Homework 2 Solutions

Problem 1 In solving this problem, we will need to calculate some moments of the Gaussian distribution. The brute-force method is to integrate by parts but there is a nice trick. The following integrals should be known:

\[
\int_0^\infty e^{-ax^2} \, dx = \frac{1}{\sqrt{a}} \sqrt{\frac{\pi}{2}}
\]

\[
\int_0^\infty xe^{-ax^2} \, dx = \frac{1}{2a}
\]

Suppose we now want to calculate \(\int_0^\infty x^2e^{-ax^2} \, dx\) or \(\int_0^\infty x^3e^{-ax^2} \, dx\). We can evaluate these integrals by differentiating the above expressions. For example:

\[
\frac{d}{da} \left( \int_0^\infty e^{-ax^2} \, dx \right) = \int_0^\infty (-x^2)e^{-ax^2} \, dx = \frac{d}{da} \left( \frac{1}{\sqrt{a}} \sqrt{\frac{\pi}{2}} \right) = -\frac{\sqrt{\pi}}{2} \frac{1}{2a^{3/2}}
\]

\[
\frac{d}{da} \left( \int_0^\infty xe^{-ax^2} \, dx \right) = \int_0^\infty x^3e^{-ax^2} \, dx = \frac{d}{da} \left( \frac{1}{2a} \right) = -\frac{1}{2a^2}
\]

\[
\frac{d}{da} \left( \int_0^\infty (x^2)e^{-ax^2} \, dx \right) = \int_0^\infty (-x^4)e^{-ax^2} \, dx = \frac{d}{da} \left( \frac{1}{4} \frac{3}{2a^{5/2}} \right) = -\frac{\sqrt{\pi}}{4} \frac{3}{2a^{5/2}}
\]

Which painlessly implies:

\[
\int_0^\infty x^2e^{-ax^2} \, dx = \frac{\sqrt{\pi}}{2} \frac{1}{2a^{3/2}}
\]

\[
\int_0^\infty x^3e^{-ax^2} \, dx = \frac{1}{2a}
\]

\[
\int_0^\infty x^4e^{-ax^2} \, dx = \frac{3\sqrt{\pi}}{8a^{5/2}}
\]

(a) We are considering the Maxwell velocity distribution function:

\[
p(v)dv = 4\pi \left( \frac{1}{2\pi\tau/m} \right)^{3/2} e^{-mv^2/2\tau}v^2dv
\]

\[
 = Ce^{-av^2}v^2dv
\]

where \(C = 4\pi \left( \frac{1}{2\pi\tau/m} \right)^{3/2}\) and \(a = \frac{m}{2\tau}\). The most probable speed, \(v_{\text{prob}}\), is the speed which maximizes \(p(v)\).

\[
\frac{dp}{dv} = (\text{constant}) \times \left( 2ve^{-av^2} + v^2e^{-av^2}(-2av) \right) = 0
\]

\[
\Rightarrow v_{\text{prob}} = \sqrt{\frac{1}{a}} = \sqrt{\frac{2\tau}{m}}
\]

The average speed is calculated using our Gaussian integrals:

\[
\langle v \rangle = \int_0^\infty vp(v)dv = C \int_0^\infty v^3e^{-av^2}dv = \frac{C}{2a^2} = \frac{1}{2} 4\pi \left( \frac{1}{2\pi\tau/m} \right)^{3/2} \left( \frac{2\tau}{m} \right)^2
\]

\[
\Rightarrow \langle v \rangle = \sqrt{\frac{8\tau}{\pi m}}
\]
Similarly:

\[
<v^2> = \int_0^\infty v^2 p(v) dv = C \int_0^\infty v^4 e^{-v^2/2\tau} dv = C \frac{3\sqrt{\pi}}{8\sqrt{2} \tau} = 4\pi \left( \frac{1}{2\pi \tau/m} \right)^\frac{3}{2} \frac{3\sqrt{\pi}}{8} \left( \frac{2\tau}{m} \right)^{\frac{3}{2}} = \frac{3\tau}{m}
\]

\[v_{rms} = \sqrt{<v^2>} = \sqrt{\frac{3\tau}{m}}
\]

(b) For $N_2$, the molecular weight is approximately $m_{N_2} = 28m_p$ where $m_p = 1.67 \times 10^{-27}$ kg. Putting in the numbers gives:

\[v_{prob} = \sqrt{\frac{2\tau}{m}} = \sqrt{\frac{2(1.38 \times 10^{-23} J(293K))}{28 \times 1.67 \times 10^{-27} kg}} = 415 \text{ m/s}
\]

\[<v> = 468 \text{ m/s}
\]

\[v_{rms} = 507 \text{ m/s}
\]

**Problem 2**

Figure 1: The figure shows the system at time $t$. Particles with velocity $(v_x, v_y, v_z)$ must be in volume $dV$ in order to hit area $A$ by the time $t + dt$.

See figure . We first determine the contribution of those particles having velocity $v = (v_x, v_y, v_z)$ (known henceforth as $v$-particles) to the flux. If our hole has area $A$, then in a time interval $dt$, only those $v$-particles in the volume $dV$ will leave the hole. We may calculate $dV$:

\[dV = Adt(v \cos \theta)
\]

where $v = |v|$. The number of $v$-particles in the volume $dV$, which we call $n(v)dv$, is given by the number of $v$-particles in the entire volume times the ratio $dV/V$. The number of $v$-particles (actually the number of particles with velocities between $v$ and $v + dv$) in the entire volume $V$ is proportional to the Maxwell velocity distribution function.

\[n(v)dv = \frac{C dV}{V} \exp(-\frac{mv^2}{2\tau})dv
\]

\[= C'(Adt) \exp(-\frac{mv^2}{2\tau})v^3dv \cos \theta \sin \theta d\theta d\phi
\]
where \( C \) and \( C' \) are constants. The previous expression gives the number of \( v \)-particles leaving the hole of area \( A \) in time \( dt \). The flux of \( v \)-particles, which we call \( F(v) \), is defined as this expression divided by \( Adt \):

\[
F(v)dv = C' \exp\left(-\frac{mv^2}{2\tau}\right)v^3 dv
\]

So we have calculated the velocity distribution of the flux. In order to get a speed distribution, we must integrate over solid angle.

\[
F(v)dv = \int_{0}^{2\pi} d\phi \int_{0}^{\pi/2} d\theta F(v) = D \exp\left(-\frac{mv^2}{2\tau}\right)v^3 dv
\]

where \( D \) is a constant. Note that the \( \theta \) integration was only over \([0, \frac{\pi}{2}]\) because the range \([\frac{\pi}{2}, \pi]\) corresponds to particles moving away from the hole. We can get \( D \) by requiring our function to be normalized.

\[
\int_{0}^{\infty} F(v)dv = D \int_{0}^{\infty} v^3 \exp\left(-\frac{mv^2}{2\tau}\right) dv = D \frac{2}{m} \left(\frac{2\tau}{m}\right)^{2} = 1
\]

\[
\Rightarrow D = 2 \left(\frac{m}{2\tau}\right)^{2}
\]

**Problem 3** A single spin can be in one of two energy states: \(+E\) and \(-E\). The single particle partition function is given by:

\[
Z(\tau) = e^{E/\tau} + e^{-E/\tau}
\]

The partition function for \( N \) particles is a product of the single particle functions:

\[
Z_N(\tau) = Z(\tau)^N = (e^{E/\tau} + e^{-E/\tau})^N
\]

In particular, there is no factor of \( N! \) in the denominator because the spins are distinguishable, being labeled by their lattice positions. If the spins were not fixed in space but instead could move from site to site, then we would need the \( N! \). While this does not affect the energy, it will affect the entropy.

The free energy is obtained in the usual way:

\[
F(\tau) = -\tau \ln Z(\tau) = -N \ln(e^{E/\tau} + e^{-E/\tau})
\]

and the entropy:

\[
S(\tau) = - \left(\frac{\partial F}{\partial \tau}\right)_V = -N \left( - \ln(e^{E/\tau} + e^{-E/\tau}) - \tau \left( -\frac{E}{2\tau} e^{E/\tau} + \frac{E}{2\tau} e^{-E/\tau} \right) \right)
\]

\[
= N \left( \ln(e^{E/\tau} + e^{-E/\tau}) - \frac{E}{\tau} \tanh \frac{E}{\tau} \right)
\]

and the energy:

\[
U = F + \tau S = -NE \tanh \frac{E}{\tau}
\]

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**Problem 4** Suppose we have two systems which interact sufficiently weakly that their interaction energy may be ignored. The fact that they interact at all implies they should be at the same temperature. A state of the combined system is specified by giving the single system states of individual systems. The combined partition function is:

\[ Z_{\text{tot}} = \sum_{\text{states of 1}} \sum_{\text{states of 2}} e^{-(E_1 + E_2)/\tau} \]

\[ = \sum_{\text{states of 1}} e^{-E_1/\tau} \sum_{\text{states of 2}} e^{-E_2/\tau} \]

\[ = Z_1 \cdot Z_2 \]

**Problem 5**

(a) The states of our system are uniquely specified by the number of open links. The state having \( n \) open links corresponds to an energy of \( n\epsilon \). Thus:

\[ Z = \sum_{n=0}^{N} e^{-(\epsilon/\tau)n} = \frac{1 - \exp(-N\epsilon/\tau)}{1 - \exp(-\epsilon/\tau)} \]

(b) Let \( x = \epsilon/\tau \). In the limit \( x > 1 \):

\[ \sum_{n=0}^{N} ne^{-(\epsilon/\tau)n} = -\frac{d}{dx}Z = -\frac{e^{-x}(1 - e^{-(N+1)x})}{(1 - e^{-x})^2} + \frac{(N + 1)e^{-(N+1)x}}{1 - e^{-x}} \]

\[ \sim e^{-x} \]

**Problem 6**

(a) This problem is the same as having a one-dimensional chain of spins. The spin on each lattice site can point left or right. If \( 2s \) is the “right excess”, then:

\[ g(N, s) = \binom{N}{\frac{1}{2}N + s} \]

is the number of configurations with that right excess. Because the energy of the system only depends on the magnitude of \( s \), we can find the total number of states with a given \( |s| \):

\[ g(N, s) + g(N, -s) = \frac{2N!}{(\frac{1}{2}N + s)!(\frac{1}{2}N - s)!} \]

(b) To find the entropy, we make use of the Stirling approximation and also the fact that \( s \ll N \) (here we write \( s \) but mean \( |s| \)):

\[ \sigma(l) = \ln(g(N, s) + g(N, -s)) \]

\[ = \ln 2N! - \ln(\frac{1}{2}N + s)! - \ln(\frac{1}{2}N - s)! \]
\[ \sim N \ln N - \frac{N}{2} (1 + \frac{2s}{N}) \ln \frac{N}{2} (1 + \frac{2s}{N}) - \frac{N}{2} (1 - \frac{2s}{N}) \ln \frac{N}{2} (1 + \frac{2s}{N}) \]

\[ = 2g(N,0) - \frac{N}{2} (1 + \frac{2s}{N}) \ln(1 + \frac{2s}{N}) - \frac{N}{2} (1 - \frac{2s}{N}) \ln(1 - \frac{2s}{N}) \]

\[ = 2g(N,0) - \frac{N}{2} (1 + \frac{2s}{N}) (\frac{2s}{N} - \frac{2s^2}{N^2}) - \frac{N}{2} (1 - \frac{2s}{N}) (-\frac{2s}{N} - \frac{2s^2}{N^2}) \]

\[ \sim 2g(N,0) - \frac{2s^2}{N} \]

\[ = 2g(N,0) - \frac{l^2}{2N\rho^2} \]

where in the last line, we used the definition \( l = 2s\rho \).

(c) \[ f = -\tau \left( \frac{\partial \sigma}{\partial \tau} \right) = \frac{l\tau}{N\rho^2} \]

**Problem 7**: We model a single particle as a free particle in a one-dimensional box. The energy levels of this system are given by:

\[ E_n = \frac{\hbar^2 \pi^2}{2ML^2} n^2 \]

where \( n \) is a positive integer. The partition function is given by:

\[ Z_1 = \sum_{n=0}^{\infty} e^{-E_n/\tau} = \int_0^{\infty} dne^{-\alpha^2 n^2} = \sqrt{\frac{\pi}{2\alpha}} = \sqrt{\frac{M\tau}{2\pi\hbar^2}L} \]

where \( \alpha = \sqrt{\frac{\hbar^2}{2M\tau L^2}} \). The \( N \) particle partition function is given by:

\[ Z_N = \frac{Z_N^N}{N!} \]

Here the \( N! \) is needed because the particles are indistinguishable. We get the free energy by the usual method:

\[ F = -\tau \ln Z_N = -\tau \left( N \ln \sqrt{\frac{M\tau}{2\pi\hbar^2}L} - N \ln N + N \right) \]

\[ = -\tau \left( N \ln \sqrt{\frac{M\tau}{2\pi\hbar^2} \frac{L}{N}} + N \right) \]

And finally, the entropy:

\[ \sigma = -\left( \frac{\partial F}{\partial \tau} \right) = N \ln \sqrt{\frac{M\tau}{2\pi\hbar^2} \frac{L}{N}} + N + \frac{N}{2} \]

\[ = N \left( \ln \sqrt{\frac{M\tau}{2\pi\hbar^2} \frac{L}{N}} + \frac{3}{2} \right) \]

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Problem 8 The probabilities which maximized the entropy in the canonical ensemble were given by $p_i = e^{-1-\lambda_1-\lambda_2 E_i}$. We note that the probabilities must sum to 1 by definition:

$$\sum_i p_i = e^{-1-\lambda_1} \sum_i e^{-\lambda_2 E_i} = 1$$

$$\Rightarrow e^{-1-\lambda_1} = \frac{1}{\sum_i e^{-\lambda_2 E_i}} = \frac{1}{Z(\lambda_2)}$$

$$\Rightarrow p_i = \frac{e^{-\lambda_2 E_i}}{Z(\lambda_2)}$$

where the notation $Z(\lambda_2)$ identifies the sum with a partition function. The average energy and entropy of this system are given by:

$$U = \sum_i p_i E_i$$

$$\sigma = -\sum_i p_i \ln p_i$$

The parameter $\lambda_2$ may be varied, as it is something imposed on the system from the outside to maintain the average energy constraint. Varying $\lambda_2$ implies the following variations in the energy and entropy:

$$\delta U = \sum_i E_i \delta p_i$$

$$\delta \sigma = -\sum_i (\delta p_i \ln p_i + \delta p_i)$$

Because the $p_i$'s are probabilities, they must always sum to 1 meaning that the sum of their variations must give 0: $\sum_i \delta p_i = 0$. This implies:

$$\delta \sigma = -\sum_i (\delta p_i \ln p_i + \delta p_i)$$

$$= -\sum_i \delta p_i \ln p_i$$

$$= -\sum_i (\delta p_i (-\lambda_2 E_i - \ln Z(\lambda_2)))$$

$$= -\lambda_2 \sum_i E_i \delta p_i$$

Finally, we use the statistical definition of temperature: $\frac{1}{T} = (\frac{\partial \sigma}{\partial U})_V$ to conclude that $\lambda_2 = \frac{1}{T}$. 