E2341: 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). We model the described above as a zipper consisting of N parallel links that can be opened from one side of the zipper. If links $1, 2, 3, ..., p$ are opened, then the energy to open link $p + 1$ is ε and the energy to open link $p + 2$ is infinity. The last link $p = N$ cannot be opened. Each open link has g orientations corresponding to the rotational freedom about the bond. Assume a large number of links N.

(1) Define $x = ge^{-\varepsilon/T}$ and find the canonical partition function $Z(\beta, x)$.
(2) Find the average number of open links $< p >$ as a function of x.
(3) Find the linear approximation for $< p >$.
(4) Approximate $\frac{<p>}{N}$ for large x.
(5) Describe the dependence of $\frac{<p>}{N}$ 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) The partition function of one open link is $e^{-\beta\varepsilon} + e^{-\beta\varepsilon} + ... + e^{-\beta\varepsilon} = ge^{-\beta\varepsilon} = x$. For p open links we multiply the p partition functions and get $g^p e^{-\beta\varepsilon p} = x^p$. So the partition function of the system would be:

$$Z(\beta, x) = \sum_{p=0}^{N-1} x^p = \frac{x^N - 1}{x - 1}$$

(2) The average number of open links is:

$$< p >= \sum_{p=0}^{N-1} Prob(p) \cdot p = \sum_{p=0}^{N-1} \frac{x^p}{Z} \cdot p = \frac{1}{Z} x \frac{\partial}{\partial x} \sum_{p=0}^{N-1} x^p = x \frac{\partial}{\partial x} \ln(Z) = \frac{Nx^N}{x^N - 1} - \frac{x}{x - 1}$$

(3)

$$< p >= \frac{Nx^{N+1} - Nx^N - x^{N+1} + x}{x^{N+1} - x^N - x + 1}$$

Now we expand the term for $< p >$ to a series at $x = 1$. We expand the numerator and the denominator separately to a third order and then divide them. We start with the numerator:

$$Nx^{N+1} - Nx^N - x^{N+1} + x \approx \frac{1}{2}(x-1)^2[N^2 - N] + \frac{1}{6}(x-1)^3[2N^3 - 3N^2 + N]$$

The series expansion for the denominator:

$$x^{N+1} - x^N - x + 1 \approx \frac{1}{2}(x-1)^2 N + \frac{1}{6}(x-1)^3[3N^2 - 3N]$$

So we get:

$$< p >\approx \frac{\frac{1}{2}(x-1)^2[N^2 - N] + \frac{1}{6}(x-1)^3[2N^3 - 3N^2 + N]}{\frac{1}{2}(x-1)^2 N + \frac{1}{6}(x-1)^3[3N^2 - 3N]} = \frac{\frac{1}{2}(N - N^2) + \frac{1}{6}(x-1)(2N^2 - 3N + 1)}{1 + \frac{1}{6}(x-1)(3N - 3)}$$

Now we expand the term $\frac{1}{1+\frac{1}{6}(x-1)(3N-3)}$ to a series at $x=1$:

$$\frac{1}{1+\frac{1}{6}(x-1)(3N-3)} \approx 1-\frac{1}{6}(3N-3)(x-1)$$

So we have:

$$<p> \approx [\frac{1}{2}(N-N^2)+\frac{1}{6}(x-1)(2N^2-3N+1)]\cdot[1-\frac{1}{6}(3N-3)(x-1)]$$

And by taking $<p>$ to first order and taking N to be large we get:

$$<p> \approx \frac{1}{2}N[1+\frac{1}{6}N(x-1)]$$

(4)

$$\frac{<p>}{N}=\frac{x^N}{x^N-1}-\frac{1}{N}\cdot\frac{x}{x-1}=\frac{1}{1-\frac{1}{x^N}}-\frac{1}{N}\cdot\frac{1}{1-\frac{1}{x}}$$

And for large x and large N we get:

$$\frac{<p>}{N}\approx 1$$

(5) We can see that for $x=0$ we get $\frac{<p>}{N}\approx 0$. The linear approximation gives us $\frac{<p>}{N}=\frac{1}{2}$ for $x=1$.

The dependence of $\frac{<p>}{N}$ on x converges to a Heaviside step function as N becomes larger, so for $N\to\infty$ the dependence is:

$$\frac{<p>}{N}=\begin{cases} 0 & \text{for} \quad x<1 \\ \frac{1}{2} & \text{for} \quad x=1 \\ 1 & \text{for} \quad x>1 \end{cases} \equiv H(x-1)$$

(6) We first find the entropy:

$$S(x)=-\frac{\partial F(\beta,x)}{\partial T}=-\beta^2\frac{\partial}{\partial\beta}(\frac{1}{\beta}\ln(Z))=\ln(Z)+\frac{1}{\beta}\frac{\partial x}{\partial\beta}\frac{\partial}{\partial x}\ln(Z)=\ln(Z)+\beta\varepsilon x\frac{\partial}{\partial x}\ln(Z)=\ln(Z)+\beta\varepsilon<p>$$

By using L'Hopital's rule we calculate the limit of $\ln(Z)$ at $x=1$ and get $\ln(Z)\approx\ln(N)$. By assuming that $\beta\varepsilon$ is not zero we get $\ln(N)<<\beta\varepsilon\cdot<p>=\beta\varepsilon\frac{N}{2}$. So the entropy at $x=1$ is:

$$S(x=1)\approx\beta\varepsilon<p>$$

And in the neighborhood of the point $x=1$ and for $N\to\infty$ we get:

$$\frac{S(x)}{\beta\varepsilon N}\approx\frac{<p>}{N}=H(x-1)$$

We Now calculate the heat capacity:

$$C_V(x)=T\frac{\partial S(x)}{\partial T}=\beta\varepsilon x\frac{\partial S(x)}{\partial x}\Rightarrow\frac{C_V(x)}{\beta\varepsilon N}=x\frac{\partial}{\partial x}(\frac{S(x)}{N})$$

In the limit $N\to\infty$ and in the neighborhood of $x=1$ the entropy is a step function. So the heat capacity in that limit is:

$$\frac{C_V(x)}{\beta\varepsilon N}=\delta(x-1)\Rightarrow\frac{C_V(x=1)}{\beta\varepsilon N}=\infty$$

(7) The entropy which is the first derivation of the Helmholtz free energy is a step function, so the phase transition is of the first order.