PHYSICAL REVIEW E VOLUME 49, NUMBER 4 APRIL 1994

Dynamic structure factors of a dense mixture

Supurna Sinha
Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, 560 012 India
and Department of Physics, Indian Institute of Science, Bangalore, 560 012 India

(Received 22 September 1993)

We compute the dynamic structure factors of a dense binary liquid mixture. These describe dynamics on molecular length scales, where structural relaxation is important. We find that the presence of a few large particles in a dense fluid of small particles slows down the dynamics considerably. We also observe a deep narrowing of the spectrum for a disordered mixture composed of a nearly equal packing of the two species. In contrast, a few small particles diffuse easily in the background of a dense fluid of large particles. We expect our results to describe neutron scattering from a dense mixture.

PACS number(s): 61.20.Lc, 61.12.Bt, 51.10.+y

I. INTRODUCTION

The behavior of a fluid at large length and time scales is well described by hydrodynamics. In recent years hydrodynamics has been extended to molecular length scales [1]. This generalized hydrodynamic theory (GHT) was motivated by the desire to describe the neutron-scattering spectrum $S(k,\omega)$ of a dense liquid. $S(k,\omega)$, which reflects the molecular scale dynamics of the fluid, has a central diffusive peak which dramatically narrows with increasing density [2]. GHT provides a physically appealing description of this phenomenon. Structural relaxation is very slow on molecular scales in a dense liquid due to close packing of the molecules. Thus density fluctuations decay very slowly via self diffusion at $k \sim k_0$ where $S(k)$ has its maximum. The emergence of this long-lived mode leads to a reduction in the half-width of the scattering spectrum.

In the past few years, much attention has been focused on the study of the dynamical properties of dense mixtures [3]. A dense binary mixture is known to be a better glass former than a one component liquid. Therefore, an understanding of the dynamics of a dense binary mixture is of considerable interest in analyzing the slow relaxation process that ultimately leads to the glass transition.

Recently, the intermediate wave-vector dynamics of a dense binary hard-sphere mixture has been studied [4] in terms of the density fluctuations of the two species. The main approximations that have gone into this study are the following. First of all, interdiffusion has been neglected. Secondly, the wave-vector dependence of the self-diffusion coefficients has been neglected.

A more detailed analysis of a dense binary hard-sphere mixture has been carried out in Ref. [5]. Here, the full linear generalized hydrodynamics has been solved and it has been explicitly demonstrated that the density fluctuations are the only slow fluctuations on molecular length scales. In addition, both self-diffusion and interdiffusion effects with their wave-vector dependence, have been retained. Interdiffusion is a physical process special to a mixture, not shared by a one-component fluid. Therefore, inclusion of interdiffusion elicits the special characteristics of the dynamics of a mixture. The wave-vector dependence of the transport coefficients brings out the nonlocal effects arising from the short-ranged interaction potential in a dense liquid. Furthermore, the analysis presented in [5] incorporates certain additional static couplings in the extended hydrodynamic equations which had been neglected earlier.

In the present paper, we use the the density modes obtained in [5] to evaluate the dynamic structure factors of a dense binary mixture. We expect the dynamic structure factors presented here to describe the molecular-scale dynamics of a dense liquid mixture measured by neutron scattering.

The paper is organized as follows. In Sec. II we present a theoretical derivation of the partial dynamic structure factors of a dense mixture. In Sec. III we numerically calculate $S(k,\omega)$ for a few specific values of the parameters of the mixture and make some predictions. Finally, in Sec. IV we end this paper with a few concluding remarks.

II. THEORETICAL DERIVATION

The differential scattering cross section of a binary mixture measured in a neutron-scattering experiment is proportional to the dynamic structure factor $S(k,\omega)$ given by [6]

$$S(k,\omega) = x_1 b^2 S_{11}(k,\omega) + x_2 S_{22}(k,\omega) + 2\sqrt{x_1 x_2}\, b S_{12}(k,\omega), \tag{1}$$

where $x_i = n_i/(n_1+n_2)$ is the relative number concentration in the mixture of particles of component i. b is the ratio of the scattering length of the first component to that of the second. The partial dynamic structure factors $S_{ij}(k,\omega)$ $(i,j=1,2)$ appearing in (1) are given by

$$S_{ij}(k,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t} F_{ij}(k,t). \tag{2}$$

These are the temporal Fourier transforms of the time correlation functions $F_{ij}(k,t)$ defined as

$$F_{ij}(k,t) = \langle \delta n^{*}_{i\vec{k}}(0)\delta n_{j\vec{k}}(t)\rangle .$$

The brackets $\langle\,\rangle$ indicate an equilibrium grand canonical ensemble average. $\delta n_{i\vec{k}}$ $(i = 1,2)$, the fluctuation of the number density of the ith component at wave-vector $\vec{k} \neq \vec{0}$ is given by

$$\delta n_{i\vec{k}} = \frac{1}{\sqrt{N_i}} \sum_{a=1}^{N_i} e^{i\vec{k}\cdot\vec{r}^{(i)}_a}$$

for a fluid containing N_i of type i particles. a labels the particle number.

It has been shown in [5] that momentum and temperature fluctuations decay very fast on molecular length scales in a dense binary liquid mixture. Therefore the molecular-scale hydrodynamic description of such a system involves only the partial density fluctuations of the two species, which are long lived on such length scales. These fluctuations are the intermediate wave-vector extensions of the long-wavelength heat and diffusion modes.

It is convenient to consider linear combinations $a_{\mu\vec{k}}(\mu = 1,\Delta)$ of the number density fluctuations $\delta n_{1\vec{k}}$ and $\delta n_{2\vec{k}}$ that form an orthonormal set [5]. We choose

$$a_{1\vec{k}} = \frac{\delta n_{1\vec{k}}}{\sqrt{n_1 S_{11}(k)}}$$

and

$$a_{\Delta\vec{k}} = \frac{1}{\cos\alpha(k)}\left[\sin\alpha(k)\frac{\delta n_{1\vec{k}}}{\sqrt{n_1 S_{11}(k)}} - \frac{\delta n_{2\vec{k}}}{\sqrt{n_2 S_{22}(k)}}\right].$$

Here $\alpha(k)$ is given by

$$\alpha(k) = \sin^{-1}\left[\frac{S_{12}(k)}{\sqrt{S_{11}(k)S_{22}(k)}}\right],$$

with $S_{ij}(k)$ $(i,j = 1,2)$ representing the partial static structure factors of the mixture [5]. The time evolution of the densities $a_{1\vec{k}}$ and $a_{\Delta\vec{k}}$ is governed by the pseudo-Liouville operator [5]. The Laplace transform of the generalized hydrodynamic equations for the number density fluctuations of a dense binary liquid mixture may be written in the following compact matrix form:

$$[z\mathbf{1} + \mathbf{A}(k,z)]|a(\vec{k},z)\rangle = |a(\vec{k},t=0)\rangle, \tag{3}$$

where $|a(\vec{k},z)\rangle$ represents a two component column vector with $a_{1\vec{k}}(z)$ and $a_{\Delta\vec{k}}(z)$ as its entries. $a_{i\vec{k}}(z)$ $(i = 1,\Delta)$ are expressed as

$$a_{i\vec{k}}(z) = \int_0^\infty dt\, e^{-(z-L_+)t}a_{i\vec{k}} = \frac{a_{i\vec{k}}}{(z-L_+)}$$

for $\mathrm{Re}(z) > 0$, with L_+ the pseudo-Liouville operator defined as in [5]. The hydrodynamic matrix $\mathbf{A}(k,z)$ has the following elements:

$$A_{11}(k,z) = M_{11}(k,z) - \frac{\Omega_{1l}(k)^2}{\Omega_{ll}(k)},$$

$$A_{1\Delta}(k,z) = M_{1\Delta}(k,z) - \frac{\Omega_{1l}(k)\Omega_{\Delta l}(k)}{\Omega_{ll}(k)} = A_{\Delta 1}(k,z),$$

and

$$A_{\Delta\Delta}(k,z) = M_{\Delta\Delta}(k,z) - \frac{\Omega_{\Delta l}(k)^2}{\Omega_{ll}(k)}.$$

Here $M_{ij}(k,z)$ with $i,j = 1,\Delta$ and $\Omega_{ij}(k)$ with $i = 1,\Delta,l$ and $j = l$ are given in [5]. The solution to (3) can be written as

$$|a(\vec{k},z)\rangle = \mathbf{R}(k,z)[z\mathbf{1} + \mathbf{A}^d(k,z)]^{-1}\mathbf{R}^T(k,z)|a(\vec{k},0)\rangle. \tag{4}$$

In Eq. (4) $\mathbf{A}^d(k,z) = \mathbf{R}^T(k,z)\mathbf{A}(k,z)\mathbf{R}(k,z)$ is a diagonal matrix with the eigenvalues

$$z_\pm = -\frac{[A_{11}(k,z) + A_{\Delta\Delta}(k,z)] \pm \sqrt{[A_{11}(k,z) - A_{\Delta\Delta}(k,z)]^2 + 4A_{1\Delta}(k,z)^2}}{2}$$

of the matrix $\mathbf{A}(k,z)$ as its diagonal elements. The eigenfunctions $|\Theta_\alpha\rangle(\alpha = \pm)$ of the hydrodynamic matrix $\mathbf{A}(k,z)$ are column vectors with $\frac{A_{1\Delta}(k,z)}{\sqrt{A_{1\Delta}(k,z)^2+[A_{11}(k,z)-z_\alpha]^2}}$ and $\frac{[z_\alpha - A_{11}(k,z)]}{\sqrt{A_{1\Delta}(k,z)^2+[A_{11}(k,z)-z_\alpha]^2}}$ as their entries. These eigenfunctions form the two columns of the orthogonal matrix $\mathbf{R}(k,z)$ which diagonalizes $\mathbf{A}(k,z)$.

Equation (4) can therefore be recast as

$$|\delta n(\vec{k},z)\rangle = \mathbf{G}(k,z)|\delta n(\vec{k},0)\rangle, \tag{5}$$

where $|\delta n(\vec{k},z)\rangle$ is a column vector with $\delta n_{i\vec{k}}(z)$ $(i = 1,2)$ as its entries and the matrix $\mathbf{G}(k,z)$ is given by

$$\mathbf{G}(k,z) = \mathbf{B}^{-1}(k,z)\mathbf{R}(k,z) \times[z\mathbf{1} + \mathbf{A}^d(k,z)]^{-1}\mathbf{R}^T(k,z)\mathbf{B}(k,z).$$

Here $\mathbf{B}(k,z)|\delta n(\vec{k},z)\rangle = |\delta a(\vec{k},z)\rangle$. In terms of components Eq. (5) reads

$$\delta n_i(\vec{k},z) = G_{ij}(k,z)\delta n_j(\vec{k},t=0). \tag{6}$$

Multiplying both sides of Eq. (6) by $\delta n_l(-\vec{k},t=0)$ and taking a thermal average we obtain the partial dynamic structure factors

$$S_{il}(k,z) = \sum_{j=1}^{2} G_{ij}(k,z)S_{jl}(k).$$

Finally the partial dynamic structure factors appearing in Eq. (2) are given by

$$S_{ij}(k,\omega) = \lim_{\epsilon \to 0} \frac{\mathrm{Re}[S_{ij}(k, z = \epsilon - i\omega)]}{\pi}.$$

We insert the explicit expressions for $S_{ij}(k,\omega)$ $(i,j = 1,2)$ in Eq. (1) to obtain the dynamic structure factors $S(k,\omega)$, which are in turn proportional to the differential neutron-scattering cross sections.

III. RESULTS

We present results for a mixture of hard spheres of diameters σ_1 and σ_2 $(\sigma_2 > \sigma_1)$, number densities n_1 and n_2 and of total packing fraction $\eta = \frac{\pi}{6}[n_1\sigma_1^3 + n_2\sigma_2^3] = 0.46$. The diameter ratio σ_1/σ_2 is taken to be 0.7. We vary the concentration $x_2 = n_2/(n_1+n_2)$ of larger spheres keeping η constant. We have chosen the ratio b of the scattering lengths of the two species to be 0.7. Finally we consider mixtures of spheres of equal masses. This is done mainly to focus on the role of structural parameters in slowing down the dynamics.

Figures 1 and 2 show $S^*(k,\omega)$ [i.e., $S(k,\omega)$ scaled with its value at $\omega = 0$] as a function of the frequency ω scaled with a time t_E given by $\frac{1}{t_E} = \frac{4\sqrt{\pi}n\sigma_{12}^2\chi_{12}}{\sqrt{2\beta\mu_{12}}}$, with n the total number density of the fluid, $\sigma_{12} = \frac{\sigma_1+\sigma_2}{2}$, χ_{12} the pair correlation function at contact between type 1 and type 2 spheres and $\mu_{12} = m_1m_2/(m_1+m_2)$ the reduced mass. All plots of $S^*(k,\omega)$ have been made for $k\sigma_{12} = 2\pi$. We notice that in Fig. 1, the curve for $x_2 = 0.01$ is significantly narrower than that for $x_2 = 0.9$. This observation can be interpreted as follows. A dense liquid mixture consisting of a few large particles suspended in a liquid of small particles slows down the dynamics on molecular length scales more easily than a liquid with a few small particles in the background of large ones. This is due to the fact that large spheres diffuse very slowly in a matrix of small ones. In contrast, the diffusion coefficient of small spheres being large, they diffuse faster in a background of large ones. This observation agrees with recent molecular dynamic simulations in dense mixtures [7], where the authors find that a liquid mixture with a majority of large spheres is easier to crystallize compared to one which consists mainly of small spheres. This stems from the difference in the rate of diffusion of the two species as mentioned above.

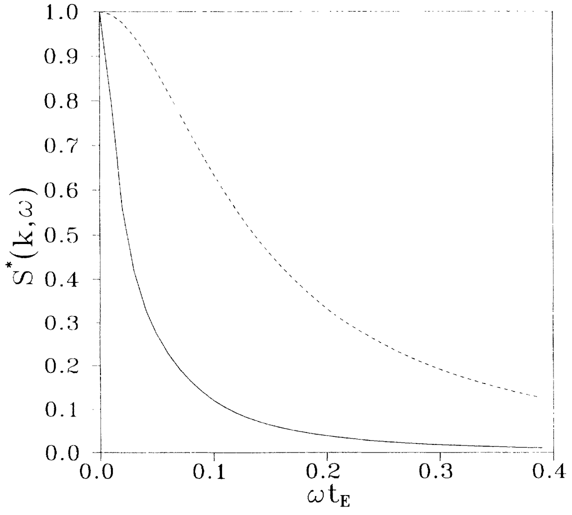

FIG. 1. The reduced dynamic structure factor $S^*(k,\omega) = \frac{S(k,\omega)}{S(k,0)}$ plotted against the reduced frequency ωt_E for $k\sigma_{12} = 2\pi$ and for $x_2 = 0.01$ (solid line) and $x_2 = 0.9$ (dashed line).

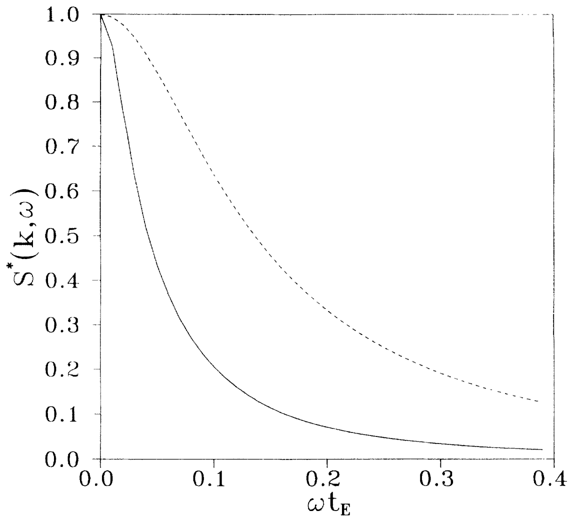

FIG. 2. Same as Fig. 1 for $x_2 = 0.9$ (dashed line) and $x_2 = 0.2$ (solid line).

In Fig. 2 we notice that a compositionally disordered mixture $(x_2 = 0.2)$ characterized by nearly equal packing fractions $(\eta_1 = 0.58\eta,\ \eta_2 = 0.42\eta)$ of the two species, undergoes a dramatic narrowing reflecting the emergence of a very slow dynamical process. In contrast, dynamical relaxation is relatively faster in a mixture consisting mainly of large spheres $(x_2 = 0.9)$. In a disordered liquid mixture, due to a difference in the sizes of the two species, the dynamics is slowed down considerably. This happens because both small as well as large spheres can be trapped in a cage formed by the other particles, resulting in the formation of peaks in $S_{ij}(k)$ $(i,j = 1,2)$ at well separated values of the wave vector. In contrast, in a liquid consisting mainly of large spheres, caging is relatively ineffective due to the ease of movement of small particles in the matrix of large ones.

IV. CONCLUSION

We have obtained the dynamic structure factors of dense mixtures on molecular scales by confining ourselves to the modes of total density fluctuations and interdiffusion, which govern the slow dynamics on such length scales. The relaxation of density fluctuations on molecular scales depends more strongly on the structural parameters, such as the size ratio, than on the mass ratio of the two species [5,8]. This is a consequence of the crucial dependence of the dynamics on the rigid static structure of a dense liquid on molecular scales. Therefore, we have considered mixtures of equal masses but different *sizes*. We have confined ourselves to mixtures of not too disparate scattering lengths in order to have comparable contributions from the two species to the total $S(k,\omega)$.

Comparison with earlier work: Our present analysis is more complete compared to previous work [4] in that it takes into account effects of interdiffusion, wave-vector dependence of transport coefficients, and incorporates a few additional static couplings in the extended hydrodynamic equations which had been neglected earlier. We have checked that our results converge to that of [4] in the appropriate limit. We would like to point out that the half-widths evaluated from our theory differ from those predicted by [4]. For instance for $x_2 = 0.5$ we find that the half-width predicted by [4] is about 1.5 times that obtained from the present theory. This observation points to the fact that inclusion of the additional effects incorporated in the present analysis makes a significant difference to the dynamic structure factor of a dense mixture on molecular scales. Whether the present analysis improves over the earlier theory can only be settled by future neutron-scattering experiments.

As mentioned in Sec. III, we have demonstrated that our quantitative evaluation of $S(k,\omega)$ confirm the qualitative observations made in [7] regarding the difference in the dynamics of slowing down between a mixture consisting of a few large particles and one containing a few small particles. Earlier researchers [6] had focused on neutron scattering in dilute to moderate density ($\eta << 0.46$) fluid mixtures. They had mainly concentrated on unusual sound propagation in such systems. The regime of density considered here is quite different. We have looked at high density mixtures where structural relaxation is important and the sound modes are overdamped. Our results are applicable to dense liquid mixtures below the glass transition packing fraction.

ACKNOWLEDGMENTS

It is a pleasure to thank M. C. Marchetti for suggesting the problem and for her critical comments. I have benefited from stimulating discussions with A. K. Sood. This work has been supported by the National Science Foundation under Contract No. DMR-91-12330 and the Jawaharlal Nehru Centre for Advanced Scientific Research and was begun at the Department of Physics, Syracuse University.

[1] I. M. de Schepper and E. G. D. Cohen, Phys. Rev. A **22**, 287 (1980); J. Stat. Phys. **27**, 223 (1982); T. R. Kirkpatrick, Phys. Rev. A **32**, 3130 (1985).

[2] P. G. de Gennes, Physica **25**, 825 (1959).

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

[4] G. V. Vijayadamodar and B. Bagchi, J. Chem. Phys. **93**, 689 (1990).

[5] M. C. Marchetti and S. Sinha, Phys. Rev A **41**, 3214 (1990).

[6] E. G. D. Cohen and I. M. de Schepper, Nuovo Cimento D **12**, 521 (1990).

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

[8] J. N. Roux, J. L. Barrat and J. P. Hansen, J. Phys. Condens. Matter **1**, 7171 (1989).