0.1 Zipper model

Lecture 9.
Friday 8th November, 2019.
Compiled: Thursday 15th September, 2022.

The Zipper model is an unusually simple and interesting member of the class of one dimensional systems which exhibit a phase transition. It is a model introduced by Kittel [**?**] to describe oligomers undergoing *denaturation transition*. Simplest model of DNA thermal denaturation transition (no bubbles). Better model for the denaturation of short oligomers.

The hypothesis are: the binding energy between two bases located at the end of the molecule is smaller than the one for pairs away from the ends. The unbinding starts and develops from the ends as a *zipper*.

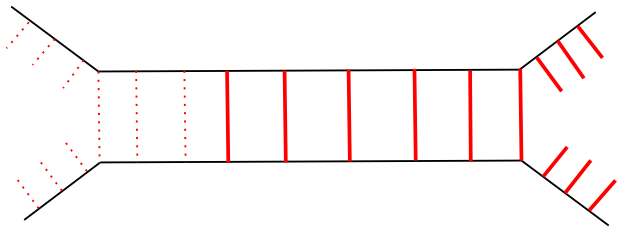

Figure 1: Sequential unzipping from the ends.

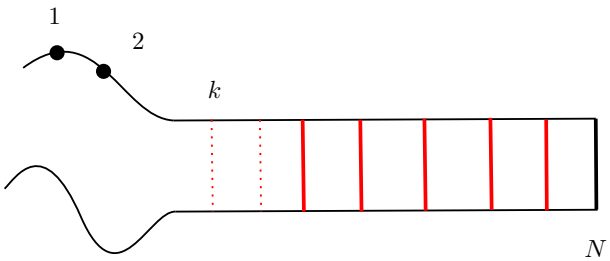

Figure 2: Open and closed links in a single-ended zipper.

In this denaturation transition we do not allow bubbles. Let us consider first the single-ended zipper, i.e. a molecular zipper of N parallel links that can be opened only from one end as in Figure 2. The single-ended zipper is simpler than any related problem which has been treated, and it offers a good way to introduce a biophysics example into a course of statistical mechanics.

If the first k bonds (or links) are open (unbounded pairs) the energy to open the $k+1$ is ε_0. Note that if at least one of the previous k bond is closed the energy needed to open the $k+1$ band is infinite! We specify further that the last link, $k = N$, cannot be opened; this minor features serves only to distinguish one end from the other, and we shall say that the zipper is open when $N - 1$ links are open.

We suppose that there are G orientations which each open link can assume: that is, the open state of a link is G-fold degenerate, corresponding to the rotational freedom of a link. Hence, once a bond is open it can orient itself in G different ways. In other words, there is an entropy

$$S_0 = k_B \log G \tag{1}$$

associated to each open band. In the problem of DNA the empirical value of G may be of the order of 10^4.

Partition function

Let us suppose that the energy required to open the first k links is ε_0. If k links are open, the degeneracy is G^k, and the contribution of this configuration to the partition function is

$$G^k e^{-k\varepsilon_0/k_BT}$$

By summing over the possible values of k, the partition function is

$$Z_N(T, G, \varepsilon_0) = \sum_{k=0}^{N-1} G^k e^{-k\varepsilon_0/k_BT} = \sum_{k=0}^{N-1} e^{k(S_0T-\varepsilon_0)/k_BT} \tag{2}$$

Let us call

$$\chi \equiv Ge^{-\varepsilon_0/k_BT} \tag{3}$$

and simplify the previous expression

$$Z_N = \sum_{k=0}^{N-1} \chi^k = \frac{1-\chi^N}{1-\chi} \tag{4}$$

We see immediately there is a single pole singularity.

The free energy is

$$F_N = -k_BT \ln Z_N = -k_BT \ln \left[\frac{1-\chi^N}{1-\chi}\right] \tag{5}$$

We can now compute some observables of interest. The correct procedure is to evaluate thermodynamic quantities for finite N and then to examine the limit $N \to \infty$.

Calculate average number of open links

The thermodynamic average number of open links is

$$\langle k \rangle_N \equiv \frac{\sum_{k=0}^{N-1} k\chi^k}{\sum_{k=0}^{N-1} \chi^k} = \chi \frac{\mathrm{d}}{\mathrm{d}\chi} \ln Z_N = \frac{N\chi^N}{\chi^N - 1} - \frac{\chi}{\chi - 1} \tag{6}$$

The function is plotted in Figure 3. We examine the behaviour of $\langle k \rangle_N$in the vicinity of the point $\chi_c = 1$ for which the denominators are equal to zero (pole).

Remark. In this model, we consider the average number of open links instead of the magnetization.

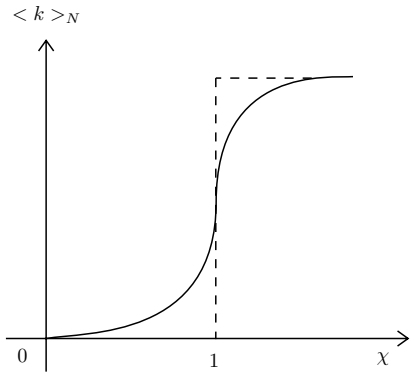

Figure 3: Thermodynamic average number of open links in a single-ended zipper of N links.

In order to analyze what happens near 1, we expand $\chi \equiv 1 + \varepsilon$:

$$\begin{aligned}
\log Z_N(\chi) &= \log\left[\frac{1-(1+\varepsilon)^N}{1-(1+\varepsilon)}\right] \\
&= \log\left[\frac{1-(1+\varepsilon N + \frac{N(N-1)}{2!}\varepsilon^2 + \frac{N(N-1)(N-2)}{3!}\varepsilon^3 + O(\varepsilon^4))}{\varepsilon}\right] \\
&= \log\left[N + \frac{N(N-1)}{2}\varepsilon + \frac{N(N-1)(N-2)}{6}\varepsilon^2 + \dots\right] \\
&= \log N + \log\left[1 + \frac{N-1}{2}\varepsilon + \frac{(N-1)(N-2)}{6}\varepsilon^2\right] \\
&= \log N + \log\left[1 + \frac{N\varepsilon}{2} + \frac{N^2\varepsilon^2}{6} + \dots\right] \\
&= \log N + \left(\frac{N\varepsilon}{2} + \frac{N^2\varepsilon^2}{6} + \dots\right) + \frac{1}{2}\left(\frac{N\varepsilon}{2} + \frac{N^2\varepsilon^2}{6} + \dots\right)^2 + \dots \\
&= \log N + \frac{N\varepsilon}{2} + \frac{N^2\varepsilon^2}{24} + \dots
\end{aligned} \tag{7}$$

By doing the same for $\langle k\rangle_N = \frac{N\chi^N}{\chi^N-1} - \frac{\chi}{\chi-1}$, one gets

$$\langle k\rangle_N = \frac{N}{2}\left(1 + \frac{N\varepsilon}{6} - \frac{N^3\varepsilon^3}{360} + \dots\right) \tag{8}$$

this is true for $N \gg 1, \varepsilon \ll 1$.

At the transition point $\chi_c = 1$, where $\varepsilon = 0$:

$$\langle k\rangle_N \simeq \frac{N}{2}$$

We can define the variation (slope per site) as a response function (the derivative with respect to the parameter):

$$\frac{1}{N}\frac{\mathrm{d}\langle k\rangle}{\mathrm{d}\varepsilon} \simeq \frac{N}{12} - \frac{N^3\varepsilon^3}{240} + \dots \tag{9}$$

is a maximum at $\varepsilon = 0$, and the slope at the transition point becomes infinite as $N \to \infty$ (linearly). The response function diverges linearly to N, this is a good signal that we have a transition.

Transition temperature

The temperature T_c corresponding to the pole $\chi_c = 1$ is given by

$$Ge^{-\varepsilon_0/k_BT_c} = 1$$

Hence,

$$T_c = \frac{\varepsilon_0}{k_B \log G} \tag{10}$$

Note that as $G \to 1$, $T_c \to 0$. For $G = 1$ there is no solution at a finite temperature and hence the model does not display a phase transition for any finite T! This is telling you that if $G = 1$ what is important it is the energy, you have no entropy as disorder. At that point everything can happen.

There is a finite transition temperature if $G > 1$. One might perhaps argue that the model is now not strictly one-dimensional, for the degeneracy G arises from the rotational freedom of an open link.

Remark. Despite the model is 1-dim, for $G > 1$ there is a phase transition. This is due to two contributions:

1. Existence of forbidden configuration (infinite energy). It is a necessary condition, but not sufficient, for a phase transition in $d = 1$ with finite range interactions.

2. A further requirement may be that the degeneracy of the excited state (G) of a structural unit must be higher than the degeneracy of the ground state[1].

Unwinding from both ends

When the zipper is allowed to unwind from both ends, there are $k+1$ ways in which a total of k links may be opened, so that the partition function for a double-ended zipper of N links is

$$Z_N(T, G, \varepsilon_0) = \sum_{k=0}^{N-1} (k+1) G^k e^{-k\varepsilon_0/k_B T} \tag{11}$$

and to this should be added a term for the state of N open links. This terminal term for a simple zipper is $G^N \exp(-N\varepsilon_0/k_B T)$.

0.1.1 Transfer matrix method for the Zipper model

The idea is: we want to map the Zipper model to an Ising model. The spin like model consists on associating to each bond a spin such that $S_i = 0$ if the i-esim bond is *closed* , while $S_i = 1, \ldots, G$ if the i-esim bond is *open* with G possible orientations. Therefore,

- Case: $S_i \neq 0$ open. We have two subcases:
  - S_{i-1} open: $S_{i-1} \neq 0 \Rightarrow E(S_i \neq 0 | S_{i-1} \neq 0) = \varepsilon_0$.
  - S_{i-1} closed: $S_{i-1} = 0 \Rightarrow E(S_i \neq 0 | S_{i-1} = 0) = \varepsilon_0 + V_0$
- Case: $S_i = 0$ closed. We have $E(S_i = 0) = 0$ irrespective of S_{i-1}.

Hence, considering all these cases, the energy results

$$E(S_i, S_{i-1}) = (\varepsilon_0 + V_0 \delta_{S_{i-1},0})(1 - \delta_{S_i,0}) \tag{12}$$

The boundary condition is $S_N = 0$ (always closed). The full Hamiltonian of the model can be written as (it could be also a function of delta, but it is not a problem):

$$\mathcal{H}_N = \varepsilon_0(1 - \delta_{S_1,0}) + \sum_{i=2}^{N-1} (\varepsilon_0 + V_0 \delta_{S_{i-1},0})(1 - \delta_{S_i,0}) \tag{13}$$

The Kittel's version is obtained by assuming $V_0 = \infty$.

The partition function is

$$Z_N = \sum_{\{S\}} \exp(-\beta \mathcal{H}_N)$$

In order to implement the transfer matrix formalism we rewrite Z_N as follows

$$Z_N = \sum_{\{S\}} e^{-\beta\varepsilon_0(1-\delta_{S_1,0})} \prod_{i=1}^{N-2} e^{-\beta\varepsilon_0(1-\delta_{S_{i+1},0})} \Big[1 + (e^{-\beta V_0} - 1)\delta_{S_i,0}(1 - \delta_{S_{i+1},0})\Big] \tag{14}$$

[1] In the mean-field approximation no transition can occur if the degeneracy of the ground state is higher than that of the excited state.

Let us consider the Kittel model, the condition $V_0 = \infty$ implies $\exp(-\beta V_0) = 0$. Hence, we can define the transfer matrix as

$$\mathbb{T} = \{\langle S|\,\mathbb{T}\,\big|S'\big\rangle \equiv t_{S,S'}\} \tag{15}$$

where

$$t_{S,S'} = e^{-\beta\varepsilon_0(1-\delta_{S',0})}[1 - \delta_{S,0}(1-\delta_{S',0})] \tag{16}$$

or in matrix form

$$\mathbb{T} = \begin{bmatrix} 1 & 0 & \ldots\ldots 0 \\ 1 & a & \ldots\ldots a \\ \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots \\ 1 & a & \ldots\ldots a \end{bmatrix}, \qquad \text{with } a \equiv e^{-\beta\varepsilon_0}$$

The first think to notice is that the constraint that the bond S_{i+1} cannot be open if bond S_i is closed ($S_i = 0$) yields the null entries in the first row of $\mathbb{T}$. This violates the hypothesis of the Perron-Frobenius theorem!

The matrix $\mathbb{T}$ has three different eigenvalues

$$\lambda_1 = Ga, \quad \lambda_2 = 1, \quad \lambda_3 = 0 \tag{17}$$

The partition function can be written as

$$Z_N = (1, a, \ldots, a)\mathbb{T}^{N-2}\begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix} \tag{18}$$

Moreover, we have

$$\lambda_1 \to \vec{\mathbf{v}}_1 = \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 1 \end{pmatrix}, \qquad \lambda_2 \to \vec{\mathbf{v}}_2 = \begin{pmatrix} 1-Ga \\ 1 \\ \vdots \\ 1 \end{pmatrix}$$

and we can then write

$$\begin{pmatrix} 1 \\ a \\ \vdots \\ a \end{pmatrix} = \frac{a(1-Ga)-1}{1-Ga}\vec{\mathbf{v}}_1 + \frac{1}{1-Ga}\vec{\mathbf{v}}_2$$

$$\begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix} = \frac{-Ga}{1-Ga}\vec{\mathbf{v}}_1 + \frac{1}{1-Ga}\vec{\mathbf{v}}_2$$

Therefore,

$$Z_N = \frac{1-(Ga)^N}{1-Ga} = \frac{1-(Ge^{-\beta\varepsilon_0})^N}{1-Ge^{-\beta\varepsilon_0}} = \frac{1}{1-Ge^{-\beta\varepsilon_0}}(-\lambda_1^N + \lambda_2^N) \tag{20}$$

Since in the thermodynamic limit only the contribution of the largest eigenvalue matters for f_b we have

$$f_b = -k_B T \ln \max(\lambda_1, \lambda_2)$$

Remark. Given that the λ_1 and λ_2 are positive, analytic function of T ($\lambda_1 = Ga, \lambda_2 = 1$). In order to have a phase transition (i.e. non analiticity of f_b) the two eigenvalues must cross for a given value of T. It is true if and only if:

$$Ga_c = 1 \Leftrightarrow Ge^{-\beta_c \varepsilon_0} = 1 \Leftrightarrow T_c = \frac{\varepsilon_0}{k_B \ln G} \tag{21}$$

that agree with previous calculation (see Eq.(10)).

0.2 Transfer matrix for $2-dim$ Ising

The two-dimensional Ising model for a system of interacting spins on a square lattice is one of the very few nontrivial many-body problems that is exactly soluble and shows a phase transition [**?**]. The exact solution in the absence of an external magnetic field ($H = 0$) was first given almost eighty years ago in a famous paper by Onsager [**?**], using the theory of Lie algebras. In particular, from Onsager's solution we can see that already in two dimensions an Ising model can exhibit phase transitions, showing a non null spontaneous magnetization for temperatures low enough.

Let us therefore consider a two-dimensional Ising model, defined on a lattice made of N rows and M columns, as in Figure 4. We apply periodic boundary conditions to the system in both directions (geometrically, this can be thought of as defining the model on a torus), and we consider only nearest neighbour interactions. The spin in a site is identified by $S_{\text{site}} = S_{m,n}$.

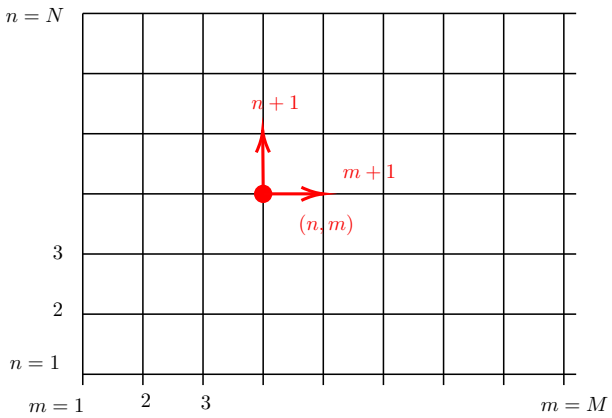

Figure 4: 2-dimensional Ising lattice of N rows and M columns.

We consider a set of spin arranged on a square lattice, interacting only with nearest neighbors and with a magnetic field $H \neq 0$. The reduced Hamiltonian of the system will be:

$$\begin{aligned} -\beta\mathcal{H}_\Omega(\{S\}) &= K\sum_{\langle ij\rangle} S_i S_j + h\sum_i S_i \\ &= K\sum_{n=1}^{N}\sum_{m=1}^{M}(S_{m,n}S_{m+1,n} + S_{m,n}S_{m,n+1}) + h\sum_{n=1}^{N}\sum_{m=1}^{M} S_{m,n} \end{aligned}$$

This can be rewritten as follows:

$$-\beta\mathcal{H}_\Omega(\{S\}) = \sum_{m=1}^{M}\left[E_2(\mu_m, \mu_{m+1}) + E_1(\mu_m)\right] \tag{22}$$

where

$$E_1(\mu_m, h) = K\sum_{n=1}^{N} S_{m,n}S_{m,n+1} + h\sum_{n=1}^{N} S_{m,n} \tag{23a}$$

$$E_2(\mu_m, \mu_{m+1}, h) = K\sum_{n=1}^{N} S_{m,n}S_{m+1,n} \tag{23b}$$

the first equation is the one body interaction, while the second equation represents the interaction between nearest neighbours columns (two body interaction).

Moreover, μ is a N dimensional vector; in particular, each μ_m represents the set of N spins along column m:

$$\mu_m = \{S_{m,1}, S_{m,2}, \ldots, S_{m,N}\} \tag{24}$$

We can write a transfer matrix between columns, permitting to transfer along the m. As for the $d = 1$ case we can make the Hamiltonian symmetric:

$$-\beta\mathcal{H}_\Omega(\{S\}) = \sum_{m=1}^{M}\left[E_2(\mu_m, \mu_{m+1}) + \frac{1}{2}(E_1(\mu_m) + E_1(\mu_{m+1}))\right] \tag{25}$$

We have

$$\begin{aligned} Z_{N,M} &= \sum_{\mu_1}\cdots\sum_{\mu_M}\exp\left[\sum_{m=1}^{M}\left[E_2(\mu_m, \mu_{m+1}) + \frac{1}{2}(E_1(\mu_m) + E_1(\mu_{m+1}))\right]\right] \\ &= \sum_{\mu_1}\cdots\sum_{\mu_M}\left[\prod_{m=1}^{M}\exp\left[E_2(\mu_m, \mu_{m+1}) + \frac{1}{2}(E_1(\mu_m) + E_1(\mu_{m+1}))\right]\right] \\ &= \sum_{\mu_1}\cdots\sum_{\mu_M}\langle\mu_1|\,\mathbb{T}\,|\mu_2\rangle\langle\mu_2|\,\mathbb{T}\,|\mu_3\rangle\ldots\langle\mu_N|\,\mathbb{T}\,|\mu_1\rangle \end{aligned} \tag{26}$$

where

$$\langle\mu_m|\,\mathbb{T}\,|\mu_{m+1}\rangle = \exp\left[E_2(\mu_m, \mu_{m+1}) + \frac{1}{2}(E_1(\mu_m) + E_1(\mu_{m+1}))\right] \tag{27}$$

Remark. In the 2x2 transfer matrix in the 1-dim case we have two possible values. Now, we have to do the same in principle, but we have to do for all of the (24).

Remark. $\mathbb{T}$ is a matrix of dimension $2^N \times 2^N$, hence, in the thermodynamic limit is an infinite matrix (violation of Perron-Frobenius).

If we can find the set of eigenvalues $\lambda_+ > \lambda_- \geq \lambda_1 \geq \cdots \geq \lambda_{2^N-2}$ of the $2^N \times 2^N$ matrix, we have

$$Z_{N,M} = \mathrm{Tr}\big(\mathbb{T}^M\big) = \sum_{i=\pm,1}^{2^N-2}\lambda_i^M(N) \tag{28}$$

To find the eigenvalues of $\mathbb{T}$ given by (27) is highly non trivial. The big problem it is that in the thermodynamic limit is that the dimension of the transfer matrix goes to infinity, then it is difficult to be diagonalized. This was first achieved by Onsanger in 1944, as said, for the case $H = 0$ and in the $N \to \infty$ limit. Onsanger has shown that the free energy of the system is given by

$$f_b(T) = -k_BT\log\left(2\cosh(2\beta J)\right) - \frac{k_BT}{2\pi}\int_0^{2\pi}\log\left[\frac{1}{2}\left(1 + \sqrt{1 - g^2\sin^2(\Phi)}\right)\right]\mathrm{d}\Phi \tag{29}$$

where

$$g = \frac{2}{\cosh(2\beta J)\coth(2\beta J)}$$

and also that the magnetization is:

$$m = \begin{cases} \left[1 - \sinh^{-4}(2\beta J)\right]^{1/8} & T < T_c \\ 0 & T > T_c \end{cases} \tag{30}$$

where T_c is the temperature given by the condition

$$2\tanh^2\left(\frac{2J}{k_B T_c}\right) = 1$$

which yields the numeric result:

$$\Rightarrow T_c \simeq 2,264 J/k_B \neq 0$$

hence, we have a phase transition at a critical temperature T_c different from 0!

Onsager also showed that the critical exponents of this model are:

$$\alpha = 0, \quad \beta = \frac{1}{8}, \quad \gamma = \frac{7}{4}$$

where $\alpha = 0$ because the specific heat diverges logarithmically for $T \sim T_c$:

$$c \propto A\left[-\ln\left(1 - \frac{T}{T_c}\right) + B\right]$$

It means that the specific heat displays at the transition a logarithmic divergence (no power law!).