

**Examination D-CHAB Fall 2024:
Statistical Physics for CSE**

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HIL F75

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Problem statements in English

- Write your **name** and **identification (Legi) number** on **each** sheet of paper you hand in.
- The use of laptops, cell phones, calculators, books, course material, *etc.* is **not allowed** (exception: language dictionaries).
- You may use the **question sheets** to report your answers (or part of them).
- Please, clearly **highlight** (*e.g.* underline or frame) your **final answers** to the problems.
- Keep your answers **short**, but **clear**.
- The five problems of the examination have **equal weights** in the final mark.

1 Concepts and Understanding (F2024.1)

For each of the following items, **answer** the question(s) in a **clear** and **concise** way.

- a. Considering a system of N atoms with Cartesian coordinates $\mathbf{r}^N = \{\mathbf{r}_i, i = 1, 2, \dots, N\}$ and a potential energy $\mathcal{V}(\mathbf{r}^N)$, describe the working principle of the **Metropolis Monte Carlo approach** to sample the configurational space of the system according to a canonical distribution at a given reference temperature T . Your description should be sufficiently precise to permit a practical implementation of the algorithm into a program. In addition, explain the compromise involved in the selection of an appropriate step size.
- b. Classical force fields typically include four types of **covalent (bonded) interaction terms**. List these four types and, for each of them, provide the three following things:
 - A simple drawing representing the atoms and the internal coordinate involved.
 - A brief explanation of the role of the term in the force field.
 - A simple functional form that can be used in practice to represent the corresponding interaction.

2 Fundamental Equations (F2024.2)

For each of the following items, **write down** the relevant equation(s), **explain the meaning** of all the involved symbols, **state the SI units** of these quantities, and **answer** the additional questions.

- a. Consider a **classical system of particles** described by a generalized-coordinate vector $\mathbf{q} = \{q_m, m = 1, 2, \dots, M\}$, along with either a generalized-velocity vector $\dot{\mathbf{q}} = \{\dot{q}_m, m = 1, 2, \dots, M\}$ (where the dot over a symbol denotes its time derivative) or a conjugate-momentum vector $\mathbf{p} = \{p_m, m = 1, 2, \dots, M\}$. The kinetic energy is \mathcal{K} and the potential energy is \mathcal{V} .
- Write down the definition of the Lagrangian \mathcal{L} as well as the Lagrangian equations of motion.
 - Show that the Lagrangian equations of motion are equivalent to the Newtonian ones in a Cartesian coordinate system.
 - Write down the definition of the Hamiltonian \mathcal{H} as well as the Hamiltonian equations of motion.
 - Show that the Hamiltonian equations of motion are equivalent to the Newtonian ones in a Cartesian coordinate system.
 - State what the value of the Hamiltonian represents in physical terms.
 - State under which conditions the Hamiltonian of a system is a conserved (time-independent) quantity.
- b. Consider a **quantum-mechanical system** with M accessible states $m = 0, 1, \dots, M - 1$ distributed over J energy levels $j = 0, 1, \dots, J - 1$ of degeneracies g_j . The energies of the M states are labelled E_m and the energies of the J levels are labelled E_j . It is assumed that the ground state has an energy of zero ($E_0 = 0$). One considers the situation of a canonical ensemble of such systems at a temperature T (it is assumed that the volume is irrelevant).
- Give the result of the expression $\sum_{j=0}^{J-1} g_j$.
 - Write the expression for the partition function Z , using either a sum over the M states or a sum over the J levels.
 - Write the expression for the free energy F .
 - Write the expression for the average energy using either a sum over the M states or a sum over the J levels.

3 Derivations (F2024.3)

For each of the following items, **derive** the required expression analytically (*i.e.* it is not sufficient to only give the final result!), and **answer** the additional questions.

- a. The **Stirling approximation**, which plays a central role in statistical mechanics, provides a simple approximation for $\ln N!$ that is accurate in the limit of large N .

- Write the expression for the Stirling approximation to $\ln N!$.
- Provide a simple derivation for this expression. *Hint:* Approximate a sum of logarithms by the corresponding integral.
- Consider a statistical-mechanical ensemble with K systems distributed over M states. The population vector, specifying the number of systems found in each state, is $\mathbf{n} = \{n_m \mid m = 0, 1, \dots, M-1\}$ and satisfies $\sum_{m=0}^{M-1} n_m = K$. The associated statistical weight $W(\mathbf{n})$ is given by

$$W(\mathbf{n}) = \binom{K}{n_0, n_1, \dots, n_{M-1}} = \frac{K!}{\prod_{m=0}^{M-1} n_m!}.$$

Use the Stirling approximation to show that in the limit of large K one has

$$K^{-1} \ln W(\mathbf{n}) \approx - \sum_{m=0}^{M-1} p_m \ln p_m \quad \text{with} \quad p_m = \frac{n_m}{K}.$$

- b. For a pure substance at a given pressure P and temperature T , the **molar isochoric heat capacity** c_V and the **molar isobaric heat capacity** c_P are connected by the equation

$$c_P - c_V = \frac{T v \alpha_P^2}{\kappa_T},$$

where v is the molar volume, κ_T the compressibility, and α_P the expansivity. The latter quantities are defined by

$$v = \frac{V}{n}, \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T, \quad \text{and} \quad \alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P,$$

where V is the volume and n the number of moles. Using these equations:

- Prove that for any pure substance, one has $c_P > c_V$.
- Derive an expression for the difference $c_P - c_V$ in the special case of an ideal gas. *Hint:* The result is a constant, *i.e.* independent on the nature of the gas.

4 Explicit Calculations (F2024.4)

For each of the following items, **calculate** the numerical result paying particular attention to the **units**, and **answer** the additional questions.

- a. The van der Waals interaction energy between two non-bonded atoms is described in a force field by a **Lennard-Jones potential energy** of the form

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

where r is the distance between the atoms, σ the collision diameter, and ϵ the well depth. The position of the minimum on this function is noted r_m . Approximate values of σ and ϵ for the interaction between two xenon atoms are 0.4 nm and 2 kJ·mol⁻¹, respectively.

- Sketch the curve of V_{LJ} as a function of r (specify clearly the location of the zero on both axes), and indicate where σ , r_m and ϵ can be read on the graph.
- Calculate the value of r_m . For this, use the approximation $2^{1/n} \approx 1 + (1/n) \ln 2$ with $\ln 2 \approx 0.69$.
- Calculate the value of the Lennard-Jones potential energy and of the corresponding force for two xenon atoms at a distance $r = \sigma$ (for the force, use a negative sign if the force is attractive and a positive sign if it is repulsive).
- Perform the same calculations for a distance $r = r_m$.

5 Algorithms and Implementation (F2024.5)

For each of the following items, **write the code** of a C++ function performing the required task (or, at least, the pseudo-code; the exactness of your C++ syntax will not be graded), and **answer** the additional questions.

- a. Write a C++ function `Thermo` that implements a **weak-coupling (Berendsen) thermostat** within a molecular dynamics code for simulating a monoatomic fluid of N atoms. This function will be called after each timestep of the simulation, and should rescale all the atomic velocities with a factor λ given by

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

where \mathcal{T} is the instantaneous temperature of the system (calculated from the current atomic velocities), T_{ref} is the reference temperature of the thermostat, Δt is the simulation timestep, and τ is the thermostat coupling time. The function declaration reads

```
void Thermo (int N, double m[], double kb, double dt,
             double tau, double Tref, double v[]);
```

The input arguments are `N` for the number of atoms, `m[0..N-1]` for the atomic masses, `kb` for the Boltzmann constant (k_B), `dt` for the timestep (Δt), `tau` for the coupling time (τ), and `Tref` for the reference temperature T_{ref} . On input, the array `v[0..3N-1]` contains the current atomic velocities (with the x -, y - and z -components listed in sequence for each atom in turn). On output, the same array should be returned with the rescaled velocities. In addition, answer the following questions:

- Assuming an ideal gas (zero potential energy), describe how the instantaneous temperature will relax with time t from a given initial temperature T_{ini} to the target temperature T_{ref} , in the form of an equation and a graph for $\mathcal{T}(t)$.
- Explain what happens in the limiting case where τ is set equal to Δt .
- Assuming that the units of mass, velocity, and temperature in the simulation code are $\text{g}\cdot\text{mol}^{-1}$, $\text{nm}\cdot\text{ps}^{-1}$, and K, respectively, state in which SI units k_B should be provided.