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REVIEW

Phase Transitions and Zeros of the Partition Function: An introduction

Petrus Henrique Ribeiro dos Anjos

Instituto de Física, Universidade Federal de Catalão, Catalão, GO, Brazil.

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Abstract:

In this revision, I provide a brief and pedagogical introduction to the relation of phase transitions and the zeros of the statistical mechanical partition function.

Keywords: phase transitions; statistical mechanics; partition function; zeros of polynomials

1. Introduction

First of all, I would like to thank the opportunity to present these notes. In particular, I wish to thank the 1st Multidisciplinary Symposium in Materials of the Brazilian Central West to give me the challenge to talk to a much diverse audience. This symposium is relevant to promote a cross-pollination between the various areas that contribute to the science of materials. In this spirit, I believe that disclosing modern methods used by physicists and mathematicians in the study of the phase transition phenomena is of particular relevance. Phase transitions are everywhere in science. Boiling of water, denaturation of a protein, or formation of a percolation cluster in a random graph are examples of phase transitions. The key idea is that at each "phase", the system has uniform physical properties. During a phase transition certain properties of the system change, often discontinuously, as a result of the change of some external condition, such as temperature, pressure, or others. A prototypical example of a phase transition is the liquid-gas transition. Crossing the coexistence curve, by varying e.g., the temperature, one can move between vapor and liquid phases. The study of phase transitions is of great interest due to both its practical importance and theoretical richness. The rigorous mathematical understanding of the phase transition phenomena is the holy grail of thermodynamics with implications in almost all areas of natural sciences.

Let k denote the Boltzmann constant and $\beta = 1/kT$ to be the inverse temperature. Mathematically, we say that a system with free energy $f(\beta, X)$ (where X denote the other relevant parameters) undergoes a phase transition if some derivative of f becomes ill-defined at some point (β, X). Paul Ehrenfest classified phase transitions based on the behavior of the (density of) free energy f as a function of other thermodynamic variables (see ref. [1]). Under this scheme, a phase transition was labeled by the lowest derivative of f that is discontinuous at the transition. First-order (or discontinuous) phase transitions exhibit a discontinuity in the first derivative of f with respect to some thermodynamic variable. For instance, the various liquid-gas transitions are classified as first-order transitions because they involve a discontinuous change in density, which is the (inverse of the) first derivative of f with respect to pressure. The open-closed transition of the molecular zipper (see [2]) is also a first order phase transition. Second-order phase transitions are continuous in the first derivative (the order parameter, which is the first derivative of the free energy with respect to the external field, is continuous across the transition) but exhibit discontinuity in a second derivative of the free energy. Examples of second order phase

*Corresponding author. E-mail: petrus@ufg.br

transition include the ferromagnetic phase transition in materials such as iron, where the magnetization, which is the first derivative of f with respect to the applied magnetic field strength, increases continuously from zero as the temperature is lowered below the so-called the Curie temperature [3]. In this case, the magnetic susceptibility, the second derivative of the free energy with respect to the external field, changes discontinuously. Under the Ehrenfest classification scheme, there could in principle be third, fourth, and higher-order phase transitions which correspond to discontinuities on high order derivatives of f. For example, I will argue atsection 4.3 that the Berezinskii-Kosterlitz-Thouless transition (BKT transition, see [4]) is an infinity order phase transition.

The connection between the microscopic mechanical properties and the macroscopic thermodynamic properties of the system are the object of study the Statistical Physics. In these notes, I will consider physical systems that are in thermal equilibrium with its environment. This means that our system and its vicinity (the energy reservoir) will be allowed to exchange energy between them. But the vicinity of our system will be assumed to be in some sense big enough so that the energy it gives or receives from the system will not change the reservoir, which will be characterized by a quantity that we call temperature T. So, we are saying that the typical variation of energy of our system will be small enough in comparison to the energy required to change the temperature of its surroundings. For simplicity, let $s = \{s_1, s_2, \cdots, s_N\}$ be the set of possible microstates of our system. The first issue in a statistical mechanics problem is to obtain p_n the probability of finding the system in the state s_n. Such the probability distribution $p_1, \cdots, p_N$ must satisfy the following conditions:

$$\sum_{n=1}^{N} p_n = 1, \qquad \sum_{n=1}^{N} E_n p_n = E$$

where En is the energy of the microstate s_n and E is the expectation value of the energy of the system, which is constant since we are considering that the system is in equilibrium. Furthermore, the probability distribution must maximize the statistical entropy of such distribution, i.e.

$$S(p_1, \cdots, p_n) = -k \sum_{n=1}^{N} p_n \ln p_n$$

These requirements implies that (see ref. [5] for more details)

$$p_n = \frac{e^{\frac{-E_n}{kT}}}{Z} \equiv \frac{e^{-\beta E_n}}{Z}$$

where Z is the so called partition function, which is given by

$$Z = \sum_{n=1}^{N} e^{-\beta E_n}$$

The partition function Z is a central object in (equilibrium) statistical mechanics and one of the most important objects in these notes. It encodes how the probabilities are partitioned among the microstates and actually allow us to calculate all the thermodynamic properties of the system (see Supporting Information).

Around 1950, providing a microscopic description of first- and second-order phase transitions became a true challenge that culminated in the development of various mathematical and computational techniques such as scaling theories and then renormalization group methods [6]. Although these techniques are computationally very effective in giving the critical point where the phase transition occurs, they fail to explain many important aspects of the phase transition phenomena. Specially, it is not clear how the (density of) free energy f can develop singularities at the first-order phase transitions, since, at finite volume, $f_N \propto \ln Z_N$, and Z_N is a sum of non-negative analytic functions. To address this problem, we will follow the ideas introduced by Lee and Yang and treat the partition function as a function of some complex control parameter (see refs. [7] and [8]). Here in particular, we consider complex temperatures following the prescription introduced by M. Fisher (see ref [9]). Singularities of the free energy (or others thermodynamic potentials), are given by the zeros of the partition function. At the thermodynamic limit, it is possible that those zeros accumulate at the physical transition point. This approach, that was later on generalized and extended to various systems, provides a lot of information about equilibrium phase transitions. To be more precise, if the function $\rho(x, y)$ denote the density of (complex) zeros of the partition function, then the partition

function Z is a functional of ρ and therefore every (equilibrium) thermodynamic property of the system is also a functional of ρ.

For practical and pedagogical purposes these notes are organized as follows. In section 2, we analyze a simple example of a physical system that undergoes a phase transition; we explicitly obtain the partition function for this system, show the existence of the phase transition and calculate the corresponding critical temperature. In section 3, we present a brief but self-contained exposition of the relationship of zeros of a partition function to the phase transitions of the system it describes. In particular, we have constructed an analogy between two-dimensional electrostatics and the thermodynamic properties of the system. In this analogy, the role of electric charges is played by the zeros of the partition function. In section 4, we use this analogy to characterize the nature of the critical point. In section 5, we discuss the key ideas used to implement this strategy to numerically obtain the critical temperature. We reserve section 6 to final comments.

2. A Simple Example: The Molecular Zipper

The so-called Molecular Zipper is a simple statistical physics model of the unraveling of a long chain of links (used as a toy model for DNA). The model became quite popular since it balances a great and interesting deal of physics with relatively simple calculations. The model was proposed in [2] and was one of the first one-dimensional models that exhibit a phase transition.

Suppose that a zipper in equilibrium with a heat bath (inverse temperature β) has N links. Each link can be closed with energy 0 or open with energy ϵ (this corresponds to the chemical energy necessary to open that link). The zipper can only unzip from one end and the final link can never be open (shown as a thick black square on the right side of Figure 1 below). This prevents the zipper from disconnecting and drifting apart. The k –th link can only open if all links before it are also open$(1,2,\cdots,k-2,k-1)$. When a link is closed there is only one possible configuration, however, when the link is open, the two pieces of the link are free to spin around and assume G different positions. We say that an open link has a degeneracy G. The orientation of the link does not change the energy stored in the link, so these setups all have the same energy.

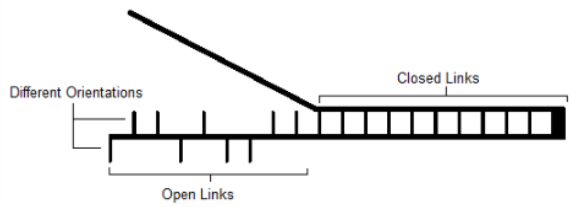

Figure 1. The Single Ended Molecular Zipper.

Let $\sigma = (\sigma_1, \sigma_2, \cdots, \sigma_N)$, such that $\sigma_k = 0$ if the k-th link is closed and $\sigma_k \in \{1,\cdots,G\}$ if the link is open. The "rules" of our zipper, also, impose that if $\sigma_k = 0$ then $\sigma_{k+1} = 0$. Imposing that the final link is always closed means that $\sigma_N = 0$. Each σ describes a distinct configuration or microstate of the zipper. Due to the restricted way that the chain of N links can unravel, it can only be in certain specific energy states. In fact, if the first n links are open, then the total energy of the system is equal to $E_n = n\epsilon$. Also, there are G^kdistinct configurations with energy $k\epsilon$. Therefore, the partition function of this model is given by

$$Z_N = \sum_{\sigma} e^{-\beta E(\sigma)} = \sum_{n=0}^{N-1} \sum_{\{\sigma: E(\sigma)=n\epsilon\}} e^{-\beta E(\sigma)} = \sum_{n=0}^{N-1} G^n e^{-\beta\epsilon n}. \quad (1)$$

For simplicity, let $z = Ge^{-\beta\epsilon}$, so our partition function becomes a polynomial in z:

$$Z_N = \sum_{n=0}^{N-1} z^n = 1 + z + \cdots + z^{N-1}.$$

Now, note that the partition function is just a geometric series and therefore

$$Z_N = \frac{1-z^N}{1-z}. \quad (2)$$

Now, the average fraction of open links is given by

$$\hat{\rho}_N(z) = \frac{\langle n \rangle}{N} = \frac{\sum_n n\, p_n}{N} = \frac{\sum_n n z^n}{N Z_N} = \frac{z}{N}\frac{d \ln Z_N}{dz}. \quad (3)$$

This leads to

$$\hat{\rho}_N(z) = \frac{1}{N}\frac{z}{1-z} - \frac{z^N}{1-z^N}.$$

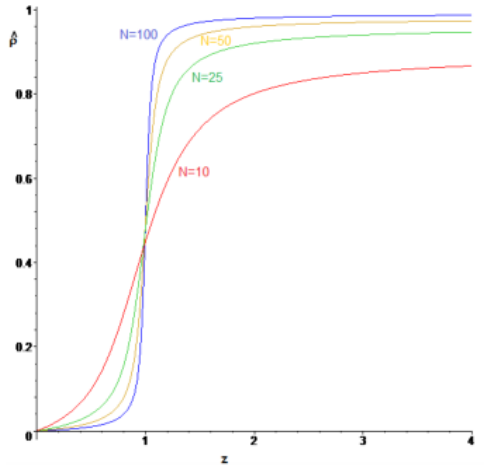

Figure 2. The average fraction of open links for a Molecular Zipper with $N = 10,25,50,100$ links.

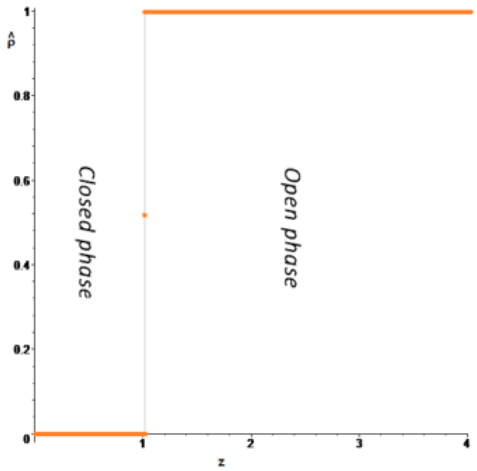

Figure 3. The average fraction of open links for an infinite long Zipper.

In Figure 2, we see how the average fraction of open links behaves as a function of $z = Ge^{-\beta\epsilon}$ for different sizes of the Zipper (N). We notice that the behavior changes when z approaches 1. In addition, this change of behavior becomes more pronounced as N becomes larger. The limit $N \to +\infty$ is called thermodynamic limit, we find that

$$\lim_{N\to+\infty} \hat{\rho}_N(z) = \hat{\rho}(z) = \begin{cases} 0 & z < 1 \\ \frac{1}{2} & z = 1 \\ 1 & z > 1 \end{cases}$$

We can see how $\hat{\rho}(z)$, the "density" of open links in an infinity long zipper, behaves as a function of z in Figure 3. Note that for $z < 1$ almost all links are closed, while for $z > 1$ almost all links are open. We can say that $z = 1$ separates two very distinct behaviors: the open phase and the closed phase of the zipper. That is a phase transition.

To continue our investigation, we now calculate the free energy of the zipper. The free energy per link is given by

$$f_N(z) = \frac{1}{N\beta} \ln Z_N = \frac{1}{N\beta} (\ln|z^N - 1| - \ln|z - 1|)$$

As $N \to +\infty, f_N \to f$, which is given by

$$f(z) = \begin{cases} 0 & z \leqslant 1 \\ \frac{1}{\beta} \ln z & z > 1 \end{cases}$$

The behavior of the free energy as a function of z is shown in the Figure 4 bellow.

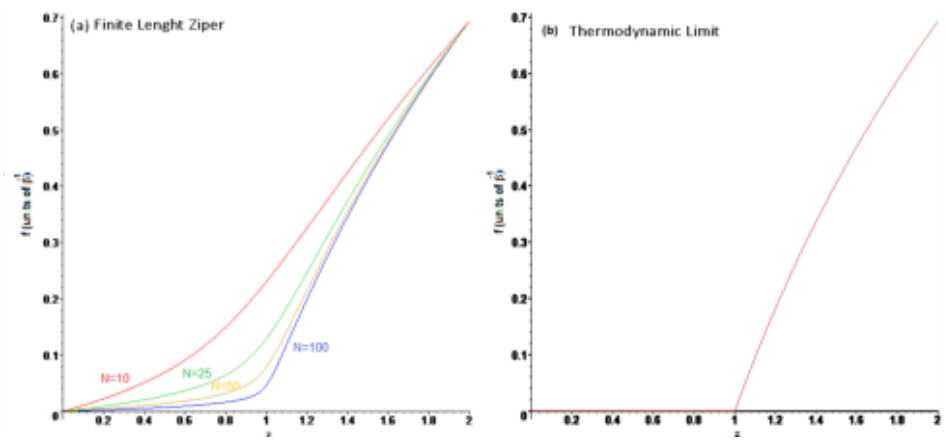

Figure 4. (a) Free energy per link for a Zipper with $N = 10,25,50,100$ links. (b) Free energy per link for a Zipper in the thermodynamic limit ($N \to +\infty$).

Note that at the critical point z = 1, the behavior of df/dz abruptly changes. Of course, following our discussion on the previous section and from eq.3, the singular behavior of f at $z = 1$ leads to the discontinuous change of $\hat{\rho}(z)$ at the same point. Roughly speaking, for $z < 1$ (low temperatures) the Zipper is using energy to break its bonds (and therefore raising its entropy). When $z = 1$ Zipper "melts", i.e. all its links suddenly open. From $z > 1$ (high temperatures) the energy becomes available for other uses.

We should take a minute here to ask if both $z < 1$ and $z > 1$ are physically acceptable situations. It quite important to stress that the degeneracy $G \geq 2$ implies that the situation $z = Ge^{-\beta\epsilon} \geq 1$ can be obtained. In fact, in the real world, we cannot control G or ϵ; they are fixed values for a given molecular zipper. However, we can control the temperature of the heat bath T. So the critical situation occurs when

$$\ln G = \beta_c \epsilon \Leftrightarrow T_c = \frac{\epsilon}{k \ln G}.$$

So, for $G \geq 2$, we can observe a change from the "closed phase" (for small temperatures) to the "open phase" (high temperatures). In this situation at the critical temperature T_c the molecule melts, i.e. almost all links suddenly open. This is a first order phase transition. Since the entropy (per link) s of the system is given by $\frac{\partial f}{\partial T}$ (see the Appendix), then ΔL the (specific) latent heat is given by

$$\Delta L = T_c\big(s(T_c^+) - s(T_c^-)\big) = kT_c \ln G = \epsilon$$

Now, we continue our analysis by noting that any singular behavior of $f_N \propto \ln Z_N$ must be associated with the zeros of the partition function Z_N. Analyzing the zeros of Z_N, we first note that $z = 1$ is not a zero since $Z_N(1) = N$, so the zeros are given by

$$z = e^{2\pi i \frac{n}{N}}.$$

That means the zeros lie on the unit circle. As $N \to +\infty$, all $z = e^{2\pi\,\alpha i}$ with α a rational number between 0 and 1, will be a zero. The distribution of the zeros of Z_N and the distribution in the thermodynamic limit are shown in Figure 5.

At the thermodynamic limit the zeros accumulate around the critical point $z = 1$, leading to the phase transition. Also, for $|z| < 1$, we have

$$Z_N \to \frac{1}{1-z}$$

as $N \to +\infty$, the behavior $\hat{\rho}(z) = 0$ will hold for all complex z inside the unit circle. Outside the unit circle, i.e. for $|z| > 1$, $\hat{\rho}_N$ asymptotically grows as

$$\hat{\rho}_N \to \frac{z^N}{z^N - 1} \neq 0.$$

So, the limit distributions of zeros (i.e. the unit circle) establish a boundary between the two phases. In the next section, we will develop these ideas in a more general context.

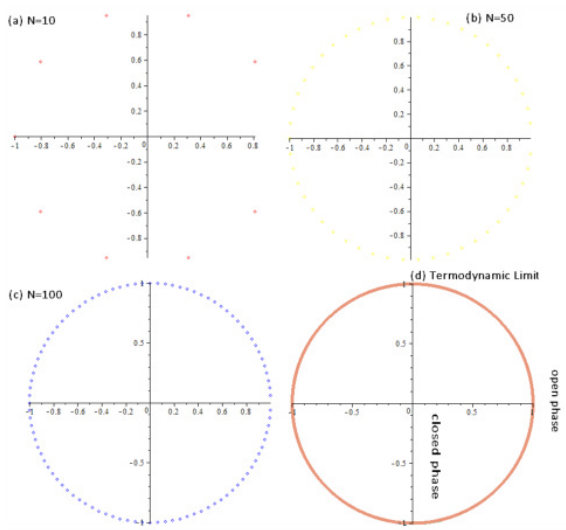

Figure 5. The distribution of the zeros of the partition function of the Molecular Zipper: (a)N = 10 links. (b) N = 50 links. (c) N = 100 links (d) Thermodynamic Limit.

3. Zeros of the Partition Function

In this section we examine the relationship of zeros of a partition function to the phase transitions of the system it describes. We try to present a brief but self-contained exposition of the fundamental ideas, but the whole topic is quite large. For a more detailed and mathematically rigorous presentation, we suggest ref. [10].

Here, we assume that the energies of the microstates of the system are discrete and given by $E_n = \epsilon_0 + \epsilon n$, where ϵ_0 is the ground state energy and ϵ is the lowest energy difference. Without loss of generality the ground state energy can be taken to be $\epsilon_0 = 0$. So the partition function can be written as a polynomial in some variable z,

$$P_N(z) = a_0 + a_1 z + \cdots + a_N z^N \qquad (4)$$

where $a_n \geq 0$, for $n = 0, \cdots, N-1$ and $a_N > 0$. From the fundamental theorem of algebra P_N has exactly N roots (which can be degenerated) and can be completely specified by knowing its roots $r_n, n = 1, \ldots, N$, and the leading coefficient a_N. In fact, we can write

$$P_N(z) = a_N \prod_{n=1}^{N} (z - r_n). \qquad (5)$$

Since we are considering all coefficients $a_n \geq 0$, we see that P_N has no roots in the positive real line (in fact, for $z > 0$, we have $P_N(z) > 0$). Furthermore, since all coefficients are real, then if r is a root of P_N, then $\bar{r}$ (the complex conjugate or r) is also a root. This means the zeros must be symmetrically distributed around the real axis and never touch the positive real axis (no zero of $P_N(z)$ can be real and positive). Figure 6 gives an example of such distribution for $N < +\infty$.

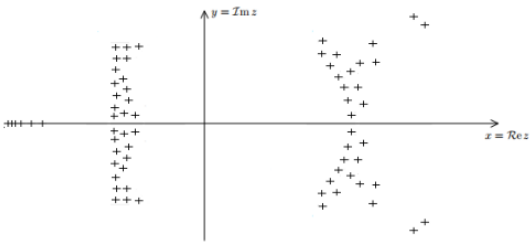

Figure 6. Example of a distribution of zeros for N finite.

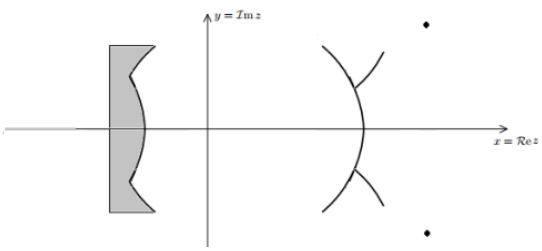

Figure 7. Example of a distribution of zeros in the thermodynamic limit.

As the system grows, more microstates become acceptable ($N \to +\infty$). The number of zeros will grow and can accumulate in areas, curves and points of the complex plane. Especially in the thermodynamic limit a pair of zeros can become closer to the positive real axis. Figure 7 show an example of such limit distribution.

We now define for all complex z, except for the zeros $z = r_n = x_n + iy_n$, the (complex density of) free energy

$$f_N(z) = \frac{1}{N\beta} \ln P_N(z) \qquad (6)$$

This free energy can be rewritten using the factorization of eq. 5 to obtain

$$f_N(z) = \frac{\ln a_n}{N\beta} + \sum_{n=1}^{N} \frac{\ln(z - r_n)}{N\beta}. \qquad (7)$$

The last equation can be written in terms of the density of the zeros of the partition function, giving us

$$f_N(z) = \frac{\ln a_n}{N\beta} + \int_{\mathbb{R}^2} \rho_N(x,y) \ln(z - x - iy)\, dxdy.$$

where $\rho_N(x,y)$ is the density of zeros of the partition function Z_N. While N is finite, this density is simply given by

$$\rho_N(x,y) = \frac{1}{N} \sum_{n=1}^{N} \delta(x - x_n)\delta(y - y_n) \qquad (8)$$

where $x_n + iy_n$ is a zero of the partition function and $\delta(x)$ is the Dirac Delta function, which can be roughly defined by the relations

$$\delta(x) = 0\ \forall x \neq 0 \text{ and } \int_{-\infty}^{+\infty} f(x)\delta(x)dx = f(0), \forall f \text{ continous.}$$

Now we note that a Taylor series expansion of $f_N(z)$ around any point z which is not a zero of $P_N(z)$ has a finite radius of convergence (given by the distance to the nearest zero from z). This implies that $f_N(z)$ is analytic in any region of the complex plane that has no partition function zeros. Since a phase transition correspond to a discontinuity in a derivative of the free energy, we see that such a transition can only occur at a point z_c in the complex plane if there is at least one zero of the partition function Z_N within any arbitrarily small region around the point z_c. If N, the number of partition function zeros r_n is finite, only at the isolated points r_n, we can identify a phase transition (at this points f exhibits a logarithmic singularity). Since such a point cannot lie on the positive real axis, there is no scope for a physical

phase transition in a finite system. However, if the partition function zeros accumulate towards a point x_c on the real axis as we increase the number of zeros N to infinity there is the possibility of a phase transition.

In order to deal with the thermodynamic limit (see ref. [11] for rigorous considerations) we shall assume that the limit

$$\lim_{N\to\infty} f_N(z) = f(z)$$

exists and we may write

$$f(z) = \frac{1}{\beta}\int_{\mathbb{R}^2} \rho(x,y)\ln(z - ix - iy)\,dxdy + const.$$

the constant term above is physically irrelevant (it can be eliminated by changing the ground state energy ϵ_0 to an adequate value) and we will neglect it in the following. Here $\rho(x,y)$ is the local density of zeros in the thermodynamic limit, i.e.

$$\lim_{N\to\infty} \rho_N(z) = \rho(z)$$

From eq. 8, we see that

$$\int_{\mathbb{R}^2} \rho(x,y)dxdy = 1 \qquad (9)$$

Now, we remark that $f(z)$ is a complex-valued function which is analytic outside the regions containing zeros (i.e. f is analytic when $\rho(x,y) = 0$). To get a further understanding on f, we decompose it in its real and imaginary parts, i.e. we write

$$\beta f(z) = \phi(z) + i\,\psi(z) = \mathrm{Re}\, f(z) + i\,\mathrm{Im}\, f(z)$$

where

$$\phi(z) = \int_{\mathbb{R}^2} \rho(x,y)\ln|z - x - iy|\,dxdy \qquad (10)$$

and

$$\psi(z) = \int_{\mathbb{R}^2} \rho(x,y)\arg(z - x - iy)\,dxdy \pmod{2\pi} \qquad (11)$$

So, from basic complex analysis (see ref. [12] for a fast introduction to complex functions), Cauchy-Riemann equations must hold everywhere $f(z)$ is analytic. So, if $z \in \mathbb{C}$ is not a zero, then

$$\frac{\partial\phi}{\partial x}(z) = \frac{\partial\psi}{\partial y}(z) \text{ and } \frac{\partial\phi}{\partial y}(z) = -\frac{\partial\psi}{\partial x}(z).$$

So everywhere f is analytic, we must have that

$$\vec{\nabla}\phi \cdot \vec{\nabla}\psi = 0 \text{ i.e. } \vec{\nabla}\phi \perp \vec{\nabla}\psi \qquad (12)$$

Also, if z is not a zero of the partition function, i.e. $\rho(z) = 0$, then Cauchy-Riemann equations also implies that

$$\nabla^2\phi(z) = 0 \text{ and } \nabla^2\psi(z) = 0, \text{ if } \rho(z) = 0$$

Now, we desire to obtain an expression for the density $\rho(z)$ in terms of the free energy $f(z)$. First, we note that

$$\nabla^2 \ln|x + iy| = 2\pi\delta(x)\delta(y).$$

That is $\ln|x + iy|$ is the kernel (or Green function) of the two-dimensional Laplacian. So, we find that

$$\nabla^2\phi(z) = \nabla^2\int_{\mathbb{R}^2} \rho(x',y')\ln|z - x' - iy'|dx'dy' = \int_{\mathbb{R}^2} \rho(x',y')\nabla^2\ln|z - x' - iy'|dx'dy'$$
$$= 2\pi\int_{\mathbb{R}^2} \rho(x',y')\delta(x - x')\delta(y - y')dx'dy'$$

where we used $z = x + iy$. So, we see that

$$\nabla^2\phi(z) = 2\pi\rho(z). \qquad (13)$$

This equation is familiar from electrostatics (although in two-dimensions). In this sense, $\phi(z)$ is analogous to an electrostatic potential, $-\vec{\nabla}\phi(z)$ is analogous to a static electric field and $\rho(z)$ is analogous to a density of electric charges.

4. The Nature of the Critical Point

Up to now, we consider the problem of the location of the phase transition point, i.e. how, when knowing the partition function (in the thermodynamic limit), can one locate a phase transition point by investigating the zeros of this partition function with respect to a control parameter of the system. In this section we wish to consider a slightly related problem, namely, the

characteristics of the transition, i.e. how can one extract information on the nature of the phase transition (e.g. if it is a discontinuous or continuous one) from the properties and distribution of these zeros.

Here, we put forward the electrostatics analogy and note that as long as we can integrate $\rho(z)$ over bounded regions containing any singularities of f, the free energy will be a continuous function (see ref. [13]). We shall employ this idea to derive a rule for locating phase boundaries given a partition function. Suppose that around points z_1 and z_2 in the complex plane, one has distinct analytic expressions for $\phi_1(z)$ and $\phi_2(z)$, this means $\phi_1 \neq \phi_2$ (i.e. they not the same function over the entirety complex plane). In order to guarantee that the potential is continuous at all points on the complex plane, we must have a phase boundary $\mathcal{C}$ at those values of z for which the condition

$$\phi_1(z) = \phi_2(z). \tag{14}$$

holds. This is the scenario of a phase transition as we describe in the introduction of this chapter. The change of behavior from ϕ_1 to ϕ_2 is delimited by the zeros of the partition function. Now, assume that the boundary between the region where $\phi_1(z)$ and $\phi_2(z)$ holds are given by a curve. So by continuity, the analytic expressions for $\phi_1(z)$ and $\phi_2(z)$ must hold on the phase boundary $\mathcal{C}$, so since $\phi_1(z)$ and $\phi_2(z)$ are different functions, some derivatives of $\phi(z)$ will be different at these values of z (i.e. at the zeros of the partition function) and we expect the density of zeros at these points to be non-zero.

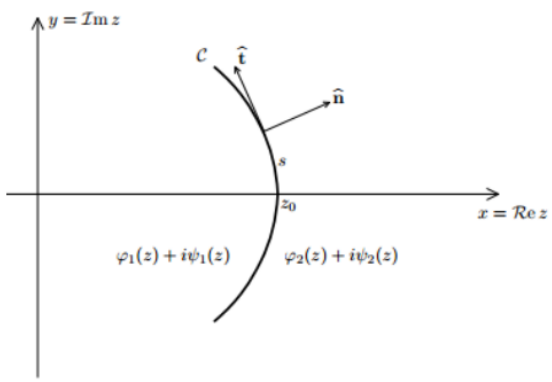

Figure 8. A phase boundary.

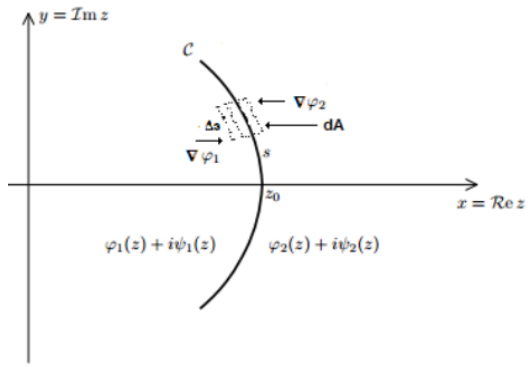

Figure 9. Application of the divergence theorem.

In the case of a "physical phase transition", a solution of eq. 14 describes a curve C that intersects the positive real z axis at a point z_0 (see Figure 8). At this point, we now understand that in the case of a phase transition the zeros must pinch the positive real axis $z_0$in the thermodynamic limit. At this situation, we say that a physical phase transition to take place, we are interested in the density of zeros per unit length of this curve $\mathcal{C}$. Now, let s be the arc length measured along $\mathcal{C}$ from the transition point z_0. Let $\lambda(s)$ to be the line density of zeros along the curve $\mathcal{C}$. Consider a short section of the curve $\mathcal{C}$ with length Δs enclosed by a closed curve γ, that delimits an area dA, and has two sides parallel to $\mathcal{C}$ and the other two sides perpendicular to $\mathcal{C}$ (see Figure 9). Integrating the density $\rho(z)$ over this area we have that

$$\int_{dA} \rho(x,y)dA = \lambda(s)\Delta s.$$

On the other hand, the divergence theorem applies here (see Figure 9) so

$$\int_{\gamma} \vec{\nabla}\,\phi(z)dz = \int_{dA} \nabla^2\phi(z)\, dA.$$

So we see that

$$2\pi \int \lambda(s)ds \;= \Delta s\left(\vec{\nabla}\phi_2(z) - \vec{\nabla}\phi_1(z)\right) \cdot \hat{n}(z) \tag{15}$$

where $\hat{n}(z)$ is a unitary vector normal to the curve $\mathcal{C}$ at the point z (see Figure 8). At that point, eq.12 reads

$$\vec{\nabla}\phi(z) \cdot \hat{n}(z) = \vec{\nabla}\psi(z) \cdot \hat{t}(z) \tag{16}$$

where $\hat{t}(z)$ is the unit vector tangent to the curve $\mathcal{C}$ at the point z (see Figure 8). So, we can recognize the scalar product in eq. 16 as the directional derivative of ψ along the curve $\mathcal{C}$. Putting this together with our expression for the line density of charges, we find that

$$\lambda(s) = \frac{1}{2\pi}\frac{d}{ds}\left(\psi_2(z) - \psi_1(z)\right). \qquad (15)$$

Let us now assume that in the thermodynamic limit, there is a phase transition at the point $z_0 > 0$. Then, either side of the transition the free energy f is analytic so it can be written as a Taylor series. For $\mathrm{Re}(z - z_0) < 0$, we have the series

$$\beta f_1(z) = \beta f_1(z_0) + a_1(z - z_0) + b_1(z - z_0)^2 + c_1(z - z_0)^3 + \cdots$$

while for $\mathrm{Re}(z - z_0) > 0$, we have the Taylor series

$$\beta f_2(z) = \beta f_2(z_0) + a_2(z - z_0) + b_2(z - z_0)^2 + c_2(z - z_0)^3 + \cdots$$

Now, we note that the free energy must be real along the real z axis, so the coefficients a_k, b_k and c_k $(k = 1,2)$ must also be real. Since ϕ , the real part of $f(z)$ is continuous across the phase boundary curve, then eq. 14 must hold for both z and z_0. Therefore, writing $z = x + iy$ and $z_0 = x_0$, we find that $(k = 1,2)$

$$\phi_k(z) = \phi(x_0) + a_k(x - x_0) + b_k[(x - x_0)^2 - y^2] + c_k\,[(x - x_0)^3 - 3y^2(x - x_0)] + \cdots$$

Similarly, we find that

$$\psi_k(z) = a_k y + b_k[2y(x - x_0)] + c_k[3y(x - x_0)^2 - y^3] + \cdots$$

We now consider how the curve boundary $\mathcal{C}$ behaves near the critical point. In particular, we will show that the angle with which the zeros line cross the critical point can be used to classify the phase transition.

4.1 First order Phase Transition

In a first order phase transition, the first derivative of βf is discontinuous across the phase boundary curve. This means $a_1 \neq a_2$. Assume that $b_1 \neq b_2$. Therefore, up to the second order,

$$a_1(x - x_0) + b_1[(x - x_0)^2 - y^2] = a_2(x - x_0) + b_2[(x - x_0)^2 - y^2].$$

Therefore,

$$y^2 = (x - x_0)^2 + \frac{a_2 - a_1}{b_2 - b_1}(x - x_0) + \mathcal{O}((x - x_0)^3 - 3y^2(x - x_0))$$

and we see that near the transition point x_0, the curve of zeros is a hyperbola that passes smoothly through the transition point. Hence the tangent to the curve of zeros is parallel to the imaginary axis at x_0 as shown in Figure 10.

The density of zeros at the transition point z_0 is nonzero at a first-order phase transition (i.e. one at which the first derivative of the free energy is discontinuous). In fact, eq. 15 implies that

$$\lambda(0) = \frac{a_2 - a_1}{2\pi}.$$

Recalling that the coefficients $a_k = \frac{\partial f_k}{\partial z}(z_0)$ and using that $z = e^{-\beta\epsilon}$, a simple application of the chain rule gives the (density of) entropy s at each side of the transition

$$s_k(z_0) = \frac{\partial f_k}{\partial T}(z_0) = \frac{a_k}{\beta}\frac{\partial z}{\partial T}(z_0) = a_k\frac{\epsilon}{T_c}z_0,$$

where $T_c = -\frac{\epsilon}{k\ln z_0}$ denotes the critical temperature. Therefore ΔL, the latent heat of the system is given by

$$\Delta L = T_c(s_2(T_c) - s_1(T_c)) = 2\pi\lambda(0)z_0\epsilon.$$

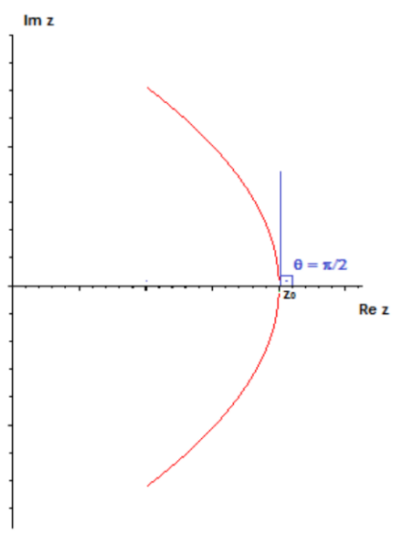

Figure 10. How the zeros approach a critical point in a first order phase transition.

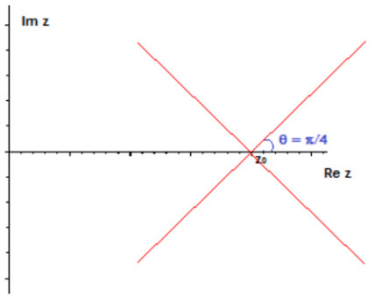

Figure 11. How the zeros approach a critical point in a second order phase transition.

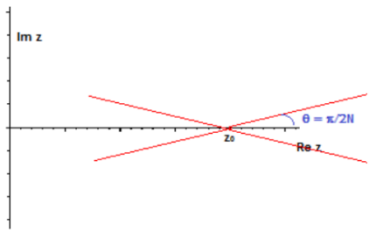

Figure 12. How the zeros approach a critical point in a N-th order phase transition.

4.2 Second-order phase transition

In a second order phase transition, the second derivative of f is discontinuous across the the phase boundary curve. Then $a_1 = a_2$ but $b_1 \neq b_2$, we have that the curve $\mathcal{C}$ obeys the equation

$$y = \pm(x - x_0).$$

So, in the vicinity of z_0 it consists of two straight lines that make an angle of $\pm\frac{\pi}{4}$ with the real axis (and $\frac{\pi}{2}$ between them) and meet at z_0 as shown in Figure 11.

Over the curve $y = (x - x_0)$ the imaginary part of f is given by

$$\psi_k(x + i(x - x_0)y) = ay + 2b_k y^2 + \mathcal{O}(y^3).$$

The length of the curve s between $z_0 = x_0$ and $z = x + i(x - x_0)$ satisfies $s_2 = 2y^2$, then eq. 17 implies that

$$\lambda(s) = \frac{1}{2\pi}\frac{d}{ds}(b_2 - b_1)s^2 = s\left(\frac{b_2 - b_1}{\pi}\right)$$

This shows that in a second-order phase transition, the density of partition function zeros decreases linearly to zero at the phase transition point.

Second-order phase transitions include the ferromagnetic phase transition observed in materials such as iron, where the magnetization (which is the first derivative of the free energy with respect to the applied magnetic field) increases continuously from zero as the temperature is lowered below a critical temperature called the Curie temperature (the temperature at which the material lose its permanent magnetic properties, to be replaced by the magnetic properties induced by the external magnetic field). The magnetic susceptibility, the second derivative of the free energy with the field, changes discontinuously.

4.3 Higher-order phase transitions

If the discontinuities appear at higher orders derivatives of the complex-valued free energy, then one can repeat the above type of reasoning to find the equation of $\mathcal{C}$ and the density of zeros in the vicinity of the transition point z_0.

As an example, we consider a third order phase transition, i.e. the third derivative of f is discontinuous across the the phase boundary curve. This means $a_1 = a_2$ and $b_1 = b_2$, but $c_1 \neq c_2$. This implies that, up to the fourth order, the curve $\mathcal{C}$ obeys the equation

$$y = \pm\frac{\sqrt{3}}{3}(x - x_0)$$

So, in the vicinity of z_0 it consists of two straight lines that make an angle of $\pm\frac{\pi}{6}$ (since $\tan\frac{\pi}{6} = \frac{\sqrt{3}}{3}$) with the real axis. The length of the curve s between $z_0 = x_0$ and z satisfies $s = 2y$, then eq. 17 implies that

$$\lambda(s) = \left(\frac{c_2 - c_1}{2\pi}\right)\frac{d}{ds}(3y(s)(x(s) - x_0)^2 - y^3(s))$$
$$= 4\left(\frac{c_2 - c_1}{\pi}\right)\frac{dy^3}{ds} = 3\left(\frac{c_2 - c_1}{2\pi}\right)s^2$$

More generally, write $z - z_0 = s\,e^{i\alpha}$ and let $f_k(z) = a_0^{(k)} + a_1^{(k)}z + a_2^{(k)}z^2 + \cdots$. So, we have that

$$f_k(z) = \sum_n a_n^{(k)} s^n e^{in\alpha}.$$

If we examine a n-th order phase transition the first different coefficient will be the n-th coefficient, i.e. $a_k^{(1)} = a_k^{(2)}$ for $0 \leq k \leq n - 1$, and $a_n^{(1)} \neq a_n^{(2)}$. So, we must have $a_n^{(1)}\cos n\,\alpha = a_n^{(2)}\cos n\,\alpha$. Therefore, the curve $\mathcal{C}$ does not cross smoothly the real axis but approaches it at an angle $\pm\frac{\pi}{2n}$.

from above and below as shown in Figure 12. So, for a sufficiently small arc length, the application of eq. 17 yields

$$\lambda(s) = \left(\frac{a_n^{(2)} - a_n^{(1)}}{2\pi}\right) n s^{n-1}.$$

This result suggests that for a n-th order transition $f_2(z) - f_1(z) \sim z^n$.

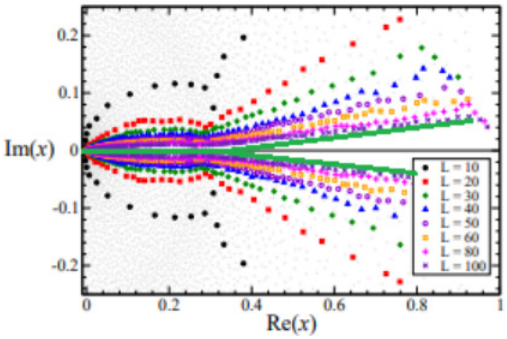

Figure 13. Zoom on the real positive semi-axis of the Fisher zeros map on the $x = e^{-\beta\epsilon}$ plane for the 2D classical XY-model in a $L \times L$ square lattice. Adapted from [14]. The solid green line plots the expected limit $L \to +\infty$ limit.

A particular interesting case of phase transition is the BKT transition. It is a transition from bound vortex-antivortex pairs at low temperatures to unpaired vortices and anti-vortices at T_c. The nature of this transition is completely different from the usual first order (discontinuous or with latent heat) or second order (without latent heat) phase transitions. Long range order does not exist and the two-point correlation function has an algebraic decay at low temperatures ($T < T_c$) and an exponential decay for high temperatures ($T > T_c$). The most famous example is the BKT transition in the two-dimensional XY model (see [4]). B.V. Costa et al studied the zeros of the partition function for this model in ref. [14], their results are shown in Figure 13. We see that in the thermodynamic limit the line of zeros attack the real positive semi-axis at a zero angle. The attack angle allows us to state that this is an infinite-order phase transition. There are many other examples of infinite-order phase transitions. They are continuous but break no symmetries. Many quantum phase transitions, e.g., in two-dimensional electron gases, belong to this class.

5. Numerical Computations

In the two last sections, we present a systematic approach to the problem of phase transition. Unfortunately, only a few special cases are accessible to a complete analytical description (such as the Molecular Zipper or the Ising model in one- and two-dimensions (see refs. [17] and [18])). Note that the thermodynamic limit of ρ the density of zeros is quite hard to obtain and even for a moderate size systems the quantity Z_N is not simple to be calculated. The best we can do is to numerically estimate ρ_N for N large enough, and use finite size scaling analysis to estimate the behavior of the thermodynamic limit (see ref. [19]). The computational approach to the study of phase transitions consists of two steps: the gathering of data in the form of a Monte Carlo simulation, followed by a numerical analysis of appropriate quantities. In our case, the Monte Carlo simulation is used to approximate the coefficients $g(E)$ of the polynomial

$$Z_N = \sum_E g(E) e^{-\beta E}$$

For a fixed (inverse) temperature β and size N of the system, the process has the following steps: (a) Begin with an initial microstate s_0. (b) Compute the energy E_0 of this microstate. (c) Randomly, choose a new microstate s_1. (d) Calculate E_1. (e) if $E_1 \leq E_0$ accept s_1 and return to step (c). (e') if $E_1 > E_0$, accept $s_1$with probability $p = e^{-\beta\delta E}$, where $\delta E = E_1 - E_0$, and return to step (c). We register the number of accepted microstates for each energy level and produce a histogram. If the size of the system N is large enough, this process will lead to a flat histogram. When the histogram is considered flat enough, we stop the process as shown in Figure 14.

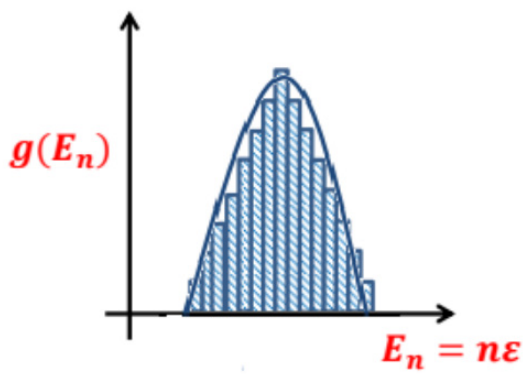

Figure 14. A "flat histogram" generated by a Monte Carlo Simulation.

The coefficients of the polynomial Z_N are approximated by the corresponding numbers of the histogram up to a multiplicative constant (which is irrelevant for the analysis of the zeros).

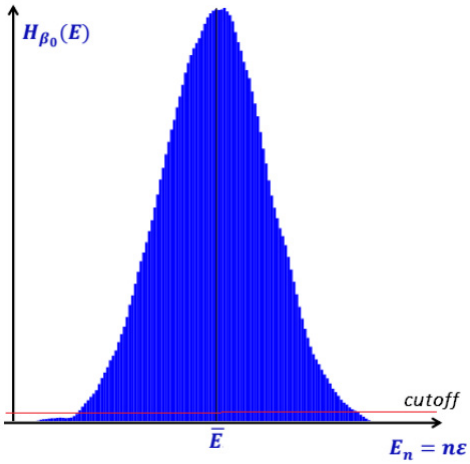

Figure 15. A histogram for EPD method and the cutoff.

In principle, we can numerically compute the zeros of Z_N with an arbitrary (fixed) precision δz. Let z_1 be the closest root to the positive real half-axis (called the dominant zero). If $\mathrm{Im}\, z_1 > \delta z$, i.e. z_1 is not close enough to the real axis, we increase the size N of the system and rerun our algorithm. Otherwise, $\mathrm{Im}\, z_1 < \delta z$ and we estimate the critical point by putting $z_c = \mathrm{Re}\, z_1$. The other roots allow us to estimate the density of zeros ρ and therefore all the thermodynamics of the system. The results shown in Figure 13 are obtained using this method.

5.1. Energy Probability Distribution Zeros

The use of Monte Carlo techniques requires the construction of the density of states in large intervals of energy (or, if allied with finite size scaling, the estimation of quantities like the specific heat or susceptibilities in a wide range of temperatures). Although many of these techniques are well developed, they are also demands time when the system size becomes large. In this subsection, we discuss a method to study the critical behavior of a system based on the partial knowledge of the complex Fisher zeros set of the partition function. This method is originally presented in ref. [15].

To introduce the method, fix a β_j and let $\hat{z} = e^{-\beta_j \epsilon} z$. Therefore, we write the partition function as a polynomial in $\hat{z}$,

$$Z_N = \sum g(n\epsilon) z^n = \sum g(n\epsilon) z^n = \sum g(n\epsilon) e^{+n\beta_j \epsilon} \hat{z}^n = \sum h_{\beta_j}(n\epsilon) \hat{z}^n.$$

The coefficient $h_{\beta_j}(n\epsilon)$ of the new polynomial is nothing but the unnormalized canonical energy probability distribution (EPD). Clearly, there is an one-to-one correspondence between the Fisher zeros z and the EPD zeros $\hat{z}$, since they are related through a trivial conformal transformation.

Note that for β_j close to the critical (inverse) temperatureβ_c, the critical EPD zero $\hat{z}_c \approx 1$. So with this transformation, we can "filter" the region where the dominant zero is located and still have the relevant information about the phase transition. For finite systems, a small imaginary part of z_c is expected. Indeed, we may expect that the dominant zero is the one with the smallest imaginary part on the real positive region regardless the choice of β_j. Once we locate the dominant zero, its distance to 1 allows us to compute $\Delta\beta$ and an estimate for the critical β_c.

An algorithm following those ideas is: (a) For a fixed β_j construct a histogram for the coefficients $h_{\beta_j}(n\epsilon)$. (b) Find the zeros of $\sum h_{\beta_j}(n\epsilon)\, \hat{z}^n$ near $\hat{z} = 1$. Let $\hat{z}_1$be the dominant zero. (c) If $|\hat{z}_1 - 1|$ is small enough (i.e. is less than the precision with which the roots of the polynomial are computed) then stop. (c') Otherwise compute $\beta_{j+1} = \beta_j - \frac{\ln \mathrm{Re}\, z_1}{\epsilon}$ and return to step (a).

For estimating the critical temperature, this procedure has a clearly advantage since we can search for roots only near $\hat{z} = 1$. Furthermore, usually, the histogram for $h_{\beta_j}(n\epsilon)$ is highly concentrated near the average energy (see Figure 15). Note that very small coefficients $h_{\beta_j}(n\epsilon)$ are related with states with a very small probability to occur and are not pertinent to the phase transition. Thus, for $\beta_j \approx \beta_c$, we can judiciously discard small values of $h_{\beta_j}(n\epsilon)$. Say we discard every $h_{\beta_j}(n\epsilon)$ smaller than some cutoff criteria. Those small values of $h_{\beta_j}(n\epsilon)$ generally related to very high energy states, as a consequence, we do not have to deal with high degree polynomials with coefficients spanning over many orders of magnitude. The advantage is that the "relevant" polynomial used to approximate

the partition function has fewer roots with its coefficients ranging in a narrow region. The method is iterative, so that, the transition temperature can be (in principle) approached at will.

6. Forewords

This In these notes, we have shown a general mathematical approach to the study of phase transitions. We described how partition function zeros are related to phase transitions:

1. The accumulation of zeros of the partition function along the (physically accessible) real, positive semi-axis of the complex z indicates the location of the phase transition point(s);
2. The density of zeros near such an accumulation point determines the order and strength of the transition (according to Ehrenfest's classification scheme) at that point.

Also, we obtained a rule (eq. 14) for locating phase boundaries and a method (eq. 17) for finding the density of zeros along such boundaries. We show that first-order (continuous) transitions exhibit a nonzero density of partition functions zeros at the transition point. On the other hand the density of zeros decays as a power-law to zero at the transition point when the associated phase transition is continuous. Here, we chose to make a quite general analysis (although not quite rigorous). So far, our presentation does not follow the footprints of history. In fact, zeros in the complex fugacity (or chemical potential) plane offer a much more comfortable scenario and are the ones first studied in refs [7] and [8], today those zeros are commonly named Lee-Yang zeros. Zeros in the complex temperature plane (see ref. [9]), called Fisher zeros, and appeared some years after. Of course, in the equilibrium theory, these intensive "field-like" quantities play similar mathematical roles and one can just as easily generalize physical "field-like" variables (such as temperature) or fugacity-like variables (such as the quantity z considered above) to the complex plane without altering the properties of the partition function zero densities at first-order and high-orders phase transitions described above.

Despite the apparently wide generality of the partition theory of equilibrium phase transitions, demonstrating its validity in the general statistical mechanics scenario is a difficult task (although there are works in this direction, such as [16]). A key problem is that the location of the zeros is very particular to each partition function. Usually determining the partition function for an arbitrarily large system is a challenging task. In some fortunate cases, one can rely on specific properties of a particular partition function (see ref. [10] for a myriad of examples). But, in general, the only hope is to compute the partition function (and its zeros) through numerical procedures. We briefly discussed some of those methods in section 5.

We conclude by pointing out that the use of partition function zeros are a research field with increasing interest and activity. It worth to mention that beyond theoretical and computational approach, at least in the Lee-Yang formalism (complex fugacity zeros), the nature and existence of the zeros of the partition function was verified experimentally (see refs. [20] and [21]).

Supporting Information

Calculating Thermodynamic Quantities in the canonical ensemble

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