

## Ex2360: The zipper model for DNA molecule

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### The problem:

The DNA molecule forms a double stranded helix with hydrogen bonds stabilizing the double helix. Under certain conditions the two strands get separated resulting in a sharp phase transition (in the thermodynamic limit). One can describe the DNA molecule using the zipper model. 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  $\epsilon$ , the zipper can unzip only from one side such that the  $p$ 'th link might open only if all of the links to its unzipped side are open. The last link  $p = N$  cannot be open. Each open link has  $g$  orientations corresponding to the rotational freedom about the bond.

Assume a large number of links.



- (1) Define  $x = ge^{-\beta\epsilon}$  and find the canonical partition function  $Z(\beta, x)$ .
- (2) Find the average number of open links  $\langle p \rangle$  as a function of  $x$ .
- (3) Find the linear approximation for  $\langle p \rangle$ .
- (4) Approximate  $\frac{\langle p \rangle}{N}$  for large  $x$ .
- (5) Describe the dependence of  $\frac{\langle p \rangle}{N}$  on  $x$ .
- (6) Find expressions for the entropy  $S(x)$  and the heat capacity  $C_V(x)$  at  $x = 1$ .
- (7) What is the order of the phase transition?

### The solution:

- (1) Assuming there are  $p$  open links, the hamiltonian of the system is  $\mathcal{H} = p\epsilon$ , taking into consideration the number of orientations, the partition function is

$$Z(\beta, x) = \sum_{p=0}^{N-1} g^p e^{-\beta p\epsilon} = \sum_{p=0}^{N-1} x^p = \boxed{\frac{x^N - 1}{x - 1}} \quad (1)$$

- (2) The probability to find an open link is  $\frac{x^p}{Z}$ , thus the average number of open links

$$\langle p \rangle = \sum_{p=0}^{N-1} \frac{x^p}{Z} p = \frac{1}{Z} x \frac{\partial}{\partial x} \sum_{p=0}^{N-1} x^p = x \frac{\partial}{\partial x} \ln(Z) = \boxed{\frac{Nx^N}{x^N - 1} - \frac{x}{x - 1}} \quad (2)$$

Another way is noticing that  $\langle p \rangle = \frac{U}{\epsilon}$ , where  $U$  is the energy of the system defined  $U = -\frac{\partial}{\partial \beta} \ln(Z)$ . Thus,

$$\langle p \rangle = -\frac{1}{\epsilon} \frac{\partial}{\partial \beta} \ln(Z) = \frac{1}{\epsilon} x \epsilon \frac{\partial}{\partial x} \ln(Z) = \frac{N x^N}{x^N - 1} - \frac{x}{x - 1} \quad (3)$$

Which is the same as equation (2).

(3) Expand (2) around  $x = 1$  is equivalent to expand it around  $\eta = 0$  where  $\eta = x - 1$ , thus we can write

$$\langle p \rangle = \frac{N\eta(1+\eta)^N - (1+\eta)\left((1+\eta)^N - 1\right)}{\eta\left((1+\eta)^N - 1\right)} \quad (4)$$

Expanding the term  $(1+\eta)^N$  up to third order,

$$\langle p \rangle \approx \frac{N\eta(1 + N\eta + \frac{1}{2}N^2\eta^2 + \frac{1}{6}N^3\eta^3 + O(\eta^4)) - (1+\eta)(N\eta + \frac{1}{2}N^2\eta^2 + \frac{1}{6}N^3\eta^3 + O(\eta^4))}{\eta(N\eta + \frac{1}{2}N^2\eta^2 + \frac{1}{6}N^3\eta^3 + O(\eta^4))} \quad (5)$$

After some algebra we get

$$\langle p \rangle = \frac{(\frac{N}{2} - 1) + \eta(\frac{1}{3}N^2 - \frac{1}{2}N) + \eta^2(\frac{1}{6}N^3 - \frac{1}{6}N^2)}{1 + \frac{1}{2}N\eta + \frac{1}{6}N^2\eta^2} \quad (6)$$

Expanding the denominator  $(1 + \frac{1}{2}N\eta + \frac{1}{6}N^2\eta^2)^{-1} \approx 1 - \frac{1}{2}N\eta + \frac{1}{12}N^2\eta^2$  we get,

$$\langle p \rangle = \left( (\frac{N}{2} - 1) + \eta(\frac{1}{3}N^2 - \frac{1}{2}N) + \eta^2(\frac{1}{6}N^3 - \frac{1}{6}N^2) \right) \left( 1 - \frac{1}{2}N\eta + \frac{1}{12}N^2\eta^2 \right) \quad (7)$$

Taking up to first order at  $\eta$  and  $N$  to be large we get,

$$\langle p \rangle = \frac{N}{2} + \frac{1}{12}N^2\eta \quad (8)$$

Finally,

$$\boxed{\langle p \rangle \approx \frac{N}{2} \left[ 1 + \frac{N}{6}(x - 1) \right]} \quad (9)$$

(4) Using (2) we get

$$\frac{\langle p \rangle}{N} = \frac{1}{1 - \frac{1}{x^N}} - \frac{1}{N} \frac{1}{1 - \frac{1}{x}} \quad (10)$$

Thus for large  $x$  and large  $N$  we get

$$\boxed{\frac{\langle p \rangle}{N} \approx 1} \quad (11)$$

Which means that all the links are open.

(5) Looking at the linear approximation we found for  $\langle p \rangle$  at equation (9) and taking the limits  $N \rightarrow \infty$  and  $x \rightarrow 0$  we get  $\frac{\langle p \rangle}{N} = 0$ .

Substituting  $x = 1$  at (9) we get  $\frac{\langle p \rangle}{N} = \frac{1}{2}$ .

Considering equation (11) we get that  $\frac{\langle p \rangle}{N}$  behaves like heaviside function

$$\frac{\langle p \rangle}{N} = \begin{cases} 0 & x < 1 \\ \frac{1}{2} & x = 1 = H(x - 1) \\ 1 & x > 1 \end{cases} \quad (12)$$

(6) The entropy is proportional to the derivative of the free energy with regard to  $T$

$$S = -\frac{\partial F}{\partial T} = -\beta^2 \frac{\partial}{\partial \beta} \left( \frac{1}{\beta} \ln(Z) \right) = \ln(Z) - \beta \frac{\partial x}{\partial \beta} \frac{\partial}{\partial x} \ln(Z) = \ln(Z) - \beta(-\epsilon x) \frac{\partial}{\partial x} \ln(Z) \quad (13)$$

Thus,

$$S = \ln(Z) + \beta \epsilon \langle p \rangle \quad (14)$$

Taking the limit of  $\ln(Z)$  for  $x \rightarrow 1$  using L'Hopital's rule we get that  $\ln(Z) \approx \ln(N)$ . But, according to (12) we see that for this limit  $\langle p \rangle \sim N$ , and we know that  $N \gg \ln(N)$  for large  $N$ .

Thus,

$$\boxed{S(x) \Big|_{x=1} \approx \beta \epsilon \langle p \rangle} \quad (15)$$

The heat capacity is defined,

$$C_V = T \frac{\partial S}{\partial T} = \beta \epsilon x \frac{\partial S}{\partial x} = \beta \epsilon x N \delta(x - 1) \quad (16)$$

Thus at the limit  $x \rightarrow 1$

$$\boxed{C_V \rightarrow \infty} \quad (17)$$

(7) The entropy, which is a first derivative of the free energy, is discontinuous, thus this is a first order phase transition.