Problem 1:

(a)

$$T(E,N) = \sum_{\substack{N_+ = 0,1,\dots,\frac{E}{\varepsilon} \\ N_+ + N_- = \frac{E}{\varepsilon}}} \frac{N!}{N_0!\, N_+!\, N_-!}$$

let $E = 0 \Rightarrow N_+ = N_- = 0$ and $\underbrace{T(E,N) = 1}_{\text{all nuclei in } m_s = 0 \text{ level}}$

let $E = \varepsilon \Rightarrow$ 1 nucleus in $\underbrace{m_s = +1}_{N \text{ ways of doing this}}$ or in $\underbrace{m_s = -1}_{N \text{ ways of doing this}}$

$\rightsquigarrow 2N$ microstates

In the equation, we will have two terms:

1) $N_+ = 0,\ N_- = 1$ and 2) $N_+ = 1,\ N_- = 0$

$$\frac{N!}{(N-1)!\,0!\,1!} \qquad \frac{N!}{(N-1)!\,1!\,0!}$$

let $E = 2\varepsilon$: 2 nuclei in $m_s = +1$ or 2 nuclei in $m_s = -1$

or 1 nucleus in $m_s = -1$ and 1 in $m_s = +1$

number of pairs

number of pairs

$$\frac{N(N-1)}{2} + \frac{N(N-1)}{2} + N(N-1) = 2N(N-1)$$

In the eq.: same terms

We can also think about part (a) in the following way:

let $N_+ = 0$: we then have two levels, namely $m_s = 0$ and $m_s = -1$ levels

$$\Rightarrow \text{numbers of states is } \underbrace{\frac{N!}{N_-!\,N_0!}}_{\substack{\text{two-level system}\\ \text{with the constraint}\\ \text{that } E \text{ fixed and}\\ N = N_- + N_0}}$$

let $N_+ = 1$: again two levels but only $N-1$ particles

$$\Rightarrow \text{numbers of states } \underbrace{\frac{(N-1)!}{N_-!\,N_0!}}_{\substack{N-1 \text{ particles}\\ \text{distributed among}\\ \text{two levels}}} \cdot N$$

the particle in $m_s = +1$ can be distributed in N different levels

let $N_+ = 2$: again think of $m_s = -1$ and 0 as two-level system

$$\Rightarrow \text{numbers of states } \underbrace{\frac{(N-2)!}{N_-!\,N_0!}}_{\substack{N-2 \text{ particles}\\ \text{distributed among}\\ \text{two levels}}} \underbrace{\frac{N(N-1)}{2}}_{\substack{\text{can distribute}\\ \text{the two } N_+\\ \text{particles in}\\ \frac{N(N-1)}{2} \text{ ways}}} = \frac{N!}{N_-!\,N_0!\,N_+!}$$

(b) Entropy $S(E,N) = k \log\left(\Gamma(E,N)\right)$

So: we need to express N_0, N_+, and N_- in terms of E and N.

$$N_+ + N_- = \frac{E}{\varepsilon} \quad (*) \qquad \& \qquad N_0 + N_+ + N_- = N$$

$$\Downarrow$$

$$N_- = \frac{E}{\varepsilon} - N_+ \qquad\qquad N_0 = N - (N_+ + N_-)$$

$$= N - \frac{E}{\varepsilon}$$

using (*)

$$\Rightarrow \Gamma(E,N) = \sum_{N_+ = 0,1,\ldots,\frac{E}{\varepsilon}} \frac{N!}{\left(N - \frac{E}{\varepsilon}\right)!\, N_+!\, \left(\frac{E}{\varepsilon} - N_+\right)!}$$

$$= \frac{N!}{\left(N - \frac{E}{\varepsilon}\right)!} \sum_{N_+ = 0,1,\ldots,\frac{E}{\varepsilon}} \frac{1}{N_+!\, \left(\frac{E}{\varepsilon} - N_+\right)!}$$

(c)

at $T=0 \rightsquigarrow E=0 \rightsquigarrow$ one micro state

$\Rightarrow \; S = k \log 1 = 0$

physically: we have no choice

we may think of this as a maximally ordered state

Problem 2:

(a) $\Delta S \geq 0$

the entropy in equilibrium never goes down

(i.e., S wants to be maximal)

(b) $\Delta A \leq 0$

the Helmholtz free energy in equilibrium never increases (i.e., A wants to be minimal)

(c) microcanonical $\boxed{S = k \log(\Gamma(E, V, N))}$

canonical $Q = e^{-\beta A}$ or $\boxed{A = -kT \log(Q(T, N, V))}$

grandcanonical $\mathcal{Q} = \sum_{N=0}^{\infty} (e^{\beta\mu})^N Q(z, N, V)$

$$\downarrow$$

$$z = e^{\beta\mu}$$

$$\boxed{PV = kT \log(\mathcal{Q}(z, N, V))}$$

(d) microcanonical : all states are equally likely

let E_s be the energy of the microstate of interest

$\Rightarrow$ probability $= \frac{1}{\Gamma(E_s)}$

(one over the total # of states consistent with macro variables)

canonical $\dfrac{e^{-\beta E_s}}{\sum_j e^{-\beta E_j}}$

grandcanonical $\dfrac{e^{-\beta(E_s - \mu N_s)}}{\sum_{j,N} e^{-\beta(E_j - \mu N)}}$

let N_s be the # of particles of the microstate of interest

Problem 3:

(a) $dU = T\,dS - P\,dV + \mu\,dN$ (*) ; $U = U(S, V, N)$

dU: extensive; T: intensive; dS: extensive; P: intensive; dV: extensive; μ: intensive; dN: extensive

extensive : double the system size and quantity increases proportional

intensive : independent of system size

(b) $A = U - TS$

$dA = dU - T\,dS - S\,dT$

$\overset{(*)}{=} T\,dS - P\,dV + \mu\,dN - T\,dS - S\,dT$

$= -P\,dV + \mu\,dN - S\,dT$ (*')

→ assembly : V, N, T

$G = A + PV$

$dG = dA + V\,dP + P\,dV$

$\overset{(*')}{=} -P\,dV + \mu\,dN - S\,dT + V\,dP + P\,dV$

$= \mu\,dN - S\,dT + V\,dP$ (*'') → assembly : N, T, P

$$H = G + TS$$

$$dH = dG + T\,dS + S\,dT$$

$$\overset{(*'')}{=} \mu\,dN - \underline{S}\,dT + V\,dP + T\,dS + S\,\underline{d}T$$

$$= \mu\,dN + V\,dP + T\,dS$$

$\rightarrow$ assembly: N, P, S

(d) from dU:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

(c) Different experimental situations "require" different assemblies

from dA:

$$-P = \left(\frac{\partial A}{\partial V}\right)_{N,T}$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}$$

$$-S = \left(\frac{\partial A}{\partial T}\right)_{N,V}$$

from dG:

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{N,P}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

from dH:

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{P,S}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{N,S}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}$$

Problem 4:

(a) Start will all spin down

$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \cdots \quad \downarrow \quad \downarrow \quad \downarrow$$
$$J \quad J \quad J \qquad\qquad J \quad J$$

$\Rightarrow E = (N-1) J \quad \rightsquigarrow$ 1 micro state

but: this is equivalent to all up $\Rightarrow$ 2 microstates

Let us introduce a "kink":

$$\downarrow \quad \downarrow \quad \downarrow \quad \cdots \quad \downarrow \quad \uparrow \quad \uparrow \quad \uparrow \cdots \uparrow$$
$$J \quad J \qquad\qquad -J \quad J$$

$\Rightarrow E = (N-2) J - J = (N-3) J$

there are $N-1$ ways to introduce the kink

$\Rightarrow N-1$ microstates

but this is equivalent to

$\uparrow \uparrow \uparrow \uparrow \cdots \uparrow \downarrow \downarrow \downarrow \cdots \downarrow$

$\Rightarrow 2(N-1)$ microstates

For 2 kinks: $E = (N-3) J - 2J = (N-5) J$

there are $\frac{(N-1)(N-2)}{2}$ to introduce the kinks

again, we need a factor of two $\Rightarrow$

$2 \frac{(N-1)(N-2)}{2}$ micro states

For n kinks, the energy is:

$$E = (N - 2n - 1) J \quad , \; n \text{ can take the values } 0, 1, \ldots, N-1$$

So, the short answer for part (a) is: $E = \pm (N-1) J$

$E = \pm (N-3) J$

$\vdots$

(b) The number of microstates are already discussed above. Let's rewrite this in a general form:

$$2 \frac{(N-1)!}{(N-1-n)! \; n!}$$

see part (a) for the explanation

this is the number of ways we can distribute n kinks among $N-1$ possible slots

(c) $$Q(N,T) = \sum_{\substack{\text{all states} \\ (\text{use label } j)}} e^{-\beta E_j}$$

$$= \sum_{n=0}^{N-1} 2 \frac{(N-1)!}{(N-1-n)! \, n!} \, e^{-\beta (N-2n-1) J}$$

If desired, we could replace n by E:

from $E = (N-2n-1) J$, we find $\frac{E}{J} - N + 1 = -2n$

$$\Rightarrow n = \frac{N}{2} - \frac{1}{2} - \frac{E}{2J}$$

Problem 5:

To get a first feel for this problem, let us consider a zipper consisting of 4 links.

link 1 : open or closed

link 2 : open or closed

link 3 : open or closed

link 4 : open or closed

$\Rightarrow 2^4 = 16$ possibilities

what are the allowed energies?

all closed: $4\varepsilon_0$ $\rightarrow$ multiplicity 1

3 closed, 1 open: $3\varepsilon_0 + \varepsilon_1$ $\rightarrow$ multiplicity 4

2 closed, 2 open: $2\varepsilon_0 + 2\varepsilon_1$ $\rightarrow$ multiplicity 6

1 closed, 3 open: $\varepsilon_0 + 3\varepsilon_1$ $\rightarrow$ multiplicity 4

4 open : $4\varepsilon_1$ $\rightarrow$ multiplicity 1

We are interested in the probability of the first link to be open. Of the states listed above, the following fulfill this criterium:

$\hookrightarrow$ underlined in purple

$E = 4\varepsilon_0$: cccc

$E = 3\varepsilon_0 + \varepsilon_1$: ccco, ccoc, cocc, occc

$E = 2\varepsilon_0 + 2\varepsilon_1$: ccoo, coco, cooc, occo, ococ, oocc

$E = \varepsilon_0 + 3\varepsilon_1$: cooo, ocoo, ooco, oooc

$E = 4\varepsilon_1$: oooo

I am listing all states

In the canonical ensemble, each state has a probability of $\dfrac{e^{-\beta E}}{Q}$

In this case, the Energy can be written as

$E = \varepsilon_0 N_{closed} + \varepsilon_1 N_{open}$ where $N = N_{closed} + N_{open}$;

N_{closed} can take the values $N, N-1, N-2, \ldots, 0$ (equivalently, N_{open} can take the values $N, N-1, N-2, \ldots, 0$)

For $N_{open} = 0$: probability for link 1 to be open is 0.

For $N_{open} = 1$: there are N such states but only 1 of these has the open link at position 1 (1 out of N)

For $N_{open} = 2$: there are $N(N-1)/2$ such states, but only $N-1$ of these have the open link at position 1 ($N-1$ out of $N(N-1)/2$)

For $N_{open} = 3$: there are $N(N-1)(N-2)/6$ such states, but only $(N-1)(N-2)/2$ have the open link at position 1 ($(N-1)(N-2)/2$ out of $N(N-1)(N-2)/6$)

⋮

So: In general we have:

For N_{open} links, the probability that the first link is open is

$$\frac{\dfrac{(N-1)!}{(N-N_{open})!\,(N_{open}-1)!}}{\dfrac{N!}{(N-N_{open})!\,N_{open}!}} = \frac{N_{open}}{N}$$

$= g_{N_{open}}$ (multiplicity factor)

So: This can now be used in the canonical ensemble

$$P_1^{open} = \frac{\sum_{N_{open}=1}^{N} \frac{N_{open}}{N} e^{-\beta(\varepsilon_1 N_{open} + (N-N_{open})\varepsilon_0)}}{\underbrace{\sum_{N_{open}=0}^{N} g_{N_{open}} e^{-\beta(\varepsilon_1 N_{open} + (N-N_{open})\varepsilon_0)}}_{Q}}$$

probability for the first link to be open

multiplicity factor

I used: $Q = \sum_{N_{open}}^{N} g_{N_{open}} e^{-\beta(\varepsilon_1 N_{open} + (N-N_{open})\varepsilon_0)}$

with $g_{N_{open}} = \dfrac{N!}{(N-N_{open})!\,N_{open}!}$

What is the probability that the second link is open?

We must have that the first link is open.

For $N_{open} = 0$: probability $= 0$

$N_{open} = 1$: probability $= 0$

$N_{open} = 2$: probability $= 1$ (1 out of $N(N-1)(N-2)/2$)

$N_{open} = 3$: probability $= N-1$

In general: $\dfrac{(N-2)!}{(N-N_{open})!\,(N_{open}-2)!}$

see next page for a derivation

Then $$\frac{\dfrac{(N-2)!}{(N-N_{open})!\,(N_{open}-2)!}}{\dfrac{N!}{N_{open}!\,(N-N_{open})!}} = \frac{N_{open}(N_{open}-1)}{N(N-1)}$$

$$\Rightarrow P^{open}_{1+2} = \frac{\sum_{N_{open}=2}^{N} \frac{N_{open}(N_{open}-1)}{N(N-1)}\, e^{-\beta(\varepsilon_1 N_{open} + (N-N_{open})\varepsilon_0)}}{Q}$$

probability that first and second link are open (at fixed temperature T)

If the number of open links is N_{open}, we have

$$\frac{N!}{N_{open}!\,(N-N_{open})!} \quad \text{states}$$

How many of these states have a configuration in which the first link is open?

→ I will place one of the open links at position 1. Then I have another $N_{open}-1$ links that need to be placed among $N-1$ slots

$$\Rightarrow \frac{(N-1)!}{(N-1-(N_{open}-1))!\,(N_{open}-1)!}$$

$$= \frac{(N-1)!}{(N-N_{open})!\,(N_{open}-1)!}$$

How many states of these states have a configuration in which the first and the second link are open?

→ I will place two of the open links in positions 1 and 2. Then I have another $(N_{open}-2)$ links that need to be placed among $N-2$ slots

$$\Rightarrow \frac{(N-2)!}{(N-N_{open})!\,(N_{open}-2)!}$$

Average number of open links?

$$\langle N_{open} \rangle = \frac{\sum_{N_{open}=0}^{N} N_{open}\, g_{N_{open}}\, e^{-\beta\left(N_{open}(\varepsilon_1-\varepsilon_0)+N\varepsilon_0\right)}}{Q}$$

$$= \frac{e^{-\beta\varepsilon_0 N}}{Q} \sum_{N_{open}=0}^{N} N_{open}\, g_{N_{open}}\, e^{-\beta N_{open}(\varepsilon_1-\varepsilon_0)}$$

$$= \frac{e^{-\beta\varepsilon_0 N}}{Q} \cdot \frac{1}{(\varepsilon_1-\varepsilon_0)}\left(-\frac{\partial}{\partial\beta} \sum_{N_{open}}^{N} g_{N_{open}}\, e^{-\beta N_{open}(\varepsilon_1-\varepsilon_0)}\right)$$

I already calculated the partition function earlier.

Parts a – c could have been done in the microcanonical ensemble. In this case, it would have been more natural to calculate the partition function at the end.

The discussion so far does not exclude configurations such as o c o o ... c c o, etc. So: If we keep all configurations, we don't really have a "zipper". The next few pages discuss how to exclude such configurations.

"Zipper problem"

We have open and closed links in a line

link 1	link 2	link 3	link 4	link 5	...
o/c	o/c	o/c	o/c	o/c	

In general, this means that we have 2^N configurations (assuming there are N links).

For example: $N = 3 \Rightarrow$

c c c
c o o
o c o
o o c
c c o
o c c
o o c
o o o

If we think about DNA as a zipper, then we might say that only the following configurations are relevant:

c c c
o c c
o o c
o o o

$\downarrow$ we assume that replication of the DNA starts with opening the DNA (the zipper) from the left

If we want to eliminate the configurations that do not belong to this class of "zipper opening" configurations from our state space, we can assign an infinite energy to them.

E.g.: o c o $\rightarrow E = \infty \Rightarrow \underbrace{e^{-\beta E} = 0}_{\text{vanishing Boltzmann factor}}$

If we do this, we are left with $N+1$ allowed configurations

c - - - - c $\quad E = N\varepsilon_0$

o c - - - c $\quad E = (N-1)\varepsilon_0 + \varepsilon_1$

o o c ... c $\quad E = (N-2)\varepsilon_0 + 2\varepsilon_1$

$\vdots$

2 DNA have formed $\longrightarrow$ o o ----- o $\quad E = N\varepsilon_1$

Assume: $\varepsilon_1 > \varepsilon_0$ (there is a barrier to opening the DNA)

Let N_{open} be the number of open links.

$$\Rightarrow E = (N - N_{open})\varepsilon_0 + N_{open}\varepsilon_1$$

$\Rightarrow$ the canonical partition function of the system is:

$$Q = \sum_{N_{open}=0}^{N} e^{-\beta[(N-N_{open})\varepsilon_0 + N_{open}\varepsilon_1]}$$

$$= e^{-\beta N\varepsilon_0} \sum_{N_{open}=0}^{N} e^{-\beta N_{open}(\varepsilon_1 - \varepsilon_0)}$$

now: $$\sum_{k=0}^{n} r^k = \frac{1-r^{n+1}}{1-r}$$

$$\Rightarrow Q = e^{-\beta N \varepsilon_0} \sum_{N_{open}=0}^{N} \left(e^{-\beta(\varepsilon_1-\varepsilon_0)}\right)^{N_{open}}$$

$$= e^{-\beta N \varepsilon_0} \frac{1-e^{-\beta(\varepsilon_1-\varepsilon_0)(N_{open}+1)}}{1-e^{-\beta(\varepsilon_1-\varepsilon_0)}}$$

What is the probability for the first link to be open? All configurations but the first have an open first link.

weight of all state

subtracting weight of cc---c configuration

$$\Rightarrow P_{1,open} = \frac{Q - e^{-\beta N \varepsilon_0}}{Q}$$

First and second link open?

$e^{-\beta N \varepsilon_0} e^{-\beta(\varepsilon_1-\varepsilon_0)}$

$$\Rightarrow P_{2,open} = \frac{Q - e^{-\beta N \varepsilon_0} - e^{-\beta[(N-1)\varepsilon_0 + \varepsilon_1]}}{Q}$$

$$\leq P_{1,open}$$

What is the average number of open links?

As can be seen above, the number of open links ~~4~~ changes from $N_{open} = 0$ to $N_{open} = N$ as the configuration changes from $cc\cdots c$ to $oo\cdots o$.

Thus:

$$\langle N_{open} \rangle = \frac{\sum_{N_{open}=0}^{N} N_{open} e^{-\beta[(N-N_{open})\varepsilon_0 + N_{open}\varepsilon_1]}}{Q}$$

$$= \frac{-\frac{1}{(\varepsilon_1-\varepsilon_0)\beta} \frac{\partial}{\partial \beta} Q}{Q}$$

$$= \frac{1}{\beta(\varepsilon_0-\varepsilon_1)} \frac{\partial}{\partial \beta}\left(\log Q\right)$$