

Phase transitions in two-component systems

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The general case of a phase transition in systems consisting of two Ising sublattices is studied by Wilson's method. Both the Baxter (energy-energy) and Ising (spin-spin) interaction between the sublattices are studied. It is shown that, if the sublattices have different transition temperatures, the behavior of the thermodynamic quantities in such a system corresponds isomorphously to the behavior in the one-component Ising model. The thermodynamics of the critical point of a two-component mixture is considered in the framework of the lattice-gas model. It is shown that the phase transitions of the mixture and of the pure substance are isomorphous along the path $\mu + f\tau = \text{const}$, where f is a constant (in contrast to the "decorated" model, in which the path $\mu = \text{const}$ is isomorphous).

1. INTRODUCTION

The general case of a phase transition in systems consisting of two Ising sublattices is studied in this paper using Wilson's method^[1,2]. As a perturbation, interactions of both the Baxter (energy-energy) and Ising (spin-spin) types between the sublattices are considered. Wilson and Fisher showed^[2] that the Baxter model consisting of two identical sublattices (the XY-model) has critical indices that differ from the corresponding indices of the Ising model. In Sec. 2 we consider a model consisting of two sublattices with different transition temperatures T_{10} and T_{20} (without taking their interaction into account). It is assumed that $\Delta\tau_0 = (T_{10} - T_{20})/T_{10} \ll 1$. As a perturbation, a Baxter interaction is "switched on" between the sublattices. Such a system has two phase-transition points T_{C1} and T_{C2} . Far from the transition points, $\tau = (T - T_C)/T_C \gg \Delta\tau_0$ (T is the temperature), the critical indices (c.i.) of the XY-model obtain, and in the immediate vicinity of T_C we have the c.i. of the one-component Ising model; the coefficient of the temperature singularity in this region is a nonanalytic function of the parameter $\Delta\tau_0$.

In Sec. 3, together with the Baxter interaction, Ising interactions are studied as a perturbation. It is shown that the problem can be reduced to the previous one by a simple change of variables. The particular case of identical sublattices with a weak Ising interaction between them (of order ν) is discussed. Such a system has Ising-model c.i. in the whole temperature range $\tau \ll 1$. The shift in the critical temperature when the perturbation is switched on is proportional to $\nu^{1/\gamma}$ (γ is the susceptibility exponent in the Ising model); this has been shown earlier by another method^[3,4]. If the shift in the critical temperature when the perturbation is switched on is a nonanalytic function of the magnitude of the perturbation, the isomorphism of the phase transitions in the perturbed and unperturbed systems is violated^[5]. This can occur both as a result of a change in the critical indices, and as a result of the fact that the coefficient $C(\nu)$ of the temperature singularity becomes a nonanalytic function of ν . In the present case, the isomorphism is violated as a result of the nonanalytic dependence of $C(\nu)$ on ν .

The results obtained are extrapolated to the case $\Delta\tau_0 \sim 1$ or $\nu \sim 1$. Then the phase transition near the point T_{C1} or T_{C2} in the two-component model is isomorphous to the transition in the one-component Ising model.

In Sec. 4 we consider a lattice model of the critical point of a two-component mixture. The interaction between the sublattices in this model, unlike the cases analyzed in the previous Sections, contains terms that are cubic in the spins.

In previous work^[6-8] it has been assumed that a phase transition in two-component equilibrium mixtures in a variable chemical potential is isomorphous to the phase transition in the pure substance.

The principal result of the latter part of the paper is a proof of the isomorphism assumed in^[6-8]. Unlike the decorated Ising model^[9], in which the isomorphous path is determined by the condition $\mu = \text{const}$, in our case the analogous condition has the form $\mu + f\tau = \text{const}$, where f is a certain constant.

2. THE BAXTER MODEL WITH DIFFERENT SUBLATTICES

1. We shall write the Hamiltonian of the system, which consists of two interacting sublattices, in the continuous Wilson model in the form

$$H = H_0 + H_1, \\ H_0 = r s_{n,i}^2 - \mu s_{n,i}^4 - K_1 \sum_j s_{n,i} s_{n+i,j} - K_2 \sum_{j,l} s_{n,i} s_{n+i,j} s_{n+2s_{n+i,j},l} \\ H_1 = -K_4 s_{n,1} s_{n,2}, \quad (1)$$

where $s_{n,i}$ is the spin variable belonging to the site n and takes all values from $-\infty$ to ∞ ; the index $i = 1, 2$ labels the two sublattices; $K_i = J_i/T$; J_i are the exchange integrals; r and μ are constants. Repeated indices are to be summed over.

The first two terms in H_0 are added in order to suppress the contribution of large values of $s_{n,i}$ to the partition function. The third term represents the energy of the spins within each sublattice. It is assumed that only nearest-neighbor spins interact. The fourth term is the Baxter interaction (of the energy-energy type). The Hamiltonian H_1 , which is assumed to be small, describes the Ising interaction of the different sublattices.

2. Following Wilson^[1], we change from $s_{n,i}$ to the variable $s_{l,i}(x)$, which depends on the continuous spatial coordinate x . The variable $s_{l,i}(x)$ characterizes the state of a block of length 2^l . The interaction between these blocks is described by an effective Hamiltonian H_l of the form

$$H_i = - \int \left\{ \frac{1}{2} [\nabla s_{i,i}(x)]^2 + Q_i[s_{i,i}(x)] \right\} dx. \quad (2)$$

The function $Q_i(z_i)$ is calculated from the recursion formula

$$Q_{i+1}(z_i) = -2^d \{ \ln [I_i(2^{1-d/2}z_i)] - \ln I_i(0) \}, \quad (3)$$

$$I_i(z_i) = \int_{-\infty}^{\infty} dy_1 dy_2 \exp \left[-y_1^2 - \frac{1}{2} Q_i(z_i - y_1) - \frac{1}{2} Q_i(z_i + y_1) \right].$$

where the dimensionless variables y_i and z_i are introduced in place of $s_{i,i}(x)$. The details of the notation are given in the papers^[1,2].

The susceptibility is calculated from the formula

$$\chi = \sum_n \langle (s_{0,1} + s_{0,2})(s_{n,1} + s_{n,2}) \rangle = g(k) |_{k=0}. \quad (4)$$

In accordance with^[1], we have

$$g(k) |_{k=0} = 2^d R_i(0) |_{l \rightarrow \infty}, \quad (5)$$

$$R_i(0) = \frac{1}{I_i(0)} \int_{-\infty}^{\infty} dy_1 dy_2 (y_1 + y_2)^2 \exp[-y_1^2 - Q_i(y_1)].$$

The function

$$Q_0(y_i) = Q_{0,0}(y_i) - \nu_0 y_1 y_2, \quad (6)$$

$$Q_{0,0}(y_i) = r_{i,0} y_1^2 + u_{1,0} y_1^4 + u_{2,0} y_1^2 y_2^2 + u_{3,0} y_2^4,$$

corresponds to the case under consideration, where $r_{i,0} = (2/K_i \rho_0)(r - K_i d)$, ρ_0 and $u_{s,0}$ are constants, and d is the dimensionality of space.

Wilson and Fisher^[2] considered a model in which $r_{1,0} = r_{2,0}$, $u_{1,0} = u_{3,0}$ and $\nu_0 = 0$ (cf. (6)). They showed that when the inequality $0 < u_{2,0} < 6u_{1,0}$ is fulfilled, the system has XY-model c.i. and that only in the cases $u_{2,0} = 0$ or $u_{2,0} = 6u_{1,0}$ will the c.i. of the Ising model obtain.

We begin our study of Eqs. (3) with the case of two sublattices with close, but not equal, transition temperatures, with a Baxter interaction between the sublattices ($\nu_0 = 0$, $r_{1,0} - r_{2,0} \ll 1$ or $(J_1 - J_2)/J_1 \ll 1$).

In accordance with the initial value Q_0 defined by formula (6) we shall seek the solution of Eqs. (3) in the form

$$Q_i(y_i) = r_{i,0} y_1^2 + u_{1,0} y_1^4 + u_{2,0} y_1^2 y_2^2 + u_{3,0} y_2^4. \quad (7)$$

Substitution of formula (7) into (3) leads to recursion relations for $r_{i,l}$ and $u_{s,l}$ for small values of $a_{s,l}$:

$$r_{1,i+1} = 4r_{1,i} + 4(3u_{1,i} g_{1,i} + 1/2 u_{2,i} g_{2,i}),$$

$$r_{2,i+1} = 4r_{2,i} + 4(3u_{3,i} g_{3,i} + 1/2 u_{2,i} g_{2,i}), \quad (8a)$$

$$u_{1,i+1} = 16 \cdot 2^{-d} (u_{1,i} - 9u_{1,i}^2 g_{1,i}^{-1} / u_{2,i} g_{2,i}^2),$$

$$u_{2,i+1} = 16 \cdot 2^{-d} (u_{2,i} - 2u_{2,i}^2 g_{1,i} g_{2,i} - 3u_{1,i} u_{2,i} g_{1,i} - 3u_{2,i} u_{3,i} g_{2,i}^2),$$

$$u_{3,i+1} = 16 \cdot 2^{-d} (u_{3,i} - 9u_{3,i}^2 g_{1,i}^{-1} / u_{2,i} g_{2,i}^2), \quad (8b)$$

where $g_{i,l} = (1 + r_{i,l})^{-1}$.

Following the paper^[2], we shall calculate the c.i. for a space of $d = 4 - \epsilon$ dimensions, where $\epsilon \ll 1$. We shall assume that the initial values $r_{i,0}$ and $u_{s,0}$ are of order ϵ . From the definitions of $r_{1,0}$ (cf. (6)), it can be seen that $r_{1,0}$ and $r_{2,0}$ can be small quantities simultaneously if $(K_1 - K_2)/K_1$ is also of order ϵ , as will be assumed.

3. In the first stage, we shall obtain the solution of Eqs. (8) in the region $r_{i,l} \ll 1$ or $g_{i,l} \approx 1$, when Eqs. (8b) have the form

$$u_{1,i+1} = (1 + \epsilon \ln 2) u_{1,i} - 9u_{1,i}^2 / u_{2,i}^2,$$

$$u_{2,i+1} = (1 + \epsilon \ln 2) u_{2,i} - 2u_{2,i}^2 - 3u_{1,i} u_{2,i} - 3u_{2,i} u_{3,i}, \quad (9)$$

$$u_{3,i+1} = (1 + \epsilon \ln 2) u_{3,i} - 9u_{3,i}^2 / u_{2,i}^2.$$

Eqs. (9) give six possible limiting values $u_{s,l} = u_{s,0}$ ($l \gg 1$):

- 1) $u_1 = u_2 = u_3 = 0$ - the Gaussian model;
- 2) $u_2 = 0$, $u_1 = u_3 = (\epsilon \ln 2)/9$ - the Ising model;
- 3) $u_1 = u_3 = (\epsilon \ln 2)/18$, $u_2 = 6u_1$ - the Ising model;
- 4) $u_1 = u_3 = (\epsilon \ln 2)/10$, $u_2 = 2u_1$ - the XY-model;
- 5) $u_1 = u_2 = 0$, $u_3 = (\epsilon \ln 2)/9$ - the Ising model;
- 6) $u_2 = u_3 = 0$, $u_1 = (\epsilon \ln 2)/9$ - the Ising model. (10)

The first four solutions were found by Wilson and Fisher^[2].

A study of the stability of all six solutions with allowance for the fact that the $u_{1,l} \neq u_{3,l}$ shows that the fourth solution is the most stable. The other solutions are realized only in those cases when the relation $u_{s,0} = \varphi u_{s,0}$, where φ is a nonzero constant, holds between the initial and limit values of $u_{s,l}$. For example, the fifth solution can be realized only when $u_{1,0} = u_{2,0} = 0$. In all the other cases, the solution for large l corresponds to the XY-model.

We shall find the critical indices close to one of the critical points (T_{c1} , for definiteness).

In solving Eqs. (8a) we can distinguish three characteristic regions. Firstly, we have the region

$$r_{1,i} \ll 1, \quad r_{2,i} \ll 1. \quad (11a)$$

This is a region far from the critical point in temperature: $\tau \gg \Delta\tau_0$.

Further, we have the regions

$$r_{1,i} \ll 1, \quad r_{2,i} \gg 1, \quad (11b)$$

$$r_{1,i} \gg 1, \quad r_{2,i} \gg 1. \quad (11c)$$

The inequalities (11b) and (11c) define regions in which $\tau \ll \Delta\tau_0$. The region (11b) is intermediate in l , and (11c) corresponds to asymptotically large values of l .

In the region (11a), the values $r_{i,l}$ are found from the linearized equations (8a), which for the stable solution $u_2/2 = u_1 = u_3 = (\epsilon \ln 2)/10$ (the fourth solution in (10)) have the form

$$\Delta r_{1,i+1} = 4\Delta r_{1,i} - 12u_1 \Delta r_{1,i} - 4u_1 \Delta r_{2,i},$$

$$\Delta r_{2,i+1} = 4\Delta r_{2,i} - 12u_1 \Delta r_{2,i} - 4u_1 \Delta r_{1,i}. \quad (12)$$

We give the solution of this system satisfying the initial conditions $r_{i,0} = (2/K_i \rho_0)(r - K_i d) + 16u_{1,0}/3$:

$$\Delta r_{1,i} = A\lambda_1^i + B\lambda_2^i, \quad \Delta r_{2,i} = -A\lambda_1^i + B\lambda_2^i, \quad (12')$$

where $\lambda_1 = 4 - 8u_1$ and $\lambda_2 = 4 - 16u_1$ are the eigenvalues of the determinant of the system of equations (12), and

$$A = \frac{\Delta r_{1,0} - \Delta r_{2,0}}{2} = \frac{r}{\rho_0} \frac{K_2 - K_1}{K_1 K_2},$$

$$B = \frac{\Delta r_{1,0} + \Delta r_{2,0}}{2} = \frac{1}{\rho_0} \left[\frac{r(K_1 + K_2)}{K_1 K_2} - 2d \right] + \frac{16}{3} u_{1,0}.$$

The solution found corresponds to the region (11a) and is valid for $1 \ll l$, where

$$l \sim \min \{ \ln A, \ln B \}. \quad (13)$$

As we shall see below (cf. also^[1,2]), the phase-transition temperatures are determined on the condition that

the expressions $\Delta r_{1,l}$ vanish. It can be seen from the solutions obtained above that the difference $\Delta r_{1,l} - \Delta r_{2,l}$ increases with increasing l and that $\Delta r_{1,l}$ and $\Delta r_{2,l}$ vanish at different temperatures. Therefore, near one of these temperatures, e.g., T_{C1} , for $l > l_1$ we have the region (11b).

Putting $g_{2,1} \approx 0$ in this region, from (8) we obtain equations for $r_{1,l}$:

$$\begin{aligned} r_{1,l+1} &= 4r_{1,l} + 12u_{1,l}g_{1,l}, \\ u_{1,l+1} &= (1 + \epsilon \ln 2)u_{1,l} - 9u_{1,l}^2g_{1,l}^2, \end{aligned} \quad (14)$$

which coincide with the corresponding equations of the one-component Ising model^[2]. As is well known, the solution of the system of equations (14) has the form

$$\begin{aligned} r_{1,l} &= a\tau\lambda^{-l/\epsilon} \ln 2, \quad \lambda = 4^{-1/\epsilon} \ln 2, \\ a &= \text{const.} \end{aligned} \quad (15)$$

For very large l (the region (11c)), from Eqs. (8a) we obtain

$$r_{1,l} = \bar{A}2^{2l}, \quad r_{2,l} = \bar{B}2^{2l}, \quad Q_l = 2^{2l}(\bar{A}y_1^2 + \bar{B}y_2^2), \quad (16)$$

where \bar{A} and \bar{B} are functions of the temperature. The quantity \bar{A} is found by matching the solutions (15) and (16) and equals

$$\bar{A} \sim \tau^\gamma, \quad (17)$$

$$\gamma = 2 \ln 2 / \ln \lambda. \quad (18)$$

By means of the expression found for Q_l we calculate the susceptibility from formulas (4) and (5):

$$\chi = 1/\bar{A} + 1/\bar{B}. \quad (19)$$

It can be seen from (19) that the quantity γ defined in (18) is the susceptibility exponent. Thus, in the immediate vicinity of the transition point, the system has the critical indices of the Ising model.

The temperature of the phase transitions are determined from the condition that \bar{A} and \bar{B} in (19) vanish. \bar{A} vanishes at the same point as the coefficient of λ^l in (15). For an estimate of the coefficient in (15), we can make use of the expression (12') for $\Delta r_{1,l}$ with $l \sim 1$. Neglecting terms of the type $u_{1,l} \sim \epsilon \ln \epsilon$ in the zeroth approximation in ϵ , from the condition $\Delta r_{1,l} |_{l \sim 1} = 0$ we find

$$T_{c1} = J_1 d/r, \quad T_{c2} = J_2 d/r. \quad (20)$$

The coefficients of the temperature singularities of the thermodynamic quantities, e.g., in the susceptibility χ , are estimated most simply by matching χ in the regions $\tau \ll \Delta\tau_0$ and $\tau \gg \Delta\tau_0$. In the first region,

$$\chi = \chi_0 \tau^{-\gamma}, \quad (21a)$$

where χ_0 is the coefficient, independent of τ , that we need to estimate.

In the second region,

$$\chi = \chi_0 \tau^{\gamma} \tau^{-\gamma\tau}, \quad (21b)$$

where χ_0 , χ_{XY} and γ_{XY} are respectively the coefficient and exponent of the susceptibility of the XY-model. By matching formulas (21a) and (21b) for $\tau \sim \Delta\tau_0$, we find

$$\chi_0 \sim \chi_0 \tau^{\gamma} \Delta\tau_0^{-\gamma\tau}, \quad (22)$$

i.e., χ_0 is a nonanalytic function of the parameter $\Delta\tau_0$. If $\Delta\tau_0 \sim 1$, the c.i. of the Ising model obtain in the whole temperature region $\tau \ll 1$.

3. ALLOWANCE FOR ISING INTERACTION BETWEEN THE PLANES

1. In the preceding sections we have calculated the c.i. of a system described by the Hamiltonian H_0 (or $Q_{0,0}$) in formulas (2) and (4). Here we shall consider the effect of the perturbation H_1 in the case of two identical sublattices ($J_1 = J_2$, $r_{1,0} = r_{2,0} = r_0$).

We observe that the system of recursion equations (3) is invariant under unitary transformations of the coordinates y_1, y_2 (z_1, z_2). In fact, if in Eqs. (3) we change from the variables y_i to \bar{y}_i and, by means of the same unitary transformation, from z_i to \bar{z}_i , then y_i^2 goes over into \bar{y}_i^2 and $Q_1(z_i \pm y_i)$ into $\bar{Q}_1(\bar{z}_i \pm \bar{y}_i)$; then the formulas (3) will have the same form as in the initial variables. In accordance with what has been said, by making the change of variables $\bar{y}_1 = 2^{-1/2}(y_1 + y_2)$, $\bar{y}_2 = 2^{-1/2}(y_1 - y_2)$ in formula (6), we obtain

$$\bar{Q}_0(\bar{y}_i) = \bar{r}_{1,0}\bar{y}_1^2 + \bar{r}_{2,0}\bar{y}_2^2 + \bar{u}_{1,0}\bar{y}_1^4 + \bar{u}_{2,0}\bar{y}_2^4 + \bar{u}_{1,0}\bar{y}_2^4, \quad (23)$$

where

$$\begin{aligned} \bar{r}_{1,0} &= r_0 - 1/2\nu_0, & \bar{r}_{2,0} &= r_0 + 1/2\nu_0, \\ \bar{u}_{1,0} &= 1/2u_{1,0} + 1/4u_{2,0}, \\ \bar{u}_{2,0} &= 3u_{1,0} - 1/2u_{2,0}, \end{aligned}$$

and the function $\bar{Q}_1(\bar{y}_i)$ satisfies the system of recursion relations (3) and (8); we can make use of the solution of this system obtained in the preceding Section (ν_0 plays the role of $\Delta\tau_0$). In accordance with this, for ferromagnetic interactions the formula (21a) holds in the region $\tau \ll \nu_0$ and (21b) holds in the region $\tau \gg \nu_0$, where χ_0 is given by the expression (22) with $\Delta\tau_0$ replaced by ν_0 .

The case of two identical sublattices with a weak interaction between them of the type $\nu_0 y_1 y_2$ was treated in^[3,4] by the method of expanding in irreducible correlators. The Baxter interaction was not taken into account. It was found that the shift in the transition temperature when the interaction between the planes is switched on is proportional to $\nu_0^{1/\gamma}$. In^[5], it was shown that if the shift in the critical temperature is nonanalytic in the magnitude of the perturbation, the phase transitions in the perturbed and unperturbed systems are not isomorphous. We shall obtain these results using Wilson's method and shall also calculate the c.i. of the perturbed system.

By making use of the expressions (23) for $\bar{u}_{1,0}$ and $\bar{u}_{2,0}$ and putting $\bar{u}_{2,0} = 0$ (the Baxter interaction is absent), we obtain $\bar{u}_{2,0} = 6\bar{u}_{1,0}$, i.e., the third solution in formula (10) holds and $\bar{u}_2 = 6\bar{u}_1$. From (8a) we obtain an equation for

$$\bar{r}_{1,l+1} = 4\bar{r}_{1,l} + 12\bar{u}_{1,l}(\bar{g}_{1,l} + \bar{g}_{2,l}), \quad (24)$$

$$\bar{r}_{2,l} = 4\bar{r}_{2,l} + 12\bar{u}_{1,l}(\bar{g}_{1,l} + \bar{g}_{2,l}),$$

where $\bar{g}_{i,l} = (1 + \bar{r}_{i,l})^{-1}$.

The solution of the system of equations (24) in the region (11a) has the form

$$\bar{r}_{1,l} = a\tau_0\lambda^l - \nu_0 2^{2l}, \quad \bar{r}_{2,l} = \bar{a}\tau_0\lambda^l + \nu_0 2^{2l}, \quad (25)$$

where $\tau_0 = (T - T_0)/T_0$, T_0 is the critical temperature of the unperturbed system, and λ is defined by formula (15).

The critical temperature T_C can be found from the condition $\bar{r}_{1,l} |_{l \sim l_1} = 0$ (analogously to the derivation of formulas (20)).

The quantity \bar{l}_1 is estimated from the conditions

$\bar{\tau}_{0c} \lambda^{l_1} \sim \nu_0 2^{2l_1} \sim 1$, $\tau_{0c} = (T_c - T_0)/T_0$. Hence, taking formula (18) into account, we have

$$\tau_{0c} \sim \lambda^{-\tilde{\tau}_i} \sim 2^{-\tilde{\tau}_i \ln \lambda / \ln 2} \sim \nu_0^{\ln \lambda / 2 \ln 2} \sim \nu_0^{1/2}, \quad (26)$$

which is in agreement with the results of [3, 4].

In the region $\tau \gg \nu_0^{1/\gamma}$ (the parameter ν_0 can tend to zero), the modes y_1 and y_2 give an approximately equal contribution, whereas in the region $\tau \ll \nu_0^{1/\gamma}$ the mode \bar{y}_2 makes no contribution to the singular part of the thermodynamic quantities. Therefore, the coefficient of the temperature singularities of the thermodynamic quantities changes by a factor of two on passing from one temperature region to the other, in agreement with the conclusions of [5].

4. PHASE TRANSITION IN MIXTURES

We shall write the Hamiltonian of a two-component mixture of liquids or gases in the framework of the lattice model:

$$H = V_{pg, ij} n_{pi} n_{gj}, \quad (27)$$

where $V_{pg, ij}$ is the interaction potential of two particles positioned in the cells i and j . The indices p and g , which take two values, label the particles from the first and second components; n_{pi} and n_{gj} are the occupation numbers of the cells i and j . Repeated indices are to be summed over.

We introduce the two spin variables $\sigma_i^{(1)} = \pm 1$ and $\sigma_i^{(2)} = \pm 1$. Let the values $\sigma_i^{(1)} = \pm 1$ correspond to particles of the first and second components in the cell i , and the values $\sigma_i^{(2)} = \pm 1$ to an occupied and empty cell respectively. The occupation numbers can be expressed by the formulas

$$\begin{aligned} n_{1i} &= 1/4 (1 + \sigma_i^{(2)}) (1 + \sigma_i^{(1)}), \\ n_{2i} &= 1/4 (1 + \sigma_i^{(2)}) (1 - \sigma_i^{(1)}). \end{aligned} \quad (28)$$

Substitution of $n_{p,i}$ into formula (27) in the particular case

$$\begin{aligned} V_{11, ij} &= V_{22, ij} & \mu_1 &= \mu_2 = \mu, \\ V_{12, ij} &\ll V_{11, ij} & |T_{10} - T_{20}| &\ll T_{10}, \end{aligned} \quad (29)$$

which is chosen for reasons of simplicity, leads to the following value Q_0 , which contains linear and cubic terms in y :

$$\begin{aligned} Q_0 &= \bar{r}_i y_i^2 + \bar{u}_i y_i^4 + \bar{u}_2 y_i^2 y_2^2 + \bar{u}_3 y_2^4 + h y_2 + \bar{\lambda} y_i^2 y_2, \\ \bar{r}_i &= (2/R_{i0}) (r - R_i d), \quad R_{1,2} = (V_{11, ij} \mp V_{12, ij}) / 8T \end{aligned} \quad (30)$$

(the upper sign defines \bar{K}_1 , and the lower defines \bar{K}_2), and

$$|R_1 - R_2| \sim V_{12}/T \ll R_1, \quad \bar{\lambda} = \bar{u}_2 = R_1, \quad h = 2R_2 - \mu/2T.$$

With the aid of the expression for Q_0 , the effective Hamiltonian H is determined by the expression (2), the partition function being calculated from the formula

$$Z = \iint dy_1 dy_2 \exp[-H(y_1, y_2)], \quad (31)$$

where functional integration is performed over the y_i .

Adding and subtracting $n_{1,i}$ and $n_{2,i}$ in (28), we have

$$n_i = n_{1i} + n_{2i} = 1/2 (1 + \sigma_i^{(2)}), \quad \Delta n_i = 1/2 (1 + \sigma_i^{(2)}) \sigma_i^{(1)}, \quad (32)$$

where n_i is the total density of the substance and Δn_i is the difference in the concentrations of particles of the first and second types. It can be seen from (32) that the parameter y_2 defines the density, and y_1 defines

the difference in the concentrations of the two types of particles. From experiment, it is known that mixtures have, in the general case, two critical points: one higher in temperature—the liquid-vapor critical point—and one lower—the liquid-liquid phase-separation point. At the liquid-vapor critical point a nonzero order parameter y_2 arises, leading to the appearance of a liquid and a gaseous phase with different densities. At the phase-separation point, the order parameter y_1 appears.

The conditions (29) mean that the Hamiltonian is invariant with respect to interchange of $n_{1,i}$ and $n_{2,i}$; particles of the first and second type appear symmetrically in this expression, i.e., at temperatures above the phase-separation point the concentration $c = 0.5$. From symmetry arguments it can also be seen that the concentration derivative of the critical temperature (for $c = 0.5$) equals zero.

In analyzing critical phenomena in mixtures, a number of authors [6-8] have made the following assumption: the thermodynamic functions (specific heat, order parameter, susceptibility) calculated at constant chemical potential of the impurity are isomorphous to the corresponding functions of the pure substance [10]. This assumption was based on a calculation of the thermodynamic quantities for "decorated" models, in which the assumption formulated above is exact. The difference between the "decorated" model and the model considered in this section is that in the "decorated" model there is only one phase-transition point.

In this section we shall show that a model containing two critical points (liquid-vapor and liquid-liquid) is also isomorphous to the pure substance. However, in contrast to the "decorated" model, this isomorphism holds not at constant chemical potential but at constant $\psi = \mu + f\tau_2$, where f is a constant and $\tau_i = (T - T_{ci})/T_0$.

To prove this statement, we shall study the expression (31) near the higher (liquid-vapor) critical point, at which the order parameter y_2 is nonanalytic. We shall calculate the integral over the nonsingular variable y_1 . (This method was pointed out to the authors by A. M. Polyakov.) We introduce the Hamiltonian $\tilde{H}(y_2)$ by the formula

$$H(y_2) = -\ln \int dy_1 \exp[-H(y_1, y_2)]. \quad (33)$$

We represent $H(y_1, y_2)$ in (33) in the form

$$H(y_1, y_2) = H_1(y_1) + H_2(y_2) + H_{int}(y_1, y_2), \quad (34)$$

where

$$H_2(y_2) = \int \frac{d^d k}{(2\pi)^d} (r_2 + k^2) y_2^2(k) + \bar{u}_2 \int \delta \left\{ \sum_{i=1}^4 k_i \right\} \prod_{j=1}^4 y_2(k_j) \frac{d^d k_j}{(2\pi)^d},$$

$$H_1(y_1) = \int \frac{d^d k}{(2\pi)^d} (r_1 + k^2) y_1^2(k),$$

$$H_{int} = \bar{u}_1 \int \delta \left\{ \sum_{i=1}^4 k_i \right\} \prod_{j=1}^4 y_1(k_j) \frac{d^d k_j}{(2\pi)^d} + \bar{u}_2 \int y_1(k_1) y_1(k_2) y_2(k_3) y_2(k_4)$$

$$\times \delta \left\{ \sum_{i=1}^4 k_i \right\} \prod_{j=1}^4 y_1(k_j) \frac{d^d k_j}{(2\pi)^d} + \bar{\lambda} \int y_1(k_1) y_1(k_2) y_2(k_3) \delta \left\{ \sum_{i=1}^3 k_i \right\} \prod_{j=1}^3 \frac{d^d k_j}{(2\pi)^d}.$$

Expanding the right-hand side of formula (33) in a series in H_{int} , we obtain (taking only the connected diagrams into account; cf. Sec. 15 of [11])

$$\begin{aligned} \tilde{H}\{y_2\} = & -\beta \left[\text{diagram 1} + \text{diagram 2} + \text{diagram 3} \right] \\ & + \frac{\beta^2}{2} \left[\text{diagram 4} + \text{diagram 5} + \text{diagram 6} \right] \\ & + \text{diagram 7} + \text{diagram 8} \\ & + \text{diagram 9} + \text{diagram 10} + \dots \end{aligned} \quad (35)$$

Here the dashed lines correspond to $y_2(g)$, the solid lines to

$$G_i(k) = \int y_i^2(k) e^{-\beta H_i(y_i)} dy_i / \int e^{-\beta H_i(y_i)} dy_i = \frac{1}{k^2 + \tau_i},$$

and the vertices have the form

$$\begin{aligned} \text{---} \langle \text{---} &= \tilde{\lambda}, & \text{---} \times \text{---} &= \tilde{u}_2, & \times &= \tilde{u}_1. \end{aligned}$$

Momentum conservation is satisfied at each vertex. The integration is performed over all the independent momenta. Thus, e.g., the diagram

$$\text{---} \langle \text{---}$$

is equal to

$$\beta^2 \tilde{\lambda}^2 \int y_2^2(g) G_i(k) G_i(g-k) \frac{d^d g}{(2\pi)^d} \frac{d^d k}{(2\pi)^d}. \quad (36)$$

Since the external lines in each diagram correspond to the critical mode, their characteristic momenta are equal to $g \sim r_C^{-1}(\tau_2) \rightarrow 0$ as $T \rightarrow T_{C2}$. But the main contribution to the integrals over the momenta of the internal lines is given by scales of order $r_C^{-1}(\tau_1) \gg r_C^{-1}(\tau_2)$. Expanding, therefore, all the integrands in a series in the parameter $(g/k)^2 \sim (r_C(\tau_1)/r_C(\tau_2))^2$, it is not difficult to estimate any diagram. In particular, in the zeroth approximation in $(g/k)^2$, the integral (36) equals

$$I = \beta^2 \tilde{\lambda}^2 \int y_2^2(g) \frac{d^d g}{(2\pi)^d} \int G_i^2(k) \frac{d^d k}{(2\pi)^d} \sim \beta^2 \tilde{\lambda}^2 (\Delta\tau)^{(d-4)/2} \int y_2^2(g) \frac{d^d g}{(2\pi)^d}. \quad (37)$$

It can be seen that this diagram does not contain any singularities in τ_2 or g , and renormalizes the first term in H_2 in formula (34). It is easy to see that all the other diagrams in the expression (35) also have no singularities in τ_2 and g , and renormalize the corresponding coefficients in the Hamiltonian H_2 . Thus, we obtain

$$H(y_2) = \sum_i \{ [\nabla y_2(\mathbf{r}_i)]^2 + \bar{r}_2 y_2^2(\mathbf{r}_i) + \tilde{\lambda} y_2^3(\mathbf{r}_i) + \tilde{u}_2 y_2^4(\mathbf{r}_i) + \tilde{h} y_2(\mathbf{r}_i) \}, \quad (38)$$

in which all the coefficients of the powers of y_2 are analytic functions of the variables τ_2 and μ .

In the Hamiltonian $\tilde{H}\{y_2\}$ all terms proportional to y_2^m with $m > 4$ have been omitted, since they make no contribution to the singular part of the free energy.

The expression $\tilde{H}\{y_2\}$ differs in its form from the Hamiltonian of the one-component Ising model only by the presence of the term proportional to y_2^3 , which can be eliminated by the linear replacement $y_2 = y_2 + t$ with the appropriate choice of t . The Hamiltonian $H\{y_2'\}$ is isomorphous to the corresponding Hamiltonian of the one-component Ising model. The path

$$\mu = \mu_c + f\tau_2, \quad (39)$$

corresponds to zero external field, in accordance with what has been stated above.

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103