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Universality of the high-temperature viscosity limit of silicate liquids

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We investigate the high-temperature limit of liquid viscosity by analyzing measured viscosity curves for 946 silicate liquids and 31 other liquids including metallic, molecular, and ionic systems. Our results show no systematic dependence of the high-temperature viscosity limit on chemical composition for the studied liquids. Based on the Mauro-Yue-Ellison-Gupta-Allan (MYEGA) model of liquid viscosity, the high-temperature viscosity limit of silicate liquids is $10^{-2.93}$ Pa·s. Having established this value, there are only two independent parameters governing the viscosity-temperature relation, namely, the glass transition temperature and fragility index.

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Shear viscosity is perhaps the single most important property of glass-forming liquids, since adequate control of flow behavior is essential for all steps of industrial glass production. It is also critical for understanding the relaxation characteristics of liquids, as in the well-known Angell plot[1] where the logarithm of viscosity, $\log_{10}\eta$, is plotted as a function of the T_g-scaled inverse temperature, T_g/T. Here, T_g is the glass transition temperature, defined as the temperature at which the liquid viscosity equals 10^{12} Pa·s, and T is absolute temperature. The slope of the Angell curve at T_g defines the fragility index m,

$$m \equiv \left. \frac{\partial \log_{10}\eta}{\partial(T_g/T)} \right|_{T=T_g}. \tag{1}$$

Fragility is a common measure of the slowing down of liquid dynamics upon cooling through the glass transition.

According to Angell,[1] liquids can be classified as either "strong" or "fragile" depending on whether they exhibit an Arrhenius or super-Arrhenius scaling of viscosity with temperature, respectively. The degree of non-Arrhenius scaling varies greatly among different glass-forming liquids and reflects the second derivative of the viscosity curve with respect to inverse temperature. With the assumption of a universal high-temperature limit of viscosity, η_∞, Angell proposed that this non-Arrhenius character is directly connected to the fragility index, m, a first-derivative property of the viscosity curve at T_g.[2] However, the assumption of a universal high-temperature limit of viscosity, which enables this direct connection between first- and second-derivative properties, has not yet been validated by a systematic analysis of experimental data.

In this Brief Report, we analyze viscosity-temperature curves of 946 silicate liquids and 31 other liquids, including water and silica, as well as borate, metallic, molecular, and ionic liquids. Our results show that there is no systematic dependence of η_∞ on composition and point to a narrow spread around $\eta_\infty = 10^{-2.93}$ Pa·s for silicate liquids. This result implies the existence of a universal high-temperature limit of viscosity, indicating that the fragility index m does have a direct relationship to the non-Arrhenius scaling of liquid viscosity (a measure of curvature), at least for silicate liquids. Our results indicate that there are only two independent parameters governing the viscosity of silicate liquids: T_g and m. This simplifies the process for modeling the composition dependence of liquid viscosity and is an indication of the universal dynamics of silicate liquids at the high-temperature limit.

To evaluate η_∞, we analyze experimental viscosity data using three of the most popular three-parameter equations for liquid viscosity. First, we consider the Vogel-Fulcher-Tammann (VFT) equation, which is historically the most frequently applied model,

$$\log_{10}\eta = \log_{10}\eta_\infty + \frac{A}{T - T_0}. \tag{2}$$

Here, η_∞, A, and T_0 are fitting parameters. VFT works well for most classical oxide liquids with low fragility, but it does not apply well for higher fragility liquids.[2] A major drawback of VFT is that it breaks down at low temperatures due to divergence at $T = T_0$.[3–6] Hence, it often overpredicts viscosity values at low temperatures.

Avramov and Milchev (AM) proposed an alternative three-parameter equation that describes the kinetics of the molecular motion in undercooled melts using an atomic hopping approach.[7] The AM equation is

$$\log_{10}\eta = \log_{10}\eta_\infty + \left(\frac{\theta}{T}\right)^{\alpha}, \tag{3}$$

where η_∞, θ, and α are treated as fitting parameters. The AM equation does not suffer from the problem of dynamic divergence at finite temperature; however, this equation gives a divergence of configurational entropy in the high-temperature limit.[8,9]

Finally, based on energy landscape analysis and the temperature-dependent constraint model for configurational entropy,[10–12] the recent Mauro-Yue-Ellison-Gupta-Allan (MYEGA) equation[9] was derived as

$$\log_{10}\eta = \log_{10}\eta_\infty + \frac{K}{T}\exp\left(\frac{C}{T}\right). \tag{4}$$

This model provides a physically realistic and accurate description of liquid dynamics[9, 13–15] since it is the only approach that accounts for a reasonable extrapolation of configurational entropy in both the high- and low-temperature limits. It should be mentioned that in the high-temperature limit, VFT can be derived as a simple approximation to MYEGA through a Taylor series expansion.[13] This implies that VFT is a reasonable approximation at high temperatures but becomes less accurate as temperature is decreased.

All of the aforementioned models have the high-temperature limit of viscosity, η_∞, as a common parameter. However, direct measurement of η_∞ is not possible, so the value of η_∞ must be obtained either through extrapolation of measured viscosity data or through a separate model designed specifically for η_∞. According to the viscous flow theories of Frenkel[16] and Eyring,[17] the high-temperature viscosity limit is $\eta_\infty = 10^{3.5\pm1}$ Pa·s. However, this is a rough estimate since they describe the temperature dependence of viscosity using an Arrhenius equation, which does not account for liquid fragility. The η_∞ values of some glass-forming liquids were also determined by Barrer,[18] where the viscosity data are also simply fitted by the Arrhenius equation. The obtained η_∞ values are scattered over several orders of magnitude and are nonphysically described as a function of temperature. Kobeko[19] showed a value equal to $\eta_\infty = 10^{-3\pm1.5}$ Pa·s for all liquids. Russell *et al.*[20] fitted the viscosity data of 333 silicate melts using the VFT and Adam-Gibbs (AG) models and obtained a high-temperature limit as $\eta_\infty = 10^{-4.3\pm0.74}$ and $10^{-3.2\pm0.66}$ Pa·s, respectively. Recently, Giordano *et al.*[21] obtained a common high-temperature viscosity limit for silicate melts of $\eta_\infty = 10^{-4.6}$ Pa·s based on the VFT equation. However, these previously obtained values of η_∞ were obtained using a fairly limited range of compositions.

We begin our investigation by fitting the three viscosity models (VFT, AM, and MYEGA) to measured viscosity data for 946 different silicate liquids from Corning Incorporated, in addition to 6 borate,[22] 11 metallic,[23] 4 molecular,[9] and 9 ionic liquids.[24] The fitting was done using a constrained Monte Carlo algorithm to avoid becoming trapped in local minima. The 946 Corning liquids cover a wide range of composition space, from simple calcium aluminosilicate ternaries through complex borosilicates with up to eleven unique oxide components.[25] Overall, the compositions cover a range of fragility values from 25.9 to 73.8. Each composition is represented by 6–13 data points in the range of 10 to 10^6 Pa·s, obtained via a rotating spindle method. Most are also represented by data points at $10^{6.6}$ Pa·s (the softening point, obtained via parallel plate viscometry) and 10^{11} Pa·s (obtained via beam bending viscometry). The measured isokom (i.e., constant viscosity) temperatures are accurate to within ±1 K. Figure 1 shows the root mean square (RMS) error of the viscosity fit to 946 Corning compositions as a function of each composition, plotted from highest to lowest error. MYEGA provides the best fit with the lowest root mean square (RMS) error for the whole range of compositions, as compared to VFT and AM, although the difference between MYEGA and VFT models is subtle. The superior fitting quality of MYEGA is due to its derivation from physically realistic considerations in both the high- and low-temperature limits; hence, it is expected to yield the most accurate value of η_∞.[9] In Fig. 1, we also consider a recent viscosity model by Elmatad, Chandler, and Garrahan (ECG), in which the viscosity curves are considered to be parabolic in inverse temperature space.[26] However, this model provides a significantly worse fitting quality compared to the other three models, and due to its parabolic form, the extrapolation of η_∞ is not physically meaningful. Therefore, we consider only the VFT, AM, and MYEGA models in the remainder of our analysis.

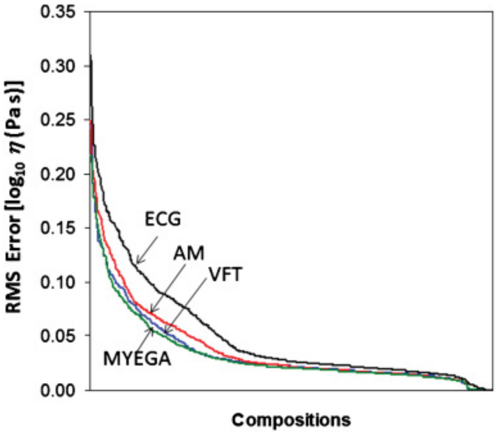

FIG. 1. (Color online) Root mean square error of the viscosity models when fitting measured data of 946 Corning compositions.

Figure 2 shows the fitted values of $\log_{10}\eta_\infty$ for the Corning liquids. The straight lines in the figure represent the average values of η_∞ obtained from the three models. The average value of $\log_{10}\eta_\infty$ predicted by MYEGA is −2.93, which is in line with previous estimates.[19,20] AM produces an unrealistically high value of η_∞[9] due to an unphysical divergence of configurational entropy in the high-temperature limit. In contrast, VFT produces comparatively low values of η_∞ as a by-product of its unphysical divergence of viscosity at low temperatures. Our results show that the lowest standard deviation of $\log_{10}\eta_\infty$ for all the compositions occurs using the MYEGA model ($\sigma = 0.337$, compared to 0.343 and 0.519 for VFT and AM, respectively). The difference among these models reflects the fact that $\log_{10}\eta_\infty$ is an extrapolated quantity well beyond the range of measurements.[20,27] Since MYEGA produces the most accurate fits and is physically derived, the value yielded by this equation is expected to be reasonable.[9]

The next question is whether the scatter in Fig. 2 is due to stochastic measurement error or if it is the result of an actual

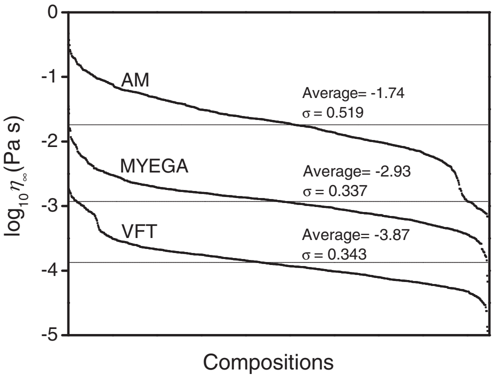

FIG. 2. $\text{Log}_{10}\,\eta_\infty$ values obtained by fitting three viscosity models to 946 Corning compositions. The straight lines represent the average $\log_{10}\eta_\infty$ values, and σ is the standard deviation.

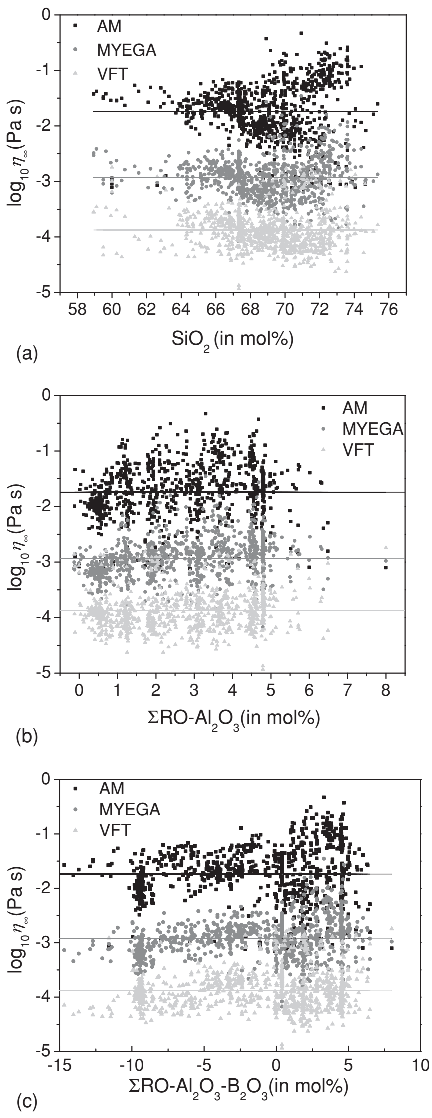

FIG. 3. Log_{10} η_∞ values of 946 Corning compositions plotted as a function (a) SiO$_2$, (b) $\sum$RO–Al$_2$O$_3$, and (c) $\sum$RO–Al$_2$O$_3$–B$_2$O$_3$ content. $\sum$RO represents the total concentration of alkaline earth oxide as measured through x-ray fluorescence. The straight lines are the average values.

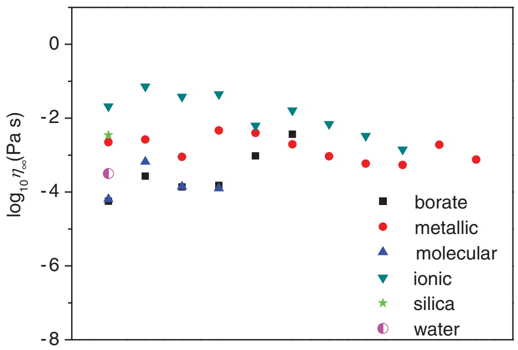

FIG. 4. (Color online) Log_{10} η_∞ values obtained by fitting MYEGA to several borate,[22] metallic,[23] molecular,[9] and ionic[24] liquids, and water.[28] The abscissa represents an arbitrary composition space.

dependence of $\log_{10}\eta_\infty$ on composition. In order to answer this question, we analyze the fitted values of $\log_{10}\eta_\infty$ as a function of every composition variable. For example, Fig. 3 shows the $\log_{10}\eta_\infty$ values for different alkaline earth boroaluminosilicate compositions as a function of alkaline earth concentration. Within the error range of the data, there is no trend of η_∞ with composition, and η_∞ has a fairly narrow spread around $10^{-2.93}$ Pa·s. Similar results are obtained when plotting $\log_{10}$ η_∞ versus any composition variable. These results suggest that the value of η_∞ is independent of composition and that the scattering of the data is due to the experimental noise and differences in the range of temperatures over which viscosity is measured.

The range of liquid fragility values (m) of the 946 glass compositions investigated is between 25.9 and 73.8. In order to find out whether relatively strong liquids (i.e., with $m < 25$) show similar η_∞ values to $10^{-2.93}$ Pa·s, we also analyze the viscosity data of silica, an archetypical strong glass-former. Here, we obtain a value of $\eta_\infty = 10^{-2.46}$ Pa·s for Corning code 8655 high-purity fused silica (HPFS). In addition, we obtain the η_∞ values of several fragile liquids with $m > 75$, e.g., o-terphenyl ($m = 99$) and 4Ca(NO$_3$)$_2$-6KNO$_3$ ($m = 115$), by fitting their viscosity data to the MYEGA equation. We plot the η_∞ values of the two liquids in Fig. 4, along with those of other nonsilicate liquids, such as borate,[22] metallic,[23] molecular,[9] and ionic liquids[24] and water.[28] Although there are significantly less statistics here compared to the silicate compositions, we find that the values of η_∞ do indeed fall near 10^{-3} Pa·s for all of these liquids. However, the viscosity data of more nonsilicate liquids need to be analyzed to judge whether a universal η_∞ value exists for all the glass-forming liquids.

The narrow spread of η_∞ points to a common underlying physics of silicate liquids at the high-temperature limit. It should be noted that the high-temperature limit refers to the viscosity of a *liquid* at high temperature. In other words, it does not involve the gaseous state, but rather a superheated liquid state. In his early work, Angell suggests that the value of η_∞ is determined by the liquid quasi-lattice vibration time ($\tau_\infty \approx 10^{-14}$ s), which is the time between successive assaults on the energy barrier for atomic rearrangements.[1] Maxwell's relation ($\eta_\infty = G_\infty \tau_\infty$, where G_∞ is the shear modulus at infinite frequency at temperature above T_g, and τ_∞ is the structural relaxation time at infinite temperature) was used to calculate the high-temperature viscosity limit from $\tau_\infty \approx 10^{-14}$ s[20,21] For oxide liquids, G_∞ varies only slightly with temperature and was measured over a large range of temperatures above T_g to be around 29 GPa.[29] However, for some organic liquids, both G_∞ and τ_∞ vary with composition and temperature.[30–32] In our view, any explanation of η_∞ based on vibrations is not correct, since at infinite temperature, the system is not really vibrating. Rather, it is exploring the upper region of the energy landscape dominated by high entropy and low activation barriers.[33] Moreover, the atoms have an infinite amount of thermal energy to overcome any barrier, so they do not even see the activation barriers at all and hence cannot be vibrating. Therefore, a more physically realistic explanation of η_∞ is needed.

For this explanation, we turn to the topological constraint approach of Phillips and Thorpe,[11,12] which states that the atomic structure of a glass-forming liquid may be treated as a network of bond constraints. By comparing the average number of constraints per atom (n) to the network dimensionality (d), the network can be floppy (underconstrained), isostatic (optimally constrained), or stressed-rigid (overconstrained). When $n < d$, the network is underconstrained and contains low-frequency deformation modes (so-called "floppy modes"). The network is optimally rigid when $n = d$, and it is stressed-rigid when $n > d$. Based on this original work of Phillips and Thorpe, Gupta and Mauro[10] presented a topological modeling approach incorporating a temperature dependence of constraints. At infinitely high temperature, any constraint is easily broken and hence does not contribute to the rigidity of the network. In a three-dimensional space, the atomic degrees of freedom, $f = d - n$, i.e., the number of low-frequency "floppy modes," is equal to $d = 3$ for any system. In other words, in the infinite temperature limit, all three degrees of freedom are floppy for each atom, so each atom has three continuous modes of deformation, independent of atom type, and the configurational entropy has achieved its maximal value. Hence, all silicate liquids will exhibit the same flow behavior in the high-temperature limit. We are in a three-dimensional space; however, if we were operating in a different dimensional space (i.e., $d = 2$ or $d = 4$), there would exist different values of η_∞. We thus argue that our result of a convergence of η_∞ values at $10^{-2.93}$ Pa·s for silicate liquids is physically meaningful in terms of constraint theory. The narrow spread of the high-temperature viscosity limit is an implication of the universal dynamics of silicate liquids at the high-temperature limit.

In summary, by analyzing 946 silicate liquids and 31 nonsilicate liquids, we find that there is a narrow spread of high-temperature limit of viscosity around 10^{-3} Pa·s for silicate liquids. This implies that silicate liquids have a universal value of η_∞. Thus, in accordance with the work of Angell, the non-Arrhenius scaling of liquid viscosity can be quantified through the fragility index m of the liquid. Moreover, by defining the high-temperature viscosity limit as a fixed value, i.e., $\log_{10} \eta_\infty = -3$, the MYEGA model contains only two fitting parameters. This result simplifies the modeling process of the compositional dependence of viscosity and indicates a common underlying physics of silicate liquids at the high-temperature limit.

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