

# What Can We Learn by Squeezing a Liquid?

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Relaxation times  $\tau(T,v)$  for different temperatures,  $T$ , and specific volumes,  $v$ , collapse to a master curve vs  $Tv^\gamma$ , with  $\gamma$  a material constant. The isochoric fragility,  $m_v$ , is also a material constant, inversely correlated with  $\gamma$ . From these experimental facts, we obtain a three-parameter function that accurately fits  $\tau(T,v)$  data for several glass-formers over the supercooled regime, without any divergence of  $\tau$  below  $T_g$ . Although the values of the three parameters depend on the material, only  $\gamma$  significantly varies; thus, by normalizing material-specific quantities related to  $\gamma$ , a universal power law for the dynamics is obtained.

## Introduction

By cooling a liquid in a time shorter than the crystallization time, a metastable equilibrium is reached, called the supercooled state. A liquid can also be supercooled more rapidly and effectively by squeezing (i.e., applying hydrostatic pressure). Herein we discuss how the fundamental difference between these two thermodynamic routes to vitrification yields insights into the physics underlying the metastable supercooled state.

Certainly the most intriguing phenomenon observed on cooling glass-forming liquids and polymers is the dramatic slowing down of their structural dynamics, by more than 14 orders of magnitude over a relatively small temperature range. Eventually, the structural relaxation time  $\tau$  becomes so large that molecular motions (other than vibrations and very restricted reorientations) cease, at least on the experimental time scale. Thus, macroscopically the system behaves as a solid, even though no apparent changes have transpired in its microscopic structure. Gaining a molecular-level understanding of this phenomenon is considered one of the most challenging problems of condensed matter physics.

In a typical experiment, a sample is cooled at some rate and below a certain temperature (the glass temperature  $T_g$ ), this cooling rate becomes comparable with  $\tau^{-1}$ , whereby the system cannot attain thermodynamic equilibrium in the time of the measurement. Consequently,  $T_g$  is rate dependent, making its definition somewhat arbitrary. Typically for dielectric relaxation measurements  $T_g$  is taken such that  $\tau(T_g) = 100$  s (we use this herein), while for viscosity measurements  $\eta(T_g) = 10^{12}$  Pa s.

A popular classification of the effect of temperature on the dynamics is the fragility or “steepness index”,<sup>1–3</sup> defined as  $m_P = \partial \log(x)/\partial(T_g/T)|_{T=T_g, P=\text{const}}$ , where  $x$  can be  $\tau$  or  $\eta$ . For small molecules and polymers, this parameter varies at atmospheric pressure over the range  $35 \leq m_P \leq 214$ ,<sup>4–7</sup> which reveals the drastic differences in the vitrification process among different materials. However, currently there is no accepted molecular-level interpretation of fragility.

The two pathways to  $T_g$  (cooling and compression) have an interesting difference: an isobaric change of  $T$  alters both  $V$  and  $T$  while an isothermal change of  $P$  only affects  $V$ . Consequently, using high-pressure measurements, it is possible to deconvolute the relative effects of  $T$  and  $V$  on the dynamics, which is of fundamental importance in assessing theoretical models and their foundation.

High-pressure experiments over the past few years on an extended number of glass-formers<sup>8–11</sup> have established unambiguously that both temperature and volume govern the temperature dependence of the relaxation time, at least at atmospheric pressure. Therefore, a complete model of the glass transition should be able to provide an equation for the dependence of  $\tau$  on both temperature and volume. Recently, it has been shown<sup>12–15</sup> that the behavior of  $\tau(T,v)$  can be rescaled onto a master curve when plotted vs  $Tv^\gamma$ .

$$\tau(T,v) = \mathcal{F}(Tv^\gamma) \quad (1)$$

where  $v$  is the specific volume and  $\gamma$  a material constant. Therefore, the relevant variable to describe structural relaxation times is the product  $Tv^\gamma$ .

This scaling was first observed for *ortho*-terphenyl (OTP)<sup>16,17</sup> for  $\gamma = 4$  (the value predicted for a simple Lennard-Jones 6-12 potential<sup>18,19</sup>) and then shown to be generally valid with  $0.13 \leq \gamma \leq 8.5$  for various materials.<sup>12–15</sup> Equation 1 can describe dielectric,<sup>12–15</sup> light scattering,<sup>17,20</sup> and viscosity measurements,<sup>21</sup> with comparable values obtained for  $\gamma$ . The scaling behavior has also been confirmed in simulations.<sup>22</sup>

The scaling provides a straightforward deconvolution of the effects of  $T$  and  $v$ . If the behavior of the relaxation time at constant pressure is known, it is possible to determine the behavior at constant volume using the equation of state  $v(T,P)$  and the value of  $\gamma$  for the particular glass-former.<sup>23</sup> Defining the isochoric fragility as  $m_v = \partial \log(x)/\partial(T_g/T)|_{T=T_g, V=\text{const}}$ , from eq 1 it follows that  $m_P$  can be calculated from  $m_v$  as<sup>12,13</sup>

$$m_P = m_v(1 + \gamma\alpha_P T_g) \quad (2)$$

where  $\alpha_P$  ( $\equiv 1/V\partial V/\partial T|_P$ ) is the isobaric (volume) expansion coefficient at  $T_g$ . Actually, this relation is valid for any  $T$  as long as  $\alpha_P$  is determined at the same  $T$  ( $\gamma$  being constant). Very

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generally, if  $\alpha_p \geq 0$  (which is true except for anomalous cases such as water), then  $0 \leq m_v \leq m_p$ , with  $m_v$  being smaller than  $m_p$  since the former does not include the effect of volume changes. The two limiting cases  $m_v = m_p$  and  $m_v = 0$  correspond to  $\tau$  being a sole function of  $T$  and  $V$ , respectively.

In addition to eq 2, there are two other independent relations:<sup>24</sup> (i) comparing the value of  $m_v$  and  $m_p$  for more than 38 glass-formers (the second determined at atmospheric pressure), the two fragilities are found to be linearly correlated,  $m_p = (37 \pm 3) + (0.83 \pm 0.05)m_v$ ; (ii)  $m_v$  is related to  $\gamma$  according to  $\gamma = -1.042 + 217/m_v$ . The consequence of these two correlations is the unobvious result that the temperature behavior, for both the isobaric and the isochoric conditions, is related to the parameter  $\gamma$  which describes (viz., eq 1) the dependence of the relaxation time on volume. Thus, the scaling exponent (whose physical interpretation has been discussed previously<sup>12,25</sup>) serves as a “new” metric to classify glass-formers. Indeed, herein we go a step further and identify from  $\gamma$  a variable which unifies the behavior of all glass-formers.

## Results

An equation has been found which best describes (using the fewest parameters)  $\tau(T, v)$  over temperatures and volumes ranging from the glass transition up to temperatures at which the behavior becomes activated<sup>26</sup>

$$\log[\tau(T, v)] = \log(\tau_\infty) + B((T_g v_g^\gamma / T v^\gamma))^D \quad (3)$$

where  $\tau_\infty$ ,  $B$ , and  $D$  are constants with  $\tau_\infty$  the limiting value of  $\tau$  at high temperatures.  $v_g$  is the specific volume at the glass transition (note from eq 1 it follows that  $T v^\gamma$  at the glass transition is a constant for every condition of  $T$  and  $v$ ). This equation can be derived from a model relating the dynamics to the system entropy.<sup>26</sup>

Assuming a linear relationship between  $m_v$  and  $m_p$ ,  $m_p = a + b m_v$  with  $a$  and  $b$  constants, then for  $m_v = 0$ ,  $m_p = m_p^{\min} = a$ , while  $m_v = m_p = m_p^{\max}$ , and hence it follows that  $b = 1 - m_p^{\min}/m_p^{\max}$ . The linear relationship between  $m_p$  and  $m_v$  can be rewritten as

$$m_p = m_p^{\min} + \left(1 - \frac{m_p^{\min}}{m_p^{\max}}\right) m_v \quad (4)$$

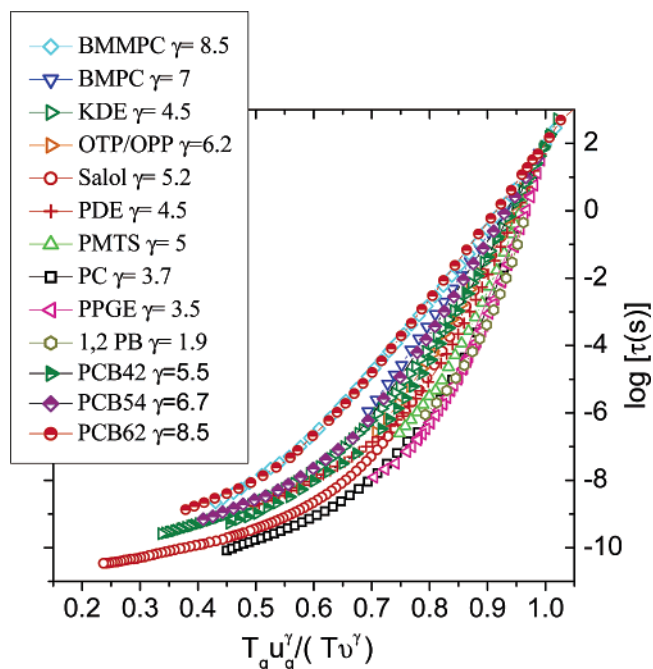
Combining eq 2 with eq 4 yields

$$\gamma = \frac{m_p^{\min}}{\alpha T_g} \left( \frac{1}{m_v} - \frac{1}{m_p^{\max}} \right) \quad (5)$$

Comparing eq 5 with the empirical correlation found between  $\gamma$  and  $m_v$ , we obtain  $(m_p^{\min}/m_p^{\max}) = 1.04 \times \alpha T_g$ . Thus, to a good approximation

$$\frac{m_p^{\min}}{m_p^{\max}} \cong \alpha T_g \quad (6)$$

Equation 6 agrees with results from the empirical correlation between  $m_v$  and  $m_p$ ,  $m_p^{\min} = 37 \pm 3$  and  $m_p^{\max} = 231 \pm 72$ .<sup>24</sup> From eq 6,  $\alpha T_g = m_p^{\min}/m_p^{\max} = 0.16 \pm 0.06$ , in good agreement with the literature; that is, the Boyer–Bondi rule  $\alpha T_g$



**Figure 1.** Relaxation times for representative glass-formers vs the variable  $T v^\gamma$  normalized by its value at the glass transition. The abbreviations in the caption are 1,1'-di(4-methoxy-5-methylphenyl)-cyclohexane (BMMPC),<sup>30</sup> 1,1'-bis(*p*-methoxyphenyl)cyclohexane (BMPC),<sup>9</sup> cresolphthalein-dimethyl ether (KDE),<sup>41</sup> (OTP/OPP),<sup>31</sup> phenyl salicylate (salol),<sup>32</sup> phenylphthalein-dimethyl ether (PDE),<sup>38</sup> poly(methyltolylsiloxane) (PMTS),<sup>33</sup> propylene carbonate (PC),<sup>34</sup> poly(phenyl glycidyl ether)-*co*-formaldehyde (PPGE),<sup>35</sup> 1,2-polybutadiene (1,2PB),<sup>36</sup> chlorinated biphenyl 42 (PCB42),<sup>37</sup> 54% chlorinated biphenyl (PCB54),<sup>37</sup> and chlorinated biphenyl 62 (PCB62).<sup>37</sup>

$= 0.16\text{--}0.19$ .<sup>27</sup> Accordingly, we substitute eq 6 in eq 5 finding

$$\gamma = \frac{m_p^{\max}}{m_v} - 1 \quad (7)$$

Defining  $m_p^\infty = 2 - \log(\tau_\infty)$  (which represents the limiting Arrhenius slope at  $T_g$ , similar to the parameter used in refs 28 and 29), it is easy to see that  $B = m_p^\infty$  and eq 3 is rewritten as  $\log[\tau(T, v)] = 2 - m_p^\infty + m_p^\infty((T_g v_g^\gamma / T v^\gamma))^D$ . Calculating  $m_v$ , we obtain  $m_v = D m_p^\infty$ , so that

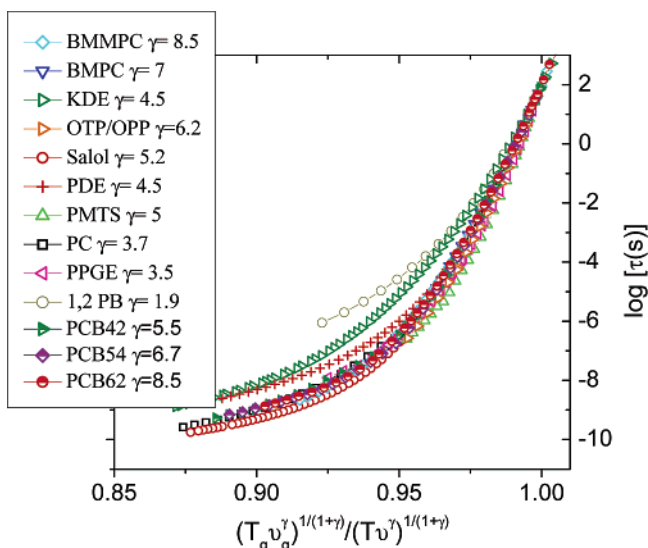
$$\log[\tau(T, v)] = 2 - m_p^\infty + m_p^\infty((T_g v_g^\gamma / T v^\gamma))^{m_v/m_p^\infty} \quad (8)$$

In Figure 1, the relaxation times are shown for several glass-formers vs  $T v^\gamma$  normalized by its value at the glass transition. This plot is similar to the more usual fragility plot, but Figure 1 is not restricted to the isobaric  $T$ -dependence; all conditions of  $T$  and  $v$  are considered. It can be seen that the rapidity of approach to the glass transition is different for each material; in fact, in this plot, the steepness index at the glass transition is equal to  $m_v$ .<sup>23</sup>

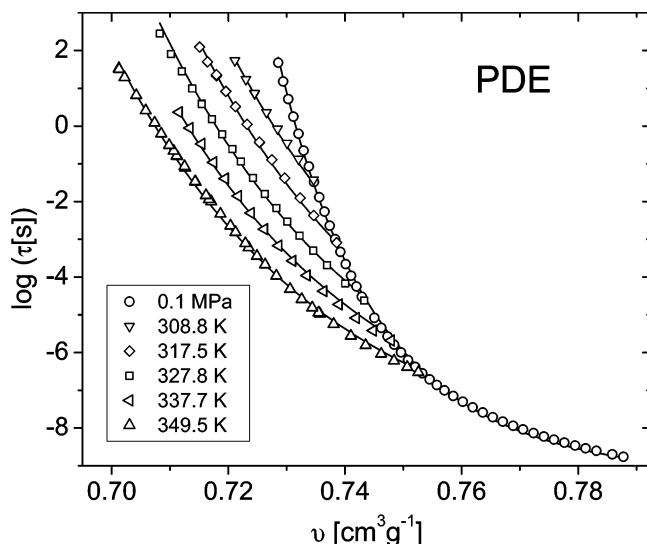
If  $T_g$  and  $v_g$  are known, then eq 8 has only three free parameters ( $\gamma$ ,  $m_v$ ,  $m_p^\infty$ ). By using eq 7 relating  $m_v$  to  $\gamma$ , we can reduce this to two parameters ( $\gamma$ ,  $m_p^\infty$ )

$$\log[\tau(T, v)] = 2 - m_p^\infty + m_p^\infty \left( (T_g^{1/1+\gamma} v_g^{\gamma/1+\gamma} / T^{1/1+\gamma} v^{\gamma/1+\gamma}) \right)^{m_p^{\max}/m_p^\infty} \quad (9)$$

Since  $m_p^\infty = 2 - \log(\tau_\infty)$ , where  $\tau_\infty$  is the high-temperature limiting value of  $\tau$ , we expect its value to be similar for many materials  $m_p^\infty \sim 12$  (see refs 26 and 39 and also data herein).



**Figure 2.** Relaxation times for the same glass-formers in Figure 1 vs the variable  $(Tv^\gamma)^{1/(1+\gamma)}$  normalized by its value at the glass transition.

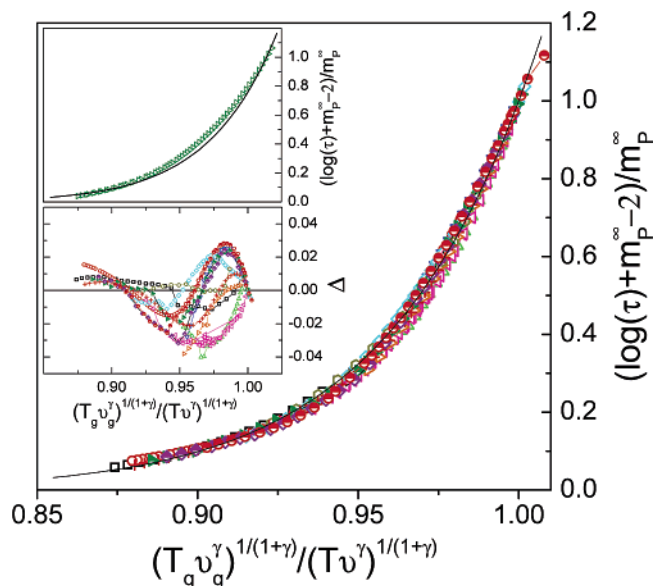


**Figure 3.** Relaxation times for PDE<sup>38</sup> vs specific volume. Data correspond to an isobar at atmospheric pressure and five isotherms at the indicated temperatures. The solid lines are fits to eq 9, taking  $T_g = 293.7$  K and  $v_g = 0.72867$  cm<sup>3</sup> g<sup>-1</sup>, which yields  $m_p^\infty = 11.4 \pm 0.1$ ,  $m_p^{\max} = 264 \pm 1$ , and  $\gamma = 4.37 \pm 0.01$ .

Interestingly, this roughly corresponds to the value of  $\log(\tau_\infty)$  beyond which the behavior becomes Arrhenius ( $\log(\tau(T_A)) \sim -10.2$ ).<sup>40</sup>

Furthermore, since  $m_p^{\max}$  is a number, it follows from eq 9 and the assumption that  $m_p^\infty$  is constant for all materials that all data should rescale onto a single universal curve when plotted vs  $(Tv^\gamma)^{1/(1+\gamma)}$  normalized by its value at the glass transition (Figure 2).

In Figure 2, all the curves have the same slope at  $T_g$ , and the data indeed almost scale onto a single curve. This result is important since the parameter  $\gamma$  is determined from the scaling (eq 1) of  $\tau(T, v)$  data (or it can be obtained from PVT data<sup>10</sup>);  $\gamma$  is not directly related to the rapidity of the variation of  $\tau$  with  $T$ . Exceptions to the general behavior in Figure 2 are noted for three materials: PDE, KDE, and 1,2-PB, which deviate for short  $\tau$ ; nevertheless, eq 9 still accurately describes the data for these materials. We illustrate this in Figure 3 for PDE, with the fit to eq 9, shown as a solid line, obtained using the known values of



**Figure 4.** Relaxation time divided by the estimated value of  $m_p^\infty$  for each material;  $m_p^\infty = 12.35$  for BMMPC, 12 for BMPC, 11.3 for KDE, 12.4 for OTP/OPP, 12.65 for salol, 11.5 for PDE, 12.7 for PMTS, 12.3 for PC, 12 for PPGE, 9.71 for 1,2PB, 12.2 for PCB42, 12.2 for PCB54, and 12.2 for PCB62. The symbols are the same as those in Figure 2, and the solid line corresponds to eq 11. In the top insert are the results for KDE along with eq 11. The lower insert shows the difference between the data of the main figure and eq 11.

$T_g = 293.7$  K (at ambient  $P$ ) and  $v_g = 0.72867$  cm<sup>3</sup> g<sup>-1</sup>. The values of  $m_p^\infty$ ,  $m_p^{\max}$ , and  $\gamma$  are given in the figure caption.

To determine if the deviation in Figure 2 is due to differences in  $m_p^\infty$  among materials, in Figure 4 we plot the function

$$\frac{\log[\tau(T, v)] - 2 + m_p^\infty}{m_p^\infty} = \left( (T_g^{1/(1+\gamma)} v_g^{\gamma/(1+\gamma)} / T^{1/(1+\gamma)} v^{\gamma/(1+\gamma)}) \right)^{m_p^{\max}/m_p^\infty} \quad (10)$$

using the values of  $m_p^\infty = 2 - \log(\tau_\infty)$  reported in the caption. In practice, the left term represents the change of  $\log(\tau)$  from its asymptotic value at high  $T$  normalized by the total change up to  $T_g$ , removing the intrinsic differences in  $\log(\tau_\infty)$ , which depend on molecular details. The agreement is now quite good, with only KDE showing any appreciable deviation (as shown in the insert to Figure 4). The origin of this deviation is unclear; however, KDE has peculiar behavior, for example, behaving as a fragile liquid for some properties but as an intermediate liquid for others.<sup>41</sup> Its molecular structure is very close to that of PDE, but its temperature dependence is markedly different.<sup>42</sup>

In Figure 4, we also show (solid line) the function

$$g(T, v) = (T_g^{1/(1+\gamma)} v_g^{\gamma/(1+\gamma)} / T^{1/(1+\gamma)} v^{\gamma/(1+\gamma)})^{22} \quad (11)$$

which accurately describes the master curve. From the mean value of  $m_p^\infty$ , we estimate  $m_p^{\max} = 22 \times m_p^\infty = 22 \times 12 \pm 0.8 = 263 \pm 18$ , which is consistent with the value of  $m_p^{\max}$  determined from the correlation between  $m_v$  and  $m_p$ .<sup>24</sup> The deviation of the behavior of each material from eq 11,  $\Delta = \{\log[\tau(T, v)] - 2 + m_p^\infty\} / m_p^\infty - g(T, v)$ , is displayed in the insert to Figure 4. The small deviation ( $|\Delta| < 0.03$  for all the materials considered herein) demonstrates the robustness of the proposed scaling.

From the scaling in Figure 4, it is evident that the parameters  $m_p^\infty$  and  $m_p^{\max}$  are about constant among different materials. These quantities represent the activation energies at the glass



transition normalized by thermal energy for the two limiting conditions, respectively. The quantity  $m_p^\infty = 2 - \log(\tau_\infty)$  is related to the activation energy when the thermal energy is much higher than the intermolecular barriers, so that differences in molecular structure are minimized. Note that the values for the “analogous”  $m_p^\infty$  reported in the literature from fitting the Vogel–Fulcher–Tamman (VFT) equation<sup>43–45</sup> to  $\tau$  are generally larger. This is a consequence of the inability of the VFT equation to fit simultaneously data both close to  $T_g$  and at short relaxation times.<sup>23,38,46–49</sup> Extrapolation of the VFT equation deduced for  $\tau$  in the vicinity of  $T_g$  to higher temperatures underestimates  $\tau$  (larger  $m_p^\infty$ ) than the values actually measured.<sup>38,48,49</sup>

The parameter  $m_p^{\max}$  represents the maximum fragility, in the limit  $\gamma \rightarrow 0$  for which the relaxation time becomes a function of temperature alone. This corresponds to completely jammed dynamics, such that motion can only occur cooperatively, through rearrangement of many neighboring molecules. The effective activation energy barrier is much larger than the thermal energy. In this limit, the dynamics depends only on  $T$ , so that  $m_V = m_p$ . The very high activation energy reflects not a single energy barrier but rather the contribution from many different local barriers. When the activation energy becomes so large relative to the thermal energy, the molecular details are less important and an average value of  $m_p^{\max}$  gives a fair representation of the behavior. In this case, the motion is a cumulative result of many activated jumps; the effective activation energy is very high even though the single jump barriers may be small. The effect of small changes in the intermolecular barrier (i.e., those due to changes in volume) will be minimized. This interpretation reconciles the observation that, for a given material, the effect of temperature becomes more important close to  $T_g$  as the motion becomes more cooperative.

The universal behavior in Figure 4 shows that the different dynamics ( $58 \leq m_p \leq 95$  for the materials considered) reflects primarily  $\gamma$  varying between 8.5 and 1.9. This strong relationship between the volume dependence of the relaxation times and their temperature sensitivity is evidence that the volume dependence reflects the nature of the intermolecular potential, which in turn governs the effect of temperature. Thus, fundamentally,  $\gamma$ , while used to describe the volume dependence of  $\tau$ , effectively describes the intermolecular potential, in particular the steepness of the repulsive interactions.

## Summary

Equation 1 has been firmly established by different experimental techniques. Moreover, a recent paper<sup>23</sup> showed the existence of a correlation between the isochoric,  $m_V$ , and the isobaric,  $m_p$ , fragilities, with the former further correlated with the parameter  $\gamma$ . Combining the idea that  $\tau(T, v)$  approaching  $T_g$  is related to  $\gamma$ , with the fact that the high-temperature limiting dynamics of glass-formers is approximately universal, we find that the relaxation behavior in toto can be characterized by  $\gamma$ . Herein, these ideas are quantified by incorporating the correlations between  $m_V$  and  $m_p$  and  $m_V$  and  $\gamma$  in eq 8 to show that indeed the various dynamics of supercooled liquids are governed mainly by  $\gamma$ . A universal law (eq 9) is found, which describes the evolution of the dynamics with changing temperature and density for all polymeric and molecular glass-formers in the range from very short times up to the glass transition. This equation has three parameters ( $\gamma$ ,  $m_p^{\max}$ ,  $m_p^\infty$ ) which depend on the material, but only  $\gamma$  shows a significant variation, whereas  $m_p^{\max}$  and  $m_p^\infty$  are almost constants. The parameter  $\gamma$  takes into

account the different effects of  $T$  and  $V$  on the dynamics, so that once the material-specific quantities related to  $\gamma$  have been normalized (see eq 11), a universal power law is obtained for the dynamics of glass-forming systems. A noteworthy consequence of this universal behavior is the absence of any divergence in the description of the glass transition; that is, no underlying transition needs to be invoked to interpret the slowing down of the dynamics.

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