Physics 112 Fall 2017
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Homework 3 Solutions

Problem 1: Energy Fluctuations

a) <u>Kittel 3.4</u>

From the definition of mean square fluctuation we have

$$
\begin{aligned}
(\triangle\epsilon)^2 &= <(\epsilon-<\epsilon>)^2> = <\epsilon^2 - 2\epsilon<\epsilon> + <\epsilon>^2> \\
&= <\epsilon^2> - <\epsilon>^2 .
\end{aligned}
$$

We also have

$$
U = \frac{1}{Z}\sum_s \epsilon_s e^{-\epsilon_s/\tau}
$$

and so

$$
\begin{aligned}
\frac{\partial U}{\partial \tau} &= \frac{1}{Z}\sum_s \frac{\epsilon_s^2}{\tau^2}e^{-\epsilon_s/\tau} - \frac{1}{Z^2}\left(\sum_s \frac{\epsilon_s}{\tau^2}e^{-\epsilon_s/\tau}\right)\left(\sum_s \epsilon_s e^{-\epsilon_s/\tau}\right) \\
\implies \tau^2\frac{\partial U}{\partial \tau} &= \frac{1}{Z}\sum_s \epsilon_s^2 e^{-\epsilon_s/\tau} - \frac{1}{Z^2}\left(\sum_s \epsilon_s e^{-\epsilon_s/\tau}\right)^2 \\
&= <\epsilon^2> - <\epsilon>^2 = (\Delta\epsilon)^2
\end{aligned}
$$

as desired.

b) Using our result from a) and the fact that $U = \frac{3}{2}N\tau$ for an ideal gas, we have

$$
\begin{aligned}
(\Delta U)^2 &= \tau^2\frac{\partial U}{\partial \tau}\Big|_V \\
&= \tau^2 \cdot \frac{3}{2}N
\end{aligned}
$$

and so

$$
\begin{aligned}
\frac{\sqrt{(\Delta U)^2}}{U} &= \frac{\sqrt{\frac{3}{2}N\tau^2}}{\frac{3}{2}N\tau} \\
&= \sqrt{\frac{2}{3N}}.
\end{aligned}
$$

Using $\sqrt{\frac{2}{3N}} = 0.1$ we get $N = \frac{200}{3}$. So to have the energy fluctuations of an ideal gas to be on the order of 10% or more, you need to have fewer than 67 particles.

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Problem 2, Kittel 3.6: Diatomic Molecules

a) As the problem reminds you, it is important to remember that the partition function is defined as a sum over all *microstates*, not energy levels. To write the partition function as a sum over energy levels, you must include the degeneracy (or multiplicity) of each level. We know for a molecule with total angular momentum j the possible values of j_z are $-j, -j+1, \cdots, j-1, j$. This gives a multiplicity of $2j+1$ for each energy level at fixed j, so the partition function is:

$$Z_R = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\epsilon_0/\tau}.$$

b) For the high temperature limit $\tau \gg \epsilon_0$ the thermal energy is much larger than the spacing between energy levels, so we can convert the sum into an integral over j:

$$
\begin{aligned}
Z_R(\tau \gg \epsilon_0) &= \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\epsilon_0/\tau} \\
&\approx \int_0^\infty (2j+1) e^{-j(j+1)\epsilon_0/\tau} \, dj \\
&= \left(-\frac{\tau}{\epsilon_0}\right) \int_0^\infty \frac{\partial}{\partial j} \left(e^{-j(j+1)\epsilon_0/\tau}\right) dj \\
&= \left(-\frac{\tau}{\epsilon_0}\right) e^{-j(j+1)\epsilon_0/\tau} \Big|_0^\infty . \\
&= \frac{\tau}{\epsilon_0}
\end{aligned}
$$

c) In the low temperature limit, $\tau \ll \epsilon_0$, higher j terms in the partition function quickly decay exponentially, so we can approximate the sum by just keeping the first two terms:

$$
\begin{aligned}
Z_R(\tau) &= \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\epsilon_0/\tau} = 1 + 3e^{-2\epsilon_0/\tau} + 5e^{-6\epsilon_0/\tau} + \cdots \\
&\approx 1 + 3e^{-2\epsilon_0/\tau}.
\end{aligned}
$$

d) U and C_V can easily be calculated in the two limits:

i) $\tau \gg \epsilon_0$

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = \frac{\tau^2}{\epsilon_0} \frac{1}{Z} = \frac{\tau^2/\epsilon_0}{\tau/\epsilon_0} = \tau$$

$$C_V = \left. \frac{\partial U}{\partial \tau} \right|_V = 1.$$

We see that $C_V \to 1$, or in terms of conventional temperature T, $C_V \to k_b$. (Note that you can define C_V in terms of a derivative with respect to T or τ: $C_V = \frac{\partial U}{\partial \tau}$ or $C_V = \frac{\partial U}{\partial T}$. These different definitions give the specific heat in different units, so make sure you understand which definition, and therefore units, you are using.) This of course agrees with the equipartition theorem: there are two axes around which a diatomic molecule can rotate (make sure you understand why there are only two, not three), and each of these degrees of freedom get $\frac{1}{2}k_bT$ of energy.

ii) $\tau \ll \epsilon_0$

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = \frac{\tau^2}{Z} \frac{\partial}{\partial \tau} \left(1 + 3e^{-2\epsilon_0/\tau} \right) \approx 6\epsilon_0 e^{-2\epsilon_0/\tau}$$

$$C_V = \left. \frac{\partial U}{\partial \tau} \right|_V = \frac{12\epsilon_0^2}{\tau^2} e^{-2\epsilon_0}/\tau,$$

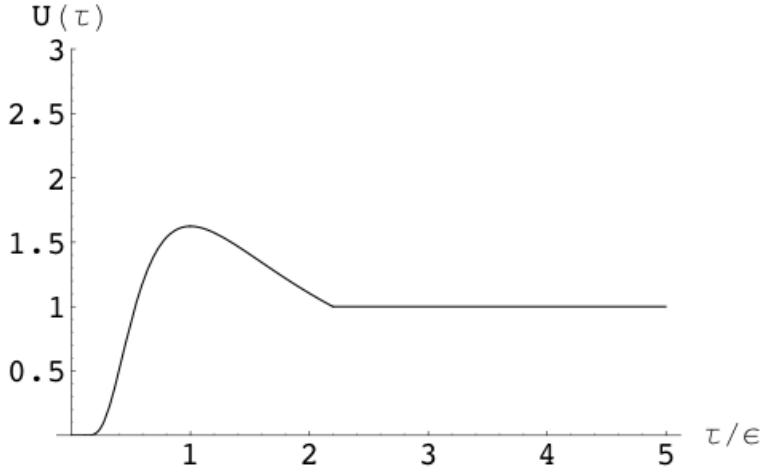e) The heat capacity and energy are plotted in Figures 1 and 2.

Figure 1: Heat capacity vs. temperature (the label $U(\tau)$ on the vertical axis should read $C(\tau)$)
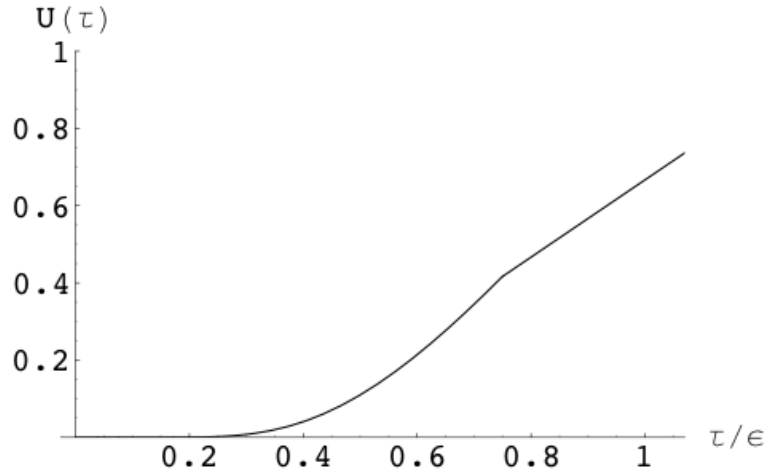
Figure 2: Energy vs. temperature

Problem 3: DNA denaturation

a) Kittel 3.7

Because the zipper can only open from one end, there is one state for each number of open links s, each having the energy $s\epsilon$. So the partition function is:

$$
\begin{aligned}
Z &= 1 + e^{-\epsilon/\tau} + e^{-2\epsilon/\tau} + \cdots + e^{-(N-1)\epsilon/\tau} + e^{-N\epsilon/\tau} \\
&= \sum_{s=0}^{N} e^{-s\epsilon/\tau} = \sum_{s=0}^{N} \left(e^{-\epsilon/\tau} \right)^s \\
&= \frac{1 - e^{-(N+1)\epsilon/\tau}}{1 - e^{-\epsilon/\tau}}.
\end{aligned}
$$

where we've used the formula for a finite geometric series: $\sum_{n=0}^{N} r^n = \frac{1-r^{N+1}}{1-r}$.

In the limit $\epsilon \gg \tau$ we can neglect the $e^{-(N+1)\epsilon/\tau}$ term in Z, obtaining

$$
Z = \frac{1}{1 - e^{-\epsilon/\tau}} \approx 1 + e^{-\epsilon/\tau}.
$$

We can then calculate

$$
\begin{aligned}
<s> &= \frac{\sum_{s=0}^{N} s e^{-s\epsilon/\tau}}{\sum_{s=0}^{N} e^{-s\epsilon/\tau}} = -\frac{1}{Z} \frac{\partial Z}{\partial(\beta\epsilon)} \\
&= \frac{e^{-\epsilon/\tau}}{1 - e^{-\epsilon/\tau}} \approx e^{-\epsilon/\tau}.
\end{aligned}
$$

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b) If we allow the zipper to open from either end, for a given number of open links s clearly there are at least two states corresponding to opening s links from either the right or left side. We also have to consider that we could open some links on the left and some on the right at the same time, so in general there will be even more degenerate states. For a given s we could open s links on the left and none on the right, $s-1$ on the left and 1 on the right, all the way up to no links on the left and s on the right. This means each energy level, $s\epsilon$, is $s+1$ fold degenerate; however when $s = N$, the entire zipper is open, so there is only one non-degenerate state. When we write our partition function as a sum over energies instead of states we need to take into account this degeneracy:

$$
\begin{aligned}
Z &= 1 + 2e^{-\epsilon/\tau} + 3e^{-2\epsilon/\tau} + \cdots + Ne^{-(N-1)\epsilon/\tau} + e^{-N\epsilon/\tau} \\
&= \sum_{s=0}^{N-1}(s+1)e^{-s\epsilon/\tau} + e^{-N\epsilon/\tau} \\
&= \sum_{s=0}^{N-1} se^{-s\epsilon/\tau} + \sum_{s=0}^{N} e^{-s\epsilon/\tau} \\
&= -\frac{\partial}{\partial(\beta\epsilon)}\left(\frac{1 - e^{-N\beta\epsilon}}{1 - e^{-\beta\epsilon}}\right) + \frac{1 - e^{-(N+1)\epsilon/\tau}}{1 - e^{-\epsilon/\tau}} \\
&= \frac{1 - Ne^{-N\beta\epsilon} + (N-2)e^{(N+1)\beta\epsilon} + e^{-(N+2)\beta\epsilon}}{(1 - e^{-\beta\epsilon})^2}.
\end{aligned}
$$

Problem 4, Kittel 3.10: Rubber Band

a) Because each link in our chain has two possible orientations, the number of configurations with s links to the right (and $N - s$ links to the left) is the same as the multiplicity of a paramagnet with spin excess s (in the paramagnet each spin also has two possible orientations). However, unlike in the magnet where s and $-s$ are different states because the magnetization is a vector, the length of the rubber band (the observable quantity) is the same if there are s links to the right and and $N - s$ links to the left or if there are $N - s$ links to the right and s links to the left (the polymer links are like vectors with no head). So the multiplicity of a state of length $l = 2s\rho$ is the sum of the multiplicities $g(N, s)$ and $g(N, -s)$:

$$
g(N, s) + g(N, -s) = 2\frac{N!}{(N/2 + s)! \, (N/2 - s)!}.
$$

b) You know how it works by now: using the Stirling approximation for $|s| \ll N$ gives

$$\sigma(l) \;=\; \ln g = \ln\left(2\frac{N!}{(N/2+s)!\,(N/2-s)!}\right)$$
$$=\; \ln 2 + \ln N! - \ln(N/2+s)! - \ln(N/2-s)! \approx \ln(2g(N,0)) - 2s^2/N$$
$$=\; \ln[2g(N,0)] - l^2/2N\rho^2,$$

We see that the entropy of the rubber band decreases as it's stretched.

c) To find the force, use the expression derived in the problem:

$$f = -\tau\frac{\partial\sigma}{\partial l}\bigg|_U = \frac{\tau l}{N\rho^2}.$$

We can see that at a constant tension, a rubber band will contract as it's heated up; compare this to most solids which expand when heated. It's all about entropy: we know that entropy increases with temperature, and in our rubber band entropy increases with *decreasing* length. Think about what this tells you about the entropy/size relationship for most other solids, and why.

Problem 5: Entropy of Mixing

a) i) If the particles of gas a are distinguishable from those of gas b (but all gas a particles are indistinguishable from one another), then the partition functions of the individual gases just multiply:

$$Z_N = \frac{Z_a^{N_a}}{N_a!}\frac{Z_b^{N_b}}{N_b!}.$$

ii) If the particles of gas a and b are indistinguishable from one another, then their single particle partition functions must be the same: $Z = Z_a = Z_b$. So now we just need to write down the partition function for $N = N_a + N_b$ indistinguishable particles:

$$Z_N = \frac{Z_1^N}{N!} = \frac{Z_a^{N_a}Z_b^{N_b}}{(N_a+N_b)!}.$$

b) The free energy is easily calculated as $F = -\tau\ln Z_N$, with $Z_a = Z_b = Z$:

i) distinguishable

$$F_{\text{dis}} = -\tau\ln\left(\frac{Z_a^{N_a}}{N_a!}\frac{Z_b^{N_b}}{N_b!}\right) \approx -\tau N\ln Z + \tau N_a(\ln N_a - 1) + \tau N_b(\ln N_b - 1)$$

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ii) indistinguishable

$$F_{\text{indis}} = -\tau \ln \left(\frac{Z^N}{N!} \right) \approx -\tau N \ln Z + \tau N (\ln N - 1).$$

c) Using the relationship between free energy and entropy $\sigma = -\frac{\partial F}{\partial \tau}$ we can find the difference in entropy in the two cases:

$$\sigma_{\text{dis}} = -\left. \frac{\partial F_{\text{dis}}}{\partial \tau} \right|_V = N \ln Z - N_a (\ln N_a - 1) - N_b (\ln N_b - 1)$$

$$\sigma_{\text{indis}} = -\left. \frac{\partial F_{\text{indis}}}{\partial \tau} \right|_V = N \ln Z - N (\ln N - 1)$$

$$S_{\text{mix}} = k_b (\sigma_{\text{dis}} - \sigma_{\text{indis}}) = -k_b \left[N_a \ln N_a + N_b \ln N_b - N \ln N \right]$$

$$= -k_b \left[N_a \ln \left(\frac{N_a}{N} \right) + N_b \ln \left(\frac{N_b}{N} \right) \right]. \tag{-4}$$

d) The ratio of the multiplicities in the two cases is (using (**??**))

$$\frac{g_{\text{dis}}}{g_{\text{indis}}} = e^{\sigma_{\text{dis}} - \sigma_{\text{indis}}}$$

$$= \left(\frac{N}{N_a} \right)^{N_a} \left(\frac{N}{N_b} \right)^{N_b}.$$

If $N_a = N_b = N/2$ this becomes

$$\frac{g_{\text{dis}}}{g_{\text{indis}}} = 2^{N_a} 2^{N_b} = 2^N.$$

This extra multiplicity comes from the fact that even once we choose N orbitals to put our particles in (consistent, of course, with the given temperature τ), we must still make a choice about which *type* of particle, a or b, to put in each orbital. Assuming that we've selected N distinct orbitals, this contributes an additional multiplicity of (approximately) 2^N.

Problem 6: Thermal Expansion and Anharmonicity

a) In this problem the energy is continuous, $E(x) = U(x) = ax^2$, so the sums in the partition function and thermal averages become integrals: $Z(x) = \int_{-\infty}^{\infty} dx \, e^{-U(x)/\tau} = \int_{-\infty}^{\infty} dx \, e^{-ax^2/\tau}$. We can express the average displacement as the weighted integral:

$$< x > = \frac{\int_{-\infty}^{\infty} x e^{-ax^2/\tau} dx}{\int_{-\infty}^{\infty} e^{-ax^2/\tau} dx}$$

b) In the above expression the integrand is an odd function integrated over an interval symmetric about zero, so $\int_{-\infty}^{\infty} x e^{-ax^2/\tau} dx = 0$ and hence $< x >= 0$.

c) To get a nonzero coefficient of thermal expansion we must include anharmonic terms in the potential, $U(x) = ax^2 - bx^3$:

$$< x > \quad = \quad \frac{\int_{-\infty}^{\infty} x e^{-\left(ax^2 - bx^3\right)/\tau} dx}{\int_{-\infty}^{\infty} e^{-\left(ax^2 - bx^3\right)/\tau} dx}$$

d) For $b/\tau \ll 1$ we can expand the cubic part of the exponential:

$$< x > \quad = \quad \frac{\int_{-\infty}^{\infty} x e^{-ax^2/\tau} e^{bx^3/\tau} dx}{\int_{-\infty}^{\infty} e^{-(ax^2 - bx^3)/\tau} dx} = \frac{\int_{-\infty}^{\infty} x \left(1 + \frac{b}{\tau} x^3 + \cdots\right) e^{-ax^2/\tau} dx}{\int_{-\infty}^{\infty} \left(1 + \frac{b}{\tau} x^3 + \cdots\right) e^{-ax^2/\tau} dx}$$

$$\approx \quad \frac{\int_{-\infty}^{\infty} \left(x + \frac{b}{\tau} x^4\right) e^{-ax^2/\tau} dx}{\int_{-\infty}^{\infty} \left(1 + \frac{b}{\tau} x^3\right) e^{-ax^2/\tau} dx} = \frac{\frac{3\sqrt{\pi} \frac{b}{\tau}}{4(\frac{a}{\tau})^{5/2}}}{\sqrt{\frac{\pi}{(\frac{a}{\tau})}}} = \frac{3b\tau}{4a^2}.$$

We've used the fact that the integrals over odd powers of x are zero (for the same reasons as in (b)) and the Gaussian integrals are given by: $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$ and $\int_{-\infty}^{\infty} x^4 e^{-ax^2} dx = \frac{3\sqrt{\pi}}{a^{5/2}}$. When the anharmonic term is included, we see that the average displacement will increase linearly with temperature, and so we expect the solid to expand as the temperature increases.