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Mode-coupling theory of the stress-tensor autocorrelation function of a dense binary fluid mixture

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We present a generalized mode-coupling theory for a dense binary fluid mixture. The theory is used to calculate molecular-scale renormalizations to the stress-tensor autocorrelation function (STAF) and to the long-wavelength zero-frequency shear viscosity. As in the case of a dense simple fluid, we find that the STAF appears to decay as $t^{-3/2}$ over an intermediate range of time. The coefficient of this long-time tail is more than two orders of magnitude larger than that obtained from conventional mode-coupling theory. Our study focuses on the effect of compositional disorder on the decay of the STAF in a dense mixture.

1 Introduction

In a simple fluid the five conserved densities relax very slowly at small wave vectors. The nonlinearities in the hydrodynamic equations provide a further mechanism for slowing down the decay of fluctuations and are responsible for the long-time algebraic tails of the correlation functions that determine the transport coefficients [1]. The coefficients of the algebraic tails arising from these long-wavelength or conventional mode-coupling effects are, however, often much smaller than those observed by molecular dynamics. In particular, the conventional mode-coupling theory yields a coefficient of the long-time tail of the stress-tensor autocorrelation function (STAF) of a dense hard-sphere fluid which is 500 times smaller than observed in simulations [2]. It has been shown that this difference can be accounted for in terms of finite-wave-vector or generalized mode-coupling effects [3]. In a dense fluid density fluctuations relax slowly even on molecular length scales. As a consequence, density nonlinearities lead to a renormalization of the transport coefficients via a finite-wave-vector mode-coupling mechanism [4,3] that can qualitatively account for the size of the coefficient of the long-time tail of the STAF [2] for the shear-dependent viscosity [5,6] observed in computer simulations. In addition they provide a good description of the behavior of the velocity autocorrelation function at intermediate times [7]. A self-consistent implementation of the generalized mode-coupling theory also predicts, at a critical density, the transition to a glassy state where structural relaxation is frozen [4,8-10]. On the other hand, a more detailed analysis has shown that the transition is an artifact of the approximation used and is cutoff when additional couplings are included [11]. The generalized mode-coupling theory has, however, provided considerable insight into the dynamical properties of dense simple liquids. In particular, it gives an adequate description of the slowing down of the dynamics of dense fluids of moderate viscosity, in a regime above the glass transition were the relaxa- tion is highly cooperative and nonexponential [12,13].

In this paper we are interested in the mode-coupling contribution to the shear viscosity and in the long-time behavior of the stress-tensor autocorrelation function of a dense binary fluid mixture. In a recent paper [14], Erpen- beck reported molecular-dynamic studies of an isotopic hard-sphere mixture at moderate densities and concluded that in this case the size of the coefficient of the long-time tail of the time-correlation function for the shear viscosity observed in the simulations agrees with the prediction of conventional mode-coupling theory. In mixtures, as in one-component fluids, the conventional mode-coupling contribution to the STAF only accounts for the kinetic part of the correlation function. The kinetic contribution dominates at low and moderate densities and in this regime the conventional mode-coupling theory agrees with the simulations. Even in one-component fluids [15] it is only at high densities ($n\sigma^3 \geq 0.7$) that the largest contribution to the correlation function is the potential one and the observed coefficient of the $t^{-3/2}$ tail of the STAF is much larger than predicted by conventional mode-coupling theory. The situation should not be different for mixtures. The agreement of the simulations with conventional mode-coupling theory can only occur at the relatively moderate densities considered by Erpenbeck. His observations do not preclude the possibility of obtaining large finite-wave-vector mode-coupling corrections to the stress-tensor autocorrelation function at higher densities. To our knowledge such effects have not yet been investigated in computer simulations of mixtures.

Here we evaluate the generalized (to include finite-wave-vector effects) mode-coupling contribution to the STAF and to the shear viscosity of a binary mixture of hard spheres of different sizes and masses. The generalized mode-coupling theory takes into account that in a dense viscous liquid structural rearrangements are very slow due to a close packing of the molecules. The slow dynamics of density fluctuations on molecular length scales affects the macroscopic transport properties through a nonlinear mode-coupling mechanism [4,3]. At large wave vectors the most important of these contributions involves the product of two density fluctuations [16,3]: this contribution is the slowest decaying and has the largest amplitude. In the case of a one-component fluid, the dynamics slows down significantly at only one value of the wave vector corresponding to the location of the first maximum of $S(k)$ [17]. In contrast, in a dense mixture of spheres of different sizes fluctuations in the mass densities of both species can be long-lived on molecular length scales [18] and the dynamics can slow down over a range of wave vectors. In paper I [18] we obtained a set of linear generalized hydrodynamic equations that describe the dynamics of the density fluctuations of the two species down to molecular scales. We found that when the packing fractions of the two species are comparable and all three partial static structure factors of the mixture are peaked, the density fluctuations of the two species decay very slowly at two length scales corresponding to the molecular diameters of the two species. We now consider the nonlinear generalized hydrodynamic equations and discuss the renormalization of the transport coefficients by density nonlinearities. The interplay of the density fluctuations of the two components leads to finite-wave-vector mode-coupling corrections to the correlation functions which determine the transport coefficients.

We are interested in a binary mixture of hard spheres as the simplest model where one can study in some detail the role of compositional disorder in slowing down the fluid dynamics. Compositional disorder seems to be an essential feature of the simplest glass formers (metallic glasses). Our work is focused towards understanding how the structural relaxation of the two species and interdiffusion affect the dense fluid dynamics. We choose to study the mode-coupling correction to the stress-tensor autocorrelation function which determines the shear viscosity as the simplest of the various mode-coupling effects in a mixture.

The self-consistent implementation of the generalized mode-coupling theory of binary mixtures has been discussed recently by several authors as a model of the glass transition [19,20]. Our work differs from this work on mixtures because here we simply study the mode-coupling corrections to lowest order in perturbation theory, without attempting any self-consistent closure. We do so for two reasons. First we believe that one needs to understand well the simplest perturbation theory before making it self consistent. Second, and most importantly, it has been shown [3] that for one-component fluids a naive mode-coupling theory of the type we discuss here describes well the slowing down of the dynamical properties above the glass transition, in a regime of moderate viscosity where the dynamics is cooperative (and therefore nonexponential), but not yet activated [12]. Our objective is to put the description of the dynamics of dense mixtures in this regime on the same solid footing as that of one-component fluids.

The outline of the paper is as follows. In Sec. II the. basic theory used here is described. The perturbation theory in the nonlincarities in the hydrodynamic equations is then outlined in Sec. III, where an expression for the renormalized shear viscosity is obtained. In Sec. IV we present our results for the STAF and the shear viscosity for hard-sphere fluid mixtures. We analyze the concentration dependence of the STAF for a mixture and conclude the paper by discussing our results and by making some remarks about connections to earlier theoretical studies and computer simulations.

2 Nonlinear generalized hydrodynamics

The hydrodynamic properties of a binary fluid mixture are described in terms of the six conserved densities: the mass densities $\rho_1(\mathbf{r}, t)$ and $\rho_2(\mathbf{r}, t)$ p.(r,t) of the two species, the total momentum density $\mathbf{g}(\mathbf{r}, t)$, and the energy density $e(\mathbf{r}, t)$ [18]. We begin by writing a set of hydrodynamic equations that have the same structure both at large and short (molecular) length scales. The starting point for the derivation of these generalized hydrodynamic equations is the free-energy functional for an inhomogeneous equi- librium binary fluid mixture, given by

$$F = \int d\mathbf{r} \left[\frac{g_1^2}{2\rho_1} + \frac{g_2^2}{2\rho_2} \right] + F_V. \tag{2.1}$$

The potential part F_V of the free-energy functional can be written exactly in the form of an expansion in the fluctuations $\delta n_s(\mathbf{r}, t) - n_{0s}$ of the number density $n_s(\mathbf{r}, t)$ of species s, with $s = 1, 2$, from its equilibrium value n_{0s}, [21]

$$\frac{\delta F_V}{\delta \rho_s} = \frac{k_B T}{m_s} \Bigg\{ \ln[\lambda_{Ts}^3 n_s(\mathbf{r})] - \sum_{s'=1}^{2} \int d\mathbf{r}' C_{ss'}(|\mathbf{r} - \mathbf{r}'|) \delta n_{s'}(\mathbf{r}', t)$$
$$- \frac{1}{2} \sum_{s'=1}^{2} \sum_{s''=1}^{2} \int d\mathbf{r}' \int d\mathbf{r}'' C_{ss's''}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \delta n_{s'}(\mathbf{r}', t) \delta n_{s''}(\mathbf{r}'', t) + \cdots \Bigg\}. \tag{2.2}$$

Here m_s is the mass of a particle of type s, T is the temperature, $\lambda_{Ts} = (\hbar^2/2\pi m_s k_B T)^{1/2}$ is the thermal wave-lngth of particles of type s and $C_{ss'}(|\mathbf{r} - \mathbf{r}'|)$ and $C_{ss's''}(\mathbf{r}, \mathbf{r}'\mathbf{r}'')$

are the equilibrium two-particle and three-particle direct correlation functions. From this free energy, nonlinear fluctuating hydrodynamic equations can be derived by the standard Poisson bracket method outlined in Appendix A [22]. Here we neglect temperature fluctuations since they do not play an important role in determining the renormalization to be discussed in Sec. III. The equations for the partial mass densities of the two species and the total momentum density are

$$\partial_t \rho_1(\mathbf{r},t) + \mathbf{nabla} \cdot \left[\frac{\rho_1}{\rho}\mathbf{g}(\mathbf{r},t)\right] = -G_1(\mathbf{r},t) + f_1(\mathbf{r},t), \tag{2.3}$$

$$\partial_t \rho_2(\mathbf{r},t) + \mathbf{nabla} \cdot \left[\frac{\rho_2}{\rho}\mathbf{g}(\mathbf{r},t)\right] = -G_2(\mathbf{r},t) + f_2(\mathbf{r},t), \tag{2.4}$$

$$\begin{aligned}\partial_t g_\alpha(\mathbf{r},t) + \delta_\beta \left[\frac{g_\alpha g_\beta}{\rho}\right] \quad &+ \sum_{i=1}^{2} \rho_s \partial_\alpha \left[\frac{\delta F_V}{\delta \rho_s}\right] \\ &= -G_{g_\alpha}(\mathbf{r},t) + f_{g_\alpha}(\mathbf{r},t).\end{aligned} \tag{2.5}$$

Here $G_1(\mathbf{r},t)$ and $G_2(\mathbf{r},t)$ account for diffusive dissipation of species type 1 and 2, respectively, and $G_{g_\alpha}(\mathbf{r},t)$ corresponds to viscous dissipation. We write these terms in the form

$$G_s(\mathbf{r},t) = \partial_\alpha \sum_{s'=1}^{2} \int d\mathbf{r}' \gamma_{ss'}^{\alpha\beta}(\mathbf{r},\mathbf{r}';n_s)\partial'_\beta \left[\frac{\delta F}{\delta \rho_{s'}(\mathbf{r}')}\right], \tag{2.6}$$

for $s = 1, 2$, and

$$G_{g_\alpha}(\mathbf{r},t) = \int d\mathbf{r}' \Gamma_{\alpha\beta}(\mathbf{r},\mathbf{r}';n_s) \frac{\delta F}{\delta g_\beta(\mathbf{r}')}. \tag{2.7}$$

From the equation of continuity for the total density fluctuations $\rho(\mathbf{r},t) = \rho_1(\mathbf{r},t) + \rho_2(\mathbf{r},t)$, it follows that $G_1(\mathbf{r},t) + G_2(\mathbf{r},t) = 0$. As we have seen in I, the only fluctuations that are slowly varying on molecular length scales are the fluctuations of the partial densities of the two species. Large-wave-vector momentum fluctuations relax on short-time scales and momentum behaves like a nonhydrodynamic (nonconserved) variable. We have therefore written $G_1(\mathbf{r},t)$ and $G_2(\mathbf{r},t)$ in a form explicitly consistent with the general structure of dissipative terms pertaining to conserved variables. The form of $G_{g_\alpha}(\mathbf{r},t)$ corresponds to that of dissipation associated with a non-conserved variable [23]. On the other hand, it should be kept in mind that our dissipative kernels $\gamma_{ss'}^{\alpha\beta}$ $\Gamma_{\alpha\beta}$ are nonlocal and reproduce the well-known transport coefficients in the long-wavelength limit.

In the above equations $f_1(\mathbf{r}, t)$, $f_2(\mathbf{r}, t)$, and $f_{g_\alpha}(\mathbf{r}, t)$ are Gaussian random fluctuating forces which are related to the corresponding linearized dissipative kernels through the fluctuation-dissipation theorem. The random forces have zero average and correlations given by

$$\langle f_s(\mathbf{r}, t) f_{s'}(\mathbf{r}', t')\rangle = 2k_BT\gamma_{ss'}^{\alpha\beta}(\mathbf{r}, \mathbf{r}')\partial_\alpha\partial'_\beta\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \tag{2.8}$$

$$\langle f_{g_\alpha}(\mathbf{r}, t) f_{g_\beta}(\mathbf{r}', t')\rangle = 2k_BT\Gamma_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'). \tag{2.9}$$

Equations (2.3)-(2.5) follow from general considerations if one neglects temperature fluctuations and non-Markovian effects.

To complete the equations, one needs to specify the dissipative kernels. We will neglect dissipative nonlinearities in our analysis. For a dense one-component fluid a theory that only retains thermodynamic nonlinearities predicts a $t^{-3/2}$ tail for the STAF with a coefficient that is a factor of 2 smaller than that observed in simulations [7]. The inclusion of dissipative nonlinearities accounts for this factor-of-2 difference [17]. For simplicity here we neglect dissipative nonlinearities and assume $\Gamma_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; n_s) \simeq \Gamma_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; n_{s0})$ and $\gamma_{ss'}^{\alpha\beta}(\mathbf{r}, \mathbf{r}'; n_s) \simeq \gamma_{ss'}^{\alpha\beta}(\mathbf{r}, \mathbf{r}'; n_{s0})$. The simple fluid results indicate that even with this approximation the theory will provide a semi-quantitative description of the behavior of the STAF at intermediate times. We also neglect convective non-linearities which are responsible for the asymptotic $t^{-3/2}$ tails in the STAF. At high density the coefficient of the asymptotic tail is much smaller that the contribution discussed here.

It is convenient for the discussion below to consider the Fourier transform of the generalized hydrodynamic equations (2.3)-(2.5). The Fourier components of momentum fluctuations are separated into longitudinal and transverse parts,

$$\mathbf{g}(\mathbf{k}, t) = \hat{\mathbf{k}} g_l(\mathbf{k}, t) + \sum_{i=1,2} \hat{\mathbf{k}}_\perp^i g_{Ti}(\mathbf{k}, t), \tag{2.10}$$

where $\hat{\mathbf{k}} = \mathbf{k}/k$ is a unit vector along $\mathbf{k}$ and $\hat{\mathbf{k}}_\perp^i$ are unit vectors normal to $\mathbf{k}$. After neglecting convective and dissipative nonlinearities and retaining only quadratic nonlinearities in the density fluctuations, the Fourier-transformed equations are given by

$$\partial_t \rho_s(\mathbf{k},t) + ik\frac{\rho_s 0}{\rho 0} g_l(\mathbf{k},t) = \frac{k^2}{\beta}\sum_{s',s''=1}^{2} \gamma_{ss'}(K)[\delta_{s's''} - n_{s'}C_{s's''}(k)]\frac{\delta n_{s''}(\mathbf{k},t)}{\rho_{s'0}} + f_s(\mathbf{k},t), \tag{2.11}$$

for $s = 1, 2$, and

$$\begin{aligned}[\partial_t + \gamma_L(k)]g_l(\mathbf{k},t) + ik \quad & \sum_{s,s'=1}^{2}[\delta_{ss'} - n_s C_{ss'}(k)]\delta_{n_{s'}}(\mathbf{k},t) \\ & = I_L(\mathbf{k},t) + F_L(\mathbf{k},t)\end{aligned} \tag{2.12}$$

$$[\partial_t + \gamma_T(k)]g_{T_i}(\mathbf{k},t) = I_{T_i}(\mathbf{k},t) + f_{T_i}(\mathbf{k},t). \tag{2.13}$$

In writing the above equations we have used that for an isotropic fluid

$$\Gamma_{\alpha\beta}(\mathbf{k}) = \rho_0[\hat{k}_\alpha \hat{k}_\beta \gamma_L(k) + (\delta_{\alpha\beta} - \hat{k}_\alpha \hat{k}_\beta)\gamma_T(k)], \tag{2.14}$$

$$\gamma_{ss'}^{\alpha\beta}(k) = \delta_{\alpha\beta}\gamma_{ss'}(k). \tag{2.15}$$

In the long-wavelength-limit the viscous kernel $\Gamma_{\alpha\beta}(\mathbf{k})$ reduces to the usual combination of gradients and bare shear and bulk viscosities η_s and ζ,

$$\lim_{k\to 0}\Gamma_{\alpha\beta}(\mathbf{k}) = k_\alpha k_\beta(\zeta + \frac{4}{3}\eta_s) + (k^2\delta_{\alpha\beta} - k_\alpha k_\beta)\eta_s. \tag{2.16}$$

The diffusion kernels $\gamma_{ss'}(k)$ are related to the diffusion constants $D_{ss'}$ of a binary mixture, according to

$$D_{ss'} = \lim_{k\to 0}\frac{k_B T}{\sqrt{m_s \rho_s m_{s'} \rho_{s'}}}\gamma_{ss'}(k). \tag{2.17}$$

Finally, the nonlinearities in Eqs. (2.12) and (2.13) are given by

$$\begin{aligned}I_L(\mathbf{k},t) = \frac{1}{2}\sum_{s,s'=1}^{2} \quad & \int \frac{d\mathbf{q}}{(2\pi)^3}[V_{ss'}^L(\mathbf{k},\mathbf{q}) + V_{s's}^L(\mathbf{q},\mathbf{k})] \\ & \times \delta_{n_s}(\mathbf{q},t)\delta_{n_{s'}}(\mathbf{k}-\mathbf{q},t),\end{aligned} \tag{2.18}$$

$$I_{T_i}(\mathbf{k},t) = \frac{1}{2}\sum_{s,s'=1}^{2} \int \frac{d\mathbf{q}}{(2\pi)^3}[V_{ss'}^{T_i}(\mathbf{k},\mathbf{q}) + V_{s's}^{T_i}(\mathbf{q},\mathbf{k})] \times\delta_{n_s}(\mathbf{q},t)\delta_{n_{s'}}(\mathbf{k}-\mathbf{q},t), \tag{2.19}$$

with

$$V_{ss'}^{T_i}(\mathbf{k},\mathbf{q}) + V_{s's}^{T_i}(\mathbf{q},\mathbf{k}) = \frac{\hat{\mathbf{k}}_\perp^i\cdot\mathbf{q}}{\beta}[C_{ss'}(|\mathbf{k}-\mathbf{q}|) - C_{ss'}(q)], \tag{2.20}$$

$$\begin{aligned} V_{ss'}^{L}(\mathbf{k},\mathbf{q}) + V_{s's}^{L}(\mathbf{q},\mathbf{k}) &= \frac{\hat{\mathbf{k}}_\perp^i\cdot\mathbf{q}}{\beta}[C_{ss'}(|\mathbf{k}-\mathbf{q}|) - C_{ss'}(q)], \\ &+ \frac{k}{\beta}\sum_{s''=1}^{2} n_{0_{s''}} C_{ss's''}(\mathbf{q}-\mathbf{k};-\mathbf{q}). \end{aligned} \tag{2.21}$$

The linearized form of Eqs. (2.3)-(2.5) is identical to the linear equations obtained in paper I for a binary fluid of hard spheres from the Enskog theory. For the case of hard-sphere fluids one can derive explicit analytical expressions for the dissipative kernels. These expressions were obtained in I. The viscous kernels are given by

$$\gamma_L(k) = \frac{2}{3\rho}\sum_{s,s'}\frac{2\mu_{ss'}\sqrt{n_s n_{s'}}}{t_{E_{ss'}}} d_1(k\sigma_{ss'}), \tag{2.22}$$

$$\gamma_T(k) = \frac{2}{3\rho}\sum_{s,s'}\frac{2\mu_{ss'}\sqrt{n_s n_{s'}}}{t_{E_{ss'}}} d_2(k\sigma_{ss'}), \tag{2.23}$$

where $t_{E_{ss'}}$, is the Enskog mean free time between collisions,

$$\frac{1}{t_{E_{ss'}}} = \frac{4\sqrt{\pi n_s n_{s'}}\sigma_{ss'}^2}{(2\beta\mu_{ss'})^{1/2}}\chi_{ss'}, \tag{2.24}$$

with $\mu_{ss'} = m_s m_s'/(m_s+m_{s'})$ and $chi_{ss'}$ the pair correlation function of species s and s' evaluated at contact, $chi_{ss'} = g_{ss'}(r=\sigma_{ss'})$. The functions $d_1(x)$ and $d_2(x)$ are defined in terms of the spherical Bessel functions $j_l(x)$ as $d_1(x) = 1 - j_0(x) + 2j_2(x)$ and $d_2(x) = 1 - j_0(x) - j_2(x)$. The four ditTusion kernels $\gamma_{ss'}(k)$ are related via the

Onsager reciprocity relations, which require $\gamma_{11}(k) = \gamma_{22}(k) = -\gamma_{12}(k) = -\gamma_{21}(k)$. Therefore there is only one independent diffusion constant in a binary mixture. For hard-sphere fluids it is given by

$$\gamma_{11}(\mathbf{k}) = \frac{3}{2}\left[\sum_{s,s'} \frac{2\mu_{ss'}}{\sqrt{m_s m_{s'} \rho_s \rho_{s'}} t_{E_{ss'}}} d_{ss'}(k\sigma_{ss'})\right]^{-1} \tag{2.25}$$

where

$$d_{ss'}(x) = \frac{\rho_s}{\rho_{s'}} - (-1)^{s+s'}[j_0(x) - 2j_2(x)] \tag{2.26}$$

This concludes the derivation of the nonlinear generalized hydrodynamic equations. In the next section we describe the perturbation theory to evaluate the mode-coupling contribution to the STAF.

3 Mode-coupling theory

We are interested in evaluating the generalized mode-coupling contribution to the coefficient of shear viscosity η_s and to the corresponding STAF, $\rho_\eta(t)$. They are related by the Green-Kubo formula,

$$\eta_s = \beta \int_0^\infty dt \rho_\eta(t). \tag{3.1}$$

The shear viscosity governs the decay of the transverse momentum fluctuations, $C_T(\mathbf{k}, t) = \langle g_T(\mathbf{k}, t) g_T(-\mathbf{k}, 0)\rangle$. When nonlinearities are neglected, the generalized hydrodynamic equations discussed in Sec. II give

$$[\partial_t + \gamma_T(k)] C_T^{(0)}(\mathbf{k}, t) = 0, \tag{3.2}$$

where

$$\lim_{k\to 0} \gamma_T(k) = k^2 \eta_E / \rho_0,$$

with η_E the Enskog shear viscosity of a mixture [24,25]. The solution to (3.2) is obtained immediately,

$$\begin{aligned} C_T^{(0)}(\mathbf{k},t) \qquad &= e^{-\gamma_T(k)t} C_T(k,0) \\ &\simeq e^{\eta_E k^2 t/\rho_0} C_T(k,0), \end{aligned} \tag{3.3}$$

where the second equality applies in the limit $k \to 0$ and $C_T(k,0) = \rho/\beta$. When quadratic nonlinearities are retained in Eq. (2.13), we obtain

$$[\partial_t + \gamma_T(k)] C_T(\mathbf{k},t) = \frac{1}{2} \sum_{s,s'=1}^{2} \int' \frac{d\mathbf{q}}{(2\pi)^3} [V_{ss'}^T(\mathbf{k},\mathbf{q}) + V_{s's}^T(\mathbf{q},\mathbf{k})] \langle \delta n_s(\mathbf{q},t) \delta n_{s'}(\mathbf{k}-\mathbf{q},t) g_T(-\mathbf{k},0) \rangle, \tag{3.4}$$

where the prime on the integral sign denotes a short distance cutoff. The effect of the nonlinearities on the right-hand side of Eq. (3.4) can be approximately incorporated by a perturbation theory that reexpresses the correlation function on the right-hand side of Eq. (3.4) in terms of $C_T(\mathbf{k},t)$. The theory is described in Appendix B. Equation (3.4) is then recast in a form where the contribution from nonlinearities enters as a non-Markovian renormalization of the transverse damping γ_T,

$$[\partial_t + \gamma_T(k)] C_T(\mathbf{k},t) = \int_0^t d\tau \sum_\eta (\mathbf{k}, t-\tau) C_T(\mathbf{k},\tau) = 0, \tag{3.5}$$

with

$$\sum_\eta (\mathbf{k},t) = \frac{1}{2} \sum_{\mu,\nu=\pm} \int^t \frac{d\mathbf{q}}{(2\pi)^3} |A_{\mu v}(\mathbf{k},\mathbf{q})|^2 e^{[z_\mu(\mathbf{q}) + z_\nu(\mathbf{k}-\mathbf{q})]t} \tag{3.6}$$

and

$$|A_{\mu,\nu}(\mathbf{k},\mathbf{q})|^2 \sum_{s,s'=1}^{2} \sum_{s'',s'''=1}^{2} [V_{ss'}^T(\mathbf{k},\mathbf{q}) + V_{s's}^T(\mathbf{q},\mathbf{k})] \alpha_{ss'}^{\mu}(\mathbf{q}) [V_{s''s'''}^T(\mathbf{k},\mathbf{q}) + V_{s''s'''}^T(\mathbf{q},\mathbf{k})] \alpha_{s''s'''}^{\nu}(\mathbf{k}-\mathbf{q}). \tag{3.7}$$

Explicit expressions for the amplitudes $\alpha_{ss'}^{\mu}$ are given in Appendix B.

It is convenient to consider the Laplace transform of (3.5),

$$[z + \gamma_T^R(k,z)] \tilde{C}_T(\mathbf{k},z) = C_T(\mathbf{k}, t=0), \tag{3.8}$$

where

$$\tilde{C}_T(\mathbf{k},z) = \int_0^\infty dt\, e^{-zt} C_T(\mathbf{k},t) \tag{3.9}$$

for Re$(z) > 0$. The renormalized transverse dissipative kernel γ_T^R is the sum of its bare part $\gamma_T(k)$ and a mode-coupling contribution $\delta\gamma_T^{\mathrm{mc}}$

$$\gamma_T^R(K, z) = \gamma_T(k) + \delta\gamma_T^{\mathrm{mc}}(k, z), \tag{3.10}$$

with

$$\delta\gamma_T^{\mathrm{mc}}(K, z) = \int_0^\infty dt\; e^{-zt} \sum_\eta(\mathbf{k}, t). \tag{3.11}$$

The long-wavelength limit of the transverse dissipative kernal $\gamma_T^R(\mathbf{k}, z)$ defines the frequency-dependent shear viscosity $\eta_s^R(z)$ according to

$$\lim_{k\to 0} \gamma_T^R(\mathbf{k}, z) = k^2 \eta_s^R(z). \tag{3.12}$$

The mode-coupling contribution to the renormalized viscosity, $\eta_s^R(z) = \eta_E + \delta\eta_s^{\mathrm{mc}}(z)$, is then given by

$$\delta\eta_s^{\mathrm{mc}}(z) = \lim_{k\to 0} \frac{1}{k^2} \int_0^\infty dt\; e^{-zt} \sum_\eta(\mathbf{k}, t). \tag{3.13}$$

By comparing Eqs. (3.1) and (3.13), we see that the long-wavelength limit of $\sum_\eta(\mathbf{k}, t)$ also determines the mode-coupling contribution to the STAF $\rho_\eta(t)$ according to

$$\delta\rho_\eta^{\mathrm{gen}}(t) = \lim_{k\to 0} \frac{1}{k^2} \sum_\eta(\mathbf{k}, t). \tag{3.14}$$

Finally, $\delta\rho_\eta^{\mathrm{gen}}(t)$ and $\delta\eta_s^{\mathrm{mc}}$ are explicitly given by

$$\delta\rho_\eta^{\mathrm{gen}}(t) = \frac{1}{2} \sum_{\mu,\nu=\pm} \int^t \frac{d\mathbf{q}}{(2\pi)^3} |A_{\mu\nu}(\mathbf{0}, \mathbf{q})|^2 \times e^{[z_\mu(\mathbf{q}) + z_\nu(-\mathbf{q})]t}\,, \tag{3.15}$$

and

$$\delta\eta_s^{\mathrm{mc}} = \frac{1}{2} \sum_{\mu,\nu=\pm} \int^t \frac{d\mathbf{q}}{(2\pi)^3} \frac{|A_{\mu\nu}(\mathbf{0}, \mathbf{q})|^2}{[z_\mu(\mathbf{q}) + z_\nu(-\mathbf{q})]}\,. \tag{3.16}$$

4 Results

In this paper we have used a generalized mode-coupling theory that takes into account molecular scale effects to compute the STAF of a dense binary-fluid mix- ture. As in the case of a one-component fluid of packing fraction $\eta = (\pi/6)n\sigma^3 = 0.46$, in a dense mixture the coefficient of the long-time tail of the STAF evaluated from generalized mode-coupling theory is about two orders of magnitude larger than the corresponding coefficient obtained from conventional mode-coupling theory.

Here, we consider a mixture of hard spheres of sizes σ_1 and σ_2, with $\sigma_2 > \sigma_1$. As discussed in paper I, the slowing down of the dynamics of the dense mixture on short length scales is directly related to the short-range correlations that characterize the fluid structure and that show up as peaks in the partial static structure factors. These are in turn determined by the relative packing fractions of the two species, $\eta_1 = \pi n_1 \sigma_1^3/6 = \eta x_1 \alpha^3/(x_2 + x_1\alpha^3)$ and $\eta_2 = \pi n_2 \sigma_2^3/6 = \eta x_2/(x_2 + x_1\alpha^3)$, where $\eta = \eta_1 + \eta_2$ is the total packing fraction and $x_l = n_1/n$ and $x_2 = n_2/n$, with $n = n_1 + n_2$, are the concentrations. Notice that in our calculation we keep η constant $\eta = 0.46$ in all the data discussed below), while changing the concentration x_2 of the large spheres. Finally, in this paper we only present results for mixtures of spheres of equal masses. This is done mainly to dissociate the role of the structural parameters from the role of the mass ratio in slowing down the dynamics. All times are normalized to an Enskog time t_E given by

$$\frac{1}{t_E} = \frac{4\sqrt{\pi}(n_1 + n_2)\sigma_{12}^2}{(2\beta\mu_{12})^{1/2}}\,\chi_{12}\;. \tag{4.1}$$

This time scale is neither the Enskog mean free time of a hard-sphere fluid of type-l nor type-2 spheres. It is chosen because it depends only weakly on the concentration of each species.

We first discuss the conventional mode-coupling contribution to the STAF of a mixture, denoted by $\delta\rho_\eta^{\text{conv}}(t)$. As in one-component fluids, one finds $\delta\rho_\eta^{\text{conv}}(t) \simeq At^{-3/2}$ [26]. This algebraic tail arises from the slow decay of fluctuations in the conserved densities at long wave-lengths and the feedback from these long-lived fluctuations through the convective nonlinearities in the hydrodynamic equations. It describes the true asymptotic long-time behavior of the correlation function. The coefficient A was evaluated many years ago by Pomeau [26] and, as in one-component fluids, it was found to be very small. In Fig. 1 we show $\delta\tilde{\rho}_\eta^{\text{conv}}(t) = (\beta t_E/\eta_E/\eta_E)\delta\rho_\eta^{\text{conv}}(t)$ as a function of $(t/t_E)^{-3/2}$ for three values of the concentration $x_2 = n_2/n$ of larger particles. Here η_E is the Enskog shear viscosity of the mixture [24]. The coefficient of the long-time tail, given by the slope of the straight lines of Fig. 1, has a weak dependence on the concentration x_2. The slope is also quite independent on the total packing fraction η.

The conventional mode-coupling contribution to the STAF should be compared to the generalized mode- coupling contribution in Eq. (3.15) and denoted here by $\delta\rho_{\eta}^{\mathrm{gen}}(t)$. Equation (3.15) can be written as a one-dimensional integral over the magnitude q of wave vector. This integral has been evaluated numerically using an upper cutoff $q_{\max}\sigma_{12} = 20$. We have checked that the contribution to the integral from reduced wave vectors larger than 20 is negligibly small. In Fig. 2 we show the generalized mode-coupling contribution $\delta\tilde{\rho}_{\eta}^{\mathrm{gen}}(t)$ as a function of $(t/t_E^{-3/2}$ for a packing fraction $\eta = 0.46$. The curves are well approximated by straight lines over a range of time scales, indicating that the generalized mode-coupling contribution to the STAF appears to decay as $\sim t^{-3/2}$ in this region. The generalized mode-coupling contribution evaluated here describes the decay of the correlation function over the intermediate time scales that are generally accessible to computer simulations. It is very hard to probe by simulations the truly; asymptotic long-time behavior of the correlation functions described by the conventional long-time tails.

The apparent failure of our curves in Figs. 1 and 2 to reduce to the result obtained for a one-component fluid in the limit of either small ($x_2 = 0.01$) or large ($x_2 = 0.9$) concentration of large spheres is only an artifact of our choice of the units of time [here we have scaled time with t_E given by Eq. (4.1)]. If in each case ($x_2 << 1$ and $x_2 \simeq 1$) we scale the time with the Enskog mean free time of the majority component, t_{E11} and t_{E22}, respectively [see Eq. (2.24)], then our results for $x_2 = 0.01$ and $x_2 = 0.9$ are essentially identical to those for a one-component fluid.

By comparing Figs. 1 and 2 we see immediately that at the large values of the density considered here the generalized mode-coupling contribution to the STAF is about two orders of magnitude larger than the conventional mode-coupling contribution (the vertical scales in Figs. 1 and 2 differ by a factor of 10^3). We also find that $\delta\rho_{\eta}^{\mathrm{gen}}(t)$ depends strongly on the fluid density. For $\eta = 0.23$ (the value used in Erpenbeck's simulations) $\delta\rho_{\eta}^{\mathrm{gen}}(t)$ is smaller than $\delta\rho_{\eta}^{\mathrm{conv}}(t)$. This is consistent with the fact that the generalized mode-coupling contribution accounts for the potential part of the correlation function that dominates at high density. One of the factors that controls its size is the height of the first peaks of the static structure factors of the fluid, which in turn are large only at high density.

The generalized mode-coupling contribution given in Eq. (3.15) is the sum of four terms, corresponding to the coupling of two density modes (- -), the coupling of two diffusion modes (+ +), and two equal terms corresponding to the coupling of one diffusion mode and one density mode (+ - and - +). In Figs. 3-5, we show separately these contributions to the STAF as well as their sum for three values of the concentration x_2 For a small ($x_2 = 0.01$, Fig. 3) and a large ($x_2 = 0.9$, fig. 5) concentration of large spheres the generalized mode-coupling contribution to the STAF is dominated by only one of these four terms. For $x_2 << 1$ the density mode

($z-$) describes the relaxation of total density fluctuations which are mainly determined by the majority component (type 1, in this case). The coupling of two of these density modes gives then the dominant generalized mode-coupling contribution to the STAF. For $x_2 \simeq 1$ it is the mode we label diffusion mode ($z+$) that describes the relaxation of density fluctuations and the coupling of two of these modes dominates the mode-coup1ing contribution to the STAF. At an intermediate value of the concentration of large spheres ($x_2 = 0.2$, Fig. 4) we find that the contributions from all four terms in Eq. (3.15) are of comparable magnitude. For large or small values of the concentration of one of the two species (here the large spheres), the mixture resembles a one-component fluid and the density fluctuations of the majority component govern the slow structural relaxation of the fluid. The effect of diffusion of the low-concentration component on slowing down the decay of the STAF appears to be small. For the intermediate value of the concentration the packing fractions of the two species are comparable and the mixture structurally resembles a metallic glass. The mixture is structurally very disordered and all three partial static structure factors are peaked at well-separated values of the wave vector, determined by the sizes of the two species. As discussed in paper I, fluctuations in the density of both species decay slowly at molecular length scales. The two extended modes of diffusion and total density fluctuations cannot be decoupled: both soften appreciably at large wave vectors and contribute to the mode-coupling integral. There is therefore a range of large wave vectors where density fluctuations decay slowly. This should be contrasted to what happens in the case of a simple fluid, where the mode-coupling integrals are dominated by the single value of the wave vector corresponding to the first maximum of the static structure factor.

We now discuss in some detail the effect of compositional disorder on the decay of the STAF in a dense mixture. For the present discussion we normalize all times to t^* given by

$$\frac{1}{t^\star} = \frac{4\sqrt{\pi}(n_1\sigma_1^2 + n_2\sigma_2^2)}{(2\beta\mu_{12})^{1/2}} \left(x_1^2\chi_{11} + x_2^2\chi_{22} + 2x_1x_2\chi_{12}\right) . \tag{4.2}$$

This time scale, unlike t_E, has the feature of going to the one-component fluid limit for $x_2 << 1$ and $x_2 \simeq 1$.

We first consider the case of conventional mode-coupling. In Fig. 6(a) we show $\delta\rho_\eta^{rmconv*}(t) = (\beta t^*/\eta_E)\delta\rho_\eta^{rmconv}(t)$ as a function of (t/t^*) for three small values of the concentration $x_2 = n_2/n$ of larger particles. Increasing the concentration of large particles in a fluid of small spheres slightly shifts the characteristic time scale governing the decay of the STAF to larger times. For a given value of (t/t^*), the STAF of the mixture is then larger than that of a one-component fluid. This is, however, a very small effect and it is entirely due to the concentration dependence of the Enskog shear viscosity of the fluid. A similar behavior is observed when small particles are added to a fluid of large particles [see Fig. 6(b)].

The concentration dependence of a generalized mode-coupling contribution to the STAF is quite different. In Figs. 7(a) and 7(b) we display $\delta\rho_\eta^{\mathrm{gen}*}(t) = (\beta t^*/\eta_E)\delta\rho_\eta^{\mathrm{gen}}(t)$ as a function of (t/t^*) for various values of the concentration $x_2 = n_2/n$ of larger particles. For values of x_2 close to 1 [Fig. 7(b)], when the large spheres are much more abundant than the small spheres, increasing the fraction of small spheres results in a shift of the characteristic time regime where the mode-coupling contribution to the STAF is large to shorter times. The shift is in the opposite direction as compared to that observed for the conventional contribution and it is more pronounced. A similar behavior is also observed for small values of x_2 [Fig. 7(a)].

A comparison of Figs. 6 and 7 shows that the concen- tration dependence of $\delta\rho_\eta^{\mathrm{gen}}(t)$ is stronger than that of $\delta\rho_\eta^{\mathrm{conv}}(t)$. This indicates that the degree of compositional disorder in the fluid plays a role in the dense fluid dynamics.

In order to assess more precisely when compositional disorder enhances large-wavevector mode-coupling effects, we have also evaluated the mode-coupling contribution to the shear viscosity, $\delta\rho_{\mathrm{mc}}^{\mathrm{gen}}$. In Fig. 8 we show $\delta\rho_{\mathrm{mc}}^{\mathrm{gen}}/\eta_E$ as a function of x_2 for a few values of the size ratio α. Here η_E is the Enskog shear viscosity of the mixture. In order to properly interpret the results displayed in Fig. 8 it is important to first clarify the concentration dependence of the Enskog shear viscosity. At the high densities considered here the Enskog shear viscosity of a hard-sphere fluid is dominated by the potential contribution. For a one-component fluid this is given by $\eta_E^V = \frac{4}{15}\sqrt{\pi m/\beta}[(n\sigma^3)^2\chi/\sigma^2]$. If the reduced density $n\sigma^3$ is kept fixed, then $\eta_E^V \sim 1/\sigma^2$ and the viscosity decreases as the sphere diameter increases (the pair correlation at contact χ only depends on $n\sigma^3$). The Enskog shear viscosity η_E of a binary mixture depends on the concentration x_2 of larger particles and reduces to the Enskog viscosity of a fluid of hard spheres of size σ_1, η_{E1}, for $x_2 = 0$, and to the Enskog viscosity of a fluid of hard spheres of size $\sigma_2 > \sigma_1$, η_{E2}, for $x_2 = 1$, with $\eta_{E2} < \eta_{e1}$. Compositional disorder always increases the bare viscosity in the sense that for $x_2 << 1$, $\eta_E > \eta_{E1}$ and for $x_2 \simeq 1$, $\eta_E > \eta_{E2}$.

In contrast we see from Fig. 8 that the concentration dependence of the generalized mode-coupling contribution $\delta\eta_s^{\rm mc}$ (relative to η_E) is quite different. The dashed line in the figure indicates the value of $\delta\eta_s^{\rm mc}/\eta_E$ for a one-component hard-sphere fluid with $n\sigma^3 = 0.88$ as obtained before by other researchers [27]. Our results show that in a mixture with a small fraction of large spheres (a colloidal suspension) the generalizai mode-coupling corrections are larger than in a one-component fluid. This corresponds to the fact that the motion of large spheres in a dense background fluid is very slow. Shear relaxation also gets slower as the size difference increases (smaller α). On the other hand, in a mixture containing a small fraction of small spheres in a fluid of large spheres ($x_2 \sim 1$) the generalized mode-coupling correction to the shear viscosity, while still larger than the one-component value, is considerably smaller than obtained in a colloidal-fluid-like mixture ($x_2 << 1$). This is because small spheres can move rather easily through a matrix of large spheres. These considerations are strictly meaningful only for $\alpha = 0.5$ and $\alpha = 0.7$, that is, for mixtures of spheres of rather disparate sizes. The $\alpha = 0.9$ value shows how the curves converge to the one-component fluid limit. Our findings are in agreement with the results of simulations of mixtures by Mountain and Thirumalai [28]. These authors reported that a mixture with a small fraction of small particles can crystallize more easily than a mixture with a few large particles, due to the fact that small particles can move more easily in a matrix of large particles compared to large particles in a matrix of small particles.

5 Discussion

In this paper we have formulated a generalized mode-coupling theory for a dense binary fluid mixture that takes into account the slowing down of the fluid dynamics at molecular scales due to the closely packed fluid structure. This has been used to evaluate the renormalization of the STAF due to density nonlinearities in the hydrodynamic free energy. As in the case of a one-component fluid [3], in a dense fluid mixture the long-time tails in the STAF are about two orders of magnitude larger than the conventional long-wavelength contributions. The concentration dependence of $\delta\tilde{\rho}_{\eta}^{\mathrm{gen}}(t)$ is stronger than that of $\delta\tilde{\rho}_{\eta}^{\mathrm{conv}}(t)$. This clearly indicates that at high densities the degree of compositional disorder in the fluid affects the static fluid structure and plays an important role in slowing down the fluid dynamics. In this section we make a few comments on the results obtained in this paper.

(1) In our analysis we have considered a dense binary mixture of different sizes and equal masses at different values of the concentration. The packing fraction of each species is the main parameter controlling the static structural properties of dense fluids at molecular length scales. For this reason concentration and size ratio have qualitatively the same effect on the short-wavelength dynamics. We find that at intermediate values of the concentration when the fluid is structurally disordered, there is a finite range of wave vectors over which the dynamics slows down and consequently the mode-coupling integrands are large over a range of length scales. This is reflected in the fact that all possible couplings of the density fluctuations of the two species make comparable contributions to the total $\delta\tilde{\rho}_{\eta}^{\mathrm{gen}}(t)$. The presence of a range of length scales and hence a distribution of time scales for a disordered dense binary mixture that we predict is a characteristic feature of glass-forming liquids [29]. In contrast, in a simple fluid the mode-coupling integrands are very sharply peaked at the position of the first maximum of the static structure factor. The presence of compositional disorder shifts the time regime where the generalized mode-coupling contribution to the STAF is large to shorter times. In order to test our results one needs to perform molecular-dynamics simulations for mixtures of dissimilar sizes at high densities.

(2) In this paper we only considered mixtures of spheres of equal masses. This choice was motivated by our desire to focus on the role of frustration caused by size difference in slowing down the fluid dynamics. In addition, both our

previous work [18] and computer simulations [20] have indicated that the slowing down of the dynamics in a dense, closely packed binary mixture depends more weakly on the mass ratio than on the size ratio of the two species.

(3) The nonlinear fluctuating hydrodynamic equations presented here can also be used to discuss the mode-coupling theory of the glass transition in fluid mixtures. In this case the mode-coupling contribution to the time- dependent density-density correlation function is evaluated self-consistently. The self-consistent mode-coupling theory of mixtures has been discussed by other authors [19]. It involves a considerable amount of computation that tends to obscure the physics. It would be interesting to consider a simplified model obtained, for instance, by replacing the static partial factors of the mixture by constant values with appropriate wave-vector cutoffs or by Lorentzians. A calculation of this type has been carried out by Mazenko and Valls [30] for a one-component fluid.

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Appendix A

In deriving the nonlinear fluctuating generalized hydrodynamic equations of a binary fluid mixture we follow the approach described by Ma and Mazenko [22]. The Langevin equation governing the time evolution of the hydrodynamic variables denoted by ψ_i may be written formally as

$$\delta_t \psi_1(t) = V_i[\psi] - L_{ij} \frac{\delta F}{\delta \psi_j(t)} + f_i(t) \ . \tag{A1}$$

The reversible part of the dynamics is given by

$$V_i[\psi] = Q_{ij}[\psi] \frac{\delta F}{\delta \psi_j(t)} - \frac{1}{\beta} \frac{\delta \mathbf{Q}_{ij}[\psi]}{\delta \psi_j(t)} \ , \tag{A2}$$

where $\mathbf{Q}_{ij}[\psi] = \{\psi_i, \psi_j\}$ is the Poisson bracket between the variables ψ_i and $F[\psi]$ is the free-energy functional given in Sec. II. The damping coefficients L_{ij} and the thermal noise f_i pertain to the dissipative part of the dynamics. The noise f_i obeys the fluctuation dissipation relation

$$\langle f_i(t) f_j(t') \rangle = 2 k_B T L_{ij} \delta(t - t') \ . \tag{A3}$$

For our binary mixture the relevant hydrodynamic variables are $\{\psi_i\} = (\rho_s, g)$. The Poisson brackets needed in the hydrodynamic equations are

$$\{\rho_s(\mathbf{r}), g_\alpha(\mathbf{r}')\} = -\partial_\alpha \delta(\mathbf{r} - \mathbf{r}') \rho_s(\mathbf{r}') \ , \tag{A4}$$

$$\{g_\alpha(\mathbf{r}, g_\alpha(\mathbf{r}')\} = \partial'_\alpha \delta(\mathbf{r} - \mathbf{r}') g_\beta(\mathbf{r}) - \partial_\beta(\mathbf{r} - \mathbf{r}) g_\alpha(\mathbf{r}') \ . \tag{A5}$$

Appendix B

In this appendix we brietly describe the perturbation theory that leads to Eq. (3.5). In order to close Eq. (3.4) we need to construct an equation for the correlation function of three phase functions appearing on the right-hand side of Eq. (3.4). This is done most simply by using the invariance of equilibrium correlation functions under time translations,

$$\begin{aligned}&\langle\delta n_s(\mathbf{q},t)\delta n_{s'}(\mathbf{k}-\mathbf{q},t)g_T(-\mathbf{k},0)\rangle\\ &=\langle\delta n_s(\mathbf{q},0)\delta n_{s'}(\mathbf{k}-\mathbf{q},0)g_T(-\mathbf{k},-t)\rangle\ .\end{aligned}\tag{B1}$$

By letting $t\to -t$ and $\mathbf{k}\to -\mathbf{k}$ in Eq. (2.13), multiplying the resulting equation with two density fluctuations, and taking the ensemble average, we then obtain

$$\begin{aligned}&[-\partial_t+\gamma_T(k)]\langle\delta n_s(\mathbf{q},0)\delta n_{s'}(\mathbf{k}-\mathbf{q},0)g_T(-\mathbf{k},-t)\rangle\\ &=\frac{1}{2}\sum_{s'',s'''=1}^{2}\int\frac{d\mathbf{q}'}{(2\pi)^3}[V^T_{s''s'''}(-\mathbf{k},\mathbf{q}')+V^T_{s'''s''}(\mathbf{q}',-\mathbf{k})]\\ &\langle\delta n_{s''}(\mathbf{q}',-t)\delta n_{s'''}(-\mathbf{k}-\mathbf{q},-t)\delta n_s(\mathbf{q},0)\delta n_{s'}(\mathbf{k}-\mathbf{q},0)\rangle\ .\end{aligned}\tag{B2}$$

We then perform a cluster expansion of the four-point correlation function on the right-hand side of Eq.(B2) and neglet cumulants. With this approximation Eq.(B2) becomes

$$\begin{aligned}&[\partial_t+\gamma_T(k)]\langle\delta n_s(\mathbf{q},0)\delta n_{s'}(\mathbf{k}-\mathbf{q},0)g_T(-\mathbf{k},-t)\rangle\\ &\simeq\frac{1}{2}\sum_{s'',s'''=1}^{2}\int\frac{d\mathbf{q}'}{(2\pi)^3}[V^T_{s''s'''}(-\mathbf{k},\mathbf{q}')+V^T_{s'''s''}(\mathbf{q}',-\mathbf{k})]\\ &\langle\delta n_{s''}(\mathbf{q}',t)\delta n_s(\mathbf{q},0)\rangle\langle\delta n_{s'''}(-\mathbf{k}-\mathbf{q},t)\delta n_{s'}(\mathbf{k}-\mathbf{q},0)\rangle\ .\end{aligned}\tag{B3}$$

The time dependence of the density-density correlation on the right-hand side of Eq.(B3) is now evaluated from Eqs.(2.11) and (2.12) by neglected nonlinearities. The most important contribution to the mode-coupling integrals comes from wave vectors near the peaks of the static structure factors. Momentum fluctuations of such large wave vectors decay rapidly and one can neglect the time derivative in Eq.(2.12) as compared to the viscous damping γ_L in treating all except the largest time scales. The longitudinal momentum can then be eliminated between Eqs.(2.11) and (2.12). The resulting two coupled linear equations for density fluctuations are given by

$$\partial_t \delta n_s(\mathbf{q},t) + q^2 b_{ss'}(q)\delta n_{s'}(\mathbf{q},t) = 0 \ , \tag{B4}$$

where summation over s' is intended, and

$$b_{ss'}(q) = \frac{n_s g_{s'}(q)}{\beta\rho\gamma_L(q)} + \frac{\gamma_{ss'}}{\beta m_s}\frac{f_{s'}(q)}{\rho_{s'}} \ , \tag{B5}$$

with

$$\begin{aligned} g_1(q) &= \frac{1}{\Delta(q)}[S_{22}(q) - \sqrt{n_2/n_1}S_{12}(q)] \ , \\ g_2(q) &= \frac{1}{\Delta(q)}[S_{11}(q) - \sqrt{n_1/n_2}S_{12}(q)] \ , \\ f_1(q) &= \frac{1}{\Delta(q)}\left[S_{22}(q) + \frac{m_1}{m_2}\sqrt{n_1/n_2}S_{12}(q)\right] \ , \\ f_2(q) &= \frac{1}{\Delta(q)}\left[S_{11}(q) + \frac{m_2}{m_1}\sqrt{n_2/n_1}S_{12}(q)\right] \ , \end{aligned} \tag{B6}$$

with $\Delta(q) = S_{11}(q)S_{22}(q) - S_{12}^2(q)$. The approximate modes obtained from Eqs.(B4) were discussed in paper I, where it was shown that this simple approximation is indeed accurate at large wave vectors. The time decay of the density-density correlation function is then governed by two relaxation rates that we label density mode $[z-(q)]$ and diffusion mode $[z+(q)]$,

$$z\pm(q) = \frac{q^2}{2}(b_{11}+b_{22}) \pm \frac{q^2}{2}[(b_{11}-b_{22})^2 + 4b_{12}b_{21}]^{1/2} \ . \tag{B7}$$

The density-density correlation functions are given by

$$\langle \delta n_s(\mathbf{q},t)\delta n_{s'}(-\mathbf{q},0)\rangle = \sum_{\mu=+,-}\alpha^{\mu}_{ss'}(\mathbf{q})e^{z_\mu(q)t} \ , \tag{B8}$$

where

$$\begin{aligned} \alpha^{\mu}_{1s'}(\mathbf{q}) &= \mu\frac{\sqrt{n_1 n_{s'}}S_{1s'}(q)(b_{22}+z_\mu) - \sqrt{n_2 n_{s'}}S_{2s'}(q)b_{12}}{[(b_{11}-b_{22})^2 + 4b_{12}b_{21}]^{1/2}} \ , \\ \alpha^{\mu}_{2s'}(\mathbf{q}) &= \mu\frac{\sqrt{n_2 n_{s'}}S_{2s'}(q)(b_{11}+z_\mu) - \sqrt{n_1 n_{s'}}S_{1s'}(q)b_{21}}{[(b_{11}-b_{22})^2 + 4b_{12}b_{21}]^{1/2}} \ . \end{aligned} \tag{B9}$$

The partial static structure factors are defined as $\langle \delta n_s(\mathbf{q}) \delta n_{s'}(-\mathbf{q}) \rangle = \sqrt{n_s n_{s'}} S_{ss'}(q)$. Finally the eigenvalues given in Eq.(B7) can be rewritten in the more transparent form presented in paper I and rewritten here for completeness,

$$
\begin{aligned}
z \pm (q) = & -\frac{q^2}{2} \left[\frac{1}{\rho \chi_T(q) \gamma_L(q)} + \frac{\gamma_{11}(q)}{\beta} \left\{ \frac{f_1(q)}{m_1 \rho_1} + \frac{f_2(q)}{m_2 \rho_2} \right\} \right] \\
& \pm \frac{q^2}{2} \left\{ \left[\frac{1}{\rho \chi_T(q) \gamma_L(q)} - \frac{\gamma_{11}(q)}{\beta} \left[\frac{f_1(q)}{m_1 \rho_1} + \frac{f_2(q)}{m_2 \rho_2} \right] \right]^2 - \frac{4 \gamma_{11}(q)}{\rho \beta^2 \gamma_L(q)} \left[\frac{f_1(q)}{m_1} - \frac{f_2(q)}{m_2} \right]^2 \right\}^{1/2} .
\end{aligned}
\tag{B10}
$$

Here $\chi_T(q)$ is the generalized isothermal compressibility, defined as

$$
\chi_T(q) = \chi_T^0 \frac{s_{11}(q) S_{22}(q) - S_{12}^2(q)}{x_2 S_{11}(q) + x_1 S_{22}(q) - 2\sqrt{x_1 x_2} S_{12}(q)} \; , \tag{B11}
$$

with $chi_T^0 = \beta/n$ the ideal-gas compressibility.

Finally, by inserting the solution of Eq.(B3) on the right-hand side of Eq.(3.4) and replacing $C_T^{(0)}(\mathbf{k}, \tau) = (\rho/\beta) e^{-\gamma_T(k)\tau}$ with $C_T(\mathbf{k}, \tau)$ in the mode-coupling integral, we immediately obtain Eq.(3.5). The derivation described here is entirely phenomenological. It can, however, be shown that the same result is obtained by using diagrammatic methods [1,22].

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