PHYSICAL REVIEW E **75**, 061203 (2007)

Scaling of the structural relaxation in simulated liquid silica

A. Le Grand, C. Dreyfus, C. Bousquet, and R. M. Pick
I.M.P.M.C., Université Pierre et Marie Curie-Paris 6 and CNRS-UMR 7590, Paris, France

(Received 2 November 2006; revised manuscript received 7 February 2007; published 19 June 2007)

A scaling law for the α relaxation time τ, involving the ratio of a density-dependent energy to the thermal energy, has been found to hold in many fragile glass-forming liquids. This scaling has been recently linked to a local quantity $n_{loc}(\rho,T)$ relating the variation of τ with density to its variation with temperature. In many fragile liquids, the variation of $n_{loc}(\rho,T)$ is weak enough to take it as constant over the experimental temperature and density domain. We show that simulated liquid silica has an opposite behavior; close to T_g, n_{loc} is negative for moderate densities and exhibits a significant variation with ρ and T, reaching positive values for higher temperature and/or densities. Moreover, those variations linearly correlate to a measure of the bonding properties of the liquid.

DOI: 10.1103/PhysRevE.75.061203 PACS number(s): 61.20.−p, 64.70.Pf, 66.10.−x, 66.20.+d

The main characteristic of supercooled liquids is the huge variation of several quantities such as the shear static viscosity η or the structural relaxation time τ [1] when the liquid, avoiding crystallization, goes from the liquid to the glassy state: throughout the transition, these coefficients increase by more than 14 orders of magnitude [2]. Although the liquid-glass transition is still not fully understood, several major advances have been performed during the last decades, one of them being the classification into strong and fragile glass-forming liquids according to the behavior of the structural relaxation time τ when plotted in the Angell diagram [2,3]. Actually, no consensus has been reached so far on an analytical expression of τ versus temperature at ambient pressure, although the most commonly used is the Vogel-Fulcher law: $\ln(\tau/\tau_0)=B/k_B(T-T_0)$ where τ_0, B, and T_0 are the relaxation time at high temperature, an activation energy, and a temperature located below the liquid-glass transition temperature, T_g, respectively.

Only quite recently have experimental developments allowed the extension of the measurements over a significant pressure range [4,5]. In order to take into account the increase of relaxation time due to increased pressure, extensions of the Vogel-Fulcher law under the form $\tau=\tau(T,P)$ have been proposed [6]. Though such an expression is mathematically correct, another formulation can also be used and leads to more insight. Let us express τ under the form

$$\tau=\tau(\Gamma(\rho,T)), \tag{1}$$

where ρ is the mass density. Recent experiments [7–13] have shown that, for a large number of organic and polymeric, fragile and intermediate glassformers, the use of the equation of state (EOS), $\rho=\rho(T,P)$, enables one to write the control parameter $\Gamma(\rho,T)$ in the simple form

$$\Gamma(\rho,T)=\frac{E(\rho)}{k_BT}. \tag{2}$$

Γ is separable into the ratio of an energy $E(\rho)$ to the Boltzmann factor k_BT. In addition, in many [13,14], but not all [15], glass-forming liquids where Eq. (2) holds, the whole α dynamics measured in dielectric absorption is determined by the value of Γ: the spectra measured at different temperatures and pressures, but for the same relaxation time τ, can be superimposed over a large frequency range around $\omega\tau=1$.

Furthermore, it was found that for all the liquids studies so far, $E(\rho)$ could be expressed as [8,10–13]

$$E(\rho)=E_0\left(\frac{\rho}{\rho_0}\right)^n, \tag{3}$$

where E_0, ρ_0, and n are, respectively, a material-dependent energy, a reference density, and a positive number [16]. The parameter n is estimated by optimizing the collapse on a single curve, $\tau=\tau(\rho^n/T)$, of the various relaxation times measured at variable temperatures and pressures. Obtained that way, n is an averaged quantity; i.e., it does not depend on T and/or ρ. Yet there is no reason for Eqs. (2) and (3) to be valid over the whole part of the (ρ,T) plane where the system is a liquid: for example, the pressure exerted on the system might lead to progressive but substantial changes in the bonding between molecules or atoms [17], liable to alter the simplicity of these equations. A change of fragility and/or the impossibility of scaling the relaxation times have been recently reported [18] in different hydrogen-bonding liquids and proposed to originate from such an effect.

The purpose of this report is to make use of a local quantity—i.e., defined at each thermodynamic state—$n_{loc}(\rho,T)$, in order to avoid the averaging process on temperature and density implicitly involved in the determination of n. Let us consider a small increase $\delta\tau$ of the relaxation time $\tau(\rho,T)$. $\delta\tau$ can be written as

$$\frac{\delta\tau}{\tau}=\frac{T}{\tau}\left(\frac{\partial\tau}{\partial T}\right)_\rho\frac{\delta T}{T}+\frac{\rho}{\tau}\left(\frac{\partial\tau}{\partial\rho}\right)_T\frac{\delta\rho}{\rho}=\frac{T}{\tau}\left(\frac{\partial\tau}{\partial T}\right)_\rho\left(\frac{\delta T}{T}-n_{loc}\frac{\delta\rho}{\rho}\right), \tag{4}$$

where $n_{loc}(\rho,T)$ is given by

$$n_{loc}=-\frac{\dfrac{\rho}{\tau}\left(\dfrac{\partial\tau}{\partial\rho}\right)_T}{\dfrac{T}{\tau}\left(\dfrac{\partial\tau}{\partial T}\right)_\rho}. \tag{5}$$

The numerator and denominator of Eq. (5) are the dimensionless coefficients introduced by Win and Menon [19] which they called, respectively, "generalized isothermal fragility with respect to ρ" and "generalized isochoric fragility with respect to T." In their dielectric study of glycerol, they pointed out the link between the exponent n of the scaling law, Eq. (3), and the ratio of these fragilities, a link which was later also mentioned by Casalini *et al.* [20]. When determining the ratio, Eq. (5), at each thermodynamic state, Win and Menon found n_{loc} varying between 1.2 and 1.7, a variation that they tentatively attributed to the different parts of the potential explored when varying the density. Simultaneously, they obtained a rather poor scaling of τ using Eqs. (1)–(3), the best exponent being $n=1.4$. Yet in a similar dielectric study of glycerol, Reiser *et al.* [21] found that the same n value gave a rather convincingly scaling of their own data.

If n_{loc} is independent of ρ and T, all the solutions of the partial differential equation for τ, Eq. (5), are functions of the form $\tau=\tau(\rho^n/T)$ with $n=n_{loc}$. $n_{loc}=n=\text{const}$ is thus a necessary and sufficient condition for the set of equations (2) and (3) to be valid. Vice versa, to ascertain the possible variation of n_{loc} requires knowledge of the partial derivatives of τ over a large range of temperature and density. For the time being, the relative temperature and density ranges explored in most of the experiments are not larger than 30% [8,10–13,18–21]. The systematic variations of n_{loc} are smaller than or of the same order as their experimental uncertainties. As an example, the estimates of n_{loc} from the photon correlation data in ortho-terphenyl (*o*TP), discussed in [12], yield a mean value 4.25 with a dispersion of 0.15 while the fit of $\tau(\rho,T)$ leads to $n=4.1\pm0.1$. So far, even in experiments exploring a larger temperature and/or density domain [10–13,18–21] than in this *o*TP experiment, one can find a value of n leading to a scaling, Eq. (3), of all the data, and the example of glycerol given above illustrates the difficulty of ascertaining a variation of n_{loc}.

Numerical simulations provide an alternative, powerful, route to obtain $n_{loc}(\rho,T)$, as they allow for much larger variations of ρ and T. Liquid silica [22,23] has been extensively studied that way in a very large temperature and density domain. Moreover, simulated silica is extremely interesting because, as in water [24], the diffusion coefficients, here for oxygen and silicon, increase with increasing density in some regions of the (ρ,T) phase diagram. This implies a corresponding decrease of the structural relaxation time. According to Eq. (5), it means that n_{loc} must be negative in these regions, a situation not found in the usual glassformers. In this paper, it will be shown that, as expected, the large variations of ρ or T offered by these computations allow one to invalidate Eq. (3) and that these variations of n_{loc} are quantitatively correlated with the change of bonding which simultaneously takes place.

Simulations of silica properties have been recently performed between 2500 K and 7000 K and between 2.3 g cm^{-3} and 4.2 g cm^{-3}, and have yielded the translational diffusion coefficients $D(\rho,T)$ of oxygen [22] or of silicon [23]. Horbach and Kob [25] found that the results of similar simulations performed at ambient pressure are in reasonable agreement with those obtained on the real strong glass-forming liquid silica. From these diffusion coefficients, we first derived a relaxation time τ using the Einstein relation between τ and D, $\tau=AT/D(\rho,T)$, and assuming the coefficient A to be only weakly dependent on ρ and T [26] compared to the four orders of magnitude variation of D. The numerical determination of the partial derivatives $\left(\frac{\partial\tau}{\partial\rho}\right)_T$ and $\left(\frac{\partial\tau}{\partial T}\right)_\rho$, Eq. (5), was performed as follows: first, the relaxation times at constant density and variable temperature are fitted by Vogel-Fulcher laws while those at constant temperature and variable density are fitted by sigmoid curves; second, the partial derivatives of these analytical expressions are calculated at every temperature and density.

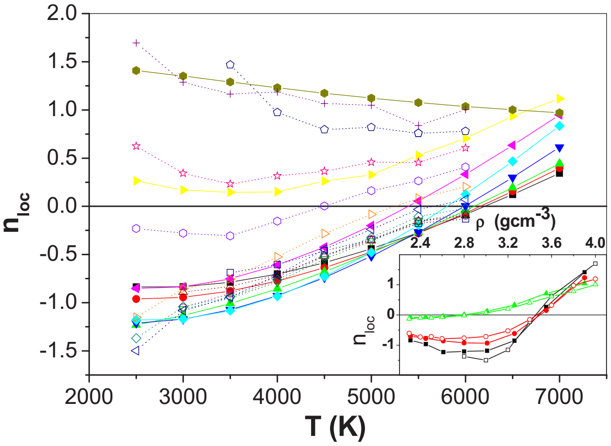

FIG. 1. (Color online) Thermal variation of n_{loc} in simulated SiO$_2$ at different densities: From [23], silicon atom: $\rho=2.31$ g cm^{-3} (■), 2.45 g cm^{-3} (●), 2.61 g cm^{-3} (▲), 2.8 g cm^{-3} (▼), 3.01 g cm^{-3} (♦), 3.26 g cm^{-3} (◀), 3.55 g cm^{-3} (▶), 3.9 g cm^{-3} (⬢). From [22], oxygen atom: $\rho=2.3$ g cm^{-3} (□), 2.4 g cm^{-3} (○), 2.5 g cm^{-3} (△), 2.6 g cm^{-3} (▽), 2.8 g cm^{-3} (◇), 3.0 g cm^{-3} (◁), 3.2 g cm^{-3} (▷), 3.4 g cm^{-3} (⬡), 3.6 g cm^{-3} (☆), 3.8 g cm^{-3} (⬠), 4.0 g cm^{-3} (+). Inset: density variation of n_{loc} at different temperatures: From [23], $T=2500$ K (■), 4000 K (●), 6000 K (▲). From [22], $T=3000$ K (□), 4000 K (○), 6000 K (△).

The variation of n_{loc} with temperature along various isochors is shown in Fig. 1 [27]. In the inset, n_{loc} is reported versus density for three temperatures $T=2500$ K, 4000 K, and 5500 K. The error Δn_{loc} in n_{loc} introduced by our numerical method has been estimated by considering the maxima of the diffusion coefficient of the oxygen atom plotted versus the density reported in [22]. These maxima are located around $\rho=3.4$ g cm^{-3} for temperatures between 2500 K and 4000 K, and, following Eq. (5), they represent points of the phase diagram for which $n_{loc}=0$. The nonzero values of n_{loc} obtained by our computational method for the same temperatures and densities provide an estimate $\Delta n_{loc}\approx0.25$ of the numerical accuracy. Such values are not expected to change much with temperature and density. The values of n_{loc} obtained from the diffusion coefficients of oxygen and silicon are in good agreement and, when calculated for the same density, are within this numerical accuracy. In a large density range (2.3 g cm$^{-3}<\rho<3.3$ g cm^{-3}), n_{loc} is approximately density independent and varies only weakly with temperature. Its mean value below $T=4000$ K is $n_{loc}=-1.0$, and in the broader temperature domain 2500 K$<T<7000$ K, it can be linearly approximated by

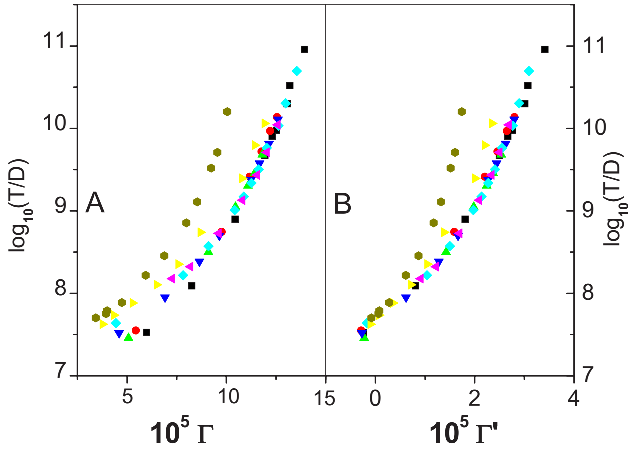

FIG. 2. (Color online) Scaling of the relaxation time of Si atoms in simulated SiO_2 [23]: (A) $\log_{10}(T/D)$ vs $\Gamma=\rho^n/T$, with $n=-1.05$ (best fit); (B) $\log_{10}(T/D)$ vs $\Gamma'=\rho^n(1+\alpha T)/T$ with $n=-2.0$ and $\alpha=1.55\times10^{-4}$ (best fit). Same symbols as in Fig. 1. Note that the scaling does not work for $\rho=3.55\text{ g cm}^{-3}$ and $\rho=3.9\text{ g cm}^{-3}$, even in (B).

$$n_{loc}=-2.0+3.1\times10^{-4}T.$$

On the contrary, for densities $3.3\text{ g cm}^{-3}<\rho<3.8\text{ g cm}^{-3}$, n_{loc} depends strongly on the density while its temperature dependence is still weak. Although for $\rho>3.8\text{ g cm}^{-3}$ simulation data are scarce, the variation of n_{loc} with density and temperature seems again weak in this domain.

The variation of n_{loc} reported in Fig. 1 is another, original, way of describing the variation of the diffusion coefficients already reported in [22,23]. Furthermore, a new and important fact emerges: the density-independent and weak temperature-dependent variation of n_{loc} for $\rho<3.3\text{ g cm}^{-3}$ contrasts with its strong variation with density for $\rho>3.3\text{ g cm}^{-3}$. Figure 1 also calls for three remarks.

(i) Qualitatively, as could be anticipated, the scaling $\Gamma\propto\rho^n/T$ is appropriate only in a relatively narrow T and ρ range: as soon as the variation of T and/or ρ exceeds 50%, it becomes inadequate. This is shown in Fig. 2(A) where τ is plotted versus Γ for $n=-1.05$ (best fit coefficient). The scaling is good for the temperature-density range ($T=2500-4000$ K; $\rho=2.3-3.3\text{ g cm}^{-3}$), but fails above 4000 K for the lower densities and at all temperatures for densities higher than 3.3 g cm^{-3}.

(ii) A second, phenomenological, remark is related to the systematic variation of n_{loc} with temperature observed in Fig. 1. Assuming that the density dependence of n_{loc} can be neglected with respect to its temperature dependence and solving the partial derivatives equation defining n_{loc}, Eq. (5), one finds that the control parameter Γ is still the product of the function $E(\rho)$ given by Eq. (3) by a function of T. Yet that function is no longer the inverse of the Boltzmann factor but takes the form $f(T)/k_BT$, where $f(T)$ describes the renormalization of the energy numerator of Eq. (2) by the temperature. In particular, when n_{loc} may be represented, as is the case here, by $n_{loc}=n(1+\alpha T)$, $f(T)$ is also given by the linear function $1+\alpha T$, with $n<0$ and $\alpha<0$. Figure 2(B) shows that this new form of scaling is very effective over the whole temperature range for densities $2.3\text{ g cm}^{-3}<\rho<3.3\text{ g cm}^{-3}$, even if it appears unphysical at high temperatures, $f(T)$ becoming negative for $T=7000$ K. It is quite remarkable that such a correction is sufficient to obtain an effective scaling in the case of simulated silica which, at first sight, is so different from the usual organic glass-forming liquids, particularly concerning the large change of its structure with density and/or temperature.

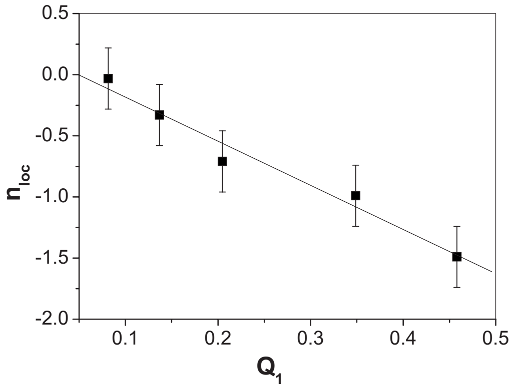

FIG. 3. n_{loc} as a function of Q_1, relative weight of the tetrahedral order with respect to the full distribution of the local order parameter q [22] (see text).

(iii) Our final and most important remark is related to a possible interpretation of the ρ and T dependence of n_{loc} shown in Fig. 1. Our motivation for the introduction of n_{loc} was the idea that Eq. (2) should not remain valid when, e.g., pressure would modify the bonding between the constituents of the supercooled liquid. We can substantiate this idea through the use of one of the results of Shell *et al.* [22] who defined a local orientational order parameter q. The latter is related to the mean angle θ between two Si-Si bonds involving the same Si atom. With their definition, $q=1$ for a tetrahedral environment ($\theta=109°$) and 0.375 for an octahedral one ($\theta=90°$). The q distribution has been computed [22] for the density $\rho=3\text{ g cm}^{-3}$ at different temperatures and exhibits a bimodal shape, indicating that these two different environments are simultaneously present in the liquid. The first mode has a maximum at $q\approx0.9$, characterizing a high, local, Si-Si tetrahedral order; the second maximum is at $q\approx0.45$ and corresponds approximately to a local octahedral arrangement. This bimodal distribution can be correctly described as the sum of two Gaussian curves centered at those two q values and with relative weights Q_1 and $Q_2=1-Q_1$, respectively. For the q distributions at $\rho=3\text{ g cm}^{-3}$ reported in [22], the weight Q_1 varies from 0.45 for $T=2500$ K to 0.05 for $T=5500$ K, with no information at higher temperatures. The plot of n_{loc} versus Q_1 is shown in Fig. 3; its linear variation shows quantitatively the direct relation between the dynamical quantity n_{loc} and the structural quantity Q_1.

To summarize, a weak variation with temperature and density of $n_{loc}(\rho,T)$, defined by

$$\frac{\delta\tau}{\tau}\propto\frac{\delta T}{T}-n_{loc}\frac{\delta\rho}{\rho}, \tag{6}$$

mathematically translates in the scaling law Eq. (3). This variation is not always weak: simulated silica is a counterexample. At densities lower that 3.3 g cm^{-3}, it exhibits a large variation with temperature, passing from a negative (n_{loc}= −1.0) value at low temperature to a positive value at 7000 K. We have shown that this variation correlates linearly with the change of bonding in the liquid. This suggests that the understanding of the structural arrest may be more complex in a strong glass-forming liquid like silica than in the fragile ones because it likely involves changes in the local environment of a bonded atom that do not take place in the fragile liquids.

We thank M. S. Shell and I. Saika-Voivod for sending us data on simulated SiO_2. We also thank A. Patkowski, J. Gapinski, and W. Steffen for fruitful discussions on the glass-forming liquids problem.

---

[1] From here on, the discussion will be based on the relaxation time τ, although it could as well involve the viscosity η.

[2] W. Götze, in *Liquids, Freezing, and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Plenum, New York, 1989), p. 287; C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. **88**, 3113 (2000).
[3] C. A. Angell, in *Relaxation in Complex Systems*, edited by K. L. Ngai and G. B. Wright, National Technical Information Service (U.S. Department of Commerce, Springfield, VA, 1985).
[4] G. Floudas, Prog. Polym. Sci. **29**, 1143 (2004).
[5] M. Paluch, J. Gapinski, A. Patkowski, and E. W. Fischer, J. Chem. Phys. **114**, 8048 (2001); A. Patkowski, M. Paluch, and H. Kriegs, *ibid.* **117**, 2192 (2002).
[6] G. Fytas, T. Dorfmüller, and C. H. Wang, J. Phys. Chem. **87**, 5041 (1983); M. Paluch, R. Casalini, A. Best, and A. Patkowski, J. Chem. Phys. **117**, 7624 (2000).
[7] C. Alba Simionesco, D. Kivelson, and G. Tarjus, J. Chem. Phys. **116**, 5033 (2002).
[8] C. Dreyfus, A. Aouadi, J. Gapinski, M. Matos-Lopes, W. Steffen, A. Patkowski, and R. M. Pick, Phys. Rev. E **68**, 011204 (2003).
[9] G. Tarjus, D. Kivelson, S. Mossa, and C. Alba Simionesco, J. Chem. Phys. **120**, 6135 (2004).
[10] R. Casalini and C. M. Roland, Phys. Rev. B **69**, 094202 (2004); Phys. Rev. E **69**, 062501 (2004).
[11] C. Alba-Simionesco, A. Caillaux, A. Alegria, and G. Tarjus, Europhys. Lett. **68**, 58 (2004).
[12] C. Dreyfus, A. Le Grand, J. Gapinski, W. Steffen, and A. Patkowski, Eur. Phys. J. B **42**, 309 (2004).
[13] C. M. Roland, S. Hensel-Bielowska, M. Paluch, and R. Casalini, Rep. Prog. Phys. **68**, 1405 (2005).
[14] S. Hensel-Bielowka, S. Pawlus, C. M. Roland, J. Ziolo, and M. Paluch, Phys. Rev. E **69**, 050501(R) (2004).

[15] This property was not found to hold in several hydrogen-bonded glass-forming liquids where the discrepancy has been attributed to a change of chemical structure [13].

[16] Other forms have been successfully tested on some glassformers [9,12]; they will not be considered here.

[17] See, e.g., *Science and Technology of High Pressure*, edited by M. H. Manghani, W. J. Nellis, and M. Nicol (Universities Press, Hyderabad, 2000).
[18] K. Grzybowska, S. Pawlus, M. Mierzwa, M. Paluch, and K. L. Ngai, J. Chem. Phys. **125**, 144507 (2006); A. Grzybowski, K. Grzybowska, J. Ziolo, and M. Paluch, Phys. Rev. E **74**, 041503 (2006); C. M. Roland, S. Bair, and R. Casalini, J. Chem. Phys. **125**, 124508 (2006).
[19] K. Z. Win and N. Menon, Phys. Rev. E **73**, 040501(R) (2006).
[20] R. Casalini, K. J. McGrath, and C. M. Roland, J. Non-Cryst. Solids **352**, 4905 (2006).
[21] A. Reiser, G. Kasper, and S. Hunklinger, Phys. Rev. B **72**, 094204 (2005).
[22] M. S. Shell, P. G. Debenedetti, and A. Z. Panagiotopoulos, Phys. Rev. E **66**, 011202 (2002).
[23] I. Saika-Voivod, F. Sciortino, and P. H. Poole, Phys. Rev. E **69**, 041503 (2004).
[24] J. Jonas, T. Defries, and D. J. Wilbur, J. Chem. Phys. **65**, 582 (1976); C. A. Angell, E. D. Finch, and P. Bach, J. Chem. Phys. **65**, 3063 (1976); F. X. Prielmeier, E. W. Lang, R. J. Speedy, and H.-D. Lüdemann, Phys. Rev. Lett. **59**, 1128 (1987).
[25] J. Horbach and W. Kob, Phys. Rev. B **60**, 3169 (1999).

[26] A has been calculated at ambient pressure in Ref. [25]. It decreases only by a factor 3 between 2900 K and 6250 K.

[27] Note that, while the values of n_{loc} reported in Fig. 1 correspond to a large relative variation of temperature, $\Delta T/T_g \sim 3.5$, τ (cf. Fig. 2) varies only by a factor of 10^4. Conversely, a relative variation of temperature $\Delta T/T_g \sim 1$ in a fragile glass-forming liquid like *o*TP corresponds to τ varying by a factor of 10^{12}.