1 Perron-Frobenius theorem

The **Perron-Frobenius theorem** states that for a real square matrix with strictly positive entries $a_{ij} > 0$:

- the largest eigenvalue λ is strictly positive.
- there exists a corresponding eigenvector x with every entry $x_i > 0$.
- λ is non-degenerate.
- if μ is any other eigenvalue, then $|\mu| < \lambda$.

Show the theorem assuming that the matrix is symmetric. Although not necessary, this simplifies the proof. Make extensive use of the Rayleigh quotient, defined for a vector $\boldsymbol{x} \neq 0$ and the matrix a_{ij}, as

$$R(\boldsymbol{x}) = \frac{\sum_{ij} a_{ij} x_i x_j}{\sum_i x_i^2}. \tag{1}$$

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2 Gaussian Integrals

1. Univariate Gaussian: show that with a Gaussian weight of mean x_0 and variance σ^2:
$$\left\langle e^{kx} \right\rangle = \exp\left(kx_0 + \frac{\sigma^2 k^2}{2}\right).$$
Remember that a Gaussian weight (distribution) reads:
$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x_0)^2}{2\sigma^2}}.$$
Further reading: properties of the cumulant generating function $\log\left\langle e^{kx}\right\rangle$ for an arbitrary probability distribution (see Wikipedia page).

2. Multivariate case of a Gaussian distribution, where the probability density is proportional to
$$p(x_1, x_2, \ldots, x_n) \propto \exp\left(-\frac{1}{2} A_{ij} x_i x_j\right)$$
with Einstein's summation convention and A a symmetric and positive definite matrix. Compute the normalization factor, in terms of $\det A$. **Hint**: the variable change $y_i = O_{ij} x_j$ where O_{ij} is an orthogonal matrix has a unit Jacobian.

3. It is useful to introduce the conjugate vector with coordinates $X_i = A_{ij} x_j$. Show that $\langle x_i X_j \rangle = \delta_{ij}$: compute $\langle x_i x_j \rangle$ and $\langle X_i X_j \rangle$.

4. Going further, show that:
$$\langle x_i f(x) \rangle = \langle x_i x_j \rangle \left\langle \frac{\partial f(\boldsymbol{x})}{\partial x_j} \right\rangle \tag{2}$$
Using repeatedly this relation allows to show that even moments of the distribution can be expressed in terms of a product of second order moments only. This is a facet of Wick theorem.

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3 Warming up: partition function of the one dimensional Ising model

We consider the N-spin Hamiltonian

$$H = -J \sum_{i=1}^{N-1} S_i S_{i+1} \tag{3}$$

where the state variables S_i take values ± 1, and boundary conditions at $i = 1$ and $i = N$ are free. Write the partition function Z. From the set $\{S_i\}$, one introduces a new set with $\tau_i = S_i S_{i+1}$, for $1 \leq i \leq N - 1$. Why can the corresponding view be qualified as dealing with a gas of domain walls? Compute Z as the partition function of the gas of walls. What is the free energy? Does it exhibit a fingerprint of phase transition?

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4 Still the Ising chain: transfer matrix approach

We add a magnetic field to the above Hamiltonian

$$H = -J \sum_{i=1}^{N-1} S_i S_{i+1} - h \sum_{i=1}^{N-1} S_i, \tag{4}$$

and take periodic boundary conditions: $S_1 = S_N$. The system is thermalized at inverse temperature β (up to Boltzmann constant), so that the probability of a given microscopic configuration is $\exp(-\beta H)/Z$, Z being the partition function. The corresponding thermal averages are denoted $\langle ... \rangle$.

1. Put the partition function in the form,

$$Z = \sum_{\{S_i\}} \prod_{i=1}^{N-1} T(S_i, S_{i+1}) \tag{5}$$

2. Introduce a 2×2 matrix $\mathbb{T}$ such that $\mathbb{T}_{S,S'} = T(S, S') = \langle S \,|\, \mathbb{T} \,|\, S' \rangle$.

3. Write Z as a function of $\mathbb{T}$.

4. What are the eigenvalues $t_\pm$ of $\mathbb{T}$, with $t_+ > t_-$?

5. Express the free energy per spin, f, as a function of $t_\pm$. How does the result simplify in the thermodynamic limit $N \to \infty$? How does this result compare to the $h = 0$ calculation for free boundary conditions?

6. We are interested in the mean magnetization per spin, $m = \langle S_i \rangle$. Provide the expression of m as a function of $\mathbb{T}$ and the matrix

$$\widehat{\sigma} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{6}$$

Who is the guy on the stamp? What is he doing here?

7. Find another expression of m as a function of a derivative of f, and show that in the thermodynamic limit, we have

$$m = \frac{\sinh(\beta h)}{\sqrt{\sinh^2(\beta h) + \exp(-4\beta J)}}. \tag{7}$$

Draw the curves $m(h)$ for various temperatures. Conclusion?

8. We now take the vanishing field limit $h = 0$. Express the correlation function $\langle S_i S_{i+k} \rangle$ as a function of $\mathbb{T}$ and $\widehat{\sigma}$.

9. Taking the thermodynamic limit in the previous expression (at fixed k), show that the correlation function becomes exponential. How does the correlation length depend on temperature? Conclude. Here, it is useful to provide the expression of the eigenvectors $|v_+\rangle$ and $|v_-\rangle$ of $\mathbb{T}$. How does $\widehat{\sigma}$ act on them?

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5 Not done yet: back to Ising correlation function

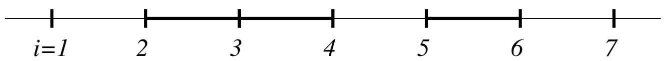
We aim at computing the correlation function $\langle S_i S_j \rangle$ for the one-dimensional ferromagnetic Ising model ($J > 0$), without a magnetic field. We shall assume free boundary conditions. Noting that

$$e^{K S_i S_{i+1}} = \cosh(K) + S_i S_{i+1} \sinh(K), \tag{8}$$

the N spin partition function can be written

$$Z = (\cosh \beta J)^{N-1} \sum_{\{S_i\}_{1 \le i \le N}} \prod_{i=1}^{N-1} \left[1 + (\tanh \beta J) S_i S_{i+1}\right]. \tag{9}$$

It is then convenient to associate a graph to each term in the expansion of the product. For instance, for the term $(\tanh \beta J)^3 (S_2 S_3)(S_3 S_4)(S_5 S_6)$:



where a thick segment joins nearest neighbors that are present in the term under consideration. Under which condition does a graph provide a non-vanishing contribution to the partition function? Compute Z, thereby recovering a known result. Using similar arguments, show that the correlation function reads

$$\langle S_i S_j \rangle = \exp(-|i - j|/\xi), \tag{10}$$

where ξ is the correlation length (provide its expression). Show that $\xi \to \infty$ in the limit $T \to 0$. Of which phenomenon is this the signature? What happens with periodic boundaries?

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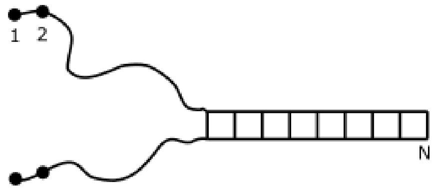
6 A special one-dimensional setting: the zipper model

The Kittel zipper model[1] is the simplest model for DNA denaturation transition and it turns out to provide an insightful approach for the denaturation of short oligomers.

Hypothesis. The binding energy of the bases located at the end of the molecule is smaller than that for pairs away from the ends: the molecule unbinds from the ends like a zipper. Here we simplify and we consider a single end. If the first k bonds are open, the energy to open the



$(k+1)$-th bond is equal to ϵ_0. If at least one of the previous k bond is still closed, the energy to open it is infinite (vanishing contribution to the partition function). Once a bond is open, it can orient itself in G ways: we then associate an entropy to each open bond $S_0 = k_B \log G$ and if k bonds are open, the associated Boltzmann weight is:

$$G^k e^{-\beta k \epsilon_0}.$$

The term G^k accounts for the G multiple orientations of each of the k open bonds. By summing over the possible values of k (with the boundary condition that the N-th bond cannot be open) the partition function reads:

$$Z_N = \sum_{k=0}^{N-1} G^k e^{-\beta k \epsilon_0} = \sum_{k=0}^{N-1} e^{\beta k (S_0 T - \epsilon_0)}. \tag{11}$$

1. Carry out the sum (it is a geometric series) and show that Z_N is equal to:

$$Z_N = \frac{1 - x^N}{1 - x}$$

   with $x = G e^{-\beta \epsilon_0}$.

2. Compute the free energy and the average open bond number $\langle k \rangle_N$. Can you identify any special $x^\star$? How is $x^\star$ related to the temperature? What is its physical meaning?

3. Study the vicinity of x^* by changing variable $x = x^\star + \epsilon$ and expanding around $\epsilon = 0$. Focus on $\langle k \rangle_N$ and $\frac{1}{N} \frac{d\langle k \rangle_N}{d\epsilon}$ (which is the slope of the average open bonds).

4. In the thermodynamic limit $N \to \infty$, in which sense is there a phase transition and how does it relate to G?

We can rewrite (a more general version of) the Hamiltonian in a spin-like fashion, with $S_i = 0, 1, \ldots G$:

$$H = \epsilon_0 (1 - \delta_{S_1,0}) + \sum_{i=2}^{N-1} (\epsilon_0 + V_0 \delta_{S_{i-1},0})(1 - \delta_{S_i,0}) \tag{12}$$

The symbol $\delta_{S,0}$ is the Kronecker delta: $\delta_{S,0} = 1$ iff $S = 0$, otherwise $\delta_{S,0} = 0$. The variable S_i is the bond variable at each "site" i and accounts for the possible $G+1$ states the bond can be

[1] V.S. thanks Professor Enzo Orlandini (UniPD) for introducing this model. Original source: C. Kittel, Am. J. Phys. **37**, 917 (1969) here

in: if $S_i = 0$, the bond is closed; for $S_i = 1, \dots, G$, the bond is open and it is in one of the G possible orientations (which energetically are all equivalent). We introduced a new term that depends on V_0, which is the energy cost needed in order to open a bond when a previous one is still closed. In the case of the already analyzed zipper model, $V_0 \to \infty$: this precludes the opening of a bond following a closed one.
The boundary condition reads $S_N = 0$ (the last bond remains closed). In Figure 1, we show two possible configurations with the Ising-like picture.

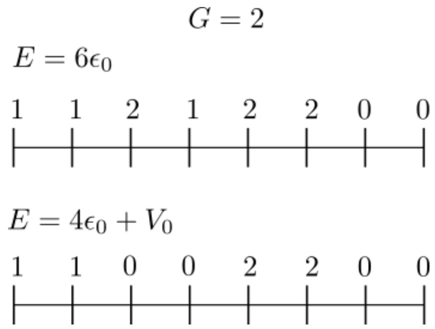


Figure 1: Ising-like picture of the zipper model. Each site represents a bond, that can be in one of three states (denoted 0, 1 and 2). Here, two examples of the configurations for $G = 2$ are shown. Top panel: there are 6 consecutive open bonds and the last two are closed, hence we have an energy $E = 6\epsilon_0$. Bottom panel: the first two open bonds account for $2\epsilon_0$; the third and the fourth are closed and do not contribute to the energy; the fifth bond is open, and follows a closed one; this results in an energy penalty V_0, in addition to ϵ_0. The sixth bond is open, follows an other open bond, and thus contributes an energy cost ϵ_0. Putting all together, the energy is $E = 4\epsilon_0 + V_0$. In the limit $V_0 \to \infty$ (the zipper model limit) this configuration is forbidden since $E \to \infty$.

We rewrite the Hamiltonian in this more complex and general form in order to implement the transfer matrix method. The partition function, starting from equation (12) and using the properties of the Kronecker delta $\delta_{S,0}$, reads::

$$Z_N = \sum_{\{S_i=0,\dots,G\}} e^{-\beta\epsilon_0(1-\delta_{S_1,0})} \prod_{i=1}^{N-2} e^{-\beta\epsilon_0(1-\delta_{S_{i+1},0})} \left[1 + (e^{-\beta V_0} - 1)\delta_{S_i,0}(1-\delta_{S_{i+1},0})\right] \qquad (13)$$

1. By taking $V_0 \to \infty$, identify the transfer matrix $\mathbb{T}$. Note that, at variance with the Ising spin 1/2 model (that had 2 possible values for the spins, hence a 2×2 transfer matrix), $\mathbb{T}$ now is a $(G+1) \times (G+1)$ matrix.

2. What can be said about the eigenvalues of $\mathbb{T}$? Make use of the Perron-Frobenius theorem.

3. Can you solve for the eigenvalues and the eigenvectors? If not, you can compute them for the cases $G = 1, 2$.

4. As a function of G, what can we say about the set of eigenvalues and eigenvectors?

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7 Transition in a binary alloy

Certain binary alloys such as brass (CuZn) exhibit a transition between different solid phases. At very small temperature, the two types of atoms are organized periodically, while at larger temperature, the corresponding lattice is still present, but the atoms are randomly arranged. The goal is here to show that this phenomenon is akin to the paramagnetic-ferromagnetic transition, as exhibited by Ising model.

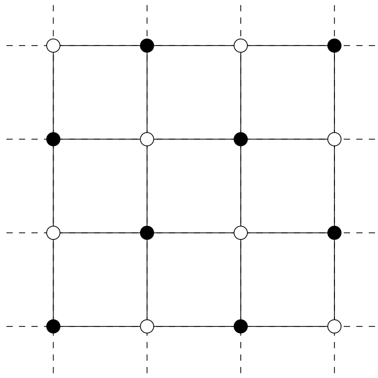

Figure 2: Schematics of the lattice. Sub-lattices of α and β types are shown with filled and empty disks.

We consider a cubic lattice in dimension d, with length L (even in terms of lattice constant, that shall be taken as our unit length), with periodic boundary conditions. We note $N = L^d$ the number of lattice sites. The lattice is divided in two sub-lattices α and β (see figure 2, where $d = 2$). $N/2$ atoms of type A and an equal amount of atoms of type B occupy the lattice sites. Only nearest neighbor interactions are accounted for, and the energy between neighbors is denoted ε_{AA}, ε_{AB} and ε_{BB} depending on the configuration.

1. Whats is, as a function of d, the number z of nearest neighbors for a given site? What is the total number of links within the lattice?

2. One denotes by N_{ij} the number of links of type ij in the system. Express N_{AA} and N_{BB} as a function of N_{AB}. Show then that the total energy can be put in the form
$$E = \frac{zN}{4}\left(\varepsilon_{AA} + \varepsilon_{BB}\right) + N_{AB}\left(\varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}\right). \tag{14}$$
Establish a condition on $(\varepsilon_{AA}+\varepsilon_{BB})/2-\varepsilon_{AB}$ such that at vanishing temperature, all atoms of a given species lie on one of the two sub-lattices. One can then refer to this situation as that of the *ordered crystal*. And what if this condition is not fulfilled?

3. For each site l of the lattice, one introduces a variable $S_l = \pm 1$: $S_l = 1$ if the atom is on an α-lattice site and is of type A, or is of type B on a β-lattice site; $S_l = -1$ otherwise. Show that the energy can be written as
$$E = E_0 - J \sum_{\langle lm \rangle} S_l\, S_m, \tag{15}$$
where the summation runs over pairs of nearest neighbors. Give the expression of E_0 and J.

4. Which condition on the magnetization of each of the two sublattices does follow from the conservation of the number of atoms of each type? Is it a real constraint in the thermodynamic limit?

5. Under which condition on d does the system exhibit a phase transition? How does the critical temperature depend on J? What is then the critical temperature of the original alloy model?

6. Recall the behavior of the order parameter $\langle S_l \rangle$ for model (15) as a function of temperature. What is the corresponding order parameter for the binary alloy?

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8 Mean-field approximation of the Ising model

We start from a standard Ising model in a d dimensional lattice, with Hamiltonian

$$H = -J \sum_{\langle i,j \rangle} S_i S_j - h \sum_i S_i. \tag{16}$$

The sum $\sum_{\langle i,j \rangle}$ must be interpreted as $\frac{1}{2} \sum_i \sum_{j \in \partial i}$ where ∂i denotes the set of neighbors of i. In a d-dimensional setting on a cubic lattice, each site has $z = 2d$ neighbors.

1. By introducing the average magnetization

$$m = \frac{1}{N} \sum_i S_i$$

   rewrite the Hamiltonian as a function of the spin fluctuations $\delta S_i = S_i - m$.

2. The (naive) mean-field approximation consists in neglecting the terms of order $O(\delta S_i \delta S_j)$ of the Hamiltonian. What is the resulting H_{MF}?

3. The Hamiltonian H_{MF} is now linear in S_i. Compute the partition function Z_{MF}.

4. We used the average magnetization m in the Hamiltonian H_{MF}; however, this quantity is NOT a free parameter, and must be fixed self-consistently. Making use of the following relation

$$m = \frac{1}{\beta N} \frac{\partial \log Z_{MF}}{\partial h}, \tag{17}$$

   derive the self-consistency equation for the magnetization m.

5. For the moment, set $h = 0$ in equation (17). Discuss the physical properties of the magnetization m. Do you observe a phase transition?

6. Now consider $h > 0$ and discuss the changes in the physics of the magnetization.

N.B.: further reading on the possible pitfalls of such mean-field approaches: R. Agra *et al.*, Eur. J. Phys. **27**, 407 (2006) ; cond-mat/0601125.

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9 The Curie-Weiss model

We consider an N-spin Ising system with Hamiltonian

$$H = -\frac{J}{2N} \sum_{i,j=1}^{N} S_i S_j - h \sum_{i=1}^{N} S_i. \tag{18}$$

1. Why does such a description qualify as "mean-field"? How important are the underlying geometric features of the system?

2. Why was the coupling constant J multiplied by the factor $1/N$?
3. The system is at thermal equilibrium. Show that the partition function can be written

$$Z = \sum_m \mathcal{N}_m^N \, e^{-\beta N(-Jm^2/2 - hm)}. \tag{19}$$

Give $\mathcal{N}_m^N$ and specify the values allowed for m in the summation.

4. Making use of Stirling approximation for the factorial function, rewrite the free energy per spin $f(\beta, h)$ as

$$f(\beta, h) = \inf_m \widehat{f}(m; \beta, h). \tag{20}$$

5. Plot $\widehat{f}(m; \beta, h = 0)$ versus m, for different temperatures. What is the temperature T_c where a qualitative change is observed?
6. What is the effect of the external field h on those curves?
7. We define $m_*(\beta, h)$ as the minimizer in Eq. (20). What is the implicit equation fulfilled by this quantity?
8. The spontaneous magnetization is defined as

$$m_{\rm sp} = \lim_{h \to 0^+} m_*(\beta, h).$$

What is the shape of this function? Compute the β-exponent ruling the behavior in the vicinity of the critical temperature:

$$m_{\rm sp} \propto (T_c - T)^\beta.$$

9. Plot the mean energy per spin, $\langle H \rangle / N$ as a function of temperature for $h = 0$. What is then the behavior of the specific heat

$$C(T) = \frac{d}{dT} \frac{\langle H \rangle}{N}$$

What critical exponent does account for its behavior?

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10 Landau theory

Landau developed a method to study phase transitions in different systems (such as the Ising model); he suggested that the free energy of a system in the vicinity of its critical temperature T_c should:

- be analytic (w.r.t. some order parameter like the magnetization in Ising systems)
- obey the symmetries of the underlying Hamiltonian

By using these two assumptions one can write down an effective free energy describing the system in interest. We now focus on the Ising model. The Ising model in a lattice obeys the $\mathbb{Z}_2$ symmetry i.e. if we flip sign of all the S_i, the Hamiltonian does not change (if there is no external magnetic field). Hence the effective free energy should not depend on the sign of magnetization (which changes sign under $\mathbb{Z}_2$ transformation). Given these property a first free energy can be written as:

$$F(m,T) = F_0 + a_0(T)m^2 + \frac{b_0(T)}{2}m^4 + \dots \tag{21}$$

The quantity F_0 is a constant term which does not affect the results while $a_0(T)$ and $b_0(T)$ are two parameters depending on the temperature. For the system to be thermodynamically stable, we should require a positive $b_0(T) > 0$ and for simplicity, we assume $b_0(T) = b_0$. As for $a_0(T)$, it should change sign (and we will see why) at the critical temperature T_c; hence we expand $a_0(T) \approx a_0(T - T_c)$. We end up with:

$$F(m,T) = F_0 + a_0(T - T_c)m^2 + \frac{b_0}{2}m^4. \tag{22}$$

Since the system minimizes the free energy, we should find the optimal $m^\star$ by taking the derivative of $F(m,T)$ w.r.t. m.

1. Find the stationary point of $F(m,T)$ i.e. $\frac{\partial F(m,T)}{\partial m} = 0$.
2. To find the minima, study the sign of $\frac{\partial^2 F(m,T)}{\partial m^2}$.
3. How in this setting does the phase transition occur?
4. Introduce now a magnetic field by adding a term $-hm$ to the free energy. How do the previous minima change? Notice that by adding this term we explicitly break the $\mathbb{Z}_2$ symmetry (as in the Hamiltonian with external magnetic field).
5. Do you see any resemblance of this approach with the Curie-Weiss model? What about the critical exponents?

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