

## Reply to "Comment on 'Translation-rotation paradox for diffusion in fragile glass-forming liquids'"

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We discuss several aspects of the fluidized domain model advanced earlier to explain rotational and translational diffusion rates for fragile glass formers and, in particular, we point out weaknesses in the preceding Comment [Sillescu, Phys. Rev. E **53**, 2992 (1996)]. Recent experimental results are cited to refine estimates of domain characteristics for orthoterphenyl at  $T_g$  and to suggest that domain heterogeneity in space and time underlies stretched exponential relaxation behavior for rotational motion.

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## I. INTRODUCTION

The metastable states of supercooled liquids, and the vitreous materials that they produce upon cooling below the glass transition temperature  $T_g$ , provide a rich array of fascinating phenomena. This seems to be particularly true for the group of substances that in Angell's classification scheme [1] fall under the heading "fragile glass formers." These typically display strongly non-Arrhenius temperature dependence of shear viscosity  $\eta(T)$  above  $T_g$  and a substantial sudden drop in heat capacity upon cooling through  $T_g$ . It seems to be generally accepted that this "fragile" behavior indicates the presence, and limited exploration, of a rugged potential energy hypersurface [2].

Recent experimental studies of translational and rotational diffusion rates in fragile glass formers seemed at first to present a conceptual puzzle. The Stokes-Einstein-Debye (SED) model of a spherical molecule executing Brownian motion in a uniform viscous medium well describes both of the measured diffusion rates in the equilibrium and the moderately supercooled liquid regimes, using the measured  $\eta(T)$ . This agreement continues down to  $T_g$  for rotational diffusion, but for translational diffusion below  $1.2 T_g$  the rates are "too fast" by SED standards, by a factor  $\mu$  that reaches or exceeds  $10^2$  at  $T_g$  [3].

## II. FLUID DOMAIN PARAMETERS

Reference [3] presented a "fluidized domain" model to demonstrate a mechanism for decoupling of the translational and rotational diffusion rates in the neighborhood of  $T_g$ . Its basic concept was selective bottlenecking mediated by thermally activated excitations that locally and cooperatively rearrange relatively large groups of molecules. While these activated domains would be expected to vary considerably from one to the next, only a select few *average* properties were required to demonstrate the viability of the proposed mechanism. The four key averages chosen were domain volume ( $v_0$ ), appearance rate ( $r_0$ ), lifetime ( $t_0$ ), and internal viscosity [ $\eta_0 < \eta(T)$ ].

The major objective of Ref. [3] was to show that ap-

propriate combinations of  $v_0$ ,  $r_0$ ,  $t_0$ , and  $\eta_0$  could cause rotational diffusion to continue to adhere to the SED norm, while translational diffusion manifested large enhancement factors  $\mu \sim 10^2$ . In view of the various constraints that had to be observed by the parameter quadruplet, it was important to exhibit at least one consistent set obeying those constraints. The first column of Table I repeats the numerical values given in Ref. [3] for orthoterphenyl (OTP) at its glass transition ( $T_g \simeq 240$  K). These were offered as an "existence proof" for the postulated mechanism, but the specific values selected were described as "rough and frankly speculative." Clearly, more experimental input was required to refine the parameter quadruplet.

In the preceding Comment [4], Sillescu offers a scheme to effect just such a refinement. The domain parameters emerging from this analysis appear for comparison in column 2 of Table I. While this alternative set remains substantially consistent with the selective bottlenecking mechanism, the picture of the glassy medium it elicits is rather different: the mean domain size  $v_0$  has been reduced by an order of magnitude, while the volume fraction  $\phi_0$  interior to the fluidized domains has increased by more than three orders of magnitude.

The key ingredient in the development of Ref. [4] is selection of "the shortest rotational correlation time of the correlation time distribution." Sillescu claims to be able to do this at  $T_g$  from the Kohlrausch (Williams-Watts) relaxation-function exponent  $\beta$ , appearing in Fig.

TABLE I. Fluidized domain model parameter sets for OTP at  $T_g$ .

	Ref. [3]	Ref. [4]	Present Work
$v_0$ ( $\text{\AA}^3$ )	$3.40 \times 10^6$	$3.43 \times 10^5$	$1.70 \times 10^5$
$r_0$ ( $\text{cm}^{-3}\text{s}^{-1}$ )	$2.11 \times 10^{13}$	$4.49 \times 10^{13}$	$2.11 \times 10^{15}$
$t_0$ (s)	0.426	$6.5 \times 10^3$	0.426
$\eta_0$ (P)	$1.22 \times 10^6$	$4 \times 10^9$	$6.10 \times 10^6$
$n_0^a$	$10^4$	$1.01 \times 10^3$	500
$\phi_0^a$	$3.06 \times 10^{-5}$	0.1	$1.53 \times 10^{-4}$

<sup>a</sup> $n_0$  = mean number of molecules contained in a fluidized domain;  $\phi_0$  = volume fraction within fluidized domains.

1 of Chang *et al.* [5]. Examination of that figure and extrapolation over a few degrees to the glass transition indicates that  $\beta(T_g)$  for OTP is very small, apparently of the order of 0.1. As a result of such a small exponent, the corresponding distribution of simple exponential relaxation times is extremely broad and lacking an obvious shortest-time cutoff, as the calculations of Lindsey and Patterson clearly demonstrate [6]. Consequently, the immediate implication of Sillescu's choice of "shortest rotational correlation time," specifically,

$$\eta_0 = 10^{-3} \eta(T_g), \quad (1)$$

must be treated with great caution. In view of the fact that the other domain parameters offered in Ref. [4] follow from (1), they, too, should be viewed with caution.

It should be mentioned in passing that the relatively large fluidized volume fraction shown in column 2 of Table I may not be fully consistent with the presumption of compact and independently acting domains. The critical percolation threshold for a close-packed array of independent regions that qualify to become fluidized is only about 0.2 [7]. Even somewhat below this threshold (i.e., around 0.1) many pairs or higher-order groupings of regions would join together to present ramified nonconvex domains that are fluidized. Of course this is not likely with the substantially smaller volume fraction of column 1 in Table I.

Time-resolved optical spectroscopy of size-variable probe molecules in deeply supercooled OTP [8] provides an alternative means to refine the fluidized domain model parameters. This experimental technique indicates that probe rotational diffusion rates near  $T_g$  are size-dependent, just as the SED picture requires. But in addition, these rotational rates actually deviate slightly in the positive direction from the SED absolute prediction (though far less than do translational diffusion rates). These features suggest that mean domain size  $v_0$  is substantially smaller than that shown in column 1 of Table I, and perhaps smaller even than shown in column 2. One must bear in mind while making such an inference that non-OTP probes might locally perturb the OTP-medium dynamics, acting perhaps as reinforcing elements that slightly resist fluidizing excitations; and the larger the probe, the greater the local perturbation.

Column 3 of Table I presents an alternative parameter set more nearly in accord with Ref. [8] and the concepts of the preceding paragraph. They were chosen subject to the constraint given by the fixed value ( $10^2$ ) of

$$\mu = r_0 v_0 t_0 \eta(T_g) / \eta_0. \quad (2)$$

TABLE II. Characteristic times relevant to the selective bottlenecking mechanism. All times are in seconds. The hydrodynamic radius  $R$  has been set at  $3.5 \text{ \AA}$  for OTP.

	Ref. [3]	Ref. [4]	Present work
$4\pi\eta_0 R^3 / k_B T_g$	$1.98 \times 10^{-2}$	65.0	$9.92 \times 10^{-2}$
$t_0$	0.426	$6.50 \times 10^3$	0.426
$\pi\eta_0 v_0^{2/3} R / k_B T_g$	9.16	$6.50 \times 10^3$	6.21

Furthermore, the combination  $(r_0 v_0)^{-1}$  in the fluidized domain model is essentially the stress relaxation time, as well as the rotational relaxation time; to be consistent with the presence of a glass transition at  $T = T_g$ , it should equal or exceed the laboratory measurement time. The values listed in column 3 imply that  $(r_0 v_0)^{-1}$  is about  $2.8 \times 10^3 \text{ s}$ .

### III. DISCUSSION

The revised domain parameters, column 3, present a picture of dynamic fluctuations in OTP at  $T_g$  that contrasts sharply with that proposed by Sillescu in the preceding Comment [4]. Our domain volume fraction  $\phi_0$  is far below any worrisome percolation threshold [7], unlike the Sillescu case. Furthermore  $t_0$  in the present work lies nearly four orders of magnitude below the stress relaxation time, so repeated appearance and disappearance of many fluidized domains mediate stress relaxation in an initially stressed sample. In the Sillescu scenario,  $t_0$  is only one order of magnitude smaller than the stress relaxation time  $(r_0 v_0)^{-1}$ .

The key attribute of the fluidized domain model is its capacity to produce the selective bottlenecking phenomenon, and this stems from an ascending order of three characteristic times [Eq. (3.4) of Ref. [3]], namely, the intradomain rotational relaxation time ( $4\pi\eta_0 R^3 / k_B T$ ), average domain lifetime ( $t_0$ ), and translational diffusion time to pass across a domain diameter ( $\pi\eta_0 v_0^{2/3} R / k_B T$ ). Table II shows the numerical values for each of these corresponding to the three parameter sets under consideration, and once again the present analysis contrasts starkly with that of Ref. [4]. In particular the present work places  $t_0$  within a factor of about 4 of the intradomain relaxation time to accommodate the small deviations from SED behavior discovered in Ref. [8]; Sillescu imposes the much larger (and in our view physically unwarranted) factor  $10^2$ .

Cicerone and Ediger [9] have recently published the results of photobleaching experiments on OTP that clearly demonstrate that the medium near  $T_g$  is dynamically heterogeneous. In the present context this should be interpreted to mean (a) that fluidized domains are broadly distributed in each of their properties about the mean values  $v_0$ ,  $t_0$ , and  $\eta_0$ , and (b) that domain appearance and disappearance processes, while random in the large, have significant spatial correlation. Neither of these features violates either the original presentation of the fluidized domain model or its present version. However, Sillescu appears to overlook both (a) and (b) in his preceding Comment, and reaches the conclusion that the fluidized domain model (with small  $\phi_0$ ) is incapable of yielding a stretched exponential relaxation function for rotation. Instead, we would suggest that the fascinating photobleaching results [9] should form the starting point for a more penetrating model of dynamical fluctuations in glass-forming substances, specifically addressing (a) and (b) above.

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