Problem Set 4

① Assuming the initial temperature is 25°C (room temperature), we need to increase the temperature of water by 75°C (or by 75 K) to bringe it to boiling temperature of 100°C.

Using the definition of 1 calorie — as the amount of energy required to increase the temperature of a gram of water by 1°, we find that in order to increase the temperature by 75° we would need 75 times more calories per each gram of water. In a cup of water (~0.2 ℓ) there are about 200 grams of water, so we need

$$200 \times 75 \text{ calories.}$$

1 calorie = 4.186 J (joules) in SI units of energy.

so we would need a total of

$$200 \times 75 \times 4.2 \text{ J} = 63000 \text{ J of energy.}$$

A 800-watt oven provides

800 J/s   - joules per second - of energy.

∴ 63000 J of energy will be provided

in $\frac{63000}{800}$ seconds = 79 seconds

So it should take approximately

1 minute and 20 seconds to bring
a cup of water to boil.

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②.

a). $Z = \sum_s e^{-E_s/k_B T}$ — for the total
                                      system composed of
                                      2 __independent__ particles.

Σ over all states.

State 1:	particle 1 is in the state with energy E_{11}
	particle 2 is in the state with energy E_{21}
	Total $E_1 = E_{11} + E_{21}$
State 2:	particle 1 ————//———— E_{11}
	particle 2 ————//———— E_{22}
	Total $E_2 = E_{11} + E_{21}$
State 3:	particle 1 ————//———— E_{12}
	particle 2 ————//———— E_{21}
	Total $E_3 = E_{12} + E_{21}$
State 4:	particle 1 ————//———— E_{12}
	particle 2 ————//———— E_{22}
	Total $E_4 = E_{12} + E_{22}$

Therefore in Z we have 4 terms:

$$Z = e^{-E_1/k_BT} + e^{-E_2/k_BT} + e^{-E_3/k_BT} + e^{-E_4/k_BT}$$

$$= e^{-(E_{11}+E_{21})/k_BT} + e^{-(E_{11}+E_{22})/k_BT}$$

$$+ e^{-(E_{12}+E_{21})/k_BT} + e^{-(E_{12}+E_{22})/k_BT}$$

$$= e^{-E_{11}/k_BT}\left(e^{-E_{21}/k_BT} + e^{-E_{22}/k_BT} \right)$$

$$+ e^{-E_{12}/k_BT}\left(e^{-E_{21}/k_BT} + e^{-E_{22}/k_BT} \right)$$

$$= \underbrace{\left(e^{-E_{11}/k_BT} + e^{-E_{12}/k_BT} \right)}_{Z_1} \underbrace{\left(e^{-E_{21}/k_BT} + e^{-E_{22}/k_BT} \right)}_{Z_2}$$

$$= Z_1 \cdot Z_2$$

b). System 1: define the states via "s_1"
and energies via E_{s_1}

System 2: ————//———— "s_2" ,
energies E_{s_2}

For any pair of states s_1 and s_2, the total energy of the combined system is $E_{s_1} + E_{s_2} \overset{\text{def.}}{=} E_s$

The partition function $Z(1+2)$ of the combined system is given by

$$Z(1+2) = \sum_s e^{-E_s/k_B T} = \sum_{s_1} \sum_{s_2} e^{-(E_{s_1} + E_{s_2})/k_B T}$$

↓
over all
states
of the
combined
system

$$= \underbrace{\sum_{s_1} e^{-E_{s_1}/k_B T}}_{Z(1)} \cdot \underbrace{\sum_{s_2} e^{-E_{s_2}/k_B T}}_{Z(2)} = Z(1) \cdot Z(2)$$

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③ (a)
$$Z = \sum_s e^{-E_s/k_B T} = \sum_{s=0}^{\infty} e^{-\hbar \omega s/k_B T}$$

$$= \sum_{s=0}^{\infty} \left(e^{-\hbar \omega/k_B T} \right)^s = \frac{1}{1 - e^{-\hbar \omega/k_B T}}$$

$$\left[\text{using} \quad \sum_{q=0}^{\infty} x^q = \frac{1}{1-x} \quad , \quad \text{for} \quad x < 1 \right]$$

Thus

$$Z = \frac{1}{1 - e^{-\hbar\omega/k_B T}}$$

b) Thermal average energy U:
can be always found as

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} \quad , \quad \text{where} \quad \tau = k_B T$$

[see Week 3 – Lecture 6, p. 10]:

$$\frac{\partial \ln Z}{\partial \tau} = \frac{1}{Z} \frac{\partial Z}{\partial \tau} = \frac{1}{Z} \sum_s \frac{\partial}{\partial \tau} \left(e^{-E_s/\tau} \right) =$$

$$= \frac{1}{Z} \sum_s \frac{E_s}{\tau^2} e^{-E_s/\tau} = \frac{1}{\tau^2} \underbrace{\frac{1}{Z} \sum_s E_s \, e^{-E_s/\tau}}_{\equiv \langle E \rangle \equiv U}$$

$$= \frac{U}{\tau^2} \qquad \Longrightarrow \qquad U = \tau^2 \frac{\partial \ln Z}{\partial \tau}$$

Thus our U:

$$U = \tau^2 \frac{\partial}{\partial \tau} \left(\ln \frac{1}{1 - e^{-\hbar\omega/\tau}} \right) =$$

$$= \tau^2 \frac{\partial}{\partial \tau} \left(\ln (1 - e^{-\hbar\omega/\tau})^{-1} \right) = \tau^2 \frac{\partial}{\partial \tau} \left(-\ln (1 - e^{-\hbar\omega/\tau}) \right)$$

$$= -\tau^2 \frac{1}{1 - e^{-\hbar\omega/\tau}} \left(-e^{-\hbar\omega/\tau} \right) \left(-\hbar\omega \right) \left(-\frac{1}{\tau^2} \right) =$$

$$= \frac{\hbar\omega \, e^{-\hbar\omega/\tau}}{1 - e^{-\hbar\omega/\tau}} = \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}$$

Thus:

$$\boxed{U = \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}}$$

(c)
(d) For two ∧ harmonic oscillators, the
partition function Z_2 is
(independent)

$$Z_2 = Z \cdot Z, \qquad \text{where} \qquad Z = \frac{1}{1 - e^{-\hbar\omega/k_B T}}$$

or

$$Z_2 = (Z)^2$$

Similarly, for N independents harmonic oscillators, the partition function would be

$$Z_N = (Z)^N = \frac{1}{\left(1 - e^{-\hbar\omega/k_B T}\right)^N}$$

The thermal average energy:

$$U_N = \tau^2 \frac{\partial \ln Z_N}{\partial \tau} = \tau^2 \frac{\partial (\ln Z^N)}{\partial \tau} =$$

$$= \tau^2 \, N \, \frac{\partial \ln Z}{\partial \tau} = N \cdot \underbrace{\left(\tau^2 \frac{\partial \ln Z}{\partial \tau} \right)}_{\text{from (b) - thermal average energy of one harmonic oscillator}}$$

Therefore

$$U_N = NU = \frac{N\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \quad ,$$

which is the same result as in Group Problem 1.

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④ **A two level system**

(a)
$$Z = \sum_s e^{-E_s/\tau} = g_0 e^{-0/\tau} + g_1 e^{-E/\tau}$$

$$= g_0 + g_1 e^{-E/k_B T}$$

$(\tau \equiv k_B T)$

↳ in the sum over all states there are g_0 states (multiplicity g_0) of energy $E_0 = 0$ and g_1 states (multiplicity g_1) of energy $E_1 = E$

Probability to be in a state with energy $E_0 = 0$

$$P(0) = \frac{e^{-0/\tau}}{Z} = \frac{1}{g_0 + g_1 e^{-E/k_B T}}$$

or $E_1 = E$

$$P(E) = \frac{e^{-E/k_B T}}{Z} = \frac{e^{-E/k_B T}}{g_0 + g_1 e^{-E/k_B T}}$$

(b) $U = $ (explicitely) $\langle E \rangle = $

$$= \sum_s E_s P(E_s) = \frac{1}{Z} \sum_s E_s e^{-E_s/\tau}$$

over all states

$$= \frac{g_0 \cdot 0 \cdot e^{-0/\tau} + g_1 E e^{-E/\tau}}{g_0 + g_1 e^{-E/\tau}}$$

$$= \frac{g_1 E e^{-E/\tau}}{g_0 + g_1 e^{-E/\tau}} = \frac{g_1}{g_0} \frac{E e^{-E/\tau}}{\left(1 + \frac{g_1}{g_0} e^{-E/\tau}\right)}$$
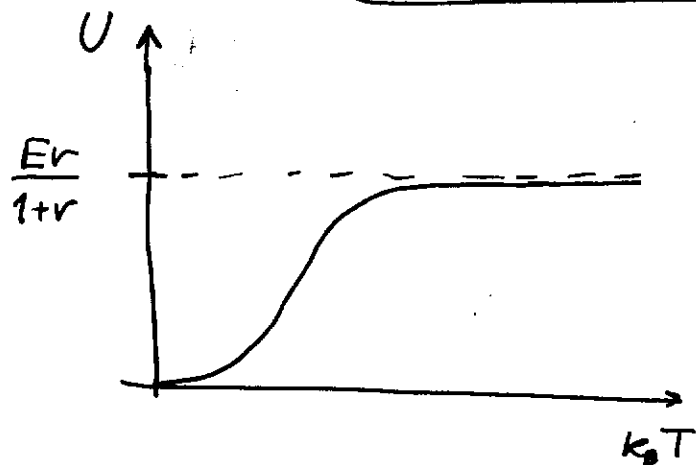
$$= \frac{r E e^{-E/\tau}}{\left(1 + r e^{-E/\tau}\right)} = \frac{r E}{e^{E/\tau} + r}$$
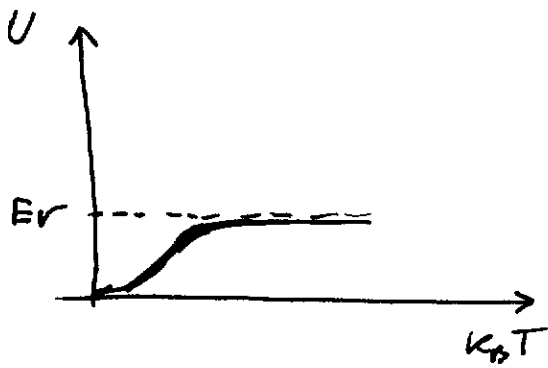
Thus:

$$\boxed{U = \frac{r E}{r + e^{E/k_B T}}}$$
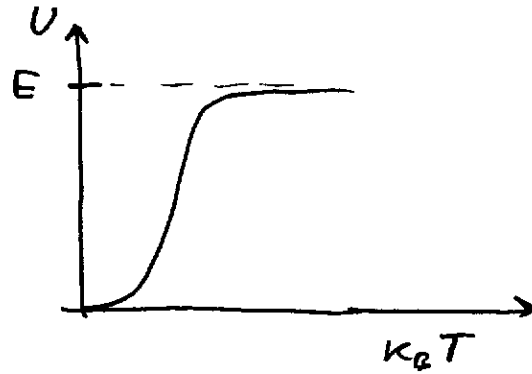
where

$$\boxed{r \equiv \frac{g_1}{g_0}}$$

For small r

(r << 1) — more states at $E = 0$

$$\frac{Er}{1+r} \simeq Er$$

For large r

(r >> 1) — more states at $E_1 = E$

$$\frac{Er}{1+r} \simeq E$$

Low temperature limit of U :

$$\tau = K_B T << E \quad , \quad \text{then} \quad e^{E/k_B T} >> 1$$

and for any finite value of the ratio r, one can take the limit of very low temperatures so that

$$e^{E/k_B T} >> r \qquad \text{as well.}$$

So

$$U = \frac{rE}{r + e^{E/k_B T}} \quad \text{becomes}$$

$$U \simeq \frac{rE}{e^{E/k_B T}} = rE\, e^{-E/k_B T}$$

High temperature limit of U:

$\tau = K_B T \gg E$, then $e^{E/k_B T} \simeq 1 + \dfrac{E}{k_B T} + \dots$

$$\left(\frac{E}{k_B T} \ll 1 \right)$$

and therefore

$$U \simeq \frac{r E}{r + 1 + \frac{E}{k_B T}} \simeq \frac{r E}{1 + r}$$
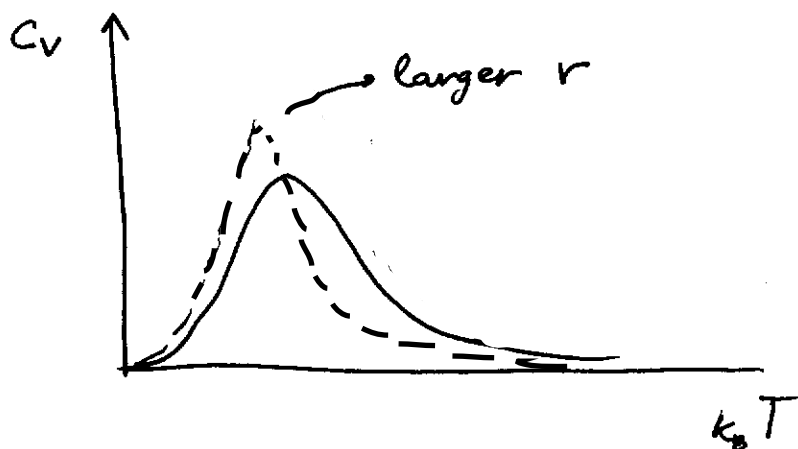

Heat capacity

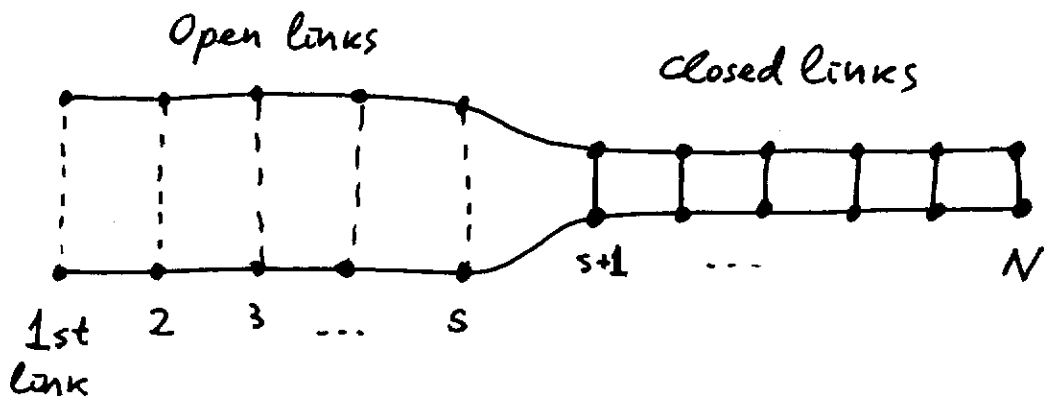$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V} = \dots$$

$$\frac{C_V}{K_B} = r \left(\frac{E}{k_B T} \right)^2 \frac{e^{E/k_B T}}{\left(e^{E/k_B T} + r \right)^2}$$

$$\left(r \equiv \frac{g_1}{g_0} \right)$$

Sketch

⑤ Zipper problem: DNA model

Open links   Closed links

1st link   2   3   ...   s   s+1   ...   N

Define the states of the zipper by **s** - the number of the last open link.

If a link is open then its energy is ϵ ;
if a link is closed then its energy is 0.

If there are s open links, then the energy of the system in that state is
$E_s = s\epsilon$.

Possible states:

No. of open links s		Energy E_s	
0	(all links are closed)	0	⎫
1		ϵ	
2		2ϵ	⎬ N+1 states
⋮			
s		$s\epsilon$	
⋮			
N	(all are open)	$N\epsilon$	⎭

The partition function Z :

$$Z = \sum_{s} e^{-E_s/kT}$$

$\left(\begin{smallmatrix} \text{all} \\ \text{states} \end{smallmatrix}\right)$

$\hookrightarrow$ there are $N+1$ states, therefore $N+1$ terms in the sum

$$= e^{-0/\tau} + e^{-\epsilon/\tau} + e^{-2\epsilon/\tau} + \cdots + e^{-N\epsilon/\tau}$$

$\underbrace{}_{N+1 \text{ terms}}$

(where we have defined $\tau \equiv k_B T$)

Thus

$$Z = \sum_{s=0}^{N} e^{-s\epsilon/\tau} = \sum_{s=0}^{N} \left(e^{-\epsilon/\tau}\right)^s$$

Defining $x \equiv e^{-\epsilon/\tau}$, we have

$$\sum_{s=0}^{N} x^s = \frac{1-x^{N+1}}{1-x} \qquad - \text{ geometric series from } s=0 \text{ to } s=N$$

Thus

$$\boxed{Z = \frac{1-x^{N+1}}{1-x}} \qquad \text{where } x = e^{-\epsilon/\tau} \qquad \underline{(1)}$$

or, in explicit form:

$$Z = \frac{1-\left(e^{-\epsilon/\tau}\right)^{N+1}}{1-e^{-\epsilon/\tau}} = \frac{1-e^{-\epsilon(N+1)/\tau}}{1-e^{-\epsilon/\tau}} \qquad \underline{(2)}$$

b)

$P(s)$ — probability of the state with s open links; it is given by the ratio of the respective Boltzmann factor $e^{-E_s/kT} = e^{-s\epsilon/kT}$ to the partition function Z

($E_s = s\epsilon$ is the respective energy of the state with s open links)

Therefore

$$P(s) = \frac{e^{-s\epsilon/kT}}{Z}$$

c) Thermal average energy of the system at temperature T

$$U \equiv \langle E \rangle = \sum_s E_s \, P(E_s) \qquad \left(P(E_s) \equiv P(s) \right)$$

$$= \frac{1}{Z} \sum_{s=0}^{N} \underbrace{E_s}_{s\epsilon} e^{-s\epsilon/kT} = \frac{\epsilon}{Z} \sum_{s=0}^{N} s \, e^{-s\epsilon/kT}$$

Can writhe this down as $U = \epsilon \langle s \rangle$

since we recognise $\dfrac{1}{Z} \displaystyle\sum_{s=0}^{N} s \, e^{-s\epsilon/kT} = \langle s \rangle$

as the definition of the thermal average number of open links

$$\langle s \rangle = \sum_{s=0}^{N} s \, P(s) = \frac{1}{Z} \sum_{s=0}^{N} s \, e^{-s\epsilon/k_B T}$$

Or, in terms of $x = e^{-\epsilon/kT}$

$$\langle s \rangle = \frac{1}{Z} \sum_{s=0}^{N} s \left(e^{-\epsilon/kT} \right)^s = \frac{1}{Z} \sum_{s=0}^{N} s \, x^s \qquad (3)$$

Thus U can be calculated as

$$\boxed{U = \epsilon <s>}\ ,\quad \text{where} \quad <s> \quad \text{is}$$

calculated   in   part (d)   below.

d). $<s> - ?$

$$<s> = \frac{1}{Z} \sum_{s=0}^{N} s x^{s}$$

First, lets   rewrite Z in terms of x

$$Z = \sum_{s=0}^{N} e^{-E_s/kT} = \sum_{s=0}^{N} e^{-s\epsilon/kT} = \sum_{s=0}^{N} x^{s}$$

By comparing this expression for Z with

$<s> = \frac{1}{Z} \sum_{s=0}^{N} s x^{s}$ one   can see   that

differentiating Z with respect to x

will give rise   in   terms   that are present

in the sum   for $<s>$

$\left[\text{note that}\quad \dfrac{d}{dx}(x^{s}) = s x^{s-1}, \text{ so that}\right.$

$$x \cdot \frac{d}{dx}(x^{s}) = s x^{s} \quad \Big]$$

So, it   is easy to see that

$$x \frac{dZ}{dx} = x \cdot \frac{d}{dx}\left(\sum_{s=0}^{N} x^{s}\right) = x \cdot \sum_{s=0}^{N} s x^{s-1} = \sum_{s=0}^{N} s x^{s}$$

Therefore $<s> = \dfrac{1}{Z} \displaystyle\sum_{s=0}^{N} s x^{s} = \dfrac{1}{Z} \cdot x \cdot \dfrac{dZ}{dx} = x \cdot \dfrac{d \ln Z}{dx}$

The explicit final result for Z in terms of x was (see page 12, Eq.(1))

$$Z = \frac{1 - x^{N+1}}{1 - x}$$

So, by taking $\ln Z$ and differentiating it with respect to x gives

$$\langle s \rangle = x \frac{d \ln Z}{dx} = x \frac{1}{Z} \frac{dZ}{dx} =$$

$$= x \frac{1}{Z} \frac{d}{dx} \left(\frac{1 - x^{N+1}}{1 - x} \right)$$

$$\boxed{\frac{1 - x^{N+1}}{1 - x}}$$

$$= x \cdot \frac{1}{\left(\frac{1 - x^{N+1}}{1 - x} \right)} \cdot \frac{-(N+1) x^{N}(1-x) + (1 - x^{N+1})}{(1-x)^2}$$

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

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

Thus $\boxed{\langle s \rangle = -\frac{(N+1) x^{N+1}}{1 - x^{N+1}} + \frac{x}{1 - x}}$ with $x = e^{-\epsilon/kT}$

$$(4)$$

Substituting $x = e^{-\epsilon/kT}$, we obtain:

$$\langle s \rangle = \frac{e^{-\epsilon/kT}}{1 - e^{-\epsilon/kT}} - \frac{(N+1)\, e^{-(N+1)\epsilon/kT}}{1 - e^{-(N+1)\epsilon/kT}}$$

or

$$\boxed{\langle s \rangle = \frac{1}{e^{\epsilon/kT} - 1} - \frac{N+1}{e^{(N+1)\epsilon/kT} - 1}} \qquad (5)$$

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*) Low - temperature limit for $\langle s \rangle$ - ?

Low-T limit corresponds to

$$kT \ll \epsilon$$

kT is the thermal energy scale;
"low-T" has to be defined (understood)
relative to something — as in

$$k_0 T \ll \text{"a characteristic energy scale in the problem"}$$

$\hookrightarrow$ this role is taken by our ϵ, which is the "quantum" of energy corresponding to 1 open link

Thus, low-T limit means

$$kT \ll \epsilon \qquad (\text{or } kT/\epsilon \ll 1)$$

In this limit $(\kappa T \ll \epsilon)$ our parameter $x = e^{-\epsilon/\kappa T}$ is going to be $x \ll 1$ (as $e^{-\epsilon/\kappa T} = \dfrac{1}{e^{\epsilon/\kappa T}} \ll 1$, for $\kappa T \ll \epsilon$)

We now apply $x \ll 1$ to our general result for $\langle s \rangle$, Eq. (4) [page 15]

$$\langle s \rangle = \frac{x}{1-x} - \frac{(N+1) x^{N+1}}{1 - x^{N+1}}$$

Here we first note that if $x \ll 1$ then x^{N+1} is also much smaller than 1, $x^{N+1} \ll 1$. Therefore, we can neglect x and x^{N+1} compared to 1 in the denominators of each term:

$$\langle s \rangle \simeq x - (N+1) x^{N+1} = x \left(1 - (N+1) x^N \right)$$

For any given N (fixed), taking the limit $x \to 0$ will make $(N+1) x^N \ll 1$ so

$$\langle s \rangle \simeq x \quad \text{in the limit} \quad x \to 0$$

Thus

$$\langle s \rangle \simeq x = e^{-\epsilon/\tau} = \frac{1}{e^{\epsilon/\kappa T}} \quad \text{as} \quad x \to 0$$

$x \to 0$ ~~implies~~ corresponds to $T \to 0$

So $\langle s \rangle = \dfrac{1}{e^{\epsilon/\kappa T}} \xrightarrow[T \to 0]{} 0$ exponentially fast

Thus, the low-T limit for $\langle s \rangle$ is

$$\langle s \rangle \simeq \frac{1}{e^{\epsilon/\kappa T}} \xrightarrow[T \to 0]{} 0$$

— the thermal average number of open links goes to zero as the temperature approaches zero! This makes sense: almost all links are closed at very low T (and the number of open links grows with T) [i.e. the DNA molecule is ~~__~~ fully "zipped" or folded at very low T].

**) High-temperature limit $\kappa T \gg \epsilon$

($\epsilon/\kappa T \ll 1$ or $T \to \infty$ as the limiting behavior).

def $x = \frac{\epsilon}{\kappa T} \ll 1$ in the high-T limit.

For simplicity, lets also assume that T is so high that $N \cdot \frac{\epsilon}{\kappa T}$ is also $\ll 1$ (for any large but finite N, and fixed ϵ, can choose T to be so high that

$$N \cdot \frac{\epsilon}{\kappa T} \ll 1)$$

Thus, we assume that $Nx \ll 1$ (then $x \ll 1$ follows, for any $N > 1$)

Lets now Taylor expand

$$e^{Nx} \simeq 1 + Nx + \frac{1}{2}N^2x^2 + \cdots \qquad (Nx \ll 1)$$

and

$$e^x \simeq 1 + x + \frac{1}{2}x^2 + \cdots \qquad (x \ll 1)$$

Note that we are keeping the quadratic terms in the expansion, because otherwise (by keeping only linear terms) the approximate result for $\langle s \rangle$ in the limit $Nx \ll 1$ would be

$$\langle s \rangle \simeq \frac{1}{0} - \frac{1}{0} = \infty - \infty \qquad \text{— undefined.}$$

With the quadratic terms kept, we get from Eq. (5) — rewritten in terms of x

$$\langle s \rangle = \frac{1}{e^x - 1} - \frac{N+1}{e^{(N+1)\epsilon/kT} - 1}$$

(before applying the above Taylor expansions, we ignore 1 in $N+1$ as $N \gg 1$

$$= \frac{1}{e^x - 1} - \frac{N}{e^{Nx} - 1}$$

$$\simeq \frac{1}{1 + x + \frac{1}{2}x^2 - 1} - \frac{N}{1 + Nx + \frac{1}{2}N^2x^2 - 1}$$

$$= \frac{1}{x\left(1 + \frac{1}{2}x\right)} - \frac{1}{x\left(1 + \frac{1}{2}Nx\right)}$$

We now use the Taylor expansion of

$$\frac{1}{1+\alpha x} \simeq 1 - \alpha x + \cdots \qquad \text{for } \alpha x \ll 1$$

where $\alpha = \frac{1}{2}$ for the first term and $\alpha = \frac{1}{2}N$ for the second term.

Then:

$$\langle s \rangle \simeq \frac{1}{x}\left(1 - \frac{1}{2}x\right) - \frac{1}{x}\left(1 - \frac{1}{2}Nx\right)$$

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

Thus

$$\boxed{\langle s \rangle \simeq \frac{N}{2}} \qquad \text{at very high } T \qquad \left(\frac{kT}{N\epsilon} \gg 1\right)$$

↳ half of the links get open at very high $-T$, which makes sense.

Why not **all** of the links get open? i.e. why we don't get $\langle s \rangle \simeq N$ (or $U = \epsilon N$) at very high $-T$, which would be more intuitive?

- The situation is similar to that of a two-state (two-level) system analysed in Lecture 6, which had $U = \frac{E}{2}$ at high T.

This is similar to the situation that we had in a two level system in Lecture 3: closed link can be associated with ground state at energy 0, open link – with excited state at energy ε. At very high T the probability of a two-state system to be in the excited state becomes equal to the probability for it to be in its ground state, i.e. in an ensemble of two-state (two-level) systems at very high T, approximately the half of the members of the ensemble would be in the excited state and the other half - in the ground state. All of them being in the excited state would have to correspond to a negative-temperature situation, which is not what we intend to treat here in the zipper problem. With this comment in mind, the result $<s> \approx N/2$ is still in agreement with our intuition/expectation: as T is raised, more and more links become open. Why not all of them become open in this model at very high T? Because our model is very simple; in a more involved model (such as if we assumed that the open links can have different relative orientations in a 3D space, which would effectively imply a multi-level system, rather than a two-level system) we would get the desired result of $<s> \approx N$, but such an involved model is harder to treat in a 3rd year course.

For further info: see [C. kittel, Amer. J. Phys. **37**, 917 (1969)], which shows that there is even a phase transition in the more advanced model.

Sketch of the full numerical result from

$$<s> = \frac{1}{e^{\varepsilon/kT} - 1} - \frac{N+1}{e^{(N+1)\varepsilon/kT} - 1}$$

for $N = 100$