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KINETIC PHENOMENA NEAR THE CRITICAL POINT OF BINARY MIXTURES

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A hydrodynamical method is proposed which enables one to establish a connection between the singular parts of the kinetic coefficients (the viscosity η, the thermal conductivity κ, and the coefficient α which determines the diffusion) which depend upon the nearness to the critical point and the singularities of a product of thermodynamic quantities, namely, the product of the correlation radius r_0 of the fluctuations in the concentration and the derivative $(\partial\mu/\partial c)_{p,T}$ of the chemical potential with respect to the concentration. The results depend on the ratio of the singular ($\Delta\xi$) and regular (ξ_0) parts of the kinetic coefficients, extrapolated from the far region. In the region $\Delta\xi < \xi_0$ all coefficients increase upon approach to a critical point: $\Delta\eta, \Delta\kappa, \Delta\alpha \sim [r_0(\partial\mu/\partial c)_{p,T}]^{-1}$. If $\Delta\xi \geq \xi_0$ then the coefficient of thermal conductivity remains finite; as for the remaining coefficients one can only assert that $\Delta\eta\cdot\Delta\alpha \sim [r_0(\partial\mu/\partial c)_{p,T}]^{-1}$. The coefficient of thermal diffusion does not have a part which increases as the critical point is approached.

1. METHOD OF INVESTIGATION

THE critical points of binary mixtures are characterized by the vanishing of the first two derivatives of the chemical potential of each component with respect to the concentration:

$$\left(\frac{\partial\mu}{\partial c}\right)_{p,T}=\left(\frac{\partial^2\mu}{\partial c^2}\right)_{p,T}=0. \quad (1)$$

A sharp increase in the mean square of the fluctuations of the concentration $\langle\Delta c^2\rangle$ and of the integral of the correlation function $W_{cc}(r)$ of these fluctuations already follows from the definition of the critical points[1]:

$$\langle\Delta c^2\rangle\equiv\langle[c(\mathbf{r})-c_0]^2\rangle\sim(\partial c/\partial\mu)_{p,T};\quad\int W_{cc}(\mathbf{r})d^3\mathbf{r}\sim(\partial c/\partial\mu)_{p,T}. \quad (2)$$

Upon approach to a critical point it is necessary to take into consideration nonlocal and nonsynchronous relations between thermodynamic quantities (spatial and temporal dispersion[2]), which leads to finite expressions in (2). At the same time the correlation radius of the fluctuations in the concentration, which characterizes the distances over which correlation of the fluctuations is essential, increases as a critical point is approached and, according to estimates from experiments on scattering, reaches a value of 10^{-4} to 10^{-5} cm.

Thus, the specific properties of the critical region consist in the appearance of a new characteristic distance r_0, and also $a \ll r_0 \ll L$, where a is the average distance between particles and L is the size of the container.

It is natural that one should expect anomalies in the kinetic properties associated with a displacement of the liquid's particles over distances of the order of or larger than r_0, whereas for a displacement over a distance of order a the particles "do not know" about the critical state. In other words, if the kinetic coefficients are represented in the form of a sum of two parts: $\xi = \xi_0 + \Delta\xi$, defined respectively by scales of order a and r_0, then upon approach to a critical point the strong dependence on $(T - T_c)/T_c$ can apparently only be associated with the "singular" part of the kinetic coefficients, but not with the "regular" part.

Such an assumption is confirmed by the fact that different methods of investigation of one and the same substance (ethane) lead to different results;[1)] in neutron scattering experiments (the characteristic displacements of the particles are of order $a \sim 10^{-7}$ to 10^{-8} cm) no anomalies in the particles' motion were observed in the critical region,[3] in spin-echo experiments (displacements of order $r_0 \sim 10^{-4}$ to 10^{-5} cm) the decrease of the self-diffusion amounts to several tens of a percent,[4] and an abrupt slowing down of the diffusion is observed by chemical methods[5] (displacements of order $L \sim 1$ cm).

The goal of our calculation is to obtain the temperature dependence of the singular parts $\Delta\xi$ of the kinetic coefficients, which determine the macroscopic properties of the liquid, whereas one can hardly determine the regular part without microscopic considerations.

Two assumptions are made as the basis of the calculation. First, since we are interested in the behavior of a liquid over macroscopic distances of the order of r_0, as the equations of motion we take the equations of hydrodynamics for an inhomogeneous and nonstationary mixture. A "hydrodynamical volume" has linear dimensions larger than a but smaller than r_0, i.e., here only a partial averaging over the fluctuations is carried out.

Later on external currents will be introduced into the equations of hydrodynamics, and the changes of the fluctuations caused by these currents will be determined. In the entropy production due to these fluctuations a final averaging of the fluctuations is carried out over distances larger than or of the order of r_0, but smaller than the dimensions of the system L; this also leads to the appearance of singularities with respect to $(T - T_c)/T_c$ in the kinetic coefficients.

The second assumption concerns the form of the

[1)] We compare experiments near the critical point of the pure substance [3,4] and diffusion in this substance, [5] which, however, is not essential for the qualitative considerations presented here.

equation of state which must be added to the system of hydrodynamical equations. Generally speaking the fluctuations are independent or are only correlated, i.e., there is not a unique relation between them. However, in the same way that the two scales of distance indicated above exist, it is natural to also assume that two scales of characteristic times exist: a time for dissipation of the fluctuations in the concentration, which tends to infinity upon approach to the critical point, and a time for the establishment of equilibrium in the remaining variables, whose fluctuations do not possess anomalies at the critical point. Such an "adiabatic approximation" means that for a given nonequilibrium (fluctuation) distribution of the concentration, the remaining thermodynamical variables assume definite values, i.e., one is able to formulate an equation of state in the sense of a nonlocal and nonsynchronous relation between the change of the chemical potential μ and the distribution of the concentration c:[2)]

$$\mu(\mathbf{r},t)-\mu_0=\int\frac{\partial\mu}{\partial c}(\mathbf{r}-\mathbf{r}',t-t')c(\mathbf{r}',t')d^3\mathbf{r}'\,dt' +\frac{\partial\mu}{\partial T}T(\mathbf{r},t)+\frac{\partial\mu}{\partial p}p(\mathbf{r},t). \tag{3}$$

Here and in what follows the kernel of the integral operators, which determine the spatial-temporal dispersion, will be denoted in the same way as the corresponding thermodynamical derivatives to which the zero-Fourier components of the kernel reduce.

The assumptions indicated above lead to a complete system of equations of the form

$$L_1\{\varphi\}+L_2\{\varphi,\varphi\}=0,\ \varphi=\{\mathbf{v},\rho,\mu,t\}. \tag{4}$$

The general scheme of the subsequent calculations consists in the following.[3)] Let us represent all variables φ in the form of a sum of fluctuating parts φ_{fl} and averaged parts φ_{av} which are determined by the external gradients (for example, the velocity gradient $\epsilon_v \equiv \partial v_{\mathrm{av}_x}/\partial y$):

$$\varphi=\varphi_{\mathrm{fl}}+\varphi_{\mathrm{av}}. \tag{5}$$

Expanding the fluctuating quantities in a series in powers of the external gradients

$$\varphi_{\mathrm{fl}}=\varphi_{\mathrm{fl}}{}^0+\varepsilon\varphi_{\mathrm{fl}}{}^1, \tag{6}$$

we isolate the terms of corresponding order in ϵ in the system of equations (4).

The equation of zero order in ϵ

$$L_1\{\varphi_{\mathrm{fl}}{}^0\}+L_2\{\varphi_{\mathrm{fl}}{}^0,\varphi_{\mathrm{fl}}{}^0\}=0 \tag{7}$$

describes the equilibrium thermal fluctuations in the absence of external gradients. The method of investigation of Eqs. (7), which is based on the fluctuation-dispersion theorem and associated with the introduction of the so-called external forces[7] into the system of linearized equations, enables one to investigate the correlation properties of the fluctuations.

From the equations of first order in ϵ

$$L_1\{\varphi_{\mathrm{fl}}{}^1\}=-L_2\{\varphi_{\mathrm{fl}}{}^0,\varphi_{\mathrm{av}}\} \tag{8}$$

one can find the change of the thermal fluctuations due to the presence of the external currents.

Finally, the last stage of the calculations consists in an evaluation of the entropy production and the identification of the coefficients for the squares of the external gradients with the singular parts of the kinetic coefficients:

$$\frac{\partial}{\partial t}\int\rho s\,d^3\mathbf{r}=\sum_{\{\varphi\}}\int\xi_\varphi(\nabla\varphi_{\mathrm{fl}}{}^1)^2d^3\mathbf{r}\equiv V\Delta\xi_\varphi\varepsilon_\varphi{}^2, \tag{9}$$

where V denotes the volume of the system.

Assigning the external gradients in a different way we arrive at a system of equations which expresses the singular parts of the kinetic coefficients in terms of the kernel $\partial\mu/\partial c$ of the equation of state (3) and the parameters of the hydrodynamical equations, in particular, in terms of the kinetic coefficients themselves.

As one would expect, the hydrodynamical method which we are using does not enable us to directly determine the singularities of the kinetic coefficients. With its aid one can only find relations between the singularities of different equilibrium and kinetic quantities.

In Sec. 2 the correlators of the hydrodynamical quantities in binary mixtures and in the presence of spatial and temporal dispersion are obtained from the system of equations (7). The solution of Eqs. (8) for the fluctuations which are changing due to the external currents and an analysis of expression (9) for the entropy production comprise the contents of Sec. 3. Finally, in Sec. 4 the obtained formulas are analyzed, and the nature of the singularities of the kinetic coefficients near the critical point of binary mixtures is clarified.

2. HYDRODYNAMICAL FLUCTUATIONS IN BINARY MIXTURES IN THE PRESENCE OF DISPERSION

The total system of hydrodynamical equations contains the equation of state and the conservation laws for the mass of the mixture, the mass of each component, momentum, and energy:

$$\frac{d\rho}{dt}=-\rho\operatorname{div}\mathbf{v};\ \rho\frac{dc}{dt}=-\operatorname{div}\mathbf{j};\ \rho\frac{d\mathbf{v}}{dt}=-\nabla p+\operatorname{div}\sigma_{ik}';$$
$$\rho T\frac{ds}{dt}=-\operatorname{div}(\mathbf{q}-\mu\mathbf{j})-\mathbf{j}\nabla\mu+\sigma_{ik}'\frac{\partial v_i}{\partial x_k}. \tag{10}$$

We shall assume that taking account of spatial-temporal dispersion reduces to the appearance of a nonlocal and nonsynchronous relation in the well-known expressions for the currents:[8]

$$\begin{aligned}\sigma_{ik}'&=\int\eta(\mathbf{r}-\mathbf{r}',t-t')\left(\frac{\partial v_i}{\partial x_k'}+\frac{\partial v_k}{\partial x_i'}\right)d^3\mathbf{r}'\,dt'\\&+\delta_{ik}\int\left[\zeta(\mathbf{r}-\mathbf{r}',t-t')-\frac{2}{3}\eta(\mathbf{r}-\mathbf{r}',t-t')\right]\frac{\partial v_m(\mathbf{r}',t')}{\partial x_m'}d^3\mathbf{r}'\,dt';\\ q_m-\mu j_m&=-\int[T_0\beta(\mathbf{r}-\mathbf{r}',t-t')\nabla_m\mu(\mathbf{r}',t')\\&+\gamma(\mathbf{r}-\mathbf{r}',t-t')\nabla_mT(\mathbf{r}',t')]\,d^3\mathbf{r}'\,dt';\\ j_m&=-\int[\alpha(\mathbf{r}-\mathbf{r}',t-t')\nabla_m\mu(\mathbf{r}',t')+\beta(\mathbf{r}-\mathbf{r}',t-t')\nabla_mT(\mathbf{r}',t')]d^3\mathbf{r}'dt'.\end{aligned} \tag{11}$$

Finally, in order to solve the system of equations (10) it is necessary to use the relations which connect the

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[2)] Temporal dispersion, as usual, takes the retardation in time into account. Of course, it does not have a rigorous thermodynamical meaning and corresponds to the fact that averaging over the time is equivalent to averaging over ensembles. However, the presence or absence of temporal dispersion does not affect the final results.

[3)] An analogous calculation for a pure substance was carried out by us earlier. [2,6]

entropy with the other thermodynamical quantities. With dispersion taken into account, these relations have the form

$$\frac{ds}{dt} = \int \Big[\frac{\partial s}{\partial T}(\mathbf{r}-\mathbf{r}', t-t')\frac{dT(\mathbf{r}', t')}{dt'} + \frac{\partial s}{\partial \mu}(\mathbf{r}-\mathbf{r}', t-t')\frac{d\mu(\mathbf{r}', t')}{dt'} + \frac{\partial s}{\partial \rho}(\mathbf{r}-\mathbf{r}', t-t')\frac{d\rho(\mathbf{r}', t')}{dt'} \Big] d^3\mathbf{r}'\, dt'. \tag{12}$$

In order to study the correlation properties of the equilibrium fluctuations, one can apply the fluctuation-dissipation theorem which, as is well-known,[7,8] establishes a relation between the properties of these fluctuations and the generalized susceptibilities—the linear responses of the system to an external influence.

One can combine these two problems into one by introducing the so-called external forces f^{ex} into the equations of motion of the quantities x of interest to us, assuming that these forces produce the given fluctuations. Then the solution of the equations of motion

$$x_m(\mathbf{r}, t) = \sum_n \int \alpha_{mn}(\mathbf{r}-\mathbf{r}', t-t') f_n^{\mathrm{ex}}(\mathbf{r}', t')\, d^3\mathbf{r}'\, dt' \tag{13}$$

immediately determines the correlation properties of the quantity x, notably the Fourier components of the correlation function are expressed in terms of the generalized susceptibility α_{mn}:

$$\langle x_m(\mathbf{r}, t) x_n(\mathbf{r}', t')\rangle_{\omega,\mathbf{k}} = \frac{i\hbar}{4\pi}(2\pi)^3 \operatorname{cth}\frac{\hbar\omega}{2T}\left[\alpha_{mn}(\omega, \mathbf{k}) - \alpha_{mn}^*(\omega, \mathbf{k})\right]$$
$$\approx \frac{iT}{2\pi}(2\pi)^3 \frac{1}{\omega}\left[\alpha_{mn}(\omega, \mathbf{k}) - \alpha_{nm}^*(\omega, \mathbf{k})\right]. \tag{14}$$

In Eq. (14) it is taken into consideration that in the classical case of interest to us $\coth(\hbar\omega/2T)$ can be replaced by $2T/\hbar\omega$.

The correspondence between the quantities x and f^{ex} is established with the aid of the expression for the rate of change of the entropy:

$$\frac{\partial}{\partial t}\int \rho s\, d^3\mathbf{r} = -T_0 \sum_m \int d^3\mathbf{r} f_m(\mathbf{r}, t) x_m(\mathbf{r}, t)\, d^3\mathbf{r}. \tag{15}$$

Thus, the scheme for application of the fluctuation-dissipation theorem is as follows: 1) selection of the quantities x_m of interest to us; 2) determination according to Eq. (15) of the corresponding generalized forces f_m^{ex}; extraction of the solutions of the linear equations of motion for x_m in terms of the external forces f_m^{ex} in the form (13); (4) expression of the correlators (14) in terms of the generalized susceptibilities α_{mn} found in (13).

Proceeding to a realization of this scheme, we shall utilize the following expression for the production of entropy in a binary mixture:[8]

$$\frac{\partial}{\partial t}\int \rho s\, d^3\mathbf{r} = -\int \frac{(\mathbf{q}-\mu\mathbf{j})\nabla T}{T_0^2} d^3\mathbf{r} - \int \frac{1}{T_0}\mathbf{j}\nabla\mu\, d^3\mathbf{r} + \frac{1}{2}\int \frac{\sigma_{ik}'}{T_0}\left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i}\right) d^3\mathbf{r}. \tag{16}$$

From a comparison of (15) and (16) we define three types of generalized forces and coordinates:

$$x_m^{(T)} = \frac{ik_m T}{T_0}, \quad x_m^{(\mu)} = ik_m\mu, \quad x_{mn} = {}^1\!/_2 i(k_m v_n + k_n v_m),$$
$$f_m^{(T)} = -\frac{q_m^{\mathrm{ex}} - \mu j_m^{\mathrm{ex}}}{i\omega}, \; f_m^{(\mu)} = -\frac{j_m^{\mathrm{ex}}}{i\omega}, \; f_{mn} = \frac{\sigma_{mn}^{\mathrm{ex}}}{i\omega}. \tag{17}$$

In (17) and everywhere below, unless explicitly stated otherwise we shall use the Fourier components of the corresponding quantities, defined in the following way:

$$\varphi(\mathbf{r}, t) = \int \frac{d^3\mathbf{k}}{(2\pi)^3} d\omega\, \varphi(\omega, \mathbf{k})\, e^{i(\mathbf{kr}-\omega t)}. \tag{18}$$

Now let us write down the linearized equations (3) and (10)—(12) with the external currents (17) introduced into them, where we choose as the independent variables the chemical potential $\mu = (\mu_1/m_1) - (\mu_2/m_2)$ of the mixture, the density of the mixture ρ, and the temperature T. Such a choice of variables is convenient since the derivatives of the corresponding thermodynamical potential with respect to ρ, μ, and T do not have singularities at the critical point. In addition, the fluctuations of only one of these variables—the density—increase anomalously upon approach to the critical point. Actually, together with the fluctuations in the concentration (2) the fluctuations of all three quantities φ increase provided $\partial\varphi/\partial c$ remains finite or decreases more slowly than the square root of the fluctuations in the concentration, whereas according to Eq. (1) $(\partial\mu/\partial c)_{p,T}$ abruptly decreases as the critical point is approached and so does $(\partial T/\partial c)_{p,\mu}$ (it follows from experiment that $(\partial\mu/\partial T)_{p,c}$ is finite); meanwhile $(\partial\rho/\partial c)$ remains finite.

The system of the linearized equations of hydrodynamics in the variables ρ, μ, and T with external forces may be reduced to the following form:4)

$$T_0 G_4(\omega, \mathbf{k})\frac{T(\omega, \mathbf{k})}{T_0} + i\omega T_0 p_T \frac{\rho(\omega, \mathbf{k})}{\rho_0} + G_2(\omega, \mathbf{k})\mu(\omega, \mathbf{k}) = -ik_m(q_m^{\mathrm{ex}} - \mu j_m^{\mathrm{ex}}),$$
$$T_0 p_T k^2 \frac{T(\omega, \mathbf{k})}{T_0} - \rho_0 G_1(\omega, \mathbf{k})\frac{\rho(\omega, \mathbf{k})}{\rho_0} - \rho_0^2 c_\rho k^2 \mu(\omega, \mathbf{k}) = k_m k_n \sigma_{mn}^{\mathrm{ex}}, \tag{19}$$
$$G_2(\omega, \mathbf{k})\frac{T(\omega, \mathbf{k})}{T_0} - i\rho_0^2 c_\rho \omega \frac{\rho(\omega, \mathbf{k})}{\rho_0} + G_3(\omega, \mathbf{k})\mu(\omega, \mathbf{k}) = -ik_m j_m^{\mathrm{ex}},$$

where the following notation has been introduced

$$G_1(\omega, \mathbf{k}) = \omega^2 - k^2 p_\rho + \frac{i\omega k^2}{\rho_0}\left(\frac{4}{3}\eta + \zeta\right), \quad G_2(\omega, \mathbf{k}) = -i\omega\rho_0 T_0 s_\mu + T_0\beta k^2,$$
$$G_3(\omega, \mathbf{k}) = -i\omega\rho_0 c_\mu + \alpha k^2, \; G_4(\omega, \mathbf{k}) = -i\omega\rho_0 T_0 s_T + \gamma k^2, \tag{20}$$
$$\alpha = \alpha(\omega, \mathbf{k})\ldots, \quad c_\rho = (\partial c/\partial\rho)_{T,\mu}\ldots,$$

All of the "thermodynamical derivatives" appearing in Eqs. (19) and (20) are functions of ω and k so that strictly speaking only the components with $\omega = 0$ and $\mathbf{k} = 0$ have thermodynamical meaning.

For an unbounded medium the system of Eqs. (19) has the following solutions:

$$\frac{T}{T_0} = \frac{1}{\Delta}\{-iA_{11}k_m(q_m^{\mathrm{ex}} - \mu j_m^{\mathrm{ex}}) - A_{21}k_m k_n \sigma_{mn}^{\mathrm{ex}} - iA_{31}k_m j_m^{\mathrm{ex}}\},$$

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4) In order to obtain Eqs. (19) the equalities

$$\left(\frac{\partial c}{\partial T}\right)_{\mu,\rho} = \left(\frac{\partial s}{\partial \mu}\right)_{T,\rho} \text{ and } \rho_0^2\left(\frac{\partial c}{\partial \rho}\right)_{T,\mu} = -\left(\frac{\partial p}{\partial \mu}\right)_{T,\rho}$$

were utilized which, generally speaking, are valid only in thermodynamics, i.e., for $\omega = 0$ and $\mathbf{k} = 0$. If the fulfillment of these qualities is not required then, performing the following transformations we arrive at susceptibilities (23) for which the principle of symmetry of the kinetic coefficients (the Onsager relations) will be satisfied only upon fulfillment of the indicated equalities. This is associated with the "quasistatistical character" of the thermodynamical states we are considering.

$$\begin{aligned}\frac{\rho}{\rho_0} &= \frac{1}{\Delta}\{iA_{12}k_m(q_m{}^{\text{ex}} - \mu j_m{}^{\text{ex}}) + A_{22}k_mk_n\sigma_{mn}{}^{\text{ex}} + iA_{32}j_m{}^{\text{ex}}\},\\ \mu &= \frac{1}{\Delta}\{-iA_{13}k_m(q_m{}^{\text{ex}} - \mu j_m{}^{\text{ex}}) - A_{23}k_mk_n\sigma_{mn}^{\text{ex}} - iA_{33}j_m{}^{\text{ex}}\}, \qquad (21)\\ v_\alpha &= \frac{1}{\Delta}\{A_{21}k_\alpha k_m(q_m{}^{\text{ex}} - \mu j_m{}^{\text{ex}}) + A_{23}k_\alpha k_m j_m{}^{\text{ex}}\} + iM_{\alpha m}k_n\sigma_{mn}^{\text{ex}},\end{aligned}$$

where

$$M_{\alpha m} = \frac{1}{-i\rho_0\omega + \eta k^2}\Big\{\delta_{\alpha m} + \frac{k_\alpha k_m}{\Delta}[T_0p_TA_{21} - [\rho_0p_\rho - i\omega\,({}^1\!/_3\eta + \zeta)]A_{22} - \rho_0{}^2c_\rho A_{23}]\Big\}.$$

The determinant of the system of equations (19) enters into formula (21):

$$\Delta = \begin{vmatrix} T_0G_4 & i\omega T_0p_T & G_2\\ T_0p_Tk^2 & -\rho_0G_1 & -\rho_0{}^2c_\rho k^2\\ G_2 & -i\rho_0{}^2c_\rho\omega & G_3\end{vmatrix}, \qquad (22)$$

and also the minors A_{ij} of this determinant.

Now introducing the generalized forces and coordinates (17) into (21), we obtain relations of the type (13), from which one can easily find the generalized susceptibilities α:

$$\begin{gathered}\alpha_{mn}^{\text{TT}} = -i\omega\frac{A_{11}}{\Delta}k_mk_n, \quad \alpha_{mn}^{\mu\mu} = -i\omega\frac{A_{33}}{\Delta}k_mk_n; \quad \alpha_{mn}^{\text{T}\mu} = -i\omega\frac{A_{31}}{\Delta}k_mk_n,\\ \alpha_{mn,\,r}^{\text{T}} = \alpha_{r,\,mn}^{\text{T}} = \omega\frac{A_{21}}{\Delta}k_mk_nk_r; \quad \alpha_{mn,\,r}^{\mu} = \alpha_{r,\,mn}^{\mu} = \omega\frac{A_{23}}{\Delta}k_mk_nk_r,\\ \alpha_{mn,\,pr} = -\frac{i\omega}{4}[k_r(k_mM_{np} + k_nM_{mp}) + k_p(k_mM_{nr} + k_nM_{mr})].\end{gathered} \qquad (23)$$

From (23) it is easy to see that upon fulfillment of the equalities indicated in the footnote to formula (19), the susceptibilities satisfy the symmetry relations of the kinetic coefficients (the Onsager relations), which have the following form in the ω, **k**-representation:

$$\alpha_{mn}(\omega, \mathbf{k}) = \pm\,\alpha_{nm}(\omega, -\mathbf{k}), \qquad (24)$$

where the ± signs refer to the cases when the generalized coordinates x_m and x_n, respectively, have the same or different symmetries with respect to a change of the sign of the time.

Now substituting (23) into (14) and taking the definition of the generalized coordinates (17) into account, we obtain the desired correlation functions:

$$\begin{gathered}\langle\rho\rho\rangle_{\omega,\mathbf{k}} = -\frac{T_0}{\pi}(2\pi)^3\frac{\rho_0{}^2k^2}{\omega}\operatorname{Im}\Big(\frac{A_{22}}{\Delta}\Big);\\ \langle TT\rangle_{\omega,\mathbf{k}} = -\frac{T_0}{\pi}(2\pi)^3T_0{}^2\operatorname{Im}\Big(\frac{iA_{11}}{\Delta}\Big);\\ \langle\mu\mu\rangle_{\omega,\,\mathbf{k}} = -\frac{T_0}{\pi}(2\pi)^3\operatorname{Im}\Big(\frac{iA_{33}}{\Delta}\Big); \qquad (25)\\ \langle\rho T\rangle_{\omega,\,\mathbf{k}} = -\frac{T_0}{\pi}(2\pi)^3\frac{T_0\rho_0k^2}{\omega}\operatorname{Im}\Big(-\frac{iA_{21}}{\Delta}\Big);\\ \langle T\mu\rangle_{\omega,\,\mathbf{k}} = -\frac{T_0}{\pi}(2\pi)^3T_0\operatorname{Im}\Big(\frac{iA_{31}}{\Delta}\Big); \quad \langle v_mv_n\rangle_{\omega,\,\mathbf{k}} = \frac{T_0}{\pi}(2\pi)^3\operatorname{Im}(iM_{mn}).\end{gathered}$$

Now let us verify that the expressions obtained above for the correlators do not contradict the well-known thermodynamical formulas[1] and reduce to them if dispersion is neglected.

Taking the inverse Fourier transform in the correlator $\langle\rho\rho\rangle_{\omega,\mathbf{k}}$ and using the Kramers-Kronig relations[1] for the integration over ω, we obtain

$$\langle\rho(\mathbf{r}, t)\rho(\mathbf{r}', t)\rangle = T_0\rho_0\int\frac{d^3\mathbf{k}}{(2\pi)^3}\frac{\exp[i\mathbf{k}(\mathbf{r} - \mathbf{r}')]}{p_\rho(0, \mathbf{k})}. \qquad (26)$$

The same limiting transformation for the correlator of the temperature leads to the following result:

$$\langle T(\mathbf{r}, t)T(\mathbf{r}', t)\rangle = \frac{T_0}{\rho_0}\int\frac{d^3\mathbf{k}}{(2\pi)^3}\frac{\exp[i\mathbf{k}(\mathbf{r} - r')]}{(\partial s/\partial T)_{\rho,c}(0, \mathbf{k})}. \qquad (27)$$

It is not difficult to verify that the correlators $\langle\rho \mathrm{T}\rangle$ and $\langle\rho\mu\rangle$ give zero upon integration over ω, which corresponds to statistical independence of the corresponding fluctuations.

Expressing the correlator of the concentrations in terms of the correlators of the thermodynamical quantities (25), we arrive at the well-known expression:

$$\langle c(\mathbf{r}, t)c(\mathbf{r}', t)\rangle = \frac{T_0}{\rho_0}\int\frac{d^3\mathbf{k}}{(2\pi)^3}\frac{\exp[i\mathbf{k}(\mathbf{r} - \mathbf{r}')]}{(\partial\mu/\partial c)_{p,T}(0, \mathbf{k})}, \qquad (28)$$

which gives the correct expression for the thermodynamical fluctuations of the concentration[1] if dispersion is neglected.

I. M. Khalatnikov has calculated the correlators of the external forces in the hydrodynamical equations of a superfluid liquid (without dispersion).[9] Our Eqs. (19), written in the form $x_m = \alpha_{mn}^{-1}f_n^{\text{ex}}$, also enable us to find the correlators of the external forces

$$\langle f_m{}^{\text{ex}}f_n{}^{\text{ex}}\rangle_\omega = -\frac{T_0}{\pi\omega}\operatorname{Im}\alpha_{mn}^{-1},$$

which coincides with the results of article [9] in the absence of dispersion.

3. EVALUATION OF THE SINGULAR PARTS OF THE KINETIC COEFFICIENTS

According to the general plan of the calculation indicated in Sec. 1, we must now determine the change of the thermal fluctuations (φ_{fl}^1) associated with the external influences (the "average" quantities) applied to the system. Substituting (5) and (6) into the system of hydrodynamics (10), eliminating the velocity, and collecting terms of first order in the external gradients, we obtain

$$\begin{gathered}T_0G_4(\omega, \mathbf{k})\frac{T_{\text{fl}}{}^1(\omega, \mathbf{k})}{T_0} + i\omega T_0p_T\frac{\rho_{\text{fl}}{}^1(\omega, \mathbf{k})}{\rho_0} + G_2(\omega, \mathbf{k})\mu_{\text{fl}}{}^1(\omega, \mathbf{k}) = R_1(\omega, \mathbf{k}),\\ T_0p_Tk^2\frac{T_{\text{fl}}{}^1(\omega, \mathbf{k})}{T_0} - \rho_0G_1(\omega, \mathbf{k})\frac{\rho_{\text{fl}}{}^1(\omega, \mathbf{k})}{\rho_0} - \\ -\rho_0{}^2c_\rho k^2\mu_{\text{fl}}{}^1(\omega, \mathbf{k}) = -R_2(\omega, \mathbf{k}), \qquad (29)\\ G_2(\omega, \mathbf{k})\frac{T_{\text{fl}}{}^1(\omega, \mathbf{k})}{T_0} - i\rho_0{}^2c_\rho\omega\frac{\rho_{\text{fl}}{}^1(\omega, \mathbf{k})}{\rho_0} + G_3(\omega, \mathbf{k})\mu_{\text{fl}}{}^1(\omega, \mathbf{k}) = R_3(\omega, \mathbf{k}),\end{gathered}$$

where

$$\begin{aligned}R_1(\mathbf{r}, t) &= -(\rho_0T_{\text{fl}}{}^0 + T_0\rho_{\text{fl}}{}^0)\frac{\partial s_{\text{av}}}{\partial t} - (\rho_0T_{\text{av}} + T_0\rho_{\text{av}})\frac{\partial s_{\text{fl}}{}^0}{\partial t}\\ &\quad - \rho_0T_0\mathbf{v}_{\text{av}}\nabla s_{\text{fl}}{}^0 - \rho_0T_0\int\mathbf{v}_{\text{fl}}{}^0(\mathbf{r}', t')[s_T(\mathbf{r} - \mathbf{r}'\ t - t')\nabla T_{\text{av}}(\mathbf{r}', t')\\ &\quad + s_\mu(\mathbf{r} - \mathbf{r}', t - t')\nabla\mu_{\text{av}}(\mathbf{r}', t')]\,d^3\mathbf{r}'\,dt' +\\ &\quad + \eta\Big(\frac{\partial v_{\text{av}\,i}}{\partial x_k} + \frac{\partial v_{\text{av}\,k}}{\partial x_i}\Big)\Big(\frac{\partial v^0_{\text{fl}\,i}}{\partial x_k} + \frac{\partial v_{\text{fl}\,k}}{\partial x_i}\Big) + 2\Big(\zeta - \frac{\eta}{3}\Big)\frac{\partial v_{\text{av}\,i}}{\partial x_i}\frac{\partial v^0_{\text{fl}\,k}}{\partial x_k}; \qquad (30)\\ R_2(\mathbf{r}, t) &= \operatorname{div}R_2' - \Big[\frac{\partial}{\partial t} - \frac{1}{\rho_0}\Big(\zeta + \frac{4}{3}\eta\Big)\Delta\Big]R_2''\\ &\equiv -\operatorname{div}\Big\{\rho_0[(\mathbf{v}_{\text{av}}\nabla)\mathbf{v}_{\text{fl}}{}^0 + (\mathbf{v}_{\text{fl}}{}^0\nabla)\mathbf{v}_{\text{av}}] + \Big(\rho_{\text{av}}\frac{\partial\mathbf{v}_{\text{fl}}{}^0}{\partial t} + \rho_{\text{fl}}{}^0\frac{\partial\mathbf{v}_{\text{av}}}{\partial t}\Big)\Big\}\\ &\quad + \Big[\frac{\partial}{\partial t} - \frac{1}{\rho_0}\Big(\zeta + \frac{4}{3}\eta\Big)\Delta\Big]\operatorname{div}(\rho_{\text{fl}}{}^0\mathbf{v}_{\text{av}} + \rho_{\text{av}}\mathbf{v}_{\text{fl}}{}^0);\\ R_3(\mathbf{r}, t) &= -\rho_{\text{fl}}{}^0\frac{\partial c_{\text{av}}}{\partial t} - \rho_{\text{av}}\frac{\partial c_{\text{fl}}{}^0}{\partial t} - \rho_0\mathbf{v}_{\text{av}}\nabla c_{\text{fl}}\end{aligned}$$

$$-\rho_0\int \mathbf{v}_{\mathrm{fl}}^{0}(\mathbf{r}',t')[c_T(\mathbf{r}-\mathbf{r}',t-t')\nabla T_{\mathrm{av}}(\mathbf{r}',t')$$
$$+c_\mu(\mathbf{r}-\mathbf{r}',t-t')\nabla\mu_{\mathrm{av}}(\mathbf{r}',t')]\,d^3r'\,dt'.$$

The left hand side of Eqs. (29) represents the system of linearized equations (19); its determinant and the matrix of the minors of this determinant are given above (see Eq. (22)). Only the terms responsible for the dissipation of energy and momentum, each of which is the product of the average quantities and the thermal fluctuations ($\varphi_{\mathrm{fl}}^{0}$) which were investigated in Sec. 2, remain on the right-hand sides of these equations.

The solution of the system of equations (29) has the form

$$\frac{T_{\mathrm{fl}}^{1}(\omega,\mathbf{k})}{T_0}=\sum_{i=1}^{3}\frac{A_{i1}(\omega,\mathbf{k})R_i(\omega,\mathbf{k})}{\Delta(\omega,\mathbf{k})};\quad \frac{\rho_{\mathrm{fl}}^{1}(\omega,\mathbf{k})}{\rho_0}=$$
$$=-\sum_{i=1}^{3}\frac{A_{i2}(\omega,\mathbf{k})R_i(\omega,\mathbf{k})}{\Delta(\omega,\mathbf{k})};\quad \mu_{\mathrm{fl}}^{1}(\omega,\mathbf{k})=\sum_{i=1}^{3}\frac{A_{i3}(\omega,\mathbf{k})R_i(\omega,\mathbf{k})}{\Delta(\omega,\mathbf{k})};\tag{31}$$
$$v_{\mathrm{fl},m}^{1}(\omega,\mathbf{k})=-\frac{ik_m}{\Delta(\omega,\mathbf{k})}[A_{21}(\omega,\mathbf{k})R_1(\omega,\mathbf{k})+A_{23}(\omega,\mathbf{k})R_3(\omega,\mathbf{k})]$$
$$+M_{m\alpha}(\omega,\mathbf{k})R_{2\alpha}'(\omega,\mathbf{k})+\frac{ik_m}{\rho_0}\left(\zeta+\frac{\eta}{3}\right)\frac{R_2''(\omega,\mathbf{k})}{-i\omega\rho_0+\eta k^2},$$

and the function $M_{m\alpha}(\omega, \mathbf{k})$ is defined in Eq. (21).

Now let us consider the additional production of entropy associated with these transformed fluctuations, for which in the general formula (16) we substitute expression (11) for the currents of the fluctuating quantities. Expanding the integrand in a Fourier series and carrying out the averaging over distances larger than the correlation radius, we obtain

$$\frac{\partial}{\partial t}\int\rho s\,d^3\mathbf{r}=\sum_{m,\,n=1}^{3}\int(\mathbf{k}'\mathbf{k}'')\frac{D_{mn}(\omega',\mathbf{k}';\omega'',\mathbf{k}'')}{\Delta(\omega',\mathbf{k}')\Delta(\omega'',\mathbf{k}'')}\langle R_m(\omega',\mathbf{k}')R_n(\omega'',\mathbf{k}'')\rangle$$
$$\times\exp\{i[(\mathbf{k}'+\mathbf{k}'')\mathbf{r}-(\omega'+\omega'')t]\}\,d^3\mathbf{k}'\,d^3\mathbf{k}''\,d\omega'\,d\omega''\,d^3\mathbf{r}+\left(\frac{\partial s^1}{\partial t}\right)_{\mathrm{visc}},\tag{32}$$

where

$$D_{mn}(\omega',\mathbf{k}';\omega'',\mathbf{k}'')=\gamma(\omega',\mathbf{k}')A_{m1}(\omega',\mathbf{k}')A_{n1}(\omega''\mathbf{k}'')$$
$$+\frac{\alpha(\omega'\ \mathbf{k}')}{T_0}A_{m3}(\omega',\mathbf{k}')A_{n3}(\omega'',\mathbf{k}'')+\frac{\beta(\omega',\mathbf{k}')}{T_0}A_{m1}(\omega',\mathbf{k}')A_{n3}(\omega'',\mathbf{k}'')$$
$$+\frac{\beta(\omega'',\mathbf{k}'')}{T_0}A_{m3}(\omega',\mathbf{k}')A_{n1}(\omega'',\mathbf{k}'').\tag{33}$$

The term $(\partial s^1/\partial t)_{\mathrm{visc}}$ in Eq. (32) determines the entropy production associated with the viscosity which, as it turns out, does not have any singularities in the critical region.

The averaging of the integrand in (32) leads to the appearance in the integrals (32) of the correlators of the thermal fluctuations (25), i.e., the integral over the frequencies in (32) reduces to expressions of the form

$$I_1=\int\frac{\Phi_1(\omega,\mathbf{k})\,d\omega}{\Delta^2(\omega,\mathbf{k})\Delta^{*2}(\omega,\mathbf{k})};$$
$$I_2=\int\frac{\Phi_2(\omega,\mathbf{k})\,d\omega}{\Delta(\omega,\mathbf{k})\Delta^*(\omega,\mathbf{k})(\omega\rho_0+i\eta k^2)(\omega\rho_0-i\eta k^2)}.\tag{34}$$

We shall evaluate the integrals (34) with the aid of the theory of residues. The poles of the integrands correspond to the solutions of the equations $\Delta(\omega, \mathbf{k}) = 0$, $\Delta^*(\omega, \mathbf{k}) = 0$, and $\omega\rho_0 \pm i\eta k^2 = 0$. For an exact evaluation of these integrals it is necessary to know the spatial-temporal dispersion of all of the liquid's parameters; however, one can estimate the singular part of these integrals without this. In fact, let $\omega_{\mathrm{min}}(\mathbf{k})$ be the lowest root of the equation $\Delta^*(\omega, \mathbf{k}) = 0$, where $\omega_{\mathrm{min}}(\mathbf{k}) \to 0$ as $\mathbf{k} \to 0$ and as the temperature approaches the critical temperature. An analysis of expression (22) indicates that such a root exists and under the natural assumptions

$$\rho_0^{-1}c_\mu^{-1}p_\rho^{-1}(^4\!/_3\eta+\zeta)(T_0\alpha\gamma-T_0^2\beta^2)k^2\ll\rho_0T_0(\gamma+T_0\alpha\mu_T^2+2T_0\beta\mu_T)\tag{35}$$

it is given by

$$\omega_{min}(\mathbf{k})=i\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\frac{(T_0\alpha\gamma-T_0^2\beta^2)k^2}{T_0(\gamma+T_0\alpha\mu_T^2+2T_0\beta\mu_T)\rho_0}.\tag{36}$$

We notice that $(\partial\mu/\partial c)_{p,T}(\omega, \mathbf{k})$ enters into Eq. (36); this derivative decreases abruptly (like a step-function with respect to $(T - T_c)/T_c$) as $\omega \to 0$ and $\mathbf{k} \to 0$. In the final analysis it is precisely this quantity which determines the singularities of the kinetic coefficients at the critical point. The remaining roots of the equation $\Delta^*(\omega, \mathbf{k})$ do not contain $(\partial\mu/\partial c)_{p,T}$, and therefore if they decrease as the critical point is approached, they do so according to a weaker law (logarithmic or close to it). In what follows we do not consider the singularities in the kinetic coefficients corresponding to these poles.

Now let us substitute $\Delta^*(\omega, \mathbf{k})$ in the form

$$\Delta^*(\omega,\mathbf{k})=[\omega-\omega_{\mathrm{min}}(\mathbf{k})]\Delta_1^*(\omega,\mathbf{k}).\tag{37}$$

Since the remaining roots of the equation $\Delta^*(\omega, \mathbf{k}) = 0$, and also the "viscous" pole $\omega_{\mathrm{visc}}(\mathbf{k}) = i[\eta(\omega_{\mathrm{visc}}, \mathbf{k})k^2/\rho_0]$ are much larger than $\omega_{\mathrm{min}}(\mathbf{k})$, it follows that

$$\Delta_1^*[\omega_{\mathrm{min}}(\mathbf{k}),\mathbf{k}]\approx\Delta_1^*(0,\mathbf{k}).\tag{38}$$

A comparison of expressions (34) and (32) enables one to determine the explicit form of the functions $\Phi_1(\omega, \mathbf{k})$ and $\Phi_2(\omega, \mathbf{k})$, from which it is clear that the residue at the pole $\omega = \omega_{\mathrm{min}}(\mathbf{k})$ gives the major contribution to the integrals, i.e.

$$I_1(\mathbf{k})=\frac{\pi i}{2}\frac{\omega_{min}(\mathbf{k})\Phi_1[\omega_{min}(\mathbf{k}),\mathbf{k}]}{\Delta^2(0,\mathbf{k})\Delta^{*2}(0,\mathbf{k})}.\tag{39}$$

Similarly

$$I_2(\mathbf{k})=\pi i\frac{\omega_{min}(\mathbf{k})\Phi_2[\omega_{min}(\mathbf{k}),\mathbf{k}]}{\Delta(0,\mathbf{k})\Delta^*(0,\mathbf{k})k^4\eta^2[\omega_{min}(\mathbf{k}),\mathbf{k}]}.\tag{40}$$

Proceeding now to the integration of expressions (39) and (40) over the wave vector $\mathbf{k}$, first we note that, for all reasonable forms of the function $\mu_c(\mathbf{k})$ (for example, according to Ornstein-Zernike $\mu_c = a + bk^2$), small wave vectors, $k \lesssim r_0^{-1}$, give the major contribution to the terms in (32) which depend on $(T - T_c)/T_c$. Therefore, integration over $\mathbf{k}$ may approximately be reduced to the substitution $\mathbf{k} \to r_0^{-1}$ in the integrands (the "scaling-law hypothesis"). Physically such an approximation is quite natural since altogether there is only one distinguished scale, the correlation radius r_0. Thus we obtain

$$\int I_1(\mathbf{k})d^3\mathbf{k}\approx\frac{\pi i}{2}\frac{\omega_{min}(r_0^{-1})\Phi_1[\omega_{min}(r_0^{-1}),r_0^{-1}](r_0^{-1})^3}{\Delta^2(0,r_0^{-1})\Delta^{*2}(0,r_0^{-1})},$$
$$\int I_2(\mathbf{k})d^3\mathbf{k}\approx\pi i\frac{\omega_{min}(r_0^{-1})\Phi_2[\omega_{min}(r_0^{-1}),r_0^{-1}](r_0^{-1})^3}{\Delta(0,r_0^{-1})\Delta^*(0,r_0^{-1})\eta^2[\omega_{min}(r_0^{-1}),r_0^{-1}](r_0^{-1})^4}\tag{41}$$

The subsequent calculation in general form would be overly cumbersome; therefore, as is usually done in kinetic problems, we consider two cases corresponding to different external gradients being applied to the system.

1. $v_{av_x} = \epsilon_v y$; $v_{av_y} = v_{av_z} = 0$; $\nabla\mu_{av} = 0$; $\nabla T_{av} = 0$. For such a choice of the initial problem expressions (30) for R_1, R_2, and R_3 are appreciably simplified. The explicit form of the quantities $\Phi_1(\omega, \mathbf{k})$ and $\Phi_2(\omega, \mathbf{k})$ in Eq. (41) may be obtained by substitutions into the integral (32) of expressions (30) and (32) evaluated at the points $\omega = \omega_{min}(r_0^{-1})$ and $k = r_0^{-1}$. In this connection it turns out that the terms which are singular in $(T - T_c)/T_c$ are only associated with the fluctuations in the density, which one would expect since it is precisely these fluctuations (together with the fluctuations of the concentration) which increase anomalously as the critical point is approached.

Expression (32) for the entropy production now takes the form (9). Identifying the coefficient associated with ϵ_v^2 with the singular part of the viscosity, after certain transformations we obtain

$$\Delta\eta \sim \rho_0^2 \int \frac{k_x^2 k_y^2}{k^2} \{T_0 s_\rho c_\rho [D_{13}(\omega, \mathbf{k}; -\omega, -\mathbf{k}) + D_{31}(\omega, \mathbf{k}; -\omega\ -\mathbf{k})] + T_0^2 s_\rho^2 D_{11}(\omega, \mathbf{k}; -\omega, -\mathbf{k}) + c_\rho^2 D_{33}(\omega, \mathbf{k}; -\omega, -\mathbf{k})\} \frac{\langle\rho\rho\rangle_{\omega,\mathbf{k}}\, d^3\mathbf{k}\, d\omega}{\Delta(\omega, \mathbf{k})\, \Delta^*(\omega, \mathbf{k})}. \tag{42}$$

Substituting the values of the correlator of the density obtained from Eq. (25) into Eq. (42), we arrive at an expression of the form (34), and according to the scheme of calculation (34)—(41) we finally obtain

$$\Delta\eta \sim \frac{r_0^{-1}}{(\partial\mu/\partial c)_{p,T}} \frac{1}{\alpha}\left[1 + \frac{T_0(\alpha\mu_T + \beta)^2}{\alpha(\gamma - \beta^2 T_0/\alpha)}\right]; \tag{43}$$

$$(\partial\mu/\partial c)_{p,T} \equiv (\partial\mu/\partial c)_{p,T}(\omega_{\min}(r_0^{-1}),\ r_0^{-1}).$$

2. $\nabla\mu_{av} = \epsilon_\mu$; $\nabla T_{av} = \epsilon_T$; $v_{av} = 0$. We assume that there is no substantial pressure gradient, $p_{av} = 0$. In this connection, one should consider all derivatives appearing in the system of equations (29) for p = const. Thus, for example, $s_T(\omega, \mathbf{k})$ now denotes the kernel of the operator connecting the Fourier components of the entropy and of the temperature, which reduces to the thermodynamical derivative $(\partial s/\partial T)_{\mu,p}$ at $\omega = 0$ and $k = 0$.

In contrast to the preceding case, now the thermal fluctuations of the density do not give any contribution to the part of the integral (32) which depends on $(T - T_c)/T_c$, i.e., they do not lead to anomalies of the kinetic coefficients at the critical point. This is associated with the fact that the density fluctuations in R_i now appear only in the form $\partial\rho_{fl}^0/\partial t$ (see Eq. (30)), which leads to the appearance of an extra factor $\omega_{min}(k)$ in (41) and leads to the vanishing of the singularities associated with fluctuations of the density.

However, the fluctuations of the velocity turn out to be important. In fact in the formulas for $R_1(\omega, \mathbf{k})$ and $R_2(\omega, \mathbf{k})$, as one can easily verify by substitution of (12) into (30) and changing to Fourier components, side by side with $v_{fl}^0(\omega, \mathbf{k})$ stands the factor $c_\mu(\omega, \mathbf{k})$ which increases as the critical point is approached, and also the quantities $s_T(\omega, \mathbf{k})$ and $c_T(\omega, \mathbf{k})$ are proportional to $c_\mu(\omega, \mathbf{k})$.

After substitution of these terms into formula (32), the expression for the production of entropy reduces to

$$\frac{\partial}{\partial t}\int \rho s\, d^3\mathbf{r} \sim V\left(\frac{\Delta\alpha}{T_0}\varepsilon_\mu^2 + \frac{\Delta\gamma}{T_0^2}\varepsilon_T^2 + 2\frac{\Delta\beta}{T_0}\varepsilon_T\varepsilon_\mu\right), \tag{44}$$

where the singular parts of the kinetic coefficients are given by

$$\Delta\alpha \sim \rho_0^2 T_0 \int \frac{k^2 c_\mu^2(\omega, \mathbf{k})\langle v^0_{fl\ x} v^0_{fl\ x}\rangle_{\omega,\mathbf{k}}}{\Delta(\omega, \mathbf{k})\,\Delta^*(\omega, \mathbf{k})}[T_0^2\mu_T^2 D_{11} + D_{33} + \mu_T(D_{13} + D_{31})]\, d^3\mathbf{k}\, d\omega; \quad \Delta\beta = -\mu_T\Delta\alpha; \quad \Delta\gamma = T_0\mu_T^2\,\Delta\alpha. \tag{45}$$

Substitution of the correlator $\langle v_{fl,x}^0 v_{fl,x}^0\rangle_{\omega,\mathbf{k}}$ from (25) into Eq. (45) and evaluation of the resulting integral according to Eqs. (34)—(41) leads to the following result:

$$\Delta\alpha \sim \frac{r_0^{-1}}{(\partial\mu/\partial c)_{x,T}} \frac{1}{\eta(\omega_{min}, r_0^{-1})}; \quad \Delta\beta = -\mu_T\Delta\alpha; \quad \Delta\gamma = T_0\mu_T^2\,\Delta\alpha.$$

Thus, we have obtained four relations (43) and (46) for the parts of the kinetic coefficients of a binary mixture which are singular in $(T - T_c)/T_c$.

4. DISCUSSION OF THE RESULTS

The kinetic coefficients $\eta[\omega_{min}(r_0^{-1}), r_0^{-1}]$, $\gamma[\omega_{min}(r_0^{-1}), r_0^{-1}]$, $\alpha[\omega_{min}(r_0^{-1}), r_0^{-1}]$, and $\beta[\omega_{min}(r_0^{-1}), r_0^{-1}]$ appear in the right-hand sides of formulas (43) and (46); these coefficients determine the energy, momentum, and mass currents according to expression (11), i.e.,

$$\eta = \eta_0 + \Delta\eta;\ \gamma = \gamma_0 + \Delta\gamma,\ \alpha = \alpha_0 + \Delta\alpha;\ \beta = \beta_0 + \Delta\beta, \tag{47}$$

where η_0, γ_0, α_0, and β_0 do not depend on the nearness to the critical point.

Relations (43) and (46) represent the equations for the quantities $\Delta\eta$, $\Delta\gamma$, $\Delta\alpha$, and $\Delta\beta$ whose values depend on the relationships between the regular and singular parts of the kinetic coefficients.

Not too near a critical point, when $\Delta\eta < \eta_0$, $\Delta\gamma < \gamma_0$, $\Delta\alpha < \alpha_0$, and $\Delta\beta < \beta_0$ Eqs. (43) and (46) give the following results for the singular parts of the kinetic coefficients:

$$\Delta\eta, \Delta\gamma, \Delta\alpha, \Delta\beta \sim \frac{r_0^{-1}}{(\partial\mu/\partial c)_{p,T}[\omega_{min}(r_0^{-1}), r_0^{-1}]}. \tag{48}$$

The ratio r_0^{-1}/μ_c increases upon approach to the critical point. In order to obtain the dependence on $(T - T_c)/T_c$ we shall utilize asymptotic estimates for r_0^{-1} and for the thermodynamic quantity μ_c, assuming that the dispersion of μ_c for small ω and k (for $T \to T_c$: $r_0^{-1} \to 0$ and $\omega_{min} \to 0$) is not important. Then if we use the estimates of scaling-law theory[10] $r_0 \sim ((T - T_c)/T_c)^{-\nu}$ and $\mu_c \sim ((T - T_c)/T_c)^{\gamma}$ with $\nu = 2/3$ and $\gamma = 4/3$, then in the region where the singular parts of the kinetic coefficients are small in comparison with the regular parts ($\Delta\eta < \eta_0$, $\Delta\gamma < \gamma_0$, $\Delta\alpha < \alpha_0$, and $\Delta\beta < \beta_0$) we have

$$\Delta\eta,\ \Delta\gamma,\ \Delta\alpha,\ \Delta\beta = ((T - T_c)/T_c)^{-2/3}. \tag{49}$$

According to the classical theory of Gibbs-Landau[1] $\nu = 1/2$, $\gamma = 1$, and

$$\Delta\eta,\ \Delta\gamma,\ \Delta\alpha,\ \Delta\beta \sim ((T - T_c)/T_c)^{-1/2}. \tag{50}$$

Such an increase continues as long as the corrections to the kinetic coefficients which are due to proximity to the critical point do not become of the order of the regular parts extrapolated from the far region. However, if

$\Delta\eta \gtrsim \eta_0$, $\Delta\gamma \gtrsim \gamma_0$, $\Delta\alpha \gtrsim \alpha_0$, and $\Delta\beta \gtrsim \beta_0$, then the four relations (43) and (46) asymptotically (in $(T - T_c)/T_c$) reduce to

$$\Delta\alpha\,\Delta\eta \sim \frac{r_0^{-1}}{(\partial\mu/\partial c)_{p,T}};\quad \Delta\beta = -\mu_T\,\Delta\alpha;\quad \Delta\gamma = T_0\mu_T^2\,\Delta\alpha \qquad (51)$$

and one can only assert that either the viscosity increases without limit at the critical point and then α, β, and γ remain finite or, on the other hand, α and together with it β and γ increase, but the viscosity remains finite as the temperature approaches the critical temperature.

Such a situation occurs even in a pure substance.[6] Apparently in both of these cases the proximity to the critical point which is experimentally attainable corresponds to case (48) but not (51).

In actual experiments the quantities α, β, and γ are not themselves measured, but rather certain combinations[8] of these quantities are measured: the diffusion coefficient $D = \alpha\mu_c$, the coefficient of thermal diffusion $k_T D = T_0(\alpha\mu_T + \beta)$, and the coefficients of thermal conductivity which are measured differently. Let us consider the behavior of these quantities as the temperature approaches the critical temperature.

The abrupt decrease of the coefficient of diffusion near the critical point is a well-known fact,[5] which follows immediately from the definition (1) of the critical point. It is of interest, however, that due to the growth of α (at least in the region of validity of formulas (48)) the decrease of D goes according to a slower law than μ_c. Actually $\Delta\alpha$ increases upon approach to the critical point, and according to estimates from scaling-law theory (49) and from the classical theory (50): $r_0^{-1} \sim \mu_c^{1/2}$, i.e., $\Delta\alpha \sim \mu_c^{1/2}$ and the "singular" part of the diffusion coefficient $\Delta D \sim \mu_c^{1/2}$ but it is not proportional to μ_c. If the growth of $\Delta\alpha$ is maintained into the region of validity of formula (56), then such a law governing the change of the diffusion coefficient holds over the entire neighborhood of the critical point.

This result is apparently confirmed experimentally in a recently published article[11] where, for the diffusion coefficient of the isobutyric-acid-water system, it was observed that $D \sim \mu_c^{1/2}$ in the temperature interval down to $(T - T_c)/T_c \lesssim 10^{-4}$.

From formula (46) it follows that the coefficient of thermal diffusion $\alpha\mu_T + \beta$ does not have any singularities which are associated with the decrease of μ_c upon approach to the critical point, but in general it may only have weak (logarithmic or close to it) singularities, which we have not taken into consideration. Thus, it follows from our calculation that the coefficient of thermal diffusion cannot increase strongly upon approach to the critical point (although its "composite parts" $\alpha\mu_T$ and β increase).

The coefficient of the so-called pure thermal conductivity is defined as the coefficient of proportionality between the heat flux and the temperature gradient in that case when no matter transport is present. Assuming $j_{av} = 0$ in (11) and eliminating $\nabla\mu_{av}$ from the expression for the heat flux q, one can easily verify that the coefficient of thermal conductivity is given by $\gamma - (\beta^2 T_0/\alpha)$. In the region of validity of formula (48) this coefficient grows according to the law (49) or (50)), but for $\Delta\eta \gtrsim \eta_0$, $\Delta\alpha \gtrsim \alpha_0$, if this region is accessible to experiment, from (51) it is seen that $\Delta(\gamma - \beta^2 T_0/\alpha)$ is bounded, i.e., the growth of the coefficient of thermal conductivity is retarded in the immediate vicinity of the critical point, and it apparently remains finite at the critical point.

We note that in the experiments[12] known to us, no substantial dependence of the coefficient of thermal conductivity on $(T - T_c)/T_c$ was observed, which is in agreement with our results.

The coefficient of thermal conductivity, determined under the condition that c_{av} = const, equals $\gamma + \alpha T_0\mu_T^2 + 2\beta T_0\mu_T$ and, as is clear from (46), in general it does not have any singularities in the critical region.

Finally, the coefficient of thermal conductivity, determined under the condition that μ_{av} = const (i.e., the changes of the temperature and concentration cancel each other), is equal to γ, and its behavior was discussed above (see Eqs. (48) and (51)).

In conclusion, let us compare our results with the article by Swift,[13] which is devoted to this same problem. From simple physical considerations Swift attempts to establish an isomorphism between the critical point of a pure substance, near which the singularities of the kinetic coefficients were calculated by him earlier,[14] and the critical point of a binary mixture. In order to do this it is necessary to make the assumption (in our opinion, this is not completely obvious) that the coefficient of thermal conductivity does not have any singularities at the critical point of the binary mixture.

In addition, Swift utilized all of the assumptions in the article by Kadanoff and Swift[14] which have been discussed by us previously.[6] We note that the characteristic frequency $\omega_{min}(k)$ given by Eq. (36), which appears in the singular parts of the kinetic coefficients, is a combination of the diffusive and heat-conducting hydrodynamical branches. Such a frequency does not appear in article[13] or in other treatments which are based on a simple dynamical theory of similarity, where the hydrodynamical states which are in local-equilibrium are assumed in advance to be noninteracting. The indicated difference finally leads to the result that in formula (3) for the diffusion coefficient given in article[13] the viscosity at the high frequency $\omega_\eta = i\eta k^2/\rho_0$ appears, whereas in our formula (46) the viscosity enters at the low frequency $\omega_{min}(k)$. Therefore, it appears to us that Swift's assertion about the finite value of the viscosity at the critical point is unproved.

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