

Physics 3410 Homework #10

4 problems
Solutions

▷ 1.

Fun with standard deviations. We showed in class that $\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$. Now

(a) Show that, for a system in equilibrium with a reservoir at temperature T , the average value of E^2 is

$$\langle E^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

(b) The standard deviation of the energy (that is, the size of its fluctuations around the average) is defined as

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

Prove that the standard deviation is related to the heat capacity $C = \frac{\partial \langle E \rangle}{\partial T}$ by the formula

$$\sigma_E = kT \sqrt{C/k}$$

Answer:_____

(a) The average of any quantity in a Boltzmann-factor situation is

$$\langle X \rangle = \frac{1}{Z} \sum_s X_s e^{-\beta E_s}$$

so

$$\langle E^2 \rangle = \frac{1}{Z} \sum_s E_s^2 e^{-\beta E_s}$$

Now let's take the second derivative of Z :

$$\frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial^2}{\partial \beta^2} \sum_s e^{-\beta E_s} = \sum_s (-E_s)^2 e^{-\beta E_s} = \sum_s E_s^2 e^{-\beta E_s}$$

Comparing this with $\langle E^2 \rangle$ above gives us

$$\langle E^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

as desired.

(b) We can write the standard deviation σ_E as

$$\begin{aligned}\sigma_E^2 &= \langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(-\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 \\ &= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2\end{aligned}$$

We can write the heat capacity as

$$\begin{aligned}C &= \frac{\partial \langle E \rangle}{\partial T} \\ &= -\frac{\partial}{\partial T} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) \\ &= -\frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) \\ &= \frac{1}{k} T^{-2} \left(\frac{\partial 1/Z}{\partial \beta} \frac{\partial Z}{\partial \beta} + \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \right) \\ &= \frac{1}{k T^2} \left(\frac{\partial 1/Z}{\partial \beta} \frac{\partial Z}{\partial \beta} + \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \right) \\ &= \frac{1}{k T^2} \left(-\frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 + \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \right) \\ &= \frac{1}{k T^2} \sigma_E^2 \\ \implies \sigma_E &= \sqrt{C k T^2} = k T \sqrt{C/k}\end{aligned}$$

This means that the larger the heat capacity of a system, the larger the fluctuations in the energy: the amount of energy in iron is more consistent than the amount of energy in the same amount of water (higher heat capacity). That seems weird at first, because you'd think that something with a large heat capacity (higher thermal "inertia" as it were) would have smaller fluctuations. The key is that the object with larger heat capacity will also have more *energy*, so while the fluctuations might be larger in magnitude they will be smaller in proportion to the total energy. Statisticians talk about the *coefficient of variation*

$$CV = \frac{\sigma_E}{\langle E \rangle}$$

Roughly speaking, the total energy in an object with heat capacity C will be proportional to C , so the CV will be proportional to $\sqrt{C}/C = C^{-1/2}$. Thus larger heat capacity leads to smaller fluctuations relative to the total energy.

▷ **2.**

Starting from the partition function for the ideal gas that we derived in class, by way of the Helmholtz free energy, derive

- (a) The ideal gas law
- (b) The Sackur-Tetrode equation

Answer:_____

The partition function of the ideal gas is

$$Z = \frac{1}{N!} \left(\frac{V Z_{int}}{v_Q} \right)^N$$

where

$$v_Q = \left(\frac{h}{\sqrt{2\pi m}} \right)^3 \beta^{3/2}$$

and so the Helmholtz free energy is

$$F = -kT \ln Z = -kT [N \ln V + N \ln Z_{int} - N \ln v_Q - \ln N!]$$

- (a) We can get the ideal gas law by calculating the pressure.

$$\begin{aligned} P &= -\frac{\partial F}{\partial V} \\ &= -\frac{\partial}{\partial V} (-kT [N \ln V + N \ln Z_{int} - N \ln v_Q - \ln N!]) \\ &= kT \frac{\partial}{\partial V} (N \ln V) = kT \frac{N}{V} \\ \implies PV &= NkT \end{aligned}$$

- (b) The Sackur-Tetrode equation comes by finding the entropy.

$$\begin{aligned} S &= -\frac{\partial F}{\partial T} \\ &= -\frac{\partial}{\partial T} (-kT [N \ln V + N \ln Z_{int} - N \ln v_Q - \ln N!]) \\ &= k [N \ln V + N \ln Z_{int} - N \ln v_Q - \ln N!] + kT \left[N \frac{\partial \ln Z_{int}}{\partial T} - N \frac{\partial \ln v_Q}{\partial T} \right] \\ &= Nk [\ln V + \ln Z_{int} - \ln v_Q - \ln N + 1] + NkT \left[\frac{\partial \ln Z_{int}}{\partial T} - \frac{\partial \ln v_Q}{\partial T} \right] \\ &= Nk \left[\ln \frac{V}{N} + 1 - \ln v_Q - T \frac{\partial \ln v_Q}{\partial T} \right] + \left(Nk \ln Z_{int} + NkT \frac{\partial \ln Z_{int}}{\partial T} \right) \end{aligned}$$

Let's define

$$S_{int} = \left(Nk \ln Z_{int} + NkT \frac{\partial \ln Z_{int}}{\partial T} \right)$$

which is the internal entropy of the particles; if they are point particles, $Z_{int} = 1$ and $S_{int} = 0$.

Now define $A = \frac{h}{\sqrt{2\pi m}}$ so $v_Q = A^3 \beta^{3/2}$. Then

$$\begin{aligned} \ln v_Q &= \ln(A^3 \beta^{3/2}) = \frac{3}{2} \ln A^2 - \frac{3}{2} \ln kT \\ \frac{\partial \ln v_Q}{\partial T} &= -\frac{3}{2} \frac{\partial}{\partial T} \ln kT = -\frac{3}{2T} \end{aligned}$$

We know that an ideal gas obeys the equipartition theorem $U = \frac{3}{2} NkT$. Also, we know that the Sackur-Tetrode equation involves $\frac{3}{2} \ln \frac{U}{N}$, where

$$\begin{aligned} \frac{3}{2} \ln \frac{U}{N} &= \frac{3}{2} \ln \left(\frac{3}{2} kT \right) = \frac{3}{2} \ln \frac{3}{2} + \frac{3}{2} \ln kT \\ &= \frac{3}{2} \ln \frac{3}{2} + \frac{3}{2} \ln A^2 - \ln v_Q \\ \implies -\ln v_Q &= \frac{3}{2} \ln \frac{U}{N} - \frac{3}{2} \ln \frac{3}{2} - \frac{3}{2} \ln A^2 \end{aligned}$$

Substituting into S :

$$\begin{aligned} S &= Nk \left[\ln \frac{V}{N} + 1 + \frac{3}{2} \ln \frac{U}{N} - \frac{3}{2} \ln \frac{3}{2} - \frac{3}{2} \ln A^2 - T \left(\frac{-3}{2T} \right) \right] + S_{int} \\ &= Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{U}{N} + \frac{5}{2} - \frac{3}{2} \ln \frac{3}{2} - \frac{3}{2} \ln A^2 \right] + S_{int} \\ &= Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{U}{N} + \frac{5}{2} + \frac{3}{2} \ln \frac{2}{3A^2} \right] + S_{int} \end{aligned}$$

Now

$$\begin{aligned} \frac{5}{2} + \frac{3}{2} \ln \frac{2}{3A^2} &= \frac{5}{2} + \frac{3}{2} \ln \left[\frac{2}{3} \left(\frac{\sqrt{2\pi m}}{h} \right)^2 \right] \\ &= \frac{5}{2} + \frac{3}{2} \ln \frac{4\pi m}{3h^2} \end{aligned}$$

and this is the C in the Sackur-Tetrode equation. Thus

$$S = Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{U}{N} + C \right] + S_{int}$$

▷ 3.

Write the partition function of an ideal gas of carbon monoxide. Treat the vibrations in the bond between the atoms as a harmonic oscillator, and assume that the temperature is high enough so that all modes are active.

Answer:_____

The partition function of an ideal gas is

$$Z = \frac{1}{N!} \left(\frac{V Z_{int}}{v_Q} \right)^N$$

The internal partition function Z_{int} is made up of rotational and vibrational parts:

$$Z_{int} = Z_{rot} Z_{vib}$$

We derived the rotational partition function in class: $Z_{rot} = \frac{kT}{\mathcal{E}}$. The vibrational partition function is

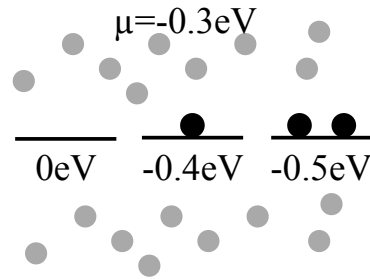
$$Z_{vib} = \sum_{n=0}^{\infty} e^{-\beta n h f} = \frac{1}{1 - e^{-\beta h f}}$$

and so

$$Z = \frac{1}{N!} \left(\frac{V k T}{\mathcal{E} (1 - e^{-\beta h f}) v_Q} \right)^N$$

▷ 4.

Consider a system (like a bonding site on a molecule) which is surrounded by a reservoir of particles having a chemical potential of $\mu = -0.3 \text{ eV}$ and temperature $T = 300 \text{ K}$. The system can be empty, or can contain one or two particles. if the system is empty, its energy is 0 eV . If it holds one particle, the system has energy -0.4 eV , and if it holds two particles, it has energy -0.5 eV .



(a) Find the Gibbs factor for each of the three possible states

(b) Find the grand partition function \mathcal{Z}

(c) What is the probability that the system is empty?

(d) What is the average occupancy \bar{n} of the system? That is, on average how many particles does it contain?

Answer:_____

(a) The Gibbs factor is given by the formula $e^{-\beta(E_s - \mu N_s)}$. The three states can be distinguished by the number of particles N_s present. Note that $kT = (8.61 \times 10^{-5} \text{ eV/K})(300 \text{ K}) = 0.0258$ so $\beta = 38.7$.

- $N_s = 0$: $e^{-(38.7)(0-(-0.3)0)} = \boxed{1}$
- $N_s = 1$: $e^{-(38.7)(-0.4-(-0.3)1)} = e^{-(38.7)(-0.1)} = \boxed{47.9}$
- $N_s = 2$: $e^{-(38.7)(-0.5-(-0.3)2)} = e^{-(38.7)(0.1)} = \boxed{0.0209}$

Note that the $N_s = 1$ state is most probable, while the $N_s = 2$ state is very improbable.

(b) The grand partition function is the sum of the Gibbs factors; thus $\boxed{\mathcal{Z} = 48.9}$.

(c) The probability that the system is empty ($N_s = 0$) is

$$P_0 = \frac{1}{48.9} = \boxed{2\%}$$

(d) The average occupancy is

$$\bar{n} = \sum_s P_s N_s = \frac{1}{48.9}(0) + \frac{47.9}{48.9}(1) + \frac{0.0209}{48.9}(2) = \boxed{0.98}$$