Time scale for the onset of Fickian diffusion in supercooled liquids

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(Dated: February 13, 2022)

We propose a quantitative measure of a time scale on which Fickian diffusion sets in for supercooled liquids and use Brownian Dynamics computer simulations to determine the temperature dependence of this onset time in a Lennard-Jones binary mixture. The time for the onset of Fickian diffusion ranges between 6.5 and 31 times the α relaxation time (the α relaxation time is the characteristic relaxation time of the incoherent intermediate scattering function). The onset time increases faster with decreasing temperature than the α relaxation time. Mean squared displacement at the onset time increases with decreasing temperature.

PACS numbers: 64.70.Pf, 61.20.Lc, 61.43.Fs

Understanding the origin of the extreme slowing down of liquids’ dynamics upon approaching the glass transition and the nature of the transition itself has been of great interest for several decades. A lot of recent activity has been stimulated by the recognition that close to the transition the liquids’ dynamics become not only very sluggish but also increasingly heterogeneous. While the presence of dynamic heterogeneities is accepted, the details of their spatial and temporal structure have been only partially established. In particular, the question of the lifetime of dynamic heterogeneities is a few times longer than the α relaxation time, other experimental studies found that at a low temperature the lifetime of dynamic heterogeneities is significantly longer than the α relaxation time. In principle, the controversy can be resolved by postulating that the temperature dependence of these two times have not been exactly the same. However, in principle, the inverse is not necessarily true. Thus, the time for the onset of Fickian diffusion then the self part of the van Hove function is Gaussian and the shape of the probability distribution is given by

$$P(\log_{10}(\delta r); t) = \ln(10)^4 \pi \delta r^3 G_s(\delta r, t).$$

This distribution is defined in such a way that the integral $\int_{x_0}^{x_1} P(x; t) dx$ is the fraction of particles whose value of log$_{10}(\delta r)$ is between $x_0$ and $x_1$. The probability distribution $P(\log_{10}(\delta r); t)$ can be obtained from the self part of the van Hove correlation function $\Gamma(\delta r, t)$, $P(\log_{10}(\delta r); t) = \ln(10)4\pi \delta r^3 G_s(\delta r, t)$. The probability distribution $P(\log_{10}(\delta r); t)$ is a convenient indicator of Fickian diffusion because if particles move via Fickian diffusion then the self part of the van Hove function is Gaussian and the shape of the probability distribution $P(\log_{10}(\delta r); t)$ is independent of time. In particular, the height of the peak of this distribution is equal to $\ln(10)\sqrt{2\pi} e^{-3/2} \approx 2.13$ and deviations from this value indicate non-Fickian particle motion. We define the time for the onset of Fickian diffusion, $\tau_F$, as the time at which the peak of $P(\log_{10}(\delta r); t)$ is equal to 90% of its value for a Gaussian distribution of displacements, $P(\log_{10}(\delta r_{\text{max}}); \tau_F) \approx 1.92$. We will discuss the threshold value of 90% together with a different indicator of Fickian diffusion at the end of this Letter.

It should be noted that a deviation of the probability distribution $P(\log_{10}(\delta r); t)$ from its universal shape expected for Fickian diffusion indicates dynamic heterogeneity. However, in principle, the inverse is not necessarily true. Thus, the time for the onset of Fickian diffusion is probably only a lower bound for the lifetime of dynamic heterogeneities.

To investigate the onset time we use the trajectories generated by an extensive Brownian Dynamics simulation study of a 80:20 Lennard-Jones binary mixture introduced by Kob and Andersen. Briefly, the potential is given by $V_{\alpha \beta} = 4\epsilon_{\alpha \beta} [\sigma_{\alpha \beta}/r]^12 - [\sigma_{\alpha \beta}/r]^6$, where $\alpha, \beta \in \{A, B\}$, and $\epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\epsilon_{BB} = 0.5$, $\sigma_{AA} = 1.0$, $\sigma_{AB} = 0.8$, and $\sigma_{BB} = 0.88$ (all the results are presented in reduced units where $\sigma_{AA}$ and $\epsilon_{AA}$ are the units of length and energy, respectively). A total of
The static structure factor is equal to 10% of its initial time
tering function for a wave vector near the peak of the
maximum value, \( \tau \). We argued in Ref. [19] that devi-
ations from a Gaussian distribution of displacements. For a comparison we also show, as a dotted line, \( P(\log_{10}(\delta r); t) \) resulting from a Gaussian distribution of displacements.

\[ N = 1000 \text{ particles were simulated with a fixed cubic box length of 9.4. The details of this study have been presented elsewhere [19, 22]} \]

In the present investigation we use only some of the temperatures simulated before: \( T = 1.0, 0.9, 0.8, 0.6, 0.55, 0.5, 0.47, \) and 0.45. The previous runs at the temperature \( T = 0.45 \) have been extended by 60%: the A particles’ mean squared displacement at the end of the extended runs is about 16. We present the results for the A particles only. The results for the B particles are qualitatively the same, although the statistics is worse due to the smaller number of B particles. The temperature dependence is presented by plotting various quantities vs. \( T - T_c \) where \( T_c = 0.435 \) is the crossover temperature [14, 21]. This is a convenient way to expand the temperature scale and it should not imply an endorsement of any particular theoretical approach.

We start by showing in Fig. 1 the probability distributions \( P(\log_{10}(\delta r); t) \) at \( T = 0.45 \) for the A particles at several times characteristic for the relaxation of the system. The first one is the time at which the non-Gaussian parameter \( \alpha_2(t) = \frac{3}{2} \langle \delta r^4 \rangle / \langle \delta r^2 \rangle^2 - 1 \) reaches the maximum value, \( \tau_{ng} \). The second one is the \( \alpha \) relaxation time, \( \tau_\alpha \), which is defined in the usual way: \( \tau_\alpha \) is the time at which the incoherent intermediate scattering function for a wave vector near the peak of the static structure factor is equal to 1/\( e \) of its initial time value, \( F_\alpha(k; \tau_\alpha) = 1/e \). The third time is the time at which a new non-Gaussian parameter \( \gamma(t) = \frac{1}{3} \langle \delta r^2 \rangle \langle 1/\delta r^2 \rangle - 1 \) [19] reaches the maximum value, \( \tau_{nnng} \). We argued in Ref. [19] that deviations of \( P(\log_{10}(\delta r); t) \) from its Fickian shape are most evident for times comparable to \( \tau_{nnng} \). The fourth time is the time at which the incoherent intermediate scattering function for a wave vector near the peak of the static structure factor is equal to 10% of its initial time value, \( F_\alpha(k; \tau_{0.1}) = 0.1 \). The final time is the onset time, \( \tau_F \), i.e. the time at which the peak of \( P(\log_{10}(\delta r); t) \) is equal to the 90% of its value for a Gaussian distribution of displacements. For a comparison we also show a \( P(\log_{10}(\delta r); t) \) resulting from a Gaussian distribution of displacements. It is clear from Fig. 4 that at shorter times, i.e. at \( \tau_{ng}, \tau_\alpha, \tau_{nnng}, \) and \( \tau_{0.1} \) the probability distributions \( P(\log_{10}(\delta r); t) \) deviate strongly from the shape resulting from a Gaussian distribution of displacements. While there are still noticeable differences even at \( \tau_F \), we believe that these are small enough to consider \( \tau_F \) the onset time for Fickian diffusion.

In Fig. 2 we show \( P(\log_{10}(\delta r); \tau_F) \) for the A particles for \( T = 1.0, 0.8, 0.6, 0.55, 0.50, 0.47, \) and 0.45. It should be noted that with decreasing temperature the probability distributions at \( \tau_F \) shift toward larger displacements. In other words, mean squared displacement at the onset of Fickian diffusion increases with decreasing temperature. The right panel indicates that the shape of \( P(\log_{10}(\delta r); \tau_F) \) is temperature-independent and, therefore, the late-time liquids’ dynamics are, up to rescaling of the time and distance scales, similar.

Fig. 3 presents our main result: comparison of the temperature dependence of of the onset time for Fick-

\[ \tau_F, \text{ i.e. the time at which the peak of } P(\log_{10}(\delta r); t) \]

in the context of the time dependence of the mean squared
having identified the Fickian crossover time, \( \tau_F \), we can define a characteristic length scale, the root mean squared displacement at the onset time, \( \langle \delta r^2(\tau_F) \rangle^{1/2} \). It follows from Figs. 2 and 3 that this length increases with decreasing temperature. Our characteristic length should be related to the so-called Fickian crossover length \( l^* \) introduced by Berthier et al. 24 The latter length was defined through the wavevector dependence of the relaxation time of a supercooled liquid. Roughly speaking, \( l^* \) is the length scale on which diffusion is Fickian on all time scales. The prediction of Ref. 23 was that this length scale changes with temperature as the square root of the product of the self-diffusion coefficient and the \( \alpha \) relaxation time; all the data pertain to the A particles. Dashed lines indicate scaling relationships \( \langle \delta r^2(\tau_F) \rangle^{1/2} \propto \tau_\alpha^{0.13} \) and \( \tau_F/\tau_\alpha \propto \tau_\alpha^{0.13} \).
for another 7 or 8 orders of magnitude of $\tau_\alpha$ (i.e., up to $\tau_\alpha$ comparable to that at the laboratory glass transition temperature), the resulting $\tau_F$ would be greater than the longest experimentally observed heterogeneity lifetime.

To summarize, we proposed a quantitative definition of the onset time for Fickian diffusion and investigated its temperature dependence in a Lennard-Jones binary mixture. We found that the onset time is considerably longer than the $\alpha$ relaxation time and, more importantly, it increases faster with decreasing temperature than the $\alpha$ relaxation time. Our definition of the onset time relies upon one particular indicator of Fickian diffusion, the probability distribution of the logarithm of single-particle displacement, $P(\log_{10}(\delta r); t)$, and upon adopting a particular numerical criterion for the onset of Fickian diffusion, peak height equal to the 90% of its Fickian value. This procedure seems reasonable in that it results in non-Fickian motion being present only at temperatures at and below $T \approx 1.0$. This temperature has been identified before as so-called onset temperature for slow dynamics. To test the robustness of our main result we also tried using a different indicator of Fickian diffusion: the new non-Gaussian parameter that we introduced recently. In this approach we defined the onset time for Fickian diffusion to be the time at which the new non-Gaussian parameter is equal to 1/3. This particular numerical value results in non-Fickian motion being present only at temperatures at and below $T \approx 0.8$. The resulting onset times are somewhat shorter than the ones presented in this Letter. However, the temperature dependence of the onset time defined using the non-Gaussian parameter is similar to that of the onset time defined using $P(\log_{10}(\delta r); t)$. More interestingly, we found that the shapes of $P(\log_{10}(\delta r); t)$ at the onset times defined using the new non-Gaussian parameter are very similar and, in particular, the height of the peak is approximately temperature independent and equal to 85% of its value for Fickian diffusion.

Finally, we would like to point out that the results presented here violate the time-temperature superposition principle: in order to superimpose the probability distributions $P(\log_{10}(\delta r); t)$ shown in the left panel of Fig. 2 we have to shift $\log_{10}(\delta r)$ by $\log_{10}(\langle \delta r^2(\tau_F) \rangle)^{1/2}$. The more usual shift procedure, agreeing with the time-temperature superposition, would involve the $\alpha$ relaxation time rather than the onset time $\tau_F$ which has temperature dependence different from $\tau_\alpha$.

G.S. thanks Mark Ediger for many discussions on dynamic heterogeneity experiments that stimulated this work. We gratefully acknowledge the support of NSF Grant No. CHE 0111152.

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