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Stokes-Einstein Relation in Supercooled Aqueous Solutions of Glycerol

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The diffusion of glycerol molecules decreases with decreasing temperature as its viscosity increases in a manner simply described by the Stokes-Einstein relation. Approaching the glass transition, this relation breaks down as it does with a number of other pure liquid glass formers. We have measured the diffusion coefficient for binary mixtures of glycerol and water and find that the Stokes-Einstein relation is restored with increasing water concentration. Our comparison with theory suggests that adding water postpones the formation of frustration domains.

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Most liquids become solids after they are cooled through their melting temperature T_m following a first order thermodynamic transition. A notable exception is a class of molecular fluids known as glass formers which can stay in a metastable state as supercooled liquids to temperatures substantially below their equilibrium melting transition. The thermodynamic properties of the supercooled liquid are a continuous extrapolation of the liquid state from above T_m. On further cooling the dynamical and transport behavior, viscosity, diffusion, and motional relaxation times, exhibits such a dramatic slowdown over a narrow temperature range, that there appears to be a transition to a rigid but amorphous solid state at a characteristic temperature T_g, called the glass transition [1,2].

According to the Stokes-Einstein (SE) relation the product of viscosity and diffusion coefficients is simply proportional to the absolute temperature [3].

$$D = \frac{k_B T}{6\pi\eta r_s}, \tag{1}$$

In Eq. (1), D is the translational diffusion coefficient, η is the viscosity, k_B the Boltzmann constant, and r_s the hydrodynamic radius. The basis for the SE relation is that the elementary units of the liquid are just Brownian particles and that the system is homogeneous. It is remarkable that many glass formers still follow this behavior even as the relaxation processes slow down. Ultimately, at low enough temperature, it fails, at least for a number of the more fragile [4] glass forming liquids.

Kivelson [1] *et al.* have developed a theory for frustration limited domains (FLD) that form at a temperature T^* above the melting temperature T_m. Although these domains are energetically favorable on a local scale their existence affects diffusional and rotational relaxation differently giving rise to breakdown of the SE relation. In this Letter we present diffusion measurements of four aqueous solutions of glycerol and compare with viscosity measurements to show that the SE relation fails for glycerol; but that this relation can be restored at low temperatures through addition of water. With the FLD theory we extract the temperatures for domain formation T^* for the four solutions and we show they are consistent with the temperatures where we first observe deviation from the SE relation, providing a direct confirmation of these theoretical ideas. To study glass formation we have measured the diffusion coefficients of binary mixtures, Fig. 1. The mixtures allow systematic and continuous control of the essential molecular interactions involved, an approach that may also prove useful for numerical simulations.

Among glass formers, glycerol is well studied having an intermediate fragility [5] $m = 53$, glass transition temperature $T_g = 190$ K, and melting temperature $T_m = 290$ K. It is strongly resistant to crystallization [6,7] as are its aqueous solutions [8–10]. For glycerol concentrations above 55% they are good single-phase glass formers [11]. The concentration dependent glass transition temperature has been measured [12,13] and can be described quite well by an empirical formula [14]: $T_g = 190w_1 + 136w_2 + 27w_1w_2$, where w_1 and w_2 denote the weight concentration of glycerol and water, respectively, such that T_g smoothly decreases with increasing water content as is shown in Fig. 2.

Samples were prepared with 100, 95, 90, and 85% glycerol by weight, using pure glycerol (99.9%, Fisher Scientific) and D_2O (99.9%, Cambridge Isotopes). The ^{1}H NMR signal, which we used for measurement of diffusion, was therefore selectively sensitive to the diffusion of the glycerol molecule. The mixtures were loaded into pyrex glass ampoules in the dry nitrogen atmosphere of a glove bag. The ampoules were flame sealed while the liquid mixture inside was frozen with liquid nitrogen. The diffusion measurements were performed by proton NMR stimulated-echo sequences in the fringe magnetic field, $H = 4.28$ T, ^{1}H frequency of 182 MHz, of a superconductive magnet with a magnetic field gradient $G = 42.3$ T/m. In order to improve signal to noise, and hence resolution in diffusion, we used the frequency jumping method developed by Sigmund and Halperin [15,16], allowing the near-simultaneous collection of data from 17 independent NMR-sample slices, each 110 microns thick.

The slowdown in dynamics of a glass former is marked by deviation of the temperature dependence of diffusion from the Arrhenius behavior that is typical at high temperatures: $\propto e^{-E/k_BT}$. The modified temperature dependence can usually be represented by the Vogel-Tamman-Fulcher (VTF) equation [17–19] which, for the diffusion coefficient D, is given by

$$D = A_0\sqrt{T}\exp\left(-\frac{B}{T - T_0}\right). \tag{2}$$

Here A_0, B, and T_0 are phenomenological constants determined from experiment. At still lower temperatures, close to T_g, the nonexponential features of relaxation, diffusion, and viscosity are often best captured by stretched exponential behavior. A theoretical basis that describes the continuous evolution of glass forming dynamics with decreasing temperature has not yet been established. Nonetheless, it is clear that the molecular interactions must play a crucial role.

The logarithm of the diffusion coefficient for glycerol is plotted as a function of the inverse temperature in Fig. 1 to emphasize deviation from Arrhenius behavior which would be a straight line in this figure. The diffusion coefficients shift to the right with increasing water content while retaining a temperature dependence similar to that for pure glycerol, at least in the high temperature region. But at lower temperatures the diffusion for solutions is softened compared to that of pure glycerol. To get a quantitative assessment, we fit the experimental diffusion coefficients to the VTF relation and present the important parameters for these fits in Fig. 2 along with T^*, determined from the viscosity data [20,21] analyzed using the FLD theory [1], and r_s, the hydrodynamic radius obtained from the SE relation, Eq. (1).

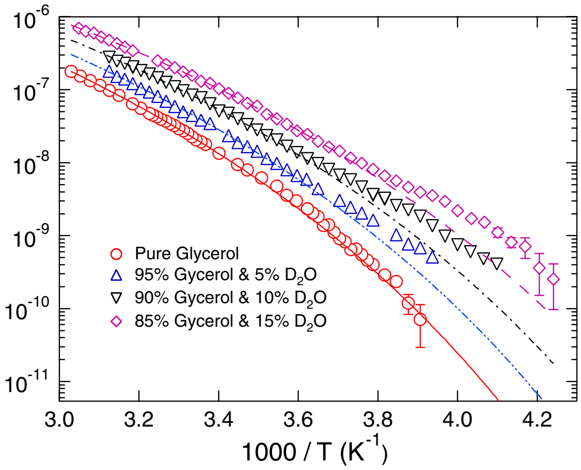

FIG. 1 (color online). The logarithm of the diffusion coefficient D of glycerol as a function of inverse temperature for various aqueous solutions of glycerol. The curves are fits to the VTF formula.

The VTF relation, Eq. (2), can be derived from a free volume theory [22]. The prefactor A_0 in this relation is a constant, at most a weak function of water concentration; the activation energy B was found to be a weak, but systematically decreasing, function of water concentration; and the temperature T_0 corresponds to full arrest of the molecular dynamics at a temperature where there would be zero free volume. This temperature should be less than, but closely related to, the glass transition temperature [2]. A direct comparison between the two is given in Fig. 2, showing that T_0 scales with T_g.

The VTF fits shown in Fig. 1 were performed for diffusion coefficients in the high temperature region. They deviate from the experimental values at low temperature where $D \approx 10^{-8}$ cm^2 s^{-1}. In order to understand the failure of the VTF formula at low temperature, we return to the free volume theory from which the VTF relation is derived. In this theory, the diffusion of the molecule is associated with the potential cage formed by its neighbors [22], such that the molecular interactions are described in a mean-field way. In the case of glycerol and its aqueous solutions, the dominant molecular interaction is hydrogen bonding (H bonding) and the potential cage should arise from these bonds. Numerous theoretical investigations on H bonding have been conducted for glycerol, water and other H bonding dominated alcohols [23–26] and it has been shown that the detail of H bonding and its effects are

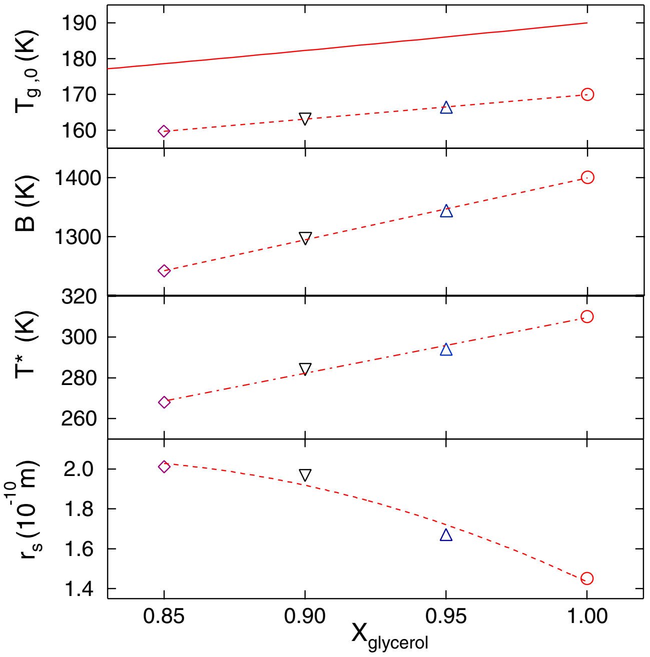

FIG. 2 (color online). VTF parameters, the domain formation temperature T^*, and the hydrodynamic radius r_s as a function of glycerol concentration in aqueous solutions. The solid curve is the glass transition temperature T_g, taken from the empirical formula given in the text. It closely parallels the VTF parameter T_0. The dashed lines are guides to the eye.

complex: one molecule can have different H bonding states depending on the number of bonds; and H bonding can be distinguished as either intermolecular or intramolecular [23], affecting diffusion differently. The lifetime of the H bond is also temperature dependent [23,24]. The more intermolecular H bonding a molecule has, the more of an obstacle there is to diffusion. This intuitive idea is confirmed in calculations by Marti *et al.* [25] for water and by Matsumoto *et al.* [26] for methanol. The molecular dynamics calculations by Chelli *et al.* [23] and Padro *et al.* [24] indicate that the average number of H bonds per molecule is higher for glycerol than water, and their lifetime in glycerol is about 6 times longer [24]. The average lifetime of a H bond in glycerol can be described by an Arrhenius equation [23] but the state of H bonding also varies with temperature [23]. This complicated situation goes beyond the simple free volume picture [22] and leads to failure of the VTF relation at low temperature where these additional temperature dependences come into play.

Fits to the SE relation in the high temperature limit give the results for r_s in Fig. 2 with a satisfying consistency for different water mixtures but systematically increasing by 25% over the range of water concentrations. In terms of H bonding we argue that a dynamical complex of glycerol and water in binary mixtures is the relevant elementary unit, akin to the ideal Brownian particle, having a larger effective radius than pure glycerol which increases systematically with water content. The increase in the diffusion coefficient of glycerol with dilution in aqueous mixtures can be ascribed to the decrease in the effective interaction between these Brownian clusters that we associate with the weaker intermolecular H bonding in water.

In Fig. 3 we show the temperature dependence relative to the glass transition of $D\eta/T$, normalized at high temperature. The viscosity data for pure glycerol are taken from smooth fits of two data sets [20,21] which are consistent with each other to $\approx 3\%$. The viscosity of the aqueous solutions are taken from smooth fits to the data by Segur *et al.* [20]. At temperatures $T/T_g < 1.62$ we resolve a breakdown in the SE relation for pure glycerol beyond the estimated measurement error in diffusion which is represented by the scatter in our data. The temperature at which this breakdown is observed moves to lower temperature with increasing amounts of water. In fact, for the 85% sample the SE relation holds over the entire range for which there are viscosity data available. The behavior of pure glycerol we report here matches qualitatively that of other glass formers where larger deviations from the SE relation are observed at temperatures closer to their glass transition. Collectively, these results on glass formers are consistent with theoretical models that have recently been proposed [27] suggesting failure in the SE relation irrespective of fragility.

For pure liquids, such as glycerol, Arrhenius behavior is observed at high temperatures in both diffusion and viscosity. So it is natural to expect the SE relation to hold there. But at lower temperature, where VTF behavior is observed, it is not obvious that the SE relation should remain valid; or if not, what might be the mechanism responsible for its failure. One important aspect of this problem is that the viscous relaxation process is microscopic while the measurement of diffusion is macroscopic, meaning that the former is on the molecular length scale and the latter on the length scale of tens of microns. So a possible explanation for breakdown of the SE relation could be ascribed to local domain or cluster formation which can lead to dynamical heterogeneity [1,27–30].

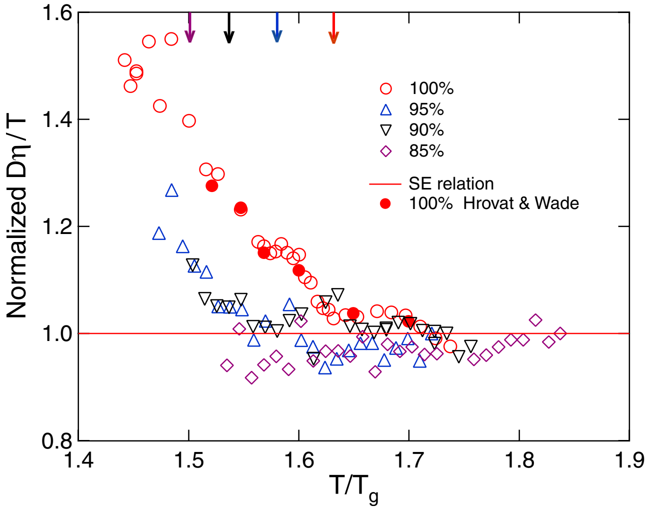

FIG. 3 (color online). Breakdown of the Stokes-Einstein relation through comparison of diffusion and a smoothed interpolation to viscosity data [20,21] for aqueous solutions of glycerol. For comparison the diffusion data of Hrovat and Wade are also shown for pure glycerol [34] with the same normalization. The validity of the Stokes-Einstein relation is limited to high temperatures. The lower limit of temperature in this figure is determined by the availability of viscosity data in aqueous mixtures. The four arrows on the top axis indicate T^*, the domain formation temperature. From left to right they are for 85, 90, 95, and 100% glycerol solutions, and are qualitatively consistent with onset for breakdown of the SE relation.

Kivelson *et al.* [1] suggested that the breakdown of the SE relation is due to dynamical heterogeneity, resulting from formation and growth of frustration limited domains below a temperature T^*. We have analyzed the viscosity data [20,21] using the FLD theory [1] to find T^* plotted in Fig. 2, and given in Fig. 3 by vertical arrows. The temperature where deviation from the SE relation appears in Fig. 3, is qualitatively consistent with the domain formation temperature T^*. In particular, they both decrease systematically with increasing water content, suggesting that the breakdown of the SE relation is controlled by the birth of these frustrated domains.

It is now well established experimentally that the SE relation fails for certain fragile glass formers in their pure form such as ortho-terphenyl [31] and tris-napthylbenzene

[32], and now for glycerol, a significantly less fragile material. However, Chang and Sillescu [33] did not find such breakdown behavior for glycerol. This is in contrast to our preliminary work [16] and that which we report here. There are significant differences ($\approx 30\%$) in the absolute values of the diffusion coefficients for pure glycerol measured by Chang and Sillescu [33] as compared with other workers [34,35], including the more precise measurements of Hrovat and Wade [34] which we have confirmed and extended to lower temperatures; see Fig. 3. This discrepancy is outside the possible error in our measurements of diffusion and it is most likely that there is systematic error in the Chang and Sillescu data that accounts for their claim that glycerol obeys the SE relation over this temperature range. We also note that the work of these authors is inconsistent with the FLD theory.

In conclusion, we have measured the diffusion coefficient of glycerol in aqueous solution. We have found that VTF behavior fails as a phenomenological form for the temperature dependence of the diffusion coefficient, but with a range of validity that extends to lower temperature with increasing water content. Similarly, we find that the SE relation breaks down for these aqueous mixtures but at a temperature that decreases progressively with increasing water content. These observations are consistent with expectations from frustration limited domain theory [1,27]. Finally, we remark that the mechanism responsible is most likely the heteromolecular hydrogen bonding which postpones the formation of domains and inhibits the breakdown of the Stokes-Einstein relation as temperature is decreased. We find that the effective intermolecular interaction from hydrogen bonding can be conveniently controlled using binary solutions.

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