Translation-rotation paradox for diffusion in fragile glass-forming liquids

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Translational and rotational diffusion rates in low-molecular-weight liquids tend to conform well to the predictions of the classic Stokes-Einstein-Debye model if temperature T is not too low. Specifically, the diffusion constants D_{trans} and D_{rot} are proportional to $T/\eta(T)$, where η is the shear viscosity. However, fragile glass formers seem to present a paradox: near the glass transition temperature T_g this proportionality continues for D_{rot}, but D_{trans} can be enhanced by 10^2. A "fluidized domain" model is proposed to explain these observations. Owing to a suitable combination of domain parameters (mean size, lifetime, concentration, internal viscosity), the observed diffusion rate discrepancy can indeed be rationalized. Rough estimates for these domain parameters are provided for two fragile glass formers (ortho-terphenyl and 1,3,5-tri-α-naphthyl benzene) at their respective T_g's.

I. INTRODUCTION

Metastable forms of matter provide a rich source of useful materials and of challenging research problems. Glasses arguably are the most significant of these metastable forms from both of those perspectives. The present paper attempts to explain a puzzling phenomenon uncovered recently by experiments on the so-called fragile glass formers, namely, a paradoxical discrepancy between the rates of rotational and of translational diffusion as the supercooled liquid approaches its glass transition region [1–3].

The following Sec. II briefly summarizes the experimental background, invoking the classic Stokes-Einstein-Debye hydrodynamic model [4–7] of a spherical Brownian particle in a viscous medium as the "behavior standard" for rotational and translational diffusion. Section III then presents our model of "fluidized domains" for motions in strongly supercooled liquids, and shows how, in principle, it can rationalize the otherwise puzzling experimental observations. Some plausible (but not irrevocable) numerical estimates of parameters in our fluidized domain picture appear in Sec. IV; these relate specifically to the experimentally favored fragile glass formers ortho-terphenyl (OTP) and 1,3,5-tri-α-naphthyl benzene ($T\alpha$NB). Section V concludes the paper with some discussion and suggestions for future research.

II. EXPERIMENTAL BACKGROUND

As a liquid has its temperature reduced through the melting point T_m and into the supercooled regime, kinetic and relaxation processes markedly decelerate. This causes the shear viscosity $\eta(T)$ to rise rapidly from its value of a few centipoise at T_m. If crystal nucleation can be avoided, upon further cooling the liquid typically undergoes a glass transition at a temperature T_g where $\eta(T_g)$ is in the range of 10^{11}–10^{13} P and structural relaxation times equal or begin to exceed the duration of conventional experiments. Additional cooling below this glass transition temperature produces breaks or discontinuities in properties such as thermal expansion, heat capacity, and even viscosity itself [8,9].

It is useful to classify glass-forming liquids between the extremes of "strong" and "fragile" behavior, as advocated by Angell [10,11]. The covalently bonded network materials SiO_2 and GeO_2 exemplify the "strong" limit, and display the key characteristics: (a) Arrhenius temperature dependence for $\eta(T)$ through the entire stable and metastable liquid range and (b) very small change in heat capacity C_p across T_g. By contrast the "fragile" limit exhibits (a) strongly non-Arrhenius $\eta(T)$ behavior and (b) substantial drop in $C_p(T)$ as T declines through T_g; the organic materials orthoterphenyl [12], Salol [13], and 1,3,5-tri-α-naphthyl benzene [14] provide examples.

It has become traditional to interpret rotational and translational diffusion of individual molecules in liquids in terms of the elementary Stokes-Einstein-Debye model [4–7]. This model examines the Brownian motion of a perfect sphere of the appropriate size embedded in a uniform incompressible fluid with shear viscosity $\eta(T)$ equal to that measured for the substance of interest. Conventional low-Reynolds-number hydrodynamics [5] describes the flow of this medium around the moving sphere. Assuming that "sticking" boundary conditions apply at the sphere surface, the Stokes-Einstein-Debye model assigns the following values to the translational and rotational diffusion constants:

$$D_{\text{trans}} = \frac{k_B T}{6\pi\eta R} ,$$

$$D_{\text{rot}} = \frac{k_B T}{8\pi\eta R^3} ,$$

(2.1)

where k_B is Boltzmann's constant, and R is the radius of the molecular sphere. Notice that D_{trans} and D_{rot} have different dimensions; they respectively measure the rates of increase with time of mean-square positional and angular displacements of the Brownian particle:

$$\langle (\delta \mathbf{r})^2 \rangle \cong 6D_{\text{trans}} \delta t \ ,$$

$$\text{(2.2)}$$

$$\langle (\delta \theta)^2 \rangle \cong 4D_{\text{rot}} \delta t \ .$$

The Stokes-Einstein-Debye model is remarkably successful in organizing and rationalizing data for a wide range of liquids in their stable range ($T \geq T_m$), and in the slightly to moderately supercooled regime ($T \geq 1.2T_g$). While $\eta(T)$ varies over several orders of magnitude for any given substance, measured values of D_{trans} and D_{rot} typically conform to Eqs. (2.1) with apparent hydrodynamic radii R that are virtually T independent, and of the proper molecular magnitude [15–17]. To be sure, the R values that emerge are somewhat smaller than precise molecular structure would suggest, but deviations from the assumed spherical molecular shape, boundary condition, and surrounding medium nonuniformity could easily account for the mismatch. In any case, the temperature variations of D_{trans} and D_{rot} in this temperature range appear closely to track that of T/η.

Recent experimental data on deeply supercooled fragile liquids [1–3] has begun to upset this comfortable situation. On the one hand, translational diffusion occurs "too fast" near T_g in comparison with the prediction of the first of Eqs. (2.1) using the $T \cong T_m$ value for R and the measured $\eta(T)$. Upon approaching T_g the discrepancy involves a factor of about 10^2 and is therefore unlikely to be due to a simple change in boundary condition or shift in molecular size and shape. On the other hand, the rotational diffusion rate continues to conform reasonably well to the second of Eqs. (2.1) while translational motions manifest great enhancement. Explaining this seemingly paradoxical discrepancy is obviously an important issue for comprehensive understanding of the glass state.

III. FLUIDIZED DOMAIN MODEL

Description of diffusive motion in the strongly supercooled liquids that are the subject of this paper requires identification of excitation processes that permit molecular rearrangement and structural relaxation. Our view is that the medium near T_g is largely uniform, but contains a small concentration of structural excitations that at any instant are spatially localized. It is not necessary to be overly specific about the nature of these thermal excitations, except to say that within their domains of localization they tend to "unbundle" molecules from what would otherwise be more favorable packing geometries (i.e., lower in local potential energy). As a result, the domain interior becomes "fluidized" temporarily while the excitation remains present. Eventually the unbundled and more mobile domain molecules find, and settle back into, another favorable packing and become substantially immobilized as the excitation disappears. At any arbitrarily chosen time, the system displays a sparse collection of these fluidized domains dispersed throughout an essentially solid matrix that fills the remainder of the volume.

Quite naturally the fluidized domains can be expected to vary in size and shape. But in the absence of compel-

ling evidence to the contrary it seems reasonable to suppose that they are relatively compact. For present purposes it suffices to describe the fluidized domains near T_g by four temperature-dependent average characteristics:

    (1) domain volume v_0;
    (2) domain appearance rate per unit volume r_0;
    (3) domain lifetime t_0;
    (4) domain internal viscosity η_0.

The last of these must reflect the fluidized nature of the domains, and so must be substantially less than the macroscopically measured viscosity η.

The domain appearance rate and lifetime together determine c_0, the concentration (number density) of fluidized domains,

$$c_0 = r_0 t_0 \ . \tag{3.1}$$

The volume fraction ϕ_0 of the system that is interior to the domains is therefore

$$\phi_0 = c_0 v_0 = r_0 t_0 v_0 \ ; \tag{3.2}$$

this assumes that the molecular number density is the same within fluidized domains as in the surrounding solid matrix, both therefore equaling the macroscopic number density ρ. The mean number of molecules within a domain is

$$n_0 = \rho v_0 \ . \tag{3.3}$$

The central notion which makes this picture useful near T_g is that the infrequency of appearance of domains bottlenecks both rotational and translational diffusion, but large domain size disproportionately compensates that bottlenecking just for translational motion. Only the early portion of lifetime t_0 contributes to rotational relaxation of the domain's contents if t_0 is large, but if at the same time v_0 is itself sufficiently large the entire interval t_0 contributes to the system's overall translational diffusion rate. Not surprisingly, this scenario of differential bottlenecking requires both t_0 and domain linear size $v_0^{1/3}$ to be quite large on the scale of molecular dimensions.

The combination of circumstances just described implies that the intradomain rotational relaxation time must be much less than t_0, which itself must be much less than the mean time required for a molecule to diffuse distance $v_0^{1/3}$ across a domain. Intradomain rotational and translational diffusion can be described crudely (but adequately for present purposes) by Stokes-Einstein-Debye expressions (2.1) and (2.2) with viscosity η_0. Consequently, we require

$$\frac{4\pi \eta_0 R^3}{k_B T} \ll t_0 \ll \frac{\pi \eta_0 v_0^{2/3} R}{k_B T} \ . \tag{3.4}$$

Within the picture just described, any given molecule must await the appearance of an encompassing domain before it can rotationally relax, but once so encompassed its relaxation soon completes. Domain appearance presumably is a random process, so the rotational relaxation time τ_{rot} should be given by $(r_0 v_0)^{-1}$, and so

$$D_{\rm rot}=(2\tau_{\rm rot})^{-1}=r_0 v_0/2 \ . \tag{3.5}$$

The system's overall translational diffusion constant $D_{\rm trans}$ will nominally have the form of a simple volume average over fluidized domains and surrounding static matrix:

$$D_{\rm trans}=\phi_0(k_B T/6\pi\eta_0 R)+(1-\phi_0)\times 0$$

$$=\frac{k_B T r_0 v_0 t_0}{6\pi\eta_0 R} \ . \tag{3.6}$$

The appearance of temperature-dependent domain parameters t_0 and η_0 in this last expression, but not in Eq. (3.5) for $D_{\rm rot}$, ultimately allows for an explanation of the translation-rotation paradox.

The shear viscosity $\eta(T)$ controls the rate of shear stress relaxation. The characteristic time (Maxwell relaxation time [8]) is given by

$$\tau_s=\eta/G_\infty \ , \tag{3.7}$$

where G_∞ is the high-frequency shear modulus for the medium, not expected to have substantial temperature dependence near T_g. In the present view, the appearance rate of fluidized domains also controls stress relaxation. Suppose the entire sample were initially placed in a state of uniform shear stress. Subsequent appearance of a fluidized domain would permit molecular rearrangement within its volume v_0 that could thereby release stress over substantially the same volume. Because these events occur randomly throughout the entire system at rate r_0 per unit volume, stress relaxation (and thus η itself) will be proportional to $(r_0 v_0)^{-1}$. This is the same combination of characteristic domain parameters that appears in $D_{\rm rot}$, Eq. (3.5); it does *not* include the remaining characteristic parameters t_0 and η_0 that appear in $D_{\rm trans}$, Eq. (3.6). Acknowledging that T itself varies rather little over the affected temperature range near T_g, we conclude that

$$\eta(T)D_{\rm rot}(T)/T\cong{\rm const} \ , \tag{3.8}$$

while

$$\eta(T)D_{\rm trans}(T)/T\cong{\rm const}\times(t_0/\eta_0) \ . \tag{3.9}$$

Consequently it is plausible that rotational diffusion should continue to adhere to the Stokes-Einstein-Debye format near T_g, while translational diffusion could deviate significantly if t_0/η_0 were to possess strong temperature dependence.

IV. NUMERICAL ESTIMATES

Neither experimental data nor theoretical analysis is sufficient at present to assign unambiguous values to v_0, r_0, t_0, and η_0 for any glass former. However, these key quantities are not arbitrary; they are subject to inequalities (3.4) if our model has merit. Furthermore, they must be consistent with the magnitudes observed for discrepancies from the Stokes-Einstein-Debye norm when T drops into the glass transition range. We now offer some rough and frankly speculative values for these four parameters, for two fragile organic glass formers at their respective T_g's, namely, orthoterphenyl (OTP), and 1,3,5-tri-α-naphthyl benzene ($T\alpha$NB). The existence of such estimates, however tentative, demonstrates that the scenario described in the preceding Sec. III can indeed be realized, and conveys a concrete sense of the molecular cooperativity involved.

Table I contains the relevant experimental properties for OTP and $T\alpha$NB. These include the melting and glass transition temperatures T_m and T_g, shear viscosities at these temperatures, and the number densities at T_g. Rough estimates of effective hydrodynamic radii R for each organic molecule have also been included.

It has been suggested [18] that fragile glass formers near T_g flow by a "tear and repair" mechanism that involves disruption of relatively weakly bonded walls between strongly aggregated or interlocked groups of molecules. We take the position now that our fluidized domains are likely to contain several, if not many, of these grains, and, therefore, to contain a rather large number of individual molecules. Therefore, we tentatively propose both for OTP and for $T\alpha$NB that $n_0(T_g)$ is 10^4. Obviously this is subject to immediate revision as appropriate experimental evidence to the contrary may appear. This number and the corresponding mean domain volumes $v_0(T_g)$ have been entered into Table II.

If the translational diffusion constant is to be some multiple μ of the Stokes-Einstein value [first of Eqs. (2.1)] at T_g, then it is easy to show that the characteristic domain parameters must satisfy the following:

$$r_0 v_0 t_0\eta/\eta_0=\mu \ . \tag{4.1}$$

As mentioned earlier, OTP measurements indicate that $\mu\cong 10^2$; while similar experiments apparently have not yet been done for $T\alpha$NB it seems sensible to suppose that approximately the same μ value applies.

The intradomain viscosity η_0 at T_g surely must be substantially less than $\eta(T_g)$. At the same time it is expected to be considerably greater than $\eta(T_m)$, the liquid's macroscopic viscosity at its melting point. A reasonable estimate is the geometric mean

$$\eta_0(T_g)\cong[\eta(T_m)\eta(T_g)]^{1/2} \ , \tag{4.2}$$

and the corresponding numbers appear in Table II.

TABLE I. Physical properties of two fragile glass formers.

	OTP[a,b]	$T\alpha$NB[c,d]
T_m(K)	329	472
T_g(K)	240	342
$\eta(T_m)$(P)	0.37	0.18
$\eta(T_g)$(P)	4×10^{12}	1×10^{13}
$\rho(T_g)$(Å^{-3})	2.94×10^{-3}	1.52×10^{-3}
R (Å)	3.5	4.4

[a]M. T. Cicerone and M. D. Ediger, Ref. [2].
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TABLE II. Suggested domain parameters for two fragile glass formers at the glass transition.

	OTP	$T\alpha$NB
n_0	10^4	10^4
$v_0(\text{Å}^3)$	3.40×10^6	6.58×10^6
$r_0(\text{cm}^{-3}\,\text{s}^{-1})$	2.11×10^{13}	3.15×10^{12}
$t_0(\text{s})$	0.426	0.647
$\eta_0(\text{P})$	1.22×10^6	1.34×10^6
$c_0(\text{cm}^{-3})$	8.99×10^{12}	2.04×10^{12}
ϕ_0	3.06×10^{-5}	1.34×10^{-5}

The two extreme members of the inequalities in (3.4) can now be evaluated. The sense of those inequalities can be optimally balanced if t_0 is chosen to be the geometric mean of its upper and lower bounds, specifically

$$t_0 \cong 2\pi\eta_0 R^2 v_0^{1/3} /(k_B T) .\qquad (4.3)$$

The implied glass-transition-temperature values appear in Table II. With this choice, the successive members of (3.4) increase by the ratio $v_0^{1/3}/(2R)$, which just exceeds 20 for both fragile glass formers considered. With t_0 thus determined, Eq. (4.1) can be used to fix r_0, the results for which also appear in Table II. This completes the selection process for the four domain parameters.

The parameter values presented in Table II can be given a rough consistency check. The rotational relaxation time that they imply, $\tau_{\text{rot}}=(r_0 v_0)^{-1}$, should be comparable to or longer than the most extended experimental observation times devoted to measurements at T_g. Otherwise, the existence of a glass transition itself would be contradicted. These rotational relaxation times are found from Table II to be 1.4×10^4 s for OTP, and 4.8×10^4 s for $T\alpha$NB. Consistency obtains.

The most striking feature displayed by Table II is the very small volume fraction of the system to be found in domains at any given instant. The great majority of the molecules are locked into the solid matrix, awaiting visitation by a domain of excitation. The mean distance between neighboring domains is about 30 domain diameters for OTP, and about 40 domain diameters for $T\alpha$NB.

V. DISCUSSION

We have proposed and investigated a "fluidized domain" model to explain the puzzling behavior of translational and rotational diffusion rates in fragile glass-forming liquids near their glass transition temperatures. Four parameters $(v_0, r_0, t_0,$ and $\eta_0)$ describing average domain behavior as a function of T appear in this model. If these quantities satisfy certain constraints it is possible to rationalize the continued adherence of rotational Brownian motion to the rate prescribed by the Stokes-Einstein-Debye model of a sphere in a viscous medium, while translational Brownian motion becomes correspondingly much faster as T declines toward T_g.

Mean domain volume (v_0), lifetime (t_0), and internal viscosity (η_0) are all expected to rise rapidly as T decreases toward T_0; the domain production rate per unit

volume (r_0) simultaneously is expected to decline. Rough estimates for these parameters at T_g for two fragile glass formers, OTP and $T\alpha$NB, were formulated in Sec. IV, and led to the picture of a vitreous solid matrix containing a sparse flickering distribution of domains.

In addition to providing a mechanism for rotational and translational diffusion, our fluidized domains presumably mediate enthalpy relaxation above T_g. The growth of $v_0(T)$ upon cooling the liquid to T_g exemplifies a basic feature of glass formers; the lower the enthalpy (essentially the molecular potential energy), the larger the group of molecules must be to be unbundled and repacked into an even more favorable arrangement. Upon passing below T_g, we expect v_0 to remain frozen at $v_0(T_g)$, so that further enthalpy relaxation becomes kinetically impossible, as experiment indeed demonstrates. But below T_g fluidized domains of that frozen size should continue to flicker into and out of existence, and can mediate very sluggish viscous flow. This sticking of domain size at v_0 (T_g) must be related to the reported change in slope of the Arrhenius plot of $\ln\eta$ versus $1/T$ at the glass transition [9,19].

We note that the "fluidized domains" central to our model bear at least a superficial resemblance to the statistically independent "cooperatively rearranging regions" postulated by the Adam and Gibbs theory of relaxation properties in glass-forming liquids [20]. However, the latter were introduced primarily as a device for configurational counting purposes, and do not have a direct and obvious connection to the translation-rotation paradox for diffusion that has motivated the present work. In fact, our fluidized domains each may encompass a large number of Adam-Gibbs regions at T_g.

Mode coupling theory [21,22] seems to provide a natural way to describe diffusive motion and viscosity in liquids, provided $T > 1.2T_g$. Unfortunately, the simple version of mode coupling theory generates an unphysical algebraic singularity around $1.2T_g$ at which η would seem to diverge and structural relaxation would be blocked. Suggestions now exist in the literature for circumventing this artifact, by inserting "barrier hopping" processes [23,24]. If the present model for understanding translational and rotational diffusion near T_g has merit for fragile glass formers, further refinement of mode coupling theory may be required to attain a comprehensive physical description.

The presence of large and widely separated fluidized domains in the medium near its glass transition temperature in principle should lead to a length-scale dependence of η. This suggests that the average hydrodynamic flow around a diffusing sphere in a fragile glass former could be described using a position-dependent viscosity. In fact, this tactic has been used to investigate the enhancement of D_{trans} compared to the Stokes-Einstein value [25], and requires a local decrease in viscosity in a zone around the diffusing sphere with a range roughly consistent with our domain model. But since a comparable enhancement experimentally does not appear for D_{rot}, the corresponding local viscosity would be a different radial function of distance from the sphere, and should de-

viate little from the macroscopic viscosity. This distinction stems of course from the different averages involved for translational and for rotation.

While the fluidized domain model seems to offer a resolution of the translation-rotation diffusion paradox, we do not know if it is unique in that respect. Some new sources of critical information are required to evaluate the model's relevance to fragile glass formers. On the one hand, experiments may have to be devised to look for wavevector and frequency dependence of viscosity near T_g to provide at least indirect evidence for flickering fluidized domains. These experiments might include the study of thickness dependence of creep properties of thin films, and the study of the radius dependence of D_{trans} for embedded Brownian particles in a given fragile glass

former. Simulation may also have an important role, since it is now possible (at least for some simple models [26]) to study in detail the many-particle collective motions that produce relaxations in "glasses." As this kind of activity matures, it should be possible to test for the presence of fluidized domains for realistically represented fragile glass formers, and if they are present to determine their average characteristics as required in our model.

ACKNOWLEDGMENT

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