

Solutions to Problem Set #8

Problem 1: Correct Boltzmann Counting

a)

$$\begin{aligned}\Phi &= V^N \left[\frac{4\pi emE}{3N} \right]^{3N/2} \\ &= V^N [2\pi emkT]^{3N/2} \quad \text{using } E = (3/2)NkT\end{aligned}$$

$$\begin{aligned}S(N, V, T) &= k \ln \Phi \\ &= k \ln \left\{ V^N [2\pi emkT]^{3N/2} \right\} \\ &= \underline{Nk \ln V + (3/2)Nk \ln[2\pi emkT]}\end{aligned}$$

Now let $N \rightarrow \lambda N$, $V \rightarrow \lambda V$, and $T \rightarrow T$. Then as a result

$$S \rightarrow \underbrace{\lambda Nk \ln(\lambda V)}_{\neq \lambda Nk \ln V} + \lambda(3/2)Nk \ln[2\pi emkT].$$

So $S \neq \lambda S$ because of the failure in the first term.

b) The pressure is the same on both sides of the partition, so

$$P = \frac{N_1 kT}{V_1} = \frac{N_2 kT}{V_2}.$$

Now make use of the definition of α .

$$\frac{N_1 kT}{\alpha V} = \frac{N_2 kT}{(1 - \alpha)V}$$

We can solve this to put N_1 and N_2 in terms of α .

$$\begin{aligned}N_2 &= \frac{1 - \alpha}{\alpha} N_1 \\ \frac{N_1}{N_1 + N_2} &= \frac{N_1}{(1 + \frac{1-\alpha}{\alpha})N_1} = \alpha = \frac{N_1}{N} \\ \frac{N_2}{N_1 + N_2} &= \frac{N_2}{(\frac{\alpha}{1-\alpha} + 1)N_2} = 1 - \alpha = \frac{N_2}{N}\end{aligned}$$

Since the mixing takes place isothermally (because for ideal gases there is no interaction between the molecules), the T term in our expression for S of each gas does not change.

$$\begin{aligned}
 \Delta S_1 &= N_1 k \ln V - N_1 k \ln \alpha V \\
 &= N_1 k \ln(1/\alpha) = \underline{Nk\alpha \ln(1/\alpha)} \\
 \Delta S_2 &= N_2 k \ln V - N_2 k \ln[(1 - \alpha)V] \\
 &= N_2 k \ln(1/1 - \alpha) = \underline{Nk(1 - \alpha) \ln(1/1 - \alpha)} \\
 \Delta S_1 + \Delta S_2 &= Nk \underbrace{\left[\underbrace{\alpha}_{+} \underbrace{\ln(1/\alpha)}_{+} + \underbrace{(1 - \alpha)}_{+} \underbrace{\ln(1/1 - \alpha)}_{+} \right]} > 0
 \end{aligned}$$

This result is correct if the two gases are different. What should we expect when the gases are the same? $\Delta E = 0$ since the internal energy of an ideal gas does not depend on the volume, $E(T, V) = E(T)$, and the initial and final temperatures are equal. $\Delta W = 0$ since no work is necessary to slide the partition in and out (there is no opposing force in the absence of friction). Using these two results in the first law, $\Delta E = \Delta W + \Delta Q$, tells us that $\Delta Q = 0$. If the process is reversible $\Delta S = \Delta Q/T$ and it follows that $\Delta S = 0$. This is not consistent with the detailed calculation above which indicated a positive ΔS , but which nowhere required that the two gases be different.

c)

$$\begin{aligned}
 \Phi &= \frac{V^N}{N!} [2\pi emkT]^{3N/2} \\
 S(N, V, T) &= Nk \ln V - Nk \ln N \quad \underbrace{+k \ln N}_{\text{neglect compared to}} \quad + (3/2)Nk \ln [2\pi emkT] \\
 &\quad \text{previous term} \\
 &= Nk \ln(V/N) + (3/2)Nk \ln [2\pi emkT]
 \end{aligned}$$

Now let $N \rightarrow \lambda N$, $V \rightarrow \lambda V$, and $T \rightarrow T$.

$$S \rightarrow \lambda Nk \ln(V/N) + \lambda(3/2)Nk \ln [2\pi emkT] = \lambda S$$

We can summarize the results for the volume-dependent part of the entropies when

the mixing involves only one gas by constructing a table.

VOLUME-DEPENDENT TERM IN THE ENTROPY			
	WITH PARTITION		WITHOUT PARTITION
OLD S	$\begin{aligned} & \alpha Nk \ln \alpha V + (1 - \alpha) Nk \ln(1 - \alpha) V \\ & = Nk [\alpha \ln \alpha V + (1 - \alpha) \ln(1 - \alpha) V] \\ & = Nk [\underbrace{\alpha \ln \alpha + (1 - \alpha) \ln(1 - \alpha)}_+ + \ln V] \end{aligned}$	\neq	$Nk \ln V$
NEW S	$\begin{aligned} & \alpha Nk \ln \frac{\alpha V}{\alpha N} + (1 - \alpha) \ln \frac{(1 - \alpha) V}{(1 - \alpha) N} \\ & = Nk [\alpha \ln(V/N) + (1 - \alpha) \ln(V/N)] \\ & = Nk \ln(V/N) \end{aligned}$	$=$	$Nk \ln(V/N)$

Problem 2: Torsional Pendulum

2) First find the Hamiltonian.

$$\mathcal{H} = T + V + \frac{1}{2} I \dot{\theta}^2 + \frac{1}{2} K (\theta - \theta_0)^2$$

Then use the canonical ensemble expression for the probability density.

$$\begin{aligned} p(\theta, \dot{\theta}) & \propto \exp\left[-\frac{\mathcal{H}}{kT}\right] \\ & \propto \exp\left[-\frac{\dot{\theta}^2}{2(kT/I)}\right] \exp\left[-\frac{(\theta - \theta_0)^2}{2(kT/K)}\right] \end{aligned}$$

Notice two important features of this result. First, the probability density factors, $p(\theta, \dot{\theta}) = p(\theta)p(\dot{\theta})$, so θ and $\dot{\theta}$ are statistically independent. Second, the dependence on both θ and $\dot{\theta}$ has the Gaussian form. In particular, $p(\theta)$ is Gaussian with mean θ_0 and variance $\sigma_\theta^2 = kT/K$. Therefore,

$$\underline{\langle (\theta - \theta_0)^2 \rangle^{1/2} = \sqrt{\frac{kT}{K}}.}$$

b) Since θ and $\dot{\theta}$ are statistically independent, $\langle \theta \dot{\theta} \rangle = \langle \theta \rangle \langle \dot{\theta} \rangle$. By inspection, $p(\dot{\theta})$ is a zero-mean Gaussian, so $\langle \dot{\theta} \rangle = 0$ which leads to $\underline{\langle \theta \dot{\theta} \rangle = 0}$.

Problem 3: Defects in a Solid

a)

$$\begin{aligned} Z_{\text{one}} &= \sum_{\text{states}} \exp[-\epsilon_i/kT] = 2 \exp[-0/kT] + 3 \exp[-\Delta/kT] \\ &= 2 + 3 \exp[-\Delta/kT] \end{aligned}$$

$$Z_{\text{total}} = (Z_{\text{one}})^N = \underline{(2 + 3 \exp[-\Delta/kT])^N}$$

b)

$$F = -kT \ln Z = -NkT \ln(2 + 3 \exp[-\Delta/kT])$$

$$S(T, N) = - \left(\frac{\partial F}{\partial T} \right)_N = \frac{kT \ln(2 + 3 \exp[-\Delta/kT]) + 3Nk \left(\frac{\Delta}{kT} \right) \frac{\exp[-\Delta/kT]}{2 + 3 \exp[-\Delta/kT]}}{1}$$

c) In the high temperature limit where $kT \gg \Delta$, all states are equally probable for a single defect.

$$p_i = \frac{1}{5} \quad i = 1, 2, 3, 4, 5$$

$$\langle \epsilon \rangle = 0 \times 2 \times \frac{1}{5} + \Delta \times 3 \times \frac{1}{5} = \frac{3}{5} \Delta$$

$$E = N \langle \epsilon \rangle = \underline{\frac{3}{5} \Delta N}$$

Problem 4: Neutral Atom Trap

a) First write down the Hamiltonian for one atom.

$$\mathcal{H}_1 = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + ar$$

Then compute the partition function

$$Z_1 = \frac{1}{h^3} \underbrace{\int_{-\infty}^{\infty} e^{-\frac{p_x^2}{2mkT}} dp_x}_{\sqrt{2\pi mkT}} \underbrace{\int_{-\infty}^{\infty} e^{-\frac{p_y^2}{2mkT}} dp_y}_{\sqrt{2\pi mkT}} \underbrace{\int_{-\infty}^{\infty} e^{-\frac{p_z^2}{2mkT}} dp_z}_{\sqrt{2\pi mkT}} \underbrace{\int_V e^{-\frac{ar}{kT}} r^2 \sin \theta dr d\theta d\phi}_{4\pi \int_0^{\infty} \exp[-ar/kT] r^2 dr}$$

$$\begin{aligned}
&= \left(\frac{2\pi mkT}{h^2}\right)^{3/2} 4\pi \left(\frac{kT}{a}\right)^3 \underbrace{\int_0^\infty y^2 e^{-y} dy}_2 \\
&= 8\pi k^3 \left(\frac{2\pi mk}{h^2}\right)^{3/2} T^{9/2} a^{-3}
\end{aligned}$$

In order to emphasize the dependence on the important variables, this can be written in the form $Z_1 = AT^\alpha a^{-\eta}$ where

$$\underline{A = 8\pi k^3 \left(\frac{2\pi mk}{h^2}\right)^{3/2}} \quad \underline{\alpha = 9/2} \quad \text{and} \quad \underline{\eta = 3}.$$

b) Remember to include correct Boltzmann counting.

$$\begin{aligned}
Z &= \frac{1}{N!} Z_1^N \\
F &= -kT \ln Z = -kT(N \ln Z_1 - N \ln N + N) \\
&= -NkT \ln(Z_1/N) - NkT \\
S &= -\left(\frac{\partial F}{\partial T}\right)_N \\
&= Nk \ln(Z_1/N) + Nk + NkT \frac{1}{Z_1/N} (9/2) \frac{Z_1/N}{T} \\
&= \underline{Nk \ln(Z_1/N) + (11/2)Nk}
\end{aligned}$$

c)

$$dQ = 0 \quad \text{no heat is exchanged with surroundings}$$

$$dQ = dS/T \quad \text{process is said to be reversible}$$

$$\Rightarrow dS = 0, \quad S \text{ is constant}$$

$$\Rightarrow Z_1 \text{ is constant, using the result from b)}$$

$$\Rightarrow T^{9/2}/a^3 \text{ is constant and } = T_0^{9/2}/a_0^3$$

$$\left(\frac{T}{T_0}\right)^{9/2} = \left(\frac{a}{a_0}\right)^3$$

$$T = \underline{T_0 \left(\frac{a}{a_0}\right)^{2/3}}$$

Problem 5: The Hydrogen Atom

a)

$$\mathcal{H}|n, l, m \rangle = -\frac{A}{n^2}|n, l, m \rangle$$

The lowest energy, $-A$, corresponds to $|1, 0, 0 \rangle$ and is non-degenerate. The next lowest energy, $-A/4$, is four fold degenerate:

$$|2, 0, 0 \rangle, \quad |2, 1, 1 \rangle, \quad |2, 1, 0 \rangle, \quad \text{and} \quad |2, 1, -1 \rangle .$$

The ratio of the number of atoms in the first excited energy level to the number in the ground state depends on both the energies and the degeneracies.

$$\frac{N(-A/4)}{N(-A)} = \frac{4 \exp[A/4kT]}{\exp[A/kT]} = 4 \exp[-(3/4)A/kT]$$

Using the conversion factor $1\text{meV} = 11.6\text{K}$ we find that $13.6\text{eV} = 1.58 \times 10^5\text{K}$. Evaluating the above ratio gives 4.8×10^{-170} at 300K and 1.6×10^{-51} at 1000K .

b) The degeneracy of the n^{th} energy level is

$$1 + 3 + 5 + \dots + (2n - 1) = n^2.$$

The partition function for a single atom, neglecting the unbound states, is

$$Z = \sum_{\text{states } i} \exp[-\epsilon_i/kT] = \sum_{n=1}^{\infty} n^2 \exp[\alpha/n^2],$$

where $\alpha \equiv A/kT$. Since $\alpha > 0$, it follows that $\exp[\alpha/n^2] > 1$ for all n . Using this we can set a lower bound for Z , but Z diverges since the lower bound diverges.

$$\underline{Z > \sum_{n=1}^{\infty} n^2} \quad \text{which diverges}$$

c) The Coulomb potential is a mathematical oddity in that it produces an infinite number of bound states with energies less than zero. This situation is modified in the real world by the presence of walls (consider the energy levels of a particle in a box) or by the presence of other atoms. The existence of hydrogen atoms in the interstellar medium, on the other hand, probably has more to do with the absence of excitation mechanisms (non-equilibrium) than with the presence of neighboring atoms.