de Gennes slowing of density fluctuations in ordinary and supercooled liquids

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We discuss the slowing mechanisms of the intermediate scattering function for wave vectors near the position of the main peak of the structure factor. Simulation data in ordinary and supercooled liquid rubidium show that the decay rate at long times is much slower than that predicted by the usual viscoelastic theories, particularly in the quenched system. This feature is accounted for by a simple mode-coupling calculation.

In a dense fluid the intermediate scattering function $F(k,t)$ is known to exhibit a marked slowing as the wave vector k approaches the value k_m where the structure factor $S(k)$ has its main peak.[1] In fact, this sharp maximum means that the corresponding wave vectors occur with high probability in the structure of the system, thus making the temporal decay of density fluctuations with $k \approx k_m$ much slower than the one implied by the average microscopic collision rate. These arguments can be given a quantitative basis by considering the Laplace transform $\hat{F}(k,z)$ of $F(k,t)$ which satisfies the memory equation

$$\hat{F}(k,z)/S(k) = \left[z + \frac{\Omega^2(k)}{z + \hat{M}(k,z)} \right]^{-1} . \tag{1}$$

Here, $\Omega^2(k) = k^2 k_B T/mS(k)$; the second-order memory function $M(k,t)$ has an initial value $M(k,t=0) = \Omega_L^2(k) - \Omega^2(k)$, where $\Omega_L^2(k)$ is simply related to the fourth frequency moment of the dynamic structure factor $S(k,\omega)$.[2] The simplest ansatz for $M(k,t)$, referred as "viscoelastic model," assumes an exponential decay, $M(k,t) = M(k,t=0)\exp(-t/\tau_k)$ with $(\tau_k)^{-1} \approx (2/\sqrt{\pi})[M(k,t=0)]^{1/2}$.[3] For $k \approx k_m$, $\Omega^2(k)$ is much smaller than $\Omega_L^2(k)$ and the times τ_k and $[1/\Omega_L(k)]$ are "microscopic," typically $\approx 10^{-13}$ s. Outside this time scale it appears reasonable to write Eq. (1) as

$$\hat{F}(k,z)/S(k) \approx \{ z + [\Omega^2(k)/\hat{M}(k,z=0)] \}^{-1} , \tag{2}$$

namely, an exponential decay of $F(k,t)$ with a rate

$$\gamma(k) = k_B T k^2 / [mS(k) M(k,t=0) \tau_k] \tag{3}$$

which decreases considerably as $S(k)$ approaches its main peak. This simple explanation of the "de Gennes slowing" applies to systems with continuous interatomic potentials, but equivalent results have been obtained for dense hard-sphere systems.[4,5]

The validity of the result $F(k,t) = S(k)e^{-\gamma(k)t}$ for $k \approx k_m$ can be tested against molecular-dynamics (MD) simulation data. Recently, in an investigation about atomic diffusion, we performed a series of MD simulations in ordinary and supercooled liquid rubidium.[6] In particular, data for $F(k,t)$ were obtained at several state points all at the constant density $n\sigma^3 = 0.905$ (here, $\sigma = 4.405$ Å denotes the first zero of the effective pair potential developed by Price *et al.*[7]). Starting from the ordinary liquid ($T \approx 318$ K), the system was quenched down to a temperature $T \approx 270$ K and remained "stable" (i.e., unaffected by nucleation) for the whole duration of the MD runs, i.e., 400 ps. For all states the main peak of $S(k)$ occurs for $k_m \sigma \approx 6.8$.

The aforementioned exponential law with the decay rate (3) is found to agree rather well with the MD data for the ordinary liquid at 318 K;[6] the actual comparison was made at $k\sigma = 6.75$, where $S(k) = 3.12$. Only at rather long times ($t > 4$ ps) the theoretical slope $\gamma(k) = 0.39$ ps^{-1} overestimates the actual decay rate of $F(k,t)$, but the effect is not very significant because the substantial decrease already occurred at shorter times. Instead, at $T \approx 270$ K, more evident discrepancies of the viscoelastic model appear at intermediate and long times (see Fig. 1 of Ref. 6). Although this state corresponds to a relatively modest supercooling, the slowing down of $F(k\sigma = 6.75, t)$ is pronounced and by no means can be described by the simple model. In particular, at 270 K, where the MD data yield $S(k\sigma = 6.75) = 3.79$, Eq. (3) predicts a decay rate $\gamma(k) = 0.28$ ps^{-1}, to be contrasted with a MD value of 0.132 ps^{-1}, deduced by an exponential regression in the interval 4–8 ps.

The origin of this breakdown lies in the assumption of a single, microscopic decay time for the memory function $M(k,t)$. More precisely, $M(k,t)$ can also be affected by other, long-lasting decay mechanisms which involve nonlinear couplings to slowly varying dynamical variables. Mode-coupling (MC) theory provides the natural framework to investigate such phenomenon. At high densities and/or low temperatures, the dominant (i.e., the slowest) coupling occurs to density fluctuations, so that ultimately Eq. (1) becomes a rather complicated self-consistent equation for $F(k,t)$. This dynamical feedback is thought to be the origin of the structural freezing which occurs in an idealized "glass transition".[5,8,9] In our case, the memory function $M(k,t)$ is split into a fast, "binary" contribution $M_B(k,t)$ (essentially the one considered in the viscoelastic model) and a slow "collective" part which incorporates the self-consistency effect. The MC result for the latter contribution reads[10]

$$M_{\mathrm{MC}}(k,t) = (nk_B T/16\pi^3 m) \int d\mathbf{q} \, [V(\mathbf{q},\mathbf{k}-\mathbf{q})]^2 \Delta(q, |\mathbf{k}-\mathbf{q}|; t) . \tag{4}$$

Here the vertex $V(\mathbf{q},\mathbf{k}-\mathbf{q})=q^z c(q)-(\mathbf{k}-\mathbf{q})^z c(|\mathbf{k}-\mathbf{q}|)$, where $c(q)=[S(q)-1]/nS(q)$ is the direct correlation function. Moreover

$$\Delta(q,p;t)=F(q,t)F(p,t)[1-\phi(q,t)\phi(p,t)] , \quad (5)$$

where $\phi(q,t)=F_0(q,t)/F_s(q,t)$, $F_s(q,t)$ being the self-intermediate scattering function and $F_0(q,t)=\exp[-(k_BT/2m)q^2t^2]$ the free-particle limit of both F and F_s. At short times $\Delta(q,p;t)$ vanishes as t^4; in this regime the memory function is essentially $M_B(k,t)$ and the viscoelastic model appears to be justified.

The situation at intermediate and long times can, however, be quite different. Beyond a microscopic time scale the free-particle term in Eq. (5) becomes negligible and the surviving long lasting portion of Δ yields in Eq. (4) a positive, slowly decaying $M_{\mathrm{MC}}(k,t)$ which accounts for the full memory function in this regime. Thus the MC contribution leads to an increase of the area under $M(k,t)$ and after Eq. (2) we may qualitatively expect a slower decrease of $F(k\approx k_m,t)$ at long times.

An approximate evaluation of the effect can be made by noting that in Eq. (4) the slowest contributions effective in the time scale of MD simulations are those with $q\approx|\mathbf{k}-\mathbf{q}|\approx k_m$, as already pointed out.[5,6,8,11] This permits a considerable simplification of Eq. (4) which for $q\approx k_m$ becomes

$$M_{\mathrm{MC}}(k_m,t)\approx(k_BT/8\pi^2mn)A^2k_m^3[f(k_m,t)]^2[1-\phi^2(k_m,t)] , \quad (6)$$

where $f(k,t)\equiv F(k,t)/S(k)$ and A is the area under the main peak of $S(q)-1$.[6,8] As already mentioned, the term with $(F_0/F_s)^2$ has a fast temporal decay and, exactly as for the viscoelastic part M_B, its contribution to Eq. (1) may be evaluated by taking $z=0$. By performing the Vineyard approximation $f\approx F_s$, we obtain

$$\int_0^\infty dt(fF_0/F_s)^2\approx\int_0^\infty dt[F_0(k_m,t)]^2=(\pi m/k_BT)^{1/2}/2k_m\equiv\mu . \quad (7)$$

The leading MC contribution of Eq. (6) has instead a slow character and the z dependence of its Laplace transform has to be retained. For the moderately supercooled state at 270 K one may attempt to solve Eq. (6) in a perturbative way by inserting the bare viscoelastic propagator $f(k_m,t)=\exp[-\gamma(k_m)t]$. Then the memory equation (1) can be written as

$$\hat{f}(k_m,z)=\left[z+\frac{\gamma(k_m)}{1-\alpha+c\gamma(k_m)/[z+2\gamma(k_m)]}\right]^{-1} , \quad (8)$$

where the dimensionless quantities $c=A^2k_mS(k_m)/8\pi^2n$ and $\alpha=c\gamma(k_m)\mu$ fix the respective magnitudes of the slow and fast contributions to $M_{\mathrm{MC}}(k,t)$. Translating Eq. (8) in the time domain and solving the corresponding differential equation we readily obtain

$$f(k_m,t)=\exp(-\Gamma_0t)\{\cosh(\Gamma_1t)+[(\Gamma_0-\gamma')/\Gamma_1]\sinh(\Gamma_1t)\} . \quad (9)$$

Here $\Gamma_0=\gamma+\frac{1}{2}(c+1)\gamma'$ and $\Gamma_1=\frac{1}{2}\{[2\gamma+(c-1)\gamma']^2+4c\gamma'^2\}^{1/2}$, with $\gamma=\gamma(k_m)$ and $\gamma'=\gamma/(1-\alpha)$. At long times Eq. (9) yields a nearly exponential time decay with a damping rate

$$\Gamma=\gamma+\tfrac{1}{2}(c+1)\gamma'-\Gamma_1 . \quad (10)$$

The results of (9) and (10) can be checked against our MD findings at intermediate and long times. The decrease of the decay rate is already appreciable in the ordinary liquid at $T\approx318$ K, where from structural data one deduces $A\sigma=1.74$, $c=0.89$, and $\alpha=0.115$. The renormalized slope $\Gamma=0.253$ ps^{-1} is now in very good agreement with the value 0.255 ps^{-1} obtained by a best exponential fit of the MD data in the range 4–8 ps. However, at 318 K the overall effect in this time regime is not so dramatic, since $f(k,t)$ is already decreased substantially from its initial value 1 (e.g., the value at 7 ps is ≈0.1).

In the supercooled state at $T\approx270$ K the effect of the MC terms is instead much more spectacular. Here, the renormalized slope (deduced from $A\sigma\approx2.5$, $c\approx2.24$, and $\alpha\approx0.225$) turns out to be $\Gamma=0.126$ ps^{-1}, which corrects substantially the "bare" value $\gamma=0.28$ ps^{-1} and compares favorably with the best fitted MD value 0.132 ps^{-1}. The improvement for long times is apparent from Fig. 1, where the "tails" of the viscoelastic and MC theories are compared with the MD data by arbitrarily adjusting the theoretical amplitudes at 3 ps. In the time range of interest $f(k,t)$ is now considerably larger than at 318 K. The simplifying approximations somewhat affect the actual amplitudes predicted by Eq. (9), which are about 15% *higher* than the MD values. In any case, even on an absolute scale the improvement is noticeable: taking again $t=7$ ps as a typical point, Eq. (9) predicts a value 0.35, to be compared with the MD result 0.30 and with the value 0.15 of the viscoelastic model. In conclusion, the MC contribution to de Gennes slowing of density fluctuations is important, and the leading effects appear to be correctly accounted for by a relatively simple analytical approach.

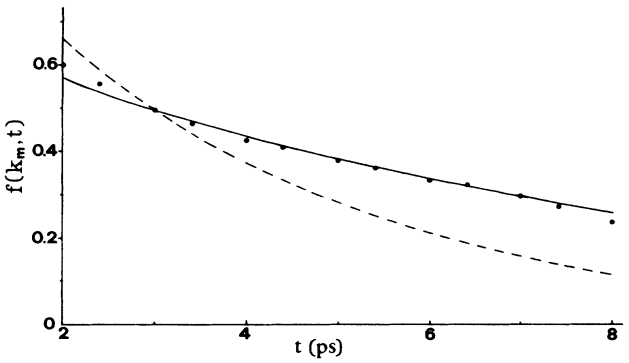

FIG. 1. Long-time behavior of the intermediate scattering function in supercooled liquid rubidium at 270 K and at a wave vector $k\sigma=6.75$. The dots are the MD results, the dashed line is the result of the viscoelastic model, and the solid line includes the mode-coupling contributions. The amplitude of both theoretical curves has been adjusted to the MD value at $t=3$ ps.

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