Examination D-CHAB Spring 2024:
Statistical Physics for CSE

24.01.2024 11:30-13:00

LFW B1

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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 (S2024.1)

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

a. Assume that a **quantum-mechanical system** has **four equidistant non-degenerate energy levels** $E_n = n\Delta E$ with $n = 0, 1, 2, 3$. Now consider a **canonical ensemble** of such systems at a temperature T, where the populations of the levels are P_n for $n = 0, 1, 2, 3$. We also define a **reduced temperature** $\tilde{T}$ as $\tilde{T} = k_B T/\Delta E$, where k_B is the Boltzmann constant.

   - Write down the equation giving P_n as a function of $\tilde{T}$.
   - Consider the four following temperatures: (1) $\tilde{T} \to 0$; (2) $\tilde{T} = 1$; (3) $\tilde{T} = 2$; (4) $\tilde{T} \to \infty$. Consider also the four following population distributions $\{P_n\}$: (A) $\{0.25, 0.25, 0.25, 0.25\}$; (B) $\{1, 0, 0, 0\}$; (C) $\{0.46, 0.28, 0.17, 0.10\}$; (D) $\{0.64, 0.24, 0.09, 0.03\}$. Without doing any complicated calculation, assign each distribution (A-D) to the corresponding temperature (1-4), and briefly explain your reasoning (answers without explanations will not be accepted).

b. Classical **force fields** typically include two types of pairwise **non-bonded interactions** that depend on the distance r_{ij} between two atoms i and j. State what are these two types of interactions, and for both of them:

   - Briefly explain the physical effects involved.
   - Give a simple functional form that can be used in practice to represent the potential-energy term as a function of r.
   - Make a sketch of the corresponding graph giving the potential energy as a function of distance r.

2 Fundamental Equations (S2024.2)

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. For a **pure substance** in a **single phase**, the pressure (P), the volume (V), the number of mols (n) and the temperature (T) are not mutually independent, *i.e.* they are connected by a so-called **equation of state**. Answer the following questions in the context of pure substances in the **gas phase**.

- Write down the ideal-gas equation of state, and explain under which assumptions (in terms of microscopic interactions) and under which circumstances (in terms of macroscopic conditions) the ideality approximation is valid.
- Write down the real-gas equation of state of van der Waals, which involves correction constants a and b, and explain what kind of effects are now approximately taken into account by the two corresponding corrections.

b. Write the equation typically used to represent the **potential energy** associated with a **bond-stretching term** in a **force field**. In addition, answer the following questions.

- State what kind of experimental or theoretical data can be used to find appropriate values for the parameters of this equation.
- Explain how to calculate (*e.g.* in a computer program) the bond distance i-j from the Cartesian position vectors $\mathbf{r}_i$ and $\mathbf{r}_j$.

c. Write the two equations defining the **leap-frog scheme** for integrating the Newtonian equations of motion based on a finite timestep Δt. In addition, answer the following questions.

- Give the order of magnitude of the error (largest neglected term) as a power of Δt.
- Explain the advantage of interleaving (asynchronous coordinates and velocities).
- Explain what trade-off is involved in the choice of a reasonable Δt, and state the order of magnitude of the Δt value typically selected in atomistic simulations (give your answer in units of second).
- Explain the relationship between the application of bond-length constraints (rather than harmonic bonds) and the choice of Δt.

3   Derivations (S2024.3)

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. An **normal (Gaussian) probability distribution** with parameters a and b is defined on the interval $]-\infty, \infty[$ by the equation

$$p(x) = c\,e^{-(x-a)^2/b}\ .$$

Use the Gaussian-integral results

$$\int_0^\infty dx\,e^{-\alpha x^2} = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{1/2} \quad,\quad \int_0^\infty dx\,x\,e^{-\alpha x^2} = \frac{1}{2\alpha} \quad\text{and}\quad \int_0^\infty dx\,x^2\,e^{-\alpha x^2} = \frac{1}{4}\left(\frac{\pi}{\alpha^3}\right)^{1/2}$$

to perform the following tasks:

- Derive the expression for the value of c, so that the distribution is normalized.
- Derive the expression for the mean μ of $p(x)$ as a function of a and b.
- Derive the expression for the variance σ^2 of $p(x)$ as a function of a and b
- If the unit of x is nanometer, give the units of $p(x)$, a, b, c, μ and σ.

b. Consider a classical molecular system with the Hamiltonian $\mathcal{H} = \mathcal{H}(\mathbf{r}, \mathbf{p})$ that depends on the Cartesian coordinate vector $\mathbf{r}$ and momentum vector $\mathbf{p}$ of the molecular system. We wish to evaluate the ensemble average A of some instantaneous observable $\mathcal{A} = \mathcal{A}(\mathbf{r})$. This can sometimes be done by performing an **unbiased simulation** using the Hamiltonian $\mathcal{H}$. In other cases, however, the sampling must be facilitated by performing a **biased sampling** with the Hamiltonian $\mathcal{H} + \mathcal{V}_B$, where $\mathcal{V}_B = \mathcal{V}_B(\mathbf{r})$ is a biasing potential-energy term. In the context of the canonical ensemble, derive the **reweighting formula**

$$A = \langle \mathcal{A} \rangle = \langle \mathcal{A}e^{+\beta \mathcal{V}_B} \rangle_B \ ,$$

where $\beta = (k_B T)^{-1}$, k_B being the Boltzmann constant and T the absolute temperature. Here, $\langle \cdots \rangle$ and $\langle \cdots \rangle_B$ stand for canonical ensemble averages over the unbiased and biased ensembles, respectively. For this, you will need to perform the following steps:

(1) write the expression for the classical canonical ensemble average $\langle \mathcal{A} \rangle$ of the observable $\mathcal{A}$ over the unbiased ensemble;

(2) write the expression for the classical canonical ensemble average $\langle \mathcal{X} \rangle$ of an observable $\mathcal{X}$ over the biased ensemble;

(3) consider the special case where one sets $\mathcal{X} = \mathcal{A}e^{+\beta \mathcal{V}_B}$.

4 Explicit Calculations (S2024.4)

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

a. The force field of a flexible water model relies on a **harmonic potential-energy** term for the H-O-H bond-angle bending of the form

$$V(\theta; \theta_o) = \frac{1}{2} k_\theta (\theta - \theta_o)^2 .$$

Here, the reference bond-angle value is $\theta_o = 105$ deg and the force constant is $k_\theta = 0.10$ kJ·mol^{-1}·deg^{-2}. Calculate the value of the potential energy for the bond-angle values $\theta = \theta_o + 5$ deg and $\theta = \theta_o - 5$ deg. Additional questions:

- Compare the resulting energy to the thermal energy RT at room temperature, using $R = 8.3$ J·K^{-1}·mol^{-1} and $T = 300$ K.

- Using this comparison, comment on the typical magnitude of the bond-angle fluctuations one should expect in molecular dynamics simulations.

b. According to the **Maxwell-Boltzmann distribution** of velocities $p(v)$, the **root-mean-square velocity** $\overline{v^2}^{1/2}$ of an atom in a monoatomic gas is given by

$$\overline{v^2}^{1/2} = \left(\frac{3k_B T}{m} \right)^{1/2} ,$$

where m is the mass, T the absolute temperature, and k_B the Boltzmann constant. Calculate the root-mean-square velocity $\overline{v^2}^{1/2}$ in m·s^{-1} of a neon atom (molar mass 20 g·mol^{-1}) at a temperature of 25 °C. For this, use the following approximate values: the gas constant (*i.e.* k_B expressed on a per-mole basis) is 8 J·mol^{-1}K^{-1}, and the absolute zero is -275 °C. Additional questions:

- State by how many percent $\overline{v^2}^{1/2}$ changes when T or when m is doubled. Provide a simple explanation for these trends in terms of the equipartition principle.

- The functional form of the Maxwell-Boltzmann distribution of velocities $p(v)$ is given by

$$p(v) = C \, v^2 \, e^{-\beta m v^2/2} ,$$

where C is a normalization constant. Sketch the curve corresponding to this distribution.

- Considering this distribution, rank the following quantities in ascending order: the mean velocity $\overline{v}$, the root-mean-square velocity $\overline{v^2}^{1/2}$, and the most probable velocity v^*.

- State how the value of $\overline{v^2}^{1/2}$ in liquid neon at a temperature T is related to the corresponding value in the gas at the same temperature T (smaller, identical, or larger; your answer must be accompanied by a brief explanation).

5 Algorithms and Implementation (S2024.5)

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 `MorseEnergy` that will calculate the potential energy of a set of N identical particles, where the interaction between any two particles is given by the **Morse function**

$$U_{\text{Morse}} = c\left\{1 - \exp\left[-a\left(r - b\right)\right]\right\}^2 \ , \tag{1}$$

where r is the interatomic distance, while a (unitless, related to the curvature at the minimum), b (distance at the minimum) and c (dissociation energy) are specified pairwise interaction parameters. The function declaration reads

```
double MorseEnergy (int N, double x[], double y[], double z[],
                    double a, double b, double c);
```

where the arrays `x[0..N-1]`, `y[0..N-1]` and `z[0..N-1]` contain the Cartesian coordinates of the N particles.