Corresponding States of Structural Glass Formers

Yael S. Elmatad,[†] **David Chandler,***[,†] **and Juan P. Garrahan**[‡]

Department of Chemistry, University of California, Berkeley, California 94720, and School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, U.K.

The variation with respect to temperature T of transport properties of 58 fragile structural glass-forming liquids (67 data sets in total) are analyzed and shown to exhibit a remarkable degree of universality. In particular, super-Arrhenius behaviors of all supercooled liquids appear to collapse to one parabola for which there is no singular behavior at any finite temperature. This behavior is bounded by an onset temperature T_o above which liquid transport has a much weaker temperature dependence. A similar collapse is also demonstrated over the smaller available range for existing numerical simulation data.

Fragile glass-forming liquids are supercooled liquids where the increase of relaxation time τ with decreasing temperature T is more rapid than that of the Arrhenius law, $\log(\tau/\tau_R) = E(1/T - 1/T_R)$. Here, τ_R refers to a relaxation time at a reference temperature T_R, and E is the activation energy over Boltzmann's constant. Most supercooled molecular liquids are of this type.[1] Figure 1 shows the collapse of transport data for these systems. Rather than linear in $1/T$, the collapsed data for $\log \tau$ is quadratic in $1/T$. The data provides no evidence for singular expressions like the Vogel–Fulcher–Tammann (VFT) $\log \tau \sim \text{const} / (T - T_K)$ or the mode-coupling $\log \tau \sim \text{const} | \log(T - T_c) |$. These singular forms are often used to fit transport data of supercooled liquids,[1] and theoretical arguments have been presented as derivations of these forms.[2] However, the data summarized in Figure 1 shows that these forms are unnecessary, suggesting that the theoretical arguments are inapplicable or incorrect.

This relaxation time τ is an "equilibrium" property. Its value is determined by the thermodynamic state of the system, and nothing more. The rate of preparation, for example, is not pertinent. In contrast, one could consider transport properties when, for example, cooling or warming rates exceed relaxation rates or at other irreversible conditions like those with which glass is manufactured. In irreversible or driven cases, transport properties can be singular.[3] However, in this article, we confine our attention to the reversible case because it is this case where the great majority of quantitative measurements have been made. It is for this case that we are showing with Figure 1 that there is no evidence of singular behavior controlled by the thermodynamic variable T.

Recently, Dyre and co-workers[4] arrived at a similar conclusion, existing transport data support neither the idea of a finite temperature divergence nor the VFT formula. All of the data considered in that work and more are treated here. Our analysis takes the further step of collapsing the data and thus demonstrating universality. A similar collapse was noted a few years ago, when Rössler and co-workers showed how seemingly varied behaviors for the transport properties of several supercooled liquids could be represented by a single function of temperature.[5] The fitting in Figure 1 differs mainly in the functional form adopted for the data collapse. This difference enables a universal fit over a range of temperatures larger than the fit suggested by Rössler.[5] For example, for liquid Ca–K–NO$_3$, Rössler et al. fit data for temperatures below $T = 381$ K, while T_o for this material is 444 K. This percentage difference is similar for all of the liquids considered by Rössler et al. The onset-like temperatures for the fits reported by Fischer[6] and by Stickel et al.[7] are somewhat closer to T_o than that of Rössler et al., but here too, the boundaries for fitted data are lower than T_o. Kivelson and co-workers[8] have proposed another collapse to a nonsingular function, but one with one more adjustable parameter than we consider.

We have used the quadratic form in earlier work.[9] This form could be interpreted in terms of a random energy model, where activation barriers are assumed to be distributed as Gaussian variables,[10] but the origin of this distribution would then remain to be explained. We arrived at the quadratic form differently, from a class of kinetically constrained models[11] where the activation energy to relax a domain of length scale ξ grows as $\log \xi$.[12] The equilibrium domain size is $\xi \simeq c^{-1/d}$, where c is an equilibrium concentration of localized excitations and d is dimensionality. The Boltzmann distribution gives $\log c \propto 1/T$, from which one predicts an activation energy that grows as $1/T$ so that $\log \tau$ grows as $1/T^2$ (to leading order in $1/T$).[12]

We expect the range of validity of this quadratic behavior to be bounded.[9] In particular, it should not apply above a temperature of T_o, where excitations facilitating molecular motions are present throughout the system. In that regime, correlated dynamics is not required for molecular motions, and accordingly, temperature variation of transport is nearly negligible.[13] The quadratic form should also not apply below another temperature, which we call T_x. The reasoning here recognizes that correlated dynamics leading to super-Arrhenius behavior[14] is the result of constraints due to intermolecular forces. At an energetic cost, E, these constraints can be avoided. The time scale to pay that cost is $\tau_x \exp(E/T)$. While this time can be very long, at a low enough temperature, it will become shorter than a super-Arrhenius time. This is the temperature T_x, below which relaxation will be dominated by dynamics that avoid constraints. Therefore, we use

$$\log(\tau/\tau_o) \simeq (J/T_o)^2(T_o/T - 1)^2, \quad T_o > T > T_x \qquad (1)$$

to fit the data in Figure 1, using J as the parameter to set the energy scale for excitations of correlated dynamics, and with the under-

* To whom correspondence should be addressed. E-mail: chandler@cchem.berkeley.edu.
† University of California.
‡ University of Nottingham.

TABLE 1: Fragile Glass Formers

system[a]	full name	T_o/K[b]	J/T_o[c]	$\log \tau_o/s$[d]	$\log \eta_o/P$[e]	Σ (Σ_{VFT})[f]	T_m/K[g]	T_g/K[h]	range/K[i]
3BRP[25]	3-bromopentane	192	4.3	−9.4		0.13 (0.13)	147	108	107−289
3Sty[26]	3-styrene	314	8.5	−6.5		0.024 (0.025)	242	237	235−280
5-PPE[23]	5-polyphenylether	398	6.2	−12.4		0.0044 (0.058)		248	248−264
AFEH[4]	2-phenyl-5-acetomethyl-5-ethyl-1,3-dioxocylohexane	285	9.4	−6.1		0.0038 (0.0096)		219	220−240
B2O3[27]	boron oxide (B_2O_3)	1066	3.3		3.0	0.095 (1.0)	723	541	533−1665
BePh[28]	benzophenone	328	6.3	−11.0		0.05 (0.052)	321	208	215−240
BN[29]	butyronitrile	135	6.6	−4.8		0.025 (0.021)	116	97	97−116
BP2IB[4]	biphenyl-2yl-isobutylate	313	6.7	−9.4		0.0063 (0.0084)		209	210−232
BPC[30]	3,3,4,4,-benzophenone-tetra-carboxylic dianhydride	432	9.9	−6.8		0.014 (0.007)		333	334−362
BSC[27]	borosilicate crown glass	2002	2.3		1.9	0.075 (0.15)		825	800−1594
CaKNO3[31]	Ca−K−NO₃	444	10.8		0.3	0.37 (0.22)		338	341−668
CN60.0[24]	soda lime silicate glass.0	1702	5.2		1.2	0.046 (0.061)		1030	1012−1809
CN60.2[24]	soda lime silicate glass.2	1668	3.2		1.8	0.086 (0.019)		820	803−1563
CN60.4[24]	soda lime silicate glass.4	1929	1.9		1.6	0.19 (0.045)		700	684−1563
Cum-1[4]	isopropylbenzene	174	8.6	−6.9		0.028 (0.018)	177	129	130−149
Cum-2[27]	isopropylbenzene	194	6.8		−0.6	0.21 (0.32)	177	129	129−306
dBAF[32]	dibutylammonium formate	220	6.6	−5.9		0.097 (0.031)		155	156−200
DBP-1[33]	dibutylphthalate	241	8.3	−6.2		0.052 (0.026)	238	179	180−224
DBP-2[27]	di-n-butylphthalate	320	4.1		−0.9	0.2 (0.36)		168	178−369
DC704[23]	tetraphenyl−tetramethyl trisiloxane	306	7.9	−9.8		0.0097 (0.019)		213	211−240
DCHMMS[34]	dichyclohexyl-methyl-2-methylsuccinate	275	10.9	−5.4		0.0072 (0.0089)		221	220−240
DEP[4,22]	diethylphthalate	262	7.3	−7.6		0.024 (0.0098)	270	185	186−222
DHIQ[23]	decahydroisoquinoline	197	25.8	−4.3		0.042 (0.077)		180	180−192
dIBP[4]	di-iso-butylphthalate	247	9.7	−5.4		0.0028 (0.02)		194	195−221
DMP[4,22]	dimethylphthalate	261	8.5	−6.4		0.017 (0.0077)	275	195	196−220
DOP[4]	dioctylphthalate	251	7.8	−5.1		0.023 (0.0036)	223	187	188−220
DPG[4,22]	dipropylene glycol	268	7.8	−5.9		0.043 (0.021)	<234	196	196−240
DPGDME[4]	dipropylglycol−dimethylether	177	9.9	−6.0		0.015 (0.022)		136	139−155
EH[35]	ether-2-ethylhexylamine	183	9.1	−5.6		0.028 (0.011)	197	140	142−166
ER[36]	diglycidylether of bisphenol A (epoxy resin)	309	14.0	−6.7		0.014 (0.035)	325	255	259−291
FAN[37]	3-fluoroaniline	225	10.3	−7.2		0.16 (0.16)		173	173−198
Gly[33]	glycerol	338	4.1	−7.7		0.033 (0.0053)	293	191	192−252
KDE[38]	cresolphthalein−dimethylether	461	7.1	−8.0		0.0095 (0.025)	387	318	315−383
mTCP[39]	m-tricresylphosphate	270	9.2	−5.6		0.018 (0.0095)	299	208	209−233
MTHF-1[4]	2-methyltetrahydrofuran	119	9.8	−6.9		0.022 (0.026)	137	92	91−108
MTHF-2[40]	2-methyltetrahydrofuran	126	8.5	−8.8		0.049 (0.11)	137	91	94−179
mTol[4,22]	m-toluidine	237	10.6	−6.6		0.01 (0.0051)	243	185	184−200
NBB[27]	n-butylbenzene	202	5.9		2.0	0.25 (0.16)	185	129	135−306
NBS[27]	NBS-711 standard	2780	1.1		1.5	0.1 (0.062)		705	665−1614
NBS 710[24]		2483	1.7		1.5	0.097 (0.018)		830	827−1776
nProp-1[40]	n-propanol	350	1.4	−10.7		0.12 (0.17)	147	99	100−300
nProp-2[27]	n-propanol	398	1.2		−2	0.21 (0.27)	147	99	104−370
NS 66[24]		2489	1.4		1.2	0.28 (0.19)		726	719−1805
NS 80[24]		2435	1.5		1.7	0.10 (0.065)		758	718−1759
OTP-1[41]	o-terphenyl	341	8.5	−8.9		0.038 (0.035)	329	243	252−282
OTP-2[15]	o-terphenyl	340	8.6		0.0	0.066 (0.064)	329	240	239−267
OTP-3[40]	o-terphenyl	357	7.7	−9.9		0.16 (0.18)	329	246	248−311
PDE[42]	phenolphthalein dimethylether	397	9.3	−7.7		0.022 (0.031)	373	294	299−333
PG[4]	1,2-propandiol (propylene glycol)	321	3.4	−7.7		0.0062 (0.0046)	214	164	180−211
PHIQ[4]	perhydroisoquinoline	208	18.5	−5.8		0.14 (0.055)		181	182−206
PPG[33]	polypropylene glycol	263	8.7	−6.1		0.049 (0.0063)	215	199	200−240
PS1[43]	titania-bearing sodium silicate melt #1	2395	1.7		1.5	0.078 (0.042)		796	837−1591
PS2[43]	titania-bearing sodium silicate melt #2	2688	1.3		1.3	0.074 (0.038)		746	784−1679
PS3[43]	titania-bearing sodium silicate melt #3	2109	1.9		1.9	0.081 (0.06)		765	815−1676
PT[33]	pyridine−toluene	146	17.5	−5.5		0.019 (0.023)		126	125−131
Sal-1[16]	salol	309	8.1	−8.5		0.05 (0.12)	315	221	218−382
Sal-2[44]	salol	299	9.1	−8.3		0.066 (0.048)	315	222	223−253
Sal-3[40]	salol	308	8.3	−8.5		0.069 (0.24)	315	221	220−309
SB[45]	sucrose benzonate	421	11.2	−5.8		0.04 (0.019)	373	340	341−400
Sqa[23]	squalane	224	8.3	−5.3		0.092 (0.053)	235	170	170−210
TANAB-1[46]	tri-α-naphtylbenzene	519	6.8		−0.9	0.082 (0.34)		335	332−584
TANAB-2[27]	tri-α-naphtylbenzene	520	6.4		−0.8	0.1 (0.21)		335	333−588
TCP[4,22]	tricresylphosphate	280	8.8	−6.3		0.012 (0.013)	240	209	216−248
tNB[47]	trisnaphthylbenzene	510	7.1	−9.2		0.019 (0.023)		342	357−405
TPG[33]	tripropylene glycol	251	8.9	−5.5		0.041 (0.0055)	232	192	192−228
TPP[48]	triphenyl phosphite	286	7.7		−0.5	0.08 (0.18)	296	204	203−291
Xyl[4]	xylitol	311	11.1	−5.8		0.026 (0.0057)	367	250	254−284

[a] Numbered footnotes refer to references with experimental data. [b] T_o is the fitted onset temperature in K. [c] J is the fitted energy scale over k_B. [d] τ_o is the fitted onset relaxation time in seconds. [e] η_o is the fitted onset viscosity in Poise. [f] Σ is the standard deviation of the quadratic form given by $(1/(N - n)\Sigma_i(\log_{10} \tau_{fit,i} - \log_{10} \tau_{data,i})^2)^{1/2}$. N is the number of fitted data points, $n = 3$ is the number of degrees of freedom for all reported fits, $i = \{1, N\}$ indexes the fitted points, Σ_{VFT} is the standard deviation for fitting the parameters τ_o^{VFT}, A and T_K of the VFT form $\tau = \tau_o^{VFT} \exp(A/(T - T_K))$. [g] T_m is the melting temperature. [h] T_g is the glass-transition temperature, i.e., where $\eta = 10^{13}$ P or $\tau = 10^2$ s. [i] The range of temperatures for the data is reported in K. For all fits, only data for $T < T_o$ are fitted.

standing that for $T > T_o$, $\log(\tau/\tau_o)$ has little temperature dependence and that for $T < T_x$, $\log(\tau/\tau_o)$ will cross over to Arrhenius temperature dependence.

The onset and crossover temperatures are material properties that may or may not fall within the range of specific experiments. For systems where T_o approaches T_x, fragile behavior
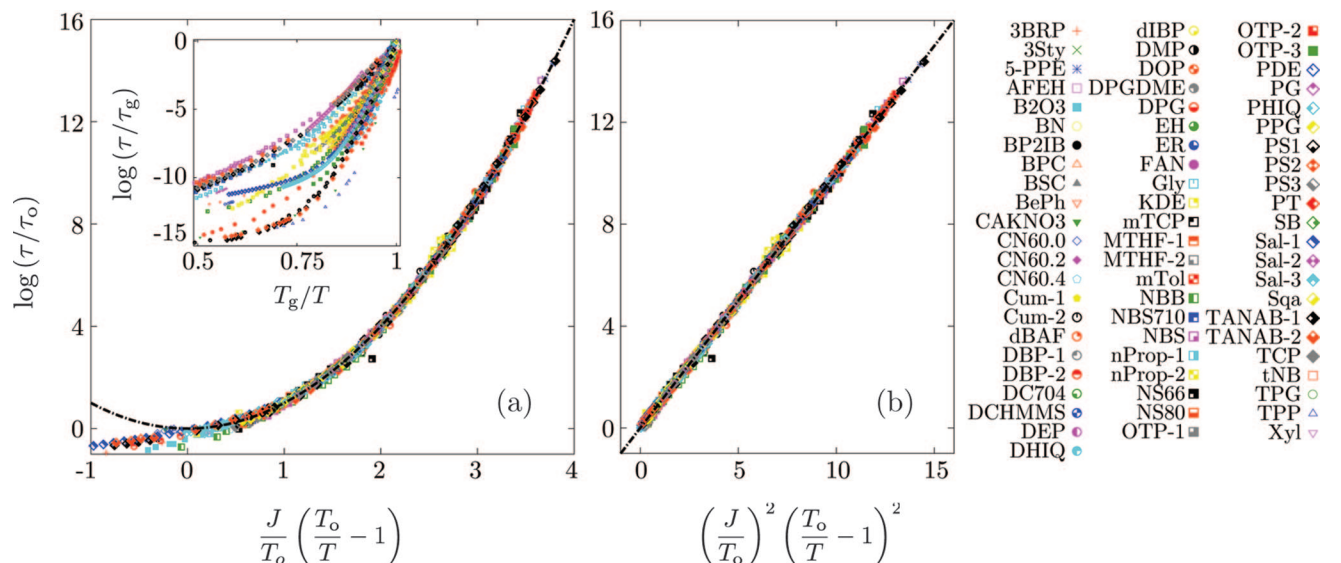
Corresponding States of Structural Glass Formers

J. Phys. Chem. B, Vol. 113, No. 16, 2009 **5565**

Figure 1. (a) Collapse to a parabolic form of the structural relaxation times, τ, and viscosities, η, as functions of temperature T for fragile glass-forming liquids. Parameters τ_o, T_o, and J are listed in Table 1. The inset shows the same data when graphed in Angell-type plots, where T_g refers to the temperature at which the viscosity of the liquid is 10^{13} Poise or when the relaxation time reaches 10^2 seconds. (b) Data for temperatures $T < T_o$ graphed as a function of the square of the collapse variable. The key at the right lists the 67 liquid data sets considered in the graphs. The meaning of each acronym is given in Table 1.
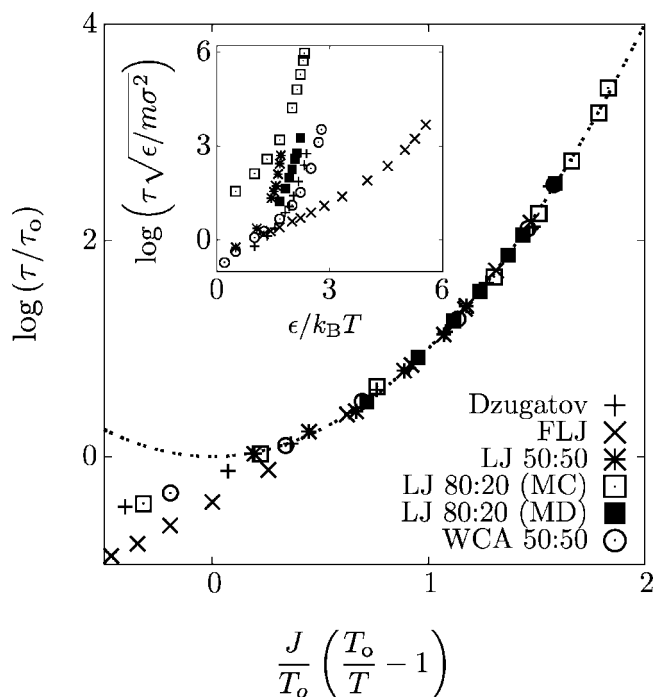
Figure 2. Collapse to a parabolic form of the structural relaxation times, τ, as a function of temperature T for simulations of models of fragile glass-forming liquids. Parameters τ_o, T_o, and J are listed in Table 2. The inset shows the same data when graphed as $\log \tau$ versus $1/T$. T is given in units of ε/k_B, and τ is in units of $(m\sigma^2/\varepsilon)^{1/2}$. Here, m is a particle mass, σ is a particle diameter, and ε is an energy parameter that characterizes interparticle interactions. Precise meaning in each case is found in refs 49−54. The meaning of each acronym is given in Table 2.

will not be observed. Most data that we have found lie in either the fragile and normal liquid regime, $T > T_x$, or in the strong regime, $T < T_x$, but not both. In earlier work,[9] we noted published transport data on two organic liquids that appear to exhibit the crossover.[15] However, for one of these, salol, other data seem to contradict this finding.[16,40] Yet, a change from super-Arrhenius to Arrhenius behavior should also be reflected in a change of

transport decoupling,[17] and this change is seen between dielectric and viscous relaxation.[18] The temperature dependence of transport[19] and of decoupling[20] in films of liquid water also suggests the presence of a crossover. Unfortunately, the amount of data available at present is too sparse to make a convincing case for the origin of this phenomenon. As such, for the present, we focus on the fragile regime.

Table 1 collects the parameters obtained in the fitting data to eq 1 with $T_o > T > T_x$. For each liquid considered, the data set for this regime contained 5 or more data points, and most contained 10 or more data points. This is the data shown in Figure 1. Some of the data refer to viscosity measurements, and others refer to relaxation time measurements. We use the same formula for both, replacing τ with η when referring to viscosity. For each liquid, the three fitting parameters are determined by minimizing the mean square deviation, Σ^2, between the data and the quadratic form for temperatures that exceed a preliminary estimate of the onset temperature. This estimate is the highest temperature at which the curvature of the data, as a function of $1/T$, appears to take on its maximum value. This estimate usually coincides closely with the value of T_o found from fitting the quadratic form. The standard deviations obtained by this fitting are noted in Table 1. Also noted in Table 1 are the standard deviations obtained by fitting the VFT form to the same data. Both the quadratic form and the VFT form have three independent parameters. Considering all 67 liquid data sets, the mean standard deviation for the parabolic form is 0.073 ± 0.073, and that for the VFT form is 0.088 ± 0.14. While the standard deviations are similar, there are at least two reasons to favor the quadratic form over the VFT form. The first[4] is that the quadratic form does not require the introduction of a metaphysical Kauzmann temperature, an implausible thermodynamic state point that, by definition, is unobservable.[21] The second is that, for approximately half of the liquids fitted, the VFT form achieves small standard deviations with a prefactor time that is less than 10 fs, which is too short to coincide with structural relaxation at any reference state of a molecular liquid.

TABLE 2: Fragile Glass-Former Simulations

system[a]	description	$T_o k_B/\varepsilon$[b]	J/T_o[c]	$\log[\tau_o/(m\sigma^2/\varepsilon)^{1/2}]$[d]	Σ[e]	range (k_B/ε)[f]
Dzugutov[49]	Dzugutov 50:50 mixture	0.8	1.8	0.3	0.053	0.42−1
FLJ[50]	Frustrated Lennard-Jones	0.3	1.6	1.5	0.0015	0.18−0.8
LJ 50:50[51]	Lennard-Jones 50:50 mixture	0.7	5.6	1.3	0.027	0.59−2
LJ 80:20 (MC)[52]	Lennard-Jones 80:20 mixture (Monte Carlo)	0.8	1.9	2.6	0.054	0.43−2
LJ 80:20 (MD)[53]	Lennard-Jones 80:20 mixture (molecular dynamics)	0.8	1.9	0.7	0.013	0.45−0.6
WCA 50:50[54]	Weeks−Chandler−Andersen 50:50 mixture	0.6	2.9	1	0.035	0.36−5

[a] Numbered footnotes refer to references with numerical data. [b] T_o is the fitted onset temperature in k_B/ε. [c] J is the fitted energy scale over k_B. [d] τ_o is the fitted onset relaxation time in units of $(m\sigma^2/\varepsilon)^{1/2}$. [e] Σ is the standard deviation of the quadratic form given by $(1/(N-n)\Sigma_i(\log_{10}\tau_{fit,i} - \log_{10}\tau_{data,i})^2)^{1/2}$. N is the number of fitted data points, $n = 3$ is the number of degrees of freedom and $i = \{1, N\}$ indexes the fitted points. [f] The range of temperatures for the data reported is in units of ε/k_B. For all fits, only data for $T < T_o$ are fitted.

The reference time, τ_o, is the time for relaxing a microscopic region of liquid at the onset temperature. We expect these times to be significantly larger than 1 ps. Similarly, we expect the reference viscosity, η_o, to be not much smaller than 1 Poise. A much smaller value can be an indication of treating a strong material as if it were fragile. For example, fitting available data for liquid 3-phenyl-1-propanol (3Ph1P)[4,22] with eq 1 yields a seemingly acceptable standard deviation of $\Sigma = 0.16$, but the energy scale compared to the reference temperature is curiously low, $J/T_o \approx 1.2$, and the reference time is unreasonably short, $\tau_o \approx 10^{-16}$ s. Instead, by fitting to the Arrhenius form with $\log(\tau_R/s) = -2.4$ at $T = T_R = 200$ K, the activation energy E and standard deviation Σ have reasonable values of $40T_R$ and 0.57, respectively. Another similar case is the liquid triphenylethylene (TPE).[23] Again, while the standard deviation $\Sigma = 0.0086$ is small, the time is unreasonably short, $\tau_o \approx 10^{-14}$ s. An Arrhenius fit for these data yields $\log(\tau_R/s) = -3.1$, $T_R = 274$ K, $E/T_R = 58$, and $\Sigma = 0.058$. The available data therefore suggest that these supercooled liquids are strong. That is, the crossover temperature is larger than any temperature for which data are available, $T_x > T_R$. Perhaps, for these liquids, or others like them, relaxation could be studied at higher temperatures to find evidence for a crossover temperature.

There is one outlying data point on the graphs of Figure 1 for so-called NS 66.[24] This occurs at a state point far separated from all of the other state points for which other data points exist. We suspect this point might be erroneous.

Figure 2 shows quadratic data collapse for data from six numerical simulations of fragile glass fomers. Here, the fitting was done using the same methods as those used to collapse the data in Figure 1a. Table 2 shows the parameters used for the data collapse. J/T_o for the numerical simulation data is comparable in magnitude to the values obtained for many of the experimental liquids. The simulation data extend over 3 or 4 orders of magnitude, while the experimental data extend over more than 10 orders of magnitude.

References and Notes

(1) See, for example: (a) Ediger, M.; Angell, C. A.; Nagel, S. *J. Phys. Chem.* **1996**, *100*, 13200–13212. (b) Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. *Appl. Phys. Rev.* **2000**, *88*, 3113–3157.

(2) See, for example: (a) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139–146. (b) Götze, W.; Sjögren, L. *Rep. Prog. Phys.* **1992**, *55*, 241–376. (c) Mézard, M.; Parisi, G. *Phys. Rev. Lett.* **1999**, *82*, 747–750. (d) Götze, W. *J. Phys.: Condens. Matter* **1999**, *11*, A1–A45. (e) Xia, X.; Wolynes, P. G. *Phys. Rev. Lett.* **2001**, *86*, 5526–5529. (f) Bouchaud, J. P.; Biroli, G. *J. Chem. Phys.* **2004**, *121*, 7347–7354.

(3) See, for example: (a) Sellitto, M.; Kurchan, J, *Phys. Rev. Lett.* **2005**, *95*, 236001. (b) Merolle, M.; Garrahan, J. P.; Chandler, D. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10837–10840. (c) Garrahan, J. P.; Jack, R. L.; Lecomte, V.; Pitard, E.; van Duijvendijk, K.; van Wijland, F. *Phys. Rev. Lett.* **2007**, *98*, 195702.

(4) Hecksher, T.; Nielsen, A. I.; Olsen, N. B.; Dyre, J. C. *Nat. Phys.* **2008**, *4*, 737–741.

(5) Rössler, E.; Hess, K.-U.; Novikov, V. *J. Non-Cryst. Solids* **1998**, *223*, 207–222.

(6) Fischer, E. W. *Physica A* **1993**, *201*, 183–206.

(7) Stickel, F.; Fischer, E. W.; Richert, R. *J. Chem. Phys.* **1996**, *104*, 2043–2055.

(8) (a) Kivelson, D.; Kivelson, S. A.; Zhao, X. L.; Nussimov, Z.; Tarjus, G. *Physica A* **1995**, *219*, 27–38. (b) Kivelson, D.; Tarjus, G.; Xiao, X. L.; Kivelson, S. A. *Phys. Rev. E* **1996**, *53*, 751–758.

(9) Garrahan, J. P.; Chandler, D. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 9710–9714.

(10) Bässler, H. *Phys. Rev. Lett.* **1987**, *58*, 767–770.

(11) (a) Fredrickson, G. H.; Andersen, H. C. *Phys. Rev. Lett.* **1984**, *53*, 1244–1247. (b) Ritort, F.; Sollich, P. *Adv. Phys.* **2003**, *52*, 219–342.

(12) (a) Sollich, P.; Evans, M. R. *Phys. Rev. Lett.* **1999**, *83*, 3238–3241. (b) Aldous, D.; Diaconis, P. *J. Stat. Phys.* **2002**, *107*, 945–975. (c) Berthier, L.; Garrahan, J. P. *J. Phys. Chem. B* **2005**, *109*, 3578–3585. (d) Ashton, D. J.; Hedges, L. O.; Garrahan, J. P. *J. Stat. Mech.* **2005**, P12010. (e) Cancrini, N.; Martinelli, F.; Roberto, C.; Toninelli, C. **2007**,arXiv:0712.1934.

(13) (a) Chandler, D.; Weeks, J. D.; Andersen, H. C. *Science* **1983**, *220*, 787–794. (b) Jonas, J. *Science* **1982**, *216*, 1179–1184.

(14) Palmer, R. G.; Stein, D. L.; Abrahams, E.; Anderson, P. W. *Phys. Rev. Lett.* **1984**, *53*, 958–961.

(15) Laughlin, W. T.; Uhlmann, D. R. *J. Phys. Chem.* **1972**, *76*, 2317–2325.

(16) Dixon, P.; Menon, N.; Nagel, S. *Phys. Rev. E* **1994**, *50*, 1717–1719.

(17) Pan, A.; Chandler, D.; Garrahan, J. P. *ChemPhysChem* **2005**, *6*, 1783–1785.

(18) Chang, I.; Sillescu, H. *J. Phys. Chem. B* **1997**, *101*, 8794–8801.

(19) Liu, L.; Chen, S.-H.; Faraone, A.; Yen, C. W.; Mou, C. Y. *Phys. Rev. Lett.* **2005**, *95*, 117802.

(20) Chen, S.-H.; Liu, L.; Fratini, E.; Baglioni, P.; Faraone, A.; Mamontov, E. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 9012–9016.

(21) Stillinger, F. H. *J. Chem. Phys.* **1988**, *88*, 7818–7825.

(22) (a) Igarashi, B.; Christensen, T.; Larsen, E. H.; Olsen, N. B.; Pedersen, I. H.; Rasmussen, T.; Dyre, J. C. *Rev. Sci. Instrum.* **2008**, *79*, 045105. (b) Igarashi, B.; Christensen, T.; Larsen, E. H.; Olsen, N. B.; Pedersen, I. H.; Rasmussen, T.; Dyre, J. C. *Rev. Sci. Instrum.* **2008**, *79*, 045106.

(23) Jakobsen, B.; Niss, K.; Olsen, N. B. *J. Chem. Phys.* **2005**, *123*, 234511.

(24) Neuville, D. R. *Chem. Geo.* **2006**, *229*, 28–41.

(25) Berberian, J. G.; Cole, R. H. *J. Chem. Phys.* **1986**, *84*, 6921–6927.

(26) Blochowicz, T. *Broadband Dielectric Spectroscopy in Neat and Binary Molecular Glass Formers Frequency and Time Domain Spectroscopy, Non-Resonant Spectral Hole Burning*. Ph.D. Thesis, Universitat Bayreuth, Bayreuth, Germany, **2003**.

(27) Tweer, H.; Simmons, J. H.; Macedo, P. B. *J. Chem. Phys.* **1971**, *54*, 1952–1959.

(28) Lunkenheimer, P.; Pardo, L. C.; Kohler, M.; Loidl, A. *Phys. Rev. E* **2008**, *77*, 031506.

(29) Ito, N.; Duvvuri, K.; Matyushov, D. V.; Richert, R. *J. Chem. Phys.* **2006**, *125*, 024504.

(30) Ngai, K. L.; Paluch, M. *J. Chem. Phys.* **2004**, *120*, 857–873.

(31) Angell, C. A. *J. Non-Cryst. Solids* **1988**, *102*, 205–221.

(32) Ito, N.; Huang, W.; Richert, R. *J. Phys. Chem. B* **2006**, *110*, 4371–4377.

(33) Olsen, N. B.; Christensen, T.; Dyre, J. C. *Phys. Rev. Lett.* **2001**, *86*, 1271–1274.

(34) Diaz-Calleja, R.; Garcia-Bernabe, A.; Sanchis, M. J.; del Castillo, L. F. *Phys. Rev. E* **2005**, *72*, 051505.

(35) Wang, L.-M.; Richert, R. *J. Phys. Chem. B* **2005**, *109*, 11091–11094.

(36) Mierzwa, M.; Pawlus, S.; Paluch, M.; Kaminska, E.; Ngai, K. L. *J. Chem. Phys.* **2008**, *128*, 044512.

(37) Wiedersich, J.; Blochowicz, T.; Benkhof, S.; Kudlik, A.; Surovtsev, N. V.; Tschirwitz, C.; Novikov, V. N.; Rossler, E. *J. Phys.: Condens. Matter* **1999**, *11*, A147–A156.

(38) Paluch, M.; Ngai, K. L.; Hensel-Bielowka, S. *J. Chem. Phys.* **2001**, *114*, 10872–10883.

(39) Blochowicz, T.; Gainaru, C.; Medick, P.; Tschirwitz, C.; Rössler, E. A. *J. Chem. Phys.* **2006**, *124*, 134503.

(40) Richert, R.; Angell, C. A. *J. Chem. Phys.* **1998**, *108*, 9016–9026.

(41) Richert, R. *J. Chem. Phys.* **2005**, *123*, 154502.

(42) Hensel-Bielowka, S.; Paluch, M. *Phys. Rev. Lett.* **2002**, *89*, 025704.

(43) Liska, M.; Simurka, P.; Antalík, J.; Perichta, P. *Chem. Geo.* **1996**, *128*, 199–206.

(44) Gainaru, C.; Rivera, A.; Putselyk, S.; Eska, G.; Rössler, E. A. *Phys. Rev. B.* **2005**, *72*, 174203.

(45) Rajian, J. R.; Huang, W.; Richert, R.; Quitevis, E. L. *J. Chem. Phys.* **2006**, *124*, 014510.

(46) Plazek, D. J.; Magill, J. H. *J. Chem. Phys.* **1966**, *45*, 3038–3050.

(47) Richert, R.; Duvvuri, K.; Duong, L.-T. *J. Chem. Phys.* **2003**, *118*, 1828–1836.

(48) Martinez, L. M.; Angell, C. A. *Nature* **2001**, *410*, 663–667.

(49) Gebremichael, Y. *Spatially Heterogeneous Dynamics and String-Like Correlated Motion in Supercooled Liquids and Polymers*. Ph.D. Thesis, University of Michigan, Ann Arbor, MI, **2004**.

(50) Shintani, H.; Tanaka, H. *Nat. Mater.* **2008**, *7*, 870–877.

(51) Lacevic, N.; Starr, F. W.; Schroder, T. B.; Glotzer, S. C. *J. Chem. Phys.* **2003**, *119*, 7372–7387.

(52) Berthier, L.; Kob, W. *J. Phys.: Condens. Matter* **2007**, *19*, 205130.

(53) Karmakar, S.; Dasgupta, C.; Sastry, S. **2008**, arXiv.org:0805.3104.

(54) Hedges, L. O.; Maibaum, L.; Chandler, D.; Garrahan, J. P. *J. Chem. Phys.* **2007**, *127*, 211101.