

Homework 7 (Due Tuesday, February 21st)

1. Consider a system of N distinguishable particles for which the energy of each particle can be either 0 or $\epsilon > 0$; the particles have no kinetic energy. Call n_0 and n_1 the number of particles in the ground and excited state, respectively.

(a) Using the microcanonical ensemble, find the entropy of such a system. Show that $S(U) = kN \ln 2$ when $U = \epsilon N/2$, which happens to be the largest possible value of the entropy.

(b) Find the temperature as a function of the internal energy, U , and show that T can be *negative*.

(c) Graph the normalized temperature, $T^* = kT/\epsilon$, versus the normalized energy $U^* = U/N\epsilon$ for $U^* = 0$ to 1. Also graph the normalized entropy, $S^* = S/Nk$, versus T^* for $T^* = -5$ to $+5$.

(d) If system A, at a negative temperature, is allowed to exchange energy with system B, at a positive temperature, does heat flow from A to B or from B to A? [Hint: Entropy must increase as the combined system approaches equilibrium].

For a description of an experiment showing a physical system at a negative temperature, see N.F. Ramsey, *Phys. Rev.* **103** 20 (1956).

2. For an ideal gas of N indistinguishable, independent particles in the extremely relativistic limit (in which the energy of a particle is pc) the canonical partition function is

$$Q(T, V, N) = \frac{1}{N!} \left[8\pi V \left(\frac{kT}{hc} \right)^3 \right]^N$$

(a) Find the average energy $\langle E \rangle = E(T, N)$.

(b) Find the pressure $P(T, V, N)$.

(c) Use the results above and thermodynamics to find the ratio of the specific heats, $\gamma = C_P/C_V$.

In each part, compare the result with the non-relativistic monatomic ideal gas.

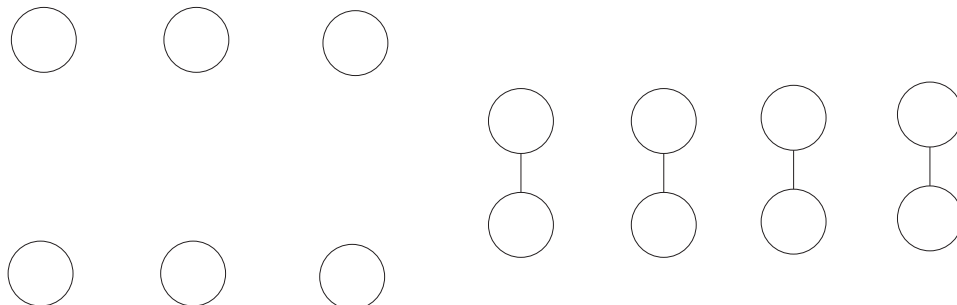


Figure 1: Zipper model for DNA molecule.

3. A simple model of a DNA molecule is to picture it as a zipper with N links, as illustrated in Fig. 1. Each link has two states: the closed state has energy 0 and the open state has energy $\epsilon > 0$. Suppose that the zipper can only open from the left end and that a link cannot open unless all links to its left are open.

- (a) Find the canonical ensemble partition function, Q , for the zipper.
- (b) Find an expression for the average number of open links, $\langle n \rangle$, in terms of the partition function.
- (c) From your result above, find the average number of open links in the limits $T \rightarrow 0$ and $T \rightarrow \infty$.
- (d) Graph the average number of open links, $\langle n \rangle$, versus kT/ϵ (from $kT/\epsilon = 0.1$ to 10^4) for $N = 100$.

Make your plot on a semilog scale with the horizontal axis being the log scale.

4. In the canonical ensemble the internal energy is not fixed but the variance about the mean turns out to be small, as you will demonstrate in this exercise.

- (a) The variance of the internal energy is defined as,

$$\text{Var}(E) = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

where

$$\langle f(E) \rangle = \sum_i^{\text{states}} f(E_i) \mathcal{P}_i$$

and $\langle E \rangle = U$. Show that in the canonical ensemble

$$\text{Var}(E) = \left(\frac{\partial^2 \ln Q}{\partial \beta^2} \right)_{V,N}$$

where Q is the partition function.

- (b) Use the result above to find $\text{Var}(E)$ for an ideal gas.
- (c) Show that the standard deviation of the energy, $\sqrt{\text{Var}(E)}$, goes as U/\sqrt{N} , which is very small for large N .

Solutions

1. (a) Call $M = U/\epsilon = n_1$ the number of quanta of energy in the system. Each particle can have either zero or one quanta of energy. The number of ways to select M distinguishable particles (which are the ones in the excited state) out of a population of N is

$$\Gamma(U) = \binom{N}{M} = \frac{N!}{(N-M)!M!}$$

Having counted states, we can now obtain the entropy using

$$\begin{aligned} S(U) &= k \ln \Gamma(U) = k \{ \ln(N!) - \ln[(N-M)!] - \ln(M!) \} \\ &\approx k \{ N \ln(N) - (N-M) \ln[(N-M)] - M \ln(M) \} \end{aligned}$$

using the approximation $\ln(x!) \approx x \ln(x) - x$. If $U = \epsilon N/2$ then $M = N/2$ and

$$S(\epsilon N/2) = k \{ N \ln(N) - \frac{N}{2} \ln[\frac{N}{2}] - \frac{N}{2} \ln(\frac{N}{2}) \} = kN \{ \ln(N) - \ln[\frac{N}{2}] \} = kN \ln 2$$

(b) To obtain the temperature, we use

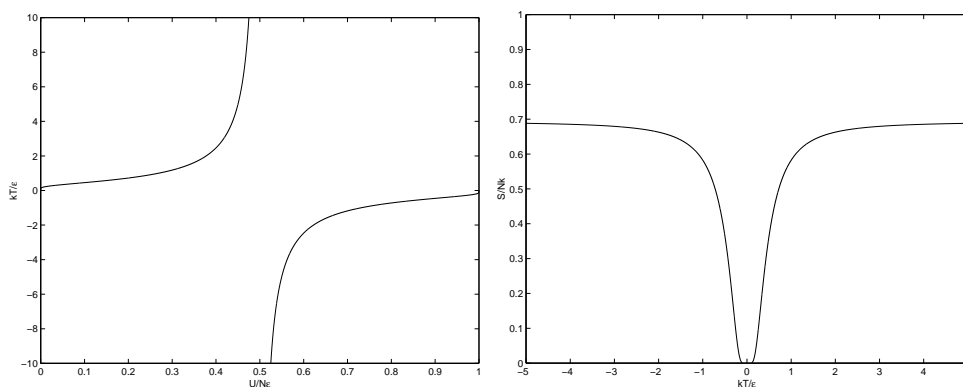
$$\frac{1}{T} = \frac{dS}{dU} = \frac{dS}{dM} \frac{dM}{dU} = \frac{k}{\epsilon} [\ln(N-M) - \ln(M)]$$

so

$$T = \frac{\epsilon}{k} \frac{1}{\ln(N-M) - \ln(M)}$$

The temperature is negative if $M > (N-M)$, that is, if there are more atoms in the excited state than in the ground state. The system is at a negative temperature when population inversion occurs (i.e., $M > N/2$). For a complete discussion, see Section 3.10 in Pathria.

(c) Your graphs should look like the figures below.



(d) A system with negative temperature has *more* energy than one with positive temperature. Also, the entropy increases with M for positive temperatures but decreases as M increases for negative temperatures ($S = 0$ for $M = 0$ and for $M = N$). So when systems at positive and negative temperatures

are brought into contact, energy (heat) flows from the negative T system (system A) to the positive T system (system B) since total entropy must increase.

2. (a) The average energy is

$$\langle E \rangle = - \left(\frac{\partial}{\partial \beta} \right)_V \ln Q = - \frac{1}{Q} \left(\frac{\partial}{\partial \beta} \right)_V Q = - \frac{1}{Q} \left(-3N \frac{Q}{\beta} \right) = 3NkT$$

Note that for the non-relativistic ideal gas $U = \frac{3}{2}NkT$.

(b) The pressure is

$$P = kT \left(\frac{\partial}{\partial V} \right)_T \ln Q = \frac{kT}{Q} \left(\frac{\partial}{\partial V} \right)_\beta Q = \frac{kT}{Q} \left(\frac{NQ}{V} \right) = \frac{NkT}{V}$$

which is the same as for the non-relativistic ideal gas.

(c) The heat capacity at constant volume is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3Nk$$

In general

$$C_P = C_V + \frac{TV\alpha^2}{K_T}$$

where α is the coefficient of thermal expansion and K_T is the isothermal compressibility. Since our equation of state is the ideal gas law, $\alpha = 1/T$ and $K_T = 1/P$, which gives $C_P = C_V + Nk = 4Nk$, thus $\gamma = C_P/C_V = 4/3$. Note that for the non-relativistic ideal gas $\gamma = 5/3$.

3. (a) By definition, the partition function is

$$Q = \sum_{states} e^{-\beta E_\nu} = \sum_{n=0}^N e^{-\beta n\epsilon} = \frac{e^{-\beta\epsilon(N+1)} - 1}{e^{-\beta\epsilon} - 1}$$

where we use the geometric progression identity,

$$\sum_{i=0}^N a^i = \frac{a^{N+1} - 1}{a - 1}$$

(b) The average number of open links is

$$\langle n \rangle = \sum_{n=0}^N n \mathcal{P}(n) = \frac{1}{Q} \sum_{n=0}^N n e^{-\beta n\epsilon} = - \frac{1}{\epsilon Q} \frac{\partial}{\partial \beta} Q = - \frac{1}{\epsilon} \frac{\partial}{\partial \beta} \ln Q$$

Note that you can also arrive at this result by using the identity $\langle E \rangle = - \frac{\partial}{\partial \beta} \ln Q$ and the fact that $\langle E \rangle = \langle n \rangle \epsilon$ for this system. After a bit of algebra one obtains the result

$$\langle n \rangle = \frac{N+1}{1 - e^{-\beta\epsilon(N+1)}} - \frac{1}{1 - e^{-\beta\epsilon}}$$

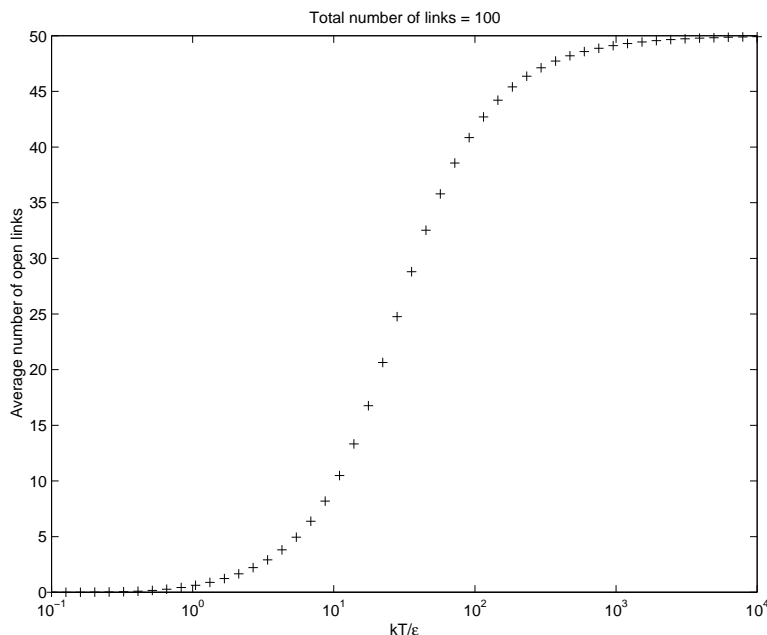


Figure 2: Graph of number of open links versus temperature for the zipper model of a DNA molecule.

(c) The limit $T \rightarrow 0$, $\beta \rightarrow \infty$ gives $\langle n \rangle = 0$ by inspection since the denominators diverge. For the high temperature limit ($\beta \rightarrow 0$) the Taylor expansion of the exponentials gives

$$\begin{aligned} \langle n \rangle &\approx -\frac{N+1}{\beta\epsilon(N+1) + \frac{1}{2}\beta^2\epsilon^2(N+1)^2} + \frac{1}{\beta\epsilon + \frac{1}{2}\beta^2\epsilon^2} \\ &\approx -\frac{1}{\beta\epsilon} \left(1 - \frac{1}{2}\beta\epsilon(N+1)\right) + \frac{1}{\beta\epsilon} \left(1 - \frac{1}{2}\beta\epsilon\right) = N/2 \end{aligned}$$

where we used the approximation $1/(1+x) \approx 1-x$ when $|x| \ll 1$. The number of open links goes to $N/2$ as $T \rightarrow \infty$ since this is the state of maximum entropy.

(d) Your graph should resemble Fig. 2.

4. (a) From the definitions,

$$\begin{aligned} \text{Var}(E) &= \langle E^2 \rangle - \langle E \rangle^2 = \sum_i^{\text{states}} E_i^2 \mathcal{P}_i - \left(\sum_i^{\text{states}} E_i \mathcal{P}_i \right)^2 \\ &= \frac{1}{Q} \sum_i^{\text{states}} E_i^2 \exp(-\beta E_i) - \left(\frac{1}{Q} \sum_i^{\text{states}} E_i \exp(-\beta E_i) \right)^2 \\ &= \frac{1}{Q} \left(\frac{\partial^2}{\partial \beta^2} \right)_{V,N} \sum_i^{\text{states}} \exp(-\beta E_i) - \left(\frac{1}{Q} \left(\frac{\partial}{\partial \beta} \right)_{V,N} \sum_i^{\text{states}} \exp(-\beta E_i) \right)^2 \\ &= \frac{1}{Q} \left(\frac{\partial^2 Q}{\partial \beta^2} \right)_{V,N} - \left(\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right)_{V,N} \right)^2 \end{aligned}$$

$$= \left(\frac{\partial}{\partial \beta} \right)_{V,N} \left[\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right)_{V,N} \right] = \left(\frac{\partial^2 \ln Q}{\partial \beta^2} \right)_{V,N}$$

(b) For an ideal gas,

$$Q = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N \quad \text{where } \lambda = \frac{h}{\sqrt{2\pi m}} \sqrt{\beta}$$

so $\ln Q = -\frac{3}{2}N \ln \beta + f(V, N)$. Thus,

$$\left(\frac{\partial \ln Q}{\partial \beta} \right)_{V,N} = -\frac{3}{2}N\beta^{-1} \quad \text{and} \quad \left(\frac{\partial^2 \ln Q}{\partial \beta^2} \right)_{V,N} = \frac{3}{2}N\beta^{-2}$$

so $\text{Var}(E) = \frac{3}{2}Nk^2T^2$. Note that in general we find that $\text{Var}(E) = C_v kT^2$.

(c) Since $U = \frac{3}{2}NkT$ we immediately see that $\sqrt{\text{Var}(E)} = \sqrt{\frac{3}{2}NkT} = U/\sqrt{\frac{3}{2}N} \propto U/\sqrt{N}$. Notice that with N as small as 10^6 particles the standard deviation of the energy is only about a tenth of one percent of the mean value.