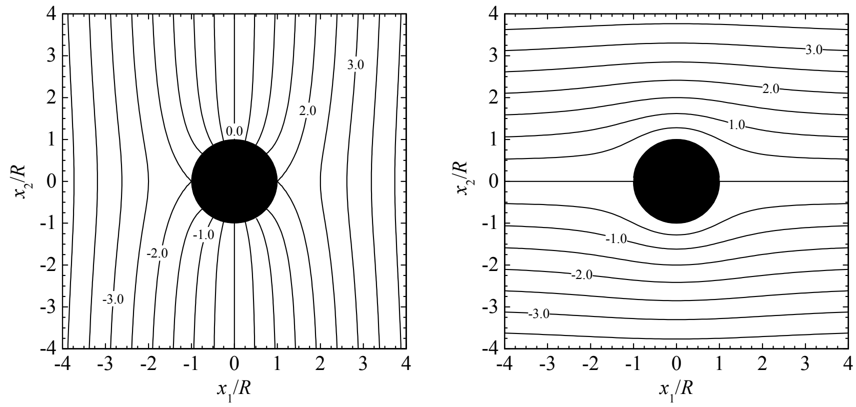

Figure C.11 Potential flow around a cylinder. Velocity potential Φ/VR contours (left) and stream function contours ψ/VR (right).

$$
\begin{aligned}
\boldsymbol{v} \cdot (\boldsymbol{\nabla} \cdot \boldsymbol{\pi}) &= \sum_{i,j,k,m=1}^{3} v_i \boldsymbol{\delta}_i \cdot \boldsymbol{\delta}_j \frac{\partial}{\partial x_j} \cdot \pi_{km} \boldsymbol{\delta}_k \boldsymbol{\delta}_m = \sum_{i,j,m=1}^{3} v_i \boldsymbol{\delta}_i \cdot \frac{\partial}{\partial x_j} \cdot \pi_{jm} \boldsymbol{\delta}_m \\
&= \sum_{i,j=1}^{3} v_i \frac{\partial \pi_{ji}}{\partial x_j} = \sum_{i,j=1}^{3} \frac{\partial}{\partial x_j} (v_i \pi_{ji}) - \sum_{i,j=1}^{3} \pi_{ji} \frac{\partial v_i}{\partial x_j} \\
&= \boldsymbol{\nabla} \cdot (\boldsymbol{\pi} \cdot \boldsymbol{v}) - \boldsymbol{\pi} : \boldsymbol{\nabla} \boldsymbol{v}.
\end{aligned}
$$

Combining the above results gives (5.49).

Exercise 5.13
For a 1-component fluid, the source terms $\pm\rho \boldsymbol{v} \cdot \boldsymbol{g}$ in the potential energy equation (5.48) and in the kinetic energy equation (5.49). In a 2-component fluid, this is no longer the case and a conversion from potential into internal energy can take place. In the potential energy equation, the generalization is $-\rho_1 \boldsymbol{v}_1 \cdot \boldsymbol{f}_1 - \rho_2 \boldsymbol{v}_2 \cdot \boldsymbol{f}_2$, whereas the generalization in the kinetic energy equation is $\boldsymbol{v} \cdot (\rho_1 \cdot \boldsymbol{f}_1 + \rho_2 \cdot \boldsymbol{f}_2)$. The no longer vanishing sum is balanced by the additional source term $\boldsymbol{j}_1 \cdot \boldsymbol{f}_1 + \boldsymbol{j}_2 \cdot \boldsymbol{f}_2$ in the internal energy equation (5.53).

Exercise 5.14
The steady state form of (5.50) with isotropic pressure tensor $\boldsymbol{\pi} = p\boldsymbol{\delta}$ gives,

$$
0 = -\boldsymbol{\nabla} \cdot \left(\boldsymbol{v} \rho \phi + \boldsymbol{v} \frac{1}{2} \rho v^2 + p \boldsymbol{v} \right) + p \boldsymbol{\nabla} \cdot \boldsymbol{v}
$$

$$
\begin{aligned}
&= -\boldsymbol{\nabla} \cdot \Big[\rho \boldsymbol{v}\Big(\phi + \frac{1}{2}v^2 + \frac{p}{\rho}\Big)\Big] + p\boldsymbol{\nabla} \cdot \boldsymbol{v} \\
&= -\Big(\phi + \frac{1}{2}v^2 + \frac{p}{\rho}\Big)\boldsymbol{\nabla} \cdot (\rho \boldsymbol{v}) - \rho \boldsymbol{v} \cdot \boldsymbol{\nabla}\Big(\phi + \frac{1}{2}v^2 + \frac{p}{\rho}\Big) + p\boldsymbol{\nabla} \cdot \boldsymbol{v} \\
&= -\rho \boldsymbol{v} \cdot \boldsymbol{\nabla}\Big(\phi + \frac{1}{2}v^2 + \frac{p}{\rho}\Big) - \frac{p}{\rho}\boldsymbol{v} \cdot \boldsymbol{\nabla}\rho,
\end{aligned}
$$

where we have used the steady state form of (5.5) in the first and third terms to go from the third to fourth line. After a minor rearrangement, we have

$$
\boldsymbol{v} \cdot \boldsymbol{\nabla}\Big(\phi + \frac{1}{2}v^2\Big) + \boldsymbol{v} \cdot \frac{\boldsymbol{\nabla} p}{\rho} = 0
$$

Now from Excercise 5.3 we have $\boldsymbol{v} = v d\boldsymbol{r}(\zeta)/d\zeta$, which when substituted in the above result gives

$$
\begin{aligned}
\frac{d\boldsymbol{r}}{d\zeta} \cdot \boldsymbol{\nabla}\Big(\phi + \frac{1}{2}v^2\Big) + \frac{d\boldsymbol{r}}{d\zeta} \cdot \frac{\boldsymbol{\nabla} p}{\rho} &= 0, \\
\sum_{i,j=1}^{3} \frac{\partial x_i}{\partial \zeta}\boldsymbol{\delta}_i \cdot \boldsymbol{\delta}_j \frac{\partial}{\partial x_j}\Big(\phi + \frac{1}{2}v^2\Big) + \sum_{i,j=1}^{3} \frac{\partial x_i}{\partial \zeta}\boldsymbol{\delta}_i \cdot \boldsymbol{\delta}_j \frac{1}{\rho}\frac{\partial p}{\partial x_j} &= 0, \\
\frac{d}{d\zeta}\Big(\phi + \frac{1}{2}v^2\Big) + \frac{1}{\rho}\frac{dp}{d\zeta} &= 0,
\end{aligned}
$$

which after integration between two points on a streamline gives (5.54).

Exercise 5.15
Since we are considering the isentropic case, we need only to consider mass (5.6) and momentum (5.35) balances:

$$
\frac{\partial \rho}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla}\rho = -\rho \boldsymbol{\nabla} \cdot \boldsymbol{v},
$$

$$
\rho\Big(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla}\boldsymbol{v}\Big) = -\boldsymbol{\nabla} p
$$

where we have set $\boldsymbol{g} = \boldsymbol{0}$. Now, since $d\rho = (\partial\rho/\partial p)_s dp = dp/{c_{\hat{s}}}^2$, where $c_{\hat{s}}$ is the isentropic speed of sound, we can write the mass balance as

$$
\frac{\partial p}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} p = -{c_{\hat{s}}}^2 \rho \boldsymbol{\nabla} \cdot \boldsymbol{v},
$$

Substitution of $\rho = \rho_0 + \delta\rho$, $p = p_0 + \delta p$ and $\boldsymbol{v} = \boldsymbol{0} + \boldsymbol{v}$ in the mass and momentum balances above gives, keeping only linear terms, the following:

$$
\frac{\partial \delta p}{\partial t} = -{c_{\hat{s}}}^2 \rho_0 \boldsymbol{\nabla} \cdot \boldsymbol{v},
$$

$$\rho_0 \frac{\partial \boldsymbol{v}}{\partial t} = -\boldsymbol{\nabla} \delta p.$$

Taking the divergence of the linearized momentum balance gives:

$$\rho_0 \frac{\partial}{\partial t}(\boldsymbol{\nabla} \cdot \boldsymbol{v}) = -\nabla^2 \delta p,$$

which when combined with the linearized mass balance gives (5.55).

Exercise 5.16
Setting $\boldsymbol{i} = \boldsymbol{0}$ in (5.61) and differentiation with respect to time gives

$$\frac{\partial^2 \boldsymbol{E}}{\partial t^2} = c \frac{\partial}{\partial t} \boldsymbol{\nabla} \times \boldsymbol{B} = c \boldsymbol{\nabla} \times \frac{\partial \boldsymbol{B}}{\partial t}.$$

Taking the curl of (5.62) gives

$$\boldsymbol{\nabla} \times \frac{\partial \boldsymbol{B}}{\partial t} = -c \boldsymbol{\nabla} \times \boldsymbol{\nabla} \times \boldsymbol{E} = -c[\boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \boldsymbol{E}) - \nabla^2 \boldsymbol{E}] = c \nabla^2 \boldsymbol{E},$$

where the first equality is obtained using (5.74) and the second using (5.59) with $\rho_{\mathrm{el}} = 0$. Combining these gives (5.75). Substitution of (5.76) in (5.75) gives

$$\left(\frac{\omega^2}{c^2} - k^2\right) \boldsymbol{E} = \boldsymbol{0},$$

which implies $k = \omega / c$. Substitution of (5.76) in (5.62) gives

$$\frac{\partial \boldsymbol{B}}{\partial t} = -c \boldsymbol{\nabla} \times \boldsymbol{E}_0 e^{i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)} = -ci \boldsymbol{k} \times \boldsymbol{E}_0 e^{i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)}.$$

Integrating, we obtain

$$\boldsymbol{B} = \frac{c}{\omega} \boldsymbol{k} \times \boldsymbol{E}_0 e^{i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)} = \boldsymbol{B}_0 e^{i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)},$$

which is (5.77) with $\boldsymbol{B}_0 = \boldsymbol{k} \times \boldsymbol{E}_0 / k$.

Now, substitution of (5.76) in (5.59) leads to $\boldsymbol{k} \cdot \boldsymbol{E}_0 = 0$, and substitution of (5.77) in (5.60) leads to $\boldsymbol{k} \cdot \boldsymbol{B}_0 = 0$. Hence, the $\boldsymbol{E}$ and $\boldsymbol{B}$ fields are orthogonal to $\boldsymbol{k}$ and from (5.62) we know they are orthogonal to each other, and therefore are transverse waves. Note that for the Poynting vector we have

$$\begin{aligned} c\boldsymbol{E} \times \boldsymbol{B} &= c\boldsymbol{E}_0 \times \boldsymbol{B}_0 e^{2i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)} = \frac{c}{k} \boldsymbol{E}_0 \times (\boldsymbol{k} \times \boldsymbol{E}_0) e^{2i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)} \\ &= \frac{c}{k}[(\boldsymbol{E}_0 \cdot \boldsymbol{E}_0)\boldsymbol{k} - \boldsymbol{E}_0(\boldsymbol{k} \cdot \boldsymbol{E}_0)] e^{2i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)} = c(\boldsymbol{E}_0 \cdot \boldsymbol{E}_0) \frac{\boldsymbol{k}}{k} e^{2i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)} \end{aligned}$$

Exercise 5.17

By applying the product rule, Maxwell's equations and the rules for double cross products, we obtain

$$\begin{aligned}
\frac{1}{c}\frac{\partial}{\partial t}(\boldsymbol{E}\times\boldsymbol{B}) &= \frac{1}{c}\left(-\boldsymbol{B}\times\frac{\partial\boldsymbol{E}}{\partial t}+\boldsymbol{E}\times\frac{\partial\boldsymbol{B}}{\partial t}\right)\\
&= -\frac{1}{c}\boldsymbol{i}\times\boldsymbol{B}-\boldsymbol{B}\times(\boldsymbol{\nabla}\times\boldsymbol{B})-\boldsymbol{E}\times(\boldsymbol{\nabla}\times\boldsymbol{E})\\
&= -\frac{1}{c}\boldsymbol{i}\times\boldsymbol{B}-\frac{1}{2}\boldsymbol{\nabla}B^2+\boldsymbol{B}\cdot\boldsymbol{\nabla}\,\boldsymbol{B}-\frac{1}{2}\boldsymbol{\nabla}E^2+\boldsymbol{E}\cdot\boldsymbol{\nabla}\,\boldsymbol{E}\\
&= -\frac{1}{c}\boldsymbol{i}\times\boldsymbol{B}+\boldsymbol{\nabla}\cdot\boldsymbol{T}-\boldsymbol{B}\,\boldsymbol{\nabla}\cdot\boldsymbol{B}-\boldsymbol{E}\,\boldsymbol{\nabla}\cdot\boldsymbol{E}\\
&= \boldsymbol{\nabla}\cdot\boldsymbol{T}-\rho_{\text{el}}\boldsymbol{E}-\frac{1}{c}\boldsymbol{i}\times\boldsymbol{B}\,.
\end{aligned}$$

The desired result (5.69) is now obtained by using the definitions (5.58) for ρ_{el} and $\boldsymbol{i}$ and the expression (5.65) for the Lorentz force.

Exercise 6.1

When generalized to k particle species, (4.53) reads

$$d\hat{u} = \hat{c}_{\hat{v}}dT+\left[T\left(\frac{\partial p}{\partial T}\right)_{\hat{v},w_\alpha}-p\right]d\hat{v}+\sum_{\alpha=1}^{k}\left[\hat{h}_\alpha-T\left(\frac{\partial p}{\partial T}\right)_{\hat{v},w_\alpha}\hat{v}_\alpha\right]dw_\alpha.$$

Noting that $\hat{v}=1/\rho$ so that $d\hat{v}=-d\rho/\rho^2$, we multiply both sides by ρ and find

$$\begin{aligned}
\rho\frac{D\hat{u}}{Dt} &= \rho\hat{c}_{\hat{v}}\frac{DT}{Dt}+\left[T\left(\frac{\partial p}{\partial T}\right)_{\hat{v},w_\alpha}-p\right]\left(-\frac{1}{\rho}\frac{D\rho}{Dt}\right)\\
&\quad+\sum_{\alpha=1}^{k}\left[\hat{h}_\alpha-T\left(\frac{\partial p}{\partial T}\right)_{\hat{v},w_\alpha}\hat{v}_\alpha\right]\rho\frac{Dw_\alpha}{Dt}.
\end{aligned}$$

Substituting for the balance laws for ρ, w_α and $\hat{u}$, this becomes

$$\begin{aligned}
-\boldsymbol{\nabla}\cdot\boldsymbol{j}_q-\boldsymbol{\pi}:\boldsymbol{\nabla}\boldsymbol{v} &= \rho\hat{c}_{\hat{v}}\frac{DT}{Dt}+\left[T\left(\frac{\partial p}{\partial T}\right)_{\hat{v},w_\alpha}-p\right]\boldsymbol{\nabla}\cdot\boldsymbol{v}\\
&\quad+\sum_{\alpha=1}^{k}\left[\hat{h}_\alpha-T\left(\frac{\partial p}{\partial T}\right)_{\hat{v},w_\alpha}\hat{v}_\alpha\right](-\boldsymbol{\nabla}\cdot\boldsymbol{j}_\alpha+\nu_\alpha\Gamma),
\end{aligned}$$

which gives the desired relation with $\boldsymbol{\pi}=p\,\boldsymbol{\delta}+\boldsymbol{\tau}$.

Exercise 6.2

Starting with $s = s(u, \rho_1, \rho_2)$, we write

$$\frac{\partial s}{\partial t} = \frac{\partial s}{\partial u}\frac{\partial u}{\partial t} + \frac{\partial s}{\partial \rho_1}\frac{\partial \rho_1}{\partial t} + \frac{\partial s}{\partial \rho_2}\frac{\partial \rho_2}{\partial t} = \frac{1}{T}\frac{\partial u}{\partial t} - \frac{\hat{\mu}_1}{T}\frac{\partial \rho_1}{\partial t} - \frac{\hat{\mu}_2}{T}\frac{\partial \rho_2}{\partial t},$$

where the second equality follows from the equations of state introduced in Chapter 4. Substitution of (5.14) and (5.51) gives,

$$\begin{aligned}\frac{\partial s}{\partial t} &= -\frac{1}{T}\Big[\boldsymbol{\nabla}\cdot(\boldsymbol{v}u + \boldsymbol{j}_q) + \boldsymbol{\pi} : \boldsymbol{\nabla}\boldsymbol{v}\Big] \\ &\quad + \frac{\hat{\mu}_1}{T}\boldsymbol{\nabla}\cdot(\boldsymbol{v}\rho_1 + \boldsymbol{j}_1) + \frac{\hat{\mu}_2}{T}\boldsymbol{\nabla}\cdot(\boldsymbol{v}\rho_2 + \boldsymbol{j}_2) - \frac{1}{T}(\nu_1\hat{\mu}_1 + \nu_2\hat{\nu}_2)\Gamma.\end{aligned}$$

Now, using (6.3) and rearranging the terms involving $\boldsymbol{\nabla}\cdot$, we can write

$$\begin{aligned}\frac{\partial s}{\partial t} &= -\frac{1}{T}(u + p - \rho_1\hat{\mu}_1 - \rho_2\hat{\mu}_2)\boldsymbol{\nabla}\cdot\boldsymbol{v} - \boldsymbol{v}\cdot\Big(\frac{1}{T}\boldsymbol{\nabla}u - \frac{\hat{\mu}_1}{T}\boldsymbol{\nabla}\rho_1 - \frac{\hat{\mu}_2}{T}\boldsymbol{\nabla}\rho_2\Big) \\ &\quad - \boldsymbol{\nabla}\cdot\frac{\boldsymbol{j}_q}{T} + \boldsymbol{\nabla}\cdot\Big(\frac{\hat{\mu}_1}{T}\boldsymbol{j}_1\Big) + \boldsymbol{\nabla}\cdot\Big(\frac{\hat{\mu}_2}{T}\boldsymbol{j}_2\Big) \\ &\quad + \boldsymbol{j}_q\cdot\boldsymbol{\nabla}\frac{1}{T} - \boldsymbol{j}_1\cdot\boldsymbol{\nabla}\frac{\hat{\mu}_1}{T} - \boldsymbol{j}_2\cdot\boldsymbol{\nabla}\frac{\hat{\mu}_2}{T} - \frac{1}{T}\boldsymbol{\tau} : \boldsymbol{\nabla}\boldsymbol{v} - \frac{1}{T}(\nu_1\hat{\mu}_1 + \nu_2\hat{\nu}_2)\Gamma.\end{aligned}$$

Using the Euler and Gibbs-Duhem relations in the first and second terms, respectively, we have

$$\begin{aligned}\frac{\partial s}{\partial t} &= -\boldsymbol{\nabla}\cdot(\boldsymbol{v}s) - \boldsymbol{\nabla}\cdot\frac{1}{T}\Big(\boldsymbol{j}_q - \hat{\mu}_1\boldsymbol{j}_1 - \hat{\mu}_2\boldsymbol{j}_2\Big) \\ &\quad + \boldsymbol{j}_q\cdot\boldsymbol{\nabla}\frac{1}{T} - \boldsymbol{j}_1\cdot\boldsymbol{\nabla}\frac{\hat{\mu}_1}{T} - \boldsymbol{j}_2\cdot\boldsymbol{\nabla}\frac{\hat{\mu}_2}{T} - \frac{1}{T}\boldsymbol{\tau} : \boldsymbol{\nabla}\boldsymbol{v} - \frac{1}{T}(\nu_1\hat{\mu}_1 + \nu_2\hat{\nu}_2)\Gamma.\end{aligned}$$

In the above expression, the second term is the entropy flux in (6.9) and the second line is the entropy production rate in (6.10).

Exercise 6.3

For a system with uniform temperature and pressure, we combine (6.17) and (6.11) to obtain

$$\boldsymbol{j}_1 = L_{11}\boldsymbol{\nabla}\left(\frac{\hat{\mu}_2 - \hat{\mu}_1}{T}\right) = -\frac{L_{11}}{Tw_2}\left(\frac{\partial\hat{\mu}_1}{\partial w_1}\right)_{T,p}\boldsymbol{\nabla}w_1 = -\rho D_{12}\boldsymbol{\nabla}w_1,$$

so that

$$\rho D_{12} = \frac{L_{11}}{Tw_2}\left(\frac{\partial\hat{\mu}_1}{\partial w_1}\right)_{T,p}$$

Using $\hat{\mu}_\alpha = \tilde{\mu}_\alpha/\tilde{M}_\alpha$ and (4.60) we obtain

$$\left(\frac{\partial\hat{\mu}_1}{\partial w_1}\right)_{T,p} = \frac{\tilde{R}T}{\tilde{M}_1}\frac{1}{x_1}\frac{dx_1}{dw_1} = \frac{\tilde{R}T}{\tilde{M}}\frac{1}{w_1}\frac{dx_1}{dw_1}$$

where the second equality follows from $x_1 = c_1/c = w_1\tilde{M}/\tilde{M}_1$. Now, since

$$w_1 = \frac{\rho_1}{\rho} = \frac{x_1\tilde{M}_1}{\tilde{M}} = \frac{x_1\tilde{M}_1}{x_1\tilde{M}_1 + x_2\tilde{M}_2}$$

and $dx_2 = -dx_1$, we obtain by a lengthy but elementary calculation

$$\frac{dx_1}{dw_1} = \frac{\tilde{M}^2}{\tilde{M}_1\tilde{M}_2},$$

so that

$$\left(\frac{\partial\hat{\mu}_1}{\partial w_1}\right)_{T,p} = \frac{\tilde{R}T\tilde{M}}{\tilde{M}_1\tilde{M}_2}\frac{1}{w_1} = \frac{\tilde{R}T}{w_1}\frac{1}{w_1\tilde{M}_2 + w_2\tilde{M}_1}$$

where the second equality follows from

$$\frac{1}{\tilde{M}} = \frac{w_1}{\tilde{M}_1} + \frac{w_2}{\tilde{M}_2},$$

Combing the above results gives

$$\rho D_{12} = \frac{\tilde{R}L_{11}}{w_1 w_2}\frac{1}{w_1\tilde{M}_2 + w_2\tilde{M}_1},$$

which is the expression in (6.25) for the diffusion coefficient D_{12}.

Exercise 6.4

Equation (5.25) for $\boldsymbol{j}_2 = -\boldsymbol{j}_1$ becomes

$$\boldsymbol{J}_1^* = \frac{1}{c\tilde{M}_1}\left[c - \rho_1\left(\frac{1}{\tilde{M}_1} - \frac{1}{\tilde{M}_2}\right)\right]\boldsymbol{j}_1 = \frac{\rho}{c\tilde{M}_1\tilde{M}_2}\boldsymbol{j}_1.$$

With $\boldsymbol{j}_1 = -\rho D_{12}\boldsymbol{\nabla} w_1$ and the relationships given in the solution to Exercise 6.3 we obtain the desired result. Similarly, using (5.27) we obtain

$$\begin{aligned}\boldsymbol{j}_1^\dagger &= \boldsymbol{j}_1 - \rho_1(\hat{v}_1\boldsymbol{j}_1 + \hat{v}_2\boldsymbol{j}_2) = (1 - \rho_1\hat{v}_1 + \rho_1\hat{v}_2)\boldsymbol{j}_1\\ &= \rho\hat{v}_2\boldsymbol{j}_1 = -\rho^2 D_{12}\hat{v}_2\boldsymbol{\nabla} w_1.\end{aligned}$$

Now, since

$$w_1 = \frac{\rho_1}{\rho} = \rho_1\hat{v} = \rho_1(w_1\hat{v}_1 + w_2\hat{v}_2)$$

we obtain

$$\frac{dw_1}{d\rho_1} = \frac{1}{\rho^2\hat{v}_2},$$

so that

$$\boldsymbol{j}_1^\dagger = -D_{12}\boldsymbol{\nabla}\rho_1.$$

Exercise 6.5

For uniform pressure, substitution of (6.17) in (6.14) gives

$$\boldsymbol{j}_1 = -\frac{L_{q1} + L_{11}(\hat{h}_2 - \hat{h}_1)}{T^2}\boldsymbol{\nabla}T - \frac{L_{11}}{\rho w_2 T}\Big(\frac{\partial \hat{\mu}_1}{\partial w_1}\Big)_{T,p}\boldsymbol{\nabla}w_1,$$

which, when compared with (6.19) leads to

$$D_{12} = \frac{L_{11}}{\rho w_2 T}\Big(\frac{\partial \hat{\mu}_1}{\partial w_1}\Big)_{T,p}, \qquad D_{q1} = \frac{L_{q1} + L_{11}(\hat{h}_2 - \hat{h}_1)}{\rho w_1 w_2 T}.$$

Similarly, substitution of (6.17) in (6.13) gives

$$\boldsymbol{j}_q = -\frac{L_{qq} + L_{q1}(\hat{h}_2 - \hat{h}_1)}{T^2}\boldsymbol{\nabla}T - \frac{L_{q1}}{\rho w_2 T}\Big(\frac{\partial \hat{\mu}_1}{\partial w_1}\Big)_{T,p}\boldsymbol{\nabla}w_1.$$

Using (6.20) and the above expression for $\boldsymbol{j}_1$ we obtain

$$\begin{aligned}\boldsymbol{j}'_q = &-\frac{L_{qq} + 2L_{q1}(\hat{h}_2 - \hat{h}_1) + L_{11}(\hat{h}_2 - \hat{h}_1)^2}{T^2}\boldsymbol{\nabla}T \\ &-\frac{L_{q1} + L_{11}(\hat{h}_2 - \hat{h}_1)}{w_2 T}\Big(\frac{\partial \hat{\mu}_1}{\partial w_1}\Big)_{T,p}\boldsymbol{\nabla}w_1,\end{aligned}$$

which, when compared with (6.18) leads to

$$\lambda' = \frac{L_{qq} + 2L_{q1}(\hat{h}_2 - \hat{h}_1) + L_{11}(\hat{h}_2 - \hat{h}_1)^2}{T^2}.$$

Substitution of (6.29) and (6.30) in (6.22) and making obvious cancelations gives,

$$[L_{q1} + L_{11}(\hat{h}_2 - \hat{h}_1)]^2 \leq [L_{qq} + 2L_{q1}(\hat{h}_2 - \hat{h}_1) + L_{11}(\hat{h}_2 - \hat{h}_1)^2]L_{11}.$$

Completing the square on the left-hand side and making further cancelations gives

$$L_{q1}^2 \leq L_{qq}L_{11}.$$

Using (6.13) and a combination of (6.11), (6.15), and (6.16), we find

$$\begin{aligned}D_{q1}^2 &\leq T\lambda D_{12}\left[\rho w_1^2 w_2\left(\frac{\partial \hat{\mu}_1}{\partial w_1}\right)_{T,p}\right]^{-1} \\ &\leq T\,\frac{L_{qq}}{T^2}\,\frac{L_{11}}{\rho w_2 T}\left(\frac{\partial \hat{\mu}_1}{\partial w_1}\right)_{T,p}\left[\rho w_1^2 w_2\left(\frac{\partial \hat{\mu}_1}{\partial w_1}\right)_{T,p}\right]^{-1}\end{aligned}$$

and hence

$$|D_{q1}| \leq \frac{\rho\sqrt{L_{11}L_{qq}}}{T\rho_1\rho_2}.$$

Exercise 6.6
From (6.26), we obtain under isothermal and isobaric conditions

$$\boldsymbol{v}_1 - \boldsymbol{v} = -D_{12}\boldsymbol{\nabla} \ln\rho_1 = -\frac{D_{12}}{k_{\rm B}T}\, k_{\rm B}T\boldsymbol{\nabla} \ln\rho_1 = -\frac{D_{12}}{k_{\rm B}T}\boldsymbol{\nabla}\frac{\tilde{\mu}_1}{\tilde{N}_{\rm A}}\,,$$

where (4.60) has been used, and hence also

$$\boldsymbol{v}_1 - \boldsymbol{v} = -\frac{D_{12}}{k_{\rm B}T}\boldsymbol{\nabla}\,\Phi^{\rm e}\,.$$

We have thus found the mobility $D_{12}/(k_{\rm B}T)$ characterizing the velocity achieved in response to an external force, and its inverse is the friction coefficient.

Exercise 6.7
For a system with uniform temperature, we combine (6.17) and (6.11) to obtain

$$\boldsymbol{j}_1 = -L_{11}\Big[\frac{1}{Tw_2}\left(\frac{\partial\hat{\mu}_1}{\partial w_1}\right)_{T,p}\boldsymbol{\nabla} w_1 - \frac{\hat{v}_2 - \hat{v}_1}{T}\boldsymbol{\nabla} p\Big].$$

Setting $D_{12} = L_{11}(\partial\hat{\mu}_1/\partial w_1)_{T,p}/(\rho w_2 T)$ we obtain the expression in (6.32). Using the results from Exercise 6.3, we find the following expression for an ideal mixture

$$\boldsymbol{j}_1 = -\rho D_{12}\boldsymbol{\nabla} w_1 - \rho w_1 w_2 D_{12}\frac{\tilde{M}_1\tilde{M}_2}{\tilde{R}T\tilde{M}}(\hat{v}_1^0 - \hat{v}_2^0)\boldsymbol{\nabla} p\,,$$

where the $\hat{v}_\alpha^0$ are the pure component specific volumes.

Exercise 6.8
Starting with $s = s(u,\rho_1,\rho_2)$, we write

$$\frac{\partial s}{\partial t} = \frac{1}{T}\frac{\partial u}{\partial t} - \frac{\hat{\mu}_1}{T}\frac{\partial\rho_1}{\partial t} - \frac{\hat{\mu}_2}{T}\frac{\partial\rho_2}{\partial t},$$

Substitution of (5.14) and (5.67) gives,

$$\begin{aligned}\frac{\partial s}{\partial t} &= -\frac{1}{T}\boldsymbol{\nabla}\cdot(\boldsymbol{v}u + \boldsymbol{j}_q) - \frac{1}{T}\boldsymbol{\tau} : \boldsymbol{\nabla}\boldsymbol{v} - \frac{p}{T}\boldsymbol{\nabla}\cdot\boldsymbol{v} + \frac{1}{T}(\boldsymbol{j}_1\cdot\boldsymbol{f}_1 + \boldsymbol{j}_2\cdot\boldsymbol{f}_2)\\ &\quad + \frac{\hat{\mu}_1}{T}\boldsymbol{\nabla}\cdot(\boldsymbol{v}\rho_1 + \boldsymbol{j}_1) + \frac{\hat{\mu}_2}{T}\boldsymbol{\nabla}\cdot(\boldsymbol{v}\rho_2 + \boldsymbol{j}_2) - \frac{1}{T}(\nu_1\hat{\mu}_1 + \nu_2\hat{\nu}_2)\Gamma.\end{aligned}$$

Neglecting flow and reaction terms, and rearranging as in Exercise 6.2, we obtain

$$\frac{\partial s}{\partial t} = -\boldsymbol{\nabla}\cdot(\boldsymbol{v}s) - \boldsymbol{\nabla}\cdot\frac{1}{T}\Big(\boldsymbol{j}_q - \hat{\mu}_1\boldsymbol{j}_1 - \hat{\mu}_2\boldsymbol{j}_2\Big)$$

$$+\, \boldsymbol{j}_q \cdot \boldsymbol{\nabla}\frac{1}{T} - \frac{1}{T}\boldsymbol{j}_1 \cdot \Big(T\boldsymbol{\nabla}\frac{\hat{\mu}_1}{T} - \boldsymbol{f}_1\Big) - \frac{1}{T}\boldsymbol{j}_2 \cdot \Big(T\boldsymbol{\nabla}\frac{\hat{\mu}_2}{T} - \boldsymbol{f}_2\Big),$$

where the second line is the expression for σ in (6.33). Rearranging terms, this can be written as

$$\sigma = -\frac{1}{T^2}[\boldsymbol{j}_q - (\hat{\mu}_1 - \hat{\mu}_2)\boldsymbol{j}_1] \cdot \boldsymbol{\nabla}T - \frac{1}{T}\boldsymbol{j}_1 \cdot (\boldsymbol{\nabla}\hat{\mu}_1 - \boldsymbol{f}_1) - \frac{1}{T}\boldsymbol{j}_2 \cdot (\boldsymbol{\nabla}\hat{\mu}_2 - \boldsymbol{f}_2).$$

From (6.9), terms in the first square brackets give $T\boldsymbol{j}_s$, so that we have found the first term in (6.34). Using (5.65), we can write

$$\begin{aligned}\boldsymbol{j}_1 \cdot (\boldsymbol{\nabla}\hat{\mu}_1 - \boldsymbol{f}_1) + \boldsymbol{j}_2 \cdot (\boldsymbol{\nabla}\hat{\mu}_2 - \boldsymbol{f}_2) &= \boldsymbol{j}_1 \cdot \boldsymbol{\nabla}(\hat{\mu}_1 - \hat{\mu}_2) - (z_1\boldsymbol{j}_1 + z_2\boldsymbol{j}_2) \cdot \boldsymbol{E} \\ &\quad - \frac{1}{c}[z_1\boldsymbol{j}_1 \cdot (\boldsymbol{v}_1 \times \boldsymbol{B}) + z_2\boldsymbol{j}_2 \cdot (\boldsymbol{v}_2 \times \boldsymbol{B})].\end{aligned}$$

For the second line, in the absence of flow, we write

$$z_1\boldsymbol{j}_1 \cdot (\boldsymbol{v}_1 \times \boldsymbol{B}) + z_2\boldsymbol{j}_2 \cdot (\boldsymbol{v}_2 \times \boldsymbol{B}) = \frac{z_1}{\rho_1}\boldsymbol{j}_1 \cdot (\boldsymbol{j}_1 \times \boldsymbol{B}) + \frac{z_2}{\rho_2}\boldsymbol{j}_2 \cdot (\boldsymbol{j}_2 \times \boldsymbol{B}) = 0.$$

Again, in the absence of flow $\boldsymbol{j}_{\text{el}} = \boldsymbol{i} = z_1\boldsymbol{j}_1 + z_2\boldsymbol{j}_2$, and the first line gives the second and third terms in (6.34). Or, using $\boldsymbol{E} = -\boldsymbol{\nabla}\phi_{\text{el}}$, we have

$$\boldsymbol{j}_1 \cdot (\boldsymbol{\nabla}\hat{\mu}_1 - \boldsymbol{f}_1) + \boldsymbol{j}_2 \cdot (\boldsymbol{\nabla}\hat{\mu}_2 - \boldsymbol{f}_2) = \boldsymbol{j}_1 \cdot \boldsymbol{\nabla}(\hat{\mu}'_1 - \hat{\mu}'_2),$$

where $\hat{\mu}'_\alpha = \hat{\mu}_\alpha + z_\alpha\phi_{\text{el}}$, which gives (6.43).

Exercise 6.9

Rearranging (6.38), we obtain

$$\boldsymbol{E} + \frac{m_{\text{el}}}{e}\boldsymbol{\nabla}\hat{\mu}_{\text{el}} = \frac{T}{L_{\text{ee}}}\boldsymbol{i} + \frac{L_{se}}{L_{ee}}\boldsymbol{\nabla}T = \frac{\boldsymbol{i}}{\sigma_{\text{el}}} + \varepsilon_{\text{el}}\boldsymbol{\nabla}T,$$

where $\varepsilon_{\text{el}} = L_{se}/L_{ee}$. Now, from (6.37) we can write

$$\begin{aligned}\boldsymbol{j}_q = T\boldsymbol{j}_s - \frac{m_{\text{el}}}{e}\hat{\mu}_{\text{el}}\boldsymbol{i} &= -L_{ss}\boldsymbol{\nabla}T + L_{ee}\Big(\boldsymbol{E} + \frac{m_{\text{el}}}{e}\boldsymbol{\nabla}\hat{\mu}_{\text{el}}\Big) - \frac{m_{\text{el}}}{e}\hat{\mu}_{\text{el}}\boldsymbol{i} \\ &= -L_{ss}\boldsymbol{\nabla}T + L_{se}\Big(\frac{T}{L_{\text{ee}}}\boldsymbol{i} + \frac{L_{se}}{L_{ee}}\boldsymbol{\nabla}T\Big) - \frac{m_{\text{el}}}{e}\hat{\mu}_{\text{el}}\boldsymbol{i} \\ &= -\lambda\boldsymbol{\nabla}T + \Big(\pi_{\text{el}} - \frac{m_{\text{el}}}{e}\hat{\mu}_{\text{el}}\Big)\boldsymbol{i},\end{aligned}$$

where $\pi_{\text{el}} = TL_{se}/L_{ee} = \varepsilon_{\text{el}}T$. To examine power generation in a thermoelectric device, we compute $\boldsymbol{i} \cdot \boldsymbol{E}$. Neglecting $\hat{\mu}_{\text{el}}$, we can write

$$\boldsymbol{i} \cdot \boldsymbol{E} = \frac{i^2}{\sigma_{\text{el}}} + \varepsilon_{\text{el}}\boldsymbol{i} \cdot \boldsymbol{\nabla}T = \frac{i^2}{\sigma_{\text{el}}} + \varepsilon_{\text{el}}\boldsymbol{i} \cdot \Big(\frac{\varepsilon_{\text{el}}T}{\lambda}\boldsymbol{i} - \frac{1}{\lambda}\boldsymbol{j}_q\Big) = (ZT+1)\frac{i^2}{\sigma_{\text{el}}} - \frac{\varepsilon_{\text{el}}}{\lambda}\boldsymbol{i} \cdot \boldsymbol{j}_q,$$

where $Z = \sigma_{\text{el}}\varepsilon_{\text{el}}^2/\lambda$.

Exercise 6.10
From Exercise 6.3, we have for $w_1 \ll 1$, the expression

$$\left(\frac{\partial \hat{\mu}_1}{\partial w_1}\right)_{T,p} = \frac{\tilde{R}T}{\tilde{M}_1 w_1}$$

Substitution in (6.42), we have for an isothermal system,

$$\boldsymbol{j}_1 = -\rho D_{12} \boldsymbol{\nabla} w_1 - \rho_1 \frac{D_{12}\tilde{M}_1}{\tilde{R}T} z_1 \boldsymbol{\nabla} \phi_{\text{el}},$$

which leads to (6.45). From Exercise 6.6, we see the term $D_{12}\tilde{M}_1/(\tilde{R}T)$ in (6.45) is the mobility of species 1. The product of mobility and force gives the species velocity, which when multiplied by the mass density, gives the mass flux due to the external force.

Exercise 6.11
As $\boldsymbol{v}_\alpha - \boldsymbol{v} = \boldsymbol{j}_\alpha/\rho_\alpha$, the two-component case of (6.54) becomes

$$-\frac{\tilde{M}_1}{\tilde{R}T} \boldsymbol{\nabla} \hat{\mu}_1 = \frac{x_2}{\mathfrak{D}_{12}} \left(\frac{\boldsymbol{j}_1}{\rho_1} - \frac{\boldsymbol{j}_2}{\rho_2}\right) = \frac{x_2}{\mathfrak{D}_{12}} \frac{\rho}{w_1 w_2} \boldsymbol{j}_1,$$

where the second equality follows since $\boldsymbol{j}_2 = -\boldsymbol{j}_1$ and $\rho_\alpha = \rho w_\alpha$. Solving for $\boldsymbol{j}_1$, we obtain

$$\boldsymbol{j}_1 = -\rho \mathfrak{D}_{12} \frac{w_1 w_2}{x_2} \frac{\tilde{M}_1}{\tilde{R}T} \boldsymbol{\nabla} \hat{\mu}_1 = -\rho \mathfrak{D}_{12} \frac{\tilde{M}_1 \tilde{M}_2}{\tilde{M}\tilde{R}T} w_1 \boldsymbol{\nabla} \hat{\mu}_1.$$

Using results from Exercise 6.3, we obtain

$$\boldsymbol{j}_1 = -\rho \mathfrak{D}_{12} \boldsymbol{\nabla} w_1,$$

which shows $\mathfrak{D}_{12} = D_{12}$.

Exercise 6.12
From the three-component version of the Gibbs-Duhem equation (4.54), we obtain

$$w_1 \boldsymbol{\nabla} \hat{\mu}_1 + w_2 \boldsymbol{\nabla} \hat{\mu}_2 + w_3 \boldsymbol{\nabla} \hat{\mu}_3 = \boldsymbol{0},$$

which allows us to write (6.49) as

$$\boldsymbol{j}_1 = -\left[L_{11} + (L_{11} + L_{12})\frac{w_1}{w_3}\right] \frac{\boldsymbol{\nabla} \hat{\mu}_1}{T} - \left[L_{12} + (L_{11} + L_{12})\frac{w_2}{w_3}\right] \frac{\boldsymbol{\nabla} \hat{\mu}_2}{T},$$
$$\boldsymbol{j}_2 = -\left[L_{12} + (L_{12} + L_{22})\frac{w_1}{w_3}\right] \frac{\boldsymbol{\nabla} \hat{\mu}_1}{T} - \left[L_{22} + (L_{12} + L_{22})\frac{w_2}{w_3}\right] \frac{\boldsymbol{\nabla} \hat{\mu}_2}{T}.$$

Substitution of (6.46) leads to the expressions

$$\begin{aligned}\boldsymbol{j}_1 = &-\frac{1}{T}\bigg\{\Big[L_{11}+(L_{11}+L_{12})\frac{w_1}{w_3}\Big]\frac{\partial\hat{\mu}_1}{\partial w_1}+\Big[L_{12}+(L_{11}+L_{12})\frac{w_2}{w_3}\Big]\frac{\partial\hat{\mu}_2}{\partial w_1}\bigg\}\boldsymbol{\nabla} w_1\\ &-\frac{1}{T}\bigg\{\Big[L_{11}+(L_{11}+L_{12})\frac{w_1}{w_3}\Big]\frac{\partial\hat{\mu}_1}{\partial w_2}+\Big[L_{12}+(L_{11}+L_{12})\frac{w_2}{w_3}\Big]\frac{\partial\hat{\mu}_2}{\partial w_2}\bigg\}\boldsymbol{\nabla} w_2\end{aligned}$$

$$\begin{aligned}\boldsymbol{j}_2 = &-\frac{1}{T}\bigg\{\Big[L_{12}+(L_{12}+L_{22})\frac{w_1}{w_3}\Big]\frac{\partial\hat{\mu}_1}{\partial w_1}+\Big[L_{22}+(L_{12}+L_{22})\frac{w_2}{w_3}\Big]\frac{\partial\hat{\mu}_2}{\partial w_1}\bigg\}\boldsymbol{\nabla} w_1\\ &-\frac{1}{T}\bigg\{\Big[L_{12}+(L_{12}+L_{22})\frac{w_1}{w_3}\Big]\frac{\partial\hat{\mu}_1}{\partial w_2}+\Big[L_{22}+(L_{12}+L_{22})\frac{w_2}{w_3}\Big]\frac{\partial\hat{\mu}_2}{\partial w_2}\bigg\}\boldsymbol{\nabla} w_2.\end{aligned}$$

For ideal mixtures (see Exercise 4.7), we write (4.60) for species β and divide by $\tilde{M}_\beta$ to convert from per mole to per mass chemical potential

$$\hat{\mu}_\beta = \hat{\mu}^0_\beta(T,p)+\frac{\tilde{R}T}{\tilde{M}_\beta}\ln x_\beta.$$

Differentiation with respect to w_α, holding temperature and pressure constant, gives

$$\Big(\frac{\partial\hat{\mu}_\beta}{\partial w_\alpha}\Big)_{T,p} = \frac{\tilde{R}T}{x_\beta\tilde{M}_\beta}\frac{\partial x_\beta}{\partial w_\alpha} = \frac{\tilde{R}T}{w_\beta\tilde{M}_\beta}\Big[\delta_{\beta\alpha}-w_\beta\tilde{M}\Big(\frac{1}{\tilde{M}_\alpha}-\frac{1}{\tilde{M}_k}\Big)\Big],$$

where the second equality follows using $x_\beta = c_\beta/c = \tilde{M}w_\beta/\tilde{M}_\beta$ and $1/\tilde{M} = \sum_{\gamma=1}^k w_\gamma/\tilde{M}_\gamma$. Substitution in the expression for $\boldsymbol{j}_1$ gives, after some tedious algebra, the following,

$$\begin{aligned}\boldsymbol{j}_1 = &-\frac{\tilde{R}\tilde{M}}{\tilde{M}_1\tilde{M}_2\tilde{M}_3 w_1 w_3}\bigg\{\Big[(1-w_2)^2\tilde{M}_2+w_2(w_1\tilde{M}_1+w_3\tilde{M}_3)\Big]L_{11}\\ &+w_1\Big[(1-w_1)\tilde{M}_1+(1-w_2)\tilde{M}_2-w_3\tilde{M}_3)\Big]L_{12}\bigg\}\boldsymbol{\nabla} w_1\\ &-\frac{\tilde{R}\tilde{M}}{\tilde{M}_1\tilde{M}_2\tilde{M}_3 w_2 w_3}\bigg\{w_2\Big[(1-w_1)\tilde{M}_1+(1-w_2)\tilde{M}_2-w_3\tilde{M}_3\Big]L_{11}\\ &+\Big[(1-w_1)^2\tilde{M}_1+w_1(w_2\tilde{M}_2+w_3\tilde{M}_3)\Big]L_{12}\bigg\}\boldsymbol{\nabla} w_2.\end{aligned}$$

Similarly, substitution in the expression for $\boldsymbol{j}_2$ gives

$$\begin{aligned}\boldsymbol{j}_2 = &-\frac{\tilde{R}\tilde{M}}{\tilde{M}_1\tilde{M}_2\tilde{M}_3 w_1 w_3}\bigg\{\Big[(1-w_2)^2\tilde{M}_2+w_2(w_1\tilde{M}_1+w_3\tilde{M}_3)\Big]L_{12}\\ &+w_1\Big[(1-w_1)\tilde{M}_1+(1-w_2)\tilde{M}_2-w_3\tilde{M}_3)\Big]L_{22}\bigg\}\boldsymbol{\nabla} w_1\end{aligned}$$

$$
- \frac{\tilde{R}\tilde{M}}{\tilde{M}_1\tilde{M}_2\tilde{M}_3 w_2 w_3}\left\{w_2\left[(1-w_1)\tilde{M}_1+(1-w_2)\tilde{M}_2-w_3\tilde{M}_3\right]L_{12}\right.
$$

$$
\left.+\left[(1-w_1)^2\tilde{M}_1+w_1(w_2\tilde{M}_2+w_3\tilde{M}_3)\right]L_{22}\right\}\boldsymbol{\nabla} w_2.
$$

Comparing these expressions with those in (6.50) we find

$$
D_{13} = \frac{\tilde{R}\tilde{M}}{\rho\tilde{M}_1\tilde{M}_2\tilde{M}_3 w_1 w_3}\left\{\left[(1-w_2)^2\tilde{M}_2+w_2(w_1\tilde{M}_1+w_3\tilde{M}_3)\right]L_{11}\right.
$$

$$
\left.+w_1\left[(1-w_1)\tilde{M}_1+(1-w_2)\tilde{M}_2-w_3\tilde{M}_3)\right]L_{12}\right\},
$$

$$
D_{12} = \frac{\tilde{R}\tilde{M}}{\rho\tilde{M}_1\tilde{M}_2\tilde{M}_3 w_2 w_3}\left\{w_2\left[(1-w_1)\tilde{M}_1+(1-w_2)\tilde{M}_2-w_3\tilde{M}_3\right]L_{11}\right.
$$

$$
\left.+\left[(1-w_1)^2\tilde{M}_1+w_1(w_2\tilde{M}_2+w_3\tilde{M}_3)\right]L_{12}\right\},
$$

$$
D_{21} = \frac{\tilde{R}\tilde{M}}{\rho\tilde{M}_1\tilde{M}_2\tilde{M}_3 w_1 w_3}\left\{\left[(1-w_2)^2\tilde{M}_2+w_2(w_1\tilde{M}_1+w_3\tilde{M}_3)\right]L_{12}\right.
$$

$$
\left.+w_1\left[(1-w_1)\tilde{M}_1+(1-w_2)\tilde{M}_2-w_3\tilde{M}_3)\right]L_{22}\right\},
$$

$$
D_{23} = \frac{\tilde{R}\tilde{M}}{\rho\tilde{M}_1\tilde{M}_2\tilde{M}_3 w_2 w_3}\left\{w_2\left[(1-w_1)\tilde{M}_1+(1-w_2)\tilde{M}_2-w_3\tilde{M}_3\right]L_{12}\right.
$$

$$
\left.+\left[(1-w_1)^2\tilde{M}_1+w_1(w_2\tilde{M}_2+w_3\tilde{M}_3)\right]L_{22}\right\}.
$$

Exercise 6.13

By combining (6.47), (6.51), and $\boldsymbol{v}_\alpha - \boldsymbol{v} = \boldsymbol{j}_\alpha/\rho_\alpha$, we obtain

$$
\sigma = \sum_{\alpha\beta=1}^{3}\rho_\alpha\rho_\beta R_{\alpha\beta}(\boldsymbol{v}_\alpha-\boldsymbol{v})\cdot(\boldsymbol{v}_\beta-\boldsymbol{v}) = \sum_{\alpha=1}^{3}\rho_\alpha^2 R_{\alpha\alpha}\boldsymbol{v}_\alpha^2 + 2\sum_{\alpha<\beta}\rho_\alpha\rho_\beta R_{\alpha\beta}\boldsymbol{v}_\alpha\cdot\boldsymbol{v}_\beta,
$$

where (6.52) and the symmetry $R_{\alpha\beta} = R_{\beta\alpha}$ have been used. We further write

$$
\sigma = \sum_{\alpha=1}^{3}\rho_\alpha^2 R_{\alpha\alpha}\boldsymbol{v}_\alpha^2 - \sum_{\alpha<\beta}\rho_\alpha\rho_\beta R_{\alpha\beta}(\boldsymbol{v}_\alpha-\boldsymbol{v}_\beta)^2 + \sum_{\alpha<\beta}\rho_\alpha\rho_\beta R_{\alpha\beta}(\boldsymbol{v}_\alpha^2+\boldsymbol{v}_\beta^2)
$$

which can be rewritten as

$$\sigma = -\sum_{\alpha<\beta} \rho_\alpha \rho_\beta R_{\alpha\beta}(\boldsymbol{v}_\alpha - \boldsymbol{v}_\beta)^2 + \sum_{\alpha\beta=1}^{3} \rho_\alpha \rho_\beta R_{\alpha\beta} \boldsymbol{v}_\alpha^2.$$

By using (6.52) again, we obtain the desired result.

Exercise 6.14
We begin by writing

$$\frac{1}{V}\frac{d\xi}{dt} = -\tilde{\Gamma} = -L_\Gamma \mathcal{A}.$$

Near equilibrium, we can write

$$\mathcal{A} \approx \mathcal{A}_{\text{eq}} + \frac{\partial \mathcal{A}}{\partial \xi}(\xi - \xi_{\text{eq}}) = \frac{\partial \mathcal{A}}{\partial \xi}(\xi - \xi_{\text{eq}}).$$

Combining (4.23) and (4.66) gives

$$dF = -SdT - pdV + \mathcal{A}d\xi.$$

so that $\mathcal{A} = (\partial F/\partial \xi)_{T,V}$. This allows us to write

$$\mathcal{A} = \Big(\frac{\partial^2 F}{\partial \xi^2}\Big)_{T,V}(\xi - \xi_{\text{eq}}) = \tilde{\nu}_\alpha^2 \Big(\frac{\partial^2 F}{\partial N_\alpha^2}\Big)_{T,V}(\xi - \xi_{\text{eq}}).$$

Combining this results with the first, we have

$$\frac{d\xi}{dt} = -L_\Gamma V \tilde{\nu}_\alpha^2 \Big(\frac{\partial^2 F}{\partial N_\alpha^2}\Big)_{T,V}(\xi - \xi_{\text{eq}}) = -\frac{1}{\tau_\Gamma}(\xi - \xi_{\text{eq}}),$$

where ${\tau_\Gamma}^{-1} = L_\Gamma V \tilde{\nu}_\alpha^2 (\partial^2 F/\partial N_\alpha^2)_{T,V}$. Integration subject to $\xi(0) = 0$ gives the desired result. Using the stability arguments in Section 4.4, the free energy is minimized at equilibrium: $(\partial^2 F/\partial N_\alpha^2)_{T,V} > 0$ so that the relaxation time τ_Γ is positive.

Exercise 6.15
With (4.60), we can write (6.57) as

$$x = \frac{1}{\tilde{R}T}\sum_{\alpha=q+1}^{k} \tilde{\nu}_\alpha \tilde{\mu}_\alpha^0 + \sum_{\alpha=q+1}^{k} \ln x_\alpha^{\tilde{\nu}_\alpha}, \qquad y = -\frac{1}{\tilde{R}T}\sum_{\alpha=1}^{q} \tilde{\nu}_\alpha^0 \tilde{\mu}_\alpha - \sum_{\alpha=1}^{q} \ln x_\alpha^{\tilde{\nu}_\alpha}.$$

Substitution in (6.58) gives

$$\tilde{\Gamma} = -L_\Gamma \left[e^{\sum_{\alpha=q+1}^{n} \frac{\tilde{\nu}_\alpha \tilde{\mu}_\alpha^0}{\tilde{R}T}} \prod_{\alpha=q+1}^{k} x_\alpha^{\tilde{\nu}_\alpha} - e^{-\sum_{\alpha=1}^{q} \frac{\tilde{\nu}_\alpha \tilde{\mu}_\alpha^0}{\tilde{R}T}} \prod_{\alpha=1}^{q} x_\alpha^{-\tilde{\nu}_\alpha} \right],$$

which, with $\Delta\tilde{g}^0 = \sum_{\alpha=1}^{k} \tilde{\nu}_\alpha \tilde{\mu}_\alpha^0$, gives (6.61), which can be written as

$$\tilde{\Gamma} = k_\mathrm{f} \prod_{\alpha=1}^{q} x_\alpha^{-\tilde{\nu}_\alpha} - k_\mathrm{r} \prod_{\alpha=q+1}^{k} x_\alpha^{\tilde{\nu}_\alpha}.$$

The rate constants for the forward and reverse reactions are given by,

$$k_\mathrm{f} = L_\Gamma e^{-\sum_{\alpha=1}^{q} \frac{\tilde{\nu}_\alpha \tilde{\mu}_\alpha^0}{\tilde{R}T}}, \qquad k_\mathrm{r} = e^{\frac{\Delta\tilde{g}^0}{\tilde{R}T}} k_\mathrm{f} = \frac{k_\mathrm{f}}{K},$$

where the equilibrium constant K is given by (4.72). At equilibrium, $\tilde{\Gamma} = 0$ so that

$$\prod_{\alpha=1}^{k} x_\alpha^{\tilde{\nu}_\alpha} = e^{-\sum_{\alpha=1}^{k} \frac{\tilde{\nu}_\alpha \tilde{\mu}_\alpha^0}{\tilde{R}T}},$$

which is expression in (4.71).

Exercise 7.1

The viscous dissipation terms in (7.3) can be written as

$$\eta\Big[[\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] : \boldsymbol{\nabla v} - \frac{2}{3}(\boldsymbol{\nabla} \cdot \boldsymbol{v})^2\Big] + \eta_\mathrm{d}(\boldsymbol{\nabla} \cdot \boldsymbol{v})^2.$$

Clearly, term the multiplied by η_d is non-negative, so we focus on the term multiplied by η.

$$\begin{aligned}
[\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] : \boldsymbol{\nabla v} - \frac{2}{3}(\boldsymbol{\nabla} \cdot \boldsymbol{v})^2 &= \frac{1}{2}[\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] : [\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] \\
&+ \frac{1}{2}[\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] : [\boldsymbol{\nabla v} - (\boldsymbol{\nabla v})^T] - \frac{2}{3}(\boldsymbol{\nabla} \cdot \boldsymbol{v})^2 \\
&= \frac{1}{2}\Big[[\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] : [\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] - \frac{8}{3}(\boldsymbol{\nabla} \cdot \boldsymbol{v})^2 + \frac{4}{3}(\boldsymbol{\nabla} \cdot \boldsymbol{v})^2\Big] \\
&= \frac{1}{2}\Big[[\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] : [\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] \\
&\qquad -\frac{4}{3}[\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] : \boldsymbol{\delta}(\boldsymbol{\nabla} \cdot \boldsymbol{v}) + \frac{4}{9}(\boldsymbol{\nabla} \cdot \boldsymbol{v})^2 \boldsymbol{\delta} : \boldsymbol{\delta}\Big] \\
&= \frac{1}{2}\Big[[\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] - \frac{2}{3}(\boldsymbol{\nabla} \cdot \boldsymbol{v})\boldsymbol{\delta}\Big] : \Big[[\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] - \frac{2}{3}(\boldsymbol{\nabla} \cdot \boldsymbol{v})\boldsymbol{\delta}\Big]
\end{aligned}$$

In the first equality, we have simply added and subtracted $1/2[\boldsymbol{\nabla v}+(\boldsymbol{\nabla v})^T] : (\boldsymbol{\nabla v})^T$. The second equality follows because the scalar product of a symmetric and antisymmetric tensor is zero. The third follows since $[\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T] : \boldsymbol{\delta} = 2\boldsymbol{\nabla} \cdot \boldsymbol{v}$, and $\boldsymbol{\delta} : \boldsymbol{\delta} = 3$. The last expression, which is the square of a difference, is of course nonnegative.

Exercise 7.2
For a single-component fluid, the last term on the right-hand side of (6.8) vanishes so that

$$\rho\hat{c}_p\Big(\frac{\partial T}{\partial t} + \boldsymbol{v}\cdot\boldsymbol{\nabla}T\Big) = -\alpha_p T\frac{Dp}{Dt} - \boldsymbol{\nabla}\cdot\boldsymbol{j}_q - \boldsymbol{\tau}:\boldsymbol{\nabla}\boldsymbol{v}$$

where we have set $\alpha_p = -1/\rho(\partial\rho/\partial T)_p$. Substitution of Fourier's law (6.4) and Newton's law of viscosity (6.6) gives (7.6).

Exercise 7.3
Using the identities in (5.45) and (5.74) in (7.2) gives

$$\begin{aligned}\rho\Big(\frac{\partial\boldsymbol{v}}{\partial t} + \frac{1}{2}\boldsymbol{\nabla}v^2 - \boldsymbol{v}\times(\boldsymbol{\nabla}\times\boldsymbol{v})\Big) &= \eta[\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\boldsymbol{v}) - \boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\boldsymbol{v})] \\ &\quad + \Big(\eta_{\rm d} + \frac{1}{3}\eta\Big)\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\boldsymbol{v}) - \boldsymbol{\nabla}p + \rho\boldsymbol{g}.\end{aligned}$$

Recognizing $\boldsymbol{w} = \boldsymbol{\nabla}\times\boldsymbol{v}$ gives (7.7).

Exercise 7.4
Substitution of (7.13) in (7.10a) gives

$$\frac{\partial\mathcal{P}}{\partial r} = \frac{\partial p^L}{\partial r} = \rho\Big(\frac{\beta R\Omega}{1-\beta^2}\Big)^2\Big[\frac{r}{(\beta R)^2} - \frac{2}{r} + \frac{(\beta R)^2}{r}\Big],$$

where we have used $\boldsymbol{g} = -g\boldsymbol{\delta}_z$. From (7.10c) we have

$$\frac{\partial\mathcal{P}}{\partial z} = \frac{\partial p^L}{\partial z} + \rho g = 0.$$

Now, we write the total differential for $p^{\rm L}$:

$$dp^{\rm L} = \frac{\partial p^{\rm L}}{\partial r}dr + \frac{\partial p^{\rm L}}{\partial z}dz.$$

Substitution and integration from $R, h(R)$ where $p^{\rm L} = 0$ to r, z gives

$$\begin{aligned}p^{\rm L}(r,z) = \frac{\rho}{2}\Big(\frac{\beta R\Omega}{1-\beta^2}\Big)^2\Big\{\frac{1}{\beta^2}\Big[\Big(\frac{r}{R}\Big)^2 - 1\Big] - 4\ln\big(\frac{r}{R}\big) - \beta^2\Big[\Big(\frac{R}{r}\Big)^2 - 1\Big]\Big\} \\ - \rho g\Big(z - h(R)\Big).\end{aligned}$$

Setting $p^{\rm L}(r, h(r)) = 0$ and solving for $h(r)$ gives

$$h(r) = h(R) - \frac{1}{2g}\Big(\frac{\beta R\Omega}{1-\beta^2}\Big)^2\Big\{\frac{1}{\beta^2}\Big[1 - \Big(\frac{r}{R}\Big)^2\Big] + 4\ln\big(\frac{r}{R}\big) + \beta^2\Big[\Big(\frac{R}{R}\Big)^2 - 1\Big]\Big\}.$$

Now, since the volume of fluid is constant, we can write

$$\pi(1-\beta^2)R^2L = \int_0^{h(r)}\int_0^{2\pi}\int_{\beta R}^{R} r\,dr\,d\theta\,dz$$
$$= 2\pi\int_{\beta R}^{R}\int_0^{h(r)} dz\,r\,dr = 2\pi\int_{\beta R}^{R} h(r)\,r\,dr.$$

Substituting $h(r)$ and integrating gives

$$h(r) = \frac{1}{2g}\Big(\frac{\beta R\Omega}{1-\beta^2}\Big)^2\Big[-\frac{2}{4}\frac{1}{\beta^2}-\frac{3}{2}+\frac{7}{r}\beta^2+\frac{1}{2}\beta^4$$
$$-3\beta^2\ln(\beta)+\left(\frac{r}{\beta R}\right)^2-4\ln\left(\frac{r}{R}\right)-\left(\frac{\beta R}{r}\right)^2\Big].$$

Finally, substitution for $h(r)$ in the expression for $p^{\mathrm{L}}(r,z)$ gives the expression in (7.14).

Exercise 7.5

If we introduce the dimensionless radius r/R and the dimensionless time $(\eta/\rho)t/R^2$, then (7.10b) becomes

$$\frac{\partial v_\theta}{\partial t} = \frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}(rv_\theta)\right] = \frac{\partial}{\partial r}\left(\frac{1}{r}\,v_\theta\right) + \frac{\partial^2}{\partial r^2}\,v_\theta,$$

so that we can identify the drift term $-1/r$ and the diffusion coefficient 2. If we further interpret $v_\theta/(\Omega R)$ as the probability density, the boundary conditions (7.11) imply probability densities 0 and 1 at the positions 1/2 and 1, respectively. The curve for $t = 0.01$ is produced by the following MATLAB® code:

```
% Simulation parameters
NTRAi=100;NTIME=1000;NHIST=100;DT=0.00001;
XMIN=0.5;DX=0.025;XMAX=1;
edges=XMIN:DX:XMAX;
centers=XMIN+DX/2:DX:XMAX-DX/2;

for K=1:NHIST
   % Generation of trajectories x
   NTRA=NTRAi;
   x=.99999999*ones(1,NTRA);
   for J=1:NTIME
      x=x-DT./x+random('Normal',0,sqrt(2*DT),[1,NTRA]);
      nm=NTRAi-length(find(and(x>XMAX-DX,x<=XMAX)));
      if nm>0
         y=.99999999*ones(1,nm);
         x=[x,y];
      end
      x(find(or(x<XMIN,x>XMAX)))=[];
      NTRA=length(x);
```

```
    end
    % Collection of NHIST histograms in matrix p
    p(K,:)=histc(x,edges)/NTRAi;
end

% Plot of simulation results
errorbar([centers NaN],mean(p),std(p)/sqrt(NHIST),'LineStyle','none')
```

Exercise 7.6

For the axisymmetric flow in spherical coordinates $v_r = v_r(r, \theta)$, $v_\theta = v_\theta(r, \theta)$, (5.43) gives,

$$w_\phi = \frac{1}{r}\frac{\partial}{\partial r}(r v_\theta) - \frac{1}{r}\frac{\partial v_r}{\partial \theta}.$$

Now, from (5.36) we find the following

$$v_r = \frac{1}{r^2 \sin\theta}\frac{\partial \psi}{\partial \theta}, \qquad v_\theta = -\frac{1}{r\sin\theta}\frac{\partial \psi}{\partial r}.$$

Substitution gives

$$w_\phi = -\frac{1}{r\sin\theta}\Big[\frac{\partial^2\psi}{\partial r^2} + \frac{\sin\theta}{r^2}\frac{\partial}{\partial \theta}\Big(\frac{1}{\sin\theta}\frac{\partial \psi}{\partial \theta}\Big)\Big],$$

which, with (7.18), gives (7.17).

Exercise 7.7

For incompressible flow, in (7.7) we can write $p \to p^{\mathrm{L}}$ and $-\boldsymbol{\nabla} p^{\mathrm{L}} + \rho \boldsymbol{g} = -\boldsymbol{\nabla}\mathcal{P}$. Taking the curl of this result, we obtain

$$\rho\Big[\boldsymbol{\nabla} \times \frac{\partial \boldsymbol{v}}{\partial t} + \frac{1}{2}\boldsymbol{\nabla} \times \boldsymbol{\nabla} v^2 - \boldsymbol{\nabla} \times \boldsymbol{v} \times (\boldsymbol{\nabla} \times \boldsymbol{v})\Big] = \eta \boldsymbol{\nabla} \times \nabla^2 \boldsymbol{v} - \boldsymbol{\nabla} \times \boldsymbol{\nabla}\mathcal{P},$$

where ρ is taken to be constant. Since $\boldsymbol{\nabla} \times \boldsymbol{\nabla} a = \boldsymbol{0}$ for any scalar a and $\boldsymbol{w} = \boldsymbol{\nabla} \times \boldsymbol{v}$, we have

$$\frac{\partial \boldsymbol{w}}{\partial t} + \boldsymbol{\nabla} \times (\boldsymbol{w} \times \boldsymbol{v}) = \nu \nabla^2 \boldsymbol{w},$$

where $\nu = \eta/\rho$. Rewriting the second term on the left-hand-side gives

$$\frac{\partial \boldsymbol{w}}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} \boldsymbol{w} - \boldsymbol{w} \cdot \boldsymbol{\nabla} \boldsymbol{v} + \boldsymbol{w}(\boldsymbol{\nabla} \cdot \boldsymbol{v}) + \boldsymbol{v}(\boldsymbol{\nabla} \cdot \boldsymbol{w}) = \nu \nabla^2 \boldsymbol{w},$$

The fourth term on the left-hand side is zero because of incompressibility and the fifth is zero because $\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} \times \boldsymbol{a} = 0$ for any vector $\boldsymbol{a}$, so that the above expression gives (7.19).

For the flow given by $v_r = v_r(r, z, t), v_z = v_z(r, z, t)$, we have

$$\boldsymbol{w} = \boldsymbol{\nabla} \times \boldsymbol{v} = \Big(\frac{\partial v_r}{\partial z} - \frac{\partial v_z}{\partial r}\Big)\boldsymbol{\delta}_\theta,$$

For the non-linear terms in (7.19), we have

$$\boldsymbol{w}\cdot\boldsymbol{\nabla}\boldsymbol{v} = \begin{bmatrix} 0 \\ w_\theta \\ 0 \end{bmatrix} \begin{bmatrix} \frac{\partial v_r}{\partial r} & 0 & \frac{\partial v_z}{\partial r} \\ 0 & \frac{v_r}{r} & 0 \\ \frac{\partial v_r}{\partial z} & 0 & \frac{\partial v_z}{\partial z} \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{v_r w_\theta}{r} \\ 0 \end{bmatrix},$$

$$\boldsymbol{v}\cdot\boldsymbol{\nabla}\boldsymbol{w} = \begin{bmatrix} v_r \\ 0 \\ v_z \end{bmatrix} \begin{bmatrix} 0 & \frac{\partial w_\theta}{\partial r} & 0 \\ -\frac{w_\theta}{r} & \frac{w_r}{r} & 0 \\ 0 & \frac{\partial w_\theta}{\partial z} & 0 \end{bmatrix} = \begin{bmatrix} 0 \\ v_r \frac{\partial w_\theta}{\partial r} + w_z \frac{\partial v_\theta}{\partial z} \\ 0 \end{bmatrix}.$$

Combining these results, we obtain

$$\frac{\partial w_\theta}{\partial t} + v_r \frac{\partial w_\theta}{\partial r} + v_z \frac{\partial w_\theta}{\partial z} - \frac{v_r w_\theta}{r} = \nu\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial w_\theta}{\partial r}\right) + \frac{\partial^2 w_\theta}{\partial z^2} - \frac{w_\theta}{r^2}\right],$$

which gives the result in (7.20).

Exercise 7.8

The equation for the wire temperature $\bar{T}$ is obtained by substitution of (4.57) and (6.4) in (5.67), which gives

$$\bar{\rho}\bar{\hat{c}}_p \frac{\partial \bar{T}}{\partial t} = \bar{\lambda}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \bar{T}}{\partial r}\right) + \boldsymbol{j}_1 \cdot \boldsymbol{f}_1,$$

where species 1 is the electrons that move in the immobile lattice of metal ions in the wire. From (5.65) and (6.37), we write the Lorentz force as follows: $\boldsymbol{f}_1 = z_1\boldsymbol{E} = (z_1/\sigma_{\rm el})\boldsymbol{i}$, where we have neglected driving forces due to temperature and chemical potential along the wire. The flux of electrons is obtained from (6.35), which gives: $\boldsymbol{j}_1 = -(m_{\rm el}/e)\boldsymbol{i} = (1/z_1)\boldsymbol{i}$. Substitution in the wire temperature equation gives

$$\bar{\rho}\bar{\hat{c}}_p \frac{\partial \bar{T}}{\partial t} = \bar{\lambda}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \bar{T}}{\partial r}\right) + \frac{P_{\rm el}}{\pi R^2},$$

where $P_{\rm el} = \pi R^2 R_{\rm el} i^2$ and $R_{\rm el} = 1/\sigma_{\rm el}$. Using the radial-average wire temperature given in (7.27), we obtain

$$\bar{\rho}\bar{\hat{c}}_p \frac{d\langle\bar{T}\rangle}{dt} = \frac{2}{R}\bar{\lambda}\frac{\partial \bar{T}}{\partial r}(R,t) + \frac{P_{\rm el}}{\pi R^2},$$

which is (7.26). Finally, if the energy flux is continuous at $r = R$, we can write $\bar{\lambda}\partial\bar{T}/\partial r(R) = \lambda\partial T/\partial r(R)$. Substitution of this in the expression for $\langle\bar{T}\rangle$ gives (7.28).

Exercise 7.9

The sample temperature T is governed by (7.22) and (7.23), with the boundary condition in (7.23b) replaced by (7.29). Using the change in variable $u = (T - T_0)/(P_{\text{el}}/4\pi\lambda)$ gives

$$\frac{\partial u}{\partial t} = \chi \frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial u}{\partial r}\Big),$$

$$u(r,0) = 0, \quad \lim_{r\to 0}\Big(r\frac{\partial u}{\partial r}\Big) = -2, \quad u(\infty, t) = 0.$$

The similarity transform $\xi = r/\sqrt{4\chi t}$ leads to the following,

$$\frac{\partial u}{\partial t} = -\frac{\xi}{2t}\frac{du}{d\xi}, \qquad \frac{\partial u}{\partial r} = \frac{1}{\sqrt{4\chi t}}\frac{du}{d\xi}.$$

This allows the problem to be written as

$$\frac{d^2 u}{d\xi^2} + \Big(2\xi + \frac{1}{\xi}\Big)\frac{du}{d\xi} = 0,$$

$$u(\infty) = 0, \quad \lim_{\xi\to 0}\Big(\xi\frac{du}{d\xi}\Big) = -2.$$

To solve this we let $Y = du/d\xi$ so that

$$\frac{dY}{d\xi} + \Big(2\xi + \frac{1}{\xi}\Big)Y = 0.$$

Integrating and using the second boundary condition gives

$$Y = \frac{du}{d\xi} = -2\xi^{-1}e^{\xi^2}$$

Integration with the first boundary condition gives

$$u(\xi) = 2\int_{\xi}^{\infty}\frac{e^{-y^2}}{y}dy$$

Finally, using the change of variable $x = y^2$ we obtain

$$u(\xi^2) = \int_{\xi^2}^{\infty}\frac{e^{-x}}{x}dx = E_1(\xi^2),$$

which is the expression given in (7.30) with $\xi = r/\sqrt{4\chi t}$.

Exercise 7.10
Setting $\rho = \rho_0$ in (7.1) gives $\boldsymbol{\nabla} \cdot \boldsymbol{v} = 0$. Setting $\rho = \rho_0$ in (7.2), except for the gravitational force term, gives

$$\rho_0\Big(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} \boldsymbol{v}\Big) = \eta \nabla^2 \boldsymbol{v} - \boldsymbol{\nabla}(p^{\mathrm{L}} + \rho_0 \phi) + (\rho - \rho_0)\boldsymbol{g},$$

where we have replaced p with p^{L} and added and subtracted $\rho_0 \boldsymbol{g}$. Substituting $\rho - \rho_0 = -\rho_0 \alpha_p (T - T_0)$, and dividing by ρ_0 gives (7.32). Setting $\rho = \rho_0$ and $\hat{c}_v = \hat{c}_p$ in (7.3), and neglecting the viscous dissipation term, gives

$$\rho_0 \hat{c}_p \Big(\frac{\partial T}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} T\Big) = \lambda \nabla^2 T,$$

which, after division by $\rho_0 \hat{c}_p$ gives (7.33).

Exercise 7.11
Using the change of variables $u = (w_{\mathrm{A}} - w_{\mathrm{A0}})/(w_{\mathrm{Aeq}} - w_{\mathrm{A0}})$, the problem in (7.38) and (7.39) becomes:

$$\frac{\partial u}{\partial t} = D_{AB} \frac{\partial^2 u}{\partial x_3^2},$$

$$u(x_3, 0) = u(\infty, t) = 0, \quad u(0, t) = 1.$$

Using the change of variables $\xi = x_3/\sqrt{4 D_{\mathrm{AB}} t}$ we obtain

$$\frac{d^2 u}{d\xi^2} + 2\xi \frac{du}{d\xi} = 0,$$

$$u(\infty) = 0, \quad u(0) = 1.$$

This problem is solved using the same method as in Exercise 7.9 and is given by

$$u = \frac{w_{\mathrm{A}} - w_{\mathrm{A0}}}{w_{\mathrm{Aeq}} - w_{\mathrm{A0}}} = 1 - \mathrm{erf}(\xi)$$

where the error function is defined in (7.46). From this solution we find

$$\frac{\partial w_{\mathrm{A}}}{\partial x_3}(0, t) = -(w_{\mathrm{Aeq}} - w_{\mathrm{A0}}) \frac{1}{\sqrt{\pi D_{AB} t}}$$

so that the mass flux of A is given by

$$(j_{\mathrm{A}})_3(0, t) = -\rho D_{\mathrm{AB}} \frac{\partial w_{\mathrm{A}}}{\partial x_3}(0, t) = \rho(w_{\mathrm{Aeq}} - w_{\mathrm{A0}}) \sqrt{\frac{D_{\mathrm{AB}}}{\pi t}}$$

The time rate of change of mass M is simply

$$\frac{dM}{dt} = A(j_{\rm A})_3(0,t) = \rho A(w_{\rm Aeq} - w_{\rm A0})\sqrt{\frac{D_{\rm AB}}{\pi t}}$$

Integration gives

$$M(t) - M(0) = \Delta M(t) = \rho A(w_{\rm Aeq} - w_{\rm A0})2\sqrt{\frac{D_{\rm AB}t}{\pi}}$$

For a film of finite thickness h, we have $\Delta M(\infty) = \rho A(w_{\rm Aeq} - w_{\rm A0})h$, so that

$$\frac{\Delta M(t)}{\Delta M(\infty)} = \frac{2}{\sqrt{\pi}}\sqrt{\frac{D_{\rm AB}t}{h^2}},$$

which is the result from (7.44) for $t \ll h^2/D_{\rm AB}$.

Exercise 7.12

For this problem we assume spherical symmetry so that all fields depend on r and t only, and if a velocity exists, it is purely radial $\boldsymbol{v} = v_r\boldsymbol{\delta}_r$. In this case, (7.34) takes the form

$$\frac{\partial w_{\rm A}}{\partial t} + v_r\frac{\partial w_{\rm A}}{\partial r} = D_{\rm AB}\Big[\frac{\partial^2 w_{\rm A}}{\partial r^2} + \frac{2}{r}\frac{\partial w_{\rm A}}{\partial r}\Big].$$

Since we have assumed ρ is constant, we have $\boldsymbol{\nabla}\cdot\boldsymbol{v} = 0$, or

$$\frac{\partial}{\partial r}(r^2 v_r) = 0,$$

which, when integrated, gives $v_r = f(t)/r^2$. Since $v_r(0,t)$ must be finite, we have $v_r(r,t) = 0$. Scaling radial position by R_0 and time by $R_0^2/D_{\rm AB}$, we obtain (7.56). The initial condition is $w_{\rm A}(r,0) = w_{\rm A0}$, and the boundary condition at the surfaces of the sphere is $w_{\rm A}(R,t) = w_{\rm Aeq}$. Also, the second term on the right hand side of (7.56) requires the boundary condition $\partial w_{\rm A}/\partial r(0,t) = 0$. Normalizing $w_{\rm A}$ with $w_{\rm A0}$ and $w_{\rm Aeq}$ gives (7.57).

Using the change of variable $u = rw_{\rm A}$, (7.56) and (7.57) become

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial r^2},$$

$$u(r,0) = 0, \qquad u(0,t) = 0, \qquad u(1,t) = 1,$$

which has the solution,[3]

$$u = r + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin(n\pi r)\exp(-n^2\pi^2 t).$$

[3] Crank, *Mathematics of Diffusion* (Oxford, 1975).

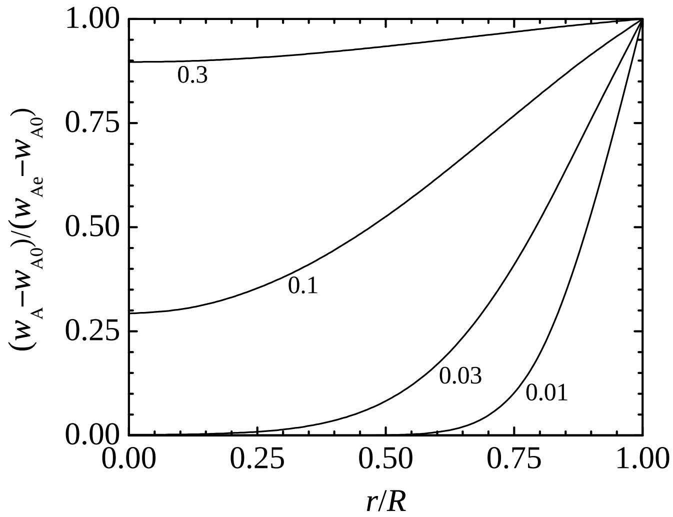

Figure C.12 Evolution of concentration profile for diffusion in a sphere given by (7.58) for $tD_{\mathrm{AB}}/R^2 = 0.01, 0.03, 0.1, 0.3$ (bottom to top).

Undoing the change in variable $w_{\mathrm{A}} = u/r$ and reintroducing the dimensional quantities gives (7.58). The concentration field from (7.58) is plotted in Figure C.12. The initial profiles in Figures 7.8 and C.12 are quite similar because the penetration is small and the effect of curvature is small. At later stages, curvature becomes important and diffusion process is faster in the spherical domain compared to the planar domain.

Exercise 7.13
Using L, L^2/χ and V to scale position, time and velocity, respectively, and ΔT to scale temperature relative to T_0 in (7.33) gives

$$\frac{\partial T}{\partial t} + \Big(\frac{VL}{\chi}\Big)\boldsymbol{v}\cdot\boldsymbol{\nabla}T = \nabla^2 T.$$

Using these and $\eta V/L$ to rescale pressure in (7.32) gives

$$\Big(\frac{\chi}{\nu}\Big)\frac{\partial \boldsymbol{v}}{\partial t} + \Big(\frac{VL}{\nu}\Big)\boldsymbol{v}\cdot\boldsymbol{\nabla}\boldsymbol{v} = \nabla^2\boldsymbol{v} - \boldsymbol{\nabla}\mathcal{P}_0 - \Big(\frac{\rho_0 L^3\alpha_p\Delta T}{\nu V}\Big)T\frac{\boldsymbol{g}}{g},$$

Choosing $V = \chi/L$ as the characteristic velocity leads to (7.59) and (7.60).

Exercise 7.14
The velocity field is postulated to have the following form: $v_r = 0; v_\theta(r,z) = rw(z); v_z = 0$, which satisfies (5.36). The boundary conditions for v_θ are $v_\theta(r,0) = 0$, and $v_\theta(r,H) = \Omega r$, so that $w(0) = 0$ and $w(H) = \Omega$. The r-, θ- and z-components of the Navier-Stokes equation (7.8) take the form:

$$\frac{\partial \mathcal{P}}{\partial r} = \rho \frac{{v_\theta}^2}{r}, \quad \frac{1}{r}\frac{\partial \mathcal{P}}{\partial \theta} = \eta\Big[\frac{\partial}{\partial r}\Big(\frac{1}{r}\frac{\partial}{\partial r}(rv_\theta)\Big) + \frac{\partial^2 v_\theta}{\partial z^2}\Big], \quad \frac{\partial \mathcal{P}}{\partial z} = 0$$

Substitution for v_θ in the θ-component gives

$$\frac{\partial \mathcal{P}}{\partial \theta} = \eta r^2 \frac{d^2 w}{dz^2} = f_1(r)$$

Integration gives

$$\mathcal{P} = f_1(r)\theta + f_2(r).$$

Now, since $\mathcal{P}(r,\theta) = \mathcal{P}(r, \theta + 2\pi)$, $f_1(r) = 0$, so that we have

$$\frac{d^2 w}{dz^2} = 0,$$

and $\mathcal{P} = f_2(r)$. Integrating and using the boundary conditions gives $w = \Omega z/H$, so that

$$v_\theta = \Omega r \frac{z}{H}$$

We now check the consistency of the velocity with the r- and z-components of the Navier-Stokes equation. Substitution of v_θ in the r-component and differentiation with respect to z gives:

$$\frac{\partial^2 \mathcal{P}}{\partial z \partial r} = 2\rho\Omega^2 \frac{r}{H^2}.$$

Differentiation of the z-component and differentiation with respect to r gives:

$$\frac{\partial^2 \mathcal{P}}{\partial r \partial z} = 0,$$

which shows the solution is inconsistent with r- and z-components of the Navier-Stokes equation. If we rescale r by R, z by H, and $\mathcal{P}$ by $\eta\Omega R/H$, we obtain

$$\frac{\partial \mathcal{P}}{\partial r} = N_{\text{Re}}\, rz^2,$$

where $N_{\text{Re}} = \rho\Omega RH/\eta$. Consistency of the solution is obtained when $N_{\text{Re}} \ll 1$, or for creeping flow, in which case $\partial\mathcal{P}/\partial r = 0$.

The torque exerted by the fluid on the lower disk is computed from (7.15), which gives

$$\boldsymbol{\mathcal{M}}_{\rm s} = \int_0^{2\pi}\int_0^R \boldsymbol{r}\times\Big[\boldsymbol{n}\cdot\boldsymbol{\pi}(r,0)\Big]rdrd\theta$$

where $\boldsymbol{r} = r\boldsymbol{\delta}_r$ and $\boldsymbol{n} = -\boldsymbol{\delta}_z$. The pressure tensor takes the form: $\boldsymbol{\pi} = \mu\frac{\Omega}{H}r(\boldsymbol{\delta}_\theta\boldsymbol{\delta}_z + \boldsymbol{\delta}_z\boldsymbol{\delta}_\theta)$ where we have set the isotropic contribution to zero. Substitution gives

$$\begin{aligned}\boldsymbol{\mathcal{M}}_{\rm s} &= -\int_0^{2\pi}\int_0^R (\boldsymbol{\delta}_r r)\times\left(\eta\frac{\Omega}{H}r\boldsymbol{\delta}_\theta\right)rdrd\theta\\ &= -\frac{\mu\Omega}{H}\int_0^{2\pi}\int_0^R r^3drd\theta\boldsymbol{\delta}_z = -\frac{\eta\Omega\pi R^4}{2H}\boldsymbol{\delta}_z,\end{aligned}$$

which gives the result in (7.61).

Exercise 7.15

As stated, the velocity field is given by $v_r = 0$, $v_\theta = v_\theta(r,\theta)$, $v_z = 0$. The velocity is constrained by $\boldsymbol{\nabla}\cdot\boldsymbol{v} = 0$, which takes the form

$$\frac{\partial v_\theta}{\partial\theta} = 0,$$

which restricts the velocity field, $v_\theta = v_\theta(r)$. The r-, θ- and z-components of the Navier-Stokes equation (7.8) can, for creeping flow, be written as,

$$\frac{\partial\mathcal{P}}{\partial r} = 0, \qquad \frac{1}{r}\frac{\partial\mathcal{P}}{\partial\theta} = \eta\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(rv_\theta)\right), \qquad \frac{\partial\mathcal{P}}{\partial z} = 0.$$

Hence, we can write the θ-component as

$$\eta r\frac{d}{dr}\left(\frac{1}{r}\frac{d}{dr}(rv_\theta)\right) = \frac{d\mathcal{P}}{d\theta} = k_1.$$

Integrating with respect to θ, we obtain

$$P = k_1\theta + k_2.$$

Hence, we can write

$$k_1 = \frac{\Delta\mathcal{P}}{\pi}, \qquad \Delta\mathcal{P} = \mathcal{P}(\alpha) - \mathcal{P}(\alpha-\pi).$$

Substitution for k_1 in the θ-component gives

$$r\frac{d}{dr}\left(\frac{1}{r}\frac{d}{dr}(rv_\theta)\right) = \frac{\Delta\mathcal{P}}{\pi\eta} = c_0,$$

which is solved subject to the boundary conditions

$$v_\theta(R) = \Omega R, \qquad v_\theta(\beta R) = 0.$$

Twice integrating the expression above we obtain

$$v_\theta = \frac{c_0}{2} r(\ln r - 1/2) + \frac{c_1}{2} r + \frac{c_2}{r}.$$

Applying the boundary conditions, we find

$$\frac{c_1}{2} = \frac{\Omega}{1-\beta^2} + \frac{c_0}{2}\Big(\frac{1}{2} - \frac{\ln R - \beta^2 \ln \beta R}{1-\beta^2}\Big), \qquad c_2 = -\frac{\Omega(\beta R)^2}{1-\beta^2} - \frac{c_0}{2}\frac{(\beta R)^2 \ln \beta}{1-\beta^2}$$

so that the velocity is given by

$$v_\theta = \frac{\Omega R}{1-\beta^2}\Big(\frac{r}{R} - \beta^2 \frac{R}{r}\Big) + \frac{R\Delta\mathcal{P}}{2\pi(1-\beta^2)\eta}\Big[\frac{r}{R}\ln\frac{r}{R} - \beta^2\Big(\frac{r}{R}\ln\frac{r}{\beta R} - \frac{R}{r}\ln\frac{1}{\beta}\Big)\Big]$$

Now, from (5.41) we have $\mathcal{P} = p^{\mathrm{L}} + \rho\phi$, where $\boldsymbol{g} = -\boldsymbol{\nabla}\phi$. Since $\boldsymbol{g} = -g\boldsymbol{\delta}_2 = -g\sin\theta\boldsymbol{\delta}_r - g\cos\theta\boldsymbol{\delta}_\theta$, we can write

$$d\phi = \frac{\partial\phi}{\partial r}dr + \frac{\partial\phi}{\partial\theta}d\theta = g\sin\theta dr + g\cos\theta r d\theta \approx gR\cos\theta d\theta.$$

Integrating from $\theta = 0$ with $\phi(0) = 0$, we obtain

$$\phi = gR\sin\theta.$$

Now, we write

$$\Delta\mathcal{P} = \mathcal{P}(\alpha) - \mathcal{P}(\alpha - \pi) = p(\alpha) + \rho\phi(\alpha) - [p(\alpha-\pi) + \rho\phi(\alpha-\pi)]$$

Now, since $p^{\mathrm{L}}(\alpha) = p_0$ and $p^{\mathrm{L}}(\alpha - \pi) = p_0$, we obtain $\Delta\mathcal{P} = 2\rho g R\sin\alpha \approx 2\rho g h$. Hence, the velocity is given by

$$v_\theta = \frac{\Omega R}{1-\beta^2}\Big(\frac{r}{R} - \beta^2 \frac{R}{r}\Big) + \frac{\rho g h R^2}{\pi(1-\beta^2)\eta}\Big[\frac{r}{R}\ln\frac{r}{R} - \beta^2\Big(\frac{r}{R}\ln\frac{r}{\beta R} - \frac{R}{r}\ln\frac{1}{\beta}\Big)\Big]$$

Now, since there can be no net flow, we can write

$$\int_{\beta R}^{R} v_\theta r dr = R^2 \int_\beta^1 v_\theta r dr = 0.$$

Substitution for v_θ gives

$$\frac{\rho g h R}{\pi\eta}\int_\beta^1 \Big[r^2\ln r - \beta^2 r^2 \ln\frac{r}{\beta} + \beta^2\ln\frac{1}{\beta}\Big]dr + \Omega\int_\beta^1 (r^2 - \beta^2)dr = 0.$$

Evaluating the integrals and solving for h, we obtain

$$h = \frac{3\pi\eta\Omega}{\rho g R}\frac{(1-\beta)(1+2\beta)}{1+\beta-\beta^3-\beta^4+6\beta^2\ln\beta}.$$

Exercise 8.1

The velocity field has the form: $v_r = v_\theta = 0, v_z = v_z(r, z)$. Since the density is constant, we apply (5.36), which gives

$$\frac{\partial v_z}{\partial z} = 0.$$

This constrains the velocity profile to be the same at each cross section along the tube: $v_z = v_z(r)$. The r-, θ- and z-components of (7.8) simplify to

$$\frac{\partial \mathcal{P}}{\partial r} = 0, \qquad \frac{\partial \mathcal{P}}{\partial \theta} = 0, \qquad \frac{\partial \mathcal{P}}{\partial z} = \eta \frac{1}{r}\frac{d}{dr}\Big(r\frac{dv_z}{dr}\Big).$$

These constrain the modified pressure $\mathcal{P} = \mathcal{P}(z)$. Integrating the z-component twice with respect to r and enforcing regularity at the origin and no slip at the tube wall $v_z(R) = 0$, we obtain

$$v_z = \frac{R^2}{4\eta}\Big(-\frac{d\mathcal{P}}{dz}\Big)\Big[1 - \Big(\frac{r}{R}\Big)^2\Big].$$

Using (8.4), we have

$$\mathcal{W} = 2\pi \int_0^R \rho v_z r dr = \frac{\rho_0 \pi R^4}{8\eta}\Big(-\frac{d\mathcal{P}}{dz}\Big),$$

or

$$\frac{\mathcal{W}}{\rho_0 \pi R^2} = V = \frac{R^2}{8\eta}\Big(-\frac{d\mathcal{P}}{dz}\Big).$$

Integration from $z = L$ with $\mathcal{P}(L) = P_L$ gives

$$\mathcal{P} = \mathcal{P}_L + \frac{8\eta V L}{R^2}\Big(1 - \frac{z}{L}\Big),$$

which leads to

$$\mathcal{W} = \frac{\rho_0 \pi R^4 (P_0 - P_L)}{8\eta},$$

where $\mathcal{P}(0) = P_0$. Since $\mathcal{P} = p^{\mathrm{L}} + \rho_0\phi$, we can write $P_0 - P_L = p^{\mathrm{L}}(0) - p^{\mathrm{L}}(L) + \rho_0[\phi(0) - \phi(L)]$. Now, since $\boldsymbol{g} = -\boldsymbol{\nabla}\phi$, we have $\partial\phi/\partial z = -\boldsymbol{g}\cdot\boldsymbol{\delta}_z$. Integration gives $\phi(0) - \phi(L) = \boldsymbol{g}\cdot\boldsymbol{\delta}_z L$ so that $P_0 - P_L = p_0 - p_L + \rho_0 \boldsymbol{g}\cdot\boldsymbol{\delta}_z L$, which gives

$$\mathcal{W} = \frac{\rho_0 \pi R^4 [(p_0 - p_L) + \rho_0 \boldsymbol{g}\cdot\boldsymbol{\delta}_z L]}{8\eta}.$$

Exercise 8.2
The velocity field has the form $v_1 = v_1(x_1, x_2), v_2 = v_3 = 0$. For constant ρ, the velocity is constrained by (5.36), or

$$\frac{\partial v_1}{\partial x_1} = 0,$$

so that $v_1 = v_1(x_2)$. Using this velocity field, we find from (7.8),

$$\frac{\partial p^{\mathrm{L}}}{\partial x_1} = \eta \frac{d^2 v_1}{dx_2^2}, \qquad \frac{\partial p^{\mathrm{L}}}{\partial x_2} = 0, \qquad \frac{\partial p^{\mathrm{L}}}{\partial x_3} = 0.$$

Applying the second and third equations, and integration of the first equation gives,

$$v_1 = \frac{1}{2\eta} \frac{dp^{\mathrm{L}}}{dx_1} x_2^2 + c_1 x_2 + c_2.$$

Applying the no-slip boundary conditions $v_1(\pm H) = 0$, we obtain

$$v_1 = -\frac{H^2}{2\eta} \frac{dp^{\mathrm{L}}}{dx_1} \Big[1 - \Big(\frac{x_2}{H} \Big)^2 \Big].$$

Similar to (8.4), we can write

$$\mathcal{W} = 2B \int_0^H \rho v_1 dx_2 = \frac{2\rho_0 B H^3}{3\eta} \Big(-\frac{dp^{\mathrm{L}}}{dx_1} \Big),$$

or

$$\frac{\mathcal{W}}{2\rho_0 B H} = V = \frac{H^2}{3\eta} \Big(-\frac{dp^{\mathrm{L}}}{dz} \Big).$$

Integration with $p^{\mathrm{L}}(L) = p_L$ and $p^{\mathrm{L}}(0) = p_0$ gives

$$\mathcal{W} = \frac{2\rho_0 B H^3 (p_0 - p_L)}{3\eta L}.$$

Exercise 8.3
For incompressible flow in a tube with $v_z = v_z(r)$, the vorticity $w_\theta = w_\theta(r)$ is simply

$$w_\theta = -\frac{dv_z}{dr}.$$

In this case, (7.20) simplifies to

$$\frac{d}{dr} \Big(\frac{1}{r} \frac{d}{dr} (r w_\theta) \Big) = 0.$$

Integrating twice and enforcing regularity at the origin gives

$$w_\theta = \frac{c_1}{2} r,$$

where c_1 is a constant. Now, from (7.7) (see Exercise 7.3), we can write

$$\frac{dp^{\mathrm{L}}}{dz} = -\eta[\boldsymbol{\nabla} \times \boldsymbol{w}]_z = -\eta \frac{1}{r}\frac{d}{dr}(r w_\theta) = -\eta c_1.$$

Integration with $p^{\mathrm{L}}(L) = p_L$ and $p^{\mathrm{L}}(0) = p_0$ gives

$$c_1 = \frac{p_0 - p_L}{\eta L},$$

so that

$$w_\theta = \frac{p_0 - p_L}{2\eta L} r.$$

Combining this with the definition for w_θ and integrating with $v_z(R) = 0$ gives (8.3).

Exercise 8.4
From (8.12), we obtain

$$\frac{\partial}{\partial r}(\rho r v_r) = -\frac{\partial}{\partial z}(\rho r v_z).$$

Analogous to (5.8), we write

$$\frac{\partial}{\partial r}\Big(\frac{\partial \psi}{\partial z}\Big) = \frac{\partial}{\partial z}\Big(\frac{\partial \psi}{\partial r}\Big).$$

Comparing the two equations, we have

$$v_r = \frac{1}{\rho r}\frac{\partial \psi}{\partial z}, \qquad v_z = -\frac{1}{\rho r}\frac{\partial \psi}{\partial r}.$$

Multiplication of the second by $2r\rho$ and integrating, we have

$$2\int_0^1 \rho v_z r dr = -2\int_0^1 d\psi = 2[\psi(0,z) - \psi(1,z)].$$

From (8.18), the left-hand side is equal to one so that we obtain the desired result.

Exercise 8.5
Setting $v_r^{(1)} = 0$ we have from (8.22),

$$\frac{\partial v_z^{(1)}}{\partial z} = 16(1 - r^2).$$

This allows us to write (8.23) as

$$\frac{\partial p^{(1)}}{\partial r} = \frac{1}{3}\frac{\partial^2 v_z^{(1)}}{\partial r \partial z} = -\frac{32}{3}r,$$

and (8.24) as

$$\frac{\partial p^{(1)}}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial v_z^{(1)}}{\partial r}\Big) - 16N_{\mathrm{Re}}(1-r^2)^2.$$

Differentiation of $\partial p^{(1)}/\partial r$ with respect to $\bar{z}$ gives $\partial^2 p^{(1)}/\partial \bar{z}\partial r = 0$ so that differentiation of the expression above for $\partial p^{(1)}/\partial \bar{z}$ with respect to r gives

$$\frac{\partial}{\partial r}\Big[\frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial v_z^{(1)}}{\partial r}\Big)\Big] = -64N_{\mathrm{Re}}r(1-r^2).$$

Integration of the above expression and applying the boundary conditions $v_z^{(1)}(1,z) = \partial v_z^{(1)}/\partial r(0,z) = 0$ leads to

$$v_z^{(1)} = -\frac{f_0}{4}(1-r^2) + \frac{2}{9}N_{\mathrm{Re}}(7 - 9r^4 + 2r^6).$$

Now, since $\langle \rho v_z \rangle = 1$ and $\langle \rho^{(0)} v_z^{(0)} \rangle = 1$, we have

$$\int_0^1 \rho^{(1)} v_z^{(0)} r dr + \int_0^1 \rho^{(0)} v_z^{(1)} r dr = 0,$$

where $\rho^{(0)} = 1$ and $\rho^{(1)} = p^{(0)} = 8(1/\beta - z)$. Substitution and performing the integrations gives $f_0/4 = 16(1/\beta - z) + 2N_{\mathrm{Re}}$. Combining these results we obtain (8.25). For $\partial p^{(1)}/\partial z$, we can now write

$$\frac{\partial p^{(1)}}{\partial z} = 64(1/\beta - z) - 8N_{\mathrm{Re}}.$$

Now, we write $dp^{(1)} = (\partial p^{(1)}/\partial r)dr + (\partial p^{(1)}/\partial z)dz$ and integrate subject to the boundary condition $p^{(1)}(1, 1/\beta) = 0$, which gives (8.26).

Exercise 8.6

We retain all assumptions made in Section 7.2 with the exception that the flow is isothermal and allow the viscosity to be temperature dependent: $\eta(T) = \eta_0[1 + A(T - T_0)]$, where η_0 and A are constants. Hence, at steady state, the velocity and temperature fields have the form $v_r = v_z = 0$, $v_\theta = v_\theta(r)$ and $T = T(r)$. It will be convenient to use dimensionless forms of the governing equations. Spatial position will be scaled by R, velocity by ΩR and temperature, relative to T_0, by $1/A$.

The r-component of the Navier-Stokes equation takes the form:

$$(1+T)\frac{d}{dr}\Big(\frac{1}{r}\frac{d}{dr}(rv_\theta)\Big)+\frac{dT}{dr}\Big(\frac{1}{r}\frac{d}{dr}(rv_\theta)\Big)=0.$$

The temperature equation can be written as follows:

$$\frac{1}{r}\frac{d}{dr}\Big(r\frac{dT}{dr}\Big)+N_{\rm Na}(1+T)\Big[r\frac{d}{dr}\Big(\frac{v_\theta}{r}\Big)\Big]^2=0,$$

where $N_{\rm Na}=\eta_0\Omega^2R^2/(\lambda/A)$. The boundary conditions for velocity are given by

$$v_\theta(\beta)=0,\quad v_\theta(1)=1,$$

and for temperature by

$$T(\beta)=0,\quad T(1)=0.$$

Note that the system ordinary differential equations for v_θ and T become decoupled and linear for $N_{\rm Na}=0$, in which case $T=0$ and v_θ is given in (7.13).

To implement the perturbation method, we write the following: $v_\theta = v_\theta^{(0)}+N_{\rm Na}v_\theta^{(1)}+...$ and $T=T^{(0)}+N_{\rm Na}T^{(1)}+...$. Substitution and collecting $(N_{\rm Na})^0$ terms we have the following:

$$(1+T^{(0)})\frac{d}{dr}\Big(\frac{1}{r}\frac{d}{dr}(rv_\theta^{(0)})\Big)+\frac{dT^{(0)}}{dr}\Big(\frac{1}{r}\frac{d}{dr}(rv_\theta^{(0)})\Big)=0,$$

$$\frac{1}{r}\frac{d}{dr}\Big(r\frac{dT^{(0)}}{dr}\Big)=0.$$

Solving for $T^{(0)}$ subject to $T^{(0)}(\beta)=T^{(0)}(1)=0$ gives $T^{(0)}=0$. We can now solve for $v_\theta^{(0)}$ subject to $v_\theta^{(0)}(\beta)=0$, $v_\theta^{(0)}(1)=1$, which gives

$$v_\theta^{(0)}=\frac{\beta}{1-\beta^2}\Big(\frac{r}{\beta}-\frac{\beta}{r}\Big).$$

Using these results and collecting $(N_{\rm Na})^1$ terms we have

$$\frac{d}{dr}\Big(\frac{1}{r}\frac{d}{dr}(rv_\theta^{(1)})\Big)=-\frac{dT^{(1)}}{dr}\Big(\frac{1}{r}\frac{d}{dr}(rv_\theta^{(0)})\Big)=-\frac{\beta^2}{1-\beta^2}\frac{dT^{(1)}}{dr},$$

$$\frac{1}{r}\frac{d}{dr}\Big(r\frac{dT^{(1)}}{dr}\Big)=-\Big[r\frac{d}{dr}\Big(\frac{v_\theta^{(0)}}{r}\Big)\Big]^2=-\frac{4\beta^4}{(1-\beta^2)^2}\frac{1}{r^4}.$$

Solving for $T^{(1)}$ subject to $T^{(1)}(\beta)=T^{(1)}(1)=0$ gives

$$T^{(1)}=\frac{\beta^2}{(1-\beta^2)^2}\Big[\beta^2-\frac{\beta^2}{r^2}+(1-\beta^2)\frac{\ln r}{\ln\beta}\Big].$$

Substitution and solving for $v_\theta^{(1)}$ subject to $v_\theta^{(1)}(\beta) = v_\theta^{(1)}(1) = 0$ gives

$$v_\theta^{(1)} = \frac{\beta^4}{(1-\beta^2)^3}\Big[\frac{1}{r} - r + \Big(\frac{2}{r} - \frac{1-\beta^2}{\beta^2 \ln\beta} r\Big)\ln r - \frac{2\ln\beta}{1-\beta^2}\Big(\frac{1}{r} - r\Big)\Big].$$

Normalizing the torque on the stationary cylinder by the result for isothermal flow given in (7.16), we can write

$$\frac{\mathcal{M}_\mathrm{s}(1-\beta^2)}{4\pi\beta^2 R^2 L\Omega\eta_0} = \frac{2}{1-\beta^2}\Big[\frac{dv_\theta}{dr}(\beta) - \frac{v_\theta(\beta)}{\beta}\Big].$$

Substitution of $v_\theta = v_\theta^{(0)} + N_\mathrm{Na} v_\theta^{(1)}$ gives the desired expression. For $A < 0$, the correction due to viscous dissipation is less than one.

Exercise 8.7

We begin with (8.31) simplifies to

$$\frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial v_z}{\partial r}\Big) = \frac{1}{\eta}\frac{dp}{dz},$$

where $p = p(z)$. Integrating twice with respect to r and using the boundary conditions in (8.15b) and (8.16b) gives

$$v_z = -\frac{R^2}{4\eta}\frac{dp}{dz}\Big[1 - \Big(\frac{r}{R}\Big)^2\Big].$$

Substitution in (8.12) gives

$$\frac{1}{r}\frac{\partial}{\partial r}(\rho r \bar{v}_r) = \frac{R^2}{4\eta}\Big[1 - \Big(\frac{r}{R}\Big)^2\Big]\frac{d}{dz}\Big(\rho\frac{dp}{dz}\Big).$$

Integrating with respect to r and using the boundary conditions in (8.15a) and (8.16a) gives (8.32). Integration of (8.32) gives

$$\rho\frac{dp}{dz} = c_0,$$

Now, using (8.18), we find $c_0 = -8\eta\rho_0 V/R^2$, which gives (8.33). Making these results dimensionless and using (8.11), we have

$$(1+\epsilon p)\frac{dp}{dz} = -8,$$

Integration subject to the boundary condition $p(1) = 0$ gives (8.34).

Exercise 8.8

Using H_0 to scale spatial position gives a properly scaled z, which suggests we use $H_0/\bar{\beta} = R$ to scale radial position, which we denote as $\bar{r}$. Similarly, we scale v_z by V, and v_r by $V/\bar{\beta}$, which we denote as $\bar{v}_r$. For flow in a tube driven by an externally imposed pressure difference, the characteristic stress is divided by the aspect ratio of the tube $\beta = R/L$. This would suggest the characteristic stress for squeezing flow is $\eta V/(H_0\bar{\beta})$. However, since the pressure gradient in squeezing flow is induced internally, it seems reasonable to include an extra factor of $\bar{\beta}$, so that stress is scaled by $\eta V/(H_0\bar{\beta}^2)$. Finally, time is scaled by H_0/V. This leads to the following dimensionless forms of the continuity and Navier-Stokes equations:

$$\frac{1}{\bar{r}}\frac{\partial}{\partial \bar{r}}(\bar{r}\bar{v}_r) + \frac{\partial v_z}{\partial z} = 0,$$

$$N_{\mathrm{Re}}\Big(\frac{\partial \bar{v}_r}{\partial t} + \bar{v}_r\frac{\partial \bar{v}_r}{\partial \bar{r}} + v_z\frac{\partial \bar{v}_r}{\partial z}\Big) = -\frac{\partial p^{\mathrm{L}}}{\partial \bar{r}} + \bar{\beta}^2\frac{\partial}{\partial \bar{r}}\Big(\frac{1}{\bar{r}}\frac{\partial}{\partial \bar{r}}(\bar{r}\bar{v}_r)\Big) + \frac{\partial^2 \bar{v}_r}{\partial z^2}$$

$$\bar{\beta}^2 N_{\mathrm{Re}}\Big(\frac{\partial v_z}{\partial t} + \bar{v}_r\frac{\partial v_z}{\partial \bar{r}} + v_z\frac{\partial v_z}{\partial z}\Big) = -\frac{\partial p^{\mathrm{L}}}{\partial \bar{z}} + \bar{\beta}^4\frac{1}{\bar{r}}\frac{\partial}{\partial \bar{r}}\Big(\bar{r}\frac{\partial v_z}{\partial \bar{r}}\Big) + \bar{\beta}^2\frac{\partial^2 v_z}{\partial z^2}$$

Velocity boundary conditions assuming no slip and impermeable disks are at the lower disk given by

$$\bar{v}_r(\bar{r},0,t) = 0 \quad v_z(\bar{r},0,t) = 0, \quad 0 \le \bar{r} \le 1,$$

and at the upper disk by

$$\bar{v}_r(\bar{r},H,t) = 0, \quad v_z(\bar{r},H,t) = -1, \quad 0 \le \bar{r} \le 1,$$

where $H = 1 - t$.

Invoking the lubrication ($\bar{\beta} \ll 1$) and creeping flow ($N_{\mathrm{Re}} = \rho V H_0/\eta \ll 1$) approximations, the z-component of the Navier-Stokes simplifies to $\partial p^{\mathrm{L}}/\partial z = 0$ so that $p^{\mathrm{L}} = p^{\mathrm{L}}(\bar{r}, t)$. The r-component of the Navier-Stokes simplifies to the following:

$$\frac{\partial^2 \bar{v}_r}{\partial z^2} = \frac{\partial p^{\mathrm{L}}}{\partial \bar{r}}.$$

Integrating twice with respect to z and using the boundary conditions above for $\bar{v}_r$ gives

$$\bar{v}_r = \frac{H^2}{2}\frac{\partial p^{\mathrm{L}}}{\partial \bar{r}}\Big[\Big(\frac{z}{H}\Big)^2 - \Big(\frac{z}{H}\Big)\Big].$$

Substitution in the continuity equation and integrating with respect to z subject to the boundary conditions above for v_z gives Reynolds equation:

$$\frac{1}{\bar{r}}\frac{\partial}{\partial \bar{r}}\Big(\bar{r}\frac{\partial p^{\mathrm{L}}}{\partial \bar{r}}\Big) = -\frac{12}{H^3}.$$

Integration with respect to $\bar{r}$ and requiring the pressure gradient be bound at $\bar{r} = 0$ gives

$$\frac{\partial p^{\mathrm{L}}}{\partial \bar{r}} = -\frac{6}{H^3}\bar{r}.$$

Substitution in the expression for $\bar{v}_r$ gives

$$\bar{v}_r = -\frac{3}{H}\Big[\Big(\frac{z}{H}\Big)^2 - \Big(\frac{z}{H}\Big)\Big]\bar{r},$$

which, when substituted in the continuity equation and is followed integration with respect to z, gives

$$v_z = 3\Big[\Big(\frac{z}{H}\Big)^3 - \frac{3}{2}\Big(\frac{z}{H}\Big)^2\Big].$$

Integrating the expression for the pressure gradient and taking $p^{\mathrm{L}}(1,t) = 0$ gives

$$p^{\mathrm{L}} = \frac{3}{H^3}(1 - \bar{r}^2).$$

To find the force on the upper disk, we use (8.39), which takes the form

$$\boldsymbol{\mathcal{F}}_{\mathrm{s}} = \int_0^{2\pi}\int_0^1 \boldsymbol{\delta}_z \cdot \boldsymbol{\pi}(r,H,t) r dr d\theta = 2\pi \int_0^1 p^{\mathrm{L}}(r,t) r dr \boldsymbol{\delta}_z,$$

where the second equality follows because $\boldsymbol{\pi}(r,H,t) = p^{\mathrm{L}}(r,t)\boldsymbol{\delta}$. Substitution for p^{L} and integration gives

$$\mathcal{F}_{\mathrm{s}} = \frac{3\pi}{2H^3}.$$

Reintroducing dimensional variables gives the Stefan equation.

Exercise 8.9

Using R_0 to scale radial position, the dimensionless tube radius is given by follows: $R(z) = 1 + \tan(\varphi)z$. Following Exercise 8.7, we have for the dimensionless pseudo-pressure field $p^{\mathrm{L}} = p^{\mathrm{L}}(z)$ and

$$\frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial v_z}{\partial r}\Big) = \frac{dp^{\mathrm{L}}}{dz},$$

which is subject to the boundary conditions in (8.15) and

$$v_r(R,z) = 0, \quad v_z(R,z) = 0, \quad 0 \le z \le 1/\beta.$$

Integration subject to the boundary conditions for v_z gives

$$v_z = - - \frac{1}{4}\frac{dp^{\mathrm{L}}}{dz}R^2\Big[1 - \Big(\frac{r}{R}\Big)^2\Big].$$

Using the continuity equation we can write

$$\frac{1}{r}\frac{\partial}{\partial r}(rv_r) = -\frac{\partial v_z}{\partial z} = \frac{1}{4}\frac{\partial}{\partial z}\Big[(R^2-r^2)\frac{dp^{\mathrm{L}}}{dz}\Big] = \frac{1}{4}(R^2-r^2)\frac{d^2p^{\mathrm{L}}}{dz^2} + \frac{1}{2}R\frac{dR}{dz}\frac{dp^{\mathrm{L}}}{dz}.$$

Integrating with respect to r and using the boundary conditions for v_r gives Reynolds equation:

$$\frac{d}{d\bar{z}}\Big(R^4\frac{dp^{\mathrm{L}}}{d\bar{z}}\Big) = 0.$$

Integration with respect to z gives

$$R^4\frac{dp^{\mathrm{L}}}{dz} = c_1,$$

Now, since

$$2\int_0^R v_z r dr = 1,$$

we find $c_1 = -8$, so that

$$v_z = \frac{2}{R^2}\Big[1-\Big(\frac{r}{R}\Big)^2\Big],$$

where $R(z) = 1 + \tan(\varphi)z$. To find p^{L}, we write

$$[1+\tan(\varphi)z]^4\frac{dp^{\mathrm{L}}}{dz} = -8,$$

Integration subject to the boundary condition $p^{\mathrm{L}}(1/\beta) = 0$ gives

$$\begin{aligned} p^{\mathrm{L}} &= \frac{8\beta/\tan(\varphi)}{3(1+\tan(\varphi)/\beta)^3}\Big[\Big(\frac{1+\tan(\varphi)/\beta}{1+\tan(\varphi)z}\Big)^3 - 1\Big] \\ &= 8(1/\beta - z)\Big[1 - 2\frac{\tan(\varphi)}{\beta}(1/\beta + z)...\Big]. \end{aligned}$$

Exercise 8.10

The average velocity is computed from the volumetric flow rate divided by the cross-sectional area of the pipe,

$$\langle v\rangle = \frac{(100,000\ \mathrm{m}^3/\mathrm{day})(1\ \mathrm{day}/24\ \mathrm{hrs})(1\ \mathrm{hr}/3600\ \mathrm{s})}{(\pi/4)(1.22\ \mathrm{m})^2} = 1\ \mathrm{m/s}.$$

The Reynolds number is found as

$$N_{\mathrm{Re}} = \frac{\rho\langle v\rangle D}{\eta} = \frac{(900\ \mathrm{kg/m}^3)(1\ \mathrm{m/s})(1.22\ \mathrm{m})}{0.01\ \mathrm{Pa\ s}} = 110,000.$$

Since the flow is turbulent, we use (8.42) to find the friction factor, which gives $f_\mathrm{s} = 0.0044$. Now, using (8.41) we have

$$-\Delta\mathcal{P} = \frac{1}{2}(900\ \mathrm{kg/m^3})(1\ \mathrm{m/s})^2\frac{(100\ \mathrm{km})(10^3\ \mathrm{m/km})}{(1.22\ \mathrm{m})/4}0.0044 = 0.6\ \mathrm{MPa}.$$

Exercise 8.11

We are setting $v_r = 0$ so that $p = p(z)$. We introduce the radial average of a quantity $\langle(..)\rangle = 2\int_0^1 (..)rdr$. Applying this to (8.12) gives

$$\frac{d}{dz}(\rho\langle v_z\rangle) = 0,$$

where ρ is uniform over the tube cross section. From the dimensionless form of (8.18), we have $\rho\langle v_z\rangle = 1$. For convenience, we write (8.14) as

$$\frac{1}{2}N_\mathrm{Re}\frac{\partial}{\partial z}(\rho v_z v_z) = -\frac{dp}{dz} + \frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial v_z}{\partial r}\Big),$$

which, when integrated over the tube cross section, gives

$$\frac{1}{2}N_\mathrm{Re}\frac{d}{dz}(\rho\langle v_z^2\rangle) = -\frac{dp}{dz} + 2\frac{\partial v_z}{\partial r}(1,z).$$

Now, for laminar flow $\langle v_z^2\rangle \approx \frac{4}{3}\langle v_z\rangle^2$, so that using $\rho\langle v_z\rangle = 1$ and (8.11) we can write,

$$-\frac{2}{3}N_\mathrm{Re}\frac{1}{\rho}\frac{d\rho}{dz} = -\frac{1}{\epsilon}\rho\frac{d\rho}{dz} + 2\rho\frac{\partial v_z}{\partial r}(1,z).$$

Integration from $z = 0$ to $z = 1/\beta$ gives

$$-\frac{2}{3}N_\mathrm{Re}\ln\Big[\frac{\rho(1/\beta)}{\rho(0)}\Big] = -\frac{1}{2\epsilon}[\rho(1/\beta)^2 - \rho(0)^2] + 2\int_0^{1/\beta}\rho\frac{\partial v_z}{\partial r}(1,z)dz.$$

Using the definition for the friction factor in (8.37), we can write

$$\frac{N_\mathrm{Re}\bar{f}_\mathrm{s}}{4} = -\frac{\beta}{\rho\langle v_z\rangle^2}\int_0^{1/\beta}\frac{\partial v_z}{\partial r}(1,z)dz \approx -\beta\int_0^{1/\beta}\rho\frac{\partial v_z}{\partial r}(1,z)dz,$$

where the second equality follows using $\rho\langle v_z\rangle = 1$ and assuming ρ is approximately constant over the length of the tube. Hence, the integrated momentum balance becomes:

$$\frac{2}{3}N_\mathrm{Re}\ln\Big[\frac{\rho(1/\beta)}{\rho(0)}\Big] = \frac{1}{2\epsilon}[\rho(1/\beta)^2 - \rho(0)^2] + \frac{N_\mathrm{Re}\bar{f}_\mathrm{s}}{2\beta}$$

Now, since $p(1/\beta) = 0$ and $p(0) = -\Delta p$, we have from (8.11) the following: $\rho(1) = 1$ and $\rho(0) = 1 - \epsilon\Delta p$, so that we obtain the desired result.

Exercise 8.12

The system we consider has volume V bound by surface $A = A_\text{s} + A_1 + A_2$ with velocity $\boldsymbol{v}_A$ and outward unit normal vector $\boldsymbol{n}$. Integration of (5.5) over V gives

$$\int_V \frac{\partial \rho}{\partial t} dV = \frac{d}{dt}\int_V \rho dV - \int_V \boldsymbol{\nabla}\cdot(\boldsymbol{v}_A \rho) dV = -\int_V \boldsymbol{\nabla}\cdot(\boldsymbol{v}\rho) dV,$$

where the first equality follows from the general transport theorem since $V = V(t)$. Using Gauss's divergence theorem (cf. footnote on p. 60) we can write

$$\frac{dM_\text{tot}}{dt} = -\int_A \rho(\boldsymbol{v}-\boldsymbol{v}_A)\cdot\boldsymbol{n} dA = -\int_{A_1+A_2} \rho\boldsymbol{v}\cdot\boldsymbol{n} dA,$$

where $M_\text{tot} = \int_V \rho dV$. The second equality follows because $\boldsymbol{v}-\boldsymbol{v}_A = \boldsymbol{0}$ on A_s and $\boldsymbol{v}_A = \boldsymbol{0}$ on A_1 and A_2. Now, since $(\rho\boldsymbol{v})_1 = -\rho_1 v_1 \boldsymbol{n}$ and $(\rho\boldsymbol{v})_2 = \rho_2 v_2 \boldsymbol{n}$, we have

$$\frac{dM_\text{tot}}{dt} = -\rho_2\int_{A_2} v_2 dA + \rho_1\int_{A_1} v_1 dA = -\rho_2\langle v_2\rangle A_2 + \rho_1\langle v_1\rangle A_1,$$

where the first equality follows because the density is uniform over A_i, and the second from the definition $\langle(..)_i\rangle = \int_{A_i}(..)_i dA/A_i$. Since $\Delta[..] = [..]_2 - [..]_1$, we obtain (8.44).

Similarly, integration of (5.32) over V and using the general transport theorem gives

$$\frac{d}{dt}\int_V \boldsymbol{m} dV - \int_V \boldsymbol{\nabla}\cdot(\boldsymbol{v}_A\boldsymbol{m}) dV = -\int_V \boldsymbol{\nabla}\cdot(\boldsymbol{v}\boldsymbol{m}+\boldsymbol{\pi}) dV + \int_V \rho\boldsymbol{g} dV.$$

Using Gauss's divergence theorem we can write

$$\frac{d\boldsymbol{M}_\text{tot}}{dt} = -\int_A \boldsymbol{n}\cdot(\boldsymbol{v}-\boldsymbol{v}_A)\boldsymbol{m} dA - \int_A \boldsymbol{n}\cdot\boldsymbol{\pi} dA + M_\text{tot}\boldsymbol{g}.$$

where $\boldsymbol{M}_\text{tot} = \int_V \boldsymbol{m} dV$. Now, as before, we take into account the different surfaces

$$\frac{d\boldsymbol{M}_\text{tot}}{dt} = -\int_{A_1+A_2} \rho\boldsymbol{v}\boldsymbol{v}\cdot\boldsymbol{n} dA - \int_{A_1+A_2} \boldsymbol{n}\cdot\boldsymbol{\pi} dA - \int_{A_\text{s}} \boldsymbol{n}\cdot\boldsymbol{\pi} dA + M_\text{tot}\boldsymbol{g},$$

where we have used $\boldsymbol{m} = \rho\boldsymbol{v}$. Neglecting extra stress ($\boldsymbol{\tau}$) contributions to the total stress at A_i, we have $\boldsymbol{\pi}_1 = -p_1\boldsymbol{n}$ and $\boldsymbol{\pi}_2 = p_2\boldsymbol{n}$, so that

$$\begin{aligned}\frac{d\boldsymbol{M}_\text{tot}}{dt} = &-\int_{A_2} \rho_2 v_2^2 dA\boldsymbol{n}_2 + \int_{A_1} \rho_1 v_1^2 dA\boldsymbol{n}_1 - \int_{A_2} p_2 dA\boldsymbol{n}_2 + \int_{A_1} p_1 dA\boldsymbol{n}_1 \\ &- \boldsymbol{\mathcal{F}}_\text{s} + M_\text{tot}\boldsymbol{g},\end{aligned}$$

where $\boldsymbol{\mathcal{F}}_{\mathrm{s}}$ is defined in (8.39). Recognizing that both ρ_i and p_i are uniform over A_i, we can write

$$\frac{d\boldsymbol{M}_{\mathrm{tot}}}{dt} = -(\rho_2\langle v_2^2\rangle + p_2)A_2\boldsymbol{n}_2 + (\rho_1\langle v_1^2\rangle + p_1)A_1\boldsymbol{n}_1 - \boldsymbol{\mathcal{F}}_{\mathrm{s}} + M_{\mathrm{tot}}\boldsymbol{g}.$$

Finally, noting that $\Delta[..] = [..]_2 - [..]_1$, we obtain (8.45).

Exercise 8.13
Integration of (5.50) over V gives

$$\int_V \frac{\partial}{\partial t}\Big(\frac{1}{2}\rho v^2 + \boldsymbol{v}\rho\phi\Big)dV = -\int_V \boldsymbol{\nabla}\cdot\Big(\boldsymbol{v}\frac{1}{2}\rho v^2 + \boldsymbol{v}\rho\phi + \boldsymbol{\pi}\cdot\boldsymbol{v}\Big)\Big]dV + \int_V \boldsymbol{\pi} : \boldsymbol{\nabla}\boldsymbol{v}dV.$$

Using the general transport theorem (see Exercise 8.12) and Gauss's divergence theorem (cf. footnote on p. 60), we obtain,

$$\frac{d}{dt}(K_{\mathrm{tot}} + \Phi_{\mathrm{tot}}) = -\int_A \Big[(\boldsymbol{v} - \boldsymbol{v}_A)\frac{1}{2}\rho v^2 + (\boldsymbol{v} - \boldsymbol{v}_A)\rho\phi + p\boldsymbol{v} + \boldsymbol{\tau}\cdot\boldsymbol{v}\Big]\cdot\boldsymbol{n}dV + \int_V p\boldsymbol{\nabla}\cdot\boldsymbol{v}dV + \int_V \boldsymbol{\tau} : \boldsymbol{\nabla}\boldsymbol{v}dV$$

where $K_{\mathrm{tot}} = \int_V \frac{1}{2}\rho v^2 dV$ and $\Phi_{\mathrm{tot}} = \int_V \rho\phi dV$. Now, using the same assumptions as in Exercise 8.12, we can write

$$\frac{d}{dt}(K_{\mathrm{tot}} + \Phi_{\mathrm{tot}}) = -\int_{A_1+A_2} \Big(\frac{1}{2}\rho v^2 + \rho\phi + p\Big)\boldsymbol{v}\cdot\boldsymbol{n}dV - \int_{A_{\mathrm{sm}}} (\boldsymbol{\pi}\cdot\boldsymbol{v})\cdot\boldsymbol{n}dV + \int_V p\boldsymbol{\nabla}\cdot\boldsymbol{v}dV + \int_V \boldsymbol{\tau} : \boldsymbol{\nabla}\boldsymbol{v}dV$$

Recognizing that both ρ and ϕ are uniform over A_1 and A_2, and using (8.47), the above expression gives (8.46).

For steady flow in a straight pipe having constant cross section, (8.46), simplifies to

$$0 = -\langle v\rangle A\Delta[\rho\phi + p^{\mathrm{L}}] + \int_V \boldsymbol{\tau} : \boldsymbol{\nabla}\boldsymbol{v}dV,$$

where we have taken the density be constant and, since there are no moving surfaces, excluded the $\dot{W}$ term. This can be rearranged to give

$$-\int_V \boldsymbol{\tau} : \boldsymbol{\nabla}\boldsymbol{v}dV = -\langle v\rangle A\Delta[\rho\phi + p^{\mathrm{L}}] = -\langle v\rangle A\Delta\mathcal{P}.$$

Combining with (8.41) gives (8.48).

Exercise 8.14

As in Exercise 8.10, we consider the steady flow of an incompressible fluid with density ρ in a pipe of constant diameter D. Since $\Delta\mathcal{P} = 0$, (8.46) simplifies to

$$\dot{W} = -\int_V \boldsymbol{\tau} : \boldsymbol{\nabla}\boldsymbol{v} dV = \frac{1}{2}\rho\langle v\rangle^3 A \frac{L}{R_{\rm hyd}} f_{\rm s} = \frac{1}{2}\rho\langle v\rangle^3 \pi D L f_{\rm s},$$

where we have used (8.48), and $A = \pi D^2/4$, $L/R_{\rm hyd} = 4L/D$. Substituting values from Exercise 8.10, we have

$$\dot{W} = \frac{1}{2}(900 \text{ kg/m}^3)(1 \text{ m/s})^3\pi(1.22 \text{ m})(10^5 \text{ m})0.0044 = 760 \text{ kW}.$$

Exercise 9.1

We treat $\bar{z}$ as a time variable with a forward Euler discretization. The finite difference scheme on a grid $r_i = 1, \ldots, N_r$, with midpoints $r_{i+1/2}$, $\Delta r = \frac{1}{N_r - 1}$ and $\bar{z}_j = 1, \ldots, N_{\bar{z}}$ takes the form

$$\frac{T_{i,j+1} - T_{i,j}}{\Delta\bar{z}} = \frac{1}{1 - r_i} \frac{r_{i+1/2}\left(\frac{T_{i+1,j} - T_{i,j}}{\Delta r}\right) - r_{i-1/2}\left(\frac{T_{i,j} - T_{i-1,j}}{\Delta r}\right)}{r_i \Delta r}.$$

The stability criterion is $\Delta\bar{z} \leq \frac{\Delta r^2}{2\alpha}$, where $\alpha = \frac{1}{1-r_i^2}$ is biggest at $N_r - 1$. The boundaries are evaluated after the interior points as $T_{1,j+1} = T_{2,j+1}$ for $\frac{\partial T}{\partial r}(0,\bar{z}) = 0$ and $T_{N_r,j+1} = T_{N_r-1,j+1} + \Delta r$ for $\frac{\partial T}{\partial r}(1,\bar{z}) = 1$ while $T(r,0) = 0$ acts as an initial condition.

```
% Simulation parameters
N=100; % Number of grid points along 0<r<1
DR=1/(N-1);
R=0:DR:1;
ALPHA=1/(1-R(N-1)^2);
DZ=DR^2/(2*ALPHA);
Z=0:DZ:1;
T=zeros(N, size(Z,2)+1); % Initialize array for temperature values
                         % including initial values

% Outer loop along z coordinate
for J=2:(size(Z,2))
    % Inner loop along radius r
    for I=2:(N-1) % Without boundaries
        T(I,J+1)=T(I,J)+DZ/DR*1/(1-R(I)^2)*1/R(I)*...
                 ((R(I)+DR/2)*(T(I+1,J)-T(I,J))/DR -...
                 (R(I) - DR/2)*(T(I,J)-T(I-1,J))/DR);
    end
    T(1,J+1)=T(2,J+1); % Boundary at r = 0
    T(N,J+1)=T(N-1,J+1) + DR; % Boundary at r = 1
end

% Plot of simulation results
```

```
figure;
axis([0 1 0 2])
hold on;
ylabel('$(T-T_0)/(q_0 R/ \lambda)$','FontSize',14,'Interpreter','latex');
xlabel('$r/R$','FontSize',14,'Interpreter','latex');

for Z_sim=[0.005 0.01 0.05 0.1 0.2 0.3 0.4]
    plot(R,T(:,round(Z_sim/DZ)),'-k')
end

for Z_approx=[0.1 0.2 0.3 0.4]
    plot(R,4*Z_approx+R.^2-R.^4/4-7/24,'--k')
end
```

Exercise 9.2
Substitution of (9.19) in (9.17) gives:

$$\sum_{i=0}^{\infty} i(i-1)a_i r^{i-2} + \sum_{i=0}^{\infty} i a_i r^{i-2} + \beta^2 \sum_{i=0}^{\infty} a_i r^i - \beta^2 \sum_{i=0}^{\infty} a_i r^{i+2} = 0,$$

$$\sum_{i=0}^{\infty} i^2 a_i r^{i-2} + \beta^2 \sum_{i=0}^{\infty} a_i r^i - \beta^2 \sum_{i=0}^{\infty} a_i r^{i+2} = 0,$$

$$-\beta^2 \sum_{i=2}^{\infty} a_{i-2} r^{i-2} + \beta^2 \sum_{i=4}^{\infty} a_{i-4} r^{i-2} + \beta^2 \sum_{i=0}^{\infty} a_i r^i - \beta^2 \sum_{i=0}^{\infty} a_i r^{i+2} = 0,$$

where the second line follows from a simple cancelation of terms, and the third from using the expression for a_i given in (9.19). Shifting the index in the sums in the first two terms causes the first and third, and second and fourth terms to cancel.

Exercise 9.3
Using $4\eta\langle v_z\rangle^2/\lambda$ to scale temperature in (9.1) gives the temperature equation for adiabatic flow for $N'_{\mathrm{Pe}} \gg 1$. Substitution of (9.6) in the temperature equation leads to the following:

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{df}{dr}\right) = c_0(1-r^2) - 4r^2.$$

Integration and using the boundary condition $df/dr(0) = 0$ gives

$$\frac{df}{dr} = \frac{c_0}{2}\left(r - \frac{r^3}{2}\right) - r^3.$$

Using the boundary condition $df/dr(1) = 0$ gives $c_0 = 4$. A second integration leads to

$$T = 4\bar{z} + \left(r^2 - \frac{r^4}{2}\right) + c_2.$$

Since this solution is valid for $\bar{z} \gg 1$, we must formulate an alternative initial condition. Applying the procedure used to derive (9.7) to the current problem we obtain:

$$\int_0^1 r(1-r^2)T dr = \bar{z}.$$

Substitution for T and integrating gives $c_2 = -1/4$, so that the temperature field is

$$T = 4\bar{z} - (r^4/2 - r^2 - 1/4).$$

Exercise 9.4
Substitution of (6.4) and (6.5) with $\boldsymbol{\nabla} \cdot \boldsymbol{v} = 0$ in (6.2) gives

$$\sigma = \frac{\lambda}{T^2} \boldsymbol{\nabla} T \cdot \boldsymbol{\nabla} T + \frac{\eta}{T} \left[\boldsymbol{\nabla} \boldsymbol{v} + (\boldsymbol{\nabla} \boldsymbol{v})^T \right] : \boldsymbol{\nabla} \boldsymbol{v},$$

or, in terms of normalized variables,

$$\frac{\sigma R^2}{\lambda} = \frac{\boldsymbol{\nabla} T \cdot \boldsymbol{\nabla} T}{[\lambda T_0/(4\eta\langle v_z\rangle^2) + T]^2} + \frac{\left[\boldsymbol{\nabla} \boldsymbol{v} + (\boldsymbol{\nabla} \boldsymbol{v})^T \right] : \boldsymbol{\nabla} \boldsymbol{v}}{\lambda T_0/(4\eta\langle v_z\rangle^2) + T},$$

The velocity is given by $\boldsymbol{v} = 2(1-r^2)$ and temperature by $T = 4\bar{z} - (r^4/2 - r^2 + 1/4)$. Substitution in the expression above gives

$$\frac{\sigma R^2}{\lambda} = \frac{16 + 4(1-r^2)^2 r^2}{[\lambda T_0/(4\eta\langle v_z\rangle^2) + 4\bar{z} - (r^4/2 - r^2 + 1/4)]^2} + \frac{4r^2}{\lambda T_0/(4\eta\langle v_z\rangle^2) + 4\bar{z} - (r^4/2 - r^2 + 1/4)}.$$

The conduction (first) and viscous dissipation (second) terms are plotted in the left and right parts, respectively, of Figure C.13.

Exercise 9.5
Introducing the change in variable $x = 1 - r$ in (9.2)-(9.4) gives, for $x \ll 1$ and neglecting curvature, the following

$$2x \frac{\partial T}{\partial \bar{z}} = \frac{\partial^2 T}{\partial x^2},$$

$$T(x, 0) = 0,$$

$$\frac{\partial T}{\partial x}(0, \bar{z}) = -1, \qquad \frac{\partial T}{\partial x}(\infty, \bar{z}) = 0,$$

where the second boundary condition applies to the center of the tube, which

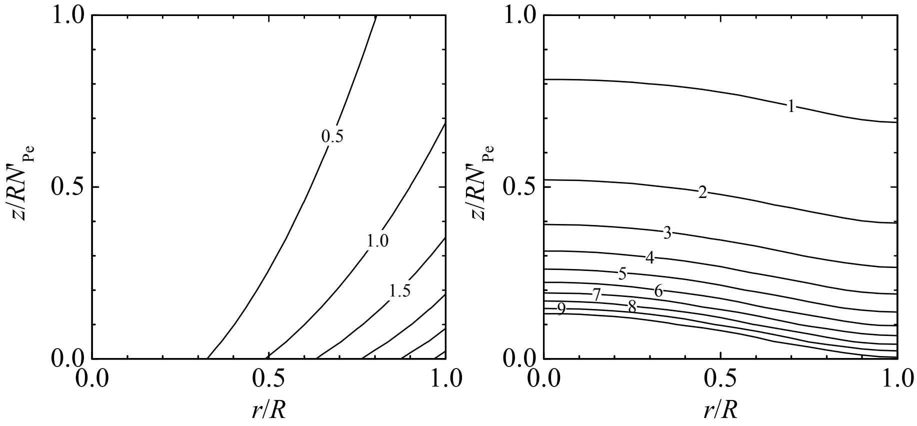

Figure C.13 Local rate of entropy production $\sigma R^2/\lambda$ for adiabatic flow in a tube for $\lambda T_0/(4\eta\langle v_z\rangle^2) = 1$. Left plot is for flow and right plot is for conduction.

is effectively at an infinite distance from the tube wall. Differentiation of the temperature equation with respect to x gives:

$$2x\frac{\partial\theta}{\partial\bar{z}} = \frac{\partial^2\theta}{\partial x^2} - \frac{1}{x}\frac{\partial\theta}{\partial x},$$

where $\theta = \partial T/\partial x$. The initial condition is replaced by

$$\theta(x, 0) = 0,$$

and the boundary conditions become

$$\theta(0, \bar{z}) = -1, \qquad \theta(\infty, \bar{z}) = 0.$$

Now, using the similarity transformation $\xi = Cx/\bar{z}^{1/3}$, the above equations take the form:

$$\frac{\partial^2\theta}{\partial\xi^2} + \Big(3\xi^2 - \frac{1}{\xi}\Big)\frac{\partial\theta}{\partial\xi} = 0,$$

$$\theta(0) = -1, \qquad \theta(\infty) = 0,$$

where for convenience we have set $C = (9/2)^{1/3}$. Integration gives

$$\frac{\partial\theta}{\partial\xi} = c_1 \exp\Big[\int -\Big(3\xi^2 - \frac{1}{\xi}\Big)d\xi\Big] = c_1\xi\exp(-\xi^3).$$

Integrating again and using the second boundary condition gives

$$\theta(\xi) = c_1 \int_\infty^\xi \bar{\xi} \exp(-\bar{\xi}^3) d\bar{\xi}.$$

Using the first boundary condition leads to

$$c_1 = \Big[\int_0^\infty \xi \exp(-\xi^3) d\xi \Big]^{-1} = \frac{3}{\Gamma(2/3)},$$

where $\Gamma(x)$ is the Gamma function, so that we have

$$\theta(\xi) = \frac{3}{\Gamma(2/3)} \int_\xi^\infty \bar{\xi} \exp(-\bar{\xi}^3) d\bar{\xi}.$$

To obtain an expression for the Nusselt number, we write (9.28) as follows:

$$N_{\text{Nu}} = 2 \frac{-\frac{\partial T}{\partial x}(0, \bar{z})}{T(0, \bar{z}) - T_{\text{fl}}(\bar{z})} = \frac{2}{T(0, \bar{z})},$$

where the second equality makes use of the boundary condition at the tube wall and the fact that the average temperature does not change from its initial value in the entrance region of the tube. Now, since $\theta = \partial T/\partial x$, integrating we can write:

$$\begin{aligned}
T(0, \bar{z}) &= \int_\infty^0 \theta dx = -\frac{x}{\xi} \int_0^\infty \theta d\xi \\
&= -\Big(\frac{9}{2}\bar{z}\Big)^{1/3} \frac{3}{\Gamma(2/3)} \int_0^\infty \int_\xi^\infty \bar{\xi} \exp(-\bar{\xi}^3) d\bar{\xi} d\xi \\
&= -\Big(\frac{9}{2}\bar{z}\Big)^{1/3} \frac{3}{\Gamma(2/3)} \Big[\xi \int_\xi^\infty \bar{\xi} \exp(-\bar{\xi}^3) d\bar{\xi} \Big|_{\xi=0}^{\xi=\infty} + \int_0^\infty \xi^2 \exp(-\xi^3) d\xi \Big],
\end{aligned}$$

where integration by parts was used to go from the second to third line. The first term in the square bracket is zero, and the second is simply 1/3. Substitution in the expression for N_{Nu} gives (9.31).

Exercise 9.6

The temperature equation for an incompressible Newtonian fluid with constant thermal conductivity λ is given in (7.21), which, neglecting viscous dissipation, we write as

$$\rho \hat{c}_p v_1 \frac{\partial T}{\partial x_1} = \lambda \Big[\frac{\partial^2 T}{\partial x_1^2} + \frac{\partial^2 T}{\partial x_2^2} \Big].$$

From Exercise 8.2, we have

$$v_1 = \frac{3}{2} V \Big[1 - \Big(\frac{x_2}{H}\Big)^2 \Big].$$

Combing these, and making x_i dimensionless with H, and temperature, relative to T_0, dimensionless by q_0/λ, we can write

$$N'_{\mathrm{Pe}}(1-x_2^2)\frac{\partial T}{\partial x_1} = \frac{\partial^2 T}{\partial x_1^2} + \frac{\partial^2 T}{\partial x_2^2},$$

where $N'_{\mathrm{Pe}} = 3VH/(2\chi)$. Using the rescaling $\bar{x}_1 = x_1/N'_{\mathrm{Pe}}$, and applying the condition $N'_{\mathrm{Pe}} \gg 1$, we obtain

$$(1-x_2^2)\frac{\partial T}{\partial \bar{x}_1} = \frac{\partial^2 T}{\partial x_2^2}.$$

The initial and boundary conditions are given by

$$T(0,x_2) = 0, \qquad \frac{\partial T}{\partial x_2}(\bar{x}_1, 0) = 0, \qquad \frac{\partial T}{\partial x_2}(\bar{x}_1, 1) = 1.$$

As in Section 9.2, we assume the following form for the temperature in the downstream region,

$$T(\bar{x}_1, x_2) = c_0\bar{x}_1 + f(x_2).$$

Substitution in the temperature equation leads to the following:

$$\frac{d^2 f}{dx_2^2} = c_0(1-x_2^2).$$

Integration and using the boundary conditions gives

$$T(\bar{x}_1, x_2) = \frac{3}{2}\bar{x}_1 + \frac{3}{4}\Big(x_2^2 - \frac{x_2^4}{6}\Big) + c_2.$$

To find c_2, we formulate an alternative initial condition by integrating the temperature equation over x_2 from $x_2 = 0, 1$, which gives

$$\int_0^1 (1-x_2^2)\frac{\partial T}{\partial \bar{x}_1}dx_2 = \frac{\partial T}{\partial x_2}(\bar{x}_1, 1) - \frac{\partial T}{\partial x_2}(\bar{x}_1, 0).$$

Applying the boundary conditions and integrating with respect to $\bar{x}_1$, leads to,

$$\int_0^1 (1-x_2^2)T dx_2 = \bar{x}_1.$$

Substitution for T and evaluating the integral gives,

$$T = \frac{3}{2}\bar{x}_1 + \frac{3}{4}\Big(x_2^2 - \frac{x_2^4}{6}\Big) - \frac{45}{122}.$$

Now, writing (9.27) in dimensionless form, we have

$$\frac{\partial T}{\partial x_2}(\bar{x}_1, 1) = \frac{N_{\mathrm{Nu}}}{2}[T(\bar{x}_1, 1) - T_{\mathrm{fl}}(\bar{x}_1)],$$

where $N_{\rm Nu} = 2hH/\lambda$, and

$$T_{\rm fl} = \frac{\int_0^1 v_1 T dx_2}{\int_0^1 v_1 dx_2} = \frac{3}{2}\bar{x}_1 - \frac{21}{80}.$$

Using the boundary condition for the temperature gradient, and substituting for T and $T_{\rm fl}$, we obtain

$$1 = \frac{N_{\rm Nu}}{2}\frac{17}{35},$$

which gives the desired result.

Exercise 9.7

The system we consider has volume V bound by surface A with velocity $\boldsymbol{v}_A$ and outward unit normal vector $\boldsymbol{n}$. Adding (5.50) and (5.51), we obtain the differential balance for total energy:

$$\frac{\partial}{\partial t}\Big(u + \frac{1}{2}\rho v^2 + \rho\phi\Big) = -\boldsymbol{\nabla}\cdot\Big(\boldsymbol{v}u + \boldsymbol{v}\frac{1}{2}\rho v^2 + \boldsymbol{v}\rho\phi + \boldsymbol{j}_q + \boldsymbol{\pi}\cdot\boldsymbol{v}\Big).$$

Integration over V gives

$$\begin{aligned}\frac{d}{dt}E_{\rm tot} &= \int_V \boldsymbol{\nabla}\cdot\Big[\boldsymbol{v}_A\Big(u + \frac{1}{2}\rho v^2 + \rho\phi\Big)\Big]dV \\ &\quad - \int_V \boldsymbol{\nabla}\cdot\Big[\boldsymbol{v}\Big(u + \frac{1}{2}\rho v^2 + \rho\phi\Big)\Big]dV - \int_V \boldsymbol{\nabla}\cdot\boldsymbol{j}_q dV - \int_V \boldsymbol{\nabla}\cdot(\boldsymbol{\pi}\cdot\boldsymbol{v})dV\end{aligned}$$

where we have used the general transport theorem (see Exercise 8.12), and the total energy is $E_{\rm tot} = \int_V (u + \frac{1}{2}\rho v^2 + \rho\phi)dV$. Using Gauss's divergence theorem, the energy balance takes the following form:

$$\frac{d}{dt}E_{\rm tot} = \int_A \Big(u + \frac{1}{2}\rho v^2 + \rho\phi\Big)(\boldsymbol{v}_A - \boldsymbol{v})\cdot\boldsymbol{n}dA - \int_A \boldsymbol{n}\cdot\boldsymbol{j}_q dA - \int_A \boldsymbol{n}\cdot(\boldsymbol{\pi}\cdot\boldsymbol{v})dA.$$

Since $\boldsymbol{v} - \boldsymbol{v}_A = \boldsymbol{0}$ on $A_{\rm s}$ and $\boldsymbol{v}_A = \boldsymbol{0}$ on A_i, the first term can be written as

$$\begin{aligned}\int_A \Big(u + \frac{1}{2}\rho v^2 + \rho\phi\Big)(\boldsymbol{v}_A - \boldsymbol{v})\cdot\boldsymbol{n}dA &= -\int_{A_1+A_2}\Big(u + \frac{1}{2}\rho v^2 + \rho\phi\Big)\boldsymbol{v}\cdot\boldsymbol{n}dA \\ &= -\Delta\Big[\Big(\langle v\rangle u + \frac{1}{2}\rho\langle v^3\rangle + \langle v\rangle\rho\phi\Big)A\Big],\end{aligned}$$

where we have taken u, ρ and ϕ to be uniform over A_i with $\langle(..)_i\rangle = \int_{A_i}(..)_i dA/A_i$. For the second term in the energy balance, we write

$$\int_A \boldsymbol{n}\cdot\boldsymbol{j}_q dA = \int_{A_1+A_2}\boldsymbol{n}\cdot\boldsymbol{j}_q dA + \int_{A_{\rm s}}\boldsymbol{n}\cdot\boldsymbol{j}_q dA = -\dot{Q}.$$

where the second equality follows by taking $\boldsymbol{j}_q = \boldsymbol{0}$ on A_i, and $\dot{Q}$ is defined in (9.25). The third term in the energy balance can be written as

$$\int_A \boldsymbol{n} \cdot (\boldsymbol{\pi} \cdot \boldsymbol{v}) dA = \int_{A_1+A_2} \boldsymbol{n} \cdot (\boldsymbol{\pi} \cdot \boldsymbol{v}) dA + \int_{A_\mathrm{s}} \boldsymbol{n} \cdot (\boldsymbol{\pi} \cdot \boldsymbol{v}) dA$$
$$= \int_{A_1+A_2} p\, \boldsymbol{v} \cdot \boldsymbol{n} dA - \dot{W}$$

where in the first line we have taken into account that $\boldsymbol{v} = \boldsymbol{0}$ on A_ss. The second line is obtained by taking $\boldsymbol{\pi} = p\boldsymbol{\delta}$ at A_i, and the rate of work done on the fluid at moving solid surfaces is given by $\dot{W} = -\int_{A_\mathrm{sm}} \boldsymbol{n} \cdot \boldsymbol{\pi} \cdot \boldsymbol{v} dA$. Combining the results above, we obtain (9.34).

Exercise 9.8
Since the tube has constant cross-section $A_1 = A_2 = \frac{\pi}{4} D^2$, and $\langle v_1 \rangle = \langle v_2 \rangle = \langle v \rangle$. Hence, the steady state form of the energy balance (9.34) simplifies to the following:

$$\langle v \rangle (h_2 - h_1) \frac{\pi}{4} D^2 = \dot{Q},$$

where we have neglected changes in potential energy, and taken $\dot{W} = 0$ since there are no moving surfaces. Since we are neglecting resistances in the steam and tube wall, the tube wall is maintained at a constant temperature $T(R, 0) = T(R, L) = T(R)$. We express $\dot{Q}$ using the log-mean temperature difference given by (9.35) so that we can write the energy balance as

$$\langle v \rangle \rho \hat{c}_p (T_2 - T_1) \frac{\pi}{4} D^2 = h_\mathrm{ln} \frac{T_2 - T_1}{\ln[T(R) - T_1] - \ln[T(R) - T_2]} (\pi D L),$$

where we have used $h_2 - h_1 = \rho \hat{c}_p (T_2 - T_1)$. Making obvious cancelations and minor rearrangements, we obtain the following:

$$L = \frac{D}{4} \frac{N'_\mathrm{Pe}}{N_{\mathrm{Nu}_\mathrm{ln}}} \ln \left[\frac{T(R) - T_1}{T(R) - T_2} \right],$$

The Reynolds number is found as follows:

$$N_\mathrm{Re} = \frac{\rho \langle v \rangle D}{\eta} = \frac{4w}{\pi D \eta} = \frac{4(4 \text{ kg/s})}{\pi (0.1 \text{ m})(0.001 \text{ Pa s})} = 51{,}000$$

For water at 25–50°C, the Prandtl number is $N_\mathrm{Pr} \approx 6$, so that $N'_\mathrm{Pe} = N_\mathrm{Re} N_\mathrm{Pr} \approx 306{,}000$. Since the flow is turbulent we use (9.33) and find $N_{\mathrm{Nu}_\mathrm{ln}} \approx 273$. Plugging these values into the expression for L gives

$$L = \frac{0.1 \text{ m}}{4} \frac{306{,}000}{273} \ln \left(\frac{75}{50} \right) \approx 11 \text{ m}.$$

Exercise 9.9

Integration of (6.1) over V gives

$$\frac{d}{dt}S_{\text{tot}} = \int_V \boldsymbol{\nabla}\cdot(\boldsymbol{v}_A s)dV - \int_V \boldsymbol{\nabla}\cdot(\boldsymbol{v}s)dV - \int_V \boldsymbol{\nabla}\cdot(\boldsymbol{j}_q/T)dV + \dot{\Sigma}$$

where $S_{\text{tot}} = \int_V s dV$ and $\dot{\Sigma} = \int_V \sigma dV$. Using Guass' divergence theorem, we obtain

$$\frac{d}{dt}S_{\text{tot}} = \int_A s(\boldsymbol{v}_A - \boldsymbol{v})\cdot\boldsymbol{n}dA - \int_A (\boldsymbol{j}_q/T)\cdot\boldsymbol{n}dA + \dot{\Sigma},$$

Recall that $A = A_1 + A_2 + A_{\text{s}}$, and that $\boldsymbol{v} - \boldsymbol{v}_A = \mathbf{0}$ on A_{s} and $\boldsymbol{v}_A = \mathbf{0}$ on A_i. We take s to be uniform over A_i and neglect $\boldsymbol{j}_q$ at A_i, so that with $\langle(..)_i\rangle = \int_{A_i}(..)_i dA/A_i$, we obtain

$$\frac{d}{dt}S_{\text{tot}} = -\Delta[\langle v\rangle sA] + \dot{S} + \dot{\Sigma},$$

where $\dot{S} = -\int_{A_{\text{s}}} \boldsymbol{n}\cdot\boldsymbol{j}_q/T dA$.

Exercise 9.10

At steady state, we write (9.36) as follows,

$$\dot{\Sigma} = \Delta[\langle v\rangle sA] + \int_{A_{\text{s}}} \frac{\boldsymbol{n}\cdot\boldsymbol{j}_q}{T}dA = \pi R^2 V\rho(\hat{s}_2 - \hat{s}_1) - 2\pi R q_0 \int_0^L \frac{1}{T(R,z)}dz.$$

For the entropy change, we can write $\hat{s}_2 - \hat{s}_1 = \hat{c}_p \ln T_2/T_1$. Substitution gives

$$\dot{\Sigma} = \pi R^2 V\rho\hat{c}_p \ln\frac{\langle T\rangle(L)}{\langle T\rangle(0)} - 2\pi R q_0 \int_0^L \frac{1}{T(r,z)}dz.$$

Changing to dimensionless variables and setting $L = RN_{\text{Pe}}$, we have

$$\frac{\dot{\Sigma}}{\pi R^2 V\rho\hat{c}_p} = \ln\frac{\beta + \langle T\rangle(1)}{\beta + \langle T\rangle(0)} - 4\int_0^1 \frac{1}{\beta + T(1,\bar{z})}d\bar{z},$$

where $\beta = \lambda T_0/q_0 R$. Substitution of (9.10) and integration gives

$$\frac{\dot{\Sigma}}{\pi R^2 V\rho\hat{c}_p} = \ln\frac{\beta + 15/4}{\beta - 1/4} - 4\ln\frac{\beta + 29/24}{\beta + 5/24}.$$

Exercise 10.1

From Figure 10.1, we postulate the velocity field to have the form $v_1 = v_2 = 0, v_3 = v_3(x_1, x_3)$. For constant ρ, the velocity is constrained by (5.36), or

$$\frac{\partial v_3}{\partial x_3} = 0,$$

so that $v_3 = v_3(x_1)$. Using this velocity field, we find from (7.8),

$$\frac{\partial \mathcal{P}}{\partial x_1} = 0, \qquad \frac{\partial \mathcal{P}}{\partial x_2} = 0, \qquad \frac{\partial \mathcal{P}}{\partial x_3} = \eta \frac{\partial^2 v_3}{\partial x_1^2}.$$

Integration of the third equation gives,

$$\frac{dv_3}{dx_1} = \frac{1}{\eta}\frac{d\mathcal{P}}{dx_3} x_1 + c_1.$$

Taking the gas to be inviscid, we have the boundary condition $\pi_{13}(0) = \tau_{13}(0) = -\eta \frac{dv_3}{dx_1}(0) = 0$ so that $c_1 = 0$. Integrating again we have

$$v_3 = \frac{1}{2\eta}\frac{d\mathcal{P}}{dx_3} x_1^2 + c_2.$$

Applying the boundary condition $v_3(h) = 0$, we obtain

$$v_3 = -\frac{h^2}{2\eta}\frac{d\mathcal{P}}{dx_3}\Big[1 - \Big(\frac{x_1}{h}\Big)^2\Big].$$

Now, we have

$$\frac{d\mathcal{P}}{dx_3} = \frac{dp^{\mathrm{L}}}{dx_3} - \rho g_3.$$

Assuming the pressure in the gas is uniform $\frac{dp^{\mathrm{L}}}{dx_3} = 0$, we have with $\boldsymbol{g} = g\boldsymbol{\delta}_3$,

$$\frac{d\mathcal{P}}{dx_3} = -\rho g.$$

Substitution gives

$$v_3 = \frac{\rho g h^2}{2\eta}\Big[1 - \Big(\frac{x_1}{h}\Big)^2\Big].$$

which is the expression in (10.2) with $V = \rho g h^2/(2\eta)$.

Exercise 10.2

Starting with (6.8), we substitute (6.20) generalized to k components

$$\rho \hat{c}_p \frac{DT}{Dt} = -\frac{T}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{p,w_\alpha} \frac{Dp}{Dt} - \boldsymbol{\nabla}\cdot\boldsymbol{j}_q' - \sum_{\alpha=1}^{k} \boldsymbol{j}_\alpha \cdot \boldsymbol{\nabla}\hat{h}_\alpha - \boldsymbol{\tau} : \boldsymbol{\nabla}\boldsymbol{v} - \Gamma \sum_{\alpha=1}^{k} \nu_\alpha \hat{h}_\alpha.$$

Neglecting viscous heating and taking the pressure to be constant, we obtain

$$\rho \hat{c}_p \Big(\frac{\partial T}{\partial t} + \boldsymbol{v}\cdot\boldsymbol{\nabla}T\Big) = -\boldsymbol{\nabla}\cdot\boldsymbol{j}_q' - \sum_{\alpha=1}^{k} \boldsymbol{j}_\alpha \cdot \boldsymbol{\nabla}\hat{h}_\alpha - \Gamma \sum_{\alpha=1}^{k} \nu_\alpha \hat{h}_\alpha.$$

Now, for an ideal mixture, we write $\hat{h}_\alpha = \hat{h}^\circ_\alpha = \tilde{M}_\alpha \tilde{h}^\circ_\alpha$ where the $\tilde{h}^\circ_\alpha$ are constant. Hence, we obtain

$$\rho \hat{c}_p \Big(\frac{\partial T}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} T \Big) = -\boldsymbol{\nabla} \cdot \boldsymbol{j}_q' - \tilde{\Gamma} \sum_{\alpha=1}^{k} \tilde{\nu}_\alpha \tilde{h}^\circ_\alpha,$$

from which (10.6) is obtained.

Exercise 10.3

From Exercise 6.12, for $w_3 \approx 1$ and $w_1 \ll 1$ and $w_2 \ll 1$, we can write

$$D_{13} = \frac{\tilde{R} L_{11}}{\rho \tilde{M}_1 w_1}, \qquad D_{12} = \frac{\tilde{R} L_{12}}{\rho \tilde{M}_2 w_2},$$

$$D_{21} = \frac{\tilde{R} L_{12}}{\rho \tilde{M}_1 w_1}, \qquad D_{23} = \frac{\tilde{R} L_{22}}{\rho \tilde{M}_2 w_2}.$$

Now, since $L_{12} \leq \sqrt{L_{11} L_{22}}$, we assume $L_{12} \ll L_{11}$ and $L_{12} \ll L_{22}$ so that the cross diffusion coefficients can be neglected. Hence, we obtain

$$\boldsymbol{j}_\alpha = -\rho D_{\alpha 3} \boldsymbol{\nabla} w_\alpha, \qquad D_{\alpha 3} = \frac{\tilde{R} L_{\alpha\alpha}}{\rho \tilde{M}_\alpha w_\alpha},$$

for $\alpha = 1, 2, ...,$ which can be generalized to a k-component system to give (10.17).

Exercise 10.4

From the given reaction, the stoichiometric coefficients are $\tilde{\nu}_{\rm A} = -1,\ \tilde{\nu}_{\rm B} = -1,\ \tilde{\nu}_{\rm C} = 2$. The mass action law in (6.61) takes the form

$$\tilde{\Gamma} = L_\Gamma \exp\left(-\frac{\tilde{\mu}^0_{\rm A} + \tilde{\mu}^0_{\rm B}}{\tilde{R} T} \right) \left[x_{\rm A} x_{\rm B} - e^{\frac{\Delta \tilde{g}^0}{\tilde{R} T}} x_{\rm C}^2 \right] = k_{\rm f} x_{\rm A} (1 - x_{\rm A} - x_{\rm C}) - k_{\rm r} x_{\rm C}^2,$$

where $k_{\rm f}, k_{\rm r}$ are the rate constants for the forward and reverse reactions. Using (4.60) for $\hat{\mu}_\alpha$ and (5.20) to eliminate $\boldsymbol{v}_\alpha$, we can write (10.8) as

$$c \boldsymbol{\nabla} x_{\rm A} = \frac{1}{\mathfrak{D}_{\rm AB}} [(1 - x_{\rm C}) \boldsymbol{J}^*_{\rm A} - x_{\rm A} \boldsymbol{J}^*_{\rm C}] + \frac{1}{\mathfrak{D}_{\rm AC}} [x_{\rm C} \boldsymbol{J}^*_{\rm A} - x_{\rm A} \boldsymbol{J}^*_{\rm C}],$$
$$c \boldsymbol{\nabla} x_{\rm C} = \frac{1}{\mathfrak{D}_{\rm CA}} [x_{\rm A} \boldsymbol{J}^*_{\rm C} - x_{\rm C} \boldsymbol{J}^*_{\rm A}] + \frac{1}{\mathfrak{D}_{\rm CB}} [(1 - x_{\rm A}) \boldsymbol{J}^*_{\rm C} - x_{\rm C} \boldsymbol{J}^*_{\rm A}],$$

where we have also used $\boldsymbol{J}^*_{\rm A} + \boldsymbol{J}^*_{\rm B} + \boldsymbol{J}^*_{\rm C} = \boldsymbol{0}$. Rearranging, we have

$$\left(\frac{1 - x_{\rm C}}{\mathfrak{D}_{\rm AB}} + \frac{x_{\rm C}}{\mathfrak{D}_{\rm AC}} \right) \boldsymbol{J}^*_{\rm A} + \left(\frac{x_{\rm A}}{\mathfrak{D}_{\rm AB}} - \frac{x_{\rm A}}{\mathfrak{D}_{\rm AC}} \right) \boldsymbol{J}^*_{\rm C} = -c \boldsymbol{\nabla} x_{\rm A},$$
$$\left(\frac{x_{\rm C}}{\mathfrak{D}_{\rm CB}} - \frac{x_{\rm C}}{\mathfrak{D}_{\rm CA}} \right) \boldsymbol{J}^*_{\rm A} + \left(\frac{1 - x_{\rm A}}{\mathfrak{D}_{\rm CB}} + \frac{x_{\rm A}}{\mathfrak{D}_{\rm CA}} \right) \boldsymbol{J}^*_{\rm C} = -c \boldsymbol{\nabla} x_{\rm C}.$$

Solving for $\boldsymbol{J}_{\mathrm{A}}^{*}$ and $\boldsymbol{J}_{\mathrm{C}}^{*}$ we obtain

$$\begin{aligned}\boldsymbol{J}_{\mathrm{A}}^{*} = &-\frac{c\mathfrak{D}_{\mathrm{AB}}[(1-x_{\mathrm{A}})\mathfrak{D}_{\mathrm{AC}}+x_{\mathrm{A}}\mathfrak{D}_{\mathrm{CB}}]}{(1-x_{\mathrm{A}}-x_{\mathrm{C}})\mathfrak{D}_{\mathrm{AC}}+x_{\mathrm{A}}\mathfrak{D}_{\mathrm{CB}}+x_{\mathrm{C}}\mathfrak{D}_{\mathrm{AB}}}\boldsymbol{\nabla}x_{\mathrm{A}}\\ &-\frac{cx_{\mathrm{A}}\mathfrak{D}_{\mathrm{CB}}(\mathfrak{D}_{\mathrm{AB}}-\mathfrak{D}_{\mathrm{AC}})}{(1-x_{\mathrm{A}}-x_{\mathrm{C}})\mathfrak{D}_{\mathrm{AC}}+x_{\mathrm{A}}\mathfrak{D}_{\mathrm{CB}}+x_{\mathrm{C}}\mathfrak{D}_{\mathrm{AB}}}\boldsymbol{\nabla}x_{\mathrm{C}},\end{aligned}$$

$$\begin{aligned}\boldsymbol{J}_{\mathrm{C}}^{*} = &-\frac{cx_{\mathrm{C}}\mathfrak{D}_{\mathrm{AB}}(\mathfrak{D}_{\mathrm{CB}}-\mathfrak{D}_{\mathrm{AC}})}{(1-x_{\mathrm{A}}-x_{\mathrm{C}})\mathfrak{D}_{\mathrm{AC}}+x_{\mathrm{A}}\mathfrak{D}_{\mathrm{CB}}+x_{\mathrm{C}}\mathfrak{D}_{\mathrm{AB}}}\boldsymbol{\nabla}x_{\mathrm{A}}\\ &-\frac{c\mathfrak{D}_{\mathrm{CB}}[(1-x_{\mathrm{C}})\mathfrak{D}_{\mathrm{AC}}+x_{\mathrm{C}}\mathfrak{D}_{\mathrm{AB}}]}{(1-x_{\mathrm{A}}-x_{\mathrm{C}})\mathfrak{D}_{\mathrm{AC}}+x_{\mathrm{A}}\mathfrak{D}_{\mathrm{CB}}+x_{\mathrm{C}}\mathfrak{D}_{\mathrm{AB}}}\boldsymbol{\nabla}x_{\mathrm{C}},\end{aligned}$$

where we have set $\mathfrak{D}_{\mathrm{CA}} = \mathfrak{D}_{\mathrm{AC}}$. These expressions, which simplify to (10.10) for $x_{\mathrm{A}} \ll 1, x_{\mathrm{C}} \ll 1$, can be written as,

$$\boldsymbol{J}_{\mathrm{A}}^{*} = -c\tilde{D}_{\mathrm{AB}}\boldsymbol{\nabla}x_{\mathrm{A}} - c\tilde{D}_{\mathrm{AC}}\boldsymbol{\nabla}x_{\mathrm{C}},$$

$$\boldsymbol{J}_{\mathrm{C}}^{*} = -c\tilde{D}_{\mathrm{CA}}\boldsymbol{\nabla}x_{\mathrm{A}} - c\tilde{D}_{\mathrm{CB}}\boldsymbol{\nabla}x_{\mathrm{C}},$$

where one can easily identify the diffusion coefficients $\tilde{D}_{\alpha\beta}$. Since we have assumed an ideal mixture c is constant, so that from (5.22) we have $\boldsymbol{\nabla}\cdot\boldsymbol{v}^{*} = 0$. Since $\boldsymbol{v}^{*} = \mathbf{0}$ on the bounding surfaces $\boldsymbol{v}^{*} = \mathbf{0}$ everywhere. Writing (5.23) for $\alpha = \mathrm{A}, \mathrm{C}$ and substituting the expressions above for $\tilde{\Gamma}$, $\boldsymbol{J}_{\mathrm{A}}^{*}$ and $\boldsymbol{J}_{\mathrm{C}}^{*}$ gives the desired results.

Exercise 10.5

For $\theta = 1$, we can write (10.19) and (10.20) as

$$\frac{\partial f}{\partial x_3} = \gamma\frac{\partial^2 f}{\partial x_1^2} + \Gamma f,$$

which are solved subject to the initial and boundary conditions

$$f(x_1, 0) = 0, \qquad f(0, x_3) = 0, \qquad f(\infty, x_3) = 0.$$

For $x_{\mathrm{C}}^{(0)}$ we have $\gamma = \beta$ and $\Gamma = N_{\mathrm{Da}}$, and for $T^{(0)}$ we have $\gamma = N_{\mathrm{Le}}$ and $\Gamma = -N_{\mathrm{Da}}$. The solution for x_{A} in (10.27) we have $\gamma = 1$ and write as $x_{\mathrm{A}}(x_1, x_3) = g(x_1, x_3, \Gamma)$. Taking the Laplace transform and solving, we obtain

$$\bar{f}(x_1, s) = \frac{1}{\gamma}\frac{\eta}{s(s-\eta)}\left(e^{-x_1\sqrt{\Gamma+s}} - e^{-x_1\sqrt{\frac{s}{\gamma}}}\right),$$

where $\eta = \frac{\gamma}{1-\gamma}\Gamma$. Using the convolution theorem, we find

$$f(x_1, x_3) = \frac{1}{\gamma}\int_0^{x_3}(e^{\eta(x_3-u)} - 1)\frac{x_1}{\sqrt{4\pi u^3}}e^{-\Gamma u - \frac{x_1{}^2}{4u}}\,du$$

$$-\frac{1}{\gamma}\int_0^{x_3}(e^{\eta(x_3-u)}-1)\frac{x_1/\sqrt{\gamma}}{\sqrt{4\pi u^3}}e^{-\frac{(x_1/\sqrt{\gamma})^2}{4u}}du.$$

Changing variable to $\xi = \frac{x_1}{\sqrt{4u}}$ in the first integral and to $\xi = \frac{x_1/\sqrt{\gamma}}{\sqrt{4u}}$ in the second, we obtain

$$\begin{aligned}
f(x_1,x_3) &= \frac{2}{\gamma\sqrt{\pi}}\int_{\frac{x_1}{\sqrt{4x_3}}}^{\infty}\left[e^{\eta\left(x_3-\frac{x_1{}^2}{4\xi^2}\right)}-1\right]e^{-\Gamma\frac{x_1{}^2}{4\xi^2}-\xi^2}d\xi \\
&\quad -\frac{2}{\gamma\sqrt{\pi}}\int_{\frac{x_1/\sqrt{\gamma}}{\sqrt{4x_3}}}^{\infty}\left[e^{\eta\left(x_3-\frac{(x_1/\sqrt{\gamma})^2}{4\xi^2}\right)}-1\right]e^{-\xi^2}d\xi \\
&= \frac{1}{\gamma}e^{\eta x_3}\frac{2}{\sqrt{\pi}}\int_{\frac{x_1}{\sqrt{4x_3}}}^{\infty}e^{-\xi^2-(\Gamma+\eta)\frac{x_1{}^2}{4\xi^2}}d\xi-\frac{1}{\gamma}\frac{2}{\sqrt{\pi}}\int_{\frac{x_1}{\sqrt{4x_3}}}^{\infty}e^{-\xi^2-\Gamma\frac{x_1{}^2}{4\xi^2}}d\xi \\
&\quad -\frac{1}{\gamma}e^{\eta x_3}\frac{2}{\sqrt{\pi}}\int_{\frac{x_1/\sqrt{\gamma}}{\sqrt{4x_3}}}^{\infty}e^{-\xi^2-\eta\frac{(x_1/\sqrt{\gamma})^2}{4\xi^2}}d\xi+\frac{1}{\gamma}\frac{2}{\sqrt{\pi}}\int_{\frac{x_1/\sqrt{\gamma}}{\sqrt{4x_3}}}^{\infty}e^{-\xi^2}d\xi.
\end{aligned}$$

This means that

$$\begin{aligned}
f(x_1,x_3) &= \frac{1}{\gamma}[e^{\eta x_3}g(x_1,x_3,\Gamma+\eta)-g(x_1,x_3,\Gamma)-e^{\eta x_3}g(x_1/\sqrt{\gamma},x_3,\eta) \\
&\quad + g(x_1/\sqrt{\gamma},x_3,0)].
\end{aligned}$$

Now, for $f(x_1,x_3)=x_{\mathrm{C}}^{(0)}$ with $\gamma=\beta=1$, we write $\Gamma+\eta\sim\eta$ so that

$$f(x_1,x_3)=g(x_1,x_3,0)-g(x_1,x_3,\Gamma),$$

where $g(x_1,x_3,0) = \mathrm{erfc}\left(x_1/\sqrt{4x_3}\right)$, which gives (10.30). Finally, for $f(x_1,x_3)=T^{(0)}$ with $\gamma=N_{\mathrm{Le}}\gg 1$, we write $\eta\sim-\Gamma=N_{\mathrm{Da}}$, so that

$$f(x_1,x_3)\simeq\frac{1}{\gamma}\left[1-e^{-\Gamma x_3}\mathrm{erfc}\left(\frac{x_1}{\sqrt{4x_3}}\right)-g(x_1,x_3,\Gamma)\right],$$

which gives (10.33).

Exercise 10.6
Integration by parts allows the given solution to be written as

$$f=\int_0^t\frac{\partial\hat{f}}{\partial t}\exp(Ct')dt'=\exp(Ct)\hat{f}-C\int_0^t\exp(Ct')\hat{f}dt',$$

from which we find

$$\frac{\partial f}{\partial t}=\exp(Ct)\frac{\partial\hat{f}}{\partial t},$$

and

$$\frac{\partial^2 f}{\partial x^2} = \exp(Ct)\frac{\partial^2 \hat{f}}{\partial x^2} - C\int_0^t \exp(Ct')\frac{\partial^2 \hat{f}}{\partial x^2}dt'.$$

$\hat{f}$ is the solution of

$$\frac{\partial \hat{f}}{\partial t} = \frac{\partial^2 \hat{f}}{\partial x^2},$$

$$\hat{f}(x,0) = 0, \qquad \hat{f}(0,t) = 1, \qquad \hat{f}(\infty,t) = 0.$$

Hence, we can write

$$\frac{\partial^2 f}{\partial x^2} = \exp(Ct)\frac{\partial \hat{f}}{\partial t} - C\int_0^t \exp(Ct')\frac{\partial \hat{f}}{\partial t}dt' = \frac{\partial f}{\partial t} - Cf.$$

Exercise 10.7

From the problem statement, we postulate $x_{\mathrm{A}} = x_{\mathrm{A}}(x_1,t)$ and $v_1^* = v_1^*(x_1,t)$. For a dilute system, we can write $\tilde{\Gamma} \approx kx_{\mathrm{A}}$. From (10.3) with constant c, we can write

$$\frac{\partial v_1^*}{\partial x_1} = -k'x_{\mathrm{A}} \approx 0,$$

where $k' = k/c$, and the approximation holds for dilute mixtures. Since $v_1^*(\infty,t) = 0$, then $v_1^*(x_1,t) = 0$. Combining (5.23) and (10.10a) we have

$$\frac{\partial x_{\mathrm{A}}}{\partial t} = D_{\mathrm{AB}}\frac{\partial^2 x_{\mathrm{A}}}{\partial x_1^2} - k'x_{\mathrm{A}}.$$

The initial and boundary conditions are given by

$$x_{\mathrm{A}}(x_1,0) = 0, \qquad x_{\mathrm{A}}(0,t) = x_{\mathrm{Aeq}}, \qquad x_{\mathrm{A}}(\infty,t) = 0.$$

The problem involves the independent quantities $x_{\mathrm{A}}/x_{\mathrm{Aeq}}, x_1, t, D_{\mathrm{AB}}, k'$ so that $n-m = 5-2 = 3$. Using the scaling $x_{\mathrm{A}}/x_{\mathrm{Aeq}} \to x_{\mathrm{A}}$, $x_1/\sqrt{D_{\mathrm{AB}}/k'} \to x_1$ and $tk' \to t$, we have

$$\frac{\partial x_{\mathrm{A}}}{\partial t} = \frac{\partial^2 x_{\mathrm{A}}}{\partial x_1^2} - x_{\mathrm{A}},$$

and

$$x_{\mathrm{A}}(x_1,0) = 0, \qquad x_{\mathrm{A}}(0,t) = 1, \qquad x_{\mathrm{A}}(\infty,t) = 0.$$

If the reaction term is dropped, this problem is equivalent to that in Exercise 7.11, which has the solution in (7.45). Hence, we write

$$\hat{x}_{\mathrm{A}} = \mathrm{erfc}\Big(\frac{x_1}{\sqrt{4t}}\Big).$$

Now, from Exercise 10.6 we can write

$$x_{\mathrm{A}} = \int_0^t \frac{\partial \hat{x}_{\mathrm{A}}}{\partial t} \exp(-t')dt',$$

which leads to the desired result.

Exercise 10.8
Dividing (10.36) by $\tilde{M}_\alpha$ and using $w_\alpha = (\tilde{M}_\alpha/\tilde{M})x_\alpha$ we obtain

$$-\boldsymbol{n} \cdot \boldsymbol{N}_\alpha = \tilde{k}_{\mathrm{m}}(x_\alpha - x_{\alpha\mathrm{fl}}) \qquad \text{at } A_{\mathrm{s}},$$

where $\tilde{k}_{\mathrm{m}} = k_{\mathrm{m}}/\tilde{M}$. Since $\boldsymbol{v}^* = \boldsymbol{0}$, using (10.10a) in we can write

$$\boldsymbol{n} \cdot cD_{\mathrm{AB}} \boldsymbol{\nabla} x_{\mathrm{A}} = \tilde{k}_{\mathrm{m}}(x_{\mathrm{A}} - x_{A\mathrm{fl}}) \qquad \text{at } A_{\mathrm{s}}.$$

For the gas absorption process shown in Figure 10.1, we have $\boldsymbol{n} = \boldsymbol{\delta}_1$, so that we obtain the boundary condition

$$\frac{\partial x_{\mathrm{A}}}{\partial x_1}(0, x_3) = \frac{\tilde{k}_{\mathrm{m}}}{cD_{\mathrm{AB}}}[x_{\mathrm{A}}(0, x_3) - x_{A\mathrm{fl}}].$$

Exercise 10.9
Integration of (5.14) over V gives

$$\frac{d}{dt}M_{\alpha,\mathrm{tot}} = \int_V \boldsymbol{\nabla} \cdot (\boldsymbol{v}_A \rho_\alpha)dV - \int_V \boldsymbol{\nabla} \cdot (\boldsymbol{v}\rho_\alpha)dV - \int_V \boldsymbol{\nabla} \cdot \boldsymbol{j}_\alpha dV + \mathcal{R}_\alpha$$

where $M_{\alpha,\mathrm{tot}} = \int_V \rho_\alpha dV$ and $\mathcal{R}_\alpha = \int_V \nu_\alpha \Gamma dV$. Using Guass' divergence theorem, we obtain

$$\frac{d}{dt}M_{\alpha,\mathrm{tot}} = \int_A \rho_\alpha(\boldsymbol{v}_A - \boldsymbol{v}) \cdot \boldsymbol{n} dA - \int_A \boldsymbol{j}_\alpha \cdot \boldsymbol{n} dA + \mathcal{R}_\alpha,$$

Recall that $A = A_1 + A_2 + A_{\mathrm{s}}$, and that $\boldsymbol{v}_A = \boldsymbol{0}$ on A_i. We take ρ_α to be uniform over A_i and neglect $\boldsymbol{j}_\alpha$ at A_i, so that with $\langle (..)_i \rangle = \int_{A_i} (..)_i dA/A_i$, we obtain

$$\frac{d}{dt}M_{\alpha,\mathrm{tot}} = -\Delta[\langle v \rangle \rho_\alpha A] - \int_{A_{\mathrm{s}}} \rho_\alpha(\boldsymbol{v}_A - \boldsymbol{v}) \cdot \boldsymbol{n} dA - \int_{A_{\mathrm{s}}} \boldsymbol{j}_\alpha \cdot \boldsymbol{n} dA + \mathcal{R}_\alpha.$$

Now, since $A_{\mathrm{s}} = A_{\mathrm{si}} + A_{\mathrm{sp}}$, and for A_{si} we have $\boldsymbol{v}_A - \boldsymbol{v} = \boldsymbol{0}$ and $\boldsymbol{j}_\alpha = \boldsymbol{0}$, this gives

$$\frac{d}{dt}M_{\alpha,\mathrm{tot}} = -\Delta[\langle v \rangle \rho_\alpha A] - \int_{A_{\mathrm{sp}}} [\rho_\alpha \boldsymbol{v} + \boldsymbol{j}_\alpha] \cdot \boldsymbol{n} dA + \mathcal{R}_\alpha,$$

where we have set $\boldsymbol{v}_A = \mathbf{0}$ on A_{sp}. This gives (10.38) with

$$\mathcal{G}_\alpha = -\int_{A_{\text{sp}}} \boldsymbol{n}_\alpha \cdot \boldsymbol{n} dA.$$

Exercise 10.10
Dividing (10.38) by $\tilde{M}_\alpha$ and setting $\mathcal{G}_\alpha = 0$ we obtain

$$\frac{d}{dt} N_{\alpha,\text{tot}} = -\Delta[c_\alpha \langle v \rangle A] + \int_V \tilde{\nu}_\alpha \tilde{\Gamma} dV.$$

Perfect mixing implies $\tilde{\Gamma}$ is uniform over V and that $c_{\alpha 2} = c_\alpha$. Taking this into account and dividing by V gives

$$\frac{dc_\alpha}{dt} = -(c_{\alpha 1} - c_\alpha)\frac{\langle v \rangle A}{V} + \tilde{\nu}_\alpha \tilde{\Gamma}.$$

At steady state, we obtain the desired result.

Exercise 11.1
From (4.55) we can write for constant T

$$\begin{aligned} d(\hat{\mu}_2 - \hat{\mu}_1) &= (\hat{v}_2 - \hat{v}_1)dp + \left[\left(\frac{\partial \hat{\mu}_2}{\partial w_1}\right)_{T,p} - \left(\frac{\partial \hat{\mu}_1}{\partial w_1}\right)_{T,p}\right] dw_1 \\ &= (\hat{v}_2 - \hat{v}_1)dp - \frac{1}{\rho \rho_2 \hat{v}_2}\left(\frac{\partial \hat{\mu}_1}{\partial w_1}\right)_{T,p} d\rho_1 \end{aligned}$$

where the second equality is obtained using (4.54). At equilibrium, the left-hand side vanishes, and we divide the above result by dr, and substitute (11.8a), which gives

$$\frac{d\rho_1}{dr} = \left(\frac{\partial \hat{\mu}_1}{\partial w_1}\right)^{-1}_{T,p} \rho^2 \rho_2 \hat{v}_2 (\hat{v}_2 - \hat{v}_1)\Omega^2 r = \frac{\tilde{M}_1}{\tilde{R}T}\rho_1 \rho^2 \hat{v}_2^0 (\hat{v}_2^0 - \hat{v}_1^0)\Omega^2 r = \Lambda_p \frac{r}{R^2}\rho_1,$$

The second equality follows for a dilute, ideal mixture using results from Exercise 6.3 and noting $\rho_2 \approx \rho$. The third equality is obtained using $\Lambda_p = s_1 \Omega^2 R^2 / D_{12}$ and the expression for s_1 in (11.18). This result can also be obtained from the steady state form of (11.15). Integration gives

$$\rho_1 = c_1 \exp\left(\frac{\Lambda_p}{2}\frac{r^2}{R^2}\right),$$

Since the total mass of the solute is constant, we can write

$$\int_{R-L}^{R+L} \rho_1 r dr = \int_{R-L}^{R+L} \rho_{10} r dr = 2RL\rho_{10},$$

so that

$$c_1 \frac{R^2}{\Lambda_p}\Big[\exp\Big(\frac{\Lambda_p(1+\beta)^2}{2}\Big) - \exp\Big(\frac{\Lambda_p(1-\beta)^2}{2}\Big)\Big] = 2RL\rho_{10}$$

Solving for c_1 and substitution gives the result in (11.30).

Exercise 11.2

Setting $D_{12} = 0$ in (11.15) gives,

$$\frac{\partial \rho_1}{\partial t} = -s_1\Omega^2 \frac{1}{r}\frac{\partial}{\partial r}(r^2\rho_1) = -2s_1\Omega^2\rho_1 - s_1\Omega^2 r\frac{\partial \rho_1}{\partial r}$$

Using the chain rule, we can write the differential for ρ_1 to obtain

$$\frac{\partial \rho_1}{\partial t} = \frac{d\rho_1}{dt} - \frac{\partial \rho_1}{\partial r}\frac{dr}{dt}$$

Comparing the last two expressions, we find

$$\frac{d\rho_1}{dt} = -2s_1\Omega^2\rho_1, \qquad \frac{dr}{dt} = s_1\Omega^2 r$$

Integration gives

$$\rho_1 = \rho_{10}\exp(-2s_1\Omega^2 t), \qquad r = c_2\exp(s_1\Omega^2 t)$$

where we have used the initial condition in (11.16) to obtain the first expression. To satisfy the boundary condition $\rho_1(R-L,t) = 0$ from (11.17), we set $c_2 = R - L$, which leads to

$$\frac{\rho_1}{\rho_{10}} = \begin{cases} 0 & \text{for} \quad R-L \le r < (R-L)\exp(s_1\Omega^2 t), \\ \exp(-2s_1\Omega^2 t) & \text{for} \quad (R-L)\exp(s_1\Omega^2 t) < r \le R+L. \end{cases}$$

Exercise 11.3

Using $r \to (r-R)/L$, $t \to D_{12}t/L^2$ and $\rho_1 \to \rho_1/\rho_{10}$ to rescale (11.15) leads to

$$\frac{\partial \rho_1}{\partial t} = \frac{1}{1+\beta r}\frac{\partial}{\partial r}\Big((1+\beta r)\frac{\partial \rho_1}{\partial r}\Big) - \frac{\beta\Lambda_p}{1+\beta r}\frac{\partial}{\partial r}\Big((1+\beta r)^2)\rho_1\Big),$$

Similarly, (11.17) takes the form

$$\frac{\partial \rho_1}{\partial r}(-1,t) = \beta(1-\beta)\Lambda_p\rho_1(-1,t), \qquad \frac{\partial \rho_1}{\partial r}(1,t) = \beta(1+\beta)\Lambda_p\rho_1(1,t).$$

For $\beta \ll 1$, the given equations neglecting curvature are obtained.

Starting from the code for the diffusing particle with drift (see code on p. 30), we only need to adjust the drift and diffusion and push back the trajectories at both boundaries. The remaining code changes concern the storage of all time steps and the plotting of selected evolution snapshots.

```
% Simulation parameters
NTRA=5000; NTIME=300; NHIST=100; DT=0.001;
XMIN=-1; DX=0.05; XMAX=1;
edges=XMIN:DX:XMAX;
centers=XMIN+DX/2:DX:XMAX-DX/2;
ALPHAp=100;
beta=0.1;

for K=1:NHIST

    % Generation of NTRA trajectories x
    x=random('Uniform',XMIN,XMAX,[1 NTRA]);
    walks=zeros(NTIME,NTRA); % Store trajectories for plot

    for J=1:NTIME
        x=x+ALPHAp*beta*DT+random('Normal',0,sqrt(2*DT),[1,NTRA]);
        x(x<-1)=-1; % Boundary at r = -1
        x(x>1)=1; % Boundary at r = 1
        walks(J,:) = x;
    end

    % Collection of NHIST histograms in matrices p_ for t=0.01,0.03,0.1,0.3
    p_t001(K,:)=histc(walks(0.01/DT,:),edges)/(DX*NTRA);
    p_t003(K,:)=histc(walks(0.03/DT,:),edges)/(DX*NTRA);
    p_t01(K,:)=histc(walks(0.1/DT,:),edges)/(DX*NTRA);
    p_t03(K,:)=histc(walks(0.3/DT,:),edges)/(DX*NTRA);
end

% Plot of simulation results
figure;
axis([-1 1 0 2])
hold on;
ylabel('$\rho_1(r,t)/\rho_{10}$','FontSize',14,'Interpreter','latex');
xlabel('$(r-R)/L$','FontSize',14,'Interpreter','latex');

errorbar([centers NaN],mean(p_t001),std(p_t001)/sqrt(NHIST),'-k')
errorbar([centers NaN],mean(p_t003),std(p_t003)/sqrt(NHIST),':k')
errorbar([centers NaN],mean(p_t01),std(p_t01)/sqrt(NHIST),'-.k')
errorbar([centers NaN],mean(p_t03),std(p_t03)/sqrt(NHIST),'--k')

l=legend('t=0.01','t=0.03','t=0.1','t=0.3');
set(l,'Location','northwest','FontSize',14)
```

Exercise 11.4

From (11.18) we can write

$$\frac{D_{12}}{\tilde{R}T} = \frac{s_1}{\tilde{M}_1(1-\rho\hat{v}_1^0)}$$

or, since $\tilde{R} = \tilde{N}_{\rm A} k_{\rm B}$, we have

$$\frac{D_{12}}{k_{\rm B}T} = \frac{\tilde{N}_{\rm A} s_1}{\tilde{M}_1(1-\rho\hat{v}_1^0)} \ .$$

which, from Exercise 6.6, we identify as the mobility coefficient.

Exercise 11.5
Writing (7.2) in component form, we have

$$\rho\Big(\frac{\partial v_j}{\partial t}+\sum_i v_i\frac{\partial v_j}{\partial x_i}\Big)=\eta\sum_i\frac{\partial^2 v_j}{\partial x_i\partial x_i}+\frac{1}{3}\eta\frac{\partial}{\partial x_j}\sum_i\Big(\frac{\partial v_i}{\partial x_i}\Big)-\frac{\partial p}{\partial x_j}+\rho g_j.$$

We transform this equation term by term, starting with the right-hand side. The last two terms become

$$\rho g_j=\rho'\sum_k Q_{kj}g'_k,\qquad \frac{\partial p}{\partial x_j}=\sum_k Q_{kj}\frac{\partial p'}{\partial x'_k}$$

where we have used (11.25a) to obtain the second result. Using (11.22) and (11.25a) we can write

$$\begin{aligned}\frac{\partial}{\partial x_j}\sum_i\Big(\frac{\partial v_i}{\partial x_i}\Big)&=\sum_k Q_{kj}\frac{\partial}{\partial x'_k}\sum_{i,l}Q_{li}\frac{\partial}{\partial x'_l}\Big(\sum_n Q_{ni}v'_n+\sum_n\frac{dQ_{ni}}{dt}x'_n-\frac{dc_i}{dt}\Big)\\&=\sum_k Q_{kj}\frac{\partial}{\partial x'_k}\sum_l\frac{\partial}{\partial x'_l}\Big(\sum_{i,n}Q_{li}Q_{ni}v'_n+\sum_{i,n}Q_{li}\frac{dQ_{ni}}{dt}x'_n-\sum_i Q_{li}\frac{dc_i}{dt}\Big)\\&=\sum_k Q_{kj}\frac{\partial}{\partial x'_k}\sum_l\Big(\frac{\partial v'_l}{\partial x'_l}\Big)\end{aligned}$$

where the third equality follows from (11.20). For the first term on the right-hand side we have

$$\begin{aligned}\sum_i\frac{\partial^2 v_j}{\partial x_i\partial x_i}&=\sum_i\sum_k Q_{ki}\frac{\partial}{\partial x'_k}\sum_l Q_{li}\frac{\partial}{\partial x'_l}\Big(\sum_n Q_{nj}v'_n+\sum_n\frac{dQ_{nj}}{dt}x'_n-\frac{dc_j}{dt}\Big)\\&=\sum_k\sum_{i,l}Q_{ki}Q_{li}\frac{\partial}{\partial x'_k}\frac{\partial}{\partial x'_l}\Big(\sum_n Q_{nj}v'_n+\sum_n\frac{dQ_{nj}}{dt}x'_n-\frac{dc_j}{dt}\Big)\\&=\sum_{l,n}Q_{nj}\frac{\partial^2 v'_n}{\partial x'_l\partial x'_l}=\sum_k Q_{kj}\sum_l\frac{\partial^2 v'_k}{\partial x'_l\partial x'_l}\end{aligned}$$

The first term on the left-hand side becomes

$$\begin{aligned}\frac{\partial v_j}{\partial t}&=\frac{\partial}{\partial t}\Big(\sum_k Q_{kj}v'_k+\sum_k\frac{dQ_{kj}}{dt}x'_k-\frac{dc_j}{dt}\Big)\\&=\sum_k Q_{kj}\frac{\partial v'_k}{\partial t}+\sum_k\frac{dQ_{kj}}{dt}v'_k+\sum_k\frac{dQ_{kj}}{dt}\frac{\partial x'_k}{\partial t}+\sum_k\frac{d^2Q_{kj}}{dt^2}x'_k-\frac{d^2c_j}{dt^2}\\&=\sum_k Q_{kj}\Big[\frac{\partial' v'_k}{\partial t}-\sum_{l,n}\Big(A_{ln}x'_n-Q_{ln}\frac{dc_n}{dt}\Big)\frac{\partial v'_k}{\partial x'_l}\Big]\end{aligned}$$

$$+\sum_k \frac{dQ_{kj}}{dt}\Big(v'_k + \sum_l \frac{dQ_{kl}}{dt}x_l + \frac{dc'_k}{dt}\Big) + \sum_k \frac{d^2Q_{kj}}{dt^2}x'_k - \frac{d^2c_j}{dt^2}$$

$$= \sum_k Q_{kj}\Big[\frac{\partial' v'_k}{\partial t} - \sum_{l,n}\Big(A_{ln}x'_n - Q_{ln}\frac{dc_n}{dt}\Big)\frac{\partial v'_k}{\partial x'_l}\Big]$$

$$+\sum_k \frac{dQ_{kj}}{dt}\Big(v'_k - \sum_n A_{kn}x'_n + \sum_n Q_{kn}\frac{dc_n}{dt}\Big) + \sum_k \frac{d^2Q_{kj}}{dt^2}x'_k - \frac{d^2c_j}{dt^2}$$

The second term on the left-hand side becomes

$$\sum_i v_i \frac{\partial v_j}{\partial x_i} = \sum_i \Big[\Big(\sum_n Q_{ni}v'_n + \sum_n \frac{dQ_{ni}}{dt}x'_n - \frac{dc_i}{dt}\Big)$$

$$\times \sum_l Q_{li}\frac{\partial}{\partial x'_l}\Big(\sum_k Q_{kj}v'_k + \sum_k \frac{dQ_{kj}}{dt}x'_k - \frac{dc_j}{dt}\Big)\Big]$$

$$= \sum_i \Big[\Big(\sum_n Q_{ni}v'_n + \sum_n \frac{dQ_{ni}}{dt}x'_n - \frac{dc_i}{dt}\Big)\Big(\sum_{l,k} Q_{kj}Q_{li}\frac{\partial' v'_k}{\partial x'_l} + \sum_k Q_{ki}\frac{dQ_{kj}}{dt}\Big)$$

$$= \sum_k Q_{kj}\Big[\sum_l \Big(v'_l - \sum_n A_{nl}x'_n - \sum_n Q_{ln}\frac{dc_n}{dt}\Big)\frac{\partial v'_k}{\partial x'_l}\Big]$$

$$+\sum_k \frac{dQ_{kj}}{dt}\Big(v'_k - \sum_n A_{nk}x'_n - \sum_n Q_{kn}\frac{dc_n}{dt}\Big)$$

Adding the last two results, we obtain

$$\frac{\partial v_j}{\partial t} + \sum_i v_i\frac{\partial v_j}{\partial x_i} = \sum_k Q_{kj}\Big(\frac{\partial' v'_k}{\partial t} + \sum_l v'_l\frac{\partial v'_k}{\partial x'_l}\Big)$$

$$+ 2\sum_k \frac{dQ_{kj}}{dt}v'_k + \sum_k \frac{d^2Q_{kj}}{dt^2}x'_k - \frac{d^2c_j}{dt^2}$$

Combining results for the left- and right-hand sides, we obtain

$$\rho'\sum_k Q_{kj}\Big(\frac{\partial' v'_k}{\partial t} + \sum_l v'_l\frac{\partial v'_k}{\partial x'_l}\Big) + \rho'\Big[2\sum_k \frac{dQ_{kj}}{dt}v'_k + \sum_k \frac{d^2Q_{kj}}{dt^2}x'_k - \frac{d^2c_j}{dt^2}\Big]$$

$$= \sum_k Q_{kj}\Big[\eta\sum_l \frac{\partial^2 v'_k}{\partial x'_l\partial x'_l} + \frac{1}{3}\eta\frac{\partial}{\partial x'_k}\sum_l\Big(\frac{\partial v'_l}{\partial x'_l}\Big) - \frac{\partial p'}{\partial x'_k} + \rho' g'_k\Big]$$

Multiplication by Q_{ij} and summing over j gives

$$\rho'\Big(\frac{\partial' v'_i}{\partial t} + \sum_l v'_l\frac{\partial v'_i}{\partial x'_l}\Big) = \eta\sum_l \frac{\partial^2 v'_i}{\partial x'_l\partial x'_l} + \frac{1}{3}\eta\frac{\partial}{\partial x'_i}\sum_l\Big(\frac{\partial v'_l}{\partial x'_l}\Big) - \frac{\partial p'}{\partial x'_i} + \rho' g'_i\Big]$$

$$= \rho' \Big[\sum_j Q_{ij} \frac{d^2 c_j}{dt^2} - \sum_{j,k} Q_{ij} \frac{d^2 Q_{kj}}{dt^2} x'_k - 2 \sum_k A_{ik} v'_k \Big],$$

Finally, differentiation of (11.24) gives

$$\sum_j Q_{ij} \frac{d^2 Q_{kj}}{dt^2} = \frac{dA_{ik}}{dt} + \sum_j A_{ij} A_{jk},$$

which when substituted in the last expression gives (11.27).

Exercise 11.6
Normalizing time by h^2/D_{12}, spatial position by h, and solute mass fraction by $M_{10}/(2h^2 B)$, we can write (11.39) and (11.42) as

$$\frac{\partial \rho_1}{\partial t} + (1 - x_2^2) \frac{\partial \rho_1}{\partial \bar{x}_1} = \frac{1}{N_{\text{Pe}}^2} \frac{\partial^2 \rho_1}{\partial \bar{x}_1^2} + \frac{\partial^2 \rho_1}{\partial x_2^2} + \Lambda_T \frac{\partial \rho_1}{\partial x_2},$$

$$\frac{\partial \rho_1}{\partial x_2}(\bar{x}_1, \pm 1, t) = -\Lambda_T \rho_1(\bar{x}_1, \pm 1, t),$$

where $N_{\text{Pe}} = 3Vh/(2D_{12})$ and $\Lambda_T = D_T \Delta T/(2D_{12})$, and we have rescaled the flow direction coordinate $\bar{x}_1 = x_1/N_{\text{Pe}}$. Applying the transverse average defined in (11.44) to each term we obtain

$$\frac{\partial \langle \rho_1 \rangle}{\partial t} = \frac{1}{N_{\text{Pe}}^2} \frac{\partial^2 \langle \rho_1 \rangle}{\partial \bar{x}_1^2} - \frac{1}{2} \int_{-1}^{1} (1 - x_2^2) \frac{\partial \rho_1}{\partial \bar{x}_1} dx_2,$$

where we have used the boundary conditions given above. This result can be written as a generalized dispersion equation of the form given in (11.45) with,

$$K_i = \frac{\delta_{i2}}{N_{\text{Pe}}^2} - \frac{1}{2} \int_{-1}^{1} f_{i-1}(1 - x_2^2) dx_2.$$

To find the equations governing the f_j, we substitute (11.43) in the equation above for ρ_1, which gives,

$$\sum_{j=0}^{\infty} \frac{\partial f_j}{\partial t} \frac{\partial^j \langle \rho_1 \rangle}{\partial \bar{x}_1^j} + \sum_{j=0}^{\infty} f_j \frac{\partial}{\partial t} \frac{\partial^j \langle \rho_1 \rangle}{\partial \bar{x}_1^j} + (1 - x_2^2) \sum_{j=0}^{\infty} f_j \frac{\partial^{j+1} \langle \rho_1 \rangle}{\partial \bar{x}_1^{j+1}}$$
$$= \frac{1}{N_{\text{Pe}}^2} \sum_{j=0}^{\infty} f_j \frac{\partial^{j+2} \langle \rho_1 \rangle}{\partial \bar{x}_1^{j+2}} + \sum_{j=0}^{\infty} \frac{\partial^2 f_j}{\partial x_2^2} \frac{\partial^j \langle \rho_1 \rangle}{\partial \bar{x}_1^j} + \Lambda_T \sum_{j=0}^{\infty} \frac{\partial f_j}{\partial x_2} \frac{\partial^j \langle \rho_1 \rangle}{\partial \bar{x}_1^j}.$$

For the second term on the left-hand side, using (11.45), we can write

$$\sum_{j=0}^{\infty} f_j \frac{\partial}{\partial t} \frac{\partial^j \langle \rho_1 \rangle}{\partial \bar{x}_1^j} = \sum_{j=0}^{\infty} f_j \frac{\partial^j}{\partial \bar{x}_1^j} \sum_{i=1}^{\infty} K_i \frac{\partial^i \langle \rho_1 \rangle}{\partial \bar{x}_1^i} = \sum_{j=0}^{\infty} \sum_{i=1}^{j} K_i f_{j-i} \frac{\partial^j \langle \rho_1 \rangle}{\partial \bar{x}_1^j}.$$

Substitution in the previous result, and rearranging terms, we find

$$\frac{\partial f_j}{\partial t} + \sum_{i=1}^{j} K_i f_{j-i} + (1 - x_2^2) f_{j-1} = \frac{1}{N_{\text{Pe}}^2} f_{j-2} + \frac{\partial^2 f_j}{\partial x_2^2} + \Lambda_T \frac{\partial f_j}{\partial x_2}.$$

For $t \gg 1$, the equation governing f_0 is given by

$$\frac{\partial^2 f_0}{\partial x_2^2} + \Lambda_T \frac{\partial f_0}{\partial x_2} = 0,$$

which has solution

$$f_0 = c_2 \exp(-\Lambda_T x_2).$$

To find c_2, we use the normalization

$$\frac{1}{2} \int_{-1}^{1} f_0 dx_2 = 1,$$

which gives

$$f_0 = \frac{\Lambda_T \exp(-\Lambda_T x_2)}{\sinh(\Lambda_T)}.$$

Now, to find K_1, we have

$$K_1 = -\frac{1}{2} \int_{-1}^{1} f_0 (1 - x_2^2) dx_2 = -\frac{1}{2} \int_{-1}^{1} \frac{\Lambda_T \exp(-\Lambda_T x_2)}{\sinh(\Lambda_T)} (1 - x_2^2) dx_2.$$

Evaluation of the integral gives (11.47).

Exercise 11.7
To obtain the solute concentration profile that is independent of $\bar{x}_1$ and time, we write

$$(j_1)_2 = 0 = -D_{12} \frac{d\rho_1}{dx_2} - D_T \rho_1 \frac{dT}{dx_2},$$

which can be rearranged to obtain

$$\frac{1}{\rho_1} \frac{d\rho_1}{dx_2} = -\frac{D_T}{D_{12}} \frac{dT}{dx_2} = -\Lambda_T,$$

where $\Lambda_T = D_T \Delta T / (2 D_{12})$. Integration gives

$$\rho_1 = c \exp(-\Lambda_T x_2),$$

where c is a constant. Substitution in the expression for the retention ratio gives,

$$R_{\text{ret}} = -\frac{4}{\Lambda_T^2}[1 - \Lambda_T \coth(\Lambda_T)],$$

which, from (11.47), we see $R_{\text{ret}} = -2K_1$. The retention ratio increases with decreasing Λ_T, or increasing retention parameter $1/\Lambda_T$.

Exercise 11.8

Substitution of $\rho_1 = \langle\rho_1\rangle + \delta\rho_1$ in the solute concentration evolution equation gives

$$\frac{\partial\langle\rho_1\rangle}{\partial t} + \frac{\partial\delta\rho_1}{\partial t} + v_z\frac{\partial\langle\rho_1\rangle}{\partial z} + v_z\frac{\partial\delta\rho_1}{\partial z} = D_{12}\Big[\frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial\delta\rho_1}{\partial r}\Big) + \frac{\partial^2\langle\rho_1\rangle}{\partial z^2} + \frac{\partial^2\delta\rho_1}{\partial z^2}\Big].$$

Application of $2/R^2\int_0^R(...)rdr$ to this equation gives

$$\frac{\partial\langle\rho_1\rangle}{\partial t} + V\frac{\partial\langle\rho_1\rangle}{\partial z} + \langle v_z\frac{\partial\delta\rho_1}{\partial z}\rangle = D_{12}\frac{\partial^2\langle\rho_1\rangle}{\partial z^2},$$

where we have used $\langle\delta\rho_1\rangle = 0$, $\langle v_z\rangle = V$ and $\partial\delta\rho_1/\partial r(R,z) = 0$. Subtracting the second result from the first gives

$$\frac{\partial\delta\rho_1}{\partial t} + (v_z - V)\frac{\partial\langle\rho_1\rangle}{\partial z} + v_z\frac{\partial\delta\rho_1}{\partial z} - \langle v_z\frac{\partial\delta\rho_1}{\partial z}\rangle = D_{12}\Big[\frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial\delta\rho_1}{\partial r}\Big) + \frac{\partial^2\delta\rho_1}{\partial z^2}\Big].$$

Now, for $t \gtrsim R^2/D_{12}$, we have $|\delta\rho_1| \ll \langle\rho_1\rangle$, and we further assume diffusion in the z-direction is negligible compared to diffusion in the r-direction. This leads to

$$\frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial\delta\rho_1}{\partial r}\Big) = \frac{V}{D_{12}}\Big(r - 2\frac{r^3}{R^2}\Big)\frac{\partial\langle\rho_1\rangle}{\partial z}.$$

Integrating twice with respect to r gives

$$\delta\rho_1 = \frac{V}{D_{12}}\frac{\partial\langle\rho_1\rangle}{\partial z}\Big(\frac{r^2}{4} - \frac{r^4}{8R^2} + c_1 + c_2\ln r\Big).$$

Enforcing regularity at $r = 0$ requires $c_2 = 0$, and since $\langle\delta\rho_1\rangle = 0$, we find $c_1 = -R^2/12$. Hence, we have

$$\delta\rho_1 = \frac{VR^2}{24D_{12}}\frac{\partial\langle\rho_1\rangle}{\partial z}\Big[6\Big(\frac{r}{R}\Big)^2 - 3\Big(\frac{r}{R}\Big)^4 - 2\Big].$$

Differentiation with respect to z, multiplication by v_z, and integrating $2/R^2\int_0^R(...)rdr$ gives

$$\langle v_z\frac{\partial\delta\rho_1}{\partial z}\rangle = -\frac{V^2R^2}{48D_{12}}\frac{\partial^2\langle\rho_1\rangle}{\partial z^2}.$$

Substitution in the equation for $\langle \delta\rho_1 \rangle$ gives

$$\frac{\partial\langle\rho_1\rangle}{\partial t} + V\frac{\partial\langle\rho_1\rangle}{\partial z} = \Big(D_{12} + \frac{V^2R^2}{48D_{12}}\Big)\frac{\partial^2\langle\rho_1\rangle}{\partial z^2} = K_{\mathrm{d}}\frac{\partial^2\langle\rho_1\rangle}{\partial z^2},$$

where $K_{\mathrm{d}} = D_{12}[1 + (1/48)N_{\mathrm{Pe}}^2]$ with $N_{\mathrm{Pe}} = VR/D_{12}$.

Exercise 11.9

From the Nernst-Planck equation (6.45) we can write for constant ρ

$$\boldsymbol{j}_1 = -\rho D_{12}\boldsymbol{\nabla}\rho_1 - \rho_1\frac{D_{12}\tilde{M}_1}{\tilde{R}T}z_1\boldsymbol{\nabla}\phi_{\mathrm{el}}.$$

The electric field across the channel is uniform so that $\boldsymbol{\nabla}\phi_{\mathrm{el}} = \Delta\phi/(2h)\boldsymbol{\delta}_2$. Substitution in (11.32) gives

$$\frac{\partial\rho_1}{\partial t} + \frac{3}{2}V\Big[1 - \Big(\frac{x_2}{h}\Big)^2\Big]\frac{\partial\rho_1}{\partial x_1} = D_{12}\Big[\frac{\partial^2\rho_1}{\partial x_1^2} + \frac{\partial^2\rho_1}{\partial x_2^2}\Big] + \frac{D_{12}}{h}\Big(\frac{z_1\Delta\phi\tilde{M}_1}{2\tilde{R}T}\Big)\frac{\partial\rho_1}{\partial x_2},$$

where the last term contains the parameter $\Lambda_\phi = z_1\Delta\phi\tilde{M}_1/(2\tilde{R}T)$.

Exercise 12.1

For $\gamma(t) = \gamma_0\sin\omega t$, from (12.1) we can write

$$\tau_{12} = -\gamma_0\omega\int_{-\infty}^{t} G(t-t')\cos(\omega t')dt',$$

or, using the change of variable $s = t - t'$

$$\begin{aligned}\tau_{12} &= -\gamma_0\omega\int_0^\infty G(s)\cos[\omega(t-s)]ds \\ &= -\gamma_0\omega\Big[\int_0^\infty G(s)\cos(\omega t)\sin(\omega s)ds + \int_0^\infty G(s)\sin(\omega t)\cos(\omega s)\Big]ds \\ &= -\gamma_0[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)]\end{aligned}$$

where G' and G'' are given in (12.6) and (12.7). Now, we write

$$\tau_{12} = -\tau_0\sin(\omega t + \delta) = -\tau_0[\cos(\delta)\sin(\omega t) + \sin(\delta)\cos(\omega t)].$$

Comparing with the last expression, we have

$$\frac{\tau_0}{\gamma_0}\cos\delta = G', \qquad \frac{\tau_0}{\gamma_0}\sin\delta = G'',$$

which gives the expression for the phase lag δ in (12.18b). Now, using (12.8), we can write

$$|G^*|^2 = (G' + iG'')(G' - iG'') = (G')^2 + (G'')^2 = \Big(\frac{\tau_0}{\gamma_0}\Big)^2,$$

or $|G^*| = \tau_0/\gamma_0$, which gives (12.18a).

Exercise 12.2
After using $e^{-i\omega t} = \cos\omega t - i\sin\omega t$ in (12.9), we obtain

$$\eta'(\omega) = \int_0^\infty G(t)\cos\omega t dt,$$

$$\eta''(\omega) = \int_0^\infty G(t)\sin\omega t dt.$$

Exercise 12.3
From (12.13), we have for simple elongation

$$\tau_{11}(t) - \tau_{33}(t) = -3\dot{\epsilon}\int_0^t G(t-t')dt' = -3\dot{\epsilon}\int_0^t G(t')dt'.$$

Equation (12.4) thus implies

$$\eta_{\mathrm{E}}^+(t) = 3\eta^+(t).$$

The factor of 3 between $\eta_{\mathrm{E}}^+(t)$ and $\eta^+(t)$ is known as the *Trouton ratio*. Similarly, for equibiaxial elongation, we have From (12.13), we have

$$\tau_{11}(t) - \tau_{33}(t) = -6\dot{\epsilon}\int_0^t G(t-t')dt' = -6\dot{\epsilon}\int_0^t G(t')dt'.$$

Equation (12.4) thus implies

$$\eta_{\mathrm{B}}^+(t) = 6\eta^+(t).$$

Exercise 12.4
It is sufficient to consider a single mode $(\eta_j/\lambda_j)\exp\{-t/\lambda_j\}$; the η_∞ contribution corresponds to a vanishing relaxation time. With the indefinite integral

$$\int \frac{\eta_j}{\lambda_j} e^{-t/\lambda_j} dt = -\eta_j e^{-t/\lambda_j},$$

we obtain $\eta^+(t)$ and $\eta^-(t)$. From the more general formula

$$\int \frac{\eta_j}{\lambda_j} e^{-i\omega t - t/\lambda_j} dt = -\frac{\eta_j}{1 + i\omega\lambda_j} e^{-i\omega t - t/\lambda_j},$$

$\eta^*(\omega)$ is obtained from (12.9). The real and imaginary parts $\eta'(\omega)$ and $\eta''(\omega)$

defined in (12.19) can then be read off from

$$\frac{\eta_j}{1+i\omega\lambda_j} = \frac{\eta_j}{1+i\omega\lambda_j}\frac{1-i\omega\lambda_j}{1-i\omega\lambda_j} = \eta_j\frac{1-i\omega\lambda_j}{1+\omega^2\lambda_j^2}.$$

According to (12.8) and (12.9), $G^*(\omega)$ is obtained as $i\omega\eta^*(\omega)$, and hence $G'(\omega) = \omega\eta''(\omega)$ and $G''(\omega) = \omega\eta'(\omega)$.

Exercise 12.5
After inserting the expression for $\eta'(\omega)$ from Table 12.1 into the Kramers-Kronig relation (12.28), we obtain

$$\eta''(\omega) = \frac{2\omega}{\pi}\sum_j \eta_j \frac{\lambda_j^2}{1+\omega^2\lambda_j^2}\int_0^\infty \frac{1}{1+\omega'^2\lambda_j^2}d\omega'.$$

By substitution, we find the final result

$$\eta''(\omega) = \frac{2\omega}{\pi}\sum_j \eta_j \frac{\lambda_j}{1+\omega^2\lambda_j^2}\int_0^\infty \frac{1}{1+z^2}dz = \sum_j \eta_j\frac{\omega\lambda_j}{1+\omega^2\lambda_j^2}.$$

Exercise 12.6
By means of (12.24), we obtain

$$\begin{aligned} G(t;T) &= \sum_j \frac{\eta_j(T)}{\lambda_j(T)}e^{-t/\lambda_j(T)} + G_0 \\ &= \sum_j \frac{\eta_j(T_0)}{\lambda_j(T_0)}e^{-t/[a_T\lambda_j(T_0)]} + G_0 = G(t/a_T;T_0). \end{aligned}$$

Equation (12.6) then implies

$$\begin{aligned} G'(\omega;T) &= \omega\int_0^\infty G(t;T)\sin\omega t dt = \omega\int_0^\infty G(t/a_T;T_0)\sin\omega t dt \\ &= a_T\omega\int_0^\infty G(t';T_0)\sin(a_T\omega t')dt' = G'(a_T\omega;T_0), \end{aligned}$$

where the substitution $t = a_T t'$ has been used. Equation (12.32) follows in the same way. Finally,

$$\eta(T) = \int_0^\infty G(t;T)dt = a_T\int_0^\infty G(t';T_0)dt' = a_T\eta(T_0).$$

Exercise 12.7
From the expression

$$\lambda_{\text{avg}} = \frac{\int_0^\infty tG(t)dt}{\int_0^\infty G(t)dt}$$

it is clear that λ_{avg} can be considered as an average weighted by the memory function of the stress–strain rate relationship. In terms of the spectrum (12.24), we have

$$\Psi_{10} = 2\sum_j \frac{\eta_j}{\lambda_j}\int_0^\infty te^{-t/\lambda_j}dt = 2\sum_j \eta_j\lambda_j,$$

and thus

$$\lambda_{\text{avg}} = \frac{\sum_j \eta_j\lambda_j}{\sum_j \eta_j}.$$

So, in the average λ_{avg}, each relaxation time is weighted by its viscosity contribution. For single-mode relaxation, we have $\lambda_{\text{avg}} = \lambda_1$.

Exercise 12.8
From the given velocity field, the rate of strain tensor takes the form

$$\dot{\boldsymbol{\gamma}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \dot{\gamma} \\ 0 & \dot{\gamma} & 0 \end{pmatrix},$$

where

$$\dot{\gamma}(\theta) = \sin(\theta)\frac{dw}{d\theta},$$

where $w(\theta)$ must satisfy the following

$$w(\pi/2) = 0, \qquad w(\pi/2-\beta) = \sin(\pi/2-\beta)\Omega.$$

The stress tensor takes the form

$$\boldsymbol{\tau} = \begin{pmatrix} \tau_{rr} & 0 & 0 \\ 0 & \tau_{\theta\theta} & \tau_{\theta\phi} \\ 0 & \tau_{\phi\theta} & \tau_{\phi\phi} \end{pmatrix},$$

where, since $\dot{\gamma} = \dot{\gamma}(\theta)$, all the components of $\boldsymbol{\tau}$ depend on θ.

For steady, creeping flow of an incompressible fluid, the r-, θ- and ϕ-components equations of motion (5.33) can be written as

$$\frac{\partial p^{\text{L}}}{\partial r} = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\tau_{rr}) - \frac{2}{r}\tau_{rr} + \frac{\tau_{\theta\theta}+\tau_{\phi\phi}}{r} = -\frac{\partial \tau_{rr}}{\partial r} - \frac{1}{r}(N_1+2N_2),$$

$$\frac{\partial p^{\rm L}}{\partial \theta} = -\frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}(\tau_{\theta\theta}\sin(\theta) + \tau_{\phi\phi}\cot(\theta) = -\frac{\partial \tau_{\theta\theta}}{\partial \theta} - \cot(\theta)N_1,$$

$$\frac{\partial p^{\rm L}}{\partial \phi} = -\frac{\partial}{\partial \theta}\left(\sin^2(\theta)\tau_{\theta\phi}\right),$$

where gravity has also been neglected. The second equalities in the r- and θ-components follow with the definitions $N_1 = \tau_{\phi\phi} - \tau_{\theta\theta}$ and $N_2 = \tau_{\theta\theta} - \tau_{rr}$. Since $p^{\rm L}(r,\theta,\phi) = p^{\rm L}(r,\theta,\phi + 2\pi)$, the ϕ-component can be integrated to obtain

$$\tau_{\theta\phi} = \frac{c_1}{\sin^2(\theta)},$$

where c_1 is a constant. The torque $\boldsymbol{\mathcal{M}}_{\rm s}$ exerted by the fluid on the stationary plate is obtained from (7.15), which we write as

$$\begin{aligned}
\boldsymbol{\mathcal{M}}_{\rm s} &= \int_0^{2\pi}\int_0^R [\boldsymbol{r} \times (\boldsymbol{n}\cdot\boldsymbol{\pi})](r,\pi/2,\phi) r dr d\phi \\
&= \int_0^{2\pi}\int_0^R [\boldsymbol{\delta}_r \times (\boldsymbol{\delta}_\theta\cdot\boldsymbol{\pi})](r,\pi/2,\phi) r^2 dr d\phi \\
&= \int_0^{2\pi}\int_0^R [\boldsymbol{\delta}_r \times (\pi_{\theta r}\boldsymbol{\delta}_r + \pi_{\theta\theta}\boldsymbol{\delta}_\theta + \pi_{\theta\phi}\boldsymbol{\delta}_\phi](r,\pi/2,\phi) r^2 dr d\phi \\
&= \int_0^{2\pi}\int_0^R [\pi_{\theta\theta}\boldsymbol{\delta}_\phi - \pi_{\theta\phi}\boldsymbol{\delta}_\theta)](r,\pi/2,\phi) r^2 dr d\phi \\
&= 2\pi \int_0^R \tau_{\theta\phi}(r,\pi/2) r^2 dr \boldsymbol{\delta}_3
\end{aligned}$$

where the second line follows since $\boldsymbol{r} = r\boldsymbol{\delta}_r$ and $\boldsymbol{n} = \boldsymbol{\delta}_\theta(\theta = \pi/2)$, and the fifth equality is obtained by replacing the spherical base vectors with rectangular base vectors. Substitution for $\tau_{\theta\phi}$ and performing the integration gives

$$\tau_{\theta\phi} = \frac{3\mathcal{M}_{\rm s}}{2\pi R^3}.$$

The r- and θ-components are incompatible unless $\dot{\gamma}$ is independent of θ, which holds for $\beta \ll 1$. In this case, integration of the differential equation for $w(\theta)$ gives

$$\dot{\gamma} = \frac{\Omega\sin(\pi/2 - \beta)}{\ln[\sin(\pi/2-\beta)] - \ln[1 + \cos(\pi/2 - \beta)]} \approx -\frac{\Omega}{\theta},$$

Integration of the r- and θ-components leads to

$$\pi_{\theta\theta}(r,\theta) = \pi_{rr}(R,\pi/2) - N_2 + (N_1 + 2N_2)\ln\left(\frac{r}{R}\right) - N_2\int_{\pi/2}^{\theta}\cot(\theta')d\theta',$$

Setting $\pi_{rr}(R,\pi/2) = p_0$, the ambient pressure, gives the following expression for the pressure tensor on the plate

$$\pi_{\theta\theta}(r,\pi/2) = p_0 - N_2 + (N_1 + 2N_2)\ln\left(\frac{r}{R}\right).$$

The force on the plate is obtained by application of (8.39), which gives

$$\begin{aligned}
\boldsymbol{\mathcal{F}}_{\mathrm{s}} &= \int_0^{2\pi}\int_0^R [\boldsymbol{n}\cdot\boldsymbol{\pi}](r,\pi/2,\phi)rdrd\phi = \int_0^{2\pi}\int_0^R [\boldsymbol{\delta}_\theta\cdot\boldsymbol{\pi}](r,\pi/2,\phi)rdrd\phi \\
&= \int_0^{2\pi}\int_0^R [\pi_{\theta r}\boldsymbol{\delta}_r + \pi_{\theta\theta}\boldsymbol{\delta}_\theta + \pi_{\theta\phi}\boldsymbol{\delta}_\phi](r,\pi/2,\phi)rdrd\phi \\
&= 2\pi\int_0^R \pi_{\theta\theta}(r,\pi/2)rdr\boldsymbol{\delta}_3.
\end{aligned}$$

Substitution for $\pi_{\theta\theta}(r,\pi/2)$ and performing the integration gives, after subtracting the contribution of the ambient pressure p_0, the following

$$N_1 = \frac{2\mathcal{F}_{\mathrm{s}}}{\pi R^2}.$$

From N_1 and the pressure distribution on the plate, N_2 can be found.

Exercise 12.9
For a generalized Newtonian fluid (12.38) in shear flow with shear rate $\dot{\gamma}$, the second invariant of $\dot{\boldsymbol{\gamma}}$ is $\sqrt{(\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}})/2} = \dot{\gamma}$. The parameters in (12.39) can be estimated as follows. For $\dot{\gamma}\to 0$, we find $\eta \to \eta_0 \approx 49,000$ Pas. For $\dot{\gamma}\to\infty$, $\eta \propto \dot{\gamma}^{n-1}$, which gives $n \approx 0.15$. Shear thinning occurs for $\lambda\dot{\gamma}\approx 1$ so that $\lambda \approx 0.85$ s.

Table C.4 *PS 200 kDa viscosity data at 180°C from Figure 12.5.*

$\dot{\gamma}[\mathrm{s}^{-1}]$	η[Pas]
0.051	47832
0.10	46670
0.20	50433
0.51	46670
1.0	38338
2.0	24630
5.0	14341
10.0	7757
20.0	4516
47.0	2057

Exercise 12.10

For a yield stress fluid (12.40) flowing with velocity field $v_1 = v_1(x_2)$, the rate of strain and stress tensors are

$$\dot{\boldsymbol{\gamma}} = \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad \boldsymbol{\tau} = \begin{pmatrix} 0 & \tau_{12} & 0 \\ \tau_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

where $\dot{\gamma} = dv_1/dx_2$. The equations of motion (5.33) reduce to

$$\frac{dp^{\mathrm{L}}}{dx_1} = -\frac{d\tau_{12}}{dx_2}$$

Setting the pressure gradient equal to $\Delta p^{\mathrm{L}}/L$ and integrating gives

$$\tau_{12} = -\frac{\Delta p^{\mathrm{L}}}{L} x_2.$$

For $x_2 = b$ we have $\tau_{12} = 2\sigma$, which gives

$$b = -\frac{2\sigma}{\Delta p^{\mathrm{L}}/L}.$$

For a Bingham fluid, (12.40) with $G \to \infty$, we have $\tau_{12} = -[\sigma + \eta dv_1/dx_2]$ for $\sqrt{(\boldsymbol{\tau} : \boldsymbol{\tau})/2} = \tau_{12} \geq 2\sigma$, and $dv_1/dx_2 = 0$ for $\tau_{12} < 2\sigma$. Since, $\tau_{12} \geq 2\sigma$ for $b < |x_2| \leq B$, substitution for τ_{12} and integrating gives

$$v_1 = \frac{\Delta p^{\mathrm{L}}}{2\eta L} x_2^2 + \frac{\sigma}{\eta} x_2 + c_2$$

Since, $v_1(B) = 0$, we have

$$c_2 = -\frac{\Delta p^{\mathrm{L}} B^2}{2\eta L} - \frac{\sigma}{\eta} B,$$

which leads to the following for the velocity

$$v_1 = \begin{cases} \frac{-\Delta p^{\mathrm{L}} B^2}{2\eta L}\left[1 - \left(\frac{b}{B}\right)^2\right] - \frac{\sigma B}{\eta}\left[1 - \left(\frac{b}{B}\right)\right] & \text{for} \quad 0 \leq |x_2| \leq b, \\ \frac{-\Delta p^{\mathrm{L}} B^2}{2\eta L}\left[1 - \left(\frac{x_2}{B}\right)^2\right] - \frac{\sigma B}{\eta}\left[1 - \left(\frac{x_2}{B}\right)\right] & \text{for} \quad b < |x_2| \leq B. \end{cases}$$

Exercise 12.11

From the definition of $\boldsymbol{c}$ in (12.57) and the evolution equation (12.45) for $\boldsymbol{\tau}$, we obtain

$$\frac{\partial \boldsymbol{c}}{\partial t} = -\boldsymbol{v} \cdot \boldsymbol{\nabla} \boldsymbol{c} + \boldsymbol{\kappa} \cdot \boldsymbol{c} + \boldsymbol{c} \cdot \boldsymbol{\kappa}^T - \frac{1}{\lambda}(\boldsymbol{c} - \boldsymbol{\delta}).$$

The chain rule

$$\frac{\partial \hat{s}}{\partial t} = \frac{k_{\rm B}}{m}\frac{\partial f}{\partial \boldsymbol{c}} : \frac{\partial \boldsymbol{c}}{\partial t}$$

leads to (12.58). The first term on the right-hand side of (12.58) represents convection for the scalar entropy per mass. The third term describes the entropy production rate due to conformational relaxation, as indicated by the occurrence of the rate parameter $1/\lambda$. The second term can neither be convection (not of divergence form) nor production (relaxation is the only dissipative process). It rather describes the exchange between conformational and thermal forms of entropy. Therefore, the second term has to cancel the stress contribution to the entropy source term in (6.2) so that, for a complex fluid, σ in (6.2) can no longer be interpreted as the entropy production rate. This cancelation requires

$$2k_{\rm B}T\frac{\rho}{m}\,\boldsymbol{c}\cdot\frac{\partial f}{\partial \boldsymbol{c}} = \boldsymbol{\tau} = G(\boldsymbol{\delta} - \boldsymbol{c})\,.$$

The modulus G can naturally be identified with $k_{\rm B}T\rho/m$ (this can actually be taken as the definition of m), so that we find

$$\frac{\partial f}{\partial \boldsymbol{c}} = \frac{1}{2}\boldsymbol{c}^{-1}\cdot(\boldsymbol{\delta} - \boldsymbol{c})\,.$$

This identity holds for the expression given in (12.59), where the integration constant is fixed such that $f(\boldsymbol{\delta}) = 0$. The tensor $\boldsymbol{c}$ is assumed to be invertible and must be positive-definite to guarantee the positivity of the last term on the right-hand side of (12.58).

Exercise 12.12

Taking the convected derivative of $\boldsymbol{\tau} = \boldsymbol{\tau}^{\rm s} + \boldsymbol{\tau}^{\rm p}$ gives the following

$$\boldsymbol{\tau}_{(1)} = \boldsymbol{\tau}^{\rm s}_{(1)} + \boldsymbol{\tau}^{\rm p}_{(1)}.$$

Multiplication by λ and adding $\boldsymbol{\tau} = \boldsymbol{\tau}^{\rm s} + \boldsymbol{\tau}^{\rm p}$ gives

$$\lambda\boldsymbol{\tau}_{(1)} + \boldsymbol{\tau} = \lambda\boldsymbol{\tau}^{\rm s}_{(1)} + \boldsymbol{\tau}^{\rm s} + \lambda\boldsymbol{\tau}^{\rm p}_{(1)} + \boldsymbol{\tau}^{\rm p}.$$

Now, since $\boldsymbol{\tau}^{\rm s} = -\eta^{\rm s}\dot{\boldsymbol{\gamma}}$, and $\lambda\boldsymbol{\tau}^{\rm p}_{(1)} = -\boldsymbol{\tau}^{\rm p} - \eta^{\rm p}\dot{\boldsymbol{\gamma}}$, we have

$$\lambda\boldsymbol{\tau}_{(1)} + \boldsymbol{\tau} = -\lambda\eta^{\rm s}\dot{\boldsymbol{\gamma}}_{(1)} - \eta^{\rm s}\dot{\boldsymbol{\gamma}} - \eta^{\rm p}\dot{\boldsymbol{\gamma}},$$

which, since $\eta = \eta^{\rm s} + \eta^{\rm p}$, can easily be rearranged to give (12.60).

Exercise 12.13

To obtain the viscometric functions given by (12.61), we must evaluate $\dot{\boldsymbol{\gamma}}$, $\dot{\boldsymbol{\gamma}}_{(1)}$ and $\dot{\boldsymbol{\gamma}} \cdot \dot{\boldsymbol{\gamma}}$ in homogeneous shear flow. For the velocity field $v_1 = v_1(x_2)$, the velocity gradient and rate of strain tensors are

$$\boldsymbol{\nabla v} = \boldsymbol{\kappa}^T = \begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad \dot{\boldsymbol{\gamma}} = \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

Since the flow is steady and homogeneous, $D\dot{\boldsymbol{\gamma}}/Dt = \mathbf{0}$. Hence, the convected derivative contains only

$$\boldsymbol{\kappa} \cdot \dot{\boldsymbol{\gamma}} = \dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\kappa}^T = \begin{pmatrix} \dot{\gamma}^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

and for $\dot{\boldsymbol{\gamma}} \cdot \dot{\boldsymbol{\gamma}}$, we have

$$\dot{\boldsymbol{\gamma}} \cdot \dot{\boldsymbol{\gamma}} = \begin{pmatrix} \dot{\gamma}^2 & 0 & 0 \\ 0 & \dot{\gamma}^2 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

Hence, for (12.61), we can write

$$\boldsymbol{\tau} = -b_1 \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} + 2b_2 \begin{pmatrix} \dot{\gamma}^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} - b_{11} \begin{pmatrix} \dot{\gamma}^2 & 0 & 0 \\ 0 & \dot{\gamma}^2 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

This gives

$$\tau_{12} = -b_1 \dot{\gamma}, \qquad \tau_{11} = (2b_2 - b_{11})\dot{\gamma}^2, \qquad \tau_{22} = -b_{11}\dot{\gamma}^2,$$

so that for the viscometric functions defined in (12.34)-(12.36) we have

$$\eta = b_1, \qquad \Psi_1 = -2b_2, \qquad \Psi_2 = b_{11}.$$

Hence, the second-order fluid predicts non-zero normal stress coefficients, but shear-rate independent viscometric functions.

Exercise 12.14

We can split the covariant equations (12.74) into the energy balance $\partial_\mu T^{\mu 0} = 0$ and the momentum balance $\partial_\mu T^{\mu j} = 0$. These balance equations can be further expanded into

$$\frac{\partial}{\partial t} T^{00} = -\frac{\partial}{\partial x^k} c T^{k0},$$

and

$$\frac{\partial}{\partial t}\frac{T^{0j}}{c} = -\frac{\partial}{\partial x^k}T^{kj} \,.$$

We can hence interpret T^{00} as the energy density, cT^{k0} as the energy flux, T^{0j}/c as the momentum density, and T^{kj} as the pressure tensor. Indeed, according to (12.91), T^{kj} has an isotropic contribution given by p_f. The contribution $\rho_\mathrm{f} c^2 u^0 u^j = \gamma^2 c\,\rho_\mathrm{f} v^j$ to T^{0j} in (12.91) is crucial to recognize the momentum density in T^{0j}/c.

By considering (12.91) in the comoving reference frame of the fluid we realize that $\alpha_{\mu\nu}$ contributes only to the pressure tensor. The four-vector $\hat{\omega}_\mu$ characterizes the non-convective part of the heat flux, but also contributes to the pressure tensor.

Exercise 12.15

The derivatives of the entropy $s_\mathrm{f} = -(1/2)H\hat{\omega}_\mu\alpha^{\mu\nu}\hat{\omega}_\nu$ are given by

$$\frac{\partial s_\mathrm{f}}{\partial \alpha^{\mu\nu}} = -\frac{1}{2}H\hat{\omega}_\mu\hat{\omega}_\nu \,, \qquad \frac{\partial s_\mathrm{f}}{\partial \hat{\omega}_\mu} = -H\alpha^{\mu\nu}\hat{\omega}_\nu \,.$$

By inserting into (12.86) we obtain the following structural contribution to the energy-momentum tensor,

$$T_\mathrm{f} H\Big(\alpha^{\mu\lambda}\hat{\omega}_\lambda\hat{\omega}^\nu + \hat{\omega}^\mu\hat{\omega}_\lambda\alpha^{\lambda\nu} - \hat{\omega}^\mu\hat{\omega}^\nu\Big) - T_\mathrm{f}^2 H\Big(\alpha^{\mu\lambda}\hat{\omega}_\lambda u^\nu + u^\mu\hat{\omega}_\lambda\alpha^{\lambda\nu}\Big) \,,$$

which is symmetric.

Exercise 13.1

As the temperature T is constant throughout the system, it does not depend on the location of the dividing surface. We can hence evaluate the derivative of $f^\mathrm{s}(T, \rho^\mathrm{s})$ with respect to ρ^s for fixed T in terms of derivatives with respect to ℓ,

$$\frac{\partial f^\mathrm{s}(T,\rho^\mathrm{s})}{\partial \rho^\mathrm{s}} = \frac{df^\mathrm{s}/d\ell}{d\rho^\mathrm{s}/d\ell} = \frac{du^\mathrm{s}/d\ell}{d\rho^\mathrm{s}/d\ell} - T\frac{ds^\mathrm{s}/d\ell}{d\rho^\mathrm{s}/d\ell}.$$

With $d\rho^\mathrm{s}/d\ell = \rho^\mathrm{I} - \rho^\mathrm{II}$ and similar results for the energy and entropy densities implied by the gauge transformations (13.1)–(13.3), we arrive at (13.5).

Exercise 13.2

From differences of the equations collected in the lines before (13.7), we get

$$U - U^\mathrm{I} - U^\mathrm{II} = T(S - S^\mathrm{I} - S^\mathrm{II}) + \tilde{\mu}(N - N^\mathrm{I} - N^\mathrm{II}) + \gamma A,$$

and

$$(S - S^{\mathrm{I}} - S^{\mathrm{II}})\, dT + (N - N^{\mathrm{I}} - N^{\mathrm{II}})\, d\tilde{\mu} + A d\gamma = 0,$$

where $V = V^{\mathrm{I}} + V^{\mathrm{II}}$ has been used. After dividing by the surface area A, introducing the various excess densities, and passing from the number to the mass excess density (and hence from $\tilde{\mu}$ to $\hat{\mu}$), we obtain the desired results.

Exercise 13.3
After performing the gauge transformations (13.1) and (13.3), (13.8) becomes

$$[s^{\mathrm{s}} + \ell(s^{\mathrm{I}} - s^{\mathrm{II}})]dT + d\gamma + [\rho^{\mathrm{s}} + \ell(\rho^{\mathrm{I}} - \rho^{\mathrm{II}})]d\hat{\mu} = 0.$$

By subtracting the original form of (13.8), we obtain

$$(s^{\mathrm{I}} - s^{\mathrm{II}})dT + (\rho^{\mathrm{I}} - \rho^{\mathrm{II}})d\hat{\mu} = 0,$$

which is the condition for the gauge invariance of the Gibbs-Duhem equation; it implies (13.9).

Similarly, after performing the gauge transformations (13.1)–(13.3), (13.7) becomes

$$u^{\mathrm{s}} + \ell(u^{\mathrm{I}} - u^{\mathrm{II}}) = T[s^{\mathrm{s}} + \ell(s^{\mathrm{I}} - s^{\mathrm{II}})] + \gamma + \hat{\mu}[\rho^{\mathrm{s}} + \ell(\rho^{\mathrm{I}} - \rho^{\mathrm{II}})].$$

By subtracting the original form of (13.7), we obtain

$$u^{\mathrm{I}} - u^{\mathrm{II}} = T(s^{\mathrm{I}} - s^{\mathrm{II}}) + \hat{\mu}(\rho^{\mathrm{I}} - \rho^{\mathrm{II}}),$$

which is the condition for the gauge invariance of the Euler equation; after using (13.9) for the entropy difference, it implies (13.10).

Exercise 13.4
The vector $\boldsymbol{n}$ has only a radial component which is equal to unity, $n_r = 1$. By writing the divergence of a vector field in spherical coordinates, we obtain

$$\boldsymbol{\nabla} \cdot \boldsymbol{n} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 n_r) = 2/r.$$

Noting that $\boldsymbol{n}$ does not change in the radial direction and specializing to the the sphere $r = R$, we obtain $\boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{n} = 2/R$, which is a special case of (13.24) for equal radii of curvature, $R_1 = R_2 = R$.

Alternatively, we can perform a more explicit pedestrian calculation based on Cartesian vector components expressed in terms of spherical coordinates to obtain $\boldsymbol{\nabla}_{\|} \cdot \boldsymbol{n}$ as

$$\frac{1}{R}\left[\begin{pmatrix} \cos\theta\,\cos\phi \\ \cos\theta\,\sin\phi \\ -\sin\theta \end{pmatrix} \frac{\partial}{\partial\theta} + \begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix} \frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right] \cdot \begin{pmatrix} \sin\theta\,\cos\phi \\ \sin\theta\,\sin\phi \\ \cos\theta \end{pmatrix}$$

$$= \frac{1}{R}\left[\begin{pmatrix} \cos\theta\,\cos\phi \\ \cos\theta\,\sin\phi \\ -\sin\theta \end{pmatrix}^2 + \begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix}^2\right] = \frac{2}{R}.$$

Exercise 13.5

From Exercise 13.4, we have $\boldsymbol{\nabla}_{\|} \cdot \boldsymbol{n} = 2/R$ so that from (13.25) we can write

$$p^{\mathrm{I}} = p^{\mathrm{II}} - \frac{2\gamma}{R}\,.$$

Since we have equilibrium, we have

$$\tilde{\mu}^{\mathrm{I}}(T, p^{\mathrm{I}}) = \tilde{\mu}^{\mathrm{II}}(T, p^{\mathrm{II}})\,.$$

Assuming ideal gas behavior, using (4.22c) we can write

$$\tilde{\mu}^{\mathrm{I}}(T, p^{\mathrm{I}}) = \tilde{\mu}^{0}(T, p_0^{\mathrm{I}}) + \tilde{R}T \ln \frac{p^{\mathrm{I}}}{p_0^{\mathrm{I}}}\,.$$

For the liquid, we use (4.20) to write

$$\tilde{v}^{\mathrm{II}} = \left(\frac{\partial \tilde{\mu}^{\mathrm{II}}}{\partial p}\right)_T\,,$$

which, assuming that the density of liquid drop $\rho^{\mathrm{II}} = \tilde{M}^{\mathrm{II}}/\tilde{v}^{\mathrm{II}}$ is constant, can be integrated to give

$$\tilde{\mu}^{\mathrm{II}}(T, p^{\mathrm{II}}) = \tilde{\mu}^{0}(T, p_0^{\mathrm{I}}) + \tilde{v}^{\mathrm{II}}(p^{\mathrm{II}} - p_0^{\mathrm{I}})\,.$$

Substitution in the equilibrium condition for chemical potential and using the first expression gives the desired result. For a drop of water with $R = 10^{-7}$ m in air $\gamma = 0.072$ N/m ar $T = 298$ K, neglecting the second term inside the square brackets, we obtain $p^{\mathrm{I}}/p_0^{\mathrm{I}} = 1.01$.

Exercise 13.6

As all interfaces are assumed to be planar, the pressure is constant throughout the entire system. Therefore, work is only done against the interfacial tension when changing the sizes of the various interfaces. For a horizontal displacement Δx to the right and a length L perpendicular to the plane of Figure 13.5 , the work is given by

$$L(-\Delta x\gamma^{\mathrm{I,S}} + \Delta x\gamma^{\mathrm{II,S}} + \Delta x\, \cos\theta\, \gamma^{\mathrm{I,II}})\,.$$

At equilibrium, we cannot gain work by any displacement Δx because otherwise the system would rearrange. Vanishing work implies Young's equation (13.29).

Exercise 13.7
The unit normal to the meniscus is given by

$$\boldsymbol{n} = -\frac{dh}{dx_1}\frac{1}{\sqrt{1+(dh/dx_1)^2}}\boldsymbol{\delta}_1 + \frac{1}{\sqrt{1+(dh/dx_1)^2}}\boldsymbol{\delta}_3$$

so that

$$\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{n} = -\frac{d^2h}{dx_1^2}\frac{1}{(1+(dh/dx_1)^2)^{3/2}}.$$

From (13.25) we can write

$$p^{\mathrm{L}} = p^{\mathrm{I}} - \gamma\frac{d^2h}{dx_1^2}\frac{1}{(1+(dh/dx_1)^2)^{3/2}}.$$

Now, since $\boldsymbol{g} = -g\boldsymbol{\delta}_3$, we have from $\boldsymbol{\nabla}p^{\mathrm{L}} = \rho\boldsymbol{g}$,

$$p^{\mathrm{L}} = p^{\mathrm{I}} - \rho g x_3.$$

Combining the last two results gives ,

$$l_{\mathrm{cap}}^2\frac{d^2h}{dx_1^2} = \left[1+\left(\frac{dh}{dx_1}\right)^2\right]^{3/2} x_3\,.$$

From Figure 13.6 it is clear that,

$$\frac{dx_1}{d\zeta} = \cos\alpha, \qquad \frac{dx_3}{d\zeta} = -\sin\alpha\,,$$

so that

$$\frac{dx_3}{dx_1} = -\tan\alpha\,.$$

Setting $h = x_3$ in the previous result and substitution gives

$$\frac{dx_3}{d\zeta} = -\sin\alpha, \qquad \frac{d\alpha}{d\zeta} = -\frac{x_3}{l_{\mathrm{cap}}^2}\,,$$

which can be written as

$$-\frac{x_3}{l_{\mathrm{cap}}^2} = \frac{d\alpha}{d\zeta} = \frac{d\alpha}{dx_3}\frac{dx_3}{d\alpha} = -\sin\alpha\frac{d\alpha}{dx_3}\,.$$

Integrating subject to $\alpha = 0$ for $x_3 = 0$ we obtain

$$x_3 = l_{\text{cap}}\sqrt{2(1-\cos\alpha)} = 2l_{\text{cap}}\sin\alpha/2\,,$$

which, for $\alpha(0) = \pi/2 - \theta$, gives (13.30). For water in air, $\gamma \approx 72$ mN/m so that $l_{\text{cap}} \approx 2.7$ mm, and for water in contact with ordinary glass, $\theta \approx \pi/6$, so that $h(0) \approx 3$ mm. Finally, substitution of this last result in the expression for $dx_3/d\zeta$, gives

$$l_{\text{cap}}\frac{d\alpha}{d\zeta} = -\frac{\sin\alpha}{\cos\alpha/2}\,,$$

which, when integrated subject to $\alpha = \alpha(0)$ for $\zeta = 0$, gives

$$\alpha = 4\tan^{-1}\left[\tan\frac{\alpha(0)}{4}e^{-\zeta/l_{\text{cap}}}\right].$$

Exercise 14.1

We start with

$$\begin{aligned}\boldsymbol{\nabla}_{\|}\cdot(\boldsymbol{v}^{\text{s}}a^{\text{s}}) &= a^{\text{s}}\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}^{\text{s}} + \boldsymbol{v}^{\text{s}}\cdot\boldsymbol{\nabla}_{\|}a^{\text{s}}\\ &= a^{\text{s}}\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}^{\text{s}}_{\text{def}} + a^{\text{s}}\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}^{\text{s}}_{\text{tr}} + \boldsymbol{v}^{\text{s}}_{\text{def}}\cdot\boldsymbol{\nabla}_{\|}a^{\text{s}} + \boldsymbol{v}^{\text{s}}_{\text{tr}}\cdot\boldsymbol{\nabla}_{\|}a^{\text{s}}\\ &= \boldsymbol{\nabla}_{\|}\cdot(\boldsymbol{v}^{\text{s}}_{\text{def}}a^{\text{s}}) + a^{\text{s}}\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}^{\text{s}}_{\text{tr}} + \boldsymbol{v}^{\text{s}}_{\text{tr}}\cdot\boldsymbol{\nabla}_{\|}a^{\text{s}}\end{aligned}$$

where we have used the general velocity decomposition in (14.11) to go from the first to second line. For the normal-parallel splitting in (14.13) we have $\boldsymbol{v}^{\text{s}}_{\text{tr}} = v^{\text{s}}_n\boldsymbol{n}$. Hence, we have $\boldsymbol{n}\cdot\boldsymbol{\nabla}_{\|} = 0$, so that for this case the last term in the third line vanishes and (14.13) is obtained.

Exercise 14.2

The unit normal is $\boldsymbol{n} = \boldsymbol{\delta}_r$ and the velocity in the bulk phases is purely radial so that $\boldsymbol{v} = v_r\boldsymbol{\delta}_r$ and $\bar{\boldsymbol{v}} = \bar{v}_r\boldsymbol{\delta}_r$. Since the interface velocity is $\boldsymbol{v}^{\text{s}}\cdot\boldsymbol{n} = dR/dt$, the expression in (14.17) is easily obtained from the jump mass balance (14.5). The momentum densities in the bulk can be written as follows: $\boldsymbol{m} = \rho v_r\boldsymbol{\delta}_r$ and $\overline{\boldsymbol{m}} = \bar{\rho}\bar{v}_r\boldsymbol{\delta}_r$. Hence, the normal component of the jump momentum balance (14.6) with $\boldsymbol{\pi}^{\text{s}} = -\gamma\boldsymbol{\delta}_{\|}$ can be written as

$$\begin{aligned}&\rho v_r(R)\Big(v_r(R) - \frac{dR}{dt}\Big) + p(R) + \tau_{rr}(R)\\ &= \bar{\rho}\bar{v}_r(R)\Big(\bar{v}_r(R) - \frac{dR}{dt}\Big) + \bar{p}(R) + \bar{\tau}_{rr}(R) - \gamma\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{n}\,,\end{aligned}$$

The extra stress in the bulk phases is given by (6.6) which take the form:

$$\tau_{rr} = -2\eta\frac{\partial v_r}{\partial r}, \qquad \bar{\tau}_{rr} = -2\bar{\eta}\frac{\partial\bar{v}_r}{\partial r}$$

Substituting these along with $\boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{n} = 2/R$ from (13.24), and using (14.17) gives the expression in (14.18).

Exercise 14.3

Since there is no mass transfer across the liquid-gas interface, we have (14.6) with the further condition that $\boldsymbol{v}^{\mathrm{s}} \cdot \boldsymbol{n} = 0$ since the interface is stationary. The unit normal to the liquid-gas interface defining the shape of the liquid jet is given by[4]

$$\boldsymbol{n} = \frac{1}{\sqrt{1 + (dR/dz)^2}}\boldsymbol{\delta}_r - \frac{dR/dz}{\sqrt{1 + (dR/dz)^2}}\boldsymbol{\delta}_z$$

so that

$$\boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{n} = \frac{1 + (dR/dz)^2 - Rd^2R/dz^2}{R[1 + (dR/dz)^2]^{3/2}} \approx \frac{1}{R},$$

where the approximation follows from $Rd^2R/dz^2 \ll dR/dz \ll 1$. Since the gas is inviscid and we are neglecting viscous effects in the liquid, the normal component of (14.6) simplifies to

$$p^{\mathrm{L}} = p^{\mathrm{I}} + \frac{\gamma}{R}.$$

Now we write (5.54) for constant ρ between for a streamline beginning at $z = 0$ to an arbitrary point along the jet

$$\frac{1}{2}\rho v_z^2(z) + \rho\phi(z) + p^{\mathrm{L}}(z) = \frac{1}{2}\rho v_z^2(0) + \rho\phi(0) + p^{\mathrm{L}}(0),$$

Substitution for p^{L} and noting $\phi = -gz$, we have

$$\frac{1}{2}\rho v_z^2(z) - \rho g z + \frac{\gamma}{R} = \frac{1}{2}\rho V^2 + \frac{\gamma}{R_0},$$

which can be rearranged to obtain

$$\frac{v_z}{V} = \left[1 + \frac{2g}{V^2}z + \frac{2\gamma}{\rho V^2 R_0}\left(1 - \frac{R_0}{R}\right)\right]^{1/2},$$

For the mass flow rate, we have

$$\mathcal{W} = \rho\pi R_0^2 V = 2\pi\int_0^R \rho v_z r dr = \rho\pi R^2 v_z\,,$$

which can used to find the desired expression for $R(z)$. This expression can be rewritten as

$$\frac{R}{R_0} = \left[1 + \frac{2}{N_{\mathrm{Fr}}}\frac{z}{R_0} + \frac{2}{N_{\mathrm{We}}}\left(1 - \frac{R_0}{R}\right)\right]^{-1/4},$$

[4] see Appendix B of Slattery et al., *Interfacial Transport Phenomena* (Springer, 2007).

where $N_{\text{Fr}} = V^2/(gR_0)$ and $N_{\text{We}} = \rho V^2 R_0/\gamma$.

Exercise 14.4

Since we are neglecting viscous forces in the liquid, the momentum balance we must solve is Euler's equation (5.40), which neglecting gravity, can be written as

$$\rho\Big(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v}\cdot\boldsymbol{\nabla}\boldsymbol{v}\Big) = -\boldsymbol{\nabla} p^{\text{L}}$$

subject to $\boldsymbol{\nabla}\cdot\boldsymbol{v} = 0$. We write the velocity and pressure fields as

$$v_r = \tilde{v}_r e^{\omega t + ikz}, \qquad v_z = \tilde{v}_z e^{\omega t + ikz}, \qquad p^{\text{L}} = p_0^{\text{L}} + \tilde{p}^{\text{L}} e^{\omega t + ikz},$$

where the perturbation amplitudes are functions of r. The constraint on the velocity takes the form

$$\frac{d\tilde{v}_r}{dr} + \frac{\tilde{v}_r}{r} + ik\tilde{v}_z = 0.$$

The r- and z-components of the momentum balance are given by

$$\rho\omega\tilde{v}_r = -\frac{d\tilde{p}^{\text{L}}}{dr}, \qquad \rho\omega\tilde{v}_z = -ik\tilde{p}^{\text{L}},$$

where we have neglected nonlinear terms because the velocity perturbations are small. Differentiating the constraint on velocity and using the momentum balance, we obtain

$$r^2\frac{d^2\tilde{v}_r}{dr^2} + r\frac{d\tilde{v}_r}{dr} - [1 + (kr)^2]\tilde{v}_r = 0,$$

which is a modified Bessel's equation having solution

$$\tilde{v}_r = c_1 I_1(kr),$$

where we have enforced regularity at the origin. From the r-component of the momentum balance, we have

$$\tilde{p}^{\text{L}} = -\frac{\rho\omega}{k} c_1 I_0(kr).$$

To find c_1, we consider the liquid-gas interface, which has unit normal given by

$$\boldsymbol{n} = \frac{1}{\sqrt{1 + (dR/dz)^2}}\boldsymbol{\delta}_r - \frac{dR/dz}{\sqrt{1 + (dR/dz)^2}}\boldsymbol{\delta}_z.$$

Since there is no mass transfer across the liquid-gas interface, we have (14.6) so that

$$\boldsymbol{v}(R, z, t)\cdot\boldsymbol{n} = \boldsymbol{v}^{\text{s}}\cdot\boldsymbol{n}.$$

Since $|dR/dz| \ll 1$, we can write this as

$$c_1 I_1(kR_0)e^{\omega t+ikz} \approx \frac{\partial R}{\partial t} = \omega \tilde{R} e^{\omega t+ikz},$$

which gives $c_1 = \omega\tilde{R}/I_1(kR_0)$. Since the gas is inviscid and we are neglecting viscous effects in the liquid, the normal component of (14.6) simplifies to

$$p^{\mathrm{L}}(R,z,t) = \gamma \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{n},$$

where we have absorbed p^{I} into p^{L}. The curvature is given by

$$\boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{n} = \frac{1+(dR/dz)^2 - R d^2R/dz^2}{R[1+(dR/dz)^2]^{3/2}},$$

which for an unperturbed surface is simply $\boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{n} = 1/R_0$ so that $p_0^{\mathrm{L}} = \gamma/R_0$. Again, since $|dR/dz| \ll 1$, we can write

$$\boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{n} \approx \frac{1}{R} - \frac{d^2R}{dz^2} \approx \frac{1}{R_0} - \frac{\tilde{R}}{R_0^2} e^{\omega t+ikz} + \tilde{R}k^2 e^{\omega t+ikz}.$$

Combining the above results, we obtain

$$\frac{\gamma}{R_0} - \frac{\rho\omega^2\tilde{R}}{k}\frac{I_0(kR_0)}{I_1(kR_0)} e^{\omega t+ikz} = \frac{\gamma}{R_0} - \frac{\gamma\tilde{R}}{R_0^2} e^{\omega t+ikz} + \gamma\tilde{R}k^2 e^{\omega t+ikz},$$

which can be rearranged to give

$$\omega^2 = \frac{\gamma}{\rho R_0^3}\frac{I_1(kR_0)}{I_0(kR_0)} kR_0[1-(kR_0)^2].$$

This result shows the liquid cylinder is unstable to disturbance having $kR_0 < 1$, or having wavelength that is larger than the circumference of the cylinder $2\pi/k > 2\pi R_0$. The wave number for the most unstable (fastest growing) disturbance is $kR_0 \approx 0.697$, or a wavelength $2\pi/k \approx 9.02 R_0$.

Exercise 14.5
From (14.23) with $e^{\mathrm{s}} = u^{\mathrm{s}}$ we can write

$$\begin{aligned}\frac{\partial^{\mathrm{s}} u^{\mathrm{s}}}{\partial t} &= -\boldsymbol{\nabla}_{\parallel} \cdot (\boldsymbol{v}^{\mathrm{s}}_{\mathrm{def}} u^{\mathrm{s}} + \boldsymbol{j}^{\mathrm{s}}_q) - u^{\mathrm{s}} \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}^{\mathrm{s}}_{\mathrm{tr}} - \boldsymbol{\pi}^{\mathrm{s}} : \boldsymbol{\nabla}_{\parallel} \boldsymbol{v}^{\mathrm{s}} - \boldsymbol{v}^{\mathrm{s}} \cdot \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{\pi}^{\mathrm{s}} \\ &+ \boldsymbol{n} \cdot \Big[(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}})(u^{\mathrm{II}} + \frac{1}{2}\rho^{\mathrm{II}} \boldsymbol{v}^{\mathrm{II}} \cdot \boldsymbol{v}^{\mathrm{II}}) + \boldsymbol{\pi}^{\mathrm{II}} \cdot \boldsymbol{v}^{\mathrm{II}} + \boldsymbol{j}^{\mathrm{II}}_q \\ &- (\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}})(u^{\mathrm{I}} + \frac{1}{2}\rho^{\mathrm{I}} \boldsymbol{v}^{\mathrm{I}} \cdot \boldsymbol{v}^{\mathrm{I}}) - \boldsymbol{\pi}^{\mathrm{I}} \cdot \boldsymbol{v}^{\mathrm{I}} - \boldsymbol{j}^{\mathrm{I}}_q \Big].\end{aligned}$$

Multiplication of (14.10) by $\boldsymbol{v}^{\mathrm{s}}\cdot$ and substitution for the last term in the first line above gives the following

$$\begin{aligned}\frac{\partial^{\mathrm{s}} u^{\mathrm{s}}}{\partial t} &= -\boldsymbol{\nabla}_{\parallel} \cdot (\boldsymbol{v}^{\mathrm{s}}_{\mathrm{def}} u^{\mathrm{s}} + \boldsymbol{j}^{\mathrm{s}}_q) - u^{\mathrm{s}} \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}^{\mathrm{s}}_{\mathrm{tr}} - \boldsymbol{\pi}^{\mathrm{s}} : \boldsymbol{\nabla}_{\parallel} \boldsymbol{v}^{\mathrm{s}} \\ &+ \boldsymbol{n} \cdot \Big[(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}})(u^{\mathrm{II}} + \frac{1}{2}\rho^{\mathrm{II}} \boldsymbol{v}^{\mathrm{II}} \cdot \boldsymbol{v}^{\mathrm{II}} - \rho^{\mathrm{II}} \boldsymbol{v}^{\mathrm{II}} \cdot \boldsymbol{v}^{\mathrm{s}}) + \boldsymbol{\pi}^{\mathrm{II}} \cdot (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}}) + \boldsymbol{j}^{\mathrm{II}}_q \\ &- (\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}})(u^{\mathrm{I}} + \frac{1}{2}\rho^{\mathrm{I}} \boldsymbol{v}^{\mathrm{I}} \cdot \boldsymbol{v}^{\mathrm{I}} - \rho^{\mathrm{I}} \boldsymbol{v}^{\mathrm{I}} \cdot \boldsymbol{v}^{\mathrm{s}}) - \boldsymbol{\pi}^{\mathrm{I}} \cdot (\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}}) - \boldsymbol{j}^{\mathrm{I}}_q \Big],\end{aligned}$$

which can be rearranged to obtain

$$\begin{aligned}\frac{\partial^{\mathrm{s}} u^{\mathrm{s}}}{\partial t} &= -\boldsymbol{\nabla}_{\parallel} \cdot (\boldsymbol{v}^{\mathrm{s}}_{\mathrm{def}} u^{\mathrm{s}} + \boldsymbol{j}^{\mathrm{s}}_q) - u^{\mathrm{s}} \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}^{\mathrm{s}}_{\mathrm{tr}} - \boldsymbol{\pi}^{\mathrm{s}} : \boldsymbol{\nabla}_{\parallel} \boldsymbol{v}^{\mathrm{s}} \\ &+ \boldsymbol{n} \cdot \Big[(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}})(h^{\mathrm{II}} + \frac{1}{2}\rho^{\mathrm{II}} \boldsymbol{v}^{\mathrm{II}} \cdot \boldsymbol{v}^{\mathrm{II}} - \rho^{\mathrm{II}} \boldsymbol{v}^{\mathrm{II}} \cdot \boldsymbol{v}^{\mathrm{s}}) + \boldsymbol{\tau}^{\mathrm{II}} \cdot (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}}) + \boldsymbol{j}^{\mathrm{II}}_q \\ &- (\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}})(h^{\mathrm{I}} + \frac{1}{2}\rho^{\mathrm{I}} \boldsymbol{v}^{\mathrm{I}} \cdot \boldsymbol{v}^{\mathrm{I}} - \rho^{\mathrm{I}} \boldsymbol{v}^{\mathrm{I}} \cdot \boldsymbol{v}^{\mathrm{s}}) - \boldsymbol{\tau}^{\mathrm{I}} \cdot (\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}}) - \boldsymbol{j}^{\mathrm{I}}_q \Big],\end{aligned}$$

or, using (14.5), we have

$$\begin{aligned}\frac{\partial^{\mathrm{s}} u^{\mathrm{s}}}{\partial t} &= -\boldsymbol{\nabla}_{\parallel} \cdot (\boldsymbol{v}^{\mathrm{s}}_{\mathrm{def}} u^{\mathrm{s}} + \boldsymbol{j}^{\mathrm{s}}_q) - u^{\mathrm{s}} \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}^{\mathrm{s}}_{\mathrm{tr}} - \boldsymbol{\pi}^{\mathrm{s}} : \boldsymbol{\nabla}_{\parallel} \boldsymbol{v}^{\mathrm{s}} \\ &+ \boldsymbol{n} \cdot \Big[(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}}) h^{\mathrm{II}} + \boldsymbol{j}^{\mathrm{II}}_q - (\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}}) h^{\mathrm{I}} - \boldsymbol{j}^{\mathrm{I}}_q \\ &+ \boldsymbol{\tau}^{\mathrm{II}} \cdot (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}}) - \boldsymbol{\tau}^{\mathrm{I}} \cdot (\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}}) \Big] \\ &+ \rho^{\mathrm{I}} (\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n} \Big[\frac{1}{2} (\boldsymbol{v}^{\mathrm{II}} \cdot \boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}} \cdot \boldsymbol{v}^{\mathrm{I}}) - \boldsymbol{v}^{\mathrm{s}} \cdot (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}}) \Big],\end{aligned}$$

Decomposing the velocity difference between the bulk phases into normal and tangential components

$$\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}} = (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}})_{\parallel} + \boldsymbol{n}\boldsymbol{n} \cdot (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}}),$$

and using (14.8) and (14.9) in the fourth line, the expression in (14.24) is obtained.

Exercise 14.6
First, we rewrite (14.25) as

$$\boldsymbol{n} \cdot \left(\boldsymbol{n}^{\mathrm{I}}_{\alpha} - \boldsymbol{v}^{\mathrm{s}} \rho^{\mathrm{I}}_{\alpha} \right) = \boldsymbol{n} \cdot \left(\boldsymbol{n}^{\mathrm{II}}_{\alpha} - \boldsymbol{v}^{\mathrm{s}} \rho^{\mathrm{II}}_{\alpha} \right) - \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{j}^{\mathrm{s}}_{\alpha} + \nu^{\mathrm{s}}_{\alpha} \Gamma^{\mathrm{s}}$$

where we have used (5.13). Dividing by $\tilde{M}_{\alpha}$ we obtain

$$\boldsymbol{n} \cdot \left(\boldsymbol{N}^{\mathrm{I}}_{\alpha} - \boldsymbol{v}^{\mathrm{s}} c^{\mathrm{I}}_{\alpha} \right) = \boldsymbol{n} \cdot \left(\boldsymbol{N}^{\mathrm{II}}_{\alpha} - \boldsymbol{v}^{\mathrm{s}} c^{\mathrm{II}}_{\alpha} \right) - \boldsymbol{\nabla}_{\parallel} \cdot \frac{\boldsymbol{j}^{\mathrm{s}}_{\alpha}}{\tilde{M}_{\alpha}} + \frac{\nu^{\mathrm{s}}_{\alpha} \Gamma^{\mathrm{s}}}{\tilde{M}_{\alpha}},$$

which can be written as

$$\boldsymbol{n} \cdot \left(\boldsymbol{N}_\alpha^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}} c_\alpha^{\mathrm{I}}\right) = \boldsymbol{n} \cdot \left(\boldsymbol{N}_\alpha^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}} c_\alpha^{\mathrm{II}}\right) - \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{J}_\alpha^{\mathrm{s}} + \tilde{\nu}_\alpha^{\mathrm{s}} \tilde{\Gamma}^{\mathrm{s}},$$

where $\boldsymbol{J}_\alpha^{\mathrm{s}} = \boldsymbol{j}_\alpha^{\mathrm{s}}/\tilde{M}_\alpha \tilde{\nu}_\alpha$, $\tilde{\nu}_\alpha^{\mathrm{s}} = \nu_\alpha^{\mathrm{s}} \tilde{M}_q^{\mathrm{s}}/\tilde{M}_\alpha$, and $\tilde{\Gamma} = \Gamma/\tilde{M}_q^{\mathrm{s}}$. Using (5.20) in this expression gives (14.27).

Exercise 14.7
As in Exercise 14.2, we have $\boldsymbol{n} = \boldsymbol{\delta}_r$, and $\boldsymbol{v} = v_r \boldsymbol{\delta}_r$ and $\bar{\boldsymbol{v}} = \bar{v}_r \boldsymbol{\delta}_r$. For this case the jump energy balance (14.26) can be written as follows:

$$\begin{aligned}
\rho\Big(v_r(R) - \frac{dR}{dt}\Big)\hat{h}^{\mathrm{I}} + (j_q)_r(R) &= \bar{\rho}\Big(\bar{v}_r(R) - \frac{dR}{dt}\Big)\hat{h}^{\mathrm{II}} + (\bar{j}_q)_r(R) \\
+ \left(\frac{1}{\bar{\rho}} - \frac{1}{\rho}\right)^{-1} &\left\{\frac{1}{2}\left(\frac{\rho + \bar{\rho}}{\rho - \bar{\rho}}\right)[\bar{v}_r(R) - v_r(R)]^2 \right. \\
&\left. + \frac{\bar{\tau}_{rr}(R)}{\bar{\rho}} - \frac{\tau_{rr}(R)}{\rho}\right\}[\bar{v}_r(R) - v_r(R)].
\end{aligned}$$

As in Exercise 14.2, we use (6.6) for the extra stress in the bulk phases. For the diffusive energy flux in the bulk phases we use (6.4), which gives

$$(j_q)_r = -\lambda \frac{\partial T}{\partial r}, \qquad (\bar{j}_q)_r = -\bar{\lambda} \frac{\partial \bar{T}}{\partial r},$$

where λ and $\bar{\lambda}$ are the thermal conductivities of phases I and II, respectively. Substitution of these expressions and using (14.17) gives

$$\begin{aligned}
\rho\Big(v_r(R) - \frac{dR}{dt}\Big)\hat{h}^{\mathrm{I}} - \lambda \frac{\partial T}{\partial r}(R) &= \bar{\rho}\Big(\bar{v}_r(R) - \frac{dR}{dt}\Big)\hat{h}^{\mathrm{II}} - \bar{\lambda} \frac{\partial \bar{T}}{\partial r}(R) \\
+ \left\{\frac{1}{2}\left(\frac{1}{\bar{\rho}} + \frac{1}{\rho}\right)\left(\frac{1}{\bar{\rho}} - \frac{1}{\rho}\right)^{-1}\right. &[\bar{v}_r(R) - v_r(R)]^2 \\
&\left. - 2\bar{\nu} \frac{\partial \bar{v}_r}{\partial r}(R) + 2\nu \frac{\partial v_r}{\partial r}(R)\right\}\Big(v_r(R) - \frac{dR}{dt}\Big),
\end{aligned}$$

which, using $\Delta\hat{h} = \hat{h}^{\mathrm{II}} - \hat{h}^{\mathrm{I}}$, is easily rearranged to give (14.28).

Taking the densities of both the particle and surrounding liquid are constant, the continuity equation (5.36) for the particle simplifies to the following: $\bar{v}_r = \bar{f}(t)/r^2$. Since the velocity must be finite at the origin, $\bar{f}(t) = 0$ and hence $\bar{v}_r = 0$. Similarly, for the surrounding fluid, $v_r = f(t)/r^2$, and using (14.17), we obtain the following

$$v_r = (1 - \epsilon)\Big(\frac{R}{r}\Big)^2 \frac{dR}{dt},$$

where $\epsilon = \bar{\rho}/\rho$. Substitution in (14.28) gives

$$-\lambda\frac{\partial T}{\partial r}(R) = -\bar{\lambda}\frac{\partial \bar{T}}{\partial r}(R) + \bar{\rho}\frac{dR}{dt}\Big[\Delta\hat{h}^{\mathrm{I}} + \frac{1}{2}(1-\epsilon^2)\Big(\frac{dR}{dt}\Big)^2 - 4\nu(1-\epsilon)\frac{1}{R}\frac{dR}{dt}\Big].$$

We now compare the magnitudes of the terms in square brackets for the melting of solid H_2O and vaporization of liquid H_2O. The table below has the necessary physical properties. For the solid-liquid phase change, $\epsilon \approx 1$ and the second and third terms inside the square brackets are negligible. For the liquid-vapor phase change, $\epsilon \ll 1$. The kinetic energy term is significant for $dR/dt \approx 10^3$ m/s or larger, and the viscous stress term is significant for $1/RdR/dt \approx 10^{10}\mathrm{s}^{-1}$ or larger. Hence, the enthalpy change dominates mechanical energy effects in all but the most extreme cases.

Table C.5 *Physical properties of* H_2O *at atmospheric pressure.*

state (T)	$\Delta\hat{h} \times 10^{-3}$[J/kg = m^2/s^2]	ρ[kg/m^3]	$\nu \times 10^6$[m^2/s]
solid (0°C)	-334	917	-
liquid (0°C)	-	1000	1.8
liquid (100°C)	-	958	0.3
vapor (100°C)	2260	0.598	2.0

Exercise 14.8

From the problem statement, we postulate the temperature and velocity fields in the solid and liquid to have the form $\bar{T} = \bar{T}(x_1, t), \bar{v}_1 = 0$ and $T = T(x_1, t), v_1 = v_1(x, t)$, respectively. The normal vector to the solid-liquid interface at $x_1 = H(t)$ is $\boldsymbol{n} = \boldsymbol{\delta}_1$, so that the jump balance for mass (14.5) gives

$$v_1(H,t) = \Big(1 - \frac{\bar{\rho}}{\rho}\Big)\frac{dH}{dt} \approx 0$$

and the jump balance for energy (14.26) simplifies to

$$\bar{\rho}\Delta\hat{h}\frac{dH}{dt} - \lambda\frac{\partial T}{\partial x_1}(H,t) = -\bar{\lambda}\frac{\partial \bar{T}}{\partial x_1}(H,t)$$

where $\Delta\hat{h} = \hat{h}^{\mathrm{II}} - \hat{h}^{\mathrm{I}}$. Since the liquid density is constant, we have

$$\frac{\partial v_1}{\partial x_1} = 0,$$

which combined with $v_1(H,t) = 0$, means $v_1 = 0$.

For convenience, we normalize temperature as follows $(T - T_1)/(T_0 - T_1) \rightarrow$

T and $(\bar{T}-T_1)/(T_0-T_1) \to \bar{T}$. Writing the temperature equation (7.21) for the solid phase, we have

$$\frac{\partial \bar{T}}{\partial x_1} = \bar{\chi}\frac{\partial^2 \bar{T}}{\partial x_1^2},$$

which is solved subject to the boundary conditions

$$\bar{T}(0,t) = 0, \qquad \bar{T}(H,t) = \Theta,$$

where $\Theta = (T_{\rm m} - T_1)/(T_0 - T_1)$. Similarly, writing the temperature equation (7.21) for the liquid phase, we have

$$\frac{\partial T}{\partial x_1} = \chi\frac{\partial^2 T}{\partial x_1^2},$$

which is solved subject to the initial and boundary conditions

$$T(x_1,0) = 1, \qquad T(H,t) = \Theta, \qquad T(\infty,t) = 1.$$

The jump energy balance becomes

$$\frac{\bar{\rho}\Delta\hat{h}}{T_0 - T_1}\frac{dH}{dt} - \lambda\frac{\partial T}{\partial x_1}(H,t) = -\bar{\lambda}\frac{\partial \bar{T}}{\partial x_1}(H,t)$$

The similarity transformation $\xi = x_1/\sqrt{4\bar{\chi}t}$ implies

$$H = \beta\sqrt{4\bar{\chi}t},$$

where β is a parameter to be determined. Transforming the jump balance for energy, we have

$$\frac{2\beta}{N_{\rm St}} - \frac{\lambda}{\bar{\lambda}}\frac{dT}{d\xi}(\beta) = -\frac{d\bar{T}}{d\xi}(\beta)$$

where $N_{\rm St} = \bar{c}_p(T_0 - T_1)/\Delta\hat{h}$. Transforming the problem for $\bar{T}$, we have

$$\frac{d^2\bar{T}}{d\xi^2} + 2\xi\frac{d\bar{T}}{d\xi} = 0,$$

which is solved subject to the boundary conditions

$$\bar{T}(0) = 0, \qquad \bar{T}(\beta) = \Theta.$$

The solution for this problem is

$$\bar{T} = \frac{\Theta}{\mathrm{erf}(\beta)}\mathrm{erf}(\xi).$$

Similarly, transforming the problem for T we obtain

$$\frac{d^2 T}{d\xi^2} + 2\alpha\xi\frac{dT}{d\xi} = 0,$$

where $\alpha = \bar{\chi}/\chi$, which is solved subject to the boundary conditions

$$T(\beta) = \Theta, \qquad T(\infty) = 1.$$

The solution for this problem is

$$T = 1 - \frac{1-\Theta}{\operatorname{erfc}(\sqrt{\alpha}\beta)}\operatorname{erfc}(\sqrt{\alpha}\xi).$$

Substituting the temperature fields in the transformed jump balance for energy leads to the transcendental equation that must be solved numerically for β.

Exercise 14.9

The analysis involves isothermal diffusion in a two-component ideal gas so it is reasonable to assume the pressure in the gas is constant. Hence, the molar density of the gas phase c is constant, and therefore we use a molar based concentration and the molar-average velocity $\boldsymbol{v}^*$ as our reference velocity. From the problem statement, we postulate the concentration and velocity fields to have the form $x_{\mathrm{A}} = x_{\mathrm{A}}(x_1, t), v_1^* = v_1^*(x, t)$, respectively. Combining (5.23) and (6.27) we obtain mass balance for species A

$$\frac{\partial x_{\mathrm{A}}}{\partial t} + v_1^* \frac{\partial x_{\mathrm{A}}}{\partial x_1} = D_{\mathrm{AB}} \frac{\partial^2 x_{\mathrm{A}}}{\partial x_1^2},$$

which is subject to the initial and boundary conditions

$$x_{\mathrm{A}}(x_1, 0) = 0, \qquad x_{\mathrm{A}}(0, t) = x_{\mathrm{Aeq}}, \qquad x_{\mathrm{A}}(\infty, t) = 0.$$

The normal vector to the liquid-gas interface at $x_1 = 0$ is $\boldsymbol{n} = \boldsymbol{\delta}_1$, so that the molar form of the jump balance for species A mass (14.27) gives

$$v_1^*(0,t)c_{\mathrm{A}}(0,t) + (J_{\mathrm{A}}^*)_1(0,t) = \bar{v}_1^*(0,t)\bar{c}_{\mathrm{A}}(0,t) = \bar{v}_1^*(0,t)\bar{c}(0,t),$$

where the overbars indicate quantities in the liquid phase. Similarly, for species B we have

$$v_1^*(0,t)c_{\mathrm{B}}(0,t) + (J_{\mathrm{B}}^*)_1(0,t) = \bar{v}_1^*(0,t)\bar{c}_{\mathrm{B}}(0,t) = 0.$$

Adding these equations we obtain

$$v_1^*(0,t)c = \bar{v}_1^*(0,t)\bar{c}(0,t).$$

Substitution in the balance for species A gives

$$v_1^*(0,t) = \frac{1}{c - c_{\mathrm{A}}(0,t)}(J_{\mathrm{A}}^*)_1(0,t) = -\frac{D_{\mathrm{AB}}}{1 - x_{\mathrm{Aeq}}}\frac{\partial x_{\mathrm{A}}}{\partial x_1}(0,t)$$

where we have used the boundary condition at $x_1 = 0$ and (6.27) to obtain the second equality. Now, since c is constant, from (5.22) we have

$$\frac{\partial v_1^*}{\partial x_1} = 0,$$

which leads to $v_1^* = v_1^*(t)$. Hence, substitution in the species A mass balance gives

$$\frac{\partial x_{\mathrm{A}}}{\partial t} - \frac{D_{\mathrm{AB}}}{1 - x_{\mathrm{Aeq}}} \frac{\partial x_{\mathrm{A}}}{\partial x_1}(0,t) \frac{\partial x_{\mathrm{A}}}{\partial x_1} = D_{\mathrm{AB}} \frac{\partial^2 x_{\mathrm{A}}}{\partial x_1^2},$$

Applying the similarity transformation $\xi = x_1/\sqrt{4D_{\mathrm{AB}}t}$ we obtain

$$\frac{d^2 x_{\mathrm{A}}}{d\xi^2} + (2\xi + \beta)\frac{dx_{\mathrm{A}}}{d\xi} = 0,$$

where

$$\beta = \frac{1}{1 - x_{\mathrm{Aeq}}} \frac{dx_{\mathrm{A}}}{d\xi}(0),$$

which is subject to the boundary conditions

$$x_{\mathrm{A}}(0) = x_{\mathrm{Aeq}}, \qquad x_{\mathrm{A}}(\infty) = 0.$$

Integrating, we find

$$\frac{dx_{\mathrm{A}}}{d\xi} = c_1 e^{-x^2},$$

where $x = \xi + \beta/2$. Integrating a second time and using the boundary condition at $\xi = 0$ gives

$$x_{\mathrm{A}} - x_{\mathrm{Aeq}} = c_1 \int_{\beta/2}^{\xi+\beta/2} e^{-x^2} dx = c_1 \frac{\sqrt{\pi}}{2}[\mathrm{erf}(\xi + \beta/2) - \mathrm{erf}(\beta/2)].$$

Applying the boundary condition at $\xi = \infty$ we obtain

$$x_{\mathrm{Aeq}} = -c_1 \int_{\beta/2}^{\infty} e^{-x^2} dx = -c_1 \frac{\sqrt{\pi}}{2}[1 - \mathrm{erf}(\beta/2)],$$

so that the solution is

$$\frac{x_{\mathrm{A}}}{x_{\mathrm{Aeq}}} = 1 - \frac{\mathrm{erf}(\xi + \beta/2) - \mathrm{erf}(\beta/2)}{1 - \mathrm{erf}(\beta/2)}.$$

Substitution in the expression for β gives

$$-\frac{\beta}{2} = \frac{x_{\mathrm{Aeq}}}{\sqrt{\pi}(1 - x_{\mathrm{Aeq}})} \frac{e^{-(\beta/2)^2}}{1 - \mathrm{erf}(\beta/2)},$$

which must be solved numerically for β. Note that $-\beta/2 = v_1^*\sqrt{t/D_{\rm AB}}$ is the dimensionless molar average velocity.

The evaporation rate is proportional to molar flux of species A at $x_1 = 0$. Using (5.20), we can write

$$(N_{\rm A})_1(0,t) = v_1^*(t)c_{\rm A}(0,t) + (J_{\rm A}^*)_1(0,t) = cD_{\rm AB}\frac{\partial x_{\rm A}}{\partial x_1}(0,t).$$

Using $\xi = x_1/\sqrt{4D_{\rm AB}t}$ and substitution of the expression for $x_{\rm A}$ gives

$$(N_{\rm A})_1(0,t) = \Big(-\frac{\beta}{2}\sqrt{\pi}\Big)c\sqrt{\frac{D_{\rm AB}}{\pi t}},$$

where the quantity in parentheses is a factor that takes into account convective transport. For $x_{\rm Aeq} = 0.25$, $-\beta/2\sqrt{\pi} \approx 1.1$, and for $x_{\rm Aeq} = 0.5$, $-\beta/2\sqrt{\pi} \approx 1.3$.

Exercise 14.10

This analysis is similar to that in Exercise 14.9. Hence, the mass balance for species A is given by

$$\frac{\partial x_{\rm A}}{\partial t} + v_1^*\frac{\partial x_{\rm A}}{\partial x_1} = D_{\rm AB}\frac{\partial^2 x_{\rm A}}{\partial x_1^2},$$

where $v_1^* = v_1^*(t)$. The initial and boundary conditions are

$$x_{\rm A}(x_1,0) = 0, \qquad x_{\rm A}(h,t) = x_{\rm Aeq}, \qquad x_{\rm A}(H,t) = x_{{\rm A}H}.$$

Choosing $\boldsymbol{n} = \boldsymbol{\delta}_1$, the normal component of the interface velocity is given by $\boldsymbol{n}\cdot\boldsymbol{v}^{\rm s} = dh/dt$. The molar form of the jump balance for species A mass (14.27) gives

$$v_1^*(t)c_{\rm A}(0,t) + (J_{\rm A}^*)_1(0,t) = (N_{\rm A})_1(0,t) = [c_{\rm A}(0,t) - \rho/\tilde{M}_{\rm A}]\frac{dh}{dt}.$$

Similarly, for species B we have

$$v_1^*(t)c_{\rm B}(0,t) + (J_{\rm B}^*)_1(0,t) = (N_{\rm B})_1(0,t) = [c - c_{\rm A}(0,t)]\frac{dh}{dt}.$$

Adding these equations and applying $c \ll \rho/\tilde{M}_{\rm A}$ we obtain

$$v_1^*(t) = -\frac{\rho}{c\tilde{M}_{\rm A}}\frac{dh}{dt}.$$

Substitution in the jump balance for species A and using (6.27) gives

$$v_1^*(t) = -\frac{D_{\rm AB}}{1 - x_{\rm Aeq}}\frac{\partial x_{\rm A}}{\partial x_1}(0,t),$$

where we have also used the boundary condition at $x_1 = h$. We also find

$$\frac{dh}{dt} = \frac{c\tilde{M}_{\rm A}}{\rho}\frac{D_{\rm AB}}{1 - x_{\rm Aeq}}\frac{\partial x_{\rm A}}{\partial x_1}(0,t).$$

Invoking the quasi-steady state approximation, the mass balance for species A can be written as

$$\frac{\partial}{\partial x_1}\Big(v_1^* c x_{\rm A} - cD_{\rm AB}\frac{\partial x_{\rm A}}{\partial x_1}\Big) = \frac{\partial}{\partial x_1}(N_{\rm A})_1 = 0,$$

or $(N_{\rm A})_1 = (N_{\rm A})_1(t)$, which implies

$$\frac{dh}{dt} = \frac{c\tilde{M}_{\rm A}}{\rho}\frac{D_{\rm AB}}{1 - x_{\rm A}}\frac{\partial x_{\rm A}}{\partial x_1}.$$

Integration over x_1 from h to H gives

$$(H-h)\frac{dh}{dt} = \frac{c\tilde{M}_{\rm A}}{\rho}\ln\Big(\frac{1 - x_{{\rm A}H}}{1 - x_{\rm Aeq}}\Big).$$

Integration over time with $h(0) = h_0$ gives the desired result.

Exercise 14.11

For a two-component system with constant $D_{\rm AB}$, we have the mass balances

$$\frac{\partial \rho}{\partial t} + v_3\frac{\partial \rho}{\partial x_3} = -\rho\frac{\partial v_1}{\partial x_3},$$

$$\rho\Big(\frac{\partial w_{\rm A}}{\partial t} + v_3\frac{\partial w_{\rm A}}{\partial x_3}\Big) = D_{\rm AB}\frac{\partial}{\partial x_3}\Big(\rho\frac{\partial w_{\rm A}}{\partial x_3}\Big).$$

Multiplying the second by $\partial\rho/\partial w_{\rm A}$ gives

$$\rho\Big(\frac{\partial \rho}{\partial w_{\rm A}}\frac{\partial w_{\rm A}}{\partial t} + v_3\frac{\partial \rho}{\partial w_{\rm A}}\frac{\partial w_{\rm A}}{\partial x_3}\Big) = D_{\rm AB}\frac{\partial \rho}{\partial w_{\rm A}}\frac{\partial}{\partial x_3}\Big(\rho\frac{\partial w_{\rm A}}{\partial x_3}\Big).$$

or

$$\rho\Big(\frac{\partial \rho}{\partial t} + v_3\frac{\partial \rho}{\partial x_3}\Big) = -\rho^2\frac{\partial v_1}{\partial x_3} = D_{\rm AB}\frac{\partial \rho}{\partial w_{\rm A}}\frac{\partial}{\partial x_3}\Big(\rho\frac{\partial w_{\rm A}}{\partial x_3}\Big).$$

where we have used the first mass balance. Now, since

$$1/\rho = \hat{v} = w_{\rm A}\hat{v}_{\rm A} + (1 - w_{\rm A})\hat{v}_{\rm B}.$$

we can write

$$\frac{\partial \rho}{\partial w_{\rm A}} = \frac{\partial(1/\hat{v})}{\partial w_{\rm A}} = -\frac{1}{\hat{v}^2}\frac{\partial \hat{v}}{\partial w_{\rm A}} = -\rho^2(\hat{v}_{\rm A} - \hat{v}_{\rm B}).$$

Substitution in the previous result gives

$$\frac{\partial v_1}{\partial x_3} = D_{\text{AB}}(\hat{v}_{\text{A}} - \hat{v}_{\text{B}})\frac{\partial}{\partial x_3}\Big(\rho\frac{\partial w_{\text{A}}}{\partial x_3}\Big).$$

The expression on right-hand side can be written as

$$\frac{\partial}{\partial x_3}\Big(\rho\frac{\partial w_{\text{A}}}{\partial x_3}\Big) = \rho\frac{\partial^2 w_{\text{A}}}{\partial x_3^2} + \frac{\partial \rho}{\partial x_3}\frac{\partial w_{\text{A}}}{\partial x_3} = \rho\frac{\partial^2 w_{\text{A}}}{\partial x_3^2} + \frac{\partial \rho}{\partial w_{\text{A}}}\Big(\frac{\partial w_{\text{A}}}{\partial x_3}\Big)^2$$

or

$$\frac{\partial}{\partial x_3}\Big(\rho\frac{\partial w_{\text{A}}}{\partial x_3}\Big) = \rho\Big[\frac{\partial^2 w_{\text{A}}}{\partial x_3^2} - \frac{\hat{v}_{\text{A}} - \hat{v}_{\text{B}}}{w_{\text{A}}(\hat{v}_{\text{A}} - \hat{v}_{\text{B}}) + \hat{v}_{\text{B}}}\Big(\frac{\partial w_{\text{A}}}{\partial x_3}\Big)^2\Big].$$

Substitution in the second mass balance the rearranged form of the first mass balance gives the desired results.

Exercise 15.1

Starting from ρ_α^{s} in any gauge, we determine ℓ in (13.4) such that

$$\sum_{\alpha=1}^{k}[\rho_\alpha^{\text{s}} + \ell(\rho_\alpha^{\text{I}} - \rho_\alpha^{\text{II}})] = \rho^{\text{s}} + \ell(\rho^{\text{I}} - \rho^{\text{II}}) = 0.$$

With the solution for ℓ, we obtain the definition

$$\bar{\Upsilon}_\alpha = \rho_\alpha^{\text{s}} - \rho^{\text{s}}\,\frac{\rho_\alpha^{\text{I}} - \rho_\alpha^{\text{II}}}{\rho^{\text{I}} - \rho^{\text{II}}}.$$

By definition, we have

$$\sum_{\alpha=1}^{k}\bar{\Upsilon}_\alpha = 0.$$

Exercise 15.2

From the decomposition of the surface pressure tensor in (15.9) we can write

$$\boldsymbol{\nabla}_\parallel \cdot \boldsymbol{\pi}^{\text{s}} = -\boldsymbol{\nabla}_\parallel \cdot (\gamma\boldsymbol{\delta}_\parallel) + \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{\tau}^{\text{s}} = \gamma(\boldsymbol{\nabla}_\parallel \cdot \boldsymbol{n})\boldsymbol{n} - \boldsymbol{\nabla}_\parallel\gamma + \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{\tau}^{\text{s}},$$

where we have used $\boldsymbol{\nabla}_\parallel \cdot (\boldsymbol{\delta}_\parallel) = -(\boldsymbol{\nabla}_\parallel \cdot \boldsymbol{n})\boldsymbol{n}$. According to (6.3), the pressure tensor in the bulk phases can be written as $\boldsymbol{\pi}^{\text{I,II}} = p^{\text{I,II}}\boldsymbol{\delta} + \boldsymbol{\tau}^{\text{I,II}}$. Substitution in the jump momentum balance in (14.10) gives the expression in (15.21).

Exercise 15.3

In the absence of mass transfer at $z = h$ with $\boldsymbol{n} = \boldsymbol{\delta}_z$, we write (15.21) as

$$\boldsymbol{0} = \tau_{zr}^{\text{II}}\boldsymbol{\delta}_r + \tau_{zz}^{\text{II}}\boldsymbol{\delta}_z + p^{\text{II}}\boldsymbol{\delta}_z - \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{\tau}^{\text{s}} + \boldsymbol{\nabla}_\parallel\gamma$$

where we have treated the gas (I) as an inviscid fluid ($\boldsymbol{\tau}^{\mathrm{I}} = \mathbf{0}$) and set $p^{\mathrm{I}} = 0$. Since $\boldsymbol{n} = \boldsymbol{\delta}_z$, we have

$$\boldsymbol{\delta}_{\|} = \boldsymbol{\delta}_r \boldsymbol{\delta}_r + \boldsymbol{\delta}_\theta \boldsymbol{\delta}_\theta, \qquad \boldsymbol{\nabla}_{\|} = \boldsymbol{\delta}_r \frac{\partial}{\partial r} + \frac{\boldsymbol{\delta}_\theta}{r} \frac{\partial}{\partial \theta}.$$

For $\boldsymbol{\tau}^{\mathrm{s}}$ we use (15.12) with $\boldsymbol{v}^{\mathrm{s}} = v_r^{\mathrm{s}}(r)\boldsymbol{\delta}_r$ so that

$$\boldsymbol{\tau}^{\mathrm{s}} = -(\eta^{\mathrm{s}} + \eta_{\mathrm{d}}^{\mathrm{s}}) \frac{1}{r} \frac{\partial}{\partial r}(r v_r^{\mathrm{s}})(\boldsymbol{\delta}_r \boldsymbol{\delta}_r + \boldsymbol{\delta}_\theta \boldsymbol{\delta}_\theta),$$

and

$$\boldsymbol{\nabla}_{\|} \cdot \boldsymbol{\tau}^{\mathrm{s}} = -(\eta^{\mathrm{s}} + \eta_{\mathrm{d}}^{\mathrm{s}}) \frac{\partial}{\partial r} \Big(\frac{1}{r} \frac{\partial}{\partial r}(r v_r^{\mathrm{s}}) \Big) \boldsymbol{\delta}_r.$$

Hence, the jump momentum balance becomes

$$\mathbf{0} = \tau_{zr}^{\mathrm{II}} \boldsymbol{\delta}_r + \tau_{zz}^{\mathrm{II}} \boldsymbol{\delta}_z + p^{\mathrm{II}} \boldsymbol{\delta}_z + (\eta^{\mathrm{s}} + \eta_{\mathrm{d}}^{\mathrm{s}}) \frac{\partial}{\partial r} \Big(\frac{1}{r} \frac{\partial}{\partial r}(r v_r^{\mathrm{s}}) \Big) \boldsymbol{\delta}_r + \frac{\partial \gamma}{\partial r} \boldsymbol{\delta}_r$$

Using (6.5) for $\boldsymbol{\tau}^{\mathrm{II}}$, the z-component gives

$$p^{\mathrm{II}} = p(r,h) = 2\eta \frac{\partial v_z}{\partial z}(r,h),$$

and the r-component gives

$$0 = -\eta \Big[\frac{\partial v_r}{\partial z}(r,h) + \frac{\partial v_z}{\partial r}(r,h) \Big] + (\eta^{\mathrm{s}} + \eta_{\mathrm{d}}^{\mathrm{s}}) \frac{\partial}{\partial r} \Big(\frac{1}{r} \frac{\partial}{\partial r}(r v_r^{\mathrm{s}}) \Big) + \frac{\partial \gamma}{\partial r},$$

which is the desired result.

Exercise 15.4

For a uniform (constant γ) interface with $\eta^{\mathrm{s}} = 0$ across which there is no mass transfer, the jump momentum balance (15.21) can be written as

$$p^{\mathrm{I}} \boldsymbol{n} + \boldsymbol{n} \cdot \boldsymbol{\tau}^{\mathrm{I}} = p^{\mathrm{II}} \boldsymbol{n} + \boldsymbol{n} \cdot \boldsymbol{\tau}^{\mathrm{II}} - \gamma (\boldsymbol{\delta}_{\|} \cdot \boldsymbol{n}) \boldsymbol{n}.$$

Since $\boldsymbol{n} \cdot \boldsymbol{\delta}_{\|} = 0$, the transverse component simplifies to

$$\boldsymbol{n} \cdot \boldsymbol{\tau}^{\mathrm{I}} \cdot \boldsymbol{\delta}_{\|} = \boldsymbol{n} \cdot \boldsymbol{\tau}^{\mathrm{II}} \cdot \boldsymbol{\delta}_{\|}.$$

For this example, $\boldsymbol{n} = \boldsymbol{\delta}_r$, so that the θ-component of the above equation is simply $\tau_{r\theta}(R,\theta) = \bar{\tau}_{r\theta}(R,\theta)$. From (6.5) we can write

$$\tau_{r\theta} = -\eta \, r \frac{\partial}{\partial r} \Big(\frac{v_\theta}{r} \Big), \qquad \bar{\tau}_{r\theta} = -\bar{\eta} \, r \frac{\partial}{\partial r} \Big(\frac{\bar{v}_\theta}{r} \Big),$$

which gives the desired result.

Now, from (15.17) with $\boldsymbol{\xi}_{\|} = \xi_{\mathrm{slip}} \boldsymbol{\delta}_{\|}$, we can write

$$(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}})_{\|} = \xi_{\mathrm{slip}} \left(\frac{\boldsymbol{\delta}_{\|} \cdot \boldsymbol{\tau}^{\mathrm{II}} \cdot \boldsymbol{n}}{\rho^{\mathrm{II}}} - \frac{\boldsymbol{\delta}_{\|} \cdot \boldsymbol{\tau}^{\mathrm{I}} \cdot \boldsymbol{n}}{\rho^{\mathrm{I}}} \right) \left(\frac{1}{\rho^{\mathrm{II}}} - \frac{1}{\rho^{\mathrm{I}}} \right)^{-1} = \xi_{\mathrm{slip}} \boldsymbol{\delta}_{\|} \cdot \boldsymbol{\tau}^{\mathrm{II}} \cdot \boldsymbol{n} \,,$$

where the second equality follows by using the transverse component of the simplified jump momentum balance given above. Again, since $\boldsymbol{n} = \boldsymbol{\delta}_r$, the θ-component of the above equation is simply $\bar{v}_\theta(R,\theta) - v_\theta(R,\theta) = \xi_{\text{slip}}\tau_{r\theta}(R,\theta)$, which gives the desired result.

Exercise 15.5

For a uniform (constant γ and T^{s}) interface with both $\eta^{\text{s}} = 0$ and $\lambda^{\text{s}} = 0$ across which there is no mass transfer, (15.20) simplifies to

$$\boldsymbol{n} \cdot \boldsymbol{j}_q^{\text{I}} = \boldsymbol{n} \cdot \boldsymbol{j}_q^{\text{II}} + (\boldsymbol{v}^{\text{II}} - \boldsymbol{v}^{\text{I}})_{\parallel} \cdot \left(\frac{\boldsymbol{\tau}^{\text{II}}}{\rho^{\text{II}}} - \frac{\boldsymbol{\tau}^{\text{I}}}{\rho^{\text{I}}} \right) \cdot \boldsymbol{n} \left(\frac{1}{\rho^{\text{II}}} - \frac{1}{\rho^{\text{I}}} \right)^{-1}.$$

Using the results from Exercise 15.4, the above expression can be written as

$$\boldsymbol{n} \cdot \boldsymbol{j}_q^{\text{I}} = \boldsymbol{n} \cdot \boldsymbol{j}_q^{\text{II}} + \xi_{\text{slip}}(\boldsymbol{\tau}^{\text{I}} \cdot \boldsymbol{n}) \cdot (\boldsymbol{\tau}^{\text{I}} \cdot \boldsymbol{n}).$$

For this example, $\boldsymbol{n} = \boldsymbol{\delta}_r$, so that the above equation is simply $j_{qr}(R,\theta) = \bar{j}_{qr}(R,\theta) + \xi_{\text{slip}}\tau_{r\theta}(R,\theta)^2$. Using (6.4), we can write

$$(j_q)_r = -\lambda \frac{\partial T}{\partial r}, \qquad (\bar{j}_q)_r = -\bar{\lambda} \frac{\partial \bar{T}}{\partial r},$$

which gives the desired result.

In the absence of mass transfer, the expressions in (15.13) and (15.14) take the following form:

$$T^{\text{I}} - T^{\text{s}} = -R_{\text{K}}^{\text{Is}} \boldsymbol{j}_q^{\text{I}} \cdot \boldsymbol{n}, \qquad T^{\text{II}} - T^{\text{s}} = R_{\text{K}}^{\text{IIs}} \boldsymbol{j}_q^{\text{II}} \cdot \boldsymbol{n}.$$

Subtracting the second from the first, we obtain

$$T^{\text{I}} - T^{\text{II}} = -(R_{\text{K}}^{\text{Is}} \boldsymbol{j}_q^{\text{I}} \cdot \boldsymbol{n} + R_{\text{K}}^{\text{IIs}} \boldsymbol{j}_q^{\text{II}} \cdot \boldsymbol{n}),$$

or, using the results from the first part

$$T^{\text{I}} - T^{\text{II}} = -(R_{\text{K}}^{\text{Is}} + R_{\text{K}}^{\text{IIs}}) \boldsymbol{j}_q^{\text{I}} \cdot \boldsymbol{n} + R_{\text{K}}^{\text{IIs}} \xi_{\text{slip}} (\boldsymbol{\tau}^{\text{I}} \cdot \boldsymbol{n}) \cdot (\boldsymbol{\tau}^{\text{I}} \cdot \boldsymbol{n}),$$

giving the desired expression.

Exercise 15.6

We use the gauge $\rho^{\text{s}} = 0$. Substitution of (14.21), (14.23) and (15.6) in (15.22) gives

$$\begin{aligned} &-\boldsymbol{\nabla}_{\parallel} \cdot (\boldsymbol{v}_{\text{def}}^{\text{s}} e^{\text{s}} + \boldsymbol{j}_q^{\text{s}} + \boldsymbol{\pi}^{\text{s}} \cdot \boldsymbol{v}^{\text{s}}) - e^{\text{s}} \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}_{\text{tr}}^{\text{s}} \\ &\quad + \boldsymbol{n} \cdot \Big[(\boldsymbol{v}^{\text{II}} - \boldsymbol{v}^{\text{s}}) e^{\text{II}} + \boldsymbol{j}_q^{\text{II}} + \boldsymbol{\pi}^{\text{II}} \cdot \boldsymbol{v}^{\text{II}} - (\boldsymbol{v}^{\text{I}} - \boldsymbol{v}^{\text{s}}) e^{\text{I}} - \boldsymbol{j}_q^{\text{I}} - \boldsymbol{\pi}^{\text{I}} \cdot \boldsymbol{v}^{\text{I}} \Big] \\ &\quad = T^{\text{s}} \Bigg\{ -\boldsymbol{\nabla}_{\parallel} \cdot \left[\boldsymbol{v}_{\text{def}}^{\text{s}} s^{\text{s}} + \frac{1}{T^{\text{s}}} \Big(\boldsymbol{j}_q^{\text{s}} - \sum_{\alpha=1}^{k} \hat{\mu}_\alpha^{\text{s}} \boldsymbol{j}_\alpha^{\text{s}} \Big) \right] - s^{\text{s}} \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}_{\text{tr}}^{\text{s}} + \sigma^{\text{s}} \end{aligned}$$

$$
\begin{aligned}
&+\boldsymbol{n}\cdot\Big[(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{s}})s^{\mathrm{II}}+\frac{1}{T^{\mathrm{II}}}\Big(\boldsymbol{j}_q^{\mathrm{II}}-\sum_{\alpha=1}^{k}\hat{\mu}_\alpha^{\mathrm{II}}\boldsymbol{j}_\alpha^{\mathrm{II}}\Big)\\
&-(\boldsymbol{v}^{\mathrm{I}}-\boldsymbol{v}^{\mathrm{s}})s^{\mathrm{I}}-\frac{1}{T^{\mathrm{I}}}\Big(\boldsymbol{j}_q^{\mathrm{I}}-\sum_{\alpha=1}^{k}\hat{\mu}_\alpha^{\mathrm{I}}\boldsymbol{j}_\alpha^{\mathrm{I}}\Big)\Big]\Big\}\\
+&\sum_{\alpha=1}^{k}\hat{\mu}_\alpha^{\mathrm{s}}\Big\{-\boldsymbol{\nabla}_\parallel\cdot(\boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}}\rho_\alpha^{\mathrm{s}}+\boldsymbol{j}_\alpha^{\mathrm{s}})-\rho_\alpha^{\mathrm{s}}\boldsymbol{\nabla}_\parallel\cdot\boldsymbol{v}_{\mathrm{tr}}^{\mathrm{s}}+\nu_\alpha^{\mathrm{s}}\Gamma^{\mathrm{s}}\\
&+\boldsymbol{n}\cdot\Big[(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{s}})\rho_\alpha^{\mathrm{II}}+\boldsymbol{j}_\alpha^{\mathrm{II}}-(\boldsymbol{v}^{\mathrm{I}}-\boldsymbol{v}^{\mathrm{s}})\rho_\alpha^{\mathrm{I}}-\boldsymbol{j}_\alpha^{\mathrm{I}}\Big]\Big\},
\end{aligned}
$$

where we have used (6.9) to replace the entropy fluxes in the bulk phases and, similarly, $\boldsymbol{j}_s^{\mathrm{s}}=(\boldsymbol{j}_q^{\mathrm{s}}-\sum_{\alpha=1}^{k}\hat{\mu}_\alpha^{\mathrm{s}}\boldsymbol{j}_\alpha^{\mathrm{s}})/T^{\mathrm{s}}$ for the entropy flux within the interface. Solving for σ^{s}, we obtain after some rearrangement of terms

$$
\begin{aligned}
T^{\mathrm{s}}\sigma^{\mathrm{s}}=&-\boldsymbol{\nabla}_\parallel\cdot(\boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}}e^{\mathrm{s}})+T^{\mathrm{s}}\boldsymbol{\nabla}_\parallel\cdot(\boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}}s^{\mathrm{s}})+\sum_{\alpha=1}^{k}\hat{\mu}_\alpha^{\mathrm{s}}\boldsymbol{\nabla}_\parallel\cdot(\boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}}\rho_\alpha^{\mathrm{s}})\\
&+T^{\mathrm{s}}\boldsymbol{j}_q^{\mathrm{s}}\cdot\boldsymbol{\nabla}_\parallel\frac{1}{T^{\mathrm{s}}}-T^{\mathrm{s}}\sum_{\alpha=1}^{k}\boldsymbol{j}_\alpha^{\mathrm{s}}\cdot\boldsymbol{\nabla}_\parallel\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\sum_{\alpha=1}^{k}\nu_\alpha^{\mathrm{s}}\hat{\mu}_\alpha^{\mathrm{s}}\Gamma^{\mathrm{s}}\\
&-\boldsymbol{v}^{\mathrm{s}}\cdot(\boldsymbol{\nabla}_\parallel\cdot\boldsymbol{\pi}^{\mathrm{s}})-\boldsymbol{\pi}^{\mathrm{s}}:\boldsymbol{\nabla}_\parallel\boldsymbol{v}^{\mathrm{s}}-\Big(e^{\mathrm{s}}-T^{\mathrm{s}}s^{\mathrm{s}}-\sum_{\alpha=1}^{k}\hat{\mu}_\alpha^{\mathrm{s}}\rho_\alpha^{\mathrm{s}}\Big)\boldsymbol{\nabla}_\parallel\cdot\boldsymbol{v}_{\mathrm{tr}}^{\mathrm{s}}\\
&+\boldsymbol{n}\cdot\Big\{(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{s}})\Big(e^{\mathrm{II}}-T^{\mathrm{s}}s^{\mathrm{II}}-\sum_{\alpha=1}^{k}\hat{\mu}_\alpha^{\mathrm{s}}\rho_\alpha^{\mathrm{II}}\Big)\\
&\qquad-(\boldsymbol{v}^{\mathrm{I}}-\boldsymbol{v}^{\mathrm{s}})\Big(e^{\mathrm{I}}-T^{\mathrm{s}}s^{\mathrm{I}}-\sum_{\alpha=1}^{k}\hat{\mu}_\alpha^{\mathrm{s}}\rho_\alpha^{\mathrm{I}}\Big)\Big\}\\
&+T^{\mathrm{s}}\boldsymbol{n}\cdot\boldsymbol{j}_q^{\mathrm{II}}\left(\frac{1}{T^{\mathrm{s}}}-\frac{1}{T^{\mathrm{II}}}\right)-T^{\mathrm{s}}\boldsymbol{n}\cdot\boldsymbol{j}_q^{\mathrm{I}}\left(\frac{1}{T^{\mathrm{s}}}-\frac{1}{T^{\mathrm{I}}}\right)\\
&-T^{\mathrm{s}}\sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\boldsymbol{j}_\alpha^{\mathrm{II}}\left(\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\frac{\hat{\mu}_\alpha^{\mathrm{II}}}{T^{\mathrm{II}}}\right)+T^{\mathrm{s}}\sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\boldsymbol{j}_\alpha^{\mathrm{I}}\left(\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\frac{\hat{\mu}_\alpha^{\mathrm{I}}}{T^{\mathrm{I}}}\right)\\
&+\boldsymbol{n}\cdot[\boldsymbol{\pi}^{\mathrm{II}}\cdot(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{s}})-\boldsymbol{\pi}^{\mathrm{I}}\cdot(\boldsymbol{v}^{\mathrm{I}}-\boldsymbol{v}^{\mathrm{s}})]+\boldsymbol{n}\cdot(\boldsymbol{\pi}^{\mathrm{II}}-\boldsymbol{\pi}^{\mathrm{I}})\cdot\boldsymbol{v}^{\mathrm{s}}.
\end{aligned}
$$

Using (15.9), along with (15.3) and (15.5), we further obtain

$$
T^{\mathrm{s}}\sigma^{\mathrm{s}}=T^{\mathrm{s}}\boldsymbol{j}_q^{\mathrm{s}}\cdot\boldsymbol{\nabla}_\parallel\frac{1}{T^{\mathrm{s}}}-\boldsymbol{\tau}^{\mathrm{s}}:\boldsymbol{\nabla}_\parallel\boldsymbol{v}^{\mathrm{s}}-T^{\mathrm{s}}\sum_{\alpha=1}^{k}\boldsymbol{j}_\alpha^{\mathrm{s}}\cdot\boldsymbol{\nabla}_\parallel\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\sum_{\alpha=1}^{k}\nu_\alpha^{\mathrm{s}}\hat{\mu}_\alpha^{\mathrm{s}}\Gamma^{\mathrm{s}}
$$

$$
\begin{aligned}
&+ \boldsymbol{n}\cdot\Big\{(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{s}})\Big(e^{\mathrm{II}}-T^{\mathrm{s}}s^{\mathrm{II}}-\sum_{\alpha=1}^{k}\hat{\mu}_\alpha^{\mathrm{s}}\rho_\alpha^{\mathrm{II}}\Big)\\
&\qquad\qquad -(\boldsymbol{v}^{\mathrm{I}}-\boldsymbol{v}^{\mathrm{s}})\Big(e^{\mathrm{I}}-T^{\mathrm{s}}s^{\mathrm{I}}-\sum_{\alpha=1}^{k}\hat{\mu}_\alpha^{\mathrm{s}}\rho_\alpha^{\mathrm{I}}\Big)\Big\}\\
&+ T^{\mathrm{s}}\boldsymbol{n}\cdot\boldsymbol{j}_q^{\mathrm{II}}\left(\frac{1}{T^{\mathrm{s}}}-\frac{1}{T^{\mathrm{II}}}\right)-T^{\mathrm{s}}\boldsymbol{n}\cdot\boldsymbol{j}_q^{\mathrm{I}}\left(\frac{1}{T^{\mathrm{s}}}-\frac{1}{T^{\mathrm{I}}}\right)\\
&- T^{\mathrm{s}}\sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\boldsymbol{j}_\alpha^{\mathrm{II}}\left(\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\frac{\hat{\mu}_\alpha^{\mathrm{II}}}{T^{\mathrm{II}}}\right)+T^{\mathrm{s}}\sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\boldsymbol{j}_\alpha^{\mathrm{I}}\left(\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\frac{\hat{\mu}_\alpha^{\mathrm{I}}}{T^{\mathrm{I}}}\right)\\
&+\boldsymbol{n}\cdot[\boldsymbol{\pi}^{\mathrm{II}}\cdot(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{s}})-\boldsymbol{\pi}^{\mathrm{I}}\cdot(\boldsymbol{v}^{\mathrm{I}}-\boldsymbol{v}^{\mathrm{s}})]+\boldsymbol{n}\cdot(\boldsymbol{\pi}^{\mathrm{II}}-\boldsymbol{\pi}^{\mathrm{I}})\cdot\boldsymbol{v}^{\mathrm{s}}-\boldsymbol{v}^{\mathrm{s}}\cdot(\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{\pi}^{\mathrm{s}}).
\end{aligned}
$$

As a next step, we rewrite the second line of expression above in terms of bulk intensive variables and use (6.3), which leads to

$$
\begin{aligned}
\sigma^{\mathrm{s}} &= \boldsymbol{j}_q^{\mathrm{s}}\cdot\boldsymbol{\nabla}_{\|}\frac{1}{T^{\mathrm{s}}}-\frac{1}{T^{\mathrm{s}}}\boldsymbol{\tau}^{\mathrm{s}}:\boldsymbol{\nabla}_{\|}\boldsymbol{v}^{\mathrm{s}}-\sum_{\alpha=1}^{k}\boldsymbol{j}_\alpha^{\mathrm{s}}\cdot\boldsymbol{\nabla}_{\|}\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\frac{1}{T^{\mathrm{s}}}\sum_{\alpha=1}^{k}\nu_\alpha^{\mathrm{s}}\hat{\mu}_\alpha^{\mathrm{s}}\Gamma^{\mathrm{s}}\\
&+\Big\{\boldsymbol{n}\cdot\Big[\rho^{\mathrm{II}}(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{s}})\frac{1}{2}\boldsymbol{v}^{\mathrm{II}2}-\rho^{\mathrm{I}}(\boldsymbol{v}^{\mathrm{I}}-\boldsymbol{v}^{\mathrm{s}})\frac{1}{2}\boldsymbol{v}^{\mathrm{I}2}\Big]\\
&\qquad\qquad +\boldsymbol{n}\cdot\big[\boldsymbol{\tau}^{\mathrm{II}}\cdot(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{s}})-\boldsymbol{\tau}^{\mathrm{I}}\cdot(\boldsymbol{v}^{\mathrm{I}}-\boldsymbol{v}^{\mathrm{s}})\big]\Big\}\frac{1}{T^{\mathrm{s}}}\\
&+\boldsymbol{n}\cdot\big[(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{s}})T^{\mathrm{II}}s^{\mathrm{II}}+\boldsymbol{j}_q^{\mathrm{II}}\big]\left(\frac{1}{T^{\mathrm{s}}}-\frac{1}{T^{\mathrm{II}}}\right)\\
&-\boldsymbol{n}\cdot\big[(\boldsymbol{v}^{\mathrm{I}}-\boldsymbol{v}^{\mathrm{s}})T^{\mathrm{I}}s^{\mathrm{I}}+\boldsymbol{j}_q^{\mathrm{I}}\big]\left(\frac{1}{T^{\mathrm{s}}}-\frac{1}{T^{\mathrm{I}}}\right)\\
&-\sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\left[(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{s}})\rho_\alpha^{\mathrm{II}}\left(\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\frac{\hat{\mu}_\alpha^{\mathrm{II}}}{T^{\mathrm{s}}}\right)+\boldsymbol{j}_\alpha^{\mathrm{II}}\left(\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\frac{\hat{\mu}_\alpha^{\mathrm{II}}}{T^{\mathrm{II}}}\right)\right]\\
&+\sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\left[(\boldsymbol{v}^{\mathrm{I}}-\boldsymbol{v}^{\mathrm{s}})\rho_\alpha^{\mathrm{I}}\left(\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\frac{\hat{\mu}_\alpha^{\mathrm{I}}}{T^{\mathrm{s}}}\right)+\boldsymbol{j}_\alpha^{\mathrm{I}}\left(\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\frac{\hat{\mu}_\alpha^{\mathrm{I}}}{T^{\mathrm{I}}}\right)\right]\\
&+\big[\boldsymbol{n}\cdot(\boldsymbol{\pi}^{\mathrm{II}}-\boldsymbol{\pi}^{\mathrm{I}})\cdot\boldsymbol{v}^{\mathrm{s}}-\boldsymbol{v}^{\mathrm{s}}\cdot\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{\pi}^{\mathrm{s}}\big]\frac{1}{T^{\mathrm{s}}},
\end{aligned}
$$

where we have used $e+p-Ts-\sum_{\alpha=1}^{k}\hat{\mu}_\alpha\rho_\alpha=\frac{1}{2}\rho\boldsymbol{v}^2$. Using (14.8) and (14.9) in the second and third lines and (14.10) in the last line of the expression above, we obtain

$$
\sigma^{\mathrm{s}}=\boldsymbol{j}_q^{\mathrm{s}}\cdot\boldsymbol{\nabla}_{\|}\frac{1}{T^{\mathrm{s}}}-\frac{1}{T^{\mathrm{s}}}\boldsymbol{\tau}^{\mathrm{s}}:\boldsymbol{\nabla}_{\|}\boldsymbol{v}^{\mathrm{s}}-\sum_{\alpha=1}^{k}\boldsymbol{j}_\alpha^{\mathrm{s}}\cdot\boldsymbol{\nabla}_{\|}\frac{\hat{\mu}_\alpha^{\mathrm{s}}}{T^{\mathrm{s}}}-\frac{1}{T^{\mathrm{s}}}\sum_{\alpha=1}^{k}\nu_\alpha^{\mathrm{s}}\hat{\mu}_\alpha^{\mathrm{s}}\Gamma^{\mathrm{s}}
$$

$$+\boldsymbol{n}\cdot\left[(\boldsymbol{v}^{\rm II}-\boldsymbol{v}^{\rm s})h^{\rm II}+\boldsymbol{j}_q^{\rm II}\right]\left(\frac{1}{T^{\rm s}}-\frac{1}{T^{\rm II}}\right)-\boldsymbol{n}\cdot\left[(\boldsymbol{v}^{\rm I}-\boldsymbol{v}^{\rm s})h^{\rm I}+\boldsymbol{j}_q^{\rm I}\right]\left(\frac{1}{T^{\rm s}}-\frac{1}{T^{\rm I}}\right)$$
$$+\frac{1}{T^{\rm s}}\left(\frac{1}{\rho^{\rm II}}-\frac{1}{\rho^{\rm I}}\right)^{-1}\left\{\frac{1}{2}\frac{\rho^{\rm I}+\rho^{\rm II}}{\rho^{\rm I}-\rho^{\rm II}}(\boldsymbol{v}^{\rm II}-\boldsymbol{v}^{\rm I})^2\right.$$
$$\left.+\boldsymbol{n}\cdot\left(\frac{\boldsymbol{\tau}^{\rm II}}{\rho^{\rm II}}-\frac{\boldsymbol{\tau}^{\rm I}}{\rho^{\rm I}}\right)\cdot\boldsymbol{n}\right\}\boldsymbol{n}\cdot(\boldsymbol{v}^{\rm II}-\boldsymbol{v}^{\rm I})$$
$$+\frac{1}{T^{\rm s}}\left(\frac{1}{\rho^{\rm II}}-\frac{1}{\rho^{\rm I}}\right)^{-1}\boldsymbol{n}\cdot\left(\frac{\boldsymbol{\tau}^{\rm II}}{\rho^{\rm II}}-\frac{\boldsymbol{\tau}^{\rm I}}{\rho^{\rm I}}\right)\cdot(\boldsymbol{v}^{\rm II}-\boldsymbol{v}^{\rm I})_{\|}$$
$$-\sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\left[(\boldsymbol{v}^{\rm II}-\boldsymbol{v}^{\rm s})\rho_\alpha^{\rm II}+\boldsymbol{j}_\alpha^{\rm II}\right]\left(\frac{\hat\mu_\alpha^{\rm s}}{T^{\rm s}}-\frac{\hat\mu_\alpha^{\rm II}}{T^{\rm II}}\right)$$
$$+\sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\left[(\boldsymbol{v}^{\rm I}-\boldsymbol{v}^{\rm s})\rho_\alpha^{\rm I}+\boldsymbol{j}_\alpha^{\rm I}\right]\left(\frac{\hat\mu_\alpha^{\rm s}}{T^{\rm s}}-\frac{\hat\mu_\alpha^{\rm I}}{T^{\rm I}}\right),$$

where we have also used $Ts = h-\sum_{\alpha=1}^{k}\hat\mu_\alpha\rho_\alpha$ and decomposed the velocity difference into normal and tangential components. This equation coincides with (15.23) when we first eliminate $\boldsymbol{m}$ and then the flat averages $\hat\mu^{\rm I}$, $\hat\mu^{\rm II}$, and $\hat\mu^{\rm s}$ from (15.23).

Exercise 15.7

For a two-component system, the entropy production terms resulting from energy and mass transfer in the first line of (15.23) can be written as

$$\sigma^{\rm s}=\boldsymbol{j}_q^{\rm s}\cdot\boldsymbol{\nabla}_{\|}\frac{1}{T^{\rm s}}-\boldsymbol{j}_1^{\rm s}\cdot\boldsymbol{\nabla}_{\|}\frac{\hat\mu_1^{\rm s}-\hat\mu^{\rm s}}{T^{\rm s}}-\boldsymbol{j}_2^{\rm s}\cdot\boldsymbol{\nabla}_{\|}\frac{\hat\mu_2^{\rm s}-\hat\mu^{\rm s}}{T^{\rm s}}=\boldsymbol{j}_q^{\rm s}\cdot\boldsymbol{\nabla}_{\|}\frac{1}{T^{\rm s}}+\boldsymbol{j}_1^{\rm s}\cdot\boldsymbol{\nabla}_{\|}\frac{\hat\mu_2^{\rm s}-\hat\mu_1^{\rm s}}{T^{\rm s}},$$

where the second equality follows from $\boldsymbol{j}_1^{\rm s}+\boldsymbol{j}_2^{\rm s}=\boldsymbol{0}$. To ensure nonnegative entropy production, we write

$$\boldsymbol{j}_q^{\rm s}=L_{qq}^{\rm s}\boldsymbol{\nabla}_{\|}\frac{1}{T^{\rm s}}+L_{q1}^{\rm s}\boldsymbol{\nabla}_{\|}\frac{\hat\mu_2^{\rm s}-\hat\mu_1^{\rm s}}{T^{\rm s}},$$
$$\boldsymbol{j}_1^{\rm s}=L_{q1}^{\rm s}\boldsymbol{\nabla}_{\|}\frac{1}{T^{\rm s}}+L_{11}^{\rm s}\boldsymbol{\nabla}_{\|}\frac{\hat\mu_2^{\rm s}-\hat\mu_1^{\rm s}}{T^{\rm s}},$$

where $L_{qq}^{\rm s}, L_{q1}^{\rm s}, L_{11}^{\rm s}$ are coefficients of a symmetric matrix. Writing

$$d\Big(\frac{\hat\mu_2^{\rm s}-\hat\mu_1^{\rm s}}{T^{\rm s}}\Big)=\frac{1}{T^{\rm s}}d(\hat\mu_2^{\rm s}-\hat\mu_1^{\rm s})-\frac{\hat\mu_2^{\rm s}-\hat\mu_1^{\rm s}}{T^{\rm s2}}dT^{\rm s}=\frac{1}{T^{\rm s}\rho_1^{\rm s}}(s^{\rm s}dT^{\rm s}+d\gamma)-\frac{\hat\mu_2^{\rm s}-\hat\mu_1^{\rm s}}{T^{\rm s2}}dT^{\rm s}$$

where the second equality is obtained using (13.17) with $\rho^{\rm s}=\rho_1^{\rm s}+\rho_2^{\rm s}=0$. Now, since $\gamma=\gamma(T^{\rm s},\hat\mu_1^{\rm s})$, we can write

$$d\gamma=\Big(\frac{\partial\gamma}{\partial T_1^{\rm s}}\Big)_{\hat\mu_1^{\rm s}}dT^{\rm s}+\Big(\frac{\partial\gamma}{\partial\hat\mu_1^{\rm s}}\Big)_{T^{\rm s}}d\hat\mu_1^{\rm s}$$

$$= -s^{\mathrm{s}} dT^{\mathrm{s}} + \rho_1^{\mathrm{s}} \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\right)_{\hat{\mu}_1^{\mathrm{s}}} dT^{\mathrm{s}} - \rho_1^{\mathrm{s}} \left[1 - \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial \hat{\mu}_1^{\mathrm{s}}}\right)_{T^{\mathrm{s}}}\right] d\hat{\mu}_1^{\mathrm{s}},$$

where the second line follows using (13.21) and (13.22). Substitution in the previous result gives

$$d\left(\frac{\hat{\mu}_2^{\mathrm{s}} - \hat{\mu}_1^{\mathrm{s}}}{T^{\mathrm{s}}}\right) = -\frac{1}{T^{\mathrm{s}2}} \left[\hat{\mu}_2^{\mathrm{s}} - \hat{\mu}_1^{\mathrm{s}} - T^{\mathrm{s}} \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\right)_{\hat{\mu}_1^{\mathrm{s}}}\right] dT^{\mathrm{s}} - \frac{1}{T^{\mathrm{s}}} \left[1 - \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial \hat{\mu}_1^{\mathrm{s}}}\right)_{T^{\mathrm{s}}}\right] d\hat{\mu}_1^{\mathrm{s}}.$$

Substitution in the expression for $\boldsymbol{j}_1^{\mathrm{s}}$ gives

$$\begin{aligned} \boldsymbol{j}_1^{\mathrm{s}} &= -\frac{1}{T^{\mathrm{s}2}} \left\{ L_{qq}^{\mathrm{s}} + L_{11}^{\mathrm{s}} \left[\hat{\mu}_2^{\mathrm{s}} - \hat{\mu}_1^{\mathrm{s}} - T^{\mathrm{s}} \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\right)_{\hat{\mu}_1^{\mathrm{s}}}\right] \right\} \boldsymbol{\nabla}_{\parallel} T^{\mathrm{s}} \\ &\quad - \frac{L_{11}^{\mathrm{s}}}{T^{\mathrm{s}}} \left[1 - \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial \hat{\mu}_1^{\mathrm{s}}}\right)_{T^{\mathrm{s}}}\right] \boldsymbol{\nabla}_{\parallel} \hat{\mu}_1^{\mathrm{s}} \\ &= -\rho_1^{\mathrm{s}} \frac{D_{q1}^{\mathrm{s}}}{T^{\mathrm{s}}} \boldsymbol{\nabla}_{\parallel} T^{\mathrm{s}} - D_{12}^{\mathrm{s}} \boldsymbol{\nabla}_{\parallel} \rho_1^{\mathrm{s}}, \end{aligned}$$

where

$$D_{12}^{\mathrm{s}} = \frac{L_{11}^{\mathrm{s}}}{T^{\mathrm{s}}} \left[1 - \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial \hat{\mu}_1^{\mathrm{s}}}\right)_{T^{\mathrm{s}}}\right] \left(\frac{\partial \hat{\mu}_1^{\mathrm{s}}}{\partial \rho_1^{\mathrm{s}}}\right)_{T^{\mathrm{s}}}$$

$$D_{q1}^{\mathrm{s}} = \frac{L_{qq}^{\mathrm{s}} + L_{11}^{\mathrm{s}} \left[\hat{\mu}_2^{\mathrm{s}} - \hat{\mu}_1^{\mathrm{s}} - T^{\mathrm{s}} \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\right)_{\hat{\mu}_1^{\mathrm{s}}}\right]}{\rho_1^{\mathrm{s}} T^{\mathrm{s}}}.$$

Similarly, substitution in the expression for $\boldsymbol{j}_q^{\mathrm{s}}$ gives

$$\begin{aligned} \boldsymbol{j}_q^{\mathrm{s}} &= -\frac{L_{qq}^{\mathrm{s}}}{T^{\mathrm{s}2}} \boldsymbol{\nabla}_{\parallel} T^{\mathrm{s}} - \frac{L_{q1}^{\mathrm{s}}}{T^{\mathrm{s}2}} \left[\hat{\mu}_2^{\mathrm{s}} - \hat{\mu}_1^{\mathrm{s}} - T^{\mathrm{s}} \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\right)_{\hat{\mu}_1^{\mathrm{s}}}\right] \boldsymbol{\nabla}_{\parallel} T^{\mathrm{s}} \\ &\quad - \frac{L_{q1}^{\mathrm{s}}}{T^{\mathrm{s}}} \left[1 - \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial \hat{\mu}_1^{\mathrm{s}}}\right)_{T^{\mathrm{s}}}\right] \left(\frac{\partial \hat{\mu}_1^{\mathrm{s}}}{\partial \rho_1^{\mathrm{s}}}\right)_{T^{\mathrm{s}}} \boldsymbol{\nabla}_{\parallel} \rho_1^{\mathrm{s}}. \end{aligned}$$

Now, since

$$\begin{aligned} \boldsymbol{j}_q^{\mathrm{s}\prime} &= \boldsymbol{j}_q^{\mathrm{s}} - \left[\hat{\mu}_1^{\mathrm{s}} - \hat{\mu}_2^{\mathrm{s}} + T^{\mathrm{s}} \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\right)_{\hat{\mu}_1^{\mathrm{s}}}\right] \boldsymbol{j}_1^{\mathrm{s}} \\ &= -\frac{1}{T^{\mathrm{s}2}} \left\{ L_{qq}^{\mathrm{s}} + 2L_{q1}^{\mathrm{s}} \left[\hat{\mu}_2^{\mathrm{s}} - \hat{\mu}_1^{\mathrm{s}} - T^{\mathrm{s}} \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\right)_{\hat{\mu}_1^{\mathrm{s}}}\right] \right. \\ &\quad \left. + L_{11}^{\mathrm{s}} \left[\hat{\mu}_2^{\mathrm{s}} - \hat{\mu}_1^{\mathrm{s}} - T^{\mathrm{s}} \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\right)_{\hat{\mu}_1^{\mathrm{s}}}\right]^2 \right\} \boldsymbol{\nabla}_{\parallel} T^{\mathrm{s}} \\ &\quad - \frac{1}{T^{\mathrm{s}}} \left\{ L_{q1}^{\mathrm{s}} + 2L_{11}^{\mathrm{s}} \left[\hat{\mu}_2^{\mathrm{s}} - \hat{\mu}_1^{\mathrm{s}} - T^{\mathrm{s}} \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\right)_{\hat{\mu}_1^{\mathrm{s}}}\right] \right\} \left[1 - \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial \hat{\mu}_1^{\mathrm{s}}}\right)_{T^{\mathrm{s}}}\right] \left(\frac{\partial \hat{\mu}_1^{\mathrm{s}}}{\partial \rho_1^{\mathrm{s}}}\right)_{T^{\mathrm{s}}} \boldsymbol{\nabla}_{\parallel} \rho_1^{\mathrm{s}} \\ &= -\lambda^{\mathrm{s}\prime} \boldsymbol{\nabla}_{\parallel} T^{\mathrm{s}} - \rho_1^{\mathrm{s}} \left[1 - \left(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial \hat{\mu}_1^{\mathrm{s}}}\right)_{T^{\mathrm{s}}}\right] \left(\frac{\partial \hat{\mu}_1^{\mathrm{s}}}{\partial \rho_1^{\mathrm{s}}}\right)_{T^{\mathrm{s}}} D_{q1}^{\mathrm{s}} \boldsymbol{\nabla}_{\parallel} \rho_1^{\mathrm{s}}, \end{aligned}$$

where

$$\lambda^{\mathrm{s}\prime} = \frac{L_{qq}^{\mathrm{s}} + 2L_{q1}^{\mathrm{s}}\Big[\hat{\mu}_2^{\mathrm{s}} - \hat{\mu}_1^{\mathrm{s}} - T^{\mathrm{s}}\Big(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\Big)_{\hat{\mu}_1^{\mathrm{s}}}\Big] + L_{11}^{\mathrm{s}}\Big[\hat{\mu}_2^{\mathrm{s}} - \hat{\mu}_1^{\mathrm{s}} - T^{\mathrm{s}}\Big(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\Big)_{\hat{\mu}_1^{\mathrm{s}}}\Big]^2}{T^{\mathrm{s}2}}.$$

Exercise 15.8

Writing the first term on the right-hand side of (14.21) as $\boldsymbol{\nabla}_\parallel \cdot (\boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}} \rho_\alpha^{\mathrm{s}}) = \boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}} \cdot \boldsymbol{\nabla}_\parallel \rho_\alpha^{\mathrm{s}} + \rho_\alpha^{\mathrm{s}} \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}}$, for two-component interface we can write,

$$\frac{\partial^{\mathrm{s}} \rho_1^{\mathrm{s}}}{\partial t} + \boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}} \cdot \boldsymbol{\nabla}_\parallel \rho_1^{\mathrm{s}} = -\rho_1^{\mathrm{s}} \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{v}^{\mathrm{s}} - \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{j}_1^{\mathrm{s}} + \nu_1^{\mathrm{s}} \Gamma^{\mathrm{s}}$$
$$+ \boldsymbol{n} \cdot \Big[(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}})\rho_1^{\mathrm{II}} + \boldsymbol{j}_1^{\mathrm{II}} - (\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}})\rho_1^{\mathrm{I}} - \boldsymbol{j}_1^{\mathrm{I}}\Big],$$

where we have used (14.11). From (14.24) with $\boldsymbol{\pi}^{\mathrm{s}} = -\gamma \boldsymbol{\delta}_\parallel + \boldsymbol{\tau}^{\mathrm{s}}$ we can write,

$$\frac{\partial^{\mathrm{s}} u^{\mathrm{s}}}{\partial t} + \boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}} \cdot \boldsymbol{\nabla}_\parallel u^{\mathrm{s}} = -(u^{\mathrm{s}} - \gamma)\boldsymbol{\nabla}_\parallel \cdot \boldsymbol{v}^{\mathrm{s}} - \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{j}_q^{\mathrm{s}} - \boldsymbol{\tau}^{\mathrm{s}} : \boldsymbol{\nabla}_\parallel \boldsymbol{v}^{\mathrm{s}}$$
$$+\boldsymbol{n} \cdot \Big[(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}})h^{\mathrm{II}} + \boldsymbol{j}_q^{\mathrm{II}} - (\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}})h^{\mathrm{I}} - \boldsymbol{j}_q^{\mathrm{I}}\Big] + \left(\frac{1}{\rho^{\mathrm{II}}} - \frac{1}{\rho^{\mathrm{I}}}\right)^{-1}$$
$$\times\left\{ \left[\frac{1}{2}\frac{\rho^{\mathrm{I}} + \rho^{\mathrm{II}}}{\rho^{\mathrm{I}} - \rho^{\mathrm{II}}}(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}})^2 + \boldsymbol{n} \cdot \left(\frac{\boldsymbol{\tau}^{\mathrm{II}}}{\rho^{\mathrm{II}}} - \frac{\boldsymbol{\tau}^{\mathrm{I}}}{\rho^{\mathrm{I}}}\right) \cdot \boldsymbol{n}\right] \boldsymbol{n} \cdot (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}}) \right.$$
$$\left. +\boldsymbol{n} \cdot \left(\frac{\boldsymbol{\tau}^{\mathrm{II}}}{\rho^{\mathrm{II}}} - \frac{\boldsymbol{\tau}^{\mathrm{I}}}{\rho^{\mathrm{I}}}\right) \cdot (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}})_\parallel \right\}.$$

In the gauge $\rho^{\mathrm{s}} = \rho_1^{\mathrm{s}} + \rho_2^{\mathrm{s}} = 0$ we can write (13.16) as

$$u^{\mathrm{s}} = T^{\mathrm{s}} s^{\mathrm{s}} + \gamma + (\hat{\mu}_1 - \hat{\mu}_2)\rho_1^{\mathrm{s}}$$
$$= \gamma - T^{\mathrm{s}}\Big(\frac{\partial \gamma}{\partial T}\Big)_{\hat{\mu}_1} + \Big[\hat{\mu}_1^{\mathrm{s}} - \hat{\mu}_2^{\mathrm{s}} + T^{\mathrm{s}}\Big(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\Big)_{\hat{\mu}_1^{\mathrm{s}}}\Big]\rho_1^{\mathrm{s}},$$

where the second equality follows using (13.21). Taking the differential of u^{s} and using (13.17) we obtain

$$du^{\mathrm{s}} = -T^{\mathrm{s}}\Big[\Big(\frac{\partial^2 \gamma}{\partial T^{\mathrm{s}2}}\Big)_{\hat{\mu}_1} - \rho_1^{\mathrm{s}}\Big(\frac{\partial^2 \hat{\mu}_2}{\partial T^{\mathrm{s}2}}\Big)_{\hat{\mu}_1}\Big] dT^{\mathrm{s}} + \Big[\hat{\mu}_1^{\mathrm{s}} - \hat{\mu}_2^{\mathrm{s}} + T^{\mathrm{s}}\Big(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\Big)_{\hat{\mu}_1^{\mathrm{s}}}\Big] d\rho_1^{\mathrm{s}}.$$

Substitution of the last two results in the balance equation for u^{s} gives

$$- T^{\mathrm{s}}\Big[\Big(\frac{\partial^2 \gamma}{\partial T^{\mathrm{s}2}}\Big)_{\hat{\mu}_1} - \rho_1^{\mathrm{s}}\Big(\frac{\partial^2 \hat{\mu}_2}{\partial T^{\mathrm{s}2}}\Big)_{\hat{\mu}_1}\Big]\Big(\frac{\partial^{\mathrm{s}} T^{\mathrm{s}}}{\partial t} + \boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}} \cdot \boldsymbol{\nabla}_\parallel T^{\mathrm{s}}\Big)$$
$$+\Big[\hat{\mu}_1^{\mathrm{s}} - \hat{\mu}_2^{\mathrm{s}} + T^{\mathrm{s}}\Big(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\Big)_{\hat{\mu}_1^{\mathrm{s}}}\Big]\Big(\frac{\partial^{\mathrm{s}} \rho_1^{\mathrm{s}}}{\partial t} + \boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}} \cdot \boldsymbol{\nabla}_\parallel \rho_1^{\mathrm{s}}\Big) = T^{\mathrm{s}}\Big(\frac{\partial \gamma}{\partial T}\Big)_{\hat{\mu}_1} \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{v}^{\mathrm{s}}$$
$$-\Big[\hat{\mu}_1^{\mathrm{s}} - \hat{\mu}_2^{\mathrm{s}} + T^{\mathrm{s}}\Big(\frac{\partial \hat{\mu}_2^{\mathrm{s}}}{\partial T^{\mathrm{s}}}\Big)_{\hat{\mu}_1^{\mathrm{s}}}\Big]\rho_1^{\mathrm{s}} \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{v}^{\mathrm{s}} - \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{j}_q^{\mathrm{s}} - \boldsymbol{\tau}^{\mathrm{s}} : \boldsymbol{\nabla}_\parallel \boldsymbol{v}^{\mathrm{s}}$$

$$+\boldsymbol{n}\cdot\left[(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{s}})h^{\mathrm{II}}+\boldsymbol{j}_q^{\mathrm{II}}-(\boldsymbol{v}^{\mathrm{I}}-\boldsymbol{v}^{\mathrm{s}})h^{\mathrm{I}}-\boldsymbol{j}_q^{\mathrm{I}}\right]$$

$$+\left(\frac{1}{\rho^{\mathrm{II}}}-\frac{1}{\rho^{\mathrm{I}}}\right)^{-1}\left\{\left[\frac{1}{2}\frac{\rho^{\mathrm{I}}+\rho^{\mathrm{II}}}{\rho^{\mathrm{I}}-\rho^{\mathrm{II}}}(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{I}})^2+\boldsymbol{n}\cdot\left(\frac{\boldsymbol{\tau}^{\mathrm{II}}}{\rho^{\mathrm{II}}}-\frac{\boldsymbol{\tau}^{\mathrm{I}}}{\rho^{\mathrm{I}}}\right)\cdot\boldsymbol{n}\right]\boldsymbol{n}\cdot(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{I}})\right.$$

$$\left.+\boldsymbol{n}\cdot\left(\frac{\boldsymbol{\tau}^{\mathrm{II}}}{\rho^{\mathrm{II}}}-\frac{\boldsymbol{\tau}^{\mathrm{I}}}{\rho^{\mathrm{I}}}\right)\cdot(\boldsymbol{v}^{\mathrm{II}}-\boldsymbol{v}^{\mathrm{I}})_{\parallel}\right\}$$

Substitution of (15.36) in the second line of the result above gives, after the cancelation of terms, the expression in (15.37).

Exercise 16.1

For $\dot{\gamma}=10\ \mathrm{s}^{-1}$, we have from Figure 12.5 $(N_1)_R = 365000$ Pa and $\tau_R =$ 365000 Pa, so that (16.8) gives

$$\frac{R_{\mathrm{ext}}}{R}\backsimeq 0.13+\left[1+\frac{1}{8}\left(\frac{365000\ \mathrm{Pa}}{79500\ \mathrm{Pa}}\right)^2\right]^{1/6}\approx 1.37.$$

Exercise 16.2

The total mass flow rate through the die of radius R can be written as

$$\mathcal{W}=\int_0^{2\pi}\int_0^R \rho v_z(r)rdrd\theta = 2\pi\rho\int_0^R v_z(r)rdr=\pi\rho\int_0^R\dot{\gamma}(r)r^2dr.$$

where the third result is obtained from integration by parts using $-\dot{\gamma}(r)=dv_z/dr$. Now using (16.4), we make a change of variable $r=(R/\tau_R)\tau_{rz}$, so that we have

$$\frac{\mathcal{W}}{\rho\pi R^3}=\frac{1}{\tau_R^3}\int_0^{\tau_R}\dot{\gamma}(\tau_{rz})\tau_{rz}^2d\tau_{rz}.$$

Differentiation with respect to τ_R gives

$$\frac{d}{d\tau_R}\left(\frac{\mathcal{W}}{\rho\pi R^3}\right)=-\frac{3}{\tau_R^4}\int_0^{\tau_R}\dot{\gamma}(\tau_{rz})\tau_{rz}^2d\tau_{rz}+\frac{\dot{\gamma}(\tau_R)}{\tau_R}$$

which is easily rearranged to give the desired expression.

Exercise 16.3

The normal vector to the interface between the fluid and die is $\boldsymbol{n}=\boldsymbol{\delta}_r$ so that $\boldsymbol{\delta}_{\parallel}=\boldsymbol{\delta}_\theta\boldsymbol{\delta}_\theta+\boldsymbol{\delta}_z\boldsymbol{\delta}_z$. Writing (15.17) with $\boldsymbol{\xi}_{\parallel}=\xi_{\mathrm{slip}}\boldsymbol{\delta}_{\parallel}$ we obtain

$$\boldsymbol{v}_{\parallel}^{\mathrm{II}}=\xi_{\mathrm{slip}}\boldsymbol{\delta}_{\parallel}\cdot\left(\frac{\boldsymbol{\tau}^{\mathrm{II}}}{\rho^{\mathrm{II}}}-\frac{\boldsymbol{\tau}^{\mathrm{I}}}{\rho^{\mathrm{I}}}\right)\cdot\boldsymbol{n}\left(\frac{1}{\rho^{\mathrm{II}}}-\frac{1}{\rho^{\mathrm{I}}}\right)^{-1}.$$

The jump balance for momentum (14.6), in the absence of mass transfer, simplifies to $\boldsymbol{n}\cdot\boldsymbol{\pi}^{\mathrm{I}}=\boldsymbol{n}\cdot\boldsymbol{\pi}^{\mathrm{II}}$ so that,

$$\boldsymbol{\delta}_{\parallel}\cdot\boldsymbol{\tau}^{\mathrm{I}}\cdot\boldsymbol{n}=\boldsymbol{\delta}_{\parallel}\cdot\boldsymbol{\tau}^{\mathrm{II}}\cdot\boldsymbol{n}$$

Combining these expressions gives

$$\boldsymbol{v}_{\|}^{\text{II}} = \xi_{\text{slip}} \boldsymbol{\delta}_{\|} \cdot \boldsymbol{\tau}^{\text{II}} \cdot \boldsymbol{n} = \xi_{\text{slip}} (\boldsymbol{\delta}_\theta \boldsymbol{\delta}_\theta + \boldsymbol{\delta}_z \boldsymbol{\delta}_z) \cdot \boldsymbol{\tau}^{\text{II}} \cdot \boldsymbol{n} = \xi_{\text{slip}} \tau_{zr}(R) \boldsymbol{\delta}_z,$$

where the third equality follows from (16.2). Now, from (16.4) and (16.5), we can write

$$\tau_{zr} = K \Big(- \frac{dv_z}{dr} \Big)^n = \frac{-\Delta p_{\text{die}}}{2L} r,$$

which can be integrated to give

$$v_z = - \Big(\frac{-\Delta p_{\text{die}}}{2KL} \Big)^{1/n} \frac{R^{1/n+1}}{1/n+1} - c_1$$

From previous results, the boundary condition at the tube wall can be written as

$$v_z(R) = \xi_{\text{slip}} \tau_{zr}(R) = \xi_{\text{slip}} K \frac{-\Delta p_{\text{die}}}{2L} R,$$

which leads to the following expression

$$v_z = \frac{nR}{1+n} \Big(\frac{-\Delta p_{\text{die}} R}{2KL} \Big)^{1/n} \Big[1 - \Big(\frac{r}{R} \Big)^{1/n+1} \Big] + \frac{-\Delta p_{\text{die}} \xi_{\text{slip}} R}{2L}.$$

Integrating over the die cross section gives the desired relationship between pressure drop and flow rate.

Exercise 16.4
Combining (16.3c) and (16.5) we obtain in the absence of an imposed pressure gradient

$$\frac{d}{dr} \Big[\Big(- \frac{dv_z}{dr} \Big)^n \Big] = 0,$$

which can be integrated twice to obtain

$$v_z = \frac{n c_1^{1/n}}{1-n} r^{-1/n+1} - c_2.$$

Applying the boundary conditions

$$v_z(R) = 0, \qquad v_z(\beta R) = V,$$

we obtain the desired velocity. Integrating over the cross section between the die and wire gives

$$\mathcal{W} = \int_0^{2\pi} \int_{\beta R}^{R} \rho v_z(r) r dr d\theta = \frac{\rho \pi R^2 V}{\beta^{1-1/n} - 1} \Big[\frac{2n}{3n-1} (1 - \beta^{3-1/n}) - (1 - \beta^2) \Big].$$

Now, since the gas is incviscid, the coating on the wire has uniform velocity V so that the mass flow rate of the coating is given by

$$\mathcal{W} = \int_0^{2\pi} \int_{\beta R}^{\kappa R} \rho V r dr d\theta = \rho \pi R^2 V (\kappa^2 - \beta^2).$$

Combining the last two expressions gives the desired relation for the coating thickness.

Exercise 16.5

At steady state, the mass flow rate through the extruder is constant and given by $\mathcal{W} = \rho B H \langle v_3 \rangle$, where

$$\langle v_3 \rangle = \frac{1}{H} \int_0^H v_3 dx_2 = -\frac{\Delta p_{\text{ext}} H^2}{12 \eta L_{\text{ext}}} + \frac{1}{2} V \cos\theta,$$

The steady state form of (9.34) is given by

$$\mathcal{W} \Delta \hat{h} = \dot{W},$$

where we have neglected changes in kinetic and potential energies and set $\dot{Q} = 0$ since we are assuming adiabatic conditions. The expression for $\dot{W}$ is given in (8.47)

$$\begin{aligned}\dot{W} &= -\int_{A_{\text{sm}}} (\boldsymbol{\pi} \cdot \boldsymbol{v}) \cdot \boldsymbol{n}(A_{\text{sm}}) dA = -\int_0^{L_{\text{ext}}} \int_{-B/2}^{B/2} \boldsymbol{\delta}_2 \cdot (\boldsymbol{\pi} \cdot \boldsymbol{v})(H) dx_1 dx_3 \\ &= V B L_{\text{ext}} [\sin\theta \tau_{21}(H) - \cos\theta \tau_{23}(H)]\end{aligned}$$

where the second line follows from $\boldsymbol{v}(H) = -V(\sin\theta \boldsymbol{\delta}_1 - \cos\theta \boldsymbol{\delta}_3)$. From (16.11) and (16.12) we have

$$\tau_{21}(H) = -\eta \frac{\partial v_1}{\partial x_2}(H) = 4 \frac{\eta V}{H} \sin\theta,$$

$$\tau_{23}(H) = -\eta \frac{\partial v_3}{\partial x_2}(H) = -\frac{H \Delta p_{\text{ext}}}{2 L_{\text{ext}}} - \frac{\eta V}{H} \cos\theta.$$

Hence, we can write

$$\dot{W} = B L_{\text{ext}} \Big[\frac{\pi^2 \Omega^2 D^2}{H} (1 + 3 \sin^2\theta) + \frac{\pi D H \Delta p_{\text{ext}}}{2 L_{\text{ext}}} \cos\theta \Big]$$

where we have used $V = \pi D \Omega$. Now, for the extruder-die system we have $\Delta \hat{h} = \hat{c}_p \Delta T + \Delta p / \rho = \hat{c}_p \Delta T$, so that the energy balance gives the following expression for the temperature rise

$$\Delta T = \frac{B L_{\text{ext}}}{\hat{c}_p \mathcal{W}} \Big[\frac{\pi^2 \Omega^2 D^2}{H} (1 + 3 \sin^2\theta) + \frac{\pi D H \Delta p_{\text{ext}}}{2 L_{\text{ext}}} \cos\theta \Big].$$

Exercise 16.6

Applying (16.23) to (16.14) we obtain

$$\frac{2}{R}v_r(R,z) + \frac{1}{R^2}\frac{d}{dz}(R^2\langle v_z(R,z)\rangle) - 2\frac{R'}{R}v_z(R,z) = 0.$$

Using (16.18) the first and third terms cancel, which gives (16.24). Setting the left-hand side of (16.16) to zero, and multiplication by r^2 and integrating gives,

$$\begin{aligned}
0 &= -\int_0^R \frac{\partial p^{\mathrm{L}}}{\partial r} r^2 dr - \int_0^R \Big[\frac{1}{r}\frac{\partial}{\partial r}(r\tau_{rr}) - \frac{\tau_{\theta\theta}}{r} + \frac{\partial \tau_{rz}}{\partial z}\Big] r^2 dr \\
&= -\int_0^R r^2 dp^{\mathrm{L}} - \int_0^R r d(r\tau_{rr}) + \int_0^R \tau_{\theta\theta} r dr - \int_0^R \frac{\partial \tau_{rz}}{\partial z} r^2 dr \\
&= -\Big[R^2 p^{\mathrm{L}}(R,z) - 2\int_0^R p^{\mathrm{L}} r dr\Big] - \Big[R^2\tau_{rr}(R,z) - \int_0^R \tau_{rr} r dr\Big] + \int_0^R \tau_{\theta\theta} r dr \\
&\quad - \frac{\partial}{\partial z}\int_0^R \tau_{rz} r^2 dr + R'R^2\tau_{rz}(R,z).
\end{aligned}$$

Dividing the last result by R^2, we obtain

$$\begin{aligned}
0 = -p^{\mathrm{L}}(R,z) + \langle p^{\mathrm{L}}\rangle - \tau_{rr}(R,z) + \frac{1}{2}(\langle \tau_{rr}\rangle + \langle \tau_{\theta\theta}\rangle) \\
- \frac{1}{R^2}\frac{\partial}{\partial z}\int_0^R \tau_{rz} r^2 dr + R'\tau_{rz}(R,z)
\end{aligned}$$

Substitution of (16.21) and (16.22) and neglecting terms of order $(R')^2$ gives (16.25). Multiplication of the left-hand side of (16.16) by r and integrating gives

$$\begin{aligned}
\int_0^R v_r \frac{\partial v_z}{\partial r} r dr + \int_0^R v_z \frac{\partial v_z}{\partial z} r dr \\
&= R v_r(R,z) v_z(R,z) - \int_0^R v_z \frac{\partial}{\partial r}(r v_r) dr + \int_0^R v_z \frac{\partial v_z}{\partial z} r dr \\
&= RR' v_z(R,z)^2 + \int_0^R \frac{\partial v_z^2}{\partial z} r dr \\
&= \frac{1}{2}\frac{d}{dz}(R^2\langle v_z^2\rangle),
\end{aligned}$$

where we have used (16.14) and (16.18) to obtain the second equality. Multiplication of the right-hand side of (16.16) by r and integrating gives

$$-\int_0^R \frac{\partial p^{\mathrm{L}}}{\partial z} r dr - \int_0^R \Big[\frac{1}{r}\frac{\partial}{\partial r}(r\tau_{rz}) + \frac{\partial \tau_{zz}}{\partial z}\Big] r dr + \int_0^R \rho g r dr$$

$$= -\frac{1}{2}\frac{d}{dz}[R^2(\langle p^{\mathrm{L}}\rangle + \langle \tau_{zz}\rangle)] + R'R^2(\langle p^{\mathrm{L}}\rangle + \langle \tau_{zz}\rangle) - R\tau_{rz}(R,z) + \frac{1}{2}R^2\rho g$$
$$= -\frac{1}{2}\frac{d}{dz}[R^2(\langle p^{\mathrm{L}}\rangle + \langle \tau_{zz}\rangle)] + \gamma R' + \frac{1}{2}R^2\rho g$$

where we have used (16.21) to obtain the third equality. Combining the last two results gives (16.26).

Exercise 16.7
For steady flow, (12.45) can be written as

$$\boldsymbol{\tau} + \lambda(\boldsymbol{v}\cdot\boldsymbol{\nabla}\boldsymbol{\tau} + \boldsymbol{\kappa}\cdot\boldsymbol{\tau} + \boldsymbol{\tau}\cdot\boldsymbol{\kappa}^T) = -\eta(\boldsymbol{\kappa} + \boldsymbol{\kappa}^T)$$

For the flow given by $v_r = v_r(r,z), v_z = v_z(r,z)$, we have

$$\boldsymbol{\kappa} = (\boldsymbol{\nabla}\boldsymbol{v})^T = \begin{bmatrix} \frac{\partial v_r}{\partial r} & 0 & \frac{\partial v_r}{\partial z} \\ 0 & \frac{v_r}{r} & 0 \\ \frac{\partial v_z}{\partial r} & 0 & \frac{\partial v_z}{\partial z} \end{bmatrix}, \qquad \boldsymbol{\tau} = \begin{bmatrix} \tau_{rr} & 0 & \tau_{rz} \\ 0 & \tau_{\theta\theta} & 0 \\ \tau_{rz} & 0 & \tau_{zz} \end{bmatrix},$$

which lead to the following for the non-linear terms

$$\boldsymbol{\kappa}\cdot\boldsymbol{\tau} = \begin{bmatrix} \tau_{rr}\frac{\partial v_r}{\partial r} + \tau_{rz}\frac{\partial v_r}{\partial z} & 0 & \tau_{rr}\frac{\partial v_z}{\partial r} + \tau_{rz}\frac{\partial v_z}{\partial z} \\ 0 & \tau_{\theta\theta}\frac{v_r}{r} & 0 \\ \tau_{rz}\frac{\partial v_r}{\partial r} + \tau_{zz}\frac{\partial v_r}{\partial z} & 0 & \tau_{rz}\frac{\partial v_z}{\partial r} + \tau_{zz}\frac{\partial v_z}{\partial z} \end{bmatrix},$$

$$\boldsymbol{v}\cdot\boldsymbol{\nabla}\boldsymbol{\tau} = \begin{bmatrix} v_r\frac{\partial \tau_{rr}}{\partial r} + v_z\frac{\partial \tau_{rr}}{\partial z} & 0 & v_r\frac{\partial \tau_{rz}}{\partial r} + v_z\frac{\partial \tau_{rz}}{\partial z} \\ 0 & v_r\frac{\partial \tau_{\theta\theta}}{\partial r} + v_z\frac{\partial \tau_{\theta\theta}}{\partial z} & 0 \\ v_r\frac{\partial \tau_{rz}}{\partial r} + v_z\frac{\partial \tau_{rz}}{\partial z} & 0 & v_r\frac{\partial \tau_{zz}}{\partial r} + v_z\frac{\partial \tau_{zz}}{\partial z} \end{bmatrix}.$$

Hence, we can write

$$\tau_{rr} + \lambda\left[v_r\frac{\partial \tau_{rr}}{\partial r} + v_z\frac{\partial \tau_{rr}}{\partial z} - 2\Big(\tau_{rr}\frac{\partial v_r}{\partial r} + \tau_{rz}\frac{\partial v_r}{\partial z}\Big)\right] = -2\eta\frac{\partial v_r}{\partial r},$$

$$\tau_{\theta\theta} + \lambda\left[v_r\frac{\partial \tau_{\theta\theta}}{\partial r} + v_z\frac{\partial \tau_{\theta\theta}}{\partial z} - 2\tau_{\theta\theta}\frac{v_r}{r}\right] = -2\eta\frac{v_r}{r},$$

$$\tau_{zz} + \lambda\left[v_r\frac{\partial \tau_{zz}}{\partial r} + v_z\frac{\partial \tau_{zz}}{\partial z} - 2\Big(\tau_{rz}\frac{\partial v_z}{\partial r} + \tau_{zz}\frac{\partial v_z}{\partial z}\Big)\right] = -2\eta\frac{\partial v_z}{\partial z},$$

$$\tau_{rz} + \lambda\left[v_r\frac{\partial \tau_{rz}}{\partial r} + v_z\frac{\partial \tau_{rz}}{\partial z} - \Big(\tau_{rr}\frac{\partial v_z}{\partial r} + \tau_{rz}\frac{\partial v_z}{\partial z} + \tau_{rz}\frac{\partial v_r}{\partial r} + \tau_{zz}\frac{\partial v_r}{\partial z}\Big)\right]$$
$$= -\eta\Big(\frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r}\Big).$$

Now, since we are assuming the dependence of v_z on r can be neglected, we can integrate the continuity equation (16.14) to obtain

$$v_r = -\frac{r}{2}\frac{\partial v_z}{\partial z}.$$

In this case, we have $\tau_{rz} = 0$, and τ_{rr} and τ_{zz} are independent of r so that

$$\tau_{rr} + \lambda\left[v_z\frac{\partial \tau_{rr}}{\partial z} + \tau_{rr}\frac{\partial v_z}{\partial z}\right] = \eta\frac{\partial v_z}{\partial z},$$

$$\tau_{zz} + \lambda\left[v_z\frac{\partial \tau_{zz}}{\partial z} - 2\tau_{zz}\frac{\partial v_z}{\partial z}\right] = -2\eta\frac{\partial v_z}{\partial z}.$$

Taking the radial average of these results and assuming the terms in square brackets can be written as the product of averages gives (16.33) and (16.34).

Exercise 16.8
Differentiation of (16.32) and substitution in (16.33) gives

$$\begin{aligned}\langle\tau_{zz}\rangle + \frac{\rho F_L}{\mathcal{W}}\langle v_z\rangle + \lambda\Big[\langle v_z\rangle\Big(\frac{d\langle\tau_{zz}\rangle}{dz} + \frac{\rho F_L}{\mathcal{W}}\frac{d\langle v_z\rangle}{dz}\Big)\\ +\Big(\langle\tau_{zz}\rangle + \frac{\rho F_L}{\mathcal{W}}\langle v_z\rangle\Big)\frac{d\langle v_z\rangle}{dz}\Big] = \eta\frac{d\langle v_z\rangle}{dz}.\end{aligned}$$

Subtracting this from (16.34) gives (16.35). Differentiating (16.35) we obtain

$$\frac{\lambda}{\eta}\frac{d\langle\tau_{zz}\rangle}{dz} = -\frac{2}{3}\lambda\frac{\rho F_L}{\eta\mathcal{W}}\frac{d\langle v_z\rangle}{dz} - \frac{1}{3}\frac{\rho F_L}{\eta\mathcal{W}}\Big(\frac{d\langle v_z\rangle}{dz}\Big)^{-1} + \frac{1}{3}\frac{\rho F_L}{\eta\mathcal{W}}\langle v_z\rangle\frac{d^2\langle v_z\rangle}{dz^2}\Big(\frac{d\langle v_z\rangle}{dz}\Big)^{-2}.$$

Substitution of these in (16.34) gives (16.36).

Exercise 16.9
It is convenient to rewrite the second-order ODE in (16.36) as two first-order ODEs by introducing the new variable

$$u_z := \frac{d\langle v_z\rangle}{dz}$$

```
% Simulation parameters
N=100; % Number of grid points along 0<z<1
DZ=1/(N-1);
Z=0:DZ:1;
V=zeros(1,N);
U=zeros(1,N);

D_R=20;
N_DE=0.05;
EPSILON=0.0685;
```

```
% Initial conditions
U(1)=1/(3*EPSILON)*(1-2/3*N_DE/EPSILON)^(-1);
V(1)=1;

for I=1:N-1
   V(I+1)=V(I)+DZ*U(I);
   U(I+1)=U(I)+DZ/V(I)^2*...
            (V(I)*(1-N_DE*U(I))*U(I)^2+1/N_DE*(V(I)-3*EPSILON*U(I))*U(I));
end

ERROR=V(end)-D_R;

% Plot of simulation results
plot(Z,V,'k')
ylabel('$\langle v_z \rangle$','FontSize',14,'Interpreter','latex');
xlabel('$z$','FontSize',14,'Interpreter','latex');
```

Exercise 16.10

Integrating (16.24), we obtain

$$R^2 \langle v_z \rangle = 1,$$

where we have used $R/R_0 \to R$. From (16.33) and (16.34) with $\lambda = 0$, we have

$$\langle \tau_{zz} \rangle - \langle \tau_{rr} \rangle = -3\eta \frac{d\langle v_z \rangle}{dz}.$$

Substitution in (16.27) and using $\mathcal{W} = \rho \pi R^2 \langle v_z \rangle$, we obtain

$$\rho R^2 \langle v_z \rangle \frac{d\langle v_z \rangle}{dz} = 3\eta \frac{d}{dz}\Big(R^2 \frac{d\langle v_z \rangle}{dz}\Big).$$

Using the first result to eliminate R and the normalizations $z/R \to z$ and $\langle v_z \rangle / V \to \langle v_z \rangle$, the desired result is obtained.

Exercise 16.11

The temperature equation (6.7) using Fourier's law (6.4) has the form

$$\rho \hat{c}_p \Big(v_r \frac{\partial T}{\partial r} + v_z \frac{\partial T}{\partial z} \Big) = \lambda \Big[\frac{1}{r} \frac{\partial}{\partial r} \Big(r \frac{\partial T}{\partial r} \Big) + \frac{\partial^2 T}{\partial z^2} \Big],$$

where we have assumed the thermal conductivity λ is constant and neglected viscous dissipation. If we further neglect axial conduction, and take the radial average (see Exercise 16.6), we obtain

$$\rho \hat{c}_p \frac{1}{2} \frac{d}{dz} (R^2 \langle v_z T \rangle) = \lambda R \frac{\partial T}{\partial r}(R, z))$$

The boundary condition at the interface between the liquid filament and ambient gas is formulated assuming local equilibrium and the absence of interfacial resistances. In the absence of mass transfer and continuity of both velocity and stress reduces (14.26) to the continuity of the energy flux across the interface: $\boldsymbol{n} \cdot \boldsymbol{j}_q^{\mathrm{I}} = \boldsymbol{n} \cdot \boldsymbol{j}_q^{\mathrm{II}}$. Thermal transport in the gas phase (I) described using a heat transfer coefficient and Newton's law of cooling (see Section 9.3). Using (9.27), we have

$$-\lambda \frac{\partial T}{\partial r}(R, z) = h[T(R, z) - T_{\mathrm{g}}],$$

where h is the heat transfer coefficient. Combining these we obtain

$$\rho \hat{c}_p \frac{d}{dz}\Big(R^2 \langle v_z \rangle \langle T \rangle\Big) = Rh[T(R, z) - T_{\mathrm{g}}],$$

where we have used the approximation $\langle v_z T \rangle \approx \langle v_z \rangle \langle T \rangle$. Since the mass flow rate is constant, we can write,

$$\hat{c}_p \mathcal{W} \frac{d\langle T \rangle}{dz} = -2\pi Rh(\langle T \rangle - T_{\mathrm{g}}),$$

where we have used $T(R, z) \approx \langle T \rangle$.

Exercise 17.1
Substitution of (17.5) and (17.6) in (17.8) gives

$$\sum_{n=0}^{\infty} \Big[A_n n R^{n-1} - B_n (n+1) R^{-(n+2)}\Big] P_n(\xi) = \beta \sum_{n=0}^{\infty} \bar{A}_n n R^{n-1} P_n(\xi)$$

from which we find $B_0 = 0$ and the following

$$B_n = (A_n - \beta \bar{A}_n) \frac{n}{n+1} R^{2n+1}$$

for $B_n \geq 1$. Similarly, substitution of (17.5) and (17.6) in (17.9) gives

$$\sum_{n=0}^{\infty} \Big[A_n R^n + B_n R^{-(n+1)}\Big] P_n(\xi) = \beta \sum_{n=0}^{\infty} \bar{A}_n n R^n P_n(\xi)$$
$$+ \lambda R_{\mathrm{K}}^{\mathrm{s}} \sum_{n=0}^{\infty} \Big[A_n n R^{n-1} - B_n (n+1) R^{-(n+2)}\Big] P_n(\xi),$$

which gives

$$\begin{aligned} \bar{A}_n &= A_n (1 - N_{\mathrm{Ka}}) + B_n [1 + (n+1) N_{\mathrm{Ka}}] R^{-(2n+1)} \\ &= A_n \frac{(n+1)(1 - N_{\mathrm{Ka}}) + n[1 + (n+1) N_{\mathrm{Ka}}]}{1 + \beta n [1 + (n+1) N_{\mathrm{Ka}}]} \end{aligned}$$

where $N_{\mathrm{Ka}} = R_{\mathrm{K}}^{\mathrm{s}} \lambda / R$, and the second line is obtained by eliminating B_n

using the expression above. Now, since $A_1 = |\boldsymbol{\nabla} T|_\infty$, and $A_n = 0$ for $n \geq 2$, we obtain

$$\bar{A}_1 = \frac{3}{2+\beta(1+2N_{\mathrm{Ka}})}A_1, \qquad B_1 = \frac{1-\beta(1-N_{\mathrm{Ka}})}{2+\beta(1+2N_{\mathrm{Ka}})}A_1 R^3$$

and $\bar{A}_n = B_n = 0$ for $n \geq 2$. Finally, since A_0 is arbitrary, we set $A_0 = T_0$, which gives the expressions in (17.10) and (17.11).

Exercise 17.2
Substitution of (17.11) in (17.9) gives

$$\begin{aligned} T(R,\theta) &= \overline{T}(R,\theta) + R_{\mathrm{K}}\lambda\Big[1 - 2\frac{1-\beta(1-N_{\mathrm{Ka}})}{2+\beta(1+2N_{\mathrm{Ka}})}\Big]\xi|\boldsymbol{\nabla} T|_\infty \\ &= \overline{T}(R,\theta) + N_{\mathrm{Ka}}\frac{3\beta}{2+\beta(1+2N_{\mathrm{Ka}})}\xi R|\boldsymbol{\nabla} T|_\infty \end{aligned}$$

which, since $\xi = \cos\theta$, clearly gives the desired expression. The temperature jump is proportional to the magnitude of the temperature gradient at the interface ($r = R$), which is largest at the poles ($\theta = 0, \pi$), and is zero at the equator ($\theta = \pi/2$).

Exercise 17.3
For this problem, (15.20) can be simplified to

$$0 = -\boldsymbol{\nabla}_\| \cdot \boldsymbol{j}_q^{\mathrm{s}} + \boldsymbol{n}\cdot\boldsymbol{j}_q^{\mathrm{II}} - \boldsymbol{n}\cdot\boldsymbol{j}_q^{\mathrm{I}}.$$

Using (6.4) and (15.11) we have

$$0 = \lambda^{\mathrm{s}}\boldsymbol{\nabla}_\| \cdot \boldsymbol{\nabla}_\| T^{\mathrm{s}} - \boldsymbol{n}\cdot\lambda^{\mathrm{II}}\boldsymbol{\nabla} T^{\mathrm{II}} + \boldsymbol{n}\cdot\lambda^{\mathrm{I}}\boldsymbol{\nabla} T^{\mathrm{I}},$$

where we have treated λ^{s} as constant. Now, since $\boldsymbol{n} = \boldsymbol{\delta}_r$, we have

$$\boldsymbol{\delta}_\| = \boldsymbol{\delta}_\theta\boldsymbol{\delta}_\theta + \boldsymbol{\delta}_\phi\boldsymbol{\delta}_\phi, \qquad \boldsymbol{\nabla}_\| = \boldsymbol{\delta}_\theta\frac{1}{R}\frac{\partial}{\partial\theta} + \frac{\boldsymbol{\delta}_\phi}{R\sin\theta}\frac{\partial}{\partial\phi},$$

and we can write this as

$$\lambda\frac{\partial T}{\partial r}(R,\theta) = \bar{\lambda}\frac{\partial\bar{T}}{\partial r}(R,\theta) - \frac{\lambda^{\mathrm{s}}}{R^2\sin\theta}\frac{\partial}{\partial\theta}\Big[\frac{\partial T^{\mathrm{s}}}{\partial\theta}(R,\theta)\sin\theta\Big].$$

Exercise 17.4
Using $\langle\boldsymbol{\nabla} T\rangle = |\boldsymbol{\nabla} T|_\infty\boldsymbol{\delta}_z$ in (17.15) and combining this with (17.14) we obtain

$$\langle\boldsymbol{j}_q\rangle = -\lambda\langle\boldsymbol{\nabla} T\rangle - \phi(\overline{\lambda} - \lambda)\frac{3}{2+\beta(1+2N_{\mathrm{Ka}})}\langle\boldsymbol{\nabla} T\rangle$$

$$= -\lambda\Big[1 + \phi\frac{3(\beta-1)}{2+\beta(1+2N_{\mathrm{Ka}})}\Big]\langle\boldsymbol{\nabla}T\rangle$$

which, when compared to (17.13), gives the expression in (17.16).

Exercise 17.5

Substitution of (17.19) in (17.21) gives

$$\begin{aligned}\frac{\partial p^{\mathrm{L}}}{\partial r} &= \frac{\eta}{r^2}\Big[\frac{\partial^2}{\partial r^2}\Big(\frac{1}{\sin\theta}\frac{\partial\psi}{\partial\theta}\Big) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\frac{1}{r^2\sin\theta}\frac{\partial\psi}{\partial\theta}\Big)\Big]\\ &= \frac{\eta}{r^2\sin\theta}\Big[\frac{\partial}{\partial\theta}\Big(\frac{\partial^2\psi}{\partial r^2}\Big) + \frac{\partial}{\partial\theta}\Big(\frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\frac{1}{\sin\theta}\frac{\partial\psi}{\partial\theta}\Big)\Big] = \frac{\eta}{r^2\sin\theta}\frac{\partial}{\partial\theta}E^2\psi\end{aligned}$$

where the last equality follows from (17.20). Similarly, substitution of (17.19) in (17.22) gives

$$\begin{aligned}\frac{\partial p^{\mathrm{L}}}{\partial\theta} &= -\frac{\eta}{r}\Big[\frac{\partial}{\partial r}\Big(r^2\frac{\partial}{\partial r}\frac{1}{r\sin\theta}\frac{\partial\psi}{\partial r}\Big) + \frac{\partial}{\partial\theta}\Big(\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}\frac{\partial\psi}{\partial r}\Big) - 2\frac{\partial}{\partial\theta}\Big(\frac{1}{r^2\sin\theta}\frac{\partial\psi}{\partial\theta}\Big)\Big]\\ &= -\frac{\eta}{\sin\theta}\Big[\frac{\partial}{\partial r}\Big(\frac{\partial^2\psi}{\partial r^2}\Big) + \frac{\partial}{\partial r}\Big(\frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\frac{1}{\sin\theta}\frac{\partial\psi}{\partial\theta}\Big)\Big] = -\frac{\eta}{\sin\theta}\frac{\partial}{\partial r}E^2\psi.\end{aligned}$$

Differentiation of $\partial p^{\mathrm{L}}/\partial r$ by θ and $\partial p^{\mathrm{L}}/\partial\theta$ by r and equating the two expressions gives

$$\frac{1}{r^2}\frac{\partial}{\partial\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}E^2\psi = -\frac{1}{\sin\theta}\frac{\partial^2}{\partial r^2}E^2\psi$$

which is easily rearranged to give (17.20).

Exercise 17.6

Substitution of $\boldsymbol{\pi} = p^{\mathrm{L}}\boldsymbol{\delta} + \boldsymbol{\tau}$ and $\boldsymbol{n} = \boldsymbol{\delta}_r$ in the expression for the force on the sphere gives

$$\begin{aligned}\boldsymbol{\mathcal{F}}_{\mathrm{s}} &= -\int_0^{2\pi}\int_0^{\pi}\Big([p^{\mathrm{L}}(R)+\tau_{rr}(R)]\boldsymbol{\delta}_r + \tau_{r\theta}(R)\boldsymbol{\delta}_\theta + \tau_{r\phi}(R)\boldsymbol{\delta}_\phi\Big)R^2\sin\theta d\theta d\phi\\ &= -2\pi R^2\int_0^{\pi}\Big([p^{\mathrm{L}}(R)+\tau_{rr}(R)]\cos\theta + \tau_{r\theta}(R)\sin\theta\Big)\sin\theta d\theta\ \boldsymbol{\delta}_3,\end{aligned}$$

where we changed base vectors from spherical to rectangular coordinate systems in the second line. Now, using $\boldsymbol{\tau} = -\eta\left[\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T\right]$ and the expressions in (17.30) and (17.31), we obtain

$$\tau_{rr}(R) = -6\frac{\eta V}{R}\frac{\Lambda_\xi}{1+3\Lambda_\xi}\cos\theta, \qquad \tau_{r\theta}(R) = \frac{3}{2}\frac{\eta V}{R}\frac{1}{1+3\Lambda_\xi}\sin\theta,$$

which, when substituted with (17.32) in the last result above, gives

$$\boldsymbol{\mathcal{F}}_{\mathrm{s}} = \frac{3\pi R\eta V}{1+3\Lambda_\xi}\int_0^{\pi}\Big([1+6\Lambda_\xi]\cos^2\theta + \sin^2\theta\Big)\sin\theta d\theta\ \boldsymbol{\delta}_3$$

$$= 6\pi R\eta V \frac{1+2\Lambda_\xi}{1+3\Lambda_\xi}\boldsymbol{\delta}_3,$$

which is the desired expression. Since $\boldsymbol{V} = V\boldsymbol{\delta}_3$, the above result is independent of coordinate system.

For a sphere moving with constant velocity through a fluid that is otherwise at rest, we have $\boldsymbol{v}(R) = \boldsymbol{v}_\mathrm{b}$ (here we assume no slip) and $\boldsymbol{v}(\infty) = \boldsymbol{0}$. In a coordinate system that moves with the sphere, we use (11.23) with $Q_{ij} = \delta_{ij}$ and write

$$\boldsymbol{v}' = \boldsymbol{v} + \frac{d\boldsymbol{c}}{dt} = \boldsymbol{v} - \boldsymbol{v}_\mathrm{b}.$$

Hence, the boundary conditions become $\boldsymbol{v}'(R) = \boldsymbol{0}$ and $\boldsymbol{v}'(\infty) = -\boldsymbol{v}_\mathrm{b}$. For steady creeping flow of an incompressible fluid, we can write (11.3) as

$$\boldsymbol{\nabla}' p^{\mathrm{L}'} = \eta\nabla'^2\boldsymbol{v}' + \rho'\Big[\frac{d^2\boldsymbol{c}}{dt^2} - \frac{d\boldsymbol{\omega}}{dt}\times\boldsymbol{r}' - 2\boldsymbol{\omega}\times\boldsymbol{v}' - \boldsymbol{\omega}\times(\boldsymbol{\omega}\times\boldsymbol{r}')\Big]$$

where gravity has also been neglected. Now, since $\boldsymbol{v}_\mathrm{b}$ is constant $d^2\boldsymbol{c}/dt^2 = \boldsymbol{0}$. and since $\boldsymbol{\omega} = \boldsymbol{0}$, all the terms in the square brackets vanish. Hence, we recover (17.18), and the expression for $\boldsymbol{\mathcal{F}}_\mathbf{s}$ holds for this case if $\boldsymbol{V} \to -\boldsymbol{v}_\mathrm{b}$.

Exercise 17.7

We have a sphere moving with constant velocity $\boldsymbol{v}_\mathrm{b} = v_\mathrm{b}\boldsymbol{\delta}_3$ through a quiescent fluid. First, we modify (17.21) and (17.22) by including the gravitational force $\rho\boldsymbol{g}$. Since $\boldsymbol{g} = -g\boldsymbol{\delta}_3$, we can write $\boldsymbol{g} = -g\cos\theta\boldsymbol{\delta}_r + g\sin\theta\boldsymbol{\delta}_\theta$. The gravitational contribution to the pressure can added to (17.32), which gives

$$p^\mathrm{L}(r,\theta) = \frac{3}{2}\frac{\eta v_\mathrm{b}}{R}\frac{1+2\Lambda_\xi}{1+3\Lambda_\xi}\Big(\frac{R}{r}\Big)^2\cos\theta - \rho g r\cos\theta$$

When this is substituted in the expression for $\boldsymbol{\mathcal{F}}_\mathrm{s}$ in Exercise 17.6, the following is obtained

$$\boldsymbol{\mathcal{F}}_\mathrm{s} = -6\pi R\eta v_\mathrm{b}\frac{1+2\Lambda_\xi}{1+3\Lambda_\xi}\boldsymbol{\delta}_3 + \frac{4}{3}\pi R^3\rho g\boldsymbol{\delta}_3,$$

where the negative sign in front of the first term reflects the fact that the sphere is moving through a quiescent fluid. The second term is the buoyant force, which is in the direction opposite the gravitational force. For a sphere moving with constant velocity, the sum of the gravitational force on the sphere and the force of the fluid on the sphere must vanish

$$-\frac{4}{3}\pi R^3\bar{\rho}g\boldsymbol{\delta}_3 - 6\pi R\eta v_\mathrm{b}\frac{1+2\Lambda_\xi}{1+3\Lambda_\xi}\boldsymbol{\delta}_3 + \frac{4}{3}\pi R^3\rho g\boldsymbol{\delta}_3 = \boldsymbol{0}$$

where $\bar{\rho}$ is the density of the sphere, or

$$\frac{4}{3}\pi R^3(\rho - \bar{\rho})g = 6\pi R\eta v_{\rm b}\frac{1+2\Lambda_\xi}{1+3\Lambda_\xi}.$$

This leads to the desired expression for the terminal velocity $v_{\rm b}$.

Exercise 17.8

For rewriting the pressure, we only need the elementary formula $\boldsymbol{r}\cdot\boldsymbol{V} = rV\cos\theta$. For rewriting the velocity field, we further need to realize that the r-component of $\boldsymbol{V}$ is $V\cos\theta$, whereas the θ-component of $\boldsymbol{V}$ is $-V\sin\theta$.

For a direct verification of the solution, the basic working horse is

$$\frac{\partial r}{\partial x_i} = \frac{\partial}{\partial x_i}\sqrt{x_1^2+x_2^2+x_3^2} = \frac{1}{2\sqrt{x_1^2+x_2^2+x_3^2}}\,2x_i = \frac{x_i}{r},$$

which implies

$$\frac{\partial r^n}{\partial x_i} = nr^{n-1}\frac{\partial r}{\partial x_i} = nr^{n-2}x_i$$

and

$$\nabla^2 r^n = \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_i}r^n = \frac{\partial}{\partial x_i}nr^{n-2}x_i = n(n-2)r^{n-4}r^2 + nr^{n-2}3 = n(n+1)r^{n-2}.$$

If we write the velocity field in the component notation

$$v_i = \left(1 - \frac{3}{4}\frac{R}{r} - \frac{1}{4}\frac{R^3}{r^3}\right)V_i - \frac{3}{4}\left(\frac{R}{r^3} - \frac{R^3}{r^5}\right)x_i x_j V_j,$$

we find

$$\begin{aligned}\frac{\partial v_i}{\partial x_i} &= \left(\frac{3}{4}\frac{R}{r^3} + \frac{3}{4}\frac{R^3}{r^5}\right)x_i V_i + \frac{3}{4}\left(3\frac{R}{r^5} - 5\frac{R^3}{r^7}\right)r^2 x_j V_j - \frac{3}{4}\left(\frac{R}{r^3} - \frac{R^3}{r^5}\right)4x_j V_j \\ &= 0,\end{aligned}$$

so that the velocity field is indeed divergence free. For $r = R$, the velocity field clearly vanishes. We further get the Stokes equation,

$$\begin{aligned}\nabla^2 v_i = &-\frac{3}{2}\frac{R^3}{r^5}V_i - \frac{3}{4}\left(6\frac{R}{r^5} - 20\frac{R^3}{r^7}\right)x_i x_j V_j - \frac{3}{4}\left(\frac{R}{r^3} - \frac{R^3}{r^5}\right)2V_i \\ &+\frac{3}{2}\left(3\frac{R}{r^5} - 5\frac{R^3}{r^7}\right)x_k\frac{\partial}{\partial x_k}(x_i x_j V_j) \\ = &-\frac{3}{2}\frac{R}{r^3}V_i + \frac{9}{2}\frac{R}{r^5}x_i x_j V_j = \frac{\partial}{\partial x_i}\left(-\frac{3}{2}\frac{R}{r^3}x_j V_j\right) = \frac{1}{\eta}\frac{\partial p^{\rm L}}{\partial x_i}.\end{aligned}$$

Exercise 17.9

The stationary spherical gas-liquid interface at $r = R$ has unit normal $\boldsymbol{n} = \boldsymbol{\delta}_r$ so that $\boldsymbol{v}^{\mathrm{s}} = \boldsymbol{v}_{\|} = v_\theta^{\mathrm{s}}\boldsymbol{\delta}_\theta$. There is no mass transfer so that from (14.7) we have

$$v_r(R,\theta) = v_r^{\mathrm{s}}(\theta) = 0.$$

Assuming no-slip, we have from (15.18)

$$v_\theta(R,\theta) = v_\theta^{\mathrm{s}}(\theta).$$

In the absence of mass transfer and setting $\boldsymbol{\tau}^{\mathrm{s}} = \boldsymbol{0}$, we write (15.21) as

$$\tau_{rr}^{\mathrm{I}}\boldsymbol{\delta}_r + \tau_{r\theta}^{\mathrm{I}}\boldsymbol{\delta}_\theta + p^{\mathrm{I}}\boldsymbol{\delta}_r = p^{\mathrm{II}}\boldsymbol{\delta}_r - \gamma(\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{n})\boldsymbol{\delta}_r + \boldsymbol{\nabla}_{\|}\gamma$$

where we have treated the gas (II) as an inviscid fluid ($\boldsymbol{\tau}^{\mathrm{II}} = \boldsymbol{0}$). Now, since $\boldsymbol{n} = \boldsymbol{\delta}_r$, we have

$$\boldsymbol{\delta}_{\|} = \boldsymbol{\delta}_\theta\boldsymbol{\delta}_\theta + \boldsymbol{\delta}_\phi\boldsymbol{\delta}_\phi, \qquad \boldsymbol{\nabla}_{\|} = \boldsymbol{\delta}_\theta\frac{1}{R}\frac{\partial}{\partial\theta} + \frac{\boldsymbol{\delta}_\phi}{R\sin\theta}\frac{\partial}{\partial\phi}.$$

The r-component of the jump balance for momentum becomes

$$p(R,\theta) = \bar{p}(R,\theta) - \gamma\frac{2}{R},$$

where we have used $\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{n} = 2/R$. The θ-component of the jump balance for momentum can be written as

$$\eta\left[\frac{\partial v_\theta}{\partial r}(R,\theta) - \frac{v_\theta(R,\theta)}{R}\right] = -\frac{1}{R}\frac{d\gamma}{d\theta} = -\frac{\gamma_T}{R}\frac{\partial T}{\partial\theta}(R,\theta),$$

where the second equality follows using $\gamma_T = d\gamma/dT^{\mathrm{s}}$. For the case of no mass transfer and no-slip, (15.20) can be simplified to

$$-T^{\mathrm{s}}\frac{d^2\gamma}{dT^{\mathrm{s}2}}\boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}}\cdot\boldsymbol{\nabla}_{\|}T^{\mathrm{s}} = T^{\mathrm{s}}\frac{d\gamma}{dT^{\mathrm{s}}}\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}^{\mathrm{s}} - \boldsymbol{n}\cdot\boldsymbol{j}_q^{\mathrm{I}},$$

where we have used $\boldsymbol{j}_q^{\mathrm{s}} = \boldsymbol{0}$ and treated the gas as an insulator ($\boldsymbol{j}_q^{\mathrm{II}} = \boldsymbol{0}$). Since γ_T is constant, the left-hand side vanishes, so that using (6.4) we have

$$0 = T^{\mathrm{s}}\frac{d\gamma}{dT^{\mathrm{s}}}\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}^{\mathrm{s}} + \boldsymbol{n}\cdot\lambda^{\mathrm{I}}\boldsymbol{\nabla}T^{\mathrm{I}}.$$

Now, since $\boldsymbol{v}^{\mathrm{s}} = v_\theta^{\mathrm{s}}(\theta)\boldsymbol{\delta}_\theta$, we can write this as

$$0 = \frac{\gamma_T T^{\mathrm{s}}}{R\sin\theta}\frac{\partial}{\partial\theta}[v_\theta^{\mathrm{s}}\sin\theta] + \lambda\frac{\partial T}{\partial r}(R,\theta),$$

which, using $v_\theta^{\mathrm{s}}(\theta) = v_\theta(R,\theta)$ and $T^{\mathrm{s}}(\theta) = T(R,\theta)$, gives the desired result.

Exercise 17.10

For large r, the terms in (17.37) decay as $1/r^2$ and $1/r^4$. For $r = R$, the terms with prefactors $5/2$ cancel each other and the only remaining term is $-\kappa_{ij}^{(0)} x_j$. For the further calculations, the representation (17.39) of the velocity field is more convenient, which has been verified in Exercise 17.11. We get

$$\frac{\partial v_i}{\partial x_i} = \frac{1}{6} R^4 \left(\kappa_{ik}^{(0)} \frac{\partial^4}{\partial x_i \partial x_j \partial x_j \partial x_k} - \kappa_{jk}^{(0)} \frac{\partial^4}{\partial x_i \partial x_i \partial x_j \partial x_k} \right) \left(5 \frac{r}{R} + \frac{R}{r} \right) = 0,$$

so that the velocity field is indeed divergence free. With the differentiation rules given in the solution to Exercise 17.8 and the results in the solution to Exercise 17.11, we further obtain

$$\begin{aligned}
\nabla^2 v_i &= \frac{1}{6} R^4 \left(\kappa_{ik}^{(0)} \frac{\partial^2}{\partial x_j \partial x_j} - \kappa_{jk}^{(0)} \frac{\partial^2}{\partial x_i \partial x_j} \right) \frac{\partial}{\partial x_k} \frac{10}{rR} \\
&= \frac{5}{3} R^3 \left(-6 \kappa_{ij}^{(0)} \frac{x_j}{r^5} + 15 \kappa_{jk}^{(0)} \frac{x_i x_j x_k}{r^7} \right) \\
&= \frac{\partial}{\partial x_i} \left(-5 R^3 \, \kappa_{jk}^{(0)} \frac{x_j x_k}{r^5} \right) = \frac{1}{\eta} \frac{\partial p^{\mathrm{L}}}{\partial x_i},
\end{aligned}$$

which means that we have verified that the proposed velocity field solves the Stokes equation.

Exercise 17.11

With the differentiation rules given in the solution to Exercise 17.8 we get

$$\begin{aligned}
\tfrac{\partial}{\partial x_i} \tfrac{\partial}{\partial x_j} \tfrac{\partial}{\partial x_k} r^n = \tfrac{\partial}{\partial x_i} \tfrac{\partial}{\partial x_j} n r^{n-2} x_k = n \tfrac{\partial}{\partial x_i} \left[r^{n-2} \delta_{jk} + (n-2) r^{n-4} x_j x_k \right] = \\
n(n-2) r^{n-4} (x_i \delta_{jk} + x_j \delta_{ik} + x_k \delta_{ij}) + n(n-2)(n-4) r^{n-6} x_i x_j x_k,
\end{aligned}$$

which leads to

$$\begin{aligned}
&\left(\kappa_{ik}^{(0)} \frac{\partial^3}{\partial x_j \partial x_j \partial x_k} - \kappa_{jk}^{(0)} \frac{\partial^3}{\partial x_i \partial x_j \partial x_k} \right) r^n = \\
&\quad 3n(n-2) r^{n-4} \, \kappa_{ij}^{(0)} x_j + n(n-2)(n-4) r^{n-6} (r^2 \kappa_{ij}^{(0)} x_j - x_i x_j \kappa_{jk}^{(0)} x_k) = \\
&\quad n(n-1)(n-2) r^{n-4} \, \kappa_{ij}^{(0)} x_j - n(n-2)(n-4) r^{n-6} \, \kappa_{jk}^{(0)} x_i x_j x_k .
\end{aligned}$$

The corresponding results for $n = 1$ and $n = -1$ are

$$-3 \kappa_{jk}^{(0)} \frac{x_i x_j x_k}{r^5} \qquad \text{and} \qquad -6 \kappa_{ij}^{(0)} \frac{x_j}{r^5} + 15 \kappa_{jk}^{(0)} \frac{x_i x_j x_k}{r^7},$$

respectively. By multiplying these results with $(5/6)R^3$ and $(1/6)R^5$, respectively, and adding them, we recover (17.37).

Exercise 17.12

We first calculate the viscous stress associated with the asymptotic form of the velocity perturbation (17.37) given by the first term,

$$\tau_{il}^{(1)} = 5\eta \frac{R^3}{r^3} \left[n_i n_j \kappa_{jl}^{(0)} + \kappa_{ij}^{(0)} n_j n_l + (\delta_{il} - 5 n_i n_l) n_j \kappa_{jk}^{(0)} n_k \right] .$$

The integrals in (17.36) consist of the following three contributions:

$$- \int_{A_{\text{eff}}} v_i^{(1)} \pi_{il}^{(0)} n_l \, dA = -5\eta \kappa_{il}^{(0)} \kappa_{jk}^{(0)} R^3 \int_{A_{\text{eff}}} n_i n_j n_k n_l \, \frac{dA}{r^2} ,$$

$$- \int_{A_{\text{eff}}} v_i^{(0)} p^{\mathrm{L}(1)} n_i \, dA = 5\eta \kappa_{ij}^{(0)} \kappa_{kl}^{(0)} R^3 \int_{A_{\text{eff}}} n_i n_j n_k n_l \, \frac{dA}{r^2} ,$$

and

$$- \int_{A_{\text{eff}}} v_i^{(0)} \tau_{il}^{(1)} n_l \, dA = 5\eta R^3 \int_{A_{\text{eff}}} \left(3 \kappa_{ij}^{(0)} \kappa_{kl}^{(0)} n_i n_j n_k n_l - \kappa_{ij}^{(0)} \kappa_{ik}^{(0)} n_j n_k \right) \frac{dA}{r^2} .$$

The first two contributions cancel. To evaluate the third contribution, we consider the average

$$\int_{A_{\text{eff}}} n_j n_k \, \frac{dA}{r^2} = 4\pi \, \frac{1}{3} \, \delta_{jk} .$$

The 4π results from the surface of the sphere, the δ_{jk} arises for symmetry reasons, and the $1/3$ is required to reproduce the correct trace. We similarly obtain

$$\int_{A_{\text{eff}}} n_i n_j n_k n_l \, \frac{dA}{r^2} = 4\pi \, \frac{1}{15} \left(\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \right) .$$

By combining all these results, we indeed realize that (17.40) follows from (17.36),

$$\dot{W} = 2\eta \kappa_{ij}^{(0)} \kappa_{ij}^{(0)} \, V_{\text{eff}} + \eta \kappa_{ij}^{(0)} \kappa_{ij}^{(0)} \, \frac{4}{3} \pi R^3 .$$

Exercise 17.13

We assume that, after a proper choice of the z-axis, the Cartesian coordinates of $\boldsymbol{x}$ and $\boldsymbol{x}'$ are given by $(0, 0, r)$ and $(r' \sin\theta \, \cos\phi, r' \sin\theta \, \sin\phi, r' \cos\theta)$, respectively. We then have

$$|\boldsymbol{x} - \boldsymbol{x}'| = \sqrt{r'^2 + r^2 - 2 r r' \xi},$$

where we have introduced $\xi = \cos\theta$. We hence have

$$\int_{V_{\text{eff}}} |\boldsymbol{x} - \boldsymbol{x}'|^Z = 2\pi \int_0^{R_{\text{eff}}} dr' \int_{-1}^{1} d\xi \, r'^2 (r'^2 + r^2 - 2 r r' \xi)^{Z/2}.$$

The integration over ξ could be performed easily. The remaining integration over r', however, would require some help from tables of integrals. We hence leave the entire integration to Mathematica®:

```
f[Z_,rp_,xi_]:=2*Pi*rp^2*(rp^2+r^2-2*r*rp*xi)^(Z/2)
I1=Integrate[f[1,rp,xi],{rp,0,Reff},{xi,-1,1},
      Assumptions->Reff>r && r>0];
I2=Integrate[f[-1,rp,xi],{rp,0,Reff},{xi,-1,1},
      Assumptions->Reff>r && r>0];
Simplify[(5*I1/R+R*I2)/(4*Pi*R^3/3)]
```

Exercise 18.1

The jump balance for solute mass (14.25) takes the form

$$\rho_1(R)\left[v(R) - \frac{dR}{dt}\right] + j_1(R) = \bar{\rho}_1(R)\left[\bar{v}(R) - \frac{dR}{dt}\right] + \bar{j}_1(R).$$

Since the bubble is treated as a single-component (solvent), $\bar{\rho}_1 \approx \bar{\rho}$ and $\bar{j}_1 \approx 0$. Hence, we can write

$$\rho_1(R)\left[v(R) - \frac{dR}{dt}\right] + j_1(R) = \bar{\rho}(R)\left[\bar{v}(R) - \frac{dR}{dt}\right],$$

or

$$\rho_0[w_1(R) - 1]\left[v(R) - \frac{dR}{dt}\right] = -j_1(R) = \rho_0 D\frac{\partial w_1}{\partial r}(R),$$

where we have used (18.8) and $\rho_1(R) = \rho_0 w_1(R)$, and the second equality follows from (6.24). Using (18.9) and rearranging terms gives (18.12).

Exercise 18.2

In the absence of mass transport, the right-hand side of (18.12) vanishes so that from (18.3) and (18.9) we have

$$v = \frac{R^2}{r^2}\frac{dR}{dt}.$$

Substitution in (18.2) gives,

$$\rho_0\Big[\Big(\frac{R}{r}\Big)^2\frac{d^2R}{dt^2} + 2\Big(\frac{R}{r^2}\Big)\Big(\frac{dR}{dt}\Big)^2 - 2\Big(\frac{R^4}{r^5}\Big)\Big(\frac{dR}{dt}\Big)^2\Big] = -\frac{\partial p}{\partial r}.$$

Integration over r leads to

$$\rho_0\Big[R\frac{d^2R}{dt^2} + \frac{3}{2}\Big(\frac{dR}{dt}\Big)^2\Big] = p(R) - p(\infty).$$

Now, using (18.10) to eliminate $p(R)$, we obtain

$$\rho_0\Big[R\frac{d^2R}{dt^2}+\frac{3}{2}\Big(\frac{dR}{dt}\Big)^2\Big]=\bar{p}-\eta\frac{4}{R}\frac{dR}{dt}-\gamma\frac{2}{R}-p(\infty),$$

which gives (18.13).

Exercise 18.3

For the isothermal case, $T=\bar{T}=T^{\mathrm{s}}=T_0$. From (15.27), we have

$$\begin{aligned}\hat{\mu}_\alpha(R)-\hat{\mu}(R)-[\hat{\mu}^{\mathrm{s}}_\alpha-\hat{\mu}^{\mathrm{s}}]=&\\ &-T_0R^{\mathrm{Is}}_{\alpha 1}\left\{\left[\rho_1(R)-\frac{1}{2}\rho(R)\right]\left(v(R)-\frac{dR}{dt}\right)+j_1(R)\right\}\\ &-T_0R^{\mathrm{Is}}_{\alpha 2}\left\{\left[\rho_2(R)-\frac{1}{2}\rho(R)\right]\left(v(R)-\frac{dR}{dt}\right)+j_2(R)\right\}\\ &=-2T_0R^{\mathrm{Is}}_{\alpha 1}\left\{\frac{1}{2}\left[\rho_1(R)-\rho_2(R)\right]\left(v(R)-\frac{dR}{dt}\right)+j_1(R)\right\},\end{aligned}$$

where we have used $R^{\mathrm{Is}}_{\alpha 2}=-R^{\mathrm{Is}}_{\alpha 1}$. Setting $\alpha=1$, we obtain

$$\begin{aligned}\hat{\mu}_1(R)-\hat{\mu}^{\mathrm{s}}_1-[\hat{\mu}_2(R)-\hat{\mu}^{\mathrm{s}}_2]=&\\ &-2T_0R^{\mathrm{Is}}_{11}\left\{\left[\rho_1(R)-\rho_2(R)\right]\left(v(R)-\frac{dR}{dt}\right)+2j_1(R)\right\}\\ &=-R^{\mathrm{s}}\rho_0\left\{[2w_1(R)-1]\left(v(R)-\frac{dR}{dt}\right)-2D\frac{\partial w_1}{\partial r}(R)\right\}\end{aligned}$$

where $R^{\mathrm{s}}=2T_0R^{\mathrm{Is}}_{11}$. Similarly, setting $\alpha=2$, we obtain

$$\begin{aligned}\hat{\mu}_2(R)-\hat{\mu}^{\mathrm{s}}_2-[\hat{\mu}_1(R)-\hat{\mu}^{\mathrm{s}}_1]=&\\ &-2T_0R^{\mathrm{Is}}_{21}\left\{\left[\rho_1(R)-\rho_2(R)\right]\left(v(R)-\frac{dR}{dt}\right)+2j_1(R)\right\}\\ &=R^{\mathrm{s}}\rho_0\left\{[2w_1(R)-1]\left(v(R)-\frac{dR}{dt}\right)-2D\frac{\partial w_1}{\partial r}(R)\right\}\end{aligned}$$

where the second equality follows since $R^{\mathrm{Is}}_{21}=R^{\mathrm{Is}}_{12}=-R^{\mathrm{Is}}_{11}$. Hence, one constitutive equation is obtained for a two-component system. Now, from (15.28), we have

$$\begin{aligned}\bar{\hat{\mu}}_\alpha(R)-\bar{\hat{\mu}}(R)-[\hat{\mu}^{\mathrm{s}}_\alpha-\hat{\mu}^{\mathrm{s}}]=&\\ &-T_0R^{\mathrm{IIs}}_{\alpha 1}\left\{\left[\bar{\rho}_1(R)-\frac{1}{2}\bar{\rho}(R)\right]\left(\bar{v}(R)-\frac{dR}{dt}\right)+\bar{j}_1(R)\right\}\\ &-T_0R^{\mathrm{IIs}}_{\alpha 2}\left\{\left[\bar{\rho}_2(R)-\frac{1}{2}\bar{\rho}(R)\right]\left(\bar{v}(R)-\frac{dR}{dt}\right)+\bar{j}_2(R)\right\}\end{aligned}$$

$$= 2T_0 R^{\mathrm{IIs}}_{\alpha 1}\frac{1}{2}\bar{\rho}\left(\bar{v}(R) - \frac{dR}{dt}\right)$$

where the second equality follows since $\bar{\rho}_1 \approx \bar{\rho}$, $\bar{\rho}_2 \approx 0$ and $\bar{j}_1 \approx 0$. Setting $\alpha = 1$ and using (18.8), we obtain

$$\bar{\hat{\mu}}_1(R) - \hat{\mu}^{\mathrm{s}}_1 - [\bar{\hat{\mu}}_2(R) - \hat{\mu}^{\mathrm{s}}_2] = \bar{R}^{\mathrm{s}}\rho_0\left(v(R) - \frac{dR}{dt}\right),$$

where $\bar{R}^{\mathrm{s}} = 2T_0 R^{\mathrm{IIs}}_{11}$, and this is the expression in (18.15). Since solvent is not transferred to or from the interface, we can set $\hat{\mu}_2(R) = \hat{\mu}^{\mathrm{s}}_2 = \bar{\hat{\mu}}_2(R)$ in (18.14) and (18.15). Using (18.9) and (18.12), we obtain (18.16) and (18.17).

Exercise 18.4

Setting $\epsilon = 1$ in (18.25) and rescaling time as $\bar{t} = N_w t$, we obtain

$$N_w\frac{\partial w_1}{\partial \bar{t}} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial w_1}{\partial r}\right)$$

$$\frac{dR}{d\bar{t}} = -\frac{\partial w_1}{\partial r}(R, \bar{t}).$$

For the case $|N_w| \ll 1$, we neglect the left-hand side of the first equation and integrate twice, which gives

$$w_1 = -\frac{f_1(t)}{r} + f_2(\bar{t}).$$

Applying the boundary conditions in (18.26), we obtain

$$w_1 = \frac{R}{r}.$$

Substitution in the second equation gives

$$\frac{dR}{d\bar{t}} = \frac{1}{R},$$

which, when integrated subject to (18.28) gives

$$R^2 = 1 + 2\bar{t},$$

which is the desired result.

Exercise 18.5

For a single-component fluid, the temperature equation (7.6) can be written as

$$\frac{\partial T}{\partial t} + \frac{f}{r^2}\frac{\partial T}{\partial r} = \frac{\chi}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right),$$

where we have used (18.3) and neglected viscous heating. The jump balance for total mass (14.17) can be written as

$$\rho_0 \left[v(R) - \frac{dR}{dt} \right] = \bar{\rho} \left[\bar{v}(R) - \frac{dR}{dt} \right].$$

For diffusion-controlled growth (collapse), the pressure within the particle is constant $\bar{p} = p_0$ and the density $\bar{\rho} = \bar{\rho}_0$, so that (18.9) becomes

$$\frac{f}{R^2} = v(R) = (1 - \epsilon)\frac{dR}{dt},$$

where $\epsilon = \bar{\rho}_0/\rho_0$. Combining these, we obtain

$$\frac{\partial T}{\partial t} + (1 - \epsilon)\frac{dR}{dt}\left(\frac{R}{r}\right)^2 \frac{\partial T}{\partial r} = \frac{\chi}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial T}{\partial r} \right),$$

which can be written in the desired dimensionless form using R_0 and $\tau = R_0^2/\chi$ to normalize radial position and time, respectively.

The jump balance for energy (14.26), neglecting mechanical energy effects interface (see Exercise 14.7), can be written as

$$\rho_0 \Big[v(R) - \frac{dR}{dt} \Big] \hat{h}(T_{\text{eq}}) - \lambda \frac{\partial T}{\partial r}(R) = \bar{\rho}_0 \Big[\bar{v}(R) - \frac{dR}{dt} \Big] \bar{\hat{h}}(T_{\text{eq}}),$$

which can be rearranged to give

$$\rho_0 \Big[v(R) - \frac{dR}{dt} \Big] \Delta\hat{h}_{\text{eq}} = -\rho_0 \Delta\hat{h}_{\text{eq}} \epsilon \frac{dR}{dt} = -\lambda \frac{\partial T}{\partial r}(R),$$

where $\Delta\hat{h}_{\text{eq}} = \bar{\hat{h}}(T_{\text{eq}}) - \hat{h}(T_{\text{eq}})$. Normalizing temperature, relative to T_0, by $T_{\text{eq}} - T_0$ leads to the desired equation, which involves the dimensionless parameter $N_{\text{St}} = \hat{c}_p(T_0 - T_{\text{eq}})/(\epsilon\Delta\hat{h}_{\text{eq}})$.

Exercise 18.6

From the problem statement, it is clear that the temperature within the solid is $\bar{T} = T_{\text{eq}}$. As in Exercise 18.5, we write the temperature equation for the liquid shell as

$$\frac{\partial T}{\partial t} + \frac{f}{r^2}\frac{\partial T}{\partial r} = \frac{\chi}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial T}{\partial r} \right).$$

The jump balance for total mass (14.17) can be written as

$$\rho \left[v(R) - \frac{dR}{dt} \right] = \bar{\rho} \left[\bar{v}(R) - \frac{dR}{dt} \right].$$

Since $\bar{v}(R) = 0$ and $\rho = \bar{\rho}$, we have $v(R) = 0$. Also, from (18.3) and (18.9), we find $f = 0$. The jump balance for energy (14.26) can be written as

$$\rho\frac{dR}{dt}\hat{h} + \lambda\frac{\partial T}{\partial r}(R) = \bar{\rho}\frac{dR}{dt}\bar{\hat{h}} + \bar{\lambda}\frac{\partial \bar{T}}{\partial r}(R),$$

which, since $\bar{T}$ is uniform, can be rearranged to give

$$\rho(\hat{h} - \bar{\hat{h}})\frac{dR}{dt} = -\lambda\frac{\partial T}{\partial r}(R),$$

Using R_0 and $\tau = R_0^2/\chi$ to normalize radial position and time, respectively, and normalizing temperature relative to T_{g} by $T_{\mathrm{eq}} - T_{\mathrm{g}}$, we have

$$\frac{\partial T}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right),$$

$$T(R,t) = 1, \qquad \frac{\partial T}{\partial r}(1,t) + N_{\mathrm{Bi}}T(1,t) = 0,$$

$$\frac{dR}{dt} = N_{\mathrm{St}}\frac{\partial T}{\partial r}(R,t), \qquad R(0) = 1,$$

where $N_{\mathrm{Bi}} = hR_0/\lambda$ and $N_{\mathrm{St}} = \hat{c}_p(T_{\mathrm{g}} - T_{\mathrm{eq}})/(\hat{h} - \bar{\hat{h}})$. Using the quasi-steady state approximation for $N_{\mathrm{St}} \ll 1$, must solve

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) = 0.$$

Integrating twice and applying the boundary conditions gives

$$T = \frac{1 + N_{\mathrm{Bi}}(1/r - 1)}{1 + N_{\mathrm{Bi}}(1/R - 1)}.$$

Substitution in the evolution equation for R gives

$$\frac{dR}{dt} = \frac{N_{\mathrm{Bi}}N_{\mathrm{St}}}{(1 - N_{\mathrm{Bi}})R^2 + N_{\mathrm{Bi}}R},$$

which, when integrated subject to the initial condition, gives the desired result. Setting $R(t_{\mathrm{melt}}) = 0$, we obtain

$$t_{\mathrm{melt}} = \frac{1 + 2/N_{\mathrm{Bi}}}{6N_{\mathrm{St}}}.$$

Exercise 18.7

The given change of variables $x = r/R$ and $w_1 = u/x$ lead to

$$\left(\frac{\partial w_1}{\partial r}\right)_t = \frac{1}{R}\left[\frac{1}{x}\left(\frac{\partial u}{\partial x}\right)_t - \frac{u}{x^2}\right]$$

$$\left(\frac{\partial w_1}{\partial t}\right)_r = \frac{1}{x}\Big[\left(\frac{\partial u}{\partial t}\right)_x - \frac{x}{R}\frac{dR}{dt}\left(\frac{\partial u}{\partial x}\right)_t + \frac{u}{R}\frac{dR}{dt}\Big].$$

Substitution in (18.25) gives

$$R^2\frac{\partial u}{\partial t} + R\frac{dR}{dt}\Big[u - x\frac{\partial u}{\partial x} + (1-\epsilon)\Big(\frac{1}{x^2}\frac{\partial u}{\partial x} - \frac{u}{x^3}\Big)\Big] = \frac{\partial^2 u}{\partial x^2}.$$

The initial and boundary conditions in (18.26) become

$$u(x,0) = 0, \qquad u(\infty,t) = 0, \qquad u(1,t) = 1.$$

Similarly, substitution in (18.27) gives

$$R\frac{dR}{dt} = -N_w\Big[\frac{\partial u}{\partial x}(1,t) - 1\Big].$$

which can be integrated subject to (18.28) to give

$$R^2 = 1 + 2N_w t - 2N_w\int_0^t \frac{\partial u}{\partial x}(1,t')dt'.$$

Combining the above results, we obtain

$$\Big[1 + 2N_w t - 2N_w\int_0^t \frac{\partial u}{\partial x}(1,t')dt'\Big]\frac{\partial u}{\partial t}$$
$$- N_w\Big[\frac{\partial u}{\partial x}(1,t) - 1\Big]\Big[u - x\frac{\partial u}{\partial x} + (1-\epsilon)\Big(\frac{1}{x^2}\frac{\partial u}{\partial x} - \frac{u}{x^3}\Big)\Big] = \frac{\partial^2 u}{\partial x^2}.$$

Using the perturbation expansion $u = u^{(0)} + N_w u^{(1)} + ...$, we obtain

$$\frac{\partial u^{(0)}}{\partial t} = \frac{\partial^2 u^{(0)}}{\partial x^2}.$$

which is solved subject to

$$u^{(0)}(x,0) = 0, \qquad u^{(0)}(\infty,t) = 0, \qquad u^{(0)}(1,t) = 1,$$

giving (see Exercise 7.11)

$$u^{(0)}(x,t) = 1 - \operatorname{erf}\Big(\frac{x-1}{2\sqrt{t}}\Big).$$

Substitution in the expression for R^2 gives (18.29).

Exercise 18.8

The similarity transformation $\xi = r/\sqrt{4t}$ leads to

$$\frac{\partial w_1}{\partial t} = -\frac{\xi}{2t}\frac{du}{d\xi}, \qquad \frac{\partial w_1}{\partial r} = \frac{1}{\sqrt{4t}}\frac{du}{d\xi},$$

and further suggests

$$R = 2\beta\sqrt{t},$$

where β is a constant to be determined. Transforming (18.25) we obtain

$$\frac{d^2 w_1}{d\xi^2} + 2\Big[\frac{1}{\xi} + \xi - (1-\epsilon)\frac{\beta^2}{\xi^2}\Big]\frac{dw_1}{d\xi} = 0,$$

and (18.26) gives

$$w_1(\infty) = 0, \qquad w_1(\beta) = 1.$$

Similarly, transforming (18.27), we obtain

$$\frac{dw_1}{d\xi}(\beta) = -2\frac{\beta}{N_w}.$$

Setting $Y = dw_1/d\xi$ we have

$$\frac{dY}{d\xi} + \Big[\frac{1}{\xi} + \xi - (1-\epsilon)\frac{\beta^2}{\xi^2}\Big]Y = 0.$$

Integration gives

$$Y = \frac{dw_1}{d\xi} = \frac{c_1}{\xi^2}\exp\Big[-\xi^2 - 2(1-\epsilon)\frac{\beta^3}{\xi}\Big]$$

Setting $\xi = \beta$, we obtain

$$c_1 = -2\frac{\beta^3}{N_w}\exp[(3-2\epsilon)\beta^2]$$

Integration gives

$$1 = 2\frac{\beta^3}{N_w}\exp[(3-2\epsilon)\beta^2]\int_\beta^\infty \frac{1}{x^2}\exp\Big[-x^2 - 2(1-\epsilon)\frac{\beta^3}{x}\Big]dx$$

which gives the desired result.

Exercise 18.9

From the given concentration field, we have,

$$\frac{\partial w_1}{\partial r} = \begin{cases} -\dfrac{2}{\delta}\left(1 - \dfrac{r-R}{\delta}\right) & \text{for } R \le r \le R+\delta, \\ 0 & \text{for } r > R+\delta. \end{cases}$$

Multiplication of (18.20) by r^2 and integrating over r from R to $R+\delta$ gives,

$$\int_R^{R+\delta}\frac{\partial w_1}{\partial t}r^2 dr = -(1-\epsilon)\frac{dR}{dt}R^2[w_1(R+\delta,t) - w_1(R,t)]$$

$$+ (R+\delta)^2 \frac{\partial w_1}{\partial r}(R+\delta, t) - R^2 \frac{\partial w_1}{\partial r}(R,t)$$
$$= (1-\epsilon)\frac{dR}{dt}R^2 - R^2 \frac{\partial w_1}{\partial r}(R,t),$$

where the second equality follows from the assumed concentration profile. Exchanging the order of integration and differentiation on the left-hand side, we obtain

$$\frac{d}{dt}\int_R^{R+\delta} w_1 r^2 dr = -\epsilon \frac{dR}{dt}R^2 - R^2 \frac{\partial w_1}{\partial r}(R,t) = \frac{1-\epsilon N_w}{3N_w}\frac{dR^3}{dt},$$

where the second equality follows using (18.27). Integration gives

$$\int_R^{R+\delta} w_1 r^2 dr = \frac{1-\epsilon N_w}{3N_w}(R^3 - 1).$$

Evaluating the integral using the given concentration field leads to

$$\frac{\delta}{R} + \frac{1}{2}\left(\frac{\delta}{R}\right)^2 + \frac{1}{10}\left(\frac{\delta}{R}\right)^3 = \frac{1-\epsilon N_w}{N_w}\frac{R^3-1}{R^3}.$$

For $\delta/R \ll 1$, we have

$$\frac{\delta}{R} \approx \frac{1-\epsilon N_w}{N_w}\frac{R^3-1}{R^3},$$

which can be combined with (18.27) to obtain the desired expression.

Exercise 19.1

To introduce the radial average temperature, we write (19.3) as follows:

$$2\int_0^1 \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) r dr + 2\int_0^1 \frac{\partial^2 T}{\partial z^2} r dr = 0,$$

which can be written as

$$2\frac{\partial T}{\partial r}(1,z,t) + \frac{\partial^2}{\partial z^2}\left[2\int_0^1 T r dr\right] = 0,$$

where we have used the boundary condition in (19.4). Using the definition $\langle T\rangle = 2\int_0^1 T\ r dr$, and the boundary condition in (19.6), we obtain

$$\frac{d^2\langle T\rangle}{dz^2} - 2\frac{h_\mathrm{g}}{R\lambda}[T(1,z,t) - T_\mathrm{g}] = 0,$$

which, setting $T(1,z,t) \approx \langle T\rangle$, gives (19.12). The same procedure leads to

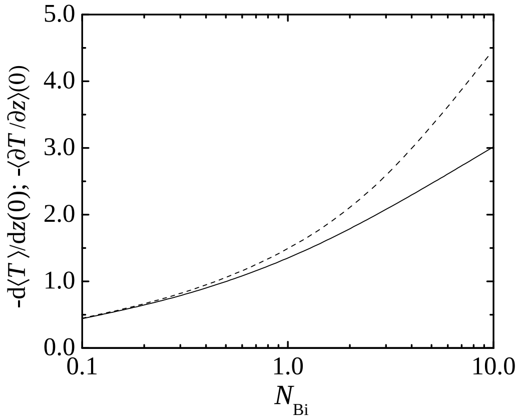

Figure C.14 Normalized temperature gradient from two-dimensional (solid curve) in (19.11) and one-dimensional (dashed curve) in (19.14) solutions for $L = 10R$.

the boundary conditions in (19.13). The solution of (19.12)–(19.13) is given by

$$\frac{\langle T\rangle - T_{\mathrm{g}}}{T_{\mathrm{s}} - T_{\mathrm{g}}} = \frac{\cosh[\sqrt{2N_{\mathrm{Bi}}}(L-x)/R] + \sqrt{N_{\mathrm{Bi}}/2}\,\sinh[\sqrt{2N_{\mathrm{Bi}}}(L-x)/R]}{\cosh(\sqrt{2N_{\mathrm{Bi}}}L/R) + \sqrt{N_{\mathrm{Bi}}/2}\,\sinh(\sqrt{2N_{\mathrm{Bi}}}L/R)}.$$

Differentiation of $\langle T\rangle$ with respect to z and setting $z = 0$ gives (19.14).

To evaluate (19.11) we need α_n, which are given in the table below. Comparison of the temperature gradient at the solid-melt interface for the one- and two-dimensional models in Figure C.14 indicates the fin approximation is valid for $N_{\mathrm{Bi}} \lesssim 1$.

Table C.6 *Roots of* $\alpha_n J_1(\alpha_n) - N_{\mathrm{Bi}} J_0(\alpha_n) = 0.$

n	N_{Bi}	0.1	0.3	1.0	3.0	10.0
1		0.4417	0.7465	1.2558	1.7887	2.1795
2		3.8577	3.9091	4.0795	4.4634	5.0332
3		7.0298	7.0582	7.1558	7.4103	7.9569
4		10.1833	10.2029	10.271	10.4566	10.9363
5		13.3312	13.3462	13.3984	13.5434	13.958
6		16.4767	16.4888	16.5312	16.6499	17.0099

Exercise 19.2
Substitution of $V = dL/dt$ and replacing $\langle \partial T/\partial z\rangle \approx d\langle T\rangle/dz$ in (19.10) gives

$$\rho(\hat{h}^{\mathrm{I}} - \hat{h}^{\mathrm{II}})\frac{dL}{dt} = -\lambda\frac{d\langle T\rangle}{dz}(0) + h_{\mathrm{m}}(T_{\mathrm{s}} - T_{\mathrm{m}})$$

Using R, R^2/χ and $T_{\mathrm{s}} - T_{\mathrm{g}}$ to normalize length, time and temperature, respectively, gives

$$\frac{dL}{dt} = N_{\mathrm{St}}\Big[-\frac{d\langle T\rangle}{dz}(0) + \bar{N}_{\mathrm{Bi}}\frac{T_{\mathrm{s}} - T_{\mathrm{m}}}{T_{\mathrm{s}} - T_{\mathrm{g}}}\Big]$$

where $N_{\mathrm{St}} = \hat{c}_p(T_{\mathrm{s}} - T_{\mathrm{g}})/(\hat{h}^{\mathrm{I}} - \hat{h}^{\mathrm{II}})$. For $L \gg 1$, the expression in (19.14) is independent of L, and for $N_{\mathrm{Bi}} = 1$, we obtain $-d\langle T\rangle/dz(0) \approx 1.4$. With $\bar{N}_{\mathrm{Bi}} = 1$, $(T_{\mathrm{m}} - T_{\mathrm{s}})/(T_{\mathrm{s}} - T_{\mathrm{g}}) = 1.1$ and $N_{\mathrm{St}} = 0.1$, we obtain $dL/dt \approx 0.13$, or $L \approx 0.13t$. For $L = 20$, $t \approx 154$ so that the time required to growth a crystal with $R = 5$ cm and $\chi = 0.1$ cm^2/s is ≈ 10 hrs.

Exercise 19.3
For steady conduction in a stationary system with a line source at $x_3 = 0$, we have $\boldsymbol{\nabla}\cdot\boldsymbol{j}_q = P_0\delta(x_1)\delta(x_2)$. When combined with (6.23) we obtain

$$k_{11}\frac{\partial^2 T}{\partial x_1^2} + k_{22}\frac{\partial^2 T}{\partial x_2^2} + k_{33}\frac{\partial^2 T}{\partial x_3^2} = -P_0\delta(x_1)\delta(x_2).$$

The boundary conditions far from the source are given by

$$T(\pm\infty, x_2, x_3) = T(x_1, \pm\infty, x_3) = T_0.$$

Heat transfer at the surfaces of the slab are governed by Newton's law of cooling, which leads to the boundary conditions

$$-k_{33}\frac{\partial T}{\partial x_3}(x_1, x_2, \pm d/2) = \pm h[T(x_1, x_2, \pm d/2) - T_0].$$

Introducing the average temperature $\langle T\rangle = \int_{-d/2}^{d/2} T dx_3/d$, we can write

$$k_{11}\frac{\partial^2\langle T\rangle}{\partial x_1^2} + k_{22}\frac{\partial^2\langle T\rangle}{\partial x_2^2} - 2\frac{h}{d}[\langle T\rangle - T_0] = -P_0\delta(x_1)\delta(x_2),$$

where we have used the last pair of boundary conditions and set $T(x_1, x_2, \pm d/2) \approx \langle T\rangle$. Using the normalized variables $x_i/d \to x_i$ and $(\langle T\rangle - T_0)/(P_0/\lambda_0) \to \langle T\rangle$, we can write

$$\alpha_1\frac{\partial^2\langle T\rangle}{\partial x_1^2} + \alpha_2\frac{\partial^2\langle T\rangle}{\partial x_2^2} - 2N_{\mathrm{Bi}}\langle T\rangle = -\delta(x_1)\delta(x_2),$$

which is solved subject to the boundary conditions

$$\langle T\rangle(\pm\infty, x_2) = \langle T\rangle(x_1, \pm\infty) = 0.$$

Using the change of variables: $x = x_1/\sqrt{\alpha_1}$ and $y = x_2/\sqrt{\alpha_2}$, we have

$$\frac{\partial^2\langle T\rangle}{\partial x^2} + \frac{\partial^2\langle T\rangle}{\partial y^2} - 2N_{\rm Bi}\langle T\rangle = -\frac{\delta(x)\delta(y)}{\sqrt{\alpha_1\alpha_2}},$$

$$\langle T\rangle(\pm\infty, y) = \langle T\rangle(x, \pm\infty) = 0.$$

To obtain a solution, we use the double spatial Fourier transform

$$\hat{\bar{a}}(\beta,\gamma) = \int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} a(x,y)e^{-i\beta x}e^{-i\gamma y}dxdy = \int\limits_{-\infty}^{\infty} \bar{a}(\beta,y)e^{-i\gamma y}dy.$$

Hence, we find

$$\langle\tilde{\bar{T}}\rangle = \frac{1}{\sqrt{\alpha_1\alpha_2}}\frac{1}{\beta^2+\gamma^2+2N_{\rm Bi}},$$

so that the solution is obtained from double inversion

$$\langle T\rangle = \frac{1}{4\pi^2}\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty}\langle\tilde{\bar{T}}\rangle e^{i\beta x}e^{i\gamma y}d\beta d\gamma = \frac{1}{4\pi^2\sqrt{\alpha_1\alpha_2}}\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty}\frac{e^{i\beta x}e^{i\gamma y}}{\beta^2+\gamma^2+2N_{\rm Bi}}d\beta d\gamma.$$

Using $e^{iz} = \cos z + i\sin z$, we can write

$$\begin{aligned}\langle T\rangle &= \frac{1}{4\pi^2\sqrt{\alpha_1\alpha_2}}\int\limits_{-\infty}^{\infty}2\int\limits_{0}^{\infty}\frac{\cos(\beta x)}{\beta^2+\gamma^2+2N_{\rm Bi}}d\beta\cos(\gamma y)d\gamma\\ &= \frac{1}{2\pi\sqrt{\alpha_1\alpha_2}}\int\limits_{0}^{\infty}\frac{e^{-\sqrt{\gamma^2+2N_{\rm Bi}}x}\cos(\gamma y)}{\sqrt{\gamma^2+2N_{\rm Bi}}}d\gamma\\ &= \frac{1}{2\pi\sqrt{\alpha_1\alpha_2}}K_0\Big(\sqrt{2N_{\rm Bi}(x^2+y^2)}\Big),\end{aligned}$$

where the second and third lines were found with the help of integration tables.

From Figure C.15 it is evident that isotherms are circular for the isotropic case and elliptic for the anisotropic case.

Exercise 19.4
We begin by writing (5.20) for O_2

$$(v_{\rm O_2})_z c_{\rm O_2} = v_z^* c_{\rm O_2} + (J^*_{\rm O_2})_z$$

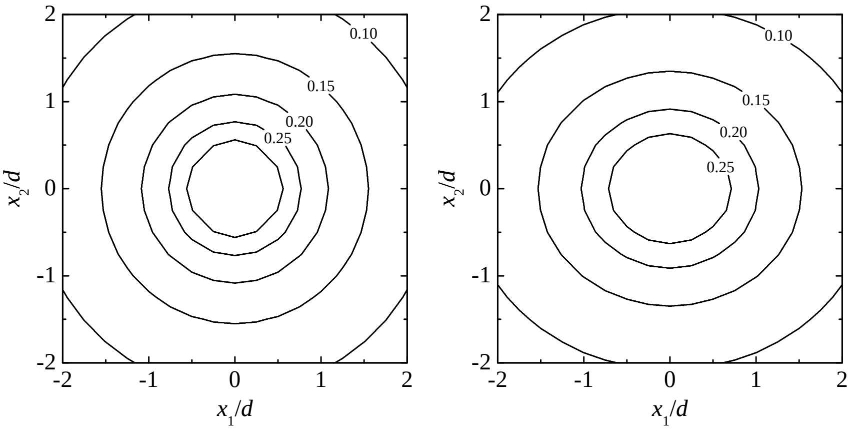

Figure C.15 Normalized temperature isotherms $(\langle T \rangle - T_0)/(P_0/\lambda_0)$ with $N_{\mathrm{Bi}} = 0.1$ for isotropic ($\alpha_1 = \alpha_2 = 1$, left) and anisotropic ($\alpha_1 = 1.3, \alpha_2 = 0.98$, right) conduction cases.

$$
\begin{aligned}
&= [x_{\mathrm{O}_2}(v_{\mathrm{O}_2})_z + (1 - x_{\mathrm{O}_2})(v_{\mathrm{SiO}_2})_z]c_{\mathrm{O}_2} - cD\frac{\partial x_{\mathrm{O}_2}}{\partial z} \\
&= x_{\mathrm{O}_2}(v_{\mathrm{O}_2})_z c_{\mathrm{O}_2} - D\frac{\partial (c_{\mathrm{O}_2}/c)}{\partial z} \\
&= x_{\mathrm{O}_2}(v_{\mathrm{O}_2})_z c_{\mathrm{O}_2} - (1 - x_{\mathrm{O}_2})D\frac{\partial c_{\mathrm{O}_2}}{\partial z},
\end{aligned}
$$

where we have used the definition of $\boldsymbol{v}^*$ and (6.27) to go from the first to second line, $(v_{\mathrm{SiO}_2})_z = 0$ and $x_{\mathrm{O}_2} = c_{\mathrm{O}_2}/c$ to go from the second to third line, and $c = c_{\mathrm{O}_2} + c_{\mathrm{SiO}_2}$ where c_{SiO_2} is constant to go from the third to the fourth line, which gives (19.16).

Exercise 19.5
We wish to transform derivatives of a function $u(x_3, t)$ to derivatives of $u(\bar{x}_3, t)$ using the change of variable $\bar{x}_3 = x_3/h$. The differential of $u(\bar{x}_3, t)$ is

$$du = \frac{\partial u}{\partial \bar{x}_3} d\bar{x}_3 + \frac{\partial u}{\partial t} dt$$

The differential for $\bar{x}_3(x_3, t)$ is

$$d\bar{x}_3 = \frac{\partial \bar{x}_3}{\partial x_3} dx_3 + \frac{\partial \bar{x}_3}{\partial t} dt = \frac{1}{h} dx_3 - \frac{\bar{x}_3}{h}\frac{dh}{dt} dt$$

Substitution gives

$$du = \frac{1}{h}\frac{\partial u}{\partial \bar{x}_3}dx_3 + \Big(\frac{\partial u}{\partial t} - \frac{\bar{x}_3}{h}\frac{dh}{dt}\frac{\partial u}{\partial \bar{x}_3}\Big)dt$$

so that

$$\frac{\partial u}{\partial x_3} = \frac{1}{h}\frac{\partial u}{\partial \bar{x}_3}, \qquad \frac{\partial u}{\partial t} = \frac{\partial u}{\partial t} - \frac{\bar{x}_3}{h}\frac{dh}{dt}\frac{\partial u}{\partial \bar{x}_3}$$

Setting $u = c_{O_2}$ and substitution in (19.19)–(19.22) gives (19.23)–(19.26).

Exercise 19.6

For $D/k^{II} \to 0$ we write (19.19)–(19.22) in terms of dimensional position and time variables

$$\frac{\partial c_{O_2}}{\partial t} = D\frac{\partial^2 c_{O_2}}{\partial x_3^2},$$

$$c_{O_2}(0,t) = 1, \qquad c_{O_2}(x_3, 0) = c_{O_2}(h,t) = 0,$$

$$\frac{dh}{dt} = -\varepsilon D\frac{\partial c_{O_2}}{\partial x_3}(h,t),$$

Using the similarity transformation $\xi = x_3/\sqrt{4Dt}$, we obtain

$$\frac{d^2 c_{O_2}}{d\xi^2} + 2\xi\frac{dc_{O_2}}{\partial \xi} = 0,$$

$$c_{O_2}(0) = 1, \qquad c_{O_2}(\beta) = 0,$$

$$\frac{dh}{dt} = -\varepsilon\sqrt{\frac{D}{4t}}\frac{\partial c_{O_2}}{\partial \xi}(\beta),$$

where $\beta = h/\sqrt{4Dt}$. The solution for c_{O_2} is

$$c_{O_2} = 1 - \frac{\mathrm{erf}(\xi)}{\mathrm{erf}(\beta)}.$$

Substitution in the evolution equation for h gives the desired expression for β, which can be written as

$$\beta^2 = \varepsilon\frac{\beta\exp(-\beta^2)}{\sqrt{\pi}\mathrm{erf}(\beta)} = \varepsilon\Big[\frac{1}{2} - \frac{\beta^2}{3} + O(\beta^3)\Big]$$

so that $\beta \approx \sqrt{\varepsilon/2}$, and $h = \sqrt{2\varepsilon Dt}$, which is equivalent to (19.28).

Exercise 19.7

For convenience, we make the change of variable $\bar{t} = \varepsilon t$. Substitution of $c_{O_2} = c_{O_2}^{(0)} + \varepsilon c_{O_2}^{(1)} + ...$ and $h = h^{(0)} + \varepsilon h^{(1)} + ...$ in (19.23)–(19.26) leads to following zero-order (ε^0) problem

$$\frac{\partial^2 c_{O_2}^{(0)}}{\partial \bar{x}_3^2} = 0,$$

$$c_{O_2}^{(0)}(0, \bar{t}) = 1,$$

$$\frac{\partial c_{O_2}^{(0)}}{\partial \bar{x}_3}(1, \bar{t}) + h^{(0)} c_{O_2}^{(0)}(1, \bar{t}) = 0,$$

$$\frac{dh^{(0)}}{d\bar{t}} = c_{O_2}^{(0)}(1, \bar{t}).$$

The solution of this problem is given in (19.27) and (19.28)

$$c_{O_2}^{(0)} = \frac{1 + (1 - \bar{x}_3)h^{(0)}}{1 + h^{(0)}}, \qquad h^{(0)} = \sqrt{1 + 2\bar{t}} - 1.$$

The first-order (ε^1) problem is given by

$$\frac{\partial^2 c_{O_2}^{(1)}}{\partial \bar{x}_3^2} = h^{(0)2} \frac{\partial c_{O_2}^{(0)}}{\partial \bar{t}} + \bar{x}_3 \frac{\partial c_{O_2}^{(0)}}{\partial \bar{x}_3}(1, \bar{t}) \frac{\partial c_{O_2}^{(0)}}{\partial \bar{x}_3} = \frac{h^{(0)3} \bar{x}_3}{(1 + h^{(0)})^3},$$

$$c_{O_2}^{(1)}(0, \bar{t}) = 0,$$

$$\frac{\partial c_{O_2}^{(1)}}{\partial \bar{x}_3}(1, \bar{t}) + h^{(1)} c_{O_2}^{(0)}(1, \bar{t}) + h^{(0)} c_{O_2}^{(1)}(1, \bar{t}) = 0,$$

$$\frac{dh^{(1)}}{d\bar{t}} = c_{O_2}^{(1)}(1, \bar{t}).$$

Integrating the first equation and applying boundary conditions leads to

$$c_{O_2}^{(1)} = \frac{h^{(0)3}}{2(1 + h^{(0)})^3} \Big[\frac{\bar{x}_3^3}{3} - \frac{(1 + h^{(0)}/3)\bar{x}_3}{1 + h^{(0)}} \Big] - \frac{h^{(1)} \bar{x}_3}{(1 + h^{(0)})^2},$$

Substitution in the evolution equation for $h^{(1)}$ gives

$$\frac{dh^{(1)}}{d\bar{t}} + \frac{h^{(1)}}{(1 + h^{(0)})^2} = -\frac{h^{(0)3}}{3(1 + h^{(0)})^4},$$

or

$$\frac{dh^{(1)}}{d\bar{t}} + \frac{h^{(1)}}{1+2\bar{t}} = \frac{(1-\sqrt{1+2\bar{t}})^3}{3(1+2\bar{t})^2}.$$

Solving subject to $h^{(1)}(0) = 0$ gives the desired expression.

Exercise 19.8
The differential for the stream function $\psi(r, z, t)$ is given by

$$d\psi = \frac{\partial \psi}{\partial r} dr + \frac{\partial \psi}{\partial z} dz.$$

From the constraint on v_r and v_z in (19.38) we obtain

$$v_r = \frac{1}{r}\frac{\partial \psi}{\partial z}, \qquad v_z = -\frac{1}{r}\frac{\partial \psi}{\partial r}$$

so that the differential becomes

$$d\psi = -rv_z dr + rv_r dz.$$

Substitution of (19.43) and (19.44) setting $\partial h/\partial r = 0$ gives

$$d\psi = r\Big[\Big(\frac{z}{h}\Big)^2 - \frac{1}{3}\Big(\frac{z}{h}\Big)^3\Big]h^3 dr + r^2\Big[\Big(\frac{z}{h}\Big) - \frac{1}{2}\Big(\frac{z}{h}\Big)^2\Big]h^2 dz.$$

Integration from $\psi(0, 0, t) = 0$ gives (19.49).

Exercise 19.9
Integration of (19.40) gives

$$\mathcal{P}(r, z, t) - \mathcal{P}(r, h, t) = \int_h^z \frac{\partial^2 v_z}{\partial z^2} dz = \frac{1}{\beta}\Big[\frac{\partial v_z}{\partial z}(r, z, t) - \frac{\partial v_z}{\partial z}(r, h, t)\Big].$$

and(19.44) integrating with the boundary condition in (19.42). Setting $\boldsymbol{g} = -\boldsymbol{\nabla}\phi = -g\boldsymbol{\delta}_z$, we can write $\mathcal{P} = p^{\mathrm{L}} + z/(\beta N_{\mathrm{Fr}})$, where $N_{\mathrm{Fr}} = (\Omega h_0)^2/g$. This allows us to rewrite the last expression as

$$p^{\mathrm{L}}(r, z, t) - p^{\mathrm{L}}(r, h, t) + \frac{z-h}{\beta N_{\mathrm{Fr}}} = \frac{1}{\beta}\Big[\frac{\partial v_z}{\partial z}(r, z, t) - \frac{\partial v_z}{\partial z}(r, h, t)\Big].$$

Now, using the boundary condition in (19.42), we obtain

$$p^{\mathrm{L}}(r, z, t) = \frac{h-z}{\beta N_{\mathrm{Fr}}} + \frac{1}{\beta}\Big[\frac{\partial v_z}{\partial z}(r, z, t) + \frac{\partial v_z}{\partial z}(r, h, t)\Big] + \frac{1}{\beta N_{\mathrm{We}}}\frac{\partial^2 h}{\partial r^2}.$$

Substitution of (19.44) gives (19.50).

Exercise 20.1

At low temperatures, a system occupies low-energy states. If there is a single ground state of lowest energy, the formula (20.3) implies that, for $T \to 0$, the entropy becomes zero. The same conclusion holds if there is a small number of ground states or if the number of ground states does not increase too strongly with system size.

Exercise 20.2

The key step for relating the canonical and microcanonical ensembles is to replace sums over microstates by sums over possible energy values and to introduce the number of microstates for a given energy value,

$$Z(T, V, \tilde{N}) = \sum_j e^{-E_j/(k_B T)} = \sum_U e^{-U/(k_B T)}\, \Omega(U, V, \tilde{N}),$$

where, for simplicity, we have assumed that the indistinguishability correction is included into Ω. By differentiation, we obtain

$$\begin{aligned}\frac{\partial}{\partial V}\left[-k_B T \ln Z(T, V, \tilde{N})\right] &= -\frac{k_B T}{Z(T, V, \tilde{N})} \sum_U e^{-U/(k_B T)}\, \frac{\partial \Omega(U, V, \tilde{N})}{\partial V} \\ &= -\frac{T}{Z(T, V, \tilde{N})} \sum_U e^{-U/(k_B T)}\, \Omega(U, V, \tilde{N}) \frac{\partial S(U, V, \tilde{N})}{\partial V} \\ &= -\frac{1}{Z(T, V, \tilde{N})} \sum_U e^{-U/(k_B T)}\, \Omega(U, V, \tilde{N})\, p(U, V, \tilde{N}) = -p(T, V, \tilde{N}).\end{aligned}$$

The differentiation with respect to $\tilde{N}$ can be carried out in an analogous way. For the derivative with respect to T we finally obtain

$$\begin{aligned}\frac{\partial}{\partial T}\left[-k_B T \ln Z(T, V, \tilde{N})\right] &= -k_B \ln Z(T, V, \tilde{N}) - \frac{k_B T}{Z(T, V, \tilde{N})} \frac{\partial Z(T, V, \tilde{N})}{\partial T} \\ &= -k_B \ln Z(T, V, \tilde{N}) - \frac{1}{T} \sum_j E_j \frac{e^{-E_j/(k_B T)}}{Z(T, V, \tilde{N})} \\ &= -k_B \ln Z(T, V, \tilde{N}) - \frac{1}{T} U(T, V, \tilde{N}) = -S(T, V, \tilde{N}).\end{aligned}$$

Exercise 20.3

At 25°C and standard pressure, we have $C_V = 75\,\mathrm{J/K}$ for 1 mol of water. For $T = 298\,\mathrm{K}$, we further have $k_B T = 4.1 \times 10^{-21}\,\mathrm{J}$. According to (20.12), these values imply temperature fluctuations of $1.3 \times 10^{-10}\,\mathrm{K}$.

Exercise 20.4
By using $U = uV$ and $C_V = V\rho\hat{c}_{\hat{v}}$, which follows by comparing the definitions in (4.35) and Table A.1, we obtain

$$\left\langle \Delta u^2 \right\rangle = \frac{\rho k_{\mathrm{B}} T^2 \hat{c}_{\hat{v}}}{V}, \qquad \left\langle \Delta T^2 \right\rangle = \frac{k_{\mathrm{B}} T^2}{\rho \hat{c}_{\hat{v}}\, V}.$$

In obtaining this result, we have used that the volume of the open subsystem in Figure 20.4 does not fluctuate.

Exercise 20.5
For fixed V and T, (20.11) leads to

$$\left\langle \Delta N^2 \right\rangle = k_{\mathrm{B}} \left[\frac{1}{T} \frac{\partial^2 F(T,N)}{\partial N^2} \right]^{-1},$$

which implies

$$\left\langle \Delta \rho^2 \right\rangle = \left[\frac{\partial^2 f(\rho,T)}{\partial \rho^2} \right]^{-1} \frac{k_{\mathrm{B}} T}{V} = \frac{\rho}{c_T^2} \frac{k_{\mathrm{B}} T}{V} = \frac{\kappa_T \rho^2 k_{\mathrm{B}} T}{V},$$

where, for the last two equalities, we have used the results of Appendix A.

Exercise 21.1
The Gaussian distribution can be given in terms of the second moments,

$$\left(\frac{3}{2\pi \langle \boldsymbol{v}^2 \rangle} \right)^{3/2} \exp\left\{ -\frac{3}{2} \frac{\boldsymbol{v}^2}{\langle \boldsymbol{v}^2 \rangle} \right\}.$$

We hence obtain

$$\begin{aligned}
\langle |\boldsymbol{v}| \rangle &= \int_0^\infty v 4\pi v^2 \left(\frac{3}{2\pi \langle \boldsymbol{v}^2 \rangle} \right)^{3/2} \exp\left\{ -\frac{3}{2} \frac{v^2}{\langle \boldsymbol{v}^2 \rangle} \right\} dv \\
&= -\int_0^\infty 2v^2 \left(\frac{3}{2\pi \langle \boldsymbol{v}^2 \rangle} \right)^{1/2} \frac{d}{dv} \exp\left\{ -\frac{3}{2} \frac{v^2}{\langle \boldsymbol{v}^2 \rangle} \right\} dv \\
&= \int_0^\infty 4v \left(\frac{3}{2\pi \langle \boldsymbol{v}^2 \rangle} \right)^{1/2} \exp\left\{ -\frac{3}{2} \frac{v^2}{\langle \boldsymbol{v}^2 \rangle} \right\} dv \\
&= -\int_0^\infty \left(\frac{8 \langle \boldsymbol{v}^2 \rangle}{3\pi} \right)^{1/2} \frac{d}{dv} \exp\left\{ -\frac{3}{2} \frac{v^2}{\langle \boldsymbol{v}^2 \rangle} \right\} dv = \left(\frac{8 \langle \boldsymbol{v}^2 \rangle}{3\pi} \right)^{1/2}.
\end{aligned}$$

The second part of (21.5) follows from $(1/2)\, m \left\langle \boldsymbol{v}^2 \right\rangle = (3/2) k_{\mathrm{B}} T$.

Exercise 21.2
The frequency of collisions between gas particles for hydrogen under normal conditions is given by

$$\frac{\langle|\boldsymbol{v}|\rangle}{l_{\mathrm{mfp}}} = \sqrt{\frac{8}{3\pi}}\frac{\sqrt{\langle\boldsymbol{v}^2\rangle}}{l_{\mathrm{mfp}}} \approx \sqrt{\frac{8}{3\pi}}\frac{1840}{0.15\cdot 10^{-6}}\frac{1}{\mathrm{s}} \approx 10^{10}\frac{1}{\mathrm{s}}.$$

Exercise 21.3
With $m = 14\mathrm{g}/\tilde{N}_{\mathrm{A}}$, $d = 2.5$ Å, and $T = 293$ K, we obtain $\eta = 1.9\cdot 10^{-5}\,\mathrm{Pas}$ from (21.12). The measured values are $\eta = 1.75\cdot 10^{-5}\,\mathrm{Pas}$ for nitrogen gas and $\eta = 1.81\cdot 10^{-5}\,\mathrm{Pas}$ for air.

Exercise 21.4
By integrating (21.22) we obtain

$$\int\left[\frac{\partial f(\boldsymbol{r},\boldsymbol{p})}{\partial t}\right]_{\mathrm{coll}} d^3p = \int w(\boldsymbol{q},\boldsymbol{q}'|\boldsymbol{p},\boldsymbol{p}')[f(\boldsymbol{r},\boldsymbol{q})f(\boldsymbol{r},\boldsymbol{q}') - f(\boldsymbol{r},\boldsymbol{p})f(\boldsymbol{r},\boldsymbol{p}')]d^3p d^3p' d^3q d^3q',$$

which can be written as the difference of two integrals. If, in the second integral, the integration variables $\boldsymbol{p},\boldsymbol{p}'$ are interchanged with $\boldsymbol{q},\boldsymbol{q}'$, the symmetry (21.20) leads to the first identity in (21.41). To prove the second identity in (21.41), one needs the additional step

$$\int \boldsymbol{p} w(\boldsymbol{q},\boldsymbol{q}'|\boldsymbol{p},\boldsymbol{p}')f(\boldsymbol{r},\boldsymbol{q})f(\boldsymbol{r},\boldsymbol{q}') = \frac{1}{2}\int(\boldsymbol{p}+\boldsymbol{p}')w(\boldsymbol{q},\boldsymbol{q}'|\boldsymbol{p},\boldsymbol{p}')f(\boldsymbol{r},\boldsymbol{q})f(\boldsymbol{r},\boldsymbol{q}'),$$

which is based on the symmetry (21.21), and the conservation of momentum expressed in (21.18). The third identity in (21.41) can be obtained in the same way, now based on the conservation of kinetic energy expressed in (21.19).

Exercise 21.5
Boltzmann's kinetic equation (21.17) in the absence of an external force and the results of Exercise 21.4 imply that the time-derivatives of the left-hand sides of (21.33)–(21.35) are obtained by replacing $f(\boldsymbol{r},\boldsymbol{p})$ by $-(\boldsymbol{p}/m)\cdot\partial f(\boldsymbol{r},\boldsymbol{p})/\partial\boldsymbol{r}$. To verify (21.36)–(21.38), one only needs to realize that some of the resulting higher moments can be rewritten in terms of the hydrodynamic variables introduced in (21.33)–(21.35). For example, from the time-derivative of (21.34), we first obtain

$$\frac{\partial}{\partial t}[\boldsymbol{v}(\boldsymbol{r})\rho(\boldsymbol{r})] = -\frac{\partial}{\partial\boldsymbol{r}}\cdot\int\frac{1}{m}\boldsymbol{p}\boldsymbol{p}\,f(\boldsymbol{r},\boldsymbol{p})d^3p,$$

and it can then be verified that the right-hand side of this equation coincides with the more complicated looking right-hand side of (21.37) [by means of (21.33) and (21.34)].

Exercise 22.1
By multiplying (22.6) by $Q_j Q_k$ and integrating over all $\boldsymbol{Q}$, we obtain after some integrations by parts

$$\frac{\partial \Theta_{jk}}{\partial t} = \int p \left(\boldsymbol{\kappa}_{lm} Q_m - \frac{2H}{\zeta} Q_l \right) \frac{\partial}{\partial Q_l} (Q_j Q_k) \, d^3 Q + \frac{2 k_{\mathrm{B}} T}{\zeta} \int p \, \frac{\partial}{\partial Q_l} \frac{\partial}{\partial Q_l} (Q_j Q_k) \, d^3 Q \, .$$

With

$$\frac{\partial}{\partial Q_l} (Q_j Q_k) = \delta_{jl} Q_k + Q_j \delta_{kl} \, ,$$

and, after a further differentiation,

$$\frac{\partial}{\partial Q_l} \frac{\partial}{\partial Q_l} (Q_j Q_k) = 2 \delta_{jk} \, ,$$

we obtain the desired result (22.7) in component form.

Exercise 22.2
If we fix the units of time and length by the conditions $\zeta/(4H) = k_{\mathrm{B}} T / H = 1$, the stochastic differential equation (22.5) for shear flow becomes

$$d\boldsymbol{Q} = \begin{pmatrix} -1/2 & \dot{\gamma} & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & -1/2 \end{pmatrix} \cdot \boldsymbol{Q} \, dt + d\boldsymbol{W} \, .$$

In the simulation code, we ignore the irrelevant component Q_3 and use the parameter SR for the dimensionless shear rate $\lambda \dot{\gamma}$.

```
% Simulation parameters
NTIME=5000; DT=0.01; SR=3.;

% Initial conditions
Q1=0; Q2=1;
Q1R=zeros(NTIME,1); Q2R=zeros(NTIME,1);

% Generation and recording of trajectory
for J=1:NTIME
    Q1=(1-DT/2)*Q1+SR*Q2*DT+random('Normal',0,sqrt(DT));
    Q2=(1-DT/2)*Q2+random('Normal',0,sqrt(DT));
    Q1R(J)=Q1; Q2R(J)=Q2;
end
Q1M=max(Q1R); Q2M=max(Q2R); % For plot axes
```

```
% Plot of dumbbell trajectory
for J=1:NTIME
    plot([0 Q1R(J)],[0 Q2R(J)],'k-','linewidth',5); hold on;
    plot([0 Q1R(J)],[0 Q2R(J)],'ko','markersize',15,'markerfacecolor','r');
    title([num2str(round(100*J/NTIME)) '%']);
    xlabel('Q_1'); ylabel('Q_2');
    axis equal; axis([-Q1M Q1M -Q2M Q2M]); hold off; pause(0.001);
end

% Plot of distribution of dumbbell end points
plot(Q1R,Q2R,'k.'); hold on;
plot(0,0,'ko','markersize',15,'markerfacecolor','r');
xlabel('Q_1'); ylabel('Q_2');
axis equal; axis([-Q1M Q1M -Q2M Q2M]);
```

Exercise 22.3

By means of the Taylor expansion of the exponential function we obtain

$$\exp\left\{\int_{t'}^{t}\boldsymbol{\kappa}(t'')dt''\right\} = \boldsymbol{\delta} + \int_{t'}^{t} dt_1\,\boldsymbol{\kappa}(t_1) + \frac{1}{2!}\int_{t'}^{t} dt_1 \int_{t'}^{t} dt_2\,\boldsymbol{\kappa}(t_1)\cdot\boldsymbol{\kappa}(t_2)$$
$$+ \frac{1}{3!}\int_{t'}^{t} dt_1 \int_{t'}^{t} dt_2 \int_{t'}^{t} dt_3\,\boldsymbol{\kappa}(t_1)\cdot\boldsymbol{\kappa}(t_2)\cdot\boldsymbol{\kappa}(t_3) + \ldots .$$

Instead of extending all integrations from t' to t and multiplying the nth term by $1/n!$, we use only one of the $n!$ possible time orderings of the integration variables $t_1, t_2, \ldots, t_n$, which is the one with $t_1 > t_2 > \ldots > t_n$. In taking the time-derivative of the right-hand-side of (22.12), the left-most integration of each term disappears and t_1 is replaced by t. Therefore, $\boldsymbol{\kappa}(t)$ multiplies the expansion (22.12) of $\boldsymbol{E}(t,t')$ from the left. The time-ordering guarantees that the factor $\boldsymbol{\kappa}(t)$ indeed appears on the left.

Exercise 22.4

If $\boldsymbol{\kappa}(t)$ is diagonal for all t, the product of any number of factors $\boldsymbol{\kappa}(t_j)$ is obtained as the corresponding product of diagonal elements. Time-ordering hence doesn't matter, and any function of a diagonal matrix is obtained as the function of the diagonal elements. For example, from (12.20) we obtain

$$\boldsymbol{E}(t,t') = \begin{pmatrix} \exp\{(t-t')\dot\epsilon\} & 0 & 0 \\ 0 & \exp\{-(t-t')\dot\epsilon/2\} & 0 \\ 0 & 0 & \exp\{-(t-t')\dot\epsilon/2\} \end{pmatrix},$$

for steady simple elongational flow.

Exercise 22.5
As the linear stochastic differential equation (22.5) contains only additive noise, it can be solved by the methods for deterministic ordinary differential equations. By the method of variation of constants, we obtain

$$\boldsymbol{Q}_t = e^{-2Ht/\zeta}\,\boldsymbol{E}(t,0)\cdot\boldsymbol{Q}_0 + \sqrt{\frac{4k_{\rm B}T}{\zeta}}\int_0^t e^{-2H(t-t')/\zeta}\,\boldsymbol{E}(t,t')\cdot d\boldsymbol{W}_{t'}\,.$$

By averaging the dyadic of $\boldsymbol{Q}_t$, using the independence of $d\boldsymbol{W}_{t'}$ and $\boldsymbol{Q}_0$, and reducing the double stochastic integral to a single time integral (by means of $\langle d\boldsymbol{W}_{t'} d\boldsymbol{W}_t\rangle = \delta(t-t')\,\boldsymbol{\delta}\,dt'dt$), we find

$$\begin{aligned}\langle\boldsymbol{Q}_t\boldsymbol{Q}_t\rangle &= e^{-4Ht/\zeta}\,\boldsymbol{E}(t,0)\cdot\langle\boldsymbol{Q}_0\boldsymbol{Q}_0\rangle\cdot\boldsymbol{E}^T(t,0)\\ &\quad+\frac{4k_{\rm B}T}{\zeta}\int_0^t e^{-4H(t-t')/\zeta}\,\boldsymbol{E}(t,t')\cdot\boldsymbol{E}^T(t,t')\,dt'\,.\end{aligned}$$

The tensor $\boldsymbol{B}(t,t') = \boldsymbol{E}(t,t')\cdot\boldsymbol{E}^T(t,t')$ occurring under the integral is known as the *Finger strain tensor*.

Exercise 22.6
We start from equilibrium, that is, from the expression $\langle\boldsymbol{Q}_0\boldsymbol{Q}_0\rangle = (k_{\rm B}T/H)\boldsymbol{\delta}$ given in (22.8). By inserting the second-moment tensor of Exercise 22.5 into the pressure-tensor expression (22.9), we obtain

$$\frac{\boldsymbol{\tau}}{n_{\rm p}k_{\rm B}T} = \boldsymbol{\delta} - e^{-4Ht/\zeta}\,\boldsymbol{B}(t,0) - \frac{4H}{\zeta}\int_0^t e^{-4H(t-t')/\zeta}\,\boldsymbol{B}(t,t')\,dt'\,.$$

The factor $4H/\zeta$ in front of the integral can be obtained by differentiating the exponential under the integral with respect to t'. An integration by parts then gives the more compact expression

$$\frac{\boldsymbol{\tau}}{n_{\rm p}k_{\rm B}T} = \int_0^t e^{-4H(t-t')/\zeta}\,\frac{\partial\boldsymbol{B}(t,t')}{\partial t'}\,dt'\,.$$

This result is a nonlinear generalization of the basic equation (12.13) of linear viscoelasticity for a single exponential shear relaxation modulus and deformations beginning at $t=0$. It is also known as the *integral formulation of the upper convected Maxwell model.*

The sparseness of the matrix

$$\boldsymbol{\kappa} = \begin{pmatrix} 0 & \dot\gamma & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{pmatrix}\,,$$

for shear flow implies that $\boldsymbol{\kappa}^n = 0$ for all $n \geq 2$, so that we find

$$\boldsymbol{E}(t,t') = \boldsymbol{\delta} + (t-t')\,\boldsymbol{\kappa}\,,$$

for steady shear flow, implying the Finger strain tensor

$$\boldsymbol{B}(t,t') = \boldsymbol{\delta} + (t-t')\,(\boldsymbol{\kappa}+\boldsymbol{\kappa}^T) + (t-t')^2\,\boldsymbol{\kappa}\cdot\boldsymbol{\kappa}^T\,,$$

or, in Cartesian components,

$$\boldsymbol{B}(t,t') = \begin{pmatrix} 1+(t-t')^2\dot\gamma^2 & (t-t')\dot\gamma & 0 \\ (t-t')\dot\gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\frac{\partial \boldsymbol{B}(t,t')}{\partial t'} = -\begin{pmatrix} 2(t-t')\dot\gamma^2 & \dot\gamma & 0 \\ \dot\gamma & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

According to the above integral formulation of the upper convected Maxwell model, the shear stress coincides with the linear viscoelastic prediction. In addition, we obtain the time-dependent first normal-stress difference

$$\frac{\tau_{11}}{n_{\rm p}k_{\rm B}T} = -2\dot\gamma^2\int_0^t e^{-(t-t')/\lambda}\,(t-t')\,dt' = -2(\lambda\dot\gamma)^2\left[1-\left(1+\frac{t}{\lambda}\right)e^{-t/\lambda}\right],$$

with $\lambda = \zeta/(4H)$, which we previously found from the differential formulation of the upper convected Maxwell model in (12.53). For small t, the first normal-stress difference is a second-order effect in t.

Exercise 22.7

By multiplying (22.14) by Q_jQ_k and integrating over all $\boldsymbol{Q}$, we obtain after an integration by parts in the convection term,

$$\frac{\partial\Theta_{jk}}{\partial t} = \int p\,\boldsymbol{\kappa}_{lm}Q_m\frac{\partial}{\partial Q_l}(Q_jQ_k)\,d^3Q + \frac{1}{\lambda}\int (p_{\rm eq}-p)Q_jQ_k\,d^3Q\,.$$

By means of

$$\frac{\partial}{\partial Q_l}(Q_jQ_k) = \delta_{jl}Q_k + Q_j\delta_{kl}\,,$$

and (22.15) we then obtain

$$\frac{\partial\Theta_{jk}}{\partial t} = \boldsymbol{\kappa}_{jm}\Theta_{mk} + \Theta_{jm}\boldsymbol{\kappa}_{km} + \frac{1}{\lambda}\Big(L^2\,\delta_{jk} - \Theta_{jk}\Big)\,,$$

which is the component version of (22.16).

Exercise 22.8

Assuming that we start the deformation of a previously undeformed material at $t = 0$, we can use the integral formulation of the upper convected Maxwell model found in Exercise 22.6 with the parameters for the temporary network model,

$$\frac{\boldsymbol{\tau}(t)}{G} = \int_0^t e^{-(t-t')/\lambda} \, \frac{\partial \boldsymbol{B}(t,t')}{\partial t'} \, dt' \, .$$

In the limit $\lambda \to \infty$, the exponential factor does not decay and can be replaced by unity, so that we get the following explicit pressure tensor for a neo-Hookean material,

$$\boldsymbol{\tau}(t) = G \int_0^t \frac{\partial \boldsymbol{B}(t,t')}{\partial t'} \, dt' = G \Big[\boldsymbol{\delta} - \boldsymbol{B}(t,0) \Big] \, .$$

This can be nicely compared to (12.17), which we write as

$$\boldsymbol{\tau}(t) = -G \boldsymbol{\gamma}(t,0) \, ,$$

as the deformation begins only at $t = 0$. For steady shear flow as an example, the solution to Exercise 22.6 gives

$$\boldsymbol{\delta} - \boldsymbol{B}(t,0) = - \begin{pmatrix} t^2\dot{\gamma}^2 & t\dot{\gamma} & 0 \\ t\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \, .$$

The difference between the neo-Hookean and the Hookean material is contained in the additional diagonal entry. As this entry is of second order in the deformation, it can be neglected for small deformations. For the large deformations possible for rubbers, however, the second-order modification becomes essential. For elongational flows, the nonlinearity of the neo-Hookean law is even more essential. According to Exercise 22.4, any linear elongation ϵ gets replaced by the exponential $e^{\epsilon} - 1$.

Exercise 22.9

The temporary network model is a single-mode Maxwell model with $G(t) = G \, e^{-t/\lambda}$. According to Table 12.1, we have

$$G'(\omega) = G \, \frac{\omega^2\lambda^2}{1+\omega^2\lambda^2} \, , \qquad G''(\omega) = G \, \frac{\omega\lambda}{1+\omega^2\lambda^2} \, .$$

For small ω, one can nicely observe the slopes 2 and 1 for G' and G'' in Figure 12.3. The modulus G can be obtained as the prefactors of $\omega^2\lambda^2$ or $\omega\lambda$, respectively, where λ can be found from the fact that $\omega\lambda = 1$ for $G' = G''$. More directly, one could obtain G as the limit of G''^2/G' for small

ω. Alternatively, G' should reach the plateaux value G for large ω (but not too large, because the model then becomes inapplicable). Still another alternative is based on the observation that, for $\omega\lambda = 1$, we have $G' = G'' = G/2$. Finally, the formula $G = n_{\rm seg}k_{\rm B}T$ provides the network strand density of the temporary network model, which is of the same order as the entanglement number density of the reptation model.

Exercise 22.10

By integrating (22.14) over all $\boldsymbol{Q}$ we get

$$\frac{d}{dt}\int p d^3Q = \int \frac{1}{\lambda}\,(p_{\rm eq} - p) d^3Q\,.$$

If $1/\lambda(\boldsymbol{Q})$ depends on $\boldsymbol{Q}$, this factor cannot be pulled out of the integral, the integral on the right-hand-side can be nonzero, and the normalization of p can change with time. Physically this means that the number of network strands changes. Only in the final approach to equilibrium, the number of network strands becomes a constant.

Exercise 23.1

Substitution of (23.3) in (23.5) gives,

$$\langle \boldsymbol{\nabla} a\rangle_{\rm s} = \boldsymbol{\nabla}(\varepsilon\langle a\rangle_{\rm s}) + \frac{1}{V_{\rm eff}}\int_{A_{\rm fs}} \boldsymbol{n} a(\boldsymbol{r}_{\rm f}) d^2\boldsymbol{r}_{\rm f}.$$

Setting $a \to 1$, we obtain

$$\boldsymbol{0} = \boldsymbol{\nabla}\varepsilon + \frac{1}{V_{\rm eff}}\int_{A_{\rm fs}} \boldsymbol{n} d^2\boldsymbol{r}_{\rm f},$$

which is the desired result. In (23.5), we set $a \to \boldsymbol{r}_{\rm f}$, to obtain

$$\langle \boldsymbol{\nabla}\boldsymbol{r}_{\rm f}\rangle_{\rm s} = \boldsymbol{\nabla}\langle \boldsymbol{r}_{\rm f}\rangle_{\rm s} + \frac{1}{V_{\rm eff}}\int_{A_{\rm fs}} \boldsymbol{n}\boldsymbol{r}_{\rm f} d^2\boldsymbol{r}_{\rm f}.$$

Since $\boldsymbol{r}_{\rm f} = \boldsymbol{r} + \boldsymbol{y}$, we can write this as,

$$\langle \boldsymbol{\delta}\rangle_{\rm s} = \boldsymbol{\nabla}\langle \boldsymbol{r}\rangle_{\rm s} + \boldsymbol{\nabla}\langle \boldsymbol{y}\rangle_{\rm s} + \frac{1}{V_{\rm eff}}\int_{A_{\rm fs}} \boldsymbol{n} d^2\boldsymbol{r}_{\rm f}\boldsymbol{r} + \frac{1}{V_{\rm eff}}\int_{A_{\rm fs}} \boldsymbol{n}\boldsymbol{y} d^2\boldsymbol{r}_{\rm f},$$

where we have used $\boldsymbol{\nabla}\boldsymbol{y} = \boldsymbol{0}$ and $\boldsymbol{\nabla}\boldsymbol{r} = \boldsymbol{\delta}$. Using (23.3), we can write $\langle\boldsymbol{\delta}\rangle_{\rm s} = \varepsilon\boldsymbol{\delta}$ and $\langle\boldsymbol{r}\rangle_{\rm s} = \varepsilon\boldsymbol{r}$ so that

$$\boldsymbol{0} = (\boldsymbol{\nabla}\varepsilon)\boldsymbol{r} + \boldsymbol{\nabla}\langle \boldsymbol{y}\rangle_{\rm s} + \frac{1}{V_{\rm eff}}\int_{A_{\rm fs}} \boldsymbol{n} d^2\boldsymbol{r}_{\rm f}\boldsymbol{r} + \frac{1}{V_{\rm eff}}\int_{A_{\rm fs}} \boldsymbol{n}\boldsymbol{y} d^2\boldsymbol{r}_{\rm f},$$

Using the first result to rewrite the first integral, we obtain the desired result.

Exercise 23.2
Assuming the particles are sufficiently dilute, we can write the integral as

$$\frac{1}{V_{\text{eff}}}\int_{A_{\text{fs}}} \boldsymbol{n}T(\boldsymbol{r}+\boldsymbol{y})dA = -\frac{k}{V_{\text{eff}}}\int_0^{2\pi}\int_0^{\pi} \boldsymbol{\delta}_r T(R,\theta)R^2 \sin\theta d\theta d\phi,$$

The temperature field in (17.11) with $\beta = N_{\text{Ka}} = 0$ and setting $r = R$ is

$$T(R,\theta) = T_0 + \frac{3}{2}|\boldsymbol{\nabla}T|_\infty R\cos\theta\,.$$

Substitution gives

$$\begin{aligned}\frac{1}{V_{\text{eff}}}\int_{A_{\text{fs}}} \boldsymbol{n}T(\boldsymbol{r}+\boldsymbol{y})dA &= -\frac{k}{V_{\text{eff}}}T_0R^2\int_0^{2\pi}\int_0^{\pi} \boldsymbol{\delta}_r \sin\theta d\theta d\phi \\ &\quad -\frac{k}{V_{\text{eff}}}\frac{3}{2}|\boldsymbol{\nabla}T|_\infty R^3\int_0^{2\pi}\int_0^{\pi} \boldsymbol{\delta}_r \cos\theta\sin\theta d\theta d\phi \\ &= -\frac{k}{V_{\text{eff}}}2\pi R^3|\boldsymbol{\nabla}T|_\infty R^3\boldsymbol{\delta}_3 = -\frac{3}{2}\phi|\boldsymbol{\nabla}T|_\infty\boldsymbol{\delta}_3,\end{aligned}$$

where $\phi = k(4/3)\pi R^3/V_{\text{eff}}$. As in Section 17.2, we write $|\boldsymbol{\nabla}T|_\infty\boldsymbol{\delta}_3 = \langle\boldsymbol{\nabla}T\rangle + O(\phi)$, so that

$$\langle\boldsymbol{j}_q\rangle = -\lambda\Big(1-\frac{3}{2}\phi\Big)\langle\boldsymbol{\nabla}T\rangle\,.$$

This leads to $\lambda_{\text{eff}}/\lambda = 1-(3/2)\phi$, which is consistent with the result in (17.16).

Exercise 23.3
Integration of

$$\frac{d}{dr}\Big(\frac{1}{r^2}\frac{d}{dr}(r^2b'_r)\Big) = 0\,,$$

gives

$$\frac{d}{dr}(r^2b'_r) = c_1r^2\,,$$

and a second integration leads to

$$b'_r = \frac{c_1}{3}r + \frac{c_2}{r^2}\,.$$

Applying the boundary conditions gives

$$c_1 = -\frac{1}{1+2(r_1/r_0)^3}, \qquad c_2 = \frac{r_1^3}{1+2(r_1/r_0)^3},$$

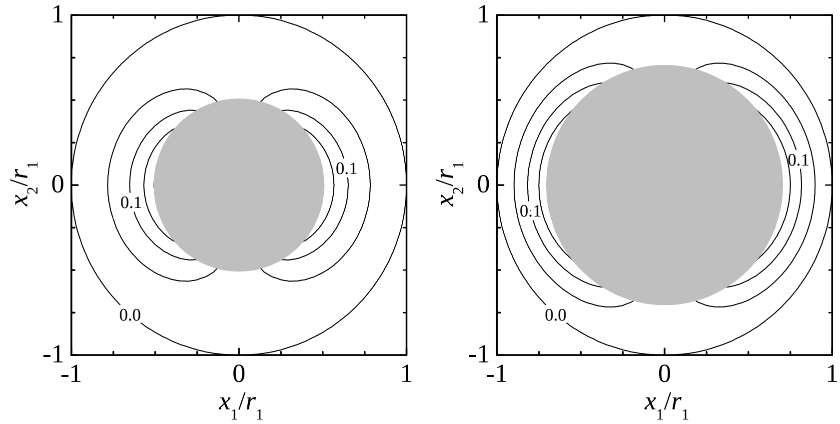

Figure C.16 Contour plots of b'_1/r_1 in x_1–x_2 plane from (23.35) for $\varepsilon = 0.875$ (left) and $\varepsilon = 0.657$ (right).

so that we obtain (23.35), which is plotted in Figure C.16. Using (23.35) in (23.30) gives,

$$\begin{aligned}\boldsymbol{D}_{\rm eff} &= D_{\rm AB}\Big[\boldsymbol{\delta} + \frac{3}{4\pi(r_1^3 - r_0^3)}\int_0^{2\pi}\int_0^{\pi} \boldsymbol{n}\boldsymbol{b}'(r_0) r_0^2 \sin\theta d\theta d\phi\Big] \\ &= D_{\rm AB}\Big[\boldsymbol{\delta} - \frac{3r_0^2 b'_r(r_0)}{4\pi r_1^3}\int_0^{2\pi}\int_0^{\pi} \boldsymbol{\delta}_r\boldsymbol{\delta}_r \sin\theta d\theta d\phi\Big] \\ &= D_{\rm AB}\Big[1 - \frac{1-\varepsilon}{3-\varepsilon}\Big]\boldsymbol{\delta} = D_{\rm AB}\frac{2}{3-\varepsilon}\boldsymbol{\delta} = D_{\rm eff}\boldsymbol{\delta}\,,\end{aligned}$$

which is the result in (23.36) with $D_{\rm eff} = D_{\rm AB} f(\varepsilon)$ with $f(\varepsilon) = 2/(3-\varepsilon)$.

Exercise 23.4

For convenience, we write (23.38) and (23.39) as

$$\frac{\partial\langle c_{\rm A}\rangle_{\rm i}}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial\langle c_{\rm A}\rangle_{\rm i}}{\partial r}\Big) - N_{\rm Da}\langle c_{\rm A}\rangle_{\rm i}$$

$$\langle c_{\rm A}\rangle_{\rm i}(r,0) = 0, \qquad \frac{\partial\langle c_{\rm A}\rangle_{\rm i}}{\partial r}(0,t) = 0, \qquad \langle c_{\rm A}\rangle_{\rm i}(R,t) = 1,$$

where we have used the normalizations $\langle c_{\rm A}\rangle_{\rm i}/c_{\rm Ag} \to \langle c_{\rm A}\rangle_{\rm i}$, $r/R \to r$ and $D_{\rm eff}t/R^2 \to 1$, and where $N_{\rm Da} = k_{\rm eff}R^2/D_{\rm eff}$. From Exercise 10.6, we can write

$$\langle c_{\rm A}\rangle_{\rm i} = \int_0^t \frac{\partial\widehat{\langle c_{\rm A}\rangle}_{\rm i}}{\partial t}\exp(-N_{\rm Da}t')dt',$$

where $\widehat{\langle c_{\mathrm{A}}\rangle}_{\mathrm{i}}$ is the solution to the problem above with $N_{\mathrm{Da}}=0$. From Exercise 7.12 we have

$$\widehat{\langle c_{\mathrm{A}}\rangle}_{\mathrm{i}} = 1 + \frac{2}{\pi}\frac{1}{r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin(n\pi r)\exp(-n^2\pi^2 t).$$

Differentiation with respect to t and substitution gives

$$\langle c_{\mathrm{A}}\rangle_{\mathrm{i}} = -2\pi\frac{1}{r}\sum_{n=1}^{\infty} n(-1)^n \sin(n\pi r)\int_0^t \exp[-(n^2\pi^2 + N_{\mathrm{Da}})t']dt',$$

which, when the integration is performed, gives (23.40).

Exercise 23.5

Since $H/R \ll 1$, the diffusion is one-dimensional so that $\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}$ is governed by

$$D_{\mathrm{eff}}\frac{d^2\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}}{dz^2} - k_{\mathrm{eff}}\langle c_{\mathrm{A}}\rangle_{\mathrm{i}} = 0\,,$$

$$\frac{d\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}}{dz}(0) = 0, \qquad \langle c_{\mathrm{A}}\rangle_{\mathrm{i}}(H) = 1,$$

which has the solution

$$\frac{\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}}{c_{\mathrm{Ag}}} = \frac{\cosh\left(\sqrt{N_{\mathrm{Da}}}\frac{z}{H}\right)}{\cosh\left(\sqrt{N_{\mathrm{Da}}}\right)}\,,$$

where $N_{\mathrm{Da}} = k_{\mathrm{eff}}H^2/D_{\mathrm{eff}}$. Substitution in (23.42) gives

$$\eta = \frac{1}{H}\int_0^H \frac{\cosh\left(\sqrt{N_{\mathrm{Da}}}\frac{z}{H}\right)}{\cosh\left(\sqrt{N_{\mathrm{Da}}}\right)}dz = \frac{\tanh(\sqrt{N_{\mathrm{Da}}})}{\sqrt{N_{\mathrm{Da}}}},$$

which gives (23.42) with $N'_{\mathrm{Th}} = \sqrt{N_{\mathrm{Da}}}$, with $L = V/A = H$.

Exercise 23.6

Using the results from Exercise 10.8 we can write the boundary condition

$$-D_{\mathrm{eff}}\frac{d\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}}{\partial r}(R) = \frac{\tilde{k}_{\mathrm{m}}}{c}[\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}(R) - c_{\mathrm{Ag}}].$$

Using the normalizations $\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}/c_{\mathrm{Ag}} \to \langle c_{\mathrm{A}}\rangle_{\mathrm{i}}$ and $r/R \to r$, the equations governing $\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}$ are given by

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}}{dr}\right) - N_{\mathrm{Da}}\langle c_{\mathrm{A}}\rangle_{\mathrm{i}} = 0$$

$$\frac{d\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}}{\partial r}(0) = 0, \qquad \frac{d\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}}{dr}(1) = -N_{\mathrm{Sh}}[\langle c_{\mathrm{A}}\rangle_{\mathrm{i}}(1) - 1],$$

where $N_{\text{Da}} = k_{\text{eff}}R^2/D_{\text{eff}}$ and $N_{\text{Sh}} = \tilde{k}_{\text{m}}R/(cD_{\text{eff}})$. To solve (see Exercise 7.12), we use $u = \langle c_{\text{A}}\rangle_{\text{i}}/r$, so that

$$\frac{d^2u}{dr^2} - N_{\text{Da}}u = 0\,,$$

$$u(0) = 0, \qquad \frac{du}{dr}(1) = -[(1 + N_{\text{Sh}})u(1) - 1].$$

The solution for u has the form

$$u = c_1 \exp(\sqrt{N_{\text{Da}}}r) + c_1 \exp(-\sqrt{N_{\text{Da}}}r)\,.$$

The first boundary condition gives $c_2 = -c_1$ so that

$$u = c_1[\exp(\sqrt{N_{\text{Da}}}r) - \exp(-\sqrt{N_{\text{Da}}}r)] = 2c_1 \sinh(\sqrt{N_{\text{Da}}}r)\,.$$

Using the second boundary condition leads to

$$2c_1 = \frac{N_{\text{Sh}}}{(1 + N_{\text{Sh}})\sinh(\sqrt{N_{\text{Da}}}) + \sqrt{N_{\text{Da}}}\cosh(\sqrt{N_{\text{Da}}})}\,,$$

so that

$$\langle c_{\text{A}}\rangle_{\text{i}} = \frac{u}{r} = \frac{N_{\text{Sh}}\sinh(\sqrt{N_{\text{Da}}}r)}{r[(1 + N_{\text{Sh}})\sinh(\sqrt{N_{\text{Da}}}) + \sqrt{N_{\text{Da}}}\cosh(\sqrt{N_{\text{Da}}})]}\,.$$

Substitution in (23.42) gives

$$\eta = \frac{3N_{\text{Sh}}[\sqrt{N_{\text{Da}}}\coth(\sqrt{N_{\text{Da}}}) - 1]}{N_{\text{Da}}[(1 + N_{\text{Sh}})\sinh(\sqrt{N_{\text{Da}}}) + \sqrt{N_{\text{Da}}}\cosh(\sqrt{N_{\text{Da}}})]},$$

which, using $N'_{\text{Th}} = \sqrt{N_{\text{Da}}}/3$, gives the desired result.

Exercise 23.7

Using $\langle \boldsymbol{v}\rangle_{\text{s}} = \varepsilon_{\text{b}}\langle \boldsymbol{v}\rangle_{\text{i}}$ and $\boldsymbol{\kappa} = \kappa_{\text{b}}\boldsymbol{\delta}$, we can write

$$\varepsilon_{\text{b}}\langle \boldsymbol{v}\rangle_{\text{i}} = -\frac{\kappa_{\text{b}}}{\eta}\boldsymbol{\nabla}\langle \mathcal{P}\rangle_{\text{i}} + \kappa_{\text{b}}\nabla^2\langle \boldsymbol{v}\rangle_{\text{i}}\,.$$

Following the approach used in Section 8.1, we postulate the intrinsic average velocity to have the form $\langle v_r\rangle_{\text{i}} = \langle v_\theta\rangle_{\text{i}} = 0, \langle v_z\rangle_{\text{i}} = \langle v_z\rangle_{\text{i}}(r, z)$. Applying the constraint

$$\frac{\partial\langle v_z\rangle_{\text{i}}}{\partial z} = 0\,,$$

we have $\langle v_z\rangle_{\text{i}} = \langle v_z\rangle_{\text{i}}(r)$. From the constrained velocity, the r- and θ-components of the momentum balance imply $\langle \mathcal{P}\rangle_{\text{i}} = \langle \mathcal{P}\rangle_{\text{i}}(z)$. This allows the z-component of the momentum balance to be written as

$$\frac{d\langle \mathcal{P}\rangle_{\text{i}}}{dz} = \frac{\eta}{r}\frac{d}{dr}\left(r\frac{d\langle v_z\rangle_{\text{i}}}{dr}\right) - \eta\frac{\varepsilon_{\text{b}}}{\kappa_{\text{b}}}\langle v_z\rangle_{\text{i}} = C\,,$$

where $C = \Delta\langle\mathcal{P}\rangle_{\mathrm{i}}/L_{\mathrm{b}}$. Introducing

$$u = -\frac{\eta}{C}\frac{\varepsilon_{\mathrm{b}}}{\kappa_{\mathrm{b}}}\langle v_z\rangle_{\mathrm{i}} - 1\,,$$

we can write

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{du}{dr}\right) - N^2 u = 0\,,$$

where we have normalized radial position $r/R_{\mathrm{b}} \to r$, and introduced $N = \sqrt{\varepsilon_{\mathrm{b}} R_{\mathrm{b}}^2/\kappa_{\mathrm{b}}}$. Using the no-slip condition $\langle v_z\rangle_{\mathrm{i}}(1) = 0$ and enforcing regularity at $r = 0$, we find

$$\langle v_z\rangle_{\mathrm{i}} = -\frac{\Delta\langle\mathcal{P}\rangle_{\mathrm{i}}\kappa_{\mathrm{b}}}{\eta L_{\mathrm{b}}\varepsilon_{\mathrm{b}}}\left[1 - \frac{I_0(Nr)}{I_0(N)}\right],$$

where $I_0(x)$ is the modified Bessel function of the first kind. To find the mass flow rate $\mathcal{W}$ we write

$$\mathcal{W} = 2\pi R_{\mathrm{b}}^2 \int_0^1 \rho\langle v_z\rangle_{\mathrm{s}} r dr = -\frac{\rho\pi R_{\mathrm{b}}^2\kappa_{\mathrm{b}}\Delta\langle\mathcal{P}\rangle_{\mathrm{i}}}{\eta L_{\mathrm{b}}}\left[1 - \frac{2I_1(N)}{NI_0(N)}\right].$$

For $\varepsilon_{\mathrm{b}} R_{\mathrm{b}}^2/\kappa \gg 1$, we obtain

$$\mathcal{W} = -\frac{\rho\pi R_{\mathrm{b}}^2\kappa_{\mathrm{b}}\Delta\langle\mathcal{P}\rangle_{\mathrm{i}}}{\eta L_{\mathrm{b}}}\,.$$

Exercise 23.8

Flow in the liquid film is governed by the constraint on velocity (5.36),

$$\frac{1}{r}\frac{\partial}{\partial r}(r v_r) + \frac{\partial v_z}{\partial z} = 0,$$

and r-component of the Navier-Stokes equations (7.8)

$$\eta\frac{\partial^2 v_r}{\partial z^2} = \frac{dp}{dr},$$

where the lubrication approximation has been invoked. Boundary conditions at the impermeable disk are given by

$$v_r(r,0) = 0, \qquad v_z(r,0) = 0,$$

and at the permeable disk by

$$v_r(r,H) = 0, \qquad v_z(r,H) = \langle v_z\rangle_{\mathrm{s}}(r,H) + \dot{H},$$

where $\langle \boldsymbol{v}\rangle_{\mathrm{s}}$ is the superficial average velocity in the porous disk. Integration of the Navier-Stokes equation with respect to z and applying the boundary conditions for v_r gives

$$v_r = -\frac{H^2}{2\eta}\frac{dp}{dr}\Big[\frac{z}{H} - \Big(\frac{z}{H}\Big)^2\Big].$$

Substitution in the constraint on velocity and integration over z from 0 to H with the boundary conditions for for v_z gives

$$\frac{1}{r}\frac{d}{dr}\Big(r\frac{dp}{dr}\Big) = \frac{12\eta}{H^3}[\langle v_z\rangle_{\rm s}(r,H) + \dot{H}],$$

which is Reynolds equation.

Flow in the porous disk is governed

$$\boldsymbol{\nabla}\cdot\langle\boldsymbol{v}\rangle_{\rm s} = 0,$$

and Darcy's law, which is obtained by dropping the second term in (23.54),

$$\langle\boldsymbol{v}\rangle_{\rm s} = -\frac{\kappa}{\eta}\boldsymbol{\nabla}\langle p^{\rm L}\rangle_{\rm i},$$

Combining these, we can write

$$\frac{1}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial\langle p^{\rm L}\rangle_{\rm i}}{\partial r}\Big) + \frac{\partial^2\langle p^{\rm L}\rangle_{\rm i}}{\partial z^2} = 0.$$

The boundary conditions for $\langle p^{\rm L}\rangle_{\rm i}$ are given by

$$\langle p^{\rm L}\rangle_{\rm i}(r,H) = p(r), \qquad \frac{\partial\langle p^{\rm L}\rangle_{\rm i}}{\partial z}(r,H+b) = 0,$$

$$\frac{\partial\langle p^{\rm L}\rangle_{\rm i}}{\partial r}(0,z) = 0, \qquad \langle p^{\rm L}\rangle_{\rm i}(R,z) = 0.$$

Also, using Darcy's law, we can write Reynolds equation as

$$\frac{1}{r}\frac{d}{dr}\Big(r\frac{dp}{dr}\Big) = -\frac{12\kappa}{H^3}\frac{\partial\langle p^{\rm L}\rangle_{\rm i}}{\partial z}(r,H) + \frac{12\eta}{H^3}\dot{H}.$$

The solution for $\langle p^{\rm L}\rangle_{\rm i}$ can be written as

$$\langle p^{\rm L}\rangle_{\rm i} = \sum_{n=1}^{\infty} A_n J_0(\alpha_n r)\cosh[\alpha_n(b+H-z)],$$

where the α_n are the roots of $J_0(\alpha_n R) = 0$, and

$$A_n = \frac{2}{R^2 J_1^2(\alpha_n R)\cosh(\alpha_n b)}\int_0^R p(r)J_0(\alpha_n r)r\,dr,$$

which follows from the orthogonality of $J_0(\alpha_n r)$. Substitution of $\langle p^{\mathrm{L}}\rangle_{\mathrm{i}}$ in Reynolds equation, we obtain

$$\frac{1}{r}\frac{d}{dr}\Big(r\frac{dp}{dr}\Big) = \frac{12\eta}{H^3}\dot{H} + \frac{12\kappa}{H^3}\sum_{n=1}^{\infty} A_n\alpha_n \sinh(\alpha_n b) J_0(\alpha_n r).$$

Integrating with respect to r using the boundary condition $p(R) = 0$, gives

$$p = -3\eta R^2 \frac{\dot{H}}{H^3}\Big[1 - \Big(\frac{r}{R}\Big)^2\Big] - \frac{12\kappa}{H^3}\sum_{n=1}^{\infty}\frac{A_n}{\alpha_n}\sinh(\alpha_n b) J_0(\alpha_n r).$$

Substitution of p in the expression for A_n gives

$$A_n = -24\eta R^2 \frac{\dot{H}}{H^3}\frac{1}{(\alpha_n R)^3 J_1(\alpha_n R)\cosh(\alpha_n b)}\Big[1 + \frac{12\kappa R}{H^3}\frac{\tanh(\alpha_n b)}{\alpha_n R}\Big]^{-1},$$

so that the pressure in the liquid film is given by,

$$p = -3\eta R^2 \frac{\dot{H}}{H^3}\Big\{\Big[1-\Big(\frac{r}{R}\Big)^2\Big] - 8\sum_{n=1}^{\infty}\frac{J_0(\alpha_n r)}{(\alpha_n R)^3 J_1(\alpha_n R)}\Big[1+\frac{H^3}{12\kappa R}\frac{\alpha_n R}{\tanh(\alpha_n b)}\Big]^{-1}\Big\}.$$

The applied force $\mathcal{F}_{\mathrm{s}}$ is obtained by integrating p over the surface of the porous disk, which gives

$$\mathcal{F}_{\mathrm{s}} = 2\pi\int_0^R p r dr = -\frac{3}{2}\eta\pi R^4 \frac{\dot{H}}{H^3}\Big\{1 - 16\sum_{n=1}^{\infty}\frac{1}{(\alpha_n R)^4\Big[1 + \frac{H^3}{12\kappa R}\frac{\alpha_n R}{\tanh(\alpha_n b)}\Big]}\Big\}.$$

Exercise 24.1

If N is the number of completed cycles and t the elapsed time, the formula for conditional probabilities implies

$$P(N|t) = c(t)\, p(t|N)\,,$$

where $c(t)$ is a normalization constant and N is assumed to be uniformly distributed (over a very large range). The probability $p(t|N)$ describes the sum of the dwell times for independent cycles. Its Fourier transform can hence be obtained from the product of the Fourier transforms of the individual cycles and steps, where the Fourier transform of exponential decay with rate Γ is $\Gamma/(\Gamma + i\omega)$. We hence have

$$P(N|t) = \tilde{c}(t)\int_{-\infty}^{\infty} e^{i\omega t}\Big[\frac{\Gamma_1\Gamma_2}{(\Gamma_1 + i\omega)(\Gamma_2 + i\omega)}\Big]^{N+1} d\omega\,,$$

where $\Gamma_1 = \Gamma_{\mathrm{A}}^- + \Gamma_{\mathrm{B}}^+$ and $\Gamma_2 = \Gamma_{\mathrm{A}}^+ + \Gamma_{\mathrm{B}}^-$ are the rates for going up and down in Figure 24.2. Note that the power $N + 1$ has been chosen because

N completed steps require that we are performing step $N + 1$ (without a completed cycle, we have the dwell time distribution of the first cycle).

It is now straightforward to calculate the desired moments of $P(N|t)$. If we multiply the above expression by z^N and sum up the geometric series over N, exponential decay with rate Γ is $\Gamma/(\Gamma + i\omega)$. We hence have

$$G_t(z) = \sum_{N=0}^{\infty} z^N P(N|t) = \tilde{c}(t) \int_{-\infty}^{\infty} e^{i\omega t} \frac{\Gamma_1 \Gamma_2}{(\Gamma_1 + i\omega)(\Gamma_2 + i\omega) - z\Gamma_1\Gamma_2} \, d\omega \,,$$

the normalization constant, first moment and second moment can be obtained by differentiation zero, one and two times with respect to z and then setting $z = 1$. For the respective Fourier transforms we find:

$$G_t(1) = \pi \tilde{c}(t) \frac{\Gamma_1 \Gamma_2}{\Gamma_1 + \Gamma_2} \left[1 - 2e^{-(\Gamma_1+\Gamma_2)t} \right] \,,$$

$$G_t'(1) = \pi \tilde{c}(t) \frac{(\Gamma_1 \Gamma_2)^2}{(\Gamma_1 + \Gamma_2)^3} \left\{ (\Gamma_1 + \Gamma_2)t - 2 + 2[(\Gamma_1 + \Gamma_2)t + 2] e^{-(\Gamma_1+\Gamma_2)t} \right\} \,,$$

and

$$\begin{aligned} G_t''(1) = \pi \tilde{c}(t) \frac{(\Gamma_1 \Gamma_2)^3}{(\Gamma_1 + \Gamma_2)^5} \Big\{ & (\Gamma_1 + \Gamma_2)^2 t^2 - 6(\Gamma_1 + \Gamma_2)t + 12 \\ & - 2[(\Gamma_1 + \Gamma_2)^2 t^2 + 6(\Gamma_1 + \Gamma_2)t + 12] e^{-(\Gamma_1+\Gamma_2)t} \Big\} \,. \end{aligned}$$

After neglecting exponentially decaying terms for large times, $G_t'(1)/G_t(1)$ and $G_t''(1)/G_t(1)$ coincide with (24.12) and (24.13).

Exercise 24.2

By means of the δ-function, the double integral in (24.18) can be reduced to the single integral

$$p(t) = \Gamma_1 \Gamma_2 \int_0^t dt_1 e^{-\Gamma_1 t_1} e^{-\Gamma_2 (t - t_1)} \,,$$

which corresponds to the convolution integral associated with the sum of independent random variables. The remaining integration of an exponential is straightforward,

$$p(t) = \Gamma_1 \Gamma_2 e^{-\Gamma_2 t} \int_0^t dt_1 e^{-(\Gamma_1 - \Gamma_2)t_1} = \Gamma_1 \Gamma_2 e^{-\Gamma_2 t} \frac{1 - e^{-(\Gamma_1 - \Gamma_2)t}}{\Gamma_1 - \Gamma_2} \,,$$

which can be rewritten as the desired result.

Exercise 24.3

From the ansatz we have $p(t, z \pm 1, j) = p(t, z, j)\, e^{\pm ika}$. By inserting the ansatz into the master equations (24.4) and (24.5) we hence obtain

$$-i\omega C_0 = C_1(\Gamma_{\mathrm{A}}^{+} e^{-ika} + \Gamma_{\mathrm{B}}^{-}) - C_0(\Gamma_{\mathrm{A}}^{-} + \Gamma_{\mathrm{B}}^{+})$$
$$-i\omega C_1 = C_0(\Gamma_{\mathrm{A}}^{-} e^{+ika} + \Gamma_{\mathrm{B}}^{+}) - C_1(\Gamma_{\mathrm{A}}^{+} + \Gamma_{\mathrm{B}}^{-})\,.$$

In matrix form, this equation can be written as

$$\begin{pmatrix} -i\omega + \Gamma_{\mathrm{A}}^{-} + \Gamma_{\mathrm{B}}^{+} & -(\Gamma_{\mathrm{A}}^{+} e^{-ika} + \Gamma_{\mathrm{B}}^{-}) \\ -(\Gamma_{\mathrm{A}}^{-} e^{ika} + \Gamma_{\mathrm{B}}^{+}) & -i\omega + \Gamma_{\mathrm{A}}^{+} + \Gamma_{\mathrm{B}}^{-} \end{pmatrix} \cdot \begin{pmatrix} C_0 \\ C_1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Nontrivial solutions C_0, C_1 exist only for zero determinant of the matrix,

$$(-i\omega + \Gamma_{\mathrm{A}}^{-} + \Gamma_{\mathrm{B}}^{+})(-i\omega + \Gamma_{\mathrm{A}}^{+} + \Gamma_{\mathrm{B}}^{-}) = (\Gamma_{\mathrm{A}}^{+} e^{-ika} + \Gamma_{\mathrm{B}}^{-})(\Gamma_{\mathrm{A}}^{-} e^{ika} + \Gamma_{\mathrm{B}}^{+})\,.$$

With the definitions (24.7), (24.14) of Γ, Γ_{tot} and the further definition $\Gamma'(k) = (\Gamma_{\mathrm{A}}^{+} e^{-ika} + \Gamma_{\mathrm{B}}^{-})(\Gamma_{\mathrm{A}}^{-} e^{ika} + \Gamma_{\mathrm{B}}^{+})$, we find the solution

$$\omega(k) = \frac{1}{2}\left[\sqrt{4(\Gamma - \Gamma'(k)) - \Gamma_{\mathrm{tot}}^2} - i\Gamma_{\mathrm{tot}}\right].$$

For small k, the Taylor expansions $e^{\pm ika} \approx 1 \pm ika - \frac{1}{2}(ka)^2$ lead to

$$\Gamma'(k) \approx \Gamma - ika(\Gamma_{\mathrm{A}}^{+}\Gamma_{\mathrm{B}}^{+} - \Gamma_{\mathrm{A}}^{-}\Gamma_{\mathrm{B}}^{-}) - \frac{1}{2}(ka)^2(\Gamma_{\mathrm{A}}^{+}\Gamma_{\mathrm{B}}^{+} + \Gamma_{\mathrm{A}}^{-}\Gamma_{\mathrm{B}}^{-})\,.$$

By inserting this result into $\omega(k)$ after expanding the square root, we obtain

$$\begin{aligned}\omega(k) = i\frac{\Gamma'(k) - \Gamma}{\Gamma_{\mathrm{tot}}} - i\frac{(\Gamma'(k) - \Gamma)^2}{\Gamma_{\mathrm{tot}}^3} &= ka\frac{\Gamma_{\mathrm{A}}^{+}\Gamma_{\mathrm{B}}^{+} - \Gamma_{\mathrm{A}}^{-}\Gamma_{\mathrm{B}}^{-}}{\Gamma_{\mathrm{tot}}} \\ &- \frac{i}{2}(ka)^2\left[\frac{\Gamma_{\mathrm{A}}^{+}\Gamma_{\mathrm{B}}^{+} + \Gamma_{\mathrm{A}}^{-}\Gamma_{\mathrm{B}}^{-}}{\Gamma_{\mathrm{tot}}} - 2\frac{\left(\Gamma_{\mathrm{A}}^{+}\Gamma_{\mathrm{B}}^{+} - \Gamma_{\mathrm{A}}^{-}\Gamma_{\mathrm{B}}^{-}\right)^2}{\Gamma_{\mathrm{tot}}^3}\right].\end{aligned}$$

In view of the definitions (24.15) and (24.16), this is the desired result. We have thus found an alternative derivation of A_0 and D_0.

Exercise 24.4

For a rough estimate, we assume that 1 kg of muscle contains 0.5 kg of myosin. For a molecular weight of about 500 kg/mol, we would have 0.001 mol of myosin per 1 kg of muscle. If each molecule performs 10 steps per second or 36000 steps per hour, 36 moles of ATP are hydrolyzed in an hour. This corresponds to some 260 kcal. A racing cyclist can burn more than 1000 kcal per hour, which would corresponds to 4 kg of muscle at maximum work rate (to be compared to a total muscle mass of about 30 kg).

Exercise 24.5

The required energy is 10 J or 2.4 cal. According to Exercise 24.4, 5 kg of muscle mass can provide 1300 kcal per hour. The required minimum time hence is $2.4/(1.3 \times 10^6)$ h or 7 ms. As the world record in weightlifting is more than 250 kg, more muscle mass must be involved.

Exercise 24.6

Differentiation of (24.29) with respect to Z and setting this result equal to zero, we obtain

$$Z_{\text{max}} = \frac{1 - \sqrt{1 - q^2}}{q}$$

Now, rearranging the second equation in (24.30) we obtain

$$\Delta\tilde{\mu}_{\text{Ca}} = -\mathcal{A}^{\text{s}} \sqrt{\frac{L_{\mathcal{A}\mathcal{A}} \tilde{M}_{\text{Ca}}^2}{L_{\text{CaCa}}}} Z$$

Setting $Z \to Z_{\text{max}}$ in the last expression and combining with the first gives

$$\Delta\tilde{\mu}_{\text{Ca}} = -\mathcal{A}^{\text{s}} \sqrt{\frac{L_{\mathcal{A}\mathcal{A}} \tilde{M}_{\text{Ca}}^2}{L_{\text{CaCa}}}} Z_{\text{max}}$$

For ideal solution behavior we have $\Delta\tilde{\mu}_{\text{Ca}} = \tilde{R}T \ln(x_{\text{Ca}}^{\text{I}}/x_{\text{Ca}}^{\text{II}})$. Combining with the last expression gives the desired result. Since $\mathcal{A}^{\text{s}} < 0$, $L_{\mathcal{A}\mathcal{A}}, L_{\text{CaCa}}$ are positive, and $q < 1$, then $x_{\text{Ca}}^{\text{I}}/x_{\text{Ca}}^{\text{II}} > 1$.

Exercise 24.7

The given reaction involves $(n = 2)$ two reactions: $\text{E}+\text{S} \rightleftarrows \text{ES}$, $\text{ES} \to \text{E}+\text{P}$. The stoichiometric coefficients for reaction 1 are $\tilde{\nu}_{\text{E},1} = \tilde{\nu}_{\text{S},1} = -1, \tilde{\nu}_{\text{ES},1} = 1, \tilde{\nu}_{\text{P},1} = 0$; for reaction 2 they are $\tilde{\nu}_{\text{E},2} = \tilde{\nu}_{\text{S},2} = 0, \tilde{\nu}_{\text{ES},2} = -1, \tilde{\nu}_{\text{P},2} = 1$. The reaction fluxes $\tilde{\Gamma}_i = -L_i(e^{x_i} - e^{y_i})$ for each reaction are

$$\tilde{\Gamma}_1 = -L_1\Big[\exp\Big(\frac{\tilde{\mu}_{\text{ES}}}{\tilde{R}T}\Big)x_{\text{ES}} - \exp\Big(\frac{\tilde{\mu}_{\text{E}} + \tilde{\mu}_{\text{S}}}{\tilde{R}T}\Big)x_{\text{E}}x_{\text{S}}\Big] = k_{1\text{f}}x_{\text{E}}x_{\text{S}} - k_{1\text{r}}x_{\text{ES}}\,,$$

$$\tilde{\Gamma}_2 = -L_2\Big[\exp\Big(\frac{\tilde{\mu}_{\text{P}}}{\tilde{R}T}\Big)x_{\text{P}} - \exp\Big(\frac{\tilde{\mu}_{\text{ES}}}{\tilde{R}T}\Big)x_{\text{ES}}\Big] = k_{2\text{f}}x_{\text{ES}}\,,$$

where second equalities follow using (4.60) and $K_2 \gg 1$, that is, the second reaction is 'irreversible.' The species mass balances in terms of the species mole fractions from Exercise 5.6, assuming both convective and diffusive mass transport can be neglected, can be written as

$$c\frac{dx_\alpha}{dt} = \sum_{j=1}^{n} \tilde{\nu}_{\alpha,j}\tilde{\Gamma}_j = \tilde{\nu}_{\alpha,1}\tilde{\Gamma}_1 + \tilde{\nu}_{\alpha,2}\tilde{\Gamma}_2 \,.$$

Hence, we can write

$$c\frac{dx_{\rm E}}{dt} = -k_{\rm 1f}x_{\rm E}x_{\rm S} + k_{\rm 1r}x_{\rm ES} \,,$$

$$c\frac{dx_{\rm ES}}{dt} = k_{\rm 1f}x_{\rm E}x_{\rm S} - k_{\rm 1r}x_{\rm ES} - k_{\rm 2f}x_{\rm ES} \,,$$

$$c\frac{dx_{\rm P}}{dt} = k_{\rm 2f}x_{\rm ES} \,.$$

Now, setting $dx_{\rm ES}/dt = 0$, we obtain

$$x_{\rm ES} = \frac{k_{\rm 1f}}{k_{\rm 1r} + k_{\rm 2f}} x_{\rm E}x_{\rm S} = K_{\rm M}^{-1} x_{\rm E}x_{\rm S} \,,$$

where $K_{\rm M} = (k_{\rm 1r} + k_{\rm 2f})/k_{\rm 1f}$. Adding this to $x_{\rm E}$ and substituting in the expression for $dx_{\rm P}/dt$ gives the desired result.

Exercise 24.8

By changing the normalization, we can rewrite (24.53) as

$$\frac{\partial}{\partial\gamma}\left\{\exp\left[\frac{\Phi(\gamma)}{\tilde{R}T}\right] p(\gamma)\right\} = \exp\left[\frac{\Phi(\gamma)}{\tilde{R}T}\right] p(\gamma)\,\frac{1}{\tilde{R}T}\frac{\partial\tilde{G}(\gamma)}{\partial\gamma} \,.$$

By means of the definition (24.41), we further obtain

$$\frac{\partial}{\partial\gamma}\left\{\exp\left[\frac{\tilde{G}(\gamma)}{\tilde{R}T}\right]\right\} = \exp\left[\frac{\tilde{G}(\gamma)}{\tilde{R}T}\right]\,\frac{1}{\tilde{R}T}\frac{\partial\tilde{G}(\gamma)}{\partial\gamma} \,,$$

which is an immediate consequence of the chain rule. The second identity in (24.53) follows by once more using the definition (24.41).

Exercise 24.9

In the absence of slippage, the cross effect reaches its maximum possible value and the Onsager matrix in the force-flux relations (24.39), (24.40) becomes degenerate, which means

$$l_{\mathcal{A}\mathcal{A}}(\gamma)\, l_{\rm CaCa}(\gamma) - l_{\mathcal{A}{\rm Ca}}(\gamma)\, l_{{\rm Ca}\mathcal{A}}(\gamma) = 0 \,.$$

According to the definitions (24.46) and (24.47) this implies $n = n'$. It has already been argued in the text that, without slippage, we have $n = 2$ because the ATPase has two binding sites for Ca^{2+} ions. A positive determinant of the Onsager matrix implies $n/n' < 1$, where n and n' have the same sign.

Exercise 24.10
According to (2.20), we have the normalized equilibrium solution

$$p_{\rm eq}(\gamma) = \exp\left[-\frac{\Phi(\gamma)}{\tilde{R}T}\right] \left\{\int_0^1 \exp\left[-\frac{\Phi(\gamma')}{\tilde{R}T}\right] d\gamma'\right\}^{-1} .$$

If we insert $c^{\rm s}_{\rm r,eq}(\gamma) = c^{\rm s,tot}_{\rm r} p_{\rm eq}(\gamma)$ into (24.51), the exponential factors cancel and we obtain (24.54).

Exercise 24.11
Equations (24.42) and (24.43) imply $\tilde{G}(1) - \tilde{G}(0) = \mathcal{A}^{\rm s}$. For small $\mathcal{A}^{\rm s}/(\tilde{R}T)$, we hence find the linearization

$$\exp\left[\frac{\tilde{G}(1)}{\tilde{R}T}\right] - \exp\left[\frac{\tilde{G}(0)}{\tilde{R}T}\right] \approx \exp\left[\frac{\tilde{G}(0)}{\tilde{R}T}\right] \frac{\mathcal{A}^{\rm s}}{\tilde{R}T} ,$$

where $\tilde{G}(0)$ in (24.41) can be evaluated at equilibrium,

$$\tilde{G}(0) \approx \Phi(0) + \tilde{R}T \ln p_{\rm eq}(0) = -\tilde{R}T \left\{\int_0^1 \exp\left[-\frac{\Phi(\gamma)}{\tilde{R}T}\right] d\gamma\right\} .$$

In the last step, the equilibrium solution given in the solution to Exercise 24.10 has been used. With (24.54) we obtain

$$\exp\left[\frac{\tilde{G}(1)}{\tilde{R}T}\right] - \exp\left[\frac{\tilde{G}(0)}{\tilde{R}T}\right] \approx \frac{\mathcal{N}_{\rm eq}}{c^{\rm s,tot}_{\rm r}} \frac{\mathcal{A}^{\rm s}}{\tilde{R}T} .$$

By comparing the linearized version of (24.48), (24.49) with (24.26), (24.27), we finally find the relation (24.52).

Exercise 25.1
For a Newtonian fluid with memory function $\zeta(t) = \zeta_0\delta(t)$ we obtain from (25.1) a Langevin equation

$$m\frac{d^2}{dt^2}\boldsymbol{r}_{\rm b}(t) = -\zeta_0 \frac{d}{dt'}\boldsymbol{r}_{\rm b}(t')dt' + \boldsymbol{f}_{\rm B}(t).$$

so that from (25.11) we have

$$\left\langle \overline{\Delta\boldsymbol{r}^2_{\rm b}[\omega]} \right\rangle_{\rm eq} = -\frac{2dk_{\rm B}T}{\omega^2\,(\zeta_0 + mi\omega)}.$$

Taking the inverse Fourier transform gives the following

$$\left\langle \Delta r_{\mathrm{b}}^2(t) \right\rangle_{\mathrm{eq}} = \frac{2dk_{\mathrm{B}}T}{\zeta_0}\Big(\frac{m}{\zeta_0} + t\Big),$$

which is diffusive for $t \gg m/\zeta_0$.

Exercise 25.2
With the definition of $h(t)$, we obtain the two-sided Fourier transform

$$\begin{aligned} h[\omega] &= \int_{-\infty}^{\infty} \int_{-\infty}^{t} f(t-t')g(t')e^{-i\omega t} dt' dt \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{t} f(t-t')g(t')e^{-i\omega(t-t')-i\omega t'} dt' dt \\ &= \int_{0}^{\infty} \int_{-\infty}^{\infty} f(s)g(t')e^{-i\omega s-i\omega t'} dt' ds = \bar{f}[\omega]\, g[\omega], \end{aligned}$$

where the substitution $s = t - t'$ has been performed.

Exercise 25.3
From the definition of $\bar{\zeta}[\omega]$ in the footnote on p. 441 we obtain

$$\bar{\zeta}[\omega]^* = \int_0^{\infty} \zeta(t)e^{i\omega t} dt = \bar{\zeta}[-\omega],$$

where the memory function $\zeta(t)$ is assumed to be real. We further have

$$\begin{aligned} \zeta[\omega] &= \int_{-\infty}^{0} \zeta(t)e^{-i\omega t} dt + \int_0^{\infty} \zeta(t)e^{-i\omega t} dt = \int_0^{\infty} \zeta(-t)e^{i\omega t} dt + \bar{\zeta}[\omega] \\ &= \int_0^{\infty} \zeta(t)e^{i\omega t} dt + \bar{\zeta}[\omega] = \bar{\zeta}[-\omega] + \bar{\zeta}[\omega] = 2\mathcal{R}\left\{\bar{\zeta}[\omega]\right\}. \end{aligned}$$

Exercise 25.4
Substituting the last line of (25.7) in (25.6) gives

$$\left\langle \boldsymbol{r}_{\mathrm{b}}[\omega]\boldsymbol{r}_{\mathrm{b}}[\omega'] \right\rangle_{\mathrm{eq}} = \frac{4\pi k_{\mathrm{B}}T\boldsymbol{\delta}\,\mathcal{R}\left\{\bar{\zeta}[\omega]\right\}\,\delta(\omega+\omega')}{\Big[H + i\omega\left(\bar{\zeta}[\omega] + mi\omega\right)\Big]\Big[H + i\omega'\left(\bar{\zeta}[\omega'] + mi\omega'\right)\Big]}.$$

The δ function implies $\omega' = -\omega$. We hence obtain

$$\left\langle \boldsymbol{r}_{\mathrm{b}}[\omega]\boldsymbol{r}_{\mathrm{b}}[\omega'] \right\rangle_{\mathrm{eq}} = \frac{4\pi k_{\mathrm{B}}T\boldsymbol{\delta}\,\mathcal{R}\left\{\bar{\zeta}[-\omega]\right\}\,\delta(\omega+\omega')}{\Big[\omega\bar{\zeta}[\omega] + i(m\omega^2 - H)\Big]\Big[\omega\bar{\zeta}[-\omega] - i(m\omega^2 - H)\Big]},$$

where, for the reformulation of the numerator, we have used the identity

$\bar{\zeta}[-\omega] = \bar{\zeta}[\omega]^*$, which implies $\mathcal{R}\left\{\bar{\zeta}[\omega]\right\} = \mathcal{R}\left\{\bar{\zeta}[-\omega]\right\}$. We rewrite this last expression in the slightly more complicated form

$$\left\langle \boldsymbol{r}_{\mathrm{b}}[\omega]\boldsymbol{r}_{\mathrm{b}}[\omega']\right\rangle_{\mathrm{eq}} = \frac{4\pi k_{\mathrm{B}}T\boldsymbol{\delta}\,\mathcal{R}\left\{\omega\bar{\zeta}[-\omega] - i(m\omega^2 - H)\right\}\,\delta(\omega+\omega')}{\omega\Big[\omega\bar{\zeta}[\omega] + i(m\omega^2 - H)\Big]\Big[\omega\bar{\zeta}[-\omega] - i(m\omega^2 - H)\Big]},$$

so that, after bringing all the real factors into the real-part operator $\mathcal{R}$ and canceling a common factor, we obtain (25.8).

Exercise 25.5

The sphere moves with velocity $\boldsymbol{v}_{\mathrm{b}} = v_{\mathrm{b}}(t)\boldsymbol{\delta}_3$. For the position vector $\boldsymbol{c}$ relating the stationary and moving coordinate systems we write

$$\frac{d\boldsymbol{c}}{dt} = -v_{\mathrm{b}}(t)\boldsymbol{\delta}_3.$$

For the time-dependent creeping flow of an incompressible fluid, we can write (11.3) as

$$\rho'\frac{\partial'\boldsymbol{v}'}{\partial t} = \eta\nabla'^2\boldsymbol{v}' - \boldsymbol{\nabla}'p^{\mathrm{L}\prime} - \rho'\frac{dv_{\mathrm{b}}}{dt}\boldsymbol{\delta}_3,$$

where we have neglected gravity and set $\boldsymbol{\omega} = \boldsymbol{0}$. Since the pseudo pressure is arbitrary, we combine it with the last term to define the modified pressure

$$\mathcal{P}' = p^{\mathrm{L}\prime} + \rho x_3'\frac{dv_{\mathrm{b}}}{dt}.$$

Hence, we can write our momentum balance for time-dependent creeping flow (dropping the primes) as

$$\rho\frac{\partial\boldsymbol{v}}{\partial t} = \eta\nabla^2\boldsymbol{v} - \boldsymbol{\nabla}\mathcal{P}.$$

Using the expressions for velocity in (17.19) and the results from Exercise 17.5, the r- and θ-components become

$$\frac{\partial\mathcal{P}}{\partial r} = \frac{\eta}{r^2\sin\theta}\frac{\partial}{\partial\theta}E^2\psi - \frac{\partial}{\partial t}\Big(\frac{\rho}{r^2\sin\theta}\frac{\partial\psi}{\partial\theta}\Big)$$

$$\frac{\partial\mathcal{P}}{\partial\theta} = -\frac{\eta}{\sin\theta}\frac{\partial}{\partial r}E^2\psi + \frac{\partial}{\partial t}\Big(\frac{\rho}{\sin\theta}\frac{\partial\psi}{\partial r}\Big)$$

Differentiation of $\partial\mathcal{P}/\partial r$ by θ and $\partial\mathcal{P}/\partial\theta$ by r and equating the two expressions gives

$$\eta\Big[\frac{1}{r^2}\frac{\partial}{\partial\theta}\Big(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\Big) + \frac{1}{\sin\theta}\frac{\partial^2}{\partial r^2}\Big]E^2\psi = \rho\Big[\frac{1}{r^2}\frac{\partial}{\partial\theta}\Big(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\Big) + \frac{1}{\sin\theta}\frac{\partial^2}{\partial r^2}\Big]\frac{\partial\psi}{\partial t},$$

which, recognizing E^2 as the operator in (17.20), is easily rearranged to give the desired result.

Exercise 25.6
Neglecting the second term in (25.17) gives

$$\bar{\zeta}[\omega] = -\frac{6\pi R i\omega}{\omega^2} G^*(\omega) = \frac{6\pi R g\lambda}{1+\lambda i\omega} = \frac{\zeta}{1+\lambda i\omega}$$

where the second equality follows for a single-mode Maxwell fluid where $G^*(\omega) = g\lambda i\omega/(1+\lambda i\omega)$, and the third from setting $\zeta = 6\pi R g\lambda$. Substitution of this result in (25.11) and setting $d = 3$ gives

$$\left\langle \overline{\Delta \boldsymbol{r}_{\mathrm{b}}^2}[\omega] \right\rangle_{\mathrm{eq}} = \frac{6k_{\mathrm{B}}T}{\zeta(i\omega)^2} \frac{1+\lambda i\omega}{1+(\tau_m/\lambda)^2(\lambda i\omega) + (\tau_m/\lambda)^2(\lambda i\omega)^2},$$

where $\tau_m = \sqrt{m\lambda/\zeta}$. Using the equivalence between the one-sided Fourier transform and the Laplace transform, we set $i\omega \to s$. Inversion to the time domain gives

$$\begin{aligned}\left\langle \Delta r_{\mathrm{b}}^2(t) \right\rangle_{\mathrm{eq}} &= \frac{6k_{\mathrm{B}}T}{\zeta\lambda(4\lambda^2-\tau_m^2)} \Bigg(4\lambda^3(t+\lambda) - (t+5\lambda)\lambda\tau_m^2 + \tau_m^4 \\ &-e^{-\frac{t}{2\lambda}} \Big[(4\lambda^4 - 5\lambda^2\tau_m^2 + \tau_m^4)\cosh(\omega_m t) - 2\omega_m\lambda\tau_m^2(3\lambda^2-\tau_m^2)\sinh(\omega_m t) \Big] \Bigg),\end{aligned}$$

where $\omega_m = \sqrt{4\lambda^2 - \tau_m^2}/(2\lambda\tau_m)$. Simplifying this expression for $\tau_m \ll \lambda$ gives

$$\left\langle \Delta r_{\mathrm{b}}^2(t) \right\rangle_{\mathrm{eq}} \approx \frac{k_{\mathrm{B}}T}{\pi R g} \left\{ 1 + \frac{t}{\lambda} - \exp\left(\frac{-t}{2\lambda}\right) \left[\cos(\omega_m t) + \frac{3\tau_m}{2\lambda}\sin(\omega_m t) \right] \right\},$$

where $\omega_m \approx 1/\tau_m$.

Exercise 26.1
We begin by writing

$$\mid \boldsymbol{R} - \boldsymbol{r}_j \mid^2 = R^2 - 2\boldsymbol{R}\cdot\boldsymbol{r}_j + r_j^2 = R^2\Big(1 - 2\frac{\boldsymbol{r}_j}{R}\cdot\frac{\boldsymbol{R}}{R} + \frac{r_j^2}{R^2}\Big) \approx R^2\Big(1 - 2\frac{\boldsymbol{r}_j}{R}\cdot\frac{\boldsymbol{R}}{R}\Big)$$

where the last expression follows since $R \gg r_j$. Taking the square root of the above result gives

$$\mid \boldsymbol{R} - \boldsymbol{r}_j \mid \approx R\Big(1 - 2\frac{\boldsymbol{r}_j}{R}\cdot\frac{\boldsymbol{R}}{R}\Big)^{1/2} \approx R - \boldsymbol{r}_j\cdot\frac{\boldsymbol{R}}{R}$$

Using this result, we write

$$e^{ik_{\mathrm{s}}|\boldsymbol{R}-\boldsymbol{r}_j|} \approx e^{i(k_{\mathrm{s}}R - \boldsymbol{r}_j\cdot k_{\mathrm{s}}\boldsymbol{R}/R)} = e^{ik_{\mathrm{s}}R}e^{-\boldsymbol{k}_{\mathrm{s}}\cdot\boldsymbol{r}_j},$$

where the last result follows since $\boldsymbol{k}_{\mathrm{s}} = k_{\mathrm{s}}\boldsymbol{R}/R$. Combining these results the expression in (26.13) is obtained.

Exercise 26.2
Using (26.23) to eliminate pressure, the evolution equations given in (7.1), (7.7) and (7.3) can be written as follows

$$\frac{\partial \rho}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} \rho = -\rho \boldsymbol{\nabla} \cdot \boldsymbol{v},$$

$$\rho\Big(\frac{\partial \boldsymbol{v}}{\partial t} + \frac{1}{2}\boldsymbol{\nabla} v^2 - \boldsymbol{v} \times \boldsymbol{w}\Big) = -\eta \boldsymbol{\nabla} \times \boldsymbol{w} + \Big(\eta_{\mathrm{d}} + \frac{4}{3}\eta\Big)\boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \boldsymbol{v}) - \frac{\rho {c_{\hat{s}}}^2}{\gamma}\Big(\alpha_p \boldsymbol{\nabla} T + \frac{\boldsymbol{\nabla}\rho}{\rho}\Big).$$

where $\boldsymbol{w} = \boldsymbol{\nabla} \times \boldsymbol{v}$ and we have neglected the gravitational force and,

$$\rho \hat{c}_{\hat{v}}\Big(\frac{\partial T}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} T\Big) = \lambda \nabla^2 T - \frac{\rho \hat{c}_{\hat{v}}(\gamma - 1)}{\alpha_p}\boldsymbol{\nabla} \cdot \boldsymbol{v},$$

where we have neglected viscous dissipation. Substitution of (26.24) in the above equations and retaining only linear terms gives

$$\frac{\partial}{\partial t}\delta\rho = -\rho_0 \boldsymbol{\nabla} \cdot \boldsymbol{v},$$

which is clearly (26.25),

$$\rho_0 \frac{\partial \boldsymbol{v}}{\partial t} = -\eta \boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \boldsymbol{v}) + \Big(\eta_{\mathrm{d}} + \frac{4}{3}\eta\Big)\boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \boldsymbol{v}) - \frac{\rho_0 {c_{\hat{s}}}^2}{\gamma}\Big(\alpha_p \boldsymbol{\nabla} \delta T + \frac{\boldsymbol{\nabla}\delta\rho}{\rho_0}\Big),$$

which, after dividing by ρ_0, gives (26.26), and

$$\rho_0 \hat{c}_{\hat{v}} \frac{\partial}{\partial t}\delta T = \lambda \nabla^2 \delta T - \frac{\rho_0 \hat{c}_{\hat{v}}(\gamma - 1)}{\alpha_p}\boldsymbol{\nabla} \cdot \boldsymbol{v},$$

which, after dividing by $\rho_0 \hat{c}_{\hat{v}} = \rho_0 \hat{c}_p/\gamma$ gives (26.27).

Exercise 26.3
From (26.29) we easily obtain

$$\frac{\partial \psi}{\partial t} = -\frac{1}{\rho_0}\frac{\partial^2}{\partial t^2}\delta\rho, \qquad \nabla^2 \psi = -\frac{1}{\rho_0}\frac{\partial}{\partial t}\nabla^2 \delta\rho,$$

Substitution in (26.30) with $\delta T = 0$ gives (26.32). Now, using $dp = c_T^2 d\rho$, we have

$$\frac{1}{c_T^2}\frac{\partial^2}{\partial t^2}\delta p = \nabla^2 \delta p + \frac{\nu_l}{c_T^2}\frac{\partial}{\partial t}\nabla^2 \delta p,$$

If we use L to rescale length, and L/c_T to rescale time, we obtain

$$\frac{\partial^2}{\partial t^2}\delta p = \nabla^2 \delta p + \frac{\nu_l}{c_T L}\frac{\partial}{\partial t}\nabla^2 \delta p,$$

which will be consistent with (5.55) from Exercise 5.15 if $L \gg \nu_l/c_T$. For air $\nu_l \approx 1.5 \times 10^{-5}$ m^2/s, $c_T \approx 340$ m/s giving $L \gg 4 \times 10^{-8}$ m. Similarly, for water $\nu_l \approx 4.3 \times 10^{-6}$ m^2/s, $c_T \approx 1500$ m/s giving $L \gg 3 \times 10^{-9}$ m. For both fluids, this critical length is roughly ten times larger than the mean-free path l_{mfp}, which is consistent with the mean-field assumption of transport phenomena.

Exercise 26.4
The velocity is decomposed into a sum of longitudinal and transverse parts:

$$\boldsymbol{v} = -\boldsymbol{\nabla}\xi + \boldsymbol{\nabla} \times \boldsymbol{a},$$

Taking the divergence of the expression above gives

$$\boldsymbol{\nabla} \cdot \boldsymbol{v} = \psi = -\nabla^2\xi,$$

since $\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} \times \boldsymbol{a} = 0$ for any vector $\boldsymbol{a}$. Taking the curl of $\boldsymbol{v}$ gives

$$\boldsymbol{\nabla} \times \boldsymbol{v} = \boldsymbol{w} = \boldsymbol{\nabla} \times \boldsymbol{\nabla} \times \boldsymbol{a} = \boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \boldsymbol{a}) - \nabla^2\boldsymbol{a},$$

since $\boldsymbol{\nabla} \times \boldsymbol{\nabla}\xi = \boldsymbol{0}$ for any scalar ξ. The second equality follows from (5.74).

Exercise 26.5
The eigenvectors $\boldsymbol{e}_i,\ i = 1, 2, 3$ are found from

$$\boldsymbol{A} \cdot \boldsymbol{e}_i = \alpha_i \boldsymbol{e}_i.$$

Hence, for $i = 1$, using (26.39) we can write

$$\begin{pmatrix} 0 & -\rho_0 & 0 \\ \frac{c_{\hat{s}}{}^2 q^2}{\gamma\rho_0} & -\nu_l q^2 & \frac{\alpha_p c_{\hat{s}}{}^2 q^2}{\gamma} \\ 0 & -\frac{\gamma-1}{\alpha_p} & -\gamma\chi q^2 \end{pmatrix} \cdot \begin{pmatrix} \rho_0 \\ c_{\hat{s}} iq f_1(iq) \\ \frac{\gamma-1}{\alpha_p} - \frac{f_2(iq)}{\hat{c}_{\hat{v}}} \end{pmatrix} = \alpha_1 \begin{pmatrix} \rho_0 \\ c_{\hat{s}} iq f_1(iq) \\ \frac{\gamma-1}{\alpha_p} - \frac{f_2(iq)}{\hat{c}_{\hat{v}}} \end{pmatrix},$$

or

$$\begin{pmatrix} -\rho_0 c_{\hat{s}} q f_1(iq) \\ -\nu_l c_{\hat{s}} i q^3 f_1(iq) + c_{\hat{s}}{}^2 q^2 - \frac{\alpha_p c_{\hat{s}}{}^2 q^2}{\gamma \hat{c}_{\hat{v}}} f_2(iq) \\ -\frac{\gamma-1}{\alpha_p} c_{\hat{s}} iq f_1(iq) - \frac{\gamma-1}{\alpha_p}\gamma\chi q^2 + \frac{\gamma\chi q^2}{\hat{c}_{\hat{v}}} f_2(iq) \end{pmatrix} = \alpha_1 \begin{pmatrix} \rho_0 \\ i c_{\hat{s}} q f_1(iq) \\ \frac{\gamma-1}{\alpha_p} - \frac{f_2(iq)}{\hat{c}_{\hat{v}}} \end{pmatrix}.$$

The first line gives

$$\alpha_1 = -c_{\hat{s}} iq f_1(iq),$$

while the second and third lead to the results in (26.42) and (26.43),

$$f_1(iq)^2 = 1 - (\nu_l/c_{\hat{s}}) iq f_1(iq) - (\alpha_p/\gamma\hat{c}_{\hat{v}}) f_2(iq),$$

$$f_2(iq) = \frac{(\gamma-1)\hat{c}_{\hat{v}}}{\alpha_p} \frac{\frac{\gamma\chi}{c_{\hat{s}}} iq}{f_1(iq) + \frac{\gamma\chi}{c_{\hat{s}}} iq}.$$

Next, for $i = 2$, using (26.40) we can write

$$\begin{pmatrix} \rho_0 c_{\hat{s}} q f_1(-iq) \\ \nu_l c_{\hat{s}} i q^3 f_1(-iq) + {c_{\hat{s}}}^2 q^2 - \frac{\alpha_p {c_{\hat{s}}}^2 q^2}{\gamma \hat{c}_{\hat{v}}} \\ -\frac{\gamma-1}{\alpha_p} c_{\hat{s}} i q f_1(-iq) - \frac{\gamma-1}{\alpha_p}\gamma\chi q^2 + \frac{\gamma\chi q^2}{\hat{c}_{\hat{v}}} f_2(-iq) \end{pmatrix} = \alpha_2 \begin{pmatrix} \rho_0 \\ -i c_{\hat{s}} q f_1(-iq) \\ \frac{\gamma-1}{\alpha_p} - \frac{f_2(-iq)}{\hat{c}_{\hat{v}}} \end{pmatrix}.$$

The first line gives

$$\alpha_2 = c_{\hat{s}} i q f_1(-iq),$$

and the second and third lead to,

$$f_1(-iq)^2 = 1 + (\nu_l/c_{\hat{s}}) i q f_1(-iq) - (\alpha_p/\gamma \hat{c}_{\hat{v}}) f_2(-iq),$$

$$f_2(-iq) = -\frac{(\gamma-1)\hat{c}_{\hat{v}}}{\alpha_p} \frac{\frac{\gamma\chi}{c_{\hat{s}}} iq}{f_1(-iq) - \frac{\gamma\chi}{c_{\hat{s}}} iq},$$

which are consistent with (26.42) and (26.43) setting $-iq \to iq$. Finally, for $i = 3$, using (26.41) we can write

$$\begin{pmatrix} -\frac{\rho_0 \chi q^2}{f_1(iq) f_1(-iq)} \\ \frac{{c_{\hat{s}}}^2 q^2}{\gamma} - \frac{\nu_l \chi q^4}{f_1(iq) f_1(-iq)} - \frac{\gamma-1}{\gamma} \frac{{c_{\hat{s}}}^2 q^2}{\gamma f_1(iq) f_1(-iq) - 1} \\ -\frac{\gamma-1}{\alpha_p} \frac{\chi q^4}{f_1(iq) f_1(-iq)} - \frac{\gamma-1}{\alpha_p} \frac{{c_{\hat{s}}}^2 q^2}{\gamma f_1(iq) f_1(-iq) - 1} \end{pmatrix} = \alpha_3 \begin{pmatrix} \rho_0 \\ \frac{\chi q^2}{f_1(iq) f_1(-iq)} \\ -\frac{(\gamma-1)/\alpha_p}{\gamma f_1(iq) f_1(-iq) - 1} \end{pmatrix}.$$

The first line leads to

$$\alpha_3 = -\frac{\chi q^2}{f_1(iq) f_1(-iq)}.$$

The third line can be written as

$$-\frac{1}{f_1(iq) f_1(-iq)} + \frac{\gamma}{\gamma f_1(iq) f_1(-iq) - 1} = \frac{1}{f_1(iq) f_1(-iq)[\gamma f_1(iq) f_1(-iq) - 1]},$$

which, by simple algebraic rearrangement, is true. The second line can be written as

$$\frac{{c_{\hat{s}}}^2 [f_1(iq) f_1(-iq) - 1]}{\gamma f_1(iq) f_1(-iq) - 1} - \frac{\nu_l \chi q^2}{f_1(iq) f_1(-iq)} = -\frac{\chi^2 q^2}{f_1(iq)^2 f_1(-iq)^2}.$$

To verify this expression, we note that the eigenvalues α_i, $i = 1, 2, 3$ for the system of equations in (26.37) are found from

$$\det(\boldsymbol{A} - \alpha\boldsymbol{\delta}) = \begin{vmatrix} -\alpha & -\rho_0 & 0 \\ \frac{{c_{\hat{s}}}^2 q^2}{\gamma\rho_0} & -\nu_l q^2 - \alpha & \frac{\alpha_p {c_{\hat{s}}}^2 q^2}{\gamma} \\ 0 & -\frac{\gamma-1}{\alpha_p} & -\gamma\chi q^2 - \alpha \end{vmatrix} = 0,$$

or

$$\alpha^3 + (\nu_l q^2 + \gamma\chi q^2)\alpha^2 + ({c_{\hat{s}}}^2 + \nu_l \gamma\chi q^4)\alpha + \chi {c_{\hat{s}}}^2 q^4 = 0.$$

Substitution of α_3 in this result verifies the last expression.

Exercise 26.6
Using $\langle c_i c_j \rangle = c'_i \delta_{ij}$, we can write (26.50) as

$$\langle \boldsymbol{x}^*(\boldsymbol{q},0)\boldsymbol{x}(\boldsymbol{q},t)\rangle = c'_1 \boldsymbol{e}_1^* \boldsymbol{e}_1 e^{\alpha_1 t} + c'_2 \boldsymbol{e}_2^* \boldsymbol{e}_2 e^{\alpha_2 t} + c'_3 \boldsymbol{e}_3^* \boldsymbol{e}_3 e^{\alpha_3 t},$$

Substitution of (26.45) and (26.46) gives

$$\begin{aligned}\langle \boldsymbol{x}^*(\boldsymbol{q},0)\boldsymbol{x}(\boldsymbol{q},t)\rangle &= c'_1 \begin{pmatrix} \rho_0 \\ -ic_{\hat{s}}q \\ \frac{\gamma-1}{\alpha_p} \end{pmatrix} \Big(\rho_0, ic_{\hat{s}}q, \frac{\gamma-1}{\alpha_p}\Big) e^{(-ic_{\hat{s}}q-\Gamma q^2)t} \\ &+ c'_2 \begin{pmatrix} \rho_0 \\ ic_{\hat{s}}q \\ \frac{\gamma-1}{\alpha_p} \end{pmatrix} \Big(\rho_0, -ic_{\hat{s}}q, \frac{\gamma-1}{\alpha_p}\Big) e^{(ic_{\hat{s}}q-\Gamma q^2)t} \\ &+ c'_3 \begin{pmatrix} \rho_0 \\ 0 \\ \frac{1}{\alpha_p} \end{pmatrix} \Big(\rho_0, 0, \frac{1}{\alpha_p}\Big) e^{-\chi q^2 t}.\end{aligned}$$

Hence, for the density fluctuations, we can write

$$\langle \widetilde{\delta\rho}^*(\boldsymbol{q},0)\widetilde{\delta\rho}(\boldsymbol{q},t)\rangle = \rho_0^2 \Big[c'_1 e^{(-ic_{\hat{s}}q-\Gamma q^2)t} + c'_2 e^{(-ic_{\hat{s}}q-\Gamma q^2)t} + c'_3 e^{-\chi q^2 t}\Big].$$

Using the constants obtained from (26.47) and (26.48) leads to,

$$\langle \widetilde{\delta\rho}^*(\boldsymbol{q},0)\widetilde{\delta\rho}(\boldsymbol{q},t)\rangle = \frac{\kappa_T \rho_0^2 k_{\mathrm{B}} T_0}{\gamma V}\Big[\frac{1}{2}\Big(e^{-ic_{\hat{s}}qt} + e^{ic_{\hat{s}}qt}\Big)e^{-\Gamma q^2 t} + (\gamma-1)e^{-\chi q^2 t}\Big],$$

which is easily rearranged to obtain (26.51). Substitution in (26.21) gives the expression in (26.52) for the dynamic structure factor $S(\boldsymbol{q},\omega)$.

Exercise 26.7
From the data in Figure 26.9, the Brillouin doublet shift is $\omega_{\mathrm{B}}/(2\pi) \approx 7.4 \times 10^9$ Hz and the half-width at half maximum $\Delta\omega_{\mathrm{B}}/(2\pi) \approx 0.31 \times 10^9$ Hz. Using $\omega_{\mathrm{B}} = c_{\hat{s}}q$, we find

$$c_{\hat{s}} = \frac{\omega_{\mathrm{B}}}{q} = \frac{2\pi(7.4 \times 10^9\ \mathrm{s}^{-1})}{3.0 \times 10^7\ \mathrm{m}^{-1}} \approx 1550\ \mathrm{m/s}.$$

For water, we have $\chi = \lambda/\rho_0\hat{c}_p \approx 1.43 \times 10^{-7}\ \mathrm{m^2/s}$, $\nu = \eta/\rho_0 \approx 1.00 \times 10^{-6}\ \mathrm{m^2/s}$ and $\gamma \approx 1.01$. Hence, $\Gamma = \frac{1}{2}[(\gamma-1)\chi + \nu_{\mathrm{l}}] \approx \frac{1}{2}\nu_{\mathrm{l}} = \frac{1}{2\rho_0}(\frac{4}{3}\eta + \eta_{\mathrm{d}})$. Using $\Delta\omega_{\mathrm{B}} = \Gamma q^2$, we have

$$\eta_{\mathrm{d}} = \frac{2\Delta\omega_{\mathrm{B}}\rho_0}{q^2} - \frac{4}{3}\eta$$

$$= \frac{2\pi(0.61 \times 10^9 \text{ s}^{-1})(998 \text{ kg/m}^3)}{(3.0 \times 10^7 \text{ m}^{-1})^2} - \frac{4}{3}(1.00 \times 10^{-3} \text{ Pa s})$$
$$\approx 3.0 \times 10^{-3} \text{ Pa s}.$$

Exercise 26.8
For mixtures, (26.29) and (26.30) are unchanged, so we write

$$\frac{\partial}{\partial t}\delta\rho = -\rho_0\psi,$$

$$\frac{\partial}{\partial t}\psi = \nu_l\nabla^2\psi - \frac{1}{\rho_0}\nabla^2\delta p,$$

where $\psi = \boldsymbol{\nabla} \cdot \boldsymbol{v}$, and we have written the last term of (26.30) in terms of pressure fluctuations $p = p_0 + \delta p$. We now write the balance equation for solute mass (5.14) as

$$\frac{\partial \rho_1}{\partial t} = -\boldsymbol{v} \cdot \boldsymbol{\nabla}\rho_1 - \rho_1\boldsymbol{\nabla} \cdot \boldsymbol{v} - \boldsymbol{\nabla} \cdot \boldsymbol{j}_1,$$

and the temperature equation (6.7) for a two-component, ideal mixture as

$$\frac{\partial T}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla}T = -\frac{\gamma - 1}{\alpha_p}(\boldsymbol{\nabla} \cdot \boldsymbol{v}) - \frac{1}{\rho\hat{c}_{\hat{v}}}\boldsymbol{\nabla} \cdot \boldsymbol{j}_q' - \frac{\gamma - 1}{\alpha_p}(\hat{v}_1^0 - \hat{v}_2^0)\boldsymbol{\nabla} \cdot \boldsymbol{j}_1,$$

where we have excluded chemical reaction, neglected viscous dissipation and used (6.20). Neglecting cross effects, from (6.18), we can write

$$\boldsymbol{j}_q' = -\lambda'\,\boldsymbol{\nabla}T.$$

For $\boldsymbol{j}_1$, we combine (6.11) and (6.17) and write,

$$\boldsymbol{j}_1 = -\rho D_{12}\boldsymbol{\nabla}w_1 + \rho w_2 D_{12}\left(\frac{\partial\hat{\mu}_1}{\partial w_1}\right)^{-1}_{T,p}\left[\frac{\hat{h}_1 - \hat{h}_2}{T}\boldsymbol{\nabla}T - (\hat{v}_1 - \hat{v}_2)\boldsymbol{\nabla}p\right],$$

which, for a dilute, ideal mixture, can be written as

$$\boldsymbol{j}_1 = -D_{12}\boldsymbol{\nabla}\rho_1 + \frac{\tilde{M}_1 D_{12}}{\tilde{R}}\left[\frac{\hat{h}_1^0 - \hat{h}_2^0}{T^2}\rho_1\boldsymbol{\nabla}T - \frac{\hat{v}_1^0 - \hat{v}_2^0}{T}\rho_1\boldsymbol{\nabla}p\right].$$

Substitution for $\boldsymbol{j}_1$ in the solute mass balance and retaining only first-order terms in the fluctuating variables we obtain,

$$\frac{\partial}{\partial t}\delta\rho_1 = -\rho_{10}\psi + D_{12}\nabla^2\delta\rho_1 - \frac{\rho_{10}D_{12}\tilde{M}_1}{\tilde{R}T_0}\left[\frac{\hat{h}_1^0 - \hat{h}_2^0}{T_0}\nabla^2\delta T - (\hat{v}_1^0 - \hat{v}_2^0)\nabla^2\delta p\right].$$

Substitution for $\boldsymbol{j}_1$ and $\boldsymbol{j}'_q$ in the temperature equation and retaining only first-order terms in the fluctuating variables we obtain,

$$\frac{\partial}{\partial t}\delta T = -\frac{\gamma - 1}{\alpha_p}\psi + \gamma\chi'\nabla^2\delta T + \frac{\gamma - 1}{\alpha_p}(\hat{v}_1^0 - \hat{v}_2^0)D_{12}\nabla^2\delta\rho_1$$
$$-\frac{\gamma - 1}{\alpha_p}(\hat{v}_1^0 - \hat{v}_2^0)\frac{\rho_{10}D_{12}\tilde{M}_1}{\tilde{R}T_0}\Big[\frac{\hat{h}_1^0 - \hat{h}_2^0}{T_0}\nabla^2\delta T - (\hat{v}_1^0 - \hat{v}_2^0)\nabla^2\delta p\Big],$$

For many systems of interest $\nu_1/D_{12} \gg 1$ so that for sufficiently long times, pressure fluctuations can be neglected $\delta p = 0$, which leads to $\psi = 0$. In this case, we have

$$\frac{\partial}{\partial t}\delta\rho_1 = D_{12}\nabla^2\delta\rho_1 - \rho_{10}D_{12}\frac{\tilde{M}_1(\hat{h}_1^0 - \hat{h}_2^0)}{\tilde{R}T_0^2}\nabla^2\delta T.$$

$$\frac{\partial}{\partial t}\delta T = \gamma\chi'\nabla^2\delta T + \frac{\gamma - 1}{\alpha_p}(\hat{v}_1^0 - \hat{v}_2^0)D_{12}\Big[\nabla^2\delta\rho_1 - \frac{\rho_{10}(\hat{h}_1^0 - \hat{h}_2^0)\tilde{M}_1}{\tilde{R}T_0^2}\nabla^2\delta T\Big].$$

If we further neglect the enthalpy of mixing $\hat{h}_1^0 - \hat{h}_2^0 \approx 0$, then the solute mass balance simplifies to

$$\frac{\partial}{\partial t}\delta\rho_1 = D_{12}\nabla^2\delta\rho_1.$$

Taking the Fourier transform, we obtain

$$\frac{\partial}{\partial t}\widetilde{\delta\rho_1}(\boldsymbol{q}, t) = -q^2 D_{12}\widetilde{\delta\rho_1}(\boldsymbol{q}, t),$$

which has the solution given in (26.53).