

Problem 1

Kittel & Kroemer, Chapter 3, problem 7 [Zipper problem]

A zipper has N links; each link has a state in which it is closed with energy 0 and a state in which it is open with energy ϵ . We require, however, that the zipper can only unzip from the left end, and that the link number s can only open if all links to the left ($1, 2, \dots, s-1$) are already open.

(a): 1 point

Show that the partition function can be summed in the form

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

Because of the requirement that it can only unzip from the left end, the zipper has $N+1$ possible states: one state where zero links are open with energy 0, one state where the leftmost link is open with energy ϵ , one state where the two leftmost links are open with energy 2ϵ , all the way up the state with all N links open, with energy $N\epsilon$. If we call the number of open links n , the partition function is

$$Z = \sum_{n=0}^N e^{-n\epsilon/\tau}.$$

The main difference with the quantum harmonic oscillator is that the sum has a finite number of terms. Let's see if we can approach the sum in a similar way as the infinite sum:

$$\begin{aligned} Z &= 1 + \sum_{n=1}^N e^{-n\epsilon/\tau} \\ &= 1 + e^{-\epsilon/\tau} \sum_{n=0}^N e^{-n\epsilon/\tau} - e^{-(N+1)\epsilon/\tau} \\ &= 1 + e^{-\epsilon/\tau} Z - e^{-(N+1)\epsilon/\tau}. \end{aligned}$$

Another cute trick! We can now solve for Z algebraically:

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

(a): 1 point

(b): 1 point

In the limit $\epsilon \gg \tau$, find the average number of open links. The model is a very simplified model of the unwinding of two-stranded DNA molecules.

[Hint: It is easier to work with the inverse temperature $\beta \equiv 1/\tau$.]

[Note: your answer to this problem shouldn't simply be 0. That result is obvious! We are interested in the *limiting behavior* of this quantity at low temperatures: is it polynomial? exponential? etc]

Since energy is the number of open links times ϵ , the average number of open links $\langle n \rangle$ is the average energy U divided by ϵ . This can be calculated from the partition function. It is easier to work with the inverse temperature $\beta \equiv 1/\tau$. Then

$$\begin{aligned}\langle n \rangle &= \frac{U}{\epsilon} = -\frac{1}{\epsilon} \frac{\partial \ln Z}{\partial \beta} \\ &= -\frac{1}{\epsilon} \frac{\partial}{\partial \beta} \ln \left[\frac{1 - e^{-\beta(N+1)\epsilon}}{1 - e^{-\beta\epsilon}} \right] \\ &= -\frac{1}{\epsilon} \frac{\partial}{\partial \beta} \left[\ln [1 - e^{-\beta(N+1)\epsilon}] - \ln [1 - e^{-\beta\epsilon}] \right] \\ &= -\frac{(N+1)e^{-\beta(N+1)\epsilon}}{1 - e^{-\beta(N+1)\epsilon}} + \frac{e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}} \\ &= -\frac{N+1}{e^{\beta(N+1)\epsilon} - 1} + \frac{1}{e^{\beta\epsilon} - 1}\end{aligned}$$

(b): 1 point

The limit $\epsilon \gg \tau$ is the same as the limit $\beta\epsilon \gg 1$. In this limit, $e^{\beta\epsilon} - 1 \approx e^{\beta\epsilon}$, and $e^{\beta(N+1)\epsilon} - 1 \approx e^{\beta(N+1)\epsilon}$. So

$$\begin{aligned}\langle n \rangle &\approx -\frac{N+1}{e^{\beta(N+1)\epsilon}} + \frac{1}{e^{\beta\epsilon}} \\ &= e^{-\beta\epsilon} \left(-\frac{N+1}{e^{N\beta\epsilon}} + 1 \right) \\ &\approx e^{-\epsilon/\tau},\end{aligned}$$

where we have switched back to the fundamental temperature τ .

Problem 2

Kittel & Kroemer, Chapter 3, problem 10 [Elasticity of polymers]

The thermodynamic identity for a one-dimensional system is

$$\tau d\sigma = dU - f dl$$

when f is the external force exerted on the line and dl is the extension of the line. By analogy with (32) we form the derivative to find

$$-\frac{f}{\tau} = \left(\frac{\partial \sigma}{\partial l} \right)_U.$$

The direction of the force is opposite to the conventional direction of the pressure.

We consider a polymeric chain of N links each of length ρ , with each link equally likely to be directed to the right and to the left.

(a): 1 point

Show that the number of arrangements that give a head-to-tail length of $l = 2|s|\rho$ is

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

We can without loss of generality assume that N is even. Let's say there are N_L links that point to the left, and N_R links that point to the right, so that $N_R + N_L = N$. Then the end-to-end distance should be $l = |\rho N_R - \rho N_L| = \rho |N_R - N_L|$. As with the spin case, we can define the "left-right excess" s as $2s = N_R - N_L$, in which case we see that $l = 2|s|\rho$. Now, like in the spin case, we have shown that the multiplicity of the state with "left-right excess" s is $g(N, s) = \frac{N!}{(\frac{1}{2}N + s)!(\frac{1}{2}N - s)!}$. But a positive and a negative "left-right excess" of the same magnitude give the same end-to-end length, since $l = 2|s|\rho$. So the multiplicity of the states with end-to-end length l is

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

(a): 1 point

(b): 1 point

For $|s| \ll N$ show that

$$\sigma(l) = \ln[2g(N, 0)] - l^2/2N\rho^2.$$

For $|s| \ll N$, we have shown in class that $g(N, s) = \frac{N!}{(\frac{1}{2}N+s)!(\frac{1}{2}N-s)!} \approx g(N, 0)e^{-2s^2/N}$. So

$$\begin{aligned}\sigma(l) &= \ln \left[\frac{2N!}{(\frac{1}{2}N+s)!(\frac{1}{2}N-s)!} \right] \\ &\approx \ln[2g(N, 0)e^{-2s^2/N}] \\ &= \ln[2g(N, 0)] + \ln e^{-2s^2/N} \\ &= \ln[2g(N, 0)] - 2s^2/N.\end{aligned}$$

(b): 1 point

Using the relation $l = 2|s|\rho$, we can write $s^2 = l^2/4\rho^2$. Thus

$$\sigma(l) \approx \ln[2g(N, 0)] - l^2/2N\rho^2.$$

(c): 1 point

Show that the force at extension l is

$$f = l\tau/N\rho^2.$$

From the introduction to this problem, we can write the force as the derivative of the entropy:

$$\begin{aligned}f &= -\tau \left(\frac{\partial \sigma}{\partial l} \right) \\ &= -\tau \frac{\partial}{\partial l} (\ln[2g(N, 0)] - l^2/2N\rho^2) \\ &= l\tau/N\rho^2.\end{aligned}$$

(c): 1 point

The force is proportional to the temperature. The force arises because the polymer wants to curl up: the entropy is higher in a random coil than in an uncoiled configuration. Warming a rubber band makes it contract; warming a steel wire makes it expand.

Problem 3

Kittel & Kroemer, Chapter 4, problem 1 [Number of thermal photons]: 2 points

Show that the number of photons $\sum \langle s_n \rangle$ in equilibrium at temperature τ in a cavity of volume V is

$$N = 2.40\pi^{-2}V(\tau/\hbar c)^3.$$

A single photon mode $\omega_n = n\pi c/L$, with $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$, behaves like a quantum harmonic oscillator, and has

$$\begin{aligned}\langle s_n \rangle &= \frac{1}{e^{\hbar\omega_n/\tau} - 1} \\ &= \frac{1}{e^{n\hbar\pi c/L\tau} - 1}.\end{aligned}$$

We can sum over all modes n to get the total number of photons (let's not forget the factor of 2 from the polarizations):

$$N \equiv 2 \sum_n \langle s_n \rangle = 2 \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \frac{1}{e^{n\hbar\pi c/L\tau} - 1}.$$

To perform this, we approximate our sums as integrals:

$$N \approx 2 \int_0^{\infty} dn_x \int_0^{\infty} dn_y \int_0^{\infty} dn_z \frac{1}{e^{n\hbar\pi c/L\tau} - 1}.$$

The integrand is spherically-symmetric and only depends on the “radius” n . It thus makes sense to transform to spherical coordinates. Because we are only integrating over one octant and the integrand is spherically symmetric, we can write our integral as

$$N = 2 \frac{1}{8} \int_0^{\infty} (4\pi n^2) dn \frac{1}{e^{n\hbar\pi c/L\tau} - 1}.$$

Defining the dimensionless variable $x \equiv n\hbar\pi c/L\tau$, so that $dx = dn \hbar\pi c/L\tau$, we have

$$N = \pi \left(\frac{L\tau}{\pi\hbar c} \right)^3 \int_0^{\infty} dx \frac{x^2}{e^x - 1}.$$

You can plug this definite integral into a calculator; its value is ≈ 2.40 . Recognizing $L^3 = V$ as the volume, we have found

$$N = 2.40\pi^{-2} \left(\frac{\tau}{\hbar c} \right)^3$$

From (23) the entropy is $\sigma = (4\pi^2 V/45)(\tau/\hbar c)^3$, whence $\sigma/N \sim 3.602$. It is believed that the total number of photons in the universe is 10^8 larger than the total number of nucleons (protons, neutrons). Because both entropies are of the order of the respective number of particles (see Eq. 3.76), the photons provide the dominant contribution to the entropy of the universe, although the particles dominate the total energy. We believe that the entropy of the photons is essentially constant, so that the entropy of the universe is approximately constant with time.

Problem 4

Kittel & Kroemer, Chapter 4, problem 7 [Free energy of a photon gas]: 3 points

(a): 1 point

Show that the partition function of a photon gas is given by

$$Z = \prod_n [1 - e^{-\hbar\omega_n/\tau}]^{-1},$$

where the product is over the modes n .

We showed in a previous homework that for two independent systems in thermal equilibrium, the partition function of the combined system is the product of the partition functions of the individual systems: $Z(\mathbf{1}+\mathbf{2}) = Z(\mathbf{1})Z(\mathbf{2})$. In a photon gas (simply a region of space with electromagnetic waves and no matter), the different modes are independent of each other. Each mode n has energies $\epsilon_s = s\hbar\omega_n$; that is, each mode has the same energy levels as a quantum harmonic oscillator. Therefore the partition function for a particular mode is the partition function for a quantum harmonic oscillator, which we showed to be $Z_n = [1 - e^{-\hbar\omega_n/\tau}]^{-1}$. Since all of the modes are independent, we can write the full partition function of the photon gas as

(a): 1 point

$$Z = Z_1 Z_2 Z_3 \cdots = \prod_n [1 - e^{-\hbar\omega_n/\tau}]^{-1}$$

(b): 1 point

The Helmholtz free energy is found directly from your result from part (a) as

$$F = \tau \sum_n \ln[1 - e^{-\hbar\omega_n/\tau}].$$

Transform the sum to an integral; integrate by parts to find

$$F = -\pi^2 V \tau^4 / 45 \hbar^3 c^3.$$

The procedure for transforming the sum to an integral is the same here as it was in the previous problem; the result is $\sum_n \rightarrow 2\frac{1}{8}4\pi \int_0^\infty n^2 dn$. So (with $\omega_n = n\pi c/L$)

$$F = \pi\tau \int_0^\infty n^2 \ln[1 - e^{-\hbar n\pi c/L\tau}] dn.$$

As before, taking $x = n\hbar\pi c/L\tau$, we have

$$F = \pi\tau \left(\frac{L\tau}{\pi\hbar c} \right)^3 \int_0^\infty x^2 \ln[1 - e^{-x}] dx.$$

Taking $dv = x^2 dx$ and $u = \ln[1 - e^{-x}]$, so that $v = \frac{1}{3}x^3$ and $du = \frac{e^{-x}}{1-e^{-x}} dx$, we can write this integral as

(b): 1 point

$$F = \pi\tau \left(\frac{L\tau}{\pi\hbar c} \right)^3 \left[\left(\frac{1}{3}x^3 \ln[1 - e^{-x}] \right)_0^\infty - \frac{1}{3} \int_0^\infty x^3 \frac{e^{-x}}{1 - e^{-x}} dx \right].$$

It turns out that the “boundary term” $(\frac{1}{3}x^3 \ln[1 - e^{-x}])_0^\infty$ equals zero; you can find the limits using l'Hopital's rule, or just by looking at a graph of $\frac{1}{3}x^3 \ln[1 - e^{-x}]$. Thus

$$\begin{aligned} F &= \pi\tau \left(\frac{L\tau}{\pi\hbar c} \right)^3 \left[-\frac{1}{3} \int_0^\infty x^3 \frac{e^{-x}}{1 - e^{-x}} dx \right] \\ &= -\frac{\pi\tau}{3} \left(\frac{L\tau}{\pi\hbar c} \right)^3 \int_0^\infty \frac{x^3}{e^x - 1} dx. \end{aligned}$$

(b): 1 point

The result of this integral is given in the text, or you can plug it into a calculator; its value is $\pi^4/15$. Thus finally

$$\begin{aligned} F &= -\frac{\pi^5\tau}{45} \left(\frac{L\tau}{\pi\hbar c} \right)^3 \\ &= -\pi^2 V \tau^4 / 45 \hbar^3 c^3, \end{aligned}$$

where $V = L^3$.