Dynamical Signature at the Freezing Transition

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Suspensions of (nearly) identical spheres have turned out to be valuable experimental model systems for exploring dynamical properties of condensed matter, particularly the dynamics of the first order freezing-melting transition and the glass transition. The dynamics of concentrated suspensions are generally pictured in terms of the cage effect: the transient localization of particles by their neighbors. Another aspect of the dynamics, best exposed by the current-current correlation function (CCCF), is backflow: a particle current in one direction must, as dictated by conservation of number density, be compensated by a current in the opposite direction. However, this aspect of the cooperation among particles in dense fluids has been rarely considered.

Recently, we have investigated the CCCF for suspensions of particles with hard-spheres like interactions via Dynamic Light Scattering (DLS) experiments as function of both volume fraction ϕ and scattering vector q [1]. The CCCF, $C(q,\tau)$, or autocorrelation function of the longitudinal current, $j(q,\tau)$, is defined as [2],

$$C(q,\tau) = q^2\langle j(q,0)j^*(q,\tau)\rangle = -\frac{d^2 f(q,\tau)}{d\tau^2} \qquad (1)$$

Here τ is the delay time, q is the scattering vector amplitude, and $f(q,\tau)$ is the coherent intermediate scattering function (ISF) or normalised autocorrelation function of the qth spatial Fourier component, $\Delta\rho(q,\tau)$ of the particle number density fluctuations,

$$f(q,\tau) = \frac{\langle \Delta\rho(q,0)\Delta\rho^*(q,\tau)\rangle}{\langle|\Delta\rho(q)|^2\rangle} \qquad (2)$$

In [1], we have found a scaling of the space and time variables of the CCCF for suspensions in thermodynamic equilibrium, below the freezing point ($\phi < \phi_f = 0.494$). However, in the metastable fluid, at volume fractions above freezing ($\phi \geq \phi_f$), this scaling fails. Failure of the scaling is identified through the appearance of an inflection point in the CCCF and is best exposed by observing a minimum in the logarithmic derivative $L(q,\tau) = dlog|C(q,\tau)|/dlog(\tau)$ (see Fig. 1). This dynamical singularity was first observed at ϕ_f and in the vicinity of the peak of the structure factor, then expanding progressively to other q's when the volume fraction is increased. At the glass point, $\phi \approx 0.565$, the CCCF at all experimentally accessible q's display an inflection point.

We now perform Molecular Dynamic (MD) simulations to confirm and better understand our experimental findings. Preliminary results are presented in Fig. 2 and confirm the appearance of a minimum in $L(q,\tau)$ around ϕ_f. Both experimental and simulation data will be presented and discussed.

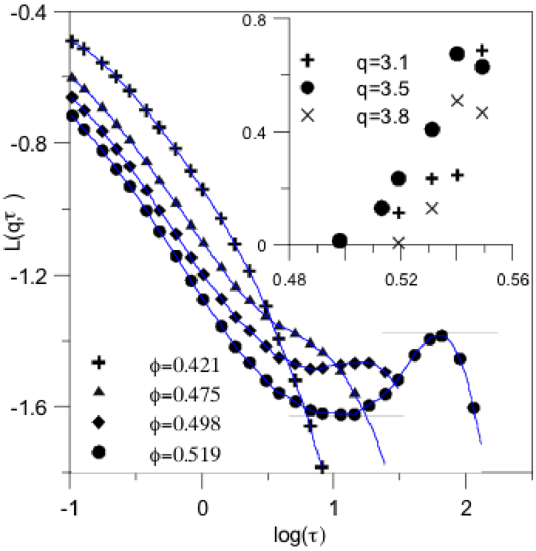

FIG. 1. Logarithmic derivative of the CCCF, $L(q,\tau)$, from DLS experiments, versus delay time τ/τ_B, normalised by the Brownian time ($\tau_B = 0.013s$) in the vicinity of the peak of the structure factor for several volume fractions as indicated.

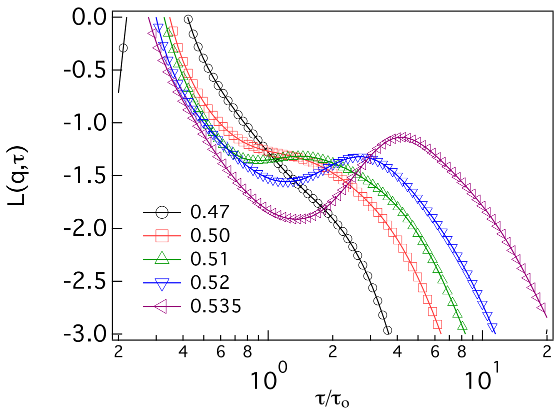

FIG. 2. Logarithmic derivative of the CCCF, $L(q,\tau)$, from MD simulation, versus delay time τ/τ_o, normalised by the thermal time (τ_o) in the vicinity of the peak of the structure factor for several volume fractions as indicated.

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[2] J.-P. Hansen and I.R. McDonald *Theory of Simple Liquids* (Academic Press, London, 1986).