

## Increase in scale length in a liquid as the glass transition temperature is approached

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A pronounced spatial dispersion has been observed for the viscosity of supercooled glycerin. This dispersion indicates a spatial scale which increases as the glass transition temperature  $T_g$  is approached. The scale length is  $120 \text{ \AA}$  at  $T - T_g = 60 \text{ K}$ .

The behavior of the properties of substances near the glass transition is intriguingly similar to events observed near second-order phase transitions: The specific heat,<sup>1-3</sup> the coefficient of thermal expansion,<sup>4</sup> and the relaxation times<sup>2,5</sup> increase anomalously near the liquid-glass transition. The relaxation is obviously not exponential.<sup>2,5</sup> To what extent the similarities stem from identical physics is not known at this point, although the possibility that the glass transition is a phase transition of a sort has been under

constant discussion in recent years.<sup>6,7</sup> For ordinary phase transitions these anomalies stem from an increase in the scale length of fluctuations in the order parameter. The nature of the "critical" fluctuations in the case of a liquid-glass transition is not known. The apparent difficulty is that the conventional research methods, based on the scattering of some sort of radiation, are ineffective here because of the high symmetry of the possible order parameter and the absence of a contribution of "critical" fluctuations to the scattering in low orders.

There is another possibility for a manifestation of a large-scale structure: in the spatial dispersion of properties that change anomalously. The property which experiences the greatest anomaly near the glass transition is the shear viscosity. In the present letter we report a study of the spatial dispersion of the viscosity of glycerin, based on measurements of this viscosity at two very different flow scale dimensions: (1) a "microscopic" scale dimension, specifically, that corresponding to the Brownian motion of polystyrene latex particles, and (2) a "macroscopic" scale dimension, in a capillary viscosimeter.

The "microscopic" viscosity is measured by light-beating spectroscopy.<sup>8</sup> This method is basically one of measuring the spectral broadening of a laser beam scattered by Brownian particles. The spectral half-width  $\Gamma$  is related to the diffusion coefficient by  $\Gamma = Dq^2$ , where  $q$  is the scattering wave vector. The viscosity  $\eta$  is determined from the Einstein-Stokes formula

$$D = kT/6\pi\eta r \quad (1)$$

where  $r$  is the radius of the latex particle,  $k$  is the Boltzmann constant, and  $T$  is the temperature.

For the present measurements, we use the correlation light-beating spectrometer described in Ref. 9. The beam from a He-Cd laser, with a wavelength of 442 nm, excites the scattering. The noise and the instability of this laser are suppressed by a system for stabilizing the output power. A constant-temperature system keeps the sample temperature constant within 0.05 K at the point of interest between  $-50^\circ\text{C}$  and  $100^\circ\text{C}$ .

Previously purified glycerin is mixed with an aqueous suspension of the latex, and then the mixture is dehydrated by pumping off the vapor as the mixture is heated to  $80^\circ\text{C}$ . The water content is no greater than 0.5%, according to measurements of the viscosity. The latex concentration is  $10^{-5}$  by weight; the average distance between particles is  $\sim 1\ \mu\text{m}$ . The radius of the particles is determined by the method of light-beating spectroscopy in measurements involving diffusion in water:  $172\ \text{\AA}$ .

We were not able to carry out measurements at temperatures below  $-40^\circ\text{C}$ . The rapid increase in the viscosity with decreasing temperature causes a pronounced contraction of the line of the scattered light. At  $T \approx -40^\circ\text{C}$  we find  $\Gamma^{-1} \approx 10^3\ \text{s}$ , comparable to the scale times for the drift of the parameters of the apparatus. The error in the measurement of  $\Gamma$  is on the order of  $\Gamma$  itself and cannot be reduced by increasing the data accumulation time.

The "macroscopic" viscosity ( $\eta_0$ ) of the same glycerin sample (with the latex) is measured by a capillary viscosimeter with a capillary diameter of 1.5 mm. Between

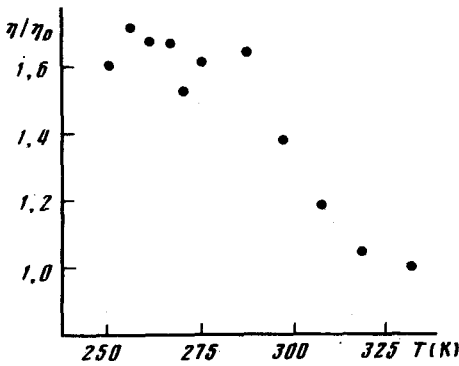


FIG. 1. Temperature dependence of the ratio of the "microscopic" and "macroscopic" viscosities,  $\eta/\eta_0$ .

+ 50°C and - 30°C the viscosity increases from 1.9 to  $7 \times 10^3$  P. The values found agree within 10% with tabulated values.<sup>10,11</sup>

Figure 1 shows the viscosity ratio  $\eta/\eta_0$  as a function of the temperature. We see that as the temperature is lowered, the viscosity values measured over the different flow scale lengths begin to differ markedly, indicating the appearance of a significant spatial dispersion. The scale length of the spatial dispersion,  $\xi$ , can be estimated from the effective renormalization of the radius of the Brownian particles. By analogy with the case of the critical point,<sup>12</sup> we rewrite (1) as

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

Figure 2 shows  $\xi$  versus  $\epsilon_T = (T - T_g) / T_g$ , where  $T_g$  is the glass transition temperature. We note that  $\xi$  reaches 120 Å at  $\epsilon_T = 0.3$ , which is in the remote neighborhood of the transition point for second-order phase transitions. This result should mean either an anomalously large nucleation size  $\xi_0 = \xi\epsilon_T^\nu$ , or an anomalously large critical index  $\nu$ . According to the approximation of a self-consistent field, we would have  $\nu = 1/2$  and thus  $\xi_0 \approx 60$  Å. If we assign  $\xi_0$  a typical molecular dimension, 5–10 Å, we find  $\nu \approx 2-3$ . We cannot accept either of these estimates as reasonable. An important point is that the anomalies in other properties also develop over a broad temperature region.<sup>1-4</sup> The reason for this behavior is not clear. One possibility is that the temperature is of secondary importance for glass-liquid transitions, and the transition results from a change in the density of the system. In Refs. 6 and 13, for example, a liquid-glass transition was achieved in a hard-sphere model, where the temperature is

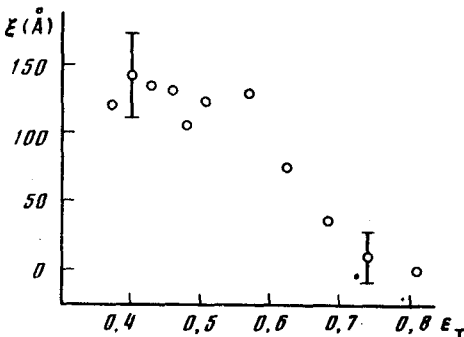


FIG. 2. Scale length of the spatial dispersion,  $\xi$ , versus the reduced temperature  $\epsilon_T$ .

by no means an important variable. The parameter which is a measure of the proximity to the transition point in this case is  $\epsilon_v = (v - v_g)/v_g$ , where  $v$  is the specific volume of the system, and  $v_g$  is the specific volume at the glass transition point. Using data<sup>14</sup> on  $v(T)$  for glycerin, we find  $\epsilon_v = 0.025$  for the points nearest the glass transition. We then find  $\xi_0 = \xi \epsilon_v^{1/2} \approx 20 \text{ \AA}$ , which is close to typical molecular dimensions.

The increase in the scale dimension in a supercooled liquid toward the transition point which we have observed is an important result. It is important for determining the actual picture of the liquid-glass transition; in particular, it may be of assistance in linking the anomalies in the thermodynamic properties to the nature of the relaxation processes on the basis of models developed for phase transitions.<sup>15,16</sup>

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