Physics 112 Problem Set 3

Holzapfel, Section 102

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1. (a) First, note that

$$\langle(\epsilon - \langle\epsilon\rangle)^2\rangle = \langle(\epsilon^2 - 2\epsilon\langle\epsilon\rangle + \langle\epsilon\rangle^2)\rangle = \langle\epsilon^2\rangle - \langle\epsilon\rangle^2$$

since expectation is a linear operator, so $\langle\epsilon\langle\epsilon\rangle\rangle = \langle\epsilon\rangle^2$.

Now,

$$U = \frac{\sum_s \epsilon_s \exp(-\epsilon_s/\tau)}{Z},$$

so

$$\frac{\partial U}{\partial \tau} = \frac{(1/\tau^2) Z \sum_s \epsilon_s^2 \exp(-\epsilon_s/\tau) - (1/\tau^2)\left(\sum_s \epsilon_s \exp(-\epsilon_s/\tau)\right)^2}{Z^2},$$

thus

$$\tau^2\left(\frac{\partial U}{\partial \tau}\right) = \frac{\sum_s \epsilon_s^2 \exp(-\epsilon_s/\tau)}{Z} - \left(\frac{\sum_s \epsilon_s \exp(-\epsilon_s/\tau)}{Z}\right)^2 = \langle\epsilon^2\rangle - \langle\epsilon\rangle^2.$$

(b) For an ideal gas, $U = \frac{3}{2}N\tau$, thus $\langle(\Delta U)^2\rangle = \frac{3}{2}N\tau^2$. So

$$\frac{\sqrt{\langle(\Delta U)^2\rangle}}{U} = \sqrt{\frac{2}{3N}}.$$

The fluctuations become 10 percent of the total energy for $N = \frac{2}{3}(10\%)^{-2} = 67$. So it takes few particles for the fluctuations in energy to become negligible.

2. (a) We sum over energy levels, multiplying each energy level by its degeneracy (multiplicity)

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

(b) For $\tau \gg \epsilon_0$, the terms in the series are so closely spaced that we can approximate the sum with an integral

$$Z_R(\tau) \approx \int_{j=0}^{\infty} (2j+1)\exp(-j(j+1)\epsilon_0/\tau)\, dj.$$

Define $u = j(j+1)\epsilon_0/\tau$. Then

$$Z_R(\tau) = \frac{\tau}{\epsilon_0} \int\limits_{u=0}^{\infty} \exp(-u)\, du = \frac{\tau}{\epsilon_0}.$$

(c) For $\tau \ll \epsilon_0$, the terms in the series die off quickly, so we can approximate the true partition function with just the first two terms

$$Z_R(\tau) \approx 1 + 3\exp(-2\epsilon_0/\tau).$$

(d) The energy $U = \tau^2 \frac{\partial \log Z}{\partial \tau}$, so in the limit $\tau \gg \epsilon_0$, $\log Z = (\log \tau - \log \epsilon_0)$ and

$$U = \tau^2 \frac{1}{\tau} = \tau.$$

In the limit $\tau \ll \epsilon_0$,

$$U = \tau^2 \frac{3\exp(-2\epsilon_0/\tau)(2\epsilon_0/\tau^2)}{1 + 3\exp(-2\epsilon_0/\tau)} = \frac{6\epsilon_0 \exp(-2\epsilon_0/\tau)}{1 + 3\exp(-2\epsilon_0/\tau)}.$$

Heat capacity is defined as $C_V = \left(\frac{\partial U}{\partial \tau}\right)_V$, so in the limit $\tau \gg \epsilon_0$, $C_V = 1$.

In the limit $\tau \ll \epsilon_0$,

$$C_V = 6\epsilon_0 \left(\frac{\exp(-2\epsilon_0/\tau)(2\epsilon_0/\tau^2)(1 + 3\exp(-2\epsilon_0/\tau)) - (\exp(-2\epsilon_0/\tau))(3\exp(-2\epsilon_0/\tau))(2\epsilon_0/\tau^2)}{(1 + 3\exp(-2\epsilon_0/\tau))^2} \right)$$

$$C_V = 12 \left(\frac{\epsilon_0}{\tau}\right)^2 \left(\frac{\exp(-2\epsilon_0/\tau)}{(1 + 3\exp(-2\epsilon_0/\tau))^2} \right)$$

but for $\tau \ll \epsilon_0$, $3\exp(-2\epsilon_0/\tau) \ll 1$, so

$$C_V \approx 12 \left(\frac{\epsilon_0}{\tau}\right)^2 \exp(-2\epsilon_0/\tau).$$

(e) See attached.

3. (a) Since each open link has energy ϵ, and we have $s \in [0, N]$ open links, the partition function is

$$Z = \sum_{s=0}^{N} \exp(-s\epsilon/\tau),$$

and the sum of this geometric series is just

$$Z = \frac{1 - \exp(-(N+1)\epsilon/\tau)}{1 - \exp(-\epsilon/\tau)}.$$

Now, we calculate the (expected) energy of the system

$$
\begin{aligned}
U &= -\tau^2 \frac{\partial \log Z}{\partial \tau} \\
&= \left[-\tau^2 \frac{1-\exp(-\epsilon/\tau)}{1-\exp(-(N+1)\epsilon/\tau)}\right] \times
\end{aligned}
$$

$$
\left[\frac{-(N+1)(\epsilon/\tau^2)\exp(-(N+1)\epsilon/\tau)(1-\exp(-\epsilon/\tau)+(\epsilon/\tau^2)\exp(-\epsilon/\tau)(1-\exp(-(N+1)\epsilon/\tau))}{(1-\exp(-\epsilon/\tau))^2}\right]
$$

$$
= \frac{-\epsilon\exp(\epsilon/\tau)}{\exp(\epsilon/\tau)-\exp(-N\epsilon/\tau)} \frac{(N+1)\exp(-N\epsilon/\tau)(1-\exp(-\epsilon/\tau))-(1-\exp(-(N+1)\epsilon/\tau))}{\exp(\epsilon/\tau)-1}.
$$

For $\epsilon \gg \tau$, $\exp(-\epsilon/\tau) \to 0$, $\exp(-N\epsilon/\tau) \to 0$, and $\exp(2\epsilon/\tau) \gg 1$, so

$$
U \approx \frac{-\epsilon\exp(\epsilon/\tau)}{\exp(2\epsilon/\tau)}(-1) = -\epsilon\exp(-\epsilon/\tau).
$$

Since each link has energy ϵ, the expected number of open links is $\langle s\rangle = -U/\epsilon \approx \exp(-\epsilon/\tau)$.

(b) If the zipper can be opened from the right or the left, there are $(s+1)$ ways to achieve a state with s open links (except there is still only one way to achieve a state with all N links open). So the partition function is

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

4. (a) The length of the chain is the number of “excess links” in either the right or left direction, mutiplied by the length of a single link. Let N_R be the total number of links facing right, and N_L be the total number of links facing left, with $N = N_R + N_L$.

First, consider $N_R > N_L$. So $l = (N_R - N_L)\rho$, which implies $2s = N_R - N_L$. The total number of ways to arrange these N links, N_R facing right and N_L facing left, is

$$
g_R = \frac{N!}{(N_L)!(N_R)!} = \frac{N!}{(\frac{1}{2}N+s)!(\frac{1}{2}N-s)!}.
$$

But the situation is exactly symmetric for $N_L < N_R$. That is, we can have a chain of the same length with $N_L > N_R$. So

$$
g = g_L + g_R = \frac{2N!}{(\frac{1}{2}N+s)!(\frac{1}{2}N-s)!}.
$$

(b) The entropy is

$$
\sigma(s) = \log(g(N,s)) = \log(2N!) - \log\left[\left(\frac{1}{2}N+s\right)!\right] - \log\left[\left(\frac{1}{2}N-s\right)!\right].
$$

Using the Stirling approximation,

$$\sigma(s) = \log(2N!)$$
$$- \left[\left(\frac{1}{2}N+s\right)\log\left(\frac{1}{2}N+s\right) - \left(\frac{1}{2}N+s\right) + \left(\frac{1}{2}N-s\right)\log\left(\frac{1}{2}N-s\right) - \left(\frac{1}{2}N-s\right)\right]$$
$$\sigma(s) = \log(2N!) + N$$
$$- \left[\left(\frac{1}{2}N+s\right)\left(\log\left(\frac{N}{2}\right) + \log\left(1+\frac{2s}{N}\right)\right) + \left(\frac{1}{2}N-s\right)\left(\log\left(\frac{N}{2}\right) + \log\left(1-\frac{2s}{N}\right)\right)\right].$$

Since $s \ll N$, we use the approximation $\log(1+x) \approx x$ for small x.

$$\sigma(s) = \log(2N!) + N - \left[\left(\frac{1}{2}N+s\right)\left(\log\left(\frac{N}{2}\right) + \frac{2s}{N}\right) + \left(\frac{1}{2}N-s\right)\left(\log\left(\frac{N}{2}\right) - \frac{2s}{N}\right)\right]$$
$$\sigma(s) = \log(2N!) + N - \left[N\log\left(\frac{N}{2}\right) + \frac{4s^2}{N^2}\right]$$

Note that

$$N\log\left(\frac{N}{2}\right) - N = 2\left(\frac{N}{2}\log\left(\frac{N}{2}\right) - \frac{N}{2}\right) \approx 2\log\left(\left(\frac{N}{2}\right)!\right) = \log\left[\left(\left(\frac{N}{2}\right)!\right)^2\right]$$

and

$$\log(2N!) - \log\left[\left(\left(\frac{N}{2}\right)!\right)^2\right] = \log[2g(N,0)].$$

Since $s^2 = l^2/4p$,

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

(c) Taking the derivative, $(\partial\sigma/\partial l)_U = -2l/N\rho^2$, and since $-f/\tau = (\partial\sigma/\partial l)_U$, $f = 2l\tau/N\rho^2$.

5. (a) Distinguishable: $Z = Z_a^{N_a} Z_b^{N_b}/N_a!N_b!$. Indistinguishable: $Z = Z_a^{N_a} Z_b^{N_b}/(N_a+N_b)!$.

(b) The free energy $F = -\tau\log Z$. Assume $Z_a = Z_b$, and note that $N = N_a + N_b$. In the distinguishable case, using the Stirling approximation,

$$\log Z_{dist} = N\log Z_a - (N_a\log N_a - N_a + N_b\log N_b - N_b),$$

and in the indistinguishable case

$$\log Z_{indist} = N\log Z_a - (N\log N - N),$$

where Z_a is the single-particle entropy, which for an ideal gas is $Z_a = (m\tau/2\pi h)^{3/2}V$. Calculation of the free energy is trivial.

(c) The entropy is $S = -k_b(\partial F/\partial\tau) = k_b(\log Z + \tau\partial(\log Z)/\partial\tau)$. Note that the second term is the same for the indistinguishable and distinguishable cases, since $\partial(\log Z_{dist})/\partial\tau = \partial(\log Z_{indist})/\partial\tau$.

So, the difference in entropy between the distinguishable and indistinguishable cases is

$$\Delta S = k_b(\log Z_{dist} - \log Z_{indist}) = -k_b(N_a \log N_a + N_b \log N_b - (N_a + N_b)\log N)$$
$$\Delta S = -k_b\left[N_a \log\left(\frac{N_a}{N}\right) + N_b \log\left(\frac{N_b}{N}\right)\right].$$

(d) The difference in entropy can be expressed

$$\Delta S = k_b(\log g_{dist} - \log g_{indist}) = k_b \log(g_{dist}/g_{indist}),$$

so

$$\frac{g_{dist}}{g_{indist}} = \exp\left(\frac{\Delta S}{k_b}\right).$$

When $N_a = N_b = N/2$,

$$\Delta S = -2k_b\frac{N}{2}\log\left(\frac{1}{2}\right) = Nk_b \log 2.$$

6. (a)

$$\langle x\rangle = \frac{\int_{-\infty}^{\infty} x\exp(-ax^2/\tau)\,dx}{\int_{-\infty}^{\infty} \exp(-ax^2/\tau)\,dx}.$$

(b) The top integral in (a) is the integral of an odd function over all real numbers, which evaluates to zero. So $\langle x\rangle = 0$, independent of temperature.

(c)

$$\langle x\rangle = \frac{\int_{-\infty}^{\infty} x\exp(-(ax^2 - bx^3)/\tau)\,dx}{\int_{-\infty}^{\infty} \exp(-(ax^2 - bx^3)/\tau)\,dx}.$$

(d) Note that $\exp(bx^3/\tau) = 1 + (bx^3/\tau) + \mathcal{O}(b^2)$. So to first order in b,

$$\langle x\rangle = \frac{\int_{-\infty}^{\infty} x\exp(-ax^2/\tau)\exp(bx^3/\tau)\,dx}{\int_{-\infty}^{\infty} \exp(-ax^2/\tau)\exp(bx^3/\tau)\,dx} = \frac{\int_{-\infty}^{\infty} (x + (bx^4/\tau))\exp(-ax^2/\tau)\,dx}{\int_{-\infty}^{\infty} (1 + (bx^3/\tau))\exp(-ax^2/\tau)\,dx}.$$

Now,

$$\int_{-\infty}^{\infty} (x + (bx^4/\tau))\exp(-ax^2/\tau)\,dx = \frac{3\sqrt{\pi}b}{4\tau(a/\tau)^{5/2}},$$

since the first term is odd, and

$$\int_{-\infty}^{\infty} (1 + (bx^3/\tau)) \exp(-ax^2/\tau)\, dx = \frac{\sqrt{\pi}}{(a/\tau)^{1/2}}.$$

since the second term is odd. So

$$\langle x \rangle = \frac{3b}{4a^2}\tau,$$

which implies a thermal expansion coefficient of $3b/4a^2$.