Note on Singularity of Specific Heat in the Second Order Phase Transition

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Singularity of specific heat near the transition point is investigated in terms of the distribution of zeros of the partition function in the complex temperature plane. In the case of a centrally symmetric two-dimensional distribution of zeros, the singularity of the radial distribution function of zeros reflects directly the anomaly of specific heat. Consequently, it is shown that in general the specific heat does not necessarily take the same critical indices above and below the transition point. The modified Slater KDP model solved exactly by Wu gives a nice example to our theory. The radial distribution function of zeros in the complex $z(=e^{\varepsilon/kT})$ plane for this model is given by the equation $g(r)=1/(\pi^2 r\sqrt{4-r^2})$. Then, the singularity of the specific heat for this model takes the form

$$C^+ \sim (T-T_c)^{-1/2} \text{ for } T>T_c$$

and

$$C^- = 0 \text{ for } T<T_c.$$

§ 1. Introduction

The concept of complex magnetic field has been proved to be very useful for the purpose of investigating critical behaviors in magnetic systems.[1]-[5] The concept of complex temperature is also powerful in studying the singularity of specific heat in a phase transition.[3],[6]-[10] We are particularly interested in the relation between critical indices above and below the Curie point. If we accept the axiom that the thermodynamic potential of a system can be continued analytically beyond the critical point, the same critical indices are obtained above and below the transition point.[3],[4],[11]-[14]

In the present paper, the singularity of specific heat is discussed from the viewpoint of distribution of zeros in the complex temperature plane. Recently, Abe has asserted the equality of the critical indices of specific heat above and below the transition point, assuming that the zeros of the partition function for a system lie on a straight line or an infinite sum of straight lines in the complex temperature plane.[9] This assumption about the distribution of zeros is too severe to explain a variety of the second order phase transitions. Here, it is shown that in general the specific heat does not necessarily take the same critical indices above and below the transition point. That is, in general, the specific

heat may behave as follows (or may have more complex singularity, which is not considered here),

$$C^+ \sim (T - T_c)^{-\alpha} \tag{1·1}$$

and

$$C^- \sim (T_c - T)^{-\alpha'}, \tag{1·2}$$

where α' is not necessarily equal to α. The above properties of the specific heat are exemplified in terms of a centrally symmetric two-dimensional distribution of zeros in the complex temperature plane.

§ 2. Zeros of the canonical partition function

The partition function of a system with N particles may be expressed as follows,[6]-[9]

$$\mathcal{E}_N(z) = \mathcal{E}_N(0) \prod_k (1 - z/z_k), \tag{2·1}$$

where z is a parameter which represents a function of temperature and $\{z_k\}$ are zeros of the partition function $\mathcal{E}_N(z)$. When the partition function $\mathcal{E}_N(z)$ is a polynomial of z, as in the case of the Ising model and the Slater KDP model,[15]-[18] the expression (2·1) is self-evident. Otherwise, the number of the zeros of the partition function may be infinite even for N finite, so that there arises a problem whether the expression (2·1) converges or not. Here, this problem remains untouched, and hereafter we will study the system of which the partition function is given by the expression (2·1).

In the limit of N infinite in Eq. (2·1), the free energy per particle is

$$F(z) = -kT \lim_{N \to \infty} \frac{1}{N} \log \mathcal{E}_N(z)$$

$$= F(0) - kT \iint \log \left(1 - \frac{z}{z(x, y)} \right) g(x, y) \, dx \, dy, \tag{2·2}$$

where

$$z(x, y) = x + iy,$$

and $g(x, y)$ is the distribution function of zeros at a point $z(x, y)$ in the complex z-plane. Owing to the hermiticity of the Hamiltonian, the distribution function satisfies the following symmetry relation about the real axis in the complex z-plane,

$$g(x, -y) = g(x, y). \tag{2·3}$$

In terms of Eq. (2·3), the free energy can be expressed by the following integral,

$$F(z) - F(0) = -\frac{kT}{2} \iint \log\left[\frac{(z-x)^2 + y^2}{x^2 + y^2}\right] g(x, y)\, dx\, dy \,, \tag{2.4}$$

$$= -\frac{kT}{2} \iint \log\left[\frac{z^2 + r^2 - 2zr\cos\varphi}{r^2}\right] g(r\cos\varphi, r\sin\varphi)\, r\, dr\, d\varphi \,. \tag{2.5}$$

The energy of the system is given by

$$E = \frac{\partial}{\partial\left(\frac{1}{T}\right)}\left(\frac{F}{T}\right) = -k\frac{\partial z(T)}{\partial\left(\frac{1}{T}\right)} E_{\text{sing}}(z) + \frac{\partial}{\partial\left(\frac{1}{T}\right)}\left(\frac{F(0)}{T}\right), \tag{2.6}$$

where

$$E_{\text{sing}}(z) = \iint \frac{z-x}{(z-x)^2 + y^2}\, g(x, y)\, dx\, dy \tag{2.7}$$

or

$$E_{\text{sing}}(z) = \int_0^\infty \int_0^{2\pi} \frac{z - r\cos\varphi}{z^2 + r^2 - 2zr\cos\varphi}\, g(r\cos\varphi, r\sin\varphi)\, r\, dr\, d\varphi \,. \tag{2.8}$$

For brevity, let us consider a centrally symmetric distribution function

$$g(x, y) = g(r). \tag{2.9}$$

The general case will be discussed in the Appendix. Then, Eq. (2.8) in terms of Eq. (2.9) is

$$E_{\text{sing}}(z) = \frac{1}{z} \int_0^\infty g(r)\, dr \int_0^\pi \left(r + \frac{z - ar}{a - \cos\varphi}\right) d\varphi \,, \tag{2.10}$$

where

$$a = \frac{z^2 + r^2}{2zr}. \tag{2.11}$$

The integration over φ in Eq. (2.10) gives the following results,

$$E_{\text{sing}}(z) = \frac{\pi}{z} \int_0^\infty g(r)\, r[1 + \text{sign}(z^2 - r^2)]\, dr \,, \tag{2.12}$$

where we have used the formula

$$\int_0^\pi \frac{d\varphi}{a - \cos\varphi} = \frac{\pi}{\sqrt{a^2 - 1}} \qquad \text{for } a > 1 \,. \tag{2.13}$$

As the parameter z can be taken as a positive function of temperature, the final expression for $E_{\text{sing}}(z)$ becomes of the form

$$E_{\text{sing}}(z) = \frac{2\pi}{z} \int_0^z g(r) r \, dr \,. \tag{2.14}$$

This final result can be easily interpreted in an electrostatic analogue,[1],[9] where $E_{\text{sing}}(z)$ is the electric field (at the point z) produced by the charge distribution $g(r)$ which is uniform in the direction to the xy plane (for example, see Figs. 1~3). Then, the specific heat corresponding to the energy $E_{\text{sing}}(z)$ is given in the following simple form

$$C_{\text{sing}}(z) = \frac{1}{z} \frac{d}{dT} \{z E_{\text{sing}}(z)\} = 2\pi g(z) \frac{dz}{dT} \,. \tag{2.15}$$

From this expression for the specific heat, we find that if the radial distribution function $g(r)$ is regular in the whole range of r, the specific heat has no singularity (there occurs no phase transition), and also we find that, in general, if all the derivatives of $g(r)$ up to the $(n-1)$-th order are continuous, and the n-th derivative is divergent or discontinuous, then the system shows the $(2+n)$-th order phase transitions. In particular, if $g(r)$ diverges at $r = r_c$, then we can classify the singularities of the specific heat in the following way.

i) If the distribution function takes the following form near the critical point, as is shown in Figs. 1-a and 1-b,

$$g(r) \simeq \begin{cases} (r_c - r)^{-\alpha} & \text{for} \quad r < r_c, \\ 0 & \text{for} \quad r > r_c, \end{cases} \tag{2.16}$$

then the singularity of the specific heat is

$$C_{\text{sing}} \simeq \begin{cases} (r_c - z)^{-\alpha} & \text{for} \quad z(T) < r_c \\ 0 & \text{for} \quad z(T) > r_c. \end{cases} \tag{2.17}$$

An example in this case will be discussed in the following section.

ii) If the distribution function takes the following form, as is shown in Figs. 2-a and 2-b,

$$g(r) \simeq \begin{cases} 0 & \text{for} \quad r < r_c \\ (r - r_c)^{-\alpha'} & \text{for} \quad r > r_c, \end{cases} \tag{2.18}$$
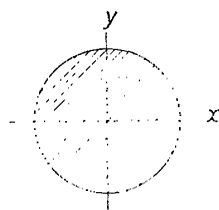

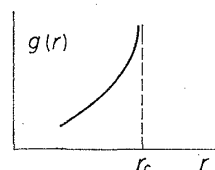Fig. 1-a. Zeros distribute inside the circle of the radius r_c.

Fig. 1-b. Illustrating a schematic distribution function which is divergent just below r_c.
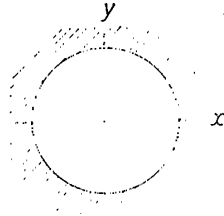
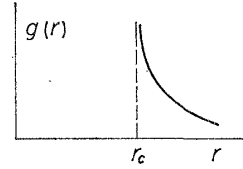Fig. 2-a. Zeros distribute outside the circle of the radius r_c.

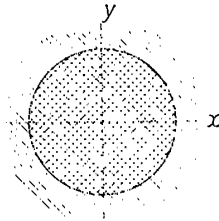Fig. 2-b. Illustrating a schematic distribution function which is divergent just above r_c.

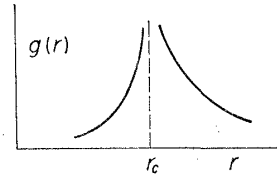Fig. 3-a. Zeros distribute both inside and outside the circle of the radius r_c.

Fig. 3-b. Illustrating a schematic distribution function which is divergent both above and below r_c.

then, the singularity of the specific heat is

$$C_{\text{sing}} \simeq \begin{cases} 0 & \text{for} \quad z < r_c \\ (z - r_c)^{-\alpha'} & \text{for} \quad z > r_c. \end{cases} \tag{2.19}$$

iii)   If the distribution function takes the following form, as is shown in Figs. 3-a and 3-b,

$$g(r) \simeq \begin{cases} (r_c - r)^{-\alpha} & \text{for} \quad r < r_c \\ (r - r_c)^{-\alpha'} & \text{for} \quad r > r_c, \end{cases} \tag{2.20}$$

then, the singularity of the specific heat is

$$C_{\text{sing}} \simeq \begin{cases} (r_c - z)^{-\alpha} & \text{for} \quad z < r_c \\ (z - r_c)^{-\alpha'} & \text{for} \quad z > r_c. \end{cases} \tag{2.21}$$

§ 3.   An example of the modified Slater KDP model

Recently, Wu has solved exactly the Slater model of the two-dimensional potassium dihydrogen phosphate crystal (KDP) under the additional assumption that the dipoles are excluded from pointing along one direction of the crystal axis.[17]   In the Slater KDP model,[15] we consider a diamond-type lattice (four nearest neighbors to each site) with directed arrows attached to all the lattice bonds.   The rule is that there are always two arrows pointing toward and two arrows pointing away from a given lattice site.   Then there are altogether six
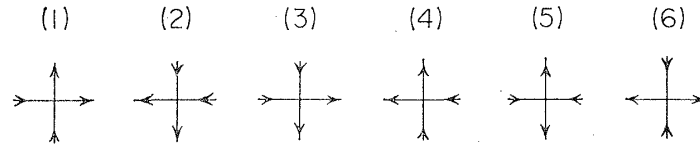
Fig. 4. Energies $e_1=e_2=0$, $e_3=e_4=e_5=e_6=\varepsilon>0$ are associated with the six configurations.

possible arrow configurations that can be associated to a site. A zero site energy is associated with two of the six configurations and an energy $\varepsilon>0$ with the remaining four (see Fig. 4). Wu has imposed the further restriction that only one of the zero-energy configuration is allowed. By the use of a Pfaffian, he has obtaided the exact partition function for an infinite rectangular lattice wrapped around a torus. The solution is

$$\log \varXi = \frac{N}{8\pi^2} \int_0^{2\pi} d\theta \int_0^{2\pi} d\varphi \log [1 + 2e^{-2\varepsilon/kT}$$

$$+ 2e^{-2\varepsilon/kT} \cos(\theta - \varphi) - 2e^{-\varepsilon/kT}(\cos\theta + \cos\varphi)],$$

which is easily rewritten in the following form,

$$\log \varXi = \frac{N\varepsilon}{kT} + \frac{N}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \log f(\theta, \varphi, z) d\theta d\varphi, \tag{3·2}$$

where

$$f(\theta, \varphi, z) = [z - (\cos\theta + \cos\varphi)]^2 + (\sin\theta + \sin\varphi)^2 \tag{3·3}$$

and

$$z = z(T) = e^{\varepsilon/kT}. \tag{3·4}$$

Now, the zeros of the partition function are given by the solution

$$z = x + iy = \cos\theta + \cos\varphi \pm i(\sin\theta + \sin\varphi) \tag{3·5}$$

for the equation

$$f(\theta, \varphi, z) = 0. \tag{3·6}$$

Then, we obtain

$$\begin{cases} x = \cos\theta + \cos\varphi \\ y = \pm(\sin\theta + \sin\varphi). \end{cases} \tag{3·7}$$

The distribution function $g(x, y)$ for this model is calculated from the Jacobian,

$$g(x, y) = 2 \cdot \frac{\partial(\theta, \varphi)}{\partial(x, y)} \cdot \frac{1}{8\pi^2}, \tag{3·8}$$

where the factor 2 arises from the fact that the set of the variables θ and φ is

the double-valued function of the set of the variables x and y. In terms of Eqs. $(3 \cdot 7)$ and $(3 \cdot 8)$ we can easily find that

$$g(x, y) = \frac{1}{\pi^2 \sqrt{x^2 + y^2} \sqrt{4 - x^2 - y^2}} \qquad (3 \cdot 9)$$

which is centrally symmetric, and consequently can be written as

$$g(x, y) = g(r) = \frac{1}{\pi^2 r \sqrt{4 - r^2}}. \qquad (3 \cdot 10)$$

This distribution function is just of type (i) discussed in the previous section, where $\alpha = 1/2$ and $r_c = 2$. Therefore, from Eq. $(2 \cdot 15)$ the singular part of the specific heat takes the form

$$C_{\text{sing}} = 2\pi g(z) \frac{dz}{dT} = -\frac{\varepsilon}{\pi k T^2} \cdot \frac{1}{z} \left(z^{-2} - \frac{1}{4} \right)^{-1/2}. \qquad (3 \cdot 11)$$

Finally, the specific heat is expressed by

$$C^+ = -k \frac{dz}{d\left(\frac{1}{T}\right)} C_{\text{sing}}(z) = \frac{\varepsilon^2}{\pi k T^2} \left(e^{-2\varepsilon/kT} - \frac{1}{4} \right)^{-1/2} \qquad \text{for } T > T_c$$

and

$$C^- = 0 \qquad \text{for } T < T_c; \ T_c = \varepsilon/(k \log 2). \qquad (3 \cdot 12)$$

Of course, these final results have already been obtained by Wu. Here, we want to emphasize that the different behaviors of the specific heat above and below the transition point can be easily understood from the partition function in the complex temperature plane.

Acknowledgements

Appendix

From the symmetry relation $(2 \cdot 3)$, the distribution function can be expanded in terms of Legendre polynomials as follows,

$$g(r, \varphi) = g(r, -\varphi) = \sum_{n=0}^{\infty} g_n(r) P_n(\cos \varphi) \qquad (A \cdot 1)$$

where

$$g_n(r) = \frac{2n+1}{2} \int_0^\pi g(r, \varphi) P_n(\cos \varphi) \sin \varphi d\varphi. \qquad (A \cdot 2)$$

Then, the singular part of the energy in terms of $(2 \cdot 8)$ is

$$E_{\text{sing}}(z) = \sum_{n=0}^{\infty} E_{\text{sing}}^{(n)}(z), \tag{A·3}$$

where

$$E_{\text{sing}}^{(n)}(z) = \frac{1}{z} \int_0^\infty g_n(r) \int_0^\pi \left(r + \frac{z - ar}{a - \cos\varphi}\right) P_n(\cos\varphi)\,d\varphi \tag{A·4}$$

and

$$a = (z^2 + r^2)/(2zr). \tag{A·5}$$

Here, let us investigate the properties of functions $\{f_n(a)\}$ defined by

$$f_n(a) = \int_0^\pi \frac{P_n(\cos\varphi)}{a - \cos\varphi}\,d\varphi. \tag{A·6}$$

From the recurrence formula for Legendre polynomials

$$(n+1)P_{n+1}(z) - (2n+1)zP_n(z) + nP_{n-1}(z) = 0, \tag{A·7}$$

we obtain the recurrence equation

$$(n+1)f_{n+1}(a) - (2n+1)af_n(a) + nf_{n-1}(a) = -R_n, \tag{A·8}$$

with

$$R_n = \int_0^\pi P_n(\cos\varphi)\,d\varphi = \begin{cases} 0 & \text{for } n \text{ odd,} \\ \pi\left[\dfrac{(n-1)!!}{n!!}\right]^2 & \text{for } n \text{ even,} \end{cases} \tag{A·9}$$

$$f_0(a) = \frac{\pi}{\sqrt{a^2 - 1}} \tag{A·10}$$

and

$$f_1(a) = \pi\left(\frac{a}{\sqrt{a^2 - 1}} - 1\right). \tag{A·11}$$

Consequently, the function $f_n(a)$, in terms of Eqs. (A·8), (A·9), (A·10) and (A·11) takes the form

$$f_n(a) = \frac{A_n(a)}{\sqrt{a^2 - 1}} + B_n(a), \tag{A·12}$$

where $A_n(a)$ and $B_n(a)$ are polynomials of the variable a. Therefore, the singular part of the energy becomes

$$E_{\text{sing}}^{(n)}(z) = \frac{1}{z} \int_0^\infty g_n(r)\,dr\,\{rA_n(a)\,[1 + \text{sign}(z^2 - r^2)]$$

$$+ r(R_n - A_n(a)) + (z - ar)B_n(a)\}$$

$$= \frac{2}{z} \int_0^z g_n(r) \, r A_n(a) \, dr + \widetilde{R}_n(z), \tag{A·13}$$

where

$$\widetilde{R}_n(z) = \frac{1}{z} \int_0^\infty g_n(r) \, \{r(R_n - A_n(a)) + (z - ar) B_n(a)\} \, dr \tag{A·14}$$

which shows the lower singularity than the first term in Eq. (A·13) in the case of the singular distribution function $g_n(r)$, and cousequently $\widetilde{R}_n(z)$ can be neglected in our discussion.

Thus, the singular part of the specific heat can be expressed in the following way,

$$C_{\mathrm{sing}}(z) \simeq \sum_{n=0}' 2 A_n(1) \frac{dz}{dT} g_n(z). \tag{A·15}$$

This means that in general the distribution function of zeros reflects directly the anomaly of the specific heat.

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