

## Nonlinear Effects in the Shear Viscosity of Critical Mixtures

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(Received June 16, 1967)

Unless the velocity gradient is small, the shear viscosity of fluids generally depends on the velocity gradient  $d$ , hence extra nonlinear terms in  $d$  appear in the hydrodynamic equations. We extend the method developed by Kawasaki and by Deutch and Zwanzig for studying the usual linear shear viscosity of critical mixtures to the investigation of the nonlinear terms which appear in the power series expansion of this effective shear viscosity  $\eta(d)$ . By the symmetry consideration we obtain

$$\eta(d) = \eta^{(0)} + \eta^{(1)}d^2 + \eta^{(2)}d^4 + \dots$$

$\eta^{(1)}$  is found to increase as  $\kappa^{-9}$  near the critical point, where  $\kappa^{-1}$  is a parameter which measures the correlation range of concentration fluctuations assuming the Ornstein-Zernike type for the correlation, indicating the importance of the nonlinear effects near the critical point since  $\eta^{(0)}$  increases only as  $\kappa^{-1}$ . This  $\eta^{(1)}$  agrees with Botch and Fixman's except for a small correction to the numerical coefficient. On the other hand the  $k$ -integral contained in  $\eta^{(2)}$  has been found to diverge as  $k^{-3}$  at small  $k$  even when  $\kappa \neq 0$ , where  $k$  is a wave vector characterizing the local concentration fluctuation. Similar divergences appear in the two dimensional mixture already in  $\eta^{(1)}$  which diverges as  $\ln k$ , and in the linear bulk viscosity which again diverges as  $\ln k$ . The nature and possible consequences of these divergences are discussed.

### § 1. Introduction

Near the critical point the thermodynamic fluctuations of certain macroscopic variables increase enormously and the nonlinear effects are expected to be important as a consequence. In fact W. Botch and M. Fixman found that the shear viscosity of the binary mixture depends nonlinearly on the velocity gradient  $d$  near the critical point.<sup>1)</sup> They extended Fixman's calculation of the shear viscosity<sup>2)</sup> to the next nonvanishing order in  $d$  to obtain this result.

Fixman has shown that the anomaly of the shear viscosity of the binary mixture comes from the anomalous increase of the concentration fluctuation near the critical point.<sup>2)</sup> He calculated the entropy production rate in the stationary state in the presence of the velocity gradient and identified the shear viscosity with the coefficient of the square of the velocity gradient. However, the relation between the shear viscosity obtained in this manner and the one which enters the hydrodynamic equations is not necessarily transparent.

On the other hand Kawasaki,<sup>3),\*)</sup> and Deutch and Zwanzig<sup>4)</sup> adopted the expression for the viscosity which is written in terms of the time correlation function of the flux. They incorporated the Fixman's idea that the anomalous behavior is due to the anomaly of the concentration fluctuation, and then, assumed that the temporal development of the flux obeys the phenomenological equation. Their result turned out to be identical to Fixman's. In this correlation function approach the viscosity is closely connected with the local stress tensor and the extension to the nonlocal case is obvious.<sup>3)</sup>

In this paper we study the nonlinear contribution to the local stress tensor in the stationary case. For this purpose we adopt the correlation function approach. This approach is considered to be suited for treating the nonlinear case as a natural extension of the linear case. For this it is necessary to expand the local stress tensor in powers of the velocity gradient and express each coefficient in terms of the appropriate correlation functions.

There are several methods for obtaining the correlation function expression for the transport coefficient in the case of the thermal disturbance;<sup>5)</sup> e.g. (i) use of the initial local equilibrium ensemble<sup>6)</sup> (ii) use of the Fokker-Planck equation<sup>7)</sup> (iii) indirect Kubo method,<sup>8)</sup> etc. We extend here the method (i) due to Mori to the nonlinear case. Section 2 is devoted to this procedure. The resulting expression is evaluated using the method which is a slight modification of that of Kawasaki.<sup>3)</sup> The  $d^2$  term in the nonlinear shear viscosity obtained here is identical to Botch and Fixman's except for a small correction to the numerical coefficient. In § 3 we present this calculation. However, if we continue further, some sort of the divergence difficulty begins to appear in the  $d^4$  term. This problem will be discussed in § 4. Finally, we note that this problem is of interest also from the point of view of the general nonlinear transport theory, since we still do not have a satisfactory general formalism of the nonlinear transport as in the linear case.\*\*)

## § 2. Nonlinear contribution to the local stress tensor

All the macroscopic properties of the system can be obtained from the knowledge of the distribution function of the system after averaging. Most systems are described by macroscopic variables after a certain transient time. To obtain such a macroscopic description, we shall start here from the local equilibrium distribution<sup>6)</sup> and consider the simple case that the temperature and the number density are spatially uniform and stationary in time, and only the local velocity differs from zero.

\*) Hereafter we shall refer to this as Ref. I.

\*\*) When we have the so-called mechanical disturbance, the formal extension of the linear response theory to non-linear problems appears to be more or less straightforward.<sup>14)</sup> However, if the disturbances are of thermal nature such as those associated with heat transport, viscosity, diffusion, etc., the situation is rather unsatisfactory.

Then the local equilibrium distribution function can be written as<sup>6)</sup>

$$f_i^N(\mathbf{x}) = \exp(-\beta U^{-1}H) / \int \exp(-\beta U^{-1}H) d\mathbf{x}^N, \quad (2.1)$$

where  $d\mathbf{x}^N = d\mathbf{x}_1 \cdots d\mathbf{x}_N$  [ $\mathbf{x}_i$ , ( $i=1 \cdots N$ ) is the coordinate of the  $i$ -th particle in phase space and  $N$  the total number of particles.] and  $H$  is the system Hamiltonian given by

$$H = \sum_{j=1}^N \frac{p_j^2}{2m_j} + \frac{1}{2} \sum_{j \neq l} u_{jl}, \quad (2.2)$$

where  $u_{jl}$  is the interaction potential. Furthermore,  $U$  is a pseudo-canonical transformation operator which generates the local equilibrium distribution function (2.1) from the equilibrium one and has the following properties:

(i) For an arbitrary phase space function  $G$ ,

$$\langle G \rangle_i = \int G f_i^N d\mathbf{x}^N = \int (UG) f_0^N d\mathbf{x}^N = \langle UG \rangle_0, \quad (2.3)$$

where  $\langle \cdots \rangle_i$  stands for the local equilibrium average and  $\langle \cdots \rangle_0$  the equilibrium one. We have used here that by (2.1)

$$f_i^N = U^{-1} f_0^N,$$

where

$$f_0^N = e^{-\beta H} / \int e^{-\beta H} d\mathbf{x}^N \quad (\text{equilibrium distribution function}),$$

and  $d\mathbf{x}^N$  is invariant under the pseudo-canonical transformation  $U$ .

(ii)  $f_i^N$  is defined such that the local velocity  $\mathbf{v}(\mathbf{r})$  alone differs from its equilibrium value. Namely,

$$\left. \begin{aligned} \langle \mathbf{j}(\mathbf{r}) \rangle_i &= \langle U\mathbf{j}(\mathbf{r}) \rangle_0 = \rho_0 \mathbf{v}(\mathbf{r}), \\ \langle \rho(\mathbf{r}) \rangle_i &= \langle U\rho(\mathbf{r}) \rangle_0 = \rho_0, \\ \langle H(\mathbf{r}) \rangle_i &= \langle UH(\mathbf{r}) \rangle_0 = \langle H(\mathbf{r}) \rangle_0 + \frac{1}{2} \rho_0 v(\mathbf{r})^2. \end{aligned} \right\} \quad (2.4)$$

Here  $\mathbf{j}(\mathbf{r})$ ,  $\rho(\mathbf{r})$  and  $H(\mathbf{r})$  are the molecular expression for the local mass current density, the local mass density and the local Hamiltonian density, respectively, defined as<sup>6)</sup>

$$\begin{aligned} \mathbf{j}(\mathbf{r}) &= \sum_j \mathbf{p}_j \delta(\mathbf{r}_j - \mathbf{r}), \\ \rho(\mathbf{r}) &= \sum_j m_j \delta(\mathbf{r}_j - \mathbf{r}), \\ H(\mathbf{r}) &= \sum_j \frac{p_j^2}{2m_j} \delta(\mathbf{r}_j - \mathbf{r}) + \frac{1}{2} \sum_j \sum_l u_{jl} \delta(\mathbf{r}_j - \mathbf{r}). \end{aligned} \quad (2.5)$$

Here  $\rho_0$  is the equilibrium mass density. Now a  $U$  satisfying these properties is

$$U\mathbf{p}_j = \mathbf{p}_j + m_j \mathbf{v}(\mathbf{r}_j), \quad U\mathbf{r}_j = \mathbf{r}_j. \quad (2.6)^*)$$

Then

$$\left. \begin{aligned} U^{-1}H &= H + R, \\ R &\equiv - \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{v}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \rho(\mathbf{r}) v(\mathbf{r})^2 d\mathbf{r}. \end{aligned} \right\} \quad (2.7)$$

Now we introduce the Liouville operator  $L$  by

$$iL = \sum_i \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial}{\partial \mathbf{r}_i} - \sum_{i < j} \frac{\partial u_{ij}}{\partial \mathbf{r}_{ij}} \cdot \left( \frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right). \quad (2.8)$$

Then for an arbitrary dynamical variable  $G$

$$e^{itL}G(0) = G(t).$$

Therefore we obtain from (2.1) and (2.7)

$$f^N(t) = e^{-itL}f_l^N = e^{-\beta R(-t)}f_0^N \quad (2.9)$$

and

$$\frac{\partial f^N(t)}{\partial t} = \beta \dot{R}(-t)f^N(t).$$

This can be solved by iteration,

$$f^N(t) = f_l^N + \sum_{n=1}^{\infty} \frac{\beta^n}{n!} \int_0^t ds_1 \cdots \int_0^t ds_n \dot{R}(-s_1) \cdots \dot{R}(-s_n) f_l^N. \quad (2.10)$$

Now we consider the local stress tensor  $\mathbf{J}(\mathbf{r})^{**})$

$$\begin{aligned} \mathbf{J}(\mathbf{r}) &= \sum_j \frac{1}{m_j} \mathbf{p}_j \mathbf{p}_j \delta(\mathbf{r}_j - \mathbf{r}) - \frac{1}{2} \sum_{j \neq l} \sum_{j \neq l} \mathbf{r}_{jl} \frac{\partial u_{jl}}{\partial \mathbf{r}_{jl}} \delta(\mathbf{r}_j - \mathbf{r}) \\ &= P_0 \mathbf{1} + \mathbf{j}(\mathbf{r}) \mathbf{v}(\mathbf{r}) + \mathbf{v}(\mathbf{r}) \mathbf{j}(\mathbf{r}) - \rho(\mathbf{r}) \mathbf{v}(\mathbf{r}) \mathbf{v}(\mathbf{r}) + \mathbf{J}_v^*(\mathbf{r}) \end{aligned} \quad (2.11)$$

where  $\mathbf{1}$  is a unit dyadic,

$$P_0 = \langle J^{xx}(\mathbf{r}) \rangle_0 \quad (\text{equilibrium pressure})$$

and

\*)  $U$  is not a genuine canonical transformation operator. However, since it conserves volume elements in the phase space, it is quite similar to the true canonical transformation.

\*\*) We also define the following quantities:

$$\mathbf{J}^* = \mathbf{J} - P_0 \mathbf{1}, \quad \mathbf{J}_v = \mathbf{J}_v^* + P_0 \mathbf{1}.$$

$$\begin{aligned} \mathbf{J}_v^*(\mathbf{r}) = & \sum_j \frac{1}{m_j} [\mathbf{p}_j - m_j \mathbf{v}(\mathbf{r}_j)] [\mathbf{p}_j - m_j \mathbf{v}(\mathbf{r}_j)] \delta(\mathbf{r}_j - \mathbf{r}) \\ & - \frac{1}{2} \sum_{j \neq l} \sum \mathbf{r}_{jl} \frac{\partial u_{jl}}{\partial \mathbf{r}_{jl}} \delta(\mathbf{r}_j - \mathbf{r}) - P_0 \mathbf{1}. \end{aligned} \quad (2.12)$$

One can easily verify that

$$\begin{aligned} U \mathbf{J}_v^*(\mathbf{r}) &= \mathbf{J}(\mathbf{r}) - P_0 \mathbf{1}, \\ U^{-1} \mathbf{J}(\mathbf{r}) &= \mathbf{J}_v^*(\mathbf{r}) + P_0 \mathbf{1}. \end{aligned} \quad (2.13)$$

We now perform the average of (2.11) with  $f^N(t)$  to obtain the local stress tensor  $\mathbf{P}(\mathbf{r})$  which appears in hydrodynamic equations.

After all, what we need is a part of the stress tensor  $\mathbf{P}(\mathbf{r})$  that is related to the viscosity, which we denote by  $\mathbf{P}^*(\mathbf{r})$  and is obtained by (2.10) as follows:

$$\begin{aligned} \mathbf{P}^*(\mathbf{r}) &= \int \mathbf{J}_v^*(\mathbf{r}) f^N(t) d\mathbf{x}^N \\ &= \langle \mathbf{J}_v^*(\mathbf{r}) \rangle_t + \sum_{n=1}^{\infty} \frac{\beta^n}{n!} \int_0^t ds_1 \cdots \int_0^t ds_n \langle \mathbf{J}_v^*(\mathbf{r}) \dot{R}(-s_1) \cdots \dot{R}(-s_n) \rangle_t. \end{aligned} \quad (2.14)$$

Here  $t$  is chosen such that  $\tau_h \gg t \gg \tau_{\text{micro}}$  ( $\tau_h$  is a relaxation time of hydrodynamic scale and  $\tau_{\text{micro}}$  is the microscopic relaxation time<sup>6)</sup>). Such a choice of  $t$  is necessary because we start with the local equilibrium ensemble and pursue the time development of the flux with the exact dynamics. More detailed discussion of this with the use of the projection operator technique will be given in Appendix A.

From (2.13) and (2.3), we have

$$\langle \mathbf{J}_v^*(\mathbf{r}) \rangle_t = \langle U \mathbf{J}_v^*(\mathbf{r}) \rangle_0 = \langle \mathbf{J}(\mathbf{r}) \rangle_0 - P_0 \mathbf{1} = 0. \quad (2.15)$$

Use of (2.7) and (2.11) yields

$$\begin{aligned} \dot{R} = & - \sum_{\alpha\beta} \int [j_\alpha(\mathbf{r}) - \rho(\mathbf{r}) v_\alpha(\mathbf{r})] v_\beta(\mathbf{r}) \frac{\partial v_\alpha(\mathbf{r})}{\partial r_\beta} d\mathbf{r} \\ & - \int \mathbf{J}_v^*(\mathbf{r}) : \nabla \mathbf{v}(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (2.16)$$

where we have also used the following equations of motion:

$$\left. \begin{aligned} \frac{d}{dt} \rho(\mathbf{r}, t) &= -\nabla \cdot \mathbf{j}(\mathbf{r}, t), \\ \frac{d}{dt} \mathbf{j}(\mathbf{r}, t) &= -\nabla \cdot \mathbf{J}(\mathbf{r}, t). \end{aligned} \right\} \quad (2.17)$$

Now we consider the shear flow of the form

$$v_x = v_z = 0, \quad v_y(\mathbf{r}) = xd, \quad (2.18)$$

where  $d$  is the magnitude of velocity gradient.

In this case (2.16) is simplified to

$$\dot{R} = - \int J_v^{xy}(\mathbf{r}) d\mathbf{r} \cdot d, \quad (2.19)$$

where we have used that  $J_v^{*xy} = J_v^{xy}$ . Then noting (2.15), (2.14) reduces to

$$P^{*xy}(\mathbf{r}) = \sum_{n=1}^{\infty} \frac{(-d\beta)^n}{n!} \int_0^{\infty} dt_1 \int d\mathbf{r}_1 \cdots \int_0^{\infty} dt_n \int d\mathbf{r}_n \langle J_v^{xy}(\mathbf{r}, 0) J_v^{xy}(\mathbf{r}_1, -t_1) \cdots \\ \cdots \times J_v^{xy}(\mathbf{r}_n, -t_n) \rangle_t. \quad (2.20)$$

In (2.20) we have taken the time  $t$  to infinity since we are concerned with the quasi-stationary case where  $\tau_h = \infty$  (see also Appendix A).

In this way we obtain an expression for the local stress tensor. Dividing this formula by  $-d$ , the nonlinear viscosity  $\eta(d)$  is obtained.

We rewrite (2.20) using (2.3) and (2.13), that is,  $J^{xy} = UJ_v^{xy}$  as,

$$P^{*xy} = \sum_{n=1}^{\infty} \frac{(-\beta d)^n}{n!} \int_0^{\infty} dt_1 \int d\mathbf{r}_1 \cdots \int_0^{\infty} dt_n \int d\mathbf{r}_n \langle J^{xy}(\mathbf{r}, 0) [UJ_v^{xy}(\mathbf{r}_1, -t_1)] \cdots \\ \cdots \times [UJ_v^{xy}(\mathbf{r}_n, -t_n)] \rangle_0^*) \quad (2.21) \\ = \sum_{n=1}^{\infty} \frac{(-\beta d)^n}{n!} \int_0^{\infty} dt_1 \int d\mathbf{r}_1 \cdots \int_0^{\infty} dt_n \int d\mathbf{r}_n \langle J^{xy}(\mathbf{r}, 0) \tilde{J}^{xy}(\mathbf{r}_1, -t_1) \cdots \tilde{J}^{xy}(\mathbf{r}_n, -t_n) \rangle_0.$$

$J^{xy}(\mathbf{r}_i, -t_i)$  in the second line is obtained by replacing the Liouville operator  $iL$  by  $i(L + dL')$  in  $J^{xy}(\mathbf{r}_i, -t_i)$ , where

$$iL' \equiv \sum_i \left( x_i \frac{\partial}{\partial y_i} - p_i^x \frac{\partial}{\partial p_i^y} \right). \quad (2.22)$$

The proof of this and the properties of the operator  $iL'$  will be given in Appendix B.

Furthermore (2.21) can be written as follows:

$$P^{*xy} = \frac{1}{V} \sum_{n=1}^{\infty} \frac{(-\beta d)^n}{n!} \int_0^{\infty} dt_1 \int_0^{\infty} dt_2 \cdots \int_0^{\infty} dt_n \langle I^{xy}(0) \tilde{I}^{xy}(-t_1) \cdots \tilde{I}^{xy}(-t_n) \rangle_0, \quad (2.23)$$

where  $I^{xy} \equiv \int d\mathbf{r} J^{xy}(\mathbf{r})$  and  $V$  is the volume of the system.

### § 3. Calculation of the nonlinear shear viscosity

In our earlier work<sup>3)</sup> the anomaly in the shear viscosity of critical binary

<sup>\*)</sup> Here  $\mathbf{r}_j$  should not be confused with the coordinate of the  $j$ -th particle.

mixture near the critical point is related to the anomalous increases of long range concentration fluctuations and the relaxation times associated with them near the critical point, and the flux entering the expression for the shear viscosity is expanded in the power series of the local concentration fluctuations whose temporal developments are assumed to obey the phenomenological diffusion law.

We adopt the same assumption regarding the flux and write

$$J^{xy}(\mathbf{r}) = f \frac{\partial c(\mathbf{r})}{\partial x} \frac{\partial c(\mathbf{r})}{\partial y}, \quad (3.1)$$

where  $c$  is the local concentration and  $f$  a constant defined in Ref. I. Then  $I^{xy}$  in Eq. (2.23) becomes

$$I^{xy} = f \int d\mathbf{r} \frac{\partial c}{\partial x} \frac{\partial c}{\partial y} = \frac{(2\pi)^6}{V} f \sum_{\mathbf{k}} k_x k_y [c_{\mathbf{k}} c_{-\mathbf{k}} - \langle c_{\mathbf{k}} c_{-\mathbf{k}} \rangle_0], \quad (3.2)$$

where

$$c_{\mathbf{k}} \equiv (2\pi)^{-3} \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} [c(\mathbf{r}) - \langle c(\mathbf{r}) \rangle_0].$$

By making use of the result of Appendix B the temporal development of the concentration fluctuation  $c_{\mathbf{k}}(t)$  is governed by the following equation which is an extension of that in Ref. I:

$$\frac{\partial c_{\mathbf{k}}}{\partial t} - dk_y \frac{\partial}{\partial k_x} c_{\mathbf{k}} = -\gamma k^2 (k^2 + \kappa^2) c_{\mathbf{k}} \quad (t > 0), \quad (3.3)^*$$

where  $\kappa$  is the inverse of the correlation length of local concentration fluctuations, and vanishes at the critical point.

From (3.3)  $A_{\mathbf{k}} \equiv c_{\mathbf{k}} c_{-\mathbf{k}}$  in (3.2) obeys the following equations ( $t > 0$ ):

$$\frac{\partial A_{\mathbf{k}}(t)}{\partial t} - dk_y \frac{\partial}{\partial k_x} A_{\mathbf{k}}(t) = -2\gamma k^2 (k^2 + \kappa^2) A_{\mathbf{k}}(t), \quad (3.4a)$$

$$\frac{\partial A_{\mathbf{k}}(-t)}{\partial t} + dk_y \frac{\partial}{\partial k_x} A_{\mathbf{k}}(-t) = -2\gamma k^2 (k^2 + \kappa^2) A_{\mathbf{k}}(-t). \quad (3.4b)$$

Here we have used the fact that on reversing the direction of the time, the term which contains dissipation should have its sign reversed.

$A_{\mathbf{k}}(t)$  enters (2.23) in the following integrated form, which is by the use of (3.4b) reduced to

$$\begin{aligned} \int_0^\infty dt A_{\mathbf{k}}(-t) &= \left( \frac{1}{\mathcal{D}_{\mathbf{k}}} - d \frac{1}{\mathcal{D}_{\mathbf{k}}} S_{\mathbf{k}} \frac{1}{\mathcal{D}_{\mathbf{k}}} + d^2 \frac{1}{\mathcal{D}_{\mathbf{k}}} S_{\mathbf{k}} \frac{1}{\mathcal{D}_{\mathbf{k}}} S_{\mathbf{k}} \frac{1}{\mathcal{D}_{\mathbf{k}}} - \dots \right) A_{\mathbf{k}}(0) \\ &\equiv O_p^{-d}(\mathbf{k}) A_{\mathbf{k}}(0), \end{aligned} \quad (3.5)$$

\* Hereafter, for simplicity, we write  $A(t)$  for  $\tilde{A}(t)$  whose temporal development is governed by the Liouville operator  $i(L + dL')$ .

where

$$\mathcal{D}_k \equiv 2\gamma k^2 (k^2 + \kappa^2),$$

$$S_k \equiv k_y \frac{\partial}{\partial k_x}.$$

This defines a new operator  $O_p^{-d}(\mathbf{k})$ . We used here the well-known expansion formula for operators  $A$  and  $B$

$$\frac{1}{A+B} = \frac{1}{A} - \frac{1}{A} B \frac{1}{A} + \frac{1}{A} B \frac{1}{A} B \frac{1}{A} - \dots.$$

Equation (2.23) now becomes

$$P^{*xy} = - \left( \sum_{n=1}^{\infty} \eta_n(d) \right) d = -\eta(d) d, \quad (3.6)^{*}$$

where  $\eta(d) = \sum_{n=1}^{\infty} \eta_n(d)$  and

$$\eta_n(d) \equiv \frac{\beta^n (-d)^{n-1}}{n! V} \int_0^{\infty} dt_1 \dots \int_0^{\infty} dt_n \langle I^{xy}(0) I^{xy}(-t_1) \dots I^{xy}(-t_n) \rangle_0. \quad (3.7)$$

Equation (3.6), however, is not itself a simple power series expansion in  $d$  because  $I^{xy}(-t_i)$  in  $\eta_n(d)$  follows the equation which contains  $d$  in its temporal development. See (3.4).

Hereafter we shall calculate  $\eta_n(d)$  using the random phase approximation (R.P.A.) in the same way as in Ref. I. Before going further, we note that the average  $\langle \dots \rangle_0$  in (3.7) must be replaced by a connected average  $\langle \dots \rangle_{oc}$ . In the connected average none of the  $I^{xy}$ 's in  $\langle \dots \rangle_{oc}$  are statistically independent of one another (this may be also termed the cumulant average). We shall discuss this in Appendix C in more detail.

In the following calculations we make use of the R.P.A. and adopt the Ornstein-Zernike form for the correlation of the local concentration fluctuation. Namely,

$$\langle |c_k|^2 \rangle_0 = \frac{V \xi_1}{k^2 + \kappa^2}, \quad (3.8)$$

where  $\xi_1$  is a parameter defined in Ref. I which is finite at the critical point.

The evaluation of  $\eta_n(d)$  is performed in Appendix D, and we obtain

$$\eta_1(d) = \frac{2\beta}{V} \left\{ \frac{(2\pi)^6}{V} f \right\}^2 \sum_{\mathbf{k}} k_x k_y O_p^{-d}(\mathbf{k}) \{ k_x k_y \langle |c_{\mathbf{k}}|^2 \rangle_0^2 \}. \quad (3.9)$$

For  $n \geq 2$  we have similarly

\*)  $P^{*xy}$  differs in its sign from that of usual hydrodynamics (see, Landau and Lifshitz; Fluid Mechanics), but this is due to the difference of its definition.



$$\eta_n(d) \equiv \frac{2^n \beta^n (-d)^{n-1}}{V} \left\{ \frac{(2\pi)^6}{V} f \right\}^{n+1} \sum_{\mathbf{k}} k_x k_y O_p^{-d}(\mathbf{k}) \{k_x k_y \langle |c_{\mathbf{k}}|^2 \rangle^{n+1} \times [O_p^d(\mathbf{k}) k_x k_y]^{n-1}\}, \quad (3.10)$$

where

$$O_p^d(\mathbf{k}) = \frac{1}{\mathcal{D}_{\mathbf{k}}} + d \frac{1}{\mathcal{D}_{\mathbf{k}}} S_{\mathbf{k}} \frac{1}{\mathcal{D}_{\mathbf{k}}} + d^2 \frac{1}{\mathcal{D}_{\mathbf{k}}} S_{\mathbf{k}} \frac{1}{\mathcal{D}_{\mathbf{k}}} S_{\mathbf{k}} \frac{1}{\mathcal{D}_{\mathbf{k}}} + \dots$$

Substituting (3.8) into (3.9) and (3.10) and using the relation  $(2\pi)^6 f = (\beta \xi_1)^{-1}$  (see. Ref. I),  $\eta_1, \dots, \eta_n$  can be evaluated. Equations (3.9) and (3.10) are now expressed in terms of power series in  $d$ . Thus we define  $\eta_{ik}$  which is a portion of  $\eta_i$  that contributes to the nonlinear shear viscosity of the order of  $d^{i+k-1}$ .

With this definition we obtain  $\eta_{ik}$  from (3.9) and (3.10):

$$\eta_{10} = \frac{k_B T}{\gamma V} \sum_{\mathbf{k}} \frac{(k_x k_y)^2}{k^2 (k^2 + \kappa^2)^3} = \frac{k_B T}{\gamma (2\pi)^3} \int d\mathbf{k} \frac{(k_x k_y)^2}{k^2 (k^2 + \kappa^2)^3} = \frac{k_B T}{160\pi\gamma\kappa}. \quad (3.11)$$

This agrees with the linear shear viscosity which is obtained in Ref. I.

Next,  $\eta_{11}$  vanishes because of the symmetry and  $\eta_{12}$  gives the first non-vanishing nonlinear contribution. From Eq. (3.9),  $\eta_{12}$  is obtained in the form

$$\begin{aligned} \eta_{12} &= \frac{2k_B T}{(2\pi)^3} \frac{d^2}{(2\gamma)^3} \int d\mathbf{k} k_x k_y \frac{1}{k^2 (k^2 + \kappa^2)} k_x \frac{\partial}{\partial k_y} \frac{1}{k^2 (k^2 + \kappa^2)} k_x \frac{\partial}{\partial k_y} \frac{k_x k_y}{k^2 (k^2 + \kappa^2)} \\ &= -\frac{2k_B T d^2}{(2\pi)^3 (2\gamma)^3} \int d\mathbf{k} k_x^4 \left( \frac{1}{k^2 (k^2 + \kappa^2)} - \frac{4k^2 + 2\kappa^2}{k^4 (k^2 + \kappa^2)^2} k_y^2 \right) \times \frac{1}{k^2 (k^2 + \kappa^2)} \\ &\quad \times \left\{ \frac{1}{k^2 (k^2 + \kappa^2)^3} - \frac{8k^2 + 2\kappa^2}{k^4 (k^2 + \kappa^2)^4} k_y^2 \right\} \\ &= -\frac{25k_B T d^2}{3 \times 2^{12} \pi \gamma^3 \kappa^9}. \end{aligned} \quad (3.12)$$

Equations (3.11) and (3.12) then yield

$$\begin{aligned} \eta_{12} &= -\frac{125}{384} \times \frac{d^2}{\gamma^2 \kappa^8} \eta_{10} \\ &\equiv -0.3255 \times \frac{d^2}{\gamma^2 \kappa^8} \eta_{10}. \end{aligned} \quad (3.13)$$

(3.13) is the same as the result given by Botch and Fixman.<sup>1),\*)</sup>

To this must be added the contributions from  $\eta_2$  and  $\eta_3$  to the nonlinear

\*) In Botch and Fixman's work there was a divergent integral at small  $k$  values. They removed this divergence by the method of the Schwartz distribution or by deforming a path of integration so as to avoid the divergence. This procedure has been justified *a posteriori* by our calculation. However, in general it is rather doubtful that one can always remove the divergence of this sort using the method of the distribution. See §4.

shear viscosity of the order of  $d^2$ . That is, since  $\eta_{20}=0$  because of the symmetry, we obtain

$$\begin{aligned}\eta_{21} &= -\frac{k_B T d^2}{2^3 \pi^3 \gamma^3} \int d\mathbf{k} \frac{(k_x k_y)^3}{(k^2 + \kappa^2)^3} \times \frac{1}{k^4 (k^2 + \kappa^2)^2} k_x \frac{\partial}{\partial k_y} \frac{k_x k_y}{k^2 (k^2 + \kappa^2)} \\ &= -\frac{k_B T d^2}{2^3 \pi^3 \gamma^3} \int d\mathbf{k} \frac{k_x^4 k_y^2}{k^4 (k^2 + \kappa^2)^5} \left\{ \frac{1}{k^2 (k^2 + \kappa^2)} - k_y^2 \frac{4k^2 + 2\kappa^2}{k^4 (k^2 + \kappa^2)^2} \right\} \\ &= -\frac{k_B T d^2}{15 \times 2^{11} \pi^3 \gamma^3 \kappa^9}\end{aligned}\quad (3.14)$$

and

$$\begin{aligned}\eta_{30} &= \frac{k_B T d^2}{2^3 \pi^3 \gamma^3} \int d\mathbf{k} \frac{(k_x k_y)^4}{k^6 (k^2 + \kappa^2)^7} \\ &= \frac{k_B T d^2}{15 \times 2^{12} \pi^3 \gamma^3 \kappa^9}.\end{aligned}\quad (3.15)$$

Equations (3.14) and (3.15) give a correction to  $\eta_{12}$ , but it is numerically very small and is roughly evaluated to be 0.6% of  $\eta_{12}$ .

Finally the power series expansion of the nonlinear shear viscosity  $\eta(d)$  up to the order of  $d^2$  becomes

$$\eta(d) = \frac{k_B T}{160 \pi \gamma \kappa} \left( 1 - 0.3281 \frac{d^2}{\gamma^2 \kappa^8} + \dots \right). \quad (3.16)$$

Thus the coefficient of  $d^2$  of the nonlinear shear viscosity diverges as  $\kappa^{-9}$  near the critical point. Therefore, nonlinear effect is expected to increase rapidly near the critical point.

By a simple dimensional analysis we see that the higher order terms in  $d$  contain higher powers in  $\kappa^{-1}$ .  $d$  has a dimension of the inverse of time and the dimensionless expansion parameter which appears in the power series expansion in  $d$  should be  $(d/\gamma\kappa^4)$ . Therefore, we get a factor  $\kappa^{-8}$  for each additional power of  $d^2$ . Physically this occurs because near the critical point the correlation range of the concentration fluctuation increases enormously in space as well as in time, and the effect of this is more enhanced in higher order terms. Furthermore, as we shall see in the next section, there arise divergence difficulties that the coefficients of the expansion of higher than  $d^4$  diverge even when  $\kappa$  is finite.

#### § 4. Higher order contributions in $d$

In the preceding section we have obtained  $\eta(d)$  up to the order of  $d^2$ . The next order non-vanishing contribution appears in the order of  $d^4$ . Unfortunately, however, its coefficient diverges at the lower limit of the  $k$ -integral even though we are not at the critical point. To demonstrate the divergence,

it is sufficient to consider the terms which dominate at small  $k$ . Thus the most divergent contribution  $\eta_{14}^{\text{M.D.}}$  to  $\eta_{14}$  is obtained from Eq. (3.9):

$$\begin{aligned}\eta_{14}^{\text{M.D.}} &= \frac{k_B T d^4}{2^4 \gamma^5 \kappa^{10}} \frac{1}{V} \sum_{\mathbf{k}} \frac{k_x^6 k_y}{(k^2 + \kappa^2)^2} \left[ \frac{1}{k^2} \frac{\partial}{\partial k_y} \right]^4 \frac{k_y}{k^2} \\ &= \frac{k_B T d^4}{2^4 \gamma^5 (2\pi)^3 \kappa^{17}} \times \left( -\frac{160\pi}{1287} \right) \times \int_0^\infty \frac{dm}{m^4 (m^2 + 1)^3}.\end{aligned}\quad (4.1)$$

Thus at the lower limit of the  $k$ -integral (or the  $m$ -integral) it diverges as  $k^{-3}$  (or  $m^{-3}$ ).  $\eta_2$  also contains a divergent integral, but the degree of the divergence is  $k^{-1}$  and is weaker than (4.1). Furthermore, the coefficient of  $d^6$  in  $\eta_1$  diverges as  $k^{-7}$  and so on.

Similarly for the nonlinear shear viscosity of the two-dimensional binary mixture the logarithmic divergence appears already at the order of  $d^2$ .

That is,

$$\begin{aligned}\eta_{12} &= -\frac{2k_B T d^2}{(2\pi)^2 (2\gamma)^3 \kappa^{10}} \int dm \frac{1}{m^2 (m^2 + 1)} m_x^4 \left\{ \frac{1}{m^4 (m^2 + 1)^4} - \frac{4(3m^2 + 1)}{m^6 (m^2 + 1)^5} m_y^2 \right. \\ &\quad \left. + \frac{4(2m^2 + 1)(4m^2 + 1)}{m^8 (m^2 + 1)^6} m_y^4 \right\} \\ &= -\frac{2k_B T d^2}{2\pi (2\gamma)^3 \kappa^{10}} \times \frac{7}{32} \times [-\ln m_0],\end{aligned}\quad (4.2)$$

where  $m_0$  is the cutoff at the lower limit of the integral. The divergences of this type appear to be associated with the use of the phenomenological theory such as the diffusion equation (3.3) to describe the time evolution of the fluxes entering the expression for the transport coefficients rather than with the fact that we are concerned with the nonlinear effects. In fact the linear bulk viscosity of two-dimensional critical mixture [see references 4) and 9) for the calculation of the bulk viscosity] diverges logarithmically owing to the same cause. This is due to the fact that in this phenomenological approach there appear in the time correlation functions of fluxes the parts with long life-times which decay as certain inverse powers of the time even when we are not near the critical point, and use of the R.P.A. in our calculation appears to be irrelevant. This long life-time part gives a negligible contribution to the three dimensional linear transport coefficients except near the critical point.

This sort of the divergences do not occur if we use the method of the continued fraction<sup>10)</sup> for the calculation of the two-dimensional bulk viscosity.<sup>11),\*)</sup> However, if we use this method to study the linear shear viscosity of three

\*) The calculation which makes use of the continued fraction is usually performed by retaining a few lower order terms correctly and by replacing the rest by its high temperature value. Therefore, we cannot settle this problem unless the convergence of the continued fraction is guaranteed.

dimensional critical mixtures, no anomalous peak appears at the critical point, while if we use our phenomenological approach, the shear viscosity exhibits the anomalous peak like  $\kappa^{-1}$ . [See (3.11).] The existing experiments seem to support the latter result.<sup>12)</sup>

It is beyond the scope of this paper to settle the question whether the divergences appearing in Eqs. (4.1), (4.2) and in the bulk viscosity of the two-dimensional mixture are real or spurious. For this purpose it is necessary to investigate very carefully the basis of our phenomenological approach.\*) This problem is now under investigation. However, if these divergences should turn out to be real, we should re-sum all the divergent contributions. Then it could lead to the interesting possibility that the nonlinear viscosities (hence, hydrodynamic equations) for binary solutions may not be analytic functions of the velocity gradient even if we are away from the critical point.

### Acknowledgements

The authors wish to express their sincere thanks to Professor H. Mori for his enlightening discussions and valuable suggestions.

### Appendix A

We here re-derive the expression for the local stress tensor (2.23) by using Mori's projection operator technique and make a few remarks.

We suppose that at the time zero the system is in the local equilibrium state which may be far from the equilibrium. Namely, we write [see (2.1) and (2.7)],

$$f^N(t=0) = f^N = \frac{1}{Z} e^{-\beta[H+R(0)]} \quad (\text{A} \cdot 1)$$

which then yields for  $t > 0$ ,

$$f^N(t) = \frac{1}{Z} e^{-\beta[H+R(-t)]}, \quad (\text{A} \cdot 2)$$

where  $Z$  normalizes the distribution function.

We apply here Mori's theory.<sup>13)</sup> A difficulty arises because in the nonlinear problem it is not easy to find consistently the temporal variation of the macroscopic parameters characterizing the local equilibrium (e.g. velocity gradient, etc.). However, if we can assume that the system is under the quasi-stationary condition such that the variation of the macroscopic parameters are infinitesimally

\*) One may of course cast our phenomenological approach into a form which makes use of Mori's general theory of Brownian motion<sup>13)</sup> as has been done in Ref. I, Appendix A. Then, one has to worry about the terms which have been left out and which contain Mori's random force  $f(t)$ , for which it is still rather difficult to say anything very definite regarding the present problem.

slow, we can still apply Mori's theory by taking  $f_i^N$  instead of  $f_0^N$  to define the projection operator.

Thus we write

$$R(-t) = R_{-t} + R'(-t), \quad (\text{A} \cdot 3)$$

where

$$R_{-t} = \mathcal{P}_t R(-t), \quad R'(-t) = (1 - \mathcal{P}_t) R(-t) \quad (\text{A} \cdot 4)$$

and  $\mathcal{P}_t$  is the projection operator defined with  $f_i^N$  in Eq. (A.7) below.

At  $t=0$ ,

$$R_{-t} = R(0), \quad R'(0) = 0. \quad (\text{A} \cdot 5)$$

According to Mori, we then obtain

$$R'(-t) = -i \int_0^t ds e^{-i(t-s)(1-\mathcal{P}_t)L} (1 - \mathcal{P}_t) L \mathcal{P}_t R(-s), \quad (\text{A} \cdot 6)$$

where

$$\mathcal{P}_t G \equiv \mathbf{A}^* \cdot \langle \mathbf{A} \mathbf{A}^* \rangle_t^{-1} \cdot \langle \mathbf{A} G \rangle_t. \quad (\text{A} \cdot 7)$$

Here  $\langle \dots \rangle_t$  is the ensemble average with  $f_i^N$  under the quasi-stationary condition with  $R_{-t} \equiv R(0)$ , and  $\mathbf{A}$  is a column matrix composed of all the macroscopic variables and  $\mathbf{A}^*$  is a conjugate matrix of  $\mathbf{A}$ .

Therefore,  $f^N(t)$  becomes

$$f^N(t) = f_i^N \exp \left[ \beta \int_0^t ds e^{-i(t-s)(1-\mathcal{P}_t)L} (1 - \mathcal{P}_t) i L \mathcal{P}_t R(-s) \right]. \quad (\text{A} \cdot 8)$$

We now choose the following  $R$ :

$$R \equiv - \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{v}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \rho(\mathbf{r}) v^2(\mathbf{r}) d\mathbf{r}. \quad (\text{A} \cdot 9)$$

The equations of motion then yield

$$\begin{aligned} \dot{R} \equiv & - \int \mathbf{J}_v^*(\mathbf{r}) : \nabla \mathbf{v}(\mathbf{r}) d\mathbf{r} - \sum_{\alpha\beta} \int [j_\alpha(\mathbf{r}) - v_\alpha(\mathbf{r}) \rho(\mathbf{r})] \\ & \times v_\beta(\mathbf{r}) \frac{\alpha v_\alpha(\mathbf{r})}{\alpha r_\beta} d\mathbf{r}. \end{aligned} \quad (\text{A} \cdot 10)$$

In defining the projection operator, the choice of the set of macroscopic variables  $\mathbf{A}$  is irrelevant as long as they are equivalent sets. Therefore, we choose  $U^{-1}\mathbf{A}$ ,  $U^{-1}\mathbf{A}^*$  instead of  $\mathbf{A}$ ,  $\mathbf{A}^*$ . ( $U$  is the pseudo-canonical transformation operator introduced in § 2.) We then obtain by using (2.3)

$$\begin{aligned} \mathcal{P}_t G &= U^{-1} \mathbf{A}^* \cdot \langle (U^{-1} \mathbf{A}) (U^{-1} \mathbf{A}^*) \rangle_t^{-1} \cdot \langle (U^{-1} \mathbf{A}) G \rangle_t \\ &= U^{-1} \mathbf{A}^* \cdot \langle \mathbf{A} \mathbf{A}^* \rangle_0^{-1} \cdot \langle \mathbf{A} U G \rangle_0 = U^{-1} \mathcal{P}_0 U G, \end{aligned} \quad (\text{A} \cdot 11)$$

where  $\mathcal{P}_0$  is the projection operator introduced by Mori which is defined with the equilibrium ensemble.\*)

Since in the quasi-stationary state we have

$$\mathcal{P}_l R(-s) = R_{-s} \cong R(0), \quad (\text{A} \cdot 12)$$

(A·8) becomes as follows:

$$f^N(t) = f_l^N \exp \left[ \beta \int_0^t ds e^{-i(t-s)(1-\mathcal{P}_l)L} (1-\mathcal{P}_l) \dot{R}(0) \right], \quad (\text{A} \cdot 13)$$

and, since

$$\begin{aligned} \mathcal{P}_l j_\alpha &= j_\alpha, \quad \mathcal{P}_l \rho(\mathbf{r}) = \rho(\mathbf{r}), \\ (1-\mathcal{P}_l) \dot{R} &= - \int (1-\mathcal{P}_l) \mathbf{J}_v^*(\mathbf{r}) : \nabla \mathbf{v}(\mathbf{r}) d\mathbf{r} \\ &= - \int (1-\mathcal{P}_l) U^{-1} \mathbf{J}^*(\mathbf{r}) : \nabla \mathbf{v}(\mathbf{r}) d\mathbf{r} \\ &= - U^{-1} \int (1-\mathcal{P}_0) \mathbf{J}^*(\mathbf{r}) : \nabla \mathbf{v}(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (\text{A} \cdot 14)$$

Thus the average of  $\mathbf{J}_v^*$  is, by using (2·3) and  $U i L = i(L + dL') \cdot U$ ,

$$\begin{aligned} \bar{\mathbf{J}}_v^* &= \langle \mathbf{J}_v^* \exp \left[ -\beta \int_0^t ds e^{-i(t-s)(1-\mathcal{P}_l)L} U^{-1} (1-\mathcal{P}_0) \int \mathbf{J}^*(\mathbf{r}) : \nabla \mathbf{v}(\mathbf{r}) d\mathbf{r} \right] \rangle_t \\ &= \langle \mathbf{J}^* \exp \left[ -\beta \int_0^t ds e^{-i(t-s)(1-\mathcal{P}_0)(L+dL')} (1-\mathcal{P}_0) \int \mathbf{J}^*(\mathbf{r}) : \nabla \mathbf{v}(\mathbf{r}) d\mathbf{r} \right] \rangle_0, \end{aligned} \quad (\text{A} \cdot 15)$$

where  $L'$  is defined by (2·22).

If we assume  $\nabla \mathbf{v} \equiv \mathbf{d} = \text{constant tensor}$ , (A·15) reduces to

$$\bar{\mathbf{J}}_v^* = \frac{1}{V} \langle \mathbf{I}^* \exp \left[ -\beta \int_0^t ds \{ e^{-i(t-s)(1-\mathcal{P}_0)(L+dL')} \} (1-\mathcal{P}_0) \mathbf{I}^* : \mathbf{d} \right] \rangle_0, \quad (\text{A} \cdot 16)$$

where  $\mathbf{I}^* \equiv \int \mathbf{J}^*(\mathbf{r}) d\mathbf{r}$ .

Furthermore, if the only non-vanishing component of  $\mathbf{d}$  is  $\partial v_y / \partial x = d$ , we obtain

$$\bar{J}_v^{xy} = \frac{1}{V} \langle I^{xy} \exp \left[ -\beta \int_0^t ds e^{-i(t-s)(1-\mathcal{P}_0)(L+dL')} I^{xy} d \right] \rangle_0, \quad (\text{A} \cdot 17)$$

where  $I^{xy} \equiv \int J^{xy}(\mathbf{r}) d\mathbf{r}$ .

\*) More precisely, Mori's  $\hat{\mathcal{Q}}$ .

Under the quasi-stationary condition, the upper limit of the time integral may be taken to infinity, and we obtain

$$\begin{aligned}\bar{J}^{xy} &= \frac{1}{V} \langle I^{xy} \exp[-\beta \int_0^t ds e^{-is(1-\mathcal{P}_0)(L+dL')} I^{xy} d] \rangle_0 \\ &\cong \frac{1}{V} \langle I^{xy} \exp[-\beta d \int_0^\infty ds e^{-is(1-\mathcal{P}_0)(L+dL')} I^{xy}] \rangle_0 \\ &= -\eta(d)d.\end{aligned}\quad (\text{A}\cdot 18)$$

Here  $\eta(d)$  is the effective shear viscosity given by

$$\begin{aligned}\eta(d) &= \frac{1}{Vd} \langle I^{xy} [1 - \exp\{-\beta d \int_0^\infty ds e^{-is(1-\mathcal{P}_0)(L+dL')} I^{xy}\}] \rangle_0 \\ &= \sum_{n=1}^\infty \frac{\beta^n (-d)^{n-1}}{n! V} \langle I^{xy} [\int_0^\infty ds e^{-is(1-\mathcal{P}_0)(L+dL')} I^{xy}]^n \rangle_0.\end{aligned}\quad (\text{A}\cdot 19)$$

Now we investigate the effect of  $\mathcal{P}_0$ .  $I^{xy}$  is translationally invariant in the limit of infinite volume  $V$ , that is, for an arbitrary constant vector  $\mathbf{a}$ ,

$$I^{xy}(\mathbf{r}_i \rightarrow \mathbf{r}_i + \mathbf{a}) = I^{xy}(\mathbf{r}_i), \quad (\text{A}\cdot 20)$$

and the same is true for the quantities of the type

$$(iL)^n (iL')^m (iL)^l (iL')^p \dots I^{xy}. \quad (\text{A}\cdot 21)$$

For an arbitrary translationally invariant quantity  $G$ , we then obtain the following expression:

$$\mathcal{P}_0 G = \mathbf{A}_0^* \cdot \langle \mathbf{A}_0 \mathbf{A}_0^* \rangle^{-1} \cdot \langle \mathbf{A}_0 G \rangle,$$

where  $\mathbf{A}_0$  and  $\mathbf{A}_0^*$  are the limit  $q \rightarrow 0$  of the macroscopic variables  $\mathbf{A}_q$  and  $\mathbf{A}_q^*$  having a wave vector  $\mathbf{q}$ . Therefore, we obtain

$$\mathcal{P}_0 iL G = \mathbf{A}_0^* \cdot \langle \mathbf{A}_0 \mathbf{A}_0^* \rangle^{-1} \cdot \langle \mathbf{A}_0 \dot{G} \rangle = -\mathbf{A}_0^* \cdot \langle \mathbf{A}_0 \mathbf{A}_0^* \rangle^{-1} \cdot \langle \mathbf{A}_0 G \rangle = 0,^{*)} \quad (\text{A}\cdot 22)$$

because  $\dot{A}_0 = 0$  for any macroscopic variable  $A_q$  associated with the constants of motion. Therefore, in (A.19) we are allowed to replace  $(1-\mathcal{P}_0)L$  by  $L$ .

Next we consider the effects of  $\mathcal{P}_0$  in  $(1-\mathcal{P}_0)L'$ . In (A.19) after expanding in  $dL'$  there appear terms of the following type:

$$\langle F(t_1) (1-\mathcal{P}_0) iL' G(t_2) \rangle_0, \quad t_2 < 0 \text{ and } t_1 > 0, \quad (\text{A}\cdot 23)$$

where we may assume that

\*) Hereafter in this appendix we assume that the temporal development of an arbitrary quantity  $G$  is governed with the Liouville operator  $iL$ .

$$\langle F(t_1) \rangle_0 = \langle (1 - \mathcal{P}_0) iL' G(t_2) \rangle_0 = 0.$$

The role of  $\mathcal{P}_0$  in (A·23) is to remove any possible secular terms contained in  $\langle F(t_1) iL' G(t_2) \rangle_0$  which remain non-zero in the limit  $t_1 \rightarrow \infty$  or  $t_2 \rightarrow -\infty$  or both. Therefore, if  $\langle F(t_1) iL' G(t_2) \rangle_0$  does not contain any secular term, the  $\mathcal{P}_0$  term in (A·23) should vanish. This appears to be the case with our theory which uses the diffusion type equation to describe the time evolution of the flux.

## Appendix B

In this Appendix we shall derive (2·22) and study its property. Let  $F(\{\mathbf{r}_j\}, \{\mathbf{p}_j\})$  be an arbitrary phase space function. Then use of (2·6) and (2·8) yields

$$UiLF(\{\mathbf{r}_j\}, \{\mathbf{p}_j\}) = \sum_i \left\{ \frac{\mathbf{p}_i + m_i \mathbf{v}(\mathbf{r}_i)}{m_i} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i \cdot \frac{\partial}{\partial [\mathbf{p}_i + m_i \mathbf{v}(\mathbf{r}_i)]} \right\} \times F(\{\mathbf{r}_j\}, \{\mathbf{p}_j + m_j \mathbf{v}(\mathbf{r}_j)\}), \quad (\text{B} \cdot 1)$$

where  $\mathbf{F}_i$  is the force acting on the  $i$ -th particle and  $\partial/\partial \mathbf{r}_i$  on the right-hand side does not operate on  $\mathbf{r}_i$  in the argument of  $\mathbf{v}$ . If we remove this restriction on  $\partial/\partial \mathbf{r}_i$ , (B·1) is then modified to

$$\sum_i \left\{ \frac{\mathbf{p}_i + m_i \mathbf{v}(\mathbf{r}_i)}{m_i} \cdot \left[ \frac{\partial}{\partial \mathbf{r}_i} - m_i \frac{\partial}{\partial \mathbf{r}_i} \mathbf{v}(\mathbf{r}_i) \cdot \frac{\partial}{\partial \mathbf{p}_i} \right] + \mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right\} UF(\{\mathbf{r}_i\}, \{\mathbf{p}_i\}).$$

If we set  $v_x = v_z = 0$  and  $v_y(\mathbf{r}) = x d$ , this reduces to

$$i(L + dL') UF(\{\mathbf{r}_j\}, \{\mathbf{p}_j\}),$$

where

$$iL' = \sum_j \left( x_j \frac{\partial}{\partial y_j} - p_j^x \frac{\partial}{\partial p_j^y} \right). \quad (\text{B} \cdot 2)$$

We next consider a density function  $G(\mathbf{r}, t)$  of the form

$$G(\mathbf{r}, t) = \sum_i g_i \delta(\mathbf{r}_i(t) - \mathbf{r}), \quad (\text{B} \cdot 3)$$

where  $g_i$  is a quantity pertaining to the  $i$ -th particle such as mass, charge, etc., and does not depend on  $\mathbf{r}_i, \mathbf{p}_i$ .

The temporal development of  $G$  with  $i(L + dL')$  is

$$\begin{aligned} \frac{\partial G(\mathbf{r}, t)}{\partial t} &= i(L + dL') G(\mathbf{r}, t) = i(L^t + dL'^t) G(\mathbf{r}, t) \\ &= iL^t G(\mathbf{r}, t) - dx \frac{\partial}{\partial y} G(\mathbf{r}, t), \end{aligned}$$

where  $L^t$  and  $L'^t$  are  $L$  and  $L'$ , respectively, which are time-displaced by  $t$  with the Liouville operator  $L + dL'$ . That is,



$$\frac{\partial G(\mathbf{r}, t)}{\partial t} + dx \frac{\partial}{\partial y} G(\mathbf{r}, t) = iL' G(\mathbf{r}, t). \quad (\text{B} \cdot 4)$$

In obtaining this result, we have used

$$\begin{aligned} iL' G(\mathbf{r}, t) &= iL' \sum_i g_i \delta(\mathbf{r}_i(t) - \mathbf{r}) \\ &= \sum_i x_i(t) \frac{\partial}{\partial y_i(t)} g_i \delta(\mathbf{r}_i(t) - \mathbf{r}) \\ &= - \sum_i x \frac{\partial}{\partial y} g_i \delta(\mathbf{r}_i(t) - \mathbf{r}) \\ &= -x \frac{\partial}{\partial y} G(\mathbf{r}, t), \end{aligned}$$

where  $\mathbf{r}_i(t)$  is  $\mathbf{r}_i$  which is time-displaced by  $t$  with the Liouville operator  $L + dL'$ . It can be seen from (B·4) that the time displacement by the operator  $idL'$  just describes the change of  $G$  due to the drift term in the hydrodynamic equations.

### Appendix C

We shall prove here that Eq. (3·7) can be expressed in the connected or cumulant average  $\langle \dots \rangle_{oc}$ . The normalization of the distribution function gives

$$\int d\mathbf{x}^N f^N(t) = \int d\mathbf{x}^N f_t^N. \quad (\text{C} \cdot 1)$$

This is rewritten using Eq. (2·10) as

$$\sum_{n=1}^{\infty} \frac{\beta^n}{n!} \int_0^t ds_1 \cdots \int_0^t ds_n \langle \dot{R}(-s_1) \cdots \dot{R}(-s_n) \rangle_t = 0. \quad (\text{C} \cdot 2)$$

In a similar way to that we derived Eq. (2·23), (C·2) becomes

$$\sum_{n=1}^{\infty} \frac{(-\beta d)^n}{n!} \int_0^{\infty} ds_1 \cdots \int_0^{\infty} ds_n \langle \tilde{I}^{xy}(-s_1) \tilde{I}^{xy}(-s_2) \cdots \tilde{I}^{xy}(-s_n) \rangle_0 = 0. \quad (\text{C} \cdot 3)$$

Equation (2·23) is then rewritten by the definition of the connected average as

$$\begin{aligned} &\sum_{n=1}^{\infty} \frac{(-\beta d)^n}{n!} \int_0^{\infty} ds_1 \cdots \int_0^{\infty} ds_n \left\{ n \langle I^{xy} \tilde{I}^{xy}(-s_1) \rangle_{oc} \langle \tilde{I}^{xy}(-s_2) \cdots \tilde{I}^{xy}(-s_n) \rangle_0 \right. \\ &\quad + \frac{n(n-1)}{2} \langle I^{xy} \tilde{I}^{xy}(-s_1) \tilde{I}^{xy}(-s_2) \rangle_{oc} \langle \tilde{I}^{xy}(-s_3) \cdots \tilde{I}^{xy}(-s_n) \rangle_0 \\ &\quad \left. + \cdots + \right\} \end{aligned}$$

$$+ {}_nC_i \langle I^{xy} \tilde{I}^{xy}(-s_1) \cdots \tilde{I}^{xy}(-s_i) \rangle_{oc} \langle \tilde{I}^{xy}(-s_{i+1}) \cdots \tilde{I}^{xy}(-s_n) \rangle_0 \\ + \cdots \}.$$

We rearrange the terms in this expression as

$$\begin{aligned} & (-\beta d) \int ds_1 \langle I^{xy} \tilde{I}^{xy}(-s_1) \rangle_{oc} \left( 1 + \sum_{n=2}^{\infty} \frac{(-\beta d)^{n-1}}{(n-1)!} \int_0^{\infty} \cdots \int_0^{\infty} ds_2 \cdots ds_n \langle \tilde{I}^{xy}(-s_2) \cdots \tilde{I}^{xy}(-s_n) \rangle_0 \right) \\ & + \cdots \\ & + \frac{(-\beta d)^i}{i!} \int_0^{\infty} \cdots \int_0^{\infty} ds_1 \cdots ds_i \langle I^{xy} \tilde{I}^{xy}(-s_1) \cdots \tilde{I}^{xy}(-s_i) \rangle_{oc} \left( 1 + \sum_{n=i+1}^{\infty} \frac{(-\beta d)^{n-i}}{(n-i)!} \right. \\ & \quad \left. \times \langle \tilde{I}^{xy}(-s_{i+1}) \cdots \tilde{I}^{xy}(-s_n) \rangle_0 \right) \\ & + \cdots \\ & = \frac{(-\beta d)}{1!} \int_0^{\infty} ds_1 \langle I^{xy} \tilde{I}^{xy}(-s_1) \rangle_{oc} \times \left( 1 + \sum_{n=1}^{\infty} \frac{(-\beta d)^n}{n!} \int_0^{\infty} \cdots \int_0^{\infty} ds_1 \cdots ds_n \langle \tilde{I}^{xy}(-s_1) \cdots \tilde{I}^{xy}(-s_n) \rangle_0 \right) \\ & + \cdots \\ & + \frac{(-\beta d)^i}{i!} \int_0^{\infty} \cdots \int_0^{\infty} ds_1 \cdots ds_i \langle I^{xy} \tilde{I}^{xy}(-s_1) \cdots \tilde{I}^{xy}(-s_i) \rangle_{oc} \\ & \quad \times \left( 1 + \sum_{n=1}^{\infty} \frac{(-\beta d)^n}{n!} \int_0^{\infty} \cdots \int_0^{\infty} ds_1 \cdots ds_n \langle \tilde{I}^{xy}(-s_1) \cdots \tilde{I}^{xy}(-s_n) \rangle_0 \right) \\ & + \cdots. \end{aligned} \tag{C.4}$$

Because of (C.3), we finally obtain for (C.4) the following:

$$\sum_{n=1}^{\infty} \frac{(-\beta d)^n}{n!} \int_0^{\infty} \cdots \int_0^{\infty} ds_1 \cdots ds_n \langle I^{xy} \tilde{I}^{xy}(-s_1) \cdots \tilde{I}^{xy}(-s_n) \rangle_{oc},$$

where  $\langle I^{xy} \tilde{I}^{xy}(-s_1) \cdots \tilde{I}^{xy}(-s_n) \rangle_{oc}$  is the connected average of the product of  $\tilde{I}^{xy}(-s_i)$  such that none of the  $I^{xy}$ 's is statistically independent from the rest.

## Appendix D

We first write the two properties of the  $\delta$ -function which are necessary for subsequent calculations in this Appendix.

For an arbitrary function  $f(x)$ , we have

$$\begin{aligned} \text{(i)} \quad & f(x') \delta(x-x') = f(x) \delta(x-x'), \\ \text{(ii)} \quad & \frac{\partial}{\partial x'} \{f(x') \delta(x-x')\} = -f(x) \frac{\partial}{\partial x} \delta(x-x') \end{aligned}$$

We now derive Eqs. (3.9) and (3.10) from

$$\eta_n(d) = \frac{\beta^n (-d)^{n-1}}{n! V} \int_0^\infty dt_1 \cdots \int_0^\infty dt_n \langle I^{xy} \tilde{I}^{xy}(-t_1) \cdots \tilde{I}^{xy}(-t_n) \rangle_{oc}. \quad (\text{D} \cdot 1)$$

First note that we can prove the following equation by using the properties of the  $\delta$ -function (although we treat here the particular case  $n=2$  explicitly, the extension to cases with general  $n$  is obvious.).

$$\begin{aligned} & \sum_{\mathbf{k}, \mathbf{k}', \mathbf{k}''} k_x k_y k_x' k_y' k_x'' k_y'' O_p^{-d}(\mathbf{k}) O_p^{-d}(\mathbf{k}') \delta(\mathbf{k} - \mathbf{k}') \delta(\mathbf{k}' - \mathbf{k}'') f(\mathbf{k}) \\ &= \sum_{\mathbf{k}, \mathbf{k}', \mathbf{k}''} k_x k_y k_x' k_y' O_p^{-d}(\mathbf{k}) O_p^{-d}(\mathbf{k}') k_x'' k_y'' \delta(\mathbf{k}' - \mathbf{k}'') \delta(\mathbf{k} - \mathbf{k}') f(\mathbf{k}) \\ &= \sum_{\mathbf{k}, \mathbf{k}'} k_x k_y k_x' k_y' O_p^{-d}(\mathbf{k}) O_p^{-d}(\mathbf{k}') k_x' k_y' \delta(\mathbf{k} - \mathbf{k}') f(\mathbf{k}) \quad (\text{use (i)}) \\ &= \sum_{\mathbf{k}, \mathbf{k}'} k_x k_y O_p^{-d}(\mathbf{k}) f(\mathbf{k}) k_x' k_y' O_p^{-d}(\mathbf{k}') k_x k_y \delta(\mathbf{k} - \mathbf{k}') \quad (\text{use (i)}) \\ &= \sum_{\mathbf{k}, \mathbf{k}'} k_x k_y O_p^{-d}(\mathbf{k}) f(\mathbf{k}) k_x k_y k_x' k_y' O_p^{-d}(\mathbf{k}') \delta(\mathbf{k} - \mathbf{k}'). \end{aligned} \quad (\text{D} \cdot 2)$$

We also have the following identity:

$$\begin{aligned} & k_x' k_y' \frac{1}{\mathcal{D}_{\mathbf{k}'}} S_{\mathbf{k}'} \frac{1}{\mathcal{D}_{\mathbf{k}}} \delta(\mathbf{k} - \mathbf{k}') \\ &= k_x' k_y' \frac{1}{\mathcal{D}_{\mathbf{k}'}} S_{\mathbf{k}'} \frac{1}{\mathcal{D}_{\mathbf{k}}} \delta(\mathbf{k} - \mathbf{k}') \quad (\text{use (i)}) \\ &= -k_x' k_y' \frac{1}{\mathcal{D}_{\mathbf{k}'}} \frac{1}{\mathcal{D}_{\mathbf{k}}} S_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}') \quad (\text{use (ii)}) \\ &= -\frac{1}{\mathcal{D}_{\mathbf{k}}} S_{\mathbf{k}} k_x' k_y' \frac{1}{\mathcal{D}_{\mathbf{k}'}} \delta(\mathbf{k} - \mathbf{k}') \\ &= -\frac{1}{\mathcal{D}_{\mathbf{k}}} S_{\mathbf{k}} \frac{1}{\mathcal{D}_{\mathbf{k}}} k_x k_y \delta(\mathbf{k} - \mathbf{k}') \quad (\text{use (i)}). \end{aligned} \quad (\text{D} \cdot 3)$$

Repeated use of (D.3) yields

$$k_x' k_y' O_p^{-d}(\mathbf{k}') \delta(\mathbf{k} - \mathbf{k}') = O_p^d(\mathbf{k}) k_x k_y \delta(\mathbf{k} - \mathbf{k}'). \quad (\text{D} \cdot 4)$$

Using (D.4), (D.2) becomes

$$\begin{aligned} & \sum_{\mathbf{k}, \mathbf{k}'} k_x k_y O_p^{-d}(\mathbf{k}) f(\mathbf{k}) k_x k_y O_p^d(\mathbf{k}) k_x k_y \delta(\mathbf{k} - \mathbf{k}') \\ &= \sum_{\mathbf{k}} k_x k_y O_p^{-d}(\mathbf{k}) [f(\mathbf{k}) k_x k_y \{O_p^d(\mathbf{k}) k_x k_y\}]. \end{aligned} \quad (\text{D} \cdot 5)$$

It is easy to generalize Eq. (D.5) by repeating the same procedure.

We now derive Eq. (3.10) [(3.9) is a special case of (3.10) with  $n=1$ ]. Using Eqs. (3.2) and (3.5), Eq. (D.1) becomes

$$\begin{aligned}
\eta_n(d) &= \frac{\beta^n (-d)^{n-1}}{n! V} \left\{ \frac{(2\pi)^6}{V} f \right\}^{n+1} \sum_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{n+1}} k_{1x} k_{1y} k_{2x} k_{2y} \cdots k_{n+1x} k_{n+1y} \\
&\quad \times O_p^{-d}(\mathbf{k}_2) \cdots O_p^{-d}(\mathbf{k}_{n+1}) \langle (c_{\mathbf{k}_1} c_{-\mathbf{k}_1} - \langle c_{\mathbf{k}_1} c_{-\mathbf{k}_1} \rangle_0) \times \cdots \\
&\quad \times (c_{\mathbf{k}_n} c_{-\mathbf{k}_n} - \langle c_{\mathbf{k}_{n+1}} c_{-\mathbf{k}_{n+1}} \rangle_0) \rangle_{0c} \\
&= \frac{\beta^n (-d)^{n-1}}{n! V} \left\{ \frac{(2\pi)^6}{V} f \right\}^{n+1} S_n \sum_{\mathbf{k}_1, \dots, \mathbf{k}_{n+1}} k_{1x} k_{1y} \cdots k_{n+1x} k_{n+1y} \\
&\quad \times O_p^{-d}(\mathbf{k}_2) \cdots \times O_p^{-d}(\mathbf{k}_{n+1}) \delta(\mathbf{k}_1 - \mathbf{k}_2) \times \cdots \\
&\quad \times \delta(\mathbf{k}_n - \mathbf{k}_{n+1}) \langle |c_{\mathbf{k}_1}|^2 \rangle_0^{n+1}, \tag{D.6}
\end{aligned}$$

where  $S_n$  arises when we use the random phase approximation to replace the cumulant average of the product of  $n+1$  factors  $c_{\mathbf{k}_i} c_{-\mathbf{k}_i} - \langle c_{\mathbf{k}_i} c_{-\mathbf{k}_i} \rangle_0$  ( $i=1, \dots, n+1$ ) by the sum of the products of  $\langle |c_{\mathbf{k}}|^2 \rangle_0$ . If we note that  $O_p^{-d}(-\mathbf{k}) = O_p^{-d}(\mathbf{k})$ , each product turns out to be the same and appears  $S_n$  times.  $S_n$  is the number of ways of ordering the  $n+1$  factors  $c_{\mathbf{k}_i} c_{-\mathbf{k}_i} - \langle c_{\mathbf{k}_i} c_{-\mathbf{k}_i} \rangle_0$  into a ring multiplied by  $2^n$ , because for fixed  $\mathbf{k}_1$ , either  $\mathbf{k}_i$  or  $-\mathbf{k}_i$  equals  $\mathbf{k}_1$  for  $i=2, 3, \dots, n+1$ . Namely,

$$S_n = 2^n \times n!. \tag{D.7}$$

Using (D.2) and (D.5) repeatedly and also (D.7), (D.6) finally becomes

$$\begin{aligned}
\eta_n(d) &= \frac{2^n \beta^n (-d)^{n-1}}{V} \left\{ \frac{(2\pi)^6}{V} f \right\}^{n+1} \sum_{\mathbf{k}} k_x k_y O_p^{-d}(\mathbf{k}) [k_x k_y \langle |c_{\mathbf{k}}|^2 \rangle_0^{n+1} \\
&\quad \times \{O_p^d(\mathbf{k}) k_x k_y\}^{n-1}]. \tag{D.8}
\end{aligned}$$

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**Note added in proof:** In the vicinity of the critical point where the diffusion constant vanishes, the terms in the diffusion equation which are nonlinear in the concentration fluctuation should become important in addition to the terms with higher spatial derivatives of  $c(\mathbf{r})$  which have been considered already. The former result from the concentration dependence of the diffusion constant  $D(c)$ . Then the equation of motion for  $c(\mathbf{r})$  is

$$\frac{\partial c(\mathbf{r})}{\partial t} = D(c)\nabla^2 c + \frac{dD(c)}{dc}(\nabla c)^2 - \gamma \nabla^4 c.$$

Though these nonlinear terms have not been considered in the problem of critical mixture so far,<sup>1)-4)</sup> the appearance of the divergences necessitates the study of the effects of these nonlinear terms.