

## Enhanced diffusion upon approaching the kinetic glass transition

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(Received 13 March 1995)

The apparent failure of the Stokes-Einstein law in strongly supercooled liquids has provoked recent experimental and theoretical studies. In an attempt to explain this phenomenon, we study the diffusion in a dynamically disordered continuum in which small, compact regions of greater diffusivity appear and disappear in time. Within the confines of the model, we show that a systematic increase in the ratio of the diffusivity of fluidized domains to the background diffusivity appears to be the single most important factor in explaining the deviation from the Stokes relation.

PACS number(s): 64.70.Pf, 66.10.Cb, 05.60.+w

### I. INTRODUCTION

For many liquids under normal conditions, the translational diffusion constant of a tagged particle obeys the Stokes-Einstein law relatively well [1,2],

$$D = \frac{k_b T}{b\pi\eta R}, \quad (1)$$

where  $k_b$  is Boltzmann's constant,  $T$  is the temperature,  $\eta$  is the transverse viscosity of the fluid system,  $R$  is the radius of the diffusing particle, and  $b$  is either 4 or 6 depending upon the boundary conditions at the surface of the Brownian particle. From a molecular point of view, the conditions for which Eq. (1) ought to be valid correspond to the motion of a large, massive particle immersed in a fluid of small, light molecules. More precisely, the Stokes law should apply in the limits  $(m/M) \rightarrow 0$  and  $(\xi/R) \ll 1$ , where  $m$  and  $M$  are the masses of the fluid and Brownian particle, respectively, and  $\xi$  is the correlation length for fluid correlation functions in the absence of the tagged particle [3–5]. Therefore, it is remarkable that the Stokes-Einstein formula works reasonably well to relate the diffusion coefficient of a constituent particle or a small tracer molecule to the shear viscosity of the liquid medium.

However, recent experimental and simulation data on strongly supercooled “fragile” glass-forming liquids have shown significant deviations from the Stokes-Einstein relation [6–11]. Specifically, the Stokes-Einstein law works well until a particular temperature that is identified as  $T_c$  in the glass transition literature [12–14].  $T_c$  appears at about  $1.3T_G$  (the glass transition temperature) where the viscosity  $\eta$  is 100–1000 P, corresponding to relaxation times in the mesoscopic regime ( $10^{-11}$ – $10^{-9}$  s). The temperature dependence of the viscosity changes from an Arrhenius to a Vogel-Fulcher-like dependence at  $T_c$ . Below this critical temperature, the prediction of ordinary incompressible hydrodynamics underestimates the diffusion coefficient by as much as a factor of  $10^2$  near the kinetic glass transition. According to mode-coupling theories of the glass transition, this critical crossover behavior is associated with the smearing out of the ideal

transition due to activated hopping processes [14]. Specifically, hopping presumably corresponds to activated, correlated jump motions of molecules which restore ergodicity via an extremely slow relaxation of the underlying metastable structure.

Molecular dynamics simulations of tagged particle motion have confirmed that diffusive behavior changes from liquid- or Brownian-motion-like to jump diffusion below  $T_c$  [8–10]. While diffusion occurs continuously in a normal and slightly supercooled liquid, particles near  $T_g$  remain trapped for hundreds of Einstein periods before hopping to neighboring sites. Such jumps are rare events, and molecules experience on average only a few jumps during the entire duration of the molecular dynamics (MD) run. Deviation from normal diffusive behavior can also be seen from the density autocorrelation function, namely [8]

$$G_s(\vec{r}, t) = \frac{1}{N} \sum_{i=1}^N \langle \delta(\vec{r}_i(t) - \vec{r}_i(0) - \vec{r}) \rangle. \quad (2)$$

where  $\vec{r}_i(t)$  denotes the position of particle  $i$  at time  $t$ . Hopping behavior is characterized by the presence of a secondary peak in  $G_s$  located at approximately the radius of the diffusing species.

Recent investigators have proposed a “fluidized” domain model to account for the discrepancy from the Stokes-Einstein relation [15,16]. In brief, it is postulated that thermal fluctuations create domains that are temporarily more fluidized than the background. These domains result from the disentangling of molecules from more energetically favorable packing geometries, local fluctuation in the molecular number density, or a combination of both effects. Regardless, these structural excitations allow for greater diffusivity than the solidlike matrix in the surroundings and create the hopping transport seen in MD experiments.

### II. JUMP-DIFFUSION MODEL

We consider a dynamical version of the “two-zone” model which closely follows Zwanzig's treatment of percolation in a dynamically disordered continuum [17,18].

In the following, we present a brief summary of the results of [18] for completeness. Specifically, the diffusion that occurs in an inhomogeneous medium characterized by a fluctuating diffusion coefficient  $D(\vec{r}, t)$  is described by the equation

$$\frac{\partial}{\partial t} C(\vec{r}, t) = \vec{\nabla} \cdot [D(\vec{r}, t) \vec{\nabla} C(\vec{r}, t)], \quad (3)$$

where  $C(\vec{r}, t)$  is the concentration of the diffusing particles. For simplicity, it is assumed that fluctuations in  $D$  occur within compact spherical domains of radius  $\sigma$  with the fluidized regions of diffusivity  $D_1$  (as opposed to  $D_2$  of the background). These regions appear and disappear in time with a relaxation time  $\tau$ , and, for a given  $\vec{r}$ , the time independent probability that  $D$  is  $D_1$  (or  $D_2$ ) is  $p_1$  (or  $p_2$ ). Quite naturally, a more realistic model should incorporate a distribution of domain sizes and a corresponding set of relaxation times.

Using a mean-field approximation, one may focus on a spherical region of radius  $\sigma$  centered at the origin. The diffusion constant within the sphere fluctuates between  $D_1$  and  $D_2$ , while the diffusion constant outside is taken to be a constant value  $D_{\text{eff}}$ . The problem thus reduces to a coupled set of differential equations where we would like to determine the dependence of  $D_{\text{eff}}$  on the other parameters of the model. By matching the values and radial derivatives (multiplied by the appropriate diffusion coefficients) of the steady state solutions in the inner and outer regions and eliminating constants after some straightforward algebra, Zwanzig [18] obtains a highly implicit expression for  $D_{\text{eff}}$ :

$$D_{\text{eff}} \left[ \frac{D_{\text{eff}} - \langle D \rangle}{D_1 - D_2} \right] \left[ \frac{i\alpha\sigma h_1'(i\alpha\sigma)}{h_1(i\alpha\sigma)} \right] = p_1 p_2 \frac{(D_1 - D_2) D_{\text{eff}}}{\langle D \rangle} + \frac{D_1 D_2}{\langle D \rangle} \left[ \frac{D_{\text{eff}} - \langle D \rangle}{D_1 - D_2} \right] \left[ \frac{i\beta\sigma j_1'(i\beta\sigma)}{j_1(i\beta\sigma)} \right], \quad (4)$$

where  $\alpha^2 = 1/D_{\text{eff}}\tau$ ,  $\beta^2 = \langle D \rangle / D_1 D_2 \tau$ ,  $h_1$  is the spherical Hankel function of order 1 ( $h_1(x) = [-(1/x) - (i/x^2)]e^{ix}$ ),  $j_1$  is the spherical Bessel function of order 1 [ $j_1(x) = (\sin x/x^2) - (\cos x/x)$ ], and  $\langle D \rangle = p_1 D_1 + p_2 D_2$ .

### III. RESULTS

The preceding expression can be simplified into a more manageable form by introducing the definitions of dimensionless variables:

$$\frac{D_1}{D_2} = \gamma, \quad \frac{D_{\text{eff}}}{D_2} = \tilde{D}, \quad \frac{\tau D_2}{\sigma^2} = \tilde{\tau}, \quad (5)$$

yielding, as a result,

$$-\tilde{D}(\tilde{D} - 1 - (\gamma - 1)p_1)f(\alpha\sigma) = \frac{p_1(1 - p_1)(\gamma - 1)^2 \tilde{D}}{(1 + (\gamma - 1)p_1)} + \frac{\gamma}{(1 + (\gamma - 1)p_1)}(\tilde{D} - 1 - (\gamma - 1)p_1)g(\beta\sigma), \quad (6)$$

where  $\alpha\sigma = (1/\tilde{D}\tilde{\tau})^{1/2}$ ,  $\beta\sigma = ([1 + (\gamma - 1)p_1]/\gamma\tilde{\tau})^{1/2}$ ,  $f(x) = (2 + 2x + x^2)/(1 + x)$ , and  $g(x) = [2x \coth x - (x^2 + 2)]/(1 - x \coth x)$ . It is easy to verify that the trivial conditions  $\gamma = 1$  or  $p_1 = 0$  yield  $\tilde{D} = 1$  as a solution.

Next, we choose values for the various parameters of the model guided by physical intuition gained from MD simulations. First, we take  $p_1$  to be small and a constant with respect to temperature, and we also propose that the size of the domain can be to a good approximation taken as a constant with  $\sigma$  somewhat larger than  $R$  (radius of diffusing particle). We believe that the probability and size of these fluctuations show only weak temperature dependences that can be neglected in our simple model. The relaxation time of the fluctuations (which is related to Maxwell's relaxation time  $\tau_M = \eta/G_\infty$ ) is expected to increase dramatically with a decrease in temperature. However, this rapid rise is tamed since  $\tau$  appears in the dimensionless combination  $\tau D_2/\sigma^2$ , where  $D_2$  decreases rapidly with the lowering of temperature. In fact, since  $D_2$  roughly goes as  $\tau_M^{-1}$  (or  $\tau^{-1}$ ),  $\tilde{\tau}$  is expected to have a weak temperature dependence, and its slight variation cannot account for the significant increase of  $\tilde{D}$  below  $T_c$ . A physical interpretation can be given for  $\tilde{\tau}$  by writing it as  $\tau/\tau_\sigma$ , where  $\tau_\sigma$  is roughly the mean time the diffusing particle spends within a sphere of radius  $\sigma$  with a diffusivity  $D_2$ . We expect  $\tilde{\tau} < 1$  (how small depending on the size of  $\sigma$ ) since, on the time scale  $\tau_\sigma$  of the diffusing species, the fluctuations are fast, which is the same scenario as for the diffusion of a tagged particle in a liquid under normal conditions. There is of course another time scale for diffusion in the fluidized domains, which is simply  $\tau_\sigma/\gamma$ .

We are thus led to the conclusion that the enhancement of  $\tilde{D}$  below  $T_c$  is most likely associated with a significant increase in  $\gamma$  or  $D_1/D_2$ . Figures 1 and 2 show the variation of  $\tilde{D}$  with  $\gamma$  given plausible sets of values for  $p_1$  and  $\tilde{\tau}$ . Note in Fig. 2 that a ratio of the order of  $10^3$  for  $D_1/D_2$  gives an enhancement of the effective diffusion constant by a factor of  $10^2$  that is observed near the kinetic glass transition.

For  $\gamma$  not too large, an expansion of  $\tilde{D}$  in terms of the small parameter  $p_1$  is possible, with the result

$$\tilde{D} = 1 + p_1(\gamma - 1) \left[ 1 - \frac{(\gamma - 1)}{f \left[ \left[ \frac{1}{\tilde{\tau}} \right]^{1/2} \right] + \gamma g \left[ \left[ \frac{1}{\gamma\tilde{\tau}} \right]^{1/2} \right]} \right] + O(p_1^2). \quad (7)$$

It is also interesting to note that  $D_{\text{eff}} \rightarrow \langle D \rangle = p_1 D_1 + p_2 D_2$  as  $\tilde{\tau} \rightarrow 0$ .

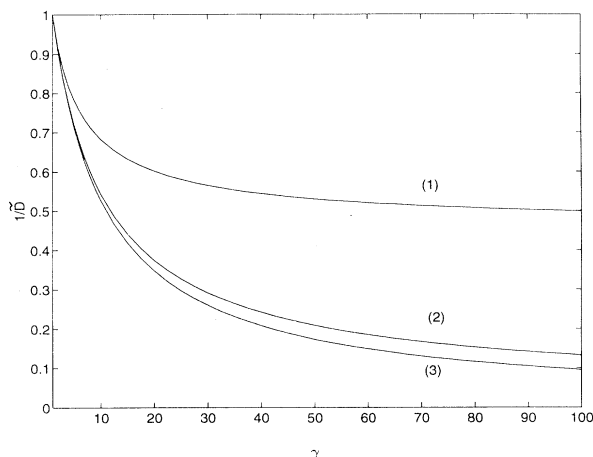


FIG. 1. Plot of  $\tilde{D}^{-1}$  vs  $\gamma$  for three different values of  $\tilde{\tau}$  given  $p_1 = \frac{1}{10}$ . The values of  $\tilde{\tau}$  are  $10^{-1}$ ,  $10^{-3}$ , and  $10^{-5}$  for curves 1, 2, and 3, respectively.

#### IV. CONCLUSIONS

Within the confines of the model, the above results should perhaps be expected. Given that the probability for the appearance of a fluidized domain is small, the effect of these regions on the effective diffusion constant is significant only if the diffusivity within the spheres is much greater than the background diffusion constant. As a liquid is supercooled below  $T_c$ , particle transport becomes increasingly dominated by the appearance of these fluidized regions that allow much greater mobility than the solidlike matrix of the surrounding. In a dense liquid, molecules are temporarily trapped in a “cage” of surrounding molecules. This cage effect introduces time dependent potential barriers that hinder the relaxation of the configurational degrees of freedom. Under normal conditions, these cages have a characteristic lifetime of a few collision times. However, when a liquid is supercooled, particle trapping becomes increasingly more effective and eventually yields partial localization of particles within metastable clusters. Structural relaxation creates domains that are less constricted and allows the trapped particles to jump to adjacent sites.

Although we have considered a simple, dynamic two-zone model where the fluctuations in diffusivity are spatially and temporally uncorrelated, we emphasize that hopping transport is not a strictly local process. From a molecular perspective, jump diffusion is most likely a medium assisted process where there is a feedback mechanism between short wavelength or local disturbances and long wavelength fluctuations [14].

Recently, Stillinger and Hodgdon suggested that spontaneous fluctuations create large domains of low viscosity to account for the different behavior of the translational and rotational coefficients near the glass transition tem-

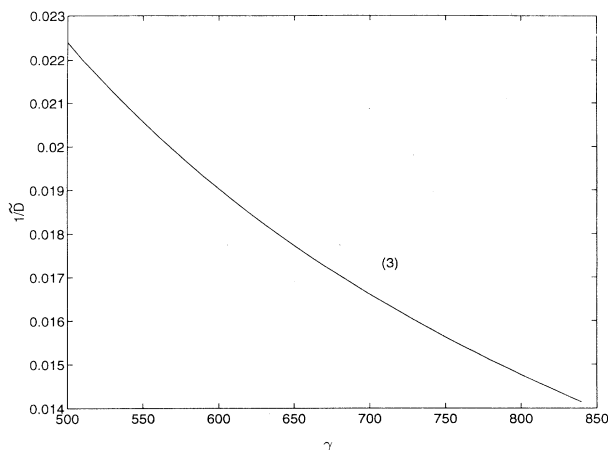


FIG. 2. Plot of  $\tilde{D}^{-1}$  vs  $\gamma$  for curve 3 of Fig. 1, showing a diffusivity enhancement of the order of  $10^2$ .

perature [16]. The large size of the domains was proposed to account for the continued adherence of the rotational Brownian motion to the Stokes-Einstein-Debye model for a sphere rotating in a viscous continuum [2]. However, observations from time resolved spectroscopy of molecular rotation are inconsistent with a model with large domains [19,20]. In particular, probe rotation was found to depend significantly upon probe size, with all probes smaller than the domain size suggested. As mentioned previously, it is our view that the most relevant domain size affecting molecular motion in strongly supercooled liquids corresponds to dimensions not significantly larger than ten times the radius of the diffusing molecule itself. Obviously, domain sizes smaller than the tagged species cannot accommodate its passage and can be neglected, while the creation of larger domains is increasingly less probable, i.e.,  $p_1$  is a decreasing function of the size  $\sigma$ . The structure of a fluid near  $T_g$  appears to be essentially homogeneous on large length scales, and it is unlikely that large fluidlike domains can have a significant effect on particle transport. The model used in this paper is not sufficiently detailed to explain differences in behavior between translational and rotational motion. While translational motion may be enhanced by local density fluctuations, rotational relaxation depends not only on density but on the symmetry of the arrangement of host molecules around the rotational probe. Unless the local density fluctuation is approximately symmetric, translation and rotation will be affected differently.

#### ACKNOWLEDGMENT

One of us (C.Z.-W.L.) would like to acknowledge partial financial support by the National Science Foundation.

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