

Statistical Physics B

Mid-term exam, 15/11/2021
09:15 — 12:00

Problem 1 (8 points):

Consider a container divided into k cells of equal volume. We randomly place N identical (but distinguishable) particles into the container. A macrostate $\{N_1, \dots, N_k\}$ is characterized by specifying the number N_i ($i \in \{1, \dots, k\}$) of particles in each of the cells.

- (4 points) Express the number of microstates Ω as function of $\{N_i\}_{i \in \{1, \dots, k\}}$. Don't just write down the formula. Argue for it.
- (4 points) For $N_i \gg 1$ (and $\sum_i N_i = N$) demonstrate that $\ln \Omega$ attains a stationary value for the uniform distribution, where $N_i = N/k$.

Problem 2 (24 points):

Consider a classical gas of diatomic molecules. The gas is contained in a closed container of volume V and at the thermal equilibrium at temperature T . We also know number of molecules, it is equal to N .

The molecules do not interact with each other. We approximate the intramolecular interaction by the quadratic term (see the Hamiltonian below). Such approximation is valid in the regime when $ar^2 \gg kT$. When solving the problem assume that this condition always holds.

- (2 points) The motion of a single molecule consists of a linear motion in all the 3 dimensions, a rotational motion and a vibrational motion. Count the degrees of freedom and use the equipartition theorem to predict the internal energy of the gas. Compute the heat capacity and specify which part of it comes from linear, rotational and vibrational modes.
- (4 points) The Hamiltonian of a single molecule is

$$H(\vec{q}_1, \vec{p}_1, \vec{q}_2, \vec{p}_2) = \frac{|\vec{p}_1|^2}{2m} + \frac{|\vec{p}_2|^2}{2m} + \frac{a}{2}(|\vec{q}_1 - \vec{q}_2| - r)^2. \quad (1)$$

Here \vec{q}_1 and \vec{q}_2 are positions of the two particles building up the molecule, \vec{p}_1 and \vec{p}_2 are their momenta, and r is the equilibrium distance between the molecules. By going to the center of mass frame of the reference the Hamiltonian becomes

$$H(\vec{R}, \vec{P}, \vec{q}, \vec{p}) = \frac{|\vec{P}|^2}{2M} + H_{\text{int}}(\vec{q}, \vec{p}), \quad H_{\text{int}}(\vec{q}, \vec{p}) = \frac{|\vec{p}|^2}{2\mu} + \frac{a}{2}(|\vec{q}| - r)^2, \quad (2)$$

where \vec{P} is the momentum of the center of mass, \vec{p} is the relative momentum and \vec{q} is the relative position. Moreover $M = 2m$ is the total mass of the molecule and $\mu = m/2$ is the reduced mass. Consider a single particle partition function and show that it can be written as

$$Q_1(V, T) = V \frac{(2\pi M k T)^{3/2}}{h^3} \times j(T), \quad (3)$$

where $j(T)$ takes into the account the internal motion (accounting for the rotational and vibrational contributions to the partition function). At this stage you don't have to compute $j(T)$.

Write down a formula for the partition function for N indistinguishable molecules.

- (4 points) Consider now the thermodynamics of the gas. Derive expression for the equation of state and the internal energy. Your answer should involve, so far unknown, function $j(T)$. Compute the heat capacity. Compare your results with the ideal gas of monatomic particles of mass M . What would $j(T)$ be then equal to? Based on your result, which measurement can reveal internal structure of the molecules of the gas?

4. (2 points) We inspect now the form of the $j(T)$. By going to the spherical coordinates (given by q, θ, ϕ and p, p_θ, p_ϕ) the Hamiltonian of the internal motion becomes

$$H_{\text{int}}(\vec{q}, \vec{p}) = H_{\text{rot}}(q, \theta, p_\theta, p_\phi) + H_{\text{vib}}(q, p_q), \quad (4)$$

where

$$H_{\text{rot}}(q, \theta, p_\theta, p_\phi) = \frac{1}{2\mu q^2} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right), \quad H_{\text{vib}}(q, p_q) = \frac{p_q^2}{2\mu} + \frac{a}{2}(|q| - r)^2. \quad (5)$$

Note that both contributions depend on q . Under which condition, in the rotational part, we can take $q = r$? With this approximation $j(T)$ factorizes into

$$j(T) = j_{\text{rot}}(T) \times j_{\text{vib}}(T). \quad (6)$$

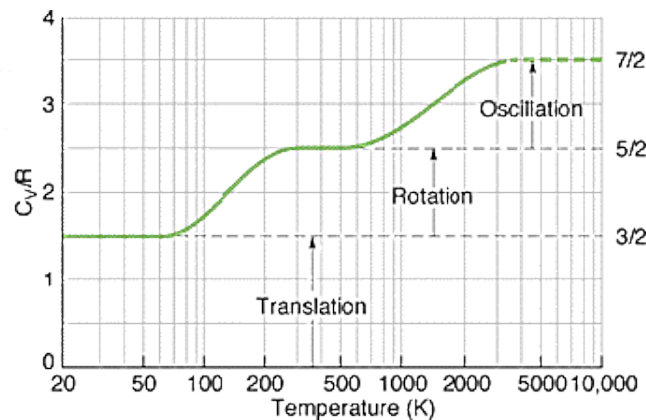
Write down expressions (in the form of integrals over the appropriate configurational spaces) for both contributions.

5. (4 points) We focus now on the vibrational part of the problem. Evaluate $j_{\text{vib}}(T)$ by performing the integral over possible configurations. You might want to use here the condition $ar^2 \gg kT$.
6. (2 points) Establish the contribution from vibrational modes to the internal energy and compare with the result found in part 1). If you see a discrepancy explain its origin.
7. (4 points) The vibrational part of the Hamiltonian given above can be seen as the leading expression for an actual intermolecular potential. We can include a quartic correction

$$H_{\text{vib}}(p, q) = \frac{a}{2}(q - r)^2 + \frac{b}{24}(q - r)^4. \quad (7)$$

where b is a constant such that $br^2 \ll a$. Recompute $j_{\text{vib}}(T)$ in this situation using that b is relatively small to expand the integrals in the zeroth and first order in b . Compute the internal energy including the leading correction in b . Compare again with the predictions of the equipartition theorem. If you see a discrepancy explain its origin.

8. (2 points) The figure below shows the dependence of the heat capacity on temperature of a typical diatomic gas as measured in an experiment. Discuss your predictions in the view of the presented data (note that the assumption $ar^2 \gg kT$ is irrelevant for this discussion). Why the experimental predictions (correctly) depend on the temperature?



Good luck!

Useful formulas

- Gaussian integrals

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}.$$

$$\int_{-\infty}^{\infty} x^4 e^{-x^2} dx = \frac{3\sqrt{\pi}}{4}.$$

- Thermodynamics

$$A(N, V, T) = -kT \ln Q_N(V, T).$$

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T, N}, \quad S = - \left(\frac{\partial A}{\partial T} \right)_{V, N}, \quad \mu = \left(\frac{\partial A}{\partial N} \right)_{T, V}$$