COMMENTS

Comment on "Translation-rotation paradox for diffusion in fragile glass-forming liquids"

Hans Sillescu

Institut für Physikalische Chemie, Universität Mainz, Jakob-Welder-Weg 15, D-55099 Mainz, Germany

F. H. Stillinger and J. A. Hodgdon [Phys. Rev. E **50**, 2064 (1994)] have proposed a "fluidized domain" model to explain that the diffusion coefficient ratio $D_{\text{trans}}/D_{\text{rot}}$ increases by a factor of $\sim 10^2$ on approaching the glass transition from above in fragile liquids. In their numerical estimates they make ad hoc assumptions that lead to a very small volume fraction $\phi_0 \sim 10^{-5}$ of the fluidized domains. It is shown how these assumptions can be avoided and $\phi_0 \sim 10^{-1}$ results from experimental values of D_{trans}, D_{rot}, and the width of the D_{rot} distribution. A modification of the Stillinger-Hodgdon model can be derived from the two-state model of Beckert and Pfeifer [Ann. Phys. (Leipzig) **16**, 262 (1965)] and yields experimental estimates of a few nanometers for the fluidized domains.

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Stillinger and Hodgdon [1] (SH) have assumed in their model that a supercooled liquid contains "fluidized domains" of volume v_0 and volume fraction ϕ_0 having a lifetime t_0 which is subject to the condition

$$\tau_0^{\text{rot}} = 1/2D_0^{\text{rot}} \ll t_0 \ll v_0^{2/3}/6D_0^{\text{trans}} , \tag{1}$$

where the diffusion coefficients D_0^{trans} and D_0^{rot} obey the Stokes-Einstein-Debye (SED) relation

$$D_0^{\text{trans}} = k_B T/6\pi\eta_0 R = \tfrac{4}{3}R^2 D_0^{\text{rot}} \tag{2}$$

with the shear viscosity η_0 inside the fluidized domains. This results in the important relations for the mean diffusion coefficient in the whole liquid [see Eqs. (3.5) and (3.6) of SH]:

$$D_{\text{rot}} = \phi_0/2t_0 , \tag{3}$$

$$D_{\text{trans}} = \phi_0 D_0^{\text{trans}} . \tag{4}$$

In order to obtain numerical estimates of v_0, t_0, etc., they make three *ad hoc* assumptions.

(1) The number of molecules in a fluidized domain is

$$n_0 = \rho v_0 \sim 10^4 , \tag{5}$$

where ρ is the number density.

(2) The viscosity η_0 is given by the geometric mean

$$\eta_0(T_g) \cong [\eta(T_m)\eta(T_g)]^{1/2} \tag{6}$$

of the experimental shear viscosities η at the melting and glass temperatures, T_m and T_g, respectively.

(3) The lifetime t_0 of a fluidized domain is given by the geometric mean of the upper and lower bounds of the ine-

qualities in Eq. (1):

$$t_0 \cong 2\pi\eta_0 R^2 v_0^{1/3}/k_B T . \tag{7}$$

For orthoterphenyl (OTP), these assumptions yield $\eta/\eta_0 \cong 3.3 \times 10^6$ and $t_0 = 0.43$ s at T_g (see Table II of SH). From the observation [2] that the experimental translational diffusion coefficient of fragile liquids D_{trans} is larger than the SED prediction $D_{\text{SED}}^{\text{trans}} = k_B T/6\pi\eta R$ by a factor μ they obtain from Eq. (4):

$$\phi_0 = D_{\text{trans}}/D_0^{\text{trans}} = \mu D_{\text{SED}}^{\text{trans}}/D_0^{\text{trans}} = \mu\eta_0/\eta . \tag{8}$$

The experimental value $\mu \sim 10^2$ in OTP at T_g yields $\phi_0 \cong 3.1 \times 10^{-5}$ (Table II of SH).

The three assumptions of SH are not necessary and can be replaced by experimental data as follows. The viscosity η_0 inside the fluidized domains can be estimated via Eq. (2) from the shortest rotational correlation time of the correlation time distribution, which is known to extend over about three decades in OTP at T_g as estimated from the Kohlrausch parameter β in Fig. 1 of Ref. [3]. Since the mean correlation time τ_{rot} is dominated by the large values of the correlation time distribution and obeys the SED relation, Eq. (2), with the experimental shear viscosity η instead of η_0 one obtains [4]

$$\tau_{\text{rot}}\tau_0^{\text{rot}} = \eta/\eta_0 \sim 10^3 , \tag{9}$$

which is much smaller than the SH estimate of 3.3×10^6 from Eq. (6). Hence, Eq. (8) yields the large value of $\phi_0 \sim 10^{-1}$ and from Eq. (3) we obtain [5] $t_0 \cong 6.5 \times 10^3$ s if the SED value of D_{rot} is used with η instead of η_0. These numbers are obtained without any change of the SH

model by just replacing their arbitrary geometric mean estimates of Eqs. (6) and (7). Of course, the large ϕ_0, value provides a rather different picture of a glass-forming liquid at T_g, since now the fractions of fluidized and solidified domains are of the same order of magnitude [4]. This suggests the following modification of the SH model, which allows one to replace the *ad hoc* assumption of $n_0 \sim 10^4$ [Eq. (5)] by an experimental quantity.

The second inequality of Eq. (1), $t_0 \ll v_0^{2/3}/6D_0^{\text{trans}}$, is applied twice by SH, first for the estimate of t_0, which is not necessary as we have shown, and second, to rationalize translational diffusion under the condition of the extremely small volume fraction of the fluidized domains $\phi_0 \sim 10^{-5}$, which requires that the mean square displacement during the lifetime t_0 inside a fluidized domain, $\langle r(t_0)^2 \rangle^{1/2} = (6t_0 D_0^{\text{trans}})^{1/2}$, is much less than the domain size. This assumption is not necessary with our much larger ϕ_0. Furthermore, our much larger η_0 yields from Eqs. (2) and (9) at T_g [5]

$$\langle r(t_0)^2 \rangle^{1/2} = (6t_0 D_0^{\text{trans}})^{1/2} = (t_0 k_B T_g / \pi \eta_0 R)^{1/2}$$
$$= 7.0 \text{ nm} , \quad (10)$$

which is of the order of the domain size $v_0^{1/3} = 15.0$ nm *assumed* by SH in Eq. (5) (Table II of SH). However, their assumption is not necessary since we see from Eq. (1) that the lifetime t_0 is sufficiently long for a molecule to diffuse over a distance [5] which is obtained in many experiments as the size of cooperative domains at T_g [6]. Therefore, we propose to do without the assumption of Eq. (5) and replace the second inequality in Eq. (1) by an *equality*:

$$t_0 \cong v_0^{2/3}/6D_0^{\text{trans}} . \quad (11)$$

This yields with Eq. (10) the domain size [5]

$$v_0^{1/3} \cong \langle r(t_0)^2 \rangle^{1/2} = 7.0 \text{ nm} . \quad (12)$$

With this new *assumption* the modified SH model becomes physically equivalent to a model of the present author (see *Note added in proof* of Ref. [3]), both being based upon a two-state model published in 1965 by Beckert and Pfeifer [7,8]. Here, the molecules are exchanged between two states ("phases") which can be identified with "fluidized domains" and "solidified domains." If τ_f ($= t_0$) is the lifetime of a molecule in a fluidized domain the detailed balance condition requires that the solidified molecules have lifetimes

$$\tau_s = \tau_f(1-\phi_0)/\phi_0 , \quad (13)$$

where ϕ_0 is the volume fraction of the fluidized molecules. If one assumes that rotational correlation times τ_{lf}^{rot} and τ_{ls}^{rot} of the Legendre polynomials $P_l(\cos\theta)$ of order l in the f and s states are subject to the inequalities

$$\tau_{lf}^{\text{rot}} \ll \tau_f, \tau_s \ll \tau_{ls}^{\text{rot}} , \quad (14)$$

where τ_f and τ_s may differ considerably [see Eq. (13)] one obtains for the rotational correlation functions [7]

$$g_l(t) = \phi_0 \exp(-t/\tau_{lf}^{\text{rot}}) + (1-\phi_0) \exp(-t/\tau_s) , \quad (15)$$

and for the mean rotational correlation time

$$\tau_l^{\text{rot}} = \int_0^\infty g_l(t)dt \approx \tau_s(1-\phi_0) = \tau_f(1-\phi_0)^2/\phi_0 . \quad (16)$$

It should be noted that Eqs. (13)–(16) are in harmony with the SH model in the limit $\phi_0 \ll 1$. However, the time constants of Eq. (15) given by $\tau_{\text{solid}} = t_0(1-\phi_0)/\phi_0 = 1.4 \times 10^4$ s and $\tau_{\text{fluid}} = 4\pi\eta_0 R^3/k_B T = 2.0 \times 10^{-2}$ s (for OTP at T_g) in the SH model cannot mimic a "distribution of correlation times" because of the tiny weight of $\phi_0 = 3 \times 10^{-5}$ for τ_{fluid}. This is clearly inconsistent with experiment, since it implies that the molecules cannot move at all during the time τ_{solid} and the resulting rotational correlation time $\tau_{\text{rot}} \approx \tau_{\text{solid}}$ is much larger than the experimental value [3]. On the other hand, our modification yields $\tau_{\text{solid}} = \tau_s = 5.8 \times 10^4$ s (4.9×10^3 s) and $\tau_{\text{fluid}} = \tau_{lf}^{\text{rot}} = 66$ s (5.3 s) with weights 0.9 and 0.1, respectively. The numbers in parentheses obtained from Ref. [5] should be used for comparison with experiment, which yields $\tau_{\text{rot}} \approx 0.9\tau_{\text{solid}} = 4.4 \times 10^3$ s. Of course, this is still a very rough order of magnitude estimate. In quantitative comparisons with experiments one should use stretched exponentials in Eq. (15), which amounts to a multistate instead of a two-state model, and is certainly a more realistic description of the continuous distributions of correlation times found in experiments. It should be noted that the division of a broad distribution of correlation times into a "slow" and a "fast" part and a distribution of rates for exchange between these parts provide a useful approximation in recent four dimensional (4D) NMR experiments [9,10], where the exchange between the correlation times within each part of the distribution has a negligible effect. That the nonexponential relaxation functions in glass forming liquids originate from a distribution of correlation times related to spatial heterogeneities has been proven by recent NMR [11] and photobleaching [12] experiments. The (reduced) 4D NMR experiments [9,13] prove that the exchange times between these inhomogeneities are of the same order of magnitude as the slow part of the correlation time distribution.

In conclusion, we have shown that the "fluidized domain" model proposed by SH becomes inconsistent with experiment because of their arbitrary *ad hoc* assumptions, Eqs. (5)–(7), introduced in order to obtain numerical estimates. We proposed alternative assumptions which are in harmony with experiment and are believed to be physically more plausible. Of course, only rough estimates can be expected from any two-state model [7,8], which should, however, be consistent with experiment.

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[4] It should be noted that the values of $\eta/\eta_0 \sim 10^3$ and $\mu \sim 10^2$ provide only a very crude estimate of ϕ_0. However, no glass-forming system is known to us where this estimate would yield $\phi_0 > 1$.

[5] In the NMR experiments of [2] one obtains a rotational correlation time for $l = 2$ which suggests $D_{rot} = 1/6\tau_{rot} = \phi_0/6t_0$ in place of Eq. (3). Furthermore, one should use the hydrodynamic radius of orthoterphenyl, $R_H = 0.22$ nm obtained in [2], rather than the value $R = 0.35$ nm given in Table I of SH. This yields $t_0 = 5.4 \times 10^2$ s and $\langle r(t_0)^2 \rangle^{1/2} = 2.5$ nm instead of the values 6.5×10^3 s and 7.0 nm given in the text. However, we stay with the numbers of SH in the text in order to be consistent with their other estimates.

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