

## 8.08 Statistical Physics II

Intro to Gases and Equipartition Theorem  
(Dated: February 14, 2011)

1. Consider a 1D hard-sphere gas with molecule diameter  $a$ . Calculate the equation of state.

**Solution:**

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i=2}^N V(x_i - x_{i-1} - 1)$$

The partition function is

$$Z = \frac{1}{h^N} \int_0^L dx_1 \int_{x_1}^L dx_2 \dots \int_{x_{N-1}}^L dx_N e^{-\beta \sum_{i=1}^N V(x_i - x_{i-1})} \int_{-\infty}^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \dots \int_{-\infty}^{\infty} dp_N e^{-\beta \sum_{i=1}^N p_i^2/2m}$$

We change variables to  $\delta_i = x_i - x_{i-1}$  which gives

$$Z = \frac{1}{\lambda^N} \int_0^L d\delta_1 \int_{x_1}^{L-\delta_1} d\delta_2 \dots \int_{x_{N-1}}^{L-\sum \delta_i} dx_N e^{-\beta \sum_{i=1}^N V(\delta_i)}$$

where  $\lambda = h/\sqrt{2\pi m kT}$

We then define the Gibbs partition function as the Laplace transform of the partition function

$$G = \int_0^{\infty} dL e^{-\beta PL} Z$$

Since in the Gibbs partition function the value of  $L$  is taken from zero to infinity, the upper limits of the internal integrals will be taken to infinity, while the lower limit of the integrals will be  $a$ . So

$$G = \frac{1}{\lambda^N (\beta P)^2} \left[ \int_a^{\infty} d\delta e^{-\beta P \delta} \right]^{N-1} = \frac{1}{\lambda^N} \frac{1}{(\beta P)^{N+1}} (e^{-\beta Pa})^{N-1}$$

The mean length is given by  $L = -kT \frac{\partial \ln G}{\partial P} = \frac{(N+1)kT}{P} + (N-1)a$  and the equation of state becomes

$$[L - (N-1)a]P = (N+1)kT$$

The excluded volume here is easily visualized and our intuition agrees with the exact calculation.

2. Consider a heteronuclear diatomic molecule with moment of inertia  $I$ . In this problem, only the rotational motion of the molecule should be considered.

- (a) Using classical statistical mechanics, calculate the specific heat  $C(T)$  of this system at temperature  $T$ .
- (b) In quantum mechanics, this system has energy levels  $E_j = \frac{\hbar^2}{2I} j(j+1)$ ,  $j = 0, 1, 2, \dots$ . Each level is  $(2j+1)$ -fold degenerate. Using quantum statistical mechanics, find expressions for the partition function  $Z$  and the average energy  $\langle E \rangle$  of this system, as a function of temperature. Do not attempt to evaluate these expressions.
- (c) By simplifying your expressions in (b), derive an expression for the specific heat  $C(T)$  that is valid at very low temperatures. In what range of temperatures is your expression valid?
- (d) By simplifying your answer to (b), derive a high-temperature approximation to the specific heat  $C(T)$ . What is the range of validity of your approximation?

**Solution:**

- (a) The system has two rotational degrees of freedom, so  $\langle E \rangle = 2 \cdot \frac{1}{2} kT = kT$  and  $C = \frac{d\langle E \rangle}{dT} = k$

(b) The partition function is  $Z = \sum_{j=0}^{\infty} (2j+1)e^{-\beta E_j}$  and the average energy is  $\langle E \rangle = \frac{\sum_{j=0}^{\infty} E_j (2j+1)e^{-\beta E_j}}{\sum_{j=0}^{\infty} (2j+1)e^{-\beta E_j}} = \frac{-\partial \ln Z}{\partial \beta}$

(c) As  $T \rightarrow 0$  we keep only the first two terms in the partition function, so  $Z \approx 1 + 3e^{-\beta E_1} \Rightarrow \ln Z \approx 3e^{-\beta E_1}$ . The average energy is  $\langle E \rangle = \frac{-\partial \ln Z}{\partial \beta} = 3E_1 e^{-E_1/kT}$  and the specific heat  $C = \frac{\partial \langle E \rangle}{\partial T} = \frac{3E_1^2}{kT^2} e^{-E_1/kT}$

The validity of the above expression requires  $5e^{-\beta E_2} \ll 3e^{-\beta E_1}$  and  $3e^{-\beta E_1} \ll 1$ , so  $kT \ll \hbar^2/I$

(d)  $Z \approx \int_0^{\infty} dj (2j+1)e^{-\beta \hbar^2 j(j+1)/2I} = -\frac{2I}{\beta \hbar^2} [e^{-\beta \hbar^2 j(j+1)/2I}]_0^{\infty} = \frac{2I}{\beta \hbar^2}$

$\ln Z \approx \ln \beta + \text{const}$  so  $\langle E \rangle = 1/\beta = kT$  This is the classical result. Finally  $C = \frac{\partial \langle E \rangle}{\partial T} = k$

3.  $10^{10}$  weakly interacting spinless particles, each with the mass of the electron, are identical in appearance, but obey classical statistics. They are confined in a cubical box which is  $10^{-6} \text{cm}$  on an edge. Each particle undergoes a potential interaction with the box which is of two sorts. One is attractive and leads to a bound state well localized near the center of the box and having an energy of  $-1 \text{eV}$ . The other interaction is a strong repulsion which prevents the particle from escaping through the walls of the box. Find at what temperature the pressure in the box is one atm.

**Solution:**

$$Z = \left[ e^{U/kT} + \frac{4\pi V}{h^3} \int_0^{\infty} e^{-p^2/2mkT} p^2 dp \right]^N, \text{ where } U = 1\text{eV}$$

$$\text{Thus } Z = \left[ e^{U/kT} + V \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right]^N \text{ and } P = kT \frac{\partial \log Z}{\partial V} = \frac{NkT}{V} \left[ 1 + \frac{h^3 e^{U/kT}}{V(2\pi mkT)^{3/2}} \right]^{-1}$$

Inverting the formula and plugging in the numbers gives us the required temperature.

4. An assembly of  $N$  particles of spin  $\frac{1}{2}$  are lined up on a straight line. Only nearest neighbors interact. When the spins of the neighbors are both up or down, their interaction is  $J$ . When one is up and one is down, the interaction energy is  $-J$ . What is the partition function of the assembly at temperature  $T$ ?

**Solution:**

There are  $N$  spins, so  $N-1$  pairs. Of these we have  $N_p$  parallel and  $N_a$  antiparallel. Since  $N_a + N_p = N - 1$  the energy for a given configuration is

$$E = J(N_p - N_a) = 2N_p + 1 - N$$

. The partition function is

$$Z = \sum e^{-E/kT}$$

There are  $\frac{(N-1)!}{N_a!N_p!}$  permutations, hence

$$Z = 2 \sum \frac{(N-1)!}{N_a!N_p!} e^{-\frac{J(2N_p+1-N)}{kT}} = 2e^{J(N-1)/kT} \sum \frac{(N-1)!}{(N-1-N_p)!N_p!} e^{-2JN_p/kT}$$

The sum is just the expansion of  $1 + e^{-2J/kT}$ , so

$$Z = 2e^{J(N-1)/kT} (1 + e^{-2J/kT})^{N-1} = 2^N \cosh(J/kT)^{N-1}$$

5. Assume a two level system consisting of  $N$  particles with energy gap  $\Delta$ . The partition function is  $Z = (1 + \exp(-D/kT))^N$ . The average energy of the system is

$$E = N \frac{\Delta \exp(-D/kT)}{1 + \exp(-D/kT)}$$

. The number of particles in the excited state is

$$n = N \frac{\exp(-D/kT)}{1 + \exp(-D/kT)}$$

. For high temperature  $n \rightarrow N/2$ , while for low temperature  $n \rightarrow N \exp(-D/kT)$

6. From thermodynamical principles, determine the vapor pressure  $P_r$  for a very small droplet of liquid of radius  $r$ , in terms of the vapor pressure  $P_\infty$  of a large body of the same liquid, having a negligible surface to volume ratio.

**Solution:**

$$G = M_1 g_1 + M_2 g_2 + 4\pi\gamma r^2$$

where  $\gamma$  is the surface tension,  $M_1$  is the mass of the droplet and  $M_2$  the mass of its vapor.  $g_1$  and  $g_2$  are Gibbs energies per unit mass.

Setting  $\delta G = 0$  we get

$$0 = \delta M_1 (g_1 - g_2) + 8\pi\gamma r \frac{\partial r}{\partial M_1} = \delta M [g_1 - g_2 + 2\gamma/(\rho r)]$$

where  $\rho$  is the mass density of the droplet. Hence in equilibrium  $g_1 - g_2 = 2\gamma/(\rho r)$

For a given phase  $V = \frac{\partial G}{\partial P}$ , so  $1/\rho = \frac{\partial g}{\partial P}$

Differentiating with respect to  $P$  at constant temperature gives us

$$1/\rho_{\text{vapor}} - 1/\rho_{\text{droplet}} = -\frac{2\gamma}{\rho r^2} \frac{\partial r}{\partial P}$$

Assuming that  $\rho_{\text{vapor}} \ll \rho_{\text{droplet}}$  and the vapor is a perfect gas

$$P \frac{\partial r}{\partial P} = -\frac{kT}{M} \frac{\rho r^2}{2\gamma}$$

Integrating, this gives  $P = P_\infty \exp(2M\gamma/\rho kTr)$