Second-order phase transition in inhomogeneous bodies

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The problem of the singularities of thermodynamic functions at the transition point in substances with fixed impurities is discussed. The critical exponents are found by the ϵ-expansion method.

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1. INTRODUCTION

There is a widely held conviction that in bodies with random inhomogeneities a second-order transition is not accompanied by those thermodynamic singularities that are characteristic of transitions in homogeneous bodies. It is not always stated specifically in this case, but it is frequently implied, that the following is meant: if the inhomogeneities have a large but finite correlation radius, then the free energy can be calculated by ascribing to each point of space a free-energy density $f(T, T_c)$ that has a singularity at $T = T_c$, and T is a random quantity. The summation of contributions of various sections of a sample into a total free energy is equivalent in this case to averaging over the possible values of T_c. The singularity is smoothed out as a result of this averaging.

The foregoing reasoning presupposes in essence that the main contribution to the thermodynamics is due to short-range order fluctuations, and therefore if the correlation radius of the inhomogeneities is large enough, the free energy can be described by a local density with a random T_c. In fact, as is well known, the main contribution to the thermodynamics in the vicinity of the transition point is made by long-wave fluctuations. Close enough to the transition point, the fluctuation wavelength becomes larger than the radius of the inhomogeneities. Under these conditions the picture becomes essentially nonlocal and it is necessary to take into account jointly the interaction of the fluctuations and their scattering by the inhomogeneities.

Another aspect of the phenomenon is that the inhomogeneities do not destroy the long-range order in a three-dimensional object, and therefore at low temperatures a magnet, for example, has a nonzero spontaneous moment M proportional to the volume. At high temperatures there is no spontaneous moment. There exists therefore a temperature T* above which there is no spontaneous moment and below which there is. We shall show that T* does not coincide with the Curie point T_c of a homogeneous substance. For the sake of argument we consider a magnet in which some of the sites are occupied by nonmagnetic atoms. If $T < T_c$ but $T - T_c$ is small, then the entire sample cannot go over into the magnetic state. There exist, of course, regions of dimension $R \sim (T_c - T)^{-1/2}$ in which, for accidental reasons, there are no impurities and in which a macroscopic moment $S \sim (T_c - T)^{-3/2}$ is produced. But the probability of such impurity-concentration fluctuations is exponentially small: $w \sim \exp\{-(T_c - T)^{-3/2}\}$. Therefore regions with macroscopic moments are at exponential distances from one another and the coupling between the moments is weak. Thermal fluctuations destroy this coupling, the moments of the individual regions do not correlate, and the spontaneous moment is equal to zero. With further decrease of temperature, the old regions grow and new regions with macroscopic moment appear. The distance between such regions decreases, their moments become more correlated, and at sufficiently low temperature T* a nonzero spontaneous moment M first appears. It can be shown that as T → T* the fluctuations of the impurity concentration can be regarded as Gaussian and δ-correlated.

The foregoing reasoning shows that as T → T* the correlation radius increases without limit and the spontaneous moment is produced at T = T* not jumpwise, but continuously. These circumstances indicate that the temperature T* is a singular point of the thermodynamic quantities. The purpose of the present paper is to calculate the critical exponents at the point T = T*. To this end, the problem is solved in the four-dimensional case, and the Wilson ϵ-expansion is then used.[1]

2. DIAGRAM TECHNIQUE AND SELECTION OF GRAPHS

The Hamiltonian of the four-dimensional problem is given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{imp},$$

$$\mathcal{H}_0 = \frac{1}{2}\sum_{\mathbf{k}} (\mu + s\mathbf{k}^2)\,|\varphi_{\mathbf{k}}{}^{\alpha}|^2 + \frac{b}{4}\sum_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4=0} \varphi_{\mathbf{k}_1}{}^{\alpha}\varphi_{\mathbf{k}_2}{}^{\alpha}\varphi_{\mathbf{k}_3}{}^{\beta}\varphi_{\mathbf{k}_4}{}^{\beta}, \tag{1}$$

$$\mathcal{H}_{imp} = \sum_{a}\sum_{\mathbf{q},\mathbf{k}} V_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}_a}\varphi_{\mathbf{k}}{}^{\alpha}\varphi^{\alpha}_{\mathbf{q}-\mathbf{k}}, \tag{2}$$

$\alpha, \beta = 1, 2, \ldots, n$, $\mathcal{H}_0$ is the Hamiltonian of impurity-free matter, and $\mathcal{H}_{\text{imp}}$ is the energy of the interaction of the order-parameter fluctuations with the impurities. In the long-wave region of interest to us, we can neglect the dependence of the impurity potential V_q on the momentum transfer **q**. In addition, it is assumed that V is small and that the Born approximation can be used.

Using the known impurity diagram technique,[2] we obtain a graphic equation for the self-energy part Σ, shown in Fig. 1. The contribution of diagram 1a must be combined with the quantity μ from (1). It then becomes clear that this diagram describes a transition-temperature shift proportional to the impurity concentration. The

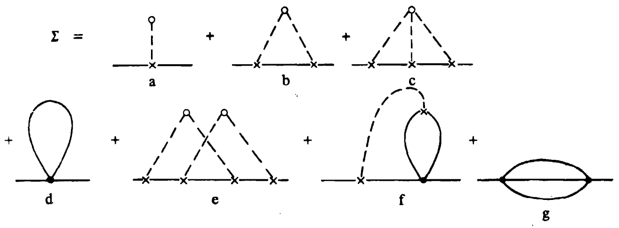


FIG. 1

contribution of diagram 1c and of the more complicated diagrams of this type is smaller than the contribution of 1b, since the potential is small. Such diagrams will henceforth be disregarded. In the retained diagram, the impurity dashed lines thus join the crosses pairwise. Separation of graphs of this type corresponds to Gaussian impurity-concentration fluctuations.

The calculations can be carried out in analogy with the theory of phase transitions in impurity-free four-dimensionless models.[3] The contribution made to Σ from diagrams 1b and 1d is equal to

$$\Sigma_b=\Sigma_{0b}+u(\Sigma+\mu)\ln\frac{\Lambda^2}{\Sigma+\mu},$$
$$\Sigma_d=\Sigma_{0d}-\gamma(\Sigma+\mu)\ln\frac{\Lambda^2}{\Sigma+\mu}; \tag{3}$$
$$\gamma=bT/64\pi^2s^2,\ u=cV^2/16\pi^2s^2, \tag{4}$$

where c is the impurity concentration, $\Lambda^2 = s/a^2$, and a is the interatomic distance.

As seen from (3), scattering by the impurities leads to self-action of the fluctuations of the order parameter φ. The sign of this self-action corresponds to attraction, which is perfectly natural, since u has appeared in second order in the impurity potential V. The constant parts of Σ_{0b} and Σ_{0d} leads to a shift of T_c, and the logarithmic terms of (3) are gathered, after summation with other terms of this type, into $m^2 = G^{-1}(\mathbf{k} = 0)$. Owing to the presence of logarithmic divergences, m^2 is a nonanalytic functions of T − T*. The dependence of the Green's function G(**k**) on the momentum **k** is given by the unrenormalized Hamiltonian (1). The corrections to this relation are given by diagrams e, f, and g (Fig. 1) and are proportional respectively to

$$\gamma^2\ln[\Lambda^2/(\mu+\Sigma)],\ \gamma u\ln[\Lambda^2/(\mu+\Sigma)],\ u^2\ln[\Lambda^2/(\mu+\Sigma)].$$

In the principal logarithmic approximation, these corrections can be neglected and the Green's function can be written in the form

$$G^{-1}(T,\mathbf{k})=m^2(T)+s\mathbf{k}^2. \tag{5}$$

The temperature T* should be determined from the condition

$$m^2(T=T^*)=0.$$

3. EQUATIONS FOR THE AMPLITUDES

To derive the equations for the amplitudes it is necessary to separate the "parquet" diagrams and to discard the "nonparquet" ones. Typical diagrams are shown in Fig. 2. There are separately drawn diagrams for the four-point vertex U that can be cut through the dashed lines, and for the uncuttable four-point vertex Γ. The parquet diagrams are of the type b, c, d, e a-d als g, h, i. Diagrams f and j are nonparquet, and their contribution is proportional to $\gamma^4\ln[\Lambda^2/(\mu+\Sigma)]$ or $u^2\ln[\Lambda^2/(\mu+\Sigma)]$, and therefore this contribution can be neglected in the principal logarithmic approximation. The summation of the parquet diagrams can be carried out by Sudakov's standard method. As a result, the equations for the vertices Γ and U take the form

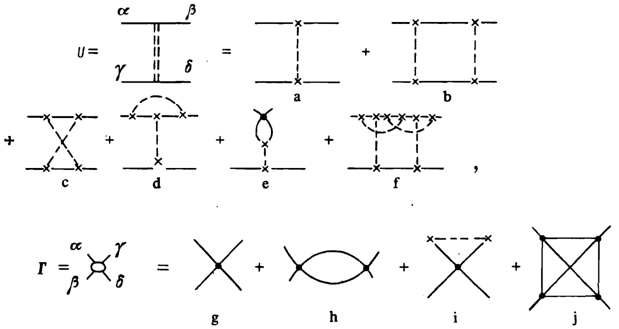


FIG. 2

$$U_{\alpha\beta\gamma\delta}=U(x)\delta_{\alpha\beta}\delta_{\gamma\delta},\ \Gamma_{\alpha\beta\gamma\delta}$$
$$=\Gamma(x)(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})/3, \tag{6}$$
$$\frac{d\Gamma}{dx}=-\Gamma\left(\frac{n+8}{3}\Gamma-6U\right), \tag{7}$$
$$\frac{dU}{dx}=-2U\left(\frac{n+2}{3}\Gamma-2U\right); \tag{8}$$
$$U(0)=u,\quad \Gamma(0)=\gamma,\quad x=\ln\frac{\Lambda^2}{m^2, sk^2}. \tag{9}$$

The system of equations (7) and (8) can be integrated in quadratures, but it is more convenient to trace the trajectories of the solutions in the phase plane of the variables U and Γ. Such a diagram is shown in Fig. 3 for the cases n = 2, 3. It is seen from this diagram that the amplitudes approach asymptotically the stable separatrix

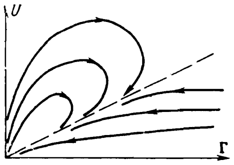


FIG. 3

$$U=(4-n)\Gamma/6.$$

Therefore as x → ∞ we have

$$\frac{d\Gamma}{dx}\approx-\frac{1}{3}(n-1)\Gamma^2, \tag{10}$$
$$\Gamma\approx3/4(n-1)x,\ U\approx(4-n)/8(n-1)x. \tag{11}$$

For n ≥ 4 the separatrix coincides with the abscissa axis. All the trajectories are in the form of lobes that approach the origin asymptotically along the abscissa axis. In the asymptotic region we have

$$U\ll\Gamma,\ \Gamma\approx3/(n+8)x. \tag{12}$$

Thus, at n ≥ 4 the quantity U decreases more rapidly than Γ. Therefore in this case the singularities as T → T* in inhomogeneous matter are analogous to the singularities at the transition point of impurity-free matter.

At n = 1, Eqs. (7) and (8) take the form

$$\frac{dU}{dx}=-2U(\Gamma-2U),\quad \frac{d\Gamma}{dx}=-3\Gamma(\Gamma-2U). \tag{13}$$

The system (13) is degenerate, its right-hand sides vanish along an entire line on the (ΓU) plane, namely the straight line Γ = 2U. This results in the presence of an integral $R = \Gamma^2/U^3 = \gamma^2/u^3$, and also in a dependence of the asymptotic values of Γ and U on the unrenormalized constants γ and u. All these unusual properties of Eqs. (13) are due to the fact that their right-hand sides are proportional to each other. This is an accidental symmetry, and the exact Gell-Mann–Low function does not, of course have this symmetry. Therefore to solve the problem in the case n = 1 the principal logarithmic approximation is not enough, we need also take into account the next term of the Gell-Mann–Low expansion in powers of the amplitudes. This will be done in Sec. 5.

4. CALCULATION OF THE CRITICAL EXPONENTS

Returning to the case n = 2 and 3, let us find the three-point scalar vertex $\mathcal{T}_{\alpha\beta} = \mathcal{T}(x)\delta_{\alpha\beta}$. The diagrams for $\mathcal{T}$ are shown in Fig. 4. The equation for $\mathcal{T}$ and its solution are

$$\frac{d\mathcal{T}}{dx} = -\mathcal{T}(x)\left[\frac{n+2}{3}\Gamma(x) - U(x)\right], \quad \mathcal{T}(0) = 1, \tag{14}$$

$$\mathcal{T}(x) = \exp\left\{-\int_0^x\left[\frac{n+2}{3}\Gamma(y) - U(y)\right]dy\right\}. \tag{15}$$

In the asymptotic region we can use formulas (11). As a result we have

$$\mathcal{T} \sim x^{-3n/8(n-1)}. \tag{16}$$

The anomalous part of the specific heat is proportional to the polarization operator Π:

$$\Pi = \int_0^x dy\mathcal{T}^2(y) \sim \int_0^x \frac{dy}{y^{6n/8(n-1)}}. \tag{17}$$

At n = 2 and 3 we have $6n/8(n-1) > 1$. Therefore the integral in (17) tends to a finite limit as $x \to \infty$. This means that the heat capacity C remains finite as $T \to T^*$, and only its derivative experiences an infinite discontinuity.

The transition to the dimensionality d = 3 can be effected by the Wilson ϵ-expansion method.[1] In this way we obtain for the susceptibility exponent$^{1)}$

$$\gamma = 1 + 3n\varepsilon/16(n-1). \tag{18}$$

The exponent η of the correlation function is equal to

$$\eta = n(5n-8)\varepsilon^2/256(n-1)^2. \tag{19}$$

In concluding this section, a remark on the thermodynamics at $T < T^*$. In this case the free energy can be expressed in the form of a sum of connected ring diagrams on which condensate ends are superimposed. It should be recalled that this sum does not contain diagrams that can be made non-connected by cutting the impurity dashed lines. Therefore the equation of state is constructed in analogy with the impurity-free case, and it contains the vertex Γ but not the vertex U. The stability condition, just as in the impurity-free case, is $\Gamma > 0$. The Appendix contains a solution of the problem of the transition in a magnet with cubic anisotropy in the presence of impurities.

5. CRITICAL EXPONENTS IN THE ONE-COMPONENT MODEL

As already noted, in the one-component case n = 1 it is necessary to calculate the Gell-Mann–Low function with accuracy to third order in the amplitudes. To this end there is no need to take the nonparquet diagrams into account, but the parquet diagrams must be calculated with nonlogarithmic accuracy.$^{2)}$ It is convenient to use the method of Tsuneto and Abrahams.[4] As a result we can write the equations for the amplitudes in the form

$$\frac{d\Gamma}{dx} = -3\Gamma(\Gamma-2U) + 6\Gamma(2\Gamma^2 - 8\Gamma U + 7U^2), \tag{20}$$

$$\frac{dU}{dx} = -2U(\Gamma-2U) + 2U^2(11U^2 - 12\Gamma U + 2\Gamma^2). \tag{21}$$

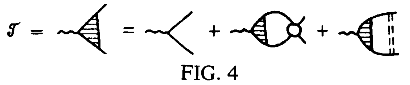


FIG. 4

From (20) and (21) we can obtain an equation for the quantity $R = \Gamma^2/U^2$:

$$\frac{dR}{dx} = R\left(\frac{2}{\Gamma}\frac{d\Gamma}{dx} - \frac{3}{U}\frac{dU}{dx}\right) = 6R(2\Gamma^2 - 4\Gamma U + 3U^2). \tag{22}$$

At $\Gamma = 2U$ the derivative is $dR/dx = 18RU^2$. Thus, R is approximately conserved in the initial stage and is equal to $R_0 = \gamma^2/u^3$. Very soon, however, Γ and U become equal respectively to γ^* and $u^* = \gamma^*/2 = 4u^3/\gamma^2$. Subsequently $\Gamma = 2U$ with accuracy to quadratic terms, R increases, and U decreases in proportion to $x^{-1/2}$.

Changing over to the ϵ-continued quantities, we obtain

$$\Gamma = 2U, \; U = Wp^{\varepsilon}, \; W = \varepsilon^{1/2}/6. \tag{23}$$

From this we get an expression for the exponents γ and η:

$$\gamma = 1 + \varepsilon^{1/2}/6, \; \eta = -\varepsilon/76. \tag{24}$$

The fact that η is negative should not be surprising. After all, positiveness of η can be derived only from the spectral expansion. In the theory considered here there are neither unitarity relations nor a spectral expansion. The general renormalizability of the theory can nevertheless be proved. Indeed, if we average, in analogy with Wilson's reasoning, over the small-scale fluctuations and renormalize the interaction Γ, the effective scatter of the transition temperatures U, and the correlation function G, then the initial sum of diagrams will reduce to a sum of diagrams of the same type, but the cutoff limit Λ is then changed, and the nonrenormalized quantities are replaced by renormalized ones. This was indeed done in the language of diagram summation.

6. CONCLUSION

Thus, the notion that there exists a transition temperature T^* below which a spontaneous moment is produced and the correlation radius tends to infinity encounters no significant difficulties. The calculation of the critical exponents by the ϵ-expansion method do not guarantee, of course, correctness of the obtained values. However, the qualitative behavior can apparently be discerned correctly by this method. Among the general qualitative conclusions of the present paper are the following:

1. The specific heat remains constant as $T \to T^*$.
2. The susceptibility, to the contrary, increases more rapidly as $T \to T^*$ than in accord with the Curie-Weiss law.
3. If the impurity concentration is such ($u \gg \gamma$) that the influence of the impurities sets in earlier as the transition point is approached than the effects of the thermodynamic fluctuation, then an extensive intermediate region exists between the region where the self-consistent field theory is valid and the critical asymptotic region. In the left-hand side of Fig. 5 is shown schematically the temperature dependence of the reciprocal susceptibility χ^{-1} and of the spontaneous moment M for this case.
4. At very low impurity concentrations ($u \ll \gamma$), similarity theory is first applicable, with exponents corresponding to impurity-free matter, and as the temperature T^* is approached closer, the exponents change and tend asymptotically to new values that take the presence of the impurities into account. The right-hand side of Fig. 5 shows the temperature dependences of χ^{-1} and M in this case.

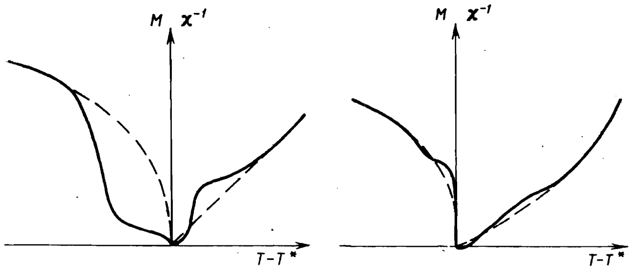


FIG. 5

If the inhomogeneities have a large radius, then the averaging procedure discussed in the Introduction is valid in a wide range of temperatures, and a singularity appears only very close to the transition point. This is the situation, apparently, in the case of a polycrystalline sample and in similar cases. In addition, the theory developed presupposed that during the time of observation a thermodynamic equilibrium manages to become established over all the degrees of freedom with the exception of the impurity diffusion. This is the situation in superconductors and in most magnets. In structure transitions it may turn out that the time of relaxation of the order parameter in an inhomogeneous sample is comparable with the impurity-diffusion time.

The author is grateful to A. I. Larkin and A. A. Migdal, and also to L. P. Gor'kov and A. M. Plyakov, for useful discussions.

APPENDIX

We write the Hamiltonian of pure impurity-free matter in the form

$$\mathscr{H}=\frac{1}{2}\sum_{\mathbf{k},\alpha}(\tau+s\mathbf{k}^2)|\varphi_{\mathbf{k}}^{\alpha}|^2+\frac{1}{4}\sum_{\substack{\alpha,\beta\\ \mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4=0}}[\gamma_1\varphi_{\mathbf{k}_1}^{\alpha}\varphi_{\mathbf{k}_2}^{\alpha}\varphi_{\mathbf{k}_3}^{\beta}\varphi_{\mathbf{k}_4}^{\beta}+\gamma_2\varphi_{\mathbf{k}_1}^{\alpha}\varphi_{\mathbf{k}_2}^{\alpha}\varphi_{\mathbf{k}_3}^{\alpha}\varphi_{\mathbf{k}_4}^{\alpha}]. \qquad (A.1)$$

The invariant amplitude has a standard tensor structure

$$\Gamma_{\alpha\beta\gamma\delta}=\Gamma_1(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})/3+\Gamma_2 g_{\alpha\beta\gamma\delta},$$

$$g_{\alpha\beta\gamma\delta}=\begin{cases}1, \alpha=\beta=\gamma=\delta\\ 0, \text{ in all remaining cases.}\end{cases}$$

The impurities alter mainly τ. Therefore $U_{\alpha\beta\gamma\delta} = U\delta_{\alpha\beta}\delta_{\gamma\delta}$. The parquet equations are written in the form

$$\frac{d\Gamma_1}{dx}=-\Gamma_1\left(\frac{n+8}{3}\Gamma_1+2\Gamma_2-6U\right), \quad \Gamma_1(0)=\gamma_1,$$

$$\frac{d\Gamma_2}{dx}=-\Gamma_2(4\Gamma_1+3\Gamma_2-6U), \quad \Gamma_2(0)=\gamma_2,$$

$$\frac{dU}{dx}=-2U\left(\frac{n+2}{3}\Gamma_1+\Gamma_2-2U\right), \quad U(0)=u. \qquad (A.2)$$

The most important property of the solutions of the system (A.2) is the conservation of the initial signs of Γ_1, Γ_2, and U. The initial value U(0) = u is always positive. It is therefore convenient to seek the solutions of the homogeneous system (A.2) in the form $\Gamma_1 = U\Phi_1(U)$, $\Gamma_2 = U\Phi_2(U)$. As a result (A.2) becomes

$$\frac{d\Phi_1}{dz}=-\Phi_1\left(\frac{4-n}{3}\Phi_1-2\right), \quad \frac{d\Phi_2}{dz}=-\Phi_2\left[\frac{2}{3}(4-n)\Phi_1+\Phi_2-2\right],$$

$$U\frac{dz}{dU}=-\frac{1}{2}\left(\frac{n+2}{3}\Phi_1+\Phi_2-2\right)^{-1}, \quad \frac{dU}{dx}=-2U^2\left(\frac{n+2}{3}\Phi_1+\Phi_2-2\right). \qquad (A.3)$$

By virtue of the system (A.3) we have dz/dx = (dz/dU) × (dU/dx) = U > 0. Therefore z is a monotonic function of x. The system (A.3) has an integral of motion I:

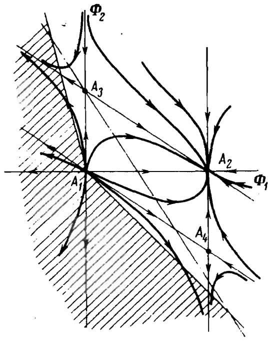
$$I=\left(\Phi_2+\frac{4-n}{3}\Phi_1\right)\left(2-\frac{4-n}{3}\Phi_1\right)\Big/\Phi_2=\text{const.} \qquad (A.4)$$

The first two equations of the system (A.3) can be integrated in quadratures, but it is more convenient to investigate the solutions qualitatively. To this end we must find and reclassify the singular points $A_1(0, 0)$—unstable node; $A_2[6/(4-n), 0]$—stable node; $A_3(0, 2)$—saddle; $A_4[6/(4-n), -2]$—saddle. The separatrices are the coordinate axes and the line $\Phi_1 = 6/(4-n)$. The other separatrices can be found by using the integral of motion (A.4). It turns out that both new separatrices are also straight lines, $\Phi_2 + \Phi_1(4-n)/3 = 0$ and $\Phi_2 - 2 + \Phi_1(4-n)/3 = 0$. Figure 6 shows the plane of the variables Φ_1 and Φ_2 and the trajectories of the solutions of the system (A.3). The shaded region is the one in which the stability conditions

$$\Phi_1+\Phi_2>0, \quad n\Phi_1+\Phi_2>0. \qquad (A.5)$$

are violated. The dash-dot line $\Phi_2 - 2 + \Phi_1(n+2)/3 = 0$ subdivides the plane into regions of monotonic variation of U.

FIG. 6



The final results of the qualitative investigation can be formulated as follows:

1. If the conditions

$$\Phi_1^{(0)}>0, \quad \Phi_2^{(0)}+\frac{4-n}{3}\Phi_1^{(0)}>0, \qquad (A.6)$$

are satisfied for the initial values of γ_1, γ_2, and u, then the trajectories of the solutions tend to the node A_2. The problem becomes isotropic and has the asymptotic solution considered in the text.

2. If the conditions (A.6) are not satisfied, then the stability conditions (A.5) are violated at finite x. In this case the system experiences a first-order transition.

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[1] After this paper was completed, the author has learned of the results of T. Lubenski and A. B. Harris, who obtained with the aid of a recurrence formula the same value of the exponent γ. The author thanks L. P. Gor'kov for the possibility of seeing a preprint of this paper.

[2] Strictly speaking, in the first nonlogarithmic order it is necessary to renormalize also the Green's function. This changes the critical exponents by an amount of the order of the exponent η of the Green's function (η is numerically small). The exponents given in the text were calculated in first nonvanishing order in η.

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