Second-Order Phase Transition in the Three-Dimensional Model of a Ferroelectric

G. V. RYAZANOV

L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences

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An exact calculation is presented for the vicinity of a second-order transition point for a three-dimensional model of a ferroelectric with hydrogen bonds. This is a Slater model in which the external strong electric field makes the partition function of one of the configurations vanish. A model of this type was first calculated in the two-dimensional case by Wu. The small parameter is the deviation of the temperature from the transition point. Interesting features of the model are the simplifications which appear just in the vicinity of the transition point. Thus the path density (see the article) vanishes at the transition point. Below the transition point the specific heat is zero, and above the point it possesses a logarithmic singularity.

THE principal task of the theory of second-order phase transitions is to calculate the thermodynamic functions in the vicinity of the transition point. A general shortcoming of the existing approximate theories, experiments, and computer calculations is that the errors have not been estimated. At the same time, there are many considerations that point to a sharp growth in the values of the errors near the transition point. Exactly-solvable models are therefore of particular interest.

At the present time there are two known exactly-solvable models with short-range action: the two-dimensional Ising model, calculated by Onsager, and the two-dimensional Slater model (ferroelectric model, calculated by Sutherland[1] and Lieb[2]). There is also the Wu model[3], which is apparently the simplest system having a second-order phase transition. The Wu model can be calculated both by the Onsager method and by the Sutherland-Lieb method. The generalized Wu model was calculated in[4] by the Vdovichenko method[5].

The purpose of the present paper is to calculate the three-dimensional Wu model. The methods mentioned above are not suitable for three-dimensional models, and our calculation is based on a generalization of a method described in[6].

The model is shown in Fig. 1. The lines joining the lattice points are hydrogen bonds. The protons, one per bond, are located near one of the ends of the bond. For each point, 16 configurations are possible, six of which (neutral configurations) are shown in Fig. 2a. Each configuration s is ascribed an energy ϵ_s (see Fig. 2b) and a statistical weight $\exp(-\epsilon_s/kT)$. The problem consists of calculating the sum over all the configurations—the partition function ($\{s\}$ denotes the set of the parameters specifying the proton configuration):

$$Z=\prod_{\{s\}}\exp\left\{-\frac{1}{KT}\Sigma\varepsilon_s\right\}. \qquad (1)$$

We assume that the energy level of the charged configurations lies so high that it suffices to take into account only six neutral configurations in the partition function (1). The energies of these six configurations depend on the molecule located at the lattice point (for the ferroelectric KH_2PO_4 these are the PO_4 ions) and on the external field; in the Wu model, we chose the energy values indicated in Fig. 2b.

The summation procedure can be made more lucid by representing the bonds in which the proton is located near the upper end (see Fig. 2a) by a solid line

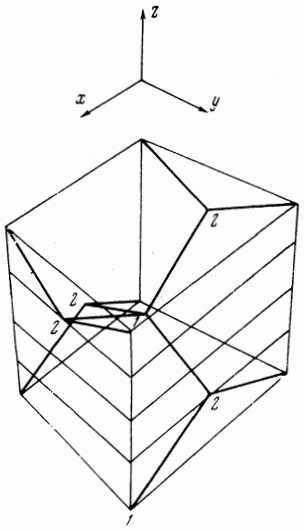

FIG. 1. Hydrogen bonds inside one cell of the crystal.

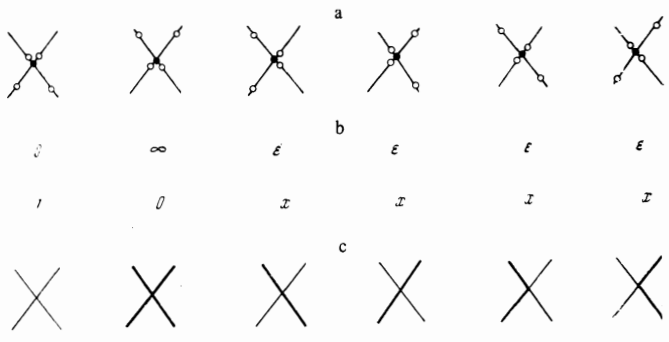

FIG. 2. Neutral proton configurations for one point: a—possible proton configurations; b—energy levels and statistical weight; c—corresponding path configurations. Each upper and each lower pair of bonds pertaining to one point lie in mutally perpendicular planes.

joining the points, and by not showing at all the bonds in which the proton is located near the lower end. For the six neutral points we obtained the configurations of Fig. 2c.

We see that any arrangement of the protons in the lattice (provided the electron neutrality condition is satisfied) can be represented by an aggregate of paths going from point to point in vertical direction without interruptions and without turning back. For a crystal with an edge (height) L, the partition function in the W Wu takes the form

$$Z = \sum_n e^{-n\epsilon L/kT}\Omega_n(L), \tag{2}$$

where Ω_n is the number of ways by which n paths can pass through the lattice from the lower limit to the upper one without meeting even in a single point. The problem of calculating the partition function of the three-dimensional Ising model can also be reduced to a calculation of the number of non-self intersecting paths[5]. In the Ising model, however, backward turns are permitted, and this complicates the problem greatly.

We introduce the following notation: $x = \exp(-\epsilon/kT)$; S is the area of the base of the crystal. Since $\Omega_n(L) < (2^L S)^n$ (the number of paths without limitations on the encounters), we have

$$Z = \sum_n [S(2x)^L]^n \varphi_n(L), \tag{3}$$

where $\varphi_n(L) < 1$ is a factor taking into account the interaction of the paths.

At $x < 1/2$, the expression in the square brackets $S(2x)^L \to 0$, and therefore when $x < 1/2$ we have for the partition function $Z = 1$.

At $x > 1/2$, the growth of the factor $[S(2x)^L]^n$ with increasing n is offset, at sufficiently large n, by the factor $\varphi_n(L)$. If x exceeds 1/2 only slightly (the temperature is close to the transition point), then n is small compared with S and the problem reduces to a calculation of $\varphi_n(L)$ at a small average path density.

At first glance it seems that this problem can be resolved by writing the kinetic equation for the paths in the low-density approximation. Thus, Belyĭ and Ovchinnikov[7] consider the related problem of random walks of particles that are annihilated by collisions, taking as the basis the kinetic equation for the number of mutual distances between particles, However, the approximations usually made in the derivation of the corresponding three-dimensional kinetic equations become doubtful in the present case. In the two-dimensional case (and all the more in the one-dimensional one) the particles interact more intensely than in the three-dimensional case, and therefore the picture of freely moving (in the first approximation) particles is incorrect even in the case of a low density and a small interaction radius. This will be seen from the calculation presented below.

On the other hand, the replacement of ρ and ρ^2 (ρ is the density) by their mean values, which was carried out in[7], raises doubts precisely because of the small radius and the strong fluctuations of the interactions, i.e., it may happen that the fluctuations of ρ and the random approaches of the particles associated with these fluctuations are more important than the value of the average density of the particles or of the particle pairs.

Indeed, as shown in[6], for the random walk of one particle over a lattice with randomly scattered forbidden points, the contribution of the fluctuations will be of the order of $1/|\ln\rho|$, i.e., this contribution decreases very slowly, although it can be made small as $\rho \to 0$. At the present time, an analogous problem is being considered, the role of forbidden points is being played by the particles themselves, and therefore the fluctuations should decrease. Since the contribution of the fluctuations is small, the point motion, which contributes only to the value of the fluctuations, does not change the result[6]. We obtain, in accordance with[6], $\varphi_n(L) \sim \exp(-SL\rho^2/4\pi|\ln\rho|)$, where $\rho = n/S$. However, the consistent calculation differs strongly from the calculation in[6], although it retains its main features.

We introduce the symbol $W(x_1, x_2, \ldots, x_n, t)$ for the probability that n particles will end up, after t transitions along the z axis, at the points $x_1, x_2, \ldots, x_n$, respectively, of a two-dimensional plane (x, y). As seen from Fig. 1, there are two types of points in the lattice, marked 1 and 2. It is therefore convenient to introduce the quantity $W_i(x_1, x_2, \ldots, x_n t)$ where the index i takes on values 1 and 2, and W_i denotes the probability of finding the first particle at a point of type i with coordinates x_1, the second at a point of type i with coordinates x_2, etc. The length along the axis is measured in units of one-quarter of the edge of the unit cell (see Fig. 1). The quantities φ_n in the partition function (2) are connected with W_i by the obvious relation

$$\varphi_n^{(i)}(L) = \sum_{x_1, x_2, \ldots, x_n} W_i(x_1, x_2, \ldots, x_n, 4L). \tag{4}$$

The calculation is then carried out as follows. From the exact recurrence relation for W_i with respect to t, we obtain an expression for the binary function $W_i(x, y, t+1)$ at the instant $t+1$ in terms of the binary, ternary, and quaternary functions of the instant t. At low density, all these functions can be expressed in terms of the binary function, and then we obtain a closed equation which can subsequently be solved. However, the calculation differs significantly from the usual calculation of a low-density gas. This difference is connected with the two-dimensional character of the gas. Unlike in the three-dimensional case, we obtain here, in addition to the usual terms connected with the scattering of the particles by one another, also the effective interaction with the neighbors. At low density ρ, this interaction takes in $\ln^2\rho$ neighbors and the problem is solved under the assumption that the radius of this interaction is large. Some interest attaches also to the method by which the total energy is transformed into two-particle energy in the derivation of the equation for the binary function.

Let us proceed to the calculation. If we disregard the path interaction, then the recurrence relation for W_i take the form

$$W_1(t+1) = \hat{L}W_2(t), \quad W_2(t+1) = \hat{M}W_1(t), \tag{5}$$

where (k_S and l_S are the coordinates of the point x_S)

$$\hat{L}W_2\begin{pmatrix} k_1 \dots k_n \\ l_1 \dots l_n \end{pmatrix} t = \frac{1}{2^n}\sum_{\sigma_s=\pm 1} W_2\begin{pmatrix} k_1 \dots k_n \\ l_1+\sigma_1 \dots l_n+\sigma_n \end{pmatrix} t,$$

$$\hat{M}W_1\begin{pmatrix} k_1, \dots, k_n \\ l_1, \dots, l_n \end{pmatrix} t = \frac{1}{2^n}\sum_{\sigma_s=\pm 1} W_1\begin{pmatrix} k_1+\sigma_1, \dots k_n+\sigma_n \\ l_1, \dots, l_n \end{pmatrix} t.$$

In accordance with the summation rule described above only one path passes through each point in the Wu model. Therefore the transitions into one and the same point should be discarded from (5). In order to cause the contributions of these transitions to vanish, we add them in (5) with a minus sign. To abbreviate the notation, we introduce the symbols

$$\frac{1}{2}\sum_{\sigma=\pm 1} W_2\left(\mathbf{x}_1, \dots \begin{matrix} k_s \\ l_s-\sigma \end{matrix} \dots, \mathbf{x}_n\right) = W_2(\mathbf{x}_1, \dots, \mathbf{x}_s', \dots \mathbf{x}_n),$$

$$\frac{1}{2}\sum_{\sigma=\pm 1} W_1\left(\mathbf{x}_1, \dots \begin{matrix} k_s+\sigma \\ l_s \end{matrix} \dots, \mathbf{x}_n\right) = W_1(\mathbf{x}_1 \dots \mathbf{x}_s' \dots \mathbf{x}_n),$$

$\delta_{sp} = \delta_{k_s k_p}\delta_{l_s l_p}$ are the Kronecker symbols. We obtain

$$W_1(t+1) = \hat{L}W_2(t) - G(t), \quad W_2(t+1) = \hat{M}W_1(t) - F(t), \quad (6)$$

where

$$G = \sum_{p\neq s}\delta_{ps}W_2(\mathbf{x}_1', \dots, \mathbf{x}_n'),$$

$$F = \sum_{p\neq s}\delta_{ps}W_1(\mathbf{x}_1', \dots, \mathbf{x}_n'). \quad (7)$$

From (6) and (7), after summing with respect to $\mathbf{x}_s$, we obtain with the aid of (4) analogous relations for φ_n. We introduce first a special symbol for a binary function of two close values of the arguments

$$W_1(\mathbf{x}', \mathbf{x}') = \frac{1}{2}\sum_{\sigma=\pm 1} W_1\begin{pmatrix} k+\sigma & k-\sigma \\ l & l \end{pmatrix}$$

$$W_2(\mathbf{x}', \mathbf{x}') = \frac{1}{2}\sum_{\sigma=\pm 1} W_2\begin{pmatrix} k & k \\ l+\sigma & l-\sigma \end{pmatrix}.$$

We obtain

$$\varphi_n^{(1)}(t+1) = \varphi_n^{(2)}(t) - n(n-1)\sum_{\mathbf{x}} W_2^{(n)}(\mathbf{x}', \mathbf{x}', t),$$

$$\varphi_n^{(2)}(t+1) = \varphi_n^{(1)}(t) - n(n-1)\sum_{\mathbf{x}} W_1^{(n)}(\mathbf{x}', \mathbf{x}', t). \quad (8)$$

To find the binary function that enters here, we integrate Eqs. (6) with respect to all but two variables $\mathbf{x}_s$. We obtain

$$W_1(\mathbf{x}, \mathbf{y}, t+1) = W_2(\mathbf{x}', \mathbf{y}', t) - \delta_{\mathbf{x},\mathbf{y}}W_2(\mathbf{x}', \mathbf{y}', t) - (n-2)W_2(\mathbf{x}', \mathbf{x}', \mathbf{y}, t)$$
$$-(n-2)W_2(\mathbf{x}', \mathbf{y}', \mathbf{y}', t) - (n-2)(n-3)\sum_{\mathbf{z}} W_2(\mathbf{x}', \mathbf{y}', \mathbf{z}', \mathbf{z}', t),$$

$$W_2(\mathbf{x}, \mathbf{y}, t+1) = W_1(\mathbf{x}', \mathbf{y}', t) - \delta_{\mathbf{x},\mathbf{y}}W_1(\mathbf{x}', \mathbf{y}', t) - (n-2)W_1(\mathbf{x}', \mathbf{x}'\ \mathbf{y}'\ t)$$
$$-(n-2)W_1(\mathbf{x}', \mathbf{y}', \mathbf{y}', t) - (n-2)(n-3)\sum_{\mathbf{z}} W_1(\mathbf{x}', \mathbf{y}', \mathbf{z}', \mathbf{z}', t). \quad (9)$$

The first term in the right-hand side is the free random walk, the second term occurs when the two paths in the left-hand side of (9) come close together, the third and fourth terms occur when one of the these paths comes close to the remaining n − 2 paths, and the fifth occurs when the paths which do not enter in the left side come close together. The quantities W_1 and W_2 denote everywhere functions that are symmetrized with respect to their arguments

At low density or at a large interaction radius (in this case both conditions are satisfied, as seen from (13), the interaction radius being of the order of $(1-\lambda)^{-1/2}$ or, according to (15), $(|\ln\rho|/\rho)^{1/2} > 1/\sqrt{\rho}$ at small values of ρ), we neglect the triple collisions and represent the normalized probability in the form (we put here $\varphi_n^{(1)} = \varphi_n^{(2)} = \varphi_n$, this follows from the symmetry of the lattice).

$$\frac{W_1^{(n)}(\mathbf{x}', \mathbf{y}', \mathbf{z}'\ \mathbf{z}')}{\varphi_n} = \frac{W_1^{(n)}(\mathbf{x}', \mathbf{y}')}{\varphi_n}\frac{W_1^{(n)}(\mathbf{z}', \mathbf{z}')}{\varphi_n}.$$

Substituting this expression in the last term of (9), we obtain with the aid of (8) the following expression for this term:

$$(n-2)(n-3)\sum_{\mathbf{z}} W_2^{(n)}(\mathbf{x}', \mathbf{y}', \mathbf{z}', \mathbf{z}')$$
$$= \frac{(n-2)(n-3)}{\varphi_n} W_2^{(n)}(\mathbf{x}', \mathbf{y}')\sum_{\mathbf{z}} W_2^{(n)}(\mathbf{z}', \mathbf{z}')$$
$$= -\frac{(n-2)(n-3)}{n(n-1)}\left(\frac{\varphi_n(t+1)}{\varphi_n(t)} - 1\right) W_2^{(n)}(\mathbf{x}', \mathbf{y}').$$

If we seek $W_2^{(n)}(t)$ in the form $W_2^{(n)}(t) = W_2(\lambda_n)\lambda_n^t$, then we obtain at large values of n the following expression for the last term in (9):

$$-\left(1-\frac{4}{n}\right)(\lambda_n - 1)W_2^{(n)}(\mathbf{x}', \mathbf{y}').$$

The purpose of the subsequent calculations is to find the smallest eigenvalue λ_n. The quantity λ_n is connected with the single-particle value λ sought in[6] by the relation $\lambda_n = \lambda^n$. Therefore, to be able to use the method of[6], we write down a recurrence relation of the type (9) not for $W_i(\mathbf{x}, \mathbf{y})$, but for the partially normalized binary function $W_i^{(n)}(\mathbf{x}, \mathbf{y})/\varphi_{n-2}$, which depends on t, roughly speaking, like λ^{2t}.

We introduce the notation $p_i^{(n)}(\mathbf{x}, \mathbf{y}) = W_i^{(n)}(\mathbf{x}, \mathbf{y})/\varphi_{n-2}$. From (8) and (9) we obtain an analogous expression for p (we assume here in (9)

$$W_2(\mathbf{x}', \mathbf{x}', \mathbf{y}') = W_2(\mathbf{x}', \mathbf{x}')\frac{W_2(\mathbf{y}')}{\varphi_n} = \frac{W_2(x', x')}{S}$$

and recognize that $n \gg 1$):

$$p_1(\mathbf{x}, \mathbf{y}, t+1) = p_2(\mathbf{x}', \mathbf{y}', t) - \delta_{\mathbf{x},\mathbf{y}}p_2(\mathbf{x}', \mathbf{y}', t)$$
$$-nS^{-1}[p_2(\mathbf{x}', \mathbf{x}', t) + p_2(\mathbf{y}', \mathbf{y}', t)] - \nu p_2(\mathbf{x}', \mathbf{y}', t),$$

$$p_2(\mathbf{x}, \mathbf{y}, t+1) = p_1(\mathbf{x}', \mathbf{y}', t) - \delta_{\mathbf{x},\mathbf{y}}p_1(\mathbf{x}', \mathbf{y}', t)$$
$$-nS^{-1}[p_1(\mathbf{x}', \mathbf{x}', t) + p_1(\mathbf{y}', \mathbf{y}', t)] - \nu p_1(\mathbf{x}', \mathbf{y}', t), \quad (10)$$

where

$$\nu = (1 - 4/n)(\lambda_n - 1) - \lambda_{n-2} + 1.$$

In the momentum representation we obtain for the functions $p_i(\mathbf{k}, \mathbf{q})$, where $\mathbf{k} = (k_1, k_2)$ and $\mathbf{q} = (q_1, q_2)$ the system of algebraic equations ($p(t) = p(\lambda)\lambda^{2t}$)

$$\lambda^2 p_1 = (\cos k_2 \cos q_2 + \nu)p_2 - G,$$
$$\lambda^2 p_2 = (\cos k_1 \cos q_1 + \nu)p_1 - F, \quad (11)$$

where ($\rho = n/S$)

$$G(\mathbf{k}, \mathbf{q}) = \sum_{\mathbf{x},\mathbf{y}} e^{i(\mathbf{kx}+i\mathbf{qy})}\{\delta_{\mathbf{x},\mathbf{y}}p_2(\mathbf{x}', \mathbf{y}') - \rho[p_2(\mathbf{x}', \mathbf{x}') + p_2(\mathbf{y}', \mathbf{y}')]\},$$

$$F(\mathbf{k}, \mathbf{q}) = \sum_{\mathbf{x},\mathbf{y}} e^{i(\mathbf{kx}+i\mathbf{qy})}\{\delta_{\mathbf{x},\mathbf{y}}p_1(\mathbf{x}'\ \mathbf{y}') - \rho[p_1(\mathbf{x}', \mathbf{x}') + p_1(\mathbf{y}'\ \mathbf{y}')]\}. \quad (12)$$

The solution of these equations is

$$p_1 = -\{\lambda^2 G + [\cos k_2 \cos q_2 + \nu]F\} / D,$$
$$p_2 = \{\lambda^2 F + [\cos k_1 \cos q_1 + \lambda]G\} / D,$$
$$D = \lambda^4 - [\cos k_1 \cos q_1 + \nu][\cos k_2 \cos q_2 + \nu]. \quad (13)$$

If we now rewrite (13) in the coordinate representation and take in the left-hand side $p_i(x, y)$ at two close points, then we obtain a closed system of equations for $p_i(x', x')$.

At large t (and at corresponding values of λ close to unity) the particle spreads out over a region of the order of $\sqrt{t}$. At the same time, it is seen from the expression for D in (13) (it will be shown below that ν is small) that the main contribution is made by momenta on the order of $\sqrt{1-\lambda^2}$, i.e., dimensions of the order of $(1-\lambda^2)^{-1/2}$ are close, according to (15), to $(|\ln\rho|/\rho)^{1/2}$. Under these conditions, the dependence of p on the absolute value of the coordinates can be neglected, and we can put $p_i(x', x') = C_i$ (constants). Substituting this value in (12), we obtain

$$G = C_2[\delta(k+q) + 2\rho\delta(k)\delta(q)],$$
$$F = C_1[\delta(k+q) + 2\rho\delta(k)\delta(q)]. \quad (14)$$

Substituting these expressions in (13), we change over to the coordinate representation and take $p_i(x, y)$ at two closed points. From the symmetry of the lattice (or from the symmetry of the equations for $p_i(x', x')$) it follows that $C_1 = C_2 = C$. We obtain in place of (13) the two identical relations,

$$\left[\ln(1-\lambda^2-\nu) - \frac{\rho}{2\pi(1-\lambda^2-\nu)}\right] C = 0.$$

From this at $\nu \ll 1 - \lambda^2$ (it will be shown below that this is actually the case)

$$\lambda = 1 - \rho/4\pi|\ln\rho|. \quad (15)$$

The quantities φ_n can be obtained from the relation

$$\frac{\varphi_n}{\varphi_{n-2}} = \sum_{x,y} p(x, y) = \tilde{p}(0, 0),$$

where $\tilde{p}(0, 0)$ is the Fourier transform of $p(x, y)$ at zero momenta.

From (13) and (14) it follows that

$$\varphi_n / \varphi_{n-2} = \tilde{p}(0, 0) = C / S(\lambda^2 - 1 - \nu).$$

Since $C(t) \sim \lambda^{2t} = \exp(-\rho t/4\pi |\ln\rho|)$, we have

$$\varphi_n \sim \lambda^{nt} = \exp\{-n\rho t/4\pi|\ln\rho|\} = \exp\{-St\rho^2/4\pi|\ln\rho|\}.$$

After substituting in (3) and integrating with respect to ρ, we obtain ($\tau = 2(x - \frac{1}{2}) \ll 1$)

$$Z = \begin{cases} \exp\{-4\pi\tau^2 \ln\tau \cdot LS\}, & \tau > 0, \\ 1, & \tau < 0. \end{cases}$$

The specific heat per unit cell (per group of four points):

$$C_v = \begin{cases} 4\pi k \ln\tau, & \tau > 0, \\ 0, & \tau < 0. \end{cases}$$

It remains to show that $\nu \ll 1 - \lambda^2$. Substituting (15) in the expression for ν in (10), we obtain

$$\nu \sim \frac{\rho}{\ln^2\rho} \exp\{-n\rho/\pi|\ln\rho|\} \ll 1 - \lambda^2 = \rho/\pi|\ln\rho|.$$

for all n.

[1]B. Sutherland, Phys. Rev. Lett. **19**, 103 (1967).
[2]E. H. Lieb, Phys. Rev. Lett. **19**, 108 (1967).
[3]F. I. Wu, Phys. Rev. Lett. **18**, 605 (1967).
[4]G. V. Ryazanov, Zh. Eksp. Teor. Fiz. **59**, 1000 (1970) [Sov. Phys. JETP **32**, 544 (1971)].
[5]L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964.
[6]G. V. Ryazanov, Teoret. i mat. fizika (in press).
[7]A. A. Belyĭ and A. A. Ovchinnikov, Teor. Eksp. Khim. **3**, 451 (1967).

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