

1 Ripasso: Ising 1d

In alcuni metalli, abbassando la temperatura sotto un valore detto di Temperatura di Curie, una frazione finita degli spin degli atomi si allinea, dando origine ad una magnetizzazione del materiale. Il modello di Ising offre una rappresentazione cruda del fenomeno, che però ha svolto nella storia della meccanica statistica un ruolo cruciale, essendo un modello risolvibile analiticamente in una e due dimensioni. Il modello di Ising è definito su un reticolo (lineare, quadrato, cubico...). Su ognuno degli N siti reticolari è collocato uno spin s che può avere solo due orientazioni, up ($s = 1$) e down ($s = -1$). Spin adiacenti interagiscono con un potenziale $-\epsilon s_i s_j$. Valori di ϵ positivi indicano un ferromagnete, ϵ negativi un anti-ferromagnete. L'Hamiltoniana del modello è (indicando con $\langle i, j \rangle$ le coppie di spin adiacenti)

$$\mathcal{H}\{s_i\} = - \sum_{\langle i, j \rangle} \epsilon s_i s_j - H \sum_{i=1}^N s_i$$

La funzione di partizione nel canonico è data dalla somma sui 2^N stati

$$Q(H, T) = \sum_{s_1} \sum_{s_2} \dots \sum_{s_N} e^{-\beta \mathcal{H}\{s_i\}}$$

La magnetizzazione $M = \langle \sum_{i=1}^N s_i \rangle$ la possiamo calcolare come derivata rispetto ad H di $\ln Q(H, T)$

$$M = \frac{1}{\beta} \frac{\partial \ln Q}{\partial H} = - \frac{\partial A}{\partial H} = \frac{1}{Q} \sum_{s_1} \sum_{s_2} \dots \sum_{s_N} \left(\sum_{i=1}^N s_i \right) e^{-\beta \mathcal{H}\{s_i\}} = \langle \sum_{i=1}^N s_i \rangle$$

2 Ising 1D

In una dimensione, con condizioni al contorno periodiche ($s_{N+1} = s_1$),

$$\mathcal{H}\{s_i\} = - \sum_{i=1}^N \epsilon s_i s_{i+1} - H \sum_{i=1}^N s_i$$

e, simmettizzando il termine con il campo magnetico

$$Q(H, T) = \sum_{s_1} \sum_{s_2} \dots \sum_{s_N} e^{-\beta \sum_{i=1}^N (-\epsilon s_i s_{i+1} - \frac{H}{2}(s_i + s_{i+1}))}$$

Se definiamo una matrice P

$$P = \begin{bmatrix} e^{\beta(\epsilon+H)} & e^{-\beta\epsilon} \\ e^{-\beta\epsilon} & e^{\beta(\epsilon-H)} \end{bmatrix}$$

possiamo riscrivere la funzione di partizione come

$$Q(H, T) = \sum_{s_1} \sum_{s_2} \dots \sum_{s_N} \langle s_1 | P | s_2 \rangle \langle s_2 | P | s_3 \rangle \dots \langle s_N | P | s_1 \rangle$$

e poiche' $\sum_{s_k} |s_k\rangle \langle s_k| = 1$,

$$Q(H, T) = \sum_{s_1} \langle s_1 | P^N | s_1 \rangle = \text{Tr} P^N = \lambda_+^N + \lambda_-^N$$

dove λ_+ e λ_- sono gli autovalori di P e abbiamo sfruttato la invarianza della traccia. Per N grandi solo il maggiore tra λ_+ e λ_- conta.

Per chiarire perche' $\sum_{s_k} |s_k\rangle \langle s_k| = 1$ considerate un caso specifico, per esempio

$$\sum_{s_2} \langle s_1 | P | s_2 \rangle \langle s_2 | P | s_3 \rangle$$

che riconoscerete come la somma equivalente al prodotto riga per colonna della moltiplicazione di P per P , trovando cosi che

$$\sum_{s_2} \langle s_1 | P | s_2 \rangle \langle s_2 | P | s_3 \rangle = \langle s_1 | P^2 | s_3 \rangle$$

2.1 $H = 0$

Quando $H = 0$,

$$P = \begin{bmatrix} e^{\beta\epsilon} & e^{-\beta\epsilon} \\ e^{-\beta\epsilon} & e^{\beta\epsilon} \end{bmatrix}$$

e il determinante $|P - \lambda I| = 0$ diviene (indicando $x = e^{\beta\epsilon}$)

$$|P - \lambda I| = (x - \lambda)^2 - \frac{1}{x^2} = 0 \rightarrow \lambda_{\pm} = x \pm \frac{1}{x}$$

e, poiche' $e^x + e^{-x} = 2 \cosh(x)$

$$\lambda_{\pm} = e^{\beta\epsilon} \pm e^{-\beta\epsilon} \quad Q_N = 2^N [\cosh^N(\beta\epsilon) + \sinh^N(\beta\epsilon)]$$

2.2 $H \neq 0$

In questo caso, chiamando $x = \exp(\beta\epsilon)$ e $y = \exp(\beta H)$

$$P = \begin{bmatrix} xy & \frac{1}{x} \\ \frac{1}{x} & \frac{x}{y} \end{bmatrix}$$

così che,

$$\begin{aligned}
 (xy - \lambda) \left(\frac{x}{y} - \lambda \right) - \frac{1}{x^2} &= 0 & \lambda^2 - \lambda \left(xy + \frac{x}{y} \right) + x^2 - \frac{1}{x^2} &= 0 \\
 \lambda_{\pm} &= \frac{1}{2} \left(\left(xy + \frac{x}{y} \right) \pm \sqrt{x^2 y^2 + \frac{x^2}{y^2} + 2x^2 - 4x^2 + \frac{4}{x^2}} \right) \\
 &= \frac{x}{2} \left[\left(y + \frac{1}{y} \right) \pm \sqrt{\left(y - \frac{1}{y} \right)^2 + \frac{4}{x^4}} \right] = x \left[\frac{1}{2} \left(y + \frac{1}{y} \right) \pm \sqrt{\frac{1}{4} \left(y - \frac{1}{y} \right)^2 + \frac{1}{x^4}} \right] \\
 \lambda_{\pm} &= e^{\beta\epsilon} \left[\cosh(\beta H) \pm \sqrt{\sinh^2(\beta H) + e^{-4\beta\epsilon}} \right]
 \end{aligned}$$

e per grandi N

$$A = -k_B T \ln Q = -k_B T \ln \lambda_+ = -\epsilon - k_B T \ln \left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta\epsilon}} \right]$$

La magnetizzazione per spin la otteniamo derivando A rispetto ad H (cambiando di segno) trovando

$$\begin{aligned}
 M &= -\frac{\partial A}{\partial H} = \frac{k_B T}{\left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta\epsilon}} \right]} \left[\beta \sinh(\beta H) + \beta \frac{\sinh(\beta H) \cosh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta\epsilon}}} \right] = \\
 &= \frac{\sinh(\beta H)}{\left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta\epsilon}} \right]} \left[1 + \frac{\cosh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta\epsilon}}} \right] = \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta\epsilon}}}
 \end{aligned}$$

Poiché $\sinh(0) = 0$, $M(H = 0, T) = 0$. Per nessuna temperatura finita, il sistema in una dimensione si magnetizza spontaneamente.

Troviamo dunque che in assenza di campo, nonostante ci aspettiamo che spin adiacenti siano orientati nella stessa maniera, non è presente magnetizzazione. Il sistema apparirà come una sequenza di spin spesso paralleli con un numero di inversioni di segno che determinano in media magnetizzazione nulla.



Possiamo capire meglio perché la magnetizzazione è sempre nulla (eccetto che strettamente a $T = 0$) considerando l'energia libera in funzione del numero di "interfacce", chiamando interfaccia il luogo dove due spin successivi hanno segno opposto. Lo stato

fondamentale (l' unico con $M = 1$) non ha interfacce ed ha una energia per spin pari a $A(0) = -N\epsilon$. Lo stato con una interfaccia ha energia libera $A(1) = -N\epsilon + 2\epsilon - T \ln N$ dove abbiamo aggiunto l'energia associata all' aver flippato tutto gli spin a destra dell' interfaccia in modo coerente. Il termine entropico $\ln N$ indica gli N luoghi dove possiamo collocare l' interfaccia. Continuando troviamo $A(3) = -N\epsilon + 4\epsilon - T \ln[N(N-1)/2]$ e cosi via. Un grafico dell' energia libera in funzione del numero di interfacce vi fa vedere che per $N \rightarrow \infty$ il minimo di A si ha per un numero di interfacce diverso da 0. Lo stato con una interfaccia (e $M = 0$!) diventa infatti piu' stabile dello stato fondamentale (con $M = 1$) gia' per $T = \frac{2\epsilon}{\ln N}$

3 Stretching DNA — Nelson Chapter 9

In this lecture we go back to what we have learned for polymers to attempt to evaluate the response of DNA in double helix form to an external force. We will investigate several regimes, from very weak forces where we already know the answer from the ideal polymer theory to forces able to elongate the polymer significantly, for which one need to develop better models.

4 The force extension curve can be measured for single DNA molecules

From the initial studies of Bustamente's group, we have now a well precise characterization of DNA behavior. Experimentally one end of the DNA is attached to a surface and the other end is attached to a gold nanoparticle and driven by an optical trap. In this set-up forces (in the pN scale) and displacement (in the 100 nm range) can be simultaneously measured.

Let us look at some of the available experimental data. To get a clear picture, we'd like to pass from pulling on rubber bands, with zillions of entangled polymer chains, to pulling on individual polymer molecules with tiny, precisely known forces. S. Smith, L. Finzi, and C. Bustamante accomplished this feat in 1992; a series of later experiments improved both the quality of the data and the range of forces probed, leading to the picture shown in Figure 9.3. Such experiments typically start with a known piece of DNA, for example lambda-phage DNA with $L_{tot} = 16.5\mu\text{m}$ and 10416 basepairs. One end is anchored to a glass slide, the other to a micrometer-sized bead, and the bead is then pulled by optical or magnetic tweezers. Figure 9.3 shows five distinct regimes of qualitative behavior as the force on the molecule increases:

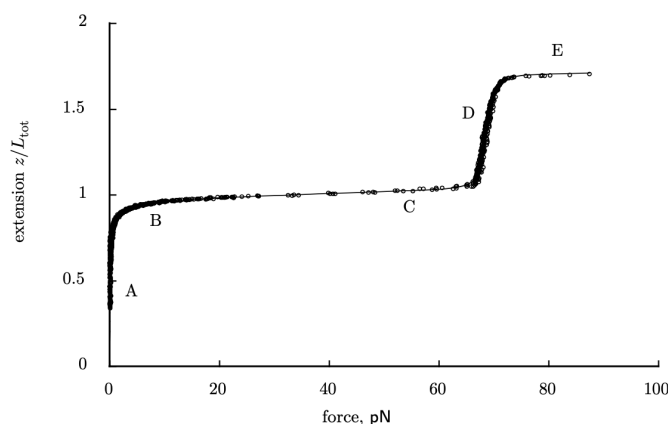


Figure 9.3: (Experimental data with fit.) Force f versus relative extension z/L_{tot} for a DNA molecule made of 10416 basepairs, in high-salt solution. The regimes labeled A, B, C, D, and E are described in the text. The extension z was measured by video imaging of the positions of beads attached to each end; the force was measured using the change of light momentum exiting a dual-beam optical tweezers apparatus (see Section 6.7 on page 199). L_{tot} is the DNA's total contour length in its relaxed state. The quantity z/L_{tot} becomes larger than one when the molecule begins to stretch, at around 20 pN. The solid curve shows a theoretical model obtained by a combination of the approaches in Sections 9.4.1' and 9.5.1 (see for example Cizeau & Viovy, 1997). [Experimental data kindly supplied by S. B. Smith; theoretical model and fit kindly supplied by C. Storm.]

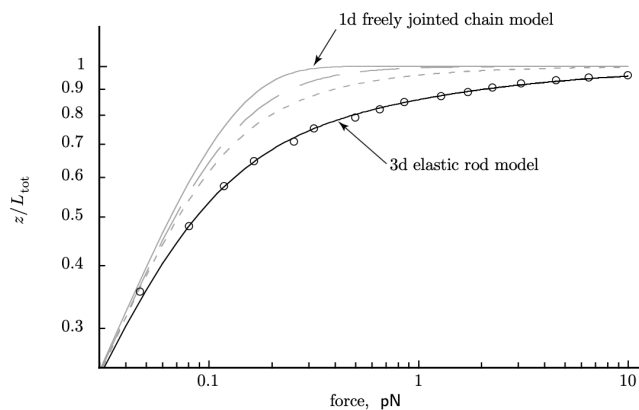


Figure 9.4: (Experimental data with fits.) Log-log plot of relative extension z/L_{tot} at low applied stretching force f for lambda phage DNA in 10 mM phosphate buffer. The points show experimental data corresponding to the regions A–B in Figure 9.3. The curves show various theoretical models discussed in the text. For comparison, in each model the value of L_{seg} has been adjusted so that all the curves agree at low force. *Top curve*: one-dimensional freely jointed chain (Equation 9.10), with $L_{\text{seg}}^{(1d)} = 35$ nm. *Dashed gray curve*: one-dimensional cooperative chain (see Your Turn 9h(b)), with $L_{\text{seg}}^{(1d)}$ held fixed at 35 nm and γ very large. *Dotted gray curve*: three-dimensional FJC (Your Turn 9e), with $L_{\text{seg}} = 104$ nm. *Black curve through data points*: three-dimensional elastic rod model (Section 9.4.1' on page 341), with $A = 51$ nm. [Data kindly supplied by V. Croquette; see also Bouchiat et al., 1999.]

- A. At very low stretching force, $f < 0.01pN$, the molecule is still nearly a random coil. Its ends then have a mean-square separation given by

$$R_{ee} = L_0 N^{1/2}$$

where L_0 is the Khun length and $N = L_{tot}/L_0$ and L_{tot} the maximum extension of the double strand molecule

Figure 9.3 shows that for zero applied force, the extension of the DNA is less than $0.3 L_{tot}$, or 1060 nm, so we conclude that

$$L_0 \sqrt{L_{tot}/L_0} < 0.3L_{tot} \quad \rightarrow \quad L_0 < (0.3)^2 L_{tot} \approx 300nm$$

- B. At higher forces the relative extension begins to level off as it approaches unity. At this point the molecule has been stretched nearly straight.
- C. At forces beyond about 10 pN, the extension actually exceeds the total contour length of the relaxed molecule: The molecule begins to stretch.
- D. At around $f = 65pN$ we find a remarkable jump, as the molecule suddenly extends to about 1.6 times its relaxed length. This is called "overstretching transition".
- E. Still higher forces again give elastic behavior, until eventually the molecule breaks.

4.1 Region A: Independent spin model at work

A simple two-state system qualitatively explains DNA stretching at low force. We wish to compute the entropic force f exerted by an elastic rod subjected to thermal motion. This may seem like a daunting prospect. The stretched rod is constantly buffeted by the Brownian motion of the surrounding water molecules, receiving kicks in the directions perpendicular to its axis. Somehow all these kicks pull the ends closer together, maintaining a constant tension if we hold the ends a fixed distance z apart. How could we calculate such a force?

Let's start with a very simple model, in which the DNA double helix is described as a random coil polymer composed by N non-interacting segments. For simplicity we also work in one dimension. We assume that each link has a two-state variable σ , which equals +1 if the link points forward (along the applied force), or -1 if it points backward (against the force). The total extension z is then the sum of these variables:

$$z = L_0 \sum_{i=1}^N \sigma_i$$

In the polymer-stretching system U_{ext} goes up as the chain shortens:

$$U_{ext} = const - fz$$

where f is the applied external stretching force. Neglecting the constant term, the system's partition function is

$$Z = \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} e^{-\beta(-fL_0^{1d} \sum_{i=1}^N \sigma_i)}$$

and

$$\begin{aligned} \langle z \rangle &= \frac{\sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} \left(L_0^{1d} \sum_{i=1}^N \sigma_i \right) e^{-\beta(-fL_0^{1d} \sum_{i=1}^N \sigma_i)}}{Z} = \\ \langle z \rangle &= \frac{\sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} \left(L_0^{1d} \sum_{i=1}^N \sigma_i \right) e^{\beta f L_0^{1d} \sum_{i=1}^N \sigma_i}}{\sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} e^{\beta f L_0^{1d} \sum_{i=1}^N \sigma_i}} = \\ &= \frac{\partial}{\partial(\beta f)} \ln \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} e^{\beta f L_0^{1d} \sum_{i=1}^N \sigma_i} = \\ &= \frac{\partial}{\partial(\beta f)} \ln \left(\sum_{\sigma_1=\pm 1} e^{\beta f L_0^{1d} \sigma_1} \sum_{\sigma_2=\pm 1} e^{\beta f L_0^{1d} \sigma_2} \dots \sum_{\sigma_N=\pm 1} e^{\beta f L_0^{1d} \sigma_N} \right) \\ &= \frac{\partial}{\partial(\beta f)} N \ln(e^{\beta f L_0^{1d}} + e^{-\beta f L_0^{1d}}) = \\ &= N L_0^{1d} \frac{e^{\beta f L_0^{1d}} - e^{-\beta f L_0^{1d}}}{e^{\beta f L_0^{1d}} + e^{-\beta f L_0^{1d}}} \end{aligned}$$

Recalling that NL_0^{1d} is the total length L_{tot} of the DNA molecule we find

$$\frac{\langle z \rangle}{L_{tot}} = \tanh(\beta f L_0^{1d})$$

For small applied forces f , $\tanh(\beta f L_0^{1d}) \approx \beta f L_0^{1d}$ such that the DNA molecule behaves as a spring

$$\frac{\langle z \rangle}{L_{tot}} = \beta f L_0^{1d} \quad \langle z \rangle = \frac{f N (L_0^{1d})^2}{k_B T}$$

of (entropic) elastic constant such that $k_{el} \langle z \rangle = f$

$$k^{el} = k_B T \frac{1}{(L_0^{1d})^2 N}$$

. We thus recover the result we knew already from the physics of an ideal polymer.

But we have now in addition also the possibility to estimate the behavior of the polymer for large applied forces $\tanh(\beta f L_0^{1d}) \approx 1$ and

$$\frac{\langle z \rangle}{L_{tot}} = 1$$

4.2 Region A (better model) Ising model at work

The next step is to account for some interaction (cooperativity in biological terminology) between adjacent segments, still retaining the one dimension approximation. We can add to the hamiltonian a term $\sum_i -\gamma k_B T \sigma_i \sigma_{i+1}$ such that there is a preferential gain in parallel alignment ($2\gamma k_B T$) respect to antiparallel one.

This additional contribution transforms the "non-interacting paramagnet" into a "1D-Ising" type model. The partition function is indeed now

$$\begin{aligned} Z &= \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} e^{-\beta(-fL_0^d \sum_{i=1}^N \sigma_i - \gamma k_B T \sum_i \sigma_i \sigma_{i+1})} \\ &= \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} e^{\alpha \sum_{i=1}^N \sigma_i + \gamma \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1}} \end{aligned}$$

where we have defined $\alpha = \beta f L_0^d$. As before we need to compute

$$\langle z \rangle = L_0^d \frac{\partial}{\partial \alpha} \ln Z$$

The partition function can be simmetrized

$$Z = \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} e^{\alpha \sum_{i=1}^N \frac{\sigma_i + \sigma_{i+1}}{2} + \gamma \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1}} e^{\alpha \sigma_1 / 2} e^{\alpha \sigma_N / 2}$$

To calculate Z we apply the transfer matrix method. If we define a matrix

$$P = \begin{bmatrix} e^{\gamma + \alpha} & e^{-\gamma} \\ e^{-\gamma} & e^{\gamma - \alpha} \end{bmatrix}$$

$$Z = \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} \langle \sigma_1 | P | \sigma_2 \rangle \langle \sigma_2 | P | \sigma_3 \rangle \dots \langle \sigma_{N-1} | P | \sigma_N \rangle e^{\alpha \sigma_1 / 2} e^{\alpha \sigma_N / 2}$$

and since $\sum_{\sigma_k} |\langle \sigma_k \rangle| = 1$,

$$Z = \sum_{\sigma_1=\pm 1} \sum_{\sigma_N=\pm 1} \langle \sigma_1 | P^{N-1} | \sigma_N \rangle e^{\alpha \sigma_1 / 2} e^{\alpha \sigma_N / 2}$$

By calling λ_+ and λ_- the two eigenvalues of P , and performing the sum using the eigenvalues of P ,

$$Z_N = p \lambda_+^{N-1} + q \lambda_-^{N-1} \sim \lambda_{max}^{N-1}$$

where p and q are two constants and $\lambda_{max} = \max(\lambda_+, \lambda_-)$. As a result, for large N ,

$$\langle z \rangle = L_0 (N-1) \frac{\partial}{\partial \alpha} \ln \lambda_{max}$$

To evaluate the eigenvalues of P , let's call $x = \exp(\alpha)$ and $y = \exp(\gamma)$ such that

$$P = \begin{bmatrix} e^{\gamma+\alpha} & e^{-\gamma} \\ e^{-\gamma} & e^{\gamma-\alpha} \end{bmatrix} = \begin{bmatrix} xy & \frac{1}{x} \\ \frac{1}{y} & \frac{x}{y} \end{bmatrix}$$

such that

$$(xy - \lambda) \left(\frac{x}{y} - \lambda \right) - \frac{1}{x^2} = 0 \quad \rightarrow \quad \lambda^2 - \lambda \left(\frac{x}{y} + xy \right) + x^2 - \frac{1}{x^2} = 0$$

$$\begin{aligned} \lambda_{\pm} &= \frac{\left(\frac{x}{y} + xy \right) \pm \sqrt{\left(\frac{x}{y} + xy \right)^2 - 4x^2 + \frac{4}{x^2}}}{2} = x \left[\frac{1}{2} \left(\frac{1}{y} + y \right) \pm \sqrt{\frac{1}{4} \left(\frac{1}{y} - y \right)^2 + \frac{1}{x^2}} \right] \\ &= e^{\gamma} \left[\frac{1}{2} (e^{-\alpha} + e^{\alpha}) \pm \sqrt{\frac{1}{4} (e^{-\alpha} - e^{\alpha})^2 + e^{-4\gamma}} \right] = e^{\gamma} \left[\cosh \alpha \pm \sqrt{(\sinh \alpha)^2 + e^{-4\gamma}} \right] \end{aligned}$$

For small α (small f) (see alpha-wolfram)

$$\frac{\partial}{\partial \alpha} \ln \lambda_+ = \frac{\partial}{\partial \alpha} \left[\ln(e^{-2\gamma} + 1) + \frac{\alpha^2}{2e^{-2\gamma}} \right]$$

$$\langle z \rangle = N \frac{\alpha}{e^{-2\gamma}} = N \frac{\beta f L_0}{e^{-2\gamma}}$$

hence again an elastic response with elastic constant

$$k^{el} = \frac{f}{\langle z \rangle} = k_B T \frac{e^{-2\gamma}}{N L_0^2}$$

4.3 A general formalism

Let's look at the double helix as a tube structure and let's look how we can describe the deformation of the tube and the associated energy cost. For each infinitesimal segment ds , we can define

- the stretch $u(s)$, quantifying the normalised length change: $u(s) = \Delta(ds)/ds$ (a scalar quantity)
- the bend $\vec{\beta}(s)$, quantifying the change in direction: $\vec{\beta} = d\hat{t}/ds$, (a vector quantity)
- the twist $\omega(s)$, quantifying the change in rotation of the angle ϕ in the segment ds : $\omega(s) = d\phi/ds$, (a scalar quantity).

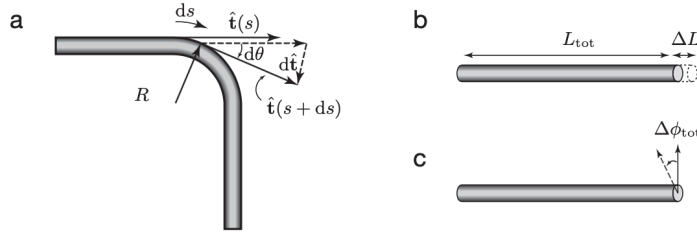


Figure 9.1: (Schematic.) (a) Definition of the bend vector, $\beta = d\hat{\mathbf{t}}/ds$, illustrated for a circular segment of a thin rod. The parameter s is the contour length (also called "arc length") along the rod. The tangent vector $\hat{\mathbf{t}}(s)$ at one point of the rod has been moved to a nearby point a distance ds away (dashed horizontal arrow), then compared with the tangent vector there, or $\hat{\mathbf{t}}(s+ds)$. The difference of these vectors, $d\hat{\mathbf{t}}$, points radially inward and has magnitude equal to $d\theta$, or ds/R . (b) Definition of stretch. For a uniformly stretched rod, $u = \Delta L/L_{\text{tot}}$. (c) Definition of twist density. For a uniformly twisted rod, $\omega = \Delta\phi_{\text{tot}}/L_{\text{tot}}$.

In the context of DNA, we can think of the stretch as measuring how the contour length of a short tract of N basepairs differs from its natural (or "relaxed") value of $(0.34\text{nm})xN$. We can think of the bend as measuring how each basepair lies in a plane tilted slightly from the plane of its predecessor. To visualize twist density, we first note that the relaxed double helix of DNA in solution makes one complete helical turn about every 10.5 basepairs. Thus we can think of the twist density as measuring the rotation $\delta\phi$ of one basepair relative to its predecessor, minus the relaxed value of this angle. More precisely,

$$\omega = \Delta\phi - \omega_0 \quad \text{where} \quad \omega_0 = \frac{2\pi}{10.5b.p.} \frac{1b.p.}{0.34} \approx 1.8\text{nm}^{-1}$$

To write the elastic energy cost E of deforming the tube (or any long, thin elastic rod) we divide the rod arbitrarily into short segments of length ds . Then E should be the sum of terms $dE(s)$, coming from the deformation of the segment at each position s . By analogy to the Hooke relation, we now argue that $dE(s)$ should be a quadratic function of the deformations, if these are small. The most general expression we can write is

$$dE = \frac{1}{2}k_B T \left[A\beta^2 + Bu^2 + C\omega^2 + 2Du\omega \right] ds$$

The phenomenological parameters A , B , and C have dimensions L , L^{-1} , L respectively; D is dimensionless. The quantities $Ak_B T$ and $Ck_B T$ are called the rod's *bend stiffness* and *twist stiffness* at temperature T , respectively. It is convenient to express these quantities in units of $k_B T$, which is why we introduced the bend persistence length A and the twist persistence length C . The remaining constants $Bk_B T$ and $Dk_B T$ are called the "stretch stiffness" and "twist-stretch coupling", respectively.

Note that not all possible quadratic terms are found in the expression for dE . The origin of this is routed in the different properties of the terms. For example, the energy

must be a scalar, whereas $\omega\vec{\beta}$ is a vector; terms of this sort have the wrong geometrical status to appear in the energy. In some cases we can simplify the energy expression even further. First, many polymers consist of monomers joined by single chemical bonds. The monomers can then rotate about these bonds, destroying any memory of the twist variable, so that there is no twist elasticity: $C = D = 0$. In other cases, the polymer is free to swivel at one of its attachment points, again leaving the twist variable uncontrolled; then ω again drops out of the analysis. A second simplification comes from the observation that the stretch stiffness $k_B T B$ has the same dimensions as a force. If we pull on the polymer with an applied force much less than this value, the corresponding stretch u will be negligible, and we can forget about it, treating the molecule as an inextensible rod, that is, a rod having fixed total length. Making both these simplifications leads us to a one-parameter phenomenological model of a polymer, with elastic energy

$$E = \frac{1}{2} k_B T \int_0^{L_{tube}} ds A \vec{\beta}^2$$

This equation describes a thin, inextensible, rod made of a continuous, elastic material. Other authors call it the "Kratky-Porod" or "wormlike chain" model (despite the fact that real worms are highly extensible). It is certainly a simple, ultra-reductionist approach to a complex molecule. Nevertheless, below will show that it leads to a quantitatively accurate model of the mechanical stretching of DNA.

4.4 A is the persistence length

Let's now demonstrate that A is indeed the persistence length of the tube. To do so, we will evaluate the correlation function of the directions along the tube

$$\langle \hat{t}(s_1) \cdot \hat{t}(s_2) \rangle$$

and demonstrate that it decays as an exponential, whose scale is the persistence length.

Let's call the point at s_1 the A point, the point in s_2 the C point and B an intermediate point between s_1 and s_2 .

If we consider the tangent vectors $\hat{t}(A)$, this can be split into the component parallel to $\hat{t}(B)$ and a perpendicular component $\hat{t}_\perp(A)$. Similarly, $\hat{t}(C)$ can be split into a component parallel to $\hat{t}(B)$ and a perpendicular component $\hat{t}_\perp(C)$.

Then

$$\hat{t}(A) \cdot \hat{t}(C) = (\hat{t}(A) \cdot \hat{t}(B))(\hat{t}(C) \cdot \hat{t}(B)) + \hat{t}_\perp(A) \cdot \hat{t}_\perp(C)$$

where we have split the scalar product in two contributions: first the product of the components in the direction $\hat{t}(B)$ and second the scalar product of the remaining perpendicular components.

If we use $\hat{t}(B)$ as z -axis, and defining θ and ϕ the polar angles respect to $\hat{t}(B)$ we can rewrite

$$\hat{t}(A) \cdot \hat{t}(C) = \cos \theta(A) \cos \theta(C) + \sin \theta(A) \sin \theta(C) \cos \phi(C)$$

(it is equivalent to select as reference system the directions $\hat{t}(B)$ and $\hat{t}_\perp(A)$ and their vector product).

The energy of bending does not depend on ϕ . Hence the angle ϕ has to be randomly distributed between 0 and 2π , resulting in a null thermodynamic averaging of $\cos \phi(C)$. Then

$$\langle \hat{t}(A) \cdot \hat{t}(C) \rangle = \langle \cos \theta(A) \cos \theta(C) \rangle$$

Considering that the energy expression does not couple distinct segments ($E = \frac{1}{2}k_B T \int_A^C ds A \vec{\beta}^2 = \frac{1}{2}k_B T \int_A^B ds A \vec{\beta}^2 + \frac{1}{2}k_B T \int_B^C ds A \vec{\beta}^2$) there will be no correlations between $\theta(A)$ and $\theta(C)$ and thus

$$\langle \hat{t}(A) \cdot \hat{t}(C) \rangle = \langle \cos \theta(A) \rangle \langle \cos \theta(C) \rangle$$

The fact that the correlation function factorises implies that

$$\langle \hat{t}(s_A) \cdot \hat{t}(s_C) \rangle = \langle \hat{t}(s_A) \cdot \hat{t}(s_B) \rangle \langle \hat{t}(s_B) \cdot \hat{t}(s_C) \rangle = e^{q(s_B - s_A)} e^{q(s_C - s_B)} = e^{q(s_C - s_A)}$$

and for very small $s_C - s_A$,

$$\langle \hat{t}(s) \cdot \hat{t}(s + ds) \rangle = 1 + qds$$

We now consider a reference system (ζ, η, ξ) in which $\hat{t}(s) = \hat{\zeta}$. Then after a small ds (considering only bending, e.g. changes in the orthogonal directions)

$$\hat{t}(s + ds) = \frac{\hat{\zeta} + \psi_\xi \hat{\xi} + \psi_\eta \hat{\eta}}{\sqrt{1 + \psi_\xi^2 + \psi_\eta^2}}$$

and

$$\langle \hat{t}(s) \cdot \hat{t}(s + ds) \rangle = \langle \frac{1}{\sqrt{1 + \psi_\xi^2 + \psi_\eta^2}} \rangle = 1 - \frac{1}{2} \langle \psi_\xi^2 \rangle - \frac{1}{2} \langle \psi_\eta^2 \rangle$$

which implies that

$$qds = -\frac{1}{2} (\langle \psi_\xi^2 \rangle + \langle \psi_\eta^2 \rangle)$$

The associated energy cost is, being

$$\vec{\beta} = \frac{\hat{t}(s + ds) - \hat{t}(s)}{ds} = \frac{1}{ds} \frac{\left(1 - \sqrt{1 + \psi_\xi^2 + \psi_\eta^2}\right) \hat{\zeta} + \psi_\xi \hat{\xi} + \psi_\eta \hat{\eta}}{\sqrt{1 + \psi_\xi^2 + \psi_\eta^2}}$$

The norm of $\vec{\beta}$ is then

$$\vec{\beta}^2 = \frac{1}{ds^2} \frac{\left(1 - \sqrt{1 + \psi_\xi^2 + \psi_\eta^2}\right)^2 + \psi_\xi^2 + \psi_\eta^2}{1 + \psi_\xi^2 + \psi_\eta^2}$$

which for small angles gives (calling $\psi_\xi^2 + \psi_\eta^2 = y^2$)

$$\bar{\beta}^2 = \frac{1}{ds^2} \frac{(1 - \sqrt{1 + y^2})^2 + y^2}{1 + y^2} \approx \frac{1}{ds^2} \frac{[1 - (1 - y^2/2)]^2 + y^2}{1 + y^2} \approx \frac{y^2}{ds^2} \approx \frac{\psi_\xi^2 + \psi_\eta^2}{ds^2}$$

Then the energy associated to the infinitesimal bend deformation

$$dE = \frac{1}{2} k_B T A \bar{\beta}^2 ds = \frac{1}{2} k_B T A (\psi_\xi^2 + \psi_\eta^2) \frac{1}{ds}$$

Since the energy is quadratic in the two terms, each will in average contribute $k_B T/2$, and hence

$$k_B T = \frac{1}{2} k_B T A (\langle \psi_\xi^2 \rangle + \langle \psi_\eta^2 \rangle) \frac{1}{ds}$$

or

$$\langle \psi_\xi^2 + \psi_\eta^2 \rangle = \frac{2ds}{A}$$

As we had seen before $\langle \psi_\xi^2 + \psi_\eta^2 \rangle = -2qds$, proving that

$$q = -\frac{1}{A}$$

or equivalently that A is indeed the persistence length.

5 Small and large deformation regimes. (from Physical Biology of the cell)

Now that we have learned how to write the energy of the tube, we can write the partition function over a sum of all possible tube conformation, each of them weighted by the Boltzmann factor

$$Z = \int \mathcal{D}\mathbf{t}(\mathbf{s}) \int \exp\left(-\frac{\xi_p}{2} \int_0^L \beta^2 ds\right)$$

In the present of an external force pulling on the tube, the partition function becomes

$$Z(f) = \int \mathcal{D}\mathbf{t}(\mathbf{s}) \int \exp\left[-\frac{\xi_p}{2} \int_0^L \beta^2 ds + f \int_0^L t_z(s)\right]$$

5.1 small forces

In the limit of small forces, one can expand the force part

$$Z(f) = \int \mathcal{D}\mathbf{t}(s) \int \exp \left[-\frac{\xi_p}{2} \int_0^L \beta^2 ds \right] \left(1 + f \int_0^L t_z(s) ds + \frac{[f \int_0^L t_z(s) ds]^2}{2} \right)$$

obtaining, (since

$$\frac{1}{Z(0)} \int e^{-\beta E(s)} f(s) ds = \langle f(s) \rangle_0$$

where the average $\langle \dots \rangle_0$ is over the $f = 0$ ensemble)

$$Z(f) = Z(0) \left(1 + \frac{1}{2} \langle \int_0^L \int_0^L t_z(s) t_z(s') ds ds' \rangle_0 \right)$$

Since in equilibrium $\langle t_z(s) t_z(s') \rangle = \frac{1}{3} \langle \mathbf{t}(s) \cdot \mathbf{t}(s') \rangle = \exp[-|s - s'|/\xi_p]$ one gets

$$\langle \int_0^L \int_0^L t_z(s) t_z(s') ds ds' \rangle_0 = \frac{1}{3} \int_0^L \int_0^L \exp[-|s - s'|/\xi_p] ds ds' =$$

and splitting the integral to eliminate the absolute value

$$\begin{aligned} \int_0^L \int_0^L \exp[-|s - s'|/\xi_p] ds ds' &= \xi_p^2 \int_0^{L/\xi_p} dy \left[\int_0^y dx \exp[-(y - x)] + \int_y^{L/\xi_p} dx \exp[-(x - y)] \right] \\ &= \xi_p^2 \left[\int_0^{L/\xi_p} e^{-y} dy \int_0^y dx e^x + \int_0^{L/\xi_p} e^y dy \int_y^{L/\xi_p} dx e^{-x} \right] \\ &= \xi_p^2 \left[\int_0^{L/\xi_p} e^{-y} dy (e^y - 1) + \int_0^{L/\xi_p} e^y dy (-e^{-L/\xi_p} + e^{-y}) \right] \\ &= \xi_p^2 \int_0^{L/\xi_p} dy \left[1 - e^{-y} - e^{-L/\xi_p} e^y + 1 \right] = \xi_p^2 \left[2 \frac{L}{\xi_p} - e^{-L/\xi_p} - 1 + e^{-L/\xi_p} \right] \\ &= 2L\xi_p \end{aligned}$$

Thus

$$Z(f) = Z(0) \left(1 + \frac{f^2}{2} \frac{1}{3} 2L\xi_p \right) = Z(0) \left(1 + \frac{f^2 L \xi_p}{3} \right)$$

Finally exploiting the relation between the derivative of the log of the partition function with f one finds

$$\frac{\langle z \rangle}{L} = \frac{2f\xi_p}{3}$$

that confirms that the displacement is linear in the force. This result is identical to the one we have derived before with the Ising model with the proper association of ξ_p with the Kuhn segment.

5.2 Large forces

The limit of large forces can also be calculated analytically. In the case of large forces, \mathbf{t} is essentially oriented in the direction of the force. Then $t_z \approx 1$ and t_x and t_y are approximatively small. Then

$$\mathbf{t} = (t_x, t_y, (1 - t_x^2 - t_y^2)^{0.5}) = \left(t_x, t_y, 1 - \frac{t_x^2 + t_y^2}{2} \right)$$

with t_x and t_y small. In this limit,

$$\langle z \rangle = \int_0^L t_z(s) ds = \int_0^L \left(1 - \frac{t_x^2 + t_y^2}{2} \right) ds = L - \int_0^L \left(\frac{t_x^2 + t_y^2}{2} \right) ds$$

and

$$\begin{aligned} \left(\frac{d\mathbf{t}}{ds} \right)^2 &= \left(\frac{dt_x}{ds} \right)^2 + \left(\frac{dt_y}{ds} \right)^2 + \left(-\frac{1}{2} \frac{d(t_x^2 + t_y^2)}{ds} \right)^2 \approx \\ &\approx \left(\frac{dt_x}{ds} \right)^2 + \left(\frac{dt_y}{ds} \right)^2 \end{aligned}$$

Then the energy can be written as:

$$\begin{aligned} E_{tot} &= \int_0^L \left[\frac{k_B T \xi}{2} \left(\frac{d\mathbf{t}}{ds} \right)^2 - f z(s) \right] ds = \\ &= \frac{\xi_p k_B T}{2} \int_0^L ds \left[\left(\frac{dt_x}{ds} \right)^2 + \left(\frac{dt_y}{ds} \right)^2 \right] - f k_B T \int_0^L ds \left(1 - \frac{t_x^2 + t_y^2}{2} \right) \end{aligned}$$

If we expand each component of the rod profile in Fourier series, (where $\omega_n = \frac{2\pi}{L}n$, but we drop the index n for simplicity)

$$t_\alpha(s) = \mathcal{R} \sum_{\omega} e^{i\omega s} t_\alpha(\omega)$$

where the symbol \mathcal{R} indicates the real part. Then

$$\begin{aligned} \int_0^L t_\alpha(s) ds &= \int_0^L ds \sum_{\omega} \sum_{\omega'} e^{i\omega s} e^{-i\omega' s} t_\alpha(\omega) t_\alpha^*(\omega') = \\ &= \sum_{\omega} \sum_{\omega'} \delta(\omega - \omega') t_\alpha(\omega) t_\alpha^*(\omega') = \sum_{\omega} |t_\alpha(\omega)|^2 \end{aligned}$$

and

$$\int_0^L \left(\frac{dt_\alpha}{ds} \right)^2 ds = \int_0^L \left| (i\omega) \sum_{\omega} e^{i\omega s} t_\alpha(\omega) \right|^2 ds = \omega^2 \sum_{\omega} |t_\alpha(\omega)|^2$$

With the Fourier series expression, the energy can be written as or

$$\begin{aligned} E_{tot} &= \frac{\xi_p k_B T}{2} \left[\omega^2 \left(\sum_{\omega} (|t_x(\omega)|^2 + |t_y(\omega)|^2) \right) \right] - f k_B T L + f k_B T \sum_{\omega} [|t_x(\omega)|^2 + |t_y(\omega)|^2] \\ &= \frac{k_B T}{2} \left[(f + \xi_p \omega^2) \left(\sum_{\omega} [t_x(\omega)^2 + t_y(\omega)^2] \right) \right] - f k_B T L \end{aligned}$$

Now, in the calculation of the partition function, we need to sum over all possible contours. This is equivalent to sum over all possible values of $t_x(\omega)$ and $t_y(\omega)$. Then making use of the equipartition theorem stating that each quadratic contribution to the Hamiltonian originates an average energy contribution equal to $k_B T/2$, one can thus write

$$\frac{k_B T}{2} \langle (f + \xi_p \omega^2) |t_x(\omega)|^2 \rangle = \frac{k_B T}{2}$$

such that (similarly for t_y)

$$|t_x(\omega)|^2 = \frac{1}{f + \xi_p \omega^2}$$

$$\frac{\langle z \rangle}{L} = 1 - \frac{1}{L} \int_0^L \left(\frac{|t_x|^2 + |t_y|^2}{2} \right) ds = 1 - \frac{1}{L} \sum_{\omega} [|t_x(\omega)|^2 + |t_y(\omega)|^2] = 1 - \frac{1}{L} \sum_{\omega} \frac{2}{f + \xi_p \omega^2}$$

Transforming the sum into an integral (and remembering that $\int_0^\infty \frac{1}{1+x^2} dx = \frac{\pi}{2}$)

$$\sum_{\omega} \frac{1}{f + \xi_p \omega^2} = \frac{L}{2\pi} \int_0^\infty \frac{d\omega}{f + \xi_p \omega^2} = \frac{L}{2\pi} \frac{\pi}{2\sqrt{f\xi_p}}$$

one obtains

$$\frac{\langle z \rangle}{L} = 1 - \frac{2}{L} \frac{L}{2\pi} \frac{\pi}{2\sqrt{f\xi_p}} = 1 - \frac{1}{2} \frac{1}{\sqrt{f\xi_p}} \quad (1)$$

5.3 Asymptotic and interpolation

The results in the low and high force limit can be "merged" in an empirical expression by the following form

$$\xi f = \frac{\langle z \rangle}{L} + \frac{1}{4(1 - \langle z \rangle / L)^2} - \frac{1}{4}$$

Indeed, from Eq. 1,

$$\left(\frac{\langle z \rangle}{L} - 1\right)^2 = \frac{1}{4} \frac{1}{f\xi_p}$$

and

$$f\xi_p = \frac{1}{4} \left(\frac{\langle z \rangle}{L} - 1\right)^{-2}$$

The merged expression, in the limit of $\langle z \rangle \approx L$ is composed only of the divergent term $\frac{1}{4(1-\langle z \rangle/L)^2}$. Instead for $\langle z \rangle \ll L$, we can expand

$$\xi f = \frac{\langle z \rangle}{L} + \frac{1}{4} \left(1 + 2\frac{\langle z \rangle}{L}\right) - \frac{1}{4} = \frac{\langle z \rangle}{L} + \frac{1}{2} \frac{\langle z \rangle}{L} = \frac{3}{2} \frac{\langle z \rangle}{L}$$

recovering the result for small forces.

6 Elastic rod in 3 dimensions

Even though we found that the 1d cooperative chain fit the experimental data slightly better than the one-dimensional ideal chain, still it is clear that this is physically a very unrealistic model: We assumed a chain of straight links, each one joined to the next at an angle of either zero or 180! Really, each basepair in the DNA molecule is pointing in nearly the same direction as its neighbour. We did, however, discover one key fact, that the effective segment length L_0 is tens of nanometers long, much longer than the thickness of a single basepair (0.34 nm). This observation means that we can use the phenomenological elastic energy formula as a more accurate Hamiltonian. Thus, "all" we need to do is to evaluate the partition function, to get the force-extension relation of the three-dimensional elastic rod model. The required analysis was begun in the 1960's by N. Saito and coauthors, then completed in 1994 by J. Marko and E. Siggia, and by A. Vologodskii. (For many more details see Marko & Siggia, 1995.) Unfortunately, the mathematics needed to carry out the program just sketched is somewhat involved. But when faced with such beautifully clean experimental data as those in the figure, and with such an elegant model we really have no choice but to go at least some distance and compare them carefully. We will treat the elastic rod as consisting of N discrete links, each of length l . Our problem is more difficult than the one-dimensional chain because the configuration variable is no longer the discrete, two-valued $\sigma = \pm 1$, but instead the continuous variable \vec{t}_i describing the orientation of link number i . Thus the transfer matrix T has continuous indices.

First of all let's see how we can write the Hamiltonian of the continuum elastic model

$$E = \frac{1}{2} k_B T \int_0^{L_{tube}} ds A \vec{\beta}^2$$

for a chain of N segments of length l

$$\begin{aligned}
H = \sum_i E_i &= \frac{1}{2} k_B T l A \left(\frac{\hat{t}_{i+1} - \hat{t}_i}{l} \right)^2 = \frac{1}{2} k_B T A \frac{1}{l} [2(1 - \hat{t}_{i+1} \cdot \hat{t}_i)] = \frac{1}{2} k_B T A \frac{1}{l} [2(1 - \cos(\Theta_{i,i+1}))] \\
&= \frac{1}{2} k_B T A \frac{1}{l} \Theta_{i,i+1}^2
\end{aligned}$$

where $\Theta_{i,i+1}$ is the angle between two successive versors.

Adding now the force (in the direction of \hat{z})

$$H_{ext} = fl \sum_{i=1}^N \cos \theta_i$$

and then write the partition function as a function of the applied force f

$$\begin{aligned}
Z(f) &= \int d\hat{t}_1 \dots d\hat{t}_N e^{-\beta(H + H_{ext})} \\
Z(f) &= \int d\hat{t}_1 \dots d\hat{t}_N e^{-\frac{A}{2l} \Theta_{i,i+1}^2} e^{\beta fl \sum_i^{N-1} \frac{\cos \theta_i + \cos \theta_{i+1}}{2}} e^{\beta fl \frac{\cos \theta_1 + \cos \theta_N}{2}}
\end{aligned}$$

The $\langle z \rangle$ vs f for this partition function has been evaluated by Marko and Siggia in 1995 with a generalization of the transfer matrix method, resulting in a prediction depending only on one fit parameter A ,

The transfer matrix is now a function

$$T(\hat{t}, \hat{n}) = \exp \left\{ \frac{\beta fl}{2} (\hat{t} \cdot \hat{z} + \hat{n} \cdot \hat{z}) + \frac{A}{l} (\hat{n} \cdot \hat{t} - 1) \right\}$$

The theoretical result can be compared (successfully) with experimental data as shown in the figure

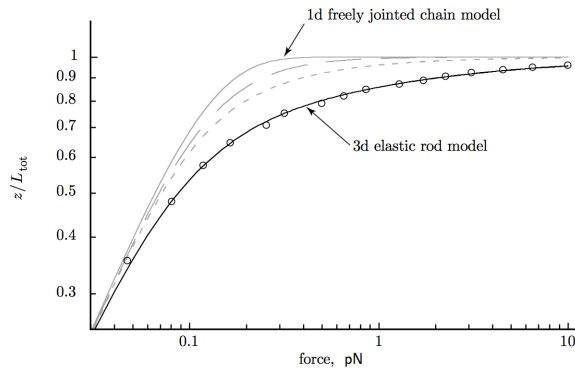


Figure 1: Comparison between experimental data and theoretical predictions at different level of complexity

6.1 Overstretching DNA - D - transition from B-form

Overstretching DNA DNA in its ordinary state adopts a conformation called the "B" form (Figure 2.17), in which the two chains of bases each stack on each other like the steps of a spiral staircase. The sugar-phosphate backbones of the two chains then wind around the center line. That is, the two backbones are far from being straight. The distance traveled along the molecule's axis when we take one step up the staircase is thus considerably shorter than it would be if the backbones were straight. It suggests that pulling on the two ends could alter the equilibrium between B-DNA and some other, "stretched", form, in which the backbones are straightened. Figure 9.3 shows this overstretching transition as region "D" of the graph. At a critical value of the applied force, DNA abandons the linear-elasticity behavior and begins to spend most of its time in a new state, about 60% longer than before. A typical value for f_{crit} in lambda phage DNA is 65 pN. The sharpness of this transition implies that it is highly cooperative.

6.2 Unzipping DNA

Unzipping DNA It is even possible to tear the two strands of DNA apart without breaking them. F. Heslot and coauthors accomplished this in 1997 by attaching the two strands at one end of a DNA duplex to a mechanical stretching apparatus. They and later workers found the average force needed to "unzip" the strands to be about 10-15 pN.

7 Helix-Coil: another application of the Ising model

Some similar approaches can be also applied to describe the helix-coil transition of polypeptide chains. The simplest proposed model is again a one-dimensional chain model in which $\sigma_i = \pm 1$ indicates the state (helix or coil) of the monomer. In the case of a polypeptide, being in helix ($\sigma = 1$) means the presence of an hydrogen-bond between peptide i and peptide $i + 4$. If we assume that the energy E_{coil} of the coil and the energy E_{helix} of the helix conformation are different (a new HB is formed, but some HBs with the solvent are lost), then

$$\Delta E_{bond} \equiv E_{helix} - E_{coil}$$

Associated to this energetic change there is also an entropic contribution ΔS_{bond} , an entropy change that sum up all entropic contributions associated to the cross-over from coil to helix. Indeed, the entropy changes both for the restriction of the molecular orientations in the helix state ($\Delta S < 0$) and for the change in solvent entropy ($\Delta S > 0$). What bias one state respect to the other is the change in free energy

$$\Delta F_{bond} = \Delta E_{bond} - T\Delta S_{bond}$$

In the bio-litterature, $\alpha \equiv -\Delta F_{bond}/2k_B T$ is called the propagation parameter. Similarly, the melting temperature T_m is defined as $T_m \equiv \Delta E_{bond}/\Delta S_{bond}$, such that when $T = T_m$, $\Delta F_{bond} = 0$ and hence both states have the same free-energy.

7.1 Simplest model for melting (non-interacting spins)

In the simplest model, all units are independent. Hence the partition function is easily written as

$$Z = \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_{N-4}=\pm 1} e^{-\beta \sum_{i=1}^{N-4} \Delta F_{bond}(\sigma_i+1)/2}$$

and we can estimate the fraction of monomers in helix conformation as

$$f_{helix} = \frac{1}{N-4} \left\langle \sum_{i=1}^{N-4} (\sigma_i + 1)/2 \right\rangle$$

7.2 Some special energy for initiating the helix: Ising model in 1d again

The formation of the first helix piece in a sequence otherwise random is associated to a different change in free energy, since four different monomers need to acquire a specific orientation to form a double helix. Extending a helical section requires the immobilization of two flexible bonds, but creating a helical section in the first place requires that we immobilize all the bonds between units i and $i + 4$. That is, the polymer must immobilize one full turn of its nascent helix before it gains any of the benefit of forming its first H-bond.

This can be empirically quantified in a quantity $\gamma \equiv \Delta F_{initiation}/4k_B T$, commonly called the cooperativity parameter. Note that this "initiator" energy is requested every time a coil segment turns into a helix segment. If we indicate with σ_i the status of monomer i , then every time $\sigma_i \sigma_{i+1} = -1$ this free-energy cost has to be added. As a result, the partition function of this model is

$$Z = e^{-(N-1)\beta\gamma} \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} e^{-\beta(\alpha \sum_{i=1}^N \sigma_i + \sum_{i=1}^{N-1} \gamma \sigma_i \sigma_{i+1})}$$

To double check this way of expressing the Hamiltonian, consider a case in which all σ_i are -1 , which we could consider the ground state with energy $E_{gs} = -N\alpha$. Now, if we change one site we have a new energy $E_{firstexcitedlevel} = -(N-1)\alpha + \alpha + 4\gamma$, since there are 2 interfaces created by the change $\sigma_i = -1 \rightarrow \sigma_i = +1$ and each interface changes from $\sigma_i \sigma_{i+1} = 1$ to $\sigma_i \sigma_{i+1} = -1$, contributing with e^γ to $e^{-\gamma}$.

The change in energy of creating one helix is thus $E_{firstexcitedlevel} - E_{gs} = 2\alpha + 4\gamma$. The change of sign of another σ next to the interface does produce only the 2α change.

To calculate the degree of helicity

$$\langle \sigma \rangle \equiv \frac{1}{N} \left\langle \sum_{i=1}^N \sigma_i \right\rangle$$

it is now sufficient to calculate

$$\langle \sigma \rangle = \frac{1}{N} \frac{d}{d\alpha} \ln Z(\alpha)$$

Since the partition function is identical to the one we have studied with the transfer matrix method previously we can immediately conclude that

$$\langle \sigma \rangle \sim \frac{\sinh \alpha}{\sqrt{\sinh^2 \alpha + e^{-4\gamma}}}$$

This expression properly fits the data for very long polypeptide. For short polypeptide one can not limit the calculation to the largest eigenvalues. One needs to keep both α_+ and α_- to account for end-effects.

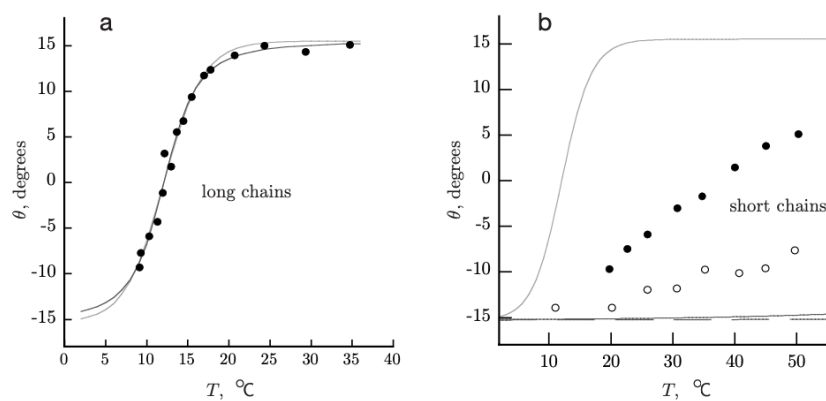


Figure 9.8: (Experimental data with fits.) Effect of changing the degree of cooperativity. (a) *Dots*: The same long-chain experimental data as Figure 9.6. *Dark gray curve*: best fit to the data holding the cooperativity parameter γ fixed to the value 2.9 (too much cooperativity). The curve was obtained by setting $\Delta E_{\text{bond}} = 0.20k_{\text{B}}T$, with the other three parameters the same as in the fit shown in Figure 9.6. *Light gray curve*: best fit to the data fixing $\gamma = 0$ (no cooperativity). Here ΔE_{bond} was taken to be $57k_{\text{B}}T$. (b) *Solid and open dots*: The same medium- and short-chain data as in Figure 9.6. The curves show the unsuccessful predictions of the same two alternative models shown in panel (a). *Top curve*: the model with no cooperativity gives no length dependence at all. *Lower curves*: in the model with too much cooperativity, short chains are influenced too much by their ends, and so stay overwhelmingly in the random-coil state. Solid line, $N = 46$; dashed line, $N = 26$.