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α- and β-relaxations in supercooled binary liquids

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Abstract. The α- and β-relaxations in a disparate-size binary liquid near the glass transition have been investigated within a mode-coupling theory. We focus our attention on the α- and β-peaks in the frequency-dependent susceptibility and their dependence on the concentrations of big and small particles. For the 1:1 mixture of big and small particles (size ratio = 0.2), a large peak appears in the susceptibility of the small particles in the frequency range of the β-relaxation, which corresponds to the fast relaxation of the small particles within the random potential produced by the big particles. The intensity of this peak grows further as the concentration of the small particles (c_1) is decreased. For large c_1, on the other hand, the peak becomes lower than the α-peak and the susceptibility is similar to that of a one-component liquid.

1. Introduction

Diffusion of small particles in a random matrix is one of the interesting problems in condensed matter physics. This problem is closely related to rapid hydrogen transfer in amorphous metals, glassy ionic conductors, molecular diffusion in amorphous polymers and so on. Recently we have extended the mode-coupling theory of glass transitions [1, 2] to multi-component systems and applied it to a disparate-size binary hard-sphere mixture to study the liquid–glass transition of the mixture as well as the delocalization of small particles in a glassy matrix. In our previous papers [3, 4] we showed that for the diameter ratio $\delta = \sigma_1/\sigma_2 = 0.2$, the localization of the big particles occurs at $\eta \cong 0.52$ corresponding to the liquid–glass transition, while the small particles are localized at $\eta \cong 0.53$, where η is the total packing fraction $\eta = (\pi/6)n_2\sigma_2^3(1+c_1\delta^3/(1-c_1))$ and $c_1 = N_1/N$. The transition at $\eta \cong 0.53$ is not the normal liquid–glass transition but the localization–delocalization transition within the random potential produced mainly by the big particles.

In this paper we extend the analysis to examine the density relaxation of the same mixture in the liquid phase. We focus our attention on the α- and β-peaks in the generalized susceptibility and their dependence on the concentration c_1.

2. Theory

The theory is summarized as follows. The space and time variations of the partial density relaxation functions

$$\Phi_{ss'}(q,t) \propto \sum_{i,j} \left\langle \exp\left\{-\mathrm{i}\boldsymbol{q}\cdot\left[\boldsymbol{r}_j^{(s)}(t) - \boldsymbol{r}_i^{(s')}(0)\right]\right\}\right\rangle$$

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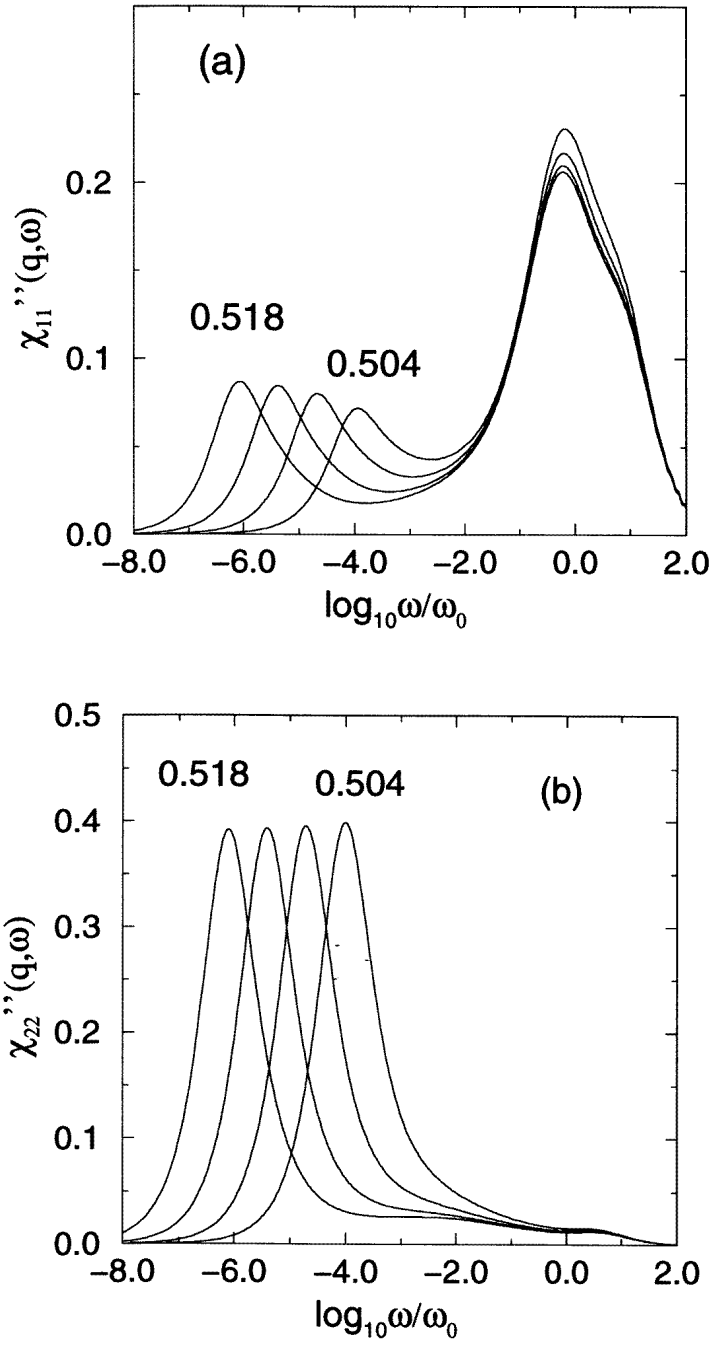

Figure 1. The susceptibility spectra of the small particles (a) and the big particles (b) for $c_1 = 0.5$ at $\eta = 0.504$, 0.512, 0.516 and 0.518. Here $\omega_0^{-1} = [k_B T/(m_2\sigma_2^2)]^{1/2}$ is the unit of time in our numerical calculations.

($s, s' = 1, 2$ denoting particle species) are described by the 2×2 matrix equation of motion

$$\ddot{\Phi}(q,t) + \Omega^2(q) \cdot \Phi(q,t) + \int_0^t \mathrm{d}t' \; K(q, t-t') \cdot \dot{\Phi}(q,t') = 0 \tag{1}$$

where $K(q,t)$ is the relaxation-kernel matrix;

$$K_{ss'}(q,t) = \frac{v_s^2}{n_{s'}V} \sum_{ll'} \sum_{\boldsymbol{k}} k_z u_{ls}(k)[k_z u_{l's'}(k)\Phi_{ll'}(k,t)\Phi_{ss'}(\kappa,t) + \kappa_z u_{l's'}(\kappa)\Phi_{ls'}(k,t)\Phi_{sl'}(\kappa,t)] + \Gamma_{ss'}(q)2\delta(t) \tag{2}$$

with abbreviations $n_s = N_s/V$, $v_s^2 = k_B T/m_s$, $k_z = \boldsymbol{k} \cdot \boldsymbol{q}/q$, and $\kappa = \boldsymbol{q} - \boldsymbol{k}$. Here the microscopic frequency $\Omega_{ss'}^2(q) = q^2 \, v_s^2 [S(q)^{-1}]_{ss'}$ and $u_{ss'}(q) = -k_B T\{\delta_{ss'} - [S(q)^{-1}]_{ss'}\}$ are determined by the static structure factors $S_{ss'}(q)$. The quickly decaying last term in equation (2) (regular part) describes binary collision effects, while the $\boldsymbol{k}$-integral approximates multiple-collision processes of the dense liquid causing strong dynamical feedback. The latter is crucial for the slow dynamics in the supercooled and glassy phases. The coupled equations (1) and (2) are solved numerically by iteration. For the binary hard-sphere mixture the static structure factor is supplied by the solution of the Percus–Yevick equations in terms of analytic formula [5]. This most simple model for the static structure of a hard-sphere mixture is known to become inadequate for size ratios $\delta < 2$ in combination with packing fractions $\eta_1 \approx \eta_2$, for which a phase separation will occur [6]. However, in the calculations presented here, the ratio of the partial packing fraction is $\eta_1/\eta_2 = 0.9 \times 10^{-3}, 0.8 \times 10^{-2}$ and 0.072 for $c_1 = 0.1$, 0.5 and 0.9, respectively. Thus, the system is away from the region of phase separation even for the largest c_1, and we consider the PY hard-sphere system an adequate model of a disparate-size binary liquid in the parameter range studied.

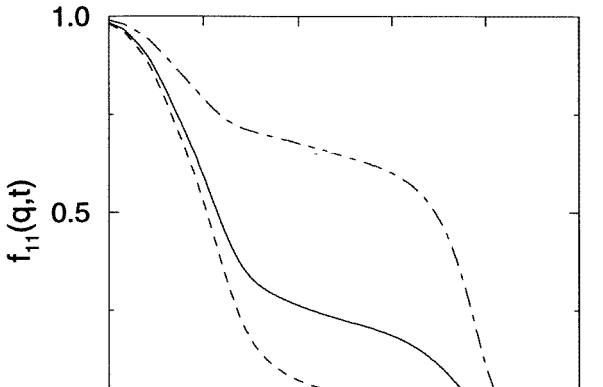

Figure 2. The density relaxation function of the small particles $f_{11}(q,t)$ for $c_1 = 0.1$ (dashed line), 0.5 (solid line) and 0.9 (chain line) at $\eta = 0.516$. The wavenumber is $q = 7.05\sigma_2^{-1}$.

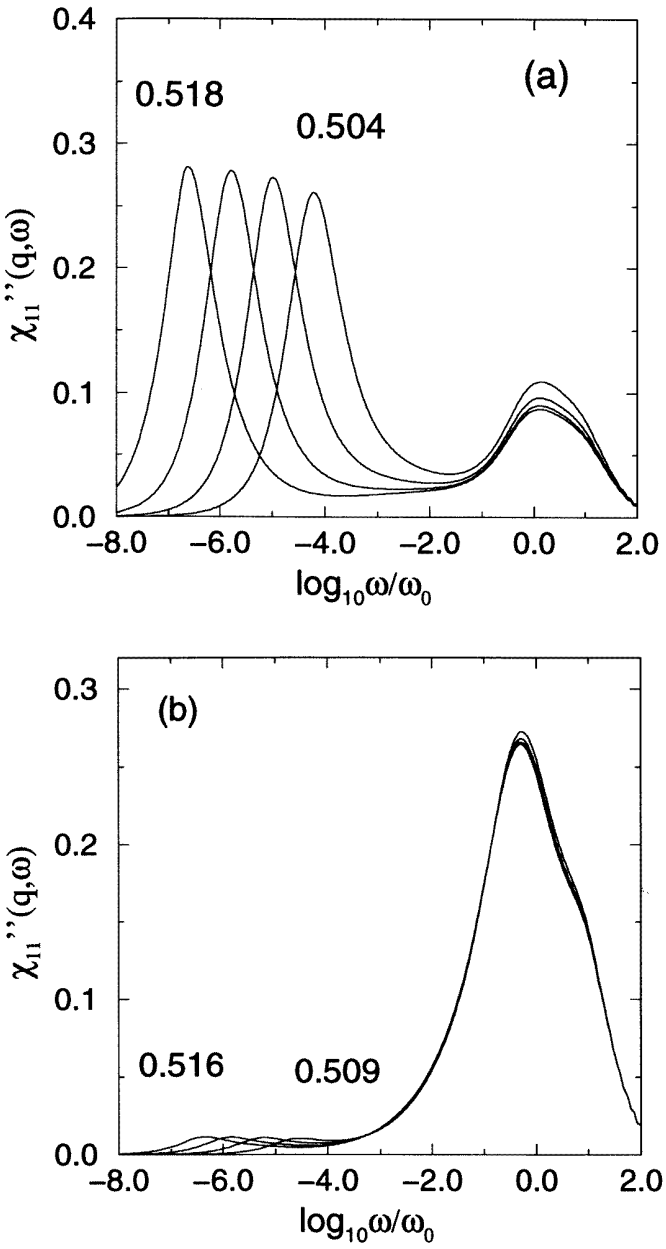

Figure 3. (a) The susceptibility of $\chi_{11}''(q,\omega)$ for $c_1 = 0.9$ and $\eta = 0.504$, 0.512, 0.516 and 0.518. (b) $\chi_{11}''(q,\omega)$ for $c_1 = 0.1$ and $\eta = 0.509$, 0.513, 0.515 and 0.516. The wavenumber is $q = 7.05\sigma_2^{-1}$.

3. Results

Figure 1 shows the susceptibility $\chi_{ss}''(q,\omega)$ for $\delta = 0.2$ and $c_1 = 0.5$ at $q = 7.05\sigma_2^{-1}$ (the main peak of $S_{22}(q)$). The characteristics of $\chi_{22}''(q,\omega)$ are similar to those of a one-

component liquid [7]; that is, it consists of a large α-peak in the low-frequency regime and a microscopic peak at $\omega/\omega_0 \sim 10$, which is overdamped in the present model. The β-peak is observed only at $\eta = 0.518$ with low intensity and it merges with the high-frequency wing of the α-peak for larger η. In the susceptibility of the small particles, on the other hand, we find a large peak at $10^{-1} < \omega/\omega_0 < 1$ with a shoulder at high frequencies. This high-frequency shoulder arises from the microscopic oscillation corresponding to the second term in equation (1). Although the large peak in $\chi''_{11}(q,\omega)$ is expected to arise from the β-process, the characteristics of the peak are different from those of the β-peak found in a one-component liquid in two ways; firstly, the intensity of the peak is much higher than that of the α-peak, and secondly, the peak frequency is about two decades higher than that of the β-peak of the big particles. Therefore, we call the peak in $\chi''_{11}(q,\omega)$ the β'-peak to distinguish it from the β-peak of the big particles. The β'-peak is considered to arise from the fast relaxation of the small particles within the random potential which is produced mainly by the big particles. The α-peaks appearing in both $\chi''_{22}(q,\omega)$ and $\chi''_{11}(q,\omega)$ correspond to the decay of the random potential. Note that the diffusion constant of the big particles near the transition point $\eta = 0.52$ is about 10^5 times smaller than that of the small particles [3]. Therefore, on the time-scale of the density relaxation of the small particles, the big particles are almost frozen and produce an almost static random potential which serves as a cage potential for the small particles.

Let us investigate the c_1-dependence of the α- and β-relaxations. Figure 2 shows the normalized density relaxation function

$$f_{ss'}(q,t) = \Phi_{ss'}(q,t)/[\Phi_{ss}(q,t=0)\Phi_{s's'}(q,t=0)]^{1/2}$$

for $c_1 = 0.1$, 0.5 and 0.9. The plateau in the β-relaxation regime becomes lower as c_1 is decreased, which reflects the small values of the long-time limit of $f_{11}(q,t)$ (Debye–Waller factor) at low concentration c_1. (See figure 2 of reference [8].) Note that $f_{11}(q,t)$ for $c_1 = 0.1$ is similar to the incoherent part of the density relaxation function of the small particles [9]. In figure 3 we plot $\chi''_{11}(q,\omega)$ at $c_1 = 0.9$ and 0.1 for several values of η. For $c_1 = 0.9$, the intensity of the α-peak is higher than that of the β'-peak and $\chi''_{11}(q,\omega)$ is similar to figure 1(b). This means that the system is like a one-component system of the *small* particles when c_1 is large (as far as the number density is concerned) and the random potential is produced by both the big and small particles. For $c_1 = 0.1$, on the other hand, the system is like a one-component system of the *big* particles. As a result, the behaviour of the small particles is similar to that of a single impurity atom in a random potential and the intensity of the α-peak becomes extremely low. These results are consistent with the interpretation of the peaks given above. The difference in $\chi''_{11}(q,\omega)$ among $c_1 = 0.1$, 0.5 and 0.9 originates from the different plateau values in $f_{11}(q,t)$ shown in figure 2.

4. Summary

In this paper we investigated the α- and β-processes in a disparate-size binary liquid near the glass transition. For a 1:1 mixture we observed a large β'-peak in $\chi''_{11}(q,\omega)$ corresponding to the fast relaxation of the small particles within a random potential. This β'-peak grows further and the α-peak becomes lower as the concentration c_1 is decreased. On the other hand, the intensity of the β'-peak decreases for large c_1 and $\chi''_{11}(q,\omega)$ becomes similar to $\chi''_{22}(q,\omega)$. These results show that the dynamics of the small particles are greatly different from what we find in a one-component system. This points out the necessity to treat the multi-component theory when comparing the theoretical predictions with experimental data.

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