Perspective: Searching for simplicity rather than universality in glass-forming liquids

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This article gives an overview of experimental results on dynamics in bulk glass-forming molecular liquids. Rather than looking for phenomenology that is universal, in the sense that it is seen in all liquids, the focus is on identifying the basic characteristics, or "stylized facts," of the glass transition problem, i.e., the central observations that a theory of the physics of glass formation should aim to explain in a unified manner. *Published by AIP Publishing.* https://doi.org/10.1063/1.5048093

I. INTRODUCTION

Glasses are amorphous solids which are traditionally formed by cooling liquids well below their melting point.[1–3] Some materials are better glass formers than others, but almost all liquids can form glasses, ranging from inorganic glasses such as classical window glass to metallic systems,[4] polymers,[5] and organic molecular liquids. It is commonly recognized that the glass transition plays a central role in many phenomena both in nature and in application, for example in pharmaceutical[6] and food science.[7] Yet, there is still no consensus on how to understand the fundamental mechanisms governing the glass transition.[1–3] In this perspective we review the experimental knowledge of the dynamics that lead to the glass transition in bulk molecular liquids. The focus is on identifying simple behavior—that may not be universal—but could be the starting point for our understanding of the glass transition phenomenon.

A. What is the glass transition?

The classical signature of the glass transition is a kink in the temperature dependence of volume (and enthalpy) as shown in Fig. 1. This kink on the volume curve translates to a jump in its derivative, and the thermal expansion coefficient is lower than the glass transition temperature, T_g, than above, shown as the red curve in Fig. 1. The exact value of T_g depends on the cooling rate; faster cooling gives a higher T_g than a slow cooling rate. The cooling rate dependence is a signature of the fact that the glass transition is not a thermodynamic phenomenon but rather governed by dynamics of the liquid.

The key to understanding the behavior seen in Fig. 1 is therefore to consider the thermal expansion coefficient as a dynamic quantity. When the temperature of a liquid is changed, the volume changes in two steps: (i) a fast isostructural volume change analogous to the volume change in crystalline solids where the distance between molecules is changed but structure remains unchanged and (ii) a structural volume change during which the packing of the atoms or molecules in the liquid changes. The structural rearrangement brings the

liquid into equilibrium and is referred to as the relaxation of the liquid. The isostructural changes happen on the phonon time scale of picoseconds, whereas the time scale of the structural change depends on the mobility of the molecules, which in turn depends on temperature and density.

Figure 2 shows the linear dynamic expansion coefficient measured isothermally at different temperatures of a molecular liquid close to the glass transition. The experiment monitors the volume relaxation after a very small jump in temperature ($\Delta T < 0.2$ K) from which the time-dependent thermal expansion coefficient can be determined as $\alpha(t) = \frac{1}{V}\frac{\Delta V(t)}{\Delta T}$.[9] At time $t = 0$, α is zero. The experiment cannot resolve the fast isostructural volume change, which is seen as a short-time plateau in these data. This plateau level corresponds to the thermal expansion coefficient of a glass formed *at that*
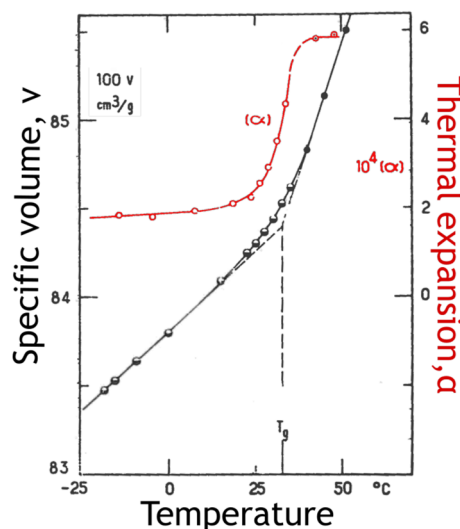

FIG. 1. Illustration of the signature of the glass transition in polyvinyl acetate in a cooling ramp. Black data points show the specific volume as a function of temperature. The glass transition gives rise to a kink in the curve, which manifests as an abrupt change in the value of the thermal expansion coefficient $\alpha = 1/v \, dv/dT$ (red data points) at the glass transition temperature, T_g. Figure from Ref. 8. Adapted with permission from A. J. Kovacs, J. Polym. Sci. **30**, 131 (1958). Copyright 1958 John Wiley and Sons.
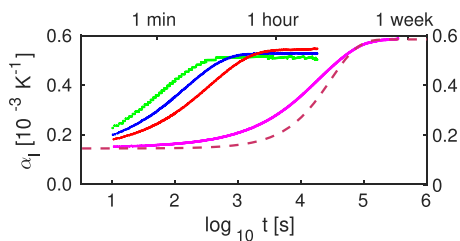
FIG. 2. Dynamic linear thermal expansion coefficient of tetramethyl tetraphenyl trisiloxane (DC704) close to the glass transition (T_g = 210 K): T = 211 K (green), 210 K (blue), 209 K (red), and 205 K (magenta). The dashed line shows an exponential curve for comparison (from Ref. 9). Reproduced with permission from Niss *et al.*, Phys. Rev. E **85**, 041501 (2012). Copyright 2012 American Physical Society.

temperature—not to be confused with the glassy α in a cooling ramp experiment.

The equilibrium value of the expansion coefficient, which is reached after the structural relaxation, gives another plateau in the long-time limit. It is seen directly in the raw data of Fig. 2 that the time scale of the transition between these plateaus—referred to as the structural relaxation time or the alpha relaxation time, τ_α—is strongly temperature dependent: A temperature change of ~3% gives rise to an increase in time scale of more than 2 orders of magnitude.

A conventional cooling ramp experiment as illustrated Fig. 1 will measure the long-time equilibrium value of the expansion coefficient, when the relative cooling rate, $q_c = \frac{1}{T}\frac{dT}{dt}$, is smaller than the inverse relaxation time. However, as temperature is lowered, the cooling rate will overtake the structural relaxation rate, and the measured expansion coefficient in the ramp will be the short-time isostructural plateau value at T_g. The transition between these two regimes is the glass transition. The transition is continuous but relatively sharp, because although an intermediate temperature range exists where the cooling rate and the relaxation time more or less match, this range is narrow due to the dramatic temperature dependence of the structural relaxation time.

Along with the slowing down of the structural relaxation observed in the expansion coefficient, there is a similar slowing down in other response functions, e.g., the specific heat and the mechanical moduli. The transport properties, e.g., viscosity and diffusion constant, likewise has a strong temperature dependence. The viscosity, which is roughly proportional to the structural relaxation time, reaches a value of 10^{12} Pa s around the glass transition temperature.

B. Focus on simplicity

There is no controversy about the explanation of the glass transition on the above-mentioned level.[1–3] The open questions concern the nature of the structural relaxation and what drives the increase of the relaxation time on cooling. Understanding the glass transition therefore implies understanding the dynamics of the equilibrium liquid. The thermodynamics, in particular the changes in entropy, as the glass transition is approached is usually part of reviews on the glass transition phenomenology as it is believed to play a central role for the glass transition. We refer to other reviews for this discussion (e.g., Refs. 1–3, 10, and 11). Likewise, we do not discuss

elastic models, which have been promoted by our group[12,13] and others.[14,15] The focus of this perspective is solely on the phenomenology of the dynamics in bulk equilibrium liquids. We address the question of *how* this phenomenology looks. Or put in other words, what is it a model or theory needs to account for in order to explain the dynamics of viscous liquids.

The basic phenomenology illustrated in Fig. 1 is independent of the atomic or molecular details and interactions, and this has led to the hope of finding a unified model or theory of the glass transition. On the experimental side, the ambition has consequently been to a search for "universal" phenomenology, which in practice led to two complementary experimental strategies. The first strategy, looking for universalities, is driven by the idea that the fundamental phenomenology should be seen in all glass formers including systems with different microscopic interactions. This strategy led to several highly cited papers 10–20 years ago,[16–20] in which data sets from 10 to 100 glass-forming liquids demonstrate correlations between different experimental properties, e.g., a correlation between the Poisson ratio and the temperature dependence of the relaxation time.[19] However, as more systems were studied, these results have been found to hold only for a limited set of glass formers.[21–23] The other strategy is clever new experiments performed on one "archetypical" glass former, based on the idea that since the glass transition is universal, it is irrelevant which exact system one studies. This strategy has also led to several high-profile papers over the decades, with glycerol being the traditional "fruitfly" of the community.[24–27]

In contrast to the search for universality, there are also results and ideas pointing in the direction of some glass formers being simpler than others. Notably, the study of the pressure dependence of liquid dynamics has demonstrated that hydrogen-bonded liquids display a more complex relaxation behavior than van der Waals-bonded liquids.[28–33] This inspires the idea that it may be possible (and useful) to understand the glass transition in its simplest form, before moving to the more general and probably more complex scenario. A prerequisite for doing so is to achieve a picture of what the phenomenology of the glass transition is in the simplest case. While going through different aspects of the dynamics, our focus in this perspective is therefore on identifying what we believe to be signs of simplicity.

Knowledge about the phenomenology of the dynamics in glass-forming liquids is growing in an incremental way, based on continuous development of the experimental techniques. For example, new techniques for studying dynamic properties are added, allowing properties to be accessed in a larger dynamic range,[34–39] larger range in pressure is reached,[40,41] and higher precision is achieved.[9,42,43] As these developments come along, they move from being unique, specialized techniques used by mainly one or a few groups, to being commercially available (e.g., high-frequency dielectric spectroscopy and AC calorimetry), which means that larger sets of samples are studied. It is the accumulated progress of numerous small developments, which has lead to the picture we have today—where liquid dynamics has been measured in a dynamical range spanning up to 18 orders of magnitude, in

large part of the pressure–temperature phase diagram and with a variety of different techniques.

C. Structure of the paper

The simplest models for molecular motion would lead to an exponential relaxation function. However, the relaxation found in glass formers is highly stretched and covers several decades in time scale. An exponential curve is included in Fig. 2 to illustrate the difference. A main question regarding liquid dynamics is **why is the structural relaxation nonexponential?**[1,44]

As it is also seen in Fig. 2 and mentioned above, the structural relaxation time increases rapidly with decreasing temperature. This would also be expected from an Arrhenius model, which is often observed for chemical reactions. However, the structural relaxation time of most liquids increases much faster with decreasing temperature than one would expect from an Arrhenius model. The second main question can be phrased, **Why is the temperature dependence of the relaxation time non-Arrhenius?**[1,44]

This perspective is structured around these two main questions. We do *not* attempt to answer the questions, but to go into what is experimentally established regarding the spectral shape and the temperature dependence of the alpha relaxation.

In Sec. II, we focus on the spectral shape of the relaxation, how can it be characterized and how it depends on temperature and density. In Sec. III, we focus on the relaxation time scale, how it depends on temperature and density, as well as the differences observed depending on the experimental observable. Finally, we summarize what we believe to be the characteristic simple features of viscous liquid dynamics that a theory should encompass.

II. SPECTRAL SHAPES

Viscous liquid dynamics can be probed in many different ways. The example above was the thermal expansion, but many coefficients that we usually consider a (possibly temperature dependent) scalar, such as mechanical moduli, heat capacity, and dielectric constant, become time dependent with a long-time liquid-like behavior and a short-time solid-like behavior. Experimentally it is often easier to probe these properties as a function of frequency rather than time, but the two domains are equivalent and linked through the Fourier–Laplace transform. The frequency-dependent functions thus are complex with a real part and an imaginary part. Figure 3 shows time-domain relaxation functions and the equivalent imaginary part of their Laplace transforms.

Figures 4(a) and 4(b) of real and imaginary parts of the dielectric spectra of glycerol over an extremely broad range of frequencies and temperatures clearly illustrate the high- and low-frequency plateaus in the real part. The dominant (alpha) peak in the imaginary part moves many decades from 10 GHz at the highest temperature to 100 μHz at the lowest temperature. At around 1 THz, a temperature-independent peak emerges as the alpha peak moves away. This peak has been identified with the so-called boson peak[45] which is connected
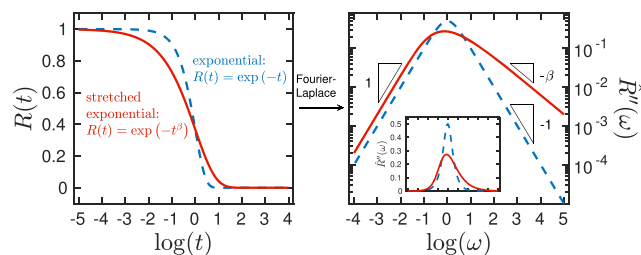

FIG. 3. Illustration of a stretched exponential compared with an exponential relaxation curve. The left figure shows the time domain. The right figure shows the imaginary part of its Fourier–Laplace transform, corresponding to a relaxation spectrum measured in the frequency domain; the main figure is a log–log plot whereas the inset is a log–lin plot.

to vibrations (e.g., Ref. 46 and references herein). As the alpha relaxation separates out from the temperature-independent fast relaxation and vibration, additional, less intense,
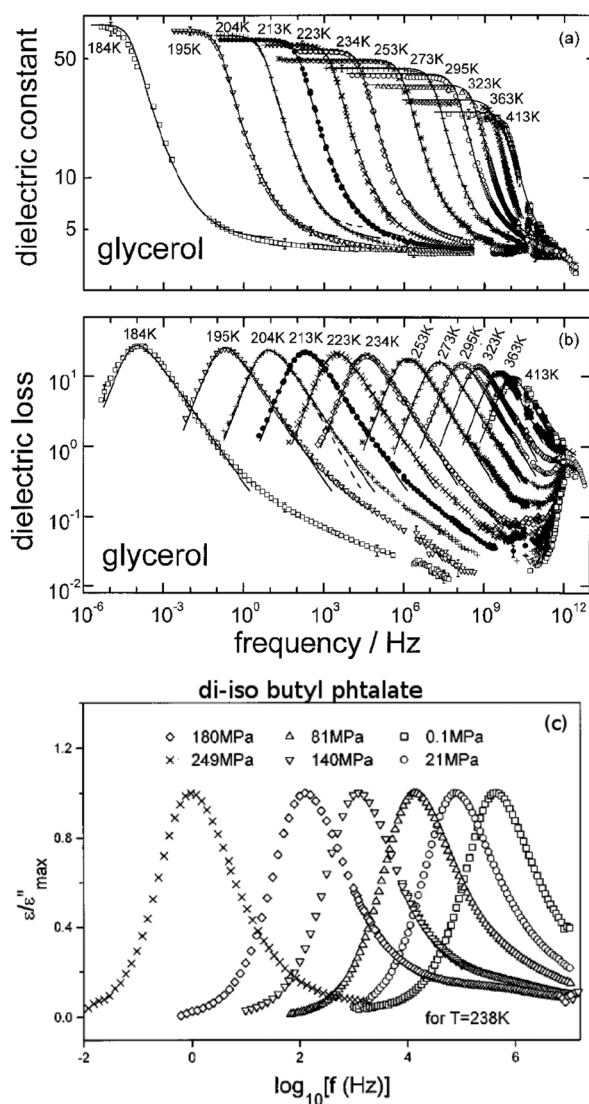

FIG. 4. Broadband spectra of dynamics in glass formers at different temperatures. [(a) and (b)] Real and imaginary part of dielectric spectra of glycerol at different temperatures under isobaric conditions (from Ref. 47). Reprinted with permission from P. Lunkenheimer and A. Loidl, Chem. Phys. **284**, 205 (2002). Copyright 2002 Elsevier. (c) Imaginary part of the dielectric constant of di-isobutyl phthalate at different pressures along an isotherm (from Ref. 49). Reprinted with permission from Paluch *et al.*, Phys. Rev. E **54**, 4008 (1996). Copyright 1996 American Physical Society.

features appear in the spectrum.[34,47,48] We will refer to these as secondary relaxations.

A similar phenomenology is seen when varying pressure instead of temperature. Figure 4(c) shows dielectric spectra for di-isobutyl phthalate at a range of pressures for single temperature. As pressure is increased from ambient pressure to 249 MPa, the alpha peak shifts six decades down in frequency and a secondary peak emerges.

A. Alpha relaxation

Focusing on the alpha peak in Fig. 4, a characteristic asymmetric shape emerges with a high-frequency power law of $\varepsilon'' \propto \omega^{-a}$, where $0 < a < 1$, whereas the low-frequency part usually follows $\varepsilon'' \propto \omega$. This is the signature of the "stretched" behavior observed in the time domain: instead of a sharp Lorentzian monodisperse peak, the peak spreads over many decades in frequency as also schematically illustrated in Fig. 3. The characteristic asymmetric alpha relaxation peak may be fitted by a number of empirical equations which all quantify the deviation from exponential behavior in terms of limiting high- and low-frequency power-law behaviors. The common knowledge dictates a broadening of the alpha peak (a decreasing) on cooling, which is documented in several studies, e.g., Refs. 48 and 50. However, there are numerous examples of liquids with a temperature-independent stretching both at low temperatures close to T_g [e.g., TPP,[51] tetramethyl tetraphenyl trisiloxane (DC704) and 5PPE,[52] 4-methyl-tetrahydrofuran and cumene,[53] 4-methyl-heptane,[54] and dicyclohexyl-methyl-2-methylsuccinate (DCMMS)[55]] and in the high-temperature limit,[56] and sometimes even a narrowing (a increasing) with decreasing temperature, e.g., in sucrose benzoate,[57] DHIQ,[52,58] and sorbitol.[53] A comprehensive collection and characterization of shapes of dielectric spectra can be found in Ref. 53.

Dielectric spectroscopy (DS) data are by far the most abundant data in the viscous liquid and glass community, because the technique is easily applicable and extremely versatile. Thus many observations and insights on liquid dynamics are obtained through dielectric spectra, and theories and models are primarily tested on dielectric data.

More direct measurements of the flow properties of liquids, such as complex mechanical moduli, display characteristics similar to the dielectric response. In Fig. 5, the broadband spectrum of the longitudinal modulus for the silicone oil DC704 reveals an analogous behavior to that observed in Fig. 4. Although the alpha peak displayed in other response functions is asymmetric, the overall shape of the relaxation may differ between different response functions.[52,59–64] Figure 6 shows a direct comparison of the (normalized) dielectric loss peak and the (normalized) shear mechanical loss peak, which clearly demonstrates that the dielectric alpha peak is much more narrow than the mechanical counterpart in the case of glycerol. Perhaps, this is no surprise because the figure compares a susceptibility to a modulus function, but it shows that conclusions on the spectral shape can depend on which response function is considered. Interestingly, the same figure shows that dielectric and mechanical alpha shapes are indistinguishable for DC704, which was also shown to be the
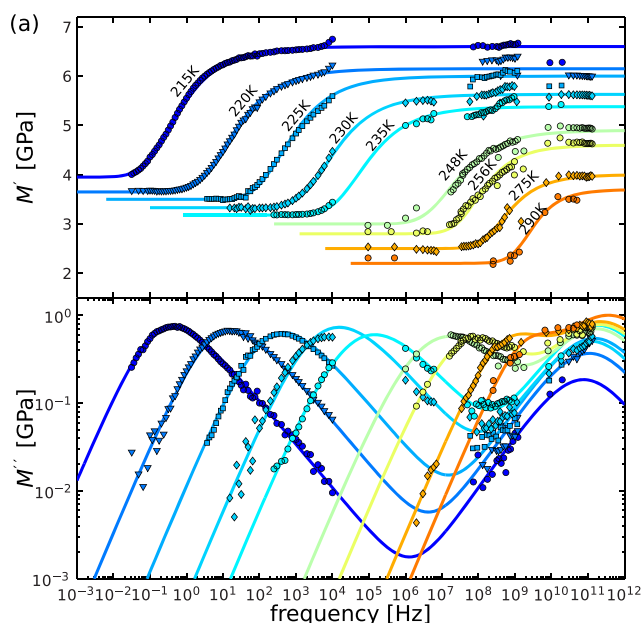

FIG. 5. Broadband mechanical spectra. [(a) and (b)] Real and imaginary part of the frequency-dependent longitudinal modulus of tetramethyl tetraphenyl trisiloxane (DC704) from Ref. 39. Reproduced with permission from Hecksher *et al.*, Proc. Natl. Acad. Sci. U. S. A. **114**, 8710 (2017). Copyright 2017 PNAS.

case for shear and bulk modulus alpha loss peaks of the same substance.[38]

So, it appears that some liquids have the simple behavior that the relaxation shape is unchanged with experimental probe [e.g., DC704 and 5PPE,[38] dibutyl-phtalate (DBP) and DC705[64]] whereas for others show a more complex scenario with probe-dependent relaxation spectra (e.g., glycerol,[59,65] m-toluidine,[60] and 1,2-propanediol[64]).

B. Secondary relaxation(s)

Secondary relaxations are the less intense and less temperature-dependent processes that appear in the spectrum as the alpha relaxation peak moves down in frequency on lowering the temperature or increasing pressure as shown in Figs. 4 and 5. The faster relaxation is often referred to as the beta relaxation.
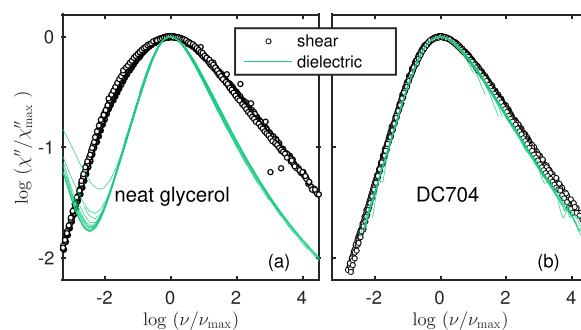

FIG. 6. Comparing dielectric and shear mechanical spectral shapes of glycerol and tetramethyl tetraphenyl trisiloxane (DC704) from Ref. 65. Spectra from several temperatures are superimposed by scaling to the peak. The dielectric and shear mechanical spectra are very different in glycerol, whereas they are barely distinguishable in the case of DC704. Reproduced with permission from Jensen *et al.*, Phys. Chem. Chem. Phys. **20**, 1716 (2018). Copyright 2018 Royal Society of Chemistry.

In most liquids, there are one or more distinct peaks between the alpha and the boson peak, when the alpha relaxation is well separated from the boson peak, e.g., sorbitol[66] and diisobutyl phthalate.[49,67] In some liquids, there is only a wing on the high-frequency flank of the alpha relaxation (see, e.g., glycerol in Fig. 4), and it was earlier suggested to classify liquids according to whether they exhibit a secondary peak or just a wing.[68] The secondary relaxations usually become more resolved as temperature is decreased (or pressure increased) because their characteristic time scale is less sensitive to thermodynamic parameters than the alpha relaxation, and the excess wing has in some cases been shown to develop into an actual peak as it is separated from the alpha relaxation.[47,69] These results suggest that there is no intrinsic difference between the secondary relaxation and the excess wing. On the other hand, there are also reports that the excess wing and the secondary relaxation are two distinct processes, and it has been suggested that both are present in all glass formers though with different relative amplitudes.[70] Yet some liquids seem to be devoid of any secondary features, at least within the experimental resolution, as in the case of the silicone oil DC704 (see Fig. 5).

Secondary relaxations have mainly been studied by dielectric spectroscopy, but it can also be seen in mechanical spectra if measured at high enough frequency. Figure 7 shows real and imaginary part of the shear modulus of a low molecular weight polyisobutylene (PIB680) from mHz to kHz, where a clear secondary peak around 100 Hz emerges as the temperature is lowered. For liquids studied by both DS and mechanical spectroscopy, it turns out that if secondary relaxation is present in DS, there is a secondary relaxation in the mechanics as well. Usually, the secondary process is more pronounced in the mechanics, i.e., the relative intensity between secondary and alpha relaxation in the mechanics is higher.[71] The secondary relaxation was believed to be invisible to photon correlation spectroscopy (PCS) techniques,[72] although this technique is sensitive to dipole rotation, but it was recently shown that in at least one case the alpha and a secondary relaxation were both clearly resolved in PCS spectrum.[73]

In some systems, especially polymers, secondary relaxations can be identified as various intramolecular modes. But there are also claims of an omnipresent secondary relaxation in rigid systems, and this process is referred to as the "genuine" beta relaxation or the Johari–Goldstein (JG) beta process.[74] In practice, it is very difficult to distinguish between the different types of secondary relaxations, and secondary relaxations can be due to system-specific reasons even in the case of apparently rigid molecules. For example, a decoupling between in-plane and out-of-plane rotation is reported to give rise to the secondary relaxation in 5H-5-methyl-6,7-dihydrocyclopentapyrazine (MDCP).[75]

All in all, it is hard to pin down the intrinsic features of the phenomenology of secondary relaxations. A genuine JG has been reported in molecular dynamics simulations in several works (see, e.g., Ref. 76), albeit not for a single component, "neat" system. Experimentally, however, there is no clear-cut, model-free way to distinguish between different secondary features in a spectrum. Thus, it remains an open question whether a JG beta relaxation is a crucial part of the phenomenology of glass-forming liquids. For the majority of liquids, secondary relaxations are two to three orders of magnitude weaker in relaxation strength than the alpha relaxation; for some, there are even no visible secondary features. This means that the beta in general accounts for a minor part of the total relaxation of the liquid.

C. Isochronal superposition

Since both temperature and pressure can be used to tune the position of the loss peak on the frequency axis, it is possible to find different state points (pairs of temperature and pressure) that have the same relaxation time. State points with the same relaxation time map out a line in the phase diagram termed *isochrones*. This is schematically illustrated in the phase diagram in Fig. 8. Isobars in this diagram would be horizontal lines, whereas isotherms [e.g., the spectra in Fig. 4(c)] would be vertical lines. The red lines marks logarithmically equidistant isochrones, and with a pragmatic definition of T_g as the temperature where the relaxation time reaches 100 s, the glass transition line is itself an isochrone. The blue lines are isochores, illustrating that even at constant density there is a glass transition.
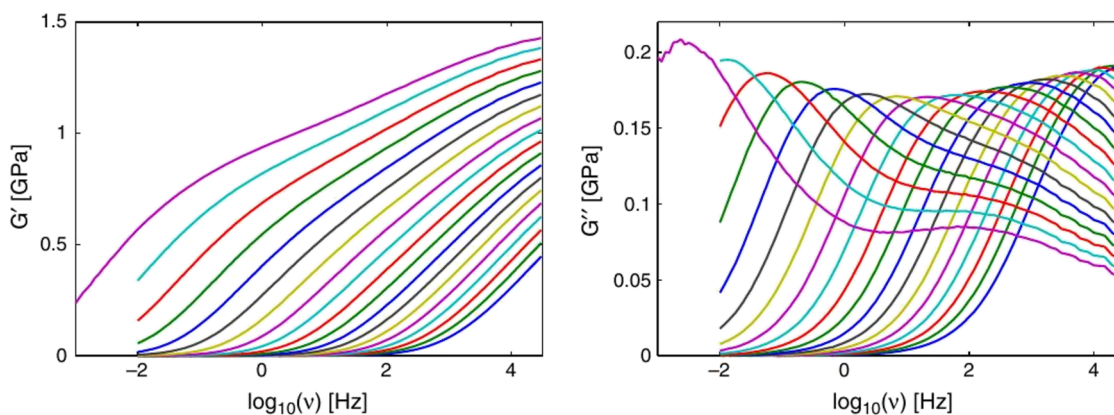

FIG. 7. Shear modulus of a low molecular weight polyisobutylene (PIB680) showing the emergence of a beta relaxation peak in the spectrum as the temperature is lowered and the alpha relaxation moves to lower frequency (from Ref. 71). Reprinted with permission from Jakobsen *et al*, J. Non-Cryst. Solids **357**, 267–273 (2011). Copyright 2011 Elsevier.
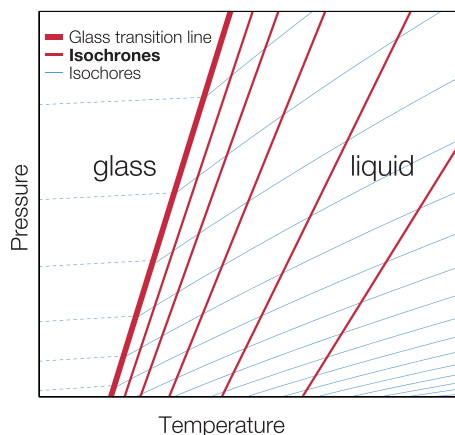
FIG. 8. Schematic illustration of the phase diagram of glass-forming liquids. The isochrones are lines along which the alpha relaxation time is constant. The glass transition as observed by a given cooling rate is also an isochrone.

It is in many cases found that the shape of the relaxation spectrum is invariant along an isochrone. This means that when the relaxation time coincides for two different state points, the entire spectrum is identical within experimental uncertainty. This striking experimental observation is referred to as isochronal superposition (IS). Figure 9 illustrates the principle for a number of different systems. In 1998, Tölle *et al.* first observed IS for ortho-terphenyl (oTP) by quasielastic neutron scattering,[77] and the phenomenon was further investigated for a range of samples by Roland *et al.*[28] and Ngai *et al.*[78] using dielectric spectroscopy [Fig. 9(a)]. By today IS is well established as a phenomenological fact when it comes to the alpha relaxation of van der Waals-bonded liquids (e.g., Refs. 28–31 and 78–81). IS can be rationalized in terms of isomorph theory,[32,82] which is expected to hold for van der Waals-bonded liquids, but not for hydrogen-bonded liquids. Consistent with this, IS has been seen to break down for the alpha relaxation of glycerol under pressures in the GPa range [see first plot
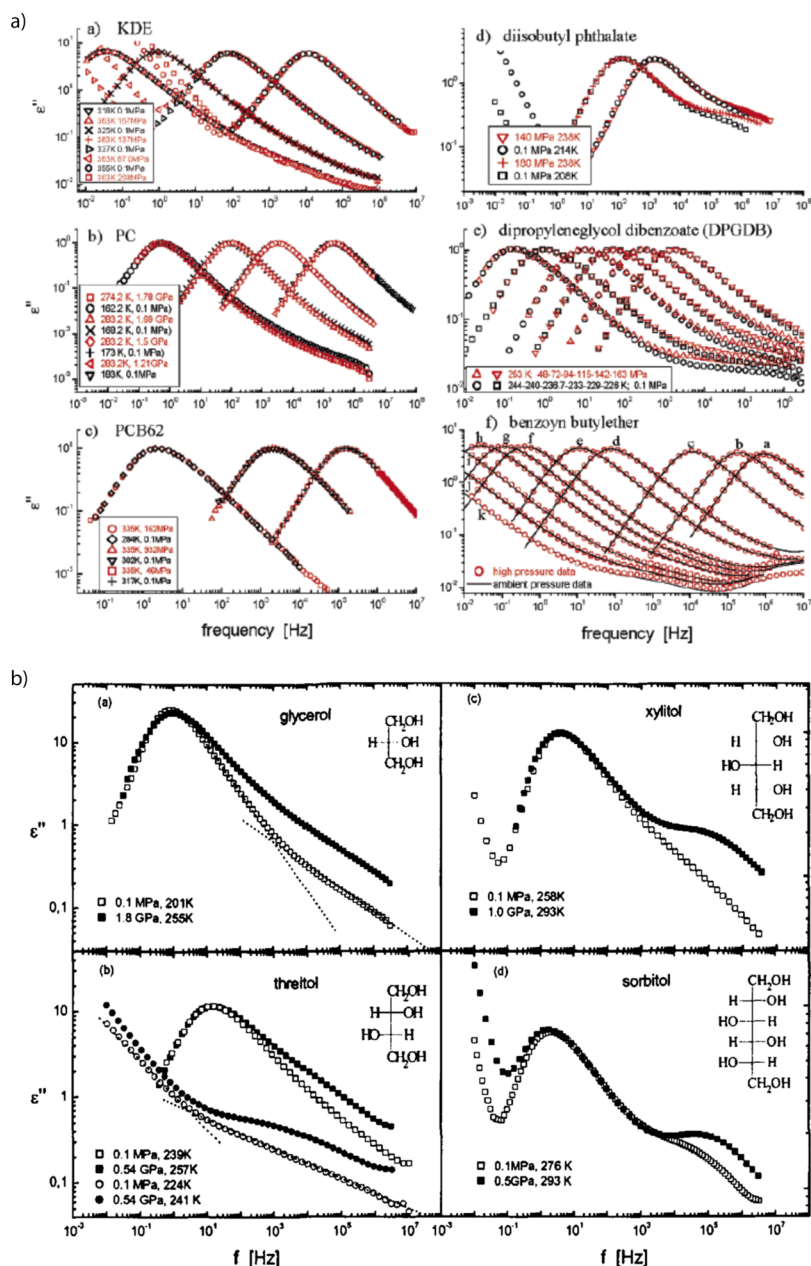

FIG. 9. Isochronal superposition. (a) Data from six different liquids at different temperature and pressures.[78] The black curves are ambient pressure data, whereas the red curves are measured at elevated pressures in the 100 MPa range. It is seen that the spectral shapes of low- and high-pressure data are identical when the relaxation time is the same, which is a demonstration of isochronal superposition (IS). Reprinted with permission from Ngai *et al.*, J. Phys. Chem. B **109**, 17356 (2005). Copyright 2005 American Chemical Society. (b) Data from four polyalcohols (glycerol, threitol, xylitol, and sorbitol) showing clearly that IS is not obeyed in these liquids.[29] Reprinted with permission from Hensel-Bielowka *et al.*, Phys. Rev. E **69**, 050501(R), 2004. Copyright 2004 American Physical Society.

in Fig. 9(b)].[83] A quantitative comparison of IS in hydrogen-bonded liquids and van der Waals liquids[81] also showed that IS worked better for the studied van der Waals liquids than the hydrogen-bonded liquids. However, in general, IS works well for the alpha relaxation also of hydrogen-bonded liquids.[29–31] The difference between the two classes of liquids is mainly seen when considering secondary relaxations and excess wings, where IS breaks down for hydrogen-bonded liquids but works to a higher degree for van der Waals liquids, compare Figs. 9(a) and 9(b).[28–31] In fact, IS has been demonstrated to collapse short- and long-time dynamics separated by more than 14 orders of magnitude for two van der Waals liquids.[33]

D. Time–temperature superposition

For some liquids, the shape of the alpha relaxation does not change with temperature, the spectrum simply shift in frequency. The principle is called time–temperature superposition (TTS). TTS was originally introduced in the field of polymer rheology (where it is referred to as thermorheological simplicity) as an assumption used to build master curves from a narrow experimental frequency window.[84–87] However, with the development of broadband techniques, notably, dielectric spectroscopy and shear mechanical spectroscopy, it has been possible to demonstrate that a range of systems obeys TTS to a very high degree, e.g., dielectric oTP data[88] [shown in Fig. 10(a)] and shear mechanical DC704 data[38] [shown in Fig. 10(b)]. Broadband techniques have also revealed that ironically TTS is not, in general, obeyed in polymers.[89,90]

TTS is a much older concept than IS, yet TTS is in fact a stronger result, in the sense that it requires a higher level of simplicity than IS. TTS appears to be valid for a subset of the liquids that obey IS. Whereas IS refers to the dynamics in the situation where the alpha relaxation has the same time scale, TTS describes a situation where the times scale changes by many orders of magnitude, yet the spectral shape shows no sign of changes. If both TTS and IS are obeyed, it follows that the spectral shape of the alpha relaxation is in fact invariant in the entire phase diagram. This simple relaxation behavior is sometimes referred to as time–temperature–pressure superposition (TTPS). It not a universal behavior; in fact, it is only reported so far in a few systems (salol,[91] DGEBA,[92] and DC704[80]).

TTS is never obeyed at very high temperatures (low viscosity) where the alpha relaxation is merged with the vibrations, secondary relaxation, and boson peak. At lower temperatures, it is only possible to observe TTS directly in the data if no additional relaxations can be observed in the spectrum. As mentioned, secondary relaxations typically have much weaker temperature dependence than the alpha relaxation, and the gradual separation of the two processes on cooling leads to break down of TTS in the measured data. Likewise, an additional slow mode because of macromolecular or supramolecular dynamics will also lead to break down of TTS in the measured alpha relaxation.[65] It is however often possible to fit the relaxation data of spectra with several spectral contributions using functions for the full spectrum in which the shape of the alpha relaxation is kept fixed.[39,71,93,94] This could indicate that TTS of the alpha relaxation is a more general behavior than what can be observed directly in the raw data.

E. Time–aging time superposition

So far, we have only addressed equilibrium properties and linear response measurements. But as the liquid is cooled and the relaxation time becomes longer and longer, it also gets
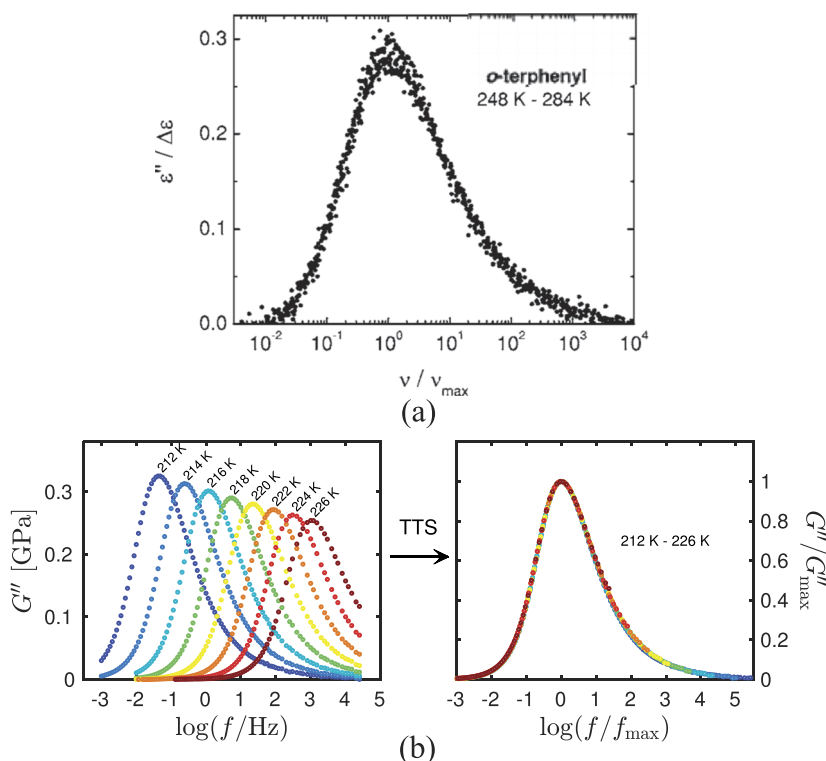

FIG. 10. Time–temperature superposition. (a) Imaginary part of dielectric from oTP in the temperature range 248 K to 284 K. The data are scaled to the dielectric relaxation strength and the peak maximum. The collapse of the data demonstrates TTS to a high degree. From Ref. 88. Reproduced with permission from R. Richert, J. Chem. Phys. **123**, 154502 (2005). Copyright 2005 AIP Publishing LLC. (b) Imaginary part of shear mechanical modulus of DC704 in a temperature range from 212 K to 226 K scaled with the peak maximum and peak position. The collapse of the data shows that the data obey TTS to a very high degree. Data from Ref. 38.

experimentally possible to monitor the liquid's properties as it equilibrates. These physical aging measurements give access to off-equilibrium dynamics.

There are two different traditions for doing aging measurements; one approach is to define various temperature ramp protocols usually involving temperatures both far above and below T_g. In this approach, it is the hysteresis effects close to T_g, which is the object of study, e.g., in Refs. 95 and 96. The other approach is closer to the linear response measurements discussed above. Here, the liquid's properties are monitored isothermally during equilibration, and with this approach, one obtains relaxation curves that resemble the linear response in the time domain as seen in Fig. 2. However, during aging, the relaxation rate of the liquid is changing over time eventually reaching the equilibrium relaxation rate of the aging temperature, $1/\tau(T_{aging})$, leading to self-retardation for temperature down jumps—the relaxation rate becomes slower and slower as the structure is changing during aging—and self-acceleration for up jumps.[97,98] Consequently, a temperature down-jump and temperature up-jump of the same magnitude to the same temperature has very different shapes. This is a clear sign of nonlinearity and is known as "asymmetry of approach," see Fig. 11.

Isothermal aging of liquid's properties may be monitored by any favorite technique or quantity, e.g., refractive index,[99,100] volume/density,[98,101] mechanical moduli,[102] dielectric constant,[42,103,104] or x-ray photon correlation spectroscopy.[105]

Isothermal aging is always probed at a high frequency or short acquisition time compared with the structural relaxation time, because significant structural changes would occur during the measurement if acquisition time is long. Sometimes a short time or frequency interval is measured as a function of aging time, i.e., the onset of a full spectrum in the chosen observable. Surprisingly, these snapshots of a spectrum in many cases have the same shape.

The principle is illustrated in Fig. 12 in the case of a polycarbonate,[106] where a step deformation of the sample is
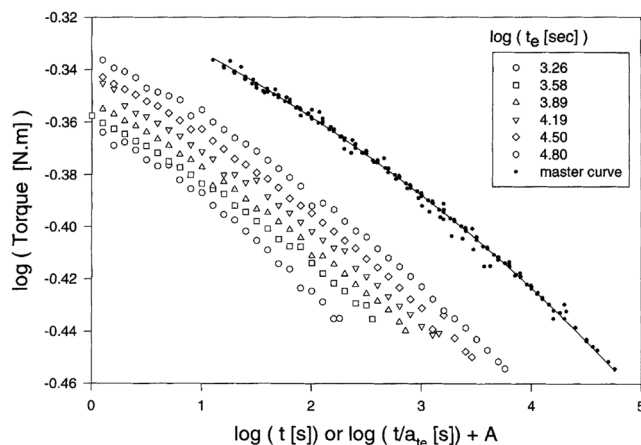

FIG. 12. Example showing time–aging time superposition. Open symbols show torque relaxation as a function of time after a deformation at different aging times. Closed symbols show the same data plotted as a function of material time as defined in Eq. (1). From Ref. 106. Reproduced with permission from P. A. O'Connell and G. B. McKenna, Polym. Eng. Sci. **37**, 1485 (1997). Copyright 1997 John Wiley and Sons.

applied for a short time at different aging times and the torque relaxation is measured subsequently. Clearly, these short-time response curves can be superposed by shifting the curves. This tells us that the shape of the linear response spectrum measured out of equilibrium is identical to the equilibrium spectral shape, and the spectrum simply shifts on the time or frequency axis as the liquid slowly comes into equilibrium. This remarkable experimental fact is a demonstration of time–aging time superposition (TAS). Assuming TAS holds, the obtained shift factors in this procedure may be interpreted as (proportional to) the "instantaneous relaxation rate" $(1/\tau(t))$.

The concept of a structure-dependent relaxation rate was introduced already by Tool,[107,108] who quantified it in terms of a fictive temperature, T_f. The idea was refined and extended to nonexponential relaxation by Narayanaswamy,[109] who proposed a linearization of aging experiments through the material time. The material time is found by counting the
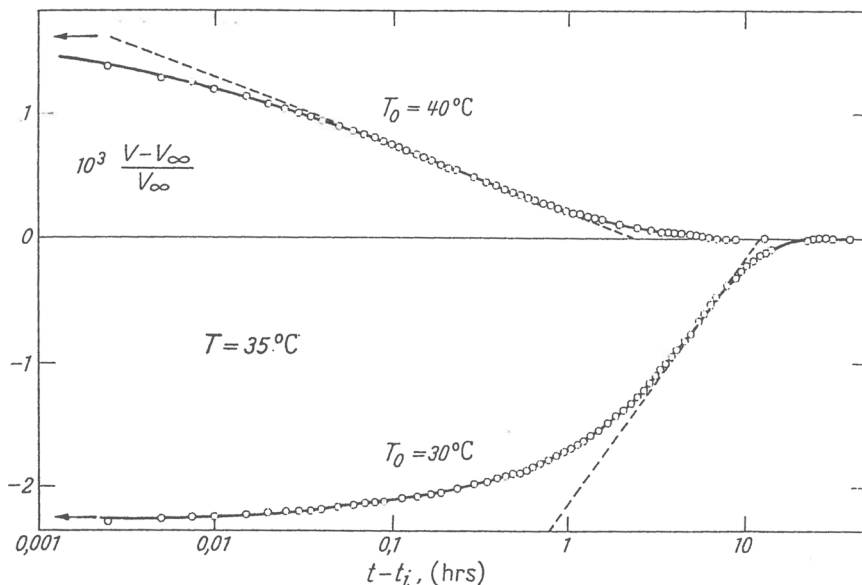

FIG. 11. Asymmetry of approach. Temperature up-jump and down-jump of the same magnitude to the same temperature has very different shape, clearly demonstrating the nonlinearity of the experiment. From Ref. 97. Reprinted with permission from A. J. Kovacs, Adv. Polym. Sci. **3**, 394 (1963). Copyright Springer 1964.

"ticks" of the internal clock, i.e., integrating the instantaneous relaxation rate

$$\tilde{t} = \int_{-\infty}^{t} \frac{dt'}{\tau(t')}, \tag{1}$$

where $\tilde{t}$ is the material time. In Narayanaswamy's seminal paper, TAS is merely a necessary assumption that nevertheless leads to a surprisingly efficient description not only of isothermal aging experiments, but any temperature protocol including temperature ramps and several subsequent temperature jumps.

Temperature-jump aging studies (as the example shown in Fig. 12) however seem to—in many cases—confirm that the internal clock and TAS is valid, e.g., in Refs. 42, 43, and 110. TAS implies TTS, but TAS does not follow from TTS; other scenarios for the off-equilibrium time evolution of the spectral shape are compatible with TTS, see, e.g., Ref. 111.

So far there is not really any classification as to which types of liquids that comply with TAS. Tool–Narayanaswamy formalism has been used for many classes of liquids, but a direct demonstration of TAS has only been given for some molecular liquids (e.g., Ref. 42) and polymers (e.g., Ref. 106).

III. TIME SCALES

The non-Arrhenius temperature dependence of the relaxation time is often illustrated by an Angell plot, which shows the logarithm of the relaxation time (or viscosity) as a function of the inverse temperature normalized with the glass transition temperature, T_g. An example is shown in Fig. 13. This classical figure shows viscosities but the same behavior is seen for relaxation times because the two are roughly proportional. In an Angell plot, Arrhenius behavior

FIG. 13. Angell plot. Viscosity (which is roughly proportional to relaxation time) as a function of T/T_g for different glass-forming liquids. A large curvature in this plot corresponds to a large value of the fragility index m. Reprinted from C. A. Angell, "Strong and fragile liquids," in *Relaxations in Complex Systems* (U.S. GPO, Washington, 1985), pp. 3–11.

gives a straight line. However, most liquids trace out a distinctly convex curve. All curves meet more or less in two points: by definition at the glass transition temperature ($T_g/T = 1$) and the high-temperature limit ($T_g/T \rightarrow 0$), which is essentially the molecular/microscopic vibration time ($\tau \sim 10^{-13}$–10^{-14} s).

Inspired by the Angell plot, the deviation from Arrhenius behavior can be quantified by the Angell fragility index, which is defined as the derivative of the curve in this plot evaluated at T_g, $m = d \log \tau / d(T_g/T)|_{T=T_g}$ [112] and essentially quantifies the steepness of the curve at T_g.

The fragility index takes the value of approximately 16 for an Arrhenius liquid, inorganic glasses have low fragility indices in the range of 20s, and for organic glass formers, it is often around 80, whereas it can exceed 100 for polymers.

A. Functional form of the temperature dependence

Characterizing the temperature dependence of the relaxation time with just one parameter, the fragility index, implicitly relies on the assumption that there is a universal functional form that can describe the curve shape in the Angell plot with just one parameter. The Vogel-Fulscher-Tammann (VFT) function is the most commonly used to fit data,[114–116]

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

However, there is no agreed-upon function to describe data because none of the existing functions perform well on all systems, even if an additional parameter is introduced.[117–119]

One of the main controversies in the field is the question of whether the relaxation time diverges at finite temperature as suggested by the VFT function. Ten years ago, one of us showed that a detailed analysis of the temperature dependence of the relaxation time in equilibrium does show no evidence for a diverging time scale.[117,120] Many alternatives to the VFT function with no divergence has been suggested[20,118,119,121] and more recent phenomenological studies suggest a limit in the activation energy, thus implying no divergence in time scale at finite temperatures.[122] On the other hand, there is also no solid evidence that there is no divergence.

To address this question, attempts have been made to go below T_g and reach longer relaxation times. One approach is through aging measurements.[101,123,124] In these studies, the VFT extrapolation from above T_g generally overestimates the actual measured relaxation times. The aging approach for reaching longer relaxation times cannot take us very far down in temperature because of its dramatic temperature dependence. Important progress in equilibrating glasses far below T_g has been made by the development on ultrastable (vapor-deposited) glasses,[125,126] and these glasses have been used to estimate relaxation times far below the conventional T_g.[127] The use of 20 million-year-old amber[128,129] is an example of another strategy to estimate longer relaxation times than those that can be measured directly. In these types of studies, it is necessary to infer extra assumptions to extract relaxation times. The analysis in Ref. 127, for example, relies on the suggested connection between nonergodicity factor and fragility.[18] Yet, within these assumptions, there is no clear support of
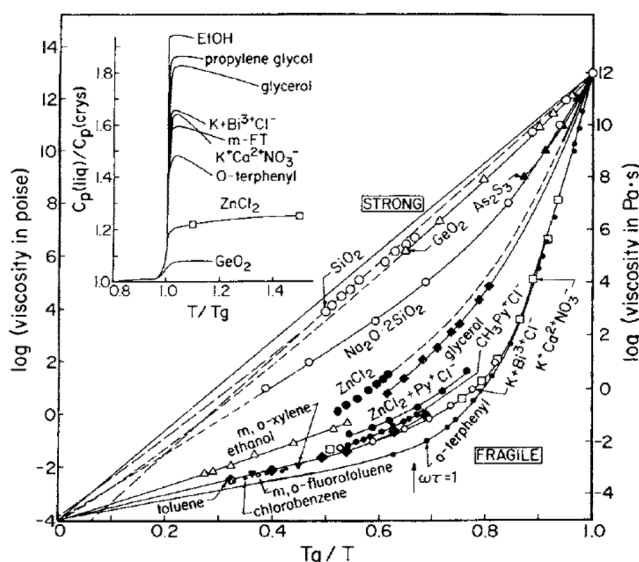
diverging time scale at finite temperatures.[127,129] The question thus remains unanswered, and it is in fact very hard, if not impossible, to tackle by experiments, because it involves measuring time scales that grossly exceed the time scale we live on.

B. Pressure dependence and density scaling

The fragility index, m, is originally taken at constant pressure, because this is where the data was obtained, and to be precise, it is sometimes referred to as the isobaric fragility. On cooling at constant pressure, the relaxation time is affected both by the decreasing available volume and the decreasing thermal energy. The isobaric fragility does not separate these two effects. To do so, the structural relaxation has to be mapped out in the two-dimensional phase diagram. Based on high-pressure data, a number of different indices have been suggested to quantify the relative effect of temperature and density on the relaxation time.[130–135] The essence is that two independent numbers replace the single well-known fragility parameter to account for the two dimensionality of the phase diagram. A pragmatic choice is to stick to the original isobaric fragility parameter $m_p = d \log \tau / d (T_g/T)|_{T=T_g}^p$ and add an isochoric fragility parameter $m_\rho = d \log \tau / d (T_g/T)|_{T=T_g}^\rho$. Isochoric measurements are not easy to realize, but the m_ρ is well defined and can be found from high-pressure dynamic data along with an equation of state.[131,133–135] In computer simulations, it is natural to work with isochoric conditions, and fragilities reported in simulations were originally isochoric by default (e.g., Ref. 136).

If changes in density play a minor role compared with the effect of temperature, then there is little difference between isobaric and isochoric cooling. This is typically the case for hydrogen bonding systems, which have values of m_p/m_ρ that are close to 1, e.g., glycerol has $m_p/m_\rho \simeq$ 1.1.[137] The effect of density is often more significant in van der Waals-bonded liquids; oTP, which is another classical glass-forming liquid, has $m_p/m_\rho \simeq 1.8$[137] whereas 1,1-bis(p-methoxyphenyl)cyclohexane (BMPC) has as high a value as $m_p/m_\rho \simeq 2.7$.[138] This high value of the m_p/m_ρ ratio shows that density is the dominant factor in the slowing down of the alpha relaxation.

An important finding from high-pressure studies is density scaling. Density scaling (or thermodynamic scaling) refers to the fact that the relaxation time is a function of a single scaling variable $\Gamma = \Gamma(\rho, T)$ rather than being an independent function of temperature and density.[134,137,138] The functional form of $\Gamma(\rho, T)$ is fitted well with density to some power γ over temperature $\Gamma(\rho, T) = \rho^\gamma/T$[134,139] for experimental data in a large range. Figure 14 shows an example of density scaling in phenylphthalein-dimethylether. Density scaling is found to work for van der Waals-bonded liquids with the exponent γ taking values in the range 3–8 both for the alpha relaxation and viscosity,[134,140] and to our knowledge, there are no examples of breakdown of density scaling for the alpha relaxation of van der Waals-bonded liquids. In recent studies, power-law density scaling was shown to work for the alpha relaxation over an impressive range, both at pressures far up in the GPa range[40] as well as over an extended
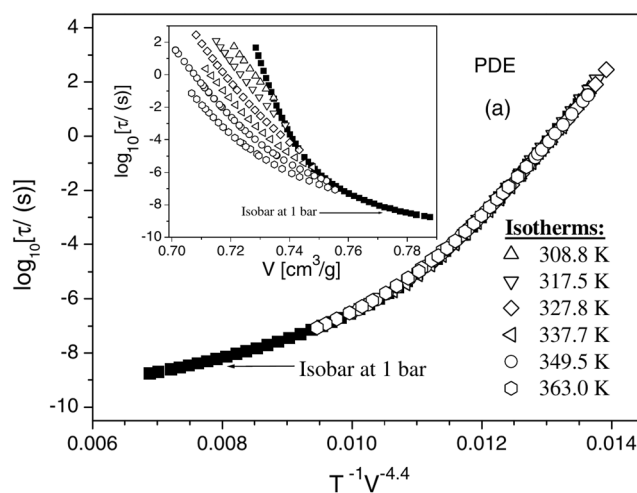

FIG. 14. Density scaling. The figure shows collapse of the structural relaxation times of phenylphthalein–dimethylether as a function of the scaling variable $\Gamma = \rho^{4.4}/T$. The inset shows the relaxation time at different isoterms as a function of volume. From Ref. 147. Reproduced with permission from M. Paluch, K. Grzybowska, and A. Grzybowski, J. Phys.: Condens. Matter **19**, 205117 (2007). Copyright 2007 IOP Publishing.

dynamical range from nanosecond to second[141] for the small molecular van der Waals-bonded glass-former cumene. Density scaling has also been found to work for some hydrogen-bonding liquids[31,134,141] and ionic liquids,[140,142] whereas for other hydrogen-bonded liquids, it breaks down, e.g., for propyleneglycols.[143] When density scaling works in hydrogen-bonding liquids, it is always with low values of the scaling exponent γ; sorbitol is an extreme case reported to have $\gamma = 0.13$.[138] Low values of γ mean that density has very little influence on the alpha relaxation time and lead to low values of the m_p/m_ρ ratio,[134,135,144] which as mentioned above are common for hydrogen-bonding systems. Density scaling can be explained in terms of repulsive power-law potentials on a microscopic scale,[77,138,145] and by isomorph theory,[32,146] however, these explanations are not expected to work for hydrogen-bonded systems. The quite different phenomenology of the hydrogen-bonded systems, in terms of low values of γ and m_ρ/m_p, also suggests that the underlying reason for density scaling could be different for these liquids, as it was already discussed in the 2005 review on pressure effects on glass formation by Roland et al.[134]

C. Time-scale decoupling

So far we have discussed the temperature and density dependence of the alpha relaxation time as if it was uniquely determined for a given system. However, the value of the alpha relaxation time found at the same temperature and pressure by different experimental techniques can differ by up to several decades. This also means that when using the dynamic definition of the glass transition temperature, $\tau(T_g) = 100$ s, the value of T_g will differ by some degrees depending on the experimental observable used to estimate it.

What about the temperature *evolution* of different dynamical probes? In some cases, also the temperature dependence of the dynamics differs depending on which property is monitored.

The classical example of this is translational-rotational decoupling which refers to the situation, where rotation slows down more dramatically on cooling than self diffusion,[148] when T_g is approached. Similarly, studies comparing DC conductivity and dielectric alpha relaxation time have demonstrated translational-rotational decoupling as a function of pressure.[149] Most works on translational-rotational decoupling involve the monitoring of some probe molecule from which the behavior of the host liquid is inferred, whereas only a few look directly at the liquid itself, e.g., Ref. 150. Here decoupling occurs at $T/T_g \approx 1.2$ and grows to about 2 decades at T_g, which is still modest when compared with an overall slowing down of the dynamics of 14–16 decades.

Time-scale decoupling should be understood broadly as a difference in the temperature dependence of the alpha relaxation time scales determined from different experimental observables, e.g., dielectric permittivity and dynamic thermal expansion. The degree of decoupling may be quantified through a *time-scale index* defined as the logarithm ratio of the alpha relaxation time of two different experimental observables at a given temperature. A constant time-scale index means that the index is temperature independent, i.e., there is *no decoupling* of the alpha relaxation time scales. The degree of decoupling depends on the sample studied and the type of different data that are compared.[52,151–153]

Differences in the relaxation time depending on technique are not surprising, and it does not change the fundamental questions of the non-Arrhenius and nonexponential behavior. However, if very different temperature dependencies of dynamic time scales found for the same liquid was the predominant behavior, the question of what governs the relaxation time would be somewhat ill posed; each observable would need its own set of parameters.

In the context of identifying the simplest behavior, it is important to stress that in some systems there is no detectable difference in the temperature dependence of the relaxation time found by different techniques all the way down to T_g. This has for example been seen by comparing DC conductivity and dielectric relaxation in salol, phenolphthalein-dimethyl-ether and propylene carbonate[151] and by comparing shear mechanical and dielectric relaxation times of *m*-toluidine.[152] The identical temperature dependence has been found to hold over more than six decades for the oils DC704 and 5PPE when comparing seven different time scales[154] as shown in Fig. 15. For 5PPE, the time scales of dielectric and calorimetric relaxation has been found to follow each other over almost ten decades[155] as well as at elevated pressure.[156] Similarly, it has been shown that viscosity and rotational relaxation time have the same temperature and pressure dependence in oTP, salol, and dibutyphthalate.[139]

Again it is not a universal behavior. Yet, it is clear that systems exist where the temperature and pressure dependence of the alpha relaxation time is uniquely given, independent on which dynamic property is monitored. The determination of the alpha relaxation time becomes nontrivial in the case where the alpha relaxation merges with other faster or slower relaxation processes. In addition, the determined temperature dependence of the relaxation time will depend on fitting procedure as soon as there is a deviation from TTS. It is
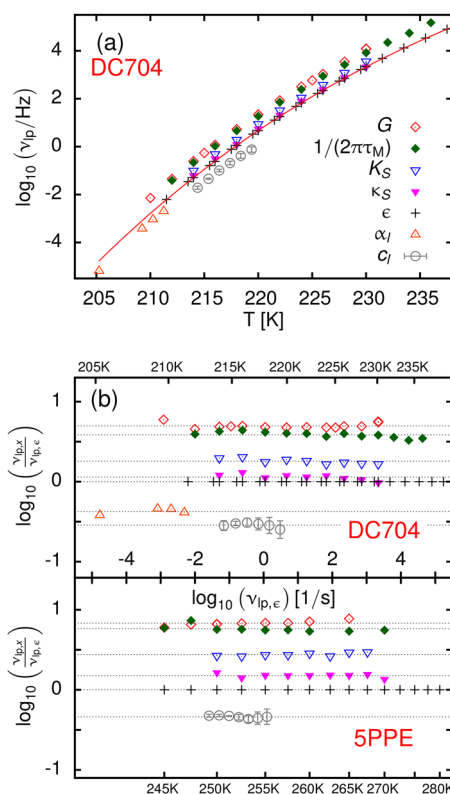

FIG. 15. Relaxation map and time-scale index of loss peak frequencies of five different response functions: complex dielectric constant ε, bulk modulus K (and derived compressibility $\kappa = 1/K$), shear modulus G (and derived Maxwell frequency, $1/2\pi\tau_M$), longitudinal specific heat c_l, and thermal expansion coefficient α_l. (a) The time scales of the functions are not identical, but proportional over 6–7 decades in frequency at temperatures close to the glass transition. Full line is an extrapolated fit to the dielectric data. (b) The time-scale index of the loss peak frequencies of these response functions with respect to the dielectric loss peak frequency, $\log(\nu/\nu_\varepsilon)$. From Ref. 154. Reproduced with permission from B. Jakobsen *et al.*, J. Chem. Phys. **136**, 081102 (2012). Copyright 2012 AIP Publishing LLC.

therefore possible that a temperature-dependent time scale index in some cases can be due to a poor determination of the alpha relaxation time. From Ref. 52, it is clear that decoupling seen in the times scales naively determined from loss peak maxima is larger in systems with larger beta relaxation. This observation leads to the speculation that no decoupling could be the underlying behavior of the alpha relaxation.

IV. SUMMARIZING THE SIMPLEST LINEAR PHENOMENOLOGY AND THE OPEN QUESTIONS

The now-more-than-20-years-old quote from Nobel Laureate Anderson, "The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of the glass and the glass transition," is still used frequently in talks and grant applications in the field of glass-forming liquids and glasses. Yet, the most striking thing is that not only does the problem remain unsolved, but we have no coherent consensus about what it would imply to solve the problem. There are decades of experimental work but no clear agreement on what the key phenomenology is. In this perspective, we have outlined a range of simple features found in the dynamics of some glass formers.

The structural alpha relaxation is merged with local vibrational dynamics at high temperatures and low densities, but the processes separate already when the structural relaxation time reaches the nanosecond time scale. On further cooling, the separation grows to more than 13 orders of magnitude until the alpha relaxation time scale reaches hours and surpasses the experimentally accessible window. Thirteen orders of magnitude is a tremendous range; it corresponds to the span between a second and a million years. Yet, for some liquids, the alpha relaxation changes remarkably little over this range and behaves in a surprisingly simple manner. We believe it is an important experimental task to characterize the relaxation in liquids in its simplest form. Based on the current knowledge as described in this perspective, we propose the simple relaxation scenario to be summarized in the following points:

1 Time–temperature–pressure superposition (TTPS): the spectral shape of the alpha relaxation is independent of temperature and pressure.
2 Probe independent relaxation function: the spectral shape is identical for (possibly a subset of) different response functions.
3 Constant time-scale index: the temperature and density dependence of the alpha relaxation time is the same for different response functions.
4 Density scaling: the alpha relaxation time depends only on a single scaling parameter $\Gamma(\rho, T)$, which in a large range is described by $\Gamma(\rho, T) = \rho^{\gamma}/T$.

Far from all liquids exhibit this simple behavior. Although the last point, density scaling, has been shown for a large set of samples, all four items have only been confirmed for DC704 and 5PPE. Other candidates include oTP and cumene that also show simple behavior, but for which, for instance, decoupling of different response functions has not been tested in detail. In the case of oTP, however, translational–rotational decoupling has been demonstrated,[150,157] which suggests that some degree of translational–rotational decoupling is present even in the case of the simplest relaxation scenario.

Although simple relaxation is not general, we believe that it is too remarkable to be a mere coincidence. Liquids complying with the simple relaxation scenario still exhibit the hallmark features of dynamics of glass-forming liquids: non-exponential alpha relaxation and non-Arrhenius temperature dependence of the relaxation time, thus cementing the origin of the two non's as the central questions that need to be answered to understand the dynamics of glass-forming liquids and the glass transition. The question of whether the nonexponential and the non-Arrhenius behaviors are connected as it has been suggested decades ago[17] still remains open. It is also possible that the simple relaxation scenario is connected to a specific alpha spectral shape, e.g., a high-frequency power law of −1/2 as suggested in Ref. 53.

Another question, which our simple relaxation scenario touches on, is the role of the secondary relaxation. This relaxation is not given much attention in the theoretical literature, but there is a large experimental literature, including phenomenological models, which claim the secondary relaxation to be a necessary precursor of the alpha relaxation.[158]

Although one or more secondary relaxations are seen in the relaxation spectrum of many liquids, there are also liquids with no visible secondary relaxations. It may be claimed that there is always a secondary relaxation, however possibly too weak to be experimentally resolved, though this type of hypothesis is difficult to test. The liquids we have identified with simple phenomenology all have a very weak or no secondary relaxation, and we find it unlikely that such a weak process—even if present—plays a crucial role for the alpha relaxation.

Our approach in identifying the simplest experimental phenomenology is inspired by isomorph theory.[82] Isomorph theory is atypical in physics because it is not universal and only approximate. It predicts dynamic invariance along certain lines in the (ρ, T) phase diagram (termed isomorphs), but only for a subset of liquids (and solids) identified as those with strong correlations between potential energy and virial.[159] Model liquids shown to have isomorphs have van der Waals-like interaction potentials, while exceptions are liquids with directional bonds, i.e., covalently or hydrogen bonded liquids, and liquids with strong Coulomb interactions such as molten salts.

Several of the experimental traits that we have listed for the simple liquid dynamics are compatible with isomorph theory, in particular, density scaling and IS. However, the experimental reality seems to be even simpler than what isomorph theory predicts: some liquids obey TTPS, which is a stronger claim than IS. Isomorph theory predicts certain sets of fundamental thermodynamic response functions to be proportional[160] (e.g., isobaric specific heat, isothermal compressibility, and isobaric thermal expansion[161]), but has no predictions regarding the spectral shapes of shear modulus and dielectric susceptibility. Yet, experiments reveal that some liquids display the same dielectric and mechanical spectral shape and proportional time scales as a function of temperature. And although isomorph theory contains simplicity for a class of liquids and explains many experimental observations, it does not offer insights on the origin of nonexponential relaxation and non-Arrhenius temperature dependence of the relaxation time.

Over the years, ideas, models, and theories of the origin of the glass transition have been proposed, e.g., Refs. 1, 15, and 162–165, but none of them have been generally accepted. Theories tend to focus on the temperature dependence of the relaxation time, and they do not directly address the experimental features described in this perspective. The shoving model, for instance, only considers a connection between instantaneous shear modulus and structural relaxation time and does not hold predictions regarding the spectral shape or consider the relaxation time as probe dependent.[1] Perhaps including more experimental facts in the requirement for a model would help determine the correct approach to understanding the glass transition. We believe that the simple relaxation scenario will be a useful guideline for further development of simple models and serve as a test for more advanced theories, by requiring that the predicted results should be consistent with this scenario. Deviations from a theoretical prediction can often be explained due to peculiarities of a given sample. However, it would be counter intuitive (and aesthetically

displeasing), if simplicity has to be explained be a sample-specific reason. For example, we believe that a remarkable observation like the invariant shape of the alpha relaxation as it changes time scale by many orders of magnitude (TTPS) should be naturally consistent with—or even better: a consequence of—a correct model or theory of the glass transition.

There are two related ideas that play a role in many of the models and theories: (i) the notion of heterogeneous dynamics in which the stretched exponential is a signature of a sum of independent exponential relaxations[166] and (ii) the concept of a growing length scale which is driving the rapid increase in relaxation time on cooling (Ref. [167] and references herein). We believe it is challenging to reconcile these ideas with the simple relaxation scenario put forward here. If the characteristic length governing the dynamics grows dramatically, the most obvious expectation would be that the spectral shape of the relaxation would also change—unless the spectral shape is robust with regard to details in the microscopic mechanism for some specific reason, a possibility we discuss below. Similarly, the notion of independent modes would *a priori* lead to deviations from TTPS and TAS. TTPS and TAS in a situation with heterogeneous relaxation imply that all the different relaxation modes depend in the same way on density, temperature, and nonequilibrium state. This is of course possible, but such a model would most likely require more assumptions. The obvious expectation of a growing characteristic length scale governing the slowing down of the dynamics is—in our opinion—that the time-scale index would be temperature (and pressure) dependent, because different dynamic observables would depend in differently on the length scale. Though it is a controversial,[168] a similar idea was recently put forward by Wyart and Cates,[169] who argued that a growing length scale as the driving factor for the increasing relaxation time should lead to larger decoupling between relaxation times and transport properties.

The focus of this perspective is on the how phenomenology of the macroscopic dynamics and the glass transition looks. This is what a model our theory in our opinion should aim to explain. Besides the type of experimental results discussed here, there is also work aiming more directly at testing the models that are on the market. Along the lines of experiments aiming to elucidate not only *how* but also *why* the glass transition takes place, there is a large literature going back several decades aiming at quantifying a growing length scale in glass-forming liquids, e.g., Refs. [26] and [170–173]. There is continuous progress in this field (e.g., Ref. [167]), but the length scales found are generally modest (5–10 molecular diameters) and the role of a growing length is still debated. Likewise, there has for decades been clear experimental evidence that the dynamics is heterogeneous (e.g., Refs. [24], [166], [174], and [175]), and there is also new experimental development in this field (e.g., recent work on metallic glasses[176]). However, it is not clear whether we can think of dynamics as independent modes the way it has sometimes been suggested.

Besides the *why* questions of the glass transition, some *how* questions are also still open in the simple relaxation scenario. For example, whether or not there is a fundamental alpha relaxation shape and whether or not there is a fundamental shape of the relaxation time as a function of the scaling parameter $\Gamma(\rho, T)$? Thus, there is a further need for precise experiments. Glycerol is, as mentioned in the Introduction, the most studied glass former, probably because of its excellent glass-forming ability and large signal in many experimental probes. But perhaps glycerol is not the best for identifying the salient features of viscous liquid dynamics. On the contrary, glycerol appears to show a rather complicated relaxation behavior, because of the hydrogen-bonding network. The community is becoming aware of this: a central paper on growing length scales in 2005 from Berthier *et al.*[26] showed data just from glycerol whereas a 2016 advancement with several of the same authors included data on glycerol *and* the van der Waals-bonded liquid propylene carbonate.[167] We propose that the community chooses new fruitflies and the focus should be on liquids that obey a simple relaxation scenario when addressing generic questions regarding the glass transition. It may not be realistic to understand all aspects of the dynamics of all glass-forming systems in one universal framework. The first step in understanding the phenomenon could therefore be to understand viscous slowing down and the glass transition in the simplest case.

How could the simple relaxation scenario put forward here be related to a more general model or theory for the glass transition?

One possibility is that the mechanisms of the alpha relaxation itself are fundamentally different in different systems, either completely different—leaving little hope for a universal understanding and the glass transition—or different in the sense that the alpha relaxation is governed by several parameters, where a part of the parameter space leads to the simple behavior.

Alternatively, deviations from simplicity could be due to system-specific complications, whereas the *underlying* alpha-relaxation governing the glass transition always remains simple, a viewpoint that has some experimental support.[51,53,177] Numerous specific dynamic features could lead to more complex relaxation behavior, even if the underlying alpha relaxation is simple. For instance, long range hydrogen bonding networks giving an additional slow polymer-like mode or intramolecular modes leading to additional fast relaxations with a temperature dependence different from that of the alpha relaxation.

There are conceptions that offer a possible origin of simplicity. Here, we will mention two.

In the first idea, the mechanism for structural relaxation is identical at all temperatures—only the speed of the dynamics is changed. In the general notion of structural relaxation as the system crossing barriers in the energy landscape, this would correspond to the system crossing the same (high) barriers to become ergodic at all temperatures. The transitions occur more and more rarely as the temperature is lowered.

In the second idea, the routes for relaxation change with temperature. At high temperatures, relaxation proceeds as transitions over high-energy barriers, whereas at low temperatures, different routes over smaller barriers in the high-dimensional energy landscape relax the system. In this picture, the energy landscape could be fractal so the distribution of relevant barriers is the same at all temperatures or it could be different

distributions that simply average out to give the same macroscopic behavior. There is some evidence of the latter in a recent work, where the random barrier model[178] is shown to fit fluidity data for a wide range of liquids.[177] This model gives the same spectral shape regardless of the distribution used for the barriers.[178]

In this perspective, our focus has been on molecular liquids. However, the glass transition is a phenomenon which can be observed in all classes of liquids, including inorganic glasses and liquid metals. To understand the role of the simplicity, it is important to include other types of glass formers. The isomorph theory suggests that simple systems should be found among van der Waals liquids and metals.

The conjectured four criteria for simple relaxation may not be the right criteria, but the value of simplicity as a route to understanding viscous liquids does not depend on these specific criteria. We believe, from an Occam's razor type argument, that a model or theory of the glass transition should include the simplest phenomenology found among glass formers. We do not claim that the simple phenomenology is universal in the sense that it is found in all liquids, but there is a striking simplicity in the phenomenology of some liquids, which a model should be able to capture in a natural manner.

ACKNOWLEDGMENTS

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