

Physics 504: Statistical Mechanics
Department of Physics, UIUC
Spring Semester 2013
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Problem Set No. 2:
The Canonical Ensemble
Due Date: Monday February 18, 2013, 9:00 am

In this problem set we will consider the statistical mechanics of a set of N molecules at temperature T in a volume V . We will assume that the molecules are planar (“benzene-like”), each with mass M and moment of inertia I with respect to the z -axis, which we will take to be perpendicular to the plane of the molecule. We will consider a simplified system in which each molecule has only one vibrational degree of freedom with effective mass μ and spring constant K . We will also assume that the system is a dilute gas so that we can neglect the interactions between molecules. Under these assumptions the quantum mechanical Hamiltonian of the system is given by

$$\begin{aligned} H &= H_{\text{translations}} + H_{\text{rotations}} + H_{\text{vibrations}} \\ &= \sum_{i=1}^N \frac{\vec{P}_i^2}{2M} + \sum_{i=1}^N \frac{L_{z,i}^2}{2I} + \sum_{i=1}^N \left[\frac{p_i^2}{2\mu} + \frac{K}{2} q_i^2 \right] \end{aligned}$$

Here we have denoted by \vec{P}_i the momentum of the center of mass of the i -th molecule, $L_{z,i}$ is the z -component of the angular momentum of the i -th molecule about its own z -axis, and p_i and q_i are the canonical momentum and coordinate for the vibrational degree of freedom of the molecule.

In what follows we will assume that the temperature T is high enough so that we can use a purely classical treatment of the translational degrees of freedom. However, the rotational and vibrational degrees of freedom will be treated quantum mechanically.

The rotational Hilbert space is spanned by the kets $\{|\ell_i\rangle\}$, where the integers ℓ_i are related to the eigenvalues of $L_{z,i}$ by

$$L_{z,i}|\ell_i\rangle = \hbar\ell_i|\ell_i\rangle$$

Likewise, the vibrational Hilbert space is spanned by the kets $\{|n_i\rangle\}$, where $|n_i\rangle$ are the eigenstates of the harmonic-oscillator vibrational degree of freedom of each molecule. In what follows we will write the vibrational part in terms of the creation and annihilation operators a_i^\dagger and a_i of the i -th vibrational oscillator,

$$H_{\text{vibrations}} = \sum_{i=1}^N \hbar\omega \left(a_i^\dagger a_i + \frac{1}{2} \right)$$

where $[a_i, a_j^\dagger] = \delta_{ij}$ and

$$\begin{aligned} |n_i\rangle &= \frac{1}{\sqrt{n_i!}} (a_i^\dagger)^{n_i} |0_i\rangle \\ a_i |0_i\rangle &= 0 \\ a_i^\dagger a_i |n_i\rangle &= n_i |n_i\rangle \end{aligned}$$

and $\omega = \sqrt{K/\mu}$.

1. For what range of densities $n = N/V$ it is correct to treat the translational degrees of freedom classically? Justify your answer.
2. Show that for this system the partition function factorizes, *i. e.*

$$Z = Z_{\text{translations}} Z_{\text{rotations}} Z_{\text{vibrations}}$$

Show that a consequence of this results is that the free energy is a sum of three terms

$$F = F_{\text{translations}} + F_{\text{rotations}} + F_{\text{vibrations}}$$

Find explicit expressions for all three terms. Note: the vibrational partition function is a simple geometric series and you should sum it; leave the rotational partition function in the form of a series.

3. (a) Find an explicit expression for $F_{\text{translations}}$ as a function of N , V and T . Show that it is *extensive*.
 (b) Use your result to compute the contribution of the translational degrees of freedom to the specific heat at constant volume c_V .
4. (a) Derive an expression for $F_{\text{rotations}}$ valid for all temperatures. Show that it is also extensive. What is the dimensionless parameter that controls the behavior of this free energy? Note: for the purposes of this item you may write your result for $F_{\text{rotations}}$ in terms of a series.
 (b) Derive an expression for the contribution of the rotational degrees of freedom to the internal energy $U_{\text{rotations}}$ of the system valid for all temperatures. You may write your result in terms of a series.
 (c) Find an approximate expression for $U_{\text{rotations}}$ valid at *low temperatures*.
 (d) Use this result to compute the contribution of the rotational degrees of freedom to the specific heat at low temperatures. What is the form of its temperature dependence? Give a qualitative argument to explain this result.
 (e) Use the Poisson Summation Formula (given below) to find an expression for $U_{\text{rotations}}$ valid at *high temperatures*.

- (f) What prediction do you find for the behavior of the rotational specific heat at high temperatures? What is the asymptotic value of the rotational specific heat at high temperatures? Compare this result with the specific heat for an ideal gas and give an explanation for the differences you found.
5. (a) Consider now the vibrational degrees of freedom. Derive an explicit and exact expression for the free energy $F_{\text{vibrational}}$ valid for all temperatures.
- (b) Use the result derived above to find an expression for the internal energy $U_{\text{vibrations}}$ and of the specific heat $C_{\text{vibrations}}$ valid for *all temperatures*.
- (c) Find an approximate expression for $C_{\text{vibrations}}$ valid at *low temperatures*; low compared to what? Compare your result for the low temperature form of $C_{\text{vibrations}}$ with that of $C_{\text{vibrations}}$. Do they have the same temperature dependence? Explain.
- (d) Derive an approximate expression for $C_{\text{vibrations}}$ valid at *high temperatures*. Compare this result with the specific heat of an ideal gas of point particles and with the high temperature specific heat of the rotational degrees of freedom. Explain the differences and similarities that you found.
6. Write an expression for the *total entropy* of the system in the limits of (a) low temperature and (b) high temperature. determine which degrees of freedom give the dominant contribution in each regime and explain your answer physically.
7. Find a general formula for the fluctuations of the total internal energy at a given temperature T .

Useful Mathematical Formulae:

Geometric Sum:

$$\sum_{n=0}^{\infty} e^{-nA} = \frac{1}{1 - e^{-A}}$$

Poisson Summation Formula:

$$\sum_{n=-\infty}^{\infty} e^{-\frac{A}{2}n^2} = \int_{-\infty}^{\infty} dx \sum_{m=-\infty}^{\infty} e^{2\pi imx - \frac{A}{2}x^2} = \sum_{m=-\infty}^{\infty} \sqrt{\frac{2\pi}{A}} e^{-\frac{2\pi^2}{A}m^2}$$

Stirling's approximation:

$$\log N! = N \log N - N + O(\log N)$$