# Logarithmic Singularity of Specific Heat near the Transition Point in the Ising Model*) 

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#### Abstract

Logarithmic singularity of specific heat near the transition point is studied in the case of the Ising model with ferromagnetic nearest neighbor interaction. The parameter appearing in high temperature expansion is extended to the whole complex plane and the analytical behavior of thermodynamic functions is examined. A distribution of roots which are derived from a certain algebraic equation plays an important role of determining the singularity of specific heat. A strikingly simple distribution of roots is shown to lead to the singularity consistent with experiment. Comparison of the theory with experiment on the liquid-gas transition at the critical point is discussed.


## § 1. Introduction

Recently, the behavior of specific heat in the immediate vicinity of transition point has been studied both experimentally and theoretically, in particular for the phase transition of second order. In most cases, the experimental results are well described by the equations

$$
\begin{align*}
C & =-\alpha \ln \left|T-T_{c}\right|+\Delta_{+}, \quad\left(T>T_{c}\right), \\
& =-\alpha \ln \left|T-T_{c}\right|+\Delta_{-}, \quad\left(T<T_{c}\right),
\end{align*}
$$

where $T$ is the absolute temperature, $T_{c}$ the transition temperature, and usually an inequality $\Delta_{+}<\Delta_{-}$holds. For instance, $C_{p}$ for the $\lambda$-transition in liquid helium, ${ }^{1)} C_{v}$ near the critical point of argon, ${ }^{2)}$ oxygen ${ }^{3)}$ and helium, ${ }^{4)} C_{p}$ of $\mathrm{CoCl}_{2} \cdot 6 \mathrm{H}_{2} 0$ near its Néel point ${ }^{5}$ ) are all expressible in the form of Eq. (1.1). Other examples are found in the work of Yamamoto et al. ${ }^{6)}$

On the other hand, several authors ${ }^{77}$ have developed diagrammatic methods for the study of logarithmic singularity of specific heat. Unfortunately, however, these theories cannot reproduce the known exact results when applied to the two-dimensional Ising model. Since the above methods are too complicated to

[^0]overcome this difficulty, we will take here quite a different approach to the problem which is originally due to Fisher. ${ }^{8)}$

This paper is devoted to a simple and concise explanation of where the above anomaly of specific heat comes from. We will restrict ourselves to a study of the Ising model with ferromagnetic nearest neighbor interaction. In $\S 2$ we extend the parameter $\omega$ appearing in high temperature expansion to the whole complex plane and study the analytical behavior of thermodynamic functions. A distribution of roots which are derived from a certain algebraic equation is shown to play an important role of determining the singularity at the transition point. Examples are demonstrated for one- and two-dimensional models. We show in §3 that a very simple distribution of roots can lead to the singularity of Eq. (1-1). In order to get some relevance of this distribution with the known facts of the three-dimensional Ising model, we study in §4 low temperature series expansion for the simple cubic lattice. On the basis of the results obtained in $\S 4$, we discuss in $\S 5$ a comparison of the theory with experiment.

## § 2. Phase transition of the Ising model

We consider a crystal composed of $N$ lattice points, each occupied by an Ising spin taking values $\pm 1$. We assume nearest neighbor interaction and introduce the following notations: $K=\beta J, \beta=1 / k T$, where $J$ is the exchange energy, $k$ the Boltzmann constant. On the basis of high temperature expansion, the partition function $Q$ is written as $^{9}{ }^{9}$

$$
Q=2^{N}(\operatorname{ch} K)^{M} F(\omega),
$$

where $M$ is the total number of nearest neighbor pairs, i.e. $M=z N / 2$ with $z$ the coordination number, and $F(\omega)$ is expressed as ${ }^{9}$

$$
F(\omega)=\sum a_{n} \omega^{n} .
$$

Here $\omega$ is defined by $\omega=$ th $K$, and $a_{n}$ is the number of closed diagrams constructed with $n$ nearest neighbor lines in the lattice $\left(a_{0}=1\right)$. In these diagrams, each vertex should receive even number of lines.

If $N$ is finite, $n$ in Eq. (2-2) should terminate at some finite value. In other words, $F(\omega)$ is a polynomial in $\omega$ of finite degree in this case. Therefore we can factorize it and write

$$
F(\omega)=\prod_{i}\left(1-\frac{\omega}{\omega_{i}}\right),
$$

where $\omega_{i}$ is a root of the algebraic equation $F(\omega)=0$, and the product extends over all roots of $F(\omega)$. It is evident that none of these roots can be real and positive, since all the coefficients in the polynomial $F(\omega)$ are positive. It is also clear that if $\omega_{i}$ is a root, so is its conjugate complex $\omega_{i}{ }^{*}$.

From Eqs. (2•1) and (2.3), we find

$$
\frac{\ln Q}{N}=\ln 2+\frac{z}{2} \ln (\operatorname{ch} K)+\frac{1}{N} \sum_{i} \ln \left(1-\frac{\omega}{\omega_{i}}\right) .
$$

If we restrict ourselves to the ferromagnetic interaction ( $J>0$ ), the quantity $\omega$ is by definition real, taking a value between 0 and 1 . But, in discussing the phase transition, it is convenient to extend $\omega$ to the whole complex plane and study the analytical behavior of thermodynamic functions. Fisher ${ }^{8)}$ has already discussed the singularity of specific heat of the two-dimensional case along this line. It should be noted that this is analogous to the Yang-Lee theory of condensation ${ }^{10}$ in which the fugacity was allowed to take complex values.

The last term in Eq. (2-4) has a logarithmic singularity at $\omega=\omega_{i}$. However, for a finite system, none of the roots lie on the real and positive axis in the $\omega$-plane, so that no singularity appears on the physical domain, and consequently no phase transition takes place. This is of course a well-known fact of phase transition. On the contrary, in the limit $N \rightarrow \infty$, it is possible to have a real root $\omega_{c}$ between 0 and 1 . In this case, the phase transition should occur. Also, one would expect that in this limit a distribution of roots has some simple regularity. Since it will turn out that this distribution near $\omega_{c}$ determines the property of singularity of thermodynamic functions, let us discuss it in two exactly solvable examples.

First, in the one-dimensional model, $F(\omega)$ is given by $F(\omega)=1+\omega^{N}$, so that all the roots lie on the unit circle. No phase transition occurs at finite temperature.

Next, in the case of simple quadratic lattice, the distribution of roots was fully studied by Fisher ${ }^{8)}$ on the basis of the Onsager solution. ${ }^{11}$ Therefore, we are not going to enter into the details but quote only the results below. In this case, the loci of roots are two circles having the same radius $\sqrt{2}$ whose centers are located at the points 1 and -1 , respectively, on the real axis. Thus, in the neighborhood of $\omega_{c}(=\sqrt{2}-1)$, the roots are continuously distributed on the line perpendicular to the real axis. We will hereafter call this line the singular line. It is convenient to write these roots as $\omega^{\prime}=\omega_{c}+i y$, and introduce a distribution function $g(y)$ which is so defined that the number of roots divided by $N$ in the interval between $y$ and $y+d y$ be $g(y) d y$. It is clear that a relation

$$
g(-y)=g(y)
$$

is valid. Then, neglecting all the terms regular at $\omega=\omega_{c}$, we have from Eq. (2.4)

$$
\frac{\ln Q}{N}=\int_{-Y}^{Y} \ln \left(1-\frac{\omega}{\omega_{a}+i y}\right) g(y) d y
$$

where $Y$ is an appropriate cutoff parameter. It will turn out that the final result is independent of $Y$.

Now, the energy $E$ of the system is given by

$$
E=-(\partial / \partial \beta) \ln Q .
$$

By the use of Eqs. (2.5) and (2.6), Eq. (2.7) is reduced to

$$
\frac{E}{N J}=\frac{2\left(\omega_{c}-\omega\right)}{\operatorname{ch}^{2} K} \int_{0}^{Y} \frac{g(y)}{\left(\omega_{c}-\omega\right)^{2}+y^{2}} d y .
$$

Since we are interested in the vicinity of transition point, ch $K$ in Eq. (2.8) may be replaced by $\operatorname{ch} K_{c}$, where $K_{c}$ is the critical value of $K$.

The function $g(y)$ plays an important role of determining how the energy behaves near the transition point. For instance, if $g(y)$ is constant, it is discontinuous at $\omega=\omega_{c}$. This is characteristic of the phase transition of first order. Therefore $g(y)$ should vanish at $y=0$ in order to have the phase transition of second order. As a matter of fact, for the system under consideration, $g(y)$ is shown to be

$$
g(y)=y / \pi \omega_{c}{ }^{2}, \quad(y>0) .
$$

Substituting Eq. (2.9) in Eq. (2•8), we find

$$
-\frac{E}{N J}=-\frac{2\left(\omega_{c}-\omega\right) \ln \left|\omega_{c}-\omega\right|}{\pi \omega_{c}{ }^{2} \operatorname{ch}^{2} K_{c}},
$$

from which the specific heat is calculated as

$$
C=\partial E / \partial T=\partial E / \partial \omega \cdot \partial \omega / \partial T,
$$

namely

$$
\frac{C}{N k}=-\frac{2 K_{c}{ }^{2} \ln \left|T-T_{c}\right|}{\pi \omega_{c}{ }^{2} \operatorname{ch}^{4} K_{c}} .
$$

It is easily proved that Eq. (2.12) is exactly the same as the more familiar form ${ }^{11)}$

$$
C / N k=-(2 / \pi)[\ln \cot (\pi / 8)]^{2} \ln \left|T-T_{c}\right| .
$$



Fig. 1. A two-dimensional distribution of roots.

In this way, we are led to the logarithmic singularity of specific heat at the transition point. The reasons why we have such a singularity are very simple: first, the roots are distributed on the singular line, and secondly, the distribution function is proportional to $y$.

If the roots in the immediate neighborhood of $\omega_{c}$ form a two-dimensional distribution (Fig. 1), this would correspond again to some sort of phase transition. It is generally believed, however, that the line distribution is more natural than the two-dimensional one. ${ }^{8}$ ) Therefore, let us assume the former distribution
in the following, retaining the discussion of the latter distribution to another paper.

## § 3. Asymmetric distribution of roots

One of the characteristic features of the two-dimensional Ising model discussed in $\S 2$ is that the specific heat near the transition point is symmetric about $T_{c}$. In other words, in this case a relation


Fig. 2. Asymmetric distribution of roots. $\Delta_{+}=\Delta_{-}$holds in Eq. (1.1). However, this relation is expected to be no longer applicable to the threedimensional Ising model, where the method due to series expansion yields an asymmetric form of specific heat. In this section, we are going to discuss a plausible situation in the three-dimensional case, in particular a condition under which a relation $\Delta_{+}<\Delta_{-}$ can be derived.

The symmetric behavior of specific heat in the two-dimensional case is due to the fact that the singular line is perpendicular to the real axis; there is no distinction between the case $\omega>\omega_{c}$ and that $\omega<\omega_{c}$. Therefore, in order to differentiate these two cases, it is necessary to introduce some asymmetric distribution of roots. One of the simplest ways of doing so is to assume that the singular line makes an angle $\varphi$ different from $90^{\circ}$ with the real axis (Fig. 2).

Let the point on singular line be $\omega^{\prime}$. On the upper half plane, it is expressed as

$$
\omega^{\prime}=\omega_{c}+y e^{i \varphi} .
$$

We further assume that the distribution function is still proportional to $y$ and put

$$
g(y)=A y .
$$

Under these assumptions, it is proved that the specific heat has precisely the same anomaly as in Eq. (1•1).

Repeating the procedure which led to Eq. (2.8), we find

$$
\frac{E}{N J}=\frac{2 A}{\operatorname{ch}^{2} K} \int_{0}^{Y} \frac{y\left(\omega_{c}-\omega\right)+y^{2} \cos \varphi}{\left(\omega_{c}-\omega\right)^{2}+2 y\left(\omega_{c}-\omega\right) \cos \varphi+y^{2}} d y
$$

The right-hand side is easily calculated by means of elementary integration. The parameter $Y$ is allowed to tend to infinity if the relevant integral converges in this limit. Such a procedure yields either a constant term or small correction terms to the final result. In this way, the integral in Eq. (3.3) is shown to be for $\omega \simeq \omega_{c}$

$$
\begin{aligned}
& \left(\omega_{c}-\omega\right) \cos 2 \varphi \ln \left|\omega_{c}-\omega\right|-\left(\omega_{c}-\omega\right) \varphi \sin 2 \varphi, \quad\left(\omega_{c}>\omega\right), \\
& \left(\omega_{c}-\omega\right) \cos 2 \varphi \ln \left|\omega_{c}-\omega\right|-\left(\omega-\omega_{c}\right)(\pi-\varphi) \sin 2 \varphi, \quad\left(\omega_{c}<\omega\right) .
\end{aligned}
$$

Therefore we have for the specific heat

$$
\begin{align*}
\frac{C}{N k} & =\frac{2 A K^{2}}{\operatorname{ch}^{4} K}\left(\cos 2 \varphi \ln \left|T-T_{c}\right|-\varphi \sin 2 \varphi\right),\left(T>T_{c}\right), \\
& =\frac{2 A K^{2}}{\operatorname{ch}^{4} K}\left(\cos 2 \varphi \ln \left|T-T_{c}\right|+(\pi-\varphi) \sin 2 \varphi\right),\left(T<T_{c}\right) .
\end{align*}
$$

Thus the specific heat is expressed as

$$
C / N k=-\alpha \ln \left|T-T_{c}\right|+\Delta_{ \pm}, \quad\left(T \gtrless T_{c}\right),
$$

which is the same as Eq. (1.1).
It is convenient to introduce a quantity $\gamma$ defined by

$$
\gamma=\left(\Delta_{-}-\Delta_{+}\right) / \alpha .
$$

From Eq. (3.4) we have

$$
\gamma=-\pi \tan \cdot 2 \varphi,
$$

that is, the quantity $\gamma$ depends on a single parameter $\varphi$ in our treatment. From the conditions that $\alpha>0$ and $\gamma>0$, we find an inequality for $\varphi$

$$
\pi / 4<\varphi<\pi / 2 .
$$

If one puts $\varphi=\pi / 2$, the results obtained here are naturally reduced to those found in § 2 .

In closing this section, we would like to mention some remarks on the assumption of Eq. (3.2). An additional term $B y^{2}$ to Eq. (3.2) is shown to yield a correction of the order of $\left(T-T_{e}\right) \ln \left|T-T_{c}\right|$ to Eq. (3.5). This is negligible near the transition point. Therefore, the present assumption may be replaced by an alternative statement that $g(y)$ can be expanded in powers of $|y|$.

## § 4. Low temperature series expansion

In order to find some connection between the distribution of roots discussed in $\S 3$ and the known facts of the three-dimensional Ising model, let us examine here low temperature series expansion, restricting ourselves to the simple cubic lattice. It will turn out in $\S 5$ that the analytical behavior of thermodynamic functions deduced from this expansion yields a rough estimate of $\varphi$.

In low temperature expansion, all the thermodynamic functions are expanded in powers of $u$ defined by $u=\exp (-4 K)$. For example, if we express the free energy per spin in the form $-(z J / 2)-k T \ln \Lambda, \ln \Lambda$ is expanded as
$\ln \Lambda=\sum_{n=0}^{\infty} b_{n} u^{n}$

$$
=u^{3}+3 u^{5}-3 \frac{1}{2} u^{6}+15 u^{7}-33 u^{8}+104 \frac{1}{3} u^{9}-280 \frac{1}{2} u^{10}+\cdots .
$$

Recently, Sykes, Essam and Gaunt ${ }^{12}$ ) have calculated the above series up to the term of the order of $u^{18}$. It is easily seen that the $u$ is related with the $\omega$ by an equation

$$
\omega=(1-\sqrt{u}) /(1+\sqrt{u}) \text { or } u=(\omega-1)^{2} /(\omega+1)^{2} .
$$

Let us now denote the value of $u$ corresponding to the real phase transition by $u_{c}$ and the radius of convergence of (4-1) by $r$. It should be stressed that $r$ is not necessarily equal to $u_{c}$. This is a well-known fact since the work of Wakefield ${ }^{183}$ ) but let us discuss it below in some detail.

The critical value of $\omega$ estimated from high temperature expansion ${ }^{14)}$ is given by $\omega_{c} \simeq 0.218$, or we get $u_{c} \simeq 0.412$ by Eq. (4.2). On the other hand, when $\Lambda$ is expanded in powers of $u^{1 / 2}$, its radius of convergence is about 0.57 according to Domb's estimate. ${ }^{15}$ ) Thus, we find $r \simeq 0.57^{2}=0.325$, and it follows that $r<u_{c}$. In order to check this point further, we have applied the CauchyHadamard formula

$$
r=\lim _{n \rightarrow \infty}\left|b_{n}\right|^{-1 / n}
$$

By using the results of Sykes et al., ${ }^{12)}$ we have calculated $\left|b_{n}\right|^{-1 / n}$ up to $n=18$ and plotted them against $1 / n$. The plots show a fairly good linear relation between these two quantities, and an extrapolation to $n \rightarrow \infty$ leads to $r \simeq 0.296$.

Furthermore, an application of the Pade approximant method reveals the state of affairs more clearly. We have calculated the Pade approximants $P_{2}{ }^{2}$, $P_{3}^{3}, \cdots$ up to $P_{7}^{7}$ for $\ln \Lambda / u^{3}$, and found the locations of singular points. The results are: (a) there is a singular point on the real and positive axis which appears to correspond to $u_{c}$, and (b) there are always singular points on the real and negative axis for each Padé approximant. We have studied the singular point with the least absolute value among these, and the results are shown in Table I. It is then clear that this singular point determines the radius of convergence, and we get $r \simeq 0.308$ from $P_{7}^{7}$.

Table I. Location of singular point on the real and negative axis derived from Pade approximant.

| $P_{2}{ }^{2}$ | $P_{3}{ }^{3}$ | $P_{4}{ }^{4}$ | $P_{5}{ }^{5}$ | $P_{6}{ }^{6}$ | $P_{7}{ }^{7}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| -0.388 | -0.311 | -0.334 | -0.322 | -0.306 | -0.308 |

From these considerations, we can conclude that the analytical property of $\ln A$ in the $u$-plane is as such as shown in Fig. 3, where crosses are singular points. That is, the convergence of power series in Eq. (4.1) is limited by the unphysical singular point at $-r$, but not by the physical one at $u_{c}$ which is outside the circle of convergence.

The fact that there is a singular point at $-r$ can be seen from the general


Fig. 3. Singular points of free energy in the $u$-plane.
features of Eq. (4.1), without recourse to the detailed calculations. We need, however, Pringsheim's theorem : ${ }^{16)}$ if all the coefficients in a given power series $P(z)$ are positive, then there should be a singular point $z_{e}$ on the real and positive axis, $z_{c}$ being equal to the radius of convergence. As a corollary, if the coefficients in a given power series are alternate in sign, then there should be a singular point on the real and negative axis, whose absolute value is equal to the radius of convergence. Since the coefficients in Eq. (4.1) so far calculated are alternate in sign except for the first few terms, the above corollary applies and it follows our result. In connection with this, it should be noted that all the coefficients have a definite sign in low temperature series for the two-dimensional case or in high temperature series so far known for the threedimensional case. Therefore, by means of Pringsheim's theorem, the convergence of these series is limited by the physical singular point.

It is easily seen from Eq. (4.2) that the circle of convergence in the $u$ plane is mapped to a circle in the $\omega$-plane. If we denote the real and the imaginary parts of $\omega$ by $\xi$ and $\eta$, respectively, the equation of the circle in the $\omega$-plane is given by

$$
\begin{align*}
& (\xi-X)^{2}+\eta^{2}=R^{2}, \\
& X=(1+r) /(1-r), R=2 \sqrt{r} /(1-r) .
\end{align*}
$$

It is to be noted that all the thermodynamic functions are regular inside the above circle and that the point $\omega_{c}$ is outside it. (In the two-dimensional case the $\omega_{c}$ is on the circle.) We also express the point in the $\omega$-plane corresponding to $-r$ in the $u$-plane by $\omega_{0}$. If we write $\omega_{0}$ as $\omega_{0}=\hat{\xi}_{0}+i \eta_{0}, \hat{\xi}_{0}$ and $\eta_{0}$ are calculated to be

$$
\xi_{0}=(1-r) /(1+r), \eta_{0}= \pm 2 \sqrt{r} /(1+r) .
$$

It is clear that the point $\omega_{0}$ lies on the circle (4.3) and is a singular point of thermodynamic functions.

## § 5. Discussion

We are now in a position to discuss quite a rough estimate of $\varphi$. In doing so, we notice that the singular line is subject to the following two conditions: (a) the point $\omega_{0}$ should lie on the singular line, and (b) the singular line should be the tangent to the circle $(4 \cdot 3)$ at the point $\omega_{0}$. The latter condition is seen from the following consideration: if the singular line crosses the circle, the thermodynamic functions are singular inside the circle; this is contradictory to
what we have seen at the end of $\S 4$.
If the singular line is a straight line, it is impossible to satisfy simultaneously the above two conditions. However, if one assumes the singular line to be a parabola represented by


Fig. 4. A schematic representation of the behavior of singular line. Here the singular line is indicated by a dotted one.

$$
\eta=c\left(\xi-\omega_{c}\right)+d\left(\xi-\omega_{c}\right)^{2}
$$

it is possible to fulfil the two conditions (Fig. 4). In fact, we find

$$
\begin{gather*}
c=2 \eta_{0} /\left(\xi_{0}-\omega_{c}\right)+\left(\xi_{0}-X\right) / \eta_{0} \\
d=-\left(\xi_{0}-X\right) / \eta_{0}\left(\xi_{0}-\omega_{c}\right)-\eta_{0} /\left(\xi_{0}-\omega_{c}\right)^{2} .
\end{gather*}
$$

If we put $\omega_{c} \simeq 0.218$ and $r \simeq 0.296$, we have $c \simeq 3.618$ and $d \simeq-3.183$. Since the relation $c=\tan \varphi$ holds, $\varphi$ is estimated from the numerical value of $c$. In this way, $r$ is calculated by means of Eq. (3.7), and we get $\gamma \simeq 1.9$. If we adopt $r \simeq 0.308$ determined from the Pade method, we get a slightly smaller value of $r$, i.e. $r \simeq 1.7$. Since our calculation of $r$ involves some uncertainty, we are satisfied by saying that the theoretical value of $\gamma$ is about 2 . In comparing this result with experiment, we notice that the Ising model is mathematically equivalent to the classical lattice gas. ${ }^{17)}$ Furthermore, as Yang and Yang ${ }^{18)}$ have shown, the specific heat at a constant volume near the critical point of lattice gas corresponds to that of the Ising model without magnetic field. Thus, it is appropriate to employ the liquid-gas transition at the critical point for comparison. In Table II, the results of $\gamma$ derived from the experimental data on argon, ${ }^{2)}$ oxygen ${ }^{3)}$ and helium ${ }^{4}$ are shown. Experimental results are about two or three times as large as theoretical one. It would be interesting to see how the theoretical $\gamma$ changes with the crystal structure, and this is being under the way. It is also interesting to study the distribution of roots for a finite Ising modcl; this is being investigated by Suzuki, Kawabata and Katsura. ${ }^{19}$ )

Table II. Numerical values of $\gamma$.

| ${ }^{3} \mathrm{He}$ | ${ }^{4} \mathrm{He}$ | A | $\mathrm{O}_{2}$ | Theory (sc) |
| :---: | :---: | :---: | :---: | :---: |
| 5.9 | 5.8 | 5.6 | 5.0 | $\sim 2$ |

In our conjecture, the distribution function is assumed to be proportional to $y$. This assumption should of course be testified in some way or other. We hope, however, that some of the essential features of logarithmic singularity of specific heat associated with the phase transition are revealed by the present method. It is also possible to derive a singularity of the form $\left|T-T_{c}\right|^{-\alpha}$ in a similar way. This will be a subject of a forthcoming paper.

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