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ISING LATTICE CONTAINING IMPURITIES

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The phase transition in an Ising lattice containing impurities that are in thermodynamic equilibrium with the lattice is considered. For the partition function of a lattice containing impurities, an expression is obtained in the form of a certain contour integral of the partition function for the pure lattice. The dependence of the phase-transition temperature on the concentration is obtained. It is shown that the presence of impurities in a lattice leads to the result that a third-order phase transition develops instead of a second-order phase transition.

1. A solution of the question as to how impurities affect the nature of the phase transition in a ferromagnet is of considerable interest. However, contemporary mathematical methods of statistical physics do not enable us to give a reliable answer to this question in general form; therefore it is reasonable to resort to a simple model in order to obtain exact results. We shall use the two-dimensional Ising model (see, for example,[1,2]) with an interaction between nearest neighbors. In this model the atoms are located on the lattice sites, and the state of each atom is characterized by a spin variable σ having two values ± 1. It is assumed that the interaction energy between two nearest neighbors is given by $J\sigma_1\sigma_2$ (J is the interaction constant). Now let us imbed in this lattice impurities which, by intruding between neighboring atoms, change the intensity of the interaction between them. The total energy of such a lattice containing impurities depends on the configuration of spins and on the way in which the impurities are distributed. Our goal is to find the partition function Z_s,

$$Z_s = \sum_{[\sigma],\,Q} \exp[-\beta E(Q,[\sigma])], \tag{1}$$

where the summation goes over all spin configurations $[\sigma]$ and over all ways Q of distributing s impurities over the lattice. The free energy obtained from (1) gives us information about a system in which the impurities are able to reach thermodynamic equilibrium with the lattice. If we wanted to study the properties of a system containing impurities that are randomly distributed but fixed on their own sites, then it would be necessary to average the free energy with respect to the distribution of impurities.[3] However, this is a more complicated problem (see, for example,[4]).

2. Now let us show that the partition function for a lattice containing impurities may be expressed in terms of a certain contour integral of the partition function Z for the pure lattice. The latter obviously can be written in the form

$$Z = \sum_r g(r)\, x^{N-r} y^r,$$

where N is the total number of bonds in the lattice (we shall call a line joining two neighboring atoms a bond), r is the number of negative bonds (lines which join atoms with oppositely directed spins), $x = y^{-1} = \exp(\beta J)$, and $g(r)$ is the number of spin configurations for a lattice containing r negative bonds.[1] Let us consider some configuration with r negative bonds, and let us distribute s impurities between the atoms of the lattice in all possible ways. The number of ways to arrange p impurity atoms on $N - r$ positive bonds and $s - p$ atoms on r negative bonds is $C^p_{N-r}C^{s-p}_r$. At the same time x^p is replaced by u^p and y^{s-p} by v^{s-p} ($u = v^{-1} = \exp(\beta J_1)$, where J_1 is the new coupling constant obtained as a result of screening). Thus, the contribution of a single configuration with r negative bonds to Z_s is

$$x^{N-r}y^r \sum_p C^p_{N-r} C^{s-p}_r u^p v^{s-p} x^{-p} y^{-s+p} = \frac{1}{2\pi i}\oint \frac{dz}{z^{s+1}} (x+zu)^{N-r}(y+zv)^r. \tag{2}$$

The integral in (2) is taken around the circumference of a circle with center at the point $z = 0$. It is important to note that only the order of the terms in the sum in Eq. (2) depends on the arrangement of the spin configuration of the lattice, but not the magnitude of the contribution itself. This circumstance enables one to relate Z_s and Z since $g(r)$ will contain terms of the form (2):

$$Z_s = \frac{1}{2\pi i}\oint \frac{dz}{z^{s+1}} \sum_r g(r)\,(x+zu)^{N-r}(y+zv)^r = \frac{1}{2\pi i}\oint \frac{dz}{z^{s+1}} (x+zu)^N Z\left(\frac{y+zv}{x+zu}\right). \tag{3}$$

For specific calculations it is convenient to make the change of variable $zuy(1 + zuy)^{-1} = t$ in expression (3). Then

$$Z_s = \frac{u^s x^{N-s}}{2\pi i} \int_{a-i\infty}^{a+i\infty} \frac{S[y^2(1-t)+v^2 t]\,dt}{t^{s+1}(1-t)^{N-s+1}}, \tag{4}$$

where

$$0 < a < 1 \text{ and } S(z) = \sum_r g(r) z^r.$$

The function $S(z)$ is well known only for planar Ising lattices (see[1,2]) although formula (4) itself is also valid for the three-dimensional case.

3. In what follows we shall be interested in the free energy per bond F_c of a lattice with impurities as $N \to \infty$, $s \to \infty$ and $c = s/N$ (c denotes the concentration of impurities); therefore the integral appearing in expression (4) can be found by the saddle-point method. Since the pre-exponential factors do not give any contribution to the free energy as $N \to \infty$, then the whole

calculation apparently reduces to the determination of F_c at the saddle point:

$$Z_s \sim \exp(-\beta N F_c).$$

The quantity F_c is related to the free energy F of a pure lattice by the formula

$$-\beta F_s = F(\eta) - c \ln \xi - (1-c) \ln (1-\xi) + c\beta J_1 + (1-c)\beta J, \quad (5)$$

where $\eta = (1-\xi)y^2 + \xi v^2$ and the saddle point ξ is determined from the condition $\partial(\beta F_c)/\partial\xi = 0$, which is more conveniently written, using the variable η, in the form

$$-\frac{c}{\eta - y^2} + \frac{1-c}{v^2 - \eta} + F'(\eta) = 0. \quad (6)$$

In the case of a square lattice the expression for $F(\eta)$ is well known (see, for example,[1,2]):

$$F(\eta) = \frac{1}{4} \ln \eta (1-\eta^2) + \frac{1}{8\pi} \int_0^{2\pi} \ln [A - \cos\varphi + \sqrt{(A-\cos\varphi)^2 - 1}]\, d\varphi, \quad (7)$$

where $A = (1+\eta^2)^2/2\eta(1-\eta^2)$. Equations (5) and (6) determine the temperature dependence of F_c.

A phase transition occurs at $\eta = \eta_0 = \sqrt{2} - 1$ (at this point $F(\eta)$ has a singularity). Since $A(\eta)$ has a minimum at $\eta = \eta_0$, one can easily show, by using formula (7), that $F'(\eta_0) = \sqrt{2}/4$. Substituting this number into Eq. (6), we obtain the dependence of the phase transition temperature on the concentration:

$$-\frac{c}{\eta_0 - y^2} + \frac{1-c}{v^2 - \eta_0} + \frac{\sqrt{2}}{4} = 0. \quad (8)$$

We shall find an explicit solution of this equation in two cases: 1) the impurity completely breaks the bond ($J_1 = 0$); 2) the impurity changes the sign of the interaction ($J_1 = -J$).

In the first case $v = 1$ and Eq. (8) gives

$$y_\lambda^2 = \frac{1-2c}{1+\sqrt{2}-2c},$$

where $y_\lambda = \exp[-J/T_\lambda(c)]$ and T_λ is the phase-transition temperature. For $c = 0.5$ the value of T_λ tends to zero, i.e., the phase transition disappears. A similar calculation for hexagonal and triangular lattices shows that in those cases the phase transition disappears when the concentration equals $(15 - 5\sqrt{3})/18$ or $(3 + 5\sqrt{3})/18$, respectively.

In the second case $v = y^{-1}$, and from Eq. (8) we find

$$y_\lambda^4 = \frac{4c - 2 + \sqrt{2}}{4c - 2 - \sqrt{2}}.$$

This expression is negative for $2 - \sqrt{2} < 4c < 2 + \sqrt{2}$, i.e., there is no phase transition in this range of concentrations. For $4c < 2 - \sqrt{2}$ a phase transition occurs into a ferromagnetic state, and for $4c > 2 + \sqrt{2}$ a phase transition occurs into an antiferromagnetic state. The dependence of T_λ on c for various cases is graphically shown in Fig. 1.

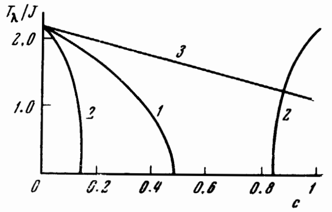

FIG. 1. Dependence of the phase-transition temperature on the impurity concentration for various disturbances of the bonds. $J_1 = 0$ for curve 1, $J_1 = -J$ for curve 2, and $J_1 = (1/2)J$ for curve 3.

4. In order to find out how the impurities influence the behavior of the heat capacity near a phase-transition point, let us consider the solution of Eq. (6) for small deviations of η from η_0 and T from $T_\lambda(c)$. For simplicity we shall assume that the bonds are completely broken ($v = 1$) and the concentration is small. Without these assumptions the result remains qualitatively the same, but the calculations become more cumbersome. Thus, we transform Eq. (6), taking $\eta = \eta_0 + \delta$ and $y^2 = y_\lambda^2 + \delta_0$ where $\delta, \delta_0 \ll 1$. As a result we obtain

$$\delta - \delta_0 - \frac{c}{\alpha} \delta \ln |\delta| = 0. \quad (9)$$

Here $\alpha = \pi(\sqrt{2} + 1)^3/2$. Let us make the substitution $\delta = \gamma \exp(\alpha/c)$. Then for γ we have the simpler equation:

$$\delta_0 = \frac{c}{\alpha} \exp\left(\frac{\alpha}{c}\right) \gamma \ln \frac{1}{|\gamma|}.$$

Hence

$$\gamma = \alpha\delta_0/c \exp\left(\frac{\alpha}{c}\right) \ln \frac{1}{|\gamma|}. \quad (10)$$

Let us substitute this expression for γ into the right hand side of Eq. (10). Then neglecting terms $\sim \ln \ln |\delta_0|^{-1}/\ln |\delta_0|$, we obtain the following expression for δ:

$$\delta \approx -\frac{\alpha\delta_0}{\alpha + c \ln c - c \ln |\delta_0|}. \quad (11)$$

For $|\delta_0| \gg \exp(-\alpha/c)$ expression (11) gives $\delta \approx \delta_0$, but for $|\delta_0| \ll \exp(-\alpha/c)$ we have $\delta \approx -\alpha\delta_0/c \ln|\delta_0|$.

Now let us expand expression (5) for the free energy F_c near a critical point in powers of δ and δ_0, and we retain the terms proportional to δ_0^2 and $\delta\delta_0$ (the terms $\sim\delta^2$ give a contribution which is $1/\ln |\delta_0|$ times smaller). We write down only the terms of second order (the terms of first order vanish because of condition (6), and the terms of zero order do not give any contribution to the heat capacity):

$$\beta F_c = -\frac{c}{2} \frac{\delta_0^2 - 2\delta\delta_0}{(\eta_0 - y_\lambda^2)^2} - \frac{1}{2\alpha} \delta^2 \ln |\delta|.$$

From Eq. (6) one can easily find, having expanded $F'(\eta)$ in a power series,

$$-\frac{1}{\alpha} \delta \ln |\delta| = c\delta_0/(\eta_0 - y_\lambda^2)^2.$$

Then expressing $\eta_0 - y_\lambda^2$ in terms of c and taking expression (11) into consideration, we obtain (in the region $\delta_0 \ll \exp(-\alpha/c)$)

$$\beta F_c = -\frac{c}{2} \frac{\delta_0^2 - \delta\delta_0}{(\eta_0 - y_\lambda^2)^2} = -\frac{(1+\sqrt{2})^4}{16c} \delta_0^2 \left[1 + \frac{\alpha}{c \ln |\delta|}\right]. \quad (12)$$

In order to calculate the heat capacity it is convenient to change from the variable δ_0 to $\tau = (T - T_\lambda)/T_\lambda$ according to the formula $\delta_0 = 2Jy_\lambda^2\tau/T_\lambda$. One can easily find the heat capacity from Eq. (12), setting $y_\lambda^2 = \sqrt{2} - 1$, correct to within terms $\sim c$:

$$C = -T \frac{\partial^2 F}{\partial T^2} \approx \frac{(1+\sqrt{2})^2}{2c} \frac{J^2}{T_\lambda^2} \left[1 + \frac{\alpha}{c \ln |\tau|}\right].$$

A graph of the heat capacity is shown in Fig. 2.

5. Thus, we see that at the critical point the heat

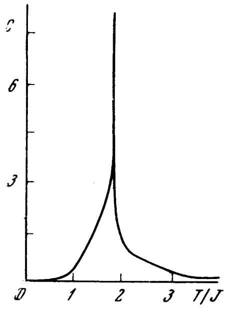

FIG. 2. Behavior of the heat capacity as a function of the temperature for impurity concentration c = 0.2 ($J_1 = 0$).

capacity remains finite, but its derivative tends to infinity like $-1/\tau \ln|\tau|$, that is, the impurities change a second-order phase transition into a third-order phase transition. However, this unusual behavior of the heat capacity will be observed only in an expontially narrow range of temperatures, $\tau \leq \exp(-\alpha/c)$, and since the value of α is numerically large ($\alpha \approx 19$), this region will remain very narrow even for high impurity concentrations. Outside of this region $\delta \approx \delta_0$, and the heat capacity will exhibit the usual logarithmic dependence.

It is not difficult to extend the results obtained above to the three-dimensional case. Numerical calculations show that at a critical point the free energy of a three-dimensional Ising lattice has a singularity of the form $|\tau|^{2-\alpha}$ where $\alpha = 1/8$. The solution of Eq. (6) near $|\tau| = 0$ then gives $C \sim |\tau|^{\alpha/(1-\alpha)} \sim |\tau|^{1/7}$ for the singular part of the heat capacity, that is, the heat capacity even in this case will be finite at the critical point.

The question as to what will happen if the impurities are distributed not on the bonds but on the lattice sites remains open. Then each impurity breaks k bonds (k is the number of nearest neighbors); however, this is still not the complete story since, let us say, two impurities may break either 2k bonds or 2k − 1 if they are nearest neighbors. If the impurity concentration is not large and one can neglect those impurity configurations in which the impurities are distributed on neighboring sites, then one would think that the results of the present article should remain valid for this case as well. It is possible, of course, that the singularity will not be unique since as the temperature is lowered the impurities may start to condense into drops, and still a phase transition of the first kind will occur. Then it is impossible to neglect configurations in which the impurities are nearest neighbors, but this condensation will occur at a temperature which is substantially more dependent on the concentration than T_λ is; therefore these two singularities may be separated by an appreciable temperature interval. (As c decreases the condensation temperature tends to zero but T_λ remains finite.)

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[1] Gordon F. Newell and Elliott W. Montroll, Rev. Mod. Phys. **25**, 353 (1953).

[2] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Izd. Nauka, 1964, Sec. 141 (English Transl., Addison-Wesley, 1958).

[3] R. Brout, Phys. Rev. **115**, 824 (1959).

[4] M. A. Mikulinskii, Zh. Eksp. Teor. Fiz. **53**, 1071 (1967) [Sov. Phys.-JETP **26**, 637 (1968)].

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