Faculty of Engineering and Physical Sciences
Department of Physics

Year 2, Energy and Entropy
Problem Set 4

Partition function, Z

1. Consider a system with 3 energy levels. The levels or states have energies $-\epsilon$, 0 and ϵ. Find

(a) the partition function Z of the system,

(b) the Helmholtz free energy F of the system,

(c) the probability of being in the middle-energy state when $\epsilon = kT$,

(d) the mean energy of the system at very high temperatures, temperatures such that $kT \gg \epsilon$,

(e) and the mean energy of the system at very low temperatures, temperatures such that $kT \ll \epsilon$.

Comment on the following:

f) Consider the dimensionless reduced heat capacity C_V/k. If $\epsilon = 10^{-20}J$, then is C_V/k large or small at the temperatures: i) 10K,ii) 1000K, iii) 10^6K? Here large means of order unity, while small means much less than one.

g) If the energy levels of the system have energies 0, ϵ and 2ϵ, instead of the $-\epsilon$, 0 and ϵ as above, is: i) the energy different?, ii) the heat capacity different?

2. Show that the Helmholtz free energy, F, of a set of N localized particles, each of which can exist in levels of energy $0, \epsilon, 2\epsilon$ and 3ϵ having degeneracies $1, 3, 3$ and 1 respectively, is

$$F = -3Nk_BT \ln\left(1 + \exp\left(-\frac{\epsilon}{k_BT}\right)\right).$$

3. The partition function of a system is given by the equation

$$Z = e^{aT^3V}$$

where a is a constant. Calculate the pressure, the entropy, and the internal energy of the system.

4. The position-dependent part of the partition function Z of a classical particle is

$$Z = \int \exp\left[-u(x)/k_BT\right] \mathrm{d}x$$

where $u(x)$ is the energy of the particle at position x, k_B is Boltzmann's constant and T is the temperature. If $u(x) = 0$ in the range from $x = 0$ to $x = L$ but is infinite outside this range obtain an expression for Z. Use this expression for Z to obtain an expression for the Helmholtz free energy F. Then using the fact that the pressure p is related to the Helmholtz free energy F by

$$p = -\frac{\partial F}{\partial L}$$

obtain an expression for the pressure p. If $L = 1\text{nm}$, and $T = 1000\text{K}$, calculate the pressure.

5. A binary alloy is composed of N_A atoms of type A and N_B atoms of type B. Each A-type atom can exist in its ground state or in an excited state of energy ϵ (all other states are of such high energy that they can be neglected). Each B-type atom similarly can exist in its ground state of energy zero or an excited state of energy 2ϵ. The system is in equilibrium at temperature T.

(a) Calculate the Helmholtz potential of the system.

(b) Calculate the heat capacity of the system.

Heat capacity of crystalline solids

6. Calculate the entropy of the lattice vibrations of a solid as described by the Einstein theory. Obtain limiting expressions for the entropy valid at low and at high temperature.

Obtain an equation for the mean quantum number, $\bar{n}$, of an Einstein oscillator as a function of the temperature. Calculate $\bar{n}$ for $k_BT/\hbar\omega = 0, 1, 100$.

7. Describe the Debye model for the internal energy of a solid, and obtain the result

$$U = \int_0^{\omega_D} \frac{V\omega^2}{2\pi^2 s^3} \frac{\hbar\omega}{e^{\hbar\omega/(k_BT)} - 1} d\omega$$

for each phonon polarization of speed s. Sketch the form of the integrand, and estimate the energy of the phonons which make the largest contribution to the internal energy of silicon at 30K and at the Debye temperature (625K). The average speed of sound in silicon is 7000ms^{-1}.

Fluctuations

8. Using the partition function, show that the mean square fluctuation in the energy of a system is

$$\langle \Delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = k_B T^2 C_V$$

where C_V is the heat capacity.