Examination D-CHAB Fall 2022:
Statistical Physics for CSE

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HPH G3

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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 (F2022.1)

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

a. The ergodic theorem relates two types of averages, involved in statistical mechanics and in molecular dynamics, respectively. Give a precise statement of this theorem, and describe its limitations in practical situations.

b. The SHAKE algorithm permits to enforce bond-lengths constraints in molecular dynamics simulations carried out with Cartesian coordinates. Answer the following questions concerning SHAKE.

- State the three main reasons why the use of constrained bonds is to be preferred over that of flexible bonds.
- State the two simplifications that are made in SHAKE for solving the system of equations involved in constraining all the bonds in a molecule.
- Considering a diatomic molecule (two atoms, one bond), illustrate with a drawing how the SHAKE coordinate resetting operates to correct a free-flight step into a constrained step.
- Explain why the SHAKE algorithm is an iterative (rather than a one-step) procedure.
- State under which circumstances the algorithm may fail to converge.

c. A fellow student expresses the opinion that the bit sequence (0,0,0,0,0,0,1,1,1,1,1,1) has a lower entropy than the bit sequence (0,0,1,1,0,1,1,0,0,1,0,1), because the values are cleanly separated in the first sequence but randomly mixed in the second one. Do you agree or disagree? (or, possibly, complain about an ill-formulated statement). Your answer must be accompanied with a brief explanation.

2 Fundamental Equations (F2022.2)

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 equation for the Coulomb interaction between two atoms with partial charges q_1 and q_2 at a distance r_{12}. Sketch the graph of the function, considering two possible situations depending on the signs of the charges.

b. The microscopic (instantaneous) configuration of a classical system of N particles is determined by the $3N$-dimensional Cartesian position and momentum vectors $\mathbf{r}$ and $\mathbf{p}$ of the system. The system is confined (using either fixed walls or periodic boundary conditions) to a volume $\mathcal{V}$.

  - Write the expression for the microscopic observable $\mathcal{P}(\mathbf{r}, \mathbf{p}, \mathcal{V})$ that corresponds to the pressure in the system.
  - Discuss this expression in the context of a monoatomic gas, considering both the ideal- and the real-gas situations.
  - Give the equation connecting $\mathcal{P}$ to its canonical ensemble average P.

3 Derivations (F2022.3)

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. Consider a Hamiltonian $\mathcal{H}(\lambda) \doteq \mathcal{H}(\mathbf{r}, \mathbf{p}; \lambda)$ that depends on the Cartesian coordinate vector $\mathbf{r}$ and momentum vector $\mathbf{p}$ of a molecular system, as well as on a coupling parameter λ. In the context of a canonical ensemble, derive the thermodynamic integration (TI) formula

$$\frac{dF(\lambda)}{d\lambda} = \left\langle \frac{\partial \mathcal{H}}{\partial \lambda} \right\rangle ,$$

which relates the λ-derivative of the Helmholtz free energy F to the ensemble average of the λ-derivative of the Hamiltonian $\mathcal{H}$. For this, you will need to: (i) write the equation connecting the Helmholtz free energy F to the canonical partition function Z; (ii) write the equation for the classical partition function Z (as determined by the Hamiltonian $\mathcal{H}$); (iii) use these two expressions to formulate $dF/d\lambda$; (iv) recast the resulting expression in the form of a canonical ensemble average $\langle ... \rangle$.

b. A computer program has to perform some operation on all the possible permutations of an ensemble of N objects. Show that the computational scaling of this program is $\mathcal{O}[(N/e)^N]$ where e is the Euler number, *i.e.* that in the limit of large N, the required computer time will increase in proportion to $(N/e)^N$. For this, you will need to: (i) find the mathematical expression for the number of permutations; (i) use an appropriate approximation for this number, valid in the limit of large N.

4 Explicit Calculations (F2022.4)

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 term 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 argon atoms are 0.3 nm and 1 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 argon 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 (F2022.5)

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 `VelAutoCorrel` that will calculate the velocity auto-correlation function $c(\tau)$ considering a simulation of N atoms carried out for a duration t_{sim}, according to the equation

$$c(\tau) = \left\langle \frac{1}{N} \sum_{n=1}^{N} \mathbf{v}_n(t+\tau) \cdot \mathbf{v}_n(t) \right\rangle_t \ ,$$

where $\mathbf{v}_n(t)$ is the Cartesian velocity vector of atom n in the trajectory frame at time t, and $\langle \cdots \rangle_t$ indicates averaging over all possible time origins t from 0 to $t_{sim} - \tau$. In practice, the trajectory is discretized using a timestep Δt, so that time is specified by an integer index $k = 0, 1, ..., k_{max} - 1$ as $t = k\Delta t$, where k_{max} is the the total number of trajectory frames (*i.e.* $k_{max}\Delta t = t_{sim}$). The function declaration reads

```
void VelAutoCorrel ( int N, int kmax, double v[][3*N], double c[] );
```

Provided to the function are the number `N` of atoms, the number `kmax` of trajectory frames, and the trajectory array `v`, in which `v[k][3*n+i]` contains the ith component (0,1,2 for x,y,z) of $\mathbf{v}_n(k\Delta t)$. The function should fill the array `c` with the values of $c(k\Delta t)$ for $k = 0, 1, ..., k_{max}-1$. Additional questions:

- Explain why, in practice, the curve calculated for $c(\tau)$ will become increasingly "noisy" as τ approaches t_{sim}.

- The integral of $c(\tau)$ from 0 to ∞ is related to an important transport property of the system. State which property and write the connecting equation (due to Green and Kubo).

- There is an alternative route for calculating the same property. State what observable has to be calculated from the trajectory and write the connecting equation (due to Einstein).