DESCRIPTION OF THE PRIMARY RELAXATION IN SUPERCOOLED LIQUIDS THROUGH THE TIMESCALE STEEPNESS FUNCTION.

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Abstract

The primary relaxation in glass forming supercooled liquids (SCLs) above the glass transformation temperature $T_g$ is discussed in terms of the first-order (steepness) and the second-order (curvature) temperature derivatives of the observed primary relaxation timescale. We report new insights into the problem of the domain of the Vogel-Fulcher-Tamman (VFT) equation, raised by Stickel et al. (J. Chem. Phys. \textbf{102}, 6251 (1995), \textit{ibid.} \textbf{104}, 2043 (1996)) and discussed by Richert and Angell (\textit{ibid.} \textbf{108}, 9016 (1998)). A new ergodic-cluster Gaussian statistical approach to the problem is given based on Onsager’s thermodynamic principle. The primary relaxation is described by the VFT equation below the crossover temperature $T_c$ (known from mode coupling theory (MCT)), and above $T_c$ by an extended (VFTE) equation obtained after accounting for cluster-size fluctuations. The timescale is parametrized by a finite number of observable
parameters such as the steepness function \( m_T \) at \( T_g \), the MCT slowing-down exponent \( \gamma_c \), and the VFT and VFTE strength indices \( D_g \) and \( D_c \). The latter are defined at \( T_g \) and \( T_c \), respectively, for the strongly and moderately SCL states, which show absolute thermodynamic instability at the same VFT temperature \( T_0 \), associated with the Kauzmann temperature. For both states the limiting cluster-size characteristics are derived from experiment. A thermodynamic-dynamic correspondence is established between the dynamic VFT equation and the thermodynamic Adam and Gibbs model. As a by-product, self-consistent equations for the excess heat capacity, entropy, and for the glass-transition characteristic temperatures \( T_0 \), \( T_g \), and \( T_c \) are deduced. The problem of the "irregular" SCLs, which are not consistent with the standard VFT equation, such as salol, ortho-terphenyl, and bis-methoxy-phenyl-cyclohexane, is also discussed.

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I. INTRODUCTION

The understanding of noncrystalline liquids and the formation of glasses by a dynamical slowing-down, and a rapid increase in viscosity at the glass transition temperatures $T_g$ (near $2/3$ of the melting point $T_m$) is currently seen as a major intellectual challenge in condensed matter physics [1]. There is therefore intense interest in studies, experimental and theoretical, including simulations, of the temperature dependence of the transport properties of supercooled liquids (SCLs). In particular, data on the primary relaxation times $\tau_T^{(\text{exp})}$ that are determined from dynamic experiments that study viscoelastic, dielectric, conductivity, light scattering and mechanical relaxation data of glass formers [2], offer one of the main keys to the problem [1,3–5].

 Unlike the slow secondary relaxation process which has a constant activation energy $\approx 24k_BT_g$ (established in Ref. [6] for the Arrhenius relaxation, where $k_B$ is Boltzmann’s factor), the thermally equilibrated SCL states, observed within the temperature domain $T_g \leq T < T_m$, exhibit a pseudo-Arrhenius form, i.e., $\tau_T = \tau_\infty \exp(E_T/k_BT)$, and are discussed traditionally in terms of the SCL activation energy $E_T$. The most widely employed Vogel-Fulcher-Tammann (VFT) timescale fitting phenomenological form with the activation energy $E_T = B/(T - T_0)$ is introduced by the fictive critical temperature $T_{cr}$ ($= T_0$, VFT temperature). $T_0$ lies below the thermodynamic glass transition temperature $T_g$ established by thermodynamic experiments such as scanning calorimetric or volume-expansion data. Analysis of the temperature-derivative behavior of the $\alpha$-relaxation timescale $\tau_T$ given by Stickel et al. in Refs. [7, 8], as improved and extended by Richert and Angell’s analysis of the thermodynamic data in Ref. [10], determined the real temperature observation domain, or observation window, of the VFT form. Overall $\tau_T$ fitting forms, distinct from the VFT, were proposed within the whole SCL observation window by Kivelson et al. in Ref.11 or by Schulz in Ref. [12] that, respectively, admits the ”avoided critical points” [13] ($T_{cr} > T_m$), or rules out the non-zero critical temperatures ($T_{cr} = 0$).

Within the context of first-and-second-order phase-transition approaches to the problem
of the liquid-to-glass transition (see Refs. [14–23]) the dramatic increase of the relaxation
times $\tau^{(\text{exp})}_T$ observed in SCLs upon cooling, is due to the growth of underlying correlation-
length scales. The lengthscale peculiarities, even when being experimentally established,
do not often lead to a clear physical understanding. In the case of the VFT form the
physical meaning of the experimentally determined VFT temperature $T_0$, is justified by its
closeness to the thermodynamic Kauzmann temperature $T_K$. At this critical temperature
($T_K = T_{cr}$) the excess liquid-over-solid SCL entropy, or configurational entropy, vanishes.
This property is thought to be associated with the absolute thermodynamic instability of
the thermally equilibrated states of the SCLs with respect to liquid-to-solid rearranging
processes that extend from the ergodic region ($T_g \leq T < T_m$) to lower temperatures. The
theoretically motivated ergodic instability (caused by divergence of the zero moment of the
relevant relaxation-time distribution function [19]) establishes the thermodynamic-dynamic
(TD-D) correspondence equation, $T^{(\text{TD})}_K = T^{(D)}_0 \equiv T_0$. This equation was experimentally
justified by Angell [3] within a certain range of experimental scatter which often lies [24]
inside the error of experimentally measured characteristic temperatures.

Thermodynamic models for SCLs are commonly tested by the $\tau^{(\text{exp})}_T$ fitting analysis. The
VFT form has proved to be ineffective for establishing simultaneously all three adjustable
parameters ($\tau^{(\text{VFT})}_\infty$, $B$ and $T_0$) within the overall fitting analysis of the observed SCL vis-
cosity (see discussion in Ref. [11]). An improved analysis for the tested forms was proposed
in Refs. [7–9] on the basis of fitting experimental data $\tau^{(\text{exp})}_T$ and additionally their first-
order ($d \log \tau^{(\text{exp})}_T /dT$ ) and second-order ($d^2 \log \tau^{(\text{exp})}_T /dT^2$ ) derivatives. These temperature-
derivative analyses permit one to exclude the unknown fitting parameters, step-by-step, by
making the three-parameter fitting procedure self-consistent. As a result, the validity of the
VFT form, when tested within the whole ergodic relaxation range, was questioned [4] for all
SCLs investigated above the so-called $\alpha$-$\beta$-relaxation bifurcation temperature $T_B$. Notably,
this crossover temperature was often found close to other known crossover temperatures $T_x$
and $T_c$ introduced, respectively, as a scaling temperature by Rössler and co-workers [25]
and as the dynamic critical temperature of the mode coupling theory (MCT). Within these
studies one can admit that to a good approximation, $T_B = T_x = T_c$ (see e.g. Table II in Ref. [10]).

Physically, the MCT crossover temperature $T_c$ signals structural transformations, or liquid-solid-like restructuring in SCLs, from moderately supercooled states of "weakly coupled fluids" ($T_c \leq T < T_m$) to strongly supercooled states of "strongly coupled fluids" ($T_g \leq T < T_c$) as discussed in Ref. [4]. The analyses given in Refs. [7–10] in terms of the first order derivatives (related to the timescale steepness) and the second-order derivatives (related to the timescale curvature) of the temperature dependence, clearly distinguish the two regions, similar to the case of the MCT theory [4], below and above the dynamical crossover temperature $T_B$, associated here with $T_c$. The data for moderately SCL (or weak-SCL) states in all glass forming liquids that have been studied are in a good quantitative agreement with the modified VFT form given as the high-T VFT (HT-VFT) version in the old canonical VFT form but with new adjustable parameters, including the HT-VFT characteristic temperature $T_0^{(HT)}(\approx T_g$, see Table II in Ref. [8]). This fundamental finding is exemplified by the case of the simple molecular liquid propylene carbonate (PC) in Fig.1. As seen from the analysis given in Fig.1, the validity of the canonical VFT form is limited by the temperature domain $T_g \leq T < T_c$, corresponding to the strongly SCL states, characterized by relaxation times $10^{-7} \lesssim \tau_T^{(exp)}/s \leq 10^{2}$, or by viscosities $10^4 \lesssim \eta_T^{(exp)}/P \lesssim 10^{13}$.

Another interesting description of the SL states is also provided by analysis of the thermodynamic (heat capacity) data that was elucidated by Richert and Angell [10] on the basis of the configurational entropy $S_c$ data. This data is schematically plotted in Fig.2.

Careful complex dynamic-thermodynamic analyses enabled one to establish a physical meaning for the standard VFT fitting form, that was justified in terms of the thermodynamic Adam-Gibbs model (AGM) introduced in Ref. [14]. The VFT form is therefore treated as the VFT equation that provides a good description of the observed dynamic and thermodynamic relaxation of the strong-SCL states (see AG-line in Fig.2). Within the context of percolation theory [20], $T_0$ may be associated with the critical temperature where the correlation length of the strong-SCL states diverges in accordance with the thermodynamic instability at the
Kauzmann temperature $T_K$. A microscopic version of this kind of instability was given by Bender and Shlesinger Ref. [27] by invoking a defect-aggregation mechanism that was recently justified [28] for PC by the pressure-dependent experiments.

In reality, strong-SCL ergodic states do not survive below $T_g$ (see solid squares in Fig.2). As shown in Ref. [29], this is due to the ergodic-to-nonergodic crossover from the short-range strong liquid correlations, characteristic of solids, to somewhat long-range weak liquid correlations, characteristic of gases. Conversely, no physical justification was given for the HT-VFT form introduced in Refs. [7–10]. The main aim of the current study is to provide a physical description of the weak-SCL states on the basis of both the extended thermodynamic AGM and the dynamic VFT equations.

The old idea that anomalous temporal (non-Debye) and anomalous temperature (non-Arrhenius) behaviors related to the SCL relaxation, may be attributed to rearranging regions [22], or domains [21], or droplets [20] or clusters [29] of different size and structure, is still widely explored and remains fruitful. There is today considerable direct evidence for the existence of these kinds of regions. They have been observed on a microscopic scale by multidimensional NMR, photobleaching, excess light scattering and dielectric hole burning, as reviewed in Ref. [1], and by X-ray scattering data, discussed in Ref. [22]. The percolation theory, improved by mesoscopic-domain energy-size scaling, as shown by Chamberlin in Ref. [30], provided a description in detail of the observed relaxation function. An alternative percolation-theory approach, combined with the relaxation-time cluster-size scaling law, proposed in Ref. [32] shed light on some universal features of the primary relaxation near $T_g$ in the structural and orientational glasses [33]. Additional cluster-approach studies of the dynamical spectra with accounting of the MCT scaling forms, explained the mechanisms [34] for the primary relaxation in polymers and those of the secondary relaxation in SCLs. Furthermore, exploration of Stauffer’s cluster-size scaling form, based on the percolation theory, made it possible [29] to justify the underlying ergodic-nonergodic transition that emerges at the ergodic crossover temperature $T_E$ ($\leq T_g$), where the cluster-size Gaussian distribution of the strong-SCL states is transformed upon cooling into the Poisson form (see
also discussions in Refs. [19,35]).

In the current study we extend the cluster approach to the problem of relaxation of ergodic states in SCLs. We will demonstrate that the structural heterogenous fluctuations, being small in the case of the strong-SCL state, are responsible for moderately SCL behavior as revealed in Refs. [4][10] by deviations from the standard VFT fitting form. The paper is organized as follows. In Sec. II we discuss phenomenological descriptions of the observed primary relaxation timescale in terms of the known fitting forms and macroscopic parameters commonly used by experimentalists. Instead of the frequency observation windows, given by $1/\tau^{(\text{exp})}_T$, which are distinct for different dynamic experiments, the timescale is introduced through the temperature domains for the SCL excitations established with the help of the characteristic temperatures. In Sec. III we give the dynamic and thermodynamic description of SCLs based on the statistical approach to the rearranging regions introduced by Adam and Gibbs. By accounting for their size fluctuations, we develop extended versions for the AGM and the VFT equations. The qualitative and quantitative analyses of the proposed physically justified fitting forms are given in Sec. IV. The conclusions are summarized in Sec. V.

II. MACROSCOPIC PARAMETRIZATION OR THE PRIMARY RELAXATION TIMESCALE

A. Strongly Supercooled Liquids

It was experimentally proved by Richert and Angell in Ref. [10] that the widely employed AGM equation

$$\log_{10} \tau^{(AG)}_T = A + \frac{C}{TS_c(T)}$$

(1)

and the phenomenological VFT form given in the two equivalent forms, namely

$$\log_{10} \tau^{(VFT)}_T = \log_{10} \tau^{(VFT)}_\infty + \frac{B}{T - T_0},$$

(2)
\[ \tau_T^{(VFT)} = \tau_\infty^{(VFT)} \exp \frac{DT_0}{T - T_0} \]  

are self-consistent when subject to the conditions \( A = \log \tau_\infty^{(VFT)} \) and \( T_0 = T_K \). These equations apparently work well in describing the strong-SCL state relaxation in terms of the MCT within the temperature domain \( T_g \leq T < T_c \). This domain was studied simultaneously on the basis of dynamic and thermodynamic experimental data, more precisely, through the primary relaxation timescale \( \tau_T^{(exp)} \), deduced from the dielectric loss spectra, and the configurational entropy:

\[ S_c(T) \equiv \Delta S_T = \int_{T_K}^{T} \Delta C_T T^{-1} dT \]

with the excess liquid-over-solid isobaric specific heat capacity \( \Delta C_T = C_p^{(Liq)} - C_p^{(Sol)} \). Accounting for the fact that at high enough temperatures \[ [10, 36, 37] \Delta C_T^{(exp)} \propto T^{-1}, \] the configurational entropy \[ (4) \] was given \[ [10, 38] \] in explicit form, namely

\[ S_c(T) = \Delta S_\infty \left( 1 - \frac{T_K}{T} \right) \text{ with } \Delta S_\infty = \frac{C_B}{B} \]  

that establishes useful relations between the observed model parameters. It has been demonstrated \[ [10] \] that unlike the VFT form, restricted by the strong-SCL states, Eq.\((5)\) does a good job within the whole range of the thermally equilibrated states (see solid line in Fig.2).

The theoretical foundation of the experimental findings by Richert and Angell are not limited by the aforesaid TD-D correspondence equation \[ [10] \], i.e., \( T_K^{(TD)} = T_0^{(D)} \equiv T_0 \). One can see that the existence of the strongly SCL states, based on the dynamic VFT equation and the thermodynamic AGM within observation windows, evidently requires in addition \( T_g^{(TD)} = T_g^{(D)} \equiv T_g \). Here the characteristic temperature \( T_g^{(TD)} \) is introduced as a thermodynamic parameter derived from the maximum of \( C_p^{(Liq)}(T_g^{(TD)}) \), observed by the scanning calorimetry, and the corresponding laboratory glass-point \( T_g^{(D)} \) that is deduced from the dynamic experiments and defined \[ [2] \] by the equation \( \tau_T^{(exp)} = 10^2 s \) given at \( T = T_g^{(D)} \).

Unlike the case of the first TD-D equation, there is no systematic study to verify the precision of the second equation. Except for the case of SCLs (see e.g. Fig.2 in Ref. \[ [39] \]) there is even
no accepted international convention on the definition of the thermodynamic value $T_g^{(TD)}$ for the various glass forming materials.

Furthermore, Eqs. (1, 2) cannot be extrapolated to high temperatures beyond their temperature domain. Hence, the justification given in Ref. [10] for the VFT and the ADM corresponding macroscopic equations, i.e., $B = C/\Delta S_\infty$ and $A = \log \tau_\infty^{(VFT)}$, should be reconsidered. The same equations might be introduced by application of the ergodic hypothesis employed for SCLs in Ref. [29]. This means that the strongly SCL states, that emerge above the crossover-ergodic-temperature $T_E$ (see Eq. (7) in Ref. [29]), can be introduced through certain observables estimated by thermodynamic and dynamic averages. Physically, this corresponds to the fact that the thermally equilibrated states are equivalent to ergodic states observed in the dynamical experiments. If this is true, this requires new equations for the ergodic time scale and length scale given, respectively, by

$$
\tau_\infty^{(VFT)} = \tau_\infty^{(AG)} \equiv \tau_a \quad \text{and} \quad z_\infty^{(VFT)} = z_\infty^{(AG)} \equiv z_a. \quad (6)
$$

In other words, Eq. (6) introduces the minimum magnitudes for temporal and size characteristics necessary employed for the mesoscopic description of the SCL states.

### B. Moderately Supercooled Liquids

In contrast to the second-order thermodynamic transition approach, MCT treats the liquid-to-glass structural transformation as a dynamic process driven by liquid density fluctuations. In the idealized version of MCT [4] the ergodic-to-nonergodic transition occurs at a unique crossover temperature $T_c (= T_{cr})$ at which neutron spin scattering measurements signal the appearance of the glassy-like correlations given by the so-called non-ergodic parameter, which is analogous to the Edwards-Anderson spin-glass order parameter in the case of weak-SCL states. Moreover, the MCT predicts [4] the algebraic-type scaling for the primary relaxation timescale, namely

$$
\tau_T^{(MCT)} = \frac{\tau_\infty^{(MCT)}}{(T - T_c)^\gamma_c} \quad \text{for} \quad T_c < T_y \leq T < T_A < T_m \quad (7)
$$
with the slowing-down exponent $\gamma_c$. This observable is rather sensitive to the location of $T_c$ as well to the temperature region of the fitting experimental curve [1, 7, 8, 11, 40]. The temperature domain of Eq.(7) is much narrower than that for the case of the HT-VFT form given [1] by $T_B < T < T_A$, where $T_A$ is the Arrhenius crossover temperature. A temperature $T_y$ is introduced in Eq.(7) to designate the lowest temperature point where the algebraic MCT form fits experimental data (see Fig.1). Unlike the first estimates reported for the slowing-down exponents that exceeded magnitudes of 5.5 in SCLs (see Table1 in Ref. [40]), the values established by the MCT Eq.(7) in glass-forming materials are in the range, $2 < \gamma_c < 3$ for liquids Eq.(7), and $3 \leq \gamma_c < 4$ for polymers. For macroscopic observable parameters of the timescale in glass forming molecular liquids and polymers see, respectively, cases A and B in Table 1.

C. Fragility and Characteristic Temperatures

One of the salient features of the primary relaxation is the so-called time-temperature superposition principle [4]. Its physical justification has not yet been established but it is employed effectively to scale the dielectric loss spectra [4]. Meanwhile, analyses of a number of the $\alpha$-timescale characteristics near $T_g$ for several experimental studies of glass forming materials [2], have revealed a number of underlying temporal-spatial correlations in explicit form. The analysis was given [2] in terms of the phenomenological relation, i.e., $m_g = (250 - 320) \beta_g$ expressed through the fragility [2] $m_g$ that is related to the steepness index [10], and the Kohlrausch-Williams-Watts (KWW) stretched exponent [1] $\beta_g$.

Incorporation [32] of the growth-correlation scaling law, employed in the order-disorder kinetic transition theory [12], into the relaxation function of the SCLs led to a description [33] of the aforesaid temporal-spatial correlations for the dynamical exponents in a form $\beta_g = (1 + m_g/m_0^*)^{-1}$ where $m_0^*$ is a universal parameter (because it is material-independent) within a certain glass family. In addition, the equation for the growth-correlation dynamic exponent, i.e., $z_g = m_g/3m_0^*$, was established in Ref. [33] (see also proposal by Ngai in Ref.
Within MCT, the characteristic temperatures, as well as the dynamical exponents, are treated as certain equilibrium thermodynamic parameters, which, as demonstrated in Ref. [23], are not independent. This statement is exemplified by the widely employed equation [13]

$$\frac{T_g}{T_0} = \frac{m_g}{m_g - m_g^*}, \text{ with } m_g^* = \log_{10} \frac{\tau_g^*}{\tau_a},$$

(8)

where $m_g^* = 16 \pm 2$ is the universal parameter known as the lower fragility limit [2]. As follows from Eq.(8), the uncertainty in the $m_g^*$, caused by deviation of the inclination of the straight lines in Fig. 3, is due to the uncertainty of the timescale unit parameter $\tau_\infty^{(VFT)} = \tau_a = 10^{-14\pm1}s$, given by Eqs.(6), and to that of the glass-transition characteristic time $\tau_g = \tau_g^* = 10^{2\pm1}s$. Eq.(8) was first introduced in Refs. [2,45] on the basis of the VFT equation (3), namely

$$\tau_T^{(VFT)} = \tau_\infty^{(VFT)} \exp \frac{D_g}{\varepsilon_T} \text{ with } \varepsilon_T = \frac{T}{T_0} - 1 \text{ for } T_g \leq T < T_c,$$

(9)

where the timescale auxiliary function $\varepsilon_T$ is introduced.

Let us define the timescale steepness function by

$$m_T = -\frac{d \log_{10} \tau_T}{d \ln T}$$

(10)

with

$$m_T^{(VFT)} = \frac{D_g}{\ln 10 \varepsilon_T} \frac{1}{(1 + \frac{1}{\varepsilon_T})}$$

(11)

for the particular case of Eq.(8). Eq.(11), estimated at $T = T_g$, is known [45] as the fragility $m_g$ that was proposed by Angell for the strong-to-fragile classification of glass forming materials [16]. We see that unlike the case of $\tau_T^{(VFT)}$, the function $m_T^{(VFT)}$ has only two free parameters, $T_0$ and $D_g$. Moreover, the latter can be excluded from the two-equation system given by $\tau_T^{(VFT)}$ and $m_T^{(VFT)}$, using $D_g = m_g^* \varepsilon_g \ln 10$, that eventually results in the known Eq.(8).
As shown above, Eq. (8) is a formal consequence of the self-consistency between the VFT equation $\tau_g^{(VFT)}$ and its first derivative given by the observed fragility $m_g^{(VFT)}$. Physically, the existence of Eq. (8) is due to the presence of the strong-SCL states at the lowest temperature $T_g$ parametrized by these equations. One can therefore introduce a similar relation (see Eq. 8 in Ref. [23]), namely

$$\frac{T_c}{T_0} = \frac{m_g + m_c^*}{m_g - m_c^*} \text{ with } m_c^* = \log_{10} \frac{\tau_c^*}{\tau_a},$$  \hspace{1cm} (12)

associated with the weak-SCL states at the lowest temperature $T_c$. The validity of Eq. (12) was established numerically with the universal parameter $m_c^* = 7 \pm 1$ (see Fig. 2 in Ref. [23]) that corresponds to the adopted value $\tau_c^* = 10^{7 \pm 1}$ s. Eq. (12) was deduced [23] by application of the Taylor series for the steepness function (11) near $T_g$ and $T_c$ along with the following assumptions: (i) in contrast to the case of the timescale $\tau_T$, the steepness function $m_T$ is analytical and smooth beyond $T_0$; and (ii) similar to the strong-SCL state, described by $m_T^{(VFT)}$ with parameters $D_g$ and $T_0$, the weak-SCL states can be described within the scope of the HT-VFT form with help of $m_T^{(HT)}$, using $D_c^{(HT)} = m_c^* \tilde{\varepsilon}_c \ln 10$, and $\tilde{\varepsilon}_c = T_c/T_g - 1$, i.e. by the formal substitution of $T_0$ and $T_g$ in the standard VFT equation by $T_g$ and $T_c$ in the HT-VFT form, respectively. It is remarkable that the idea to introduce in Ref. [23] the steepness function $m_T$ on the basis of the HT-VFT analytical form was stimulated by the uncertainty of the fitting analyses of $\tau_T^{(exp)}$ discussed by Kivelson et al. in Ref. [11]. Experimentally, the HT-VFT form was established by the first-order derivative analyses given by Stickel et al. in Refs. [7–9].

The most striking consequence of the existence of the two distinct SCL states described at $T_g$ (in the vicinity but below $T_c$), respectively, by Eqs. (8) and (12) is an inference on the self-consistency of the principal characteristic temperatures. Indeed, excluding the fragility $m_g$ from Eqs. (8) and (12) one obtains the following characteristic-temperature equation (CTE), namely

$$\frac{T_c}{T_g} = \frac{T_g \left( \frac{m_g^2}{m_c^2} + 1 \right) - T_0}{T_g \left( \frac{m_g^2}{m_c^2} - 1 \right) + T_0},$$  \hspace{1cm} (13)
(that was analyzed analytically in Ref. 23 under the model simplification \( m_g^* = 2m_c^* \)). One can see that beyond the scope of this simplification, Eq.(13) includes the particular case of the MCT ideal liquid-to-glass transition that occurs at a unique crossover temperature given by the equation \( T_g = T_0 = T_c \).

We have shown that representation of the CTE in the form given in Eq.(13) is ensured by application of the VFT fitting forms to both the strong and the weak SCL states. On the other hand, there exist a number of fitting forms (see e.g. Refs. 27,28 and for a short review see Ref. 1) and therefore the question arises as to whether the fact of self-dependency of characteristic temperatures given through the CTE is also limited by exploration of the VFT forms.

Using the Lindeman melting criterion for the mean-square displacements of pre-transition solid-like clusters in SCLs, Novikov et al. in Ref. 25 deduced the CTE in the ”square-root” form: \( T_g^{(low)} = \sqrt{T_0T_c} \). Meanwhile it was shown 23 that \( T_g^{(low)} \) and the ”cubic-root” CTE, i.e., \( T_g^{(up)} = 3\sqrt{T_0T_c^2} \), are respectively, the lower and the upper limits of the solutions of Eq.(13) considered under the model constraint \( m_g^* = 2m_c^* \). Physically, this means that the experimental data on \( T_g^{(exp)} \) and theoretical predictions for \( T_g \), deduced from Eq.(13) under conditions \( T_0 = T_0^{(exp)} \) and \( T_c = T_c^{(exp)} \), are expected to satisfy the equation \( T_g = T_g^{(exp)} \) within the experimental error of \( \pm 5\% \) (see the last column in Table 1 in Ref. 23) and, in addition, to satisfy the inequalities \( T_g^{(low)} < T_g < T_g^{(up)} \).

Odagaki proposed a controlled-diffusion approach to the SCL glass-transition problem in Ref. 19. A glass transformation process was characterized by the critical VFT temperature \( T_0 (= T_K) \) and the crossover temperature \( T_c (= T_x) \) related to the peculiarities of the pseudo-divergent \( \alpha \)-timescale, and introduced 19 through the true divergence of the first moment of their distribution function. As a consequence the CTE in the form \( T_c\Delta S_c = 2T_g\Delta S_g \) was deduced. Taking into account that the excess entropy \( \Delta S_T \), given in Eq.(4), in real SCLs is well approximated by Eq.(5), we represent here the Odagaki CTE in the following equivalent form, namely
\[
\frac{T_g}{T_c} = \frac{1}{2} \left( 1 + \frac{T_0}{T_c} \right).
\] (14)

Again, one can see that the aforementioned MCT ideal transition is also satisfied by Eq. (14).

A comparative analysis of the distinct CTE form is given in Fig. 4 for glass forming liquids (case A) and polymers (case B). As seen from Fig. 4 the Odagaki CTE prediction (14) is very close to that given by Eq. (13) with a value for \( m_g^* / m_c^* \) that lies within the experimentally established uncertainties, i.e., \( m_g^* = 16 \pm 2 \) and \( m_c^* = 7 \pm 1 \).

III. DYNAMICS AND THERMODYNAMICS OF SUPERCOOLED LIQUID STATES

A. Cluster Statistics

Solid-like clusters were treated in Refs. [29,33,34] as short-range random-size correlated regions of SCLs that permits one, at a mesoscopic level of consideration, to employ the percolation [29,32] or controlled-diffusion [33,34] models. Within this context, clusters are equivalent to solid-like domains [13,30], or droplets [20] or CRRs (cooperatively rearranging regions) as introduced in Ref. [14]. A more detailed specification of clusters depends on ways of incorporation of short-range correlations in the description of their evolution.

We treat clusters as conglomerates of \( z \) molecules [47] that are characterized at a given temperature \( T \) and pressure \( p \) by the solid-state chemical potential \( \mu_T^{(\text{sol})}(p) \). These finite-size solid-like clusters are in thermal and mechanical contact with the remaining \( N - z \) molecules, which are in the normal liquid (NL) state and characterized by a chemical potential \( \mu_T^{(\text{liq})}(p) \).

The typical cluster, or characteristic cluster, is in dynamic equilibrium with SCL, and is introduced by the mean-size configurational average, i.e., \( < z >_{C} = z_T(p) \) through the cluster-size distribution function \( P_T(p, z) \). For the thermally equilibrated SCL states we admit the ergodicity hypothesis [29], i.e. the configurational averaged values are equal to those estimated at thermodynamic equilibrium for temperatures \( T > T_g \geq T_E \), above the ergodic-nonergodic transition temperature \( T_E \) [29].
The isobaric process, as a model mechanism of z-cluster formation, can be described by variation of the Gibbs (thermodynamic) potential $\delta G^{(sol)}(T, p, z) = -S_T^{(sol)} \delta T + \mu_T^{(sol)} \delta z$. Solidification, or cluster growth, if assumed at the thermal equilibrium temperature $T_{eq}$, is defined by minimization of the whole system potential, that gives rise to the requirements imposed on the chemical potentials, i.e., $\mu_T^{(sol)} = \mu_T^{(liq)}$, and on the entropies, with $S_T^{(sol)} < S_T^{(liq)}$, given at $T = T_{eq}$ (see e.g. Fig.15 and discussion in Ref. [48]). Stabilization of the liquid-solid boundary upon decrease of temperature below the equilibrium temperature is also ensured by minimization of the whole Gibbs potential and therefore by positivity of the excess chemical potential, i.e., $\Delta \mu_T = \mu_T^{(sol)} - \mu_T^{(liq)} > 0$ and the mesoscopic-scale configurational entropy, i.e., $\Delta S_T(z) = S_T^{(liq)}(N - z) - S_T^{(sol)}(z) > 0$ at $T < T_{eq}$ (hereafter we omit the pressure $p$ as an irrelevant parameter). Note that the macroscopic configuration entropy introduced by Eq.(4) is defined here as $\Delta S_T = \Delta S_T(z) > C$. The latter is also expected to be valid far from thermodynamic equilibrium.

Within the fluctuation mechanism for the formation of heterogeneous clusters, the probability for the formation of a solid cluster of size $z$, is formally given by the probability $P_T(z) dz$ that the thermodynamic variable $z$ lies between $z$ and $z + dz$. This probability is driven by the temperature-dependent whole-system entropy [49], namely

$$P_T(z) = \exp \frac{S_T(z)}{k_B} \approx \sqrt{\frac{2}{\pi \Delta z_T^2}} \exp \left[ -\frac{(z - z_T)^2}{2 \Delta z_T^2} \right].$$  \hspace{1cm} (15)

Here the characteristic cluster of size $z_T$ is in thermodynamic equilibrium with the thermal bath, and therefore the entropy of the whole system $S_T(z) = S_T^{(sol)} + S_T^{(liq)} + S_T^{(mix)}$ (which includes the solid-liquid mixing term $S_T^{(mix)}$) has a maximum at $z = z_T$. The cluster-size fluctuations $\Delta z_T^2 \equiv (z - z_T)^2 > C$ are introduced formally by the relation $\Delta z_T^2 = -\left( \frac{\partial^2 S_T}{k_B \partial^2 z} \right)^{-1}_{z=z_T}$, and Eq.(17) is expected to work near equilibrium, i.e., for $T \approx T_{eq}$. It is notable that the real SCLs, studied in dynamic experiments, are not close to thermodynamic equilibrium, but the Gaussian size-distribution function $P_T(z)$ of Eq. (15) was experimentally tested and justified by Chamberlin et al. in Refs. [30,35] for a number of SCLs.

Let us treat the formation of a cluster of size $z$ at fixed pressure $p$ and temperature...
$T$ as an isobaric-isothermal fluctuation process. This means that solid-like clusters are not in thermodynamic equilibrium with the fluid, i.e., $T < T_{eq}$, ($T$ refers to the solid-state subsystem and $T_{eq}$ to the thermal bath) but they appear and disappear from a fluid volume of size $z$ with a CRR frequency $\tau_T^{-1}(z)$, where $\tau_T(z)$ is the lifetime of a $z$-cluster. The probability of formation of this kind of cluster is given by $\tau_T^{-1}(z)$ and is determined from Onsager’s principle, i.e. by the aforesaid mesoscopic size-scale entropy $\Delta S_T(z)$, namely

$$\tau_T^{-1}(z) = \tau_\infty^{-1} \exp \left( \frac{\Delta S_T(z)}{k_B} \right) = \tau_\infty^{-1} \exp \left( \frac{-W_{\min}(z)}{k_B T_{eq}} \right).$$

(16)

Here $W_{\min} = \Delta G_T(z)$ corresponds to the minimum work (see e.g. Eqs.(20.8) and (114.1) of Ref. [48]) required for solidification of $z$ molecules driven by cluster-size fluctuations. Within the isobaric-isothermal mechanism, proposed by Adam and Gibbs [14], one has $\Delta G_T(z) = (\mu_T^{(sol)} - \mu_T^{(liq)})z$. As a result the exact result of Eq.(16) can be extended to non-equilibrium states with $T \approx T_{eq}$ through the relation

$$\tau_T(z) = \tau_a \exp \left( \frac{\Delta \mu_T z}{k_B T} \right)$$

(17)

which introduces the cluster mesoscopic-scale relaxation time. This in turn is related to the observed macroscopic timescale, namely

$$\tau_T \equiv < \tau_T(z) >_C = \int_0^\infty \tau_T(z) P_T(z) dz.$$

(18)

Within the proposed cluster statistical treatment, the corresponding macroscopic lengthscale is given by

$$z_T \equiv < z >_C = \int_0^\infty z P_T(z) dz.$$

(19)

On one hand, these two scales, experimentally justified above the glass transition temperature, are ensured by the thermodynamic-dynamic correspondence principle. On the other hand, the cluster-formation mechanism, specified by $P_T(z)$ through the observables given in Eqs.(18) and (19), should satisfy the constraints that are naturally required by the macroscopic and mesoscopic scales. In other words, the observables should obey the conditions $\tau_T > \tau_T^{(min)} = \tau_a$ and $z_T > z_T^{(min)} = z_a$ where the limiting mesoscopic-scale magnitudes $\tau_a$ and $z_a$ are established in Eq.(6).
B. Adam-Gibbs Model

The Adam-Gibbs molecular-kinetic theory [14] was based on Eq. (16) given for the cooperative transition probability for rearranging regions of $z$ molecules with the minimum work $W_{\text{min}}^{(AG)} = \Delta \mu^{(AG)} z$ that was estimated for the isobaric-isothermal ensemble of equivalent thermodynamic subsystems, where $\Delta \mu^{(AG)}$ is a solid-over-liquid excess chemical potential, approximated by a constant. The average transition probability $1/\tau_T^{(AG)}$ follows from the AGM macroscopic timescale, namely

$$\tau_T^{(AG)} = \tau_\infty^{(AG)} \exp \left( \frac{\Delta \mu^{(AG)} z_T^{(AG)}}{k_B T} \right).$$

(20)

The smallest CRR of a “critical size” $z_T^{(AG)}$, that still permits a transition, corresponds to the lowest critical configurational entropy for one CCR, $s^* = k_B \ln 2$, introduced as the first estimate in Ref. [14]. The configurational entropy $S_c(T)$ of the whole system given in Eqs. (4) and (5) for one mole of the SCL ($N = N_A$), consists of $N_A/z_T^{(AG)}$ of self-similar smallest CRRs and is therefore estimated here as

$$S_c(T) = s^* \frac{N_A}{z_T^{(AG)}}.$$

(21)

One can see that Eq. (21) is equivalent to Eq. (20) in Ref. [14]. Eqs. (20) and (21) deduced above result in the known Eq. (1) with the AGM parameters, namely

$$A = \log_{10} \tau_\infty^{(AG)} \text{ and } C = \frac{\Delta \mu^{(AG)} N_A s^*}{k_B}.$$

(22)

Note that the AGM was motivated to validate the phenomenological Williams-Landel-Ferry fitting form that in a way is equivalent to the VFT form.

Adopting the aforesaid TD-D correspondence established between the AGM and the VFT form given by Eq. (3), and with the help of Eqs. (3) and (20), we introduce the primary relaxation lengthscale through the relations

$$z_T^{(AG)} = \frac{z_\infty^{(AG)}}{1 - T_K/T} \quad \text{with} \quad z_\infty^{(AG)} = z_\infty^{(VFT)} = z_a = \frac{N_A s^*}{\Delta S_\infty} = \frac{k_B B}{\Delta \mu^{(AG)} \ln 10}$$

(23)

where the minimum cluster-size magnitude $z_a$ is anticipated by Eq. (3).
The CRR size-temperature behavior given by $z^{(\text{exp})}$ was experimentally studied for SCLs and for orientational-glass plastic crystals in Refs. [50, 51]. These studies as well as the findings of Ref. [10], both based on the AGM, clearly indicate that Eq.(23), and also Eq.(5), do good a job within the whole SCL ergodic temperature range, i.e., at $T \geq T_g$ (see e.g. Fig. 4 in Ref. [51] and Fig. 3 in Ref. [10]). This permits one to present the experimental result for the excess isobaric heat capacity $\Delta C^{(\text{exp})}_T \propto T^{-1}$, used above to evaluate the configurational entropy in Eq.(3), in the following equivalent form:

$$\Delta C^{(\text{exp})}_T = \Delta C^{(\text{exp})}_g \frac{T_g}{T} \text{ for } T \geq T_g.$$  \hspace{1cm} (24)

With the help of Eq.(4) one arrives at a new useful relation for the observed model parameter $\Delta S_\infty$ (see Table I in Ref. [10]) introduced in Eq. (5), namely

$$\Delta S_\infty = \Delta C^{(\text{exp})}_g \frac{m_g}{m_g - m_g^*}$$ \hspace{1cm} (25)

that though needs further experimental examination.

Finally, one can see that the CRRs can be introduced by the SCL cluster statistics on the basis of Eq. (18) with the help of $P_T^{(AG)}(z) = \delta(z - z_T^{(AG)})$. This means that the CRRs are \textit{homogeneous clusters} of characteristic size $z_T = z_T^{(AG)}$ given in Eq.(4) with negligible heterogeneous and/or thermal size fluctuations, i.e., $\Delta z_T = \Delta z_T^{(AG)} = 0$.

\textbf{C. Extension of the Vogel-Fulcher-Tamman Equation}

Within the cluster statistics approach the primary relaxation timescale is introduced by Eqs.(15),(17) and (18). A straightforward calculation using the standard integral [53]

$$\int_0^\infty \exp \left( -\frac{x^2}{4b} - ax \right) dx = \sqrt{\pi b} \left[ 1 - \text{erf} \left( a\sqrt{b} \right) \right] \exp ba^2$$ \hspace{1cm} (26)

yields

$$\tau_T = \tau_a \left[ 1 + \text{erf} \left( \frac{1 + \Delta E_T/k_BT}{\sqrt{2\Delta E_T/E_T}} \right) \right] \exp \left[ \frac{E_T}{k_BT} \left( 1 + \frac{\Delta E_T}{2k_BT} \right) \right]$$ \hspace{1cm} (27)

given in the pseudo-Arrhenius form with the cluster-energy characteristics, namely
\[ E_T = \Delta \mu_T z_T, \quad \Delta E_T = \frac{\Delta \mu_T \Delta z_T^2}{z_T}, \quad z_T = \frac{z_a}{1 - T_0/T}. \] (28)

The standard error function that emerges in Eq. (27) is bounded by one, and although it modifies the pre-exponential factor \( \tau_a \), it does not substantially modify the exponential temperature dependence of \( \tau_T \). Furthermore, the error-function term will be absorbed by \( \tau_a \).

We see that the VFT form of Eq. (27), when extended by cluster-size fluctuations, has the form of a high-\( T \) thermodynamic perturbation series. The first and second terms in the exponent describe the rigid solid clusters and their fluctuation corrections, respectively. The first term matches the rigid-cluster relaxation time given by the VFT equation and the AGM solution given by Eq. (9) and Eq. (20), respectively. The TD-D correspondence is now extended at a mesoscopic level that permits one to establish the physical meaning of the macroscopical phenomenological parameters for the strong-SCL states, namely

\[ B^{(SL)} = \frac{\Delta \mu_g z_a}{k_B \ln 10} \quad \text{and} \quad C^{(SL)} = \frac{\Delta \mu_g N_A s_c^*}{k_B \ln 10} \] (29)

under the additional condition \( \Delta \mu_g = \Delta \mu^{(AG)} \) along with Eq. (5).

Unlike the case of the thermodynamic AGM, which gives a good description \([10]\) of all the SCL states (see Fig.2) within the ergodic temperature domain, \( T_g \leq T \leq T_m \) (that means that \( C = C^{(SL)} = C^{(ML)} \) in Eq. (1)), the VFT form fails \([7–9]\) to describe weak SCL states if one uses the same critical temperature \( T_0 \). In order to incorporate the weak SCL states into the \( \alpha \)-timescale parametrized by the observed MCT parameters \( \tau^{(MCT)}_\infty, T_c, \text{ and } \gamma_c \) let us represent the exponential form (27) in the asymptotically equivalent algebraic form given by Eq. (7). Using \( \exp [c (1 + x)] = \exp [(1 + x)^c] \), one has the following high-\( T \) series with respect to the small fluctuation parameter \( \Delta E_T / k_B T \), namely

\[ \tau_T^{(V F T E)} = \tau_a \left[ \exp \left( 1 + \frac{\Delta E_T}{2k_B T} \right) \right]^{\frac{E_T}{k_B T}} = \tau_a \left[ e \left( 1 + \frac{\Delta E_T}{2k_B T} + \frac{1}{2} \left( \frac{\Delta E_T}{2k_B T} \right)^2 + \ldots \right) \right]^{\frac{E_T}{k_B T}} \propto \frac{\tau^{(M C T)}_\infty}{(1 - T_0/T)^\gamma} \text{ for } T > T_c \] (31)
denoted the VFT extended (VFTE) form. Accounting for only the two leading terms, one establishes the following relations, i.e., \( \gamma_c = E_c/k_BT_c \) and \( T_c = \Delta E_c/2k_B \) with \( \tau^{(\text{MCT})}_\infty = e^{\gamma_c}\tau_a \), that can also be represented with the help of Eq.(28) in terms of the observed MCT parameters, namely

\[
\gamma_c = \frac{\Delta \mu_c z_{\infty}^{(\text{VFTE})}}{k_BT_0 \varepsilon_c} = \frac{2}{\varepsilon_c^2} \text{ with } \varepsilon_c = \frac{T_c}{T_0} - 1
\]  

and

\[
T_c = T_0 + \frac{\Delta \mu_c z_{\infty}^{(\text{VFTE})}}{k_B \gamma_c}.
\]

Here a new model parameter \( \xi_c = \sqrt{\Delta E_T/E_T = \Delta z_T/z_T} \) is introduced \([29]\), with the aim of establishing a scale for the cluster-size fluctuations above \( T_c \). Accounting for the fact that the size fluctuations are limited, at least to \( \xi_c < 1 \), with help of Eq.(32) one arrives at a physical restriction \( \gamma_c > 2 \) that is in accord with experimental data. As a result, the \( \alpha \)-relaxation scale is now parametrized for the strong SCL states, namely

\[
\tau^{(\text{SL})}_T = \tau_a \exp \left( \frac{\Delta \mu_a z^{(\text{SL})}_a}{k_BT_0 \varepsilon_T} \right) \text{ with } \varepsilon_T = \frac{T}{T_0} - 1, \text{ for } T_g \leq T < T_c,
\]  

with the observable combinations of cluster parameters \( \Delta \mu_a z^{(\text{SL})}_a = D_g k_BT_0 \) (see Eq.(9)) and \( z^{(\text{SL})}_a = z_{\infty}^{(\text{VFTE})} \) (see also Eq.(16)). For the case of the weakly cooled states in moderately SCLs one has

\[
\tau^{(\text{ML})}_T = \tau_a \exp \left[ \frac{\Delta \mu_a z_{\infty}^{(\text{ML})}}{k_BT_0 \varepsilon_T} \left( 1 + \frac{1}{\gamma_c} \frac{\Delta \mu_a z^{(\text{ML})}_a}{k_BT_0 \varepsilon_T} \right) \right] \text{ for } T_c \leq T \leq T_m
\]  

with \( \Delta \mu_a z^{(\text{ML})}_a = \gamma_c k_B(T_c - T_0) \) that follows from Eq.(33) when \( z_{\infty}^{(\text{VFTE})} = z^{(\text{ML})}_a \). In the following sections we review experimental evidence for the proposed description of the primary relaxation through the timescale steepness and curvature.

**IV. STEEPNESS FUNCTION ANALYSIS**
A. Qualitative Analysis

We discuss two scenarios of relaxation of the SCLs observed in thermodynamic and dynamic experiments and shown in Fig. 2. The thermodynamic version is given by the AGM that describes the configurational entropy data within the whole SCL ergodic range (shown by solid squares in Fig.2). Within the context of percolation treatment, the solid clusters are apparently the same for the strongly and moderately SCL states, i.e., $z_a^{(SL)} = z_a^{(ML)} = z_a^{(AG)}$ and thermal fluctuations are negligible ($\Delta z_T^{(AG)} = 0$). The AGM excess chemical potential is approximated by a constant given at $T_g$, i.e., $\Delta \mu^{(AG)} = \Delta \mu_g$.

To describe the primary relaxation timescale observed in the dynamic experiments, we start from the trial estimate given by the thermodynamic approximation. This is formally introduced by SCL-system clusters with $z_a^{(SCL)} = z_a^{(AG)} = z_a$, but with $\Delta z_T^{(SCL)} \neq 0$, that corresponds to an extension of the AGM by cluster-size fluctuations, which strictly speaking are not observed in real thermodynamic experiments. Meanwhile the trial dynamic timescale steepness function follows from Eqs. (10) and (35), namely

$$m_T^{(SCL)} = \frac{D^{(SCL)}}{\ln 10} \frac{1}{\varepsilon_T} \left( 1 + \frac{1}{\varepsilon_T} \right) \left( 1 + \frac{2}{\gamma_c} \frac{D^{(SCL)}}{\varepsilon_T} \right)$$

with

$$D^{(SCL)} = \frac{\Delta \mu_g z_a}{k_B T_0} \quad \text{for} \quad T_g \leq T < T_m,$$

where the auxiliary timescale function $\varepsilon_T$ is given in Eq. (9). In order to employ the timescale parametrization in terms of the observed fragility $m_g$, we apply Eq. (36) at $T = T_g$. Using the relation $z_a = k_B T_0 \gamma_c \varepsilon_c / \Delta \mu_c$, one excludes the unknown parameter $z_a$. By solving Eq. (36), with respect to the MCT parameter $\gamma_c$, one obtains the trial estimate given by

$$\gamma_c = \frac{m_g^{*} \ln 10}{\frac{\Delta \mu_g \varepsilon_c}{\Delta \mu_c \varepsilon_g} \left( 1 + 2 \frac{\Delta \mu_g \varepsilon_c}{\Delta \mu_c \varepsilon_g} \right)}$$

that was analyzed in detail in Ref. [29]. Here we consider Eq. (37) as the quadratic equation with respect to the unknown factor $\Delta \mu_g / \Delta \mu_c$. This enables one to calculate the rebuilding energy per molecule near the crossover temperature, namely

$$\frac{\Delta \mu_g}{\Delta \mu_c} = \frac{\varepsilon_g}{4 \varepsilon_c} \left( \sqrt{1 + 8 \frac{m_g^{*}}{\gamma_c} \ln 10} - 1 \right).$$
The physical solutions of the quadratic equation (37) must satisfy the requirement of thermodynamic stability discussed above and given by the condition \( \Delta \mu_g \geq \Delta \mu_c \). Numerical solutions of Eq. (38) are shown in Table 2 for experimental data known for the characteristic temperatures and the slowing-down exponent \( \gamma_{c}^{(\text{exp})} \) given in Table 1. Predictions for the unknown \( \gamma_c \) are also made with the help of Eq. (37) through the overall estimates \( \Delta \mu_g^{(\text{SCL})} / \Delta \mu_c^{(\text{SCL})} = 1.2 \) and \( \Delta \mu_g^{(\text{pol})} / \Delta \mu_c^{(\text{pol})} = 1 \) adopted, respectively, for liquids and polymers. We see that no rebuilding chemical potential effects are found for the case of glass forming polymers. This can be understood as follows. In contrast to the case of molecular liquids, where application of the ergodic cluster description by the Gaussian distribution given in Eq. (13) is justified both physically and experimentally, the monomeric-segment polymers require accounting of their fractal structure even for their ergodic states 29.

The dynamic relaxation scenario given by the VFT equation is realized through rigid clusters as well as by the VFT equation extended by the cluster-size fluctuations (VFTE equation) and applied, respectively, to the strong and weak SCL states. The relevant steepness function follows immediately from the corresponding relaxation times. Hence with help of Eq. (34), one has

\[
m_T^{(\text{SL})} = \frac{D_g}{\ln 10 \varepsilon_T} \left( 1 + \frac{1}{\varepsilon_T} \right) \text{ with } D_g = \frac{\Delta \mu_g^{(S)}}{k_B T_0}.
\]

(39)

for the case of the strongly SCLs. In the case of the moderately SCLs the steepness function follows from Eq. (35), namely

\[
m_T^{(\text{ML})} = \frac{D_c}{\ln 10 \varepsilon_T} \left( 1 + \frac{1}{\varepsilon_T} \right) \left( 1 + \frac{2 D_c}{\gamma_c \varepsilon_T} \right) \text{ with } D_c = \frac{\Delta \mu_c^{(ML)}}{k_B T_0}.
\]

(40)

Qualitatively, the first-order derivative analyses of experimental data by Stickel et al., given in Refs. 7,8 points to the existence of a small kink of the steepness function near the crossover temperature \( T_c \) (see Fig. 1) 54. Formally, this means that the limit of the timescale steepness function from below \( (T \to T_c - 0 \text{ and } m_T^{(\text{SL})} \to m_c^{(\text{SL})}) \) differs with that from above \( (T \to T_c + 0 \text{ and } m_T^{(\text{ML})} \to m_c^{(\text{ML})}) \), and therefore one should expect that \( m_c^{(\text{SL})} > m_c^{(\text{ML})} \). Application of these limits to Eqs. (39) and (40) using the relation \( D_c = \gamma_c \varepsilon_c \), that follows

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from Eq.(33), results in \( D_g > 3D_c \). These qualitative findings extended by the condition of the thermodynamic cluster stability can be summarized as

\[
\frac{\Delta \mu_g}{\Delta \mu_c} \frac{z_a^{(SL)}}{z_a^{(ML)}} > 3 \quad \text{with} \quad \frac{\Delta \mu_g}{\Delta \mu_c} > 1. \quad (41)
\]

The dynamic conditions given in Eq.(41) reflect the observed dynamical crossover from moderately to strong SCLs near \( T_c \) that are associated with the dynamic reconstruction of the cluster lengthscale. To provide deeper insight into the problem we will reproduce below the fitting derivative analyses by Stickel et al. within the VFT and VFTE equations.

**B. Numerical Analysis**

1. **First-Order Derivative Timescale Steepness**

The first-order derivative analysis of the temperature behavior of the timescale was given in Refs. [7,8] with the help of a first-order derivative function, namely

\[
F_{1T} = \left( -\frac{d \log_{10} T}{d \ln T} \right)^{-1/2} = \frac{1}{\sqrt{T m_T}}. \quad (42)
\]

This function was estimated from \( \tau_T^{(exp)} \) and fitted by the VFT form, i.e. by \( F_{1T}^{(VFT)} = (1 - T_0/T) / \sqrt{B} \), and by other known fitting forms (see e.g. Fig.1). We reproduce this analysis in Figs.5 and 6 in terms of the steepness function deduced from Eq.(42), i.e., \( m_T^{(exp)} = 1/T(F_{1T}^{(exp)})^2 \), with \( F_{1T}^{(exp)} \) found by Stickel et al. by fitting with \( m_T^{(SL)} \) and \( m_T^{(ML)} \). The latter are given, respectively, in Eq.(39) and Eq.(40), with the strength indices \( D_g \) and \( D_c \) treated as adjustable parameters within the corresponding temperature regions, \( T_g \leq T < T_c \) and \( T_c \leq T < T_m \), respectively. The results of fitting analyses are accumulated in Table 3. Unlike the case of Figs.5, where the VFT temperature \( T_0 \) is treated as the same for the both states, the SCLs analyzed in Fig.6 are in conflict with the canonical VFT form for the strongly SCL states, but this is in accord with analysis given in Refs. [7,8,10].

In this case the critical temperature \( T_0 \) is not established and is therefore treated as an additional adjustable parameter for description of the moderately SCL states through the
VFTE equation. Thereby, we follow the idea that the Kauzmann temperature $T_0$ might be established beyond the VFT equation.

Our quantitative analysis of the strong-to-moderate-state crossover is in accord with the qualitative predictions given by Eq. (41). As seen from Table 3, the typical change in the ratio of strength indices $D_g/D_c$ lies between 4 and 6. Exceptions should be given for the "irregular" case of salol where the Kauzmann temperature established by the VFTE equation ($T_0 = 200K$) is rather different from those established by other methods and given in Table 1.

Adopting the trial estimate for the moderate-to-strong SCL-state crossover for the excess chemical potential, given in Table 2, one arrives at the length-scale ratio estimate $z_a^{(SL)}/z_a^{(ML)} = 3.7 - 4.7$. We see that the observed crossover, associated with the cluster reconstruction, is not caused solely by decrease of cluster-size fluctuations and/or by growth of their chemical potentials. This crossover is accompanied by the lengthscale extension, i.e., $z_a^{(SL)} > z_a^{(ML)}$.

2. Second-Order Derivative Timescale Curvature

The second-order timescale derivative-fitting analysis introduced by Stickel et al. can be treated as experimental observation of the critical temperature $T_0$ through the VFT form. This analysis was done [7,8] with the help of the second-order derivative function $F_{2T}(\equiv \Theta(T))$, introduced in Eq.(21) in Ref. [7] as

$$F_{2T} = \frac{d\log_{10} \tau_T}{dT} \left( \frac{d^2 \log_{10} \tau_T}{dT^2} \right)^{-1} = T \left( 1 - \frac{d \ln m_T}{d \ln T} \right)^{-1} \quad (43)$$

that results in $F_{2T}^{(VFT)} = -(T - T_0)/2$ for the case $\tau_T^{(VFT)}$ given in Eqs.(2) and (3). The experimental data for $\tau_T^{(exp)}$ was used to estimate $F_{2T}^{(exp)}$ by Eq.(13) and fitted to the temperature-linear function $F_{2T}^{(VFT)}$. As a result, the two distinct critical temperatures $T_0$ and $T_c$ were established for PC and 1-propanol through the VFT and HT-VFT forms (see Figs. 13 and 16 in Ref. [8], respectively). In the case of salol and PDE, only the HT-VFT
form was derived \[8\] in Figs. 8 and 11. Remarkably, in all cases the assumed kink in the function \(F^{(\text{exp})}_{1T}\) near \(T_c\) was transformed into the evident jump of the function \(F^{(\text{exp})}_{2T}\).

The \textit{curvature} of the timescale \(k_T\), closely related to the second-order derivative function given in Eq.\((43)\), can be introduced by the following relations, namely

\[
k_T \equiv \frac{d \ln m_T}{d \ln T} = \frac{1}{\ln 10} \frac{d^2 \ln \tau_T}{(d \ln T)^2} = 1 - \frac{T}{F^{(\text{exp})}_{2T}}, \tag{44}
\]

with \(k_T^{(\text{VFT})} = (3T - T_0)/(T - T_0)\). In order to describe the weakly cooled states in moderately SCLs through the curvature \(k_T^{(ML)}\) we substitute the relevant steepness function given in Eq.\((43)\). This yields

\[
F^{(ML)}_{2T} = -\frac{T}{1 + \left(\frac{\gamma c + 4D_c}{\gamma c + 4D_c} + \frac{1}{\epsilon_T + 1}\right) \left(1 + \frac{1}{\epsilon_T}\right)} \quad \text{with} \quad D_c = \frac{\Delta \mu_{c_a}^{(ML)}}{k_B T_0}, \tag{45}
\]

that leads to an expression for \(k_T^{(ML)}\) with the help of Eq.\((44)\). The typical SCL timescale curvatures are exemplified by PC and salol given in, Fig. 7 and Fig. 8, respectively. We see that both cases are distinct and that the moderately SCL states are consistent with the cluster-size fluctuation description, based on the idea of the existence of a unique thermodynamic-instability temperature \(T_K = T_0\). They are described by the VFTE timescale equation \((35)\) with the same model parameters established in the steepness timescale analysis given in Fig. 5A and 6A, respectively, for PC and salol. Conversely, in the case of salol and PDE, our attempts failed \[55\] to describe the strongly SCL states through the observed curvature with the help of various VFT-type fitting forms reviewed in Ref. \[1\], including the proposal given in Refs. \[27,28\]. Accounting for the aforesaid TD-D correspondence, we speculate that the failure of the standard VFT equation in the salol-type SCLs (that should be extended by the case of BMPC (see Fig.6C)), is due to the inapplicability of the cluster description given by the thermodynamic model of Adam and Gibbs in Ref. \[14\]. Indeed, as shown above, the main AGM constraint for the excess chemical potential, i.e., \(\Delta \mu_T = \Delta \mu_c\), works well above the SL-ML crossover temperature, but below \(T_c\) it needs to be reconsidered for the salol-type SCLs.
V. DISCUSSION AND CONCLUSIONS

The investigation of the temperature behavior of the primary relaxation timescale in SCLs plays a fundamental role in understanding the glass transition problem in general, as widely discussed in various, microscopically distinct, glass forming non-solid materials. In spite of the fact that the nature of the structural glass transformations is essentially dynamical, the process of solidification of rearranging regions, while avoiding crystallization of a given SCL as a whole system, exhibits many features of the common liquid-to-solid or disorder-to-order true thermodynamic phase transitions.

The ”pure” dynamic treatment of the glass-transition problem, given by the simplified MCT version, and the ”pure” thermodynamic treatment given by the simplified AGM, are limited in the description of the primary relaxation timescale temperature behavior. This limitation was revealed by the temperature derivative analyses given by Stickel et al., as shown in Fig.1, that clearly establish that the fitting forms for the known $\tau_T^{(MCT)}$ and $\tau_T^{(AG)}$ (given, respectively, in Eqs.(7) and (34)), fit the data only for a restricted temperature window.

The same kind of restriction applies to the analysis of the thermodynamic models \[12,13\] mentioned in the Introduction, which offer a similar overall $\tau_T$ description within the whole range of existence of the ergodic SCL states. Although these models seem to provide a good fit to $\tau_T^{(exp)}$ (by using only one adjustable parameter, as the fragility $m_g$ in the case of Ref. \[12\], or by using more than three adjustable model parameters, as in the case of Ref. \[1\]), they need to be analyzed by considering the derivative functions of the dynamical variables over the full temperature range.

As stressed by Angell et al. in Ref. \[1\], the popularity of the thermodynamic AGM among molecular-liquid phenomenologists might be compared with that of exploring the phenomenological VFT form by glass-material experimentalists. The current study develops a statistical approach for the description of CRRs, with their isobaric-isothermal mechanism of solidification that were introduced a long time ago by Adam and Gibbs in Ref. \[14\].
The application of the second-order derivative analysis for the case of salol, revealed that the widely used standard VFT form given in Eq.(16) has no observation window. This observation ended the unreserved domination of the phenomenological VFT form for fitting all dynamical data of all SCLs, and divided the SCLs in two groups, "regular" and "irregular", that, respectively, obey or do not obey the VFT equation. Meanwhile, it seems that all SCLs exhibit a jump in the timescale curvature near $T_c$ (see e.g. Figs. 7 and 8) related to the corresponding kink observed in the temperature behavior of the timescale-steepness that separates the glass forming liquids into two dynamically distinct states (see e.g. Figs. 5 and 6). Additionally, both the "regular" and "irregular" SCLs, therefore manifest the absolute thermodynamic instability at the Kauzmann temperature $T_K$, whose physical meaning is extended by the equation $T_K = T_0$.

We have discussed the SCLs in ergodic states in terms of isolated finite-size solid-like clusters observed within the window $T_g \leq T < T_m$ in the dynamic experiments through the primary relaxation timescale data $\tau_T^{(exp)}$. The cluster dynamics, introduced by the Gaussian size-distribution cluster statistics and exponential-type size-relaxation, described by Eqs.(15) and (17), respectively, is driven by the mesoscopic entropy and ensured by the Onsager thermodynamic principle.

Below the crossover temperature $T_c$, the CRRs emerges as structurally homogeneous clusters, where thermodynamic stability is guaranteed by the growth of the excess chemical potential $\Delta \mu_g$ (> $\Delta \mu_c$). This energetic change, associated with the cluster rebuilding, is justified experimentially through the analysis given in Table 2A. In turn, the homogeneous clusters are associated with the strong SCL states of the MCT, and/or with percolation theory solid-like clusters described by the VFT equation (with the activation energy $E_T^{(SL)} = \Delta \mu_g z_T^{(SL)}/T$ and the characteristic size $z_T^{(SL)} = z_a^{(SL)}/(1 - T_0/T)$, both are given in Eq.(34)). The minimum cluster size $z_a^{(SL)}$ is related to the lattice constant of the underlying percolation lattice, i.e., $z_a^{(SL)} = \left(v_0 z_a^{(SL)}\right)^{1/3}$, where $v_0$ is the molecule volume.

The experimental observation [10] of the strong-SCL ergodic states, described simultaneously by the thermodynamic AGM and the dynamic VFT equations led to formulation
of the thermodynamic-dynamic glass-transition correspondence principle. This principle is based on the physically intelligible thermodynamic-dynamic equations introduced for the critical \( T_0 \) and glass transition \( T_g \) temperatures, as well as on the ergodic hypothesis that gives rise to the temporal and spatial scale minima introduced in Eq. (6). These scales are common for both dynamic and thermodynamic experiments within the temperature domain \( T_g \leq T < T_c \). Upon cooling near and below \( T_g \), the cluster size \( z_T^{(SL)} \) and its heterogeneous fluctuations \( \Delta z_T^{(SL)} \) grow and the SL clusters show an ergodic instability caused by their maximum fluctuations [29]. The compact "ergodic" solid-like SL clusters are therefore transformed into fractal-type clusters of the holey-like (approximated by the ideal gas [27,29]) structure that is accompanied by expansion of the relevant percolation lattice, with \( \zeta_b > \zeta_a^{(SL)} \). Upon heating, the CRRs of the AGM disappear in the dynamic experiments above \( T_c \) but remain stable in calorimetric thermally equilibrated experiments (see Fig.2). Moreover, as follows from the first and second order \( T \)-derivative analyses elaborated in Refs. [7,8,10,55], the SL-cluster description given with the help of the VFT-type forms is not useful for "irregular" SCLs such as salol, PDE, and BMPC (see also steepness and curvature analyses in Figs.6A and 8, Fig.6B, and Fig.6C, respectively).

Unlike the SL states, the structurally heterogeneous clusters, denominated as ML clusters, exhibit stability in all studied SCLs. They are associated with excitations of the weak supercooled states, characteristic of the moderately SCLs within the domain \( T_c \leq T < T_m \) and introduced by the VFTE equation with the correlation length \( z_T^{(ML)} = \zeta_a^{(ML)}/(1 - T_0/T) \) described in Eq. (28). In turn, the heterogeneous cluster-size fluctuations, \( \Delta z_T^{(ML)} = (2/\gamma_c)^{1/2} z_T^{(ML)} \), are introduced with the help of the model parameter \( \xi_c \) given in Eq. (33).

Due to the common physical restriction imposed on fluctuations, which preserve the ML-cluster structure and given by \( \Delta z_T^{(ML)}/z_T^{(ML)} < 1 \), one naturally arrives at the constraint for the timescale slowing-down exponent, i.e., \( \gamma_c > 2 \).

The minimum size of the ML clusters derived from the dynamical experimental data (see Table 3) is related to the instability of heterogeneous clusters below the crossover temperature \( T_c \) that results in an expansion of the underlying percolation lattice, i.e., \( \zeta_a^{(SL)} > \zeta_a^{(ML)} \).
We see that within the context of percolation theory, the discussed cluster reconstructions near $T_g$ and $T_c$ are geometrically similar and therefore the crossover temperature $T_c$ for the moderately SCL states plays a role similar to the "crossover" temperature $T_g$ for the strong SCL states. This clarifies the effectiveness of the phenomenological HT-VFT fitting form introduced on the basis of the VFT equation with relevant substitution of the characteristic temperatures discussed in Eq.(12).

It has been justified experimentally (see analyses in Figs. 5-8) that the size fluctuations of the ML clusters, as "non-rigid" solid-like precursors of the SL clusters, grow upon the decrease of the temperature. This means that the ML clusters are characterized more as "fluid-like" rather than "solid-like" and hence might be introduced on the basis of the thermodynamic heterophase-fluctuation microscopic model proposed by Fischer and Bakai in Ref. [22]. According to this model, the ML clusters may be associated with isolated liquid-like droplets that show small heterophase fluctuations. Upon cooling, the concentration of the solid fraction grows and the liquid droplets exhibit a crossover from isolated to non-isolated long-range density fluctuations [56], related to Fischer clusters that eventually do not contribute to the primary relaxation. As seen from Fig. 5 in Ref. [22], for the case of salol, the droplet percolation crossover temperature is close to $T_c$, i.e. to that predicted by the MCT. The question therefore arises as to whether the interpercolation droplet states, given by the Gibbs potential in Eq.(2.1) in Ref. [22], enable one to describe the drastic temperature behavior observed for the timescale curvature in the window $T_g \leq T < T_c$ (see Fig.8). Furthermore, one can speculate that the thermodynamic-dynamic glass-transformation correspondence above $T_c$, can be established on the basis of the physical correspondence between the thermodynamic heterophase-fluctuation droplet model [22] and the dynamic VFTE equation given for $\tau_T^{(ML)}$ in Eq.(35).

One can expect that application of the derivative analysis by fitting the timescale steepness and curvature, in addition to the common $\tau_T^{(exp)}$ fitting, might serve as a reliable instrument to give new insights into important features of the underlying physical processes. This is related to the weak-to-strong SCL-state crossover based on the existence of the
observation windows and the steepness kink discussed above in Eqs. (3) and (11), respectively. We exemplify our statement by the Schulz model (SM) [12] that employs the concept of Goldstein’s energy landscape for SCLs. The overall ergodic-range timescale [12] can be represented here by the activation energy

\[ E_{m}^{(SM)} = E_{m}(T_{m}/T)^{\gamma_{g}} \]

where \( E_{m} \) and \( \gamma_{g} \) are thermodynamic parameters (with \( \gamma_{g} = 1 + 2\Delta c^{(SM)}/3k_{B} \), given in Eq.(26) in Ref. [12] in terms of the excess liquid-over-HT-solid isobaric specific heat capacity \( \Delta c_{g}^{(SM)} \)). Ignoring the weakly \( T \)-dependent pre-exponential factor, one can estimate the steepness function defined in Eq.(10) at \( T_{g} \), i.e., the fragility \( m_{g} \). Similar to the case of the VFT form, discussed on the basis of Eq.(8), one can solve the system of the two equations for \( m_{g} \) and \( \tau_{g} \) with respect to \( E_{m} \) and \( \gamma_{g} \). This process results in the following expression for the slowing-down exponent,

\[ \gamma_{g} = m_{g}/m_{g}^{*} \]

and offers a new equation for the Schulz model excess heat capacity, namely

\[ \Delta c_{g}^{(SM)} = \frac{3}{2}\left( \frac{m_{g}}{m_{g}^{*}} - 1 \right)k_{B}. \] (46)

We have thereby demonstrated, along with the findings given in Eq.(13) and analyzed in Fig.4 (for the self-consistent characteristic temperatures) and in Eq.(25) (for the observed excess entropy \( \Delta S_{\infty} \)), how the steepness timescale analysis can be used to verify the self-consistency of the model predictions. Both model Eqs.(25) and (46) need further testing.

We also speculate on the existence of some alternative mathematical forms for the timescale \( \tau_{T} \), whose cluster-size singular behavior near \( T_{0} \) is sufficiently affected by the excess chemical potential \( \Delta \mu_{T} \). Indeed, in the current study, the macroscopic primary relaxation timescale is introduced by the mesoscopic solid-like clusters with rearranging frequency \( \omega_{T}^{(cl)}(z) \equiv \tau_{T}^{-1}(z) = \tau_{a}\exp(-\Delta \mu_{T} z/k_{B}T) \) (see Eq.(17)). An alternative description of the random mesoscopic rearranging regions was proposed by Odagaki in Ref. [19] on the basis of the AGM treated within the controlled-diffusion approach. Formally, the rearranging regions in SCLs were introduced as random domains defined by the random excess chemical potential \( \Delta \mu \) and by the characteristic size \( z_{T}^{(AG)} \) that follows from Eq.(21) given by the AGM. The domain rearranging frequency was therefore treated as a random value \( \omega_{T}^{(dom)}(\Delta \mu) = \tau_{d}^{-1}\exp(-\Delta \mu z_{T}^{(AG)}/k_{B}T) \). In fact, the most general mathematical form
is given by \( \omega_T \equiv \tau_T^{-1}(\Delta \mu, z) = \tau_a^{-1}\exp(-\Delta \mu \ z/k_B T) \) where both \( \Delta \mu \) and \( z \) are random variables. This type of extended generalized treatment might be considered as a possible candidate to solve the problem of the primary relaxation observed in the salol-type SCLs.

Finally, we have demonstrated how the primary relaxation scale can be described by the two VFT and VFTE equations and parameterized by a finite number of observables: three principal characteristic temperatures \( T_0, T_g \) and \( T_c \); the fragility \( m_g \); the slowing-down exponent \( \gamma_c \); and the two strength indices \( D^{(SL)} = \Delta \mu_g z_a^{(SL)}/k_B T_0 \) and \( D^{(ML)} = \Delta \mu_c z_a^{(ML)}/k_B T_0 \) given in Eqs.(39) and (40), respectively. Physically, this description is justified by the stabilization of the strong and weak SCL states, realized through stabilization of the temporal and spatial scales, and related to the minimum time and size of the rearranging regions. This proposed approach is elaborated with the help of a set of “universal parameters” \( m_g^* = 16 \pm 2 \) and \( m_c^* = 7 \pm 1 \), that seems to be extended by the new ratio \( z_a^{(SL)}/z_a^{(ML)} = 4.2 \pm 0.5 \). Furthermore, one can show through application of the TD-D correspondence principle, that CRRs are observed with the minimum configurational entropy, i.e., \( \Delta s_g^{(AG)} = s_c^* = k_B \ln(2 \pm 0.25) \), as predicted by Adam and Gibbs in their pioneer work in Ref. [14]. The new result will be discussed elsewhere.

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FIGURE CAPTIONS

Fig. 1. First-order derivative function of the timescale, $10^2 \left( d \log_{10}(\tau_T)/d(1/T) \right)^{-1/2}$ versus temperature for propylene carbonate. Circles: relevant dielectric relaxation and dc conductivity experimental data $\tau_T^{(Exp)}$ from Fig. 12 in Ref. [8]. Lines: fitting forms proposed by the mode coupling theory (MCT), Adam-Gibbs model (AGM) and phenomenological VFT ($T_0 = 132K$, $B = 389K$) and the HT-VFT ($T_0^{(HT)} = 153K$, $B^{(HT)} = 158K$) forms. One can see that the AGM and VFT forms fit the strongly SCL (SL) states, shown between $T_g = 157K$ and $T_c = 176K$, and the HT-VFT form fits the moderately SCL (ML) states and even normal liquid (NL) states above the melting point $T_m = 225K$. $T_y$ is the lower temperature of the MCT form.

Fig. 2. Typical temperature behavior of the configurational entropy of supercooled liquids. Schematic representation of the thermodynamic data (solid squares), reestimated dynamic dielectric relaxation data (open circles, see Eq.(8) in Ref. [10]), and the mechanical stress relaxation data (solid circles, see Fig. 10 in Ref. [3]) data. The solid line corresponds to Eq. (5), which is common to the AGM and VFT forms for strongly SCL states, and fits the thermally equilibrated states within the whole ergodic region. Notations correspond to Fig. 1.

Fig. 3. Observation of the universal parameter $m_g^*$: scaled characteristic temperatures against scaled fragility for glass forming liquids (A) and polymers (B). Circles (A) and diamonds (B) correspond to experimental data, see Tables 1A and 1B, respectively. Solid line obeys Eq.(8) with $m_g^* = 16$.

Fig. 4. Experimental justification of the characteristic-temperature equations for supercooled liquids (A) and polymers (B). The symbols denote experimental data from Table 1.
Solid and broken lines are solutions of the CTEs, \((13)\) with fixed ratio \(m_g^*/m_c^*\), and \((14)\), respectively. Dotted lines correspond to the upper and lower limits of Eq.\((13)\) subject to the condition \(m_g^*/m_c^* = 2\).

Fig. 5. Steepness-temperature analysis of the primary timescale in supercooled liquids propylene carbonate (A), ortho-terphenyl (B) and 1-propanol (C) where the VFT equation \((9)\) is experimentally justified. Symbols correspond to the dynamical data (dielectric relaxation, dc conductivity, and viscosity) by Stickel et al. reestimated with the help of Eq.\((12)\) from Fig.12 in Ref. [8], from Fig. 6 in Ref. [9] and from Fig.15 in Ref. [8] for the cases A, B and C, respectively. Lines are given by the VFT and VFTE equations using the experimental characteristic temperatures from Table 1 and with the adjustable parameters given in Eqs.\((39)\) and \((11)\), respectively. Notations correspond to Fig. 1.

Fig. 6. Steepness-temperature analysis of the primary timescale in supercooled liquids sa-lol (A), phenolphthalein-dimethyl-ether (B) and bis-methoxy-phenyl-cyclohexane (C) where the applicability of the VFT equation \((9)\) is questioned. Symbols correspond to the dynamical data given by Stickel et al. and reestimated with the help of Eq.\((12)\) from Fig.4 in Ref. [7], from Fig.10 in Ref. [8] and from Fig.7 in Ref. [9] for the cases A, B and C, respectively. Lines and fitting parameters correspond to Fig. 5. The VFT fit is questionable at low temperatures.

Fig. 7. Curvature-temperature analysis for the primary relaxation in propylene carbonate. Symbols correspond to experimental data reestimated using Eqs.\((14)\) and \((13)\) with the help of Fig.13 in Ref. [8]. Lines are given by the VFT equation \((k_T^{(VFT)}\) ) for the strongly SCL state (SL), HT-VFTE \((k_T^{(HT-VFT)}\) ) and VFTE \((k_T^{(VFTE)}\) ) equations for the moderately SCL state (ML), all discussed in the text, with the same adjustable parameters as found in Fig. 5A.
Fig. 8. Curvature-temperature analysis for the primary relaxation in salol. Symbols correspond to experimental data reestimated from Fig. 8 in Ref. [7]. Lines represent equations given in the text with the same adjustable parameters as found in Fig. 6A.
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