Physical Examples of Phase Transition in One-Dimensional Systems with Short Range interaction

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Abstract

In this paper, we study the thermodynamic phase transition in one dimensional systems with short range interaction. We begin by reviewing some famous non-existence result, such as Landau's argument and van Hove's theorem. And we point out that the Perron-Frobenius theorem is generally used to determine whether there is phase transition in such kind of system. Then several examples that Perron-Frobenius theorem doesn't apply and exhibit phase transitions will be present.

1 Introduction

One dimensional systems are one of the most important and remarkable research areas in physics. As a matter of fact, it is generally easier to perform analytical analysis on models in one dimension compared to their higher dimensional counterparts. The exact one dimensional results often give us deep understanding about many physical phenomena, and may lead to advances in much broader contexts subsequently. For example, one way to derive the scaling laws of the Kondo problem, which is related to the anomalous behavior of resistivity in metals due to the scattering of conduction electrons with magnetic impurities, is to prove that it is equivalent to certain class of one dimensional classical statistical problem, and solve the statistical mechanics of that problem ([2]).

Despite that people have known a lot about one dimensional systems, they are still interesting areas and a continuous source of exciting new physics. In this paper, we will study some phase transitions take place in one dimensional models. Historically, there are some careless opinions about whether there are true thermodynamic phase transitions in one dimensional systems with short range interactions, and they often prevent people from considering 1 D problems correctly. We will also try to clarify them.

The structure of this paper is that, we will first discuss the generally cited 'van Hove's theorem' ([1]) that excludes phase transition in certain class of one dimensional model, which is further reinforced by Landau's argument. Then we'll present some one dimensional models that do exhibit true thermodynamic phase transitions, and talk about the conditions for 1 D phase transition to take place.

2 Non-Existence Result

The generally accepted statement that '1D system with short range interactions cannot have phase transitions' in literature is usually called the 'van Hove's theorem'. Indeed, most one dimensional systems with short range interaction do not undergo a phase transition, except maybe at zero or infinite temperature. And the most common exactly solvable examples of statistical physics such as Ising model, Potts model, etc, seem to suggest this conclusion.

One of the most famous argument is given by Landau and Lifshitz ([4]). Consider a one dimensional lattice of L sites, each site variable can take two possible states, either A or B. Let us assume the ordered phases, where all sites take state A or all sites take sate B, have the lowest energy (just like ferromagnetic spin $\frac{1}{2}$ Ising model in zero field), and assume a domain wall that divides a region of A phase from that of B will cost energy of ϵ. Then the free energy is consist of the energy cost by n domain walls $n\epsilon$, and the entropic contribution due to the number or ways of placing n walls on L sites $\simeq nT[ln(n/L) - 1]$ for $1 << n << L$.

$$F = E - TS = n\epsilon - nT[ln(n/L) - 1] \tag{1}$$

Thus to minimize the free energy, the number of domain walls will grow until it scales as L for any finite temperature. that is to say, the building of a domain wall is energetically more favorable. More and more domain walls are built and we will

not observe a state with all spins up (or down). Thus there is no phase transition in one dimension (for $T \neq 0$). Note that this argument relies on a finite energy cost for domain walls, and short range interactions so that one may ignore the interaction energy of domain walls.

We can also think of this problem from a dynamical perspective. For a disordered state to become ordered, domain walls must annihilate each other. However in one dimension system, two domain walls at opposite ends of a domain moving closer to one another can not reduce the free energy. Therefore there is no effective force to move the domain walls and eliminate domains. The system would stay in disordered states. Again, this argument requires a short range interaction so that one can ignore the energy of interaction of domain walls beyond some finite distance.

As for the finite range of the interactions, the work of Ruelle ([5]) and Dyson ([6]) proved that pair interactions decaying as $1/r^2$, r being the distance between variables represent the boundary between models with and without phase transitions.

Mathematically, people use the transfer matrix technique to address the question of phase transition in one dimension. For example, for N sites Ising model in one dimension with periodic boundary conditions, the partition sum can be written as the trace of a product of N transfer matrices T:

$$Z = Tr[T^N] = \sum_{\lambda} \lambda^N \tag{2}$$

where λ are eigenvalues of the transfer matrix. If the transfer matrix is finite and positive, the Perron-Frobenius theorem ensures that the largest eigenvalue λ_{max} is non-degenerate. Consequently in this system, as we vary some control parameters, we could expect no phase transitions which are defined rigorously as nonanalyticities of the free energy $F \sim lim_{N\to\infty}(lnZ)/N = \lambda_{max}$

The frequently cited van Hove's theorem generally referred to a paper written by him in 1950 ([8]). That paper considered phase transition in a system of N identical particles, lying on a segment of length L on positions $x_i, i = 1, \cdots, N, 0 \leq x_i \leq L$. The potential energy of the system is assumed to be continuous, bounded, and is given by

$$\mathbf{V} = \sum_{i=1, i<j}^{N} U\left(|x_i - x_j|\right) \tag{3}$$

with

$$U(\xi) = \begin{cases} +\infty, & if \quad 0 \leq \xi \leq d_0, \\ 0, & if \quad \xi \geq d_0, \end{cases} \tag{4}$$

and $0 < d_0 < d_1$. That means the system that van Hove initially considered was of hard-core segments of diameter d_0, that interact only at distances smaller than d_1. He used the transfer matrix technique that we described before, and showed that the largest eigenvalue is an analytic function and consequently it cannot have phase transitions.

Hence, we can see that it is crucial to clarify the conditions that the 1D systems have to satisfy in order for the van Hove's theorem to be applicable.

First of all, the system has to be made up of identical particles, i.e. it should be perfectly homogeneous. This is a very strong restriction. It automatically excludes any aperiodic or disordered models. Actually there is no known theorem excluding

phase transitions in one dimensional systems with any degree of inhomogeneity. Periodic systems, however, could be included in the van Hove's theorem by analyzing the transfer operator for a unite cell.

Second, there should be no external fields acting on the system, otherwise it will introduce terms depending on the position of the particles x_i alone in the potential energy. However, in van Hove's assumption, the potential energy could depend on relative interparticle distances $x_i - x_j$ only. Consider one dimensional Ising model, if we introduce a magnetic field, the system might therefore have phase transitions at non-zero temperatures.

Last, the system should be consist of hard-core particles, which means it does not apply to point-like or soft particles.

It was showed later that the second and third restriction can relax in some cases ([1]).

3 Examples of 1D Models with Phase Transition

In this part, we study some examples where there are true thermodynamic phase transitions despite of their one dimensional character and the range of their interactions, and thus summarize the conditions for phase transition to happen in this kind of systems. The first case we consider is the Kittel's Model.

3.1 Kittel's Model

The system is proposed by kittel in 1969 as a simple model of KH_2PO_4 (usually known as KDP), which exhibits a first-order transition at non zero temperature. It is in fact a single-end zipper model, and inspired in double-ended zipper models of polypeptide or DNA molecules. Consider a zipper of N links that can be opened only from one end. The energy required to open link n+1 is ϵ if all the preceding links 1,2,...n are open, and is infinite if not all the preceding links are open. The zipper is said to be open when the first N-1 links are open, as link N cannot be opened. Further, we assume that each open link can take G kinds of different orientations, i.e., the open state of a link is G-fold degenerated. As we will see below, if G=1 there is no phase transition still. We will solve Kittel's model in terms of a transfer matrix.

The Hamiltonian of this model can be written as

$$\mathscr{H}_N = \epsilon(1 - \delta_{s_1,0}) + \sum_{i=2}^{N-1}(\epsilon + V_0\delta_{s_{i-1},0})(1 - \delta_{s_i,0}) \tag{5}$$

where $s_i = 0$ means that link i is closed, $s_i = 1, 2, \cdots, G$ means that the link is open in one of the possible G states. Note that Kittel's constraint on the zipper corresponds to the choice $V_0 = \infty$, and as Link N in the zipper is always closed, we have also imposed the boundary condition $s_N = 0$.

The partition function is then be given by

$$\mathscr{Z}_N = \sum_{config.} exp(-\beta\mathscr{H}_N) \tag{6}$$

To implement the transfer matrix formalism, we rewrite the partition function as

$$\mathscr{Z}_N = \sum_{config.} e^{-\beta\epsilon(1-\delta_{s_1,0})} \prod_{i=1}^{N-2} e^{-\beta\epsilon(1-\delta_{s_{i+1},0})} \left[1 + \left(e^{-\beta V_0} - 1\right) \delta_{s_i,0}(1 - \delta_{s_{i+1},0})\right]. \quad (7)$$

Let $V_0 = \infty$, which implies that $e^{-\beta V_0} = 0$.

The transfer matrix $\mathbf{T} = (t_{s,s'})$, can therefore be defined as

$$t_{s,s'} = e^{-\beta\epsilon(1-\delta_{s',0})} \left[1 - \delta_{s,0}(1 - \delta_{s',0})\right], \quad (8)$$

or in matrix form

$$\mathbf{T} = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 1 & a & \cdots & a \\ \vdots & \vdots & & \vdots \\ 1 & a & \cdots & a \end{pmatrix}, \quad (9)$$

where $e \equiv e^{\beta\epsilon}$. The 0 entries in the first row of $\mathbf{T}$ are due to the constraint that link s_{i+1} cannot be open if link s_i is closed ($s_i = 1$).

We can thus revise the partition function as

$$\mathscr{Z}_N = (1 \quad a \quad \cdots \quad a) T^{N-2} \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix}. \quad (10)$$

Matrix $\mathbf{T}$ has three different eigenvalues, namely $\lambda_1 = Ga$, $\lambda_2 = 1$ and $\lambda_3 = 0$. The third one is $G - 1$ fold degenerate. The eigenvectors of the two nonzero eigenvalues are, respectively

$$\mathbf{v}_1 = \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 1 \end{pmatrix}, \mathbf{v}_2 = \begin{pmatrix} 1 - Ga \\ 1 \\ \vdots \\ 1 \end{pmatrix}, \quad (11)$$

so if we express

$$\begin{pmatrix} 1 \\ a \\ \vdots \\ a \end{pmatrix} = \frac{a(1 - Ga) - 1}{1 - Ga} v_1 + \frac{1}{1 - Ga} v_2, \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix} = \frac{-Ga}{1 - Ga} v_1 + \frac{1}{1 - Ga} v_2, \quad (12)$$

we finally get

$$\mathscr{Z}_N = \frac{1 - (Ga)^N}{1 - Ga} = \frac{1 - \left(Ge^{-\beta\epsilon}\right)^N}{1 - Ge^{-\beta\epsilon}} \quad (13)$$

or in another way

$$\mathscr{Z}_N = \frac{1}{1 - Ge^{-\beta\epsilon}} \left(-\lambda_1^N + \lambda_2^N\right) \quad (14)$$

The partition function now is expressed as a linear combination of N th powers of the transfer matrix eigenvalues. In the thermodynamic limit, only the contribution of the largest eigenvalue retains. Let's take $N \to \infty$, the free energy is then given by

$$f \equiv \frac{1}{N}\mathscr{F} \equiv -\frac{1}{\beta N} ln \mathscr{L}_N = -\frac{1}{\beta} ln\ max(\lambda_1, \lambda_2). \tag{15}$$

In order to create a nonanalyticity of the free energy and thus phase transition of the system, as both the eigenvalues are positive, analytic functions of β, we have to let the two eigenvalues to cross at certain β_c. Compare λ_1 and λ_2, we get that they cross at a temperature given by $\beta_c = lnG/\epsilon$, or $T_c = k_B\epsilon/lnG$. Above T_c, λ_1 is the largest eigenvalue; below T_c, λ_2 is the largest eigenvalue. At T_c, the derivative of the free energy is discontinues, indicating the existence of a phase transition. It is interesting to note that $T_c = k_B\epsilon/lnG$ is finite as long as $G > 1$. For non-degenerate case $G = 1$, the transition takes place at $T = \infty$, or, in other words, there is no phase transition.

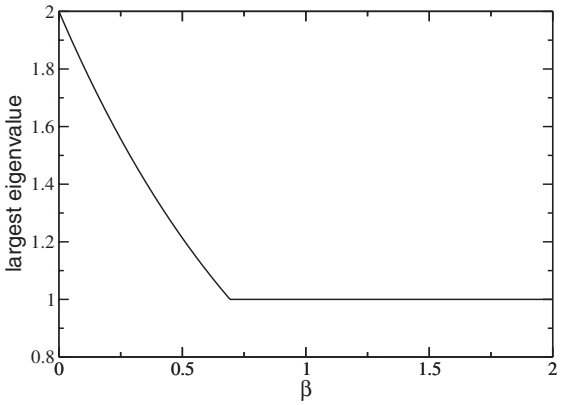

Figure 1: Largest eigenvalue of the transfer matrix for Kittel's model with G=2 vs inverse temperature, with $\epsilon = 1$. The non-analyticity takes place at $\beta = 1/ln2$

Why there is a phase transition in Kittel's model? The transfer matrices, made up from Boltzmann factors, i.e., exponentials, are always strictly positive and consequently, irreducible and analytic in β. According to the Perron-Frobenius theorem, there cannot be a phase transition under these conditions for any finite $\beta > 0$. However, in this Kittel's model, we assign an infinite energy to some configurations, thus some of the elements in the transfer matrix become zeros. This makes the phase transition to be possible.

However, it should be noted that following this assignment does not necessarily induce a phase transition in a 1 D system. As we mentioned above, the case where the open state is non-degenerate doesn't experience a phase transition at finite temperature.

3.2 Chui-Week's Model

The next example we are going to consider is proposed by Chui and Weeks. In this model, the transfer matrix has infinite size. The model is given by the following Hamiltonian

$$\mathscr{H}_N = \mathbf{J}\sum_{i=1}^{N}|h_i - h_{i-1}| - \mathbf{K}\sum_{i=1}^{N}\delta_{h_i,0}. \tag{16}$$

This is a typical model that describes surface growth. h_i stands for the height above site i of the lattice and is single-valued. Suppose the heights can only take integer values and that there is an impenetrable substrate, imposing a boundary condition $h_i \geq 0$. The first term in the Hamiltonian is the surface tension contribution to the total energy, and the second one introduces an energy binding the surface to the substrate. Interestingly, despite that this model appears to take place in two dimensions, it is essentially a model with one dimensional nature, as the height h_i could equally well represent any other magnitude, not necessarily associated to a physical dimension.

Easy to see the transfer matrix for the model is

$$(\mathbf{T})_{ij} \equiv e^{-\beta J|i-j|}\left[1 + (e^{-\beta K} - 1)\delta_{i,0}\right], \qquad i,j = 1,2,\dots\ . \tag{17}$$

Here the matrix dimension becomes infinite, due to the fact that the any site of the lattice can take infinite amount of states (height). However, the matrix is a strictly positive one, as in this case none of the entries in the matrix is zero.

Let $\omega \equiv e^{-\beta J}$, $\kappa \equiv e^{-\beta K}$, then, by considering eigenvectors of the form

$$\mathbf{v}_q \equiv (\psi_0, cos(q+\theta), cos(2q+\theta), \dots), \tag{18}$$

it can be shown that there is a continuous spectrum of eigenvalues,

$$\sigma(\mathbf{T}) = \left[\frac{1-\omega}{1+\omega}, \frac{1+\omega}{1-\omega}\right]. \tag{19}$$

In the range of temperatures such that $\kappa > 1/(1-\omega)$, there is an additional eigenvector,

$$\mathbf{v}_0 \equiv (\psi_0, e^{-\mu}, e^{-2\mu}, \dots) \tag{20}$$

with eigenvalue

$$\lambda_0 = \frac{\kappa(1-\omega^2)(\kappa-1)}{\kappa(1-\omega^2)-1}, \tag{21}$$

which, when it exists, is the largest eigenvalue. This is another case of eigenvalue corssing in the transfer matrix, which indicates the existence of a phase transition. The phase transition temperature T_c, is defined at which $\kappa = 1/(1-\omega)$. The physics of this transition is that, for temperatures below T_c, the surface is bound to the substrate and is macroscopically flat; on the contrary, above T_c, the surface becomes free and its width is unbounded. This is an example of the so called roughening (or wetting) transitions.

However, an interesting thing is that, if the substrate is not impenetrable, the variable h_i is thus not limited to positive integers, this phase transition disappears. The surface will be flat at all temperatures pinned to the line $h_i = 0$.

We could extend the range of h_i to positive real space. In this way, the transfer matrix will become an integral. Similar case is going to be studied in the next section.

3.3 Dauxois-Peyrard's Model

In this part, we want to discuss a model for DNA denatuation. This is a much more realistic model than the toy model introduced by Kittel and discussed in detail above. We will refer to it as Dauxois-Peyrard's model.

Suppose that the DNA molecule is homogeneous. The Hamiltonian is given by

$$\mathscr{H}_N = \sum_{i=1}^{N} \left[\frac{1}{2} m \dot{y}_n^2 + D \left(e^{-\alpha y_n} - 1 \right)^2 + \mathbf{W}\left(y_n, y_{n-1} \right) \right], \tag{22}$$

where the variable y_n represents the transverse stretching of the hydrogen bonds connecting the two base pairs at site n of the double helix of DNA. The first term in the hamiltonian is the kinetic energy, with m being the mass of the base pairs. The second term is a Morse potential, which stands for the hydrogen bonds between base pairs as well as the repulsion between phosphate groups and solvent effect. The last term represents the stacking energy between neighboring base pairs along each of the two strands. This is an anharmonic potential

$$\mathbf{W}(y_n, y_{n-1}) = \frac{\mathbf{K}}{2} \left[1 + \rho e^{-\alpha(y_n + y_{n-1})} \right] (y_n - y_{n-1})^2. \tag{23}$$

Once again, we write down the partition function of the model. As mentioned before, it is given in the form of an integral transfer operator

$$\mathbf{T}\phi(y) = \int_{-\infty}^{A} dx exp \left[-\beta \left(\mathbf{W}(y, x) + \frac{1}{2} \left[\mathbf{V}(y) + \mathbf{V}(x) \right] \right) \right] \phi(x), \tag{24}$$

where the upper limit in the integral, A, is a cutoff introduced for technical reasons, but the limit $A \to \infty$ is well defined.

Our problem now is that it is impossible to use analytical method to find the exact eigenvalues of the transfer operator for Dauxois-Peyrard model. However, people did analytical approximation and numerical computation and got compelling evidence for a phase transition in the anharmonic case.

Their numerical results about the transfer matrix show that its eigenvalue spectrum is very similar to that of Chui-Weeks's model we discussed before. Besides the band of the continuous spectrum, there is a single eigenvalue appears at a finite temperature. This result agrees very well with numerical simulations of the model, showing that above the critical temperature the mean value of y_n diverges, i.e. the two strands separate to a macroscopically large distance. That is to say, the double strand denaturates. While below the critical temperature the two strands remain bound.

More interestingly, the predictions of the model compared very well with experiments on short chains ([7]). A work show the comparison of theoretical calculations with the experimental melting curves was obtained in 1998. The experiment was did for three different oligonucleotides, in a 10-mM Na phosphate buffer, 0.1-mM Na_2EDTA and 200-mM NaCl, pH 6.7. One of the oligonucleotides contained 27 base pairs, and the other two had 21 base pairs. In Fig. 2 we show the experimental and computed melting curves. The Dauxois-Peyrard's Model we talk about here is thus a very realistic model, and clearly there is a phase transition in this system at finite temperature. On one hand, the Morse potential applied external field on the system; the most important reason, however, is that its transfer matrix is an integral operators indicating infinite dimensions.

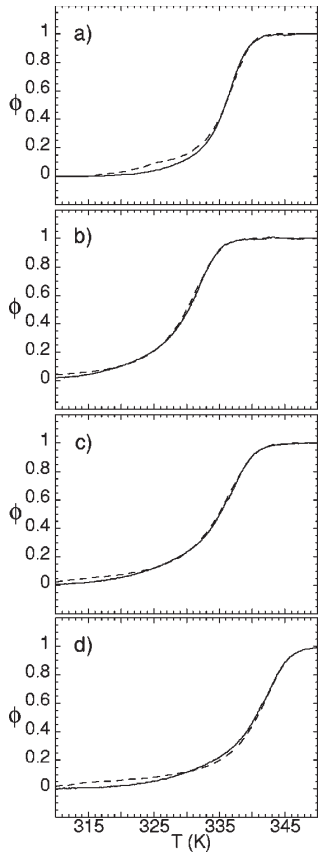

Figure 2: Experimental melting profiles (full lines) and theoretical results (dashed lines) for the three DNA chains ((c) and (d) are for the same chain at low and high concentration respectively). Here $\phi = 1 - \theta$, and θ is the average fraction of bonded base pairs

3.4 discussion

From the previous discussion, it easy to see that we usually use the Perron-Frobnius theorem to determine whether certain transfer matrix would exhibit crossing of largest eigenvalues and thus phase transition in one dimensional system. In

general, there is no transition. However, exceptions happens when the Perron-Frobenius theorem no longer applies. For example, when the transfer matrix becomes reducible, i.e. when there exist components of T^N that are zero for all values of N. This can occur at zero temperature or when some interaction strengths are set to infinity. Another case when the Perron-Frobenius theorem does not apply is when the transfer matrix becomes infinite due either to long range interactions or when the local degree of freedom at each lattice site is infinite. In this paper, we showed some one dimensional models to exemplify those cases.

Apart from what is mentioned above, from the procedure of solving the Kittel's model, we can see that the specific form of partition function is also related to the choice of boundary conditions of the system. For periodic boundary conditions, for example, $\mathscr{Z}_N = Tr(\mathbf{T}(\beta)^N)$; while for fixed boundary conditions given by two vectors f and g, the partition function takes the form $\mathscr{Z}_N = \langle f, \mathbf{T}(\beta)^N g\rangle$. Sometimes boundary conditions could suppress the eigenstates of the maximum eigenvalue as allowed states for the model and results in unusual phase transition. We will show this possibility by giving an academic example. Suppose the transfer matrix for a three state system is of the form

$$\mathbf{T} \equiv \begin{pmatrix} 3 & 1 & 1 \\ 1 & b & 1 \\ 1 & 1 & b \end{pmatrix}. \tag{25}$$

This is a positive, irreducible matrix which, according to Perron-Frobenius theorem, cannot have a phase transition. The spectrum of this matrix is

$$\sigma(\mathbf{T}) = \left\{ b-1, \frac{1}{2}\left(4+b \pm \sqrt{12-4b+b^2}\right)\right\}. \tag{26}$$

If the boundary conditions are chosen to be given by a vector orthogonal to the eigenvector of the maximum eigenvalue, $\frac{1}{2}(4+b+\sqrt{12-4b+b^2})$, in this particular case, it can be easily showed that there is a crossing of the second and third eigenvalue at $b = 3$. Therefore this model has a thermodynamic phase transition even if it is described by a positive, irreducible matrix, and this kind of phase transition only occurs for specific boundary conditions. In general, the model will behave in the usual way. Admittedly, the example we give here is more academic than physical, as in real systems, both the energy of the first state and the boundary conditions would be temperature dependent. However, it is possible for this feature to arise in more realistic systems, and lead to phase transitions.

4 conclusion

In this paper, we talked about the existence of true thermodynamic phase transitions in one dimensional systems with short range interaction. When the transfer matrix does not satisfy the condition of Perron-Frobenius theorem, which requires the matrix to be positive, irreducible, compact, phase transitions can exist. But this is not a sufficient condition. We studied several one dimensional physical models to certify this argument. And we also mentioned that even if the Perron-Frobenius theorem applies, some special boundary conditions may also result in

phase transitions. In conclusion, it is not easy to reach an 'if and only if' theorem about the existence of phase transition in one dimensional systems with short range interaction. We need to bear in mind that such kind of phase transition does exist, and we should study a particular problem carefully instead of judging it by careless generalization.

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