Zeros of the partition function for a continuum system at first-order transitions

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We extend the circle theorem on the zeros of the partition function to a continuum system. We also calculate the exact zeros of the partition function for a finite system where the probability distribution for the order parameter is given by two asymmetric Gaussian peaks. For the temperature-driven first-order transition in the thermodynamic limit, the locus and the angular density of zeros are given by $r=e^{(\Delta c/2l)\theta^2}$ and $2\pi g(\theta)=l[1+3/2(\Delta c/l)^2\theta^2]$, respectively, in the complex $z(\equiv re^{i\theta})$ plane where l is the reduced latent heat, Δc is the discontinuity in the reduced specific heat, and $z=\exp(1-T_c/T)$. [S1063-651X(96)10506-7]

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One of the fascinating subjects of equilibrium statistical mechanics is to understand how an analytic partition function acquires a singularity when the system undergoes a phase transition. For the last three decades, the main focus has been on the second-order transition. Only recently has a renewed interest in the first-order phase transition begun to emerge [1].

Since Yang and Lee [2] first published their celebrated papers on the theory of phase transitions and the circle theorem on the zeros of the partition function, there have been many attempts to generalize the theorem [3]. Fisher [4] initiated the study of zeros of the partition function in the complex temperature plane and Jones [5] proposed a scenario for the first-order transition for a continuum system. However, very little is known about the distribution of zeros for the continuum case. This is because the partition function for the continuum system is not a polynomial, in general, and the original proof of the circle theorem relied heavily on particular properties of the coefficients of a polynomial. Recently, we have been able to prove the theorem in a quite different approach [6] and this approach allows us to generalize the theorem further to the continuum case.

We found that the circle theorem follows from a certain mathematical relation that exists between a probability density function and the zeros of its characteristic function. In this paper, we prove that the zeros of the partition function can be expressed in terms of the discontinuities in the derivatives of the free energy across the phase boundary if there is a nonvanishing discontinuity in the first-order derivative, and that the zeros lie on the unit circle if the transition is symmetric. We further show that there are no zeros in the single-phase region where the probability distribution is given by a single Gaussian peak. We also calculate the zeros of the partition function exactly at the two phase coexistence point where the probability distribution is given by two asymmetric Gaussian peaks.

Furthermore, we find the finite-size scaling very similarly to that of the discrete system [6]. Therefore, this result can again be used, for a continuum system, (1) to resolve the recent controversy over equal weight versus equal height of the probability distribution functions [7–9] and (2) to distinguish the first-order transition from the second [10,6], just as we have done for the discrete system in Ref. [6].

We first note that the canonical partition function can be regarded as a moment generating function of a probability distribution function. Take, for example, a canonical partition function $Z(\beta)$ defined by $Z(\beta)=\int_{-\infty}^{\infty}e^{-\beta E}\Omega(E)dE$, where $\Omega(E)$ is the density of states at E, β is the inverse temperature $1/k_bT$, and k_b is the Boltzmann constant. We can identify this partition function as a moment-generating function $\mathcal{M}(t)$,

$$\mathcal{M}(t)\equiv Z(\beta)/Z(\beta_0)=\int_{-\infty}^{\infty}e^{tx}f(x)dx, \qquad (1)$$

where the probability density function is given by

$$f(x)=\Omega(x/\beta_0)e^{-x}\bigg/\int_{-\infty}^{\infty}\Omega(x/\beta_0)e^{-x}dx. \qquad (2)$$

In the above, $t=1-\beta/\beta_0$, $x=\beta_0E$, and β_0 is a reference inverse temperature around which the system fluctuates.

The characteristic function [11] for a probability density function $f(x)$ is defined by

$$\phi(\omega)=\int_{-\infty}^{\infty}e^{i\omega x}f(x)dx, \qquad (3)$$

where i is the imaginary unit. If $\phi(\omega)$ can be analytically continued into the complex ω plane, $\mathcal{M}(t)=\phi(-it)$ is the moment-generating function. Since the characteristic function always exists and its properties are well known [11], we will consider zeros of the characteristic function.

The logarithm of $\phi(\omega)$ is known as the second characteristic function or cumulant generating function and denoted by $\psi(\omega)$. That is,

$$\psi(\omega)=\ln[\phi(\omega)]=\sum_{s=1}^{\infty}\gamma_s\frac{(i\omega)^s}{s!}. \qquad (4)$$

The expansion coefficients, γ_s are known sth cumulants or semi-invariants and are calculable by the formula, $\gamma_s=\partial^s\psi(\omega)/\partial(i\omega)^s|_{i\omega=0}$.

Since $i\omega$ is the temperature t and $\psi=\Sigma_{s=1}^{\infty}\gamma_st^s/s!$ is the *free energy* $-\beta F(t)$ in the above example, $\gamma_1=\beta_0\langle E\rangle$ and

$\gamma_2=\beta_0^2\langle(E-\langle E\rangle)^2\rangle=C_v/k_b$, where $\langle E\rangle$ is the internal energy and C_v is the heat capacity. The higher-order cumulants are similarly related to the higher-order derivatives of the free energy.

We will consider zeros of the characteristic function in the finite region only. If the density function is not a delta function (in which case there are no zeros in the finite region) we can always divide the density function into two parts, taking a point x_* somewhere in the middle of the distribution.

That is,

$$f(x)=c[f_1(x)+af_2(x)], \tag{5}$$

where $f_1(x)=f(x)/c$ and $f_2(x)=0$ for $x<x_*$, $f_1(x)=0$ and $f_2(x)=f(x)/ac$ for $x\geqslant x_*$, $c=\int_{-\infty}^{x_*}f(x)dx$, and $a=\int_{x_*}^{\infty}f(x)dx/\int_{-\infty}^{x_*}f(x)dx$.

Consider the zeros of characteristic function

$$\phi(\omega)=\phi_1(\omega)+a\phi_2(\omega). \tag{6}$$

If $\psi_1(\omega)$ and $\psi_2(\omega)$, the cumulant generating functions of $\phi_1(\omega)$ and $a\phi_2(\omega)$ exist except at isolated zeros, then we can write Eq. (6) in terms of these cumulant generating functions as

$$\phi(\omega)=2e^{\bar{\psi}}\cosh[\tilde{\psi}(\omega)]. \tag{7}$$

In the above, $\overline{\psi}(\omega)=[\psi_1(\omega)+\psi_2(\omega)]/2$ and $\tilde{\psi}(\omega)=[\psi_2(\omega)-\psi_1(\omega)]/2$.

It should be noted that because of the factor a in $\psi_2(\omega)$, $\psi_2(0)=\ln(a)$. It should further be noted that the zeros of $\phi(\omega)$, in Eq. (6) are zeros of $\cosh[\tilde{\psi}(\omega)]$ only. This is because any zeros of $e^{\bar{\psi}}$ cancel the poles of $\cosh[\tilde{\psi}(\omega)]$. This, in turn, can be understood because Eq. (7) is nothing but $2(a\phi_1\phi_2)^{1/2}[\{\phi_1+a\phi_2\}/2(a\phi_1\phi_2)^{1/2}]$.

Therefore, the zeros of $\phi(\omega)$ may be obtained by solving

$$\tilde{\psi}(\omega)=\pm i(1/2+k)\pi\equiv iI_k, \tag{8}$$

where $k=0,1,2,\ldots$.

Now, using the cumulant expansion (4) we can write $\tilde{\psi}(\omega)$ as

$$\tilde{\psi}(\omega)=\sum_{s=1}^{\infty}\tilde{\gamma}_s\frac{(i\omega)^s}{s!}+\frac{\ln(a)}{2}, \tag{9}$$

where $\tilde{\gamma}_s=(\gamma_s^{(2)}-\gamma_s^{(1)})/2$.

If $\tilde{\gamma}_1=\{[d/d(i\omega)]\tilde{\psi}(\omega)\}_{i\omega=0}\neq 0$, we can invert the above series. We first define $\hat{\psi}(\omega)=\{\tilde{\psi}(\omega)-[\ln(a)/2]\}/\tilde{\gamma}_1$.

The local inverse function near the origin can be obtained in the power series as, using the Lagrange formula [12],

$$i\omega=\sum_{s=1}^{\infty}b_s\hat{\psi}^s, \tag{10}$$

where

$$b_s=\frac{1}{s!}\frac{d^{s-1}}{d(i\omega)^{s-1}}\left(\frac{i\omega}{\hat{\psi}(\omega)}\right)^s\Bigg|_{i\omega=0}. \tag{11}$$

It should be noted that, since $\tilde{\gamma}_s$'s are real, the b_s's are also real. The first few b_s's are $b_1=1$, $b_2=-\hat{\gamma}_2$, $b_3=2\hat{\gamma}_2^2-\hat{\gamma}_3$, $b_4=-5\hat{\gamma}_2^3+5\hat{\gamma}_2\hat{\gamma}_3-\hat{\gamma}_4$, $b_5=14\hat{\gamma}_2^4-21\hat{\gamma}_2^2\hat{\gamma}_3+3\hat{\gamma}_3^2+6\hat{\gamma}_2\hat{\gamma}_4-\hat{\gamma}_5$, [13] where $\hat{\gamma}_s=\tilde{\gamma}_s/\tilde{\gamma}_1/s!$.

Therefore, the zeros of the characteristic function $\phi(\omega)$ can be expressed by

$$i\omega_k=\sum_{s=1}^{\infty}b_s\left(\frac{iI_k-[\ln(a)/2]}{\tilde{\gamma}_1}\right)^s, \tag{12}$$

where the b_s's I_k are given by (11) and (8).

Although the dividing point x_* is arbitrary and the b_s's should not depend on x_*, $\tilde{\gamma}_s$'s have little meaning unless the original probability density function has two separate distributions over two distinct regions and x_* is taken at some point between the two regions.

For a symmetric distribution, it is convenient to shift the origin to x_* so that $f(x)=f(-x)$. Zeros are unaffected by the shift since the cumulants are invariant except for γ_1 [11] and the zeros depend only on $\tilde{\gamma}_1$, the difference between γ_1's, which is also invariant.

Since $\phi_1(-\omega)=\phi_2(\omega)$, we have $\tilde{\gamma}_s=\gamma_s^{(2)}-\gamma_s^{(1)}=0$ for even s and $\tilde{\gamma}_s=\gamma_s^{(2)}=-\gamma_s^{(1)}$ for odd s in addition to $a=1$. This makes $\tilde{\psi}(\omega)$ in Eq. (9) an odd function of $i\omega$. Therefore, the function $[i\omega/\hat{\psi}(\omega)]^s$ on the right hand side of Eq. (11) becomes even, making the odd-numbered derivatives vanish. This makes only the odd-numbered coefficients b_{2s+1} survive. Thus we have $\omega=\Sigma_{s=0}^{\infty}(-1)^s b_{2s+1}(\hat{\psi}/i)^{2s+1}$.

Finally, by substituting the solution for zeros (8) in the above, we have

$$\omega_k=\sum_{s=0}^{\infty}(-1)^s b_{2s+1}\left(\frac{I_k}{\tilde{\gamma}_1}\right)^{2s+1}, \tag{13}$$

provided that the series converges. Since b_s's are real, ω_k's are real. We now have shown that the zeros of the characteristic function of a symmetric distribution function lie on the real axis provided that the series in (12) converges. This means that in the complex $z=e^{-i\omega}$ plane, the Mellin transformation $P(z)$, defined by $P(z)=\phi[-i\ln(z)]$, [11] has zeros only on the unit circle.

For some probability distributions it is possible to calculate zeros explicitly. For example, the zeros of the characteristic function for the uniform distribution, i.e., $f(x)=1/(b-a)$ on $[a,b]$ and $f(x)=0$ elsewhere, are $\omega_k=(2\pi k)/(b-a)$, where $k=\pm1,\pm2,\ldots$. If the density function of the Gaussian distribution is $f(x)=\exp[-(x-\mu)^2/(2\sigma^2)]/\sqrt{2\pi}\sigma$, the cumulant generating function is given by $\psi(\omega)=\mu(i\omega)+1/2\sigma^2(i\omega)^2$ [11]. Since the exponential function of an arbitrary entire function cannot have zeros in the finite region [12] and $\psi(\omega)$ in the above is an entire function, $\phi(\omega)=e^{\psi(\omega)}$ cannot have zeros in the finite region.

On the other hand, if the density function of a double Gaussian peak is given by $f(x)=\exp[-(x-\mu_1)^2/$

$(2\sigma_1^2)]/\sqrt{2\pi}\sigma_1 + a\ \exp[-(x-\mu_2)^2/(2\sigma_2^2)]/\sqrt{2\pi}\sigma_2$, the cumulant generating functions for the two peaks are given by $\psi_1(\omega)=\mu_1(i\omega)+1/2\sigma_1^2(i\omega)^2$ and $\psi_2(\omega)=\ln(a)+\mu_2(i\omega)+1/2\sigma_2^2(i\omega)^2$, respectively. Therefore, $\tilde{\psi}(\omega)=\ln(a)/2+m(i\omega)+1/2\tilde{\sigma}^2(i\omega)^2$, where $m=(\mu_2-\mu_1)/2$ and $\tilde{\sigma}^2=(\sigma_2^2-\sigma_1^2)/2$. By solving Eq. (8) using the above $\tilde{\psi}(\omega)$ we obtain zeros as

$$\omega_k=\lambda_k/|\tilde{\sigma}|+i(m-|\tilde{\sigma}I_k/\lambda_k|)/\tilde{\sigma}^2, \tag{14}$$

where

$$\lambda_k=\pm\left[\left\{\left(\frac{m^2}{2\tilde{\sigma}^2}-\frac{\ln(a)}{2}\right)^2+I_k^2\right\}^{1/2}-\left(\frac{m^2}{2\tilde{\sigma}^2}-\frac{\ln(a)}{2}\right)\right]^{1/2}.$$

In the asymptotic limit where $a\to 1$ and $\tilde{\sigma}\to 0$, the zeros are given by $\omega_k=I_k/m/(1-\epsilon_k\tilde{\sigma}^2/m)+i\epsilon_k$, where $\epsilon_k=\ln(a)/2m-1/2\tilde{\sigma}^2I_k^2/m^3$. If we put $a=1$ and $\tilde{\sigma}=0$ in the above, then we have $\epsilon_k=0$, which makes the ω_k's real. This is an explicit example of the unit circle theorem shown by Eq. (13).

The above mathematical results can be readily applied to the theory of the phase transition. Let us return to the example considered in the beginning of the paper. Since the cumulants of $f(x)$ of Eq. (2) are related to the derivatives of the free energy, Eq. (12) implies that the zeros of the partition function can be expressed in terms of the discontinuities in the derivatives of the free energy, provided that the first-order derivative has a nonvanishing discontinuity. If $f(x)$ is a symmetric function, then Eq. (13) indicates that the zeros of the partition function lie on the unit circle in the complex e^t plane. Thus we have extended the Lee-Yang unit circle theorem to the continuum case.

From the general principle of statistical mechanics, $f(x)$ of (2) can be approximated by a Gaussian distribution [14]. Let N be some integer representing an extensive thermodynamic quantity, say, the number of particles of the system. Let us introduce the reduced internal energy $u=\beta_0U/N$ and the reduced specific heat $c=C_v/Nk_b$. Then by redefining $x\to x/N$, the mean and the variance of the Gaussian form become $\mu=u$ and $\sigma=\sqrt{c/N}$. Here, β_0 is the inverse temperature of a single phase. In this case, the partition function cannot have zeros as long as $f(x)$ maintains the Gaussian shape even if the system is finite so that σ remains finite.

On the other hand, if the system undergoes a first-order transition at $\beta_0=\beta_c$, then $f(x)$ is characterized by a double Gaussian peak [7,8] separated by the discontinuity of the internal energy, or the latent heat in the thermodynamic limit. Let us further assume that the ratio of the weight of the two peaks is a and that there is also a discontinuity in c, Δc. Let us designate the reduced latent heat $\Delta u\equiv u_2-u_1$ by l. Then Eq. (14) now indicates that zeros of the partition function for small values of k may be written as $\ln(r_k)=\mathrm{Re}(t_k)=-\ln(a)/Nl+1/2(\Delta c/l)(\vartheta_k/l)^2$ and $\theta_k=\mathrm{Im}(t_k)=(\vartheta_k/l)\{1+1/2(\Delta c/l)\ln(a)/Nl-1/2(\Delta c/l)^2(\vartheta_k/l)^2\}$. Here we have used $\tilde{\sigma}^2=\Delta cN/2$, $m=lN/2$, and $\vartheta_k=(1+2k)\pi/N$, with $k=0,\pm1,\pm2,\ldots$. We see that the dominant finite-size correction is the term dependent on the asymmetric factor a.

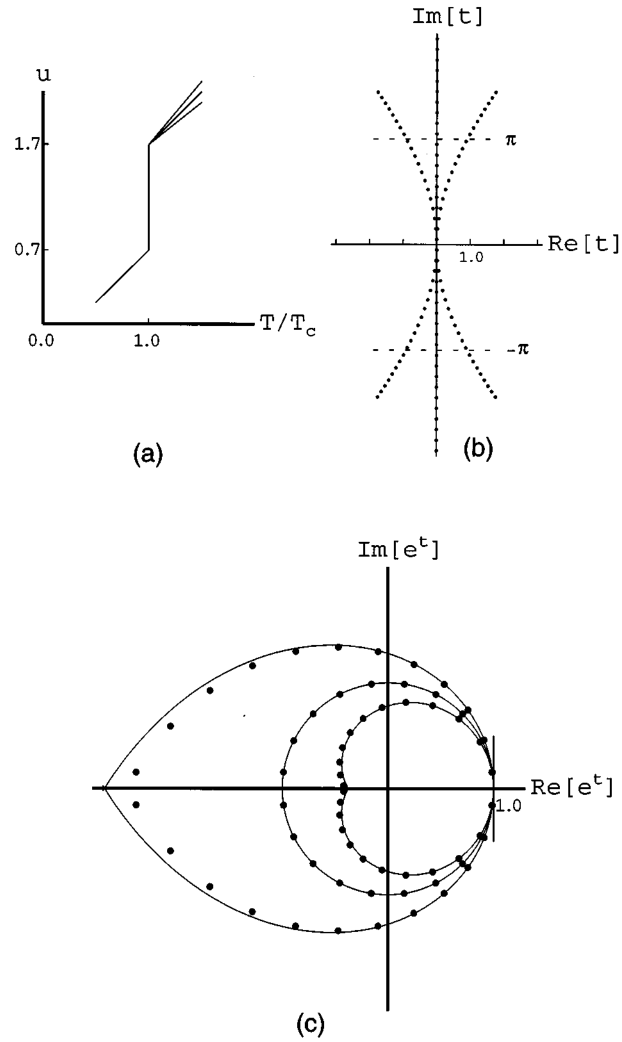

FIG. 1. (a) u as a function of $T/T_c=1/(1-t)$. $u_1=0.7$ and $c_1=1.0$ are taken arbitrarily. (b) Zeros in the complex t plane given by Eq. (14). For $\Delta c>0$, the line of zeros arches toward the positive real axis. Only zeros between the two dashed lines appear in the first Riemann sheet in the complex e^t plane. (c) Zeros in the complex e^t plane. The solid lines are the loci of the zeros in the thermodynamic limit given by (15). For $\Delta c>0$, the locus lies outside the unit circle, which corresponds to the symmetric case, $\Delta c=0$.

In the thermodynamic limit where $N\to\infty$, a dependent terms vanish, and the equation for the locus of zeros becomes

$$r=e^{(\Delta c/2l)\theta^2}, \tag{15}$$

where r_k and θ_k are replaced by the continuous variables r and θ. In Fig. 1, we plot u as a function T/T_c and zeros in the complex t and e^tplanes. $l=1.0$ and $\Delta c=\pm0.2,0$ are used in all three figures and the exact zeros given by Eq. (14) are calculated using $N=20$ and $a=1$.

The angular density of zeros defined by $Ng(\theta)=1/(\theta_{k+1}-\theta_k)$ can be written for small values of k, as

$$2\pi g(\theta)=l\{1+\tfrac{3}{2}(\Delta c/l)^2\theta^2\}. \tag{16}$$

If the transition is symmetric ($\Delta c = 0$), the locus of zeros becomes the unit circle with the uniform density $2\pi g(\theta) = l$. One should note that the equation for the locus of zeros is valid only near the real axis. This is because terms beyond the Gaussian approximation become important as the argument θ grows, i.e., for large values of k, as we have shown with an example in Ref. [6]. Finally, it should be remarked that the number of zeros in this example is infinite in the complex t plane [Fig. 1(b)]. However, only a finite number of zeros closes the circle in the complex $z = e^t$ for a finite system if we consider only the first Riemann sheet. In fact, for the symmetric case where $\Delta c = 0$, there are exactly N zeros distributed uniformly on the unit circle if we scale the energy of the system by l, so that $l = 1.0$.

For finite-size systems a Gaussian approximation is not sufficient. Although we do not have zeros in a closed form, we can calculate them from Eq. (12) by including higher-order terms with $s > 2$. For periodic boundary conditions, the discontinuity in the third-order derivatives of the free energy is proportional to N^{-1} and one in the fourth order N^{-2}, etc., as we have shown in Ref. [6]. These are the predominant finite-size corrections to the Gaussian approximation apart from the unequal weight factor, $\ln(a)/2$. For nonperiodic boundary conditions, the finite-size corrections will include surface terms proportional to $N^{-1/3}$ in addition to the bulk terms in the free energy and their derivatives [15]. The details will be published in a separate paper.

In conclusion, we have shown that the scenario for the first-order phase transition put forward by Yang and Lee [2] is valid in a continuum system. Because we have shown a formal relation between the discontinuities in the derivatives of the free energy and the distribution of zeros of the partition function, it can now be applied to any type of first-order phase transition. The results obtained in this paper include the discrete system considered in Ref. [6] as a special case. In this case we merely write the density function as a sum of weighted δ peaks as $f(x) = \Sigma_{k=0}^{N} p_k \delta(x-k)$. The characteristic function is an Nth-order polynomial $\phi(z) = \Sigma_{k=0}^{N} p_k z^k$, where we replaced ω by z as $z = e^{i\omega}$.

It can also be extended to a multiphase coexistence point. In this case, one only needs to consider the multidimensional complex space, as we have done in Ref. [6]. The existence of the formal relation presented in this paper was suspected by the original proponents of the theorem, Lee and Yang themselves. In their 1952 paper [2], they expressed their sentiment in the concluding remark by saying, '' . . . distribution (of zeros) should exhibit such simple regularities . . . . One can not escape the feeling that there is a very simple basis underlying the theorem, with much wider application, which still has to be discovered.'' We believe we have discovered this simple basis.

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