



Some considerations on the transport properties of water-glycerol suspensions

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We study the self-diffusion coefficient and viscosity of a water-glycerol mixture for several glycerol molar fractions as a function of temperature well inside the metastable supercooled regime. We perform NMR experiments and verify that the system has at different concentration a fragile-to-strong crossover accompanied by the violation of the Stokes-Einstein relation. We observe that the crossover temperature depends on the water amount. Studying the fractional representation of the Stokes-Einstein relation, we find that in these systems dynamical arrest does not exhibit criticality and the transport parameters have a universal behavior. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4939087>]

I. INTRODUCTION

Glassy materials and supercooled liquids are of wide importance in science and technology. Their behavior on approaching the glass transition presents fundamental and challenging questions that have been the subject of many studies over the past century, and what actually happens when a liquid is cooled down into its amorphous glass phase is still an unsolved problem.¹ When the liquid phase approaches the glass phase, observable quantities such as transport parameters (viscosity, self-diffusion, and relaxation times) do not undergo the critical transition invoked by many theoretical models² but continuously increase up to 13 orders of magnitude. In this frame, the so called Vogel-Fulcher-Tamman formula was considered as the signature of the criticality emerging from the temperature behavior of the transport parameters toward the glass state. Today serious arguments have been proposed to remark that this formula can be simply considered a fitting expression without any physical meaning; whereas, at the same time the importance of the glass transition temperature T_g , defined only in a heuristic qualitative way, was reconsidered.³⁻¹⁰ It is commonly accepted that two characteristic features dominate the behavior of glassy liquids evolving toward the glassy state: (i) a complicated energy landscape⁹⁻¹³ and (ii) the onset of dynamical heterogeneities in which the Stokes-Einstein relation (SER) is violated.¹⁴ It has been also proposed (see, e.g., Ref. 5) that the dynamical heterogeneities are accompanied by (i) a crossover from non-Arrhenius, multirelaxation behavior (fragile or super Arrhenius¹⁵) to Arrhenius behavior in which the activation energies are well defined (strong), (ii) a decoupling of the

translational and rotational motions,¹² and (iii) an onset of Johari-Goldstein relaxation times (β)¹⁶ and a Boson peak.^{4,14,17-19}

Water and glycerol are of special interest in the context of supercooled materials: water for its intriguing and counterintuitive chemico-physical behaviors dominated by hydrogen bond (HB) interactions²⁰⁻²³ and glycerol for its strong resistance to crystallization. Glycerol can be supercooled from its stable liquid phase above the melting temperature $T_m = 290$ K down to (and below) its estimated $T_g \approx 190$ K.²⁴ The same is true when it is in aqueous solutions.²⁴ An analysis of the translational self-diffusion and the corresponding viscosity data in the supercooled regime indicates that the SER is violated for bulk glycerol, although the corresponding temperature that falls within the range $277 < T < 300$ K differs somewhat.^{9,25}

On lowering the temperature the characteristic length scale of density fluctuations increases²⁶ favoring the formation of a dynamical tetrahedrally coordinated HB network and of clustering phenomena.²⁰ The increase of fluctuations explains the diverging-like behavior of various water thermal response and transport functions when T enters the supercooled region. When T of the stable liquid phase is lowered, both HB lifetime and cluster stability increase, and this altered local structure can, in principle, continue down into the amorphous region of the phase diagram where two glassy phases characterized by different densities have been observed.²⁷

This suggests that liquid water may also be polymorphous, i.e., a mixture of a low-density liquid and a high-density liquid. In the high T regime, the high-density liquid phase predominates, the local tetrahedrally coordinated structure is not fully developed, and a more open “ice-like” HB network appears. The anomalies in water behavior are caused by

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the presence of two local liquid structures having differing local densities. At ambient pressure, metastable supercooled water is located on the phase diagram between the melting temperature $T_M = 273$ K and the homogeneous nucleation temperature $T_H = 231$ K. Below $T_g \approx 130$ K water is a glass, above that temperature it becomes a highly viscous fluid that crystallizes at $T_X \approx 150$ K. The region between T_H and T_X , referred to as the “No-Man’s Land,” has been accessed only very recently for bulk liquid water by means of coherent X-ray scattering from individual micrometre-sized droplets.²⁸

The crystallization within the no-man’s land can be retarded somewhat by confining water within narrow nanoporous structures or mixing water with systems resistant to crystallization, such as glycerol. Studies of confined water^{29–31} have found that on decreasing T the water HB networking and the HB lifetime greatly increases, indicating the presence of a fragile-to-strong dynamic crossover (or simply dynamic crossover) at $T_L \approx 225$ K at ambient pressure. At this temperature clear signs of low-density and high-density liquid phases are observed.³⁰ This confirms that polymorphism dominates the water liquid phase and also supports the liquid-liquid phase transition hypothesis.³² A first-order phase transition at the glycerol molar fraction $X_g \approx 0.15$ suggesting the presence of a liquid-liquid phase transition was recently observed.^{33,34} This result was questioned and ascribed to ice formation.³⁵

The dynamic crossover observed in confined water in combination with a violation of the Stokes-Einstein relation^{30,31} has been identified as the Widom line, i.e., the locus of the maximum correlation length ($T_L = T_W$) where the thermodynamic response functions exhibit extrema (maximum and minimum).^{36,37} On decreasing T , T_W converges to the liquid-liquid critical point C' where the correlation length diverges. Neutron experiments performed on confined water in a wide P - T interval of the water phase diagram³⁶ strongly support this hypothesis.

We examine SER in glycerol and glycerol-water solutions at glycerol molar fractions $X_g = 1, 0.8, 0.65, 0.5,$ and 0.4 in the temperature range $228 < T < 373$ K at ambient pressure. Using viscosity data $\eta(T)$ from the literature,^{38–42} we carry out a new NMR experiment to obtain the self-diffusion $D(T)$ values. A previous experiment on the same system found (i) that the Vogel-Fulcher-Tammann behavior fails as a phenomenological form for the T dependence of D but has a range of validity that extends to lower T with increasing water content and (ii) that the SER breaks down for these aqueous mixtures but at a T that decreases progressively with increasing water content. This study used the frustration limited domain theory to explain the origin of the dynamical heterogeneities.⁴³ Because the SER violation is observed in confined water at $T_L \approx 225$ K (just at the Widom line), we examine the role of the HB tetrahedral network and how it is affected by the presence of glycerol. Note that the physical chemistry of a HB is complex, i.e., HB lifetime is influenced by both the temperature and the number of HBs in the molecule. The number of possible HBs per molecule is higher for glycerol than for water,⁴⁴ and the HB lifetime in glycerol is longer than in water. The formation of the most stable

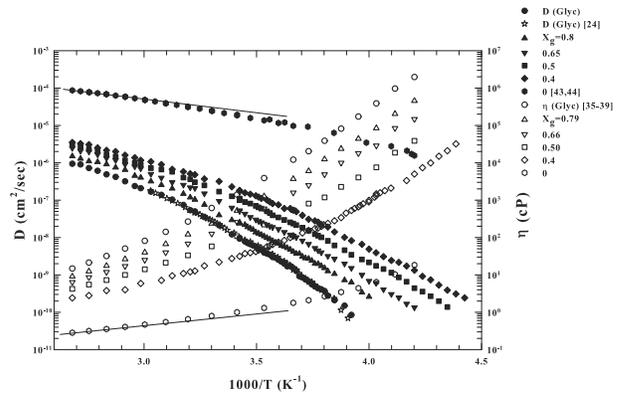


FIG. 1. Arrhenius plot (log-lin, D vs $1/T$) on a double y -axes representation of the temperature behaviors of $D(T)$ (left y -axis) and $\eta(T)$ (right y -axis) measured for water-glycerol mixtures at different concentrations. The total explored T range is 373–225 K.

configurations can be explained using an energy landscape approach.¹⁰

II. EXPERIMENTS

We carry out NMR experiments using a Bruker AVANCE NMR spectrometer operating at a 700 MHz ^1H resonance frequency, and we measure the self-diffusion D using the pulsed gradient stimulated echo (^1H -PGSTE) technique.⁴⁵ We allow the temperature of the samples to vary no more than ± 0.2 K in all of the explored T ranges. We prepare the samples at the desired glycerol molar fraction using pure glycerol (99.9%, from Fisher Scientific) and double distilled water. Because the water contribution in the NMR results resolves with respect to the glycerol spectral contribution, we can trace the self-diffusion of the water, and again we use the viscosity data supplied in the literature.^{38–42} Figure 1 uses an Arrhenius plot (log-linear, D vs $1/T$) and double y -axes to show the temperature behavior of $D(T)$ (left y -axis) and $\eta(T)$ (right y -axis) for all the studied concentrations in the 373–225 K range. Note that both the self-diffusion and the viscosity change by many orders of magnitude. The data supplied by Chen *et al.*²⁵ for pure glycerol are also shown (open stars). Chen *et al.*²⁵ studied glycerol-heavy water mixtures at several glycerol molar fractions (data not reported here). Note that the use of D_2O rather than pure water addresses the self-diffusion of the glycerol molecules in a water environment, whereas by following the water protons we measure the water molecular self-diffusion as it is affected by the presence of glycerol. In both cases, the molecular dynamics are governed by HBs between the water molecules or between the water and glycerol molecules. HBs between the glycerol molecules are possible but increasing the proportion of water causes the interactions to be dominated by the water HBs. Decreasing the temperature increases the probability that HBs will be formed and accelerates the development of the water tetrahedral HB network. Figure 1 shows $D(T)$ behavior that indicates that a decrease in temperature decreases the longitudinal mobility in both water and pure glycerol and increases system viscosity; the literature data for D of pure bulk water are also reported.^{46,47}

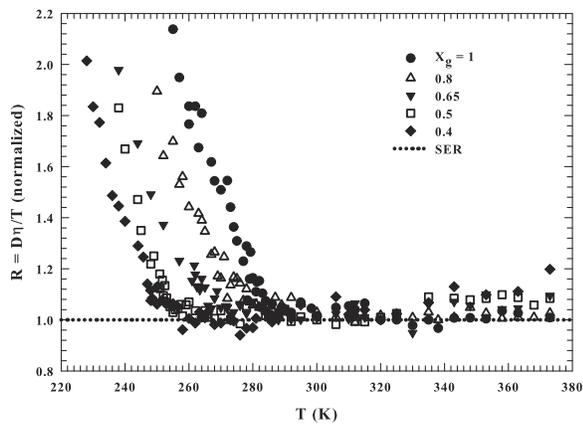


FIG. 2. The SER ratio $R = D\eta/T$ (normalized for the value at 320 K) for the pure glycerol and water-glycerol solutions at $X_g = 0.8, 0.65, 0.5$, and 0.4 as a function of the temperature. The dotted line represents the validity of the SER.

III. RESULTS

The validity of the SER can be verified using these transport data.²⁵ In the SER, the relationship between the self-diffusion coefficient D , viscosity η , and temperature T is $D \propto T/\eta$. This is usually accurate for simple liquids in high temperature regimes. In water, the SER is violated twice:⁴⁸ at $T_L \approx 225$ K (confined water³⁰) and at $T^* \approx 320$ K (bulk water⁴⁷). T^* represents also a special locus for the isothermal compressibility $K_T(T, P)$ and the thermal expansion coefficient $\alpha_P(T, P)$ in the P - T plane.²³ Figure 1 shows this as two straight lines in the high T region of the bulk water D and η data.

Figure 2 shows the SER ratio $R = D\eta/T$ normalized at 320 K for pure glycerol and the water-glycerol solution at $X_g = 0.8, 0.65, 0.5$, and 0.4 versus the temperature. The dotted line shows the validity of the SER. Note that for all concentrations there is a SER breakdown that for pure glycerol takes place at about 285 K, just near its melting temperature.^{25,49} In the water-glycerol solution, the breakdown temperature evolves inside the supercooled region by increasing the water content. Similarly, in the D_2O -glycerol system,²⁵ the SER breakdown occurs only when $X_g > 0.66$. Figure 3(a) shows the estimated SER breakdown temperatures T_L (circles) for all the studied H_2O -glycerol solutions as a function of the corresponding X_g . Note that $T_L(X_g)$ evolves linearly from the temperature of pure glycerol to the temperature of pure bulk water. Figure 3(a) also shows the T_L value (cross) measured at $X_g = 0.13$ for a H_2O -glycerol solution placed in an emulsion to retard water crystallization.³⁴ Although it is still a debated topic,³⁵ the region of diluted glycerol $0.1 < X_g < 0.2$ supports the presence of two liquid water phases with a liquid-liquid transition observed at ambient pressure.³³ Experiments performed as a function of pressure fully support the liquid-liquid critical point hypothesis for a water-glycerol metastable supercooled liquid at $X_g \approx 0.13$, $P \sim 0.05$ GPa, and $T \sim 150$ K.³⁴ The extrapolation of these latter data to pure water and a calculation based on experimental data⁵⁰ suggest that the critical temperature is located in the vicinity of 200 K. This is supported by the data in Fig. 3(a) and confirms the observation that the temperature of the SER breakdown

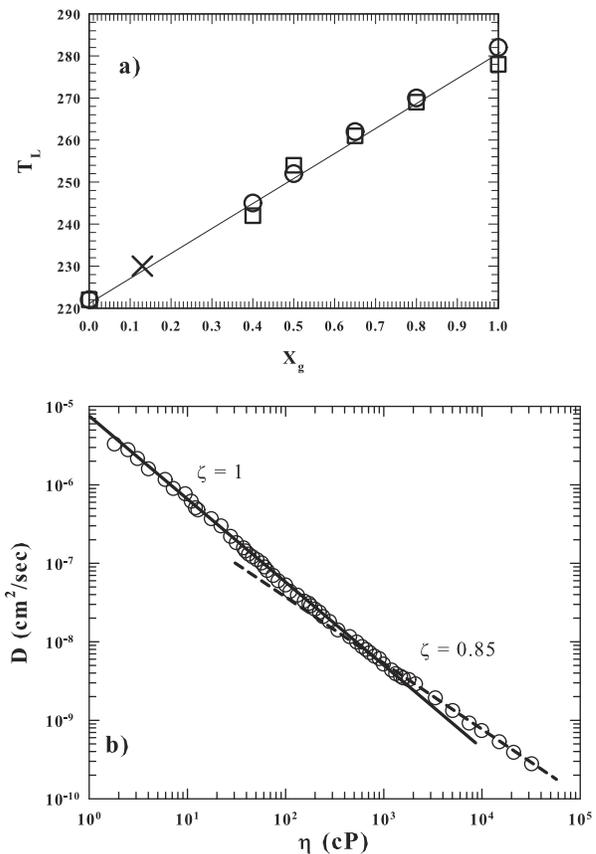


FIG. 3. (a) The SER breakdown temperatures T_L (circles) and those obtained by means of the MCT analysis (squares) versus the corresponding X_g . The cross corresponds to the T_L value measured at $X_g = 0.13$ for H_2O -glycerol solution putted in an emulsion.³⁴ (b) The scaled representation of the fractional SER with the D and η data ($X_g = 0.4$), measured at the same temperature, reported in a log-log plot as $D(\eta)$.

is coincident with the Widom temperature in confined water.^{30,31,37} Figure 3(b) uses a log-log plot to show the fractional SER $D(\eta)$ where the D and η data ($X_g = 0.4$) are measured at the same temperature. We previously demonstrated^{9,51} that SER breakdowns occurring close to T_L indicate the decoupling of transport coefficients and the existence of dynamical heterogeneities, and this implies that there are correlations between the time and length scales. In particular, before the dynamical arrest is approached the increase in time scale leads to an increase in the length scale of dynamically correlated regions in space, which suggests that supercooled liquids display dynamical scaling. Thus, below a certain temperature, the SER gives way to a fractional SER $D \sim \tau^{-\zeta}$ in which the exponent ζ is related to the characteristic spatial-temporal length scales of the “spatially” heterogeneous dynamics.^{52,53} Here the scaling exponent is $\zeta \approx 0.85 \pm 0.02$ and the onset of the breakdown of the fractional SER occurs at viscosity value $\eta \approx 1$ P. Note that the behavior of these data confirms the universality of the transport properties of supercooled liquids.^{9,51}

The universality of the ζ value indicates that the crossover from hierarchical super Arrhenius dynamics to pure Arrhenius corresponds to a dynamical transition from short length scales to long length scales.^{52,53} All the models describing the dynamical changes of the super Arrhenius

glass-forming liquids have a structural origin. This is because decreasing T increases the effective SE hydrodynamic radius (correlation length). This increase may diverge if the correlated regions show the characteristic slowing-down of critical processes. However, the originally proposed criticality cannot be observed in the transport parameters because they often evolve toward a nondivergent behavior when the temperature is lower than the glass transition temperature T_g . This behavior occurs inside the super Arrhenius region when the growth process originates in disordered and finite correlation regions (finite polydisperse dynamical clusters) where molecules are more “sluggish” than less correlated molecules. Thus, the dynamics is strongly T -dependent and the supercooling causes a slowing down up to a temperature at which only intercluster dynamics are possible. This is the crossover temperature, and above this temperature molecular motion, identified by D (or by the relaxation times and viscosity), primarily depends on intracluster dynamics.⁵¹

The polydispersity of the clusters and the interaction between them cause the hierarchical relaxation times reflected in the time dependence of the density-density correlation functions $F(q,t)$, in terms of the well-known stretched exponential decays (Williams-Watt), and in the transport parameters of the super Arrhenius behavior. The $F(q,t)$ temperature behavior can be quantified using the extended mode coupling theory (MCT), according to which the dynamic crossover is caused by a change in the dynamics from the one determined by the cage effect to one dominated by hopping processes.⁵⁴ This is reflected in the MCT primary α -relaxation time. In particular, the ideal MCT quantitatively describes the super Arrhenius region (intracluster) in terms of its scaling laws, and the MCT critical temperature T_c is coincident with the T of the dynamic crossover ($T_c \equiv T_L$).^{54,55} The intercluster hopping at $T < T_c$ causes the pure Arrhenius behavior.

IV. DISCUSSION

The existence of correlated structures in supercooled liquids not only causes the intracluster and the intercluster system dynamics but also the energy landscape scenario^{9–13} in which T_L marks the low T limit. For $T > T_L$, the onset of the molecular clustering gives rise to a multibasins energy landscape with a corresponding large frequency (and thus correlation time) distribution. In the opposite case $T < T_L$, when intercluster hopping is the dominant dynamics, there is only a two-state basin and a single frequency. Thus, each of these basins is characterized by a temperature-dependent weight factor, and system cooling not only reduces their numbers but also decreases their weight until it becomes negligible. At this stage (T_L), the only relevant dynamic is the molecule migration from one cluster to another, i.e., a process with only one typical energy scale (Arrhenius). This progressive evolution from the first energetic “configuration” to the second indicates the existence around T_L of a temperature region in which the system changes gradually from a fragile to a strong glass former. All of this constitutes the rationale for using the MCT scaling approach to analyze the transport data in the super Arrhenius regions.⁵⁵

In the previous study, the SER breakdown was observed only in high concentrations (the D₂O-glycerol system²⁵) but increasing the water content provokes a deviation from the Vogel-Fulcher-Tammann behavior for the lowest temperatures. Thus, the free volume theory that relates the molecular diffusion to cage effects (the potential cage and cages formed by glycerol and water by means of the HBs) has been considered.⁵⁶ In particular, the frustration limited domain theory approach takes into account the presence of frustration-limited clusters in one-component glass-forming liquids in the normal and supercooled regime and treats transport parameters (viscosity data, in particular) in terms of a universal scaling form: $E_\eta(T) - E_\eta(\infty) = BT^*\delta^3 = BT^*(1 - T/T^*)^3$ for $\delta \geq 0$ (where $E_\eta(T)$ is the viscosity activation free energy defined as $E_\eta(T) = RT \ln[\eta(T)/\eta(\infty)]$ and T^* is a domain formation temperature⁴³). In the D₂O-glycerol system, T^* is consistent with the SER breakdown temperature. Both decrease with increasing water content, supporting the idea that the breakdown of the SER is caused by a water-glycerol clustering process.²⁵ Note that the model of the frustration limited domain theory agrees with other models in characterizing a universality in the thermal behavior of the supercooled glass forming materials^{3–10} and suggests that (i) neither the empirical T_g nor the Vogel-Fulcher-Tammann critical temperature T_0 is fundamental to the description of supercooled liquids, but instead a temperature related to the dynamical clustering and the dynamic crossover, and (ii) all the data can be scaled and superimposed on a single universal curve.

As stated above, we measure the dynamic crossover temperature in the super Arrhenius region using ideal MCT approach to fit viscosity and diffusion data for the pure components and the studied molar fractions and using the form $D = D_0[(T - T_c)/T_c]^\theta$ (or $\eta = \eta_0[(T - T_c)/T_c]^{-\theta}$), with $T_c \equiv T_L$. According to the ideal MCT, T_c is the critical temperature and θ a non-universal exponent dependent on the system property. Figure 4 shows analyses of $D(T)$ and $\eta(T)$ in the super Arrhenius region using this procedure. The experimental data are reported on separate scales: D on the left and η on the right. Figure 4(a) shows pure glycerol, Fig. 4(b) pure water, and Fig. 4(c) the water-glycerol solution for $X_g = 0.4$. All the fitting curves are shown as dotted lines for the diffusion data and dashed lines for the viscosity fitting. Figures 4(a) and 4(c) superimpose straight lines on the experimental data below T_L , indicating that in these system there is also a low T Arrhenius behavior and hence a fragile-to-strong crossover. Figure 3(a) shows the temperatures T_L obtained by MCT analysis (squares). Note that within the experimental error they are nearly coincident with the same quantity obtained by analyzing the normalized SER ratio $R = D\eta/T$. We find the values of the exponent θ to be 2.00 ± 0.05 for pure water, 3.00 ± 0.05 for pure glycerol, 2.95 ± 0.05 for $X_g = 0.8, 0.6$, and 0.5 , and 2.80 ± 0.05 for $X_g = 0.4$. These θ values suggest that in the studied concentration range the system dynamics are largely influenced by the glycerol and reflect the situation demonstrated by MD simulations and infrared spectroscopy for which the possible number of HBs per molecule is higher for glycerol than for water.⁴⁴ In particular, the OH stretching spectra in the concentration

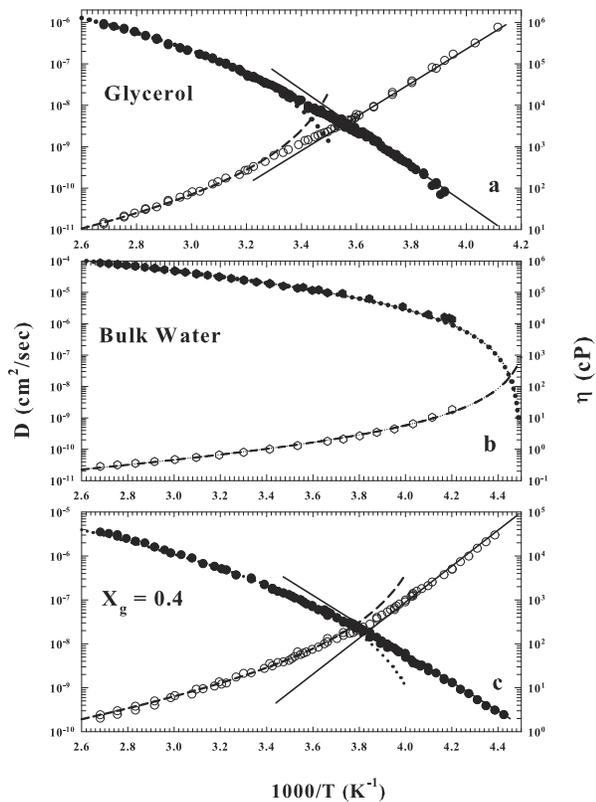


FIG. 4. The MCT analyses of $D(T)$ and $\eta(T)$ in the super Arrhenius region reported on separate scales: D on the left and η on the right. Panel (a) deals with pure glycerol, panel (b) with pure water and panel (c) with water-glycerol solution for $X_g = 0.4$. All the fitting curves are illustrated as dotted lines for the diffusion data whereas the viscosity fitting are reported as dashed lines. In the panels (a) and (c), below T_L some straight lines are superimposed to the experimental data indicating also for these systems the presence of a low T Arrhenius behavior and hence of a fragile-to-strong crossover.

range $0.27 < X_g < 1$ indicates a linearization in the glycerol-water HBs, i.e., they become progressively more linear as the glycerol concentration increases. At the same time the interaction strength increases, which causes water-glycerol mixtures to remain glassy at low temperatures. At low glycerol

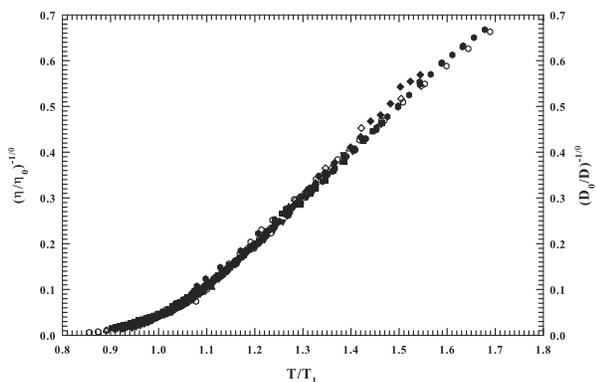


FIG. 5. Scaled representation of the MCT scaling forms used to evaluate the transport data inside the super Arrhenius temperature region: $(\eta/\eta_0)^{-1/\theta}$ and $(D_0/D)^{-1/\theta}$ versus T/T_L . The obtained master curve makes sense only for $T > T_L$ demonstrating that for pure water and glycerol and their solutions the transport parameters have a universal behavior.

concentrations, $X_g < 0.27$, there is an amount of bulk water sufficient to cause crystallization at a moderate supercooled regime.

V. CONCLUSION

These MCT results and the results of previous studies^{6-9,43,51} on supercooled glass-forming materials indicate that viscosity and diffusion data can be scaled and superimposed on a single universal curve. Figure 5 shows a plot of a scaled representation of the MCT scaling forms used to evaluate the transport data inside the super Arrhenius temperature region, $(\eta/\eta_0)^{-1/\theta}$ and $(D_0/D)^{-1/\theta}$ versus T/T_L . The obtained master curve makes sense only for $T > T_L$, demonstrating that for pure water and glycerol and their solutions the transport parameters exhibit a universal behavior. Also in these systems there is the confirmation that the dynamical arrest does not show criticality. In particular, these results show that the physics of supercooled liquids can be understood in terms of a universal dynamical crossover, rather than a low-temperature critical point T_0 .

In conclusion, we explain the breakdown of the Stokes-Einstein relation in a system characterized by strong hydrogen bonds, such as the water-glycerol mixture, and confirm that for liquid solutions (or mixtures) there is a universality behavior evidenced by molecular fluids. We use an approach based on a molecular clustering process characterizing supercooled glass-forming materials and an energy landscape representation to explain this behavior.

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