Tutorial 5, Statistical Mechanics: Concepts and applications
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Tutorial exercises

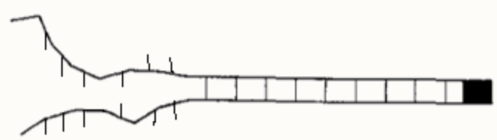
I. CAN 1D CLASSICAL SYSTEMS HAVE PHASE TRANSITIONS?

1. **Molecular zipper** *[Source: C. Kittel, American Journal of Physics* **37***, 917 (1969)]*

   [The model]

   Kittel's toy model for DNA-melting:
   DNA melting refers to the dissociation of the two strands of the double helix by an increase of temperature or change of pH.

   Suppose a zipper in a heat bath (with temperature T) has N links. Each link can either be closed with energy 0 or open with energy ϵ. However, the zipper can only unzip from one end. Thus, link number n can only open if all links before it are also open $(1, 2, ..., n-1)$. The final link can never be open (shown as a thick black square on the right side of the diagram below). This prevents the zipper from disconnecting and drifting apart. When a link is closed it can only be in one configuration. However, when the link is open, the two pieces of the link are free to spin around and assume G different positions. Thus, the open link has a degeneracy of G.



   (a) Let the number of links be N. Compute the free energy.

   : *The energy corresponding to n open links is $n\epsilon$. The number of configurations for given n is G^n. The partition function is therefore given by*

$$Z = \sum_{n=0}^{N-1} G^n e^{-\beta n \epsilon} = \frac{1-(Ge^{-\beta\epsilon})^N}{1-Ge^{-\beta\epsilon}} \,. \tag{1}$$

   The free energy reads as

$$F = -\beta^{-1} \log Z = \beta^{-1} \log \frac{1-Ge^{-\beta\epsilon}}{1-(Ge^{-\beta\epsilon})^N} \,. \tag{2}$$

   (b) Simplify the expression in the thermodynamic limit $N \to \infty$. Is the free energy an analytic function of $\beta = 1/T$? What is the difference between $G = 1$ and $G > 1$ cases?

: *If $Ge^{-\beta\epsilon} > 1$ then $(Ge^{-\beta\epsilon})^N \gg 1$, and hence*

$$F \xrightarrow{1\ll N \ (Ge^{-\beta\epsilon}>1)} -\beta^{-1} N \log[Ge^{-\beta\epsilon}] + \beta^{-1}\log[Ge^{-\beta\epsilon} - 1] + O(G^{-N} e^{N\beta\epsilon})\,. \tag{3}$$

If instead $Ge^{-\beta\epsilon} < 1$ then$(Ge^{-\beta\epsilon})^N \ll 1$, and hence

$$F \xrightarrow{1\ll N \ (Ge^{-\beta\epsilon}<1)} \beta^{-1}\log[1 - Ge^{-\beta\epsilon}] + O(G^N e^{-N\beta\epsilon})\,. \tag{4}$$

If there is only one configuration then $Ge^{-\beta\epsilon} = e^{-\beta\epsilon} < 1$ for any finite temperature and the free energy is an analytic function of the temperature. On the other hand, for $G > 1$ there is a critical temperature equal to $kT_c = \frac{\epsilon}{\log G}$ where the free energy is not smooth.

(c) Compute the average number open links at temperature T.

: *The average number open links $\langle n\rangle$ is equal to the average energy $\langle E\rangle$ per unit ϵ: $\langle n\rangle = \frac{\langle E\rangle}{\epsilon}$. Since $\langle E\rangle = -\partial_\beta \log Z$ we obtain*

$$\langle n\rangle = \frac{1}{\epsilon}\partial_\beta \log\frac{1 - Ge^{-\beta\epsilon}}{1-(Ge^{-\beta\epsilon})^N} =$$
$$\frac{1}{G^{-1}e^{\beta\epsilon}-1} - \frac{N}{G^{-N}e^{N\beta\epsilon}-1} \to \frac{1}{G^{-1}e^{\beta\epsilon}-1} + \begin{cases} N + O(NG^{-N}e^{N\beta\epsilon}) & Ge^{-\beta\epsilon} > 1 \\ O(NG^N e^{-N\beta\epsilon}) & Ge^{-\beta\epsilon} < 1\,. \end{cases} \tag{5}$$

In conclusion, at temperature higher than the critical one most of the links are open; at lower temperature most of them are close.

(d) (Optional) Let us now assume that an open link can take a given configuration $g_0 \in 1,\dots,G$ only if there are no other open links with $g < g_0$. Is there a phase transition? If yes, what is the critical temperature?

: *Let us denote the number of open links by $x_{m,j} = mG + j$, where $m = 0, 1, \dots \lfloor\frac{N-1}{G}\rfloor$ and $0 = 1, \dots, G-1$. The number of configuration that the $x_{m,j}$-th link can take is $C_{m,j} = G - j + 1$. The degeneracy $g_{m,j}$ of the $x_{m,j}$-th energy level is the product of all the $C_{m,j}$ for the links opened at that moment*

$$g_{m,j} = \Big(\prod_{m'=0}^{m}\prod_{j'=1}^{G} C_{m',j'}\Big)\Big(\prod_{j'=1}^{j} C_{m,j'}\Big) = \Big(\prod_{m'=0}^{m}\prod_{j'=1}^{G}(G-j'+1)\Big)\Big(\prod_{j'=1}^{j}(G-j+1)\Big) = \frac{G!^{m+1}}{(G-j)!} \tag{6}$$

The partition function is therefore given by

$$Z = \sum_{m=0}^{\lfloor\frac{N-1}{G}\rfloor}\sum_{j=1}^{G} g_{m,j}e^{-\beta\epsilon x_{m,j}} = \sum_{m=0}^{\lfloor\frac{N-1}{G}\rfloor}\sum_{j=1}^{G}\frac{G!^{m+1}}{(G-j)!}e^{-\beta\epsilon(mG+j)} = \sum_{j=1}^{G}\frac{G!e^{-\beta\epsilon j}}{(G-j)!}\frac{1-(G!e^{-\beta\epsilon G})^M}{1-G!e^{-\beta\epsilon G}}\,, \tag{7}$$

*where $M = \lfloor\frac{N-1}{G}\rfloor + 1$. The first sum is an analytic function of β and contributes to the free energy with an analytic additive term. The remaining part is equivalent to (**??**), but now $G!e^{-\beta\epsilon G}$ takes the place of $Ge^{-\beta\epsilon}$. In conclusion, the critical temperature is the solution of*

$$G!e^{-\beta_c\epsilon G} = 1\,, \tag{8}$$

that is to say

$$kT_c = \frac{G}{\log(G!)}\epsilon \sim \frac{\epsilon}{\log(G/e)} \tag{9}$$

2. **Ising model in a staggered field.**

Reminder: In physics, transfer matrices appear in diverse contexts. In classical statistical physics they are employed to compute partition functions. The basic idea is to construct a matrix $T(\beta)$ such that the partition function can be written in the form

$$Z = \mathrm{Tr}[T^N(\beta)W]\,, \tag{10}$$

where W is a matrix that depends on the boundary conditions and N is an integer that in one dimensional chains is proportional to the number of sites. For the sake of simplicity, let us assume that $T(\beta)$ is symmetric and therefore is diagonalizable. We have

$$F = -\beta^{-1}\log Z = -\beta^{-1}\log\left(\sum_{i=1}^{n}\lambda_i^N(\beta)\mathrm{Tr}[\Pi_i W]\right) = -\beta^{-1}N\log\left(\lambda_{\max}(\beta)\right) + O(N^0) \tag{11}$$

where n is the dimensionality of the transfer matrix (essentially the number of states each constituent can assume), $\lambda_i(\beta)$ are the eigenvalues of $T(\beta)$ and Π_i the corresponding projectors on the eigenspace (*i.e.*, if $\vec{v}_i$ is an eigenvector, $[\Pi_i]_{\ell n} = [\vec{v}_i]_\ell[\vec{v}_i]_n$).

Reminder: A matrix M is reducible if and only if it can be placed into block upper-triangular form by simultaneous row/column permutations, i.e.

$$P^t M P = \begin{pmatrix} X & Y \\ 0 & Z \end{pmatrix}\,. \tag{12}$$

where P is a permutation matrix and X and Z are square matrices. Notice that if all the elements of the matrix are non-zero then the matrix is irreducible.

Reminder: Phase transitions are generally forbidden in one dimensional systems by virtue of the following theorems:

- **Theorem 1**: *[Perron-Frobenius] Let A be an irreducible matrix with non-negative elements; the maximum eigenvalue is positive and non-degenerate.*
- **Theorem 2**: *If $T(\beta)$ is a complex matrix with elements analytic functions of β, the eigenvalues are analytic functions of β with only algebraic singularities localized at the points where eigenvalues split or coalesce (eigenvalue crossings).*

If the transfer matrix $T(\beta)$ is finite-dimensional and does not have zeros then it is irreducible and if all the elements are positive (theorem 1) there are no eigenvalue crossings and therefore $f(\beta) = -N\log\lambda_{max}(\beta)$ is an analytic function of β for all $\beta \geq 0$ (theorem 2). Since the elements of the transfer matrix are generally the exponentials of real numbers (*i.e.* strictly positive number), there can not be phase transitions at finite temperature. Can you think of any exceptions? In what circumstances would there be zeros present in the transfer matrix?

The model: We consider a classical Ising model in a staggered field:

$$E(\{s\}) = -J\sum_{\ell=1}^{L} s_\ell s_{\ell+1} - (-1)^\ell h s_\ell\,. \tag{13}$$

Here s_ℓ are classical spin variables $s_\ell \in \{-1, 1\}$, J has the dimensions of an energy, and h is the absolute value of the staggered field.

(a) Write down a transfer matrix for this model.

: *We assume that L is even. The partition function reads as*

$$Z = \sum_{\{s\}_L} \exp\Big(\beta J \sum_{\ell=1}^{L} s_\ell s_{\ell+1} + (-1)^\ell h s_\ell\Big) =$$
$$\sum_{\{s\}_L} \prod_{\ell=1}^{L/2} \exp\Big(\beta(J s_{2\ell-1} s_{2\ell} - h s_{2\ell-1})\Big) \exp\Big(\beta(J s_{2\ell} s_{2\ell+1} + h s_{2\ell})\Big) =$$
$$\sum_{\{s\}_L} \Big(\prod_{\ell=1}^{L/2-1} \mathcal{L}_{s_{2\ell-1}s_{2\ell}} \mathcal{M}_{s_{2\ell}s_{2\ell+1}} \Big) \mathcal{L}_{s_{L-1}s_L} \exp\Big(\beta(J s_L s_{L+1} + h s_L)\Big) , \quad (14)$$

where

$$\mathcal{L}_{ss'} = \exp\Big(\beta(Jss' - hs)\Big) \qquad \mathcal{M}_{ss'} = \exp\Big(\beta(Jss' + hs)\Big) . \quad (15)$$

A transfer matrix for this model is therefore

$$T = \mathcal{L}\mathcal{M} = \begin{pmatrix} e^{\beta(J-h)} & e^{-\beta(J+h)} \\ e^{-\beta(J-h)} & e^{\beta(J+h)} \end{pmatrix} \begin{pmatrix} e^{\beta(J+h)} & e^{-\beta(J-h)} \\ e^{-\beta(J+h)} & e^{\beta(J-h)} \end{pmatrix} =$$
$$\begin{pmatrix} e^{2\beta J} + e^{-2\beta(J+h)} & 1 + e^{-2\beta h} \\ 1 + e^{2\beta h} & e^{2\beta J} + e^{-2\beta(J-h)} \end{pmatrix} \quad (16)$$

(b) Show the formal structure of the partition function both for periodic ($s_{L+1} \equiv s_1$) and open ($s_{L+1} \equiv 0$) boundary conditions.

: *If periodic boundary conditions are imposed,* (**??**) *can be written as*

$$Z = \mathrm{Tr}[T^{L/2}] . \quad (17)$$

If instead $s_{L+1} \equiv 0$ we obtain

$$Z = \vec{L}^t T^{L/2-1} \mathcal{L} \vec{R} , \quad (18)$$

where

$$\vec{L} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \vec{R} = \begin{pmatrix} e^{\beta J h} \\ e^{-\beta J h} \end{pmatrix} \quad (19)$$

(c) Are there phase transitions at finite temperature?

: *There can not be phase transitions because the transfer matrix is finite-dimensional and has strictly positive eigenvalues.*

3. **Generalized Kittel's model** *[Source: J. A. Cuesta and A. Sánchez, J. Stat. Phys.* **115**, *869 (2004)]*

The model: our model can be described by the following Hamiltonian

$$H = \varepsilon(1-\delta_{s_1 0}) + \sum_{i=1}^{N-2} (\varepsilon + \Lambda\delta_{s_i 0})(1-\delta_{s_{i+1}0}) \tag{20}$$

where label $s_i = 0, 1, ..., G$ signifies the configuration of the ith link (if the i-th link is closed then $s_i = 0$, otherwise the link is in the $s_i \in (1, \dots, G)$-th state). Roughly, you can think of it as a generalized version of problem 1, where it is now possible to open links from any position in the zipper (not just the open end) at the cost of energy Λ. Λ is an auxiliary variable that is used to parametrize the forbidden configurations of the original problem.

(a) In what limit do you get the original problem 1 back?

: *We do in the limit $\Lambda \to \infty$.*

(b) Let the number of links be $N-1$. Write down a transfer matrix for the model.

: *We have the set of $N-1$ variables $x_j = 0, 1, \dots, G$ with the following meaning: if the j-th link is closed then $x_j = 0$, otherwise the link is in the $x_j \in (1, \dots, G)$-th state. The energy of a given configuration $\{x_1, \dots, x_{N-1}\}$ can be recast in the following (symmetric) form*

$$E_{\{x_1,\dots,x_{N-1}\}} = (N-1)\epsilon + \frac{\Lambda-\epsilon}{2}\delta_{x_1 0} - \frac{\Lambda+\epsilon}{2}\delta_{x_{N-1}0} + \sum_{i=1}^{N-2}\Big[\frac{\Lambda-\epsilon}{2}(\delta_{x_i 0}+\delta_{x_{i+1}0}) - \Lambda\delta_{x_i 0}\delta_{x_{i+1}0}\Big] \tag{21}$$

The first term $(N-1)\epsilon$ is constant and hence irrelevant; by neglecting it, the partition function reads as

$$Z = \sum_{\{x_1,\dots,x_{N-1}\}} \exp\Big(-\beta\frac{\Lambda-\epsilon}{2}\delta_{x_1 0}\Big) \prod_{i=1}^{N-2} \exp\Big(-\beta\frac{\Lambda-\epsilon}{2}(\delta_{x_i 0}+\delta_{x_{i+1}0}) + \beta\Lambda\delta_{x_i 0}\delta_{x_{i+1}0}\Big) \times \exp\Big(\beta\frac{\Lambda+\epsilon}{2}\delta_{x_{N-1}0}\Big) = \vec{L}^t T^{N-2}(\beta)\vec{R}\,, \tag{22}$$

where (the vectors have dimension $G+1$, the first element corresponding to $x=0$)

$$\vec{L}^t = \begin{pmatrix}\exp(-\beta\frac{\Lambda-\epsilon}{2}) & 1 & \cdots & 1\end{pmatrix} \qquad \vec{R}^t = \begin{pmatrix}\exp(\beta\frac{\Lambda+\epsilon}{2}) & 1 & \cdots & 1\end{pmatrix}, \tag{23}$$

and

$$[T(\beta)]_{xx'} = \exp\Big(-\beta\frac{\Lambda-\epsilon}{2}(\delta_{x0}+\delta_{x'0}) + \beta\Lambda\delta_{x0}\delta_{x'0}\Big) \quad , \quad x, x' = 0, 1, \dots, G \tag{24}$$

(c) Compute the free energy in the thermodynamic limit. Is it an analytic function of β if $G = 1$? And if $G > 1$?

: *The free energy can be directly obtained from the partition function:*

$$F = -\beta^{-1}\log[\vec{L}^t T^{N-2}(\beta)\vec{R}]\,. \tag{25}$$

In order to take the thermodynamic limit, we need to compute the largest eigenvalue of $T(\beta)$ and the corresponding eigenvector. We immediately see that $T(\beta)$ has G identical raws, which means that there are at least $G-1$ eigenvalues equal to zero. The largest eigenvalue can not be zero, *so we can focus on the remaining two solutions. Let us cast a generic eigenvector $\vec{v}$ in the form $\vec{v} = \begin{pmatrix} \phi & \vec{w}^t \end{pmatrix}$, where $\vec{w}$ is a vector with dimension G. The secular equation reads as*

$$\begin{aligned} e^{\beta\epsilon}\phi + e^{-\beta\frac{\Lambda-\epsilon}{2}}\vec{u}\cdot\vec{w} &= \lambda\phi \\ (e^{-\beta\frac{\Lambda-\epsilon}{2}}\phi + \vec{u}\cdot\vec{w})\vec{u} &= \lambda\vec{w}\,, \end{aligned} \tag{26}$$

where $\vec{u}^t = \begin{pmatrix} 1 & \cdots & 1 \end{pmatrix}$. Since we are looking for nonzero eigenvalues, the last equation tells us that $\vec{w}$ is proportional to $\vec{u}$: $\vec{w} = \alpha\vec{u}$. Plugging this ansatz into the secular equation gives

$$\begin{aligned} e^{\beta\epsilon}\phi + e^{-\beta\frac{\Lambda-\epsilon}{2}}\alpha G &= \lambda\phi \\ e^{-\beta\frac{\Lambda-\epsilon}{2}}\phi + \alpha G &= \lambda\alpha\,, \end{aligned} \tag{27}$$

i.e.

$$\begin{aligned} (e^{\beta\epsilon} - \lambda)\phi + e^{-\beta\frac{\Lambda-\epsilon}{2}}G\alpha &= 0 \\ e^{-\beta\frac{\Lambda-\epsilon}{2}}\phi + (G-\lambda)\alpha &= 0\,. \end{aligned} \tag{28}$$

This system has a solution only if the determinant of the matrix constructed with the coefficients is zero, that is to say

$$\det\begin{pmatrix} e^{\beta\epsilon} - \lambda & e^{-\beta\frac{\Lambda-\epsilon}{2}}G \\ e^{-\beta\frac{\Lambda-\epsilon}{2}} & G-\lambda \end{pmatrix} = 0\,. \tag{29}$$

From this we obtain

$$\lambda_\pm = \frac{G + e^{\beta\epsilon} \pm \sqrt{(G+e^{\beta\epsilon})^2 - 4Ge^{\beta\epsilon}(1-e^{-\beta\Lambda})}}{2}\,. \tag{30}$$

The discriminant is always positive, $\lambda_+ > \lambda_-$, so the leading eigenvalue is

$$\lambda_{\max} = \frac{G + e^{\beta\epsilon} + \sqrt{(G+e^{\beta\epsilon})^2 - 4Ge^{\beta\epsilon}(1-e^{-\beta\Lambda})}}{2} \tag{31}$$

Since this is an analytic function of β, also the free energy will be analytic. Now we compute the eigenvector associated with the largest eigenvalue. Plugging the expression for $\lambda_{\max}$ in the second of (**??**) *we obtain*

$$\phi = -e^{\beta\frac{\Lambda-\epsilon}{2}}\frac{G - e^{\beta\epsilon} - \sqrt{(G+e^{\beta\epsilon})^2 - 4Ge^{\beta\epsilon}(1-e^{-\beta\Lambda})}}{2}\alpha\,. \tag{32}$$

The spectral decomposition of the transfer matrix gives

$$T(\beta) \sim \lambda_{\max}\vec{v}_{\max}\vec{v}_{\max}^T \tag{33}$$

(d) Explain in what this model differs from the one of Exercise 1.

: *In the limit $\Lambda \to \infty$ the maximal eigenvalue becomes singular at $G = e^{\beta\epsilon}$, indeed*

$$\lambda_{\max} = \frac{G + e^{\beta\epsilon} + |G - e^{\beta\epsilon}|}{2} = \max(G, e^{\beta\epsilon})\,. \tag{34}$$