

Qualitative change in structural dynamics of some glass-forming systems

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Analysis of the temperature dependence of the structural relaxation time $\tau_\alpha(T)$ in supercooled liquids revealed a qualitatively distinct feature—a sharp, cusplike maximum in the second derivative of $\log\tau_\alpha(T)$ at some T_{\max} . It suggests that the super-Arrhenius temperature dependence of $\tau_\alpha(T)$ in glass-forming liquids eventually crosses over to an Arrhenius behavior at $T < T_{\max}$, and there is no divergence of $\tau_\alpha(T)$ at nonzero T . T_{\max} can be above or below T_g , depending on the sensitivity of $\tau(T)$ to a change in the liquid's density quantified by the exponent γ in the scaling $\tau_\alpha(T) \sim \exp(A/T\rho^{-\gamma})$. These results might turn the discussion of the glass transition in a different direction—toward the origin of the limiting activation energy for structural relaxation at low T .

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I. INTRODUCTION

The structural relaxation in glass-forming liquids usually shows Arrhenius-like behavior at high temperatures, $\tau_\alpha(T) = \tau_0 \exp(E_\infty/T)$, but becomes super-Arrhenius at lower temperatures [1,2]. Moreover, the steepness of the temperature dependence of $\log(\tau_\alpha)$ vs $1/T$ increases sharply with cooling [Fig. 1(a)], meaning that the activation energy for structural relaxation, $E(T)$, increases with decreasing T . This suggests that the relaxation time and activation energy might diverge at some finite, nonzero temperature, indicating the existence of an underlying phase transition at $T < T_g$ [2]. Attempts to resolve this fundamental question of $\tau_\alpha(T)$ divergence from detailed analysis of experimental data thus far have provided different conclusions [3–6]. The authors of [3] found no evidence for the divergence of the structural relaxation time. In Ref. [4] it was shown that the divergent signature of τ_α disappears below T_g in amber. On the other hand, detailed analysis of the relaxation time in poly(vinyl acetate) revealed that the Vogel-Fulcher-Tammann (VFT)-like behavior of τ_α extends far below T_g (at least by four orders of magnitude) [5,6].

To describe $\tau_\alpha(T)$ various functions have been proposed. The most common are three-parameter functions: the Vogel-Fulcher-Tammann function [7–9]

$$\tau_\alpha = \tau_0 \exp[B/(T - T_{\text{VFT}})]; \quad (1)$$

the double-Arrhenius function [10]

$$\tau_\alpha = \tau_0 \exp[(B/T)\exp(E/T)], \quad (2)$$

the function of Bässler and Avramov and Milchev [11,12]

$$\tau_\alpha = \tau_0 \exp(C/T^\alpha), \quad (3)$$

and the parabolic function [13]

$$\tau_\alpha = \tau_0 \exp[(J/T_0)^2(T_0/T - 1)^2]. \quad (4)$$

They are based on various phenomenological models, e.g., free-volume [14] and configurational entropy [15], elastic [16], random first-order transition (RFOT) [17], and facilitation [18] models, etc. These models either predict the underlying phase transition with diverging relaxation time at finite T (e.g., free volume, entropy-based Adam-Gibbs, and RFOT), or predict no divergence of $\tau_\alpha(T)$ for any T except at $T = 0$ K. These functions fit the temperature variations of the

structural relaxation time reasonably well. In some materials they provide a good description in the entire temperature range above T_g , e.g., the VFT function fits $\tau_\alpha(T)$ in polymers or glycerol very well at all T . However, they give different predictions for the divergence of $\tau_\alpha(T)$. This divergence would correspond to the divergence of the size of the cooperatively rearranging regions in the Adam-Gibbs approach [15] or of the correlation radius in the random first-order theory [17]. Even if there is no divergence of the relaxation time at nonzero T , still there is a question: Does the activation energy $E(T)$ diverge as the temperature goes to zero [as suggested by, e.g., the double-Arrhenius equation (2)]?

To have a deeper understanding of the temperature dependence of $\tau_\alpha(T)$ and to discriminate between various models one should look at more subtle features of the $\tau_\alpha(T)$ behavior. Recent developments in experimental techniques, especially in broadband dielectric spectroscopy, provide highly accurate experimental data that can reveal these subtle changes in $\tau_\alpha(T)$. Here we present an analysis of the temperature dependence of viscosity or τ_α of supercooled liquids based on their second derivative. We show that at least in some supercooled liquids there is a qualitatively distinct feature in the second derivative of $\tau_\alpha(T)$ that resembles a cusplike singularity with a sharp maximum. This maximum is not predicted by any of the three-parameter functions discussed above. The analysis presented suggests that the equilibrium $\tau_\alpha(T)$ turns to Arrhenius-like behavior also at low temperatures, so there is no divergence of $\tau_\alpha(T)$ or $E(T)$ at a finite temperature. The activation energy, in contrast, approaches some constant value apparently related to the limited activation energy required for structural relaxation.

II. DERIVATIVE ANALYSIS

As a first example, we consider the classical glass-forming liquid salicylic acid (salol) [19]. The structural relaxation time of salol can be fitted reasonably well by several of the functions discussed above [Fig. 1(a)]. The first derivative of $\log\tau_\alpha$ over T_g/T presents the apparent activation energy which increases monotonically with temperature decrease [Fig. 1(b)]. However, the second derivative of the experimental data reveals a sharp peak at a temperature $T_{\max} = 255$ K [Fig. 2(a)]. A few other independent data for $\tau_\alpha(T)$ of salol [20–22] also reproduce this cusplike peak in the second derivative. For

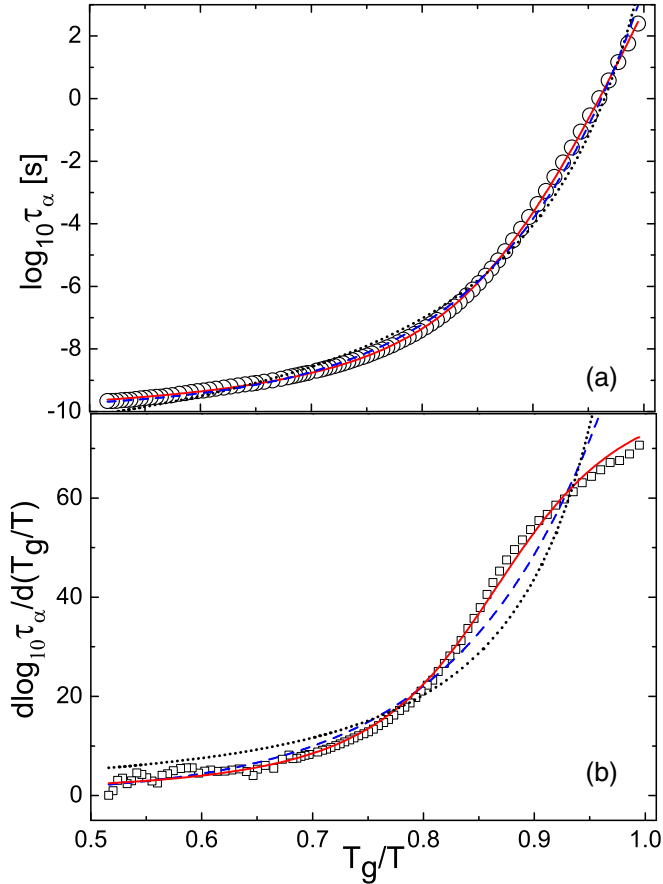


FIG. 1. (Color online) $\log_{10}\tau_\alpha$ (a) and $d\log_{10}\tau_\alpha/d(T_g/T)$ (b) of salol (symbols). Data for τ_α are from Ref. [19]. Fits of τ_α by VFT (dotted line), Mauro *et al.* [10] (dashed line), and Cole-Grest (solid red line) functions are shown.

example, the second derivative of the structural relaxation time of salol measured by a different group of researchers [20] [Fig. 2(a)] exhibits the same peak at the same T_{\max} (with accuracy better than 1 K). Similar behavior can be found in some other glass-forming systems where sufficiently accurate data on the relaxation time or viscosity are available [23–25]. For example, the second derivative of $\log\tau_\alpha(T)$ exhibits a sharp maximum in phenylphthalein dimethyl ether (PDE) and polychlorinated biphenyl with chlorine content 62% (PCB62) (Fig. 3); and the second derivative of $\log\eta$ for the covalent-bonding B_2O_3 [25] also exhibits a maximum at $T_{\max} \sim 630$ K (Fig. 4).

However, there are not many data available with the accuracy required for the second derivative analysis. The dimensionless second derivative of $\log_{10}\tau_\alpha$ or $\log_{10}\eta$ over T_g/T has amplitude about a few hundred, up to 600 (Figs. 2–6). Experimental data on the relaxation time have errors that are reflected in some scattering of the data points of $\tau_\alpha(T)$. Taking derivatives greatly increases the scattering. A simple estimation can be done based on about 20–30 experimental data points in the interval $0.5 < T_g/T < 1$. The typical interval between the data points $\Delta(T_g/T)$ in this case is about 0.02–0.03 which will enhance the error of $\log\tau_\alpha$, $\Delta\log\tau_\alpha$, in the second derivative by a factor of about $\sim 10^3$. If one wants the resulting error to be, e.g., only 10% of the actual

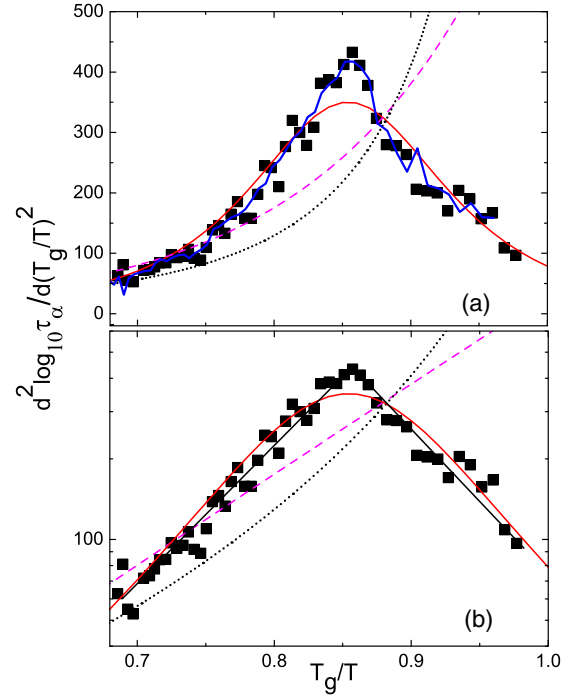


FIG. 2. (Color online) (a) Second derivative of $\log_{10}\tau_\alpha$ in salol (solid squares). Smooth solid red line is the second derivative of the Cohen-Grest function [Eq. (4)] fit of $\log_{10}\tau_\alpha$. Dashed magenta line is the second derivative of the Mauro *et al.* [10] fitting function; the dotted line is the second derivative of the VFT function. The blue solid line is the second derivative of the independent set of data for salol [20]. (b) The same (except for the data of [20]) with the vertical axis in logarithmic scale. Straight solid lines are guides for the eye.

value of the second derivative, then the error $\Delta\log_{10}\tau_\alpha \approx (\log_{10}e)\Delta\tau_\alpha/\tau_\alpha \approx 0.43\Delta\tau_\alpha/\tau_\alpha$ should be less than a few percent. The analysis of a large amount of published data revealed that the scattering of the second derivative points in most cases is too high to provide any conclusive results.

Analysis of a broad number of glass-forming liquids with sufficiently accurate data revealed some systems that do not exhibit the peak in the second derivative of $\log\tau_\alpha$ in the supercooled state. They include hydrogen-bonding liquids, polymers, and room-temperature ionic liquids (RTILs). As examples, we show the second derivative of $\log_{10}\tau_\alpha$ in glycerol and propylene carbonate (PC) (Fig. 5), and in tri-cresylphosphat (m-TKP), ethanol, polyvinylacetate (PVAc), and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([bmim][NTf2]) (Fig. 6).

III. DISCUSSION

We note that the second derivative of $\log\tau_\alpha$ over T_g/T is proportional to the first derivative of the apparent activation energy

$$E_a = d\ln\tau_\alpha/d(1/T). \quad (5)$$

The maximum in the second derivative means that the rate with which E_a is growing upon cooling drastically changes behavior at T_{\max} : The rate increases with decreasing temperature at $T > T_{\max}$, while it sharply decreases with

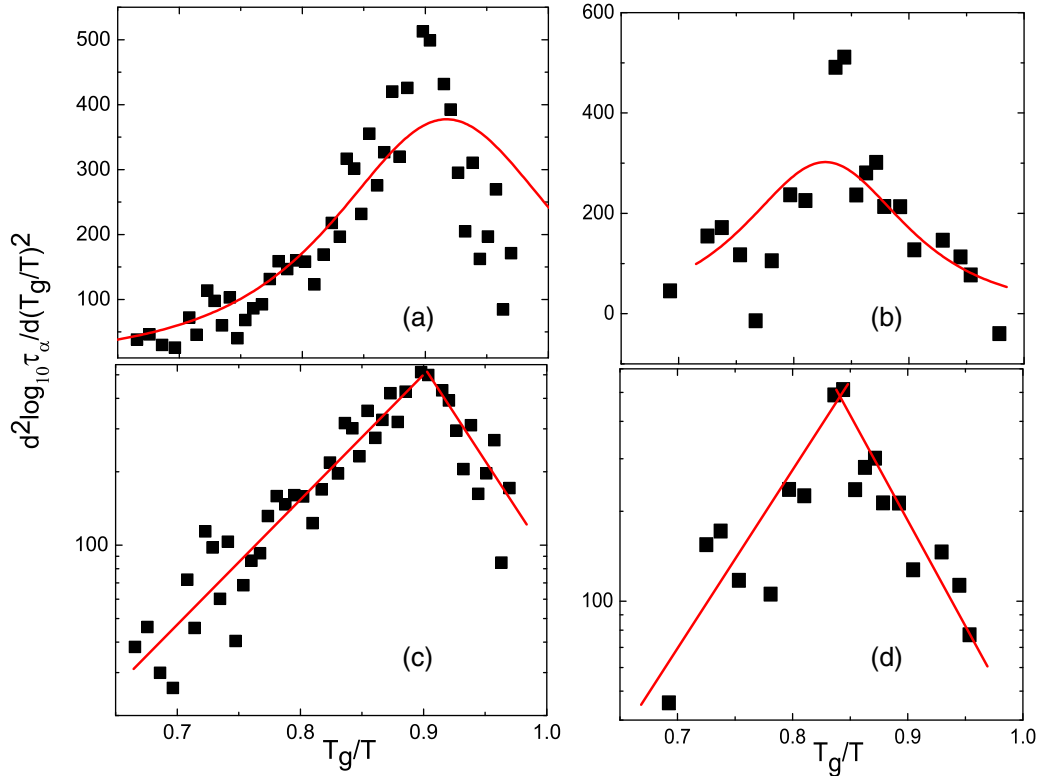


FIG. 3. (Color online) (a) Second derivative of $\log_{10}\tau_\alpha$ in phenylphthalein dimethyl ether (PDE) (symbols). Data for τ_α are from Ref. [23]. Red solid line is the second derivative of the Cohen-Grest function fit of τ_α . (b). The same for polychlorinated biphenyl with chlorine content 62% (PCB62). Data for τ_α are from Ref. [24]. (c) and (d) are the respective data in logarithmic scale (symbols) and the lines present linear approximations [Eq. (2)].

further cooling below T_{\max} . In a logarithmic scale, the peak in the second derivative of $\log\tau_\alpha$ can be described by two linear regimes with positive and negative slopes and an T_{\max} intersection at $T = T_{\max}$ (Figs. 2–4). It means that $\log_{10}[(\log_{10}\tau_\alpha)'] = a + b(T_g/T)$ where a and b are some constants, $b > 0$ at $T > T_{\max}$ and $b < 0$ at $T < T_{\max}$. This corresponds to Arrhenius behavior of $(\log_{10}\tau_\alpha)''$ with the activation energy changing sign at T_{\max} :

$$(\log_{10}\tau_\alpha)'' = A_1 \exp(E_1/T) \quad \text{at } T > T_{\max}, \quad (6a)$$

$$(\log_{10}\tau_\alpha)'' = A_2 \exp(-E_2/T) \quad \text{at } T < T_{\max}. \quad (6b)$$

For salol, $A_1 = 7.8 \times 10^{-3}$, $A_2 = 3.91 \times 10^3$, $E_1 = 2803$ K, $E_2 = 2337$ K. The apparent activation energy E_a , Eq. (5), can be obtained by integrating $(\log_{10}\tau_\alpha)''$:

$$E_a = B_1 + \frac{A_1 T_g^2 \ln 10}{E_1} \exp\left(\frac{E_1}{T}\right), \quad T > T_{\max}, \quad (7a)$$

$$E_a = E_0 - \frac{A_2 T_g^2 \ln 10}{E_2} \exp\left(-\frac{E_2}{T}\right), \quad T < T_{\max}, \quad (7b)$$

where B_1 and E_0 are constants, $B_1 = E_\infty - A_1 T_g^2 \ln 10 / E_1 \approx E_\infty$. Equations (7a) and (7b) predict that there are two Arrhenius regimes: one at high temperatures (with $E_a = E_\infty$ which is well documented [30]), and another one at low temperature ($E_a = E_0$). The activation energy rises with cooling at intermediate temperatures and then saturates at some level. A characteristic temperature interval for the decaying exponential in Eq. (7b) is $\Delta T \sim T_g^* (T_g/E_2) \sim 20$ K for salol,

i.e., the respective interval is $\Delta(T_g/T) \sim 0.1$. At such a distance from T_{\max} , the behavior of $\tau_\alpha(T)$ becomes close to the Arrhenius type again. We note that this low-temperature Arrhenius behavior is related to the equilibrium supercooled liquid and is different from the Arrhenius behavior below T_g observed in nonequilibrium glass formers. Similarly, the slowdown of the rate of increase of τ_α on lowering the temperature below T_{\max} [Fig. 1(b)] occurs at temperatures where τ_α is still short enough ($\sim 10^{-4}$ s) and the liquid is in equilibrium, so a systematic error that leads to such behavior is unlikely.

It is important to emphasize that the maximum in the second derivative challenges all the traditional three-parameter fitting functions discussed above. They produce a monotonic second derivative without any peak (some examples are shown in Fig. 3). Thus they all failed to reproduce accurately the temperature variations of $(\log\tau_\alpha)''$ in these liquids even qualitatively in this temperature range. However, there is a four-parameter function derived by Cohen and Grest (CG) [31] in the free-volume percolation model of the glass transition that has the maximum in the second derivative of $\log\tau_\alpha$:

$$\log_{10}(\tau_\alpha/\tau_0) = \frac{2B}{T - T_0 + \sqrt{(T - T_0)^2 + aT}}. \quad (8)$$

Here T_0 may be both higher and lower than T_g , depending on the material. The parameter a is determined by the anharmonicity of the intermolecular potential. It is known that the CG function fits very well the experimental data for $\tau_\alpha(T)$

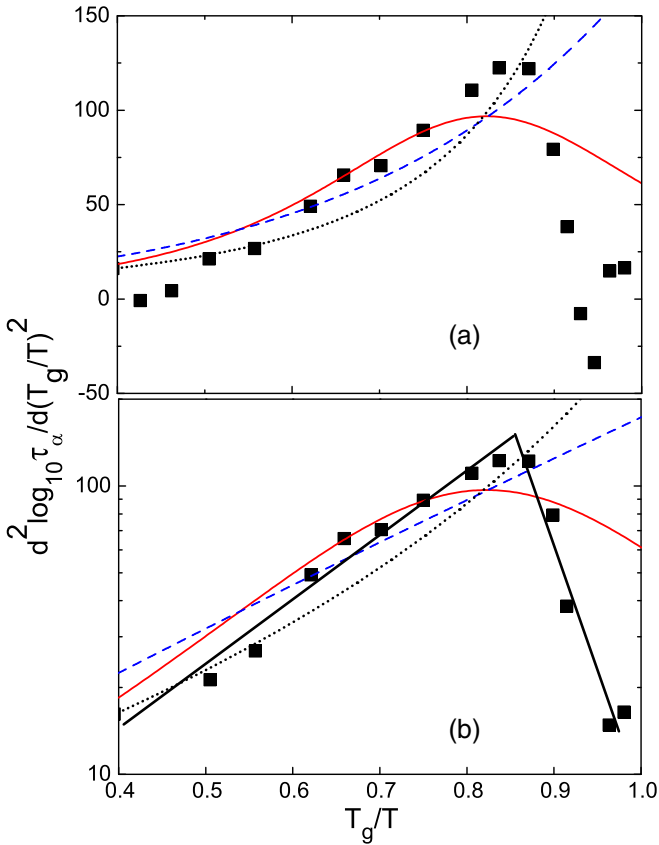


FIG. 4. (Color online) (a) Second derivative of $\log_{10}\tau_\alpha$ in B_2O_3 (solid squares). Solid red line is the second derivative of the Cohen-Grest function [Eq. (4)] fit of $\log_{10}\tau_\alpha$. Dashed blue line is the second derivative of the Mauro *et al.* [10] fitting function; the dotted line is the second derivative of the VFT function. (b) The same plot as (a) but in logarithmic scale. The data for τ_α are from Ref. [25]. Straight solid lines are guides for the eye.

and $\eta(T)$ in various glass formers at all T [31,32]. This is not surprising because the CG function has an additional parameter in comparison with the VFT function. The latter is the limiting case of the CG function at $a \rightarrow 0$. The second derivative of the CG function with respect to the inverse temperature indeed

has a maximum at

$$T_{\max} = \frac{T_0}{1 - \frac{a}{2T_0}}, \quad (9)$$

although it is not as sharp as the experimental one (Figs. 2–4). Thus, the position of the peak of the second derivative can be determined by simply fitting the experimental $\tau_\alpha(T)$ or $\eta(T)$ to the CG function [Eq. (8)]. Since the ratio a/T_0 is small, ~ 0.1 – 0.1 (Refs. [31,32]), for practical purposes T_0 gives a good estimate of T_{\max} with an accuracy of a few percent.

As it was mentioned in Sec. II, some supercooled liquids do not show the peak in the second derivative of $\tau_\alpha(T)$ (Figs. 5 and 6). A fit to the CG function [Eq. (8)] gives $T_0 \sim 160$ K for glycerol which is below its T_g [Fig. 5(a)]. This may explain why there is no peak in the second derivative of $\log\tau_\alpha$ in supercooled glycerol and some other glass formers: the peak is expected to be at temperatures below T_g , where the equilibrium supercooled state cannot be reached experimentally. As one of the consequences, a single VFT or other three-parameter function mentioned above can fit $\tau_\alpha(T)$ of glycerol and other materials with T_0 below T_g reasonably well in the entire temperature range of the supercooled state. This explains the well-known fact that $\tau_\alpha(T)$ in polymers [33], RTILs [29], and some hydrogen-bonding materials [26] can be fitted well by a single VFT function, while many molecular liquids require at least two VFT functions, one for low temperatures and another one for high temperatures [19]. We emphasize that the existence proposed here of the maximum in the second derivative of τ_α at $T_{\max} (\sim T_0)$ below T_g is a speculation based on the fit to the CG function and is not confirmed experimentally. The only justification for this point is that in all cases, when the CG fit provides $T_0 > T_g$ and the data are good enough to analyze the second derivative, there is a maximum at $T_{\max} \sim T_0$. It would be important to perform an experiment where a parameter of a glass former or external conditions, such as pressure, can be varied in order to change the ratio T_0/T_g from $T_0/T_g < 1$ to $T_0/T_g > 1$ and track the evolution of the peak of the second derivative of $\log\tau_\alpha$. We note that the CG fit in the case of propylene carbonate estimates $T_0 \sim T_g$ (Fig. 5). Although the peak is not resolved [Fig. 5(b)], the data are consistent with a possible peak at $T \sim T_g$.

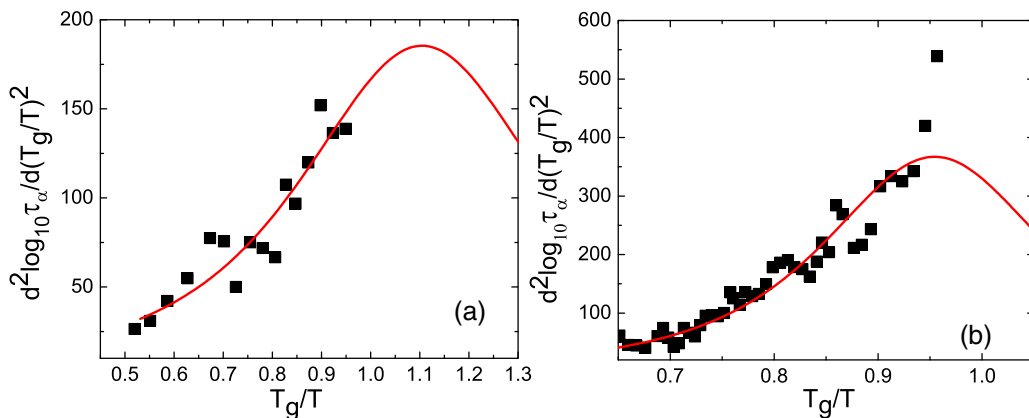


FIG. 5. (Color online) (a) Second derivative of $\log_{10}\tau_\alpha$ in glycerol (symbols). Data for τ_α are from Ref. [26]. Solid red line is the second derivative of the Cohen-Grest function (3) that fits τ_α . (b) The same for propylene carbonate; data for τ_α are from Ref. [23].

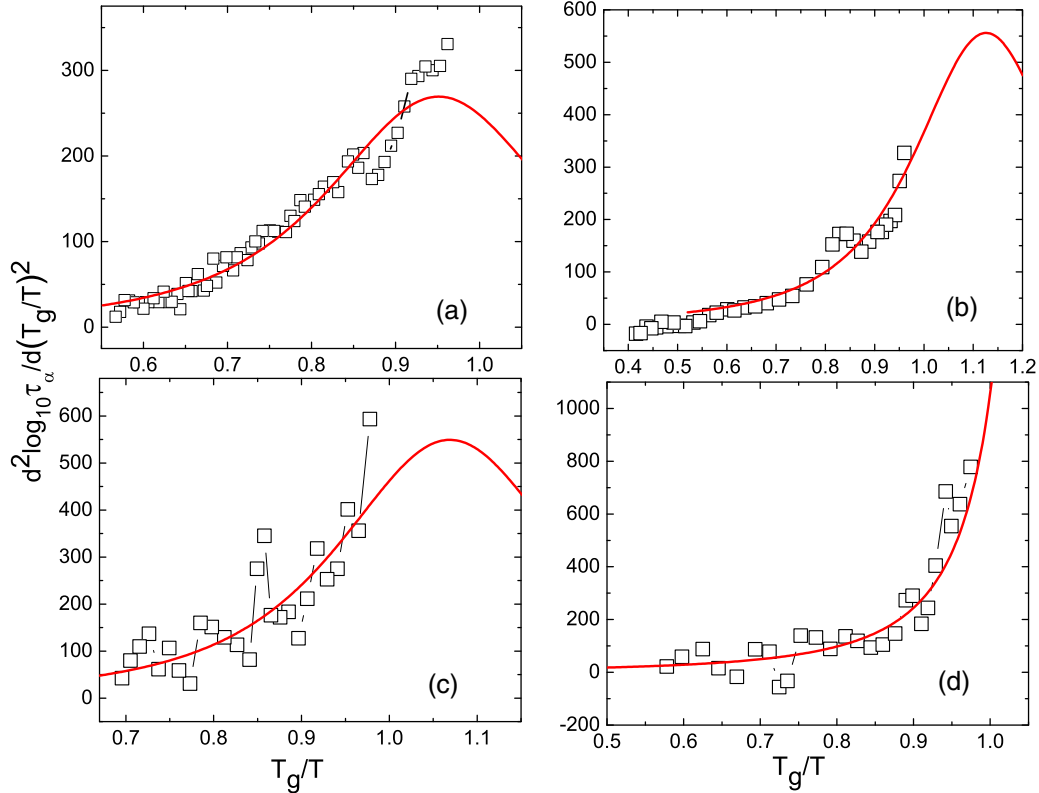


FIG. 6. (Color online) (a) Second derivative of $\log_{10}\tau_\alpha$ in tri-cresylphosphate (m-TKP) (symbols). Data for τ_α are from Ref. [27]. Solid line presents the second derivative of the Cohen-Grest function that fits τ_α . The same for (b) ethanol (data for τ_α from Ref. [23]); (c) polyvinylacetate (PVAc, data for τ_α from Ref. [28]); and (d) room-temperature ionic liquid [bmim][NTf2] (data for τ_α from Ref. [29]).

The critical question is what controls the position of T_{\max} ($\sim T_0$) with respect to T_g ? The exact physical meaning of the temperature T_{\max} is not clear, but in the CG model $T_{\max} \sim T_0 = T_1 + a/4 \sim T_1$, where T_1 is a parameter showing the sensitivity of the anharmonic part of the interparticle potential to changing volume [31]. Thus, the more strongly the anharmonicity of the potential depends on volume, the higher will be T_{\max} with respect to some reference material temperature, such as the melting or glass transition temperature. Thus, the ratio T_{\max}/T_g might correlate with the sensitivity of the structural relaxation time to changing volume. The dependence of the structural relaxation in glass-forming liquids on volume V can be characterized by the exponent γ of the so-called thermodynamic scaling [34,35]:

$$\tau_\alpha(T) = \tau_0 \exp(A/TV^\gamma). \quad (10)$$

The larger is γ the stronger is the dependence of τ_α on volume. Analysis of γ and T_0 obtained using the CG fit revealed that the ratio T_0/T_g indeed increases with increasing γ (Fig. 7). These data suggest that $T_0 > T_g$ in glass formers with $\gamma \geq 3.5-4$, which are mostly molecular liquids. The peak of the second derivative can be experimentally detected only in such liquids. Materials with $\gamma < 3.5$ (hydrogen-bonding materials, many polymers, RTILs) have $T_0 \leq T_g$. In these materials the peak is predicted to be at temperatures where the supercooled liquid falls out of equilibrium, and thus the peak cannot be observed experimentally.

The presented analysis suggests the following scenario: (i) Glass-forming liquids exhibit Arrhenius-like temperature

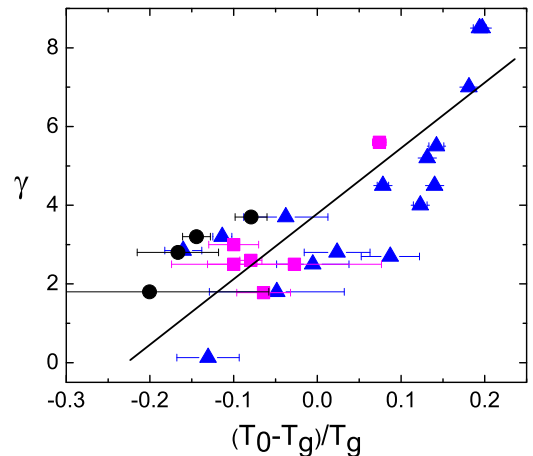


FIG. 7. (Color online) Correlation between γ and $(T_0 - T_g)/T_g$. Nonpolymeric materials (triangles, in increasing γ order): sorbitol, glycerol, propylene glycol, 3-fluoroaniline (FAN), diglycidylether of bisphenol A (DGEBA), dibutylphthalate, propylene carbonate, ortho-terphenyl (OTP), cresolphthalein dimethyl ether (KDE), phenolphthalein dimethyl ether (PDE), salol, cyclohexane polychlorinated biphenyl (PCB42), 1,1'-bis(p-methoxy phenyl) cyclohexane (BMPC), polychlorinated biphenyl (PCB62), 1,1'-di(4-methoxy-5-methyl phenyl) cyclohexane (BMMPC). Polymers (squares): 1.2 polybutadiene (PB), polystyrene (PS), polypropylene glycol (PPG), polyvinylacetate (PVAc), 1.4 polyisoprene (PI), polymethyl phenyl siloxane (PMPS); polymethyl methacrylate (PMMA) with different molecular weight (circles). The data and references are in Table I.

TABLE I. Some parameters of the glass formers used in this paper.

	T_g (K)	T_0 (K)	γ	Ref. τ_α or η	Ref. γ
Sorbitol	268	233 ± 10	0.16	[38]	[39]
Glycerol	186	177 ± 15	1.8	[26,40]	[39]
1-propanol	99	96 ± 5	1.89	[41]	[42]
Propylene glycol	168	167 ± 8	2.5	[43]	[44]
3-fluoroaniline (FAN)	172	187 ± 6	2.7	[45]	[46]
Dibutylphthalate	176	156 ± 2	3.2	[47]	[48]
propylene carbonate	159	153 ± 8	3.7	[43]	[39]
Orthoterphenyl (OTP)	244	274 ± 2	4	[49]	[39]
Cresolphthalein dimethylether (KDE)	314	358 ± 1	4.5	[24]	[39]
Phenolphthalein dimethyl ether (PDE)	294	317 ± 2	4.5	[23]	[39]
Salol	221	250 ± 1	5.2	[19]	[39]
Polychlorinated biphenyl PCB42	225	257 ± 2	5.5	[24]	[39]
1,1'-bis(p-methoxy phenyl) cyclohexane (BMPC)	243	287 ± 1	39	[27]	[39]
polychlorinated biphenyl (PCB62) chlorine content 62%	274	328 ± 1	8.5	[24]	[39]
1,1'-di(4-methoxy-5-methyl phenyl) cyclohexane (BMMPC)	263	314 ± 2	8.5	[24]	[39]
[bmim][NTf2]	181	152 ± 4	2.85	[29]	[50]
1,2 polybutadiene (PB)	253	233 ± 8	1.9	[44]	[44]
polystyrene (PS)	366	356 ± 38	2.5	[51]	[52]
polypropylene glycol (PPG)	202	182 ± 15	2.5	[53]	[39]
polyvinylacetate (PVAc)	302	278 ± 4	2.6	[28]	[39]
diglycidylether of bisphenol A (DGEBA)	254	260 ± 10	2.8	[32]	[39]
1,4 polyisoprene (PI)	202	182 ± 6	3	[54]	[39]
poly(methyl phenyl siloxane) (PMPS)	243	261 ± 2	5.6	[55]	[39]
PMMA	379	303 ± 54	1.8	[56]	[57]
PMMA decamer	288	240 ± 14	2.8	[57]	[57]
PMMA tetramer	240	205 ± 4	3.2	[57]	[57]
PMMA trimer	210	193 ± 4	3.7	[57]	[57]

dependence of the structural relaxation time (viscosity) at high temperatures; (ii) at intermediate temperatures the apparent activation energy for structural relaxation $E_\alpha(T)$ increases upon cooling, and $\tau_\alpha(T)$ exhibits super-Arrhenius behavior; (iii) this increase, however, slows down upon further cooling and (iv) eventually $E_\alpha(T)$ reaches a limiting value, leading to a low-temperature Arrhenius behavior of $\tau_\alpha(T)$ with a constant activation energy E_0 . Unfortunately, the low-temperature Arrhenius regime in pure form is not observable due to rather long relaxation time required [see, e.g., Fig. 1(b) for salol]. We want to stress here that this low-temperature Arrhenius behavior is expected in equilibrium supercooled liquids. It should not be confused with the non-equilibrium Arrhenius behavior usually observed at $T < T_g$.

In the Adam-Gibbs [15] and RFOT [17] theories, the activation energy is proportional to the volume of the cooperatively rearranging region (CRR). The crossover to the low-temperature Arrhenius regime means that the size of the CRR does not diverge with cooling, and instead, after initial growth, eventually saturates at some maximum value. Recently, the low-temperature Arrhenius regime was predicted in a string model [36]. In this model the CRR corresponds to strings comprised of fast-moving molecules. Applying the theory of living polymers to the strings, the authors showed that the string length increases upon cooling, but will saturate at some limited length at lower temperatures. This would correspond to a limited size of the CRR, and consequently of the activation

energy. In elastic models [16] the low-temperature Arrhenius behavior corresponds to the limiting value of shear modulus. In any case, regardless the microscopic mechanism, the activation energy E cannot grow to infinitely large value and will have its limit that depends on the material. Indeed, there should be a limiting energy cost for a molecule to make a relaxation motion in a supercooled liquid. Thus relaxation in any glass-forming liquid eventually will become Arrhenius-like upon cooling and no divergence of time scale at finite T should be expected.

According to Fig. 2, the third-order derivative, i.e., the slope of $(\log \tau_\alpha)''$, has a finite jump at T_{\max} in salol, and the fourth-order derivative is infinite at T_{\max} . In the Adams-Gibbs thermodynamic theory of the glass transition $\log \tau_\alpha / \tau_0 = \text{const} / T S_c(T)$ [15] where $S_c(T)$ is the configurational entropy. Thus, $S_c(T)$ should have an infinite fourth-order derivative at T_{\max} . This formally means that the system experiences a subtle fourth-order phase transition at T_{\max} . At this point we do not have a clear physical picture of the nature of this transition. We speculate that at decreasing temperature the collective relaxation eventually acquires such high activation energy and CRR size that at $T < T_{\max}$ either the CRR size is limited by the mechanism of relaxation, as in the string model [36], or other channels of relaxation with limited collectivity have equal or higher rate.

We note that the peak in B_2O_3 (Fig. 4) looks different from all other cases—it is strongly asymmetric. It is known

that B_2O_3 exhibits a structural transformation above T_g , with increasing number of B_3O_6 boroxol rings at the expense of BO_3 triangular units [37]. We cannot exclude the possibility that the observed maximum in $(\log_{10}\eta)''$ in B_2O_3 (Fig. 4) is related to this structural change. However, observation of the maximum in the second derivative of several other liquids (Figs. 2 and 3) and the correlation of T_0/T_g with the scaling parameter γ point to a more general nature of the transition.

The temperature T_{max} at which the increase in $E(T)$ starts to slow down differs with respect to T_g for different materials and it may be lower or higher than T_g depending on the sensitivity of the structural relaxation to change in volume (density) (Fig. 7). Thus there are systems where crossover to the low-temperature Arrhenius behavior is visible (e.g., salol, PDE, PCB65, B_2O_3), but there are systems where this should happen only at $T < T_g$. This explains why attempts to analyze the divergence of $\tau_\alpha(T)$ at finite T in various systems [3–6] may produce different results: There are systems (apparently with high γ) where no divergence can be obvious at $T \sim T_g$, while this regime cannot be achieved in other systems, where $T_{max} < T_g$.

IV. CONCLUSIONS

In conclusion, the second derivative of the temperature dependence of the structural relaxation time and viscosity in

some supercooled liquids exhibits a sharp maximum. Such a maximum is not predicted by traditional three-parameter functions suggested for description of $\tau_\alpha(T)$. Thus, these functions are missing important qualitative feature of the glass transition. This behavior of the second derivative suggests that the super-Arrhenius dependence of $\tau_\alpha(T)$ should eventually cross over to an Arrhenius regime on further cooling and there is a limiting value for the activation energy required for structural relaxation. The crossover to this low-temperature Arrhenius regime can be either above or below T_g , apparently depending on the sensitivity of the structural relaxation of the material to change in volume. This provides a hint as to the parameters that might define the maximum activation energy for structural relaxation of the liquid. Employing this approach might help to reveal many other peculiarities of dynamics in soft matter.

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