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Structural Relaxation in a Binary Mixture

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We study the dynamic feedback mechanism of the mode-coupling model in a binary liquid in the context of structural Glass transition. The dependence of the dynamic transition point on the mass ratio of the constituents in the mixture is studied from the model equations. The effects of slow structural relaxation on the single particle dynamics are also analyzed. The feedback effects on the tagged particle dynamics from coupling of density fluctuations show that the extrapolated self-diffusion coefficient approaches zero at a low temperature in agreement with simulation results.

§1. The model studied

The self-consistent mode-coupling theory (MCT) has provided a microscopic basis for understanding the slow dynamics in supercooled liquids. In a one component system the mode-coupling model constitutes a dynamic feedback mechanism to enhance the viscosity or equivalently reduce diffusion coefficient. We use a similar theoretical approach for a binary liquid in the context of structural Glass transition. Binary systems are particularly interesting since they are widely used for simulation studies of supercooled liquids1),2) since two component systems seem to avoid the crystallization and continue to remain in the disordered state till very high density. Density correlation function between components s and s' in the mixture is defined as, $C_{ss'}(q,t) = N^{-1}\langle \delta\rho_s(q,t)\delta\rho_{s'}(-q,0)\rangle$. Time evolution of the correlation functions is obtained in terms of the matrix equation,

$$[z\boldsymbol{I} - \boldsymbol{M}(q,z)]\boldsymbol{C}(q,z) = \boldsymbol{\chi}(q). \tag{1·1}$$

$\chi_{ss'} = a_s a_{s'} S_{ss'}$ is the equal-time density correlation function matrix. $a_s = m_s\sqrt{n_s}$ and $n_s = N_s/N$; m_s is the mass of the species s. $S_{ss'}$ is the partial structure factor between s and s'. The memory function $M(q,z)$ is expressed as

$$\boldsymbol{M}(q,z) = q^2\left[i\,\boldsymbol{M}^{\boldsymbol{B}}(q) + \rho_o\kappa\chi^{-1}(q)/\{z + i\,q^2\Gamma^R(q,z)\}\right]. \tag{1·2}$$

$\boldsymbol{M^B}_{ss'}(q) = \gamma_0(q)(-1)^{s+s'}$ is related to the bare inter-diffusion constant. $\kappa_{ss'} = x_s x_{s'}$, with $x_s = m_s n_s/\rho_o$ and $\rho_0 = m_1 n_1 + m_2 n_2$. $\Gamma^R = \Gamma_0 + \Gamma^{mc}$ with Γ^{mc} represents the mode-coupling contribution to longitudinal viscosity. Up to the one loop order, the MC contribution is given by

$$\Gamma^{mc}(q,t) = \frac{\mu_q}{2q^2}\int \frac{dk}{(2\pi)^3} V_{ss'}(q,k)\ V_{ll'}(q,k_1) C_{l's'}(k,t) C_{ls}(k_1,t), \tag{1·3}$$

where $\vec{k_1} = \vec{q} - \vec{k}$ and the vertex function is given by $V_{ss'}(q,k) = (a_s a_{s'})^{-1}[\hat{q}.k\ \ \tilde{c}_{ss'}(k) + \hat{q}.k_1\ \ \tilde{c}_{ss'}(k_1)]$, $c_{ss'}$ being the direct correlation functions for the binary liquid. $\mu_q =$

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$[n_1 S_{11} + \Re^2(2\sqrt{n_1 n_2} S_{12} + n_2 S_{22})]A^{-1}$, $A = (n_1 + \Re^2 n_2)$ and $\Re$ represents the mass-ratio, m_2/m_1.

The long time limit of the density correlation function, known as the non-ergodicity parameter (NEP), $f_{ss'}(q) = C_{ss'}(q, t \to \infty)/\sqrt{\chi_{ss}\chi_{s's'}}$. In the asymptotic limit of time ($z \to 0$), Eq. (1·1) reduce to

$$f_{ss'}(q) = \frac{\zeta_{ss'}(q)\Gamma(q)}{1 + \Omega_o(q)\Gamma(q)}, \qquad (1\cdot4)$$

with $\Gamma(q)$ being the long time limit of the memory function given by Eq. (1·3). $\Omega_o(q) = \sum_{s,s'}(a_s a_{s'}/\rho_o)S_{ss'}(q)$. The matrix $\zeta_{ss'}(q)$ is given in terms of the structure of the system, $\zeta_{ss'}(q) = a_i a_j S_{is}(q) S_{js'}(q)/(\rho_o\sqrt{S_{ss}(q)S_{s's'}(q)})$. A non-zero solution for the $f_{ss'}(q)$ at the critical point marks the dynamic transition to a non-ergodic phase.

§2. Numerical solution of MCT equations

2.1. *Mass ratio dependence of transition*

The dynamic transition of the bianary liquid as predicted in the earlier works[3] using the mode coupling approach does not depend on $\Re$. This dependence of the dynamic transition point on $\Re$ follows naturally from our model equations. We study here the model equation (1·4) with input structure factor of a binary hard sphere system. The characteristic properties for the systems are, (a) the fractional concentration of bigger particles x, (b) The size ratio $\alpha (= \sigma_1/\sigma_2)$, of the diameters of the two species, and (c) the total packing fraction $\eta = \eta_1 + \eta_2$, where $\eta_s = \frac{\pi}{6} n_s {\sigma_s}^3$, n_s being the number of particles per unit volume of sth species. For high values of the ratio, $\Re \geq 2$, i.e., the bigger sized particles with higher mass, we find that there is no significant change in the transition point. This is in qualitative agreement with the simulation studies on the binary mixtures. However, for the case of bigger particles having less inertia than the smaller particles, i.e., $\Re \leq 1$, a significant change in transition point is observed. A similar qualitative dependence on the mass-ratio is also found in the non-ergodicity parameters. Recent computer simulations demonstrate dependence of the diffusivity on the transport properties.[4]

2.2. *Single particle dynamics*

The tagged particle density correlation function is defined as, $G^s(|\vec{r} - \vec{r}'|, t) = V\langle \delta(\vec{r} - \vec{R}(t))\delta(\vec{r}' - \vec{R}(0))\rangle$, where $\vec{R}_s^\alpha(t)$: position of the αth particle of the sth species ($s = 1, 2$). In the two limiting cases of free particle ($t \to 0$) and diffusive regimes ($t \to \infty$), $G^s(r, t)$ follows Gaussian distribution in space.[5] Tagged correlation for the μth species at wave vector q, $\psi_s^\mu(q, t)$ is described by

$$\frac{\partial^2 \psi_s^\mu}{\partial t^2} + \frac{v_\mu^2}{D_\mu}\frac{\partial \psi_s^\mu}{\partial t} + q^2 v_\mu^2 \psi_s^\mu + \int_0^t d\tau K_\mu(q, t - \tau)\frac{\partial \psi_s^\mu}{\partial \tau} = 0, \qquad \mu = 1, 2, \qquad (2\cdot1)$$

where $v_\mu^2 = K_B T/m_\mu$. D_μ represents the bare self-diffusion coefficient for μth species.[6] In a dense liquid the correlated motion of the tagged particle with the surrounding bath particles is accounted through the memory function $K_\mu(q,t)$ obtained from the generalization of the one-component result,

$$K_\mu(q,t) = \lambda_\mu \int \frac{d\vec{k}}{(2\pi)^3} \sum_{\nu,\nu'} V^{\mu}_{\nu\nu'}(k)\psi_{\nu,\nu'}(k,t)\psi^{\mu}_s(|\vec{q}-\vec{k}|,t) \tag{2·2}$$

with $V^{\mu}_{\nu,\nu'}(k) = (\hat{q}.\vec{k})^2 \tilde{c}_{\nu\mu}(k)\tilde{c}_{\nu'\mu}(k)\sqrt{S_{\nu\nu}(k)S_{\nu'\nu'}(k)}$ and $\lambda_\mu = v_\mu^2/n_\mu$, n_μ is the number density corresponding to the μth species. $\widehat{q} = \vec{q}/q$.

For obtaining Eqs. (2·1) and (2·2) it is required to write down the equation for the tagged particle momentum in a TDGL form. This can be only considered approximate since the tagged particle momentum is not a conserved property.

We consider the model equations here for the Kob-Andersen (KA) binary system characterized by the Lennard Jones (LJ) interaction potential. We take $m_1 = m_2$ here. Partial structure factors are obtained from the self-consistent solution of integral equations following the method outlined in Ref. 7). The mean-square displacement $\langle r^2(t)\rangle$ crosses over from ballistic ($\sim t^2$) at short times to a diffusive behavior ($\sim t$) at longest times. Over intermediate times the growth of $\langle r^2(t)\rangle$ is substantially reduced due to the manifestation of the cage effect. From the long time fit to $\langle r^2(t)\rangle$ curve, we obtain the self-diffusion coefficients D_μ for both the species ($\mu = 1,2$) at different temperatures. Power law fits to the D_μ indicate that at a temperature around $T_c = 0.44$ the diffusion coefficients for both the species would vanish on extrapolation. This value of T_c is close to the simulation prediction for ideal glass transition temperature at $T = 0.435$[8)] which is also concluded from a similar extrapolation procedure.

In the supercooled liquid there is a fraction of particles termed as "mobile" particles, move further than what is predicted by a Gaussian approximation at a given time. These particles are identified in the present model by comparing the actual

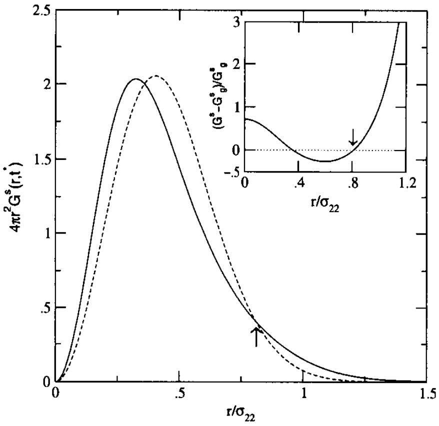

Fig. 1. Distribution of the bigger particles $4\pi r^2 G^s(r,t)$ corresponding $t = t^*$ at which the peak in $\alpha_2(t)$ occurs, at $T = 0.451$. The Gaussian distribution, $4\pi r^2 G^s_g(r,t)$, where $G^s_g(r,t) = [3/2\pi\langle r^2(t)\rangle_2]^{3/2}\exp[-3r^2/2\langle r^2(t)\rangle_2]$, is also shown with dashed curve at the same temperature. Inset shows the relative difference $(G^s(r,t) - G^s_g(r,t))/G^s_g(r,t)$ at $T = 0.451$. Arrows, both in the main figure and the inset, indicate the position of r^* (see text). σ_{22} is the hard core of the Lennard-Jones potential of species 2.

distribution for the single particle probability with a corresponding homogeneous (Gaussian) distribution.[9] It was shown in Ref. 10) that the mobile particles tend to form clusters in the system which contribute to the heterogeneous character of the system. The fraction of mobile particles,

$$\phi_M = \int_{r^*}^{\infty} d\vec{r} G^s(r,t) \tag{2·3}$$

is computed at three different temperatures, $T^* = 0.45$, 0.48 and 0.55. This fraction increases as the temperature is lowered. This is in the background of the system getting more jammed with lowering of the temperature. The fraction of mobile particles over the temperature range considered here constitutes only roughly 5.4%–6.4% of the total particles. In the computer simulation of the same system Kob et al.[9] have identified a similar fraction of particles having higher mobility.

§3. Conclusion

Earlier MCT models[11],[12] predict the dynamic transition at a much lower density in comparison to the simulation study on binary systems.[8] The present model improves this. The dynamic transition shows a dependence on mass ratio of the particles here. We have also studied the nature of the single particle dynamics in terms of the van Hove self-correlation function. Memory effects due to coupling with slowly decaying density correlations are included. As the temperature is lowered the particles tend to get more jammed with a fraction of the particles remaining more mobile. We observe a fraction of the mobile particles (5–6 %) increase with lowering of temperature and thus signifying the growing heterogeneity in the system. This is in agreement with the corresponding results from the simulation.

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