LETTERS TO THE EDITOR

NOTES

The length scale dependence of viscosity approaching the glass transition in glycerol

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As yet, there is no conclusive evidence that the glass transition is a true phase transition. In practice, the transition from a supercooled liquid to a glass is due to the liquid slowing down and falling out of equilibrium as it is cooled through the glass transition temperature T_g. Equilibrium susceptibility measurements[1] of supercooled liquids have shown that the characteristic relaxation time of the liquid is growing faster than an Arrhenius law. These observations, coupled with arguments based on the extrapolation of the thermodynamics[1-3] below T_g suggest that an underlying phase transition may be driving the dynamics of the supercooled liquid. Recently, Kiyachenko and Litvinov[4] reported the development of a scale dependence in the viscosity of glycerol upon cooling towards T_g. They suggested that their result may be evidence of such a phase transition. In their experiment, Kiyachenko and Litvinov measured the viscosity of glycerol on two different length scales as it was cooled towards the glass transition. They reported that the effective viscosity measured on a length scale of $L \sim 10$ nm grew with respect to the viscosity measured on a larger length scale, $L \sim 1$ mm, as the liquid was cooled. They interpreted this observed spatial dispersion in the viscosity in terms of a growing correlation length, ξ of critical fluctuations of the low temperature glass phase.

The technique they used to measure the viscosity on the microscopic length scale was photon correlation spectroscopy.[5] Small particles placed in a liquid diffuse through it via Brownian motion. For spherical particles, the diffusion coefficient is $D = k_B T/[6\pi\eta r]$ where k_B Boltzmann's constant, T is the temperature, η is the viscosity of the liquid, and r is the hydrodynamic radius of the particle. Monochromatic light scattered from such particles will exhibit intensity fluctuations whose power spectrum has a halfwidth of $\Gamma = Dq^2$ where q is the scattering wave vector. This relationship has proven to be quite reliable for low concentrations of particles without long-range interactions.[5] Photon correlation spectroscopy measures Γ in the time domain by directly measuring the intensity autocorrelation function of the temporal fluctuations of the scattered light

$$\langle I(t)I(0)\rangle = \langle I\rangle^2[1 + A\exp(-2\Gamma t)], \quad (1)$$

where $A \leqslant 1$ is a constant determined by the geometry. By measuring Γ as a function of temperature with small poly-

styrene spheres ($r = 17.2$ nm), Kiyachenko and Litvinov were able to measure the viscosity of glycerol on a microscopic scale.

Their measurement covered the temperature range from 50 °C down to -30 °C; note that this is very far away from $T_g = 180$ K where the viscosity reaches 10^{13} Poise. The limitation on getting closer to T_g is that the decay time, Γ^{-1}, gets too long to measure due to the increasing viscosity. They found that the ratio of the microscopic viscosity to the macroscopic viscosity increased 60% as the temperature was lowered from 50 °C to -30 °C. They interpreted this temperature dependence as due to critical fluctuations of the glass phase, obtaining the correlation length, ξ from the effective rescaling of the particle radii:

$$D = k_B T/[6\pi\eta_0(r + \xi)]. \quad (2)$$

This gave a correlation length that increased from a few Å at 50 °C to ~ 12 nm at -30 °C.

We have attempted to reproduce their results. Instead of comparing the macroscopic viscosity with the microscopic viscosity measured for a single size sphere, we have measured the viscosity for a range of sphere sizes in the hope of better characterizing the spatial dispersion. We have measured the viscosity of glycerol over the range -20 °C $< T < 100$ °C using polystyrene spheres of sizes $r = 10, 27, 55$, and 102 nm.

Our experimental arrangement is a conventional 90 degree scattering geometry.[5] The laser is a light-stabilized water-cooled argon laser running at 488 nm. The scattering cell is isolated in a dry nitrogen atmosphere at slight positive pressure. The scattered light signal is detected with a PMT and sent to an ALV 5000 correlator.

We prepared our samples in the fashion described in Ref. 4 at concentrations on the order of $\phi \sim 10^{-5}$. In order to remove the water, the samples were placed in a vacuum oven at 80 °C for 48 h. The final samples all had water content $\sim 0.2\%$ as established in the actual measurements; this will be discussed below. The size distributions of all of the polystyrene sphere samples were checked by making water samples with $\phi \sim 10^{-5}$ and measuring the intensity autocorrelation function at 25 °C. This also served to calibrate the experiment using a well understood system. The average size and polydispersity are obtained from the first and second cumulants of the intensity autocorrelation function.[5,6] The values we obtained are $r = 10.1 \pm 0.8$ nm, 27.0 ± 1.4 nm, 55.1 ± 1.9 nm, and 102.3 ± 2.1 nm. These
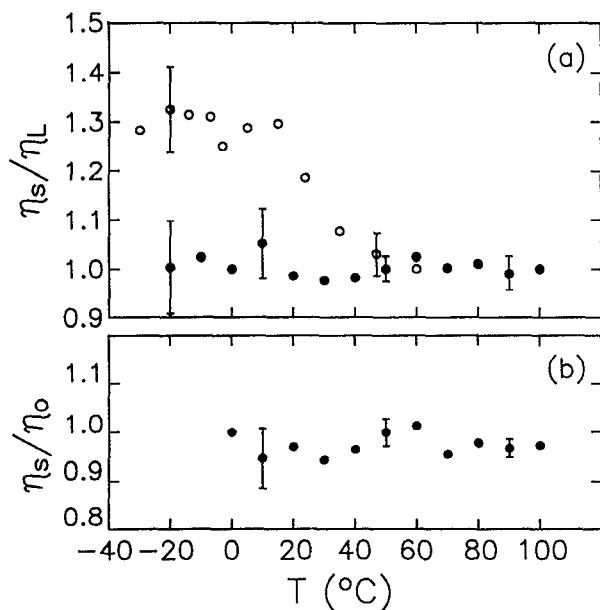
FIG. 1. (a) (●) The temperature dependence of the ratio η_s/η_L of the viscosities measured with the 27 nm and 102 nm polystyrene spheres in glycerol. (O) The behavior expected for this ratio based upon the data in Ref. 4. (b) The temperature dependence of the ratio η_s/η_0 of the viscosity measured with the 27 nm spheres to the tabulated viscosity data for pure glycerol. The ratio is uniformly low and is consistent with a 0.2% water content.

results agree well with the values quoted by the distributor (Duke Scientific) using the same technique.

We characterized the glycerol samples at 60 °C; this is above the temperature range at which Kiyachenko and Litvinov observed dispersion in the viscosity with their 17.2 nm spheres. We measured the average sphere size and polydispersity of each sample. For the three larger sizes, we obtained the same results that we obtained in water if we assumed that the glycerol samples had water concentrations of 0.2%. This was established using the tabulated viscosity data on glycerol-water solutions.[7]

In Fig. 1(a), we plot (●) the viscosity ratio, η_s/η_L, measured with the 27 nm and 102 nm spheres over the range $-20\,°C < T < 100\,°C$. There is no apparent spatial dispersion in this ratio. The 55 nm sphere data shows the same lack of dispersion and has been omitted for clarity. We also plot (O) the expectation based upon the results of Kiyachenko and Litvinov. From Eq. (2), we would expect for our measurement

$$\eta_s/\eta_L = [r_L/r_s][(r_s + \xi)/(r_L + \xi)] \qquad (3)$$

using the correlation length values of Kiyachenko and Litvinov. It is clear that our measurement disagrees with these expectations. In Fig. 1(b), we plot the ratio of the viscosity measured with the 27 nm radius spheres and the tabulated viscosity for pure glycerol: η_s/η_0. This also shows no temperature dependence. The ratio is consistently less than one, which can be accounted for by assuming that the glycerol contains 0.2% water. Using Eq. (2), our data places a limit on the correlation length: $\xi < 2$ nm at $-20\,°C$.

While the three larger size spheres exhibited no anomalous behavior in glycerol, the 10 nm spheres did behave differently. We found that the effective radius of these spheres was ~ 1.3 times larger than expected based upon our results in water. In addition, we found that the second cumulant was much larger, suggesting that some clustering of the spheres had occurred. Placing the sample cuvette in an ultrasonic cleaner for 2 min decreased the average radius and polydispersity down close to the values obtained with the water samples. Over a 24 h period, the sample reverted back to the polydisperse distribution. This suggests that the smallest spheres are somewhat less stable in glycerol than in water and precluded their use in obtaining reliable data. However, we found that the aged sample exhibited no observable temperature dependent dispersion. The measured values in the aged state are consistent with a small but significant fraction ($\sim 5\%$) of the spheres forming dimers. We suspect that the effect reported by Kiyachenko and Litvinov was due to clustering of the small spheres that they used.

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