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PHYS-3341 Statistical Physics | Prof. Itai Cohen

Solutions to Problem Set 7

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7.1 Dilute Gas in an Enclosure

(a) By symmetry we see

$$\boxed{\bar{v}_z 0}\ .$$

By the maxwell-boltzmann distribution we have

$$\overline{|v_z|} = \frac{\int_{-\infty}^{\infty} |v_z| e^{-mv_z^2/2kT} dv_z}{\int_{-\infty}^{\infty} e^{-mv_z^2/2kT} dv_z} = \frac{2\int_0^{\infty} v_z e^{-mv_z^2/2kT} dv_z}{2\int_0^{\infty} e^{-mv_z^2/2kT} dv_z} = \frac{2kT/m}{\sqrt{2\pi kT/m}} = \sqrt{\frac{2kT}{\pi m}}$$

$$\overline{v^2} = \frac{2\int_0^{\infty} v_z^2 e^{-mv_z^2/2kT} dv_z}{2\int_0^{\infty} e^{-mv_z^2/2kT} dv_z} = \frac{\frac{1}{2}\sqrt{\pi}\left(\frac{2kT}{m}\right)^{3/2}}{\sqrt{\pi}\left(\frac{2kT}{m}\right)^{1/2}} = \frac{kT}{m}$$

(b) Define $\phi(v_z)$ as the # of molecules escaping per unit time per unit z-velocity. That is $\Phi = \int_0^{\infty} \phi(v_z) dv_z$. Now $\phi(v_z) = Av_z n(v_z)$ where $n(v_z)$ is the number of molecules with z-velocity v_z per unit volume per unit z-velocity.

$$n(v_z) = \frac{N}{V} \frac{e^{-mv_z^2/2kT}}{\int_{-\infty}^{\infty} e^{-mv_z^2/2kT dv_z}}$$

$$\Rightarrow \Phi = \frac{AN}{2V} \frac{\int_0^{\infty} e^{-mv_z^2/2kT} dv_z}{\int_0^{\infty} e^{-mv_z^2/2kT dv_z}} = \frac{AN}{2V}\overline{|v_z|} = \frac{AN}{V}\sqrt{\frac{kT}{2\pi m}}$$

(c) Now assume we cover the hole with a plate and assume elastic collisions on that plate. Then the froce on that plate per unit time is

$$F = \Phi \Delta p = 2m\Phi \overline{v_{z,esc}}$$

where Δp is the average change in momentum due to an elastic collision.

$$\Rightarrow P = \frac{F}{A} = \frac{2m}{A}\Phi \overline{v_{z,esc}}$$

(d)

$$\overline{v_{z,esc}} = \frac{AP}{2\Phi m} = \frac{PV}{Nm}\sqrt{\frac{\pi m}{2kT}} = \frac{kT}{m}\sqrt{\frac{\pi m}{2kT}} = \sqrt{\frac{\pi kT}{2m}} = \frac{\pi}{2}\overline{|v_z|}$$

For an ideal gas with maxwell-boltzmann distribution we have $\overline{v_{z,esc}} > \overline{|v_z|}$. Another way of seeing this is to recognize that the escaping molecules are "pushed" preferentially on one side, giving them a greater average speed.

$\square$

7.2 Two-Dimensional Gas

> **Reif §7.7:** Monoatomic molecules adsorbed on a surface are free to move on this surface and can be traeted as a classical ideal two-dimensional gas. At absolute temperature T, what is the heat capacity per mole of molecules thus adsorbed on a surface of fixed size?

In an ideal gas the particles are non-interacting , and there are no external potentials, therefore $V = 0$. Hence we have the energy $E = K$ the kinetic energy. The equipartition theorem gives us

$$\bar{E} = \bar{K} = 2N\left(\frac{1}{2}kT\right) = NkT$$

where 2 comes from the number of dimensions and N is the number of particles.

Thus we have

$$C = \frac{\partial \bar{E}}{\partial T} = Nk = \nu R \Rightarrow \boxed{\frac{C}{n} = R}$$

□

7.3 More Oscillators

> **Reif §7.10:** A system consists of N very weakly interacting particles at a temperature T sufficiently high so that classical statistical mechanics is applicable. Each particle has mass m and is free to perform one-dimensional oscillations about its equilibrium position. Calculate the heat capacity of this system of particles at this temperature in each of the following cases:
>
> **(a)** The force effective in resotring each particle to its equilibrium position is proportional to its displacement x from this position.
>
> **(b)** The restoring force is proportional to x^3.

(a) We have an energy of the form

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

Thus there are two seperate quadratic degrees of freedom per particle, hence we have by equipartition

$$\bar{E} = NkT \qquad \Rightarrow \qquad \boxed{C = \left(\frac{\partial E}{\partial T}\right) = Nk}$$

(b) For this system we have the energy

$$E = \sum_i^N \frac{p_i^2}{m} + \frac{1}{4} k_o x_i^4$$

The classical partition function is then

$$\begin{aligned} Z &= \frac{1}{h_0^N} \prod_i^N \int_{-\infty}^{\infty} e^{-\beta p_i^2/2m} dp_i \int_{-\infty}^{\infty} e^{-\beta k_o x_i^4/4} dx_i \\ &= \left(\frac{2\pi m}{h_o^2 \beta}\right)^{N/2} \left[\beta^{-1/4} \int_{-\infty}^{\infty} e^{-k_o y^4/4} dy\right]^N \qquad \text{(where } y = \beta^{1/4} x\text{)} \\ &= \left(\frac{2\pi m}{h_o^2}\right)^{N/2} \left[\int e^{-k_o y^4/4} dy\right]^N \beta^{-3N/4} \end{aligned}$$

Since the first two terms in the product do not depend on β we must have

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{4} NkT \qquad \Rightarrow \qquad \boxed{C = \frac{3}{4} Nk}$$

□

7.4 Specific heat of graphite

Reif §7.11: Assume the following highly simplified model for calculating the specific heat of graphite, which has a highly anisotropic crystalline layer structure. Each carbon atom in this structure can be regarded as performing simple harmonic oscillations in three dimensions. The restoring forces in directions parallel to a layer are very large; hence the natural frequencies of oscillations in the x and y directions lying within the plane of a layer are both equal to a value $\omega_\parallel$ which is so large that $\hbar\omega_\parallel \gg 300k$. On the other hand, the restoring force perpendicular to a layer is quite small; hence the frequency of oscillation $\omega_\perp$ of an atom in the z direction perpendicular to a layer is so small that $\hbar\omega_\perp \ll 300k$. On the basis of this model, what is the molar specific heat (at constant volume) of graphite at 300°K?

For harmonic oscillations we have energy $E = \hbar\omega(n + \frac{1}{2})$. Adding the terms for all directions we get

$$E = \hbar\omega_\perp(n_1 + n_2 + 1) + \hbar\omega_\parallel(n_\parallel + \frac{1}{2})$$

But since the energy terms are indepedent in each direction, we can separate direction dependence of the partition function

$$Z = Z_\perp Z_\parallel$$

where both $Z_\perp$ and $Z_\parallel$ are partition functions for harmonic oscillator(s). Now using the partition function to find the specific heat is simple

$$\begin{aligned} c_V &= \frac{\partial \bar{E}}{\partial T} = -\frac{\partial^2 \ln Z}{\partial T \partial \beta} \\ &= -\frac{\partial^2 \ln Z_\perp}{\partial T \partial \beta} - \frac{\partial^2 \ln Z_\parallel}{\partial T \partial \beta} \\ &= \frac{\partial \bar{E_\perp}}{\partial T} + \frac{\partial \bar{E_\parallel}}{\partial T} \end{aligned}$$

At $300^\circ K$, since $\hbar\omega_\parallel \gg 300k$ and $\hbar\omega_\perp \ll 300k$ following the argument at p.253 of Reif we get

$$\begin{aligned} \bar{E_\perp} &= \bar{E_1} + \bar{E_2} \simeq \hbar\omega_\perp(1 + 2e^{-\beta\hbar\omega_\perp}) \\ \bar{E_\parallel} &\simeq kT \end{aligned}$$

Taking the derivative of these with respect to T,

$$\begin{aligned} \frac{\partial \bar{E_\perp}}{\partial T} &= \frac{d\beta}{dT}\frac{\partial \bar{E_\perp}}{\partial \beta} = -\frac{1}{kT^2}\hbar\omega_\perp(-2\hbar\omega_\perp e^{-\beta\hbar\omega_\perp}) \\ &= 2k(\beta\hbar\omega_\perp)^2 e^{-\beta\hbar\omega_\perp}) \\ c_V &= k + \hbar\omega_\perp(-2\hbar\omega_\perp) \\ \frac{\partial \bar{E_\parallel}}{\partial T} &= k \end{aligned}$$

Combining this we get

$$c_V = k\left[2(\beta\hbar\omega_\perp)^2 e^{-\beta\hbar\omega_\perp} + 1\right]$$

Introducing the definition of Einstein temperature $\theta_E = \frac{\hbar\omega_\perp}{k}$ and summing over all the atoms in a mole(since above result was only for one atom),

$$\boxed{c_V = R\left[2\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T} + 1\right]}$$

□

7.5 Ferro Fluids

> **Reif §7.14:** Consider an assembly of N_0 weakly interacting magnetic atoms per unit volume at a temperature T and describe the situation classically. Then each magnetic moment μ can make any arbitrary angle θ with respect to a given direction (call it the z direction). In the absence of a magnetic field, the probability that this angle lies between θ and $\theta + d\theta$ is simply proportional to the solid angle $2\pi sin\theta d\theta$ enclosed in this range. In the presence of a magnetic field H in the z direction, this probability must further be proportional to the Boltzmann factor $e^{-\beta E}$, where E is the magnetic energy of the moment μ making this angle θ with the z axis. Use this result to calculate the classical expression for the mean magnetic moment $\bar{M_z}$ of these N_0 atoms.

Following the argument given in the problem we have

$$P(\theta)d\theta \propto 2\pi sin\theta d\theta e^{\beta\mu H cos\theta}$$

for one magnetic moment. Since they are only weakly interacting, we can consider the atoms individually and sum up in the end. Since we have the proportionality of $P(\theta)$ we can find the partition function as follows:

$$Z = \int_0^\pi d\theta 2\pi sin\theta d\theta e^{\beta\mu H cos\theta} = 2\pi \int_{-1}^{1} d(cos\theta) e^{\beta\mu H cos\theta} = 2\pi \left[\frac{e^{\beta\mu H cos\theta}}{\beta\mu H}\right]_{-1}^{1} = -\frac{4\pi}{\beta\mu H} sinh(\beta\mu H)$$

To find the average magnetization of the magnetic moment in z-direction,

$$\bar{\mu_z} = \frac{\partial \ln Z}{\partial(\beta H)} = \mu coth(\beta\mu H) - \frac{1}{\beta H}$$

thus for N_0 atoms

$$\boxed{\bar{M_z} = N_0\mu \left(coth(\beta\mu H) - \frac{1}{\beta\mu H}\right)}$$

□

7.6 Mean Values

Reif §7.19: A gas of molecules, each of mass m, is in thermal equilibrium at the aboslute temperature T. Denote the velocity of a molecule by $\vec{v}$, its three cartesian components by v_x, v_y and v_z, and its speed by v. What are the following mean values:

(a) $\overline{v_x}$

(b) $\overline{v_x^2}$

(c) $\overline{v^2 v_x}$

(d) $\overline{v_x^3 v_y}$

(e) $\overline{(v_x + bv_y)^2}$ where b is a constant

(f) $\overline{v_x^2 v_y^2}$

(a) $\overline{v_x} = 0$ since v_x is an odd function.

(b) $\overline{v_x^2} = \frac{kT}{m}$ by the equipartition thereom.

(c) $\overline{v^2 v_x} = 0$ since $v^2 v_x$ is an odd function

(d) $\overline{v_x^3 v_y} = 0$ since $v_x^3 v_y$ is odd in both v_x and v_y.

(e) $\overline{(v_x + bv_y)^2} = \overline{v_x^2 + 2bv_xv_y + bv_y^2} = \frac{kT}{m} + 0 + \frac{bkT}{m} = (1+b)\frac{kT}{m}$.

(f) $\overline{v_x^2 v_y^2} = \overline{v_x^2}\;\overline{v_y^2} = \left(\frac{kT}{m}\right)^2$ since the distributions of v_x and v_y can be considered independent.

□

7.7 Isotope Separation

Reif §7.26: A vessel is closed off by a porous partition through which gases can pass by effusion and then be pumped off to some collecting chamber. The vessel itself is filled with a dilute gas consisting of two types of molecules which differ because they contain two different atomic isotopes and have correspondingly masses m_1 and m_2. The concentrations of these molecules are c_1 and c_2, respectively, and are matintained constant inside the vessel by constantly replenishing the cupply of gas in it by a steady slow flow of fresh gas through the vessel.

(a) Let c_1' and c_2' denote the concentrations of the two types of molecules in the collecting chamber. What is the ratio c_2'/c_1'?

(b) By using the gas UF_6, one can attempt to separate U^{235} from U^{238}, the first of these isotopes being the one useful in initiation of nuclear-fission reactions. The molecules in the vessel are then $U^{238}F_6^{19}$ and $U^{235}F_6^{19}$. (The concentrations of these molecules, corresponding to the natural abundance of the two uranium isotopes, are $c_{238} = 99.3$ percent and $c_{235} = 0.7$ percent.) Calculate the corresponding ratio c'_{235}/c'_{238} of the molecules collected after effusion in terms of their original concentration ratio c_{235}/c_{238}.

(a) The ratio of concentration of the molecules in the collecting chamber will be the ratio of the molecules effused through the porous partition. From (7.11.13) average number of particles that will hit, i.e. pass through, the holes per unit area is

$$\Phi_0 = \frac{\bar{p}}{\sqrt{2\pi mkT}} = \frac{nkT}{\sqrt{2\pi mkT}}$$

where $\bar{p}$ is the mean pressure of the molecules, thus can be substituted to nkT using the equation of state. T is the same for the two types of molecules thus $\Phi_0 \propto \frac{n}{\sqrt{m}}$ is the relation relevant to the ratio.

$$\boxed{\frac{c'_1}{c'_2} = \frac{c_1}{c_2}\sqrt{\frac{m_2}{m_1}}}$$

(b) For UF_6, using the result of (a) we get

$$\boxed{\frac{c'_{235}}{c'_{238}} = \frac{c_{235}}{c_{238}}\sqrt{\frac{m_{238}}{m_{235}}} = \frac{c_{235}}{c_{238}}\sqrt{\frac{352}{349}} = 1.004 \times \frac{c_{235}}{c_{238}}}$$

Although the change in concentration ratio is small, by repeatedly using effusion we can increase the concentration of U^{235} in the mixture.

□