Delocalization of Small Particles in a Glassy Matrix

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A binary mixture of hard spheres is investigated within mode-coupling theory under conditions that ensure that the large particles form an amorphous solid. The localization length of small spheres grows continuously with decreasing diameter ratio δ, diverging at a critical value $\delta_c \simeq 0.15$. Close to the localization-delocalization transition both the Lamb-Mössbauer and the Debye-Waller factors of the small particles show striking deviations from their commonly assumed wave-number dependence. Implications for quasielastic neutron scattering on hydrogen in (amorphous) metals are discussed.

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In this Letter we apply the recent mode-coupling theory of the liquid-glass transition[1] to a binary mixture of hard spheres with the aim of studying the localization-delocalization transition of a system of *interacting* small particles in a *glassy* matrix executing thermal vibrations. Having in mind the description of dynamical properties of systems such as high loads of hydrogen in metals[2] or liquids in porous media,[3] it is obvious that our model overcomes several limitations inherent in the Lorentz-gas model studied extensively in the past.[4,5]

For the numerical evaluation we choose numbers $N_1 = N_2$ of hard spheres with diameter ratio $\delta = \sigma_1/\sigma_2 \leq 1$ in a volume V. The total packing fraction $\eta = \frac{1}{6}\pi \times (N_1\sigma_1^3 + N_2\sigma_2^3)/V = 0.55$ ensures (as will be shown) that the large particles are localized in an amorphous structure for all values of δ.

We define the *Lamb-Mössbauer factor* (LMF) of species s,

$$f_s(q) = \lim_{t\to\infty} \Phi_s(q,t), \tag{1}$$

as the long-time limit of the tagged-particle–density relaxation function,[6] and correspondingly, the *Debye-Waller factor* (DWF),

$$f(q)_{ss} = \lim_{t\to\infty} \Phi(q,t)_{ss}, \tag{2}$$

derives from the sth *diagonal* element of the matrix $\Phi(q,t)_{ss'}$ of partial-density relaxation functions defined with variables $N_s(\mathbf{q})/\sqrt{S_{ss}(q)}$ normalized by partial structure factors. These two quantities coincide in an harmonic solid and they show merely quantitative differences in a glass[1] as a result of anharmonicities. They will, however, differ from each other *qualitatively* in an assembly of small particles in a glassy matrix. For $t \to \infty$, the generalized oscillator equation of motion for $\Phi_s(q,t)$ with relaxation kernel $K_s(q,t)$ reduces to the exact equation[7]

$$q^2 f_s(q) + K_s(q,\infty)[f_s(q) - 1] = 0. \tag{3}$$

Applying a mode-coupling approximation to the friction kernel we find ($s = 1,2$; $s' \neq s$)

$$K_s(q,\infty) = (1/V)\sum_{\mathbf{k}} (\mathbf{k}\cdot\mathbf{q}/q)^2 f_s(|\mathbf{q}-\mathbf{k}|)\{c_{ss}(k)^2 f(k)_{ss} S_{ss}(k) + 2c_{ss}(k)c_{ss'}(k)f(k)_{ss'}[S_{ss}(k)S_{s's'}(k)]^{1/2} + c_{ss'}(k)^2 f(k)_{s's'} S_{s's'}(k)\}. \tag{4}$$

The direct correlation functions $c_{ss'}(k)$ entering Eq. (4) represent the only external input required. We use results of the Percus-Yevick approximation[8] known to be reliable for hard spheres and available in analytical form for all values of the system parameters η, δ, and $c = N_1/(N_1+N_2)$. Figure 1(a) shows representative examples of the partial static structure factors

$$S_{ss'}(q) = [I - c(q)]^{-1}_{ss'}.$$

Evaluation of $f_s(q)$ from Eqs. (3) and (4) requires knowledge of the matrix $f(q)_{ss'}$, which we calculate from

$$\sum_\sigma \{\Omega^2(q)_{s\sigma} f(q)_{\sigma s'} + K(q,\infty)_{s\sigma}[f(q)_{\sigma s'} - \Phi(q,0)_{\sigma s'}]\} = 0, \tag{5}$$

where $\Phi(q,0)_{ss'}$ and $\Omega^2(q)_{ss'}$ are determined solely by $S_{ss'}(q)$.[7] The exact Eq. (5) is derived in a way analogous to the procedure described above. Applying a mode-coupling approximation to the friction kernel matrix $K(q,t)_{ss'}$ results in

$$K(q,\infty)_{ss'} = \sum_{\mathbf{k}} \sum_{\substack{\lambda\lambda' \\ \mu\mu'}} v(qss';k\lambda\lambda', |\mathbf{q}-\mathbf{k}|\mu\mu') f(k)_{\lambda\lambda'} f(|\mathbf{q}-\mathbf{k}|)_{\mu\mu'}, \tag{6}$$

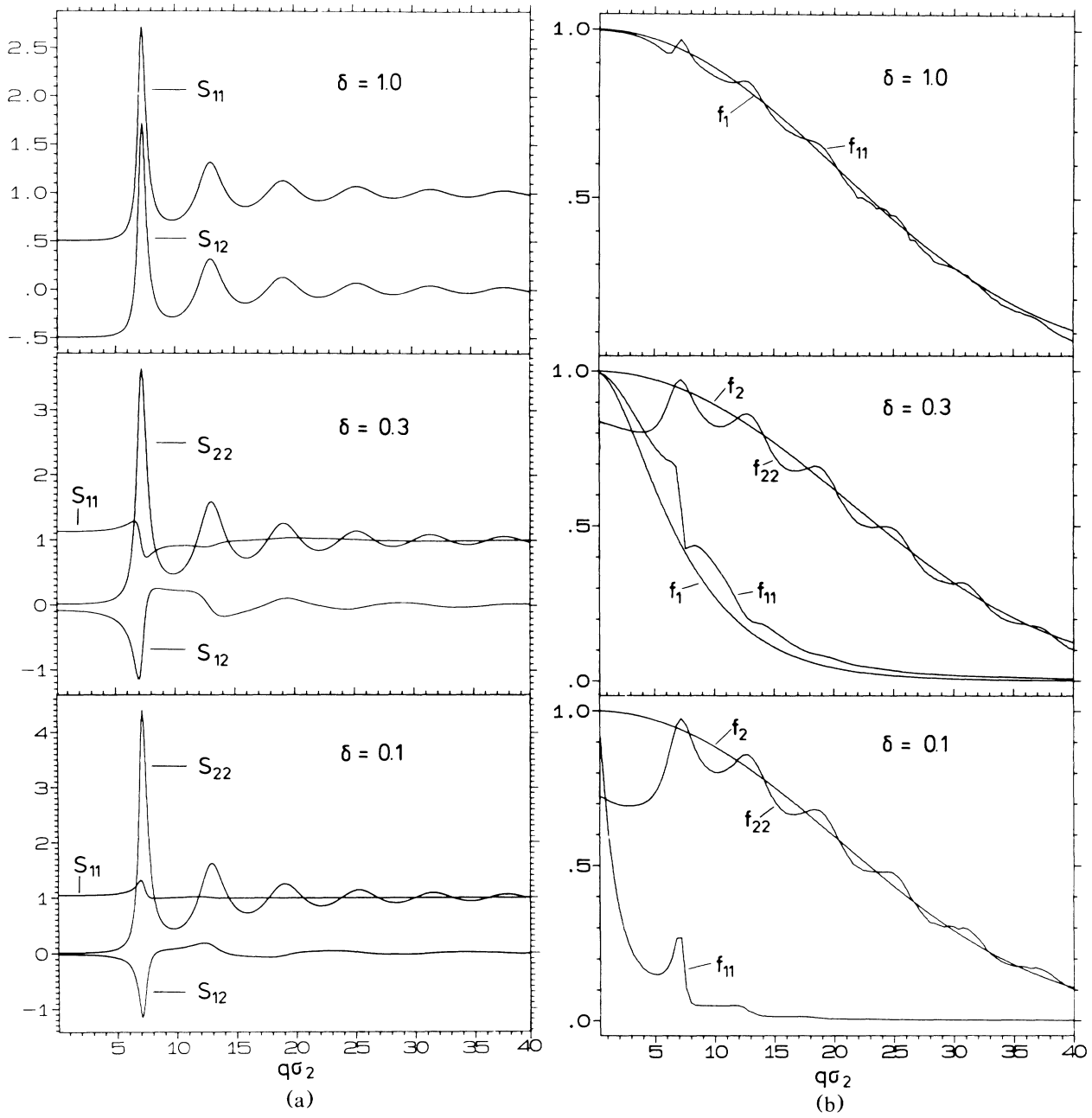

FIG. 1. (a) Structure factors and (b) glassy-matrix and small-particle properties, for $\eta=0.55$, $c=0.5$, and various δ, plotted against $q\sigma_2$.

with vertex functions v also determined by the static structure.[7] Equations (4) and (6) generalize Eqs. (2.13) and (2.12) of Ref. 1 to a binary mixture. Note that Eqs. (5) and (6) are a closed set of nonlinear integral equations for the $f(q)_{ss'}$, which was solved iteratively before iteration of Eqs. (3) and (4) to find $f_s(q)$.

Calculations were performed on a Cray X-MP/24 Computer and an accuracy of better than 5% was achieved after six to seven iterations. Starting in a state deep inside the glass, we fix η and c and decrease δ; i.e., we treat an increasingly nonideal mixture of spheres. Of course, one expects that the small particles will eventually be delocalized and form a liquid in the voids created by the large particles. This transition is, in fact, described by Eqs. (3)–(6). Representative results of the DWF with the corresponding LMF are shown in Fig. 1(b).

The nonzero DWF and LMF of species 2 in Fig. 1(b)

verify the above statement that for all δ the large particles will form an isotropic solid, which we call a "glassy matrix" in view of the liquidlike static structure factor $S_{22}(q)$, Fig. 1(a). For $\delta=1$, the LMF is well represented by a Gaussian $f_s(q)\sim\exp(-q^2 l_s^2/2)$, with a localization length $l_s=0.051\sigma_2$ for both species [see also Fig. 2(a)], and the DWF differs from the LMF only slightly. That is due to the particles oscillating harmonically about their equilibrium positions in this state deep in the glass. As δ is decreased to zero, the packing fraction $\eta_2=0.55/(1+0.45\delta^3)$ of species 2 increases by a factor 1.45. Yet Fig. 1(b) shows a slight increase of the localization length and deviations of the DWF from simple Gaussian behavior, signaling the onset of anharmonic oscillations. Obviously, the smaller the particles the more destabilizing their influence on the matrix.

Now we turn to the small-particle properties [Fig. 1(b)], which display some striking features:

(i) Contrary to the conventional liquid-glass transition, the LMF and DWF of the small particles change *continuously* with the transition driving parameter δ.[9]

(ii) A qualitative difference between LMF and DWF arises: While the half-width of $f_1(q)$ [$f_1(0)=1$ for $\delta>\delta_c$] decreases to zero as $\delta\to\delta_c$, reflecting the delocalization of the small particles, and $f_1(q)=0$ for $\delta\le\delta_c$, the DWF $f(q)_{11}$ stays *finite* even in the delocalized phase, reflecting the geometric structure of the glassy matrix. Physically this result is plausible: If the particles are sufficiently small, they are able to diffuse through the voids in the matrix, and thus their localization length is infinite, $f_1(q)=0$. On the other hand, since $f_{11}(q)\neq0$ the particles do *not* execute ergodic motion; indeed part of energetically allowed phase space is blocked permanently by the arrested large particles. The reason for $f_{11}(q)\neq0$ can be traced back to an indirect interaction between the small particles mediated by the matrix of *interacting* large particles.[7]

(iii) As $\delta\to\delta_c$ the LMF shows deviations from simple Gaussian behavior which are demonstrated in Fig. 2(a). The same phenomenon is presented in more physical terms in Fig. 2(b), where we plotted the q-dependent generalization of the localization length l_1 of the small

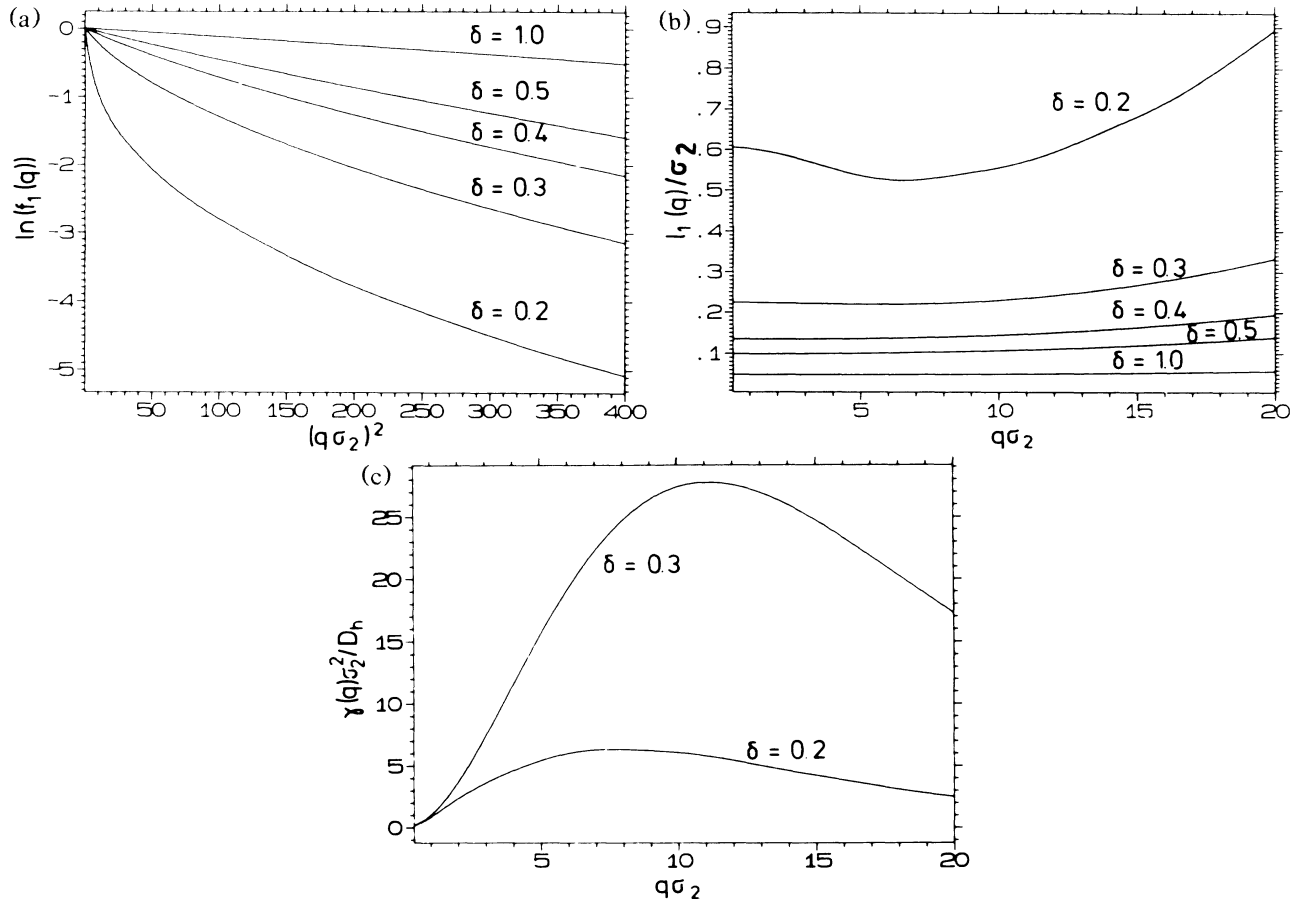

FIG. 2. (a) Logarithm of quasielastic intensity $f_1(q)$, (b) localization length $l_1(q)$, and (c) quasielastic linewidth $\gamma(q)$.

particles:

$$l_1(q) = [2/K_1(q,\infty)]^{1/2}. \quad (7)$$

From Eq. (3), non-Gaussian behavior of LMF is expected in general. It will merely coincide with a Gaussian for sufficiently small wave numbers obeying $l_1(q) \simeq l_1(0) \ll q^{-1}$. This condition is violated (except for the smallest wave numbers) as $\delta \to \delta_c$ because of the increasing localization length [Fig. 2(b)]. Note that as $\delta \to \delta_c$, $l_1(q)$ develops an anomalous initial decrease with increasing q which leads to a shallow minimum at q_0 before it grows indefinitely for large q. The minimum position q_0 coincides with the position of the first peak in $S_{22}(k)$ which is obviously the source of the hindered small-particle motion.

(iv) Finally, the δ dependence of the inverse localization length $l_1(0)^{-1}$ is well fitted by a straight line in the full interval $\delta_c < \delta \leq 1$, implying that $l_1 \propto (\delta - \delta_c)^{-1}$. Please note the strong effect of "superheating" of the small particles in the voids of the glass: $\delta_c \simeq 0.15$ corresponds to a partial packing fraction $\eta_1 = 0.55\delta^3/(0.45+\delta^3) \simeq 0.004$, while in the bulk the small spheres would melt at[1,10] $\eta_1 \approx 0.52$. Substantial superheating of bubbles of hydrogen in an α-silicon matrix has recently been observed.[11]

Here we apply the above results to *incoherent* quasielastic neutron scattering on the small particles. The low-frequency part of the incoherent scattering function in the glass takes the form

$$S_{\rm inc}^{\rm qe}(q,\omega) \simeq \pi^{-1} \frac{\gamma(q)}{\omega^2 + \gamma^2(q)} f_1(q), \quad (8)$$

with half-width

$$\gamma(q) = q^2 D_h f_1(q), \quad (9)$$

where D_h denotes a hopping-diffusion constant introduced *ad hoc* at this point. [D_h would be zero within the simple approximation Eq. (4). However, it was shown recently how dynamical processes can be incorporated into mode-coupling theory, leading to a small but finite diffusion constant in the glassy state.[12] Using similar arguments for $\Phi_1(q,t)$ we arrive at Eqs. (8) and (9).[13]] The width and intensity of the quasielastic peak are plotted in Figs. 2(c) and 2(a), respectively, for different δ. Quasielastic neutron scattering on hydrogen in amorphous solids is expected to correspond to a small value of δ; thus, the matrix effects discussed above should be observable. In fact, the characteristic non-Gaussian behavior of the integrated intensity has often been noted in experiments on hydrogen in crystalline metals.[2,14] The simple formula for the width $\gamma(q)$ in a glassy matrix is, to our knowledge, new and should be checked against experiment.

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