

Effects of density and temperature on correlations between fragility and glassy properties

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A fundamental question in condensed matter science is to understand what governs the increase of relaxation time, and ultimately the glass formation, in liquids upon cooling. This phenomenon, which can be observed in chemically very different systems ranging from metals to polymers, has had practical importance for thousands of years but remains poorly understood from a fundamental point of view. The glass transition is general but the relaxation time has qualitatively different temperature dependencies in different systems. This qualitative difference can be quantified via the “fragility.” Within the past decades a lot of experimental effort has been put into correlating isobaric fragility at atmospheric pressure with other properties of the liquid and the glass. Here we show how such correlations to the isobaric fragility in some cases reflect the effect of density on the relaxation time while they in other cases are related to the intrinsic effect of temperature on the relaxation time. We specifically demonstrate that different properties related to the vibrational dynamics in the glass might contain information about different aspects of the mechanisms that govern the viscous slowing down. This insight is central if the correlations are to be used in the development of theories and models of the glass formation.

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I. INTRODUCTION

Liquids will, in general, crystallize when they are cooled below their melting point T_m . However, at sufficiently high cooling rates most systems can be supercooled, meaning that the liquid state is maintained in a metastable equilibrium below T_m . When the liquids are further cooled their viscosity and characteristic relaxation time increase drastically. Temperature changes of just a few percent can lead to changes in the structural relaxation time (τ) of several orders of magnitude. As T decreases the relaxation time ultimately surpasses the experimental time scale and the liquid consequently falls out of its thermodynamical equilibrium. This phenomenon is referred to as the glass formation and the nonequilibrium “state” is referred to as a glass.^{1,2} The glass transition temperature T_g will naturally depend on the time scale of the specific experiment, but $\tau=100$ s is often used as a convenient definition of T_g . The viscous slowing down of the liquid relaxation and the formation of a glass are general phenomena which can be observed by numerous techniques, in chemically very diverse systems and in computer simulations. The generality of the observed behavior makes it one of the key questions in condensed matter physics to determine and understand whether there is a universal mechanism governing the slowing down of the liquid relaxation.³⁻⁵

While the viscous slowing down is universal there are still large variations to be found when comparing the temperature dependence seen in different liquids. The classification and description of systems according to this difference plays a major role in the attempt to understand the universal slowing down and the glass formation itself. The concept of “fragility”⁶ has become a standard scheme for characterizing the temperature dependence of the relaxation time of a liquid. Fragility is a measure of how far from Arrhenius this temperature dependence is, characterizing a large departure from Arrhenius behavior as *fragile* and Arrhenius behavior as *strong*. There are several more or less equivalent quantitative measures of fragility, with the “steepness index” being

the most commonly used one: $m = [\partial \log(\tau) / \partial T_g / T]_P (T = T_g)$; m ranges from 17 for strong systems to roughly 200 for the most fragile systems. During the last two decades there has been intensive experimental and theoretical effort aiming to understand which properties govern the fragility of a system, but there has been no major breakthrough.

The standard way of forming a glass is by isobaric cooling at atmospheric pressure and these conditions were implicitly assumed in Angell’s original definition of fragility. That is, the derivative is taken at a constant pressure and the fragility defined is the ambient pressure isobaric fragility, m_P . When a liquid is cooled isobarically the thermal energy decreases and the density increases at the same time.⁷ These effects both contribute to the slowing down of the relaxation in the liquid, which is seen clearly from the fact that a glass can also be formed by isochoric cooling or by isothermal compression. Hence the isobaric fragility contains information on both the effect of temperature and the effect of density on the relaxation time.

The experimental isobaric fragility has received a lot of attention in the attempts to correlate the qualitative features of the *temperature* dependence of the relaxation time to other properties of the system.⁸⁻¹³ One of the interesting questions in this context is whether the properties of the glass which are formed show a signature of the liquid fragility. This type of idea is not new but has gained growing interest in the recent years, and several correlations between glassy properties and the liquid fragility have been proposed.^{8-10,13-17} The origin of these correlations is not understood and their validity is in some cases controversial.^{18,19} The aim is to use these empirical correlations between m_P and glassy properties in the development of models and theories of the dynamics in viscous liquids. However, computer simulations and theoretical attempts to understand these correlations, and viscous slowing down, in general, mainly consider isochoric conditions, hence taking into account only the effect of temperature.²⁰⁻²³

The aim of this paper is to address the question of whether the phenomenological correlations to m_P measured

under isobaric conditions relate to the pure effect of temperature or if they are mainly related to the effect of density on the relaxation time. In Sec. II we present a general analysis of how this question can be addressed for each particular empirical correlation. This analysis is split in two parts; Sec. II A, where temperature and density effects are separated without any assumptions regarding the systems behavior, and Sec. II B where we incorporate the consequences of an empirical scaling law which, over the last five years, has been established to hold for the density and temperature dependence of the relaxation time. In Sec. III we consider a few specific correlations between fragility and glassy properties in the frame of the general analysis. Section III A regards the relation between the nonergodicity factor at T_g , $f(T_g)$, and fragility.^{9,16,17} We find based on the data available in literature that the inverse nonergodicity factor is correlated to the effect of density on the relaxation time, while it apparently holds no information about the isochoric temperature dependence of the relaxation time. In Sec. III B we consider the correlation between inverse relative boson peak intensity and fragility.¹³ The data material are extremely limited in this case, but the tentative result of our study is that the boson peak is more likely related to the effect of temperature than to the effect of density on the relaxation time. Finally, we discuss how the analysis in terms of density and temperature effects could be extended and on its consequence for the validation of correlations with fragility proposed in the literature.

II. SEPARATING DENSITY AND TEMPERATURE EFFECTS

A. General aspects of correlations between fragility and glassy properties

A scheme for quantifying the respective effect of density and temperature is to define the isochoric fragility $m_\rho = [\partial \log(\tau) / \partial T_g / T]_\rho (T = T_g)$. The formal relation between the pressure dependent isobaric fragility and the density dependent isochoric fragility can be found by considering the relaxation time as a general function of density and temperature [$\tau = \tau(\rho, T)$]. Applying the chain rule this yields

$$m_P(P) = m_\rho + \left. \frac{\partial \log(\tau)}{\partial \rho} \right|_T \left. \frac{\partial \rho}{\partial T_g / T} \right|_P = m_\rho (1 + \alpha_P / |\alpha_\tau|), \quad (1)$$

where α_P is the isobaric expansivity and α_τ is the isochronic expansivity,²⁴ that is the expansivity along a line of constant τ (in this case the T_g line, as the fragility is evaluated at $T = T_g$). m_ρ describes the pure effect of temperature, whereas the second term describes the change of the relaxation time due to the change of density in the isobaric case.^{25,26} Equation (1) has the consequence that $m_P \geq m_\rho$ because α_P is positive.⁷

To analyze the situation we consider the effect of pressure on a given liquid. A glass can also be formed at a pressure $P2$, higher than atmospheric pressure, by isobaric cooling (see Fig 1). This will lead to a higher T_g and to a different $m_P(P2)$ [where $m_P(P2)$ is, of course, evaluated at $T_g(P2)$

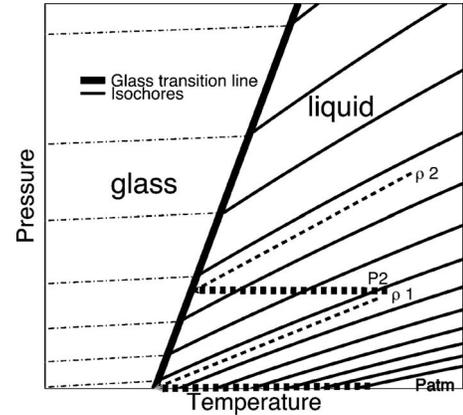


FIG. 1. Typical pressure-temperature-volume (PVT) diagram for a glass forming liquid. The glass transition line is the line where the structural relaxation time reaches $\tau = 100$ s; the glass transition line is thus a specific example of an *isochrone*. The system is out of thermodynamical equilibrium on the left-hand side of the glass transition line and the density is therefore path dependent. The thin dashed-dotted lines indicate typical glassy isochores corresponding to a density obtained by cooling isobarically after crossing the T_g line. The thin dashed lines illustrate two isochoric cooling paths in the liquid, while the bold dashed lines illustrate two isobaric cooling paths (P_{atm} and $P2 > P_{atm}$).

$> T_g(P_{atm})$]. The quantity $\alpha_P / |\alpha_\tau|$ evaluated at different P 's and at the corresponding $T_g(P)$ is, in general, pressure dependent.²⁴ This has the consequence that m_ρ and m_P will have different density and/or pressure dependencies when evaluated along the $T_g(P)$ line. Assuming that there is nothing special about ambient pressure (from the point of view of the liquid), then a strict correlation to m_P should follow this pressure dependence, where the property correlating to m_P is to be evaluated at the same high pressure.

The glass formed at T_g is a frozen-in liquid. The structure and the density get virtually frozen at T_g and the dynamics seen at high frequencies in the liquid corresponds to the dynamics of the glass. These properties vary weakly with temperature below T_g , and T_g is, in fact, the standard reference temperature used in most of the original papers when “glassy” properties are correlated to fragility.²⁷

A priori the glassy properties that are found to correlate to isobaric fragility also depend on pressure along the $T_g(P)$ line. The liquid is in (metastable) thermodynamic equilibrium at T_g hence the properties of the system at T_g depend only on T and P but not on the thermodynamic path. This means that the quantities which correlate to fragility, e.g., the nonergodicity factor,^{9,16,17} the Poisson ratio,⁸ the relative strength of the boson peak,¹³ and other properties measured at T_g , all have a well-defined pressure dependence along the $T_g(P)$ line. This pressure dependence could correspond to the pressure dependence of m_P or it could correspond to the pressure dependence of m_ρ . However, it is not possible for a quantity to have the same pressure dependence as both m_P and m_ρ because they will differ in their pressure dependence by the factor $\alpha_P / |\alpha_\tau|$ [Eq. (1)], which is in itself pressure dependent (the phenomenology is discussed in more detail in the following section). A correlation to m_ρ will mean that the property in question is related to the pure temperature depen-

dence of the relaxation. A correlation to the pressure dependent m_p signifies that the quantity in question encompasses information about both the density and the temperature dependence of the relaxation time. While a correlation to m_p/m_ρ reflects a relation to the contribution of the density effect on the relaxation time.

B. Scaling out the influence of the density on the viscous slowing down

To develop the ideas further we consider the consequence of the empirical scaling law, where the contribution of density on the relaxation time is scaled out by introducing a single density dependent energy scale:^{28,29}

$$E(\rho, T)/e(\rho) = \Phi[T/e(\rho)], \quad (2)$$

where Φ is system dependent and $E(\rho, T)$ is defined by the relation

$$\tau(\rho, T) = \tau_0 \exp[E(\rho, T)/T]. \quad (3)$$

The scaling law can also be expressed directly in terms of the relaxation time by

$$\log_{10}[\tau(\rho, T)] = F\left(\frac{e(\rho)}{T}\right), \quad (4)$$

where F and e are system dependent functions. The scaling has been found to hold for all the relevant data collected so far.^{26,28,30-34}

It is seen directly from Eq. (4) that $X(\rho, T) = e(\rho)/T(\rho)$, evaluated at T_g will have the same value at all densities $[X_g = e(\rho)/T_g(\rho)]$ if $T_g(\rho)$ is defined as at the temperature where the relaxation time has a given value (e.g., $\tau = 100$ s). Exploiting this fact, it is easy to show^{29,30} that the scaling law has the consequence that the isochoric fragility will be independent of density when evaluated at a T_g corresponding to a given relaxation time:

$$\begin{aligned} m_\rho &= \left. \frac{d \log_{10}(\tau)}{dT_g/T} \right|_{\rho} (T = T_g) = F'(X_g) \frac{dX}{dT_g/T} (T = T_g) \\ &= X_g F'(X_g). \end{aligned} \quad (5)$$

We illustrate the meaning of the result in Fig. 1 and 2. Contrarily, the isobaric fragility depends on pressure and this dependence is highly system dependent. In most systems m_p decreases with pressure making m_p approach m_ρ as the density of the system is increased; in some systems m_p changes very little, and in hydrogen bonded systems it is found that m_p increases with pressure.^{31,35} Since m_ρ is found to be density independent, it follows from Eq. (1) that the pressure dependence of $m_p(P)$ is due to a pressure dependence of α_p/α_τ .

The fact that m_ρ stays constant when evaluated at higher densities at the corresponding pressure dependent T_g while m_p changes with pressure along the same T_g line emphasizes the statement that a quantity cannot have the same pressure dependence as both m_ρ and m_p as it would have to be pressure dependent and independent at the same time.

The scaling is an empirical result and despite the variety of systems for which it has been shown to hold, there is no

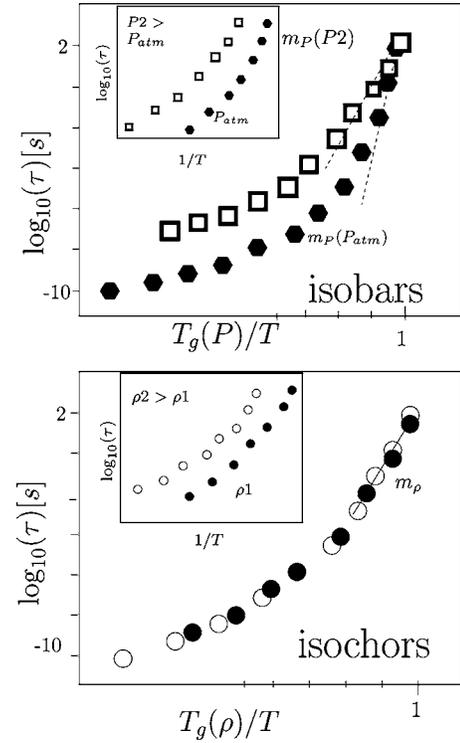


FIG. 2. Top: typical temperature dependence of the relaxation time when followed at different isobars. It is illustrated that this temperature dependence persists after scaling with $T_g(P)$ leading to a pressure dependence in m_p . The open symbols correspond to the highest pressure (P_2). (b) Bottom: typical temperature dependence of the relaxation time when followed along different isochores. The density dependence is canceled by scaling with $T_g(\rho)$ which means that m_ρ is density independent. The open symbols correspond to the highest density ($\rho_2 > \rho_1$).

guarantee that it is universal; there is, for example, no data available on strong network glasses, nor in inorganic glasses, in general. However, the scaling gives a rationalized picture of the pressure and temperature dependence of the relaxation time in the data obtained so far on polymers and molecular liquids. The emerging picture is that m_p is intrinsic to the system in the sense that it is density independent. A quantity correlating to the pure temperature dependence of the relaxation time as it is measured by m_ρ should then possess the same intrinsic characteristic and be independent of pressure along the T_g line.

For this picture to be consistent with the correlations between glassy properties and m_p , these latter should also hold when rephrased and/or replotted as correlations to m_ρ . From Eq. (1) it is seen that m_p contains m_ρ and it has consistently been found by including a large amount of fragile and intermediate systems that m_ρ does correlate to the ambient pressure m_p ,³⁶ indicating that a cross correlation to the glassy properties is possible. To test this hypothesis one must know both m_p , m_ρ and the properties suggested to correlate with fragility (nonergodicity factor, the Poisson ratio, the relative strength of the boson peak etc.). The relevant complete set of data is only available for a few of the well studied archetypal glass formers: glycerol, salol, and o-terphenyl (OTP) whom cover a range of $m_p \approx 50$ to $m_p \approx 80$ taken at T_g and ambient

pressure. However, these three liquids have very similar isochoric fragility ranging only from $m_\rho \approx 38$ to $m_\rho \approx 45$.^{25,37} Hence the difference in isobaric fragility found at ambient pressure when comparing these three liquids is not related to an intrinsically different response to temperature but rather to a different effect of the change in density upon isobaric cooling [just as it is the case for the change of $m_p(P)$ when changing pressure]. This observation leads to a quite different conjecture, namely that the correlations between m_p and glassy properties are, in fact, a reflection of the effect of density on the relaxation time.

III. SPECIFIC CORRELATIONS

A. Nonergodicity factor

To look into this problem in more detail we focus on the relation between m_p and the nonergodicity factor $f(T_g)$, because this is the case for which there is most m_p data available for comparison.

The first proposed correlation between fragility and nonergodicity factor regarded the temperature dependence in the $T=0$ limit of the glass of the inverse nonergodicity factor measured by inelastic x-ray scattering (IXS) in the low- Q region where $f(T_g)$ is weakly Q dependent (in practice $Q = 2 \text{ nm}^{-1}$).⁹ The properties of the glass are path dependent and it is therefore not clear how density and temperature effects should be properly disentangled, when considering properties measured deep in the glass. However, $1/f(T)$ is mostly found to have a linear temperature dependence; this corresponds to a harmonic approximation where density changes are neglected. This also leads to a direct correspondence between the temperature dependence of $f(T)$ and its absolute value at T_g . It was consistently shown in follow up papers (Refs. 16 and 17) that (a somewhat weaker) correlation can be found between fragility and $f(T_g)$ such that the higher the fragility the lower the $f(T_g)$.

In Fig. 3 we show $f(T_g)$ as a function of the isochoric and the isobaric fragilities, respectively. The first observation is that the originally proposed correlation to m_p is blurred when considering this particular limited set of data. The next observation is that the correlation to m_ρ is even poorer. This indicates that the correlation proposed between $f(T_g)$ and m_p is not related to the effect of the temperature on the α -relaxation time. However, there is a correlation to the ratio m_p/m_ρ (Fig. 4), thereby implying a correlation between $f(T_g)$ and the effect of density on the relaxation time.

To further examine the significance of these findings we start by noting that the scaling leads to the following relation:^{25,26}

$$m_p/m_\rho = \left(1 + \alpha_p T_g \frac{d \log e(\rho)}{d \log \rho} \right). \quad (6)$$

This expression clearly illustrates that the relative effect of density on the slowing down upon isobaric cooling can be decomposed in two parts: the temperature dependence of the density measured by $T_g \alpha_p = -[d \log \rho / d \log T]_p$ ($T = T_g$), and the density dependence of the relaxation time, which is contained in $[d \log e(\rho) / d \log \rho]$.

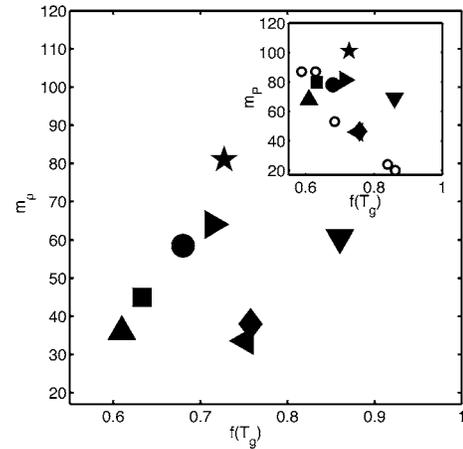


FIG. 3. Isochoric fragility as a function of a nonergodicity factor. Inset: Isobaric fragility as a function of a nonergodicity factor for the same systems. salol (▲), OTP (■), *m*-toluidine (●), PB (▶), PVAc (★), PIB (◀), glycerol (◆), and DBP (▼). In the inset we also show data from systems reported in Ref. 9 for which m_p is not known (○). It has been proposed that the deviations from the correlation to m_p can be explained if secondary relaxations contribute to the elastic intensity measured by IXS. (Ref. 53)

It has been found for all the cases studied so far that $e(\rho)$ is reasonable well described by a power law $e(\rho) \propto \rho^x$, which gives a density independent $[d \log e(\rho) / d \log \rho] = x$ (e.g., Refs. 26, 28, and 30–34). In Fig. 4 we show $f(T_g)$ versus $[d \log e(\rho) / d \log \rho]$. The amount of data is limited and the uncertainty of this type of data is large, but we clearly obtain a good correlation between the two quantities. This is quite striking because $[d \log e(\rho) / d \log \rho]$ can be determined from the dynamics of the nonviscous liquid at high temperatures²⁸ as well as from the dynamics in the viscous regime close to T_g . We speculate that the proposed correlation between $f(T_g)$ and m_p is a reminiscence of a correlation between $f(T_g)$ and $[d \log e(\rho) / d \log \rho]$, and as a result is mostly a signature of the effect of density, an effect that can be determined from

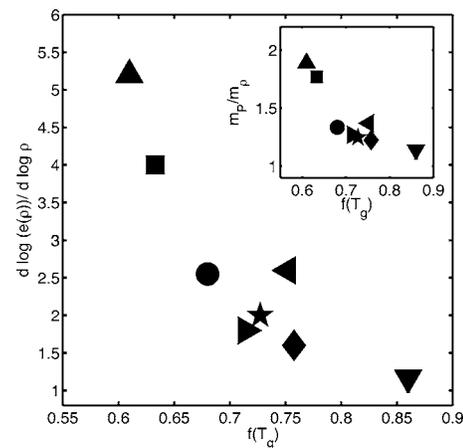


FIG. 4. (a) $\frac{d \log e(\rho)}{d \log \rho}$ as a function of the low Q nonergodicity factor $f(T_g)$. Inset: The ratio of fragilities m_p/m_ρ as a function of the low Q nonergodicity factor $f(T_g)$. salol (▲), OTP (■), *m*-toluidine (●), PB (▶), PVAc (★), PIB (◀), glycerol (◆), and DBP (▼).

the high- T behavior of liquids and polymers.²⁹ An excellent test case for this hypothesis would be to measure $f(T_g)$ on sorbitol which has a very high m_p value combined with an exceptionally low value of $[d \log e(\rho)/d \log \rho]$.^{26,38} It can also be tested by high pressure measurements. IXS data on dibutylphthalate (DBP) show no pressure dependence of f at a given T .³⁹ This means that $f(T_g)$ will decrease with pressure due to the increase in T_g . Unpublished data on polyisobutylene (PIB) point in the same direction. A decrease in $f(T_g)$ with pressure does not correspond to an inverse correlation to m_p nor to m_p/m_ρ , since these decrease with pressure. If $e(\rho)$ follows a power law, then a decrease in $f(T_g)$ with pressure is not consistent with a correlation to $[d \log e(\rho)/d \log \rho]$ either, since a power law makes $[d \log e(\rho)/d \log \rho]$ density independent.

B. The boson peak intensity

It is, of course, possible that the different glassy properties considered are related to different aspects of the temperature and density dependence of the relaxation time, though, such a conclusion would be at odds with the attempts to interrelate the different glassy properties and thereby to understand their respective correlation to m_p from a common starting point.¹⁷ In the case of the Poisson ratio and the boson peak strength there is even less data on systems where m_p is also available than for the nonergodicity factor.

The proposed relation between boson peak strength and fragility is that the higher the relative boson peak intensity is, the lower is the fragility. This has been done either by normalizing the boson peak to the Debye density of states¹⁴ or by normalizing the boson peak intensity at T_g to the intensity of quasielastic scattering at T_g .¹³ In the latter case a parameter R is defined as the quasielastic intensity divided by the boson peak intensity, and R is proposed to increase with increasing isobaric fragility. In Fig. 5 we show R as a function of, respectively, isobaric and isochoric fragility for the

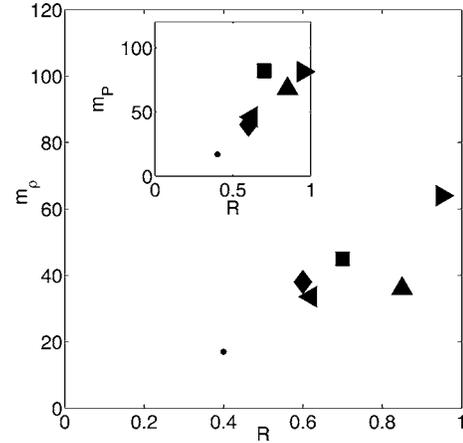


FIG. 5. The isochoric fragility as a function of the intensity of quasielastic scattering divided by the boson peak intensity measured via R as defined. (Ref. 13) Inset: the isobaric fragility as a function of R . In general we only show data when both m_ρ and m_p are available. However, we have included a limiting strong behavior which corresponds to SiO_2 of Ref. 13. We assume $m_\rho \approx m_p$ in this limit, based on Eq. (1), which yields that $m_\rho \leq m_p$. salol (\blacktriangle), OTP (\blacksquare), PB (\blacktriangleright), PIB (\blacktriangleleft), glycerol (\blacklozenge), DBP (\blacktriangledown), and the limiting strong behavior (\bullet). R for PIB is from Ref. 54; all other R values from Ref. 13. See Table I for fragility values.

systems where all the three relevant parameters are known. The data are extremely limited and it is clear that no definite conclusion can be drawn on this basis. However, the observation is that the correlation to m_ρ is comparable to the originally proposed correlation to m_p . This suggests that the boson peak intensity could be related to the pure effect of temperature on the relaxation time rather than that of density. This hypothesis implies that the relative boson peak intensity does not change with pressure along the glass transition line $T_g(P)$, a property that could easily be checked experimentally.

TABLE I. The values and references used for the plots. The parameter $f(T_g)$ is in the case of polyvinyl-acetate (PVAc), taken from Ref. 16 where $f(T_g)=1-1/[\chi_T(T_g)\rho v_l^2(T_g)]$ is used and χ_T is the isotherm compressibility and v_l is the Brillouin sound speed. For salol we calculated $f(T_g)$ from the value of the parameter α given in Ref. 9 assuming a linear temperature dependence of $1/f(T, Q=2 \text{ nm}^{-1})$, which could be a rough approximation for a fragile liquid, since $1/f(T)$ sometimes becomes nonlinear when approaching T_g . Ref. 53 For all other liquids [*o*-terphenyl (OTP), *m*-toluidine, 1,4-polybutadiene (PB), glycerol, dibutylphthalate (DBP), and polyisobutylene (PIB)] we have taken $f(T_g)$ from the IXS spectra at $Q=2 \text{ nm}^{-1}$ and $T=T_g$. The directly measured values of m_p and $[d \log e(\rho)/d \log \rho]$ are not available in the cases of PIB, DBP, and *m*-toluidine. We have therefore calculated these using the formal relations $m_\rho=m_p(1+\alpha_p/|\alpha_\tau|)^{-1}$ and $[d \log e(\rho)/d \log \rho]=(|\alpha_\tau|T_g)^{-1}$. We have used the average in the situations where we are aware of more than one literature value of a given parameter.

Compound	m_p	Refs.	m_ρ	$[d \log e(\rho)/d \log \rho]$	Refs.	$f(T_g)$	Refs.
Salol	63/68/73	41, 12, and 31	36	5.2	31	0.61	9
OTP	76/81/82	41, 12, and 31	45	4	42 and 25	0.63	9
<i>m</i> -toluidine	77/79	43 and 44	56	2.6	30	0.68	45
1,4-PB	107/60/70	41, 9, and 25	64	1.8	25	0.71	46
PVAc	95/130/78	47, 48, and 25	52/130/61	2.6/1.4	47, 48, 25, and 49	0.73	16
PIB	46	50	34	2.6	51	0.75	51
Glycerol	53/40	12 and 25	38	1.8/1.4	25, 32, and 33	0.76	9
DBP	69	52	61	1.2	30	0.86	39.

C. Other correlations

The arguments presented here could likewise be central for the analysis of the relations between m_p and other properties; e.g., the thermodynamic fragility,¹¹ the dynamic correlation length scale,⁵ and the Kohlrausch stretching parameter β_{KWW} .¹² Regarding the proposed correlation between fragility and the stretching parameter, β_{KWW} , it is interesting to note that it has recently been proposed that β_{KWW} does, in fact, stay constant as pressure is increased along T_g (or any other isochrone).⁴⁰ This behavior is consistent with a correlation to the effect of temperature on the relaxation time as measured by m_p . Moreover this means that β_{KWW} does not have the same pressure dependence as m_p .

IV. CONCLUSIONS

We provide a framework for analyzing correlations between fragility and glassy properties by disentangling temperature and density effects. We argue that properties related to the temperature dependence of the relaxation time should correlate to the isochoric fragility rather than the isobaric fragility. We moreover state that properties which are related to the effect of density on the relaxation time should correlate to the ratio between isobaric and isochoric fragility.

We find, based on the available data from the literature, that the correlation between the nonergodicity factor at T_g and $Q=2 \text{ nm}^{-1}$, $f(T_g)$, and fragility^{9,16,17} that this correlation is due to a “hidden” correlation between the nonergodicity factor and the effect of density on the relaxation time. We find that $f(T_g)$ is smaller when the effect of density on the relaxation time is larger. This means that the vibrational part

of the density fluctuations in the considered Q range are larger when the effect of density on the relaxation time is larger. This suggests that the properties which govern these density fluctuations also couple to the density dependence of the relaxation time. We also consider the correlation between relative boson peak intensity at T_g and fragility.¹³ The available data for this case are very limited but the preliminary conclusion is that this correlation might be related to the effect of temperature on the relaxation time. Apparently these two characteristic measures of the vibrational dynamics in the glass contain information about different aspects of the mechanisms that govern the viscous slowing down. We moreover point out that the pressure dependence of β_{KWW} is consistent with a correlation to m_p .

Another important issue, which could be valuably studied along similar lines, is the correlations between the temperature dependence of properties in the supercooled liquid above T_g and the fragilities evaluated at shorter relaxation times.

We believe that testing correlations of any liquid or glassy properties distinctively with m_p , m_ρ , or their ratio, will help in disentangling generic features for the understanding of the glass transition phenomenon from other more specific or *ad hoc* for the system under consideration.

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