Order-parameter and charge-density waves near the critical point in an electrolyte

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In a system that undergoes a second-order phase transition and has charges that can become redistributed (liquid or solid electrolyte, semiconductor), charge-density and order-parameter waves are produced near the phase-transition point. This state can be regarded as a special phase. The wavelength is of the order of the Debye radius, the characteristic width of the temperature interval in which they can exist is $\Delta T\sim T_cx$, where T_c is the transition temperature and x is the relative density of the charged particles. The thermodynamic singularities, the phase diagram, and the correlation functions of such a system are analyzed.

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INTRODUCTION

A substance that undergoes a second-order phase transition (and is near the critical point), can be regarded as an aggregate of weakly coupled subsystems, an interaction in one of which is in fact the direct cause of the phase transition. In the vicinity of the critical point, owing to long-wave fluctuations of the order parameter, there is produced an unusual instability with respect to even a weak interaction between the subsystem that undergoes the phase transition and the other subsystems. This instability can alter the character of the phase transition. For example, when account is taken of the interaction with other modes, a magnetic or a ferroelectric transition becomes of first order,[1] and in the presence of impurities under thermodynamic equilibrium, the singularity at the phase-transition point becomes weaker (the phase transition becomes a third order).[2-4]

These phenomena were investigated principally from the point of view of the change in the character of the singularities of the thermodynamic quantities. On the other hand, one can expect the aforementioned instability near the critical point to give rise to a new phase with interesting properties.

The purpose of the present paper is the study of the interaction of the subsystem that undergoes the phase transition with a Coulomb subsystem. In the latter there exist slowly decreasing correlations. At low densities x of the charged particles, the Debye radius r_D is large. When the critical point is approached, the correlation radius of the fluctuations of the order parameter r_c increases, and the condition $r_c\sim r_D$ is satisfied at a certain value of the temperature. In this region, at a sufficiently large interaction between the subsystems, an instability sets in with respect to formation of charge-density and order-parameter-density waves, with a wave vector $k_0\sim r_D^{-1}\sim r_c^{-1}$, which is the subject of the investigation that follows.

In contrast to the usually considered charge-density waves, which are caused by the presence of a strongly degenerate electron gas with a distinct Fermi surface,[5] these waves are not determined by the quantum character of the statistics of the charged particles. On the other hand, in contrast to the localized states investigated by Krivoglaz, Nagaev, and others,[6,7] the waves are a collective effect. We note also that Krivoglaz considered inhomogeneous states near a first-order phase transition. These states are also collective. Far from the critical point, however, such formations arise at a sufficiently large charge density and constitute distinctly separated layers of two phases. We emphasize that the waves considered by us arise at arbitrarily low density of the electrolyte and are not alternating layers of two phases, but a new phase.

1. FORMULATION OF PROBLEM

Since we are interested in long-wave inhomogeneous states ($k_0a\ll 1$, where a is the interatomic distance), we represent the Hamiltonian of the system in the form

$$H=H_1+H_2+H_3. \tag{1}$$

Here H_1 is the usual Landau functional that describes a second-order phase transition[8] and constitutes, at long-wave deviations, an addition to the thermodynamic potential Φ. The parameter $\eta(\mathbf{r})$ will for simplicity be regarded as scalar

$$H_1={}^1/_2\int[\alpha\tau\eta^2(\mathbf{r})+c(\nabla\eta)^2+{}^1/_2b\eta^4(\mathbf{r})-2h\eta(\mathbf{r})]d\mathbf{r}, \tag{2}$$

α, c, and b are the usual expansion coefficients, h is an external field conjugate to $\eta(\mathbf{r})$, and $\tau=(T-T_c)/T_c$ is the temperature.

We shall use hereafter the microscopically exact Hamiltonian H_2+H_3, which describes the charged impurities, to obtain the addition to Φ necessitated by the long-wave deviations of the charge density from zero. The Hamiltonian H_2 of the charged particles will be written in the second-quantization representation

$$H_2=\sum_a\frac{\hbar^2}{2m_a}\int\nabla\psi_a^+\nabla\psi_a\,d\mathbf{r}+\frac{1}{2}\sum_{a,b}\frac{\psi_a^+(\mathbf{r})\psi_b(\mathbf{r}')e_ae_b\psi_b(\mathbf{r}')\psi_a(\mathbf{r})}{\varepsilon|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}', \tag{3}$$

ψ_a^+ and ψ_a are the creation and annihilation operators of ions of species a, ε is the dielectric constant of the solvent, and e_a and m_a are the charge and mass of the particles of species a.

The Hamiltonian H_3 of the interaction between the ions and the molecules of the solvent are written in the

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form

$$H_3=\sum_a g_a\int\eta(\mathbf{r})\hat{n}_a(\mathbf{r})\,d\mathbf{r},\quad \hat{n}_a(\mathbf{r})=\psi_a^+(\mathbf{r})\psi_a(\mathbf{r}),\tag{4}$$

g_a is the constant of the interaction of the particles of species a with the order parameter. Expression (4) takes into account only the short-range interaction between the ions and molecules of the solvent. As for the interaction of the ions with the dipole moments of the solvent molecules, it is effectively taken into account by introducing the dielectric constant ε in expression (3). For simplicity we shall carry out the calculations that follow for a symmetrical monovalent binary electrolyte. The transition to the general case is trivial and will be carried out in the final formulas.

We write the term with the Coulomb interaction in (3) in the form

$$\frac{e^2}{2}\int\frac{\Delta\hat{n}(\mathbf{r})\Delta\hat{n}(\mathbf{r}')}{\varepsilon|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}',\quad \Delta\hat{n}(\mathbf{r})=\hat{n}_1(\mathbf{r})-\hat{n}_2(\mathbf{r}).\tag{5}$$

The interaction Hamiltonian (4) consists of two parts

$$\begin{gathered}H_3=g\int\Delta\hat{n}(\mathbf{r})\eta(\mathbf{r})\,d\mathbf{r}+g'\int\hat{n}'(\mathbf{r})\eta(\mathbf{r})\,d\mathbf{r},\\ g=(g_1-g_2)/2,\quad g'=(g_1+g_2)/2,\quad \hat{n}'(\mathbf{r})=\hat{n}_1(\mathbf{r})+\hat{n}_2(\mathbf{r}).\end{gathered}\tag{6}$$

In expressions (5) and (6) we have introduced new variables Δn and n' in place of the charged-particle densities n_1 and n_2. As follows from (5), only the variable Δn is responsible for the Coulomb interaction. Accordingly, the first term in (6) describes the interaction between two systems with slowly decreasing correlations. The second term redefines effectively the constants that enter in H (the corrections are of the order of the density x), i.e., it describes an uncharged impurity.[4] In particular, the critical temperature T_c of the solvent is shifted. We consider only the first term of H_3.

As will be seen subsequently, the interaction with the Coulomb system leads to anomalies near the critical point in the region $\tau_0\sim x$. We consider first of all the case when τ_0 is located outside the scaling region, i.e., in the region of the self-consistent field. To determine the correlation functions (CF) above the transition point we can leave out of H_1 the term with η^4 and thereby simplify the calculations substantially. In the case when τ_0 lands in the scaling region, the physical picture remains in principle the same, but the exact calculation becomes more complicated. We shall present the results for this case at the end of the paper.

2. CORRELATION FUNCTIONS

We consider the case $\tau_0\gg\mathrm{Gi}$, $\mathrm{Gi}=b^2T^2/\alpha c^3$. We denote the correlation functions for the order parameter $\eta(\mathbf{r})$ in a zero field ($h=0$) above the transition point (where $\langle\eta\rangle=0$) by G:

$$G(\mathbf{r})=\langle\eta(0)\eta(\mathbf{r})\rangle.$$

The angle brackets denote averaging over the states of a system of noninteracting particles. Outside the scaling region and neglecting the interaction with the Coulomb subsystem ($g=0$) we have

$$\begin{gathered}G_0(\mathbf{r})=\frac{1}{4\pi c}\frac{e^{-\varkappa r}}{r},\quad G_0(\mathbf{k})=\frac{T}{c}(k^2+\varkappa^2)^{-1},\\ \varkappa^2=r_c^{-2}=\gamma\tau,\quad \gamma=\alpha/c\sim a^{-2},\end{gathered}\tag{7}$$

where a is the distance between the solvent atoms.

The complete correlation function

$$D(\mathbf{r})=\langle\Delta n(0)\Delta n(\mathbf{r})\rangle$$

is obtained in the Debye-Huckel approximation ($g=0$) by summing diagrams with small momentum transfers, of the type

(8)

A wavy line corresponds here to the Coulomb potential, and is assigned the quantity $-4\pi e^2/\varepsilon k^2$. The usual lines denote the bare Green's functions of the charged particles, which we shall assume to obey classical statistics. In the calculation of the polarization operator, which is represented on the diagrams by a loop with two ends, such particles can be arbitrarily regarded in the Matsubara technique[9,10] as fermions, and after the calculations it is possible to go over to the classical limit:

$$\begin{gathered}D_0(\mathbf{r})=n_0\left[\delta(\mathbf{r})-\frac{\nu^2}{4\pi}\frac{e^{-\nu r}}{r}\right],\\ D_0(\mathbf{k})=n_0\frac{k^2}{k^2+\nu^2},\quad \nu^2=r_D^{-2}=\frac{4\pi n_0e^2}{\varepsilon T},\end{gathered}\tag{9}$$

n_0 is the mean value of the density of the charged particles of both signs, and $\delta(\mathbf{r})$ is a delta function.

Allowance for the interaction between the subsystems ($g\neq 0$) introduces into diagrams of type (8) for the complete correlation functions $G(\mathbf{r})$, $D(\mathbf{r})$, and

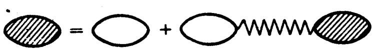
$$\Gamma(\mathbf{r})=\langle\eta(0)\Delta n(\mathbf{r})\rangle,$$

besides the Coulomb interaction of the charged particles, an additional interaction between the ions via fluctuations of the order parameter $\eta(\mathbf{r})$. In this case, when summing the most divergent diagrams of type (8), the Coulomb interaction must be replaced by the total interaction:

(10)

The dashed line denotes G_0 and the dot the interaction constant g.

As a result we obtain for the function[1] $D(\mathbf{k})$, which we represent by a shaded loop, the Dyson equation



(11)

The remaining correlation functions are expressed in terms of $D(\mathbf{k})$:

$$G=G_0+g^2G_0DG_0,\quad \Gamma=-gG_0D.\tag{12}$$

Solving (11) and substituting in (12), we obtain for

$$\begin{gathered}G(\mathbf{k})=Tc^{-1}(k^2+\nu^2)f^{-1}(\mathbf{k}),\quad D(\mathbf{k})=n_0k^2(k^2+\varkappa^2)f^{-1}(\mathbf{k}),\\ \Gamma(\mathbf{k})=-gn_0c^{-1}k^2f^{-1}(\mathbf{k}),\quad f(\mathbf{k})=(k^2+\varkappa^2)(k^2+\nu^2)-\tilde{g}^2k^2,\\ \tilde{g}^2=g^2n_0/cT.\end{gathered}\tag{13}$$

The character of the correlations in the system is determined by the correlation-function poles, i.e., by the zeros of $f(\mathbf{k})$.

We consider first the case of a weak interaction between the subsystems, $\xi<1$, $\xi=\tilde{g}/\nu$. Above the critical point (at $\tau>0$), in the temperature interval satisfying the inequality $|\varkappa-\nu|>\tilde{g}$, the zeros of $f(\mathbf{k})$ lie on the imaginary axis and the correlation functions decrease exponentially in analogy with (7) and (9). In the temperature region $|\varkappa-\nu|<\tilde{g}$, the zeros of $f(\mathbf{k})$ have nonzero real part, so that the correlation-functions oscillate in addition to being exponentially damped, i.e., they take the form

$$r^{-1}\exp(-\operatorname{Im}\mathbf{k}_0\mathbf{r})\sin(\operatorname{Re}\mathbf{k}_0\mathbf{r}+\varphi), \tag{14}$$

where $\mathbf{k}_0$ is the complex root of the equation

$$f(\mathbf{k})=0. \tag{15}$$

The most interesting is the case of strong interaction, $\xi>1$, which is in fact the subject of our study. In this case, at sufficiently high temperatures $\tau>\tau_0$, where

$$\tau_0=\gamma^{-1}(\tilde{g}-\nu)^2, \tag{16}$$

the zeros of $f(\mathbf{k})$ are complex as before, but Eq. (15) has at $\tau=\tau_0$ a real root (Fig. 1)

$$k_0^2=\nu(\tilde{g}-\nu). \tag{17}$$

The thermodynamic functions are obtained by integrating the correlation functions with respect to k. The presence of a pole on the real axis in a correlation function leads to divergences in the thermodynamic quantities (the usual situation which attests to instability of the system to the onset of a mode with $\mathbf{k}=\mathbf{k}_0$). Physically this means the appearance of waves with wave vector $\mathbf{k}_0$ and with macroscopic amplitude. In our case, charge-density waves and order-parameter-density waves appear at $\tau\leqslant\tau_0$.

3. THERMODYNAMICS OF THE SYSTEM. SELF-CONSISTENT-FIELD REGION

To consider the thermodynamics of the system, we introduce the effective Hamiltonian

$$H_{eff}\{\eta,\Delta n\}=\frac{1}{2}\int\Big[c(k^2+\varkappa^2)|\eta_{\mathbf{k}}|^2+\frac{T}{n_0}\frac{k^2+\nu^2}{k^2}|\Delta n_{\mathbf{k}}|^2$$
$$+2g\operatorname{Re}(\eta_{\mathbf{k}}\Delta n_{-\mathbf{k}})\Big]\frac{d\mathbf{k}}{(2\pi)^3}+\int\Big[\frac{b}{4}\eta^4(\mathbf{r})-h\eta(\mathbf{r})\Big]d\mathbf{r}. \tag{18}$$

As mentioned above, H_{eff} is in fact a term that must be added to the thermodynamic potential Φ in the case of long-wave deviations from the state $\eta=0$, $\Delta n=0$. Above the transition point τ_0 the Hamiltonian H_{eff} can be employed in the usual manner for the calculation of the correlation functions via thermodynamic averaging, and below the transition point it can be used to calculate the equilibrium values of $\eta_{\mathbf{k}}$ and $\Delta n_{\mathbf{k}}$ by minimizing (18). We note that the Coulomb part of (18) has a simple physical meaning. We express it in the form

$$\frac{1}{2}\int\Big[\frac{T}{n_0}|\Delta n_{\mathbf{k}}|^2+\frac{4\pi e^2}{\varepsilon k^2}|\Delta n_{\mathbf{k}}|^2\Big]\frac{d\mathbf{k}}{(2\pi)^3}.$$

The first term is a quadratic increment to the expansion of the entropy term in Φ in powers of Δn:

$$\sum_a\int Tn_a(\mathbf{r})\ln n_a(\mathbf{r})\,d\mathbf{r}.$$

The second term is the Coulomb energy. In particular, upon averaging, i.e., when $|\Delta n_{\mathbf{k}}|^2$ is replaced by $\langle|\Delta n_{\mathbf{k}}|^2\rangle$, the second term yields above the transition point the usual correlation energy E_{corr} of the Coulomb gas in the Debye approximation (Ref. 8, p. 270). Starting from expression (18), we can again obtain formulas (7), (9), and (13)–(17).

We carry out the transformation

$$\Delta n_{\mathbf{k}}=\zeta_{\mathbf{k}}-g\frac{n_0}{T}\frac{k^2}{k^2+\nu^2}\eta_{\mathbf{k}} \tag{19}$$

and change over to the dimensionless parameters

$$\eta'=b^{1/2}\alpha^{-1/2}\eta,\quad \zeta'=b^{1/2}\alpha^{-1/2}\zeta,$$
$$h'=b^{1/2}\alpha^{-3/2}h,\quad H'=b\alpha^{-2}H.$$

The Hamiltonian (18) then takes the form

$$H_{eff}\{\eta,\zeta\}=\frac{1}{2}\int\Big[\frac{1}{\gamma}\frac{f(\mathbf{k})}{k^2+\nu^2}|\eta_{\mathbf{k}}|^2$$
$$+\frac{T}{\alpha n_0}\frac{k^2+\nu^2}{k^2}|\zeta_{\mathbf{k}}|^2\Big]\frac{d\mathbf{k}}{(2\pi)^3}+\int\Big[\frac{1}{4}\eta^4(\mathbf{r})-h\eta(\mathbf{r})\Big]d\mathbf{r}. \tag{20}$$

We have left out the primes for the sake of brevity.

In accordance with the foregoing, the coefficient of $|\eta_{\mathbf{k}}|^2$ at the point $\tau=\tau_0$ vanishes and becomes negative at $\tau<\tau_0$, meaning that $\langle\eta_{\mathbf{k}_0}\rangle\neq0$. On the other hand, the coefficient of $|\zeta_{\mathbf{k}}|^2$ remains positive, therefore $\langle\zeta_{\mathbf{k}}\rangle=0$. As a result we have hereafter everywhere

$$\langle\Delta n_{\mathbf{k}}\rangle=-g\frac{n_0}{T}\frac{k^2}{k^2+\nu^2}\langle\eta_{\mathbf{k}}\rangle. \tag{21}$$

At $h\neq0$ or at sufficiently low temperatures there exists also a macroscopic mode with $k=0$. Being interested in the macroscopic characteristics of the system, we seek the function that minimizes the Hamiltonian (20) in the form

$$\eta(\mathbf{r})=\eta_0+2\eta_1\cos\mathbf{k}_0\mathbf{r}, \tag{22}$$

and regard η_0 and η_1 as the variational parameters.[2] The amplitudes η_0 and η_1 are determined from the system of equations

$$\tau\eta_0+\eta_0^3+6\eta_0\eta_1^2=h,\quad \eta_1[-(\tau_0-\tau)+3(\eta_0^2+\eta_1^2)]=0. \tag{23}$$

The system (23) has two types of solution: type I is uniform ordering ($\eta_1=0$, homogeneous phase I), and type II—non-uniform ordering [$\eta_0^2+\eta_1^2=(\tau_0-\tau)/3$, phase II consisting of charge-density and order-parameter waves].

For the sake of argument we consider an electrolyte near the liquid (L)—vapor (V) critical point of the solvent. The phase diagram of the system (23) is shown in Fig. 2, which shows only the stable states of the Hamiltonian (20) on the $P-T$ plane. The line BC is that of a second-order phase transition. Inside the loop is the region of non-uniform ordering, and the amplitude of the waves with $k=k_0$ is zero on the BC line. The points B and C are tricritical and correspond

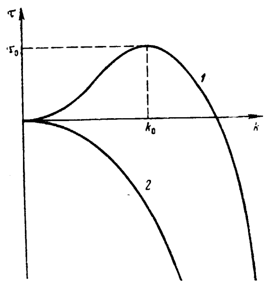


FIG. 1. Line of zeros of $f(\mathbf{k})$ in the case of strong interaction $\xi>1$ (curve 1) and of weak interaction $\xi<1$ (curve 2).

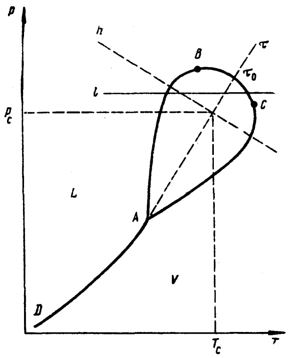


FIG. 2. Phase diagram of electrolyte near the critical point of the pure solvent (P_c, T_c). Inside the loop is the region of existence of the inhomogeneous phase.

to $\tau = 3\tau_0/4$ and $h = \pm 5\tau_0^{3/2}/12\sqrt{3}$. The value of η_1 on the first-order phase-transition lines AB and AC differs from zero. A is the triple point of coexistence of phase II and phase I with two different values of the density (liquid and vapor), separated by the first-order phase-transition line AD.

A variational solution of the type (22) is not exact. Owing to the nonlinear term in the exact solution of the minimizing equation of the functional (20), harmonics that are multiples of k_0 appear, i.e., the solution takes the form

$$\eta(\mathbf{r}) = \eta_0 + 2\sum_{n=1}^{\infty}[\eta_n^{(1)}\cos(n\mathbf{k}_0\mathbf{r}) + \eta_n^{(2)}\sin(n\mathbf{k}_0\mathbf{r})]\,. \tag{24}$$

At small $\eta_1 \sim (\tau_0 - \tau)^{-1/2}$, however, the coefficients η_n are of higher order of smallness than η_1. Therefore the solution of the system (23) for the region of the phase diagram near the line BC (on which $\eta_1 = 0$) and near the points B and C is asymptotically exact. Inside the loop, at sufficient distance from the BC line on the first-order phase-transition lines AB and AC, the value of η_1 is not small and the system (23) should have been replaced by the analogous system for $\eta_n^{(1)}$ and $\eta_n^{(2)}$. Analysis shows, however, that the results remain qualitatively the same in this case, too. The shape of the wave, however, becomes strongly anharmonic (Fig. 3). We emphasize that in this case, too, the system does not constitute alternating layers of separate phases.

We have so far disregarded completely the fluctuations of the order parameter $\eta(\mathbf{r})$. Brazovskiĭ[11] has shown that owing to the relatively large phase volume of the fluctuations with $k = k_0(\Delta\Omega \sim k_0^2\Delta k)$ in comparison with the phase volume for the states with $k = 0[\Delta\Omega \sim (\Delta k)^3]$, the phase with $k = k_0 \neq 0$ is produced via a first-order transition. A calculation similar to that of Brazovskiĭ[11] shows that the line BC is replaced by a first-order phase-transition line $B'C'$ shifted by

$$\delta\tau \sim \tau_0^{2/3}(\mathrm{Gi})^{1/3} \ll \tau_0.$$

On this line τ_1 has inside the loop the finite value

$$\eta_1 \sim \tau_0^{1/3}(\mathrm{Gi})^{1/6} \ll \tau_0^{1/2},$$

i.e., a first-order close to a second-order phase transition takes place. It is then possible to use as before the system (23) to describe the thermodynamics.

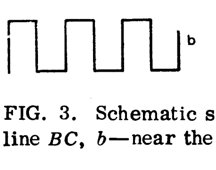


FIG. 3. Schematic shape of the wave in the loop: *a*—near the line BC, *b*—near the point A, Fig. 2.

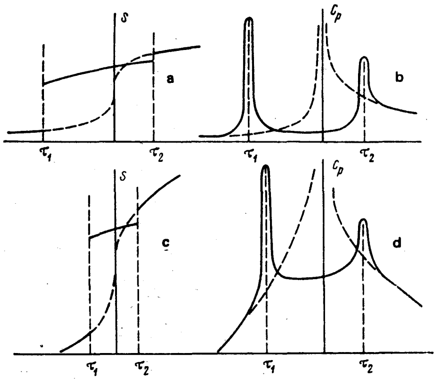


FIG. 4. Behavior of the entropy and of the heat capacity on the line l of Fig. 2 ($P > P_c$). The point τ_1 lies on the line the first-order phase-transition line AB, τ_2 lies on the line BC of a first-order phase transition close to that of second order. The dashed lines show the behavior of the quantities in the absence of interaction between the subsystems ($g = 0$). Figures a and b correspond to the case $\tau_0 \gg \mathrm{Gi}$, and c and d to the case $\tau_0 \ll \mathrm{Gi}$.

Estimates of the discontinuities of the entropy S yield $S \sim \tau_0^{2/3}(\mathrm{Gi})^{1/3}$ for a transition from the homogeneous phase outside the loop into the inhomogeneous phase via the line $B'C'$, and $S \sim \tau_0$ for a transition via AB' or AC'. Typical plots of the entropy and of the heat capacity C_p are shown in Figs. 4(a) and 4(b), and correspond to the behavior of these quantities on the line l of Fig. 2.

4. THERMODYNAMICS OF SYSTEM. SCALING REGION

In the case $\tau_0 \ll \mathrm{Gi}$ it is necessary to take into account the interaction $\eta^4(\mathbf{r})$ in (2), as a result of which H_1 takes the scale-invariant form[12]

$$H_1 = \tau^{2-\alpha}F\{\eta(\mathbf{r})/\tau^{\beta}\}, \tag{25}$$

where F is a functional. We consider the case $|\eta(\mathbf{r})| \ll \tau^{\beta}$. For functions $\eta(\mathbf{r})$ that vary slowly over distances $\sim r_c$ we then have

$$H_1 = \frac{1}{2}\int \tau^{2-\alpha}\left[A_1\frac{\eta^2(\mathbf{r})}{\tau^{2\beta}} + A_2\frac{r_c^2}{\tau^{2\beta}}(\nabla\eta)^2 + \frac{A_3}{2}\frac{\eta^4(\mathbf{r})}{\tau^{4\beta}}\right]d\mathbf{r}, \tag{26}$$

where A_1, A_2, and A_3 are constants. Taking into account the relations between the exponents, namely 2 $2 - \alpha - 2\beta = 2\mu - \zeta\mu$ and $\alpha = 2 - 3\mu$, where α, β, and μ are the critical exponents that determine the temperature dependence of the heat capacity, of the order parameter, and of the correlation radius, and neglecting the anomalous-dimensionality exponent $\zeta \sim 0.03$, we obtain

$$H_1 = \frac{1}{2} \int \omega(\mathbf{k}, \tau) |\eta_\mathbf{k}|^2 \frac{d\mathbf{k}}{(2\pi)^3} + \int \left[\frac{\tau^\mu}{4} \eta^4(\mathbf{r}) - h\eta(\mathbf{r}) \right] d\mathbf{r},$$
$$\omega(\mathbf{k}, \tau) = \gamma^{-1}[k^2 Q(kr_c) + \gamma\tau^{2\mu}]. \tag{27}$$

$Q = 1$ at $\gamma^{-1/2} k\tau \ll 1$. At $kr_c \gg 1$, i.e., in the region of rapid variation of $\eta(\mathbf{r})$ over distances $\sim r_c$, the correlation function $G(\mathbf{r}) \sim r^{-(1+\zeta)}$ and for $\zeta = 0$ we have

$$G^{-1}(\mathbf{k}) \sim \omega(\mathbf{k}, \tau) \sim \mathbf{k}^2,$$

meaning that Q is constant at $\gamma^{-1/2}/k\tau^{-\mu} \gg 1$. Therefore expression (27) remains in force at arbitrary k, where $Q(kr_c) \sim 1$.

Turning on the interaction with the Coulomb subsystem leads to an effective functional (27) with

$$\omega(\mathbf{k}, \tau) = \gamma^{-1}[k^2 + \gamma\tau^{2\mu} - \tilde{g}^2 k^2/(k^2 + \nu^2)] \tag{28}$$

that differs from (20) only in the temperature dependences of the coefficients and in a redefinition of τ_0:

$$\tau_0{}^\mu = (\tilde{g} - \nu)\gamma^{-1/2}, \quad k_0{}^2 = \nu(\tilde{g} - \nu). \tag{29}$$

The fluctuations near the point $\tau = \tau_0$ are considered in the same manner as in the preceding case. The line BC then becomes a first-order phase-transition line and is shifted by[3] $\delta\tau \sim \tau_0 \xi^{-2/3}$. The size of the jump is $\delta\eta_1 \sim \tau_0^\beta \xi^{-1/3} \tau_0^\beta$, and justifies at $\xi \gg 1$ the expansion (26) used by us near the BC line. The values of the entropy discontinuities are $S \sim \tau_0^\mu$ on the lines AB and AC and $S \sim \tau_0^\mu \xi^{-2/3}$ on the line BC. The plots of S and C_p on the line l of Fig. 2 are shown in Figs. 4(c) and 4(d).

5. CONCLUSION

If a multicomponent electrolyte is involved, it is necessary to put in all the formulas

$$\nu^2 = \sum_a \frac{4\pi n_a e_a{}^2}{\varepsilon T}, \quad \tilde{g}^2 = \frac{1}{cT} \Big(\sum_a g_a n_a e_a \Big)^2 \Big/ \sum_a n_a e_a{}^2. \tag{30}$$

The generalization for ν is obvious, the formula for $\tilde{g}$ is derived in a natural fashion in the calculations of the correlation functions for a multicomponent electrolyte by the method described above. We do not write here the expressions for the shift, which is of no importance to us, of the critical temperature T_c.

We present some estimates for the parameters of the resultant inhomogeneous state. Using expressions (7), (13), (16), and (17) we obtain

$$\tau_0{}^{2\mu} \sim xp(\xi - 1)^2, \quad k_0 = \nu(\xi - 1)^{1/2} \sim a^{-1}(xp)^{1/2}(\xi - 1)^{1/2},$$
$$p = 4\pi e^2/\varepsilon a T_c, \quad \xi = \tilde{g}/\nu \sim (g/T_c) p^{-1/2} (\mathrm{Gi})^{1/6}. \tag{31}$$

The condition for the applicability of the Debye-Hückel theory $\nu a \ll x^{1/3}$ means that

$$px^{1/3} \ll 1. \tag{32}$$

In the case of a strong local interaction, $g \gg T_c p^{1/2}$, we have $\xi \gg 1$ and

$$\tau_0{}^{2\mu} \sim xp\xi^2, \quad k_0 a \sim (xp\xi)^{1/2}. \tag{33}$$

A sufficient condition for the existence of an interval of densities x at which τ_0 lies in the region of the self-consistent field, $\tau_0 \gg \mathrm{Gi}$, is

$$p^{-3} \gg x \gg p^{-1}\xi^{-2}\mathrm{Gi}. \tag{34}$$

In estimates, in the case $x \ll p^{-1}\xi^{-2}\mathrm{Gi}$, when the inhomogeneous phase lies in the scaling region where $\mu \approx 0.63$, or when the condition (34) where $\mu = \frac{1}{2}$ is satisfied, we can use the expressions

$$\tau_0{}^{2\mu} \sim x(g/T_c)^2, \quad k_0 a \sim x^{1/3}(g/T_c)^{1/2} p^{1/4}. \tag{35}$$

As noted above, our results pertain primarily to liquid electrolytes. We present numerical estimates. Since $\xi \sim \varepsilon^{1/2}$, and for water at room temperature $\varepsilon \approx 80$, the described phenomenon could be observed for aqueous solutions of electrolytes. In this case $\xi \approx 3, p \approx 20$ and $g/T_e \approx 20$. For example, for intrinsic dissociation in the phenol–water system near the stratification critical point,[13] $T_c = 339$ K, and $x \approx 10^{-6}$, we obtain $\tau_0 \approx 10^{-3}$ (assuming that we land in the scaling region), $T_0 - T_c \approx 0.3$ K, and $k_0 \approx 10^6$ cm^{-1}.

When account is taken of the intrinsic dissociation of water into H$^+$ and OH$^-$ ions near the critical point ($T_c = 647$ K), owing to the higher T_c the smaller $\varepsilon \approx 10$, $g/T_c \approx 10$, $\xi \approx 1.3$, $p \approx 80$, and $x \approx 10^{-5}$, we obtain $\tau_0 \approx 10^{-2}$–10^{-3} and $T_0 - T_c \approx 1$ K, $k_0 \approx 10^6$ cm^{-1}.

Besides liquid electrolytes, similar phenomena can take place in solids near the point of a structural-type second-order phase transition, if the charges in these crystals can be redistributed as a result of the presence of vacancies or voids in the crystal structure.[14] The wave vector $\mathbf{k}_0$ is then fixed because of the crystallographic anisotropy, and the phenomenon consists as a manifestation of an incommensurate structure in the temperature interval between a symmetrical phase and a nonsymmetrical one.

We note in conclusion that in the case $\xi - 1 \ll 1$ the coefficient of the quadratic term in the expansion of $\omega(\mathbf{k}, \tau)$ in powers of $\mathbf{k} - \mathbf{k}_0$ is anomalously small, i.e., we find ourselves in the vicinity of the Lifshitz critical point considered in Ref. 15. This critical point is characterized by a noncommensurability parameter $\delta = 1 - \xi$ and by a dependence of the wave vector on δ: $k_0 \sim (-\delta)^{1/2}$. We point out that for the system considered by us the Lifshitz critical point coincides with the usual critical point.

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[1] The correlation function of interest to us, in the form $\langle X(\mathbf{r}_1)Y(\mathbf{r}_2)\rangle$, can be regarded as the limit, as $\tau_1 \to \tau_2$, of Matsubara Green's functions of the type $\langle T_\tau\{X(\mathbf{r}_1, \tau_1)Y(\mathbf{r}_2, \tau_2)\}\rangle$, where X and Y are arbitrary operators. These correlators are expressed by correlation functions in the frequency representation, summed over the frequencies. In the case of interest to us, however, the principal contribution is made by the zero-frequency term.[9,10]

[2] Since the system is isotropic, degeneracy is present with respect to the directions of $\mathbf{k}_0$. It can be shown, however, that a wave with a fixed direction $\mathbf{k}_0$ is thermodynamically more favored than a superposition of such waves. The concrete realization of the direction in the system is determined by

the boundary conditions, by the external fields, and by other factors.

[3)] It should be noted that the expressions for $\delta\eta$ and $\delta\tau$ contain as a factor the Ginzburg coefficient $\tilde{G}i = T^2 A_3^2 / A_1 A_2^3$ for the functional (26). The value of $\tilde{G}i$ can be obtained by matching (27) to (2) in the region $\tau \sim$ Gi. It is easy to verify that the $\tilde{G}i \sim 1$.

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Thermodynamic effects in multipulse NMR spectroscopy in solids

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We consider the behavior of multispin systems in solids under the influence of multipulse trains. An important role is played here by the small fraction of the spins whose interaction is not averaged out by the external actions because these spins are in local fields $\omega_{\text{loc}} \sim 2\pi/t_c$, where t_c is the period of the external actions. It is shown that these nonaveraged interactions play an important role in the absorption of energy from the external fields by the spin system. A method of canonical transformations is developed to study the dynamics of spin systems in arbitrary multipulse experiments. The behavior of spin systems acted upon by pulse trains that average out the dipole-dipole interaction is investigated. The nature of the damping of the longitudinal component of the magnetization in the pulse trains WHH-4 [J. S. Waugh, L. M. Huber, and U. Haeberlen, Phys. Rev. Lett. **20**, 180 (1968)] and HW-8 [U. Haeberlen and J. S. Waugh, Phys. Rev. **175**, 453 (1968)] is investigated. Solution of the equation for the spin-system density matrix yields the damping time of the transverse magnetization component as a function of the period of the pulse train and of the detuning of the RF-pulse carrier frequency from the spin Larmor-precession frequency. New pulse trains that average out dipole-dipole interactions between spin nuclei are considered.

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Recently reported multipulse NMR methods[1-3] have improved of the resolution in the spectra by a factor of several hundred, thus substantially extending the possibilities of investigating the structure of matter and dynamic processes in solids. The resolution was improved by using intense radio-frequency pulsed fields. Unlike in ordinary spectroscopy however, the fields were used not to register the absorption lines, but for dynamic averaging of the dipole-dipole interactions responsible for the broadening of the NMR spectral lines in solids. By using periodic trains of intense RF pulses (with periods t_c) it became possible to organize rapid transitions (within a time $\sim t_c$) between Zeeman levels of dipole-coupled nuclei. As a result the anisotropic dipole interactions become oscillatory with frequencies that are multiples of $2\pi/t_c$ and exceed greatly the characteristic frequency ω_{loc} of the dipole-dipole interaction.

It is well known from classical mechanics[4] that similar rapidly oscillating interactions exert on a system the same action as a suitably constructed[4] time-independent effective interaction. Unlike in mechanics, in multipulse NMR spectroscopy of solids it is necessary to deal with systems having macroscopically large numbers of degrees of freedom, i.e., with thermodynamic systems. This circumstance greatly complicates the theoretical analysis of the multipulse problem, and as

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