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Diffusion maximum as a function of size in dense liquids

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We study the diffusion of small guest particles of different sizes in a host fluid at liquid densities using molecular dynamics simulations. We observe an enhancement of the diffusivity of guest particles for a size related to the structure of the void space of the host fluid, analogous to the "levitation effect" observed for guest diffusion in porous solids. Friction and activation energy are found to be minimum for the guest size with maximum self-diffusivity. Wavelength dependent self-diffusivity indicates a monotonic and oscillatory dependence on wave number k for anomalous and linear regimes, respectively. These are associated with single and bi-exponential decay of the incoherent intermediate scattering function.

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In the past decade, studies on fluids confined within porous solids have yielded some surprizing results, several of which concern transport properties of confined fluids. For example, single file diffusion of sorbates confined within one-dimensional cylindrical pores have been found to exhibit a $\sqrt{t}$ dependence of the mean square displacement [1,2].

Another interesting observation is the maximum in self-diffusivity, D, found in confined fluids for particles with a diameter comparable to that of the void [3]. This unexpected behavior, known as the *levitation effect (LE)*, has two distinct regimes. The linear regime (LR) where $D \propto 1/\sigma_{gg}^2$ is seen for guest diameter (σ_{gg}) which are significantly smaller than the narrowest part of the void, the neck or window diameter (σ_w or σ_{neck}). The anomalous regime (AR), characterized by a maximum in D, has been observed for σ_{gg} approaching σ_w of the porous solid [see Fig. 1(a)]. This occurs due to the symmetry around the diffusant at one or more points along the diffusion path within the confining medium. This symmetry leads to mutual cancellation of forces exerted on the guest by the confining medium (e.g., zeolite, the host), for a particle in the anomalous regime [3]. For example, in zeolite Y [3] the bottleneck for diffusion is the 12-ring window made up of Si and O atoms [see Fig. 1(b)]. For the guest in the AR [the larger open circle in Fig. 1(b)], the force on it due to the zeolite atoms from a given lateral side or direction is equal and opposite to that exerted by the atoms placed diagonally opposite. This leads to negligible net force on the guest even though the guest-host interaction energy is large. Such a cancellation does not occur in the case of the smaller guest from the LR [smaller open circle, Fig. 1(b)]. The dimensionless levitation parameter defined by $\gamma \equiv 2\sigma_{\text{opt}}/\sigma_{\text{neck}}$ [$\gamma = 2.2^{1/6}\sigma_{\text{gh}}/\sigma_{\text{neck}}$, for particles interacting via purely Lennard-Jones (LJ) interaction] is close to 1 at the anomalous maximum, where σ_{opt} is the optimum distance at which interactions between the sorbate and the host medium are most favorable. LE has been found in all types of porous solids such as zeolites, aluminophosphates, etc., irrespective of the geometrical and topological details as well as chemical nature of pore network [4].

Given the ubiquity of the LE in porous solids, depending only on gross structural features, it is of interest to ask if this effect is also present in dense materials, and in particular dense liquids. This question is of great relevance since many chemical reactions as well as biochemical processes occur in solvents and their rate is often determined by how fast the products and reactants can diffuse within those solvents [5,6]. Note that, unlike porous crystalline solids, dense liquids are disordered and further that this disorder is evolving in time. So, it is not self-evident that the diffusion maximum will be seen in liquids. As the predominant interaction in most liquids (except for ionic liquids) is *via* dispersion [7], we employ the LJ potential and carry out classical molecular dynamics simulations of a binary mixture. The binary mixture we simulate consists of $N_h = 500$ host particles and $N_g = 50$ guest particles. The density we have chosen ($\rho^* = N_h/V = 0.933$; $(N_g + N_h)/V = 1.027$) is higher than that of triple point density (~ 0.7). The pairwise LJ potential is $\phi_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$ where r is the interparticle separation, and α, β index the particle type (host or guest). We use LJ interaction parameters $\epsilon_{hh} = 0.25$ kJ/mol, $\epsilon_{gg} = 0.99$ kJ/mol; $\epsilon_{gh} = 1.50$ kJ/mol and size parameters $\sigma_{hh} = 4.1$ Å, $\sigma_{gh} = \sigma_{gg} + 0.7$ Å. The σ_{gg} is varied, from 0.3 to 1.5 Å to obtain the dependence of self-diffusivity on size. The masses of the particles are chosen to be $m_h = 85.0$ a.m.u. and $m_g = 40.0$ a.m.u. All properties indicated

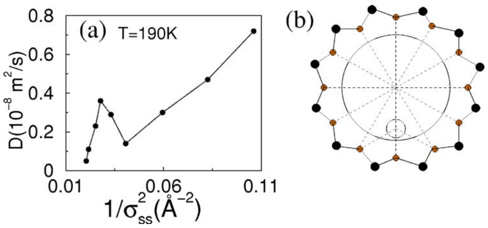

FIG. 1. (Color online) (a) Plot of self-diffusivity vs $1/\sigma_{gg}^2$ in NaY taken from Ref. [4]. (b) Explanation for (a): the bottleneck for diffusion is the 12-membered ring or window in zeolite NaY, shown with Si and O atoms as filled circles. Guest atoms are shown as open circles. For the larger guest with diameter comparable to that of the 12 ring, there is net cancellation of forces while this does not happen for the smaller guest leading to diffusion maximum.

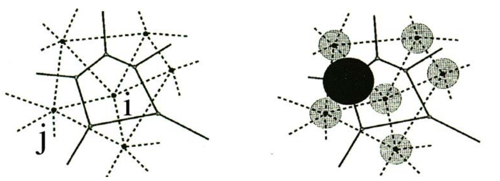

FIG. 2. (Color online) Two-dimensional illustration of the Voronoi–Delaunay dual construction. The central atom *i* is surrounded by atoms *j*. Figure has been taken from Ref. [8].

by the asterisk below are in reduced units based on the values of $\epsilon_{hh}, \sigma_{hh}$ and m_h.

Molecular dynamics simulations were carried out in the microcanonical ensemble using the velocity Verlet scheme at an average temperature $\langle T^{*} \rangle = 1.663$ or 50 K with periodic boundary conditions. Velocities were scaled to obtain the desired temperature only during equilibration. A time step of 5.0 fs was found to give adequate conservation of energy better than 1 in 10^4. Equilibration and production runs are each for 1.0 ns duration. Properties have been computed from trajectories stored every 0.25 ps. Simulations have been performed in a cubic cell of length 33.3 Å with interactions truncated at 16.5 Å.

In order to characterize the structure of the "pore space" or "void space" in the host matrix, we use the Voronoi construction, which has been employed in similar studies of liquids [8,9], and other disordered materials such as porous media and powders [10], resulting in valuable insights into the distribution of voids within these dense systems. In any specified configuration of equi-sized particles, the Voronoi polyhedron of a given particle *i* is the set (subvolume) of all points that are closer to *i* than to any other. The vertices and edges of the Voronoi polyhedra are, by construction, equally far from the closest surrounding particles. Specifically, in disordered configurations, a Voronoi vertex is equidistant from four particles, and any point on a Voronoi edge is equidistant from three particles. Therefore, a natural and convenient description of the empty or void space can be given in terms of the network formed by the edges of the Voronoi polyhedra. Specifically, one can visualize the void space as made of "pores," each of radius given by the distance of a Voronoi vertex to the surrounding particles *minus* the particle radius, and "channels" of radius given by the smallest lateral distance of a Voronoi edge and the surrounding particles *minus* the particle radius. We refer to the corresponding diameters as *void* and *neck* sizes, respectively. Figure 2 illustrates these for two dimensions. Diffusants of a given radius can find an interconnected path between voids if the intervening neck sizes are larger than the diffusant radius. However, the motion of the host atoms ensure that the void network is restructured dynamically. Thus, even a guest particle for which there is no interconnected path at a given time step manages to diffuse over a period of time. Voronoi and Delaunay tesselations have been carried out using the algorithm by Tanemura, Ogawa, and Ogita [11], as outlined in Sastry *et al.* [9]. For each molecular dynamics (MD) run, the void and neck sizes are calculated for 400 configurations (and binned with $\Delta r_v = \Delta r_n = 0.01$ Å), using the positions of the host particles. The main purpose of Voronoi analysis is to obtain the distribution of neck sizes.

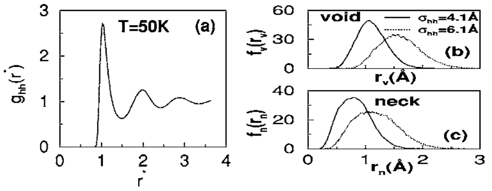

FIG. 3. (a) Host-host radial distribution function. (b) Void size and (c) neck size distribution for the dense liquid at 50 K ($T^{*} = 1.663$).

The host radial distribution function $g_{hh}(r^{*})$ [see Fig. 3(a)] corresponds to that of a typical LJ liquid. The void distribution $[f_v(r_v)]$ of the void sizes r_v as well as the neck distribution $[f_n(r_n)]$ is shown in Figs. 3(b) and 3(c). The $f_n(r_n)$ peaks at a somewhat lower value of r than $f_v(r_v)$.

Self-diffusivities of the guest particles have been computed using the Einstein relationship $D = \langle u^2(t) \rangle / 2dt$, where $d=3$ and $u^2(t)$ is the mean squared displacement. Self (D) and tracer (D') diffusivities are related to each other through a constant of proportionality c, a measure of the excluded volume [12]. As this volume is essentially constant even when the guest size is varied, D reported here reflects D' as well. The Ds are plotted in Fig. 4(a) against reciprocal of the squared sorbate diameter, $1/\sigma_{gg}^2$. For small values of σ_{gg} ($\sigma_{gg} \leqslant 0.7$ Å), the relationship $D \propto 1/\sigma_{gg}^2$ expected on the basis of kinetic theory is seen to be valid. For large values of σ_{gg}, a maximum is seen for a particular size of the guest ($\sigma_{gg} = 0.9$ Å). Calculations on a larger system with 1000 host particles or with a lower concentration of just five guests in 500 host particles yielded values of D that are same as the D reported here, within the limits of error.

Previous simulations of diffusants confined to *porous* solids suggest that the self-diffusivity exhibits a maximum when its size is comparable to the void dimension through which it is diffusing [3]. Our results confirm the existence of an anomalous maximum in self-diffusivity in *dense* liquids as well, characterized both by a disordered structure and a

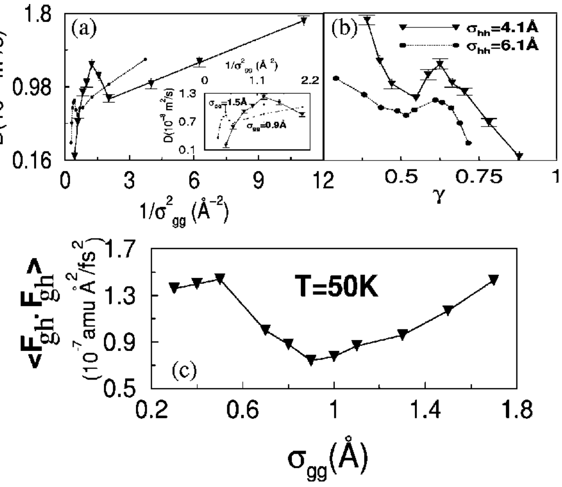

FIG. 4. Self-diffusivity D against (a) reciprocal of the squared sorbate diameter and (b) γ. (c) $\vec{F}_{gh} \cdot \vec{F}_{gh}$ for different sizes of the guest for dense liquid at $\rho^{*} = 0.933$ and $T^{*} = 1.663$.

host matrix that restructures in time. The diffusivities of the host in our system are 0.122×10^{-8} m^2/s as compared to the guest diffusivity of around 0.85×10^{-8} m^2/s. The host diffusivity is therefore only about six times slower than the guest. For diffusion within crystalline porous solids, the anomalous maximum in the self-diffusivity occurs when γ ($\gamma\equiv2\sigma_{\mathrm{opt}}/\sigma_{\mathrm{neck}}$) is close to unity. For diffusion within disordered systems [13] the maximum occurs at values of γ significantly less than unity since it should be expected that when the neck sizes are variable, the smallest of the neck sizes have a greater effect on guest diffusion, and besides, at finite temperatures, thermal motion of the host decreases the probability of passage of the diffusing guest particles through the necks.

We also carried out simulation with $\sigma_{hh}=6.1$ Å at a number density of $\rho^*=0.954$. The void and neck distributions as well as D vs $1/\sigma_{gg}^2$ and γ are shown in Figs. 3 and 4. The maximum in the neck distribution is now at 1.085 Å(0.785 Å) for $\sigma_{hh}=6.1$ Å(4.1 Å). The maximum in D is at 1.5 Å(0.9 Å) for $\sigma_{hh}=6.1$ Å(4.1 Å). The shift in the distribution maximum of neck radius on going from 4.1 to 6.1 Å is 0.3 Å. The guest particle shows a corresponding shift to larger σ_{gg} by 0.6 Å from 0.9 to 1.5 Å showing thereby that the maximum in D is related intimately to the distribution of voids.

There are a number of factors such as mass, interaction energy, size, etc. that influence the self-diffusivity of a diffusant. However, the observed maximum in self-diffusivity arising from LE has two special characteristics, as observed in previous studies. Particles that lie in the AR are characterized by (i) a lower average force [3] exerted on the guest by the host medium and friction and (ii) a lower activation energy [14] as compared to the LR. To confirm that the underlying cause for the observed maximum in D in the present case is due to LE, the force exerted on the guest by the host, $\vec{F}_{gh}$ has been computed. $\vec{F}_{gh}\cdot\vec{F}_{gh}$ is plotted in Fig. 4(c) for different sizes of guests. The force is a minimum for $\sigma_{gg}=0.9$ Å. Friction coefficients computed from the force-force autocorrelation function [15] are: 9.317 kg/s for $\sigma_{gg}=0.7$ Å (the largest sized particle in the LR) and 6.655 kg/s for $\sigma_{gg}=0.9$ Å guest. Clearly, the friction is lower for the guest in the AR. After verifying that the Arrhenius theory of activation holds, we used it to compute the activation energies from the temperature dependence of D at three different temperatures (50, 70, 100 K) (for $\sigma_{gg}=0.7$ Å, $D=0.85$, 2.04, 3.87×10^{-8} m^2/s; for $\sigma_{gg}=0.9$ Å, $D=1.23$, 1.88, 3.13×10^{-8} m^2/s). The value of activation energy E_a for $\sigma_{gg}=0.7$ Å is 1.21 kJ/mol. For $\sigma_{gg}=0.9$ Å, $E_a=0.77$ kJ/mol. These are consistent with results obtained for guests diffusing within zeolite NaY and NaCaA [14].

We now investigate the dependence of the diffusion properties on wave number k for intermediate k values. In the hydrodynamic limit ($k\to0$, $\omega\to0$), the simple diffusion model is valid and the full width at half maximum, $\Delta\omega$ of the self part of the dynamic structure factor $S_s(k,\omega)$ is proportional to $2Dk^2$. At large k, $\Delta\omega(k)/2Dk^2$ varies as $1/k$ [16]. The motion in the *intermediate range* of k values is *strongly influenced by the intermolecular potential*. Previous simulation studies [3] of guests of varying sizes in zeolites suggest that the precise nature of the intermolecular interactions plays an important role in LE. Note that the diffusion maximum is not seen in the absence of attractive $1/r^6$ term of the Lennard-Jones potential [3]. It is therefore interesting to see the behavior of $\Delta\omega(k)$ in the intermediate k region for the linear and the anomalous regimes. $S_s(k,\omega)$ of the guest was obtained from the Fourier transform of the guest intermediate scattering function $F_s(k,t)$ for several sizes of the guest. $F_s(k,t)$ was computed by taking a powder average [17].

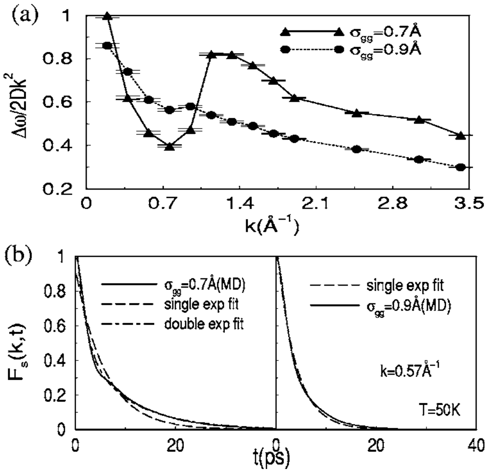

FIG. 5. (a) $\Delta\omega(k)/2Dk^2$ as a function of k at $\rho^*=0.933$ and $T^*=1.663$ or 50 K for LR and AR. (b) Intermediate scattering function, $F_s(k,t)$, for the guest in the linear ($\sigma_{gg}=0.7$ Å) and anomalous regimes ($\sigma_{gg}=0.9$ Å) for $k=0.57$ Å^{-1} are shown along with single and biexponential fit.

Previously, Nijboer and Rahman [18] and Levesque and Verlet [16] investigated the variation of the ratio $\eta=\Delta\omega/2Dk^2$ with k for pure argon for two thermodynamic states: $\rho^*=0.8442$, $T^*=0.722$, a high density fluid at low temperature and $\rho^*=0.65$, $T^*=1.872$, a low density fluid, at high temperature. These studies show that for a high density fluid, $\Delta\omega(k)/2Dk^2$ exhibits first a maximum and then a minimum as k decreases [18]. The minimum in $\Delta\omega(k)$ was found to be associated with the strong spatial correlations seen in the static structure factor, $S(k)$—i.e., a lowering of the $\Delta\omega(k)/2Dk^2$ on length scales on which strong structural correlations are observed. For the low density fluid [16], $\Delta\omega(k)/2Dk^2$ increases monotonically with decrease in k. Correlations in $S(k)$ for this fluid are weak.

A plot of $\Delta\omega(k)/2Dk^2$ is shown in Fig. 5(a) for the guest in the binary mixture, for $\sigma_{gg}=0.7$ Å (LR) and $\sigma_{gg}=0.9$ Å (AR). $\Delta\omega(k)/2Dk^2$ for $\sigma_{gg}=0.7$ Å exhibits a maximum and a minimum as k decreases but for $\sigma_{gg}=0.9$ Å the variation is nearly monotonic (slight dip could be seen due to the actual maximum close to but not at 0.9 Å). The former (LR) is akin to a high density fluid and the latter (AR) to a low density fluid at intermediate k although in both cases, the guest particles move in a high density liquid medium, with $\rho^*=0.933$. Since this density is higher than that of Nijboer and Rahman ($\rho^*=0.8442$), the nonmonotonic behavior of $\Delta\omega(k)/2Dk^2$ for the $\sigma_{gg}=0.7$ Å case is as expected. However, the *larger sized* particles from AR with $\sigma_{gg}=0.9$ Å show no lowering of self-diffusivity at intermediate k values, displaying dynamics similar to the particles in the low density, high temperature case of Nijboer and Rahman. The conclusion is that spatial correlations in the fluid at intermediate wave vectors do not affect the diffusive motion of guest particles in the AR.

This counterintuitive result is consistent with the interpretation supported by results described earlier, that in the AR, the cancellation of forces near the necks that interconnect void space through which the guest particles diffuse leads to effective barriers and friction, that are lower than in the case of smaller guest particles in the LR. Interestingly, the anomalous maximum exists even at a relatively high temperature of $T^*=1.663$. The nonmonotonic variation of $\Delta\omega(k)/2Dk^2$ for particles in the LR is likely to lead to two well separated time scales for motion. At short times, motion is facile. At larger times, the minimum in $\Delta\omega(k)/2Dk^2$ leads to slower motion. This is due to the larger activation barrier associated with passage across the neck. For particles in the AR, no such separation should arise. The signature of these should be seen in decay of density fluctuations at small k. In order to test this speculation we study the incoherent intermediate scattering function, $F_s(k,t)$ for $\sigma_{gg}=0.7$ and 0.9 Å particles, which are shown for $k=0.57$ Å^{-1} in Fig. 5(b), along with a fit to a single ($e^{-t/\tau}$) and a double exponential decay. A single exponential decay ($\tau_1=3.71$ ps) provides a good fit to the $F_s(k,t)$ for the 0.9 Å particle but not to 0.7 Å ($\tau_1=1.84$ ps; $\tau_2=9.90$ ps).

These results suggest that diffusion within liquids may strongly depend on the size of the diffusing species, with anomalously high diffusion for sizes that is related to the void structure of the medium. Many of the processes occuring in liquid medium such as chemical reactions or diffusion of electrolytes will need to be reconsidered in the light of these results. These results have implications in biological processes, as well as diffusion in amorphous solids and glasses. We have verified that ionic conductivity exhibits a similar maximum in water explaining the experimentally observed anomalous maximum in ionic conductivity. [19]

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