

Correlation-Function Approach to the Transport Coefficients near the Critical Point. I*

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A general theory is presented for the transport coefficients exhibiting anomalous peaks near the critical point, employing correlation-function expressions for transport coefficients. Recognizing that the anomaly should arise from the anomalous increase in the fluctuations of certain macroscopic variables, we attempt an expansion of the flux entering the correlation-function expression in powers of the macroscopic variables, which then are supposed to obey the macroscopic equations of motion. A general formula for the anomalous part of the transport coefficient is given, restricting ourselves to the quadratic terms in this expansion. The general theory is illustrated for the shear viscosity of critical mixtures, choosing local concentration and local temperature as macroscopic variables. The anomaly is attributed to the cooperation of the two effects: (1) anomalous increase in certain large-scale fluctuations of macroscopic variables contained in the flux, and (2) the anomalous increase in the lifetimes associated with these fluctuations. If we ignore the local temperature fluctuations, Fixman's result of the anomalous viscosity is obtained. Generalizing these results, the large frequency and wave-vector dependence which is expected for the anomalous transport coefficients near the critical point is studied explicitly for the shear viscosity. The thermal conductivity of the critical mixture is also examined, and is found to have no anomaly in the same approximation, in agreement with the existing experiments. In an appendix, a more rigorous and systematic treatment of the general theory is given with the help of Mori's general theory of Brownian motion for macroscopic variables, and we indicate a possibility of obtaining a self-consistent set of equations for general nonlocal transport coefficients.

1. INTRODUCTION

A FEW years ago Fixman presented a theory of shear viscosity of critical mixtures which successfully explained the anomalous increase of viscosity near the critical point.^{1,2} The crux of his theory is the recognition of the fact that the anomalous viscosity must arise from the anomalous increase in the concentration fluctuation on the macroscopic scale which is also responsible for the anomalies observed in various other properties near the critical point. However, the method of his calculation of viscosity is somewhat unconventional, in that he calculates the entropy production rate in the stationary state in the presence of a constant velocity gradient and identifies the coefficient of the square of the velocity gradient with the viscosity. Thus, it is not quite obvious precisely what sorts of approximations are introduced in the theory and how one can generalize the treatment so as to be applicable to other problems.

The present work has emerged from our attempt to understand Fixman's theory in more conventional terms. Retaining his basic idea that this type of anomaly comes from certain macroscopic fluctuations, we have been able to find a general and systematic way to extract the anomaly in the transport coefficients. We shall use the now familiar correlation function expression for transport coefficients.³ Our starting point of the calculation is to attempt a power-series expansion of the

flux entering the correlation function in various Fourier components of local macroscopic variables. Since the flux is essentially a microscopic quantity, this power series cannot exhaust the entire flux. However, if the basic idea adopted here is correct, the anomaly in the transport coefficients must be contained in this power series. The time-correlation function of the power series may then be evaluated using the macroscopic equations of motion which can be made nonlocal if necessary.⁴

In the next section we carry out the above program in a somewhat heuristic fashion restricting ourselves to the quadratic term of the power series (the linear term never appears). In Sec. 3, we apply the general theory to the shear viscosity of critical mixtures, where we consider the temperature fluctuation in addition to the concentration fluctuation. If we ignore the former, the result of Fixman is recovered. In Sec. 4 we consider the wave-vector (\mathbf{q}) and frequency (ω) dependence of the shear viscosity, which exhibits strong \mathbf{q} , ω dependence near the critical point. Section 5 is devoted to some comments including the discussion of thermal conductivity of critical mixtures. In Appendix A, we present a more rigorous and systematic treatment of the general theory of Sec. 2, using Mori's general theory of Brownian motion for macroscopic variables. In particular we indicate a possibility of obtaining a self-consistent set of equations which in principle determine the anomalous parts of \mathbf{q} , ω -dependent transport coefficients.

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¹ M. Fixman, *J. Chem. Phys.* **36**, 310 (1962); W. Botch and M. Fixman, *ibid.* **36**, 3100 (1962).

² M. Fixman, in *Advances in Chemical Physics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1963), Vol. VI.

³ R. W. Zwanzig, *Ann. Rev. Phys. Chem.* **16**, 67 (1965) and the references cited therein.

⁴ Use of macroscopic equations of motion in a similar context in the problems of transport and relaxation phenomena near the critical point has appeared in literature. Besides Fixman's works the reader is referred to T. Moriya, *Progr. Theoret. Phys. (Kyoto)* **28**, 371 (1962) for NMR linewidth in an antiferromagnet; P. M. Richards (unpublished) for ESR linewidths in ferro- and antiferromagnets, Kawasaki (Ref. 18) and H. Stern, *J. Phys. Chem. Solids* **26**, 153 (1965) for thermal conductivity near the magnetic transition, and Zwanzig and Mountain for one-component fluids (Ref. 27).

2. METHOD OF EXTRACTING THE CRITICAL FLUCTUATION

As pointed out in the Introduction, the present treatment starts from recognizing that the cause of the anomalies in transport coefficients at the critical point is the anomalous increase in the long-wavelength parts of fluctuations near that point. Thus, we attempt to express as much as possible the flux entering the transport coefficients in terms of the various spatial Fourier components of the local macroscopic variables of the system, supposing that the critical fluctuation is adequately described by the fluctuations of macroscopic variables. In this section we shall present a somewhat simpler, but less rigorous treatment deferring the more systematic derivation to Appendix A.

Let us now write the general correlation function expression for transport coefficients as follows:

$$\theta = \frac{w}{V} \int_0^\infty \langle J(t)J \rangle dt, \quad (2.1)$$

where J is the flux corresponding to the transport coefficient θ , w is some known function of the temperature, V the total volume of the system, $\langle \dots \rangle$ the average over the equilibrium ensemble, and we have assumed classical mechanics. Denoting the k th Fourier component of the α th macroscopic variable as $A_{\mathbf{k}}^\alpha$ we attempt the following expansion:

$$J = \sum_{\alpha\beta} \sum_{\mathbf{k}} S_{\alpha\beta}^{\mathbf{k}} A_{\mathbf{k}}^\alpha A_{-\mathbf{k}}^\beta + \dots, \quad (2.2)$$

where \dots denote the terms with higher powers of A 's and the terms which are not contained in this power series. Here use is made of the fact that J is orthogonal to the linear combinations of A 's:

$$\langle JA_{\mathbf{k}}^{\alpha*} \rangle = 0, \quad (2.3)$$

which excludes the linear term in A 's from (2.2) (also see Appendix A), and A 's are chosen such that $\langle A_{\mathbf{k}}^\alpha \rangle = 0$ and the asterisk denotes taking the complex conjugate.

For the present simplified treatment, we shall only consider the terms written explicitly in (2.2). As for the part of J which does not contain A 's, we assume that it does not give rise to anomalies in the transport coefficients because it would not involve the critical fluctuation. An analogy for ignoring the terms containing higher powers of A 's than quadratic may be found in a somewhat similar circumstance in the well-known theory of the correlation of fluctuations near the critical point of Landau and Lifshitz,⁵ where the thermodynamic potential is expanded in powers of the deviations of the local thermodynamic variables from their values in thermal equilibrium and their spatial derivatives and

only the quadratic terms have been retained. This theory describes quite well the various gross features of phase transition. The higher order terms in A 's are necessary only if we try to study more detailed features of critical phenomena in the immediate vicinity of the critical point.⁶ Similarly, we may hope that the present simplified treatment is adequate to describe gross features of the anomalies in the transport coefficients near the critical point. However, it may happen that for some particular problems the present quadratic approximation fails to describe the anomaly. Then one should be able to take as many terms in (2.2) as is necessary without difficulty. The coefficients S 's in (2.2) are determined if we ignore \dots in (2.2) by the set of equations,

$$\langle JA_{\mathbf{k}}^{\gamma*} A_{-\mathbf{k}}^{\delta*} \rangle = \sum_{\alpha\beta} \sum_{\mathbf{k}'} S_{\alpha\beta}^{\mathbf{k}'} \langle A_{\mathbf{k}'}^\alpha A_{-\mathbf{k}'}^\beta; A_{\mathbf{k}}^{\gamma*} A_{-\mathbf{k}}^{\delta*} \rangle, \quad (2.4)$$

where

$$\langle F; G \rangle \equiv \langle FG \rangle - \langle F \rangle \langle G \rangle, \quad (2.4')$$

and we have used that $\langle J \rangle = 0$. The magnitudes of \mathbf{k} or \mathbf{k}' in (2.2), (2.3), and the subsequent equations are limited below a certain cutoff k_{\max} which is much smaller than the inverse of the interparticle distance, since A 's represent macroscopic variables. The anomalous parts of the transport coefficients should be insensitive to the precise value of this cutoff as we shall see in a specific example later in Sec. 3.

The expansion of the form (2.2) is not new: It has been used in the theory of sound attenuation in liquid helium⁷ where the A 's are the phonon creation and annihilation operators and the right-hand side of (2.2) represents phonon interactions. If we remember that J is related to the time derivatives of A 's, the right-hand side of (2.2) represents the so-called mode-mode coupling familiar in plasma physics.⁸

Substituting (2.2) into (2.1), the anomalous part of the transport coefficient, $\Delta\theta$, becomes,

$$\Delta\theta = \frac{w}{V} \sum_{\alpha\beta} \sum_{\mathbf{k}} S_{\alpha\beta}^{\mathbf{k}} \int_0^\infty dt \langle A_{\mathbf{k}}^\alpha(t) A_{-\mathbf{k}}^\beta(t) J \rangle. \quad (2.5)$$

We shall now evaluate (2.5) by making use of the fact that A 's in (2.4) are the macroscopic variables, and thus their temporal development may be assumed to be governed by the macroscopic equations of motion, such as the hydrodynamic equations suitably generalized to take account of the finiteness of k which is expected to be important near the critical point. We have not considered the possible frequency dependence or the memory effects in the macroscopic equations of motion which may become important for some problems. We

⁶ M. Fixman, J. Chem. Phys. **36**, 1965 (1962).

⁷ K. Kawasaki and H. Mori, Progr. Theoret. Phys. (Kyoto) **28**, 784 (1962).

⁸ B. B. Kadomtsev, *Plasma Turbulence Theory* (Academic Press Inc., New York, 1965), Chap. II.

⁵ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958.) See also Fisher (Ref. 18) and P. Debye, J. Chem. Phys. **31**, 680 (1959).

thus write the macroscopic equations of motion as

$$\frac{d}{dt}\langle A_{\mathbf{k}}^{\alpha}(t) \rangle_1 = -\sum_{\beta} M_{\mathbf{k}}^{\alpha\beta} \langle A_{\mathbf{k}}^{\beta}(t) \rangle_1, \quad (2.6)$$

where $\langle A_{\mathbf{k}}^{\alpha}(t) \rangle_1$, is the average of $A_{\mathbf{k}}^{\alpha}(t)$ over the non-equilibrium ensemble. It is convenient to put (2.6) in the following matrix form:

$$\frac{d}{dt}\langle \mathbf{A}_{\mathbf{k}}(t) \rangle_1 = -\mathbf{M}_{\mathbf{k}} \cdot \langle \mathbf{A}_{\mathbf{k}}(t) \rangle_1, \quad (2.7)$$

where $\mathbf{A}_{\mathbf{k}}$ is the column matrix with the elements $A_{\mathbf{k}}^{\alpha}$ and $\langle \mathbf{A}_{\mathbf{k}} \rangle_1$ its nonequilibrium ensemble average. Then, our assumption is that for the purpose of evaluating (2.4) we can assume that

$$\frac{d}{dt}\mathbf{A}_{\mathbf{k}}(t) = -\mathbf{M}_{\mathbf{k}} \cdot \mathbf{A}_{\mathbf{k}}(t). \quad (2.8)$$

Since (2.5) involves $A(t)$'s in bilinear form, we need the equations of motion for $A_{\mathbf{k}}^{\alpha}A_{-\mathbf{k}}^{\beta}$ which are, by (2.6) or (2.8)

$$\begin{aligned} \frac{d}{dt}A_{\mathbf{k}}^{\alpha}(t)A_{-\mathbf{k}}^{\beta}(t) = & -\sum_{\gamma} \{M_{\mathbf{k}}^{\alpha\gamma}A_{\mathbf{k}}^{\gamma}(t)A_{-\mathbf{k}}^{\beta}(t) \\ & + M_{-\mathbf{k}}^{\beta\gamma}A_{\mathbf{k}}^{\alpha}(t)A_{-\mathbf{k}}^{\gamma}(t)\}. \end{aligned} \quad (2.9)$$

We again write (2.9) in the matrix form introducing $\mathcal{Q}_{\mathbf{k}}(t)$, which is the column matrix in the composite space of $\mathbf{A}_{\mathbf{k}}(t)$ and $\mathbf{A}_{-\mathbf{k}}(t)$ and has the following $\alpha\beta$ element:

$$\mathcal{Q}_{\mathbf{k}}^{\alpha\beta}(t) = A_{\mathbf{k}}^{\alpha}(t)A_{-\mathbf{k}}^{\beta}(t). \quad (2.10)$$

Then (2.9) can be written as

$$\frac{d}{dt}\mathcal{Q}_{\mathbf{k}}(t) = -\mathfrak{N}_{\mathbf{k}} \cdot \mathcal{Q}_{\mathbf{k}}(t), \quad (2.11)$$

where $\mathfrak{N}_{\mathbf{k}}$ is the composite matrix of $\mathbf{M}_{\mathbf{k}}$ and $\mathbf{M}_{-\mathbf{k}}$ whose $\alpha\beta\text{-}\gamma\delta$ element is given by

$$\mathfrak{N}_{\mathbf{k}}^{\alpha\beta\text{-}\gamma\delta} \equiv \delta_{\beta\delta}M_{\mathbf{k}}^{\alpha\gamma} + \delta_{\alpha\gamma}M_{-\mathbf{k}}^{\beta\delta}. \quad (2.12)$$

With this notation the integral in (2.5) is written as

$$\int_0^{\infty} dt \langle \mathcal{Q}_{\mathbf{k}}^{\alpha\beta}(t) J \rangle \quad (2.13)$$

and using the formal solution of (2.11), this expression reduces to

$$\sum_{\sigma\tau} [\mathfrak{N}_{\mathbf{k}}^{-1}]_{\alpha\beta\text{-}\sigma\tau} \langle \mathcal{Q}_{\mathbf{k}}^{\sigma\tau} J \rangle, \quad (2.14)$$

where it is assumed that the real parts of the eigenvalues of the matrix $\mathbf{M}_{\mathbf{k}}$ are positive definite.

Thus, using the definition (2.10), the transport

coefficient (2.5) becomes,

$$\Delta\theta = \frac{w}{V} \sum_{\alpha\beta} \sum_{\gamma\delta} \sum_{\mathbf{k}} S_{\alpha\beta}^{\mathbf{k}} [\mathfrak{N}_{\mathbf{k}}^{-1}]_{\alpha\beta\text{-}\gamma\delta} \langle A_{\mathbf{k}}^{\gamma} A_{-\mathbf{k}}^{\delta} J \rangle. \quad (2.15)$$

If we can calculate $S_{\alpha\beta}^{\mathbf{k}}$ from (2.4), and we know the macroscopic equations of motion (2.6), and we can compute the equal-time correlations of fluctuations appearing in (2.15), (2.15) gives the anomaly in the transport coefficient near the critical point. The anomaly arises as the result of the anomalous increase in the contributions to (2.15) from small k .

The formula (2.15) is still quite involved for actual calculation of the anomaly, and we shall introduce further approximations to simplify it. First, we use the random-phase approximation to reduce the thermal averages of the products of four A 's in (2.4) which should not be bad except, perhaps, in the immediate vicinity of the critical point, because A 's are the macroscopic variables and their fluctuations will follow the Gaussian distribution. Next we shall choose $A_{\mathbf{k}}$'s such that different $A_{\mathbf{k}}$'s are orthogonal, or are orthogonal in the limit of small k like the temperature and the concentration. That is, for small k ,

$$\langle A_{\mathbf{k}}^{\alpha} A_{\mathbf{k}'}^{\beta*} \rangle \cong \delta_{\alpha\beta} \delta_{\mathbf{k}\mathbf{k}'} \langle |A_{\mathbf{k}}^{\alpha}|^2 \rangle, \quad (2.16)$$

where we have used the fact that the system is spatially homogeneous. The error committed in (2.16) is of higher order in k and is thus assumed not to affect the anomalous part $\Delta\theta$ of θ . [However, see the discussion at the end of Sec. 3.] Then we have

$$\begin{aligned} \langle A_{\mathbf{k}}^{\alpha} A_{-\mathbf{k}}^{\beta}; A_{\mathbf{k}'}^{\gamma*} A_{-\mathbf{k}'}^{\delta*} \rangle \cong & (\delta_{\mathbf{k}\mathbf{k}'} \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\mathbf{k},-\mathbf{k}'} \delta_{\alpha\delta} \delta_{\beta\gamma}) \\ & \times \langle |A_{\mathbf{k}}^{\alpha}|^2 \rangle \langle |A_{-\mathbf{k}}^{\beta}|^2 \rangle, \end{aligned} \quad (2.17)$$

and (2.4) becomes,

$$\begin{aligned} \langle J A_{\mathbf{k}}^{\alpha*} A_{-\mathbf{k}}^{\beta*} \rangle \\ = (S_{\alpha\beta}^{\mathbf{k}} + S_{\beta\alpha}^{-\mathbf{k}}) \langle |A_{\mathbf{k}}^{\alpha}|^2 \rangle \langle |A_{-\mathbf{k}}^{\beta}|^2 \rangle. \end{aligned} \quad (2.18)$$

If we note that from the form of the expansion (2.2) we can choose

$$S_{\alpha\beta}^{\mathbf{k}} = S_{\beta\alpha}^{-\mathbf{k}}, \quad (2.19)$$

(2.15) can be finally brought to the following form:

$$\begin{aligned} \Delta\theta = \frac{w}{2V} \sum_{\alpha\beta} \sum_{\gamma\delta} \sum_{\mathbf{k}} [\mathfrak{N}_{\mathbf{k}}^{-1}]_{\alpha\beta\text{-}\gamma\delta} \langle J A_{\mathbf{k}}^{\alpha*} A_{-\mathbf{k}}^{\beta*} \rangle \\ \times \langle J A_{\mathbf{k}}^{\gamma} A_{-\mathbf{k}}^{\delta} \rangle \langle |A_{\mathbf{k}}^{\alpha}|^2 \rangle^{-1} \langle |A_{-\mathbf{k}}^{\beta}|^2 \rangle^{-1}. \end{aligned} \quad (2.20)$$

The evaluation of this expression requires quantities of the form $\langle J A_{\mathbf{k}}^{\alpha} A_{-\mathbf{k}}^{\beta} \rangle$, besides the knowledge of the macroscopic equations of motion contained in $\mathbf{M}_{\mathbf{k}}$. There appears to be, unfortunately, no general and easy way to evaluate these quantities. However, in some cases, the virial theorem⁹ can be generalized to reduce

⁹ J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, (John Wiley & Sons, Inc., New York, 1954); I. Oppenheim and P. Mazur, *Physica* 23, 197 (1957).

these quantities to more tractable ones as we shall see in Appendix B.

3. SHEAR VISCOSITY OF CRITICAL MIXTURES

In order to illustrate how the general scheme of the previous section works, we shall now consider the shear viscosity η of critical mixtures which was first studied by Fixman.¹ We then have $w=1/k_B T$, where k_B is the Boltzmann constant and T the absolute temperature. $J=I^{\alpha\beta}$, and $I^{\alpha\beta}$ is the $\alpha\beta$ component of the stress tensor defined by

$$I^{\alpha\beta} \equiv \sum_i \frac{p_i^\alpha p_i^\beta}{m_i} - \sum_{i < j} r_{ij}^\alpha \frac{\partial u_{ij}}{\partial r_{ij}^\beta}, \quad (3.1)$$

where u_{ij} is the potential of the intermolecular force between the particles i and j which is assumed to be a function only of $|\mathbf{r}_{ij}|$. m_i is the mass of the particle i .³ The macroscopic equations of motion to be used in evaluating (2.20) consist of four equations: the continuity equation, the Navier-Stokes equation, the energy transport equation, and the equation of continuity for the concentration.¹⁰ Since near the critical point, only the concentration fluctuation and the energy fluctuation become anomalously large, we may use the simplified macroscopic equations of motion for the temperature and the concentration in which the pressure is kept constant, which become in the linearized form and in the limit of small gradients,¹¹

$$\partial T / \partial t - (\rho D_T / \alpha C) \partial c / \partial t = (\lambda / \rho C) \nabla^2 T, \quad (3.2a)$$

$$\partial c / \partial t = D \nabla^2 c + (D_T / T) \nabla^2 T, \quad (3.2b)$$

where we have generally followed the notation used in Refs. 1, 10, and 11 with some alterations. c is the local concentration, D the diffusion constant, D_T the thermal diffusion coefficient, ρ the mass density, λ the thermal conductivity, C the specific heat per unit mass at the constant pressure, and α is a constant defined by

$$D = \alpha (\partial \mu / \partial c)_{P, T / \rho}, \quad (3.3)$$

where μ is the chemical potential of the second species relative to that of the first defined in Ref. 10. (See also Ref. 22.) We further simplify the treatment by ignoring the difference in the specific heats at constant pressure and at constant volume, which would not be serious for binary mixtures. At the critical point $(\partial \mu / \partial c)_{P, T}$ and hence D vanish, and C goes to infinity. Other quantities appearing in the coefficients of (3.2) appear to remain finite.¹²⁻¹⁴ In order to use these equations to calculate the anomalous part of η , $\Delta\eta$, we must generalize (3.2)

to take account of higher terms in the gradients,² which can be done most easily in Fourier space. Thus we first write (3.2) as

$$\partial T_{\mathbf{k}} / \partial t - (\rho D_T / \alpha C) \partial c_{\mathbf{k}} / \partial t = -(\lambda / \rho C) k^2 T_{\mathbf{k}}, \quad (3.4a)$$

$$\partial c_{\mathbf{k}} / \partial t = -D k^2 c_{\mathbf{k}} - (D_T / T) k^2 T_{\mathbf{k}}. \quad (3.4b)$$

Or,

$$\partial c_{\mathbf{k}} / \partial t = -D k^2 c_{\mathbf{k}} - (D_T / T) k^2 T_{\mathbf{k}}, \quad (3.5a)$$

$$\partial T_{\mathbf{k}} / \partial t = -(\rho D D_T / \alpha C) k^2 c_{\mathbf{k}} - (\rho D_T^2 / \alpha T + \lambda / \rho) / C \cdot k^2 T_{\mathbf{k}}, \quad (3.5b)$$

where

$$c_{\mathbf{k}} = (2\pi)^{-3} \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} [c(\mathbf{r}) - \langle c \rangle], \text{ etc.} \quad (3.6)$$

This is of the form of (2.6), where¹⁵

$$\langle \mathbf{A}_{\mathbf{k}}(t) \rangle_{\mathbf{i}} \equiv \begin{pmatrix} c_{\mathbf{k}} \\ T_{\mathbf{k}} \end{pmatrix}, \quad (3.7)$$

and

$$\mathbf{M}_{\mathbf{k}} \rightarrow \begin{bmatrix} D k^2 & (D_T / T) k^2 \\ (\rho D D_T / \alpha C) k^2 & (\rho D_T^2 / \alpha T + \lambda / \rho) k^2 / C \end{bmatrix} \quad \text{as } k \rightarrow 0. \quad (3.8)$$

Since D and $1/C$ vanish at the critical point, these quantities depend strongly on \mathbf{k} [also see Sec. 5] and we must replace D and $1/C$ by $D(\mathbf{k})$ and $1/C(\mathbf{k})$ which we assume to be of the following forms:

$$D(\mathbf{k}) = \gamma (\kappa_1^2 + k^2), \quad (D = \gamma \kappa_1^2), \quad (3.9)$$

$$1/C(\mathbf{k}) = g (\kappa_2^2 + k^2), \quad (C = 1/g \kappa_2^2), \quad (3.10)$$

where κ_1^2 and κ_2^2 vanish at the critical point T_c , and γ and g stay finite there. The \mathbf{k} dependence of $D(\mathbf{k})$ is mostly due to the correlation in the concentration fluctuation, see (3.17) below and Sec. 5. Here some care must be exercised in determining $\mathbf{M}_{\mathbf{k}}$ which is related to the definition of the temperature in the nonuniform situation. In our simple case, for canonical ensemble, the total energy fluctuation δE is related to the temperature fluctuation δT by $\delta E = V \rho C \delta T$ and the specific heat C is expressed as,

$$\langle (\delta E)^2 \rangle = k_B T^2 V \rho C, \quad (3.11)$$

or

$$\langle (\delta T)^2 \rangle = k_B T^2 / V \rho C. \quad (3.12)$$

See Ref. 5. Now, $C(\mathbf{k})$ is expressed in terms of the Fourier transform $\delta e_{\mathbf{k}'}$ of the local energy density fluctuation $\delta e'(\mathbf{r})$ at a fixed local concentration, $\delta e'(\mathbf{r}) = \delta e(\mathbf{r}) - (\partial E / \partial c)_{T, V} / V \cdot \delta c(\mathbf{r})$, in the following way:

$$C(\mathbf{k}) = \frac{(2\pi)^6}{k_B T^2 V \rho} \langle |\delta e_{\mathbf{k}'}|^2 \rangle \quad (3.13)$$

¹⁵ Here $c_{\mathbf{k}}$ and $T_{\mathbf{k}}$ are used to denote both the macroscopic variables and their nonequilibrium ensemble averages.

¹⁰ L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1959).

¹¹ R. D. Mountain, *J. Res. Natl. Bur. Std. A69*, 523 (1965).

¹² For D , see Ref. 2, for D_T see Refs. 2 and 13 and for λ see Ref. 14.

¹³ G. Thomaes, *J. Chem. Phys.* **25**, 32 (1956).

¹⁴ J. V. Sengers, in *Proceedings of the Conference on the Phenomena near the Critical Point*, Washington, D.C., 1965 (to be published), and the references cited therein.

which reduces to (3.11) for $k=0$ because for canonical ensemble $\int \delta c(\mathbf{r}) d\mathbf{r} = 0$. Here, $\delta e(\mathbf{r})$ and $\delta c(\mathbf{r})$ are the fluctuations of the local energy density and the local concentration, respectively. Then, (3.10) means that the energy fluctuation at a fixed local concentration has the correlation range of κ_2^{-1} which becomes infinite at T_c like $C^{1/2}$. Thus, if we define the local temperature fluctuation $\delta T(\mathbf{r})$ by

$$\delta T(\mathbf{r}) = (\rho C)^{-1} \delta e'(\mathbf{r}), \quad \text{or} \quad \delta T_k = (\rho C)^{-1} \delta e_k', \quad (3.14)$$

the temperature fluctuation has also the same correlation range κ_2^{-1} , although its magnitude nearly vanishes near T_c .¹⁶ Thus we have, using (3.13) and (3.10),

$$\langle |T_k|^2 \rangle = \frac{k_B T^2 V}{(2\pi)^6 \rho C^2} C(\mathbf{k}) = V \xi_2 / (\kappa_2^2 + k^2), \quad (3.15)$$

where

$$\xi_2 \equiv \frac{k_B T^2}{(2\pi)^6 g \rho C^2} = \frac{k_B T^2 g}{(2\pi)^6 \rho} \kappa_2^4. \quad (3.16)$$

The concentration fluctuation can be expressed near T_c in a similar form:

$$\langle |c_k|^2 \rangle = V \xi_1 / (\kappa_1^2 + k^2), \quad (3.17)$$

where¹⁷

$$\xi_1 \equiv 2(n \partial c / \partial n)^2 a / (2\pi)^5 \quad (3.18)$$

with n the number density of the 2nd species and a some constant giving the magnitude of the concentration fluctuation.^{1,18}

In determining \mathbf{M}_k , we make use of the generalized Onsager relation¹⁹ which can be written if A 's are even variables under the time reversal as,²⁰

$$(\chi_k^{-1} \cdot \mathbf{M}_k)_{\alpha\beta} = (\chi_k^{*-1} \cdot \mathbf{M}_k^*)_{\beta\alpha}, \quad (3.19)$$

where χ_k is the generalized susceptibility matrix whose $\alpha\beta$ element is,

$$\chi_k^{\alpha\beta} \equiv \langle A_k^\alpha A_k^{\beta*} \rangle / k_B T V. \quad (3.20)$$

¹⁶ Alternatively, one could define the temperature by

$$\delta T_k = [\rho C(k)]^{-1} \delta e_k'. \quad (3.14a)$$

Then the range of correlation of the local temperature fluctuation becomes very short even near T_c .

¹⁷ In taking the derivative, we use the following relation

$$V_1 dn_1 + V_2 dn_2 = 0,$$

where we write V_i , n_i for the partial molecular volume and the number density of the i th component, respectively. Therefore, $n \partial c / \partial n$ of (3.18) is $[V_1 n_2 (n_1 + n_2)]^{-1}$. See Ref. 1 and M. Fixman, J. Chem. Phys. 36, 1957 (1962).

¹⁸ κ_1^2 associated with the density fluctuation of one-component fluid is discussed in M. E. Fisher, J. Math. Phys. 5, 944 (1964) and the references cited therein. κ_1^2 for ferromagnetism is given in P. G. de Gennes, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. III, and the references cited therein. κ_2^2 for the spin system is calculated in K. Kawasaki, Progr. Theor. Phys. (Kyoto) 29, 801 (1963), Appendix.

¹⁹ H. Mori, Progr. Theoret. Phys. (Kyoto) 33, 423 (1965); 34, 399 (1965); in Proceedings of the Symposium on Inelastic Scattering of Neutrons, Brookhaven, 1965 (Brookhaven National Laboratory, 1966).

²⁰ B. U. Felderhof, J. Chem. Phys. 44, 602 (1966).

In our case, if we ignore $\langle c_k T_k^* \rangle$ because it vanishes⁵ as $k \rightarrow 0$ [see also the end of this section], we have

$$\chi_k \cong \begin{bmatrix} \langle |c_k|^2 \rangle & 0 \\ 0 & \langle |T_k|^2 \rangle \end{bmatrix} \times (k_B T V)^{-1}. \quad (3.21)$$

Thus the only restriction imposed by (3.19) is,

$$M_k^{12} / \langle |c_k|^2 \rangle = M_k^{21*} / \langle |T_k|^2 \rangle. \quad (3.22)$$

That this is satisfied in the limit of small k is seen as follows. First, there is a relation between $(\partial \mu / \partial c)_{P,T}$ and κ_1 which is the analog of the fluctuation theorem for the isothermal compressibility of the one-component fluid²¹ and near T_c is written as,²²

$$(\partial \mu / \partial c)_{P,T} \cong (\partial n / \partial c / n)^2 k_B T \kappa_1^2 / 4\pi a \rho. \quad (3.23)$$

This, together with (3.3), (3.9), and (3.18), leads to

$$\gamma = (\partial n / \partial c / n)^2 \alpha k_B T / 4\pi a \rho^2 = \alpha k_B T / (2\pi)^6 \rho^2 \xi_1. \quad (3.24)$$

We now have from (3.8), and (3.17) for $k \rightarrow 0$

$$M_k^{12} / k^2 \langle |c_k|^2 \rangle \rightarrow \kappa_1^2 D_T / V T \xi_1. \quad (3.25)$$

We also have by (3.8) and (3.15),

$$M_k^{21} / k^2 \langle |T_k|^2 \rangle \rightarrow \rho D D_T \kappa_2^2 / \alpha C V \xi_2, \quad (3.26)$$

which reduces to (3.25) if we use (3.16), (3.9), (3.10), and (3.24). For larger k , then, in order to satisfy (3.22), we assume

$$M_k^{12} = (D_T / T \kappa_2^2) k^2 (\kappa_2^2 + k^2), \quad (3.27)$$

$$M_k^{21} = (\rho \gamma D_T g \kappa_2^2 / \alpha) k^2 (\kappa_1^2 + k^2), \quad (3.28)$$

where we have made explicit the quantities κ_1^2 and κ_2^2 which vanish at T_c . The rest of \mathbf{M}_k is immediately written down:

$$M_k^{11} = \gamma k^2 (\kappa_1^2 + k^2), \quad (3.29)$$

$$M_k^{22} = (\lambda / \rho + \rho D_T^2 / \alpha T) g k^2 (\kappa_2^2 + k^2), \quad (3.30)$$

which completes the derivation of the macroscopic equations of motion.

The next step is to evaluate $\langle I^{xy} | c_k|^2 \rangle$, $\langle I^{xy} c_k T_k^* \rangle$ and $\langle I^{xy} | T_k|^2 \rangle$. The first one is obtained in Appendix B, (B20) where we set $\alpha = x$, $\beta = y$:

$$\langle I^{xy} | c_k|^2 \rangle = -k_B T k^y \frac{\partial}{\partial k^x} \langle |c_k|^2 \rangle. \quad (3.31)$$

There we present an argument that $\langle I^{xy} c_k e_k^* \rangle$ and $\langle I^{xy} | e_k|^2 \rangle$ essentially may have the properties similar to those of $k^y \partial \langle c_k e_k^* \rangle / \partial k^x$ and $k^y \partial \langle |e_k|^2 \rangle / \partial k^x$, respectively, near the critical point. Since T_k can be expressed in terms of c_k and e_k , $\langle I^{xy} c_k T_k^* \rangle$ and $\langle I^{xy} | T_k|^2 \rangle$ may also be considered to have the properties similar to

²¹ M. E. Fisher, Ref. 18.

²² This is derived by using (69), (68), (36) of Ref. 1 and the Gibbs-Duhem relation $n_1 d\mu_1 + n_2 d\mu_2 = 0$ with $\mu = \mu_1 / m_1 - \mu_2 / m_2$ where μ_i is the chemical potential of the i th component.

$k^y \partial \langle c_k T_k^* \rangle / \partial k^x$ and $k^y \partial \langle |T_k|^2 \rangle / \partial k^x$, respectively. Since $\langle c_k T_k^* \rangle$ vanishes as k goes to zero, the term $\langle I^{xy} c_k T_k^* \rangle$ has an additional factor of k compared to the other two terms, and may be neglected near T_c [see also the end of this section]. We then assume that

$$\langle I^{xy} |T_k|^2 \rangle = -k_B T' k^y \frac{\partial}{\partial k^x} \langle |T_k|^2 \rangle, \quad (3.32)$$

where T' is a constant of the magnitude of T . The difference $T' - T$ takes care of possible additional terms such as those appearing in (B25) and (B27). Use of (3.15) and (3.17) then leads to,

$$\langle I^{xy} |c_k|^2 \rangle = 2k_B T V \xi_1 k^x k^y / (\kappa_1^2 + k^2)^2, \quad (3.33)$$

$$\langle I^{xy} |T_k|^2 \rangle = 2k_B T' V \xi_2 k^x k^y / (\kappa_2^2 + k^2)^2. \quad (3.34)$$

With these preparations, we are now ready to evaluate the anomalous part of shear viscosity $\Delta\eta$, which can now be written as,

$$\Delta\eta = \frac{1}{2V k_B T} \sum_{\alpha} \sum_{\beta} \sum_{\mathbf{k}} [\mathfrak{N}_{\mathbf{k}}^{-1}]_{\alpha\alpha:\beta\beta} \times \langle I^{xy} |A_{\mathbf{k}^{\alpha}}|^2 \rangle \langle I^{xy} |A_{\mathbf{k}^{\beta}}|^2 \rangle \langle |A_{\mathbf{k}^{\alpha}}|^2 \rangle^{-2}, \quad (3.35)$$

where $A_{\mathbf{k}^{\alpha}}$ is $c_{\mathbf{k}}$ and $T_{\mathbf{k}}$, and $\mathfrak{N}_{\mathbf{k}}$ is the 4×4 matrix given by (2.12) and (3.27)–(3.30). Then, (3.35) is conveniently divided into four parts:

$$\Delta\eta = \sum_{\alpha\beta} \Delta\eta_{\alpha\beta}, \quad \alpha, \beta = 1, 2, \quad (3.36)$$

where $\Delta\eta_{\alpha\beta}$ becomes, if we write

$$\langle I^{xy} |A_{\mathbf{k}^{\alpha}}|^2 \rangle = 2k_B T_{\alpha} V \xi_{\alpha} k^x k^y / (\kappa_{\alpha}^2 + k^2)^2, \quad \alpha = 1, 2, \quad (3.37)$$

where

$$\begin{aligned} T_{\alpha} &\equiv T, & \alpha = 1 \\ &\equiv T', & \alpha = 2, \end{aligned}$$

and use (3.15) and (3.17),

$$\Delta\eta_{\alpha\beta} \equiv 2 \frac{k_B T_{\alpha} T_{\beta}}{T} \frac{\xi_{\beta}}{\xi_{\alpha}} \frac{1}{V} \sum_{\mathbf{k}} [\mathfrak{N}_{\mathbf{k}}^{-1}]_{\alpha\alpha:\beta\beta} \times (k^x k^y)^2 / (\kappa_{\beta}^2 + k^2)^2. \quad (3.38)$$

$\mathfrak{N}_{\mathbf{k}}^{-1}$ can now be regarded as a 2×2 matrix;

$$(\mathfrak{N}_{\mathbf{k}}^{-1})_{\alpha\alpha:\beta\beta} = \frac{1}{2\Delta_{\mathbf{k}}'} \begin{bmatrix} M_{\mathbf{k}}^{22}(M_{\mathbf{k}}^{11} + M_{\mathbf{k}}^{22}) - M_{\mathbf{k}}^{12} M_{\mathbf{k}}^{21} & (M_{\mathbf{k}}^{12})^2 \\ (M_{\mathbf{k}}^{21})^2 & M_{\mathbf{k}}^{11}(M_{\mathbf{k}}^{11} + M_{\mathbf{k}}^{22}) - M_{\mathbf{k}}^{12} M_{\mathbf{k}}^{21} \end{bmatrix}, \quad (3.39)$$

where

$$\begin{aligned} \Delta_{\mathbf{k}}' &\equiv (M_{\mathbf{k}}^{11} + M_{\mathbf{k}}^{22})(M_{\mathbf{k}}^{11} M_{\mathbf{k}}^{22} - M_{\mathbf{k}}^{12} M_{\mathbf{k}}^{21}) \\ &= k^6 (\lambda g \gamma / \rho) (\kappa_1^2 + k^2) (\kappa_2^2 + k^2) [\gamma (\kappa_1^2 + k^2) + g (\lambda / \rho + \rho D_T^2 / \alpha T) (\kappa_2^2 + k^2)]. \end{aligned} \quad (3.40)$$

More explicitly, using (3.27)–(3.30),

$$\begin{aligned} (\mathfrak{N}_{\mathbf{k}}^{-1})_{\alpha\alpha:\beta\beta} &= \frac{1}{2\Delta_{\mathbf{k}}'} \left[\begin{array}{cc} \{ (\lambda / \rho) (\kappa_1^2 + k^2) + (g / \gamma) (\lambda / \rho + \rho D_T^2 / \alpha T) (\kappa_2^2 + k^2) \} / (\kappa_1^2 + k^2) & (D_T / T \kappa_2^2)^2 / g \gamma \cdot (\kappa_2^2 + k^2) / (\kappa_1^2 + k^2) \\ g \gamma (\rho D_T \kappa_2^2 / \alpha)^2 (\kappa_1^2 + k^2) / (\kappa_2^2 + k^2) & [(\gamma / g) (\kappa_1^2 + k^2) + (\lambda / \rho) (\kappa_2^2 + k^2)] / (\kappa_2^2 + k^2) \end{array} \right] \end{aligned} \quad (3.41)$$

$$\Delta_{\mathbf{k}} \equiv k^2 (\lambda / \rho) [\gamma (\kappa_1^2 + k^2) + g (\lambda / \rho + \rho D_T^2 / \alpha T) (\kappa_2^2 + k^2)]. \quad (3.42)$$

This allows us to calculate $\Delta\eta$. Near T_c both κ_1 and κ_2 approach zero and, as we shall see below, contributions from small k dominate in (3.38), and give anomalously large $\Delta\eta$. In order to investigate this in more detail, we assume that $\kappa_1 \ll \kappa_2$ for the temperatures sufficiently close to T_c . This comes from the fact that the specific heat diverges much more slowly near T_c compared with $1 / (\partial \mu / \partial c)_{P,T}$ [for isothermal compressibility in a one-component fluid or magnetic susceptibility in a ferromagnet].

We now study each $\Delta\eta_{\alpha\beta}$, separately. First let us consider $\Delta\eta_{11}$. Inspection of (3.38), (3.41), and (3.42) tells us that here the major contribution comes from the

region $k \sim \kappa_1$ and we obtain

$$(\mathfrak{N}_{\mathbf{k}}^{-1})_{11:11} \cong (2k^2 \gamma)^{-1} (1 + \rho^2 D_T^2 / \alpha \lambda T) / (\kappa_1^2 + k^2). \quad (3.43)$$

$\Delta\eta_{11}$ becomes

$$\begin{aligned} \Delta\eta_{11} &= 2k_B T \frac{1}{V} \sum_{\mathbf{k}} (\mathfrak{N}_{\mathbf{k}}^{-1})_{11:11} (k^x k^y)^2 / (\kappa_1^2 + k^2)^2 \\ &= \Delta\eta_F (1 + \rho^2 D_T^2 / \alpha \lambda T), \end{aligned} \quad (3.44)$$

where

$$\Delta\eta_F \equiv \frac{k_B T}{\gamma} \frac{1}{V} \sum_{\mathbf{k}} \frac{(k^x k^y)^2}{k^2 (\kappa_1^2 + k^2)^3}. \quad (3.45)$$

This has been evaluated by changing the summation into an integral to yield

$$\Delta\eta_F = k_B T / (160\pi\gamma\kappa_1) \quad (3.46)$$

$$= (\rho n \partial c / \partial n)^2 (a/40\alpha)\kappa_1^{-1}, \quad (3.47)$$

where we have used (3.24) in the last step. Since the integral converges at large k , the upper limit k_{\max} does not affect (3.47). $\Delta\eta_F$ is the anomalous viscosity found by Fixman¹ in an entirely different way, and diverges as κ_1^{-1} near T_c . The same is true for $\Delta\eta_{11}$ which includes a finite correction due to thermal diffusion. This divergence at T_c is the result of the two cooperating factors: (1) the increase of the long-wavelength parts of the fluctuations contained in I^{xy} near T_c giving rise to the factor $(\kappa_1^2 + k^2)^{-2}$ in (3.44); (2) increase of the lifetimes of these parts of fluctuations which are given by $(\mathfrak{N}_k^{-1})_{11,11}$, (3.43) [critical slowing-down]. Neither one of them alone is enough to cause the divergence. Thus $\langle I^{xy} I^{xy} \rangle$ does not diverge at T_c . The origin of the correction to $\Delta\eta_F$ due to the thermal diffusion is traced to the correction in the lifetime, (3.43), which is also one-half of the inverse of the eigenvalues of the matrix \mathbf{M}_k .

The evaluation of the rest of $\Delta\eta_{\alpha\beta}$ is quite similar except that here the major contribution arises from $k \sim \kappa_2$. We give only the final results in the following:

$$\Delta\eta_{12} = \Delta\eta_{21} = \frac{1}{30\pi^2} \frac{k_B T'}{T} \frac{(\rho D_T)^2}{\alpha\lambda} \times \frac{Q(y)}{\gamma + g(\lambda/\rho + \rho D_T^2/\alpha T)} \frac{1}{\kappa_2}, \quad (3.48)$$

where

$$Q(y) \equiv \int_0^\infty dx \frac{x^2}{(x^2+1)(x^2+y)}, \quad (3.49)$$

$$y \equiv (\lambda/\rho + \rho D_T^2/\alpha T) / (\gamma/g + \lambda/\rho + \rho D_T^2/\alpha T). \quad (3.50)$$

$$\Delta\eta_{22} = \frac{1}{30\pi^2} \frac{k_B T'^2}{T} \frac{\rho}{\lambda g} \frac{\gamma + g\lambda/\rho}{\gamma + g(\lambda/\rho + \rho D_T^2/\alpha T)} \times R(y, z) \frac{1}{\kappa_2}, \quad (3.51)$$

where

$$R(y, z) \equiv \int_0^\infty dx \frac{x^4}{(1+x^2)^3} \frac{x^2+z}{x^2+y}, \quad (3.52)$$

$$z \equiv (\lambda/\rho) / (\gamma/g + \lambda/\rho) \quad (3.53)$$

and y is given by (3.50). In the absence of thermal diffusion, $D_T = 0$, $\Delta\eta_{12} = \Delta\eta_{21} = 0$ and

$$\Delta\eta_{22} = \frac{k_B T'^2}{T} \frac{\rho}{\lambda g} \frac{1}{160\pi\kappa_2}, \quad (3.54)$$

which becomes $\Delta\eta_F$ if we replace T' , $\lambda g/\rho$, and κ_2 by T , γ , and κ_1 , respectively.

In summary, we have obtained two kinds of corrections to Fixman's result, (3.47). The first one is $(\rho D_T)^2/\alpha\lambda T$ in (3.44) which is finite at T_c . Since the thermal diffusion ratio $k_T = D_T/D$ is small ($10^{-1} \sim 10^{-2}$) if we are far away from T_c and D_T appears to remain finite at T_c ,¹³ $\rho^2 D_T^2/\alpha\lambda T$ is usually very small. The second correction is given by (3.48) and (3.51). They are also small when $\kappa_2 \gg \kappa_1$ under which they have been derived. Therefore, the corrections to Fixman's result, $\Delta\eta_F$, considered here is of minor importance as far as the comparison with experiments is concerned. In fact, we could have obtained $\Delta\eta_F$ much more simply by ignoring the temperature fluctuation from the beginning. The main reason for going through this complicated case is that we wished to illustrate our general theory for the case where we have at least two coupled macroscopic variables.

In the example of this section, we have always ignored $\langle c_k T_k^* \rangle$ on the ground that it vanishes as $k \rightarrow 0$ which simplified the treatment somewhat. Actually, however, this must be taken with some reservation if k becomes of the order of the inverses of correlation lengths of critical fluctuations. For example, the function $k^2/(\kappa_1^2 + k^2) \times (\kappa_2^2 + k^2)$ vanishes as k goes to zero, but for $k \sim \kappa_2$ it cannot be neglected compared with $1/(\kappa_1^2 + k^2)$. Since we do not know $\langle c_k T_k^* \rangle$ near T_c , we cannot get a reliable estimate of the error committed by neglecting it, although this is expected not to change the major conclusions of this section. Thus for the moment the treatment given in this section only serves mainly for an illustrative purpose.

A similar remark also applies to the approximation (2.16) when A_k^α and $A_k^{\beta*}$ ($\alpha \neq \beta$) are not exactly orthogonal for $k \neq 0$. We can then certainly replace (2.16) by

$$\langle A_k^\alpha A_{k'}^{\beta*} \rangle = \delta_{kk'} \langle A_k^\alpha A_k^{\beta*} \rangle. \quad (2.16')$$

Then the equation determining $S_{\alpha\beta}^k$ will be still an algebraic equation which is a little more complicated than (2.18). Alternatively, we can also transform A_k^{α} 's so as to satisfy (2.16) exactly. We hope to come back to this question on another occasion.

4. NONLOCAL VISCOSITY

The study of the anomaly near T_c in the shear viscosity of Sec. 3 indicates that the anomaly arises from: (1) the anomalous increase of the long wavelength parts of the fluctuations of I^{xy} , and (2) the anomalous increase of decay times associated with these fluctuations. This immediately suggests that the shear viscosity may become nonlocal in space and time near T_c . In other words, the shear viscosity may exhibit considerable amount of wave vector (\mathbf{q}) and frequency (ω) dependence near T_c .

In order to investigate this problem, we first obtain the correlation function expression for \mathbf{q} , ω -dependent shear viscosity. Thus, let us consider the \mathbf{q} th Fourier component of the transverse part of the local momen-

tum density \mathbf{P}_q defined by

$$\mathbf{P}_q \equiv (2\pi)^{-3} \sum_j i\mathbf{q} \times \mathbf{p}_j e^{-i\mathbf{q} \cdot \mathbf{r}_j}, \quad (4.1)$$

where we assume classical mechanics. If we write the Laplace transform of the time correlation function of P_q^x as follows by taking the z axis in the direction of \mathbf{q} :

$$\int_0^\infty \langle P_q^x(t) P_q^{x*} \rangle e^{-tz} dt = \langle |P_q^x|^2 \rangle / [z + q^2 \eta(\mathbf{q}, z) / \rho], \quad (4.2)$$

where ρ is the mass density, $\eta(\mathbf{q}, z)$ can be shown to reduce to the shear viscosity η in the limit of q and z go to zero.²³ If we use the following identity due to Mori,¹⁹ which can be obtained from (A11) specializing to the case of a single macroscopic variable A [for the notation, see Appendix A]:

$$\int_0^\infty dt \langle A(t) A(0) \rangle e^{-tz} = \langle A^2 \rangle / [z - i\hat{\omega} + \varphi^L(z)], \quad (4.3)$$

we obtain

$$\eta(\mathbf{q}, z) = \frac{q^2 \rho}{(2\pi)^6 \langle |P_q^x|^2 \rangle} \int_0^\infty \langle \hat{I}_q^{yz}(t) I_q^{yz*} \rangle e^{-tz} dt, \quad (4.4)$$

where

$$I_q^{\alpha\beta} \equiv \sum_j \frac{\hat{p}_j^\alpha \hat{p}_j^\beta}{m_j} e^{-i\mathbf{q} \cdot \mathbf{r}_j} - \frac{1}{2} \sum_{j \neq l} \sum \frac{\partial u_{jl}}{\partial \mathbf{r}_{jl}^\alpha} r_{jl}^\beta e^{-i\mathbf{q} \cdot \mathbf{r}_j}, \quad \alpha \neq \beta \quad (4.5)$$

which reduces to the stress tensor $I^{\alpha\beta}$, (3.1), when q goes to zero, and $I_q^{\alpha\beta}(t)$ differs from $I^{\alpha\beta}(t)$ in that its temporal development is governed by the special Liouville operator L_1 introduced in Appendix A, (A6), which is designed to remove the secular term in $I_q^{\alpha\beta}(t)$ at long times. Thus, $\eta(\mathbf{q}, i\omega)$ is naturally regarded as a \mathbf{q} , ω -dependent shear viscosity which becomes, if we note that $(2\pi)^6 \langle |P_q|^2 \rangle = q^2 k_B T \rho V$,

$$\eta(\mathbf{q}, i\omega) = \frac{1}{k_B T V} \int_0^\infty \langle \hat{I}_q^{yz}(t) I_q^{yz*} \rangle e^{-it\omega} dt. \quad (4.6)$$

This reduces to η of Sec. 3 in the limit of small q and ω as mentioned above. It should be noted that this limit is independent of the order in which the two limits are taken in contrast to other definitions such as (4.7) below simply because $\hat{I}_q^{\alpha\beta}(t)$ does not contain secular contributions at long times even for a finite q .

Unfortunately, however, it is not yet clear how to handle in general the time correlation function of the

quantities whose temporal development is governed by L_1 . Therefore, we consider another quantity $\eta'(\mathbf{q}, i\omega)$ defined by

$$\eta'(\mathbf{q}, i\omega) = \frac{1}{k_B T V} \int_0^\infty \langle I_q^{yz}(t) I_q^{yz*} \rangle e^{-it\omega} dt, \quad (4.7)$$

in which the temporal development of $I_q^{\alpha\beta}(t)$ is governed by the ordinary dynamics. The relation between (4.6) and (4.7) is obtained as a special case of (A22) as,

$$\eta(\mathbf{q}, i\omega) = \eta'(\mathbf{q}, i\omega) / [1 - \rho^{-1} q^2 \eta'(\mathbf{q}, i\omega) / i\omega], \quad (4.8)$$

or

$$\eta'(\mathbf{q}, i\omega) = \eta(\mathbf{q}, i\omega) / [1 + \rho^{-1} q^2 \eta(\mathbf{q}, i\omega) / i\omega]. \quad (4.9)$$

If, as we said earlier, $\eta(\mathbf{q}, i\omega)$ tends to a finite limit for q , ω go to zero irrespectively of the way the limit is taken, it follows from (4.9) that

$$\lim_{\omega \rightarrow 0} \lim_{q \rightarrow 0} \eta'(\mathbf{q}, i\omega) = \eta, \quad (4.10)$$

$$\lim_{\omega \rightarrow 0} \eta'(\mathbf{q}, i\omega) = 0, \quad (q \neq 0). \quad (4.11)$$

The anomalous part of $\eta'(\mathbf{q}, i\omega)$ in the quadratic approximation can be obtained either by generalizing (2.20) or using the results of Appendix A as follows:

$$\begin{aligned} \Delta\eta'(\mathbf{q}, i\omega) &= \frac{1}{2k_B T V} \sum_{\alpha\beta} \sum_{\gamma\delta} \sum_{\mathbf{k}} [i\omega + \mathfrak{N}_{\mathbf{k}}(\mathbf{q})]_{\alpha\beta:\gamma\delta}^{-1} \\ &\quad \times \langle I_q^{yz} A_{\mathbf{k}}^{\alpha*} A_{\mathbf{q}-\mathbf{k}}^{\beta*} \rangle \langle I_q^{yz*} A_{\mathbf{k}}^{\gamma} A_{\mathbf{q}-\mathbf{k}}^{\delta} \rangle \\ &\quad \times \langle |A_{\mathbf{k}}^\alpha|^2 \rangle^{-1} \langle |A_{\mathbf{q}-\mathbf{k}}^\beta|^2 \rangle^{-1}, \quad (4.12) \end{aligned}$$

where $\mathfrak{N}_{\mathbf{k}}(\mathbf{q})$ is the composite matrix of $\mathbf{M}_{\mathbf{k}}$ and $\mathbf{M}_{\mathbf{q}-\mathbf{k}}$ whose $\alpha\beta-\gamma\delta$ element is

$$\mathfrak{N}_{\mathbf{k}}^{\alpha\beta:\gamma\delta}(\mathbf{q}) \equiv \delta_{\beta\delta} M_{\mathbf{k}}^{\alpha\gamma} + \delta_{\alpha\gamma} M_{\mathbf{q}-\mathbf{k}}^{\beta\delta}, \quad (4.13)$$

and we have assumed the form of macroscopic equations of motion (2.6) which is local in time. Here it is noted that (4.12) does not approach zero in the limit of zero ω with a finite q . This contradicts (4.11) because (4.12) contains anomalous part which dominates $\eta'(\mathbf{q}, i\omega)$ for small q and ω near T_c . This is because in the process of introducing the approximations leading to (4.12), the secular part at long times contained in (4.7) is washed out. Thus in fact we ought to identify (4.12) with the anomalous part of η , $\Delta\eta(\mathbf{q}, i\omega)$. With this new $\Delta\eta(\mathbf{q}, i\omega)$ which is finite in the limit of small q and ω irrespectively of the way the limit is taken except precisely at $T = T_c$, (4.11) is again satisfied using (4.9).

For the macroscopic equations of motion, we now choose for simplicity the simple diffusion equation instead of those of Sec. 3,

$$\partial c_{\mathbf{k}} / \partial t = -k^2 \gamma (\kappa_1^2 + k^2) c_{\mathbf{k}}. \quad (4.14)$$

²³ B. U. Felderhof and I. Oppenheim, *Physica* **31**, 1441 (1965).

²⁴ Actually, $I_q^{\alpha\beta}$ defined in this manner contains a contribution linear in A 's for $q \neq 0$ even for $\alpha \neq \beta$. This does not contribute to $\langle I_q^{yz} A_{\mathbf{k}}^{\alpha*} A_{\mathbf{q}-\mathbf{k}}^{\beta*} \rangle$ in the random-phase approximation and has been ignored.

Thus, (4.12) leads to

$$\begin{aligned} \Delta\eta(\mathbf{q}, i\omega) = & \frac{1}{2k_B T V} \sum_{\mathbf{k}} \{i\omega + k^2\gamma(\kappa_1^2 + k^2) \\ & + (\mathbf{k} - \mathbf{q})^2\gamma[\kappa_1^2 + (\mathbf{k} - \mathbf{q})^2]\}^{-1} \\ & \times |\langle I_{\mathbf{q}}^{yz} c_{-\mathbf{k}} c_{\mathbf{k}-\mathbf{q}} \rangle|^2 \langle |c_{\mathbf{k}}|^2 \rangle^{-1} \langle |c_{\mathbf{k}-\mathbf{q}}|^2 \rangle^{-1}. \end{aligned} \quad (4.15)$$

In order to obtain $\langle I_{\mathbf{q}}^{yz} c_{-\mathbf{k}} c_{\mathbf{k}-\mathbf{q}} \rangle$, we write $I_{\mathbf{q}}^{yz}$ as

$$I_{\mathbf{q}}^{yz} = \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} j^{yz}(\mathbf{r}), \quad (4.16)$$

where $j^{yz}(\mathbf{r})$ is the local stress tensor at \mathbf{r} . The explicit expression for $j^{yz}(\mathbf{r})$ can be obtained from (4.5) and (4.16), but we do not write it here because we do not need it. Let us now expand $j^{yz}(\mathbf{r})$ in powers of the local concentration $c(\mathbf{r})$ and its gradient. If we note the tensor property of $j^{yz}(\mathbf{r})$ and that it does not contain terms linear in $c(\mathbf{r})$, we will have

$$j^{yz}(\mathbf{r}) = f \frac{\partial c}{\partial r^y} \frac{\partial c}{\partial r_z} + \dots \quad (4.17)$$

The terms not written explicitly in (4.17) are of the higher orders in c and/or in the gradient and the part which is not expressed in terms of $c(\mathbf{r})$. Therefore, we may ignore them in the quadratic approximation near T_c . To determine f , we consider

$$\begin{aligned} I^{yz} = & f \int d\mathbf{r} \frac{\partial c}{\partial r^y} \frac{\partial c}{\partial r_z} \\ = & \frac{(2\pi)^6}{V} f \sum_{\mathbf{k}} k^y k^z (c_{\mathbf{k}} c_{-\mathbf{k}} - \langle c_{\mathbf{k}} c_{-\mathbf{k}} \rangle), \end{aligned} \quad (4.18)$$

where the term with $\langle c_{\mathbf{k}} c_{-\mathbf{k}} \rangle$ does not contribute because of symmetry. If we consider $\langle I^{yz} c_{\mathbf{k}} c_{-\mathbf{k}} \rangle$ and use the random-phase approximation for the average of product of four c 's, we find

$$\langle I^{yz} c_{\mathbf{k}} c_{-\mathbf{k}} \rangle = \frac{2(2\pi)^6}{V} f k^y k^z \langle |c_{\mathbf{k}}|^2 \rangle^2. \quad (4.19)$$

Using (B20) for the left-hand side, and (3.17) and (3.18) for $\langle |c_{\mathbf{k}}|^2 \rangle$, this immediately gives for f ,

$$f = k_B T / (2\pi)^6 \xi_1 = k_B T (\partial n / \partial c / n)^2 / 4\pi a. \quad (4.20)$$

The existence of such a constant f which is finite at T_c justifies *a posteriori* the local form of (4.17). Substitution of (4.17) into (4.16) leads to

$$I_{\mathbf{q}}^{yz} = (2\pi)^6 f V^{-1} \sum_{\mathbf{k}} k^y (k^z - q^z) c_{\mathbf{k}} c_{\mathbf{q}-\mathbf{k}}, \quad (4.21)$$

from which we obtain $\langle I_{\mathbf{q}}^{yz} c_{-\mathbf{k}} c_{\mathbf{k}-\mathbf{q}} \rangle$ again with the use of the random phase approximation as follows:

$$\begin{aligned} \langle I_{\mathbf{q}}^{yz} c_{-\mathbf{k}} c_{\mathbf{k}-\mathbf{q}} \rangle = & (2\pi)^6 f V^{-1} \\ & \times [k^y (k^z - q^z) + k^z (k^y - q^y)] \langle |c_{\mathbf{k}-\mathbf{q}}|^2 \rangle \langle |c_{\mathbf{k}}|^2 \rangle. \end{aligned} \quad (4.22)$$

Substituting this into (4.15) and using (3.17) and (4.20) we obtain ($q^y = 0, q^z = q$),

$$\begin{aligned} \Delta\eta(\mathbf{q}, i\omega) = & \frac{k_B T}{2V} \sum_{\mathbf{k}} \{i\omega + k^2\gamma(\kappa_1^2 + k^2) \\ & + (\mathbf{k} - \mathbf{q})^2\gamma[\kappa_1^2 + (\mathbf{k} - \mathbf{q})^2]\}^{-1} [(2k^z - q)k^y]^2 \\ & \times [\kappa_1^2 + (\mathbf{k} - \mathbf{q})^2]^{-1} (\kappa_1^2 + k^2)^{-1}. \end{aligned} \quad (4.23)$$

We now transform this first by introducing the following dimensionless variables:

$$\xi \equiv \mathbf{q} / \kappa_1, \quad \xi_1 \equiv \mathbf{k} / \kappa_1, \quad \zeta \equiv \omega / \gamma \kappa_1^4, \quad (4.24)$$

then, by changing the summation over \mathbf{k} into an integral over ξ_1 . This then leads to

$$\Delta\eta(\mathbf{q}, i\omega) = \Delta\eta_F Z(\xi, \zeta), \quad (4.25)$$

where $\Delta\eta_F$ is the anomalous shear viscosity of Fixman given by (3.45)–(3.47), and

$$\begin{aligned} Z(\xi, \zeta) = & \frac{10}{\pi^2} \int d\xi_1 [\xi_1^y (2\xi_1^z - \xi)]^2 \\ & \times \{\zeta \xi^z + \xi_1^2 (1 + \xi_1^2) + (\xi_1 - \xi)^2 [1 + (\xi_1 - \xi)^2]\}^{-1} \\ & \times (1 + \xi_1^2)^{-1} [1 + (\xi_1 - \xi)^2]^{-1}, \end{aligned} \quad (4.26)$$

where ξ is in the direction of the z axis. In particular, we find that

$$Z(0, 0) = 1. \quad (4.27)$$

Therefore, the \mathbf{q}, ω dependence of the shear viscosity is contained in $Z(\xi, \zeta)$, which is in general complex giving rise to dissipative as well as reactive parts to $\eta(\mathbf{q}, i\omega)$.

The integral (4.26) can be transformed by the change of integration variables,

$$\xi_{11} = x, \quad \xi_1^z = y + \frac{1}{2}\xi,$$

where ξ_{11} is the component of ξ_1 perpendicular to the z axis, and extending the limits of integrals to infinity we finally obtain

$$\begin{aligned} Z(\xi, \zeta) = & \frac{40}{\pi} \int_0^\infty dx \int_{-\infty}^\infty dy x^3 y^2 \\ & \times \{(1 + x^2 + y^2)^2 + \frac{1}{2}(1 + x^2 - y^2)\xi^2 + \frac{1}{16}\xi^4\}^{-1} \\ & \times \{2(x^2 + y^2)(1 + x^2 + y^2) + (x^2 + 3y^2 + \frac{1}{2})\xi^2 \\ & + \frac{1}{8}\xi^4 + i\zeta\}^{-1}. \end{aligned} \quad (4.28)$$

Near the critical point where κ_1 is very small, ξ and ζ can become appreciable even for very small q and ω . This indicates stronger \mathbf{q}, ω dependence of $\Delta\eta(\mathbf{q}, i\omega)$ closer we approach T_c as was expected. Since (4.28) is a complicated integral, we consider a few special cases to study the properties of $Z(\xi, \zeta)$.

(a) *Zero wave vector* ($\xi = 0$) and a finite frequency ω . Near T_c , ζ can become very large. Although actually the

limits of integrals are about k_{\max}/κ_1 , this is still much greater than ζ for small ω , and the limits can be taken to infinity as in (4.28) since the integrals converge. Then the most contributions come from x , $|y| \gg 1$. Therefore, one can show that (4.28) for $\xi=0$ may be approximated by

$$Z(0, \zeta) \cong \frac{2^{1/4} \times 16}{3\pi} R \zeta^{-1/4} \sim \gamma^{1/4} \kappa_1 \omega^{-1/4} \quad (4.29)$$

by (4.24), where

$$R \equiv \int_0^\infty dx \frac{x^2}{x^4 + i}. \quad (4.30)$$

Thus, if we remember that $\Delta\eta_F$ grows like κ_1^{-1} near T_c , this singularity is offset by (4.29) for a finite ω when $\kappa_1 \lesssim (\omega/\gamma)^{1/4}$.

(b) *Zero frequency ($\zeta=0$) and a finite wave vector.* Here ξ can become very large near T_c . Then the major contributions to the integrals, (4.28), come again from the region x , $|y| \gg 1$ and we have

$$\begin{aligned} Z(\xi, 0) \cong & \frac{40}{\pi} \int_0^\infty dx \int_{-\infty}^\infty dy x^3 y^2 \\ & \times \{ (x^2 + y^2)^2 + \frac{1}{2}(x^2 - y^2)\xi^2 + \frac{1}{16}\xi^4 \}^{-1} \\ & \times \{ 2(x^2 + y^2)^2 + (x^2 + 3y^2)\xi^2 + \frac{1}{8}\xi^4 \}^{-1}. \end{aligned} \quad (4.31)$$

The actual limits of integrals k_{\max}/κ_1 are very large compared to ξ for small q , and the integrals converge as in the preceding case. Then we can ignore these limits as in (4.31). Therefore, if we change variables as $x = \xi x'$, $y = \xi y'$, we see that

$$Z(\xi, 0) \sim \xi^{-1} = \kappa_1/q. \quad (4.32)$$

Thus, again the divergence κ_1^{-1} of $\Delta\eta_F$ is canceled by $Z(\xi, 0)$ for $\kappa_1 \lesssim q$.

For small values of ξ or ζ , one also obtains the following expansions of $Z(\xi, \zeta)$:

$$Z(0, \zeta) = 1 - \frac{1}{12} i\zeta + \dots, \quad (4.33)$$

$$Z(\xi, 0) = 1 - \frac{19}{56} \xi^2 + \dots. \quad (4.34)$$

These results indicate explicitly that whenever a transport coefficient tends to infinity at T_c , it is necessary to consider the strong \mathbf{q} , ω -dependence of the transport coefficient.

5. DISCUSSION

In the preceding sections, we have given the general treatment of the behavior of transport coefficients which exhibit anomalous increases near the critical point, and we have illustrated the general theory with the application to the shear viscosity of critical mixtures. The anomaly has been attributed to the two cooperative effects of the anomalous increases in certain large-scale

fluctuations and in the associated lifetimes of these fluctuations. We note, however, that the latter is actually caused by the former. In concluding this paper, let us make a few remarks:

(1) Let us now consider the thermal conductivity of critical mixtures. We can apply the treatment of Sec. 3 by replacing I^{xy} by the heat flux I_T^x . Now I_T^x consists of linear and cubic terms in particle momenta and thus changes sign under time-reversal whereas c_k and T_k do not. Therefore the quantities $\langle I_T^x | c_k |^2 \rangle$, $\langle I_T^x | T_k |^2 \rangle$ and $\langle I_T^x c_k T_k^* \rangle$ identically vanish. This means that no anomalous increase near T_c is expected for the thermal conductivity of critical mixtures at least in the quadratic approximation and with the choice of c_k and T_k as macroscopic variables, which is consistent with the existing experiments.¹⁴

(2) In the preceding section we have studied the strong \mathbf{q} , ω -dependence associated with the transport coefficient which exhibits an anomalous increase near T_c . There is another type of anomaly in which the transport coefficient vanishes at T_c . An example is the diffusion process which appears in Sec. 3 and Sec. 4. The \mathbf{q} , ω -dependent diffusion constant $D(\mathbf{q}, \omega)$ is then given by

$$D(\mathbf{q}, \omega) = \frac{1}{\langle |c_q|^2 \rangle} \int_0^\infty dt \langle \hat{j}_q(t) j_q^* \rangle e^{-it\omega}, \quad (5.1)$$

where j_q is the component in the direction of \mathbf{q} of the diffusion current \mathbf{j}_q defined by

$$\partial c_q / \partial t = -i\mathbf{q} \cdot \mathbf{j}_q,$$

and $\hat{j}_q(t)$ differs from $j_q(t)$ in that the former is governed in its temporal development by L_1 of (A6) with A given by c_q . If the conventional theory of the critical slowing-down²⁵ holds, the numerator of (5.1) remains finite near T_c and thus has no anomalous \mathbf{q} , ω dependence, whereas $\langle |c_q|^2 \rangle$ increases anomalously near T_c and has a strong \mathbf{q} dependence. Thus, for this type of anomaly, *only* the \mathbf{q} dependence becomes of importance near T_c .

(3) The question arises how our result for the anomalous shear viscosity depends on the specific choice of the Ornstein-Zernike form of correlations of fluctuations, (3.15) and (3.17). Ignoring the temperature fluctuation, we can easily generalize the result of Sec. 3 for a more general form of $\langle |c_k|^2 \rangle$ which we denote as $G(k)$. Namely, using (2.20), (3.31), and $M_k = \text{const} \times k^2/G(k)$ with $T_k = 0$, we obtain

$$\begin{aligned} \Delta\eta &= \text{const} \sum_{\mathbf{k}} M_k^{-1} \langle I^{xy} | c_k |^2 \rangle / \langle |c_k|^2 \rangle \\ &= \text{const} \sum_{\mathbf{k}} \frac{[G'(k)]^2 (k^x k^y)^2}{k^2 G(k)} \left(\frac{k^x k^y}{k} \right)^2 \\ &= \text{const} \int_0^\infty \frac{[G'(k)]^2}{G(k)} k^2 dk, \end{aligned} \quad (5.2)$$

²⁵ K. Kawasaki, Phys. Rev. **145**, 224 (1966) and the references cited therein.

where $G'(k) = dG(k)/dk$. At $T = T_c$, we may put

$$G(k) = \text{const } k^{-(2-\nu)}, \quad (5.3)$$

where ν represents the deviation from the O.Z. form of $G(k)$ (ν equals Fisher's η^{21}). The behavior of $\Delta\eta$ near T_c may be obtained by introducing κ^{-1} which is the range of correlation of concentration fluctuations as follows

$$\Delta\eta = \text{const} \int_{\kappa}^{\infty} dk k^2 \frac{[G'(k)]^2}{G(k)} = \text{const } \kappa^{-(1-\nu)}. \quad (5.4)$$

ν is usually a small number,²⁶ and $\Delta\eta$ still diverges at T_c . However, the result (5.4) should not be taken too seriously, because the quadratic approximation and the random-phase approximation were already used in arriving at this result.

Finally, we briefly mention a recent very interesting attempt made by Zwanzig and Mountain²⁷ to calculate the various transport coefficients of one-component fluid near the critical point. They adopted the model of van Kampen,²⁸ where the particles are interacting with very-long-range potentials which is essential in their treatment. They successfully explained the various features of anomalies observed experimentally. Although their theory undoubtedly contains a key to the understanding of this difficult problem, the model adopted is somewhat unrealistic because the critical point is characterized by the long-range correlations of fluctuations rather than by long-range interaction potentials. Thus it is hoped that the present theory may provide a more realistic treatment of this problem.

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APPENDIX A

Here we shall present a more systematic treatment of the general theory of Sec. 2 which enables us to generalize the results obtained there and to derive them in a more satisfactory way. In particular, we have been able to derive in the quadratic approximation the self-consistent set of equations for the anomalous parts of the wave vector (\mathbf{q}) and frequency (ω)-dependent transport coefficients.

The starting point of the present treatment is the theory of Brownian motion for the macroscopic variables recently put forward in a general form by Mori.¹⁹

²⁶ M. E. Fisher, in Proceedings of the Conference on the Phenomena near the Critical Point, Washington, D. C., 1965 (to be published).

²⁷ R. W. Zwanzig and R. D. Mountain (private communication).

²⁸ N. G. van Kampen, Phys. Rev. **135**, A362 (1964).

Therefore, we shall first summarize the relevant part of Mori's theory which is necessary for the subsequent development.

Before proceeding further, we shall introduce a set of necessary notations. Let \mathbf{A} be the column matrix representing macroscopic variables at the time zero whose element is $A_{\mathbf{k}}^{\alpha}$. $A_{\mathbf{k}}^{\alpha}$ may be a classical phase space function or a quantum operator. We introduce the classical or quantum Liouville operator L to describe the temporal development of any variable F as

$$F(t) = e^{itLF}. \quad (A1)$$

We define the inner product of two variables F and G by

$$(F, G^*) \equiv \beta^{-1} \int_0^{\beta} d\lambda \langle e^{\lambda HF} e^{-\lambda HG^*} \rangle, \quad \beta \equiv 1/k_B T, \quad (A2)$$

where H is the system Hamiltonian and G^* denotes the Hermitian conjugate operator of G for quantum mechanics. For a classical case, (F, G^*) reduces to $\langle FG^* \rangle$.

With this inner product we define the projection operator \mathcal{P}_1 which projects any variable G onto the subspace spanned by \mathbf{A} .²⁹ Namely, in matrix notation,

$$\mathcal{P}_1 G \equiv (G, \mathbf{A}^*) \cdot (\mathbf{A}, \mathbf{A}^*)^{-1} \cdot \mathbf{A}. \quad (A3)$$

Now, when the system exhibits certain collective motions such as sound waves, their frequencies of oscillation can often be described by the first moment frequency matrix $\hat{\omega}$ defined by

$$i\hat{\omega} \equiv (\dot{\mathbf{A}}, \mathbf{A}^*) \cdot (\mathbf{A}, \mathbf{A}^*)^{-1}, \quad (A4)$$

where $\dot{\mathbf{A}}$ is the time derivative of \mathbf{A} taken at $t=0$ and the matrices are constructed from all the $A_{\mathbf{k}}$'s with $|\mathbf{k}| < k_{\text{max}}$. Then we can divide $\dot{\mathbf{A}}$ into two parts:

$$\dot{\mathbf{A}} \equiv iL\mathbf{A} = i\hat{\omega} \cdot \mathbf{A} + \mathbf{f}. \quad (A5)$$

The first term represents the part of $\dot{\mathbf{A}}$ which contains the collective motion and \mathbf{f} represents the random force acting on $\dot{\mathbf{A}}$. It can then be shown that the temporal development of \mathbf{f} is described more appropriately by the modified Liouville operator L_1 rather than L , where

$$L_1 \equiv (1 - \mathcal{P}_1)L. \quad (A6)$$

That is,

$$\dot{\mathbf{f}}(t) = e^{itL_1} \mathbf{f}. \quad (A7)$$

Finally we define the damping matrix $\varphi(t)$ by

$$\varphi(t) \equiv (\mathbf{f}(t), \mathbf{f}^*) \cdot (\mathbf{A}, \mathbf{A}^*)^{-1}, \quad (A8)$$

which is related to the general wave vector and frequency-dependent transport coefficients.

With these notations Mori derived an important identity satisfied by the variable $\mathbf{A}(t)$, namely,

$$\frac{d}{dt} \mathbf{A}(t) = i\hat{\omega} \cdot \mathbf{A}(t) - \int_0^t \varphi(t-s) \cdot \mathbf{A}(s) ds + \mathbf{f}(t), \quad (A9)$$

²⁹ In Mori's paper (Ref. 19), \mathcal{P}_1 is denoted by \mathcal{P}_0 . Mori's $\mathcal{P}_1, \mathcal{P}_2, \dots$ have different meanings from ours.

where the first term on the right-hand side represents the collective motion associated with \mathbf{A} , the second the friction term with memory, and the last term represents the random force mentioned earlier. We rewrite this in terms of the Laplace transforms $\mathbf{A}^L(z)$, $\varphi^L(z)$, and $\mathbf{f}^L(z)$ defined by

$$\mathbf{A}^L(z) \equiv \int_0^\infty dt e^{-tz} \mathbf{A}(t), \quad \text{etc.}, \quad (\text{A10})$$

in the following way:

$$\mathbf{A}^L(z) = [z - i\hat{\omega} + \varphi^L(z)]^{-1} \cdot [\mathbf{A}(0) + \mathbf{f}^L(z)]. \quad (\text{A11})$$

The meaning of this equation becomes clear if we take the average over the nonequilibrium ensemble. Then \mathbf{f}^L will drop out and this represents the generalized macroscopic equations of motion. For example for a simple diffusion, we take \mathbf{A} to be the Fourier components of the local concentration c_q . Then $\hat{\omega} = 0$ and (A11) becomes a scalar equation with

$$\varphi^L(z) = q^2 D(\mathbf{q}, z), \quad (\text{A12})$$

where $D(\mathbf{q}, z)$ represents the \mathbf{q} , z -dependent diffusion constant which reduces to the ordinary diffusion constant in the limit $q, z \rightarrow 0$. Thus $\varphi^L(z)$ is in general regarded as a matrix representing the wave vector and frequency-dependent transport coefficients if we set $z = i\omega$. In the following we shall derive a set of self-consistent equations determining the part of $\varphi^L(z)$ which becomes anomalous near the critical point.

We now attempt an expansion of f 's in powers of A 's as in (2.2) for J . To do it more systematically, we construct a set of orthogonal variables from A 's in the following way. Writing A^α instead of $A_{\mathbf{k}}^\alpha$ supposing that α also specifies \mathbf{k} , consider the set of variables A^α , $B^{\alpha\beta}$, $C^{\alpha\beta\gamma}$, \dots which are linear combinations of the products of A 's. The maximum number of powers of A 's contained in each variable equals the number of indices attached, and the condition of orthogonality requires that³⁰

$$(B^{\alpha\beta}, A^\gamma) = (C^{\alpha\beta\gamma}, A^{\delta\epsilon}) = (C^{\alpha\beta\gamma}, B^{\delta\epsilon\zeta}) = \dots = 0. \quad (\text{A13})$$

As an example, let us consider $B^{\alpha\beta}$ which we write as

$$B^{\alpha\beta} = A^\alpha A^\beta - \sum_\gamma u_\gamma^{\alpha\beta} A^\gamma. \quad (\text{A14})$$

The orthogonality condition (A13) then requires that

$$(A^\alpha A^\beta, A^{\delta\epsilon}) - \sum_\gamma u_\gamma^{\alpha\beta} (A^\gamma, A^{\delta\epsilon}) = 0 \quad (\text{A15})$$

which determines $u_\gamma^{\alpha\beta}$. In a similar manner $C^{\alpha\beta\gamma}$ can be determined except for multiplicative factors. Since from (A15) $u_\gamma^{\alpha\beta}$ is of the order of A 's, $B^{\alpha\beta}$ is of the magnitude of square of A 's. Similarly, $C^{\alpha\beta\gamma}$ is of the magnitude of cube of A 's, and so on. In this sense, therefore,

the orthogonal set A^α , $B^{\alpha\beta}$, $C^{\alpha\beta\gamma}$, \dots represents the ascending powers of A 's.

In order to obtain the expansion of f 's, we now introduce the projection operators $\mathcal{P}_2, \mathcal{P}_3, \dots$ which projects any variable G onto the orthogonal subspaces spanned by the sets $B^{\alpha\beta}$, $C^{\alpha\beta\gamma}$, \dots , respectively, in analogy with \mathcal{P}_1 introduced earlier. For example,

$$\mathcal{P}_2 G = (G, \mathbf{B}^*) \cdot (\mathbf{B}, \mathbf{B}^*)^{-1} \cdot \mathbf{B}, \quad (\text{A16})$$

where \mathbf{B} and \mathbf{B}^* are the column and row matrices constructed from $B^{\alpha\beta}$ and $B^{\alpha\beta*}$, respectively, which are the obvious analog of \mathbf{A} . Because of the orthogonality of the set $\mathbf{A}, \mathbf{B}, \mathbf{C}, \dots$, the desired expansion of f^α becomes

$$f^\alpha = (\mathcal{P}_1 + \mathcal{P}_2 + \dots) f^\alpha + f_R^\alpha, \quad (\text{A17})$$

where f_R^α is the part of f^α which is outside of the subspace spanned by $\mathbf{A}, \mathbf{B}, \mathbf{C}, \dots$. Since by the definition of f^α , (A5), it is orthogonal to \mathbf{A} , that is, $\mathcal{P}_1 f^\alpha = 0$, the expansion starts from \mathcal{P}_2 in (A17). Therefore we can write (A17) as

$$f^\alpha = \sum_{\beta\gamma} S_{\beta\gamma}^\alpha (B^{\beta\gamma} - \langle B^{\beta\gamma} \rangle) + \dots, \quad (\text{A18})$$

where $S_{\beta\gamma}^\alpha$ is determined by the set of equations,

$$(f^\alpha, B^{\delta\epsilon*}) = \sum_{\beta\gamma} S_{\beta\gamma}^\alpha (B^{\beta\gamma}, B^{\delta\epsilon*}), \quad (\text{A19})$$

which is obtained from (A16) by applying \mathcal{P}_2 to (A18), and we have used the fact that $\langle f^\alpha \rangle = 0$, and

$$(F; G) \equiv (F, G) - \langle F \rangle \langle G \rangle.$$

To proceed further, we neglect all the terms not written explicitly in (A18) for studying the anomalous part of φ , $\Delta\varphi$, by the same reason by which we truncated (2.2). For obtaining $\Delta\varphi^L$, we could replace $f^\alpha(t)$ in (A8) by the first term of (A18). However, there is one difficulty, that is, the temporal development of f^α given by (A7) is different from that of \mathbf{A} and \mathbf{B} . Thus we introduce another variable $K^\alpha(t)$ defined by

$$K^\alpha(t) \equiv e^{itL} f^\alpha \quad (\text{A20})$$

and also define the matrix function $\psi^L(z)$ by

$$\psi^L(z) \equiv \int_0^\infty dt e^{-tz} (\mathbf{K}(t), \mathbf{K}^*) \cdot (\mathbf{A}, \mathbf{A}^*)^{-1}. \quad (\text{A21})$$

Then, Mori has derived a simple relation between $\varphi^L(z)$ and $\psi^L(z)$ ¹⁹;

$$\varphi^L(z) = [1 - \psi^L(z) \cdot (z - i\hat{\omega})^{-1}]^{-1} \cdot \psi^L(z). \quad (\text{A22})$$

Thus, we can study the anomalous part of ψ^L , $\Delta\psi^L$, instead of $\Delta\varphi^L$. $K^\alpha(t)$ becomes, using (A20), (A18), and (A14).³¹

$$K^\alpha(t) = \sum_{\beta\gamma} S_{\beta\gamma}^\alpha [A^\beta(t) A^\gamma(t) - \sum_\delta u_\delta^{\beta\gamma} A^\delta(t)] + \dots \quad (\text{A23})$$

³⁰ The orthogonality is required only between the variables with different number of indices.

³¹ In (A23) we suppressed $\langle B^{\beta\gamma} \rangle$ which must be subtracted from it, because $\langle B^{\beta\gamma} \rangle$ does not contribute to the final result (A25).

Denoting the Laplace transform of $K^\alpha(t)$ by $K^{\alpha L}(z)$ and using (A11), we obtain

$$\begin{aligned}
K^{\alpha L}(z) &= \sum_{\beta\gamma} S_{\beta\gamma}^\alpha \frac{1}{(2\pi i)^2} \int_c \int_c dz_1 dz_2 \\
&\times \sum_{\delta\epsilon} \left\{ \left[\frac{1}{z_1 - i\hat{\omega} + \varphi^L(z_1)} \right]_{\beta\delta} \left[\frac{1}{z_2 - i\hat{\omega} + \varphi^L(z_2)} \right]_{\gamma\epsilon} \right. \\
&\times [A^\delta + f^{\delta L}(z_1)] [A^\epsilon + f^{\epsilon L}(z_2)] \int_0^\infty dt e^{t(z_1+z_2-z)} \\
&\left. - u_\delta^{\beta\gamma} \left[\frac{1}{z - i\hat{\omega} + \varphi^L(z)} \right]_{\delta\epsilon} [A^\epsilon + f^{\epsilon L}(z)] \right\} + \dots, \quad (\text{A24})
\end{aligned}$$

where c is the contour appearing in the inverse Laplace transformation of $\mathbf{A}^L(z)$ and runs from $x - i\infty$ to $x + i\infty$, where x is a real number greater than the real parts of all the singular points of $\mathbf{A}^L(z)$. When all these singularities are located to the left of the imaginary axis, we can take $x=0$ and the time integral converges for $\text{Re}z > 0$, which we assume to be the case. Let us now consider the expansion of f^L appearing in (A24) in powers of A 's. By the definition of f 's, we have

$$(f^{\alpha L}(z), A^{\beta*}) = 0,$$

because $f^\alpha(t)$ is orthogonal to A^β at all times. This means that $f^{\alpha L}(z)$ does not contain linear terms in A 's in this expansion. Therefore, in the approximation of retaining only the quantities quadratic in A 's, all f^L in (A24) should be omitted since $u_\delta^{\beta\gamma}$ is the quantity of the order of A 's. With this resulting expression for $K^{\alpha L}(z)$, we now consider $(K^{\alpha L}(z), f^{\sigma*})$. Again noting the orthogonality of A 's and f 's, the second term of (A24) does not contribute, and we finally obtain

$$\begin{aligned}
(K^{\alpha L}(z), f^{\sigma*}) &= \frac{1}{(2\pi i)^2} \sum_{\beta\gamma} \sum_{\delta\epsilon} S_{\beta\gamma}^\alpha (A^\delta A^\epsilon, f^{\sigma*}) \int_c dz_1 \int_c dz_2 \\
&\times \left[\frac{1}{z_1 - i\hat{\omega} + \varphi^L(z_1)} \right]_{\beta\delta} \left[\frac{1}{z_2 - i\hat{\omega} + \varphi^L(z_2)} \right]_{\gamma\epsilon} \\
&\times \int_0^\infty dt e^{t(z_1+z_2-z)} + \dots, \quad (\text{A25})
\end{aligned}$$

where \dots is the contributions of higher-orders in A 's and that which comes from f_R^α of (A17). Ignoring the former contributions to be consistent with our quadratic approximation, we write (A21) as

$$\begin{aligned}
\psi^{\alpha\beta L}(z) &= \sum_\gamma (K^{\alpha L}(z), f^{\gamma*}) [(A, A^*)^{-1}]_{\gamma\beta} \\
&= \Delta\psi^{\alpha\beta L}(z) + \psi_R^{\alpha\beta L}(z), \quad (\text{A26})
\end{aligned}$$

where $\Delta\psi^L(z)$ comes from the first term of (A25) and thus represents the anomalous contribution to $\psi^L(z)$, whereas $\psi_R^L(z)$ comes from f_R^α of (A17) and is assumed

to be known smooth function of the temperature near the critical point. Since $\Delta\psi^L(z)$ is expressed in terms of $\varphi^L(z)$ by (A25), if we substitute (A26) into (A22) we obtain a self-consistent set of equations for $\varphi^L(z)$. Thus, this set of equations in principle allows us to study the anomaly of generalized nonlocal transport coefficients near the critical point contained in $\varphi^L(z)$ in the quadratic approximation once we know the equal time correlation functions appearing in (A19), (A25), and (A26) as well as the well behaved part $\psi_R^L(z)$. In practice, however, it is too involved to be useful and further reductions are necessary for specific applications. We hope to be able to report on this in future.²²

In the following, we shall use the above results to derive the results of Sec. 2 for the transport coefficients (2.1) in the limits of long wavelength and then small z . In this case $\varphi^L(z)$ reduces to $\psi^L(z)$ except for such systems as plasmas and superfluids and we can use (A25) replacing both K^α and f^α by J , and then we can set z equal to zero. We thus obtain in classical mechanics

$$\begin{aligned}
\int_0^\infty dt \langle J(t)J \rangle &= \frac{1}{(2\pi i)^2} \sum_{\alpha\beta} \sum_{\gamma\delta} \sum_{\mathbf{k}} S_{\alpha\beta}^{\mathbf{k}} \langle A_{\mathbf{k}}^\gamma A_{-\mathbf{k}}^\delta J \rangle \int_c dz_1 \\
&\times \left[\frac{1}{z_1 - i\hat{\omega}_{\mathbf{k}} + \varphi_{\mathbf{k}}^L(z_1)} \right]_{\alpha\gamma} \left[\frac{1}{z_2 - i\hat{\omega}_{-\mathbf{k}} + \varphi_{-\mathbf{k}}^L(z_2)} \right]_{\beta\delta} \\
&\times \int_0^\infty dt e^{t(z_1+z_2-z)} + \dots, \quad (\text{A27})
\end{aligned}$$

where we have written down \mathbf{k} explicitly again. We now move the integration contour very far towards the left in the complex plane in a familiar way. We are then left with the contour integrals over the small circles around each singularity in (A27). For small k , which give major contributions near the critical point, $\hat{\omega}_{\mathbf{k}}$ and $\varphi_{\mathbf{k}}^L$ are small and only the singularities clustering around the origin become significant. Then, we may ignore the z -dependence of $\varphi_{\mathbf{k}}^L(z)$. This would not be always correct since near the critical point some transport coefficients exhibit strong frequency dependence [see Sec. 4]. However, this appears to be true for the example considered in Sec. 3 and the simple diffusion equation (4.14). Equation (A27) then becomes

$$\begin{aligned}
\int_0^\infty dt \langle J(t)J \rangle &= \sum_{\alpha\beta} \sum_{\gamma\delta} S_{\alpha\beta}^{\mathbf{k}} \langle A_{\mathbf{k}}^\gamma A_{-\mathbf{k}}^\delta J \rangle \\
&\times \int_0^\infty dt \{ \exp(-t\mathbf{M}_{\mathbf{k}}) \}_{\alpha\gamma} \\
&\times \{ \exp(-t\mathbf{M}_{-\mathbf{k}}) \}_{\beta\delta} + \dots, \quad (\text{A28})
\end{aligned}$$

where

$$\mathbf{M}_{\mathbf{k}} \equiv \varphi_{\mathbf{k}}^L - i\hat{\omega}_{\mathbf{k}}. \quad (\text{A29})$$

²² A self-consistent set of equations has been used also in the theory of Zwanzig and Mountain (Ref. 27). Since the details of this theory are not yet available to the author, we do not discuss it here.

This \mathbf{M}_k clearly has the same meaning as that of Sec. 2. The integral in (A28) can be reduced by introducing the composite matrix as defined by (2.12) to yield

$$\int_0^\infty dt \{ \exp(-t\mathfrak{M}_k) \}_{\alpha\beta;\gamma\delta} = [\mathfrak{M}_k^{-1}]_{\alpha\beta;\gamma\delta}. \quad (\text{A30})$$

Now, $S_{\alpha\beta^*}$ in (A28) is determined by (A19) where f^α is replaced by J ;

$$\langle JB_k \gamma \delta^* \rangle = \sum_{\alpha\beta} \sum_{k'} S_{\alpha\beta k'} \langle B_{k'}^{\alpha\beta}; B_k \gamma \delta^* \rangle, \quad (\text{A31})$$

where

$$B_k^{\alpha\beta} = A_k^\alpha A_{-k}^\beta - \sum_\gamma u_\gamma^{\alpha\beta}(\mathbf{k}) A_0^\gamma \quad (\text{A32})$$

with u 's determined by the equations similar to (A15). Equation (A30) is slightly different from the corresponding (2.4), but becomes the same in the random-phase approximation where $u_\gamma^{\alpha\beta} = 0$. Thus, substituting (A30) into (A28), we have essentially derived (2.15), which was obtained there in a more heuristic fashion.

APPENDIX B

This Appendix is concerned with the evaluation of the quantities of the form $\langle A_k^\gamma A_{-k}^\delta J \rangle$. Although there appears to be no general way to evaluate them, there is a generalized virial theorem which can reduce them for the case of viscosity. Thus, let us consider for the system consisting of N particles the quantity of the form

$$\langle I^{\alpha\beta} G \rangle = \int d\mathbf{r}^N d\mathbf{p}^N I^{\alpha\beta} G \rho_e, \quad (\text{B1})$$

where G is any phase space function, $I^{\alpha\beta}$ the $\alpha\beta$ component of the stress tensor defined by (3.1) and ρ_e the equilibrium distribution function given by

$$\rho_e = Z^{-1} \exp(-\beta H), \quad (\text{B2})$$

where Z is the partition function and H the system Hamiltonian,

$$H \equiv \sum_i \frac{p_i^2}{2m_i} + \sum_{i<j} u_{ij} + \sum_i u_i^e, \quad (\text{B3})$$

and the integral is over the phase space of the N particles. Here u_i^e is the potential of the external force on the particle i due to the wall of the container and is nonvanishing only on the boundary. We first note the following identity:

$$I^{\alpha\beta} = \sum_i \left(p_i^\alpha \frac{\partial}{\partial p_i^\beta} - r_i^\alpha \frac{\partial}{\partial r_i^\beta} \right) H - \sum_i r_i^\alpha X_i^\beta, \quad (\text{B4})$$

where

$$X_i^\beta \equiv -\partial u_i^e / \partial r_i^\beta \quad (\text{B5})$$

is the external force on the particle i . Since the system is confined to the finite volume V by the potential u^e , if $G\rho_e$ vanishes for infinite momenta we can integrate

(B1) by parts to yield

$$\langle I^{\alpha\beta} G \rangle = k_B T \sum_i \left\langle \left(p_i^\alpha \frac{\partial G}{\partial p_i^\beta} - r_i^\alpha \frac{\partial G}{\partial r_i^\beta} \right) \right\rangle - \sum_i \langle r_i^\alpha X_i^\beta G \rangle. \quad (\text{B6})$$

The last term can be written as

$$\langle r_i^\alpha X_i^\beta G \rangle = \int d\mathbf{r}_i r_i^\alpha X_i^\beta g_i(\mathbf{r}_i), \quad (\text{B7})$$

where

$$g_i(\mathbf{r}_i) \equiv \int d\mathbf{p}^N \int d\mathbf{r}^{N-1} G \rho_e, \quad (\text{B8})$$

where the integral is over the phase space of N particles except \mathbf{r}_i . $g_i(\mathbf{r}_i)$ is almost constant inside the volume except near the boundary as long as the range of the particle correlation is short compared to the dimension of V . Now, the force due to the wall may be obtained by considering the special case of $G=1$, when (B6) becomes

$$-\sum_i \langle r_i^\alpha X_i^\beta \rangle = \langle I^{\alpha\beta} \rangle = \delta_{\alpha\beta} p V, \quad (\text{B9})$$

where p is the pressure.

We now show that the following choice of X_i^β satisfies (B9):

$$X_i^\beta = X^\beta(r_i) \equiv -N^{-1} V p n^\beta \delta^S(\mathbf{r}_i), \quad (\text{B10})$$

where \mathbf{n} is the unit vector in the direction of the outward normal to the surface element of the volume V at \mathbf{r}_i and $\delta^S(\mathbf{r})$ is a kind of delta function which vanishes except on the boundary and is normalized so that

$$\int_V \delta^S(\mathbf{r}) F(\mathbf{r}) d\mathbf{r} = \int_S F(\mathbf{r}_S) dS, \quad (\text{B11})$$

where $F(\mathbf{r})$ is any smooth function of \mathbf{r} and right-hand side represents the surface integral, \mathbf{r}_S being the value of \mathbf{r} on the surface element dS . Then, we have

$$\begin{aligned} \sum_i \langle r_i^\alpha X_i^\beta \rangle &= \frac{N}{V} \int d\mathbf{r} r^\alpha X^\beta(\mathbf{r}) = -p \int dS r^\alpha n^\beta \\ &= -p \int d\mathbf{r} \frac{\partial}{\partial r^\beta} r^\alpha = -p V \delta_{\alpha\beta}, \end{aligned} \quad (\text{B12})$$

where the Gauss theorem has been used.

Turning now to the evaluation of (B7), we have, using (B10), (B11), and the Gauss theorem

$$\begin{aligned} \langle r_i^\alpha X_i^\beta G \rangle &= -N^{-1} V p \int dS r^\alpha g_i(\mathbf{r}) n^\beta \\ &= -N^{-1} V p \int d\mathbf{r} \frac{\partial}{\partial r^\beta} [r^\alpha g_i(\mathbf{r})]. \end{aligned} \quad (\text{B13})$$

Since $g_i(\mathbf{r})$ varies with \mathbf{r} appreciably only near the boundary, if we ignore small surface contributions and use (B8), (B13) reduces to

$$\begin{aligned} \langle r_i^\alpha X_i^\beta G \rangle &= -N^{-1} V \rho \delta_{\alpha\beta} \int d\mathbf{r} g_i(\mathbf{r}) \\ &= -N^{-1} V \rho \langle G \rangle \delta_{\alpha\beta}. \end{aligned} \quad (\text{B14})$$

Substituting this into (B6) we finally obtain the generalized virial theorem as

$$\begin{aligned} \langle I^{\alpha\beta} G \rangle &= k_B T \sum_i \left\langle \left(p_i^\alpha \frac{\partial G}{\partial p_i^\beta} - r_i^\alpha \frac{\partial G}{\partial r_i^\beta} \right) \right\rangle \\ &\quad + \rho V \langle G \rangle \delta_{\alpha\beta}. \end{aligned} \quad (\text{B15})$$

Although the special form of the external force has been used in deriving this result, it should be valid for large systems in general because it is concerned with the bulk properties of the system. It is sometimes more convenient to rewrite this in a slightly different way by writing G formally as follows:

$$G = \sum_{\mathbf{k}^N} g_{\mathbf{k}^N}(\mathbf{p}^N) e^{-i\mathbf{k}^N \cdot \mathbf{r}^N}, \quad (\text{B16})$$

where \mathbf{k}^N , \mathbf{p}^N , and \mathbf{r}^N are the vectors in the $3N$ -dimensional space of N particles. Then we have

$$\left\langle r_i^\alpha \frac{\partial G}{\partial r_i^\beta} \right\rangle = \sum_{\mathbf{k}^N} \left\langle g_{\mathbf{k}^N}(\mathbf{p}^N) k_i^\beta \frac{\partial}{\partial k_i^\alpha} e^{-i\mathbf{k}^N \cdot \mathbf{r}^N} \right\rangle. \quad (\text{B17})$$

Thus we obtain

$$\begin{aligned} \langle I^{\alpha\beta} G \rangle &= -k_B T \sum_{\mathbf{k}^N} \sum_i \left\langle g_{\mathbf{k}^N}(\mathbf{p}^N) k_i^\beta \frac{\partial}{\partial k_i^\alpha} e^{-i\mathbf{k}^N \cdot \mathbf{r}^N} \right\rangle \\ &\quad + k_B T \sum_i \left\langle p_i^\alpha \frac{\partial G}{\partial p_i^\beta} \right\rangle + \rho V \langle G \rangle \delta_{\alpha\beta}. \end{aligned} \quad (\text{B18})$$

As a first example, let us consider the case when $G = |c_{\mathbf{k}}|^2$. Noting that¹⁷

$$\begin{aligned} |c_{\mathbf{k}}|^2 &= (\partial c / \partial n)^2 |n_{\mathbf{k}}|^2 \\ &= (\partial c / \partial n)^2 (2\pi)^{-6} \sum_{ij}' e^{-i\mathbf{k} \cdot \mathbf{r}_{ij}}, \end{aligned} \quad (\text{B19})$$

where $n_{\mathbf{k}}$ is the Fourier component of the number density of the second species and \sum' denotes the sum over the particles of the second species and $\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$. Use of (B18) immediately yields

$$\langle I^{\alpha\beta} |c_{\mathbf{k}}|^2 \rangle = -k_B T k^\beta \frac{\partial}{\partial k^\alpha} \langle |c_{\mathbf{k}}|^2 \rangle + \rho V \langle |c_{\mathbf{k}}|^2 \rangle \delta_{\alpha\beta}. \quad (\text{B20})$$

Thus we obtain $\langle I^{\alpha\beta} |c_{\mathbf{k}}|^2 \rangle$ from the knowledge of the pair correlation function of the concentration fluctuation $\langle |c_{\mathbf{k}}|^2 \rangle$. The same relation holds also for the ordinary density fluctuation.

As a second example, we consider the expression $\langle I^{xy} c_{\mathbf{k}} e_{\mathbf{k}}^* \rangle$ where $e_{\mathbf{k}}$ is the \mathbf{k} Fourier component of the energy density given by

$$(2\pi)^3 e_{\mathbf{k}} = \sum_i \frac{p_i^2}{2m_i} e^{-i\mathbf{k} \cdot \mathbf{r}_i} + \frac{1}{2V} \sum_q \sum_{ij} u_q^{ij} e^{-i\mathbf{k} \cdot \mathbf{r}_i + i\mathbf{q} \cdot \mathbf{r}_{ij}}, \quad (\text{B21})$$

where

$$u_q^{ij} \equiv \int u_{ij}(r) e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r}, \quad u_{ii}(r) = 0. \quad (\text{B22})$$

Then, we have

$$\langle I^{xy} c_{\mathbf{k}} e_{\mathbf{k}}^* \rangle = (\partial c / \partial n) \langle I^{xy} n_{\mathbf{k}} e_{\mathbf{k}}^* \rangle = (2\pi)^{-6} (\partial c / \partial n) \left\langle I^{xy} \sum_i' \left\{ \sum_j \frac{p_j^2}{2m_j} e^{-i\mathbf{k} \cdot \mathbf{r}_{ij}} + \frac{1}{2V} \sum_q \sum_{jl} u_q^{jl*} e^{-i\mathbf{k} \cdot \mathbf{r}_{ij} - i\mathbf{q} \cdot \mathbf{r}_{jl}} \right\} \right\rangle. \quad (\text{B23})$$

Using (B13) this reduces to,

$$\langle I^{xy} c_{\mathbf{k}} e_{\mathbf{k}}^* \rangle = -k_B T k^y \frac{\partial}{\partial k^x} \langle c_{\mathbf{k}} e_{\mathbf{k}}^* \rangle - \frac{k_B T \partial c / \partial n}{2(2\pi)^6 V} \sum_i' \sum_{jl} \sum_q u_q^{jl*} q^y \frac{\partial}{\partial q^x} \langle e^{-i\mathbf{k} \cdot \mathbf{r}_{ij} - i\mathbf{q} \cdot \mathbf{r}_{jl}} \rangle \quad (\text{B24})$$

$$= -k_B T k^y \frac{\partial}{\partial k^x} \langle c_{\mathbf{k}} e_{\mathbf{k}}^* \rangle - \frac{k_B T \partial c / \partial n}{2(2\pi)^3} \sum_{jl} \sum_q \langle n_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}_j} r_{jl}^x \partial u_{jl} / \partial r_{jl}^y \rangle, \quad (\text{B25})$$

where we have used that $n_{\mathbf{k}} \equiv (2\pi)^{-3} \sum_i' e^{-i\mathbf{k} \cdot \mathbf{r}_i}$ and

$$\partial u_{ij}(r) / \partial r_{ij}^y = -iV^{-1} \sum_q e^{-i\mathbf{q} \cdot \mathbf{r}} q^y u_q^{ij*} \quad (\text{B26})$$

which follows from (B22). By a similar but somewhat lengthy analysis, we obtain for $\langle I^{xy} e_{\mathbf{k}} e_{\mathbf{k}}^* \rangle$,

$$\begin{aligned} \langle I^{xy} |e_{\mathbf{k}}|^2 \rangle &= -k_B T k^y \frac{\partial}{\partial k^x} \langle |e_{\mathbf{k}}|^2 \rangle - \frac{k_B T}{2(2\pi)^6} \sum_{iji} \left\langle \frac{p_i^2}{2m_i} (e^{-i\mathbf{k} \cdot \mathbf{r}_{ij}} + e^{i\mathbf{k} \cdot \mathbf{r}_{ij}}) r_{ji}^x \frac{\partial u_{jl}}{\partial r_{jl}^y} \right\rangle \\ &\quad - \frac{k_B T}{4(2\pi)^6} \sum_{ijln} \left\langle e^{-i\mathbf{k} \cdot \mathbf{r}_{il}} \left(r_{ij}^x \frac{\partial u_{ij}}{\partial r_{ij}^y} u_{ln} + r_{ln}^x \frac{\partial u_{ln}}{\partial r_{ln}^y} u_{ij} \right) \right\rangle. \end{aligned} \quad (\text{B27})$$

Thus, $\langle I^{xy} c_k e_k^* \rangle$ and $\langle I^{xy} |e_k|^2 \rangle$ are not related to $\langle c_k e_k^* \rangle$ and $\langle |e_k|^2 \rangle$ respectively in a simple manner as for $\langle I^{xy} |c_k|^2 \rangle$, and there are additional terms represented by the last term of (B25) and the last two terms of (B27). Let us now consider the nature of these extra terms. First, consider the last term of (B25) which we denote as Φ_k^{xy} . Φ_k^{xy} is different from $\langle n_k e_k^{U*} \rangle$, where e_k^U corresponds to the potential energy, by the fact that u_{jl} is replaced by $r_{jl}^x \partial u_{jl} / \partial r_{jl}^y$. Thus both of them contain

the same types of the long-range particle correlations near T_c . However, the difference arises from the different symmetry property of u_{jl} and $r_{jl}^x \partial u_{jl} / \partial r_{jl}^y$. Therefore, Φ_k^{xy} vanishes as k goes to zero. In this sense Φ_k^{xy} is more similar to $k^y (\partial / \partial k^x) \langle c_k e_k^{U*} \rangle$. The same thing is also true for (B27), and the properties of its last two terms may be similar to those of $k^y \partial \langle e_k^K e_k^{U*} \rangle / \partial k^x$ and $k^y \partial \langle |e_k^U|^2 \rangle / \partial k^x$, respectively, where e_k^K corresponds to the kinetic energy.

Nuclear Spin Relaxation in Cs Metal*

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The characteristic nuclear-magnetic-resonance parameters, Knight shift, line shape and width, and relaxation times have been measured in cesium metal from the melting point to 1.6°K. The nuclear spin relaxation time T_1 is inversely proportional to the temperature from 300 to 7°K, with $T_1 T = 0.135 \pm 0.01$ sec °K. For temperatures below 7°K, the relaxation shows another contribution of unknown origin. The Knight shift increases linearly with temperature down to 4°K, following the line previously measured by Gutowsky and McGarvey at higher temperatures. Diffusion narrowing of the magnetic-resonance line is observed at 190°K, but the strong electron-nucleus interactions preclude good diffusion-constant measurements.

I. INTRODUCTION

THE alkali metals were among the first metallic systems to be extensively investigated by means of NMR techniques.¹⁻⁴ The experiments provided detailed information in two major areas of interest. (1) Measurements of the motional narrowing of the resonance line gave good data on self-diffusion, particularly in Na and Li.³ (2) The large electron-nucleus magnetic interaction allowed investigation of certain properties of the electron system such as the spatial distribution of electronic wave functions, importance of nonfree-electron effects, and spin magnetic susceptibility.

The work reported in this paper was undertaken primarily for the purpose of extending these earlier measurements to cesium. The experimental data consist of measurements of the nuclear spin-lattice relaxation time T_1 , the free induction decay time T_2 , and the Knight shift K , from the melting point 28.5°C, down to 1.6°K. After a short section discussing experimental details, we will discuss the data from three points of

view. We will analyze them for information on (1) self-diffusion, (2) properties of the electron system, and (3) the existence of an unidentified low-temperature relaxation mechanism; these three topics are covered in Secs. III, IV, and V, respectively.

II. EXPERIMENTAL DETAILS

All resonance measurements were made using transient techniques. The basic experimental apparatus, consisting of a pulsed, phase-coherent rf spectrometer, low-temperature probe, and gated integrator, has been previously described by Sundfors.⁵ In the probe used, the rotating rf field H_1 had an amplitude of about 15 G. Thus, pulse lengths of about 30 μ sec were necessary to nutate the nuclear magnetization by 90°. The T_1 measurements were made with a two-pulse sequence, observing the recovery of the free induction decay following the second pulse as a function of spacing between the pulses. The T_2 measurements were obtained from the shape of the free induction decay envelope. For some T_2 measurements, a Northern Scientific model NS-513 digital memory oscilloscope was used to improve the signal-to-noise ratio.

Most of the samples used were prepared from bulk cesium obtained from Electronics Space Products, Inc., catalog No. K999E. The impurities listed by the manufacturer are given in Table I.

A second shipment of metal from the same source, catalog No. K999J, was of higher purity, and a more

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¹ H. S. Gutowsky, Phys. Rev. **83**, 1073 (1951).

² R. E. Norberg and C. P. Slichter, Phys. Rev. **83**, 1074 (1951).

³ D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955).

⁴ R. T. Schumacher and C. P. Slichter, Phys. Rev. **101**, 58 (1956).

⁵ R. K. Sundfors, thesis, Cornell University, 1963 (unpublished).