Critical fluctuations in external fields

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A method based on the scale-transformation theory and on thermodynamic fluctuation theory is proposed for finding the correlation functions of the fluctuations of the scalar ordering parameter near critical points in the presence of external fields. The general theory is used to investigate the correlations of critical density fluctuations in a gravitational field and to describe critical opalescence in such an optically inhomogeneous medium.

In describing critical fluctuations one usually assumes that the system is isotropic, making it possible to express the fluctuational part of the free energy in terms of the corresponding scalar invariants[1-3]. In general, because of the anomalous increase of the susceptibility in the near-critical state, switching on an external field destroys the isotropy of the problem under consideration. In this case, the fluctuational nonuniformity of matter near phase-transition points and critical points depends not only on the proximity to the critical temperature but also on the characteristic field variable for each concrete problem.

On the basis of the theory of scaling laws[4-7], we develop in this paper a method for describing the correlation properties of matter in external fields near critical points. Together with the correlation length R_c of the order-parameter fluctuations, which describes the "internal" nonuniformity, in treating this problem it is necessary to introduce also an "external" length R_0 characterizing the nonuniformity created by the field. Below, the correlation properties of the systems being studied will be examined within a volume V satisfying the inequality $V \gg R_c^3 \gg a^3$, where a is the intermolecular distance. An equivalent criterion $R_0 \gg R_c$ is assumed to be fulfilled for the length characterizing the external nonuniformity, i.e., for the length associated with the characteristic functions of the problem that are dependent upon the external field.

PROBABILITY OF FORMATION OF ORDER-PARAMETER FLUCTUATIONS NEAR THE CRITICAL POINT

We shall assume that the free energy of an isothermal system with nonuniformity brought about by the existence of an external scalar field and by the presence of fluctuations can be represented in the form of a functional series in the corresponding scalar order parameter characterizing the given phase transition[8]:

$$F(\eta(\mathbf{r}))=\sum_{n=0}^{\infty}\int\limits_V\ldots\int K_n(\mathbf{r}_1,\ldots,\mathbf{r}_n)\prod_{i=1}^{n}\Delta\eta(\mathbf{r}_i)\,d\mathbf{r}_i, \qquad (1)$$

$$K_n(\mathbf{r}_1,\ldots,\mathbf{r}_n)=\frac{1}{n!}\frac{\delta^n F}{\delta\eta(\mathbf{r}_1)\ldots\delta\eta(\mathbf{r}_n)}\bigg|_{\eta(\mathbf{r})=\langle\eta(\mathbf{r})\rangle}. \qquad (2)$$

The kernels K are symmetric in the variables $\mathbf{r}_1,\ldots,\mathbf{r}_n$ inside the volume V, and $\Delta\eta(\mathbf{r}_i)$ is the deviation of the order parameter from its equilibrium value $\langle\eta(\mathbf{r}_i)\rangle$. The condition $\eta(\mathbf{r})=\langle\eta(\mathbf{r})\rangle$ means that the fluctuations of the order parameter are put equal to zero after the functional derivatives in (2) have been calculated. Then it follows from (2) that $K_0 = F(\langle\eta(\mathbf{r})\rangle)$ is the free energy of the nonuniform system in the absence of fluctuations.

In the quadratic approximation in $\Delta\eta$, the probability of formation of fluctuations of the scalar order parameter in the presence of an external field near phase-transition points has the form

$$W\sim\exp\left\{-\frac{C}{k_BT}\left[\int\limits_V K_1(\mathbf{r}_1)\Delta\eta(\mathbf{r}_1)d\mathbf{r}_1+\iint\limits_V K_2(\mathbf{r}_1,\mathbf{r}_2)\Delta\eta(\mathbf{r}_1)\Delta\eta(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2\right]\right\}, \qquad (3)$$

where C is a dimensional constant which is determined by the specific type of phase transition. On the basis of the condition for thermodynamic equilibrium of a system in an external field[2]

$$\frac{\delta F}{\delta\eta(\mathbf{r}_1)}\bigg|_{\eta(\mathbf{r})=\langle\eta(\mathbf{r})\rangle}=\mu(\langle\eta(\mathbf{r})\rangle)+U(\mathbf{r})=\text{const},$$

where $\mu(\langle\eta(\mathbf{r})\rangle)$ is the "chemical potential" conjugate to the order parameter $\eta(\mathbf{r})$ and $U(\mathbf{r})$ is the potential of the external field, and also on the basis of the reasonable equality

$$\int\limits_V\eta(\mathbf{r})d\mathbf{r}=\int\limits_V\langle\eta(\mathbf{r})\rangle d\mathbf{r},$$

the term linear in $\Delta\eta$ in the exponent is zero.

In the quadratic term, the functional derivative is represented by the formula

$$\frac{\delta^2F}{\delta\eta(\mathbf{r}_1)\delta\eta(\mathbf{r}_2)}=\frac{\delta}{\delta\eta(\mathbf{r}_2)}[t^{\beta\delta}G(y(\mathbf{r}_1))-f^*(\mathbf{r}_1)\nabla^2\eta(\mathbf{r}_1)], \qquad (4)$$

which takes into account the nonlocal spatial dependence of $\mu(\eta)$ in the sense of Lebowitz and Percus[9] and uses the scaling-theory equation of state[4-7]

$$\mu(\langle\eta(\mathbf{r})\rangle,t)-\mu(\eta_c,t)=t^{\beta\delta}G(y(\mathbf{r}));$$
$$y=\frac{\langle\eta(\mathbf{r})\rangle-\eta_c}{\eta_c t^{\beta}},\qquad t=\frac{T-T_c}{T_c},$$

where G(y) is the scaling function, and β and δ are critical indices.

From formulas (2) and (4) and the relations

$$\frac{\delta\eta(\mathbf{r}_1)}{\delta\eta(\mathbf{r}_2)}=\delta(\mathbf{r}_1-\mathbf{r}_2),\qquad \gamma=\beta(\delta-1)$$

it follows that

$$K_2(\mathbf{r}_1,\mathbf{r}_2)={}^1\!/_2\,\delta(\mathbf{r}_1-\mathbf{r}_2)[t^{\gamma}G_y'(y(\mathbf{r}_1))+b\nabla_{r_1}\nabla_{r_2}]. \qquad (5)$$

It can be shown that the quantity $b = f^*(\langle\eta(\mathbf{r})\rangle, t)$, which is related to the range of the intermolecular interaction[9,10], depends weakly on the field and temperature variables. In fact, estimates made in accordance with scaling-law theory lead to

$$b\sim[R_c(t,x)]^{\eta'},\qquad x=\frac{\langle\eta(\mathbf{r})\rangle-\eta_c}{\eta_c}=yt^{\beta}.$$

The function

$$R_c \sim \begin{cases} t^{-\nu}, & x\to 0 \\ x^{-\xi}, & t\to 0 \end{cases}.$$

By virtue of the assumed smallness of the critical index η' (in the 3-dimensional Ising model, $\eta' \approx 0.06$, $\nu \approx 2/3$, and $\xi \approx 2.16$), this justifies neglecting the dependence of b on t and $\langle\eta(\mathbf{r})\rangle$ compared with the strong temperature and field dependence of the susceptibility of the system

$$\chi \sim [t^\gamma G_y'(y(\mathbf{r}))]^{-1},$$

which for $\langle\eta\rangle = \eta_c$, is proportional to $t^{-\gamma'}$ and on the critical isotherm is proportional to $x^{1-\delta}$. In obtaining (5), we have used the criterion $R_0 \gg R_c$ and a relation of the type $|\nabla\eta(\mathbf{r})| \gg |\nabla\langle\eta(\mathbf{r})\rangle|$ which follows from this criterion.

Finally, the macroscopic distribution function of the order-parameter fluctuations takes the form

$$W \sim \exp\left\{-\frac{C}{2k_BT}\int_V [t^\gamma G_y'(y(\mathbf{r},t))\Delta\eta^2(\mathbf{r}) + b(\nabla\eta(\mathbf{r}))^2]d\mathbf{r}\right\} \qquad (6)$$

The distribution function of the Fourier components of the order-parameter fluctuations, corresponding to formula (6), is represented conveniently in the form

$$W \sim \exp\left\{-\frac{CV}{2k_BT}\sum_{\mathbf{k},\mathbf{k}'}[\varphi_{oz}(\mathbf{k}\mathbf{k}')\delta_{\mathbf{k}\mathbf{k}'} + \varphi_1(\mathbf{k}-\mathbf{k}')]\eta_\mathbf{k}\eta_{\mathbf{k}'}^*\right\}, \qquad (7)$$

$$\varphi_{oz}(\mathbf{k}\mathbf{k}') = At^\gamma + b\mathbf{k}\mathbf{k}',$$

$$\varphi_1(\mathbf{k}-\mathbf{k}') = \frac{1}{V}\int_V At^\gamma[A^{-1}G_y'(y(\mathbf{r})) - 1]e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}}d\mathbf{r};$$

A is the value of G_y' in the absence of the external field. It should be noted that the expression (6) can also be obtained by another method, based on the use of the method of the local-equilibrium distribution developed by Zubarev[11].

CORRELATION FUNCTIONS IN AN EXTERNAL FIELD

We introduce the correlation function

$$g_{\mathbf{k}\mathbf{k}'} = \frac{CV}{k_BT}\langle\eta_\mathbf{k}\eta_{\mathbf{k}'}^*\rangle,$$

associated with the covariance $\langle\eta_\mathbf{k}\eta_{\mathbf{k}'}^*\rangle$ of the Fourier components of the order-parameter fluctuations, where $\langle\ \rangle$ denotes averaging over the distribution (7). The function $g_{\mathbf{k}\mathbf{k}'}$ satisfies the integral equation

$$\sum_{\mathbf{k}_1}[\varphi_{oz}(\mathbf{k}\mathbf{k}_1)\delta_{\mathbf{k}\mathbf{k}_1} + \varphi_1(\mathbf{k}-\mathbf{k}_1)]g_{\mathbf{k}_1\mathbf{k}'} = \delta_{\mathbf{k}\mathbf{k}'}, \qquad (8)$$

the solution of which, in the case of weak nonuniformity ($\varphi_1 \ll \varphi_{0Z}$), can be written in the form

$$g_{\mathbf{k}\mathbf{k}'} = \frac{1}{\varphi_{oz}(k^2)}\left\{\delta_{\mathbf{k}\mathbf{k}'} + \sum_{n=1}^\infty(-1)^n\prod_{i=1}\frac{\varphi_1(\mathbf{k}_{i-1}-\mathbf{k}_i)}{\varphi_{o\Pi}(k_i^2)}\right\}, \qquad (9)$$

where $\mathbf{k}_0 = \mathbf{k}$ and $\mathbf{k}_n = \mathbf{k}'$.

Fourier transformation of (8) leads to the following equation for the correlation function $g(\mathbf{r}, \mathbf{r}')$ in the coordinate representation:

$$\hat{L}(\mathbf{R};\mathbf{r}',t)g(\mathbf{R},\mathbf{r}') = -\frac{V}{b}\delta(\mathbf{R}), \qquad (10)$$

$$\hat{L}(\mathbf{R};\mathbf{r}',t) = \nabla_R^2 - \varkappa^2[1+f_1(\mathbf{R}+\mathbf{r}',t)],$$

$$\mathbf{R} = \mathbf{r}-\mathbf{r}', \quad \varkappa^2 = At^\gamma/b, \quad f_1(\mathbf{r},t) = A^{-1}G_y'(\mathbf{r},t) - 1;$$

f_1 is the field function describing the effect of external forces on the correlation properties of the systems being investigated; f_1 is symmetric under inversion of the spatial coordinates and possesses the properties

$$f_1(\mathbf{r}=0, t\neq 0) = 0, \quad f_1(\mathbf{r}\neq 0, t=0) > 0.$$

Eq. (10) is the generalization, in the presence of an external field, of the well-known differential equation of the Ornstein-Zernike (0Z) theory[1-3].

In the case of smooth nonuniformity characterized by the inequality

$$\left|\frac{\mathbf{R}\nabla_{\mathbf{r}'}f_1(\mathbf{r}',t)}{f_1(\mathbf{r}',t)}\right| \ll 1, \qquad (11)$$

which in k-space is equivalent to assuming that small differences $\mathbf{k}_i - \mathbf{k}_j$ make the main contribution to $\varphi_1(\mathbf{k}_i - \mathbf{k}_j)$, the correlation function identified with the singular part of the Green function of the operator $\hat{L}(\mathbf{R}; \mathbf{r}', t)$ takes the form

$$g_0(\mathbf{r},\mathbf{r}') = \frac{V}{4\pi b}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\exp[-(b^{-1}t^\gamma G_y'(\mathbf{r}',t))^{1/2}|\mathbf{r}-\mathbf{r}'|], \qquad (12)$$

and the effective correlation length of the order-parameter fluctuations in the external field is found to be equal to

$$R_{c\ \mathrm{eff}}(\mathbf{r},t) = \left[\frac{t^{\gamma}}{b}G_y'(\mathbf{r},t)\right]^{-1/2} = \frac{R_c(t)}{[1+f_1(\mathbf{r},t)]^{1/2}}$$

In the absence of an external field ($f_1(\mathbf{r}, t) = 0$, $G_y' = A$), the expressions (9) and (12) for the correlation functions go over into the corresponding results of the 0Z theory and the surfaces of equal correlation lengths at each point of the system are spheres, all of the same radius $R_c(t) = (b/AT^\gamma)^{1/2}$. "Switching on" the field leads to the result that the correlation between two fluctuations at the points $\mathbf{r}$ and $\mathbf{r}'$ is found to depend not only on the relative distance but also on the position in space of the two fluctuations for a given $\mathbf{R}$.

In the case when the inequality (11) does not hold, for $g_1 = g - g_0$ we can write a convolution-type integral equation of the form

$$g_1(\mathbf{R},\mathbf{r}') = \hat{L}^{-1}(\mathbf{R};\mathbf{r}',t)\varkappa^2[f_1(\mathbf{R}+\mathbf{r}',t) - f_1(\mathbf{r}',t)]g_0(\mathbf{R},\mathbf{r}'). \qquad (13)$$

Solving (13) by means of Fourier transformation with respect to the coordinate $\mathbf{R}$ in a sufficiently large volume, for the correlation function $g(\mathbf{R}, \mathbf{r}')$ we have finally

$$g(\mathbf{R},\mathbf{r}') = g_0(\mathbf{R},\mathbf{r}') + \frac{1}{(2\pi)^3}\int\frac{g_{0s}(\mathbf{r}')\Phi_s(\mathbf{r}')e^{-is\mathbf{R}}ds}{1-\Phi_s(\mathbf{r}')}$$

where $g_{0s}(\mathbf{r}')$ and $\Phi_s(\mathbf{r}')$ are the Fourier transforms of $g_0(\mathbf{R}, \mathbf{r}')$ and of the function $\Phi(\mathbf{R}, \mathbf{r}') = b\kappa^2[f_1(\mathbf{R} + \mathbf{r}', t) - f_1(\mathbf{r}', t)]g_0(\mathbf{R}, \mathbf{r}')/V$.

It should be noted that the expression (12) for the correlation function $g_0(\mathbf{r}, \mathbf{r}')$ is a solution of Eq. (10) when the inequality (11) is fulfilled with "zero" boundary conditions at infinity. If we take into account the finite dimensions of real systems, the subsequent use of this expression requires specific justification. In the Appendix, a calculation is performed of the correlation function for a plane-parallel layer with reasonable boundary conditions. The Fourier transform of this correlation function is given by an expression of the following form:

$$g_0(\mathbf{k},\mathbf{k}') = \frac{1}{Vb}\int_V\frac{e^{i(\mathbf{k}'-\mathbf{k})\mathbf{r}'}}{\varkappa_{\mathrm{eff}}^2(\mathbf{r}',t)+k^2}\left\{1 - \frac{\cos k_zL_z}{\mathrm{ch}\,[\varkappa_{\mathrm{eff}}^2(\mathbf{r}',t)+k^2-k_z^2]^{1/2}L_z}\right\}d\mathbf{r}'. \qquad (14)$$

It follows from (14) that, for a system of sufficiently large volume V in the sense of the inequality

$$V^{1/3} \gg R_0 \approx f_1(\mathbf{r},t)/|\nabla f_1(\mathbf{r},t)| \gg R_c,$$

the correlation function (14) goes over into the Fourier transform of (12).

To conclude this Section, we note that the theory proposed here of critical fluctuations in external fields (applications of which will be considered below) has been developed on a thermodynamic basis, in the sense that the characteristics of the correlation functions of the order-parameter fluctuations are determined in an essential way by the scaling function $G(y)$ characterizing the equation of state near the phase-transition points. Naturally, such a phenomenological theory requires a microscopic justification.

DENSITY FLUCTUATIONS IN A GRAVITATIONAL FIELD

The anomalous increase in the susceptibility to external forces which appears in the immediate vicinity of second-order phase-transition points and critical points can lead in a number of cases to pronounced spatial nonuniformity of the substance, and this makes it possible to apply the general method developed above for calculating order-parameter fluctuations to the study of the correlation properties of these systems.

The most characteristic example of such a situation is, evidently, the critical point of a classical liquid situated in a gravitational field. The order parameter of such a system is the dimensionless deviation $\Delta\rho$ of the density from its critical value, and the field variable is the height z (measured from the level with the maximum density gradient), which is connected with the scaling function $G(y)$ by the relation

$$z^* = \rho_c gz / P_c = -t^{\beta\delta} G(y). \tag{15}$$

The function $G(y)$, which is known in scaling-law theory only for the limiting cases $y \ll 1$ (the vicinity of the critical isochore) and $y \gg 1$ (the vicinity of the critical isotherm), has the following asymptotic forms[7]:

$$G(y \ll 1) = \sum_{n=0}^{\infty} a_n y^{2n+1}, \tag{16a}$$

$$G(y \gg 1) = \sum_{n=0}^{\infty} b_n y^{\delta - n/\beta} \tag{16b}$$

(a_n and b_n are parameters of the substance in the critical state), which can be used to calculate the correlation functions of the density fluctuations in a gravitational field on the basis of the method described in the preceding Section.

Vicinity of the critical isochore ($|z^*| \ll t^{\beta\delta}$, $t > 0$). In this limiting case, it follows from (7), (15) and (16a) that

$$y(z^*, t) = \frac{\rho(z^*, t) - \rho_c}{\rho_c t^\beta} = -\frac{|z^*|}{a_0 t^{\beta\delta}} \operatorname{sign} z^*,$$
$$\varphi_{0z}(k^2) = a_0 t^\gamma + bk^2,$$
$$\varphi_1(\mathbf{k}) = \frac{3a_1}{V a_0^2 t^{\beta(\delta+1)}} \int_V z^{*2} e^{i\mathbf{k}\mathbf{r}} d\mathbf{r}. \tag{17}$$

For a layer of substance bounded in the z direction by the planes $z = \pm L$, the function $\varphi_1(\mathbf{k})$ can be calculated easily. In the case of weak nonuniformity, the covariance $\langle \rho_{\mathbf{k}} \rho_{\mathbf{k}'}^* \rangle$ of the Fourier components of the density fluctuations is, in accordance with formula (9) in the first approximation in φ_1/φ_{0Z}, equal to

$$\langle \rho_{\mathbf{k}} \rho_{\mathbf{k}'}^* \rangle = \frac{k_B T}{V P_c (a_0 t^\gamma + bk^2)} \left\{ \delta_{\mathbf{k}\mathbf{k}'} - \frac{3a_1 L^{*2} \delta(k_x, k_x') \delta(k_y, k_y')}{a_0^2 t^{\beta(\delta+1)} (a_0 t^\gamma + bk'^2)} \times \left[\frac{\sin \Delta k^* L^*}{\Delta k^* L^*} \left(1 - \frac{2}{\Delta k^{*2} L^{*2}}\right) + \frac{2 \cos \Delta k^* L^*}{\Delta k^{*2} L^{*2}} \right] \right\},$$

where

$$\Delta k^* = (k_z - k_z') P_c / \rho_c g,$$

and L^* is the result of putting $z = L$ in (15). Here the role of the dimensional constant C in the distribution (7) is played by the critical pressure P_c.

From the general formula (12) for the correlation function $g_0(\mathbf{r}, \mathbf{r}')$ in the vicinity of the critical isochore, we have

$$g_0(\mathbf{r}, \mathbf{r}') = \frac{V}{4\pi b} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \exp\left[-\frac{1}{\sqrt{b}} \left(a_0 t^\gamma + \frac{3a_1 z'^{*2}}{a_0^2 t^{\beta(\delta+1)}} \right)^{1/2} |\mathbf{r} - \mathbf{r}'| \right], \tag{18}$$

whence it follows that the long-range character $g_0(R) \sim R^{-1}$ is conserved only at the critical point itself, when $z^* \to 0$ and $t \to 0$ simultaneously, with the condition $|z^*| \ll t^{\beta\delta}$. The correlation length of the density fluctuations

$$R_{c\ \mathrm{eff}} = \left[\frac{a_0 t^\gamma}{b} + \frac{3a_1 z^{*2}}{b a_0^2 t^{\beta(\delta+1)}} \right]^{-1/2}$$

does not vary at a given height and decreases as we move away from the level with maximum density gradient.

In the case of the smooth nonuniformity created by a gravitational field, the use of the correlation function (18) leads to the following expression for the covariance of the Fourier components of the density fluctuations:

$$\langle \rho_{\mathbf{k}} \rho_{\mathbf{k}'}^* \rangle = \frac{k_B T}{P_c V} \frac{a_0^2 t^{\beta(\delta+1)}}{3a_1 L^*} \delta(k_x, k_x') \delta(k_y, k_y') \times \left\{ \frac{1}{a_0 t^\gamma} \left(\frac{3a_1}{a_0 t^\gamma + bk^2} \right)^{1/2} \left[1 + \frac{1}{2} \Delta k^{*2} \frac{a_0^2 t^{\beta(\delta+1)}}{3a_1} (a_0 t^\gamma + bk^2) \right] \times \operatorname{arctg} \frac{L^*}{a_0 t^\gamma} \left(\frac{3a_1}{a_0 t^\gamma + bk^2} \right)^{1/2} - \frac{1}{2} \Delta k^{*2} L^{*2} \right\},$$

in the derivation of which only small differences $\mathbf{k} - \mathbf{k}'$ have been taken into account.

In the vicinity of the critical isochore, the effect of the gravitational field is characterized by the function $f_1(z^*, t) = 3a_1 z^{*2}/a_0^3 t^{2\beta\delta}$; in connection with this, the length R_0 of the "external" nonuniformity turns out to be of the order of the field variable $z \ll 10^5 t^{\beta\delta}$ cm. At the same time, the length associated with the "internal" fluctuational nonuniformity coincides in magnitude with the correlation length $R_c(t) \lesssim (b/a_0 t^\gamma)^{1/2} \approx 10^{-7} t^{-\gamma/2}$ cm. Thus, for $t \approx 10^{-4}$ and the critical-index values of the 3-dimensional Ising model, the vertical coordinate ($|L| < 10^{-5/3}$ cm) of the boundaries of the region investigated is still considerably greater than $R_c \approx 10^{-9/2}$ cm, so that the use of the correlation function $g_0(\mathbf{r}, \mathbf{r}')$ determined by formula (12) can be considered to be justified in this case. As the critical temperature is approached in the limiting case $y \ll 1$ under consideration, the length R_0 of the "external" nonuniformity decreases and the length R_c of the "internal" nonuniformity simultaneously increases, so that the method proposed in this paper for calculating the critical fluctuations cannot be used.

Vicinity of the critical isotherm ($|z^*| \gg |t|^{\beta\delta}$). From the formulas (7), (15) and (16b), we have the following expressions:

$$y(z^*, t) = -t^{-\beta} \left(\frac{|z^*|}{b_0} \right)^{1/\delta} \left[1 - \frac{b_1}{\delta b_0^{1-1/\beta\delta}} \left(\frac{|z^*|}{t^{\beta\delta}} \right)^{-1/\beta\delta} + \ldots \right] \operatorname{sign} z^*;$$
$$\varphi_{0z} = bk^2, \quad T \to T_c,$$
$$\varphi_1(\mathbf{k}) = \frac{\delta b_0^{1/\delta}}{V} \int_V |z^*|^{1-1/\delta} e^{i\mathbf{k}\mathbf{r}} d\mathbf{r}. \tag{19}$$

If the expressions (9) and (19) are taken into account, in the approximation of weak nonuniformity the covariance $\langle \rho_{\mathbf{k}} \rho_{\mathbf{k}'}^* \rangle$ in the volume of the system bounded by the planes $z = L_1$ and $z = L_2$ has the form, for $T \to T_c$,

$$\langle \rho_{\mathbf{k}} \rho_{\mathbf{k}'}^* \rangle = \frac{k_B T}{V P_c b k^2} \Big\{ \delta_{\mathbf{k}\mathbf{k}'} - \frac{\delta b_0^{1/\delta} \delta(k_x, k_x') \delta(k_y, k_y')}{4(L_2^* - L_1^*) b k'^2} (i\Delta k^*)^{-2+1/\delta}$$
$$\times [1 - (-1)^{-2+1/\delta}] [\gamma(2 - 1/\delta, i\Delta k^* L_2^*) - \gamma(2 - 1/\delta, -i\Delta k^* L_2^*)$$
$$- \gamma(2 - 1/\delta, i\Delta k^* L_1^*) + \gamma(2 - 1/\delta, -i\Delta k^* L_1^*)],$$

where $\gamma(n, x)$ is the incomplete gamma-function.

In the limiting case $y \gg 1$ under consideration, the dependence of $g_0(\mathbf{r}, \mathbf{r}')$ from (12) on the field variable is given by the expression

$$g_0(\mathbf{r}, \mathbf{r}') = \frac{V}{4\pi b} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \exp\left\{ -\frac{|\mathbf{r} - \mathbf{r}'|}{R_c} \right\},$$
$$R_c = \left[\frac{b}{\delta b_0^{1/\delta} z'^{*(1-1/\delta)}} \right]^{1/2}, \qquad (20)$$

and is, naturally, stronger than for $y \ll 1$. The long-range character of the correlation function $g_0(R)$ and the singularity of the correlation length $R_c = [b/\delta b_0^{1/\delta} z'^{*(1-1/\delta)}]^{1/2}$ are found at $T = T_c$ only at the level with maximum density gradient, where $z'^* = 0$.

Near the critical isotherm, the length of the "external" nonuniformity created by the gravitational field is $R_0 \approx z \gg 10^5 t^{\beta\delta}$ cm, whereas the correlation length of the density fluctuations is $R_c(z^*, 0) \approx 10^{-7}/z^{*(\delta-1)/2\delta}$ cm. On decrease of the value of the field variable, the increase of R_c and decrease of R_0 lead to violation of the inequality $R_0 \gg R_c$, which determines the position $z = L_1$ of the lower boundary. The choice of coordinate $z = L_2$ of the upper boundary is dictated by the requirement $L_2^* \ll b_0$, which ensures that one of the parameters of the theory $(\Delta\rho(z^*, t))$ is small.

Vicinity of the coexistence curve ($|z^*| \ll |t|^{\beta\delta}$, $t < 0$). This limiting case can be treated analogously to the case of the vicinity of the critical isochore, if, as has been done previously[12,13], we assume that it is possible to sum the principal singularities of the asymptotic expansions (16a) and (16b). The corresponding calculation of the correlation function in the coordinate representation gives the following result:

$$g_0(\mathbf{r}, \mathbf{r}') = \frac{V}{4\pi b} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \exp\left\{ -\frac{1}{\sqrt{b}} \left[(\delta - 1) a_0 |t|^\gamma + \delta^{1-1/(\delta-1)} \left(\frac{b_0}{a_0} \right)^{1/(\delta-1)} \frac{|z^{*'}|}{t^\beta} \right]^{1/2} |\mathbf{r} - \mathbf{r}'| \right\}. \qquad (21)$$

Formulas illustrating the behavior of the correlation functions in the $\mathbf{k}$-representation can also be obtained easily. As can be seen from (21), the function $f_1(r, t)$ (and also, consequently, the positions of the boundaries of the region investigated) differs only by a numerical factor from the corresponding expression in the case $y \ll 1$.

CRITICAL OPALESCENCE IN AN OPTICALLY NONUNIFORM MEDIUM

The above treatment of the correlation properties of matter near a critical point in the presence of an external field is a basis for the study of molecular scattering in the near-critical state. A consistent account of the spatial nonuniformity induced by the unlimited increase of the susceptibility to external forces requires also the solution of the corresponding electrodynamic problem of the propagation of electromagnetic waves in such an optically nonuniform medium. Features of the transmission and scattering of light near the critical state of individual systems in a gravitational field have been investigated previously[14]. Solving the Maxwell equations in which the height dependence and temperature dependence (associated with the experimental and theoretical investigations of the gravitational effect[15-17,12,13]) of the dielectric permittivity of the substance are taken into account leads to the following expression for the Poynting vector of singly scattered light:

$$\langle \mathbf{S} \rangle = \frac{c}{16\pi} \left(\frac{k_0^2}{4\pi} \right)^2 \left(\rho \frac{\partial \varepsilon}{\partial \rho} \right)_T^2 \frac{1}{L_0^2} \operatorname{Re} \iint_V d\mathbf{R}\, d\mathbf{r}' \exp(-ik_0 \varepsilon_c^{1/2} \mathbf{n}_0 \mathbf{R}) \cdot$$
$$\times g(\mathbf{R}, \mathbf{r}') \varepsilon_0^{-1/2}(z', t) \left[\mathbf{n}_0 (1 + \cos^2\vartheta) + \frac{\Delta\varepsilon(z', t)}{\varepsilon_c} (\mathbf{m}_0 \cos\vartheta - \mathbf{n}_0 \cos^2\vartheta) \right] \cdot$$
$$\times \{ |A^{(-)}|^2 \exp[ik_0 \varepsilon_0^{1/2}(z', t) \mathbf{m}_0 \mathbf{R}] + |A^{(+)}|^2 \exp[-ik_0 \varepsilon_0^{1/2}(z', t) \mathbf{m}_0 \mathbf{R}] \}. \qquad (22)$$

Here $\mathbf{m}_0$ and $\mathbf{n}_0$ are unit vectors in the direction of the incident light beam and the light beam scattered through angle ϑ, $\Delta\epsilon = 3 r_c \rho_c \Delta\rho$ is the deviation of the macroscopic dielectric permittivity $\epsilon_0(z, t)$ from its critical value $\epsilon_c = 1 + 3 r_c \rho_c$, r_c is the critical refractive index, $k_0 = 2\pi/\lambda$, and $A^{(-)}$ and $A^{(+)}$ are the amplitudes of the forward and backward waves which propagate in the plane layer of thickness $\Delta z \gg \lambda$ being studied; in connection with the latter, interference terms are omitted in (22).

Using the density-fluctuation correlation functions $g(\mathbf{R}, \mathbf{r}')$ obtained earlier for the different limiting cases, we shall study the effect of nonuniformities created by a gravitational field on the integral intensity (22) of scattered radiation near a critical point.

In the limiting case corresponding to the vicinity of the critical isochore, integration of the expression (22) over the relative variable $\mathbf{R}$ with the correlation function (18) gives

$$\langle \mathbf{S}(t, \vartheta) \rangle = \frac{V}{2L^*} \operatorname{Re} \int_{-L^*}^{L^*} \mathbf{J}_0(z^*; t, \vartheta) \Big\{ \frac{|A^{(-)}|^2}{\varkappa^2(t) + d_1 z^{*2} + q_-^2 (1 + d_2 z^*)^2}$$
$$+ \frac{|A^{(+)}|^2}{\varkappa^2(t) + d_1 z^{*2} + q_+^2 (1 + d_2 z^*)^2} \Big\} dz^*; \qquad (23)$$
$$\mathbf{J}_0 = \frac{c}{16\pi} \left(\frac{k_0^2}{4\pi} \right)^2 \frac{k_B T}{b P_c L_0^2} \left(\rho \frac{\partial \varepsilon}{\partial \rho} \right)_T^2 \varepsilon_0^{-1/2} \Big\{ \mathbf{n}_0 (1 + \cos^2\vartheta)$$
$$+ \frac{\Delta\varepsilon}{\varepsilon_c} (\mathbf{m}_0 \cos\vartheta - \mathbf{n}_0 \cos^2\vartheta) \Big\},$$
$$\varkappa^2(t) = \frac{a_0 t^\gamma}{b}, \quad d_1 = \frac{3 a_1 f}{a_0^2 b t^{\beta(\delta+1)}}, \quad d_2 = \frac{3 r_c \rho_c f}{2 \varepsilon_c a_0 t^\gamma},$$

$f = 1$ in the presence of the field and $f = 0$ in its absence, and

$$q_\mp = 2^{1/2} k_0 \varepsilon_c^{1/2} (1 \mp \cos\vartheta)^{1/2}$$

is the wave-vector transfer in the directions of the forward and backward waves. The differential cross section $\langle s(z^*; t, \theta) \rangle$ from (23) for radiation scattered at a given level displays a pronounced height dependence, with a maximum at $z^* = 0$; this is fully confirmed by the experimental investigations[18,19,12]. An analysis of the angular dependence of $\langle \mathbf{s}(z^*; t, \vartheta) \rangle$ shows that, as the critical point ($z^* = 0$, $t = 0$) is approached along a direction $|z^*| \ll |t|^{\beta\delta}$, the scattering cross section should increase anomalously not only at zero angle but also in the backward direction $\vartheta = \pi$.

The expression for the projection of $\langle \mathbf{S} \rangle$ on the direction of observation $\mathbf{n}_0$ at small scattering angles:

$$\langle S(q_-^2,t)\rangle=\langle S(q_-^2,t)\rangle_{oz}\left(1-\frac{L^{*2}}{3}\frac{d_1-d_2q_-^2}{\varkappa^2(t)+q_-^2}\right),\qquad(24)$$

goes over in the absence of the external field to the well-known result of OZ theory[20]:

$$\langle S(q_-^2,t)\rangle_{oz}=I_0\frac{\pi V}{2L_0^2\lambda^4}\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_T^2\frac{k_BT(1+\cos^2\vartheta)}{P_c(a_0t^\gamma+bq_-^2)},$$

which determines the scattering power of a macroscopically uniform and isotropic medium.

In the limiting case of the critical isotherm, use of the correlation function (20) in a volume bounded by the planes $z = L_1$ and $z = L_2$ leads, in the expression for the Poynting vector:

$$\langle \mathbf{S}(t,\vartheta)\rangle=\frac{V}{L_2^*-L_1^*}\operatorname{Re}\int_{L_1^*}^{L_2^*}\mathbf{J}_0(z^*;t,\vartheta)\left(\frac{|A^{(-)}|^2}{Q_-}+\frac{|A^{(+)}|^2}{Q_+}\right)dz^*,$$

$$Q_\pm=\frac{\delta b_0^{1/\delta}z^{*(1-1/\delta)}}{b}+q_\pm\left(1+\frac{3r_c\rho_cz^{*1/\delta}}{2\varepsilon_cb_0^{1/\delta}}\right)^2,\qquad(25)$$

to the singularities noted above in the height and angular dependences of $\langle \mathbf{s}(z^*;t,\vartheta)\rangle$ for $t\to0$, $z^*\to0$ ($|t|^{\beta\delta}\ll|z^*|$). In the direction of small scattering angles for $\Delta\epsilon\ll\epsilon_0$, it follows from (25) that

$$\langle S(q_-^2,0)\rangle/\langle S(q_-^2,0)\rangle_{oz}=\frac{1}{L_2^*-L_1^*}\Big[L_2^*F\left(1,\frac{\delta}{\delta-1};\frac{2\delta-1}{\delta-1};-x_2\right)-L_1^*F\left(1,\frac{\delta}{\delta-1};\frac{2\delta-1}{\delta-1};-x_1\right)\Big],$$

$$x_{1,2}=\frac{\delta b_0^{1/\delta}f}{bq_-^2}L_{1,2}^{*(1-1/\delta)},\qquad(26)$$

where $F(a,b;c;x)$ is the hypergeometric function. The deviation, caused by switching on the external field, of the scattering cross section (26) from the corresponding result of the OZ theory is determined by the expression

$$\frac{\langle S(q_-^2,0)\rangle}{\langle S(q_-^2,0)\rangle_{oz}}\approx1-\frac{\delta^2b_0^{1/\delta}f}{(2\delta-1)bq_-^2}\frac{L_2^{*(2-1/\delta)}-L_1^{*(2-1/\delta)}}{L_2^*-L_1^*},\qquad(27)$$

in which the correction to the OZ theory increases with decreasing q_-^2 for fixed dimensions of the scattering layer.

In the vicinity of the coexistence curve, using the correlation function (21) we obtain from the general formula (22) the following expression:

$$\frac{\langle S(q_-^2,t<0)\rangle}{\langle S(q_-^2,t<0)\rangle_{oz}}=1-\frac{1}{(\delta-1)\varkappa^2(|t|)+q_-^2}\Big[\frac{3r_c\rho_c}{\varepsilon_c}\left(\delta\frac{a_0}{b_0}\right)^{1/(\delta-1)}f|t|^\beta q_-^2+\frac{1}{2}L^*\delta^{1-1/(\delta-1)}\left(\frac{b_0}{a_0}\right)^{1/(\delta-1)}f|t|^{-\beta}\Big].\qquad(28)$$

The dependences, determined by formulas (24), (27) and (28), of the reciprocal of the scattering intensity on the square of the wave-vector transfer are, generally speaking, nonlinear. Deviations of this type from OZ theory, which are usually described by introducing a critical index η', can be related naturally to the increasing effect of the nonuniformities caused by the external forces as the critical state is approached. We should expect that a linear dependence of $\langle S(q_-^2)\rangle^{-1}$ will be observed in experimental investigations of the critical opalescence in the layers of "local nonuniformity" defined by the appropriate criterion from[14].

APPENDIX

We shall consider a plane-parallel layer with parameters $-\infty<x,y<\infty$, $-L\le z\le L$. The dela-function constructed from the orthonormal eigenfunctions of the operator $\hat{L}(0;\mathbf{r}';t)=\nabla_R^2-\kappa_{eff}^2(\mathbf{r}',t)$ of the eigenvalue problem with "zero" boundary conditions at the boundaries $z=\pm L$, with the condition that the eigenvalues of the given operator satisfy the relation

$$\lambda^2=k_x^2+k_y^2+k_z^2+\varkappa_{eff}^2(\mathbf{r}',t),$$

(where $\kappa_{eff}^2(\mathbf{r}',t)=\kappa^2[1+f_1(\mathbf{r}',t)]$, k_x and k_y vary continuously from $-\infty$ to ∞, and k_z runs over the discrete series of values $k_z^2=n^2\pi^2/4L^2$ ($n=0,1,2,\ldots$)), has the form

$$\delta(\mathbf{R})=\frac{1}{8\pi^2L}\sum_{n=0}^\infty\iint_{-\infty}^{\infty}[1+(-1)^{n+1}]\cos\frac{n\pi}{2L}R_z\exp[i(k_xR_x+k_yR_y)]dk_xdk_y.$$

Then, for the singular part of the correlation function $g_0(\mathbf{R},\mathbf{r}')$, we have the expression

$$g_0(\mathbf{R},\mathbf{r}')=\frac{V}{8\pi^2Lb}\times\sum_{n=0}^\infty\int_0^\infty\int_0^{2\pi}\frac{\exp(ik_{xy}\rho\cos\varphi)[1+(-1)^{n+1}]\cos(n\pi R_z/2L)}{k_{xy}^2+n^2\pi^2/4L^2+\varkappa_{eff}^2(\mathbf{r}',t)}k_{xy}dk_{xy}d\varphi,\qquad(A.1)$$

in which we have transformed to polar coordinates

$$k_xR_x+k_yR_y=k_{xy}\rho\cos\varphi,\quad\rho=(R_x^2+R_y^2)^{1/2},\quad k_{xy}=(k_x^2+k_y^2)^{1/2}.$$

We note that the uniqueness of the division by the operator $\hat{L}(0;\mathbf{r}',t)$ implies here the rejection of the uniform solution of the equation $\hat{L}g_0(\mathbf{R},\mathbf{r}')=-V\delta(\mathbf{R})/b$.

Performing the integration in (A.1) by taking into account the well-known relations for cylindrical functions[21]

$$e^{ik\rho\cos\varphi}=J_0(k\rho)+2i\cos\varphi J_1(k\rho)+2i^2\cos2\varphi J_2(k\rho)+\ldots,\quad0<\varphi<2\pi,$$

$$\int_0^\infty\frac{kJ_0(k\rho)}{k^2+a^2}dk=K_0(\rho a),$$

we obtain

$$g_0(\mathbf{R},\mathbf{r}')=\frac{V}{4\pi Lb}\sum_{n=0}^\infty K_0\left[\rho\left(\varkappa_{eff}^2(\mathbf{r}',t)+\frac{n^2\pi^2}{4L^2}\right)^{1/2}\right][1+(-1)^{n+1}]\cos\frac{n\pi}{2L}R_z.\qquad(A.2)$$

The Fourier transform of (A.2)

$$g_0(\mathbf{k},\mathbf{k}')=\frac{1}{V^2}\iint_V g_0(\mathbf{R},\mathbf{r}')\exp\{i[\mathbf{kR}+(\mathbf{k}'-\mathbf{k})\mathbf{r}']\}d\mathbf{R}\,d\mathbf{r}'$$

after transformation to polar coordinates and integration over the angle φ takes the form

$$g_0(\mathbf{k},\mathbf{k}')=\frac{1}{VLb}\int_V\Big\{\sum_{n=0}^\infty[1+(-1)^{n+1}]\left(\int_0^\infty K_0\Big[\rho\left(\varkappa_{eff}^2(\mathbf{r}',t)+\frac{n^2\pi^2}{4L^2}\right)^{1/2}\Big]J_0(k_{xy}\rho)\rho\,d\rho\right)\int_0^L\cos\frac{n\pi}{2L}R_z\cos k_zR_z\,dR_z\Big\}e^{i(\mathbf{k}'-\mathbf{k})\mathbf{r}'}d\mathbf{r}'.\qquad(A.3)$$

Using the relations

$$\int_0^\infty\rho K_0\Big[\rho\left(\varkappa_{eff}^2(\mathbf{r}',t)+\frac{n^2\pi^2}{4L^2}\right)^{1/2}\Big]J_0(k_{xy}\rho)d\rho=\Big[k_{xy}^2+\varkappa_{eff}^2(\mathbf{r}',t)+\frac{\pi^2n^2}{4L^2}\Big]^{-1},$$

and

$$\sum_{n=0}^\infty\frac{[1+(-1)^{n+1}]\cos nx}{n^2+a^2}=\frac{\pi}{2a}\operatorname{ch}^{-1}\frac{a\pi}{2}\operatorname{sh}\left(\frac{a\pi}{2}-ax\right),\quad0<x<\pi$$

and integrating (A.3) over R_z, we finally obtain the formula (14) determining the correlation function in the bounded region.

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[1] L. Ornstein and F. Zernike, Z. Phys. 19, 134 (1918); ibid, 27, 761 (1926).

[2] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), "Nauka", M., 1964 (English translation published by Pergamon Press, Oxford, 1969).
[3] A. Munster, Theory of Fluctuations, in Collection "Termodinamika neobratimykh protsessov" (Thermodynamics of Irreversible Processes), IIL, M. (1962) (Original in Proceedings of an "Enrico Fermi Summer School"?).
[4] V. L. Pokrovskiĭ, Usp. Fiz. Nauk **94**, 127 (1968) [Sov. Phys.-Uspekhi **11**, 66 (1968)].
[5] M. E. Fisher, Rep. Prog. Phys. **30**, 615 (1967).
[6] L. P. Kadanoff, W. Götze, D. Hamblen, R. Hecht, E. A. S. Lewis, V. V. Palciauskas, M. Rayl, J. Swift, D. Aspnes, and J. Kane, Rev. Mod. Phys. **39**, 395 (1967).
[7] R. B. Griffiths, Phys. Rev. **158**, 176 (1967).
[8] J. K. Percus and S. Shanack, Preprint NYO-1480-151, N. Y. University (1970).
[9] J. L. Lebowitz and J. K. Percus, J. Math. Phys. **4**, 116 (1963).
[10] A. S. Davydov, Zh. Eksp. Teor. Fiz. **10**, 263 (1940).
[11] D. N. Zubarev, Neravnovesnaya statisticheskaya termodinamika (Nonequilibrium Statistical Thermodynamics), "Nauka", M., 1971 (English translation to be published by Plenum Press, N. Y., 1973 or 1974).
[12] A. V. Chalyĭ and A. D. Alekhin, Zh. Eksp. Teor. Fiz. **59**, 337 (1970) [Sov. Phys.-JETP **32**, 181 (1971)].
[13] L. M. Artyukhovskaya, E. T. Shimanskaya, and Yu. I. Shimanskiĭ, Zh. Eksp. Teor. Fiz. **59**, 688 (1970) [Sov. Phys.-JETP **32**, 375 (1971)].
[14] N. L. Tsyganov and A. V. Chalyĭ, Zh. Eksp. Teor. Fiz. **61**, 1605 (1971) [Sov. Phys.-JETP **34**, 856 (1972)].
[15] E. T. Shimanskaya, Yu. I. Shimanskiĭ, and A. Z. Golik, in the Collection "Kriticheskie yavleniya i fluktuatsii v rastvorakh" (Critical Phenomena and Fluctuations in Solutions), Izd. AN SSSR, M., 1960.
[16] A. V. Voronel' and M. Sh. Giterman, Zh. Eksp. Teor. Fiz. **39**, 1162 (1960) [Sov. Phys.-JETP **12**, 809 (1961)].
[17] M. Sh. Giterman and S. P. Malyshenko, Zh. Eksp. Teor. Fiz. **53**, 2079 (1967) [Sov. Phys.-JETP **26**, 1176 (1968)].
[18] A. D. Alekhin and N. P. Krupskiĭ, ZhETF Pis. Red. **14**, 581 (1971) [JETP Lett. **14**, 403 (1971)].
[19] A. D. Alekhin, A. Z. Golik, and N. K. Krupskiĭ, in the Collection "Sovremennye problemy fizicheskoĭ khimii (voprosy molekulyarnoĭ optiki)" (Modern Problems in Physical Chemistry (Topics in Molecular Optics)), Izd. MGU, M., 1970.
[20] I. L. Fabelinskiĭ, Molekulyarnoe rasseyanie sveta (Molecular Light Scattering), Nauka, M., 1965.
[21] E. T. Whittaker and G. N. Watson, A Course of Modern Analysis, Cambridge University Press, 1927: (Russ. transl., Fizmatgiz, M., 1963).

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