Little evidence for dynamic divergences in ultraviscous molecular liquids

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The physics of the ultraviscous liquid phase preceding glass formation continues to pose major problems that remain unsolved. It is actively debated, for instance, whether the marked increase of the relaxation time reflects an underlying phase transition to a state of infinite relaxation time. To elucidate the empirical evidence for this intriguing scenario, some of the most accurate relaxation-time data available for any class of ultraviscous liquids—those obtained by dielectric relaxation experiments on organic liquids just above the glass transition—were compiled. Analysis of data for 42 liquids shows that there is no compelling evidence for the Vogel–Fulcher–Tammann (VFT) prediction that the relaxation time diverges at a finite temperature. We conclude that theories with a dynamic divergence of the VFT form lack a direct experimental basis.

All liquids may be supercooled. In some cases, the liquid crystallizes spontaneously. In other cases, a marked increase in viscosity and relaxation time is observed on continued cooling, and the liquid eventually solidifies into a glass—a frozen liquid. Which of the two scenarios that prevails depends on the cooling rate. The ultraviscous liquid phase preceding glass formation has universal physical properties, independent of the nature of the chemical bonds involved: metal bonds, ionic bonds, covalent bonds, van der Waals bonds or hydrogen bonds. The universalities and the lack of understanding of the basic phenomenology continue to make this research field attractive to physicists, chemists and materials scientists alike.

The universal features[1–7] that characterize ultraviscous supercooled liquids relate, in particular, to the time dependence of relaxation functions and to the temperature dependence of the relaxation time. The former is not our focus here; it is reflected in the fact that relaxation functions are generally well fitted by the so-called stretched exponential function. The focus below is on the relaxation time, which increases markedly on cooling into the ultraviscous phase, sometimes by more than a factor of ten when temperature is lowered by just 1%. Figure 1 shows the relaxation time as a function of temperature for some typical molecular liquids. This figure raises the question: Does the relaxation time diverge at finite temperatures or only as $T \to 0$?

The average relaxation time τ is generally non-Arrhenius. That is, on cooling, τ almost always increases faster than predicted by the well-known Arrhenius equation. This is the mathematical expression that characterizes, for example, the temperature dependence of a chemical reaction time in terms of an activation energy. For ultraviscous liquids, if the temperature-dependent activation energy $\Delta E(T)$ is defined by the Arrhenius expression

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta E(T)}{k_B T}\right), \qquad (1)$$

it is generally found that $\Delta E(T)$ increases significantly on cooling. To the best of our knowledge, there are no liquids where ΔE decreases, which is in itself a striking fact.

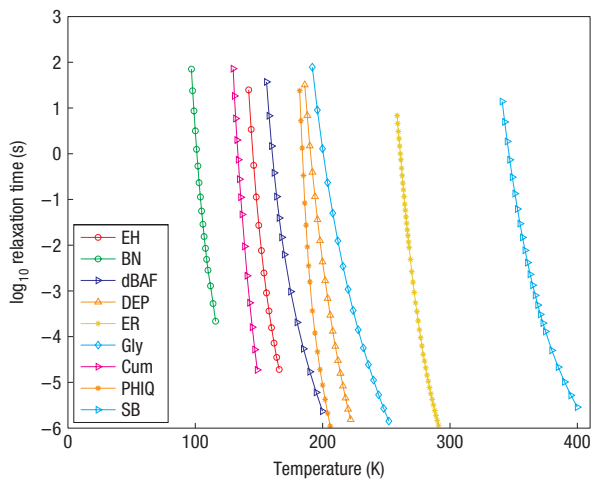

Figure 1 Relaxation time as a function of temperature for typical organic liquids supercooled into the ultraviscous phase. The relaxation time was determined as the inverse dielectric loss-peak frequency, identified by fitting data in a log–log plot around the maximum with a parabola. If a linear scale were used, the relaxation time would increase almost vertically on cooling; even on a log scale, the increase is marked. The question investigated in this article is whether or not there is reason to believe that the relaxation time diverges at some finite temperature. The full lines are drawn as guides to the eye. Table 1 explains the liquid abbreviations.

THE VFT EQUATION

The function most widely used to fit relaxation-time data is the Vogel–Fulcher–Tammann (VFT) equation dating back to the 1920s (refs 8–10):

$$\tau = \tau_0 \exp\left(\frac{A}{T - T_0}\right) \qquad (T_0 < T). \qquad (2)$$

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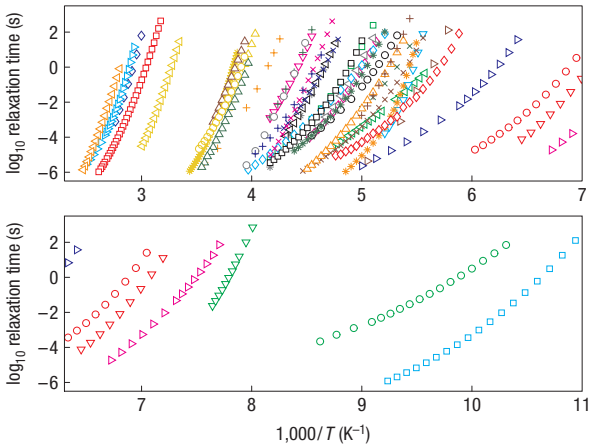

Figure 2 Relaxation time data identified from dielectric loss peaks for all of the 42 organic ultraviscous liquids used in the analysis. Both panels show the logarithm of the dielectric relaxation time as a function of inverse temperature. A straight line in this plot signals an Arrhenius temperature dependence. The liquids all exhibit the non-Arrhenius temperature dependence of the relaxation time that characterizes ultraviscous liquids. The symbols are explained in Table 1.

Table 1 Liquids included in the analysis. The name of each liquid, its abbreviation and the symbol used in the figures are listed. More details (including references, temperature, frequency intervals and some further information) are provided in the Supplementary Information.

Liquid	Abbreviation	Symbol
1,2-propandiol (propylene-glycol)	PG	◁
2-ethyl-hexylamine	EH	○
2-methyl-tetrahydrofurane	MTHF	□
2-phenyl-5-acetomethyl-5-ethyl-1,3-dioxocyclohexane	AFEH	▽
3,3,4,4-benzophenonetetracarboxylic dianhydride	BPC	◇
3-fluoro-aniline	FAN	▷
3-phenyl-1-propanol	3Ph1P	×
3-styrene	3Sty	+
5-polyphenyl-ether	5-PPE	△
benzophenone	BePh	*
biphenyl-2yl-isobutylate	BP2IB	◁
butyronitrile	BN	○
cresolphthalein-dimethylether	KDE	□
decahydroisoquinoline	DHIQ	▽
di-iso-butyl-phtalate	dIBP	◇
dibutyl-ammonium-formide	dBAF	▷
dibutyl-phtalate	DBP	×
dicyclohexyl-methyl-2-methylsuccinate	DCHMMS	+
diethyl-phtalate	DEP	△
diglycidyl-ether-of-bisphenol A (epoxy-resin)	ER	*
dimethyl-phtalate	DMP	◁
dioctyl-phtalate	DOP	○
dipropylene-glycol	DPG	□
dipropylene-glycol-dimethyl-ether	DPGDME	▽
glycerol	Gly	◇
isopropyl-benzene	Cum	▷
m-tricresyl-phosphate	mTCP	×
m-toluene	mTol	+
o-terphenyl	OTP	△
perhydroisoquinoline	PHIQ	*
phenolphthalein-dimethylether	PDE	◁
phenyl-salicylate (salol)	Sal	○
polypropylene-glycol	PPG	□
pyridine–toluene mixture	PT	▽
squalane	Sqa	◇
sucrose-benzonate	SB	▷
tetraphenyl-tetramethyl-trisiloxane	DC704	×
tricresyl-phosphate	TCP	+
triphenyl-ethylene	TPE	△
tripropylene-glycol	TPG	*
trisnaphthylbenzene	tNB	◁
xylitol	Xyl	○

This corresponds to an activation energy that increases on cooling as $\Delta E \propto T/(T - T_0)$. Although the VFT equation has few adjustable parameters, it generally gives quite good fits to data. The coefficients of the VFT equation were considered in the landmark paper published in 1955 by Williams, Landel and Ferry[11] that discussed the non-Arrhenius problem in terms of the free-volume model. In the 1970s, there were reports that the VFT equation breaks down at temperatures with long relaxation times (large viscosities)[12,13]. These 'early warnings' were to some extent forgotten or repressed, perhaps because probing the relaxation time accurately through viscosity measurements is difficult at high viscosities.

Experimentalists often regard the VFT equation as just a convenient fit to data[12]. Many theorists, on the other hand, were inspired by the VFT equation to develop theories predicting a phase transition at T_0 to a state with infinite relaxation time[14]. The first such approach was the famous Adam–Gibbs entropy model from 1965 predicting a second-order phase transition at $T = T_0$ to a state of zero configurational entropy and infinite relaxation time[15,16], a unique 'ideal glass'. A number of simplifying assumptions go into the Adam–Gibbs formalism, and in 1997 it was argued by DiMarzio and Yang[17] that even if the Adam–Gibbs idea of an underlying phase transition is accepted, the relaxation time remains finite at the transition temperature. Very recently, mathematically rigorous theorems derived by Eckmann and Procaccia[18] show that for two-dimensional soft-sphere mixtures, at least, the configurational entropy stays positive for $T > 0$.

Leading theorists such as Edwards[19,20], Anderson[21] and, more recently, Bouchaud and Biroli in 2004 (ref. 22) and Lubchenko and Wolynes in 2007 (ref. 23) have developed dynamic divergence scenarios far beyond Adam and Gibbs'. Although there are differing opinions from other famous theorists[24–27], it remains a popular idea that the marked slowing down on cooling reflects an underlying phase transition to a state of infinite relaxation time. The fact that data are usually well fitted by the VFT equation has reinforced this idea over many years[28]. Our aim is to provide an in-depth investigation of the evidence for dynamic divergences of the VFT form. Before detailing the data analysis, it should be noted that support for the idea of a dynamic divergence traditionally came from several papers reporting near equality of the VFT fitting parameter T_0 and the Kauzmann temperature T_K, the temperature where the liquid phase entropy by extrapolation below the glass transition becomes identical to the crystal phase entropy[29–31]. In 2003, however, Tanaka presented a compilation of data showing that $T_0 = T_K$ is not confirmed by experiment[32].

As is evident from the above, an important question of contemporary glass science is the following: Is there experimental evidence for the dynamic divergence predicted by the VFT equation? Answering this is important, because if there is an underlying dynamic divergence, this obviously explains the marked relaxation-time increase on cooling. By its very nature the question is subtle, however, because if the equilibrium liquid relaxation time diverges at some finite temperature, it is impossible to equilibrate the liquid at or close to that temperature. This means that no experiment can conclusively prove the existence of a dynamic divergence. To cut this science–philosophical Gordian knot, we take the following pragmatic viewpoint: the conjecture of a diverging

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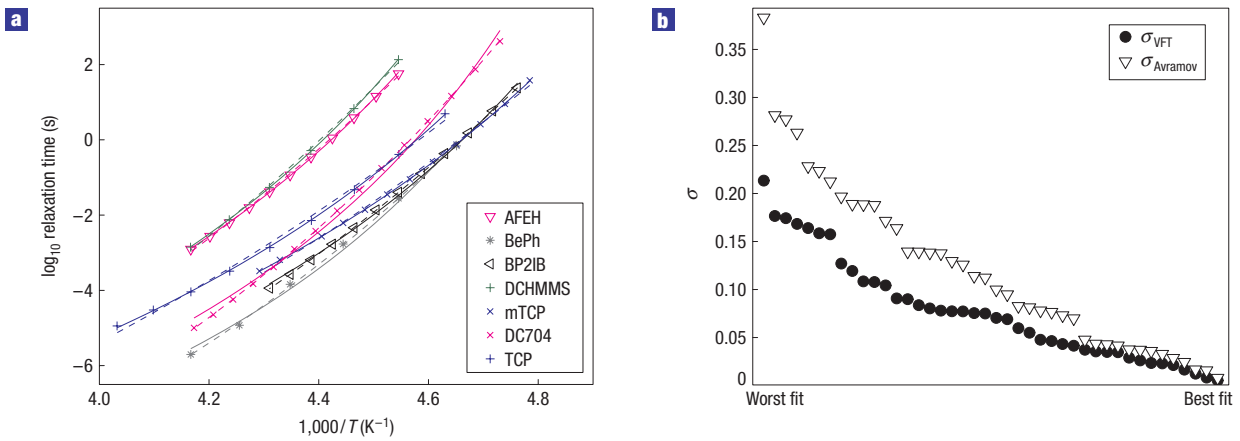

Figure 3 The VFT and Avramov equations compared with data. a, Examples of fits with the VFT equation (solid lines) and the Avramov equation (dashed lines). **b**, Standard deviation from fits to data of the two equations. The *x* axis represents the 42 liquids sorted in descending order of standard deviation for each of the two fitting functions; thus, a given position on the *x* axis generally corresponds to two different liquids. On average, the VFT equation fits data better than does the Avramov equation.

relaxation time of VFT form will be regarded as probably correct if—and only if—the VFT equation fits data considerably better than do other mathematically simple functions with the same number of fitting parameters and no dynamic divergence. To investigate this, data for a large number of liquids are needed.

DATA ANALYSIS

Accurate data are required to assess whether or not the VFT prediction of a diverging relaxation time is confirmed by experiment. Dielectric relaxation measurements give the most precise relaxation-time data, far more accurate than data from other relaxation processes or from viscosity measurements. For practical reasons, the best dielectric data for ultraviscous liquids are for organic liquids; such liquids are often easily supercooled and quite convenient to work with. Monoalcohols were omitted from the analysis because their dominant dielectric relaxation process does not relate to the calorimetric glass transition[33].

To quantify how well the VFT equation fits data, we compared the VFT equation with another popular fitting function[34–39] that is now known as the Avramov equation:

$$\tau(T) = \tau_0 \exp\left(\frac{B}{T^n}\right). \qquad (3)$$

Like the VFT equation, the Avramov equation has two parameters in addition to the prefactor τ_0, but it has no dynamic divergence. The prefactor is usually regarded as a free parameter, but we chose to fix it to $\tau_0 = 10^{-14}$ s (ref. 40). The below conclusions are not sensitive to the exact value of τ_0 if it is insisted that it should have a physically reasonable value, that is, be in (or just slightly outside) the range 10^{-14}–10^{-13} s.

At any given temperature, from the dielectric loss as a function of frequency, we define the liquid relaxation time τ as the inverse loss-peak frequency. The last of these is identified by fitting loss data as a function of log frequency close to the maximum loss with a parabola. Figure 2 shows all data analysed. All liquids exhibit the characteristic non-Arrhenius behaviour with a relaxation time that increases stronger on cooling than predicted by the Arrhenius equation (that is, equation (1) with temperature-independent activation energy). A list of all liquids included in the analysis and their corresponding symbols is given in Table 1; more details are provided in the Supplementary Information.

The fitting region was restricted to relaxation times between 1 μs and 1,000 s. This was done to avoid comparing different types of dynamic behaviour—otherwise there is the risk that we ultimately test the two equations' ability to interpolate between two different dynamics. The lower limit (1 μs) was chosen to ensure that the dynamics are well within the 'landscape dominated' domain[41,42]. The upper limit (1,000 s) was chosen to ensure that all data are true equilibrium data. A further requirement was that only data sets covering at least four decades in time measured at five or more temperatures were included in the analysis. Out of an initial collection of data for 62 liquids, 42 met these demands. The liquids represent some of the most commonly studied organic glass formers; their dielectric properties were measured by leading groups in the field. These data were supplemented by some new measurements of ours.

Equations (2) and (3) were fitted to data using the least-squares method. The procedures for selecting data and the subsequent fitting procedures were automated through MatLab routines. Examples of fits are shown in Fig. 3a with VFT fits as solid lines and Avramov fits as dashed lines. Both equations fit well with little visible difference. For a quantitative comparison of the two fitting functions, we used the standard deviation formula, $\sigma^2 = 1/(N-n)\sum_i(\log_{10}(\tau_{\mathrm{fit,i}}) - \log_{10}(\tau_{\mathrm{data,i}}))^2$, where N is the number of data points and $n = 2$ is the number of degrees of freedom. Figure 3b shows σ_{VFT} and $\sigma_{\mathrm{Avramov}}$ for all liquids, where the σ values for clarity are sorted in descending order for both fits. The VFT equation generally fits data better than does the Avramov equation.

Inspecting the fits closely—in Fig. 3a as well as those not shown—reveals that deviations are systematic. Thus, highly non-Arrhenius liquids, that is, data sets with large curvature, are generally poorly fitted by the Avramov equation. Apparently, the Avramov equation is not able to 'bend' enough to capture the curvature of these data sets. Is that a signal of the dynamic divergence predicted by the VFT equation? To investigate this possibility, we calculated how the activation energy changes with temperature using the temperature index defined[43] by

$$I = -\frac{\mathrm{d}\ln \Delta E}{\mathrm{d}\ln T}. \qquad (4)$$

The temperature index quantifies the activation-energy temperature dependence in a way that is independent of the

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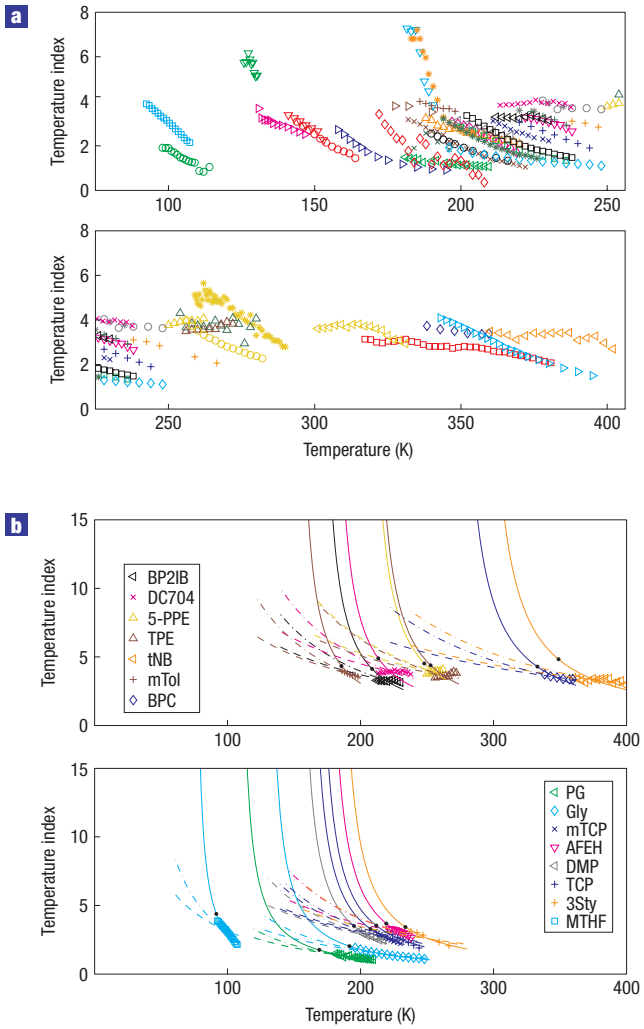

Figure 4 Temperature indices. This quantity (equation (4)) measures how fast the activation energy increases on cooling; it is plotted as a function of temperature. **a**, Temperature indices for all liquids. With few exceptions, the temperature index increases with decreasing temperature. This explains why the VFT equation fits data better than does the Avramov equation, which predicts a temperature-independent index. **b**, Temperature indices for the eight liquids where the Avramov equation (upper panel), respectively the VFT equation (lower panel), fits best. The full lines give the VFT-predicted temperature indices (equation (5)), the dashed–dotted and dashed lines, respectively, give the predictions of the two fitting functions FF1 and FF2 that do not have dynamic divergences (equations (6) and (7)). In both subfigures, the black circles mark the glass-transition temperature for each liquid.

unit system, like the Grüneisen parameter of solid-state physics quantifies the effects of thermal expansion. If for instance the temperature index is four, lowering the temperature by 1% leads to a 4% increase of the activation energy. If the glass transition temperature is defined by $\tau(T_g) = 100\,\mathrm{s}$, the temperature index is related to Angell's fragility $m \equiv \mathrm{d}\log_{10}(\tau)/\mathrm{d}(T_g/T)|_{T_g}$ by $m = c(1 + I(T_g))$, where $c = \log_{10}(\tau(T_g)/\tau_0) = 16$ (ref. 43).

For the Avramov equation, the temperature index is constant, $I_{\mathrm{Avramov}} = n - 1$. For the VFT equation, we find

$$I_{\mathrm{VFT}} = \frac{T_0}{T - T_0}. \qquad (5)$$

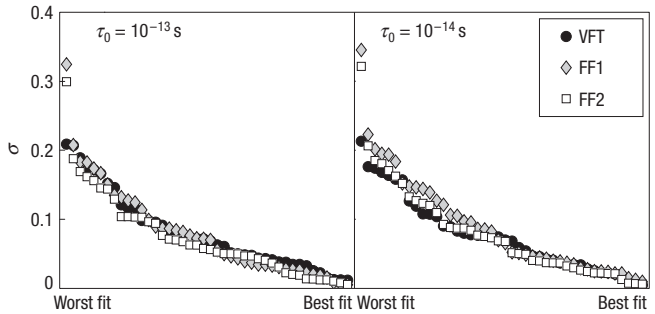

Figure 5 Standard deviation from fits to data of the VFT equation and two alternative fitting functions with the same number of parameters but no dynamic divergence, FF1 and FF2 of equations (6) and (7). The *x* axis represents the liquids sorted in descending order of standard deviation for each fitting function. For both choices of physically reasonable prefactors, the three functions fit equally well. The worst-fit outlier is perhydroisoquinoline, one of the most fragile (non-Arrhenius) liquids in the collection (compare Fig. 1).

Thus, the VFT temperature index increases on cooling and diverges at $T = T_0$. Figure 4a shows temperature indices for all 42 liquids as functions of temperature. For the vast majority of liquids, the temperature index increases with decreasing temperature. This explains why the VFT equation fits data better than the Avramov equation.

The temperature index is also useful for shedding light on how strong the evidence for a dynamic divergence is. Figure 4b (upper panel) shows the actual and the VFT-predicted temperature indices for the eight liquids that are best fitted by the Avramov equation; the lower panel shows those liquids that are best fitted by the VFT equation. The data are not inconsistent with the dynamic divergence predicted by the VFT equation, but we cannot reasonably say that there is compelling evidence for a divergent temperature index as predicted by the VFT equation. The dashed–dotted and dashed lines are the temperature indices of the two below fitting functions.

We proceed to compare the VFT function to two alternative fitting functions with temperature indices that increase on cooling, but without divergence at a non-zero temperature. Fitting functions one and two (FF1 and FF2) reflect the following temperature indices: $I = (T_1/T)^2$ and $I = (T_2 - T)/T$ $(T < T_2)$, respectively. Integrating these expressions via equation (4) leads to

$$\Delta E(T) \propto \exp\left[\frac{T_1^2}{2T^2}\right] \qquad (\mathrm{FF1}), \qquad (6)$$

$$\Delta E(T) \propto T \exp\left[\frac{T_2}{T}\right] \qquad (\mathrm{FF2}). \qquad (7)$$

Figure 5 shows the standard deviations from fitting these two functions to data compared with the VFT equation. The panels show results from two different prefactors, $\tau_0 = 10^{-13}$ s and $\tau_0 = 10^{-14}$ s. In both cases the three functions fit equally well.

OUTLOOK

The analysis was limited to non-polymeric systems because the polymer glass transition may be fundamentally different from the liquid–glass transition. The VFT equation was often used also for the polymer glass transition, however, where it is generally

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known as the Williams–Landel–Ferry equation[11]. A clever way to extend the range of relaxation times beyond those obtainable by linear relaxation experiments is to consider results from ageing experiments. Studies by McKenna, Simon, Plazek and co-workers mainly on polymeric systems show that the VFT prediction is not followed when systems are aged into equilibrium by annealing for sufficiently long time slightly below the glass-transition temperature[44–47]. Although the accuracy of these experiments is not comparable to that of dielectric relaxation experiments on the metastable equilibrium phase, it was nevertheless possible to conclude that the relaxation times deviate from the VFT equation by always increasing less markedly when lowering temperature than predicted by the VFT equation. These results are fully consistent with the above conclusion.

It is not possible to rule out that there is a dynamic divergence of the VFT form, but our findings give no indications of such a divergence. It is instructive to compare the situation to that of a second-order phase transition. This is associated with a dynamic divergence where the (maximum) relaxation time diverges as an inverse power law of the temperature distance to the transition temperature (critical slowing down). Thus, right at the phase transition, the relaxation time is infinite. Although it is not possible to experimentally definitively prove this dynamic divergence, nobody doubts it. This is because (1) the predicted mathematical form is supported by experiment, (2) the dynamic critical exponents fit theoretical predictions and (3) there is a fundamental understanding of what is going on and why relaxations slow down when the transition is approached. For ultraviscous liquids, there is no such generally agreed simple and universal model. Here, the logic was traditionally reversed. The observation that data are well fitted by the VFT equation was used to justify a search for models with a dynamic divergence. Our findings indicate that this is probably not a fruitful route. Thus, with Occam's razor in mind—'it is vain to do with more what can be done with fewer'—we suggest that in the search for the correct theory for ultraviscous liquid dynamics, theories not predicting a dynamic divergence of the VFT form should be focused on.

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Author contributions

Project planning and data analysis were carried out by T.H. and J.C.D., experimental work by A.I.N. and N.B.O.

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