Theoretical and Experimental Study of Compression Effects on Structural Relaxation of Glass-Forming Liquids

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ABSTRACT: We develop the elastically collective nonlinear Langevin equation theory of bulk relaxation of glass-forming liquids to investigate molecular mobility under compression conditions. The applied pressure restricts more molecular motion and therefore significantly slows down the molecular dynamics when increasing the pressure. We quantitatively determine the temperature and pressure dependence of the structural relaxation time. To validate our model, dielectric spectroscopy experiments for three rigid and nonpolymeric supramolecules are carried out at ambient and elevated pressures. The numerical results quantitatively agree with experimental data.

INTRODUCTION

Investigating molecular dynamics of glass-forming liquids is one of the most intriguing topics. It has been experimentally established that the structural relaxation time ($\tau_\alpha$) reflecting the time scale for liquid structure reorganization systematically deviates from the simple Arrhenius behavior during the cooling process on approaching to the glass transition temperature ($T_g$), defined by $\tau_\alpha (T_g) = 100 \text{ s.}^{1,2}$ The non-Arrhenius dependence of the structural relaxation time, $\tau_\alpha$, has a universal character because it has been observed for different groups of glass-forming liquids (van der Waals and associated liquids, polymers, ionic liquids, molten metals, etc.). However, the degree of deviation of $\tau_\alpha$ from the Arrhenius law at $T_g$ is material-dependent and is characterized by means of fragility or steepness index, $m = [\partial \log_{10} \tau_\alpha / \partial (T/T_g)]_{T_g}$. Consequently, the parameter $m$ was used to introduce the strong versus fragile liquid classification scheme. According to this classification, strong liquids reveal temperature evolution of structural relaxation time, less deviating from the Arrhenius behavior than fragile ones.

Much efforts have been spent in the last decades to formulate satisfactory models being able to capture and explain all experimentally observed features of structural dynamics of glass-forming liquids. One of such successful approaches is the elastically collective nonlinear Langevin equation (ECNLE) theory of bulk relaxation.3−9 In this theory, a single molecular motion is considered as a consequence of its interactions with the nearest neighbors and molecular cooperativity outside the cage of neighboring molecules. The treatment leads to two strongly related but distinct barriers corresponding to local and elastically collective dynamics. Plugging these two barriers into Kramer’s theory gives the structural alpha relaxation times. To determine the temperature dependence of the structural relaxation times, Mirigian and Schweizer have used a thermal mapping, which is based on an equality between hard-sphere fluid and experimental isothermal compressibility. From this, the ENCLE theory has successfully described the alpha relaxation event of polymers3,7 and thermal liquids4−6 over 14 decades in time. However, amorphous drugs and many materials have no experimental data for the thermal mapping. It is impossible to compare ECNLE calculations with experiments. Recently, Phan and his coworkers8−10 proposed another density-to-temperature conversion based on the thermal expansion process to handle this issue.

The rapid cooling of liquid to obtain the glass is not the only way. An alternative method to vitrify it is squeezing (compression).11,12 Therefore, by changing the hydrostatic pressure of liquid, one can also control its molecular dynamics.11,12 Compression brings about an increase in the molecular packing, in consequence, leading to an increase of the structural relaxation time. Numerous experimental results11,12 show that the pressure counterpart of the Arrhenius law
\[ \tau_a = \tau_0 \exp \left( \frac{P \Delta V}{k_B T} \right) \]  
(1)

derived based on transition state theory fails to grasp the pressure dependence of \( \tau_a \) where \( \Delta V \) is the activation volume, \( P \) is the pressure, and \( k_B \) is the Boltzmann constant. The experimentally measured relaxation times are found to change with pressure much faster than predicted by eq 1.2.16 It indicates that the activation volume is not constant but in general increases with increasing pressure on approaching to a glassy state. An extension of the ECNLE theory2 was introduced in 2014 to understand compression effects on the glass transition. Authors used Schweitzer’s thermal mapping associated with the compressibility data measured at different pressures. However, theoretical predictions are more sensitive to pressure than experiments. Thus, it is crucial to propose a better model to determine quantitatively the pressure-dependant structural dynamics.

The main goal of this paper is to develop the ECNLE theory in a new approach to describe the pressure dependence of \( \tau_a \). To validate our development, we implement new dielectric spectroscopy measurements on three different rigid and nonpolymeric sizable molecules at a wide range of pressures and temperatures. Then, theoretical calculations are quantitatively compared to experimental results. Theoretical limitations are clearly discussed.

### THEORETICAL METHODS

**Formulation.** To theoretically investigate the structural relaxation time of amorphous materials, these materials are described as a fluid of disconnected spheres (a hard-sphere fluid) and we formulate calculations for activation events of a single particle. The hard-sphere fluid is characterized by a particle diameter, \( d \), and the number of particles per volume, \( \rho \). According to the ECNLE theory \(^3\) the dynamic free energy quantifying interactions of an arbitrary tagged particle with its nearest neighbors at temperature \( T \) is

\[
F_{\text{dyn}}(r) = \int_0^\infty dq \frac{q^2 d[S(q) - 1]^2}{12\pi \rho \Phi [1 + S(q)]} \exp \left[ \frac{-q^2 r^2(S(q) + 1)}{6S(q)} \right] - 3 \ln \frac{r}{d}
\]

where \( \Phi = \rho d^3/6 \) is the volume fraction, \( S(q) \) is the static structure factor, \( q \) is the wavevector, and \( r \) is the displacement of the particle. The dynamic free energy is constructed without considering effects of rotational motions. We use the Percus–Yevick (PY) integral equation theory\(^4\) for a hard-sphere fluid to calculate \( S(q) \). The PY theory defines \( S(q) \) via the direct correlation function \( C(q) = [S(q) - 1]/\rho S(q) \). The Fourier transform of \( C(q) \) is\(^5\)

\[
C(r) = -\left( \frac{1 + 2\Phi}{1 - \Phi} \right)^2 + \frac{6\Phi(1 + \Phi/2)^2}{(1 - \Phi)^3} \frac{r}{d}
\]

\[
- \frac{\Phi(1 + 2\Phi)^2}{2(1 - \Phi)^3} \frac{r^3}{d} \quad \text{for} \quad r \leq d
\]

\[
C(r) = 0 \quad \text{for} \quad r > d
\]

The free energy profile gives us important information for local dynamics. For \( \Phi \leq 0.43 \), \( F_{\text{dyn}}(r) \) monotonically decreases with increasing \( r \) and particles are not localized\(^6\) In denser systems (\( \Phi > 0.43 \)), one observes that the dynamical arrest of particles within a particle cage formed by its neighbors occurs and a free-energy barrier emerges, as shown in Figure 1. We determine the particle cage radius, \( r_{\text{cage}} \) as a position of the first minimum in the radial distribution function, \( g(r) \). The localization length (\( r_L \)) and the barrier position (\( r_b \)) are the local minimum and maximum of the dynamic free energy. The separation distance between these two positions, \( \Delta r = r_b - r_L \) is a jump distance. The local energy-barrier height is calculated by

\[
F_B = F_{\text{dyn}}(r_b) - F_{\text{dyn}}(r_L).
\]

Compression effects modify the motion of a single particle. The motion of a particle is governed by both nearest neighbor interparticle interactions and applied pressure. Under a high pressure condition, when a particle is displaced by a small distance (\( r \ll d \)), the applied pressure acts on a volume \( \Delta V(r) \approx d^3 r \) and causes the mechanical work. In addition, the free and the molecular volume are reduced with compression. For simplification purposes, we suppose that the volume fraction is insensitive to pressure. Thus, we propose a new and simple expression for the dynamic free energy

\[
F_{\text{dyn}}(r) \approx \int_0^\infty dq \frac{q^2 d[S(q) - 1]^2}{12\pi \rho \Phi [1 + S(q)]} \exp \left[ \frac{-q^2 r^2(S(q) + 1)}{6S(q)} \right] - 3 \ln \frac{r}{d} + \frac{P}{k_B T} \frac{r}{d^3}
\]

(5)

The diffusion of a particle through its cage is decided by rearrangement of particles in the first shell. The reorganization process slightly expands the particle cage and excites collective motions of other particles in the surrounding medium by propagating outward radially a harmonic displacement field \( u(r) \). By using Lifshitz’s continuum mechanics analysis,\(^7\) the distortion field in a bulk system is analytically found to be

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c00860)
where $\Delta r_{\text{eq}}$ is the cage expansion amplitude,\(^1,5\) which is

$$
\Delta r_{\text{eff}} = \frac{3}{\Delta r_{\text{cage}}^3} \left[ \frac{\rho^2}{2^2} - \frac{\rho \Delta r_{\text{cage}}^3}{192} + \frac{\Delta r_{\text{cage}}^4}{3072} \right]
$$

Since $\Delta r_{\text{eff}}$ is relatively small, particles beyond the first coordination is supposed to be harmonically oscillated with a spring constant at $K_0 = \left| \partial^2 F_{\text{dyn}}(r)/\partial r^2 \right|_{r_0}$. Thus, the oscillation energy of the oscillator at a distance $r$ is $K_0 r^2/2$. By associating with the fact that the number of particles at a distance between $r$ and $r + dr$ is $\rho g(r)4\pi r^2 dr$, we can calculate the elastic energies of cooperative particles outside the cage to determine contributions of nearest neighbor interactions and collective motions of particles. The elastic barrier, $F_{\text{cage}}$, is

$$
F_{\text{cage}} = 4\pi \rho \int_{r_0}^{\infty} r^2 g(r) K_0 \frac{L_0^2(r)}{2}
$$

For $r \geq r_{\text{cage}}$, $g(r) \approx 1$. The calculations allow us to determine contributions of nearest neighbor interactions and collective rearrangements to the activated relaxation of a particle.

Due to chemical and biological complexities, conformational configuration, and chain connectivity, local and nonlocal dynamics are nonuniversally coupled. In our recent work,\(^9\) an adjustable parameter $a_i$ is introduced to scale the collective elastic barrier as $F_{\text{cage}} \rightarrow a_i F_{\text{cage}}$. The treatment has simultaneously provided quantitatively good agreements between the theory and experiment in both the dynamic fragility and temperature dependence of structural relaxation time for 22 amorphous drugs and polymers.\(^9\) According to Kramer's theory, the structural (alpha) relaxation time defined by the mean time for a particle to diffuse from its particle cage is

$$
\tau_\alpha = 1 + \frac{2\pi}{\sqrt{K_b \rho}} \frac{k_b T}{d^2} \exp \left( \frac{F_{\text{cage}} + a_i F_{\text{cage}}}{k_b T} \right)
$$

where $K_b = |\partial^2 F_{\text{dyn}}(r)/\partial r^2|_{r_0}$ is the absolute curvatures at the barrier position and $\tau_s$ is the short time scale of relaxation. The explicit expression of $\tau_s$ is\(^4,5\)

$$
\tau_s = \frac{e^3}{d_r} \left[ 1 + \frac{1}{36\pi \phi} \int_0^\infty dq q^7 \left( \frac{S(q) - 1}{q^2} \right) \right]
$$

where $\tau_e$ is the Enskog time scale, $b(q) = 1/[1 - j_0(q) + 2j_2(q)]$, and $j_n(x)$ is the spherical Bessel function of order $n$. In various works\(^3,8,9\),\(^22,23\) of thermal liquids, polymers, and amorphous drugs, $\tau_s \approx 10^{-13}$ s.

To compare our hard-sphere calculations with the experiment, a density-to-temperature conversion (thermal mapping) is required. The initial thermal mapping proposed by Schweizer\(^7\) is

$$
S_0^\text{HS}(\Phi) = \frac{(1 - \Phi)^3}{(1 + 2\Phi)^2} = S_0^\text{exp}(T, P)
$$

where $S_0$ is the isothermal compressibility. Clearly, this mapping requires experimental equation-of-state (EOS) data. The superscripts HS and exp correspond to the hard sphere and experiment, respectively. Although this mapping has successfully provided both qualitative and quantitative descriptions for $r_L(T)$ for 17 polymers and thermal liquids,\(^3,5,7\) the EOS data is unknown for our three polymers presented in the next sections.

Thus, we employ another thermal mapping\(^8\) constructed from the thermal expansion process of materials. During a heating process, the number of molecules remains unchanged while the volume of material increases linearly. This analysis leads to $\rho \approx \rho_0 [1 - \beta(T - T_0)]$.\(^8\) Here, $\beta$ is the volume thermal expansion coefficient, and $\rho_0$ and $T_0$ are the initial number density and temperature, respectively. From this, we can convert from a volume fraction to temperature of experimental material via

$$
T \approx T_0 - \frac{\Phi - \Phi_0}{\beta \Phi_0}
$$

For most organic materials and amorphous drugs (22 materials),\(^8\) $\beta \approx 12 \times 10^{-4}$ K$^{-1}$. This value is consistent with Schweizer’s original mapping.\(^7\) $\Phi_0 \approx 0.5$ is the characteristic volume fraction estimated in our prior works.\(^8\) The parameter $T_0$ captures material-specific details such as molar mass and particle size. This density-to-temperature conversion has been used in the cooperative string model for supercooled dynamics.\(^21\) In our calculations, the parameters $T_0$ and $a_i$ are tuned to obtain the best quantitative agreement between theoretical and experimental temperature dependence of structural relaxation times.

**Ultralocal Limit.** Figure 1 shows an example dynamic free energy for $\Phi \approx 0.57$ at different pressures in the unit of $k_b T/d^3$ and defines the key length and energy scales. The localization length is nearly insensitive to compression. Meanwhile, the barrier position increases and the local barrier height is raised with increasing the applied pressure. The result implies that the compression induces more constraint to the local dynamics of the tagged particle.

When the local barrier is beyond a few $k_b T$, much insight for key length scales of the dynamic free energy has been gained using the approximate “ultralocal” analytic analysis. In the ultralocal limit, since $r_L/d_i \ll 1$, high wavevectors are dominant in calculations of $F_{\text{dyn}}(r)$. We can ignore the wavevector integral below a cutoff $q$, and exploit $C(q) = -4\pi d^3 g(q) \cos(qd)/q^3$ in the exact PY theory for $q \gtrsim q_1$.\(^3,22,23\) and $S(q) \approx 1$.

Combining the analytical expression of $C(q)$ and $S(q) \approx 1$ with $[\partial F_{\text{dyn}}(r)/\partial r]_{r \rightarrow r_L} = 0$ gives a self-consistent equation for the localization length and barrier position. Now, since $q r_L/\sqrt{3} \ll 1$, one obtains

$$
r_L \equiv r_L(P) = \frac{r_L(P = 0)}{1 + \frac{q}{\sqrt{5}} \frac{d}{k_b T/d_i} \frac{1}{4q^2 d_i/\pi}}
$$

where $r_L(P = 0) = (\sqrt{5}d_i/4q^2 d_i/\pi)$ is the localization length at $P = 0$ or ambient pressure.\(^22,23\) Equation 14 quantitatively reveals how
the external pressure restricts molecular motions. The localization length is reduced with increasing the compression. In addition, the Percus–Yevick theory for the contact number\(^{19}\) gives 
\[ g(d) = \frac{(1 + \Phi/2)}{(1 - \Phi)^2}. \]
Thus, \(4\pi g^2(d)\Phi \approx 110\) for \(\Phi = 0.57\) is much larger than the considered values of \(P/(k_BT/d^3)\). This finding explains why \(r_i(P)\) is nearly unchanged, as seen in Figure 1.

When \(q_r/\sqrt{3}\) is sufficiently large, one can use 
\[ \text{erfc}(x) \approx e^{-x^2}/(\sqrt{\pi}x) \]
to approximate \(r_b\) in eq 13 and then obtain 
\[ \frac{P}{k_BT/d^3} r_b \approx 3 - \frac{12\Phi g^2(d)}{\pi^2 d} \exp\left(-\frac{q_r^2 r_b^3}{3}\right) \] (15)

The analytic form in eq 15 qualitatively indicates an increase of \(r_b\) with increasing pressure, as observed in Figure 1. Since prior works\(^{22,23}\) show very poor quantitative accuracy of eq 15 compared to the numerical predictions at ambient pressure (\(P \approx 0\)), the deviation is expected to be large at elevated pressures. Thus, we do not show the corresponding curves.

The local barrier height \(F_B\) in the ultralocal limit\(^{22,23}\) can be analytically calculated as
\[
\frac{F_B}{k_BT} = -3 \ln \left(\frac{r_b}{r_L}\right) - \frac{12\Phi g^2(d)}{\pi^2 d} \int_{q_c}^{\infty} dq \frac{q^3}{q^2} - \exp\left(-\frac{q_r^2 r_b^3}{3}\right) \right]
\] (16)

Clearly, the growth of \(r_b\) with pressure is faster than that of \(\ln (r_b)\) and it leads to the pressure-induced rise of \(F_B\). At a given compression condition, we find that \(F_B\) increases linearly with \(\Phi g^2(d)\). Thus, \(F_B\) grows with \(\Phi\). The findings are consistent with numerical results shown in the inset of Figure 1. This analysis also reveals that adding the pressure term to the dynamic free energy as written in eq 5 exhibits the same manner as using eq 2 for hard-sphere fluids at higher effective volume fractions.

In addition, based on analysis in prior works,\(^{22,23}\) one can also perform a dynamic shear modulus in the ultralocal limit as
\[
G(P) = \frac{9\Phi k_BT}{5\pi d r_L^3(P)}
\]
\[ = \frac{9\Phi k_BT}{5\pi d r_L^3(P = 0)} \left(1 + \frac{P\sqrt{\pi/3}}{k_BT/d^3} \frac{1}{4g^2(d)\Phi}\right)^2 \]
\[ G(P = 0) \left(1 + \frac{P\sqrt{\pi/3}}{k_BT/d^3} \frac{1}{4g^2(d)\Phi}\right)^2 \] (17)

Equation 17 shows that \(G(P)\) hardly changes with the applied pressure.

### EXPERIMENTAL SECTION

**Materials.** The experiments were performed on three rigid and nonpolymeric sizable molecules. Two of the tested samples are planar and linear, and their chemical structure (shown in Figure 2) differ only in the end of the group (the diphenylamine–fluorene moiety is the same). In the material referred to M67, the metoxy–OCH3 group is the end, while in the sample named M68, the end of the group is the −CF3 moiety. The third material, entitled M71, encloses the other motif (i.e., carbazole–carbazole group) compared to M67 and M68, which leads to deflection of the chemical structure. All of tested samples were synthesized by Sonogashira coupling reaction between 4-iodoanisole (M67) or 4-iodobenzotri fluoride (M68 and M71) and ethynyl derivative of the diphenylamine–fluorene motif (M67 and M68) or ethynyl derivative of carbazole–carbazole moiety. The obtained compounds were purified by column chromatography, giving 99% purity of the samples.

**Dielectric Spectroscopy at Ambient Pressure.** The isobaric dielectric measurements at ambient pressure were carried out using the Novocontrol GmbH alpha impedance analyzer in the frequency range from 10\(^{-2}\) to 10\(^{6}\) Hz at various temperature conditions (329–353 K for M67, 326–371 K for M68, and 320–386 K for M71). The temperature was controlled by the Quatro temperature controller using a nitrogen gas cryostat with temperature stability better than 0.1 K. The tested sample was placed between two stainless steel electrodes of a capacitor (20 mm diameter) with a fixed gap between electrodes (0.1 mm) provided by fused silica spacer fibers. The dielectric measurements of M67 and M68 were performed after the vitrification by fast cooling from melting point (430 and 425 K, respectively), while M71 was measured during slow cooling from 386 K.

**Dielectric Spectroscopy at Elevated Pressure.** The isothermal dielectric measurements at elevated pressure were performed utilizing a high-pressure system with an MPS micro-pump (Unipress) and an alpha impedance analyzer (Novocontrol GmbH). The pressure was controlled with an accuracy better than 1 MPa by an automatic pressure pump, and the silicone oil was used as a pressure-transmitting fluid. The sample cell was the same as used during the measurements at ambient pressure (15 mm diameter of the capacitor and 0.1 distance between electrodes provided by a Teflon spacer). To avoid contact between the sample and pressure-transmitting fluid, the capacitor was placed in a Teflon ring and additionally wrapped by a Teflon tape. The temperature was controlled by a Weiss Umwelttechnik GmbH fridge with the precision being better than 0.1 K. The measurements were performed at 347 K (5–45 MPa) for M67, 338 K (0.1–28 MPa) for M68, and 338 K (0.1–28 MPa) for M71.

### RESULTS AND DISCUSSION

Representative dielectric spectra measured for M71 above the glass transition temperature are presented in Figure 3. As can
be seen, the structural relaxation process and dc conductivity (on the low-frequency flank of the $\alpha$-process) move toward lower frequencies with decreasing temperature (or with squeezing at isothermal conditions). From analysis of the dielectric loss peak, we obtained the relaxation time, $\tau_\alpha$, using the following definition: $\tau_\alpha = 1/2\pi f_{\text{max}}$ where $f_{\text{max}}$ is the maximum frequency of the structural relaxation peak. The log $\tau_\alpha$ as a function of (i) inverse of temperature is presented in Figure 4, while (ii) log $\tau_\alpha$ as a function of $P/P_g$ is depicted in Figure 5.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** (Color online) Dielectric loss spectra of M71 measured above glass transition temperature at ambient pressure.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** (Color online) Temperature dependence of structural relaxation time of M67, M68, and M71 under ambient pressure ($P \approx 0$). Open points are experimental data, and solid curves correspond to our ECNLE calculations.

Figure 4 shows theoretical and experimental log$_{10}\tau_\alpha$ of M67, M68, and M71 under atmospheric pressure ($P \approx 0$). Open points are experimental data, and solid curves correspond to our ECNLE calculations.

Figure 5 shows theoretical and experimental log$_{10}\tau_\alpha$ of M67, M68, and M71 at 347 K, 338 K, and 338 K versus pressure normalized by $P_g$ which is defined by $\tau_\alpha(P_g) = 1\text{ s}$. Open points are experimental data, and solid curves correspond to our ECNLE calculations.

for M71. Different chemical end groups cause the different relative importance of the collective elastic distortion and give various values of $a_c$. Overall, the ENCLE calculations agree quantitatively well with experimental data.

Under high compression effects, the motion of particles has more constraint and the relaxation process is significantly slowed down. From the previous section, we know that the barrier height $F_B$ and jump distance $\Delta r = r_B - r_L$ are increased with a pressure rise. Thus, the collective barrier $F_c \sim K_0\Delta r^4$ also grows. For simplification, we assume that the correlation between local and collective molecular dynamics in substances does not change when applying pressure. In addition, the thermal expansion coefficient $\beta$ and the characteristic temperature $T_0$ are supposed to remain unchanged with pressure. The assumption allows us to calculate the pressure dependence of structural relaxation time. Since pressure entering to the dynamic free energy in eq 5 is in the unit of $k_B T/d^3$, our numerical results can be compared to experimental data without introducing additional parameters by the pressure normalization.

Theoretical calculations and experimental data for log$_{10}\tau_\alpha$ versus normalized pressure of our three materials in an isothermal condition are contrasted in Figure 5. A fixed temperature, we use eq 12 to map from temperature to a packing fraction of the effective hard-sphere fluid in ECNLE calculations. Then, the pressure dependence of physical quantities for local dynamics and the alpha relaxation time are calculated using eq 5 when varying pressure. We define the glass transition pressure $P_g$ at $\tau_\alpha(P_g) = 1\text{ s}$ to normalize pressure. One observes a quantitatively good accordance between the theory and experiment shown in Figure 5. This agreement suggests that our simple assumption of ignoring effects of chemical and biological structures seems plausible. We do not need to consider steric repulsion between molecules since the hard-sphere models are still applicable during compression. However, this simplicity may cause deviation between the theory and experiment. Numerical results in Figure 5 also reveal that our extended ECNLE theory
is a predictive approach to investigate effects of pressure when only knowing parameters $T_0$ and $\alpha_c$ from molecular mobility at ambient conditions.

To compare with the experiment in a real unit of pressure (MPa), we establish an equality between the theoretical and experiment $P_g$ to calculate the particle diameter. Results are $d = 0.434$ nm for M67, $d = 0.567$ nm for M68, and $d = 0.575$ nm for M71. Experimental data and theoretical calculations for the pressure dependence of $\tau_\alpha$ of our three pure amorphous materials in isothermal processes are shown in Figure 6. One can see better quantitative consistency between the theory and experiment than in Figure 5 since $d$ is fixed and calculated at $P = P_g$. At a high-pressure regime, molecules are incompressible, while at low pressures (and/or ambient condition), molecules are internally relaxed and their volume becomes relatively larger. The curves of ECNLE calculations are slightly above those of experimental data. The theory–experiment deviation becomes more important at low compression.

Obviously, there is no universal way to determine $d$. If the diameter $d$ is calculated at a low-pressure regime, then the behavior is reversed and theoretical predictions deviate from the experiment at high pressures. These results clearly indicate that the external pressure not only reduces the free volume but also changes the molecular size. All factors change the packing fraction $\Phi$. In Figure 7a, we show the temperature or density dependence of $\tau_\alpha$ for a representative material (M71) under various pressure conditions. Increasing the packing fraction $\Phi$ and compression slows down the molecular dynamics in the same manner. The shrinking down process of molecules under large compression can be quantified by tuning the value of $d$ to obtain the best quantitative fit between theoretical and experimental $\log_{10}\tau_\alpha(P)$.

Based on theoretical calculations in Figure 7a, one can determine $T_g(P)$ defined as $\tau_\alpha(T_g) = 1$ s and the dynamic fragility of M71.

**Figure 6.** (Color online) Logarithm of structural relaxation time of M67 at 347 K, M68 at 338 K, and M71 at 338 K versus pressure in a unit of MPa. Open points are experimental data, and solid curves correspond to our ECNLE calculations.

**Figure 7.** (Color online) (a) Logarithm of structural relaxation time of M71 at different external pressures. A horizontal blue dashed line indicates a vitrification time scale criterion of 1 s. (b) Pressure dependence of the glass transition temperature of M71. The inset shows the theoretical fragility plotted versus external pressures in the unit of $k_B T/d^3$.

Numerical results are shown in Figure 7b. Generically, both $T_g$ and $m$ increase with compression. It means that this glass former becomes more fragile at elevated pressure. In the ECNLE theory, the higher fragility corresponds to more collective elasticity or greater effects of collective motions on the glass transition. This finding is consistent with prior simulations and experiments. We can explain this behavior using a nontrivial correlation among the cooling rate ($h$), glass transition temperature, and dynamic fragility:

$$m = \frac{\partial \log_{10}(\tau_\alpha)}{\partial (T_g/T)} \bigg|_{T = T_g}$$

(18)

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$$h_{\tau_\alpha}(T_g) = \frac{T_g}{m \ln(10)}$$

(19)
Since $\eta_{s}(T_g)$ is a constant, $m$ monotonically varies with $T_g$. Consequently, at a fixed temperature, the pressure-induced slowing down of the relaxation time shifts $T_g$ toward a larger value and causes an increase of $m$. We emphasize that this analysis can be changed if glass-forming liquids have strong electrostatic interactions and chemical/biological complexities.

**CONCLUSIONS**

We have developed the ECNLE theory of bulk relaxation to capture the pressure effects on the glass transition of glass-forming liquids. Amorphous materials are described as a hard-sphere fluid. Under compression conditions, a mechanical work done by the pressure acting on a tagged particle modifies its the dynamic free energy. The free energy profile provides the pressure dependence of key physical quantities of the local dynamics by only considering nearest neighbor interactions. The localization length is slightly reduced with increasing pressure, while the barrier position and local barrier height grows. These variations in the ultralocal limit (high densities or low temperatures) have been analytically analyzed. Our calculations indicate that further restrictions apply to the local dynamics. It leads to a significantly slowing down of molecular mobility when applying pressure. The validity of our theoretical approach has been supported by dielectric spectroscopy experiments. We measured the dielectric loss spectra of three different materials to determine the alpha structural relaxation time at ambient and elevated pressures over a wide range of temperatures. Our theoretical temperature and pressure dependence of the structural relaxation time quantitatively agree with experimental data.

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Notes

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