Probing large viscosities in glass-formers with nonequilibrium simulations

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For decades, scientists have debated whether supercooled liquids stop flowing below a glass transition temperature T_{g0} or whether motion continues to slow gradually down to zero temperature. Answering this question is challenging because human time scales set a limit on the largest measurable viscosity, and available data are equally well fit to models with opposite conclusions. Here, we use short simulations to determine the nonequilibrium shear response of a typical glass-former, squalane. Fits of the data to an Eyring model allow us to extrapolate predictions for the equilibrium Newtonian viscosity η_N over a range of pressures and temperatures that change η_N by 25 orders of magnitude. The results agree with the unusually large set of equilibrium and nonequilibrium experiments on squalane and extend them to higher η_N . Studies at different pressures and temperatures are inconsistent with a diverging viscosity at finite temperature. At all pressures, the predicted viscosity becomes Arrhenius with a single temperature-independent activation barrier at low temperatures and high viscosities ($\eta_N > 10^3$ Pa·s). Possible experimental tests of our results are outlined.

glass transition | nonequilibrium systems | molecular dynamics simulations | rheology | supercooled liquids

Glass-forming liquids flow rapidly when hot but appear to become quenched into a fixed disordered structure at low temperatures. Researchers continue to debate whether this represents a transition to a new phase of matter or merely a slowing of dynamics beyond the observable range of time scales (1–12). Experimentalists typically measure the rise in the Newtonian viscosity η_N as a liquid is cooled and define the glass temperature T_g as the value where η_N reaches 10^{12} Pa·s. This temperature identifies when the dynamics become difficult to measure, rather than a fundamental transition where η_N diverges and the material enters a new state.

Perhaps the simplest model of glassy dynamics is that motion is always thermally activated. If viscous flow requires activation over a free energy barrier of height ΔH , then the viscosity will scale inversely with the activation rate:

$$\eta_N = \eta_0 \exp[\Delta H / k_B T], \quad [1]$$

where k_B is Boltzmann's constant and η_0 is a characteristic high-temperature viscosity. When ΔH is independent of temperature, plots of $\log \eta_N$ against $1/T$ form straight lines. Supercooled liquids that follow this Arrhenius behavior are called strong glass-formers (1). Fragile glass-formers show a more rapid, super-Arrhenius rise, indicating that ΔH grows with decreasing T (1). Ambient pressure data for the simple hydrocarbon molecule squalane in Fig. 1 are typical of fragile glass-formers. The slope of this curve rises by more than a factor of 3 over the experimentally accessible range from 10^{-3} to 10^8 Pa·s, indicating a proportionate increase in the activation barrier.

A central question is whether ΔH continues to rise slowly with decreasing temperature or diverges at a finite temperature T_{g0} (4, 13–15). Data for fragile glass-formers is often fitted to the Vogel–Fulcher–Tammann (VFT) model (16–18),

$$\eta_N^{\text{VFT}} = \eta_0 \exp[\Delta H_0 / k_B (T - T_{g0})], \quad [2]$$

where $\Delta H = \Delta H_0 / (1 - T_{g0}/T)$ diverges at T_{g0} and the constant ΔH_0 is the activation barrier at high temperatures. Fig. 1 shows published VFT fits to two sets of squalane data (19, 20) that illustrate a common problem. Excellent fits can be obtained to experiment, but extending data to lower temperatures frequently leads to a significant decrease in T_{g0} . Hecksher et al. have recently considered data for a wide range of molecular glass-formers and shown that they are all equally well fitted by theories where η_N diverges at a finite T_{g0} or only at zero temperature (21). They concluded that the range of data from standard viscosity measurements is too small to determine the nature of the glass transition.

In this work, we develop an approach for extending the accessible range of viscosities using nonequilibrium simulations. The approach assumes an analytic form for the shear-rate-dependent viscosity that is validated by comparing to the unusually large set of nonequilibrium and equilibrium flow measurements for squalane (19, 20, 22–27). Newtonian viscosities are obtained from two-parameter fits of this analytic form to the high-rate response. Our results agree with experimental values of η_N over 10 orders of magnitude and predict values more than 10 orders of magnitude larger. They also allow a wide range of pressures and densities to be explored. Based on these results, squalane becomes a strong glass-former with a constant energy barrier at high pressures and low temperatures. There is no indication of a finite-temperature divergence in ΔH or viscosity.

Results

Nonequilibrium Shear Stress and Viscosity. Squalane (Fig. 1) is a short hydrocarbon with side branches. The branches inhibit

Significance

As a liquid cools, molecules move more slowly and the viscosity rises. A fundamental question is whether this trend continues smoothly down to zero temperature, or if flow stops at a finite temperature where the material undergoes a transition to a glass phase. Direct measurements of growing viscosities become difficult as the time for motion exceeds years or centuries. We describe and test an approach for obtaining large viscosities using nonequilibrium molecular dynamics simulations. Results agree with existing experiments on the model glass-former squalane and allow viscosities over 10 orders of magnitude larger to be predicted. The temperature dependence at fixed pressure or density is consistent with a gradual slowing of dynamics, rather than a finite-temperature divergence in viscosity.

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Fig. 1. Newtonian viscosity of squalane as a function of temperature T . η_N is plotted against $1000/T$ for constant pressures of $P = 0.1$ MPa (red), 300 MPa (blue), and 800 MPa (green). Open symbols are our results with η_N evaluated directly from low-rate simulation data (diamonds and upside-down triangles) or obtained from Eyring fits (squares, right-side-up triangles, and circles). Filled symbols are experimental data from ref. 20 (pentagons), ref. 22 (inverted triangles), ref. 23 (triangles), and ref. 19 (circles). Error bars are shown for simulation data when they are larger than the symbol size. Dashed black lines are Arrhenius fits to data at $\eta_N > 10^3$ Pa·s with constant $\Delta H = 1.28$ eV. Red lines are VFT fits to experimental data for $T \geq 240$ K (dotted line) (23) and $T \geq 170$ K (dash-dotted line) (19) that give $T_{g0} = 139$ K and 126 K, respectively. By convention, the glass transition temperature T_g is where the viscosity is 10^{12} Pa·s. (*Inset*) Sketch of squalane showing carbon atoms (circles) and covalent carbon-carbon bonds (lines). Red, green, and blue circles indicate carbon atoms with three, two, and one hydrogen atoms, respectively.

crystallization, making squalane ideal for fundamental studies of the glass transition (19, 22, 23). It has also been widely used as a model fluid in studies of elastohydrodynamic lubrication (20, 24, 26), where lubricants are subjected to extreme pressures P and strain rates $\dot{\gamma}$. In this latter context, the nonequilibrium response of squalane has been measured as a function of $\dot{\gamma}$ for P up to ~ 1 GPa and over a wide range of T (20, 24, 25). We have used standard simulation methods (*Materials and Methods*) to determine the strain-rate-dependent shear stress σ and viscosity at corresponding state points. Although long times are required to reach equilibrium in glassy systems, sheared systems reach steady state in a time of order $1/\dot{\gamma}$, making it possible to obtain the nonequilibrium $\sigma(\dot{\gamma})$ at arbitrary density and temperature for rates as low as 10^5 s^{-1} .

Fig. 2A compares experimental and simulation results for the strain rate dependence of σ at room temperature and varying pressure P . Fig. 2B shows the nonequilibrium viscosity, $\eta \equiv \sigma/\dot{\gamma}$, calculated from the same data. Experimental data extend up to $\dot{\gamma} \sim 10^4 \text{ s}^{-1}$, and we have calculated the viscosity down to $\dot{\gamma} \sim 10^5 \text{ s}^{-1}$. For $P \leq 500 \text{ MPa}$ ($\eta_N < 10^2 \text{ Pa}\cdot\text{s}$), simulation rates are low enough to reach the constant low-rate Newtonian viscosity η_N . For larger pressures and viscosities, we determined η_N by fitting $\eta(\dot{\gamma})$ to the Eyring model (dashed lines in Fig. 2).

The Eyring model (28) is a simple extension of the activation model for viscosity (Eq. 1) that includes the effect of shear stress. The idea is that the barrier for forward hops (in the direction of shear) decreases linearly with the applied shear stress, whereas the barrier for backward hops (in the reverse direction) rises. The net flow rate $\dot{\gamma}$ can then be calculated from the difference between forward and backward hops (*SI Text*):

$$\dot{\gamma} = \frac{\sigma_E}{\eta_N} \sinh(\sigma/\sigma_E), \quad [3]$$

where η_N is given by Eq. 1 with the equilibrium barrier $\Delta H(\sigma = 0)$ for a given T and P , and the Eyring stress σ_E characterizes the rate of change of ΔH with σ : $|\partial \Delta H / \partial \sigma| \equiv k_B T / \sigma_E$. One recovers the Newtonian response at $\sigma \ll \sigma_E$. At large stresses, σ rises linearly with $\log \dot{\gamma}$. This linear behavior is clearly evident for high-viscosity systems ($\eta_N > 1$ Pa·s) in Fig. 2A and Figs. S1 and S2 and has been observed in elastohydrodynamic lubrication at high rates and pressures (26). A simple straight-line fit at large $\dot{\gamma}$ yields both the Eyring stress and Newtonian viscosity.

Fig. 2 shows that Eyring fits to simulations at $T = 293$ K and $P \geq 300$ MPa provide an excellent description of the numerical data and extrapolate smoothly to the experimental values of the Newtonian viscosity. Fits at other state points are shown in [SI Text](#). At very high rates, $\dot{\gamma} > 5 \cdot 10^9 \text{ s}^{-1}$, the stress rises above the Eyring fit. In this regime, the strain rate is approaching phonon frequencies, leading to new dissipation mechanisms. Experimental results drop slightly below the Eyring fits at the highest rates. This difference may reflect heating under these extreme rates and shear stresses (26) or expansion under shear, because experiments fix the component of the stress tensor in the vorticity direction and allow dilation (29). Both changes would reduce the viscosity compared with our simulations at fixed temperature and volume (*Materials and Methods*).

Fig. 2. Steady-state shear stress σ and viscosity η of squalane as a function of strain rate $\dot{\gamma}$. Stress σ vs. $\dot{\gamma}$ at $T = 293$ K for P from 0.1 – 955 MPa (A) and viscosity $\sigma/\dot{\gamma}$ vs. $\dot{\gamma}$ (B) for the same systems. Symbols for $\dot{\gamma} \geq 10^5$ s⁻¹ correspond to MD simulation results, whereas symbols at lower rates are from experiment (20, 24, 25). Black dashed lines are Eyring model fits to simulation data that show the expected linear dependence of stress on $\log \dot{\gamma}$ for high $\dot{\gamma}$. For $P \geq 300$ MPa, the Eyring fit extrapolates to the measured Newtonian viscosity at low rates. For $P \leq 500$ MPa, simulations reach the Newtonian limit (dotted lines) without extrapolation.

Fig. 3. Collapse of viscosity data from different T and P . Reduced viscosity η/η_N as a function of reduced strain rate $\dot{\gamma}_N/\sigma_E$ for systems with $\eta_N > 1$ Pa·s and $\dot{\gamma} \leq 3 \cdot 10^9 \text{ s}^{-1}$. Data are for $P = 0.1$ MPa (red), 300 MPa (blue), 636 MPa (black), 800 MPa (green), 875 MPa (magenta), and 955 MPa (gray) at $T = 150$ K (pentagons), 175 K (diamonds), 200 K (inverted triangles), 250 K (triangles), 293 K (circles), 313 K (squares), and 338 K (crosses). Data for $\rho = 0.95 \text{ g} \cdot \text{cm}^{-3}$ (filled brown circles) at $T = 293, 313$, and 338 K are also shown. Data from both simulations and experiments are used, and the dashed line shows the prediction of the Eyring model. *Inset* expands the low rate region.

Fig. 3 further illustrates the success of Eyring theory in describing all systems with $\eta_N \gtrsim 1$ Pa·s. Viscosity data from different temperatures are frequently collapsed by using the hypothesis of time–temperature superposition (30) (i.e., that as temperature changes, the relaxation time for all modes scales with a single characteristic relaxation time τ_R). When this hypothesis holds, plots of η/η_N against $\dot{\gamma}\tau_R$ collapse onto a universal curve, and data for each T and P reveal part of the curve. A collapse for squalane at a wide range of pressures and temperatures is shown in Fig. 3, with $\tau_R = \eta_N/\sigma_E$. Over almost 30 decades, simulation and experimental data from the glassy regime lie on the analytic solution of the Eyring model.

Variation of Newtonian Viscosity with T and P . Assuming an Eyring form for the stress vs. strain-rate curves allows us to extract a prediction for η_N from simulations at high rates as long as there is a substantial linear region in plots of σ vs. $\log \dot{\gamma}$. We find that this condition is met whenever $\eta_N \gtrsim 1$ Pa·s. Farther from the glassy regime, the response deviates from the simple Eyring form, indicating that the motion cannot be described by a single activation barrier or rearrangement mechanism. The response is better described by models with a wide range of characteristic times, such as the modified power law in the Carreau formula that is often used to model simple fluids (31). Fortunately, the rapid dynamics in this regime means that we do not need to assume any form for the viscosity. Instead, values of η_N can be determined directly from simulations up to $\eta_N \sim 10^2$ Pa·s.

We have explored the effect of temperature and pressure on viscosity over a large range of parameters by combining direct evaluations of η_N with Eyring fits. Some of the data are summarized in Fig. 1. They agree with available experimental data from 10^{-3} to 10^8 Pa·s and predict η_N up to 10^{22} Pa·s.

All of the simulation results in Fig. 1 show a cross-over from fragile, super-Arrhenius behavior to strong, Arrhenius behavior as T decreases. At each pressure, the cross-over occurs when the viscosity exceeds $\sim 10^3$ Pa·s. The corresponding cross-over temperature T_a increases with increasing pressure. Dashed fit lines in Fig. 1 show that data for $T \leq T_a$ and $\eta_N \gtrsim 10^3$ Pa·s can be described by a pressure- and temperature-independent acti-

vation barrier. Expressing the pressure-dependent η_0 in terms of T_a , we find:

$$\eta_N = \eta_a \exp[(\Delta H/k_B)(1/T - 1/T_a)], \quad T \leq T_a, \quad [4]$$

with $\eta_a = 10^3$ Pa·s, $\Delta H = 1.28$ eV, and $T_a \sim 197, 245, 292$ K for $P = 0.1, 300, 800$ MPa, respectively.

Past VFT fits to experimental data in Fig. 1 are clearly inconsistent with our extension of ambient pressure results to lower temperatures. Additional bounds on the rise in η_N are implied by our high-pressure results. For a simple molecule like squalane, viscosity rises monotonically with pressure at fixed temperature (20). Any super-Arrhenius fit to low-pressure data with $T_{g0} \gtrsim 100$ K rises rapidly above the Arrhenius behavior seen in our high-pressure results, whereas fits with $T_{g0} \lesssim 110$ K can only fit a portion of the experimental data. Thus, our extrapolated results are inconsistent with a finite temperature divergence of η_N for squalane.

Separating the Roles of T and Density. As noted in experimental and simulation studies of other fluids, measurements of η_N at constant pressure mix the effects of temperature and density ρ because of thermal expansion (32–34). Fig. 4 shows η_N as a function of ρ for different P and T . For low viscosities, the change in viscosity produced by a 10% increase in ρ is comparable with that from a similar change in T (338 to 293 K). As the viscosity increases, variations with temperature become more dramatic than changes with density. Refs. 32 and 33 showed similar behavior in experimental data for other glass-formers and concluded that temperature dominates changes in η_N at large viscosities.

Simulations allow us to easily determine the variation of η_N with T at constant density instead of constant pressure. Fig. 5 contrasts the ambient pressure data from Fig. 1 with the rise in η_N for two constant densities, 0.95 and 1.0 g/cm³. The corresponding temperatures at ambient pressure in an equilibrium fluid can be estimated by extrapolating the linear thermal expansion at $T \geq 250$ K. We find 96 and 22 K, respectively. These values overestimate the temperature because the thermal

Fig. 4. Newtonian viscosity of squalane as a function of density. Symbols indicate changes at constant $T = 150, 175, 200, 250, 293, 313$, and 338 K and at constant $P = 0.1$ MPa. Crosses, diamonds, light-side-down Janus circles, and upside-down triangles indicate results with η_N evaluated directly using low-rate simulation data. Pluses, squares, light-side-up Janus circles, and right-side-up triangles denote estimates of η_N obtained from Eyring fits. Note that the increase in η_N with fractional changes in T is larger than with fractional changes in ρ , and the difference grows at large η_N . Similar results have been obtained in experiments on other glasses (32, 33).

of the highest viscosities in Fig. 1 are impractical because the relaxation times, η_N/σ_E , become comparable to the age of the universe. However, nonequilibrium measurements can be made at experimentally accessible rates to validate our extrapolation from much higher rates. Combining experiment and simulation as in Fig. 2 may greatly reduce the uncertainty in η_N and allow tighter limits on viscosity models used in studies of a wide range of small-molecule glass-formers.

Materials and Methods

Squalane, or 2,6,10,15,19,23-hexamethyltetracosane ($C_{30}H_{62}$), is a branched alkane with a C_{24} backbone and six methyl side groups placed symmetrically about the backbone center. Past studies of squalane and similar alkanes showed that united atom (UA) potentials accurately describe the viscosity at ambient pressure (39–42). As shown in the schematic in Fig. 1, each UA represents a carbon and its covalently bonded hydrogens. UAs representing CH_3 , CH_2 and CH groups interact with different potentials.

We use the potential parameters that Mondello and Grest used for squalane (40). Within each molecule, UAs interact with a harmonic bond-stretching term, a harmonic bond-bending term, a torsional potential characterizing the rotational barrier around nonterminal bonds, and a harmonic bending term to prevent umbrella (sp_3) inversion at tertiary carbon branch points. Atoms on different molecules or separated by four or more bonds on the same molecule interact with a 6–12 Lennard–Jones potential. The model gives accurate values of the viscosity at ambient pressure, although the density is systematically too high. We checked that treating hydrogens separately by using an all-atom potential developed for high pressure (43) gave consistent results for the viscosity at a given pressure and more accurate densities.

To generate equilibrium squalane states, we prepared a melt configuration composed of $N_m = 125$ molecules ($N = 3750$ UAs) in a periodic unit cell with cubic geometry at room temperature $T = 293$ K and ambient pressure $P = 0.1$ MPa. After equilibrating this low-viscosity state, the volume was decreased over 1 ns to the estimated density for the desired pressure. The system was then equilibrated alternately at constant pressure and density over an additional 4 ns to obtain the correct density at the chosen P . The equilibration times were increased by up to a factor of 10 as P increased. States at different temperatures were created from the room-temperature state by first changing T at <15 K/ns at constant volume. The appropriate density was then found by using alternating constant pressure and density runs over 40 ns. Different seeds and protocols gave equivalent results on

the scale of the symbol size in our plots. We also found the same results for systems with eight times as many molecules (SI Text and Fig. S3).

The steady-state shear stress was obtained with standard nonequilibrium MD methods (44) in LAMMPS (45). Sample input scripts and potential parameters are available in Datasets S1–S3. The periodic box was deformed to impose simple shear (planar Couette flow) at fixed density and strain rate $\dot{\gamma} = \delta u_x / \delta y$ by using the SLLOD equations of motion (44). Here, u_x is the streaming velocity in the flow (x) direction, and the velocity gradient is along the y axis. Constant temperature was maintained with a Nose–Hoover thermostat, and we checked that it maintained constant T and did not affect the shear stress until strain rates higher than those reported here ($>10^{10} \text{ s}^{-1}$). The stress and internal structure were monitored to determine when the system reached steady state. Strains of up to 100 were required. The shear stress σ was then averaged to reduce the statistical errors, which are indicated when they are larger than symbols in the figures.

As noted in Results, our Eyring fits agree with experimental measurements of the Newtonian viscosity, but differ slightly from measurements at the highest rates for $P = 796, 875$, and 955 MPa (Fig. 2). We attribute this finding to small differences between the ensembles. There may be some heating and shear dilation in the experiments. Both effects would produce the observed decrease in experimental viscosities. A quantitative estimate of the shift is difficult because of uncertainties in the thermal and mechanical coupling between the sample and viscometer, and the shift disappears in the Newtonian limit.

To isolate the effect of temperature on the rise of viscosity and obtain stricter bounds on squalane viscosity at ambient pressure, we performed simulations at constant density. We extrapolated the high T results at ambient pressure to obtain upper bounds for the density ρ at a given temperature. For $T = 96$ K and 22 K, we find bounds of 0.95 and 1.0 g cm^{-3} , respectively. Fig. S2 shows the steady-state shear stress at $\rho = 0.95 \text{ g cm}^{-3}$. Eyring fits that are used to extract the Newtonian viscosity are also shown. Simulations of shear at a given density reach steady state in a time of order $1/\dot{\gamma}$, ensuring that we obtain converged results for σ at the chosen density and rate.

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