Denaturization of DNA

In this solution I record every physically important point but I sometimes skip mathematical steps.

a. The effective Hamiltonian $\mathcal{H}$ gives $e^{-\beta\mathcal{H}}$ as a product, with a factor of

$e^{\beta\epsilon}$	for each segment in the helical state $[h_i = 1]$,
q	for each segment in the melted state $[h_i = 0]$,
r	for each junction from helical to melted or vice versa $[(h_i - h_{i-1})^2 = 1]$.

Hence

$$\begin{aligned} e^{-\beta\mathcal{H}} &= \prod_{i=1}^{N} e^{\beta\epsilon h_i} q^{(1-h_i)} r^{(h_i-h_{i-1})^2} \\ &= \exp\left\{\beta\epsilon\sum_{i=1}^{N} h_i + \ln q \sum_{i=1}^{N}(1-h_i) + \ln r \sum_{i=1}^{N}(h_i - h_{i-1})^2\right\}. \end{aligned}$$

(We arbitrarily pick $h_0 = h_1$ to give the proper edge effect at $i = 1$. This choice of boundary condition will have no effect on bulk properties in the thermodynamic limit.) And

$$Z_N(T, \epsilon, r) = \sum_{\text{states}} e^{-\beta\mathcal{H}} = \sum_{h_1=0}^{1}\sum_{h_2=0}^{1}\cdots\sum_{h_N=0}^{1}\prod_{i=1}^{N} e^{\beta\epsilon h_i} q^{(1-h_i)} r^{(h_i-h_{i-1})^2}.$$

b. Use the slick trick! By definition

$$\theta(T) = \frac{\displaystyle\sum_{\text{states}}\left(\sum_i h_i/N\right)e^{-\beta\mathcal{H}}}{\displaystyle\sum_{\text{states}} e^{-\beta\mathcal{H}}}, \quad \text{but} \quad \frac{\partial \ln Z}{\partial \epsilon} = \frac{\displaystyle\beta\sum_{\text{states}}\left(\sum_i h_i\right)e^{-\beta\mathcal{H}}}{Z},$$

so

$$\theta(T) = -\frac{1}{N}\frac{\partial F}{\partial \epsilon}.$$

Similarly

$$J(T) = \frac{\displaystyle\sum_{\text{states}}\left(\sum_i (h_i - h_{i-1})^2\right)e^{-\beta\mathcal{H}}}{\displaystyle\sum_{\text{states}} e^{-\beta\mathcal{H}}}, \quad \text{but} \quad \frac{\partial \ln Z}{\partial r} = \frac{1}{r}\frac{\displaystyle\sum_{\text{states}}\left(\sum_i (h_i - h_{i-1})^2\right)e^{-\beta\mathcal{H}}}{Z},$$

so

$$J(T) = -\frac{r}{k_B T}\frac{\partial F}{\partial r}.$$

c.

$$\begin{aligned} Z_{N+1}^h &= Z_N^h\, e^{\beta\epsilon} + Z_N^m\, e^{\beta\epsilon} r \\ Z_{N+1}^m &= Z_N^h\, qr \; + Z_N^m\, q \end{aligned}$$

d. As with the Ising chain, in the thermodynamic limit

$$f(T,\epsilon,r) = \lim_{N\to\infty} \frac{F_N(T,\epsilon,r)}{N} = -k_B T \ln \lambda_A$$

where λ_A is the largest eigenvalue of the transfer matrix

$$\begin{pmatrix} e^{\beta\epsilon} & e^{\beta\epsilon} r \\ qr & q \end{pmatrix}.$$

To find this eigenvalue, set

$$\begin{aligned} \det \begin{pmatrix} e^{\beta\epsilon} - \lambda & e^{\beta\epsilon} r \\ qr & q-\lambda \end{pmatrix} &= 0 \\ \lambda^2 - (q + e^{\beta\epsilon})\lambda + q e^{\beta\epsilon}(1-r^2) &= 0. \end{aligned}$$

The solution of this quadratic equation is

$$\begin{aligned} \lambda &= \tfrac{1}{2}\left[(q+e^{\beta\epsilon}) \pm \sqrt{(q+e^{\beta\epsilon})^2 - 4qe^{\beta\epsilon}(1-r^2)}\right] \\ &= \tfrac{1}{2} e^{\beta\epsilon}\left[1 + qe^{-\beta\epsilon} \pm \sqrt{(1-qe^{-\beta\epsilon})^2 + 4qe^{-\beta\epsilon}r^2}\right]. \end{aligned}$$

In this form, it is clear that the square root is real, so the largest eigenvalue comes from taking the + sign in the $\pm$:

$$\begin{aligned} f(T,\epsilon,r) &= -k_B T \ln \lambda_A \\ &= -k_B T \ln\left\{\tfrac{1}{2}\left[1 + qe^{-\beta\epsilon} + \sqrt{(1-qe^{-\beta\epsilon})^2 + 4qe^{-\beta\epsilon}r^2}\right]\right\} - \epsilon \\ &= -k_B T \ln\left\{\tfrac{1}{2}\left[1 + w + \sqrt{(1-w)^2 + 4wr^2}\right]\right\} - \epsilon. \end{aligned}$$

where we have defined

$$w = qe^{-\beta\epsilon}.$$

At $T = 0$, $f = -\epsilon$ and, as expected, $F = E - TS \longrightarrow E_{\text{ground state}}$.

e. As $r \to 0$, the free energy becomes

$$\begin{aligned} f(T,\epsilon,0) &= -k_B T \ln\left\{\tfrac{1}{2}\left[1 + w + \sqrt{(1-w)^2}\right]\right\} - \epsilon \\ &= -k_B T \ln\left\{\tfrac{1}{2}\left[1 + w + |1-w|\right]\right\} - \epsilon. \end{aligned}$$

Note well! For any variable x,

$$\sqrt{x^2} \neq x, \qquad \text{instead} \qquad \sqrt{x^2} = |x|.$$

This function is smooth almost everywhere, but is non-analytic when the argument of the absolute value vanishes, i.e. when

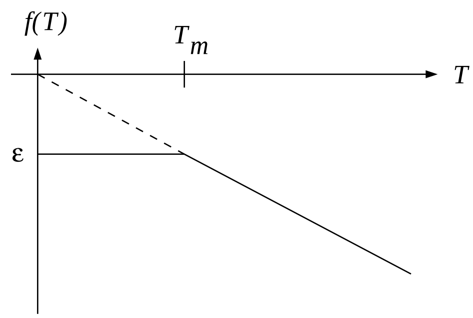
$$1 - w = 0 \qquad \text{or} \qquad T = T_m \equiv \frac{\epsilon}{k_B \ln q}.$$

In fact, the free energy behaves as

$$f(T,\epsilon,0) = \begin{cases} -k_B T \ln\left\{\frac{1}{2}[(1+w)+(1-w)]\right\} - \epsilon & \text{for } w<1,\ T<T_m \\ -k_B T \ln\left\{\frac{1}{2}[(1+w)-(1-w)]\right\} - \epsilon & \text{for } w>1,\ T>T_m \end{cases}$$

which simplifies to

$$f(T,\epsilon,0) = \begin{cases} -\epsilon & \text{for } T<T_m \\ -k_B T \ln q & \text{for } T>T_m \end{cases}$$



Other quantities of interest include the energy,

$$\frac{E(T)}{N} = \frac{\partial(f/T)}{\partial(1/T)} = \begin{cases} -\epsilon & \text{for } T<T_m \\ 0 & \text{for } T>T_m \end{cases}$$

the entropy,

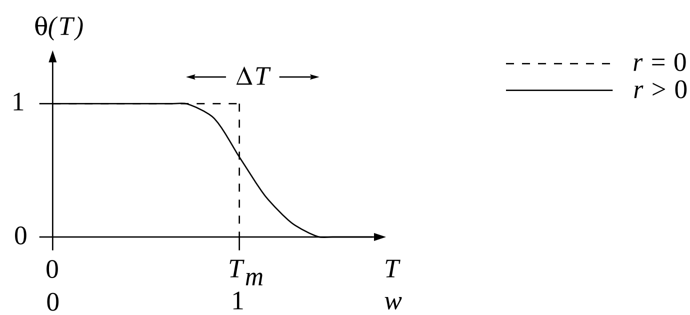
$$\frac{S(T)}{N} = -\frac{\partial f}{\partial T} = \begin{cases} 0 & \text{for } T<T_m \\ k_B \ln q & \text{for } T>T_m \end{cases}$$

and the helical fraction,

$$\theta(T) = -\frac{\partial f}{\partial \epsilon} = \begin{cases} 1 & \text{for } T<T_m \\ 0 & \text{for } T>T_m \end{cases}$$

The transition at $r=0$ is first order: the DNA is either all helical or all melted.

f. If $r \neq 0$ the free energy is analytic, so all the properties vary smoothly with temperature.



g. The exact free energy, written in a form to facilitate comparison to $r = 0$, is

$$f(T, \epsilon, r) = -k_B T \ln \left\{ \tfrac{1}{2} \left[(1+w) + |1-w| \left\{ 1 + \frac{4wr^2}{(1-w)^2} \right\}^{1/2} \right] \right\} - \epsilon.$$

Thus the criterion for "r vanishingly small" is

$$\frac{4wr^2}{(1-w)^2} \ll 1.$$

For finite r, this condition fails as $w \to 1$, i.e. near the melting transition. In fact, if $\Delta w = w - 1$, it breaks down approximately at

$$\frac{4r^2}{\Delta w^2} \approx 1$$

or

$$|\Delta w| \approx 2r.$$

So the "two-sided" ΔT, as defined in the figure above, is

$$\Delta T = 2|\Delta w| \left. \frac{dT}{dw} \right|_{w=1} = \frac{4\epsilon r}{k_B \ln^2 q}.$$

h.

$$J(T) = -N \frac{r}{k_B T} \frac{\partial f}{\partial r} = N \frac{4r^2 w}{(1+w)\sqrt{(1-w)^2 + 4r^2 w} + (1-w)^2 + 4r^2 w}.$$

At $T = T_m$, we have $w = 1$ and

$$J(T) = N \frac{r}{1+r}$$

The regime $r \ll 1$ gives $J(T) \approx Nr$.

In contrast, at $T \to 0$, we have $w \to 0$ and

$$J(T) \to N \frac{4r^2 w}{\sqrt{1 + 4r^2 w} + 1 + 4r^2 w} \to N 2wr^2.$$