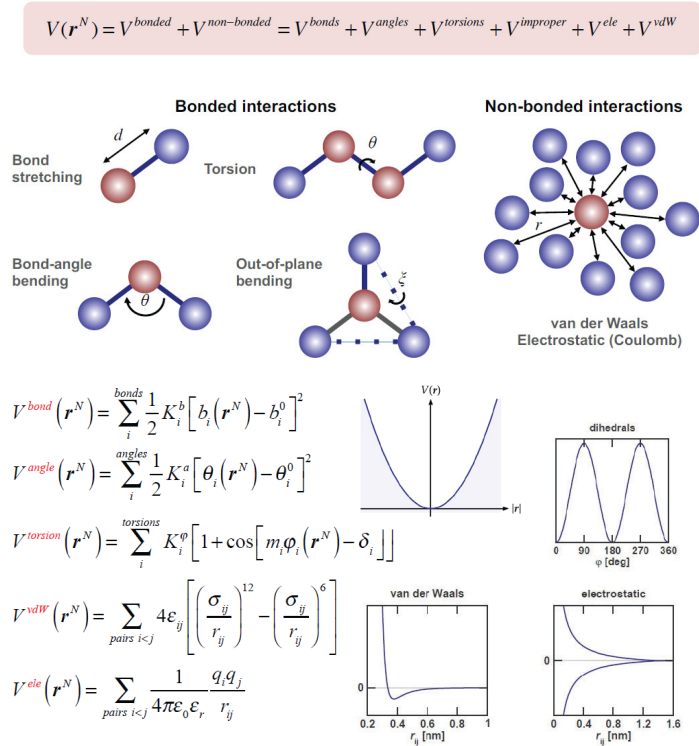


# SAMPLE SOLUTION

# 1 Concepts and Understanding (F2024.1)

Note that the answers given below are more detailed (for didactical purposes!) than what was actually expected from the students during the examination.

- a. The Metropolis Monte Carlo method is an iterative scheme to generate successive system configurations  $\mathbf{r}_k^N$  (where  $k = 0, 1, \dots, K$  is the iteration counter) according to a canonical distribution at a given reference temperature  $T$ . An initial configuration  $\mathbf{r}_0^N$  must be provided. Then, at each iteration, the algorithm consists of two steps: (i) selection of a random trial move; (ii) acceptance or rejection of this move (a rejected move leading to the repeat of the current configuration in the ensemble). The only constraint on the selection of the trial move is that the probabilities of proposing a move and that of proposing its reverse move must be the same. One possible approach (there are many!) is to select an atom at random and move it by a step of a fixed size  $\Delta r$  in a random direction. The acceptance/rejection is determined by the relative Boltzmann weights of the configurations before and after the trial move. If the potential-energy change is  $\Delta \mathcal{V}$  and the corresponding Boltzmann ratio is  $p = e^{-\beta \Delta \mathcal{V}}$  (where  $\beta^{-1} = k_B T$  with  $k_B$  the Boltzmann constant and  $T$  the temperature), the acceptance probability is  $\min\{1, p\}$ . In practice, if  $p \geq 1$  (“downhill” move with  $\Delta \mathcal{V} \leq 0$ ) the move is automatically accepted. And if  $p < 1$  (“uphill” move with  $\Delta \mathcal{V} > 0$ ), one selects a random number  $s$  between 0 and 1, and the move is only accepted if  $s < p$ . For efficiency, the choice of a step size  $\Delta r$  should compromise between two factors. If  $\Delta r$  is too large, the moves frequently place atoms too close from each other (large positive  $\Delta \mathcal{V}$ ), which induces many rejections. If  $\Delta r$  is too small, the acceptance probability is high but the rate at which the configurational space is sampled is very low. In summary, both too large and too small  $\Delta r$  lead to inefficient sampling.
- b. Covalent (bonded) terms are: bond stretching, bond-angle bending, dihedral torsion and improper-dihedral distortion (out-of-plane bending). Their roles and typical functional forms are shown in the figure below (which also includes the two non-bonded types, electrostatic and van der Waals interactions).



## 2 Fundamental Equations (F2024.2)

Note that the answers given below are more detailed (for didactical purposes!) than what was actually expected from the students during the examination. Watch out not to overlook the requirements “**explain the meaning** of all the involved symbols” and “**state the SI units** of these quantities”.

- a. The Lagrangian function  $\mathcal{L} = \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}})$  is a function of the generalized-coordinate vector  $\mathbf{q}$  and of the generalized-velocity vector  $\dot{\mathbf{q}}$ . It has the units of an energy (SI unit: J). The units of the different components  $q_m$  of  $\mathbf{q}$  can be diverse, and the corresponding components  $\dot{q}_m$  have the same units divided by time. The connection between the Lagrangian function  $\mathcal{L}$ , the kinetic energy  $\mathcal{K}$ , and the potential energy  $\mathcal{V}$  is given by

$$\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}) = \mathcal{K}(\mathbf{q}, \dot{\mathbf{q}}) - \mathcal{V}(\mathbf{q}) ,$$

where it is assumed that  $\mathcal{V}$  only depends on the generalized coordinates (as is the case for a force field). The Lagrangian equations of motion read

$$\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{q}_m} \right) = \frac{\partial \mathcal{L}}{\partial q_m} \quad \text{for } m = 1, 2, \dots, M ,$$

where  $t$  is time (SI unit: s).

In the special case of a Cartesian coordinate system (for a system of  $N$  particles), the Lagrangian becomes

$$\mathcal{L}(\mathbf{r}, \dot{\mathbf{r}}) = \mathcal{K}(\dot{\mathbf{r}}) - \mathcal{V}(\mathbf{r}) ,$$

where it is noted that the kinetic energy

$$\mathcal{K}(\dot{\mathbf{r}}) = \frac{1}{2} \sum_{n=1}^N m_n \dot{\mathbf{r}}_n^2$$

now only depends on the Cartesian velocities. One can then write

$$\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_n} \right) = \frac{d}{dt} \left( \frac{d\mathcal{K}}{d\dot{\mathbf{r}}_n} \right) = m_n \ddot{\mathbf{r}}_n \quad \text{for } n = 1, 2, \dots, N$$

and

$$\frac{\partial \mathcal{L}}{\partial \mathbf{r}_n} = - \frac{d\mathcal{V}}{d\mathbf{r}_n} = \mathbf{F}_n \quad \text{for } n = 1, 2, \dots, N ,$$

where  $\mathbf{F}$  is the force vector. This shows that the Lagrangian equations of motion become equivalent to the Newtonian ones in the special case of a Cartesian coordinate system.

The Hamiltonian function  $\mathcal{H} = \mathcal{H}(\mathbf{q}, \mathbf{p})$  is a function of the generalized-coordinate vector  $\mathbf{q}$  and of the conjugate-momentum vector  $\mathbf{p}$ . It has the units of an energy (SI unit: J). The units of the conjugate momenta are related to those of the generalized coordinate they are associated to, so that the product  $p_m q_m$  has unit of an action (SI units: J·s). The connection between the Hamiltonian function  $\mathcal{H}$ , the kinetic energy  $\mathcal{K}$ , and the potential energy  $\mathcal{V}$  is given by

$$\mathcal{H}(\mathbf{q}, \mathbf{p}) = \mathcal{K}(\mathbf{q}, \mathbf{p}) + \mathcal{V}(\mathbf{q}) ,$$

where it is assumed that  $\mathcal{V}$  only depends on the generalized coordinates (as is the case for a force field). The Hamiltonian equations of motion read

$$\dot{\mathbf{q}} = \frac{\partial \mathcal{H}(\mathbf{q}, \mathbf{p})}{\partial \mathbf{p}} \quad \text{and} \quad \dot{\mathbf{p}} = - \frac{\partial \mathcal{H}(\mathbf{q}, \mathbf{p})}{\partial \mathbf{q}} .$$

In the special case of a Cartesian coordinate system (for a system of  $N$  particles), the Hamiltonian becomes

$$\mathcal{H}(\mathbf{r}, \mathbf{p}_r) = \mathcal{K}(\mathbf{p}_r) + \mathcal{V}(\mathbf{r}) ,$$

where  $\mathbf{p}_r$  stands for the Cartesian momenta (mass times velocity), and it is noted that the kinetic energy

$$\mathcal{K}(\mathbf{p}_r) = \frac{1}{2} \sum_{n=1}^N m_n^{-1} \mathbf{p}_r^2$$

now only depends on the Cartesian momenta. The Hamiltonian equations become

$$\dot{\mathbf{r}}_n = \frac{\partial \mathcal{H}(\mathbf{r}, \mathbf{p}_r)}{\partial \mathbf{p}_{r,n}} = \frac{d\mathcal{K}(\mathbf{p}_r)}{d\mathbf{p}_{r,n}} = m_n^{-1} \mathbf{p}_{r,n}$$

and

$$\dot{\mathbf{p}}_{r,n} = -\frac{\partial \mathcal{H}(\mathbf{r}, \mathbf{p}_r)}{\partial \mathbf{r}_n} = -\frac{d\mathcal{V}(\mathbf{r})}{d\mathbf{r}_n} = \mathbf{F}_n .$$

This shows that the Hamiltonian equations of motion become equivalent to the Newtonian ones in the special case of a Cartesian coordinate system.

The value of the Hamiltonian represents the total (kinetic plus potential) energy of the system. It is a conserved quantity when the system is isolated, *i.e.* when there is no potential energy term in the Hamiltonian that couples the system to its surroundings (neither in a time-independent nor in a time-dependent fashion).

- b. The  $M$  states are distributed over the  $J$  energy levels in such a way that each level encompasses  $g_j$  degenerate states. Thus, one has

$$\sum_{j=0}^{J-1} g_j = M .$$

This quantity is unitless. Noting that  $E_0 = 0$  (so that the energies are already given relative to the ground state), the canonical partition function is

$$Z = \sum_{m=0}^{M-1} e^{-\beta E_m} = \sum_{j=0}^{J-1} g_j e^{-\beta E_j} ,$$

where  $\beta^{-1} = k_B T$  with  $k_B$  the Boltzmann constant and  $T$  the temperature. The partition function is unitless. The free energy is related to the partition function as

$$F = -\beta^{-1} \ln Z .$$

The free energy has the units of an energy (SI unit: J). Finally, the average energy is the ensemble average of the energy

$$E = \sum_{m=0}^{M-1} E_m e^{-\beta E_m} = \sum_{j=0}^{J-1} g_j E_j e^{-\beta E_j}$$

The energy has the units of an energy (SI unit: J).

### 3 Derivations (F2024.3)

a. The Stirling approximation reads

$$\ln N! \approx N \ln N - N ,$$

valid in the limit of large  $N$ . A simple derivation is as follows.

$$\ln N! = \sum_{n=1}^N \ln n \approx \int_1^N dn \ln n = [n \ln n - n]_1^N = N \ln N - N + 1 \approx N \ln N - N .$$

Considering a statistical-mechanical ensemble with  $K$  systems distributed over  $M$  states with a population vector  $\mathbf{n} = \{n_m \mid m = 0, 1, \dots, M-1\}$  satisfying  $\sum_{m=0}^{M-1} n_m = K$  and associated with a statistical weight  $W(\mathbf{n})$ , we can simplify the quantity  $K^{-1} \ln W(\mathbf{n})$  in the limit of large  $K$  using the Stirling approximation in the following way.

$$\begin{aligned} K^{-1} \ln W(\mathbf{n}) &= K^{-1} \ln \frac{K!}{\prod_{m=0}^{M-1} n_m!} = \ln K - 1 - \sum_{m=0}^{M-1} [K^{-1} n_m \ln n_m - K^{-1} n_m] \\ &= \ln K - \sum_{m=0}^{M-1} p_m \ln n_m = - \sum_{m=0}^{M-1} p_m [\ln n_m - \ln K] = - \sum_{m=0}^{M-1} p_m \ln p_m . \end{aligned}$$

This result is in essence the equivalence of the Boltzmann and Gibbs definitions of the canonical entropy.

b. For any pure substance in any phase, one has  $c_P > c_V$ , because the difference  $c_P - c_V$  is always positive. This follows from noticing that  $T$ ,  $v$ ,  $\alpha_P^2$  and  $\kappa_T$  are all positive quantities. Note that the compressibility  $\kappa_T$  is always positive (when you increase the pressure at constant temperature, the volume of a substance always decreases). However, the expansivity  $\alpha_P$  can sometimes be negative (an example is water between 0 and 4°C at ambient pressure, which slightly contracts upon increasing the temperature). But the expansivity enters the equation as a square, which is always positive.

For an ideal gas, upon inserting  $PV = nRT$ , one gets

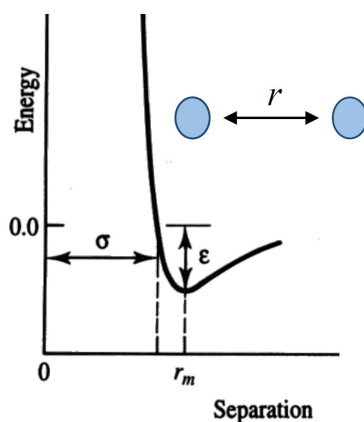
$$v = \frac{RT}{P} \quad , \quad \kappa_T = -\frac{1}{V} nRT \frac{dP^{-1}}{dP} = \frac{1}{P} \quad , \quad \text{and} \quad \alpha_P = \frac{1}{V} \frac{nR}{P} \frac{dT}{dT} = \frac{1}{T} .$$

This leads to

$$c_P - c_V = \frac{T \frac{RT}{P} \frac{1}{T^2}}{\frac{1}{P}} = R .$$

## 4 Explicit Calculations (F2024.4)

- a. A sketch of the Lennard-Jones function is shown below. The zero-distance and zero-energy points are indicated, as well as the locations where you can measure  $\sigma$ ,  $r_m$ , and  $\epsilon$ .



For the following tasks, it is useful to calculate the corresponding Lennard-Jones force  $F_{LJ}$ , *i.e.* the negative derivative of  $V_{LJ}$  with respect to  $r$

$$F_{LJ}(r) = 4\epsilon \left[ 12 \left( \frac{\sigma}{r} \right)^{12} - 6 \left( \frac{\sigma}{r} \right)^6 \right] \frac{1}{r} .$$

The sign of  $F_{LJ}$  matches the desired convention, namely it is negative if the force is attractive and positive otherwise. This is easily checked by noting that  $F_{LJ}$  is positive when  $r \rightarrow 0$  (the  $r^{-12}$  term dominates) and negative when  $r \rightarrow \infty$  (the  $r^{-6}$  term dominates). To calculate  $r_m$ , we note that the force should be zero at this point. This leads to the condition

$$12 \left( \frac{\sigma}{r_m} \right)^{12} - 6 \left( \frac{\sigma}{r_m} \right)^6 = 0 ,$$

which is satisfied when  $r_m = 2^{1/6}\sigma$ . Using the approximation  $2^{1/n} \approx 1 + (1/n)\ln 2$  with  $\ln 2 \approx 0.69$ , one has  $2^{1/6} \approx 1.115$ , so that  $r_m = 1.115 \cdot 0.4 \text{ nm}$ , that is  $0.446 \text{ nm}$ . Considering the point  $r = \sigma$ , the Lennard-Jones potential energy is zero. The corresponding force is

$$F_{LJ}(\sigma) = 4\epsilon [12 - 6] \frac{1}{\sigma} = \frac{24\epsilon}{\sigma} .$$

This gives  $24 \cdot 2 \text{ kJ} \cdot \text{mol}^{-1} \cdot 1/0.4 \text{ nm}^{-1}$ , that is  $120 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{nm}^{-1}$ . As expected, the value is positive, as we are in the repulsive range. Considering the point  $r = r_m$ , the Lennard-Jones force is zero, and the corresponding potential energy is  $-\epsilon$ , that is  $-2 \text{ kJ} \cdot \text{mol}^{-1}$ .

## 5 Algorithms and Implementation (F2024.5)

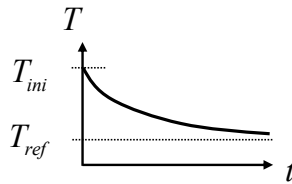
a. A possible code for the function Thermo is given below

```
void Thermo (int N, double m[], double kb, double dt,
            double tau, double Tref, double v[]);
// First calculate the current kinetic energy
double K = 0.0;
for ( int n=0; n<N; n++ ) {
    int n3 = 3*n;
    K += m[n] * ( v[n3]*v[n3] + v[n3+1]*v[n3+1] + v[n3+2]*v[n3+2] );
}
K *= 0.5;
// Next calculate the current temperature (we have 3N dof)
double T = 2.0 * K / ( 3.0 * N * kb );
// Then calculate the velocity-scaling factor
double lam = sqrt( 1.0 - dt/tau * ( T - Tref ) / T );
// Finally, scale the velocities
for ( int n3=0; n3<3*N; n3++ ) {
    v[n3] *= lam;
}
return;
}
```

Assuming an ideal gas (zero potential energy), the weak-coupling thermostat induces an exponential temperature relaxation. This corresponds to the equation

$$\mathcal{T}(t) = T_{\text{ref}} + (T_{\text{ini}} - T_{\text{ref}}) e^{-t/\tau} .$$

This is of course numerically only the case in the limit of a small timestep (compared to  $\tau$ ). This exponential relaxation with characteristic time  $\tau$  is illustrated in the graph below (assuming here  $T_{\text{ini}} > T_{\text{ref}}$ )



In the limiting case where  $\tau$  is set equal to  $\Delta t$ , the expression for the scaling factor becomes

$$\lambda = \left( 1 - \frac{\mathcal{T} - T_{\text{ref}}}{\mathcal{T}} \right)^{1/2} .$$

The kinetic energy is scaled by  $\lambda^2$  and so is the instantaneous temperature. The new temper-

ature after a single scaling is thus

$$\mathcal{T}_{\text{new}} = \mathcal{T} \left( 1 - \frac{\mathcal{T} - T_{\text{ref}}}{\mathcal{T}} \right) = T_{\text{ref}} .$$

Thus, after a single scaling,  $\mathcal{T}$  becomes  $T_{\text{ref}}$ . With this choice, the simulation will be performed at constant instantaneous temperature. This corresponds to a so-called isokinetic situation (Woodcock/Hoover-Evans thermostating).

Finally, if the units of mass and velocity are  $\text{g}\cdot\text{mol}^{-1}$  and  $\text{nm}\cdot\text{ps}^{-1}$ , respectively, then the calculated kinetic energy has units of  $\text{g}\cdot\text{mol}^{-1}\cdot(\text{nm}\cdot\text{ps}^{-1})^2$ , which is a  $\text{kJ}\cdot\text{mol}^{-1}$  (since a J is a  $\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}$ ). If the unit of temperature is K,  $k_B$  should thus be provided in  $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .