

# Nature of the breakdown in the Stokes-Einstein relationship in a hard sphere fluid

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Molecular dynamics simulations of high density hard sphere fluids clearly show a breakdown of the Stokes-Einstein equation (SE). This result has been conjectured to be due to the presence of mobile particles, i.e., ones which have the propensity to “hop” distances that are integer multiples of the interparticle distance. We conclusively show that the sedentary particles, i.e., ones complementary to the “hoppers,” obey the SE relationship to a good approximation, even though the fluid as a whole violates the SE equation at high densities. These results support the notion that the unusual diffusive behavior of supercooled liquids is dominated by the hopping particles. © 2006 American Institute of Physics. [DOI: 10.1063/1.2192769]

## I. INTRODUCTION

Typical homogeneous equilibrium liquids, far above their glass transition temperature ( $T_g$ ), obey the Stokes-Einstein (SE) equation,  $D\eta = \text{constant}$ , where  $D$  is the self-diffusion coefficient and  $\eta$  the reduced shear viscosity [ $\eta \equiv \eta_s/T$ , where  $\eta_s$  is the shear viscosity]. Recent experiments<sup>1</sup> and simulations<sup>2</sup> on supercooled liquids have shown that the structural relaxation time  $\tau$  obeys the proportionality  $\tau \propto \eta$  so that both  $D\tau$  and  $D\eta$  are essentially constant well above  $T_g$ . However, both of these relations “break down” dramatically in the immediate vicinity of  $T_g$ .<sup>3–9</sup> It is now commonly accepted that this effect results from “dynamic heterogeneity” in supercooled liquids, specifically the presence of particles having excessively high and low mobilities relative to ideal Brownian motion.<sup>1,3,5,7,8,10–18</sup> While there has been much interest in the breakdown of the Stokes-Einstein relationship, the origin of the fast and slow particles and their impact on the fluid dynamics remain somewhat unclear. This paper focuses precisely on the second issue in the representative case of a fluid of hard spheres. We show that the breakdown of the SE equation may be attributed directly to the presence of particles that “hop” distances which are integer multiples of the particle spacing, where this behavior only occurs for densities larger than a fitted value of the “mode coupling” density. The remaining “sedentary” particles, on the other hand, appear to be unaware of the breakdown of the SE relationship, and thus behave “normally.” Associated with the onset of hopping, we find also that the exchange time between these “fast” particles and the remaining sedentary particles increases strongly with increasing density. Thus dynamical heterogeneities persist for

increasing times and provide an increasingly stronger signature of their presence with increasing density, i.e., there is a more pronounced breakdown of the SE relationship.

## II. SIMULATION MODEL AND METHODS

To better understand the origins of dynamic heterogeneity, we conduct molecular dynamics (MD) simulations<sup>19,20</sup> on a polydisperse hard sphere fluid.<sup>21</sup> All spheres (either 864 or 2048 in number) are of identical mass, but their diameters ( $\sigma_i$ ) are sampled from a Gaussian distribution [mean =  $\sigma$  and standard deviation =  $0.1\sigma$ ; diameters only in the range  $(1 \pm 0.3)\sigma$ ]. The packing fraction  $\phi = \Sigma(\pi/6)\sigma_i^3/V$  ranges from 0.35 to 0.59. Initially, the particles are placed on a fcc lattice with no overlap (i.e.,  $\phi \approx 0.45–0.5$ ), simulated using MD and periodically compressed until the desired  $\phi$  is attained. All of the results discussed, which are averaged over three separate starting configurations, are for completely amorphous structures which have ceased aging.<sup>22</sup> Production runs were long enough for the mean squared particle displacement,  $\langle r^2 \rangle$ , to reach 4 for the highest  $\phi = 0.59$  and to exceed 10 for all smaller packing fractions. (All results are in reduced units where  $\sigma$  and  $\sigma/(k_B T/m)^{1/2}$  are the units of length and time, respectively.)

## III. RESULTS AND DISCUSSION

### A. Breakdown of Stokes-Einstein relationship

Figure 1(a) plots the diffusion coefficient  $D$  as a function of  $\phi$  (derived from plots of  $\langle r^2 \rangle$  vs  $t$ ). The  $D$  values, which typically have uncertainties smaller than 10%, agree with available literature values<sup>23</sup> for amorphous collections of monodisperse spheres ( $\phi < 0.55$ ). The  $D$  results are well described by the Vogel-Fulcher (VF) functional form:  $D$

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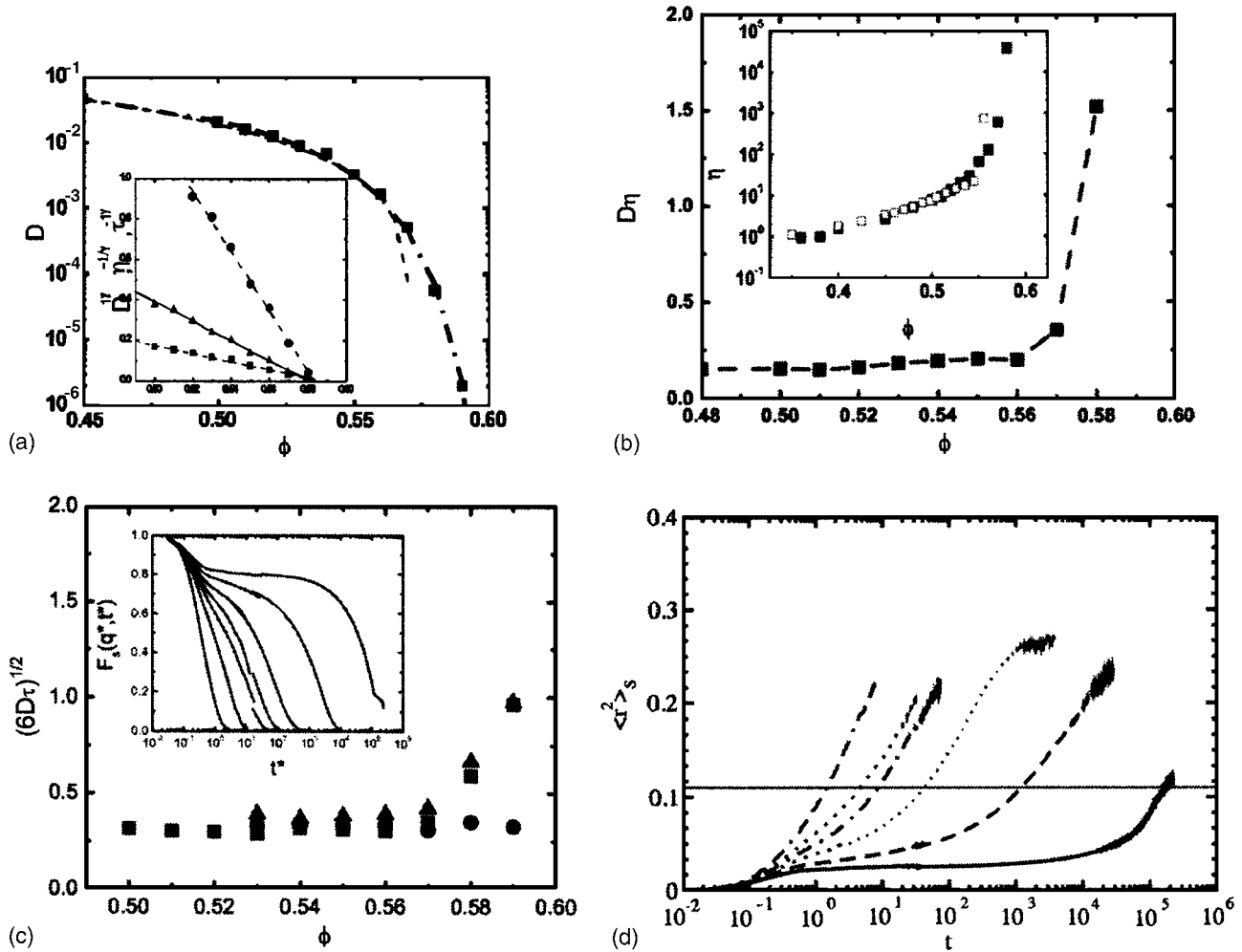


FIG. 1. (a) Plot of the diffusion coefficient  $D$  as a function of  $\phi$  (■). The dot-dashed line is a fit to the VFT equation as discussed in the text. The dashed line is from Speedy (Ref. 23). Inset: plot of  $D^{(1/\gamma)}$  (■),  $\eta^{-(1/\gamma)}$  (▲), and  $\tau^{-(1/\gamma)}$  (●) as a function of  $\phi$ . The lines are best fits. (b)  $D\eta$  as a function of  $\phi$ . Inset is a plot of  $\eta$  vs  $\phi$ . (■) our work and (□) from Ref. 19. (c) Plots of  $\sqrt{6D\tau}$  as a function of  $\phi$  (■). Also plotted are the  $\langle r^2 \rangle^{1/2}$  at  $\tau$  (▲). Finally we plot  $F_s(q^*, t)$  as a function of  $t$  (the  $q^*$  values, which correspond to the first peak of the structure factor, vary monotonically with density). From right to left these curves correspond to  $\phi=0.59, 0.58, 0.57, 0.56, 0.55, 0.53$ , and  $0.50$ . (d) Plots of the  $\langle r^2 \rangle_s$  vs time for the  $S$  particles. From right to left these curves correspond to  $\phi=0.59, 0.58, 0.57, 0.56, 0.55$ , and  $0.53$ .

$=D_0 \exp(A/[\phi - \phi_0])$ , with  $\phi_0=0.614$  [Fig. 1(a)]. The results for densities  $\phi \leq 0.57$  can also be fit well to a power law having a “critical density”  $\phi_c \approx 0.58$  and a power law exponent  $\gamma \approx 2.2$  [Fig. 1(a), inset], as in Ref. 24. Next, we consider the shear viscosity  $\eta$  calculated from a formula that is analogous to the Einstein expression for the diffusion coefficient.<sup>20</sup> Our  $\eta$  data are in good agreement with the limited published results for monodisperse hard spheres [inset to Fig. 1(b)].<sup>19,20</sup> Note that these  $\eta$  calculations require long simulation times, and we could not obtain reliable data for  $\phi=0.59$ . For  $\phi \leq 0.56$ , the  $\eta$  follows an apparent power law dependence similar to that of the  $D$  with a critical density  $\phi_c \approx 0.58$  and a power law exponent  $\gamma \approx 2.2$  [Fig. 1(a), inset]. Finally, we consider the self-intermediate scattering function [inset to Fig. 1(c)] computed at each  $\phi$  at the wave vector  $q^*$  corresponding to the first peak of the static structure factor. As expected,  $F_s(q^*, t)$  is described by a pronounced two-step decay for  $\phi \geq 0.57$ . A shoulder is observed in the range of  $0.53 \leq \phi \leq 0.57$ , and this feature is a defining characteristic of caged dynamics. The structural relaxation times  $\tau$ , i.e., times at which the  $F_s(q^*, t)$  assumes a value of

$1/e$ , also follow an approximate power law over this  $\phi$  range with a  $\phi_c \approx 0.58$  and  $\gamma \approx 2.2$  [Fig. 1(a), inset]. Note that the uncertainties in this type of power law fit are significant, so that  $\gamma \approx 1.7$  provides an equally good fit (correlation coefficient  $r > 0.99$ ). The results shown in the inset to Fig. 1(a) and in Figs. 1(b) and 1(c) suggest that  $D$ ,  $(1/\eta)$ , and  $(1/\tau)$  have essentially the same  $\phi$  dependence for  $\phi \leq 0.56$ . Thus, the relaxation time  $\tau$ , defined through a single particle correlation function, and the shear viscosity  $\eta$ , which is a collective property, have a similar density dependence. Closer examination of the data in Fig. 1(b) (not shown) suggests that  $D\eta$  is not exactly constant for  $\phi \leq 0.56$ . Rather, it increases by about 30% between  $\phi=0.52$  and  $\phi=0.56$ . This trend is in agreement with previous reports.<sup>25–27</sup> Since the onset of caging has previously been identified as occurring in the vicinity of  $\phi=0.52$ , this result suggests that the Stokes-Einstein relationship  $D\eta = \text{constant}$  does not strictly hold when caged motion occurs. However, this breakdown becomes much stronger for  $\phi \geq 0.57$  [see Fig. 1(b)]. In a similar fashion, the product  $D\tau$  also increases strongly [Fig. 1(c)] for  $\phi \geq 0.57$ . Both of these results are consistent with previous experi-

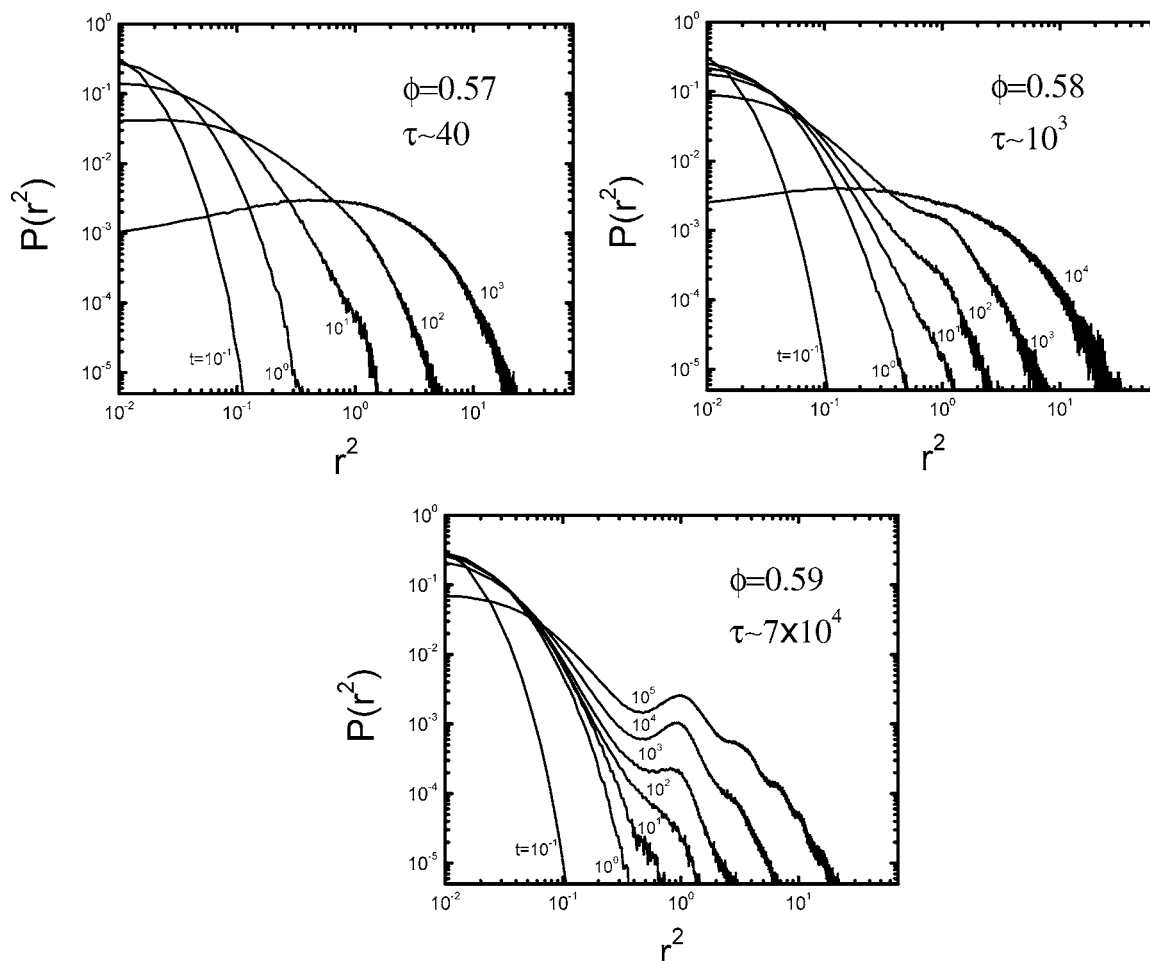


FIG. 2. Distribution  $P(r^2)$  of mean square particle displacement  $r^2$ . Data are shown for three different  $\rho$  and for a variety of times  $t=0.1, 1, 10, 100$ , etc. The  $\tau$  data for each  $\phi$  are shown in the figure.

ments and simulations.<sup>1,3,5–10,14–16,18,21,28–33</sup> In Fig. 1(c) we also show  $\langle r^2 \rangle^{1/2}$  at the structural relaxation time  $\tau$ . Evidently, both  $\sqrt{6D\tau}$  and  $\langle r^2 \rangle^{1/2}$  nearly coincide.

A number of recent computational studies of glass-forming fluids have emphasized the existence of particles that are “mobile” and “immobile” relative to Brownian motion on the time scale  $t^*$  of the maximum of the non-Gaussian parameter [ $\alpha=(3\langle r^4 \rangle/5\langle r^2 \rangle^2)-1$ ]; deviations from Fickian diffusion were assumed to be maximal in this regime.<sup>16,30</sup> These investigations have quantified the tendency of particles of excess “mobility” to become increasingly correlated in spatial position on cooling.<sup>13,30</sup> The development of a plateau in  $F_s(q^*, t)$  seems to coincide with the emergence of this dynamic heterogeneity. In our simulations, this plateau may be present for densities as low as  $\phi=0.52$ , but the crossover density is hard to precisely locate. We note that the density  $\phi$  where this dynamic heterogeneity sets in is close to theoretical estimates of the mode coupling critical density,  $\phi \approx 0.52$ .<sup>34</sup> Since this phenomenon is well documented, we focus our attention instead on a higher  $\phi$  range where basic questions remain about the nature of particle transport in glass-forming liquids.

Figure 2 shows distributions of particle displacement  $r^2$  away from their initial position ( $t=0$ ) for a range of dimensionless times. We choose three different  $\phi$  that are in close

proximity to the “critical” value  $\phi_c \approx 0.58$ , defined through the fitting of the simulation data in Fig. 1(a) (inset) to a power law form inspired by mode coupling theory. According to conventional reasoning, deviations from mode coupling theory (MCT) should arise from rare “hopping events” that allow for relaxations above  $\phi \geq \phi_c$ .<sup>5,35</sup> Consistent with this hypothesis, we find clear evidence of particle displacements to distances that are integral multiples of the intermolecular spacing for times comparable to  $\tau$ . For  $\phi=0.58$ , it is apparent that this “hoplike” motion persists for times as long as  $10\tau$ . For  $\phi=0.59$ , we find that the hopping motion persists for even longer times, emphasizing the increased difficulty in equilibrating the fluid within a reasonable time scale.

Clearly the “hopping” events deduced from Fig. 2 require something more than the dynamic heterogeneity mentioned above since they appear only at densities much higher than the onset of dynamic heterogeneity (i.e., where a plateau in the intermediate scattering function first becomes evident,  $\phi \approx 0.52$ ). On the other hand, the rare hopping particles can certainly be classified as a kind of mobile particles that is particularly well defined in these congested fluids. (Note that this definition has no evident relationship to the definition of mobile particles considered by Glotzer and co-workers.) We define hopping ( $H$ ) particles at a given time by the requirement  $r^2 \geq 0.45$ , and the complementary particles as sedentary

(S). The precise cutoff value of 0.45 corresponds to the well defined position of the first local minimum in the plots shown in Fig. 2, a quantity that appears to be independent of  $\phi$  over the range considered. Given this definition of  $H$  and  $S$  particles, an examination of the  $S$  particles at their  $\tau$  reveals an important effect. These particles exhibit *no detectable deviation* from the SE equation [Fig. 1(c)]. The finding that the  $S$  particles behave identically (on average) at all densities implies that the breakdown of the SE equation may be attributed purely to the presence of the  $H$  particles. This is our primary result. A few points need to be stressed. (i) The  $S$  particles are not diffusive at a time scale on the order of the structural relaxation time  $\tau$ . Consequently, these results represent the rms displacement of the  $S$  particles, rather than the product  $(6D\tau)^{1/2}$  for the sedentary population. (ii) The  $S$  subpopulation has a  $F_s(q^*, t)$  which is different from the quantity calculated for all the particles. This difference becomes appreciable for  $\phi \geq 0.57$ . Correspondingly, the  $\tau$  of the  $S$  subpopulation becomes larger than that of all the particles. The  $\langle r^2 \rangle^{1/2}$  values calculated at the  $\tau$  of all the particles or for the slow population are different, this difference being as large as  $\approx 20\%$  at the highest density simulated. (iii) There is a possibility that the invariance of  $\langle r^2 \rangle$  of the  $S$  particles at their  $\tau$  with  $\phi$  in Fig. 1(c) is merely a consequence of the cutoff distance (0.45) that is used in their definition. In order to convince ourselves that this is not the case, we plot the  $\langle r^2 \rangle$  of the  $S$  particles as a function of time in Fig. 1(d). (The three lower densities are shown merely for completeness, but the definition of a  $S$  particle is not appropriate for densities where particles do not hop, i.e.,  $\phi < 0.57$ ). The horizontal line in Fig. 1(d)  $\langle r^2 \rangle = 0.11$  is the average value that the  $S$  particles have moved at their  $\tau$  at each density [Fig. 1(c) shows that  $\langle r^2 \rangle^{1/2} = 0.33$  for these particles]. Clearly, in this range of time (and displacement) the  $\langle r^2 \rangle$ s are not close to the cutoff value used in their definition ( $\langle r^2 \rangle < 0.45$ ), and they are increasing smoothly as a function of time. In fact, there is only a hint of a plateau for  $\langle r^2 \rangle \sim 0.25$  for  $\phi = 0.57$ . Thus, we conclude that the  $S$  particles obey the Stokes-Einstein relationship, as mentioned before. Moreover, this result is insensitive to the cutoff value we choose to define the  $S$  particles.

One might imagine that the  $S$  particles follow the SE results simply because the removal of the  $H$  particles from the analysis leaves us with only those particles whose motion follows Gaussian statistics. However, as evidenced by the non-Gaussian parameter  $\alpha$ , the particle motion is non-Gaussian for all  $\phi \geq 0.52$ ,<sup>21,25,30</sup> whereas the  $H$  and  $S$  particles can only be distinguished for  $\phi \geq 0.57$ . Additionally, even if we consider only the  $S$  particles, we find that the non-Gaussian parameter is nonzero, and has a maximum value of  $O(1)$  (for  $\phi = 0.59$ ): the motion of these particles, thus, does not follow Gaussian statistics. More credibility for this assertion follows from the ideas of Odagaki and Hiwatari<sup>36</sup> who have suggested that the quantity  $[t^* \alpha(t^*)]$  is uniquely sensitive to the Gaussian/non-Gaussian nature of particle motion ( $t^*$  is the time where  $\alpha$  is maximum). In accord with Ref. 35, we find that  $[t^* \alpha(t^*)]^{-0.25}$  decreases monotonically with increasing density (see Fig. 3). Evi-

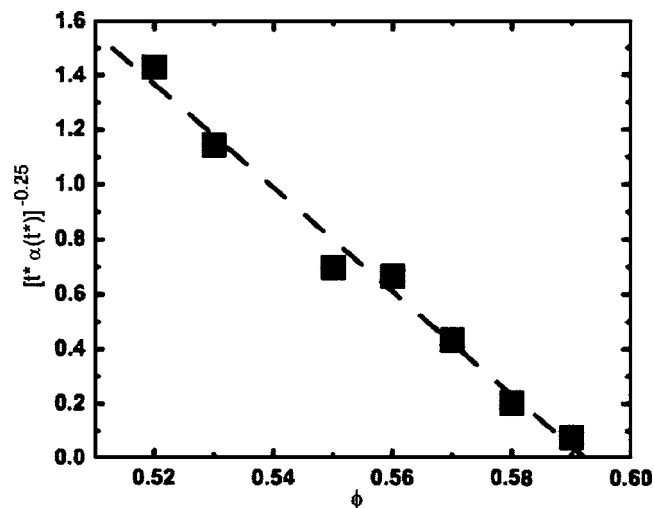


FIG. 3. Plot of  $[t^* \alpha(t^*)]^{-1/4}$  vs  $\phi$  following Ref. 35. The line is a best fit.

dently, there is no qualitative change in the non-Gaussian character of particle motion in the vicinity of  $\phi \approx 0.57$  that can be invoked to rationalize the trends reported here.

## B. Temporal exchange between $H$ and $S$ populations

Previous experimental work has established the dynamical exchange of immobile and mobile populations, and found that the exchange time is comparable to  $\tau$ , except in the immediate vicinity of the glass transition where it can be as much as 100 times larger.<sup>7</sup> We define a dynamic correlation function which can quantify the persistence of the  $H$  (or  $S$ ) particle states. Without loss of generality, we choose an arbitrary simulation time as our time origin ( $t=0$ ) and proceed to a time  $\tau$ , the structural relaxation time. At this point, we “mark” all the particles that have executed hops. We then define a function  $f_i(t) = \theta[(r_i[t+\tau] - r_i[t])^2 - 0.45]$ , where  $\theta$  is the step function, and  $f_i(t=0)$  is unity if the particle  $i$  hops between 0 and  $\tau$ . We then select new time origins  $t > 0$ , go to a time  $\tau$  from this new origin, and ask which of the marked particles continue to be  $H$  particles. We ensemble average this quantity, normalize it so that it goes from 1 to 0 as a function of time (Fig. 4),

$$C(t) = \frac{N \sum_i \langle f_i(t) f_i(0) \rangle - (\sum_i \langle f_i(0) \rangle)^2}{N \sum_i \langle f_i(0) \rangle - (\sum_i \langle f_i(0) \rangle)^2}.$$

We find that this autocorrelation function for the persistence of the  $H$  particle state  $C(t)$  takes progressively larger  $t$  to decay with increasing  $\phi$  and we define the mean exchange time by locating the point where this function assumes a value of  $(1/e)$ . In Fig. 4(b), we plot this exchange time, and the structural relaxation time as a function of  $\phi$ . Over the whole range of densities the exchange time is shorter than  $\tau$ , but there is a clear trend that these two curves will cross in the vicinity of  $\phi = 0.59$ . These results are apparently consistent with recent NMR measurements that suggest that the “lifetimes” for clusters of slow particles are comparable with  $\tau$  for temperatures roughly 10 K above the glass transition.<sup>7</sup> Further, our simulations suggest that exchange times can become longer than  $\tau$  but only in the immediate vicinity of vitrification. We are unable to equilibrate our sample for  $\phi$



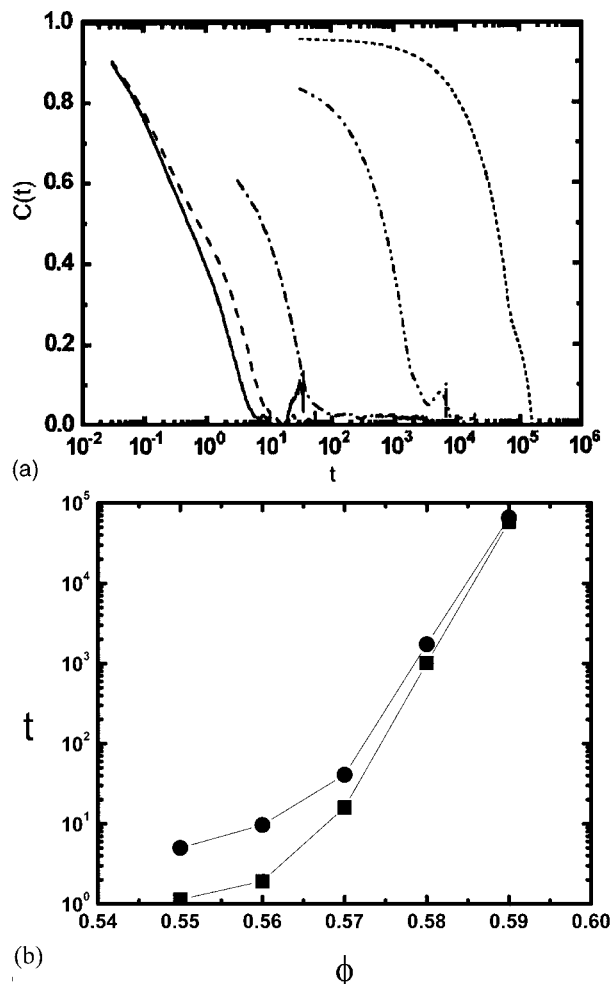


FIG. 4. (a) Plots of the correlation function for exchange  $C(t)$  as a function of  $t$ . From right to left they correspond to densities of  $\eta=0.59, 0.58, 0.57,$  and  $0.56$ . (b) Plots of exchange time [denoted by the time where  $C(t) = 1/e$ ] and structural relaxation time as a function of  $\eta$ . Lines are guides to the eyes.

greater than 0.60 (a density that was previously identified with the glass transition),<sup>11,37,38</sup> and similar difficulties are often found in real physical systems in this concentration range.

### C. Origins of hoplike motion

Finally, we comment briefly on situations where the initialization of the system did not yield amorphous samples, but rather yielded specimens where the spheres remained on a fcc lattice. For densities  $\phi \geq 0.58$ , we find that the particle “rattle” around their lattice positions, but these systems remain caged, and hence fixed in this structure for the entire duration of our simulations. For densities lower than  $\phi \approx 0.58$ , on the other hand, we find that the systems relax into an amorphous configuration by allowing for the presence of hoppers (note that the polydispersity is crucial for this process; a monodisperse fcc hard sphere system with density  $\phi > 0.545$  is in a stable, single phase crystalline state). For  $\phi < 0.53$ , the systems melt homogeneously without any  $H$  particle motion being required. To gain more insight into these results, we have calculated the rms value of the cage size relative to the interparticle spacing. First, we used the

intermediate time plateau value of  $\langle r^2 \rangle$  to define the cage size. In a second method we froze the particle positions at randomly chosen times and computed the minimum distance a particle would have to move to collide with another particle. The mean value of the square of these distances gives another physically motivated measure of cage size. The density where we just begin to see motion in the “crystalline” solid ( $\phi \sim 0.58$ ), and the last density where we can equilibrate an amorphous liquid ( $\phi = 0.59$ ), both yield cage sizes of  $\approx 0.14\sigma$ , consistent with the standard Lindemann criterion of melting. It appears that the Lindemann criterion of melting correctly anticipates both the density at which melting and vitrification occurs in these simple liquids.<sup>10,39–43</sup>

## IV. CONCLUSION

In summary, we find that an appropriately defined slow subpopulation of particles (sedentary particles) follow the Stokes-Einstein relationship even for  $\phi$  beyond the critical density  $\phi_c = 0.58$ , while the liquid as a whole violates this relationship. This observation provides conclusive evidence that the complementary “hoppers” are responsible for the breakdown of the Stokes-Einstein relationship.

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- <sup>1</sup>R. Yamamoto and A. Onuki, Phys. Rev. E **58**, 3515 (1998).
- <sup>2</sup>J. L. Barrat, J. N. Roux, and J. P. Hansen, Chem. Phys. **149**, 197 (1990).
- <sup>3</sup>L. Berthier, D. Chandler, and J. P. Garrahan, Europhys. Lett. **69**, 320 (2005).
- <sup>4</sup>H. Z. Cummins, J. Phys.: Condens. Matter **17**, 1457 (2005).
- <sup>5</sup>K. S. Schweizer and E. J. Saltzman, J. Phys. Chem. B **108**, 19729 (2004).
- <sup>6</sup>S. F. Swallen, P. A. Bonvallet, R. J. McMahon, and M. D. Ediger, Phys. Rev. Lett. **90**, 015901 (2003).
- <sup>7</sup>M. D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).
- <sup>8</sup>H. Sillescu, J. Non-Cryst. Solids **243**, 81 (1999).
- <sup>9</sup>M. T. Cicerone and M. D. Ediger, J. Chem. Phys. **104**, 7210 (1996).
- <sup>10</sup>X. Y. Xia and P. G. Wolynes, Phys. Rev. Lett. **86**, 5526 (2001).
- <sup>11</sup>E. R. Weeks, J. C. Crocker, A. C. Levitt, A. Schofield, and D. A. Weitz, Science **287**, 627 (2000).
- <sup>12</sup>P. Viot, G. Tarjus, and D. Kivelson, J. Chem. Phys. **112**, 10368 (2000).
- <sup>13</sup>D. Thirumalai and R. D. Mountain, Phys. Rev. E **47**, 479 (1993).
- <sup>14</sup>G. Tarjus and D. Kivelson, J. Chem. Phys. **103**, 3071 (1995).
- <sup>15</sup>F. H. Stillinger and J. A. Hodgdon, Phys. Rev. E **50**, 2064 (1994).
- <sup>16</sup>N. Lacevic and S. C. Glotzer, J. Phys. Chem. B **108**, 19623 (2004).
- <sup>17</sup>D. B. Hall, A. Dhinojwala, and J. M. Torkelson, Phys. Rev. Lett. **79**, 103 (1997).
- <sup>18</sup>A. Coniglio, A. de Candia, and M. Nicodemi, Nuovo Cimento Soc. Ital. Fis., D **20**, 2349 (1998).
- <sup>19</sup>H. Sigurgeirsson and D. M. Heyes, Mol. Phys. **101**, 469 (2003).
- <sup>20</sup>B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. **53**, 3813 (1970).
- <sup>21</sup>B. Doliwa and A. Heuer, Phys. Rev. E **61**, 6898 (2000).
- <sup>22</sup>W. Kob and J. L. Barrat, Phys. Rev. Lett. **78**, 4581 (1997).
- <sup>23</sup>R. J. Speedy, Mol. Phys. **62**, 509 (1987).
- <sup>24</sup>T. Voigtmann, A. M. Puertas, and M. Fuchs, Phys. Rev. E **70**, 061506 (2004).
- <sup>25</sup>C. De Michele and D. Leporini, Phys. Rev. E **63**, 036701 (2001).

- <sup>26</sup>G. Szamel and E. Flenner, *Europhys. Lett.* **67**, 779 (2004).
- <sup>27</sup>W. Kob and H. C. Andersen, *Phys. Rev. Lett.* **73**, 1376 (1994).
- <sup>28</sup>W. K. Kegel and A. van Blaaderen, *Science* **287**, 290 (2000).
- <sup>29</sup>Y. J. Jung, J. P. Garrahan, and D. Chandler, *Phys. Rev. E* **69**, 061205 (2004).
- <sup>30</sup>Y. Gebremichael, M. Vogel, and S. C. Glotzer, *Mol. Simul.* **30**, 281 (2004).
- <sup>31</sup>C. De Michele and D. Leporini, *Fractals* **11**, 139 (2003).
- <sup>32</sup>I. Chang and H. Sillescu, *J. Phys. Chem. B* **101**, 8794 (1997).
- <sup>33</sup>P. Bordat, F. Affouard, M. Descamps, and F. Muller-Plathe, *J. Phys.: Condens. Matter* **15**, 5397 (2003).
- <sup>34</sup>M. Fuchs, I. Hofacker, and A. Latz, *Phys. Rev. A* **45**, 898 (1992).
- <sup>35</sup>A. M. Puertas, M. Fuchs, and M. E. Cates, *J. Chem. Phys.* **121**, 2813 (2004).
- <sup>36</sup>T. Odagaki and Y. Hiwatari, *Phys. Rev. A* **43**, 1103 (1991).
- <sup>37</sup>W. Vanmegen and S. M. Underwood, *Phys. Rev. E* **49**, 4206 (1994).
- <sup>38</sup>P. N. Pusey and W. Vanmegen, *Nature (London)* **320**, 340 (1986).
- <sup>39</sup>T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, *Phys. Rev. A* **40**, 1045 (1989).
- <sup>40</sup>D. A. Young and B. J. Alder, *J. Chem. Phys.* **60**, 1254 (1974).
- <sup>41</sup>C. A. Murray and D. G. Grier, *Annu. Rev. Phys. Chem.* **47**, 421 (1996).
- <sup>42</sup>H. Lowen, *Phys. Rep.* **237**, 249 (1994).
- <sup>43</sup>J. H. Bilgram, *Phys. Rep.* **153**, 1 (1987).