Short-wavelength collective modes in a binary hard-sphere mixture

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We use hard-sphere generalized hydrodynamic equations to discuss the extended hydrodynamic modes of a binary mixture. The theory presented here is analytic and it provides us with a simple description of the collective excitations of a dense binary mixture at molecular length scales. The behavior we predict is in qualitative agreement with molecular-dynamics results for soft-sphere mixtures. This study provides some insight into the role of compositional disorder in forming glassy configurations.

I. INTRODUCTION

The study of short-wavelength collective modes in one-component hard-sphere fluids has greatly contributed to our understanding of the dynamical properties of dense simple fluids on molecular length scales. de Schepper and Cohen[1] used the revised Enskog kinetic equation to calculate the extension of the usual hydrodynamic modes to large wave vector k. They showed that at high density collective modes exist even for wavelengths as small as a fraction of the molecular diameter and that the neutron-scattering structure factor $S(k,\omega)$ can be represented as a superposition of Lorentzians peaked at these extended modes. This simple form of the structure factor provides, as the scattering wave vector k changes, an accurate description of both light scattering and neutron-scattering data. Alley, Alder, and Yip[2] used computer molecular dynamics for a one-component hard-sphere fluid to determine the wave-vector-dependent transport coefficients that should be used in the generalized hydrodynamic equations for hard spheres.[3] Kirkpatrick[4] established the connection between the microscopic and the phenomenological approaches using a projection operator method and a short-time approximation at the level of generalized hydrodynamics.

The main conclusion of the above authors is that in a dense fluid density fluctuations are long-lived even on molecular length scales, where they relax very slowly, essentially by self-diffusion. Physically one can interpret this slow relaxation on a molecular scale, near the wave vector k_0 where the static structure factor $S(k)$ has its first maximum, as due to structural relaxation. de Schepper and Cohen,[1] and Kirkpatrick[4] proposed a simple approximation for the decay rate of density fluctuations that is accurate for wave vectors not too small and depends explicitly on the equilibrium structural properties of the fluid through $S(k)$.[5] This simple approximation not only displays in a transparent way the physics of structural relaxation, but has also proved quite useful for considering mode-coupling effects in dense fluids.[6] It is well-known that the usual long-time algebraic tails of the correlation functions that determine the transport coefficients of a simple fluid arise because the five conserved densities relax very slowly at small wave numbers.[7] Similarly in a dense fluid density fluctuations also relax slowly for $k \sim k_0$. Density nonlinearities yield, therefore, an additional renormalization of the transport coefficients via a finite-wave-vector mode-coupling mechanism.[8] These generalized mode-coupling effects have been evaluated and have been shown to be very important in dense simple fluids.[8-10] They can qualitatively account for the large coefficient of the long-time tail of the stress tensor autocorrelation function[11,12] and for the shear-dependent viscosity[13,14] observed in computer simulations. They also provide a good description of the behavior of the velocity autocorrelation function at intermediate times.[10] Finally, a self-consistent implementation of the generalized mode-coupling theory predicts, at a critical density, the transition to a glassy state where structural relaxation is frozen.[9,15-17] Subsequently, a more detailed analysis has revealed that the transition is an artifact of the approximation used and is cut off when additional couplings are included.[18] The generalized mode-coupling theory has, however, proved quite accurate in describing the slowing down of the dynamics of dense fluids in a region of moderate viscosity, still above the glass transition, but in a regime where the relaxation is cooperative and nonexponential.[19,20] In short, considerable insight into the dynamical properties of dense liquids has been gained using the methods and ideas of generalized hydrodynamics.

In the last few years much attention has been devoted to the study of the dynamical properties of binary fluid mixtures as a simple model for some real glass-forming fluids, namely metallic glasses.[21] Several researchers have carried out molecular-dynamics simulations for simple model potentials to understand the role of the compositional disorder and the resulting jammed configurations that can occur in fluids of molecules of different sizes in slowing down the dynamics.[22-24] The study of the dynamical properties of dense mixtures on molecular length scales is therefore of great current interest. In this paper we derive a set of generalized hydrodynamic equations for a binary mixture of hard spheres of different sizes and masses and we use these equations to study the short-wavelength collective modes of the fluid. The motivation of our work is twofold. First, the study of the

extended hydrodynamic modes in mixtures is interesting *per se*. As in one-component fluids, it leads to a simple and physically appealing representation of neutron-scattering data. Our second and main motivation is to obtain a relatively simple analytical representation for the extended modes in the region of large wave vector that can be used to evaluate mode-coupling effects at finite k. The hard-sphere potential is chosen for two reasons. First, all the static properties can be evaluated explicitly in this case.[25,26] Second, a kinetic equation is available for hard spheres, the revised Enskog equation, that describes exactly the short-time dynamics at all densities and contains all important excluded volume corrections.[27] The special feature of hard spheres is that the short-time dynamics include momentum transfer, which require a finite time to develop in fluids interacting via continuous potentials. For this reason a description of the short-time dynamics of a one-component fluid of hard spheres, such as that contained in the revised Enskog equation, works well even when extended *ac hoc* to long times. This motivated Kirkpatrick[4] to use a short-time approximation at the level of the generalized hydro-dynamics to evaluate the frequency- and wave-vector-dependent transport coefficients that appear in the equations. The resulting generalized hydrodynamic equations describe well the short-wavelength collective modes of a dense hard-sphere fluid. They are only appropriate for dense fluids, where the contribution to the transport coefficients from collisional transfer is much larger than the kinetic contribution.

In this paper we follow closely the method of Kirkpatrick[4] and use an analogous short-time approximation in the generalized hydrodynamic equations of a binary hard-sphere mixture. In the case of the mixture there is an additional complication not present in a one-component fluid. Mass diffusion and thermal diffusion (i.e., diffusion due to thermal gradients) are important dissipative processes in a binary mixture that need to be taken into account when describing dynamical properties. On the other hand, all mass transport only takes place via translational motion and not via instantaneous collisional transfer. The collisional transfer contributions to the coefficients of mutual diffusion and thermal diffusion vanish identically. A short-time approximation analogous to that used by Kirkpatrick in the one-component case only keeps the instantaneous collisional transfer contributions to the transport coefficients and therefore neglects diffusion altogether. This is clearly unphysical at all values of the density. We use, therefore, a modification of the short-time approximation that is appropriate for fluid mixtures. While for all other transport coefficients we only keep the collisional transfer contributions, we evaluate approximately the frequency- and wave-vector-dependent coefficients of diffusion in a Sonine polynomial approximation.[28] The consistency and implications of this approximation will be discussed below.

Our derivation of the generalized hydrodynamic equations for a binary mixture starts from the Liouville equation. It can be shown, however, that the same results are obtained using the Enskog equation as the starting point.

The Enskog equation has been used before to describe the light scattering spectra of binary fluids[29] and to discuss neutron-scattering experiments in disparate-mass binary fluid mixtures at moderate densities.[30] Our work differs from earlier studies because it focuses on the study of the extended hydrodynamic modes at large wave vector in the high-density regime. By analyzing in detail the structure of the collective excitations of the fluid on molecular length scale we obtain a simple description of the dense mixture extended modes that can be used as an input for studying large-wave-vector mode-coupling effects at high densities.

In Sec. II we outline the formal derivation of the generalized hydrodynamic equations for a binary hard-sphere mixture. The elements of the frequency matrix appearing in these equations are evaluated exactly and the approximation used for the memory functions is described. In Sec. III we discuss the solution of the generalized hydrodynamic equations in terms of the eigenfunctions and eigenvalues of the corresponding hydrodynamic matrix. Numerical results for the extended hydrodynamic modes are presented for various values of the parameters. The paper is concluded with a brief discussion.

II. GENERALIZED HYDRODYNAMIC EQUATIONS

In this section we use the projection operator method to derive the generalized hydrodynamic equations for a binary hard-sphere mixture.[31] We consider a fluid of N_1 spherical particles of mass m_1 and diameter σ_1 and N_2 spherical particles of mass m_2 and diameter σ_2, contained in a volume Ω and interacting via the hard-sphere potential. The six conserved densities in a binary mixture are the mass densities of the two species, the three components of the total momentum density, and the energy density. The Fourier components at wave vector $\mathbf{k}$ of the fluctuations of the six corresponding microscopic densities from their equilibrium values are

$$\rho_{a\mathbf{k}} = \sum_{i=1}^{N_a} m_a e^{i\mathbf{k}\cdot\mathbf{r}_{ai}} - \Omega\rho_a\delta_{\mathbf{k},0} , \tag{2.1}$$

$$\mathbf{g}_\mathbf{k} = \sum_{a=1,2}\sum_{i=1}^{N_a} m_a \mathbf{v}_{ai} e^{i\mathbf{k}\cdot\mathbf{r}_{ai}} , \tag{2.2}$$

$$\varepsilon_\mathbf{k} = \sum_{a=1,2}\sum_{i=1}^{N_a} \frac{1}{2} m_a v_{ai}^2 e^{i\mathbf{k}\cdot\mathbf{r}_{ai}} - \Omega\frac{3n}{2\beta}\delta_{\mathbf{k},0} , \tag{2.3}$$

where $a = 1,2$ labels the species, $\mathbf{r}_{ai}$ and $\mathbf{v}_{ai}$ denote the position and velocity of the ith particle of species a, respectively, $\rho_a = m_a n_a$ is the equilibrium mass density of species a, with n_a the corresponding number density, $n = n_1 + n_2$ is the total equilibrium number density, and $\beta = 1/k_B T$. In writing (2.3) we have used that hard-sphere particles only have kinetic energy.

Our objective is to derive a set of equations for the equilibrium time correlation functions of the fluctuations in the conserved densities. The time evolution of the microscopic densities is governed by the pseudo-Liouville equation, according to

$$\partial_t \hat{a}_{\mu k}(t) = L_+ \hat{a}_{\mu k}(t) , \qquad (2.4)$$

where we have denoted the set of six microscopic densities $(\rho_{ak}, \mathbf{g_k}, \varepsilon_k)$ collectively as $\hat{a}_{\mu k}$, with $\mu = \rho_a, g, \varepsilon$. The operator L_+ in Eq. (2.4) is the forward streaming pseudo-Liouville operator for a binary hard-sphere mixture, given by[27]

$$L_+ = \sum_{a=1,2} \sum_{i=1}^{N_a} \mathbf{v}_{ai} \cdot \frac{\partial}{\partial \mathbf{r}_{ai}} + \sum_{a=1,2} \sum_{i<j=1}^{N_a} T_+(ai,aj)$$

$$+ \sum_{a=1,2} \sum_{\substack{b=1,2 \\ b\neq a}} \sum_{i=1}^{N_a} \sum_{\substack{j=1 \\ j\neq i}}^{N_b} T_+(ai,bj) , \qquad (2.5)$$

where $T_+(ai,bj)$ is the hard-sphere binary collision operator describing a collision between the ith particle of species a and the jth particle of species b. It is given by

$$T_+(ai,bj)$$

$$= \sigma_{ab}^2 \int d\hat{\sigma}\, \Theta(-\hat{\sigma} \cdot \mathbf{v}_{ai,bj}) |\hat{\sigma} \cdot \mathbf{v}_{ai,bj}| \delta(\mathbf{r}_{ai,bj} - \sigma_{ab}\hat{\sigma})$$

$$\times [\hat{\mathbf{b}}_{\hat{\sigma}}(ai,bj) - 1] , \qquad (2.6)$$

where $\sigma_{ab} = (\sigma_a + \sigma_b)/2$, $\mathbf{r}_{ai,bj} = \mathbf{r}_{ai} - \mathbf{r}_{bj}$, and $\mathbf{v}_{ai,bj} = \mathbf{v}_{ai} - \mathbf{v}_{bj}$ are the relative position and velocity of the colliding pair, $\Theta(x)$ is the unit step function and the $\hat{\sigma}$ integration is an angular integration over the unit sphere. The operator $\hat{\mathbf{b}}_{\hat{\sigma}}(ai,bj)$ transforms the velocities of the colliding particles into post-collisional velocities, according to

$$\hat{\mathbf{b}}_{\hat{\sigma}}(ai,bj)\mathbf{v}_{ai} = \mathbf{v}_{ai} - 2\frac{\mu_{ab}}{m_a}\hat{\sigma}(\hat{\sigma} \cdot \mathbf{v}_{ai,bj}) , \qquad (2.7)$$

$$\hat{\mathbf{b}}_{\hat{\sigma}}(ai,bj)\mathbf{v}_{bj} = \mathbf{v}_{bj} + 2\frac{\mu_{ab}}{m_b}\hat{\sigma}(\hat{\sigma} \cdot \mathbf{v}_{ai,bj}) , \qquad (2.8)$$

with $\mu_{ab} = m_a m_b/(m_a + m_b)$ and $\hat{\sigma}$ a unit vector along the line joining the centers of the colliding spheres at contact, directed from sphere (bj) to sphere (ai).

In deriving the generalized hydrodynamic equations, it is convenient to consider linear combinations of the densities $\hat{a}_{\mu k}$ that form an orthonormal set. Denoting this new set of microscopic densities by $a_{\mu k}$, for $\mu = 1, \Delta, l, T, t_1, t_2$, we choose

$$a_{1k} = \frac{\rho_{1k}}{m_1 [n_1 S_{11}(k)]^{1/2}} , \qquad (2.9)$$

$$a_{\Delta k} = \frac{1}{\cos\alpha(k)} \left[\sin\alpha(k) \frac{\rho_{1k}}{m_1 [n_1 S_{11}(k)]^{1/2}} \right.$$

$$\left. - \frac{\rho_{2k}}{m_2 [n_2 S_{22}(k)]^{1/2}} \right] , \qquad (2.10)$$

$$a_{lk} = \left[\frac{\beta}{\rho} \right]^{1/2} \hat{\mathbf{k}} \cdot \mathbf{g_k} , \qquad (2.11)$$

$$a_{Tk} = \beta \left[\frac{2}{3n} \right]^{1/2} \left[\varepsilon_k - \frac{3}{2\beta} \sum_{a=1,2} n_{ak} \right] , \qquad (2.12)$$

$$a_{t_i k} = \left[\frac{\beta}{\rho} \right]^{1/2} \hat{\mathbf{k}}_\perp^i \cdot \mathbf{g_k} , \qquad (2.13)$$

where $\rho = \rho_1 + \rho_2$ is the total equilibrium mass density and

$$\alpha(k) = \sin^{-1} \left[\frac{S_{12}(k)}{[S_{11}(k)S_{22}(k)]^{1/2}} \right] . \qquad (2.14)$$

Here $S_{ab}(k)$ are the partial static structure factors, defined as

$$(n_a n_b)^{1/2} S_{ab}(k) = (n_{ak}, n_{bk})$$

$$= (n_a n_b)^{1/2} [\delta_{ab} + (n_a n_b)^{1/2} h_{ab}(k)] , \qquad (2.15)$$

with $h_{ab}(k)$ the Fourier transform of the pair correlation function of species a and b. We have also defined a set of three orthonormal unit vectors $(\hat{\mathbf{k}}, \hat{\mathbf{k}}_\perp^1, \hat{\mathbf{k}}_\perp^2)$, with $\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$. The set of microscopic variables defined in Eqs. (2.9)–(2.13) satisfy

$$(a_{\mu k}, a_{vk}) = \delta_{\mu v} . \qquad (2.16)$$

We have introduced a scalar product between two arbitrary phase functions A and B, defined as

$$(A,B) = \lim_{\substack{\langle N_a \rangle, \Omega \to \infty \\ \frac{\langle N_a \rangle}{\Omega} = n_a}} \frac{1}{\Omega} \langle A^* B \rangle , \qquad (2.17)$$

where the angular brackets denote a grand canonical ensemble average for hard-sphere particles with the equilibrium distribution function in the bra vector.

We now derive equations for the time evolution of the correlation functions of the normalized densities, given by

$$C_{\mu v}(\mathbf{k},t) = (a_{\mu k}, e^{L_+ t} a_{vk}) . \qquad (2.18)$$

When using the projection operator method it is convenient to consider the Laplace transform of the correlation functions, defined as

$$\tilde{C}_{\mu v}(\mathbf{k},z) = \int_0^\infty e^{-zt} C_{\mu v}(\mathbf{k},t)$$

$$= \left[a_{\mu k}, \frac{1}{z - L_+} a_{vk} \right] , \qquad (2.19)$$

for $\mathrm{Re}(z) > 0$. The projection operator P is defined as

$$P = \sum_\mu |a_{\mu k})(a_{\mu k}| . \qquad (2.20)$$

Operating on the Laplace transform of Eq. (2.4) with P and $Q = 1 - P$, we can derive formal equations for the $\tilde{C}_{\mu v}(\mathbf{k},z)$ in a standard way. One obtains

$$[z\delta_{\mu v} + \Omega_{\mu v}(k) + \tilde{M}_{\mu v}(k,z)]\tilde{C}_{v\lambda}(\mathbf{k},z) = \delta_{\mu\lambda} , \qquad (2.21)$$

where repeated Greek indices are summed over. The frequency matrix $\Omega_{\mu v}(k)$ is given by

$$\Omega_{\mu v}(k) = -(a_{\mu k}, L_+ a_{vk}) , \qquad (2.22)$$

and $\tilde{M}_{\mu v}(k,z)$ are the memory functions

$$\tilde{M}_{\mu\nu}(k,z)=-\left[a_{\mu k},L+Q\frac{1}{z-QL_+Q}QL+a_{\nu k}\right] . \tag{2.23}$$

The elements of the frequency matrix can be evaluated immediately, with the result

$$\Omega_{1l}(k)=-ik\left[\frac{n_1}{\rho\beta S_{11}(k)}\right]^{1/2}=\Omega_{ll}(k) , \tag{2.24}$$

$$\Omega_{\Delta l}(k)=\frac{-ik}{\cos\alpha(k)}\left[\sin\alpha(k)\left[\frac{n_1}{\rho\beta S_{11}}\right]^{1/2}\right.$$
$$\left.-\left[\frac{n_2}{\rho\beta S_{22}}\right]^{1/2}\right]$$
$$=\Omega_{l\Delta}(k) , \tag{2.25}$$

$$\Omega_{ll}(k)=\frac{2}{3\rho}\sum_{a,b}\frac{2\mu_{ab}(n_a n_b)^{1/2}}{t_{Eab}}d_1(k\sigma_{ab}) , \tag{2.26}$$

$$\Omega_{lT}(k)=-ik\left[\frac{2n}{3\beta\rho}\right]^{1/2}$$
$$\times\left[1+\sum_{a,b}2\pi\frac{n_a n_b}{n}\sigma_{ab}^3\chi_{ab}\frac{j_1(k\sigma_{ab})}{k\sigma_{ab}}\right]$$
$$=\Omega_{Tl}(k) , \tag{2.27}$$

$$\Omega_{TT}(k)=\frac{2}{3\rho}\sum_{a,b}\frac{2\mu_{ab}(n_a n_b)^{1/2}}{t_{Eab}}d_3(k\sigma_{ab}) , \tag{2.28}$$

$$\Omega_{t_l t_l}=\frac{2}{3\rho}\sum_{a,b}\frac{2\mu_{ab}(n_a n_b)^{1/2}}{t_{Eab}}d_2(k\sigma_{ab}) , \tag{2.29}$$

and $\Omega_{\mu\nu}(k)=0$, for all the other values of μ and ν. In Eqs. (2.24)–(2.28) t_{Eab} is the Enskog mean free time between collisions, given by

$$\frac{1}{t_{Eab}}=\frac{4(\pi n_a n_b)^{1/2}\sigma_{ab}^2}{(2\beta\mu_{ab})^{1/2}}\chi_{ab} , \tag{2.30}$$

with χ_{ab} the pair correlation function of species a and b evaluated at contact $\chi_{ab}=g_{ab}$ ($r=\sigma_{ab}$). Also, the functions $d_i(x)$, for $i=1,2,3$, are defined in terms of the spherical Bessel functions $j_l(x)$ as

$$d_1(x)=1-j_0(x)+2j_2(x) , \tag{2.31}$$

$$d_2(x)=1-j_0(x)-j_2(x) , \tag{2.32}$$

$$d_3(x)=1-j_0(x) . \tag{2.33}$$

To obtain an explicit form of the generalized hydrodynamic equations one also needs an expression for the memory functions $\tilde{M}_{\mu\nu}(k,z)$. In general, these are complicated functions of wave vector and frequency and cannot be evaluated exactly. Motivated by the short-time approximation used to derive the Enskog kinetic equation for hard spheres, which is exact at short times and yields qualitatively correct results even at long times, Kirkpatrick suggested a short-time approximation at the level of generalized hydrodynamics.[4] This consists in re-

placing the memory functions by their high-frequency limit, i.e.,

$$\tilde{M}_{\mu\nu}(k,z)\to\lim_{z\to\infty}\tilde{M}_{\mu\nu}(k,z)=0 . \tag{2.34}$$

Within this short-time approximation the memory functions vanish and the set of generalized hydrodynamic equations only contains the elements of the frequency matrix $\Omega_{\mu\nu}(k)$. This approximation relies on the special feature of impulsive potentials that collisions are instantaneous and even in the limit $z\to\infty$ there is a nonvanishing contribution to the generalized wave-vector- and frequency-dependent transport coefficients. This is usually referred to as the collisional transfer contribution and at high density is much larger than the kinetic contribution that takes a finite time to develop. In the case of continuous potentials replacing the memory functions by their high-frequency limit amounts to neglecting dissipation altogether. The resulting generalized hydrodynamic equations are simply those of an ideal fluid. This is because correlations take a finite time to develop in fluids interacting via a continuous potential. The short-time approximation proposed by Kirkpatrick[4] works well for single-component dense hard-sphere fluids. The resulting generalized hydrodynamic equations are identical to those obtained from the Enskog equation.

When we try to implement the same short-time approximation at the level of generalized hydrodynamics in a binary hard-sphere mixture we run into a difficulty. The instantaneous collisional transfer contribution contained in the frequency matrix Ω to the generalized coefficients of diffusion and of thermal diffusion vanish. The diffusion coefficients are determined by the elements of the memory functions $\tilde{M}_{\mu\nu}(k,z)$ for $\mu=1,\Delta$ and $\nu=1,\Delta$, and the coefficients of thermal diffusion by $\tilde{M}_{\mu\nu}(k,z)$ for $\mu=1,\Delta$, and $\nu=T$, and for $\mu=T$ and $\nu=1,\Delta$. To include these dissipative processes in our generalized hydrodynamic equations we need to evaluate approximately the corresponding memory functions at a finite frequency.

The four generalized diffusion coefficients defined by the four memory functions $\tilde{M}_{\mu\nu}(k,z)$ for $\mu=1,\Delta$ and $\nu=1,\Delta$, are not independent, but are related via the Onsager reciprocal relations. There is only one independent diffusion coefficient in a binary mixture. This is easily seen by evaluating explicitly the projected mass currents $\mathbf{j}_{ak}$ defined by

$$QL_+\rho_{ak}\equiv-i\mathbf{k}\cdot\mathbf{j}_{ak} , \tag{2.35}$$

for $a=1,2$. We find

$$\mathbf{j}_{ak}=\mathbf{g}_{ak}-\frac{\rho_a}{\rho}\mathbf{g}_k , \tag{2.36}$$

where $\mathbf{g}_{ak}$ is the momentum density of species a and $\mathbf{g}_k=\mathbf{g}_{1k}+\mathbf{g}_{2k}$. One then sees immediately that

$$\mathbf{j}_{2k}=-\mathbf{j}_{1k} , \tag{2.37}$$

and the total projected mass current vanishes. Using Eqs. (2.35) and (2.36) the four memory functions determining the generalized diffusion coefficients can all be ex-

pressed in terms of a generalized coefficient of mutual diffusion $\tilde{D}(k,z)$. We find

$$\tilde{M}_{1\Delta}(k,z)=A(k)\tilde{M}_{11}(k,z)=\tilde{M}_{\Delta 1}(k,z) \ , \quad (2.38)$$

$$\tilde{M}_{\Delta\Delta}(k,z)=A^2(k)\tilde{M}_{11}(k,z) \ , \quad (2.39)$$

with

$$A(k)=\frac{\sin\alpha(k)+[m_1\rho_1 S_{11}(k)/m_2\rho_2 S_{22}(k)]^{1/2}}{\cos\alpha(k)} \ . \quad (2.40)$$

The memory function $\tilde{M}_{11}(k,z)$ is in turn given by

$$\tilde{M}_{11}(k,z)=\frac{k^2}{S_{11}(k)}\frac{m_2}{m_1}\left[\frac{n_2}{n_1}\right]^{1/2}\tilde{D}(k,z) \ , \quad (2.41)$$

with

$$\tilde{D}(k,z)=-\frac{1}{m_1 m_2(n_1 n_2)^{1/2}}\left[\hat{\mathbf{k}}\cdot\mathbf{j}_{1\mathbf{k}},\frac{1}{z-QL_+Q}\hat{\mathbf{k}}\cdot\mathbf{j}_{1\mathbf{k}}\right] \ . \quad (2.42)$$

The two coefficients of thermal diffusion are determined by the memory functions $\tilde{M}_{\mu\nu}(k,z)$ for $\mu=1,\Delta$ and $\nu=T$ (or $\mu=T$ and $\nu=1,\Delta$). They are not independent, but they are related by an Onsager relation according to

$$\tilde{M}_{\Delta T}(k,z)=A(k)\tilde{M}_{1T}(k,z) \ , \quad (2.43)$$

where $A(k)$ is given in Eq. (2.40). The generalized coefficient of thermal diffusion $\tilde{D}_T(k,z)$ is defined by

$$\tilde{M}_{1T}(k,z)=-\frac{k^2}{[S_{11}(k)]^{1/2}}\tilde{D}_T(k,z) \ , \quad (2.44)$$

with

$$\tilde{D}_T(k,z)=\frac{\beta}{m_1(n_1 n)^{1/2}}\left[\hat{\mathbf{k}}\cdot\mathbf{j}_{1\mathbf{k}},\frac{1}{z-QL_+Q}\hat{\mathbf{k}}\cdot\mathbf{j}_{T\mathbf{k}}\right] \ . \quad (2.45)$$

In Eq. (2.45) $\mathbf{j}_{T\mathbf{k}}$ is the projected heat current, defined by

$$-i\mathbf{k}\cdot\mathbf{j}_{T\mathbf{k}}=\frac{\sqrt{n}}{\beta}QL_+a_{T\mathbf{k}} \ . \quad (2.46)$$

In the limit $k\to 0$ and $z\to 0$ the Enskog thermal diffusion coefficients are small compared to the Enskog diffusion coefficients.[32,33] In addition the thermal diffusion coef-

ficients are "second-order" transport coefficients, in the sense that they are nonvanishing only when evaluated in a two-Sonine polynomial approximation. Here we assume that in the limit $z=0$ the generalized thermal diffusion coefficient is small compared to the generalized diffusion coefficient for all values of wave vector and we neglect the thermal diffusion constants in our generalized hydrodynamic equations. As a consequence, our equations contain no coupling of the densities to temperature fluctuations.

To proceed, we need an approximate expression for $\tilde{D}(k,z)$. For frequencies smaller than the inverse of the Enskog mean free time we can neglect the frequency dependence of the generalized diffusion coefficient and replace it by its value at $z=0$. The resulting generalized hydrodynamic equations apply for frequencies up to this characteristic Enskog frequency, which in a dense fluid is considerably larger than the frequency scale of conventional hydrodynamics. We then approximate

$$\tilde{D}(k,z)\approx\tilde{D}(k,z=0)$$

$$=\frac{1}{m_1 m_2(n_1 n_2)^{1/2}}\left[\hat{\mathbf{k}}\cdot\mathbf{j}_{1\mathbf{k}},\frac{1}{QL_+Q}\hat{\mathbf{k}}\cdot\mathbf{j}_{1\mathbf{k}}\right] \ , \quad (2.47)$$

and then evaluate the right-hand side of (2.47) using a first-Sonine polynomial approximation,[34] with the result[35]

$$\tilde{D}(k)=\frac{3}{2\beta m_1 m_2(n_1 n_2)^{1/2}}$$

$$\times\left[\sum_{a,b}\frac{2\mu_{ab}}{(m_a m_b\rho_a\rho_b)^{1/2}t_{Eab}}d_{ab}(k\sigma_{ab})\right]^{-1} \ , \quad (2.48)$$

where

$$d_{ab}(x)=\frac{\rho_a}{\rho_b}-(-1)^{a+b}[j_0(x)-2j_2(x)] \ . \quad (2.49)$$

Finally, we can now write the six generalized hydrodynamic equations in an explicit form. The two equations for the transverse momentum fluctuations are decoupled from the others and are given by

$$[z+\Omega_{t_i t_i}(k)]\tilde{C}_{t_i\beta}(k,z)=\delta_{t_i\beta} \ . \quad (2.50)$$

The remaining four equations for the fluctuations in the partial densities, the temperature, and the longitudinal momentum are coupled together. They are given by

$$\left[z+k^2\frac{D(k)}{S_{11}(k)}\frac{m_2}{m_1}\left[\frac{n_2}{n_1}\right]^{1/2}\right]\tilde{C}_{1\beta}(k,z)+k^2\frac{D(k)}{S_{11}(k)}\frac{m_2}{m_1}\left[\frac{n_2}{n_1}\right]^{1/2}A(k)\tilde{C}_{\Delta\beta}(k,z)-ik\left[\frac{n_1}{\beta\rho S_{11}(k)}\right]^{1/2}\tilde{C}_{l\beta}(k,z)=\delta_{1\beta} \ ,$$

$$(2.51)$$

$$\left[z+k^2\frac{D(k)}{S_{11}(k)}\frac{m_2}{m_1}\left[\frac{n_2}{n_1}\right]^{1/2}A^2(k)\right]\tilde{C}_{\Delta\beta}(k,z)+k^2\frac{D(k)}{S_{11}(k)}\frac{m_2}{m_1}\left[\frac{n_2}{n_1}\right]^{1/2}A(k)\tilde{C}_{1\beta}(k,z)$$

$$-\frac{ik}{\cos\alpha(k)}\left[\sin\alpha(k)\left[\frac{n_1}{\rho\beta S_{11}}\right]^{1/2}-\left[\frac{n_2}{\rho\beta S_{22}}\right]^{1/2}\right]\tilde{C}_{l\beta}(k,z)=\delta_{\Delta\beta} \ , \quad (2.52)$$

$$[z + \Omega_{ll}(k)]\tilde{C}_{l\beta}(k,z) - \frac{ik}{\cos\alpha(k)} \left[\sin\alpha(k) \left[\frac{n_1}{\rho\beta S_{11}} \right]^{1/2} - \left[\frac{n_2}{\rho\beta S_{22}} \right]^{1/2} \right] \tilde{C}_{\Delta\beta}(k,z) - ik \left[\frac{n_1}{\beta\rho S_{11}(k)} \right]^{1/2} \tilde{C}_{l\beta}(k,z)$$

$$+ \Omega_{lT}(k)\tilde{C}_{T\beta}(k,z) = \delta_{l\beta} , \qquad (2.53)$$

$$[z + \Omega_{TT}(k)]\tilde{C}_{T\beta}(k,z) + \Omega_{Tl}(k)\tilde{C}_{l\beta}(k,z) = \delta_{T\beta} , \qquad (2.54)$$

where to simplify the notation we let $D(k) = \tilde{D}(k, z = 0)$.

For small wave vector k the above equations reduce to the usual linearized hydrodynamic equations for a binary mixture with the exact thermodynamic coefficients and the Enskog value for the diffusion coefficients.[36] The other transport coefficients equal their Enskog values if in the latter, one retains only the collisional transfer contributions. These are in fact the instantaneous contributions that survive in the high-frequency limit considered here. In dense hard-sphere fluids the collisional transfer contribution represents the most important part of the viscosities and of the thermal conductivity. On the other hand, the collisional transfer contribution to the diffusion coefficient vanishes. Even in a dense mixture approximate hydrodynamic equations that properly incorporate interspecies diffusion can only be obtained by retaining a noninstantaneous contribution to the corresponding memory function. The approximation used here yields hydrodynamic equations that are appropriate to describe the dynamics of fluctuations in dense hard-sphere mixtures.

III. EXTENDED HYDRODYNAMIC MODES

In this section we evaluate the hydrodynamic modes that follow from Eqs. (2.50)–(2.54). We consider both the full solution of the six hydrodynamic equations as well as two approximate solutions that describe well the structure of the extended modes in the large-wave-vector region.

A. Full solution

It is convenient to rewrite the set of generalized hydrodynamic equations in a matrix form as

$$[z\underline{1} + \underline{R}(k)]\underline{\tilde{C}}(k,z) = \underline{1} , \qquad (3.1)$$

where $\underline{1}$ is a 6×6 unit matrix. The solution of (3.1) can be written in terms of the eigenvalues and eigenfunctions of the matrix $\underline{R}$. This matrix is symmetric, but not self-adjoint. It has six complex eigenvalues $z_\lambda(k)$. The right eigenfunctions $\Theta_\lambda^R(\mathbf{k})$ are six-component column vectors and the left eigenfunctions $\Theta_\lambda^L(\mathbf{k})$ are six-component row vectors. They are given by the solutions of the right and left eigenvalue problem, respectively,

$$\underline{R}(k)\Theta_\lambda^R(\mathbf{k}) = z_\lambda(k)\Theta_\lambda^R(\mathbf{k}) , \qquad (3.2)$$

$$\Theta_\lambda^L(\mathbf{k})\underline{R}(k) = z_\lambda(k)\Theta_\lambda^L(\mathbf{k}) . \qquad (3.3)$$

For normalization we require

$$\Theta_\lambda^L(\mathbf{k})\Theta_\lambda^R(\mathbf{k}) = \delta_{\lambda\lambda'} . \qquad (3.4)$$

It appears from examining Eqs. (2.50)–(2.54) that the equations for the transverse momentum fluctuations are decoupled from the others. It follows immediately that the two eigenvalues corresponding to the extension of the shear modes are

$$z_{t_i}(k) = -\Omega_{t_i t_i}(k) . \qquad (3.5)$$

Here we use the terminology shear, heat, sound, and diffusion modes to identify the extended hydrodynamic modes in order to make contact with conventional hydrodynamics in the small-k limit and maintain the continuity in k. As in a one-component fluid, the extended shear modes are always diffusive. For a simple fluid it has been shown that mode coupling effects—which are neglected here—are needed to account for the propagating shear waves observed in computer experiments.[8]

The remaining four extended hydrodynamic modes are the continuation of the two sound modes and of the heat and diffusion modes. They are determined by finding the eigenvalues and the eigenfunctions of the 4×4 matrix of the coefficients of the four coupled equations (2.51)–(2.54), as described above. The eigenvalues are found numerically as the roots of a quartic equation. The four extended modes corresponding to the two complex conjugate hydrodynamic sound modes ($\lambda = \pm$), the diffusion mode ($\lambda = D$), and the mode of heat diffusion ($\lambda = H$) are displayed as functions of wave vector in Figs. 1–4 for various values of the parameters. The frequencies of the extended modes are scaled with an Enskog time t_E, given by $t_E = (2\beta\mu_{12})^{1/2}/[4\sqrt{\pi}(n_1 + n_2)\sigma_{12}^2\chi_{12}]$. This time scale is chosen to be only a weak function of the concentration x and to reduce to the Enskog mean free time of a one-component fluid of hard spheres of diameter σ, mass m, and density $n_1 + n_2$ when $\sigma_1 = \sigma_2 = \sigma$ and $m_1 = m_2 = m$. All the results shown are for a constant value of the packing fraction $\eta = \pi/6(n_1\sigma_1^3 + n_2\sigma_2^3)$. We have chosen $\eta = 0.46$, which corresponds to the value of the packing fraction close to that observed for the freezing of a one-component hard-sphere liquid.[37] To fix a convention, we assume that the type 2 spheres are the larger ones and fix the mass ratio $m_1/m_2 = 0.5$ and the size ratio $\alpha = \sigma_1/\sigma_2 = 0.7$. Finally, we vary the concentration of large spheres, denoted by x, with $x = n_2/n$.

To a great extent the large-wave-vector structure of the extended modes (in particular, the structure of the extended heat and diffusion modes) is governed by the static structure factors $S_{ab}(k)$, which have been evaluated in the Percus-Yevick approximation.[26] The relevant parameters in determining the sharpness of the static structure factors are the packing fractions η_1 and η_2 of the two species, given by

$$\eta_1 = \frac{\pi}{6}n_1\sigma_1^3 = \frac{(1-x)\alpha^3}{x + (1-x)\alpha^3}\eta , \qquad (3.6)$$

$$\eta_2 = \frac{\pi}{6} n_2 \sigma_2^3 = \frac{x}{x + (1-x)\alpha^3} \eta \ . \qquad (3.7)$$

The packing fraction of each species can be changed by either varying the concentration x or the size ratio α. Even though these two parameters play quantitatively different roles in determining the packing fractions, similar qualitative behaviors will be obtained, for instance, in the cases of a small concentration of small spheres with an arbitrary (not too small) size ratio or an arbitrary concentration with a very small size ratio. For this reason we keep the size ratio fixed and only vary the concentration x.

The four longitudinal extended hydrodynamic modes for the case of a very small concentration of large spheres, i.e., $x = 0.01$, are shown in Fig. 1. The upper half of the figure displays the magnitude of the imaginary part of the two complex conjugate sound modes. The lower half displays the real part of the modes that describes the damping of the excitations. The value $x = 0.01$ corresponds to a very small number of large spheres immersed in a dense fluid of smaller spheres (a kind of colloidal suspension, even though the size ratio of two species is much closer to 1 here than in real colloids). The packing fractions of the two species have the values $\eta_1 = 0.97\eta$ and $\eta_2 = 0.03\eta$, and $S_{22}(k) \simeq 1$ for all values of k. The sound modes are very similar to those of a one-component hard-sphere fluid of type 1 particles. As in a

one-component fluid, the imaginary part of the sound dispersion relation vanishes over a region of wave vectors, yielding a sound propagation gap. In the propagation gap the sound modes are strongly damped. From consideration of the eigenfunctions we can see that this is because at these large wave vectors the sound modes essentially describe the decay of longitudinal momentum fluctuations, which are expected to decay on short microscopic time scales. As in a one-component hard-sphere fluid the continuation of the heat mode softens considerably at $k \simeq 2\pi/\sigma_1$, where the structure factor $S_{11}(k)$ has its first maximum. In this large-wave-vector region the heat mode governs the decay of fluctuations in the total mass density. The softening of the heat mode corresponds to the slowing down of structural relaxation on molecular length scales. In contrast with the one-component fluid, there is an additional mode that is the continuation of the mode of diffusion. For the case of a very low density of large spheres displayed in Fig. 1, the diffusion mode describes the decay of concentration fluctuations and is quite structureless.

At intermediate values of the concentration x all the partial static structure factors $S_{ab}(k)$ exhibit considerable structure as functions of k. As a consequence, fluctuations in the partial densities are strongly coupled as reflected in the modes. The solutions of the quartic eigenvalue equation for $x = 0.2$ and 0.5 are displayed in Figs. 2 and 3, respectively. The imaginary part of the sound modes exhibits a pronounced softening at large wave vector, but there is no propagation gap. The sound modes are always overdamped in the region where the imaginary part softens. The heat mode exhibits a pronounced softening near the peak of the generalized iso-
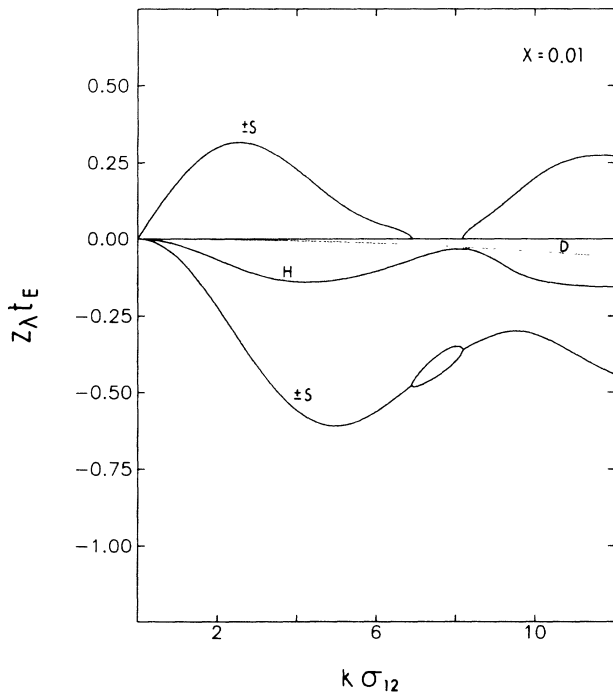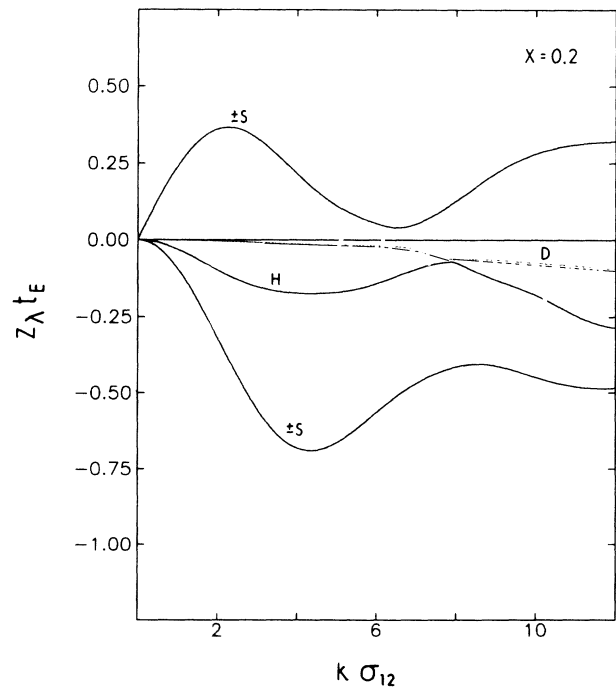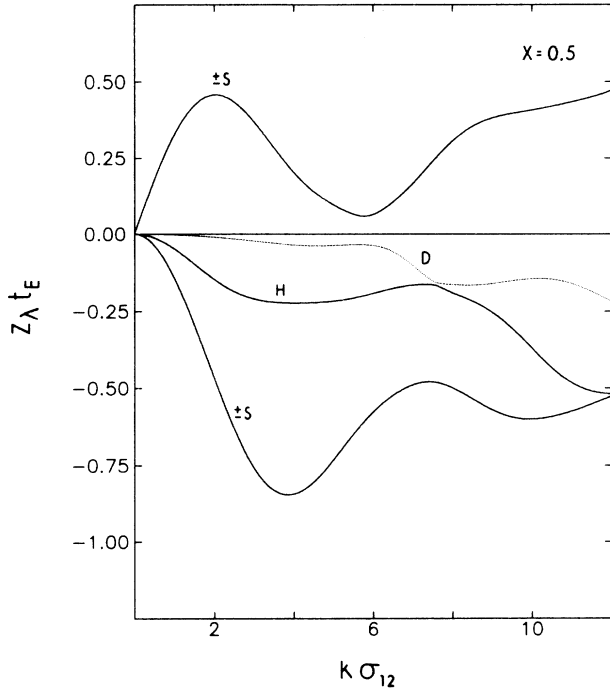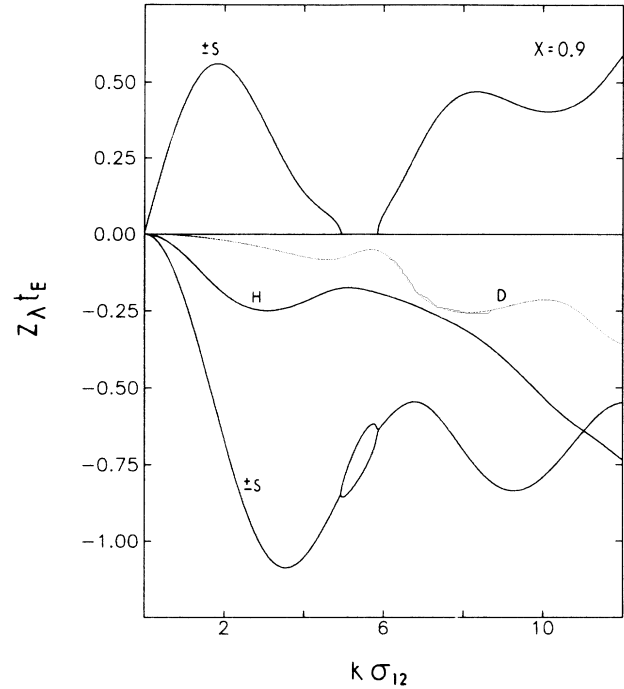

FIG. 1. Reduced eigenvalues $z_{\pm}^s(k)$, $z_H(k)$ (solid line), and $z_D(k)$ (dotted line) obtained from the full solution as functions of the reduced wave vector $k\sigma_{12}$. The upper half of the figure displays the magnitude of the imaginary part of the two complex conjugate sound modes. The lower half displays the real part of the four modes. The parameter values are $\eta = 0.46$, $x = 0.01$, $\alpha = 0.7$, and $m_1/m_2 = 0.5$.

FIG. 2. Same as Fig. 1 for $x = 0.2$.

FIG. 3. Same as Fig. 1 for $x = 0.5$.

FIG. 4. Same as Fig. 1 for $x = 0.9$.

thermal compressibility defined in Eq. (A5). The value $x = 0.2$ of the concentration (Fig. 2) corresponds to very similar values of the packing fraction of the two species ($\eta_1 = 0.58\eta$ and $\eta_2 = 0.42\eta$), while for $x = 0.5$ (Fig. 3) there is a larger packing fraction of large particles, with $\eta_1 = 0.16\eta$ and $\eta_2 = 0.74\eta$. At $x = 0.5$ the generalized compressibility is mainly determined by $S_{22}(k)$ and the softening of the heat mode occurs near $2\pi/\sigma_2$. An additional effect that takes place as x increases is that the diffusion mode acquires some structure. For both $x = 0.2$ and 0.5 there is a clear two-rate diffusion process, with a quite sudden increase in the diffusion rate at length scales of the order of the size of the large spheres. For $x = 0.5$ the diffusion mode also displays a very slight softening at $k \simeq 2\pi/\sigma_2$, due to the peak in $S_{22}(k)$.

Finally, the extended hydrodynamic modes for $x = 0.9$ are shown in Fig. 4. For this value of x the packing fraction of the smaller type 1 particles is very small, with $\eta_1 = 0.04\eta$ and $\eta_2 = 0.96\eta$. Consequently, $S_{11}(k) \simeq 1$ and $S_{22}(k)$ is sharply peaked at $k\sigma_2 \simeq 2\pi$. The sound modes resemble those of a dense fluid of type-2 spheres and the propagation gap reappears. Near $k \approx 2\pi/\sigma_2$, the location of the first maximum of $S_{22}(k)$, we obtain both a softening of the heat mode and an appreciable softening of the diffusion mode.

B. Approximate solutions

Our main interest here is in the structure of the extended hydrodynamic modes on molecular length scales, with the objective of developing a simple approximation to describe the collective excitations of the fluid in this region. A standard approximation that is made in the literature when discussing effects on molecular length scales[4,38] is

neglecting temperature fluctuations. The motivation is that temperature fluctuations of large wave vector are expected to decay on short microscopic time scales in a dense fluid and do not affect the structure of the long-lived excitations at these wave vectors. This approximation works well in one-component fluids where it has been shown that the most important aspect of the extended hydrodynamic modes, i.e., the softening of the heat mode near the first maximum of $S(k)$, is retained when temperature fluctuations are neglected.[4] It is not clear *a priori* that the approximation will work as well in mixtures for all values of the concentration.

In view of this we have evaluated the extended hydrodynamic modes for a dense binary mixture by neglecting temperature fluctuations. In this case we only have five hydrodynamic modes. The extended shear modes are still given by Eq. (3.5). The three coupled equations describing the dynamics of fluctuations in the densities and the longitudinal momentum yield a cubic eigenvalue equation that can be solved analytically. The result is, however, not very illuminating and will not be given here. The three longitudinal extended hydrodynamic modes obtained when neglecting temperature fluctuations are displayed in Figs. 5, 6, and 7 for $x = 0.01$, 0.2, and 0.9, respectively. The first observation is that neglecting temperature fluctuations leads to a gross overestimate of the size of the sound propagation gap. The same feature has been observed in a one-component hard-sphere fluid.[4] When neglecting temperature fluctuations we obtain a propagation gap for $x = 0.2$ (and $x = 0.5$—the corresponding figure is not shown), while when temperature fluctuations are included we find a deep minimum of the sound propagation at these values of the concentration, but no actual gap (see Figs. 2 and 3). In the propagation
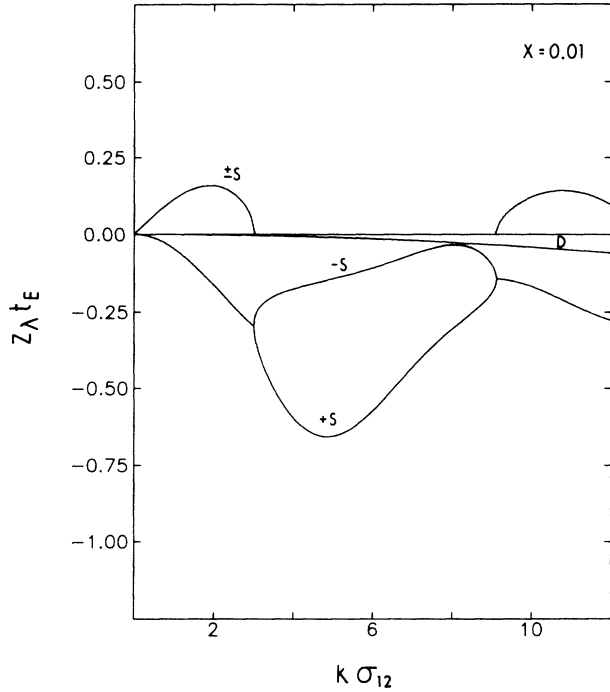
FIG. 5. Reduced eigenvalues $z^s_\pm(k)$ and $z_D(k)$ obtained when neglecting temperature fluctuations as functions of the reduced wave vector $k\sigma_{12}$. The parameter values are $\eta=0.46$, $x=0.01$, $\alpha=0.7$, and $m_1/m_2=0.5$.

FIG. 7. Same as Fig. 5 for $x=0.9$.

gap one of the sound modes is strongly damped, while the other softens considerably at a value of k near the peak of the generalized compressibility defined in Eq. (A5). This softening describes the same physics as the softening of the heat mode in the description that includes the cou-
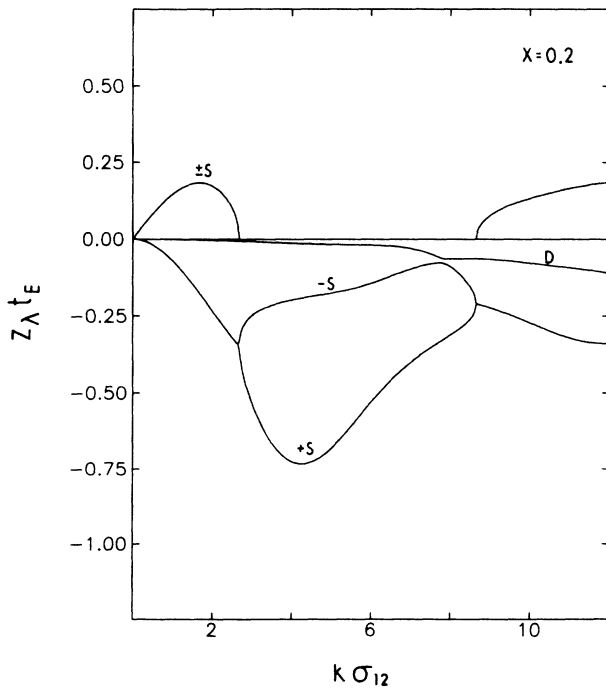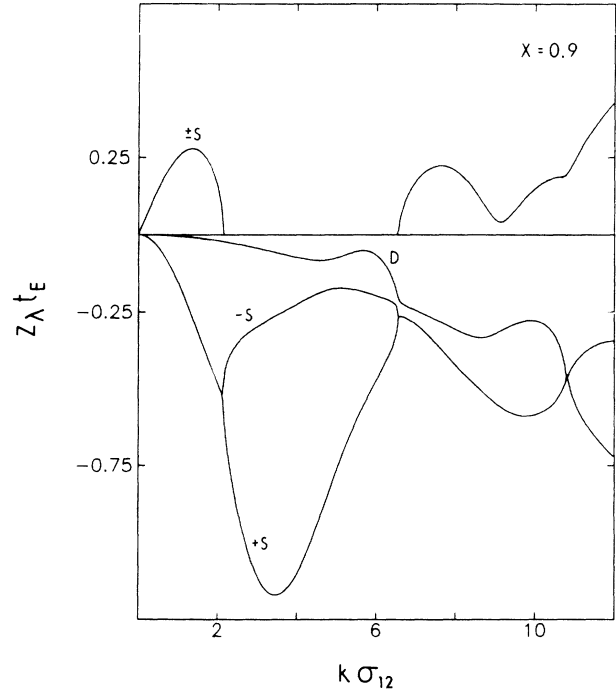

FIG. 6. Same as Fig. 5 for $x=0.2$.

pling to temperature fluctuations. In both cases it represents the slowing down of structural relaxation at molecular length scales. From consideration of the eigenfunctions we can see that in both the full solution and the approximate one the mode that softens is the relaxation rate of fluctuations in the total density of the fluid. The overdamped sound mode describes the decay of longitudinal momentum fluctuations. The extended diffusion mode obtained from this "three-mode approximation" is close to that obtained from the full solution of Sec. III A for all values of the concentration. We conclude that the essential feature of the extended modes in the large-wave-vector region are the same as when temperature fluctuations are included.

A further simplification of the description of extended hydrodynamics at large wave vectors can be obtained by observing that on physical grounds one also expects momentum fluctuations to decay on a short microscopic time on molecular length scales. This is confirmed by the results discussed above. In this large-wave-vector region where one observes the slowing down of structural relaxation the generalized viscosity $\Omega_{ll}(k)$, which governs the decay of momentum fluctuations, becomes approximately constant and large. For $zt_E<1$ one finds $z\ll\Omega_{ll}(k_0)$, where k_0 is a characteristic wave vector corresponding to a molecular length scale. One can then neglect the frequency in the momentum equation (2.53) and eliminate the momentum fluctuations from Eqs. (2.51) and (2.52), obtaining two coupled equations for the correlations functions describing the decay of density fluctuations. It is important to remark that the same equations can also be obtained by choosing a set of slow variables to be projected out containing only the two mass densities (proper-

ly orthonormalized). Physically one would indeed argue that this choice is the appropriate one for describing the decay of fluctuations on molecular length scales, where one expects that only the densities will be long lived and behave as hydrodynamic variables.

The two coupled equations for density fluctuations are given in the Appendix. Their solution yields two diffusive modes and does not reproduce conventional hydrodynamics as $k \to 0$ since the approximation of neglecting momentum fluctuations only applies for wave vectors not too small. In Figs. 8–10 we graph the extended heat and diffusion modes obtained from the quartic eigenvalue equation (solid lines) and the corresponding approximations obtained for these modes when (a) temperature fluctuations are neglected and (b) temperature and momentum fluctuations are neglected. The dotted lines represent the diffusion mode and the sound mode that softens at large wave vector obtained from solving the cubic eigenvalue equation resulting from neglecting temperature fluctuations. The dashed lines are two roots given in Eq. (A8) obtained from the simple "two-mode" approximation described in Sec. III A. The approximation obtained by neglecting both temperature and momentum fluctuations is a very good representation of the extended heat and diffusion modes at large wave vector for all values of the concentration, as shown in Figs. 8–10. The two-mode model provides therefore a simple and yet quite accurate description of the long-lived excitations of the fluid on molecular length scales. It will be particularly useful to evaluate large-wave-vector mode-coupling effects in binary mixtures.

Consideration of the eigenfunctions corresponding to the two diffusive modes obtained when neglecting temperature and momentum fluctuations suggests, for the case of very small or very large concentration x, a very simple analytical approximation for these modes. For

FIG. 9. Same as Fig. 8 for $x = 0.2$.

both small and large x the cross terms in Eqs. (A3) and (A4) coupling total mass density and concentration become very small and the two modes given in (A8) are well approximated by

$$z_-(k) \simeq -\frac{k^2}{\rho \chi_T(k) \Omega_{ll}(k)} ,$$ (3.8)

and

$$z_+(k) \simeq -k^2 D(k) \left[\frac{m_2}{m_1} \left[\frac{n_2}{n_1} \right]^{1/2} f_1(k) + \frac{m_1}{m_2} \left[\frac{n_1}{n_2} \right]^{1/2} f_2(k) \right] .$$ (3.9)

The eigenvalue $z_-(k)$ governs the relaxation of fluctuations in the total mass density. For a very low concentration of type-2 particles one finds $\chi_T(k) \simeq \chi_T^0 S_{11}(k)$, while in the opposite case of a very low concentration of type-1 particles $\chi_T(k) \simeq \chi_T^0 S_{22}(k)$. The eigenvalue $z_+(k)$ governs the relaxation of concentration fluctuations, as defined in Eq. (A2). In the case of a small concentration of large spheres (type 2), the second term in square brackets on the right-hand side of Eq. (3.9) dominates over the
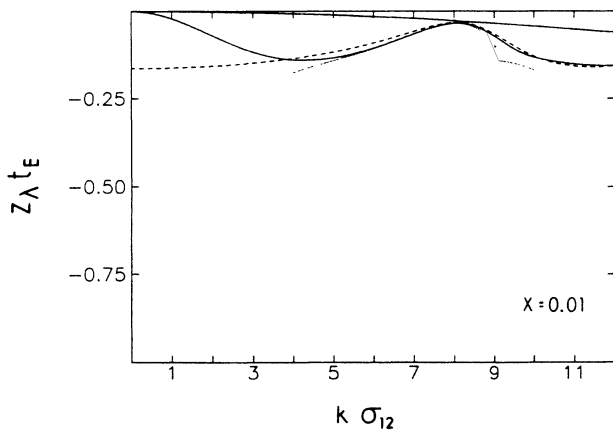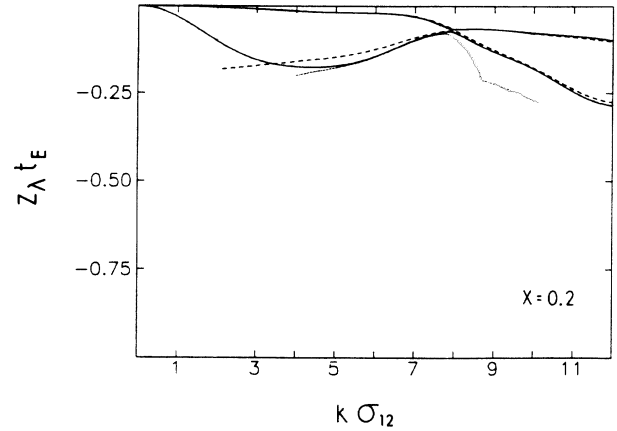

FIG. 8. Here we compare the real part of the reduced heat and diffusion modes obtained from the full solution (solid lines) to the corresponding modes obtained from the approximate solutions (explanation in text). The parameters are $\eta = 0.46$, $x = 0.01$, $\alpha = 0.7$, and $m_1/m_2 = 0.5$. For this value of x the various approximations to the diffusion mode fall on top of each other.
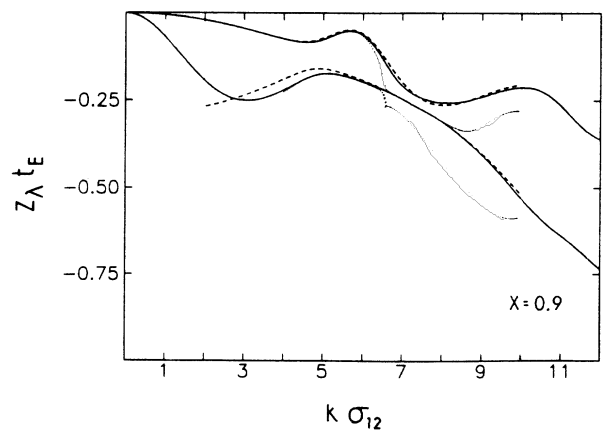

FIG. 10. Same as Fig. 8 for $x = 0.9$.

first term. The diffusion rate is determined by the diffusion coefficient of the large spheres and it is quite slow (see Fig. 2). In the opposite case of a small concentration of small spheres the first term in square brackets dominates over the second. The diffusion rate is determined by the diffusion coefficient of the small spheres and it is much faster (see Fig. 7).

IV. DISCUSSION

In this section we make a number of comments on the results obtained in this paper.

(i) In a dense binary mixture of particles of different sizes, fluctuations in the mass densities of both species can decay slowly on molecular length scales. This is in close analogy with what is observed in a one-component fluid, where at high density the decay rate of density fluctuations softens appreciably at wave vectors near the first maximum of the static structure factor.[4]

In a binary mixture, when the packing fractions of the two species are comparable, the equations that govern the decay of fluctuations of the two densities are always coupled. Our normal mode analysis of the equations identifies modes that are the extensions of the hydrodynamic diffusion and sound modes. For the value of the size ratio considered here we observe a slight softening of the extended diffusion mode near $k \simeq 2\pi/\sigma_2$ followed by a rather sharp increase of the diffusion rate and a softening of the sound damping for k near the first maximum of the generalized compressibility defined in Eq. (A5). Physically, this corresponds to the fact that both small and large spheres can be trapped in a cage by other particles, as expressed by the fact that all three static structure factors are peaked for intermediate values of x. As a consequence there may be interesting molecular scale mode-coupling effects involving the interplay of these two slow modes in a mixture. In a recent paper, Erpenbeck,[39] on the basis of molecular-dynamics studies of a moderate density isotopic mixture, concludes that the long-time behavior of the time correlation functions for the shear viscosity as well as for the other transport coefficients agree with the predictions of conventional mode coupling theory. This, however, does not preclude the possibility of obtaining finite wave-vector mode-coupling corrections at high densities.

For large or small values of the concentration x (corresponding to the case where the packing fraction of one of the two species is very small) softening of the decay rates occurs at wave vectors near the first maximum of the partial structure factor of the dense species. For small x, corresponding to a mixture with a small concentration of large spheres in a dense background of smaller spheres, the softening appears in the sound damping. For large x, corresponding to a mixture with a small concentration of small spheres in a dense fluid of larger spheres, the softening occurs in the extension of the diffusion mode. In both cases the softening describes the same physics. It corresponds to the slowing down of the decay of fluctuations in the density of the dense component at wave lengths of the order of the corresponding molecular size. At these wavelengths fluctuations in the density of the

large-concentration component decay via self-diffusion. The decay rate of fluctuations in the density of the small-concentration component is quite structureless. For both small and large x it is essentially described by a diffusion process ($\simeq Dk^2$). Here D is the diffusion coefficient of the small-concentration component. In a mixture with a small concentration x ($x = n_2/n$) of large spheres the decay rate of fluctuations in the small-concentration component is much slower than in the opposite case of a mixture with large x (see Figs. 1–4) simply because the larger and heavier spheres have a smaller diffusion coefficient. The slowing down of diffusion of larger particles in the background of smaller particles may provide us with some insight into the caging dynamics characteristic of a transition to a glassy state.

(ii) We have considered two approximations of the extended hydrodynamic modes of a binary mixture that are known to capture the essential features of the modes at large wave vectors in the case of a one-component fluid.[4]

The first consists in neglecting temperature fluctuations which are expected to decay on microscopic time scales at large wave vectors. We find that, as in a one-component hard-sphere fluid, the softening of the extended diffusion and heat mode is still present when temperature fluctuations are neglected and is comparable to the full solution for all values of the concentration. On the other hand, this approximation leads to a gross overestimate of the sound propagation gap.

Second, we have considered a very simple model where both temperature and momentum fluctuations are neglected. This approximation yields only two diffusive modes that describe the relaxation of density fluctuations and in the large-wave-vector region reproduce very closely the extended heat and diffusion modes obtained from the full solution, as shown in Figs. 8–10. This two-mode approximation yields a very good description of the long-lived collective excitations of the fluid on molecular length scales. It can be used as the starting point to analyze large-wave-vector mode-coupling effects in binary mixtures.

(iii) Mountain and Thirumalai[22] found that a situation where there is a low concentration of smaller particles in the background of larger particles is more favorable for crystallization to take place compared to a situation where there is a low concentration of larger particles. They argue that a few smaller particles find it easier to move around in the background of larger particles making the process of crystallization easier to occur. A few large particles, on the other hand, find it difficult to move around in the background of smaller particles and have a greater tendency to get caged into glassy configurations. This is consistent with our observation of a very slow diffusion of larger particles in the background of smaller particles and a fast diffusion of smaller particles in the background of larger particles.

(iv) It has been observed[1,4] that there exists a propagation gap in the sound modes around the location of the first peak of $S(k)$ in a one-component fluid. In a binary hard-sphere mixture one also observes a considerable softening of the sound propagation at large wave vectors that can be understood as arising from the competition

between elasticity and dissipation.[40] The softening depends on the relative concentration of the two species. Only in the limit of a small concentration of large spheres in a dense fluid of small spheres or a small concentration of small spheres in a dense fluid of large spheres the imaginary part of the sound dispersion vanishes and one obtains a propagation gap, as in the one-component fluid. There is no gap for intermediate values of the concentration of the two species.

(v) We have also evaluated the extended shear modes given in (2.50) for a variety of concentrations. When scaled with the Enskog mean free time t_E defined in Sec. III A, the shear modes only change very little when the concentration x ranges from $x = 0.01$ to 0.9 and resemble very closely the extended shear modes obtained previously for a one-component hard-sphere fluid.[1,4]

(vi) The results obtained here can be used to evaluate the dynamic structure factor $S(k,\omega)$ of a binary mixture. For large values of k the dominant contribution comes from the extended diffusion and heat modes. This follows both from the fact that these modes relax more slowly and that the corresponding amplitudes are larger than for the sound modes.

ACKNOWLEDGMENTS

APPENDIX

Here we consider the two generalized hydrodynamic equations for density fluctuations that are obtained when neglecting both temperature and momentum fluctuations. The two coupled equations governing the dynamics of fluctuations in the two orthonormal densities a_{1k} and $a_{\Delta k}$ can be obtained immediately by neglecting the frequency z compared to the generalized viscous damping Ω_{ll} in (2.53) and then using the resulting equation to eliminate

the momentum correlation function $\tilde{C}_{l\beta}(k,z)$ from (2.51) and (2.52). It is, however, more illuminating to consider instead the coupled equations for two different (not orthonormal) linear combinations of fluctuations in the mass densities of the two species, the total mass density

$$\rho_k = \rho_{1k} + \rho_{2k} , \tag{A1}$$

and the fluctuations in a "concentration" variable

$$c_k = \frac{\rho_2}{\rho^2} \rho_{1k} - \frac{\rho_1}{\rho^2} \rho_{2k} . \tag{A2}$$

When momentum and temperature fluctuations are neglected, the two coupled equations for the correlation functions of the total mass density and concentration fluctuations are given by

$$\left[z + \frac{k^2}{\rho \chi_T(k) \Omega_{ll}(k)} \right] \tilde{C}_{\rho\beta}(k,z)$$

$$+ \frac{k^2 \rho}{\beta \Omega_{ll}(k)} \left[\frac{f_1(k)}{m_1} - \frac{f_2(k)}{m_2} \right] \tilde{C}_{c\beta}(k,z)$$

$$= C_{\rho\beta}(k, t = 0) \tag{A3}$$

and

$$\left\{ z + k^2 D(k) \left[\frac{m_2}{m_1} \left[\frac{n_2}{n_1} \right]^{1/2} f_1(k) \right. \right.$$

$$\left. \left. + \frac{m_1}{m_2} \left[\frac{n_1}{n_2} \right]^{1/2} f_2(k) \right] \right\} \tilde{C}_{c\beta}(k,z)$$

$$+ \frac{k^2}{\rho^2} D(k)(n_1 n_2)^{1/2} [m_1 f_2(k) - m_2 f_1(k)] \tilde{C}_{\rho\beta}(k,z)$$

$$= C_{c\beta}(k, t = 0) . \tag{A4}$$

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

$$\chi_T(k) = \chi_T^0 \frac{S_{11}(k)S_{22}(k) - S_{12}^2(k)}{x S_{11}(k) + (1-x)S_{22}(k) - 2\sqrt{x(1-x)}S_{12}(k)} , \tag{A5}$$

with $\chi_T^0 = \beta/n$ the ideal gas compressibility, and

$$f_1(k) = \frac{S_{22}(k) + (m_1/m_2)(n_1/n_2)^{1/2}S_{12}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)} , \tag{A6}$$

$$f_2(k) = \frac{S_{11}(k) + (m_2/m_1)(n_2/n_1)^{1/2}S_{12}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)} . \tag{A7}$$

The eigenvalue problem corresponding to Eqs. (A3) and (A4) yields two diffusive modes, given by

$$z_{\pm}(k) = -\frac{k^2}{2} \left\{ \frac{1}{\rho \chi_T(k) \Omega_{ll}(k)} + D(k) \left[\frac{m_2}{m_1} \left[\frac{n_2}{n_1} \right]^{1/2} f_1(k) + \frac{m_1}{m_2} \left[\frac{n_1}{n_2} \right]^{1/2} f_2(k) \right] \right\}$$

$$\pm \frac{k^2}{2} \left[\left\{ \frac{1}{\rho \chi_T(k) \Omega_{ll}(k)} - D(k) \left[\frac{m_2}{m_1} \left[\frac{n_2}{n_1} \right]^{1/2} f_1(k) + \frac{m_1}{m_2} \left[\frac{n_1}{n_2} \right]^{1/2} f_2(k) \right] \right\}^2 \right.$$

$$\left. + \frac{4 D(k)(n_1 n_2)^{1/2}}{\rho \beta \Omega_{ll}(k)} \left[\frac{f_1(k)}{m_1} - \frac{f_2(k)}{m_2} \right] [m_1 f_2(k) - m_2 f_1(k)] \right]^{1/2} . \tag{A8}$$

[1]I. M. de Schepper and E. G. D. Cohen, Phys. Rev. A **22**, 287 (1980); J. Stat. Phys. **27**, 223 (1982).

[2]W. E. Alley, B. J. Alder, and S. Yip, Phys. Rev. A **27**, 3158 (1983); **27**, 3174 (1983).

[3]For a discussion of generalized hydrodynamics see, for instance, J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, New York, 1987).

[4]T. R. Kirkpatrick, Phys. Rev. A **32**, 3130 (1985).

[5]See also E. G. D. Cohen, I. M. de Schepper, and A. Campa, Physica A **147**, 142 (1987), and references therein.

[6]J. R. Dorfman and T. R. Kirkpatrick, in *Molecular-Dynamics Simulation of Statistical-Mechanical Systems, Proceedings of the International School of Physics "Enrico Fermi,"* Course XCVII, Varenna, 1985, edited by G. Ciccotti and W. G. Hoover (North-Holland, Amsterdam, 1986).

[7]See, for example, Y. Pomeau and P. Resibois, Phys. Rep. **19**, 63 (1975).

[8]T. R. Kirkpatrick, Phys. Rev. Lett. **53**, 1735 (1984).

[9]T. R. Kirkpatrick, Phys. Rev. A **32**, 3120 (1985).

[10]T. R. Kirkpatrick and J. C. Nieuwoudt, Phys. Rev. A **33**, 2658 (1986).

[11]T. R. Kirkpatrick and J. C. Nieuwoudt, Phys. Rev. A **33**, 2651 (1986).

[12]D. J. Evans, J. Stat. Phys. **22**, 81 (1980); J. J. Erpenbeck and W. W. Wood, *ibid.* **24**, 455 (1981).

[13]J. J. Erpenbeck, Phys. Rev. Lett. **52**, 1333 (1984), and references therein.

[14]T. R. Kirkpatrick, J. Noncryst. Solids **75**, 437 (1985).

[15]E. Leutheusser, Phys. Rev. A **29**, 2765 (1984).

[16]V. Bengtzelius, W. Goetze, and A. Sjolander, J. Phys. C **17**, 5915 (1984).

[17]S. P. Das, G. F. Mazenko, S. Ramaswamy, and J. Toner, Phys. Rev. Lett. **54**, 118 (1985).

[18]S. P. Das and G. F. Mazenko, Phys. Rev. A **34**, 2265 (1986).

[19]P. Taborek, R. N. Kleiman, and D. J. Bishop, Phys. Rev. B **34**, 1835 (1986).

[20]M. C. Marchetti, Phys. Rev. A **33**, 3363 (1986).

[21]See, for instance, D. R. Nelson and F. Spaepen, Solid State Phys. **42**, 1 (1989).

[22]R. D. Mountain and D. Thirumalai, Phys. Rev. A **36**, 3300 (1987).

[23]B. Bernu, J. P. Hansen, Y. Hiwatari, and G. Pastore, Phys. Rev. A **36**, 4891 (1987).

[24]H. Miyagawa, Y. Hiwatari, B. Bernu, and J. P. Hansen, J. Chem. Phys. **88**, 3879 (1988).

[25]See, for instance, J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, New York, 1987).

[26]N. W. Ashcroft and D. C. Langreth, Phys. Rev. **156**, 685 (1967).

[27]H. van Beijeren and M. Ernst, Physica **68**, 437 (1973), and references therein.

[28]J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972), pp. 175 and 189.

[29]S. Yip, L. Letamendia, and G. Nouchi, Phys. Rev. A **32**, 1082 (1985).

[30]A. Campa and E. G. D. Cohen, Phys. Rev. Lett. **61**, 853 (1988).

[31]See, for instance, K. Kawasaki, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. Green (Academic, New York, 1976), Vol. 5a, p. 166; or R. Zwanzig, in *Systems Far from Equilibrium*, edited by L. Garrido (Springer, New York, 1980), p. 198.

[32]J. M. Kincaid, E. G. D. Cohen, and M. Lopez de Haro, J. Chem. Phys. **86**, 963 (1987).

[33]For the parameter values under consideration the binary thermal diffusion ratio (which is the ratio of the binary thermal diffusion coefficient and the binary diffusion coefficient) evaluated from the Enskog equation (Ref. 32) is at most of the order of 0.1. Thermal diffusion only becomes important in mixtures with very large mass and/or size ratios.

[34]When the process of thermal diffusion is also taken into account the first-order approximation (i.e., the first nonvanishing contribution) to the two coefficients of diffusion and thermal diffusion is obtained by evaluating them in a two-Sonine-polynomial approximation (Ref. 28). The resulting diffusion coefficient differs from that obtained here.

[35]In the limit of small wave vectors $\tilde{D}(k,z=0)$ reduces to the Enskog coefficient of mutual diffusion

$$\tilde{D}(k=0,z=0)=\frac{3nm_1m_2}{8\sigma_{12}^2\chi_{12}\rho^2}(2\pi\beta\mu_{12})^{-1/2} ,$$

as given for instance in Ref. 36. In the low density limit ($\chi_{12}\approx 1$) this is identical to the low density binary diffusion coefficient (Ref. 28).

[36]M. Lopez de Haro, E. G. D. Cohen, and J. M. Kincaid, J. Chem. Phys. **78**, 2746 (1983).

[37]See, for instance, J. M. Ziman, *Models of Disorder* (Cambridge University Press, Cambridge, 1979), pp. 232–235, and references therein.

[38]N. K. Ailawadi, A. Rahaman, and R. Zwanzig, Phys. Rev. A **4**, 1616 (1971).

[39]J. J. Erpenbeck, Phys. Rev. A **39**, 4718 (1989).

[40]See, for instance I. M. de Schepper, E. G. D. Cohen, and M. J. Zuilhof, Phys. Lett. **101A**, 399 (1984).