Understanding the Stokes–Einstein relation in supercooled liquids using random pinning

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Abstract. The breakdown of the Stokes–Einstein relation in supercooled liquids is believed to be one of the hallmarks of glass transition. The phenomenon has been studied in depth over many years in efforts to understand the microscopic mechanism, without much success. Recently it was found that the violation of the Stokes–Einstein relation in supercooled liquids can be tuned by randomly pinning a set of particles in their equilibrium positions. This observation suggested a possible framework where the breakdown of the Stokes–Einstein relation in the dynamics of supercooled liquids can be studied in a systematic manner. We have performed extensive molecular dynamics simulations to understand this phenomenon by analysing the structure of appropriately defined sets of dynamically slow and fast particle clusters. The breakdown of the Stokes–Einstein relation is found to become predominant once the cluster formed by the slow particles percolates the entire system size. Finally we propose a possible close connection between fractal dimensions of these clusters and the exponents associated with the fractional Stokes–Einstein relation.

Keywords: disordered systems (theory), dynamical heterogeneities (theory), slow relaxation and glassy dynamics, structural glasses (theory)

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1. Introduction

The dynamics of supercooled liquids and the associated glass transition where viscosity or relaxation time increases dramatically with decreasing temperature still puzzle the scientific community, even after decades of research [1–8]. The viscosity change is so dramatic that with a few tens of degrees of change in temperature, viscosity can change by as much as 16 orders of magnitude, and the temperature at which viscosity reaches $10^{16}$ poise is termed the calorimetric glass transition temperature, $T_g$. The temporal density–density correlation functions in the supercooled temperature regime show multiple relaxation steps. The short timescale relaxation is termed $\beta$-relaxation [9] and the longer timescale relaxation is called $\alpha$-relaxation. One of the most puzzling phenomena observed in the long timescale $\alpha$-relaxation process is the breakdown of the famous Stokes–Einstein relation [10–12]. This is one of the hallmarks of supercooled liquids, and has been studied extensively without a clear general consensus on its molecular origin [13–25]. Thus a better understanding of this phenomenon will definitely be of immediate importance for developing the theory of glass transition.

The Stokes–Einstein relation connects the viscosity of a liquid ($\eta$) to the diffusion constant ($D$) as

$$D \propto \frac{k_B T}{\eta}$$

where $k_B$ is the Boltzmann constant. The constant of proportionality depends on the details of the probe particles used to measure the diffusion constant of the liquids. One often uses self-diffusion constants instead of tracer diffusion in the above equation for simple liquids interacting via isotropic pairwise potential. It is found that at least in
the low-temperature regime viscosity, $\eta$ is proportional to the longer $\alpha$-relaxation time, $\tau_\alpha$ [26] (see section 2 for definition), so it is customary in the literature to cast the Stokes–Einstein relation in the following form

$$D \propto \frac{k_B T}{\tau_\alpha}$$

where $\eta$ is replaced by $\tau_\alpha$. The other reason for this modification lies in the fact that calculation of $\tau_\alpha$ is much easier and more straightforward than the viscosity (notice that it has already been shown in the literature that this is not the reason for the breakdown in the Stokes–Einstein relation). Thus if one plots $D\tau_\alpha/T$ as a function of $T$, it should be a temperature-independent constant, but it turns out that for supercooled liquids this ratio becomes a strong function of temperature below a certain temperature level. Phenomenological arguments [13, 16] often assume the existence of dynamic heterogeneity [24, 27–34], which means the existence of mobile and less mobile dynamical regions in the supercooled liquid states, in order to explain the violation of the Stokes–Einstein relation. Many previous studies have indeed shown a positive correlation between Stokes–Einstein breakdown and dynamic heterogeneity [22, 33] as measured by the four-point density–density correlation function (see section 2 for definition).

Often a generalized version of the Stokes–Einstein relation [19, 47] is also used to describe the interrelationship between the diffusion constant and relaxation time in the supercooled regime with the following form:

$$D \propto \tau_\alpha^{-1+\omega}$$

where exponent $\omega$ characterizes the degree of deviation from the normal Stokes–Einstein relation. This relation is called the fractional Stokes–Einstein relation and in [19, 47], it was shown that the fractional Stokes–Einstein exponent can depend on the dimensionality of the system as well as on the details of the microscopic interaction between particles. From the mean field arguments, it is expected that $\omega$ will go to zero as one increases the spatial dimensions. This expectation is broadly supported by the results reported in [22, 48–50]. In [49] it was shown that the fractional Stokes–Einstein exponent $\omega$ actually goes to zero as the number of spatial dimensions goes to eight. This provided for the first time a direct estimate of the upper critical dimension for glass-forming liquids, above which the mean field type description of the liquids should hold [49]. Thus it would be useful if one could change the fractional Stokes–Einstein exponent with ease in model systems to gain further insight into the problem.

In [51], it was shown that one can change the fractional Stokes–Einstein exponent with ease in model systems simply by randomly pinning some fraction of particles in their equilibrium positions [35, 46, 52]. Here we will use this protocol to understand in depth the breakdown of the Stokes–Einstein relation and its relation with any underlying structural changes in the liquids. The rest of the paper is organized as follows: first, details of the model system studied are described, followed by the definitions of the different dynamical quantities calculated in this study. The details of the pinning protocol used to generate random pinning in the system are discussed subsequently. Finally we discuss the implications of the obtained results for the understanding of the breakdown of the Stokes–Einstein relation.
2. Method and simulation details

2.1. Model

We perform simulations for a model glass-forming liquid in two dimensions in this work. The model is characterized by a repulsive inverse power-law potential \( (2dR10) \) [52]. This model has been studied extensively and found to be a good glass former [52]. The interaction potential is given by

\[
V_{\alpha\beta}(r) = \epsilon_{\alpha\beta} \left( \frac{\sigma_{\alpha\beta}}{r} \right)^n
\]

where \( \alpha, \beta \in \{A, B\} \) and \( \epsilon_{\alpha\beta} = 1.0 \), for all \( \alpha \) and \( \beta \). \( \sigma_{AA} = 1.0 \), \( \sigma_{AB} = 1.18 \), \( \sigma_{BB} = 1.40 \), and \( n = 10 \). The interaction potential was cut off at \( 1.38 \sigma_{\alpha\beta} \). For this model the system sizes studies are \( N = 1000, 10\,000 \) at a number density \( \rho = 0.850 \) for many different temperatures in the range \( T \in [0.480, 3.000] \). These simulations are done in the canonical ensemble using a modified leap-frog integration scheme with the Berendsen thermostat. We have also performed simulation with another constant temperature simulation algorithm due to Brown and Clark [53]. The results do not depend on the exact algorithm used for integrating the equations of motion. We have averaged the data over 32 independent runs of length \( 100 \tau_{\alpha} \).

2.2. Pinning protocol

In this study we have pinned a fraction \( \rho \) of the total number of particles randomly from their equilibrium configurations. First we equilibrate a system of a given number of particles, \( N \), at the studied temperatures and then we choose randomly \( N_{\rho} = \rho N \) number of particles from one such equilibrated configuration and pin their positions. The advantage of such a pinning protocol is that the system with the pinned particles is already in equilibrium as the positions of the pinned particles are taken from an equilibrium configuration. This procedure bypasses re-equilibration of the system after introducing this form of quenched disorder. We then perform averaging over different realizations of these pinning positions (averaging over quenched disorder) to calculate different thermodynamic and dynamic quantities. In this study we have done averaging of 32 different realizations of disorder and we checked that this amount of averaging is enough to get reliable results. One can also pin particles in ordered arrangements with further equilibration and the results may depend on the details of the pinning protocol, but we don’t expect much qualitative change in the reported results.

2.3. Correlation functions

Dynamic heterogeneity in the system is characterized by the four-point density correlation function \( g_4(r, t) \) [54–56], which is a product of four density evaluated at two different space points and two time points. A four-point susceptibility may be defined as the \( k = 0 \) value of the Fourier transform \( g_4(k, t) \) of this function. A variant [57] of this four-point function has been used extensively in numerical studies of dynamic heterogeneity because it is easier to compute. This quantity is obtained from the overlap function \( q(t) \) defined as

\[
g_4(r, t) = \frac{1}{(2\pi)^2} \int \int g_4(k_1, k_2) e^{-i(k_1 \cdot r + k_2 \cdot r)} dk_1 dk_2
\]

where \( g_4(k, t) = \frac{1}{(2\pi)^2} \int \int g_4(k_1, k_2) e^{-i(k_1 \cdot k_2 - k_1 \cdot k_2)} dk_1 dk_2 \) and \( q(t) \) is obtained from \( g_4(k, t) \) using the relation \( q(t) = \frac{1}{4\pi^2} \int \int g_4(k, t) dk \).
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\[ q(t) = \frac{1}{N - N_p} \sum_{i=1}^{N-N_p} w(|\mathbf{r}_i(0) - \mathbf{r}_i(t)|), \]  

(5)

where \( \mathbf{r}_i(t) \) is the position of particle \( i \) at time \( t \), \( N \) is the total number of particles and \( N_p \) is the number of pinned particles. \( w(r) = 1 \) if \( r \leq a_0 \) and zero otherwise, and \( a_0 \) is a short-distance cutoff chosen to be close to the distance at which the root-mean-square displacement of the particles as a function of time exhibits a plateau (the precise choice of the value of \( a_0 \) turns out to be qualitatively unimportant). The thermal and disorder averaged overlap function is denoted as

\[ Q(t) = \langle q(t) \rangle. \]  

(6)

The fluctuations in this two-point function yield the dynamical four-point susceptibility:

\[ \chi_4(t) = \frac{1}{N - N_p} (\langle \langle q^2(t) \rangle \rangle - \langle q(t) \rangle^2) \]  

(7)

with the peak value defined as \( \chi_4^p \equiv \chi_4(t = \tau_4) \), where \( \tau_4 \) is the time at which \( \chi_4(t) \) attains its maximum value and \( \tau_4 \approx \tau_\alpha \) at all temperatures. The \( \alpha \)-relaxation time \( \tau_\alpha \) is defined using the two-point correlation function as \( Q(t = \tau_\alpha) = 1/e \). The diffusion constant \( D \) for different temperatures and pinning densities is calculated from the slope of the mean squared displacement using the relation \( \langle \Delta r^2(t) \rangle = 2dDt \) where \( d \) is the spatial dimension and in this case \( d = 2 \).

2.4. The van Hove function

The van Hove function is the probability of finding a displacement of a particle of amount \( x \) over a timescale of \( t \). The self part of this correlation function is defined as

\[ G_s(x, t) = \sum_{i=1}^{N} \delta(x - x_i(t) - x_i(0)), \]  

(8)

where \( x_i(t) \) is one of the coordinates of the position of particle \( i \) at time \( t \).

3. Results

In figure 1, we have plotted the Stokes–Einstein parameter \( D \tau_\alpha / T \) as a function of temperature for different pinning densities. One can clearly see that the quantity is fairly independent of temperature up to some temperatures for a given pinning concentration and then starts to increase rapidly, indicating the violation of the Stokes–Einstein relation in this temperature regime. The phenomenon becomes even more prominent with increasing pinning concentration and the Stokes–Einstein parameter becomes strongly temperature-dependent. The temperature at which this violation happens seems to also increase with increasing pinning concentration as shown in figure 1. Thus pinning a set of randomly chosen particles in their equilibrium positions is a good model system to systematically understand the breakdown of the Stokes–Einstein relation in supercooled liquids.

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In figure 2, we have plotted $D$ versus $\tau_{\alpha}$ in log–log plot for different pinning concentrations, $\rho$. One can clearly see that at higher temperatures this relation breaks down and one gets $D \sim \tau_{\alpha}^{-1+\omega}$ with $\omega > 0$. The straight line has slope $-1$. The exponent increases with increasing pinning concentration as shown in the right panel. Notice the significant finite size effect on the extracted exponent. $\omega$ increases faster with increasing pinning concentration for $N = 10000$ system size.

In figure 2, we have plotted $D$ versus $\tau_{\alpha}$ in log–log plot for different pinning density to understand the effect of pinning density on the fractional Stokes–Einstein relation. As in [51], we have found that at higher temperatures $D \propto \tau_{\alpha}^{-1}$, but at lower temperatures, this relation breaks down. In this low-temperature regime, data is better described by the relation $D \propto \tau_{\alpha}^{-1+\omega}$, with $\omega > 0$. We have fitted only five data points

Figure 1. The Stokes–Einstein parameter $D\tau_{\alpha}/T$ is plotted as a function of temperature for different pinning concentrations, $\rho$. One can clearly see that at high temperatures the parameter is almost independent of temperature and then starts to become temperature-dependent somewhat sharply. The temperature at which the breakdown happens increases to higher value with increasing pinning concentration.

Figure 2. Left panel: the fractional Stokes–Einstein relation, $\tau_{\alpha}$, is plotted as a function of $D$ for different pinning concentrations. One can see that at higher temperatures $D \sim 1/\tau_{\alpha}$, but at lower temperatures this relation breaks down and one gets $D \sim \tau_{\alpha}^{-1+\omega}$ with $\omega > 0$. The straight line has slope $-1$. The exponent increases with increasing pinning concentration as shown in the right panel. Notice the significant finite size effect on the extracted exponent. $\omega$ increases faster with increasing pinning concentration for $N = 10000$ system size.
in the large \( \tau_a \) region for each pinning density to get an estimate of \( \omega \). The value of the fractional Stokes–Einstein exponent \( \omega \) increases continuously with increasing pinning density, as shown in the lower panel of figure 2. We will next discuss the correlation between the different dynamical correlation functions which measure the heterogeneity present in the dynamic at the supercooled temperature regime with the breakdown of the Stokes–Einstein relation.

As discussed before, many phenomenological theories suggest that Stokes–Einstein breakdown is due to the presence of dynamic heterogeneity in the system [16, 22], and indeed some correlations were found in [22]. It was shown that a peak height of \( \chi_4 \) starts to grow rapidly at a temperature very close to the temperature where the Stokes–Einstein breakdown happens for different model systems. The behaviour was found to be independent of spatial dimensions. To see whether a similar correlation exists for the pinned system also, we have calculated the four-point susceptibility as shown in figure 3. One can see that the peak height of the \( \chi_4(t) \) increases with decreasing temperature, indicating the growth of dynamic heterogeneity in the system. On the other hand, the peak height of \( \chi_4(t) \) when plotted as a function of pinning density for a given temperature shows a completely different trend. It decreases instead of increasing with increasing pinning density. In figure 4, the peak height of \( \chi_4(t) \), \( \chi_4^P \) is plotted as a function of pinning density for different temperatures. Thus \( \chi_4^P \) does not seem to show the previously observed correlation with the breakdown of the Stokes–Einstein relation [22].

Next we check whether the exponent \( \beta \), related to the stretched exponential decay of the two-point correlation function, is correlated with Stokes–Einstein breakdown as found in previous studies [22], to get the exponent \( \beta \) by fitting the \( Q(t) \) data to the following fitting function

\[
Q(t) = A \exp \left[ -\left( \frac{t}{\tau} \right)^2 \right] + B \exp \left[ -\left( \frac{t}{\tau} \right)^\beta \right].
\]

The quality of the fitting as shown in figure 5 is reasonably good for a reliable estimate of exponent \( \beta \). \( \tau_2 \) obtained from the fits are proportional to \( \tau_n \) with a proportionality constant close to one, but in this study we have used the relation \( Q(t = \tau_n) = 1/e \) to define the \( \alpha \)-relaxation time. The fitting is done to obtain the stretched exponent \( \beta \) only.

In figure 6, we have shown the stretched exponent \( \beta \) as a function of temperature for different pinning densities and one can clearly see that \( \beta \) becomes smaller and smaller with increasing pinning density. In [22], it was shown that \( \beta \) becomes closer to one as one increases the dimensions of the system from \( d = 2 \) to \( d = 4 \) and the Stokes–Einstein breakdown also becomes less prominent with increasing dimensionality. Thus it seems that the stretched exponent \( \beta \) is a good measure of the Stokes–Einstein breakdown even for pinned systems.

Now if we assume that stretched exponential relaxation is related to hierarchical relaxation processes, we can write the longer-time part of the correlation function, \( Q(t) \), as

\[
Q(t) \sim \exp(-t/\tau_\alpha)^\beta = \int_0^\infty P(\tau) \exp(-t/\tau) d\tau
\]

where \( \beta \) will be related to the relative variance of the distribution and a smaller \( \beta \) will correspond to a larger relative width of the distribution. To ascertain that we have
calculated the distribution $P(\tau)$ by discretizing equation (10) in time and minimizing the following cost function,

$$
\chi^2 = \sum_{i=1}^{m} \left[ Q(t_i) - \sum_{j=1}^{M} P_j \exp(-t_i/\tau_j)\Delta\tau \right]^2,
$$

where $m$ is the number of time points $t_i$, two-point correlation function $Q(t)$ is obtained from simulations and $M$ is the number of discretized $\tau$ values ($\tau_j$) where we want to find out the probability density $P_j$. $\Delta\tau = \tau_{j+1} - \tau_j$ is the elementary discretization step size.

Figure 3. Four-point dynamic susceptibility, $\chi_4(t)$ as a function of time for different temperatures for pinning concentration $\rho = 0.020$. Notice the monotonic increase in the peak height of $\chi_4(t)$ with decreasing temperature.

Figure 4. Peak height of $\chi_4(t)$, $\chi_4^P$ as a function of pinning concentration for different temperatures. Notice that $\chi_4^P$ becomes smaller with increasing pinning concentration, especially at lower temperatures.
One crucial transformation which is required to get the required convergence of the $\chi^2$ minimization is to do the following variable change, $P_j = P^{\alpha}_j$, and then minimize with respect to the new variable $p_j$. This ensures the positivity of the probability \cite{58}. As shown in the top panel of figure 7, the convergence is found to be fast and one can get a reliable estimate of the underlying probability distribution of the relaxation time. We have calculated the probability for all the different temperatures at different pinning densities, but show the results for three different pinning concentrations at temperatures where $\tau_\alpha$ are comparable to each other. The results clearly show that indeed the normalized distribution tends to have a larger width with increasing pinning density. The observed bi-modality of the distribution function is also interesting.

Up to now we have shown that the peak height of $\chi_4(t)$ is not a good measure of the degree of the Stokes–Einstein violation in the pinned system, whereas the stretched

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**Figure 5.** Fitting of $Q(t)$ using equation (9) for temperature $T = 0.520$ and $\rho = 0$. The fitting observed is very good over the whole time window and thus one can be confident of the obtained values of stretched exponent $\beta$.

**Figure 6.** Stretched exponent $\beta$ as a function of $\alpha$-relaxation timescale $\tau_\alpha$ for different pinning concentrations. Notice that $\beta$ becomes significantly smaller for larger pinning concentrations at lower temperatures.
exponent $\beta$ and the associated distribution of relaxation time, $P(\tau)$, are. Next we will quantify the dynamic heterogeneity in an alternative way by identifying ‘slow’ and ‘fast’ particles over the $\alpha$-relaxation timescale as done in \cite{51} and discuss the results for the clustering properties of these slow particles in the system to elucidate their role in the breakdown of the Stokes–Einstein relation.

We will first briefly discuss the method employed to obtain the distribution of diffusion constants from the van Hove correlation function using Lucy iteration \cite{59}. This method was also recently used in \cite{60} for the diffusion processes in biological systems. We start with the assumption that particle displacements are mainly caused by diffusion processes. Due to dynamic heterogeneity in the system, at least in the supercooled temperature regime, it is not very surprising to find that there will be a distribution of local diffusivity $p(D)$. Then we can express the van Hove correlation function calculated at the $\alpha$-relaxation timescale, $G_s(x, \tau_\alpha)$, in terms of $p(D)$ as

$$G_s(x, \tau_\alpha) = \int_0^{D_0} p(D) \cdot g(x|D) \cdot dD,$$

where $g(x|D) = 1/\sqrt{4\pi D\tau_\alpha} \exp(-x^2/4D\tau_\alpha)$ and $D_0$ is the upper limit of diffusion constant and will be equal to diffusivity for a free diffusion. Now given the $G_s(x, \tau_\alpha)$, we calculate the distribution of diffusivity $p(D)$ following \cite{59} as

$$p^{n+1}(D) = p^n(D) \int_{-\infty}^{\infty} \frac{G_s(x, \tau_\alpha)}{G_s^n(x, \tau_\alpha)} g(x|D) dD,$$

where $p^n(D)$ is the estimate of $p(D)$ in the $n$th iteration with $p^0(D) = (1/D_{avg}) \exp(-D/D_{avg})$ and

$$G_s^n(x, \tau_\alpha) = \int_0^{D_0} p^n(D) \cdot g(x|D) \cdot dD.$$
Similarly
\[ P^{n+1}(D_{\tau_0}) = P^n(D_{\tau_0}) \int_{-\infty}^{\infty} \frac{G(x, \tau_0)}{G^n(x, \tau_0)} g(x|D)dx, \] (15)

where \( p(D)\,dD = P(D_{\tau_0})\,d(D_{\tau_0}) \). The choice of \( D_{\tau_0} \) as our variable is due to the fact that \( D \) changes by several orders of magnitude in the studied temperature range whereas \( D_{\tau_0} \) changes relatively modestly with decreasing temperature, making it easier to compare the distributions obtained for different temperatures (please see [51] for further details).

In figure 8, the van Hove functions are plotted for different temperatures at two different pinning densities. At higher temperatures the distribution is closer to being Gaussian and the deviation becomes much more prominent with decreasing temperature. At lower temperatures the tail of the distribution becomes exponential and it is believed to be universal in nature [34]. The lines passing though the symbols are obtained from equation (14) using the converged distribution function, \( P(D) \), from equation (15). In figure 9, we have shown the obtained distribution of diffusion constants for different pinning concentrations. For the unpinned case the distribution is bimodal below some temperatures, clearly telling us that one can identify a set of ‘slow’ and ‘fast’ moving particles over the \( \alpha \)-relaxation timescale. Notice that at much larger time than \( \tau_0 \) the dynamic heterogeneity will be averaged out in space and one expects the corresponding van Hove function to become Gaussian at much larger time. Thus at longer timescales the distribution will also loose its bimodality. However in [51] it was found that the bimodality of the distribution remains intact even for timescales that are larger than the \( \alpha \)-relaxation timescale by factor of 2–3. Thus we believe the results reported here to be qualitatively valid even for timescales larger than the typical relaxation time.

To define ‘slow’ and ‘fast’ moving particles, a cutoff value of diffusion constant \( D = D_c \) is chosen between the two prominent peaks of the distribution. This is done in such a way that at \( D_{\tau_0} \) the distribution of the diffusion constant, \( P(D_{\tau_0}) \), has a
minimum. For systems with pinning, the peak associated with the slow particles in the
distribution splits into two peaks. This can be understood as follows: with increasing
pinning density the difference in the diffusion constants between slow and fast particles
will increase strongly and there will be a set of particles that reside on the boundary of
slow-moving and fast-moving particles with intermediate diffusion constants. The split
of the first peak in $P(D_{\tau_0})$, we believe, is due to these sets of particles with intermedi-
ate values of diffusion constants. In our studies we have considered these particles also
to be part of the slow particles to make the analysis simple. As mentioned before, $P(\tau)$
also shows bimodality and it will be interesting to see whether different peaks in that
distribution actually correspond to the relaxation of slow- or fast-moving particles.

Next we have defined a cutoff distance $r_c = \sqrt{4D_{\tau_0}}$ and denoted all those particles
that have not moved a distance greater than $r_c$ over the $\tau_0$ timescale as slow-moving par-
ticles. The others that have moved beyond that critical distance are termed fast-moving
particles. Once the fast- and slow-moving particles are identified, a cluster finding algo-
rithm is used to find all the clusters formed by the slow particles. In figure 10, we have
plotted the distribution of cluster size for slow-moving particles for different temper-
atures at a pinning concentration of $\rho = 0.040$. One can see the appearance of the power
law distribution at lower temperatures with exponent $P(S) \sim S^{-3/2}$. In the right panel of
the same figure we have done the fitting to obtain the exponent of the power law decay
and the fitted value of the exponent turns out to be close to $-1.62$. At still further lower
temperatures one can see the appearance of a hump at larger cluster sizes, indicating
the existence of system-spanning clusters. Motivated by this observation we have tried
to study a possible underlying percolation transition of slow-moving particles.

In figure 11, we have plotted the probability of finding a system-spanning cluster, $P_c$,
as a function of temperature for different pinning concentrations. $P_c$ grows sharply
after a particular critical temperature and this temperature also shifts to higher val-
ues with increasing pinning concentration. Thus there is a one-to-one correspondence
between the onset of the Stokes–Einstein violation and the appearance of system-
spanning clusters. To establish a possible underlying percolation transition one needs

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Figure 9. Distribution of diffusion constants for different temperatures for
$\rho = 0.00$ (left panel) and $\rho = 0.020$ (right panel). Notice the multi-modal nature of
the distribution at lower temperatures.
to perform a detailed finite size scaling analysis, which has not been yet performed in this study due to large computational requirements; however, we checked how \( P_c \) grows for a smaller system size of \( N = 1000 \) particles. In the case of the percolation transition, one expects \( P_c \) to increase less sharply with decreasing temperature due to finite size effects. In figure 11, we have also plotted \( P_c \) as a function of temperature for system sizes \( N = 1000 \) along with \( N = 10000 \) for different pinning concentrations. \( P_c \) indeed increases less sharply with decreasing temperature for smaller system sizes. This finite size effect is evident in the data for smaller system sizes, as shown in figure 11.
size effect suggests a possible underlying percolation transition [61] associated with the Stokes–Einstein violation. It will be interesting to perform a detailed finite size scaling analysis to calculate the exponents related to this transition and its connection to slowing down in dynamics in supercooled liquids. In figure 12, the growth of the mean cluster size, $\langle S \rangle$, is plotted as a function of temperature for different pinning concentrations. The growth of this scale is very rapid and is faster for higher pinning concentrations. This is in accordance with the stronger degree of violation of the Stokes–Einstein relation with increasing pinning concentrations.

Finally, to understand the origin of the fractional Stokes–Einstein exponent, $\omega$, we have calculated the fractal dimensions of these spanning clusters using the sandbox method [62] as shown in figure 13. The fractal dimensions are in the range $D_f \in [1.5–1.8]$.
for all the temperatures and pinning concentrations. The important point to note is that the fractal dimension increases systematically with increasing pinning concentrations. Thus it seems there is a positive correlation between the fractal dimensions of the system-spanning cluster, $D_f$, and the fractional Stokes–Einstein exponent, $\omega$. At this moment we do not have a clear understanding of this correlation but the following simple arguments seem to suggest such a correlation. At higher temperatures $D \sim 1/\tau_\alpha$ and then at lower temperatures $D \sim 1/\tau_\alpha^{1-\omega}$ with $\omega > 0$, which implies that $\tau_\alpha$ increases much faster than the rate at which $D$ decreases. This difference in the change of $\tau_\alpha$ and $D$ with decreasing temperature will be much more prominent if the clusters formed by the slow-moving particles become more compact. This is due to the fact that $\tau_\alpha$ is mainly determined by the relaxation of the slow particles and breaking a compact slow cluster will take longer than breaking a less compact cluster. On the other hand, $D$ is predominantly determined by the diffusion constants of the fast-moving particles. It will be interesting to see whether such an argument works for a system where breaking a slow particle cluster is even more difficult due to bond formation, for example in the ‘patchy’ colloidal system [64].

4. Discussion

To conclude, we have performed extensive molecular dynamics simulations of a model glass-forming liquid in two dimensions to understand the breakdown of the Stokes–Einstein relation. We found that if one randomly pins a fraction of particles in their equilibrium positions then the breakdown of the Stokes–Einstein relation becomes even more dramatic. Thus supercooled liquids with random pinning can be used to study the phenomenon of the breakdown of the Stokes–Einstein relation in a more systematic way.

The main findings of this study can be summarized as follows:

- The breakdown of the Stokes–Einstein relation in supercooled liquids is enhanced by randomly pinning a fraction of the particles in the system, and the exponent associated with the fractional Stokes–Einstein relation also systematically increases with increased pinning concentration.

- The peak height of $\chi_4(t)$ does not seem to be a good measure of the Stokes–Einstein breakdown. This is in disagreement with previously reported results.

- The exponent $\beta$ related to the stretched exponential decay of the two-point density–density correlation function clearly shows strong correlation with the Stokes–Einstein breakdown, in complete agreement with previous studies.

- Appropriately defined slow-moving particles seem to form clusters with decreasing temperature. Close to the temperature where the Stokes–Einstein relation starts to break down, the cluster of these slow-moving particles percolates the whole system size. This indicates a possible deep connection between the percolation transition of the slow-moving particles and the Stokes–Einstein breakdown. To our knowledge this is the first demonstration where percolation transition is found to be associated with the breakdown of the Stokes–Einstein relation in supercooled liquids.
The mean cluster sizes of slow particles in the system grow with decreasing temperature, and the growth becomes stronger with increasing pinning concentration.

The clusters of slow particles are fractal in nature with fractal dimensions $D_f$ in the range 1.5–1.8. The fractal dimensions of these clusters increase systematically with increasing pinning concentration. Thus there is a positive correlation between the fractal dimensions and the fractional Stokes–Einstein exponent. It would be nice to further understand this correlation in other model glass-forming liquids.

The results reported in this study are from a model two-dimensional system, so it will be interesting to see whether these results also hold for model three-dimensional systems. Although we don’t expect the results to be qualitatively different in three-dimensional systems, there are studies which suggest that glass transition in two and three dimensions can be qualitatively different [63]. So a detailed study is certainly necessary.

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