Self-Diffusion in Supercooled Binary Liquids

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Frequency-dependent self-diffusion coefficients $D_s(\omega)$ for both particle species of a supercooled binary hard-sphere liquid have been calculated within a mode-coupling approximation. For a disparate-size mixture we find a glass transition at a critical packing fraction η_B in connection with the localization of the large particles only. The small spheres retain a finite mobility within the glass. It is found that a little bump appears in $D_s(\omega)$ of the small particles at low frequencies when the glass transition is approached, which implies that the diffusion mechanism of the small particles changes from fast liquidlike diffusion to slow diffusion in a random potential.

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The mode-coupling theory of the glass transition for *one-component* liquids [1–3] has been extended to *multicomponent* systems [4,5] several years ago. This generalization has cast new light on the theoretical aspects of the relaxation dynamics in nonsimple liquids, the latter showing a much richer variety of possible phenomena than simple one-component liquids. Extensive analyses have been made of the long-time limits of density-relaxation functions (nonergodicity parameters) for special examples of binary liquids, supplying us with detailed information on Debye-Waller factors (DWF) and Lamb-Mössbauer factors (LMF) [4,6–9]. From these calculations it has been predicted that there is a *new* phase between the liquid and glassy phases in disparate-size binary mixtures [4,9]. In the new phase, which we call a *delocalized* phase, a glass is formed only by the big particles, while the small particles retain a finite mobility diffusing through the voids of the glassy structure formed by the immobile big particles. The appearance of the delocalized phase will be closely related to such interesting phenomena—known from certain real glass formers—as rapid hydrogen transfer in amorphous metals and glassy ionic conductors. Both for basic theoretical aspects concerning the interplay of glass transition and delocalization transition and for possible applications in the development of amorphous batteries, it would certainly be desirable to reach a better understanding of the above phenomena than one could get from the discussion of DWF and LMF alone. In this Letter, we therefore investigate *dynamical* properties of the same binary disparate-size mixture in its supercooled-liquid phase by solving the full wave-number- and time-dependent mode-coupling equations for the system. In the following, the existence of the new phase ("liquid within the voids of a glassy structure") will be confirmed not only by the localization lengths but also by the diffusion constants of both particle species of a binary hard-spheres mixture. The change in the diffusion mechanism of the small particles near the glass transition is discussed from a dynamical viewpoint.

The basis of our calculations is the mode-coupling approximation (MCA) for multicomponent liquids [5]. It allows us to determine the set of partial-density relaxation functions of an S-component liquid ($s, s' = 1, 2, ..., S$),

$$\Phi_{ss'}(q,t) = \langle \delta N^{(s)}(\mathbf{q},t)^{\dagger} \delta N^{(s')}(\mathbf{q},0) \rangle / k_B T \,, \qquad (1)$$

with the particle density of sth species defined as

$$N^{(s)}(\mathbf{q},t) = \frac{1}{\sqrt{N_s}} \sum_{j=1}^{N_s} \exp[-i\mathbf{q} \cdot \mathbf{r}_j^{(s)}(t)] \,, \qquad (2)$$

from the following set of matrix nonlinear integro-differential equations:

$$\ddot{\Phi}(q,t) + \Omega^2(q) \star \Phi(q,t) + \int_0^t dt' \, K(q,t-t') \star \dot{\Phi}(q,t') = 0 \,, \qquad (3)$$

with initial conditions $\Phi(q,t=0) = S(q)/k_B T$ and $\dot{\Phi}(q,t=0) = 0$. Here $S(q)$ is the matrix of partial structure factors, and $\Omega^2(q) = q^2 v_{\mathrm{th}}^2 \star S(q)^{-1}$ denotes the restoring-force matrix with $[v_{\mathrm{th}}^2]_{ss'} = (k_B T / m_s)\, \delta_{ss'}$. While Eq. (3) is formally exact, the relaxation-kernel matrix $K(q,t)$ reads in MCA

$$K(q,t) = (k_B T)^2 v_{\mathrm{th}}^2 \star \int \frac{d^3k}{(2\pi)^3} [(\mathbf{k} \cdot \mathbf{q}^0)^2 \check{c}(k)^T \star \Phi(k,t) \star \check{c}(k) \circ \Phi(|\,\mathbf{q} - \mathbf{k}\,|, t) + (\mathbf{k} \cdot \mathbf{q}^0)(q - \mathbf{k} \cdot \mathbf{q}^0) \check{c}(k)^T \star \Phi(k,t) \circ \Phi(|\,\mathbf{q} - \mathbf{k}\,|, t) \star \check{c}(|\,\mathbf{q} - \mathbf{k}\,|)] \,, \qquad (4)$$

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where $\mathbf{q}^0 = \mathbf{q}/q$ and the $\star$ denotes ordinary matrix multiplication, while the $\circ$ stands for the element-wise product of matrices, $\{A \circ B\}_{ss'} = A_{ss'} B_{ss'}$. The *non-symmetric* matrix $\check{c}(q)$ is related to the Ornstein-Zernike direct correlation function $C(q)$ as $\check{c}(q) = w \star C(q)$ with $w_{ss'} = \sqrt{N_s/V}\, \delta_{ss'}$. The above equations can be solved to find the *coherent* density-correlation functions [Eq. (1)] of a multicomponent system, once the partial structure factor $S(q)$ is known as an input. For a binary mixture of hard spheres, this input is available within the Percus-Yevick approximation in analytic form [10].

The time evolution of the *incoherent* density correlation function of species s may also be expressed by the generalized oscillator equation

$$\ddot{\phi}_s(q,t) + q^2 \frac{k_B T}{m_s} \phi_s(q,t) + \int_0^t dt' K_s(q,t-t') \dot{\phi}_s(q,t') = 0, \quad (5)$$

with initial conditions $\phi_s(q,t=0) = 1$ and $\dot{\phi}_s(q,t=0) = 0$. The relaxation kernel $K_s(q,t)$ reduces in MCA to

$$K_s(q,t) = \frac{(k_B T)^3}{m_s} \int \frac{d^3k}{(2\pi)^3} (\mathbf{k} \cdot \mathbf{q}^0)^2 [\check{c}(k)^T \star \Phi(k,t) \star \check{c}(k)]_{ss} \times \phi_s(|\mathbf{q} - \mathbf{k}|, t). \quad (6)$$

Once the set of coherent density-relaxation functions $\Phi(q,t)$ for a supercooled liquid has been determined by solving Eq. (3), these functions along with the static structure factors serve as an input when solving Eqs. (5) and (6) for the incoherent density-correlation functions. Interesting quantities such as a generalized wave-number-dependent localization length $l_s(q)$ and a frequency-dependent diffusion constant $D_s(\omega)$ are determined from the incoherent relaxation kernel $K_s(q,t)$ by the following formula:

$$l_s(q) = \left[\frac{2k_B T/m_s}{K_s(q, t = \infty)} \right]^{1/2}, \quad (7)$$

$$D_s(\omega) = \mathrm{Im} \frac{k_B T/m_s}{\omega + \lim_{\epsilon \to 0} i \int_0^\infty dt\, e^{it(\omega + i\epsilon)} K_s(q = 0, t)}. \quad (8)$$

This program has been carried through for a binary ($S = 2$) hard-sphere system with size ratio $\delta = \sigma_1/\sigma_2 = 0.2$ and concentration of small spheres $c = 0.9$. In Fig. 1 we outline three phases of the system by plotting the inverse localization lengths of the small and large particles, $1/l_1(q)$ and $1/l_2(q)$, respectively, versus the total packing fraction $\eta = \eta_2[1 + c/(1-c)\delta^3]$, where $\eta_2 = (\pi/6) n_2 \sigma_2^3$ denotes the large-particle packing fraction: (i) a glass phase for $\eta > \eta_A \approx 0.53$ with all particles being localized, (ii) a "porous glass" for $\eta_A \geq \eta \geq \eta_B$ containing mobile small particles [$1/l_1(q) = 0$ and $1/l_2(q) > 0$], and finally (iii) a liquid phase for $\eta < \eta_B \approx 0.52$, in which both particle species are mobile [$1/l_2(q) = 1/l_1(q) = 0$]. We note that the localization length of the small particles increases *continuously* to infinity according to $l_1(q) \propto (\eta - \eta_A)^{-1}$ as the delocalization transition is approached [9]. Similar behavior of the localization length has been derived for a quantum particle in a *static random potential* [11,12]. In contrast to the small particles delocalizing continuously within the glassy matrix, the large particles merely exhibit a slight increase in their localization length as the packing fraction is decreased. Near the melting density, however, $l_2(q)$ grows more rapidly approaching a *finite* value at η_B which is slightly less than 10% of the diameter of large particles ($l_2^{\mathrm{crit}} \approx 0.089\sigma_2$, see below) in close agreement with *Lindemann's criterion* known for the mean-square displacement of atoms in a crystal. When passing the glass-liquid transition point η_B (towards low η), the localization length of the large particles jumps to infinity discontinuously. The large-particle behavior found in the mixture here is very similar to that predicted from MCA for the localization length in a *one-component* system [2]. Assuming the same glass-transition scenario derived by Götze and co-workers for the one-component system [3] also for the binary system, we expect a critical exponent of 1/2 for the nonergodicity parameters of the number densities [6,8] implying the large-particle localization length to vary like $(\eta - \eta_B)^{1/2}$ near η_B. Since $1/l_2(q) > 0$ at $\eta = 0.52$ and $1/l_2(q) = 0$ at $\eta = 0.519$, we can assume that $\eta_B = 0.5195$. Using this value of η_B, the calculated points in Fig. 1 are, indeed, well represented by

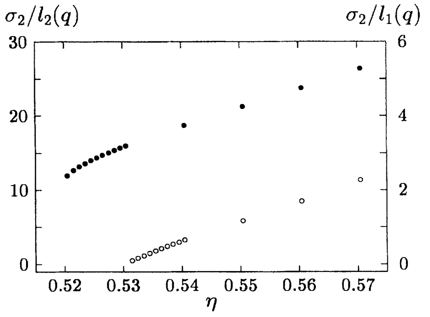

FIG. 1. Inverse localization length $\sigma_2/l_s(q)$ of the small (open circles) and large (solid circles) particles at $q\sigma_2 = 0.02$.

$$(l_2/\sigma_2)^{-1} = (l_2^{\mathrm{crit}}/\sigma_2)^{-1} + a|\eta - \eta_B|^{1/2} + b\,|\,\eta - \eta_B\,|, \quad (9)$$

with $(l_2^{\mathrm{crit}}/\sigma_2)^{-1} = 11.30$, $a = 27.11$, and $b = 174.4$. In Fig. 2 the diffusion constant $D_s(\omega)$ (in multiples of $\sigma_2^2 \omega_0$) at $\omega/\omega_0 = 10^{-6}$ ($\omega_0^2 = k_B T/m_2 \sigma_2^2$) is plotted with respect to η, where η is chosen as $\eta = \eta_B - (1/2)^n$ with $n = 3$–9. The diffusion constant of the small particles becomes more than 10^5 times larger than that of the large particles near the glass transition point η_B,

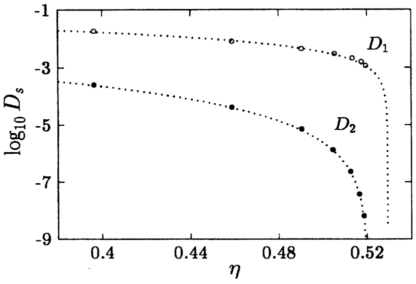

FIG. 2. Diffusion constant $D_s(\omega)$ at $\omega/\omega_0 = 10^{-6}$ for the small (open circles) and large (solid circles) particles.

implying that the large particles are almost frozen while the small particles still retain a high mobility. We note in passing that liquid Ar near its triple point would be represented by the point $\eta \approx 0.44$ and $\log_{10} D \approx -1.32$ in Fig. 2 corresponding to $D_{\mathrm{Ar}} \approx 4D_1$. The calculated points are well fitted (using the iterative nonlinear-fit procedure supplied by MATHEMATICA) by the power law $D = D_0|\eta - \tilde{\eta}|^\gamma$ with $\gamma = 1.05$ and 2.53 for $s = 1$ and 2, respectively. From the extrapolation in terms of the power law (dotted lines), the diffusion constants are found to vanish at $\tilde{\eta} = 0.53$ and 0.52 for $s = 1$ and 2, respectively, which are in good agreement with the transition points η_A and η_B identified by the divergence of the localization lengths. It is interesting to note that the exponent γ for the large particles is close to that of a one-component hard-sphere system; $\gamma = 2.58$ [13]. This confirms the validity of our assumption that—as far as the localization of large particles is concerned—the transition mechanism in a binary system at $\eta = \eta_B$ is the same as that of the liquid-glass transition for a one-component system. For the small particles, on the other hand, the power γ is greatly different from 2.58. Their behavior will be markedly different from that of one-component liquid particles emphasizing the limits of applicability of the one-component theory in the treatment of multicomponent systems. We note that, contrary to the one-component case, there is no analytic prediction of a power-law behavior of the diffusion constants near the glass transition in the case of a binary liquid. The main purpose of our power law fits in Fig. 2 is, therefore, to demonstrate the qualitative difference in the η dependence of D_1 and D_2. Figure 3 illustrates the diffusivity $D_s(\omega)$ (in multiples of $\sigma_2^2\omega_0$) for both particle species as a function of ω in a logarithmic scale. We note that a little bump appears in $D_1(\omega)$ in the small ω range ($\omega/\omega_0 < 10^{-5}$) as the glass transition is approached. This bump, which has not been predicted by a one-component theory, grows in $D_1(\omega)$ as η increases, while no bump is observed in $D_2(\omega)$ for all η of our calculations. Since the ω range of the bump is in the quasielastic region of the incoherent relaxation spectra $\phi_s(q,\omega)$, the appearance of the bump will be related to the change in the diffusion mechanism of the small particles. Our interpretation of the bump is the following. When D_1 and D_2 are large, the diffusion of both species is liquidlike (Gaussian process). For η close to η_B, however, the motion of the large particles becomes sluggish, and they are almost frozen near the transition, producing an almost static potential field which the small particles would experience when they move through the glassy matrix of the large particles. Therefore the diffusion of the small particles at $\eta \sim \eta_B$ will be similar to that of a particle moving in a static random potential, which is different from the diffusion in normal liquids. The appearance of the bump in $D_1(\omega)$ is interpreted as an indication of the change from the liquidlike diffusion to the slow diffusion in an "almost fixed" random potential.

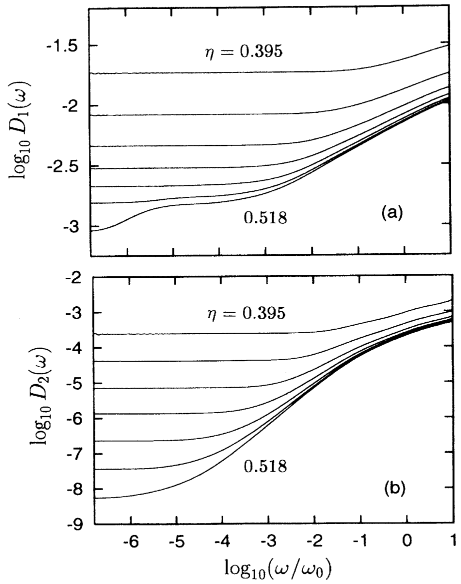

FIG. 3. Frequency-dependent diffusion constant $D_s(\omega)$ for the small (a) and large (b) particles.

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