

## Denaturation 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

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

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

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

b. Use the slick trick! By definition

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

so

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

Similarly

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

so

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

c.

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

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

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

where  $\lambda_A$  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

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

The solution of this quadratic equation is

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

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

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

where we have defined

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

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

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

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

Note well! For any variable  $x$ ,

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

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

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

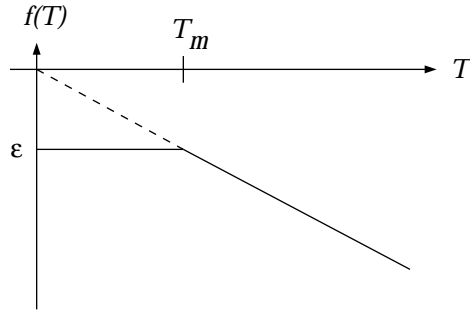
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In fact, the free energy behaves as

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

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,

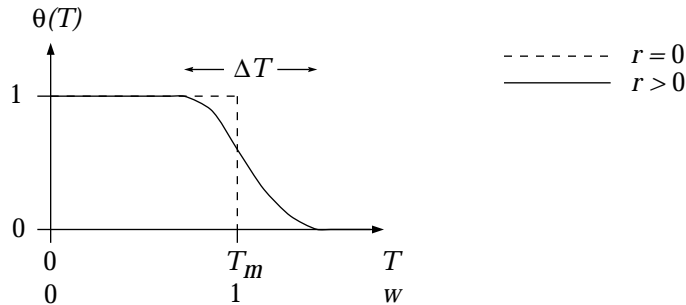
$$\frac{S(T)}{N} = -\frac{\partial f}{\partial T} = \begin{cases} 0 & \text{for } T < T_m \\ k_B \ln q & \text{for } T > T_m \end{cases}$$

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.



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

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

Thus the criterion for “ $r$  vanishingly small” is

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

For finite  $r$ , this condition fails as  $w \rightarrow 1$ , 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”  $\Delta T$ , 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  $T \rightarrow 0$ , we have  $w \rightarrow 0$  and

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