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BEHAVIOR OF KINETIC COEFFICIENTS NEAR THE CRITICAL POINT OF PURE LIQUIDS

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The infinite increase in the compressibility and correlation radius of the density fluctuations at the critical point permits the use of the hydrodynamic equations for calculation of the singularities of the kinetic coefficients of liquids in the critical region. In the region that is not too near the critical point, and when the corrections to the kinetic coefficients do not exceed the magnitude of these quantities extrapolated from a remote region, the viscosity η and the thermal conductivity κ increase as $((T - T_c)/T_c)^{-2/3}$. In the immediate vicinity of the critical point, it can only be asserted that $\eta\kappa \sim ((T - T_c)/T_c)^{-2/3}$.

1. INTRODUCTION

FOR the study of nonequilibrium properties of classical systems, the kinetic equation is ordinarily used, the form of the collision integral in which is established from a definite microscopic model. In a liquid, in contrast to a gas or a solid, the kinetic and potential energies of the molecules are quantities of the same order, which makes very difficult the systematic microscopic investigation of the kinetic properties of the liquids.

The situation is in some sense simplified near the critical point (for definiteness, we shall only speak of the liquid-vapor critical point of single-components liquids). The fact is that as the critical point is approached, the motion of the molecules of the liquid becomes correlated at large distances—the correlation radius becomes much greater than the mean distance between the molecules and increases without limit as the temperature approaches the critical.[1] Therefore, one can hope that the details of the interaction of the molecules at short distances is not too important and that complete specification of the critical point is obtained only at distances that are larger than or of the order of the correlation radius.

In correspondence with this, we assume that for the description of the singularities of the behavior of the liquid close to the critical point, it suffices to use the hydrodynamic approximation with account of the infinite increase in the compressibility as the temperature approaches the critical; this leads to the appearance of spatial and temporal dispersion of all the characteristics of the liquid in the critical region.

A liquid at the critical point is a system with random inhomogeneities (thermal fluctuations), account of which, based on the fluctuation-dissipation theorem, can be carried out with the help of the introduction of the so-called outside forces in the equation of hydrodynamics.

If the external gradients of temperature and velocity are absent, then the distribution of the fluctuations over the volume occupied by the liquid is homogeneous and therefore fluxes of energy and momentum associated with them are absent. In the presence of these same external gradients, the distribution of the fluctuations changes in space, energy and momentum fluxes appear, and the entropy of the system increases.

The equations of hydrodynamics allow us to express the energy dissipation in the system in terms of the external gradients and the correlation function of thermal fluctuations, which themselves are determined by the equations of hydrodynamics, and also by the singularities of these equations in the critical region. The coefficient entering into the entropy production expression for a quadratic gradient of the mean velocity determines the singular part of the viscosity; for a quadratic gradient of the mean temperature, it determines the singular part of the thermal conductivity.

Thus, assuming the hydrodynamic description of the singular parts of the kinetic coefficients to be valid in the critical region, we shall carry out all further calculation without additional assumptions.

The method of solution of the problem was first formulated by Lifshitz, Kaganov, and Tsukernik,[2] and was later applied in a series of other researches. However, in all cases, the inhomogeneity was governed by external conditions—by polycrystallinity,[3] by turbulent currents in the atmosphere, which manifest themselves in the appearance of a random contribution to the dielectric tensor,[4] and so forth. In our case, thermal fluctuations, which take place far from the critical point, serve as the source of the inhomogeneity.

The closeness to the critical point can be seen in the change in the contribution of the long-wave fluctuations to the kinetic coefficient. This means that an additional averaging of the hydrodynamic equations over a scale that is larger than the correlation radius but smaller than the dimensions of the system, can lead to the appearance of singularities of the kinetic coefficients in terms of $(T - T_c)$.

Another approach was used in the works of Kawasaki,[5] and also of Kadanov and Swift.[6] They used an expression for the kinetic coefficients in terms of correlation functions. The microscopic space-time correlation functions are, of course, unknown. However, it is assumed that the singularity of the kinetic coefficients is connected with fluctuations of macroscopic scales, which are described by the hydrodynamic equations. The introduction of hydrodynamic quantities into the microscopic equation for the kinetic coefficients is a separate problem, for the solution of which definite, assumptions, that are sometimes quite difficult to verify, are used.

2. FUNDAMENTAL EQUATIONS

The set of equations of hydrodynamics has the form

$$\rho\frac{d\mathbf{v}}{dt} = -\nabla p + \operatorname{div}\sigma' \qquad \frac{d\rho}{dt} + \rho\operatorname{div}\mathbf{v} = 0,$$

$$\rho T\frac{ds}{dt} = \operatorname{div}\mathbf{q} + \sigma_{ik}'\frac{\partial v_i}{\partial x_k}, \tag{1}$$

where

$$\frac{d\varphi}{dt} = \left[\frac{\partial}{\partial t} + (\mathbf{v}\nabla)\right]\varphi, \tag{2}$$

and in the case in which space-time dispersion is significant, we have for σ' and $\mathbf{q}$:

$$\sigma_{ik}'(\mathbf{r}-\mathbf{r}', \omega) = \int\left\{\eta(\mathbf{r}-\mathbf{r}', \omega)\left[\frac{\partial v_i(\mathbf{r}', \omega)}{\partial x_k'} + \frac{\partial v_k(\mathbf{r}', \omega)}{\partial x_i'} - \frac{2}{3}\delta_{ik}\frac{\partial v_l(\mathbf{r}', \omega)}{\partial x_l'}\right] + \delta_{ik}\xi(\mathbf{r}-\mathbf{r}', \omega)\frac{\partial v_l(\mathbf{r}', \omega)}{\partial x_l'}\right\}d^3\mathbf{r}',$$

$$\mathbf{q}(\mathbf{r}, \omega) = \int \varkappa(\mathbf{r}-\mathbf{r}', \omega)\nabla T(\mathbf{r}', \omega)\,d^3\mathbf{r}'. \tag{3}$$

To obtain the complete set we must add to Eqs. (1) the equation of state. Close to the critical point, because of the large compressibility and the sharp increase of the relaxation time, an essential role is played by the nonlocal and nonsynchronous connection of the change in the pressure with change in the density:[7]

$$p(\mathbf{r}, \omega) = \rho_0\int Q(\mathbf{r}-\mathbf{r}', \omega)\rho(\mathbf{r}', \omega)\,d^3\mathbf{r}' + \left(\frac{\partial p}{\partial T}\right)_\rho T(\mathbf{r}, \omega). \tag{4}$$

As is seen from (3) and (4), the functions $\eta(\omega, \mathbf{k})$, $\xi(\omega, \mathbf{k})$, $\kappa(\omega, \mathbf{k})$ and $\rho_0 Q(\omega, \mathbf{k})$ are respectively the first and second viscosity, the thermal conductivity and the isothermal compressibility, which in the case of a weak spatial dispersion is determined by the Ornstein-Zernike approximation:

$$\rho_0 Q(\mathbf{k}) = \left(\frac{\partial p}{\partial\rho}\right)_T + bk^2. \tag{5}$$

Finally, for a solution of the system (1)–(4), it is necessary to use thermodynamic considerations which connect the entropy with the density and temperature. In this case, by analogy with (3) and (4), we must take into account the spatial and temporal dispersion, which is done trivially for linear operations and is naturally generalized to the nonlinear case; for example, for the total derivative of the entropy with respect to time, we have

$$\frac{dS(\mathbf{r}, t)}{dt} = \int K_1(\mathbf{r}-\mathbf{r}', t-t')\frac{dT(\mathbf{r}', t')}{dt'}d^3\mathbf{r}'dt' + \int K_2(\mathbf{r}-\mathbf{r}', t-t')\frac{d\rho(\mathbf{r}', t')}{dt'}d^3\mathbf{r}'\,dt'. \tag{6}$$

Here, just as above, the Fourier components of the kernels $K_1(\mathbf{k}, \omega)$ and $K_2(\mathbf{k}, \omega)$ describe the dispersions of the heat capacity $c_V(\mathbf{k}, \omega)$ and of the thermal coefficient of the pressure $\beta_T(\mathbf{k}, \omega)$, respectively. We note that if the process of thermal conduction takes place at constant pressure, then,

$$\frac{dS(\mathbf{r}, t)}{dt} = \int K_3(\mathbf{r}-\mathbf{r}', t-t')\frac{dT(\mathbf{r}', t')}{dt'}d^3\mathbf{r}'dt', \tag{7}$$

where the Fourier component of the kernel $K_3(\mathbf{k}, \omega)$ describes the dispersion of the heat capacity $c_p(\mathbf{k}, \omega)$.

In the linear approximation and in the absence of external gradients, the set of equations (1)–(4) and (6) completely describes the thermal fluctuations in the medium. In the presence of external gradients, the character of the fluctuations changes. This change is described by the nonlinear terms in (1)–(4), (6).

For example, we find the equations of motion of the fluctuations in the presence of an external velocity gradient. We set

$$v_{\text{av}}^{(x)} = d\cdot ye^{-i\omega t}, \qquad v_{\text{av}}^{(y)} = v_{\text{av}}^{(z)} = 0, \tag{8}$$

where d is the gradient of the mean velocity. The specific form of the external gradient is unimportant for the results of our calculations. The choice of the initial hydrodynamic problem in the form (8) is convenient for finding the dependence of the shear viscosity on $T - T_c$ and for an account of the temporal dispersion of the viscosity.

Substituting in (1) v, T and ρ in the form

$$\mathbf{v} = \mathbf{v}_{\text{av}} + \mathbf{v}_{\text{fl}}, \quad T = T_{\text{av}} + T_{\text{fl}} \quad \rho = \rho_{\text{av}} + \rho_{\text{fl}}$$

$$\overline{\mathbf{v}_{\text{fl}}} = 0, \quad \overline{T_{\text{fl}}} = 0, \quad \overline{\rho_{\text{fl}}} = 0, \tag{9}$$

averaging the resultant system, subtracting the averaged equations from the unaveraged ones, and neglecting terms of third order in the fluctuations, we obtain the equations for the fluctuating quantities:

$$\rho_0\frac{\partial\mathbf{v}_{\text{fl}}}{\partial t} + \nabla p_{\text{fl}} - \operatorname{div}\sigma_{\text{fl}}' = \mathbf{N}_1,$$

$$\frac{\partial\rho_{\text{fl}}}{\partial t} + \rho_0\operatorname{div}\mathbf{v}_{\text{fl}} = N_2,$$

$$\rho_0 T_0\frac{\partial s_{\text{fl}}}{\partial t} - \operatorname{div}\mathbf{q}_{\text{fl}} = N_3, \tag{10}$$

where $\mathbf{N}_1$, $\mathbf{N}_2$, and $\mathbf{N}_3$ denote the terms proportional to d obtained after substitution of (9) in (1). Now, expanding the fluctuating quantities in powers of d:

$$\varphi_{\text{fl}}(\mathbf{r}, t) = \sum_n d^n\varphi_{\text{fl}\,(n)}(\mathbf{r}, t), \quad \varphi_{\text{fl}}(\mathbf{r}, t) = \begin{Bmatrix}\mathbf{v}_{\text{fl}}\\ T_{\text{fl}}\\ \rho_{\text{fl}}\end{Bmatrix} \tag{11}$$

and substituting (11) in (10), we obtain for the zeroth approximation in d the set of equations that describes the thermal fluctuations in the mean. For example, the correlation function of the density fluctuations, found from these equations, has the form[7]

$$\Psi_{\rho\rho}(\mathbf{k}, \omega) = \frac{T_0\rho_0}{\pi}(2\pi)^3\mathbf{k}^4\left\{\mu\omega^2 + \varkappa_1\mathbf{k}^2\left[\varkappa_1\mu\mathbf{k}^2 + \frac{T_0}{\rho_0^2 c_V}\left(\frac{\partial p}{\partial T}\right)_\rho^2\right]\right\}\Big/ P(\mathbf{k}, \omega)P^*(\mathbf{k}, \omega), \tag{12}$$

where

$$P(\mathbf{k}\omega) = (\omega + i\varkappa_1 k^2)(\omega^2 - k^2\rho_0 Q + i\omega k^2\mu) - \frac{T_0}{\rho_0^2 c_V}\left(\frac{\partial p}{\partial T}\right)_\rho^2\omega k^2,$$

$$\mu = \frac{1}{\rho_0}\left(\xi + \frac{4}{3}\eta\right), \qquad \varkappa_1 = \frac{\varkappa}{\rho_0 c_V}, \tag{13}$$

and η, ξ, κ, c_V, etc., are functions of $(\omega, \mathbf{k})$.

In first order in d, we obtain an inhomogeneous set of equations

$$\rho_0\frac{\partial\mathbf{v}_{\text{fl}\,(1)}}{\partial t} + \nabla p_{\text{fl}\,(1)} - \operatorname{div}\sigma'_{\text{fl}\,(1)} = \mathbf{N}_{1(0)},$$

$$\frac{\partial\rho_{\text{fl}\,(1)}}{\partial t} + \rho_0\operatorname{div}\mathbf{v}_{\text{fl}\,(1)} = N_{2(0)},$$

$$\rho_0 T_0\frac{\partial s_{\text{fl}\,(1)}}{\partial t} - \operatorname{div}\mathbf{q}_{\text{fl}\,(1)} = N_{3(0)}, \tag{14}$$

where $\mathbf{N}_{1(0)}$, $N_{2(0)}$, and $N_{3(0)}$ are obtained from $\mathbf{N}_1$, N_2, and N_3 by replacing φ_{fl} in them by $\varphi_{\text{fl}(0)}$. Leaving in $\mathbf{N}_{1(0)}$, $N_{2(0)}$, and $N_{3(0)}$ only the density fluctuations, since only these fluctuations increase anomalously as the critical point is approached,[1)] we have for the values of $N_{1(0)}$, $N_{2(0)}$, and $N_{3(0)}$

$$N_{1(0)} \approx 0, \quad N_{2(0)} \approx -\mathbf{v}_{\text{av}} \nabla \rho_{\text{fl}\,(0)},$$
$$N_{3(0)} \approx -\rho_0 T_0 \int K_2(\mathbf{r}-\mathbf{r}', t-t')\, \mathbf{v}_{\text{av}}(\mathbf{r}', t')\, \nabla \rho_{\text{fl}\,(0)}(\mathbf{r}', t')\, d^3\mathbf{r}'\, dt' \cdot \quad (15)$$

Substituting (6) and (15) in (14) and solving the set of equations (14), we obtain

$$\mathbf{v}_{\text{fl}\,(1)} \approx 0, \quad \rho_{\text{fl}\,(1)}(\mathbf{k}, \omega) \approx i K_2(\mathbf{k}\omega) \frac{\mathbf{k}^2 N_{3(0)}(\mathbf{k}, \omega)}{P(\mathbf{k}, \omega)},$$
$$T_{\text{fl}\,(1)}(\mathbf{k}, \omega) \approx -i \frac{\mathbf{k}^2 \rho_0 Q(\mathbf{k}, \omega)}{P(\mathbf{k}, \omega)} N_{3(0)}(\mathbf{k}, \omega). \quad (16)$$

3. CALCULATION OF THE SHEAR VISCOSITY

Proceeding to the calculation of the particular parts of the kinetic coefficients in a liquid close to the critical point, we write out the entropy production associated with the fluctuations:

$$\frac{\partial}{\partial t} \int \rho s\, d^3\mathbf{r} = \int \frac{1}{T_0} \sigma_{ik}'{}_{\text{fl}} \frac{\partial v_{\text{fl}}}{\partial x_k} d^3\mathbf{r} + \int \frac{1}{T_0^2} \mathbf{q}_{\text{fl}} \nabla T_{\text{fl}}\, d^3\mathbf{r}. \quad (17)$$

Substituting (3) and (16) in (17), averaging over the fluctuations, and then separating the terms proportional to the squares of the gradients of the mean velocity, we determine the value of the viscosity as the corresponding coefficient of proportionality. Then the singular part of this kinetic coefficient has the form

$$\Delta\eta(s, 0) \sim \int d^3\mathbf{k}\, d\omega \left\{ \frac{\varkappa(\mathbf{k}, \omega + s)}{T_0} \mathbf{k}^2 \mathbf{k}_x^2 W_{\rho\rho}(\mathbf{k}\omega) \right.$$
$$\left. \times \frac{\partial}{\partial \mathbf{k}_y} \left[\frac{\mathbf{k}^2 \rho_0 Q(\mathbf{k}, \omega + s)}{P(\mathbf{k}, \omega + s)} \right] \cdot \frac{\partial}{\partial \mathbf{k}_y} \left[\frac{\mathbf{k}^2 \rho_0 Q(\mathbf{k}, -\omega + s)}{P(\mathbf{k}, -\omega + s)} \right] \right\}, \quad (18)$$

where the functions $P(\mathbf{k}, \omega)$ and $W_{\rho\rho}(\mathbf{k}, \omega)$ are determined by the relations (12) and (13).

For the exact calculation of the integral (18), it is necessary to know the space-time dispersion of all the parameters of the liquid. The singular part of the integral (18) can, however, be estimated without this. Actually, let $\omega = \omega_{\min}(\mathbf{k})$ be the smallest root of the equation

$$P(\mathbf{k}, \omega) = 0, \quad (19)$$

which tends to zero as $T \to T_c$. (If there is no such root, when $\Delta\eta(s, 0)$ generally does not have a singular part in the critical region.)

We write $P(\mathbf{k}, \omega)$ in the form

$$P(\mathbf{k}, \omega) = [\omega - \omega_{min}(\mathbf{k})] P'(\mathbf{k}, \omega). \quad (20)$$

Here all the roots of the equation $P'(\mathbf{k}, \omega) = 0$ are much greater than $\omega_{\min}(\mathbf{k})$, and therefore

$$P'(\mathbf{k}, \omega_{min}) \approx P'(\mathbf{k}, 0). \quad (21)$$

It is evident from the structure of (18) that for $s \lesssim \omega_{\min}$, the principal contribution to the integral is made by the residue at the point $\omega = \omega_{\min}(\mathbf{k})$, which is easily computed and is equal to

$$\Delta\eta(s, 0) \sim \left\{ \varkappa_1 \mu \omega^2_{min} + \varkappa_1^2 \left[r_0^{-2} \varkappa_1 \mu \right.\right.$$
$$\left.\left. + \frac{T_0}{\rho_0^2 c_V} \left(\frac{\partial p}{\partial T}\right)_\rho^2 \right] r_0^{-2} \right\} c_T^4 \Big/ r_0^{13} |\omega_{min}(r_0^{-1})|^3 |P'(r_0^{-1}, 0)|^4. \quad (22)$$

For an estimate of the integral over k, we have used the idea of "scaling."[6] The functions κ and μ here are taken at the point $\{\omega_{\min}(r_0^{-1}), r_0^{-1}\}$. The root $\omega_{\min}(r_0^{-1})$ is easily estimated from (19) by using the fact that it tends to zero as $T \to T_c$. Neglecting the higher powers of ω in $P(\mathbf{k}, \omega)$, we obtain an equation for the determination of $\omega_{\min}$

$$\omega[c_s^2 + \mathbf{k}^2 \varkappa_1(\mathbf{k}, \omega) \mu(\mathbf{k}, \omega)] + i\varkappa_1(\mathbf{k}, \omega) \mathbf{k}^2 c_T^2(\mathbf{k}, \omega) = 0, \quad (23)$$

whence

$$\omega_{min}(\mathbf{k}) = -i\varkappa(\mathbf{k}, \omega_{min}) \mathbf{k}^2 \frac{c_T^2}{c_s^2 + \mathbf{k}^2 \varkappa_1(\mathbf{k}\omega_{min}) \mu(\mathbf{k}, \omega_{min})} \quad (24)$$

For the additional condition

$$c_s^2 \gg \varkappa_1 \mu \mathbf{k}^2,$$

which is always satisfied sufficiently close to the critical point, we have, after substitution of (24) in (22)

$$\Delta\eta(s, q) \sim \frac{1}{\varkappa(r_0^{-1}, \omega_{\min})} \frac{r_0^{-1}}{c_T^2} \qquad (s \lesssim \omega_{\min}, q \lesssim r_0^{-1}). \quad (25)$$

CALCULATION OF THE THERMAL CONDUCTIVITY

Calculation of the singular part of the coefficient of thermal conductivity is made in a way that is entirely similar to the calculation of the singular part of the coefficient of viscosity. Therefore, we limit ourselves to only a few remarks.

A system is considered in an external temperature gradient, which changes with time according to the law e^{-ist}. The average velocity at each point is taken to be equal to zero. The equations for the fluctuations are obtained after substitution of (9) in (1)–(4), (7), averaging of the resultant equations and subtraction of the averaged equations from the nonaveraged ones. It is essential here that, in correspondence with the footnote before Eq. (15), in this case, in addition to the density fluctuations, there should also be left terms containing the velocity fluctuations, which are proportional to $c_p(\mathbf{k}, \omega)$.

The set of equations obtained in this fashion is identical with (14), with only this difference that now $N'_{1(0)}$, $N'_{2(0)}$, $N'_{3(0)}$ are equal to

$$N'_{1(0)} \approx 0, \quad N'_{2(0)} \approx 0,$$
$$N'_{3(0)} \approx \rho_0 T_0 \int K_3(\mathbf{r}-\mathbf{r}', \omega) \nabla T_{\text{cp}}(\mathbf{r}') \mathbf{v}_{\text{fl}\,(1)}(\mathbf{r}', \omega - s) d^3\mathbf{r}'. \quad (26)$$

$\rho_{\text{fl}\,(1)}$, $T_{\text{fl}\,(1)}$ and $v_{\text{fl}\,(1)}$ are obtained in this case from (16) by substitution in them of $N'_{i\,(0)}$ for $N_{i\,(0)}$.

It is seen from (26) that in the calculation of the entropy production in the system, we now need the correlation function of the thermal fluctuations of the velocity, which is easily computed[7] and is equal to

$$W_{vv}^{(ij)}(\mathbf{k}, \omega) = \frac{T_0}{\pi} (2\pi)^3 \,\mathrm{Im} \frac{1}{\omega\rho_0 + i\eta\mathbf{k}^2} \left\{ \delta_{ij} - \frac{\mathbf{k}_i \mathbf{k}_j}{P(\mathbf{k}, \omega)} \right.$$
$$\left. \times \left[(\omega + i\varkappa_1\mathbf{k}^2) \left[\frac{i\omega}{\rho_0} \left(\xi + \frac{1}{3}\eta \right) - \rho_0 Q \right] - \frac{T_0}{\rho_0^2 c_V} \left(\frac{\partial p}{\partial T}\right)_\rho^2 \omega \right] \right\}. \quad (27)$$

Separating the term in the entropy production that is proportional to the square of the gradient of the mean temperature, we find the coefficient of thermal conductivity:

$$\Delta\varkappa(s, 0) \sim \int d^3\mathbf{k}\, d\omega \left\{ \frac{\varkappa(\mathbf{k}, \omega + s)}{T_0^2} \mathbf{k}^2 W_{vv}(\mathbf{k}, \omega) \right.$$
$$\left. \times \frac{[c_p(\mathbf{k}) \mathbf{k}^2 \rho_0 Q]^2}{P(\mathbf{k}, \omega + s) P(\mathbf{k}, -\omega + s)} \right\}. \quad (28)$$

[1)] It is assumed that the remaining thermodynamic quantities follow instantly the change in the density, i.e., the relation (4) is valid. One must also take into account velocity fluctuations if the factor in them increases as the critical point is approached.

The estimate of the singular part of this integral is carried out in a way that is completely analogous to the estimate of the singular part of the viscosity. As a result, we get for $s \lesssim \omega_{\min}$, $q \lesssim r_0^{-1}$,

$$\Delta\varkappa(s, q) \sim \frac{1}{\eta(r_0^{-1}, \omega_{\min})} \frac{r_0^{-1}}{c_T^2}. \tag{29}$$

5. BEHAVIOR OF THE VISCOSITY AND THE THERMAL CONDUCTIVITY IN THE CRITICAL REGION

The relations (25) and (29) are equations relative to the singular (dependent on $T - T_c$) parts of the kinetic coefficients $\Delta\eta$ and $\Delta\kappa$ of interest to us, since the quantities $\eta(\omega_{\min}, r_0^{-1})$ and $\kappa(\omega_{\min}, r_0^{-1})$ on the right-hand sides of these formulas are the complete kinetic coefficients, which determine the fluxes of energy and momentum in the initial equations of hydrodynamics (1)–(4), i.e.,

$$\eta = \eta_0 + \Delta\eta, \quad \varkappa = \varkappa_0 + \Delta\varkappa, \tag{30}$$

where η_0 and κ_0 do not depend on $T - T_c$.

Not too close to the critical point we have $\Delta\eta < \eta_0$ and $\Delta\kappa < \kappa_0$. Then (25) and (29) give for the singular parts of the kinetic coefficients

$$\Delta\eta \sim \frac{r_0^{-1}}{c_T^2}, \quad \Delta\varkappa \sim \frac{r_0^{-1}}{c_T^2} (\Delta\eta < \eta_0, \quad \Delta\varkappa < \varkappa_0). \tag{31}$$

We note that in the derivation of (31), it was essentially assumed that the region of validity of the similarity theory and the region in which the inequalities $\Delta\eta < \eta_0$ and $\Delta\kappa < \kappa_0$ still hold, coincide, which is generally not obvious.

In the immediate vicinity of the critical point, when the singularities of the kinetic coefficients can already be significant, Eqs. (25) and (29) become equivalent in the sense of their dependence on $T - T_c$ and reduce to the equation

$$\Delta\eta \cdot \Delta\varkappa \sim r_0^{-1}/c_T^2. \tag{32}$$

It is then seen that at least one of these quantities should increase as $T - T_c$ approaches zero.

However, we note that it follows from all the experiments performed[8,9] that the kinetic coefficients close to the critical point increase by no more than several times ten of per cent, and evidently, in all the experimentally accessible region of temperature the inequalities $\Delta\eta < \eta_0$ and $\Delta\kappa < \kappa_0$ are valid. Moreover, in the immediate vicinity of the critical point, the effect of impurities, the hydrostatic effect, and so on, become decisive; these were generally not taken into account in our analysis.

If we use the estimates of similarity theory: $r_0 \sim \tau^{-\nu}$, $c_T^2 \sim \tau^{\gamma}$ with $\nu = 2/3$, $\gamma = 4/3$, then in the region where the singular parts are not too large, we have

$$\Delta\eta \sim \tau^{-2/3}, \quad \Delta\varkappa \sim \tau^{-2/3}. \tag{33}$$

According to classical theory,[1] $\nu = 1/2$, $\gamma = 1$, and

$$\Delta\eta \sim \tau^{-1/2}, \quad \Delta\varkappa \sim \tau^{-1/2}. \tag{34}$$

The basic results of (25), (29) and (33) are identical with the results of the work of Kadanoff and Swift[6], with only this difference that in the expression for thermal conductivity in[6] the viscosity appears at the high frequency $\omega_\eta = i\eta k^2/\rho_0$, while in Eq. (29), it enters at the low frequency $\omega_\kappa = -i\kappa k^2/\rho_0 c_p$. This difference is connected with the fact that in[6] they have chosen from the beginning five hydrodynamic "local equilibrium states" whose relaxation times are determined by the viscosity at the frequency ω_η and by the thermal conductivity at the frequency ω_κ.

In contrast with[6], our formulas for the viscosity and thermal conductivity (see (18) and (28)) contain integration over the frequency ω, which leads to the intermingling of the "correlation" and "hydrodynamic" factors in the integrands of (18) and (28), and in the final analysis to the appearance of the viscosity at the frequency $\omega_\kappa = -i\kappa k^2/\rho_0 c_p$ in (29).

Such an intermingling is impossible in the formulas for the kinetic coefficients in[6], since in these formulas there is no integration over the frequencies of the intermediate states, and only the eigenfrequencies with $\eta(\omega_\eta)$ and $\kappa(\omega_\kappa)$ enter. Therefore, the statement in[6] that the viscosity at the critical point is finite seems to us somewhat without basis.

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