

Answer on Question #50679-Physics-Molecular Physics-Thermodynamics

Show that the partition function of an N-particle system is given by the expression:

$$Z_n = Z^N = \frac{V^N}{h^{3N}} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

Obtain expressions for (i) heat capacity at constant volume, (ii) average pressure exerted by the gas, and (iii) Helmholtz free energy F.

Solution

Let us now practice calculating thermodynamic relations using the partition function by considering an example with which we are already quite familiar: i.e., an ideal monatomic gas. Consider a gas consisting of N identical monatomic molecules of mass m enclosed in a container of volume V . Let us denote the position and momentum vectors of the i -th molecule by r_i and p_i , respectively. Since the gas is ideal, there are no interatomic forces, and the total energy is simply the sum of the individual kinetic energies of the molecules:

$$E = \sum_{i=1}^N \frac{p_i^2}{2m}$$

Let us treat the problem classically. In this approach, we divide up phase-space into cells of equal volume h^f . Here, f is the number of degrees of freedom, and h is a small constant with dimensions of angular momentum which parameterizes the precision to which the positions and momenta of molecules are determined. Each cell in phase-space corresponds to a different state. The partition function is the sum of the Boltzmann factor $\exp(-\beta E_r)$ over all possible states, where E_r is the energy of state r . Classically, we can approximate the summation over cells in phase-space as an integration over all phase-space. Thus,

$$Z = \int \dots \int \exp(-\beta E) \frac{d^3 r_1 \dots d^3 r_N d^3 p_1 \dots d^3 p_N}{h^{3N}}$$

where $3N$ is the number of degrees of freedom of a monatomic gas containing N molecules. The above expression reduces to

$$Z = \frac{V^N}{h^{3N}} \int \dots \int \exp\left(-\beta \frac{p_1^2}{2m}\right) d^3 p_1 \dots \exp\left(-\beta \frac{p_N^2}{2m}\right) d^3 p_N$$

Note that the integral over the coordinates of a given molecule simply yields the volume of the container, V , since the energy E is independent of the locations of the molecules in an ideal gas. There are N such integrals, so we obtain the factor V^N in the above expression. Note, also, that each of the integrals over the molecular momenta is identical: they differ only by irrelevant dummy variables of integration. It follows that the partition function Z of the gas is made up of the product of N identical factors: i.e.,

$$Z = \zeta^N,$$

where

$$\zeta = \frac{V}{h^3} \int \exp\left(-\beta \frac{p^2}{2m}\right) d^3 p.$$

The integral is easily evaluated:

$$\int \exp\left(-\beta \frac{p^2}{2m}\right) d^3p = \int_{-\infty}^{\infty} \exp\left(-\beta \frac{p_x^2}{2m}\right) dp_x \cdot \int_{-\infty}^{\infty} \exp\left(-\beta \frac{p_y^2}{2m}\right) dp_y \cdot \int_{-\infty}^{\infty} \exp\left(-\beta \frac{p_z^2}{2m}\right) dp_z$$

$$= \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}}.$$

Thus,

$$Z = \frac{V^N}{h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}.$$

(i)

$$C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V.$$

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\frac{3}{2}N}{\beta} = \frac{3}{2}NkT.$$

$$C_V = \frac{3}{2}Nk.$$

(ii)

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{1}{\beta} \frac{N}{V} = \frac{NkT}{V}.$$

(iii)

$$F = -kT \ln Z = -NkT \ln \left(\frac{V}{h^3} (2\pi mkT)^{\frac{3}{2}}\right).$$