1 The Boltzmann Factor and Partition Functions

1/25:   1. Derive the value of PV for a gas of photons in terms of the total internal energy. Use $E = h\nu$ and $p = h\nu/c$ for the photon energy and momentum, respectively, and follow a similar method to that used for an ideal gas in class.

Proof. We first seek to derive an expression for the number of collisions per second per area (of the wall of the container). Consider the number $N(v_x)$ of photons with speed v_x in the x direction. Assuming that such photons are equally distributed throughout the container, their density in any region is $N(v_x)/V$. Thus, their "flux" at the wall of the container is this density $N(v_x)/V$, times the area A of the wall, times the x-velocity v_x of the photons. Additionally, assuming elastic collisions, a single photon colliding with the wall transfers $2p_x = 2h\nu/v_x$ of momentum. It follows that the change in momentum per second of an area A of the wall (i.e., the force F at the wall) is $\frac{N(v_x)}{V}Av_x \cdot 2p_x$. But, of course, we must sum over all possible v_x; note that since all photons travel at the speed of light $c = v_x^2 + v_y^2 + v_z^2$, we must integrate from 0 to c (photons with $v_x \leq 0$ don't collide with the wall in question and no photon has $v_x > c$). It follows that

$$F = \int_0^c 2p_x \cdot \frac{N(v_x)}{V}Av_x \, dv_x$$

$$= \int_0^c 2\frac{h\nu}{v_x} \cdot \frac{N(v_x)}{V}Av_x \, dv_x$$

$$= \int_0^c 2h\nu \cdot \frac{N(v_x)}{V}A \, dv_x$$

$$= \frac{2h\nu A}{V}\int_0^c N(v_x) \, dv_x$$

$$\frac{F}{A} = \frac{2h\nu}{V}\frac{N}{2}$$

$$PV = Nh\nu$$

$$= NE$$

$$\boxed{PV = U}$$

$\square$

2. Apply the Boltzmann factor.

   (a) For N_2 at $300\,K$, give the ratio of molecules in $J = 5$ over $J = 4$. Indicate also if the transition from $J = 4$ to $J = 5$ is observable by microwave absorption spectroscopy. Data on N_2 are in Table 18.2 on McQuarrie and Simon (1997, p. 739).

   Proof. From Table 18.2, we have that $\Theta_{\text{rot}} = 2.88\,K$ for N_2. Therefore, we have that

   $$\frac{p_5}{p_4} = \frac{(2(5)+1)e^{-(2.88)(5)((5)+1)/300}}{(2(4)+1)e^{-(2.88)(4)((4)+1)/300}}$$

   $$\boxed{\frac{p_5}{p_4} = 1.11}$$

   Also, the transition from $J = 4$ to $J = 5$ is $\boxed{\text{not observable}}$ by microwave absorption spectroscopy since N_2 does not have a permanent dipole moment. $\square$

   (b) Also, for N_2 at $300\,K$, give the ratio of molecules in $n = 1$ over $n = 0$ for the vibrational states.

Proof. From Table 18.2, we have that $\Theta_{\text{vib}} = 3374\,\text{K}$ for N_2. Therefore, we have that

$$\frac{p_1}{p_0} = \frac{e^{-(3374)(1)/300}}{e^{-(3374)(0)/300}}$$

$$\boxed{\frac{p_5}{p_4} = 1.305 \times 10^{-5}}$$

$\square$

(c) Problem 18-28 (calculating a moment of inertia based on masses and distances).

The N–N and N–O bond lengths in the (linear) molecule N_2O are 109.8 pm and 121.8 pm, respectively. Calculate the center of mass and the moment of inertia of $^{14}N^{14}N^{16}O$. Compare your answer with the value obtained from Θ_{rot} in Table 18.4.

Proof. Take the middle nitrogen atom to be the center of the coordinate system and the molecular axis to be the x-axis. Let $x_1 = 109.8\,\text{pm}$ and $x_3 = 121.8\,\text{pm}$. Then the center of mass is at

$$x_{\text{CM}} = \frac{\sum_{i=1}^{3} m_i x_i}{\sum_{i=1}^{3} m_i}$$

$$\boxed{x_{\text{CM}} = 9.355\,\text{pm}}$$

It follows that the moment of inertia about an axis perpendicular to the bond axis is

$$I_B = \sum_{i=1}^{3} m_i x_i^2$$

$$= m_1(x_1 + x_{\text{CM}})^2 + m_2 x_{\text{CM}}^2 + m_3(x_3 - x_{\text{CM}})^2$$

$$\boxed{I_B = 6.727 \times 10^{-46}\,\text{kg m}^2}$$

Thus, our calculated rotational temperature is

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2 I_B k_B} = 0.5985\,\text{K}$$

which has percent error of 0.829% from 0.603 K, the value from Table 18.4. $\square$

(d) Calculate the fraction of protons in the two spin orientations for a magnetic field of 10 T at 300 K. Follow Example 17-1 and Problem 17-8.

Proof. Let $B_z = 10\,\text{T}$, $T = 300\,\text{K}$, and $\gamma = 26.7522 \times 10^7\,\text{rad}\,\text{T}^{-1}\,\text{s}^{-1}$ be the magnetogyric ratio for a proton. If N_w is the number of protons aligned with a magnetic field and N_o is the number of protons opposed to the field, then

$$\frac{N_o}{N_w} = e^{-\hbar \gamma B_z / k_B T}$$

$$\boxed{\frac{N_o}{N_w} = 1.0}$$

$\square$

(e) Problem 17-41.

The lowest electronic states of $Na_{(g)}$ are tabulated below.

Term symbol	Energy/cm^{-1}	Degeneracy
$^2S_{1/2}$	0.000	2
$^2P_{1/2}$	16 956.183	2
$^2P_{3/2}$	16 973.379	4
$^2S_{1/2}$	25 739.86	2

Calculate the fraction of the atoms in each of these electronic states in a sample of $Na_{(g)}$ at $1000\,K$. Repeat this calculation for a temperature of $2500\,K$.

Proof. At $1000\,K$, we have

$$f_{^2S_{1/2}} = \frac{2e^{-0.000/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{1.000}$$

$$f_{^2P_{1/2}} = \frac{2e^{-16956.183/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{2.546 \times 10^{-11}}$$

$$f_{^2P_{3/2}} = \frac{4e^{-16973.379/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{4.968 \times 10^{-11}}$$

$$f_{^2S_{1/2}} = \frac{2e^{-25739.86/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{8.275 \times 10^{-17}}$$

At $1000\,K$, we have

$$f_{^2S_{1/2}} = \frac{2e^{-0.000/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{0.9998}$$

$$f_{^2P_{1/2}} = \frac{2e^{-16956.183/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{5.784 \times 10^{-5}}$$

$$f_{^2P_{3/2}} = \frac{4e^{-16973.379/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{1.145 \times 10^{-4}}$$

$$f_{^2S_{1/2}} = \frac{2e^{-25739.86/k_BT}}{2e^{-0.000/k_BT} + 2e^{-16956.183/k_BT} + 4e^{-16973.379/k_BT} + 2e^{-25739.86/k_BT}} = \boxed{3.690 \times 10^{-7}}$$

$\square$

3. Problem 17-38. In the second question, in addition to the ideal monoatomic gas, apply the formula also to the case of solid obeying the law of Dulong and Petit for the average internal energy.

The following equation gives the ensemble average of E, which we assert is the same as the experimentally observed value. In this problem, we will explore the standard deviation about $\langle E \rangle$ (see MathChapter B). We will start with either the right or second from the right term below.

$$\langle E \rangle = U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = k_BT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

Differentiate again with respect to β or T to show that (MathChapter B)

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = k_BT^2C_V$$

where C_V is the heat capacity. To explore the relative magnitude of the spread about $\langle E \rangle$, consider

$$\frac{\sigma_E}{\langle E \rangle} = \frac{\sqrt{k_BTC_V}}{\langle E \rangle}$$

To get an idea of the sie of this ratio, use the values of $\langle E \rangle$ and C_V for a (monoatomic) ideal gas, namely $\frac{3}{2}Nk_BT$ and $\frac{3}{2}Nk_B$, respectively, and show that $\sigma_E/\langle E \rangle$ goes as $1/\sqrt{N}$. What does this trend say about the likely observed deviations from the average macroscopic energy?

Proof. We are given that

$$-\frac{\partial \ln Q}{\partial \beta} = \langle E \rangle$$

We can show that

$$\frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} = \frac{1}{Q}\frac{\partial^2}{\partial \beta^2}\left(\sum_j e^{-E_j\beta}\right) = \sum_j E_j^2\frac{e^{-E_j\beta}}{Q} = \sum_j E_j^2 p_j = \langle E^2 \rangle$$

Therefore,

$$k_B T^2 C_V = k_B T^2 \frac{\partial \langle E \rangle}{\partial T}$$

$$= k_B T^2 \frac{\partial \langle E \rangle}{\partial \beta} \cdot \frac{\partial \beta}{\partial T}$$

$$= k_B T^2 \frac{\partial \langle E \rangle}{\partial \beta} \cdot -\frac{1}{k_B T^2}$$

$$= -\frac{\partial \langle E \rangle}{\partial \beta}$$

$$= -\frac{\partial}{\partial \beta} \left(-\frac{\partial \ln Q}{\partial \beta} \right)$$

$$= \frac{\partial}{\partial \beta} \left(\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right)$$

$$= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} + \frac{\partial}{\partial \beta} \left(\frac{1}{Q} \right) \cdot \frac{\partial Q}{\partial \beta}$$

$$= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} + \frac{\partial}{\partial Q} \left(\frac{1}{Q} \right) \frac{\partial Q}{\partial \beta} \cdot \frac{\partial Q}{\partial \beta}$$

$$= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} - \frac{1}{Q^2} \left(\frac{\partial Q}{\partial \beta} \right)^2$$

$$= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} - \left(\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right)^2$$

$$= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} - \left(\frac{\partial \ln Q}{\partial \beta} \right)^2$$

$$= \frac{1}{Q} \cdot \frac{\partial^2 Q}{\partial \beta^2} - \left(-\frac{\partial \ln Q}{\partial \beta} \right)^2$$

$$= \langle E^2 \rangle - \langle E \rangle^2 = \sigma_E^2$$

as desired.

As to the second part of the question, plugging in the given values yields

$$\frac{\sigma_E}{\langle E \rangle} = \frac{\sqrt{k_B T C_V}}{\langle E \rangle}$$

$$= \frac{\sqrt{k_B T \cdot 3 N k_B / 2}}{3 N k_B T / 2}$$

$$= \frac{1}{\sqrt{N}} \cdot \frac{1}{\sqrt{3T/2}}$$

which will indeed behave like $1/\sqrt{N}$ as $N \to \infty$. This means that as the number of particles increase, the deviations from the average energy will grow smaller and smaller.

Performing the same analysis on a solid obeying the law of Dulong and Petit yields

$$\frac{\sigma_E}{\langle E \rangle} = \frac{\sqrt{k_B T C_V}}{\langle E \rangle}$$

$$= \frac{\sqrt{k_B T \cdot 3 N R}}{3 N R T}$$

$$= \frac{1}{\sqrt{N}} \cdot \frac{\sqrt{k_B}}{\sqrt{3RT}}$$

so $\sigma_E / \langle E \rangle$ will also behave like $1/\sqrt{N}$ as $N \to \infty$ for this type of solid. $\square$

4. (a) Problem 17-11 and also verify that the pressure derived from this partition function gives the van der Waals equation (16.5).

Although we will not do so in this book, it is possible to derive the partition function for a monoatomic van der Waals gas as

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} (V - Nb)^N e^{aN^2/V k_B T}$$

where a and b are the van der Waals constants. Derive an expression for the energy of a monoatomic van der Waals gas.

Proof. We have that

$$\ln Q = - \ln N! + \frac{3N}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) + \frac{3N}{2} \ln T + N \ln(V - Nb) + \frac{aN^2}{V k_B T}$$

$$= \frac{3N}{2} \ln T + \frac{aN^2}{V k_B T} + \text{terms not involving } T$$

Therefore,

$$\langle E \rangle = k_B T^2 \frac{\partial \ln Q}{\partial T}$$

$$= k_B T^2 \frac{\partial}{\partial T} \left(\frac{3N}{2} \ln T + \frac{aN^2}{V k_B T} \right)$$

$$= k_B T^2 \left(\frac{3N}{2T} - \frac{aN^2}{V k_B T^2} \right)$$

$$\boxed{\langle E \rangle = \frac{3}{2} N k_B T - \frac{aN^2}{V}}$$

As to the second part of the question, we have that

$$\ln Q = \ln \left(\frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \right) + N \ln(V - Nb) + \frac{aN^2}{V k_B T}$$

$$= N \ln(V - Nb) + \frac{aN^2}{V k_B T} + \text{terms not involving } V$$

Therefore,

$$\langle P \rangle = k_B T \frac{\partial \ln Q}{\partial V}$$

$$= k_B T \frac{\partial}{\partial V} \left(N \ln(V - Nb) + \frac{aN^2}{V k_B T} \right)$$

$$= k_B T \left[\frac{N}{V - Nb} - \frac{a}{k_B T} \left(\frac{N}{V} \right)^2 \right]$$

$$= \frac{N k_B T}{V - Nb} - a \left(\frac{N}{V} \right)^2$$

$$\left(P + \frac{aN^2}{V^2} \right) (V - Nb) = N k_B T$$

as desired.   □

(b) Then do Problem 17-12.

An approximate partition function for a gas of hard spheres can be obtained from the partition function of a monoatomic gas by replacing V in

$$Q(N, V, \beta) = \frac{[q(V, \beta)]^N}{N!} \qquad q(V, \beta) = \left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} V$$

with $V - b$, where b is related to the volume of the N hard spheres. Derive expressions for the energy and the pressure of this system.

Proof. We have that

$$\ln Q = N \ln q - \ln N!$$

$$= N \left(\ln \left(\frac{2\pi m}{h^2}\right)^{3/2} (V - b) - \frac{3}{2} \ln \beta \right) - \ln N!$$

$$= -\frac{3N}{2} \ln \beta + \text{terms not involving } \beta$$

Therefore,

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta}$$

$$= -\frac{\partial}{\partial \beta} \left(-\frac{3N}{2} \ln \beta \right)$$

$$= \frac{3N}{2\beta}$$

$$\boxed{\langle E \rangle = \frac{3}{2} N k_B T}$$

We also have that

$$\ln Q = N \ln q - \ln N!$$

$$= N \left(\ln \left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} + \ln(V - b) \right) - \ln N!$$

$$= N \ln(V - b) + \text{terms not involving } V$$

Therefore,

$$\langle P \rangle = k_B T \frac{\partial \ln Q}{\partial V}$$

$$= k_B T \frac{\partial}{\partial V} (N \ln(V - b))$$

$$\boxed{\langle P \rangle = \frac{N k_B T}{V - b}}$$

$\square$

5. Problem 18-14.

There is a mathematical procedure to calculate the error in replacing a summation by an integral as we do for the translational and rotational partition functions. The formula is called the Euler-Maclaurin summation formula and goes as follows.

$$\sum_{n=a}^{b} f(n) = \int_a^b f(n) \, dn + \frac{1}{2} (f(b) + f(a)) - \frac{1}{12} \left(\frac{df}{dn} \bigg|_{n=a} - \frac{df}{dn} \bigg|_{n=b} \right) + \frac{1}{720} \left(\frac{d^3 f}{dn^3} \bigg|_{n=a} - \frac{d^3 f}{dn^3} \bigg|_{n=b} \right) + \cdots$$

Apply this formula to

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty}(2J+1)e^{-\Theta_{\text{rot}}J(J+1)/T}$$

to obtain

$$q_{\text{rot}}(T) = \frac{T}{\Theta_{\text{rot}}}\left\{1 + \frac{1}{3}\left(\frac{\Theta_{\text{rot}}}{T}\right) + \frac{1}{15}\left(\frac{\Theta_{\text{rot}}}{T}\right)^2 + O\left[\left(\frac{\Theta_{\text{rot}}}{T}\right)^3\right]\right\}$$

Calculate the correction to replacing the second equation herein by an integral for $N_{2(g)}$ at $300\,\text{K}$ and $H_{2(g)}$ at $300\,\text{K}$ (being so light, H_2 is an extreme example).

6. Problem 17-33. Discuss at which temperatures the heat capacity deviates from the result given.

We will learn in Chapter 18 that the rotational partition function of an asymmetric top molecule is given by

$$q_{\text{rot}}(T) = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{8\pi^2 I_A k_B T}{h^2}}\sqrt{\frac{8\pi^2 I_B k_B T}{h^2}}\sqrt{\frac{8\pi^2 I_C k_B T}{h^2}}$$

where σ is a constant and I_A, I_B, I_C are the three (distinct) moments of inertia. Show that the rotational contribution to the molar heat capacity is $\overline{C}_{V,\text{rot}} = 3R/2$.

Proof. We have that

$$\ln q_{\text{rot}} = \frac{3}{2}\ln T + \ln \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{8\pi^2 I_A k_B}{h^2}}\sqrt{\frac{8\pi^2 I_B k_B}{h^2}}\sqrt{\frac{8\pi^2 I_C k_B}{h^2}}$$
$$= \frac{3}{2}\ln T + \text{terms not involving } T$$

It follows that

$$\langle E \rangle = k_B T^2 \frac{\partial \ln q_{\text{rot}}}{\partial T}$$
$$= k_B T^2 \frac{\partial}{\partial T}\left(\frac{3}{2}\ln T\right)$$
$$= k_B T^2 \cdot \frac{3}{2T}$$
$$= \frac{3}{2}k_B T$$

so that

$$C_{V,\text{rot}} = \frac{\partial \langle E \rangle}{\partial T}$$
$$= \frac{\partial}{\partial T}\left(\frac{3}{2}k_B T\right)$$
$$= \frac{3}{2}k_B$$
$$\boxed{\overline{C}_{V,\text{rot}} = \frac{3}{2}R}$$

Note that at temperatures for which $\boxed{\Theta_{\text{rot}} \ll T \text{ is not satisfied}}$ the above result will not hold since our derivation of the partition function relies on using this result to approximate an infinite sum as an indefinite integral. $\square$