solutions for 2nd Mid-semester Examinations, Mar 2012

1. A system of N non-interacting identical, indistinguishable particles of mass m is confined to a 1-dimensional box of length L. At absolute zero temperature, write an expression for the total energy of the system and the frequency of the lowest energy photon that can be absorbed by the system, if the particles are (a) bosons; (b) fermions.

   Ans. The particle in a box energy levels are: $E_n = \frac{n^2 h^2}{8mL^2}$.

   The frequency for the $n+1 \leftarrow n$ transition is: $\nu_{n+1 \leftarrow n} = \frac{\Delta E_{n+1 \leftarrow n}}{h} = (2n+1)\frac{h}{8mL^2}$

   Bosons: all particles will occupy the lowest $(n=1)$ energy state. $\therefore$ total energy $= N.\frac{h^2}{8mL^2}$

   $\nu_{2 \leftarrow 1} = \frac{\Delta E_{2 \leftarrow 1}}{h} = (2.1+1)\frac{h}{8mL^2} = \frac{3h}{8mL^2}$

   Fermions: Each level will be occupied by two particles of opposite spin. In all, $N/2$ levels will be occupied.

   $\therefore$ total energy $=$

   $$\sum_{n=1}^{n=\frac{N}{2}} \frac{2.n^2 h^2}{8mL^2} = \frac{h^2}{4mL^2} \sum_{1}^{\frac{N}{2}} n^2 = \frac{\left[\frac{N}{2}\left(\frac{N}{2}+1\right)(N+1)\right]}{6} \cdot \frac{h^2}{4mL^2} = \frac{N(N+1)(N+2)}{96mL^2}$$

   and $\nu_{\frac{N}{2}+1 \leftarrow \frac{N}{2}} = \frac{\Delta E_{\frac{N}{2}+1 \leftarrow \frac{N}{2}}}{h} = (2.\frac{N}{2}+1)\frac{h}{8mL^2} = \frac{(N+1)h}{8mL^2}$

2. What are the terms contributing to the cohesive energy of an ionic crystal? Obtain the cohesive energy for the NaCl crystal, given the following data:
Equilibrium Na-Cl distance=0.281nm; Madelung constant= 1.748; $\frac{1}{4\pi\epsilon_0} = 9\times10^9 \text{Nm}^2/\text{C}^2$; ionisation energy for Na=5.41eV; electron affinity for Cl=3.61 eV. Write the final result in kcal/mol.

Since $\alpha = 1.748$ and $n \approx 9$, the potential energy per ion pair is

$$U_0 = -\frac{\alpha e^2}{4\pi\epsilon_0 r_0}\left(1 - \frac{1}{n}\right) = -\frac{(9\times10^9 \text{ N}\cdot\text{m}^2/\text{C}^2)(1.748)(1.}{2.81\times10^{-10}\text{ n}}$$

$$= -1.27\times10^{-18}\text{ J} = -7.96\text{ eV}$$

Half this figure, -3.98 eV, represents the contribution per ion crystal.

Now we need the electron transfer energy, which is the sum energy of Na and the -3.61-eV electron affinity of Cl, or $+1.53$ tributes $+0.77$ eV to the cohesive energy from this source. The t is thus

$$E_{\text{cohesive}} = (-3.98 + 0.77)\text{ eV} = -3.2$$

Ans.

3. For an ideal gas at temperature T, obtain expressions for:
   (a) the number of energy states between energy ϵ and $\epsilon+d\epsilon$; (b) the distribution of molecular speeds.
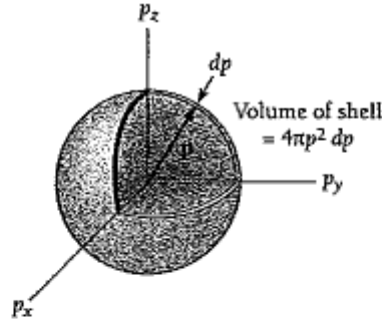

Figure 9.1 The coordinates in momentum space are p_x, p_y, p_z. The number of momentum states available to a particle with a momentum whose magnitude is between p and $p + dp$ is proportional to the volume of a spherical shell in momentum space of radius p and thickness dp.

The number of states $g(p)\ dp$ with momenta whose magnitudes are between p and $p + dp$ is proportional to the volume of a spherical shell in momentum space p in radius and dp thick, which is $4\pi p^2\ dp$. Hence

Number of
momentum states
$$g(p)\ dp = Bp^2\ dp \qquad (9.5)$$

where B is some constant. [The function $g(p)$ here is not the same as the function $g(\epsilon)$ in Eq. (9.4).]

Since each momentum magnitude p corresponds to a single energy ϵ, the number of energy states $g(\epsilon)\ d\epsilon$ between ϵ and $\epsilon + d\epsilon$ is the same as the number of momentum states $g(p)\ dp$ between p and $p + dp$, and so

$$g(\epsilon)\ d\epsilon = Bp^2\ dp \qquad (9.6)$$

Because

$$p^2 = 2m\epsilon \quad \text{and} \quad dp = \frac{m\ d\epsilon}{\sqrt{2m\epsilon}}$$

Eq. (9.6) becomes

Number of energy
states
$$g(\epsilon)\ d\epsilon = 2m^{3/2}\ B\sqrt{\epsilon}\ d\epsilon \qquad (9.7)$$

The number of molecules with energies between ϵ and $d\epsilon$ is therefore

$$n(\epsilon)\ d\epsilon = C\sqrt{\epsilon}\ e^{-\epsilon/kT}\ d\epsilon \qquad (9.8)$$

where $C(= 2m^{3/2}\ AB)$ is a constant to be evaluated.
To find C we make use of the normalization condition that the total number of molecules is N, so that

Normalization
$$N = \int_0^\infty n(\epsilon)\ d\epsilon = C \int_0^\infty \sqrt{\epsilon}\ e^{-\epsilon/kT}\ d\epsilon \qquad (9.9)$$

Ans. (a)
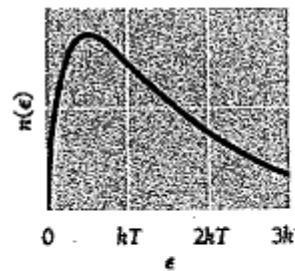

Figure 9.2 Maxwell-Boltzman energy distribution for the molecules of an ideal gas. The average molecular energy is $\bar{\epsilon} = \frac{3}{2}kT$.

The distribution of molecular speeds in an ideal gas can be found from Eq. (9.11) by making the substitutions

$$\epsilon = \tfrac{1}{2}mv^2 \qquad d\epsilon = mv\, dv$$

The result for the number of molecules with speeds between v and $v + dv$ is

Molecular-speed distribution
$$n(v)\, dv = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\, dv \qquad (9.14)$$

(b)

4. Why is the contribution of the electronic motion to the heat capacity of a metal insignificant at ordinary temperatures?

Ans.

Since Fermi energies for metals are usually several electronvolts (Table 9.2), the average electron energy in them at 0 K will also be of this order of magnitude. The temperature of an ideal gas whose molecules have an average kinetic energy of 1 eV is 11,600 K. If free electrons behaved classically, a sample of copper would have to be at a temperature of about 50,000 K for its electrons to have the same average energy they actually have at 0 K!

The failure of the free electrons in a metal to contribute appreciably to its specific heat follows directly from their energy distribution. When a metal is heated, only those electrons near the very top of the energy distribution—those within about kT of the Fermi energy—are excited to higher energy states. The less energetic electrons cannot absorb more energy because the states above them are already filled. It is unlikely that an electron with, say, an energy ϵ that is 0.5 eV below ϵ_F can leapfrog the filled states above it to the nearest vacant state when kT at room temperature is 0.025 eV and even at 500 K is only 0.043 eV.

5. Obtain an expression for the rotational quantum number for a diatomic molecule corresponding to maximum population at a given temperature [Hint: remember the degeneracy].
Ans. $N_J = N_o(2J+1)exp(-BhcJ(J+1)/kT)$ (N_J = number in level J)
Maximum population: $dN_J/dJ = 0 \implies J_{max} = (kT/2hcB)^{1/2} - \frac{1}{2}$

6. Obtain an expression for the average energy per oscillator in the cavity walls of an ideal black body. When Planck worked on the theory of black body radiation, the quantum 'mechanics' of an oscillator did not exist. Planck proposed that an oscillator may have n quanta of energy (each quantum=$h\nu$, where ν is the frequency of radiation emitted). From Maxwell Boltzmann statistics, we know that the probability of an oscillator having energy $nh\nu$ is $\propto e^{-\frac{nh\nu}{kT}}$.

Then, the average energy $=$

$$\frac{\sum_n nh\nu e^{-\frac{nh\nu}{kT}}}{\sum_n e^{-\frac{nh\nu}{kT}}}$$

Consider,

$$S = \sum_n e^{-na} = \frac{1}{1 - e^{-a}} \ (\because e^{-a} < 1); \quad \therefore \frac{dS}{da} = \sum_n n.e^{-na} = \frac{d}{da}\left(\frac{1}{1 - e^{-a}}\right) = \frac{e^{-a}}{(1 - e^{-a})^2}$$

Thus, taking $a = \frac{h\nu}{kT}$, the average energy $=$

$$h\nu \frac{\frac{e^{-a}}{(1-e^{-a})^2}}{\frac{1}{1-e^{-a}}} = \frac{e^{-a}}{1 - e^{-a}} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

If we use the results for a quantum mechanical harmonic oscillator, we will get a slightly different expression.

7. Why do we need statistics in modeling of natural systems? The role of chance is much more significant in the modeling of social processes than of natural systems in equilibrium. Comment on this statement.

Ans. Our knowledge of individual atoms or molecules is inadequate to understand the behaviour of the macroscopic systems. By the principles of quantum mechanics, the atoms or molecules are distributed in different energy eigen states, accordingly with different magnitudes of properties. In a collection of objects, there is an average behaviour over the distribution. To calculate the average behaviour, we need statistical tools. The larger the number of objects, the closer is the observed behaviour to the calculated average.

In natural systems, we have number of atoms/molecules of the order of Avogadro number, whereas in social systems, the number is much smaller. For example, the entire human population is only a few billions. Thus, the role of chance fluctuations becomes many orders of magnitude more important in social systems than in natural systems. In general, the effect of fluctuations $\propto \frac{1}{\sqrt{N}}$, where N is the number of objects in an ensemble.

8. Two diatomic molecules AB and CD are of equal reduced mass. The vibrational frequency of one is twice that of the other. How do we explain this?

   Ans. The vibrational frequency of the diatomic molecule$= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$. If the masses are identical, then the difference in frequency must be due to the difference in force constants. The force constant of one must be 4 times the other.

9. Last year's Nobel prize for chemistry went to Daniel Schechtman from Israel for his work on quasi-crystals, which has features that are abundant in motifs in old Islamic architecture. What is 'quasi' (meaning - 'resembling') about quasi-crystals?

   Ans. (From Wiki) A quasiperiodic crystal, or, in short, quasicrystal, is a structure that is ordered but not periodic. A quasicrystalline pattern can continuously fill all available space, but it lacks translational symmetry. While crystals, according to the classical crystallographic restriction theorem, can possess only two, three, four, and six-fold rotational symmetries, the Bragg diffraction pattern of quasicrystals shows sharp peaks with other symmetry orders, for instance five-fold.

rough work: