Examination D-CHAB Fall 2021: Statistical Physics for CSE

28.08.2021 10:30-11:30

HIL E4

Prof. Sereina Riniker
Prof. Philippe H. Hünenberger

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.

- You **do not** need to answer **all** questions correctly to obtain a top mark. First try to efficiently solve the easier questions, and then move to the more difficult ones.

.

1 Concepts and Understanding (F2021.1)

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

a. In thermodynamics and statistical mechanics, one distinguishes between extensive and intensive properties.

- Explain the difference between the two types of quantities.
- Give two examples of quantities belonging to each of the two types.
- State whether the ratio of two extensive quantities represents an extensive or an intensive quantity (your answer must be accompanied by a brief justification).
- State whether the product of an extensive with an intensive quantity represents an extensive or an intensive quantity (your answer must be accompanied by a brief justification).

b. Molecular simulations of condensed-phase systems are commonly carried out under periodic boundary conditions rather than considering finite systems (*e.g.* solute in a droplet of liquid surrounded by vacuum).

- Explain the concept of periodic boundary conditions.
- Explain why the use of periodic boundary conditions is to be preferred for condensed-phase systems.
- Explain when and why it may be advantageous to apply periodic boundary conditions based on a truncated-octahedral rather than a cubic computational box.
- Explain what type of preprocessing has to be performed before analyzing a trajectory generated using periodic boundary conditions in terms of a structural property, *e.g.* for calculating the radius of gyration of a protein as a function of time.

c. Coarse-grained models are sometimes employed to reduce the computational costs of molecular dynamics simulations. Answer the following questions concerning the calibration of such models.

- Explain the basic principle of the approach termed "iterative Boltzmann inversion".
- Explain the basic principle of the approach termed "force matching".
- Comment on the relative advantages and disadvantages of the two approaches.

2 Fundamental Equations (F2021.2)

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. Write down the classical Lagrangian equations of motion formulated in a generalized-coordinate system involving a generalized-coordinate vector $\mathbf{q} = \{q_m, m = 1, 2, ..., M\}$. Additional questions:

- Explain what is meant by a generalized coordinate and by a generalized-coordinate system.
- Give the connection between the Lagrangian function $\mathcal{L}$, the kinetic energy $\mathcal{K}$, and the potential energy $\mathcal{V}$.
- Show that the Lagrangian equations of motion are equivalent to the Newtonian ones in a Cartesian coordinate system.
- Given the definition of the conjugate momenta as

$$p_m = \frac{\partial \mathcal{L}}{\partial \dot{q}_m} \quad \text{for} \quad m = 1, 2, ..., M \ ,$$

where the dot over a symbol denotes its time derivative, and of the Hamiltonian $\mathcal{H}$ as

$$\mathcal{H} = -\mathcal{L} + \sum_{m=1}^{M} p_m \, \dot{q}_m \ ,$$

derive the corresponding classical Hamiltonian equations of motion.

b. Write the equation for calculating the excess chemical potential μ_{exc} of an extra particle added to a N-particles system according to the Widom particle-insertion method. Additional questions:

- State the condition that must be fulfilled in order for this equation to provide an accurate estimate of μ_{exc} based on finite (and relatively short) simulations.
- Provide an alternative strategy that one can use to calculate μ_{exc} when the above condition is not met.

3   Derivations (F2021.3)

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 Lennard-Jones potential-energy function can be written

$$U_{\mathrm{LJ}} = C_{12}r^{-12} - C_6 r^{-6} \; ,$$

where r is the distance between two particles, and C_{12} and C_6 are positive coefficients. It is also common to use different parameter pairs in place of $\{C_6, C_{12}\}$, typically $\{\epsilon, \sigma\}$ or $\{\epsilon, r_m\}$. Here, σ is the zero-point of the curve (also called collision diameter), r_m is the minimum-point of the curve (also called equilibrium distance), and ϵ is the value of the energy at this minimum (also called well depth).

- Sketch the Lennard-Jones function and indicate where σ, r_m and ϵ can be read on the graph (also specify the location of the zero on both axes).

- Derive the expressions providing σ, r_m and ϵ as a function of C_6 and C_{12}.

- Rewrite the equation for U_{LJ} using the parameter pair $\{\epsilon, \sigma\}$ or the parameter pair $\{\epsilon, r_m\}$ instead of $\{C_6, C_{12}\}$ (you need to write both equations).

b. Consider a quantum system that can exist in two states labelled 1 and 2, with energies 0 and ΔE, respectively. Consider a canonical ensemble of such systems at a given absolute temperature T.

- Write the most probable distribution of systems over states in the form of the fractions p_1 and p_2 of systems that are found in states 1 and 2, respectively.

- State the limits of p_1 and p_2 when T becomes very small ($T \to 0$) or very large ($T \to \infty$).

- Write the corresponding canonical partition function Z, free energy F, and internal energy U.

4 Explicit Calculations (F2021.4)

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

a. A mass of 1 kg is placed on the lid of a piston (cylinder) of section 10 cm^2 containing a gas. As a result of the added mass, the gas is compressed, and the lid moves down by 1 cm. Calculate the work performed by the environment (added mass + atmospheric pressure; the weight of the lid itself can be neglected) on the system. For this, use a value of 10 m·s^{-2} for the gravitational acceleration, and a value of 1 bar (10^5 J·m^{-3}) for the atmospheric pressure.

b. According to the Maxwell-Boltzmann distribution of velocities $p(v)$, the mean velocity $\bar{v}$ of an atom in a monoatomic gas is given by

$$\bar{v} = \left(\frac{8k_B T}{\pi m} \right)^{1/2} \ ,$$

where m is the mass, T the absolute temperature, and k_B the Boltzmann constant. Calculate the mean velocity $\bar{v}$ in m·s^{-1} of an argon atom (molar mass 40 g·mol^{-1}) at a temperature of 25 °C. For this, use the following approximations: the gas constant (*i.e.* k_B expressed on a per-mole basis) is 8 J·mol^{-1}K^{-1}, the absolute zero is -275 °C, and π is 3. Additional questions:

   - State by how many percent $\bar{v}$ 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 $\bar{v}$, the root-mean-square velocity $\overline{v^2}^{1/2}$, and the most probable velocity v^*.
   - State how the value of $\bar{v}$ in liquid argon 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 (F2021.5)

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 `MonteCarlo2DwithPBC` that will perform a two-dimensional Monte Carlo sampling of `N` iterations. The two variables `x` and `y` should be initialized to zero, and allowed to evolve in the ranges $[-\pi, \pi)$, thereby defining a square domain. Periodic boundary conditions should be applied at the edges of this domain, *i.e.* if a move exits the domain, the position should be reset within it by means of appropriate $\pm 2\pi$ translations. The energy function to be sampled is $c \cdot \sin(x \cdot y)$, where `c` is a force constant (units of energy). The temperature multiplied by the Boltzmann constant is provided to the function as `kbT` (units of energy), and the step size to be used for the trial moves is provided as `dr` (unitless). The function declaration reads

```
void MonteCarlo2DwithPBC (int N, double c, double kbT, double dr);
```

Your function has access to the mathematical functions `sin()` and `sqrt()`, as well as to a pseudo-random number generator function `rand()`. Each successive call to `rand()` will provide a new pseudo-random real in the range $[0; 1)$. It is also assumed that π is available through a global variable `pi`.