Statistical Physics: Workshop Problems 5

(1) A gas of N classical weakly-interacting particles is in contact with a heat bath at temperature T. The gas has a number of independent degrees of freedom.

(a) Using the Boltzmann distribution the average energy for a degree of freedom x with energy $\epsilon(x)$ is

$$\langle \epsilon(x) \rangle = \frac{\int_{-\infty}^{\infty} \epsilon(x) \exp[-\beta\epsilon(x)]dx}{\int_{-\infty}^{\infty} \exp[-\beta\epsilon(x)]dx}.$$

If $\epsilon(x) = ax^2$, where $a > 0$ and the variable x takes values in the range $-\infty < x < \infty$, obtain the average energy of a particle in this system. Note that

$$\int_{-\infty}^{\infty} \exp(-b\,x^2)dx = \sqrt{\frac{\pi}{b}}.$$

(b) Show that the internal energy U of this system of N particles, when there are η such degrees of freedom (each associated with a quadratic energy term) is

$$U = \eta\,\frac{Nk_{\mathrm{B}}T}{2}.$$

This result is known as the *Equipartition Theorem.*

(2) The heat capacity at constant volume is defined as $C_V = [dU/dT]_V$. Use the Equipartition Theorem to obtain C_V in each of the following cases (ignoring electron excitations).

(a) A gas of N monoatomic neon atoms (translational motion only).

(b) A gas of N diatomic molecules of oxygen (O_2) at room temperature, due to the translational and rotational motion only (at room temperature, these are excited mainly).

(c) A gas of N diatomic molecules of oxygen (O_2) at higher temperatures, due to the contribution of vibrations only.

(d) A gas of N diatomic molecules of oxygen (O_2) at higher temperatures, due to translations, rotations and vibrations.

(3) The vibrations of a diatomic molecule can be approximated as one dimensional harmonic oscillations with energies $\epsilon_n^{\mathrm{vibr}} = (n + 1/2)\hbar\omega$, with $n = 0, 1, 2, \ldots$ and ω is the frequency of the oscillation.

(a) Derive the single-particle partition function Z_1^{vibr} for the vibrations of a diatomic molecule.

[Hint: $1 + r + r^2 + \ldots = (1 - r)^{-1}$, for $|r| < 1$.]

(b) Derive the vibrational energy, U^{vibr}, and heat capacity at constant volume, C_V^{vibr}, for a gas of N molecules of O_2. Compare your answer with that of question (2).

(c) The characteristic temperature for the excitation of vibrations, T^{vibr}, in a diatomic molecule is defined as $k_{\mathrm{B}}T^{\mathrm{vibr}} = \hbar\omega$. Write the vibrational heat capacity in terms of the ratio T^{vibr}/T.

(d) The characteristic temperature for vibrations in O_2 is $T^{\mathrm{vibr}} = 2200$ K. At room temperature (293 K) what is the vibrational heat capacity C_V^{vibr} and the percentage contribution of the vibrations to the total heat capacity of O_2 gas at constant volume?