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Power-law behavior in the viscosity of supercooled liquids

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We present experimental results on the viscosity of supercooled aqueous solutions of lithium chloride. The viscosity scales as $(T-T_0)^\mu$ with $\mu=-2.08$ over a large temperature range. Data on other systems show that both the power-law behavior and the approximate value of the exponent μ are typical for a wide variety of fluids. The region of power-law behavior occurs at much higher temperatures and lower viscosities than are normally associated with the glass transition. The results are discussed in the context of several recent theories of structural relaxation in glassy liquids.

INTRODUCTION

As a liquid is cooled into the metastable state below its melting point, the viscosity increases until it crystalizes or vitrifies. The manner in which the viscosity approaches its value in the solid state provides important information about the mechanism of atomic mobility in the fluid and the nature of the glass transition. The temperature dependence of the viscosity of fluids is often described using the Arrhenius form $\eta \sim \exp(E/T)$ or the Vogel-Fulcher (VF) form $\eta \sim \exp[E/(T-T_0)]$. The theoretical interpretation of the Arrhenius form relies on a picture of single-particle hopping over potential barriers of uniform height; this picture is not supported by computer simulations which suggest that particle motion in viscous flow is cooperative with a broad distribution of barrier heights.[1,2] The VF equation has been justified by considering the liquid free volume required for flow.[3] At a characteristic temperature T_0 which is related to the calorimetrically defined glass transition temperature T_g, the free volume vanishes and the viscosity is predicted to diverge. In the Arrhenius form, however, the only significant temperature is $T=0$. Although both of these forms have been used with partial success in describing experimental data, neither one is considered the basis of a fundamental theory of the temperature dependence of fluid viscosity. Recently, a number of investigations of the dynamics of supercooled fluids which attempt to include the cooperative nature of the flow on a microscopic scale have been presented. These calculations, based on a hard-sphere model,[4,5] an Ising spin model,[6,7] and a general hydrodynamic description,[8–10] suggest the existence of a transition at which the viscosity diverges as $(T-T_g)^\mu$ with $\mu \cong -1.8$. In the experiments reported here, we have used an oscillating-cup viscometer to make high-precision measurements of the viscosity of aqueous solutions of lithium chloride. This system provides the opportunity of studying the viscous behavior of supercooled fluids, which range from very difficult to vitrify (pure water) to excellent glass formers (15 mol % LiCl—H_2O) by varying the salt concentration. The results show that over a broad temperature range the viscosity η scales as $(T-T_0)^\mu$ with $\mu \approx -2$. Although T_0 is not a sharp transition point and does not coincide with the glass transition temperature T_g, it appears to be a significant point which marks the boundary between two types of viscous behavior: power law for $T>T_0$ and approximately Arrhenius $\eta \sim \exp(E/T)$ for $T<T_0$. We have also found that the power law $(T-T_0)^\mu$ describes the temperature dependence of the viscosity of a surprising variety of fluid systems in the high-temperature regime better than the Arrhenius or Vogel-Fulcher forms commonly used to parametrize viscosity data. The exponent μ is not universal, but lies in the range between -1.5 and -2.3.

EXPERIMENT

The viscometer used in these measurements consists of an aluminum cup 7 mm in diameter and 13 mm high mounted on an aluminum torsion rod which forms part of a high-Q oscillator operating at $\omega=1950$ Hz. The maximum angular displacement is 3×10^{-5} rad. Details of the experimental apparatus are discussed elsewhere.[11] The frequency and amplitude of the oscillator are monitored as a function of temperature as the sample is cooled at a rate of 10 K/h. The amount of fluid which is dragged along by the walls of the cup is characterized by the viscous penetration depth δ which is given by $(2\eta/\rho\omega)^{1/2}$. In the limit where δ is much smaller than the size of the cup and the background damping is negligible, the amplitude of oscillation is proportional to $1/\delta$. The solutions were prepared from reagent-grade LiCl and high-purity water which was passed through a 0.2-μm filter before being sealed into the viscometer. The addition of LiCl to water inhibits nucleation and allows the liquid to be supercooled. Although the viscosity at room temperature is similar to pure water, the LiCl-water system is a typical example of a good glass former[12] with $T_g \sim 140$ K.

Since the oscillator amplitude is proportional to $\eta^{-1/2}$, plots of $\eta^{-1/2}$ as a function of temperature occurred naturally in the process of taking our data and also proved helpful in understanding it. Figure 1 shows such a plot for several LiCl-H_2O solutions. For concentrations less than 15 mol % LiCl, the measurement range is limited by nucleation of the solid; at nucleation, the fluid is typically supercooled by 10 °C. The 15-mol % solution can be cooled continuously into the glass phase without freezing. Above 230 K, the data can be approximately described by

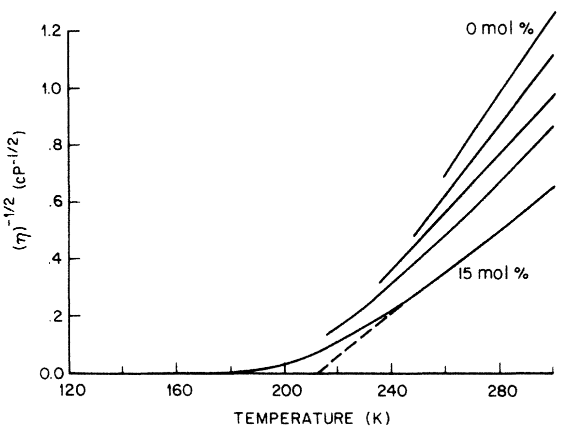

FIG. 1. $\eta^{-1/2}$ as a function of temperature for a series of solutions of LiCl in water. From top to bottom the concentrations are 0.0-, 3-, 6-, 9-, and 15-mol % LiCl. A dashed line which extrapolates the high-temperature behavior of the 15% solution, representing power-law behavior with $\mu=-2$, is included as a guide to the eye.

a family of straight lines which extrapolate to infinite viscosity in the vicinity of 210 K. The 15-mol % solution shows a linear portion from 300 to 230 K, a sharp bend centered around 200 K and a transition to a different kind of behavior in the low-temperature high-viscosity regime. The linearity of these plots above 230 K immediately indicates that $\eta \cong (T-T_0)^{\mu}$ with $\mu \approx -2$; a careful least-squares analysis for the 15-mol % solution yields $\mu=-2.08$, $T_0=207$ K. It is important to note that a best fit using the Arrhenius form shows pronounced curvature on a similar plot and is obviously an inferior way of parametrizing the data. The VF form can fit the data slightly better than the Arrhenius form, but it is still significantly worse than the simple power law. The viscosity in the transition regime centered around T_0 is only 100 times higher than the viscosity at room temperature, and is many orders of magnitude lower than the 10^{12} P usually associated with the glass transition. Since the viscosity is so low, the characteristic relaxation times are still very short compared to the time scale of the measurement, and the sample is certainly in internal equilibrium. It is also apparent from Fig. 1 that T_0 is not a real singularity since the viscosity remains finite as the sample is cooled to T_0 and below. For $T<T_0$ the viscosity is approximately Arrhenius as described in Ref. 12.

DISCUSSION

It is natural to inquire whether the viscous behavior illustrated in Fig. 1 is a special property of our experimental system, or if it is in fact typical of many dense liquids. In order to answer this question, we have carefully analyzed viscosity data for a number of diverse systems taken from literature sources.[13] For most simple liquids, a plot of $\eta^{-1/2}$ versus T shows an approximately linear segment, but no sharp bend or transition to a different low-temperature regime. This is a consequence of the fact that almost all of the available viscosity data has been obtained for temperatures above the melting temperature, while T_0 is always considerably below the melting temperature. By analogy with Fig. 1, one would expect that the high-temperature data could be described by a power law. We have found that fits to the form $A(T/T_0-1)^{\mu}$ are indeed better than fits to the Arrhenius or VF forms customarily used for viscosity data. Figure 2 shows power-law fits of the temperature dependence of the viscosity of some typical non-glass-forming liquids. Although the viscosity of these liquids varies by approximately an order of magnitude from the melting temperature to the boiling point, the power law describes the temperature variation of the viscosity in this region very well. The plots also suggest that if these fluids could be strongly supercooled, the temperature dependence of the viscosity would change character in the vicinity of T_0. Table I shows the parameters we have obtained for several liquids[15] as well as the ratio, R, of the χ^2 of the power-law fit to the VF fit to the same data; R is large if the power law is a superior fit.

In addition to these real laboratory liquids, we have examined data for molecular-dynamics simulations of supercooled Lennard-Jones argonlike liquids.[16] Although the simulation data is much noiser than laboratory data, the results are nevertheless consistent with power-law behavior. It is important to note, however, that just as in the real liquids, the viscosity at T_0 is only ~ 10 P. We have also analyzed data for several pure compounds such as isopropylbenzene and tri-α-napthylbenzene which can be cooled into the glassy state.[17,18] These materials exhibit behavior completely analogous to Fig. 1, i.e, a power-law regime, a transition region around T_0, and Arrenhius behavior at lower temperatures. As illustrated in Fig. 1, the region of power-law behavior for glass formers can be clearly identified from a plot of $\eta^{1/2}$ versus T. For the fitting procedure we have selected the temperature range by computing χ^2 as a function of the low-temperature cutoff and choosing the value at which χ^2 reaches twice its asymptotic high-temperature value. In order to show that the identification of T_0 is not dependent on the details of our plotting procedure, we have included in Figs. 3 and 4 the more conventional plot of $\log_{10}(\eta)$ versus $1/T$ for comparison. The linear portion of Figs. 3(a) and 4(a) show that the viscous behavior in the low-temperature high-viscosity regime can be described accurately with an Arrhenius form, but the description breaks down at the same T_0 obtained from the power-law fit. In contrast, the viscous behavior is smooth and regular in the vicinity of the glass-transition temperature. In fact, T_g cannot be identified from measurements of the temperature dependence of the viscosity without recourse to calorimetric data.

Figures 1–4 and Table I reinforce our viewpoint that for most liquids there exists a temperature T_0 above which the viscosity has power-law behavior. For simple liquids, measurements in the vicinity of T_0 are difficult or impossible because the lifetime of the metastable liquid is typically very short because of the high probability of

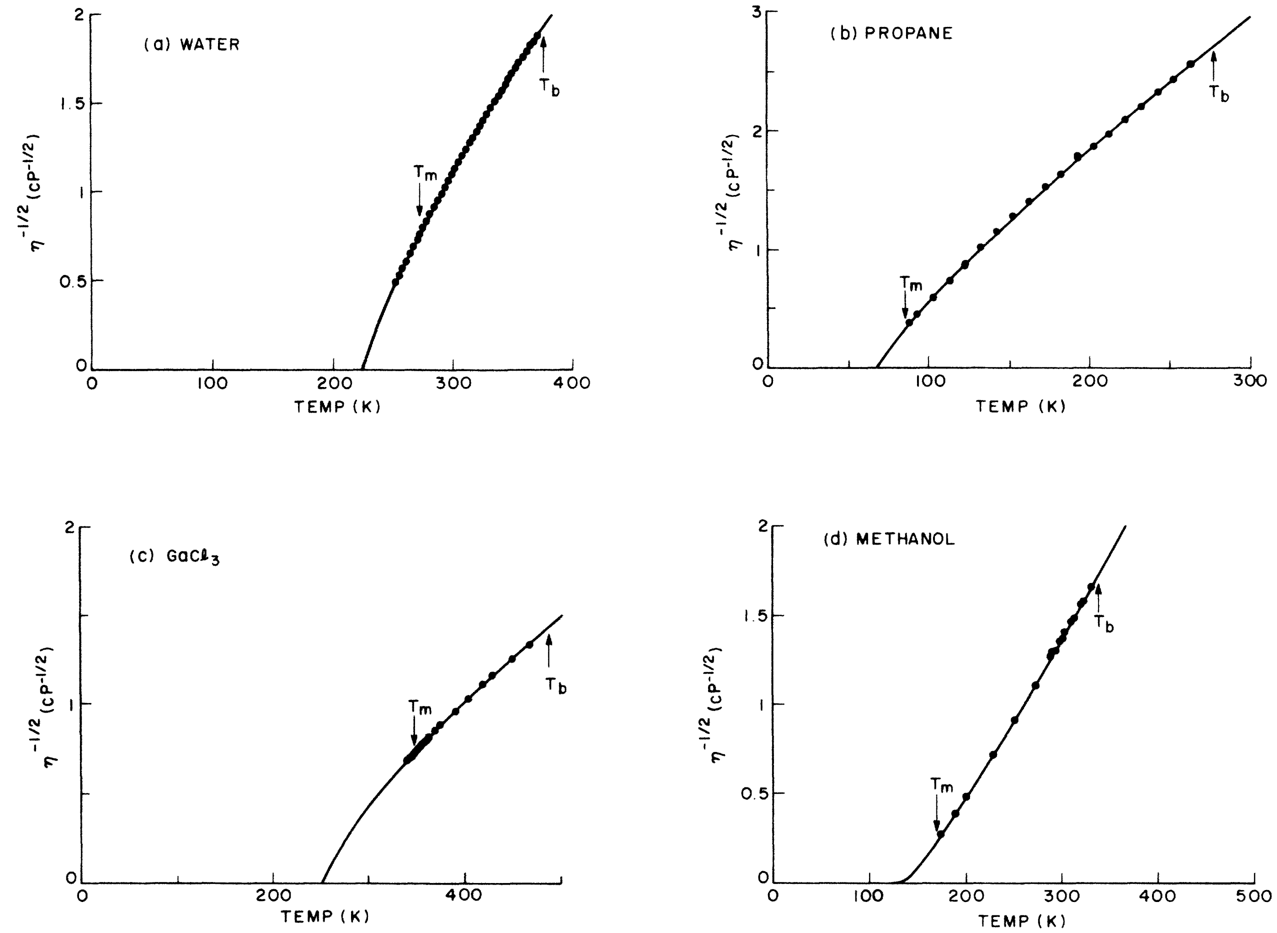

FIG. 2. $\eta^{-1/2}$ as a function of temperature. (a) Pure water; (b) propane at 3.4 atm pressure; (c) gallium chloride; (d) methanol. The arrows indicate the melting and boiling points. The solid curves are power-law fits with parameters from Table I. Data are taken from Ref. 13.

TABLE I. Best-fit parameters for the power-law form $\eta = A(T/T_0 - 1)^{\mu}$. See Eq. (1) for the definition of γ.

Name	A (cP)	$-\mu$	T_0 (K)	γ	Temperature range (K)	R	Ref.
Water (pure)	0.139	1.64	225	0.00686	250—370	2.5	13,14
Methanol	0.838	2.27	135	0.0156	170—330	3.1	13
Carbon tetrachloride	0.705	1.99	158	0.0163	260—455	1.4	13
Acetic acid	0.714	1.99	166	0.0174	305—385	1.6	13
Propane	0.981	1.69	69	0.0195	90—270	1.7	13
Benzene	0.684	2.13	145	0.0138	280—500	2.5	13
Aniline	0.284	1.71	243	0.0161	270—460	1.1	13
Toluene	0.602	2.02	148	0.0134	150—440	1.0	13
n-heptane	0.423	1.65	145	0.0197	180—375	12.0	13
Isopropyl benzene	0.485	2.02	163	0.0119	175—330	2.3	13
gallium chloride	0.430	1.50	254		340—520	1.6	13
n-dodecane	0.399	1.76	199	0.0218	260—380	1.0	13
n-tetrakosan	0.730	2.09	233		320—580	5.0	13
tri-α-napthylbenzene	0.355	2.17	424		460—580	1.0	17
Lennard-Jones argon	0.169	1.87	38		45—90	1.1	16
Argon	0.864	1.82	30	0.0178	85—125	1.0	13
Hydrogen	1.02	1.58	1.2	0.0111	14—28	1.0	13

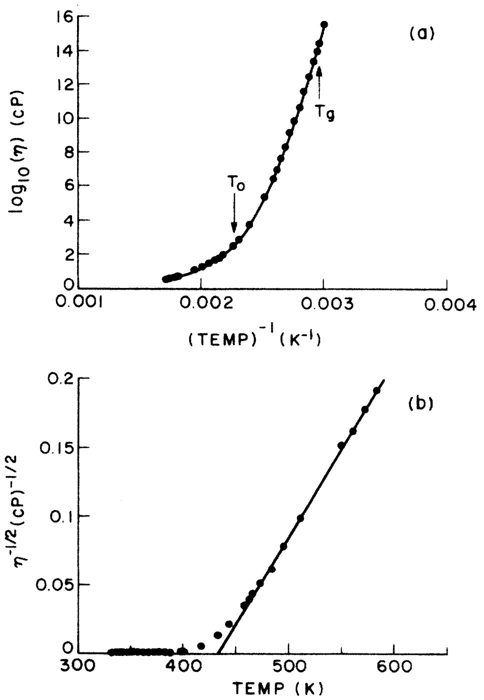

FIG. 3. Viscosity of tri-α-napthylbenzene. (a) Arrhenius plot $\log_{10}(\eta)$ vs T^{-1}. Arrows indicate the calorimetric glass transition temperature T_g and the power-law singularity temperature T_0. (b) $\eta^{-1/2}$ as a function of temperature for the same data as in (a). Straight line shows region of power-law behavior and identifies T_0. Data are taken from Ref. 17.

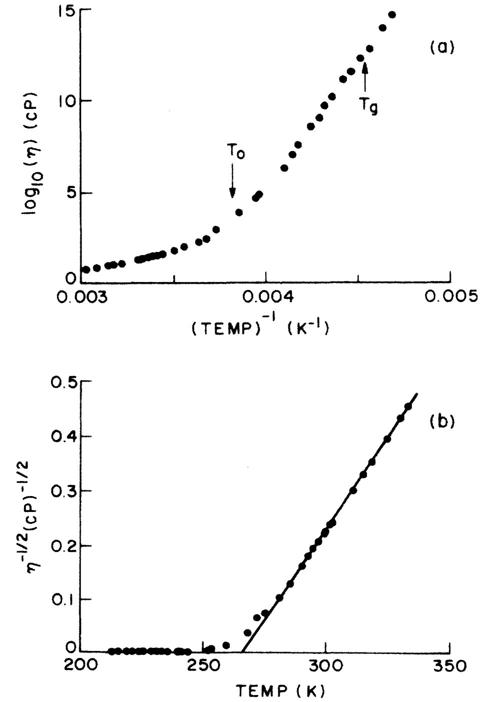

FIG. 4. Viscosity of salol. (a) Arrhenius plot $\log_{10}(\eta)$ vs T^{-1}. Arrows indicate the calorimetric glass transition temperature T_g and the power-law singularity temperature T_0. (b) $\eta^{-1/2}$ as a function of temperature for the same data as in (a). Straight line shows region of power-law behavior and identifies T_0. Data is taken from Ref. 17.

homogeneous nucleation. In glass-forming liquids, however, samples can be cooled below T_0 into a regime with a qualitatively different temperature dependence of the viscosity. Although the VF equation provides a convenient interpolation formula which approximately describes the high-temperature and transition regions,[19] it typically fails at low temperatures[17] and, in our view, obscures the fundamental difference between the low- and high-viscosity regimes. We feel that the temperature T_0 defined by the region of power-law behavior as in Table I is of more significance for classifying the flow properties of viscous and glass-forming liquids than the singularity temperature of the VF equation or the calorimetrically defined glass transition temperature T_g, since the temperature dependence of the viscosity has no singular characteristics in the vicinity of these temperatures.

A striking feature of Table I is that the exponent μ lies within a narrow range between -1.5 and -2.3. The prefactor A, however, is not constant and shows systematic dependence on the properties of the fluid. This dependence can be accounted for using the principle of corresponding states. On dimensional grounds, the viscosity of a fluid at the critical point is proportional to $\tilde{\eta}=(MT_c)^{1/2}V_c^{-2/3}$ where M is the molecular weight, T_c is the critical temperature, and V_c is the critical molar volume.[20] In order that the power-law behavior be consistent with this estimate of the critical viscosity, we must have

$$\eta=\gamma\tilde{\eta}\left[\frac{T-T_0}{T_c-T_0}\right]^{\mu}, \tag{1}$$

where γ is a constant independent of fluid properties. The fact that the variations in the computed values of γ shown in Table I are small demonstrates that this relationship is a useful universal representation of the viscosity of fluids in the low-viscosity regime. The only class of liquids which we have found which does not display the qualitative behavior illustrated in Fig. 1 are the liquid metals. The viscosity of these liquids asymptotically approaches a constant at high temperatures, and if the viscosity is fit to a power law, the exponent is typically less than 1.0, and the fit is not very good. See Fig. 5. If, however, we take the high-temperature behavior into account and analyze the divergence at low temperatures as a power law plus a constant we obtain a good fit with exponents of -1.20, -1.75, and -1.96 for Ga, Sn, and Pb, respectively.

The similarity of the behavior of the various fluids in Table I strongly suggests that the microscopic mechanism which is responsible for producing the power-law behavior is common to all of these fluids and depends only weakly on chemical details. Several recent theories[4–10] have analyzed the consequences of including nonlinear terms in the equations of motion that describe relaxation in various model systems. In each case, the analysis, which is based on a self-consistent perturbation theory, yields a transition point where the relaxation times diverge and the system behaves in some respects like a glass. Despite the distinction between T_0 and T_g, it is tempting to identify the T_0 of Table I with the transition

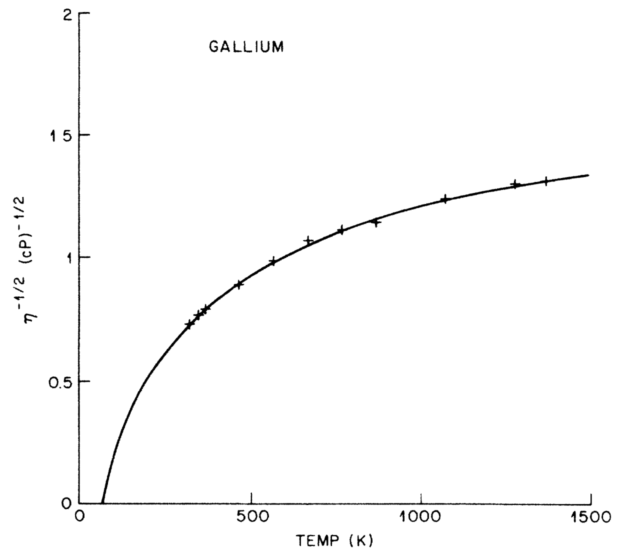

FIG. 5. $\eta^{-1/2}$ as a function of temperature for gallium. The solid curve is a fit to a power law plus a constant.

point found in these theories. The version of Das *et al.*[9] certainly satisfies the criterion of general validity, since it is applicable to any fluid described by the Navier-Stokes equations. The exponent which governs the viscosity is predicted to be nonuniversal but less than -1.5, which is in accordance with the data and analysis presented here.[21] There are, however, some important differences between the experimentally observed behavior and the theoretical predictions. In particular, the experiments show that the viscosity does not actually diverge at T_0, but smoothly crosses over to an Arrhenius-like regime. The theory predicts the correct behavior far from T_0 but breaks down in the vicinity of T_0 and below. It is perhaps not too surprising that first-order perturbation theory can describe the effects of nonlinear cooperative interactions in the region where the effects are small, but fails when these effects become large.[7]

Another possible explanation for the power-law behavior we observe is related to correlated site percolation theory, which has been invoked in several previous theories of fluid viscosity.[3,22] We wish to point out the analogy between the flow of current in a random resistor network and fluid flow in the network of solid and liquid-like cells which are hypothesized in the free-volume theories of liquids. In simple bond percolation in three dimensions, the resistance diverges with an exponent of ~ -2 which is similar to the viscosity exponent observed here for many liquids. A percolation theory of the hydrogen-bond network in water has been constructed[22] to explain the thermodynamic and transport properties of supercooled water, including the power-law divergence of the viscosity.[14] The work presented here shows that the power-law behavior of $\eta(T)$ is not an anomalous property of water, but rather is a property shared by almost all liquids, and its explanation probably depends on features more general than the high degree of bonding in liquid water.

CONCLUSION

We have presented evidence which suggests that a typical fluid has two regimes of viscous behavior in which the mechanism of flow is probably quite different. These regimes are separated by a transition region characterized by a temperature T_0 and a range of viscosities of $10-10^3$ P. For $T < T_0$ and $\eta > 10^3$ P, most fluids have approximately Arrhenius behavior. For $T > T_0$, we have shown that the temperature dependence of the viscosity of many liquids can be described more accurately by a power law than by any other commonly used functional form. The extrapolated singularity temperature T_0 lies in the supercooled metastable liquid regime, but the behavior around the singularity appears to control the temperature dependence of the viscosity even at high temperatures. For non-glass-forming liquids, the power law describes the temperature variation of the viscosity throughout the region of existence of the liquid state which typically involves variations of the viscosity by 1 to 2 orders of magnitude.

We have also found that T_0 (and in particular, not T_g) is the only temperature at which the temperature dependence of the viscosity of a typical fluid changes in a significant way. Since there is no temperature at which the viscosity of real liquids diverges, it seems that the recent mode-coupling theories[4-10] either do not describe the physics which controls the temperature dependence of the viscosity, or have relied on some mathematical approximation which is not physically justifiable. It is therefore not possible to compare directly the theoretical predictions with the experimental data. The evidence which we have presented here suggests that these theories cannot describe liquids in the vicinity of T_g, but may provide a qualitative description of the behavior for $T > T_0$. Although the power-law exponents which we observe in this restricted range are consistent with the theoretical estimates, the theories do not prepare us to expect a transition for viscosities between 10 and 1000 P, which we find is typical behavior for glass formers. A more complete theory, which explains the significance of this range of viscosities, would be required before T_0 could be associated with a mode-coupling "transition." Irrespective of any particular theoretical interpretation, the success of the power-law correlation for a wide variety of liquids suggests that T_0 has a real physical significance which has not been previously appreciated.

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[15] The liquids presented in Table I are representative of several classes of fluids which were chosen on the basis of the existence of high-quality data over a sufficiently broad temperature range that a meaningful comparison of the various functional forms could be made. For equilibrium liquids, the data typically span the entire range of existence of the dense liquid from the melting point to the boiling point at fixed pressure. The uncertainty in the exponent is approximately ±5% in all cases except for hydrogen and for the rare gases, where the liquid range is limited and the uncertainty is ±40%.

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