Mechanisms Influencing Levitation and the Scaling Laws in Nanopores: Oscillator Model Theory

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Received: November 17, 2005; In Final Form: December 26, 2005

We provide here a detailed theoretical explanation of the floating molecule or levitation effect, for molecules diffusing through nanopores, using the oscillator model theory (*Phys. Rev. Lett.* **2003,** *91,* 126102) recently developed in this laboratory. It is shown that on reduction of pore size the effect occurs due to decrease in frequency of wall collision of diffusing particles at a critical pore size. This effect is, however, absent at high temperatures where the ratio of kinetic energy to the solid−fluid interaction strength is sufficiently large. It is shown that the transport diffusivities scale with this ratio. Scaling of transport diffusivities with respect to mass is also observed, even in the presence of interactions.

1. Introduction

All materials possess interatomic voids that are typically too small for any molecular species to enter or diffuse through. However, there is a class of crystalline and amorphous solid materials that contains internal voids and apertures that are large enough for other molecules to enter and pass through.[1,2] These materials are termed nanoporous and form a class of chemically and physically rich compounds that are naturally occurring or can be synthesized. These materials find diverse applications such as adsorption and separation of mixtures, adsorptive storage, and catalysts.[3] Important examples of microporous materials are silicas such as MCM-41, activated carbons, zeolites, and carbon nanotubes. Numerous applications of such nanoporous materials are being widely studied both experimentally and theoretically and have provided an active area of research for the past two decades.[4−6]

Nanoporous materials are also important from a fundamental point of view. Geometric confinement effectively reduces the dimensionality of the system and leads to very significant changes in the thermodynamic and dynamic properties of fluids. Many physical properties change substantially when moving from three to two or one dimension. In fact, a large number of phenomena only occur in low dimensions. Low-dimensional systems have been investigated vigorously using theoretical methods and have stimulated an explosion of activity due to the radically different physical properties from their three-dimensional analogues.[7−10] Nanoporous materials provide a model system for these low-dimensional systems and make it feasible to study one- or two-dimensional systems both experimentally and computationally.

Diffusion of gases in microporous adsorbents is a field that has attracted much attention due to its importance in adsorption, separation, and heterogeneous catalysis. The understanding of the details of molecular motion in small pores is important because the rate at which the molecules access the interior space of the nanoporous materials can sometimes control the performance of adsorbents, membranes, and catalysts. The effect of molecular confinement and the interaction of intraporous fluids with the surface of confining nanoporous materials sometimes lead to peculiar dynamical properties. For example in one-dimensional nanoporous channels, particles are forced to move in a sequential order such that they are unable to pass each other when the pore dimensions and molecular dimensions are comparable. This leads to single file diffusion where the long time mean squared displacement is proportional to $t^{0.5}$, rather than t as is generally observed for Fickian diffusion.[11,12] Another interesting phenomenon observed in microporous materials is the floating molecule behavior or the levitation effect,[13] in which supermobility is attained when the molecular dimensions match closely with the pore dimensions. It is proposed that when the potential energy profile changes from a double well to a single well at the center of the pore, the van der Waals force becomes zero and the molecule appears floating in the pore. This is considered as the ideal situation to achieve supermobility.

Although the existence of the superdiffusive or "levitation" regime has been supported by other workers,[14−16] based on molecular dynamics (MD) simulations, no firm theoretical treatment of this effect has been made. These simulations of the self-diffusion of monatomic sorbates in different zeolites, while varying the Lennard-Jones (LJ) parameter, σ_{ff}, of the adsorptive, confirm the existence of an anomalous regime in which the diffusivity passes through a maximum with respect to pore size, when the particle dimension and pore dimension are comparable. The anomalous peak is found to occur at a pore diameter that is twice the equilibrium separation based on the LJ pair interaction, i.e.

$$d = 2(2^{1/6})\sigma_{fs} \tag{1}$$

where d is the pore diameter and σ_{fs} is the LJ size parameter. Although found to exist for a number of zeolite structures having different topological and geometrical features, a rigorous theoretical explanation of this effect is yet to emerge. Indeed, the region of validity of the above criterion is not obvious. For example, as shown by Rajappa and Yashonath,[17] at sufficiently high temperatures, the levitation effect is not observed. Clearly, the above criterion does not reflect the effect of temperature and therefore does not provide a sufficient condition for the existence of the effect.

Here we demonstrate that the superdiffusive motion of particles in low dimension is a direct consequence of the

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decrease in frequency of collision with the confining surfaces between which the particles undergo oscillatory motion, when the central potential barrier of the double well disappears due to the merging of the wells on reducing the pore size. The recent oscillator model theory of Bhatia and co-workers[18,19] provides a natural vehicle to study this behavior and yields valuable insight into the superdiffusive regime, while quantitatively explaining the levitation effect and also the effect of temperature. The results obtained from oscillator model theory are also validated against molecular dynamics simulations.

2. Oscillator Model Theory

As indicated above, we have followed the recent transport model of Bhatia and co-workers to determine the transport diffusivity of methane in silica pores at low density.[18,19] For particles moving in a cylindrical pore that undergo diffuse reflection upon the collision with the pore walls, the transport diffusivity can be written as[18,19]

$$D_t = \frac{k_B T}{m} \langle \tau \rangle \qquad (2)$$

where $\langle \tau \rangle$ is the mean hopping time of the trajectory in the potential field of the cylindrical pore at temperature T. To determine the hopping time, solution of the Hamiltonian equations of motions of a particle moving under a radial potential field leads to

$$\tau(r,p_r,p_\theta) = 2m \int_{r_{c0}(r,p_r,p_\theta)}^{r_{c1}(r,p_r,p_\theta)} \frac{dr'}{p_r(r',r,p_r,p_\theta)} \qquad (3)$$

where $p_r(r',r,p_r,p_\theta)$ is the radial momentum profile at position r' for a particle having radial momentum p_r at r and angular momentum p_θ, which can be written as

$$p_r(r',r,p_r,p_\theta) =$$
$$\left\{ 2m[\phi_{fs}(r) - \phi_{fs}(r')] + p_r^2(r) + \frac{p_\theta^2}{r^2}\left(1 - \frac{r^2}{r'^2}\right) \right\}^{1/2} \qquad (4)$$

Further, $r_{c0}(r,p_r,p_\theta)$ is the radial position at the point closest to the center during the oscillation and $r_{c1}(r,p_r,p_\theta)$ is the point of reflection near the wall, both of which can be obtained from the solution of

$$p_r(r',r,p_r,p_\theta) = 0 \qquad (5)$$

Upon averaging the oscillation time τ between the reflections, over the canonical distribution of r, p_r, and p_θ and substituting into eq 1, we can obtain the low-density transport diffusivity

$$D_t = \frac{2}{\pi m Q} \int_0^\infty e^{-\beta \phi_{fs}(r)} dr \int_0^\infty e^{-\beta p_r^2/2m} dp_r \times$$
$$\int_0^\infty e^{-\beta p_\theta^2/2mr^2} dp_\theta \int_{r_{c0}(r,p_r,p_\theta)}^{r_{c1}(r,p_r,p_\theta)} \frac{dr'}{p_r(r',r,p_r,p_\theta)} \qquad (6)$$

where

$$Q = \int_0^\infty r e^{-\beta \phi_{fs}(r)} dr$$

and $\phi_{fs}(r)$ is the one-dimensional radial potential due to the solid−fluid interaction in the pore. Here, $\beta = 1/k_B T$ is the Boltzmann factor. Equation 6 is valid when the intermolecular interactions between the sorbate molecules are insignificant. This theory has been tested against molecular dynamics simulations and found to be in excellent agreement with the simulation

TABLE 1: Lennard-Jones Interaction Parameters for the Solid−Solid and Fluid−Fluid Interactions

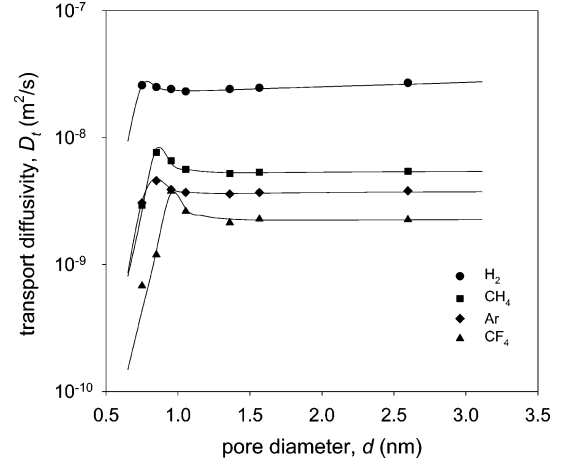|	σ (nm)	ϵ (K)
solid	0.29	290
H_2	0.2915	38
CH_4	0.375	148.0
Ar	0.3405	120
CF_4	0.4662	134.0

Figure 1. Transport diffusivity of H_2, CH_4, Ar, and CF_4 in cylindrical silica pores versus the pore diameter. The lines are from the oscillator model theory and symbols from molecular dynamics simulations.

results[18-20] for a variety of gases in silica pores. Under conditions of diffuse reflection, it is essentially exact, and can profitably be used to analyze the levitation regime.

3. Results and Discussion

We determined the transport diffusivity for Lennard-Jones (LJ) models of H_2, CH_4, Ar, and CF_4 in cylindrical silica pores of varying diameter having infinitely thick walls, using the above theory. The host matrix is modeled as a continuum solid based on an array of close packed Lennard-Jones 12-6 pseudoatoms following Nicholson and Gubbins,[21] having LJ parameters σ_{ss} and ϵ_{ss}. The potential profile due to the adsorbate−wall interaction is calculated by placing a probe molecule at a fixed radial position and summing over the interaction with all wall atoms. Such a one-dimensional radial potential profile does not consider the periodicity along the z-direction arising from the atomic roughness of the surface. This potential profile is used in eq 6 to calculate the transport diffusivity. For the solid, the parameters are the same as those determined earlier,[22] based on argon adsorption. The potential parameters used in this study for different fluid molecules are summarized in Table 1. Lorentz−Berthlot mixing rules are used to obtain the cross interaction parameters. These results are validated against molecular dynamics simulations. These simulations have been carried out in the canonical ensemble using a fifth order Gear predictor−corrector algorithm. The temperature is maintained constant using a Gaussian thermostating technique.[23] The run length is typically about 10 ns, and the transport diffusivities are calculated from the autocorrelation of the center of mass velocity vector using the Green−Kubo relation.[24]

3.1. Effect of Pore Diameter on Transport Diffusivity and Levitation Effect. Figure 1 shows the diffusivity of H_2, CH_4, Ar, and CF_4 in silica pores against the diameters of the silica pores at 50 K. In this figure, the theoretical results are plotted as lines and simulation results as symbols. From the figure it is clear that simulation results are in excellent agreement with the theory. This further validates the oscillator model theory. It is
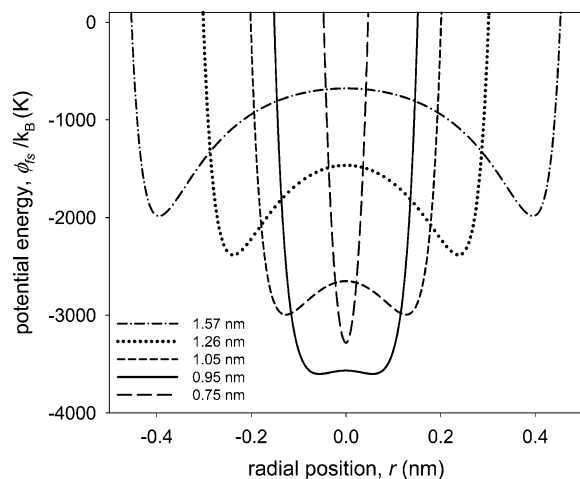
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Figure 2. Potential profile of CF_4−solid interaction at various pore diameters. The potential energy changes from double minima to a single minimum at $d = 0.95$ nm. The anomalous peak in the diffusivity occurs at this diameter.

seen that beyond a critical pore dimension, the transport diffusivity monotonically increases with increasing pore diameter. However, as is clear from Figure 1, the transport diffusivity shows a peak at sufficiently low value of the pore diameter, comparable to the Lennard-Jones parameter σ_{ff}. This is the levitation effect observed earlier in different zeolites, which is well captured by our theory. The picture becomes clearer when we examine the solid−fluid potential profiles, illustrated in Figure 2 for the case CF_4. For larger pores, the potential energy profile has a double well nature, with a barrier separating the two wells. As the diameter of the pore decreases, the barrier between the potential wells decreases and eventually a cross over from a double well to a single well at the pore center occurs. As mentioned earlier, Derouane and co-workers have stated that the supermobility occurs at this point.[13] Indeed, the peak in the transport diffusivity is found to occur around this point in our calculations. The oscillator model theory offers a clear physical explanation of this effect. According to eq 2, the transport diffusivity is directly proportional to the time of oscillation of the molecule in the radial potential energy field. At large pore dimension, the particles will be localized in either of the two double wells and the time of oscillation depends on the width of the potential well. When the diameter is decreased, the width over which the molecule oscillates also decreases, leading to reduction in oscillation time. This results in reduced diffusivity because increase in collision frequency with the pore wall enhances the rate of axial momentum loss of the confined particles. However, at sufficiently small pore dimension, when the cross over from a double well to single well occurs (at $d = 0.952$ nm in the case of CF_4 as shown in Figure 2), there is a sudden increase in the amplitude of oscillation of the molecule because of the larger width of this single well in comparison to either member of the double well. This increases the time of oscillation and results in an increase in transport diffusivity. At still lower diameters, the width over which the particle can oscillate decreases again and the diffusivity decreases. Thus, the time of oscillation goes through a minimum and maximum as we decrease the pore diameter, and this is manifested as a peak in the transport diffusivity versus diameter plot at small pore diameters. In Figure 1, the peak in the diffusivity for Ar appears wider compared to other molecules. This is because the anomalous peak in the case of Ar is less intense due to the lower value of ϵ_{fs}/k_BT, which will be discussed later.

3.2. Dependence of levitation effect on temperature and interaction strength. Figure 3a depicts the transport diffusivities
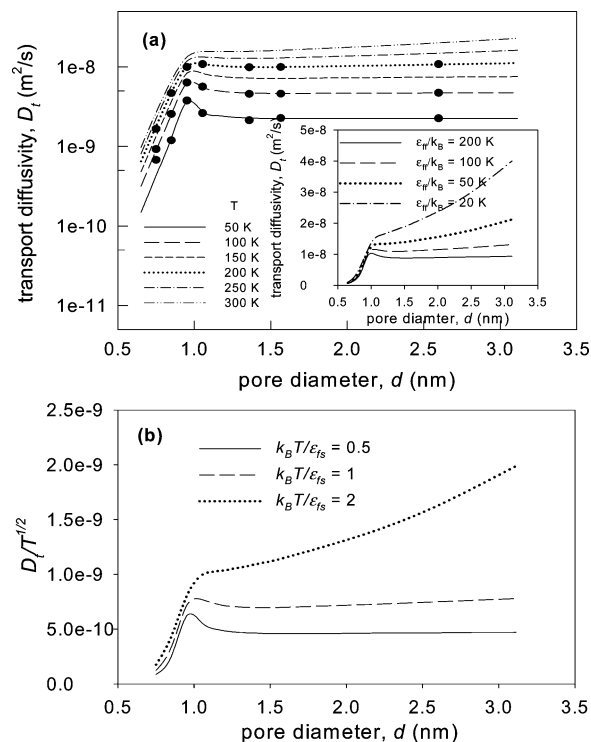

Figure 3. (a) Transport diffusivity of CF_4 in the silica pore at various temperatures. The lines represent theoretical values and the symbols molecular dynamics simulations. The dependence of the levitation effect on the fluid−fluid interaction strength, ϵ_{ff}, is shown in the inset. (b) The scaling of transport diffusivities with respect to the factor k_BT/ϵ_{fs}. The values correspond to different temperatures, 50, 100, and 150 K, keeping the ratio constant.

of CF_4 against the pore diameter at various temperatures. Here again, the simulation results are shown as symbols and theoretical results as lines. From the figure, it is clear that the floating molecule effect is predominant at lower temperatures and at high temperature it is almost nonexistent. Similar observations were made for H_2, CH_4, and Ar. Such temperature dependence was earlier reported by Rajappa and Yashonath,[17] based on molecular dynamics simulations. Thus, the oscillator model theory captures not only the levitation effect but also its temperature dependence. However, it also provides physical insight not readily obtained from simulations. At low temperatures, the particles have less kinetic energy and oscillate at the bottom of the potential well, where the amplitude of the motion is small. With reduction in pore size at low temperature, at the pore size at which the potential energy surface undergoes a transition from the double well to a single well, the amplitude of oscillation increases significantly. This results in increase in the transport diffusivity, and the anomalous peak in the transport diffusivity. However, at higher temperatures, the particles will be oscillating at a higher position above the bottom of the potential well because of higher kinetic energy, and when the potential energy surface changes from the double well to a single well, the extent of oscillation does not change significantly, leading to reduction in the intensity of the anomalous peak compared to that at low temperature. At very high temperatures, the kinetic energy of the molecules will be larger than the potential energy barrier separating the double minima and the molecules will be oscillating above the potential barrier. In this condition, when the potential profile changes from the double minima to a single minimum, the amplitude of the oscillation does not increase and the anomalous peak vanishes.

Next, we studied the effect of interaction strength on the levitation effect. For this we kept the Lennard-Jones parameter,

σ_{ff} constant and the parameter, ϵ_{ff}/k_B was varied. The mass of the molecules is taken as that of CF_4. The transport diffusivities of molecules versus pore diameter at different interaction strengths are plotted in the inset of Figure 3a. From the figure it is evident that the levitation effect is more significant for the larger interaction strength. The ratio of the diffusivity value at the peak relative to that at the diffusivity minimum is highest for $\epsilon_{ff}/k_B = 200$ K, the value being 1.1388. This ratio reduces to 1.0596 for $\epsilon_{ff}/k_B = 100$ K. It is also evident that the anomalous peak vanishes for $\epsilon_{ff}/k_B < 50$ K. This observation is very similar to the temperature dependence discussed earlier. In both cases, the kinetic energy relative to the potential barrier separating the double minima governs the existence of the anomalous peak. In the case of temperature dependence, the kinetic energy is the factor which is varying and, in this case, the potential energy barrier is varying. At large ϵ_{ff}/k_B, the solid−fluid interaction, ϵ_{fs}, and the barrier between the potential minima are also large, and the particles are less likely to cross over the barrier at large pore dimensions, while for small interaction strength the barrier is low enough such that a higher fraction of particles will be able to surmount the barrier and oscillate. Thus, when the potential profile abruptly changes from the double minima to a single minimum, the increase in the average extent of oscillation is larger for molecules having higher interaction strength than others. Consequently, the increase in diffusivity is higher in this case and the anomalous peak becomes more predominant. At low enough interaction strength, the potential energy barrier is so small that almost all of the molecules are oscillating above the barrier and do not experience an increase in the extent of oscillation when the potential profile changes from double minima to single minimum.

The above observations suggest that the diffusivity of the particles and the levitation effect depend on the factor k_BT/ϵ_{fs}, rather than on temperature or interaction strength alone. We calculated the transport diffusivities of model particles with different interaction strengths at different temperatures, while keeping the factor k_BT/ϵ_{fs} constant. The mass of the particles is kept the same as that of the CF_4 molecule. The results are plotted in Figure 3b. It is found that the ratio of transport diffusivity to the square root of the temperature, $D_t/\sqrt{T}$, scales with respect to the factor k_BT/ϵ_{fs}. In the figure, $D_t/\sqrt{T}$ is plotted against the pore diameter for different values of k_BT/ϵ_{fs}. For each value of k_BT/ϵ_{fs}, we have computed the diffusivities at three different temperatures, 50, 100, and 150 K, and all three sets give identical values for the quantity $D_t/\sqrt{T}$. Indeed such a scaling can also be derived from eq 6. Writing $\phi_{fs}(r) = 4\epsilon_{fs}V_{fs}(r)$ where the dimensionless potential energy, $V_{fs}(r)$, depends only on the size parameter σ_{fs}, and substituting $y = 4\beta\epsilon_{fs}V_{fs}(r)$, $x^2 = \beta p_r^2/2m$, $\alpha^2 = \beta p_\theta^2/2mr^2$, and $p_r(r',r,p_r,p_\theta) = \sqrt{2m/\beta}s(r',r,x,\alpha)$ in eq 6, we obtain

$$D_t = \frac{2}{\pi Q}\sqrt{\frac{2k_BT}{m}}\frac{k_BT}{4\epsilon_{fs}}\int_0^\infty \frac{e^{-y}}{V_{fs}'}V^{-1}\left(\frac{k_BTy}{4\epsilon_{fs}}\right)dy \times$$
$$\int_0^\infty e^{-x^2}dx \int_0^\infty e^{-\alpha^2}d\alpha \int_{r_{c0}(r,x,\alpha)}^{r_{c1}(r,x,\alpha)}\frac{dr'}{s(r',r,x,\alpha)} \quad (7)$$

where $V^{-1}(k_BTy/4\epsilon_{fs}) = r$, so that

$$D_t/\sqrt{T} = f\left(\frac{k_BT}{\epsilon_{fs}},\sigma_{fs},d\right) \quad (8)$$

This confirms the results from our calculations plotted in Figure 3b. All the observations made in the temperature dependence and the dependence on the interaction strength of levitation

effect can be seen in Figure 3b also, demonstrating that it is the ratio of kinetic energy to the interaction strength which controls the behavior of the transport diffusivity and thereby the levitation effect.

Another point to be noted here is that the position of the diffusivity maximum shifts from 0.952 to 1.054 nm when the factor k_BT/ϵ_{fs} changes from 0.5 to 1. Our explanation holds true for this observation also. At $k_BT/\epsilon_{fs} = 0.5$, the particles have less kinetic energy and none of the particles will be able to surmount the potential energy barrier between the double minima for the cylinder of diameter 1.054 nm and will be oscillating in either of the potential minima. However, when the factor k_BT/ϵ_{fs}, increases to 1, a greater fraction of the particles will have sufficient kinetic energy to cross over the barrier. As a result the amplitude of oscillations in this case is higher and this makes the maximum in the transport diffusivity shift from 0.952 to 1.054 nm. Thus, the critical size at which superdiffusive motion is attained is not precisely that at which the transition from a double potential well to a single potential well occurs but also depends on the temperature (i.e., kinetic energy). This shows the importance of the kinetic energy along with the potential energy profile while determining the position and intensity of the floating molecule effect. The earlier studies on the levitation effect have considered only the changes in potential energy profile while explaining this effect. Derouane and co-workers proposed that the ideal case for the molecule to be floating in the cylindrical pore is that when the potential energy profile changes from the double minima to a single minimum. Following eq 1 Yashonath and co-workers empirically proposed that the diffusivity maximum occurs when a levitation parameter defined as

$$\gamma = \frac{2(2^{1/6})\sigma_{fs}}{d} \quad (9)$$

becomes unity.[15] In both the cases, they neglected the effect of kinetic energy in defining the ideal condition for achieving the supermobility. The importance of kinetic energy is evident from the fact that the value of γ at which the peak in the diffusion coefficient occurs is always less than unity for the results obtained from molecular dynamics simulations.[14,15]

3.3. Dependence of Levitation Effect on Molecular Mass. We have also investigated the dependence of the levitation effect on the mass. In this case, we used the Lennard-Jones parameters of CF_4 for the calculations, while varying the mass systematically. The transport diffusivities of this model system for different masses are shown in Figure 4a. From the figure it appears that the anomalous peak in the diffusivity is more predominant for lighter particles and the intensity of the peak decreases for heavier particles. However, the difference in mass is not of significance in the levitation effect. To verify this, we have scaled the diffusivities inversely with the square root of molecular mass, as is well established for Fickian diffusion. These scaled diffusivities are plotted in Figure 4b, and lie on a single curve. This observation of the scaling of diffusivities with respect to mass is also verified using equilibrium molecular dynamics simulations, as shown in Figure 4b. This scaling is also readily obtained from the oscillator model theory, as can be seen from eq 7, i.e., $D_t \propto m^{-1/2}$, thus confirming the scaling with respect to mass, observed in our calculations. We have also scaled the diffusivities with the minimum value occurring just before the anomalous peak, which is plotted as the inset in Figure 4b. Again the scaled diffusivities lie on a single curve. This observation demonstrates that the molecular mass does not influence the levitation effect.
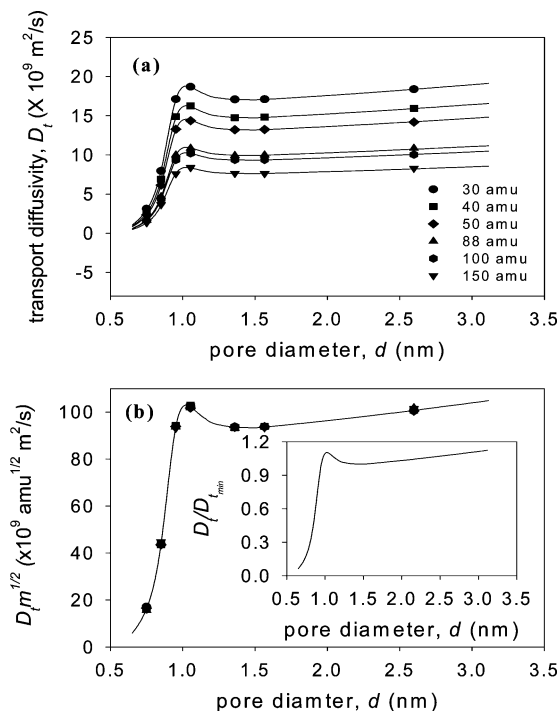
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Figure 4. Mass dependence of the levitation effect. (a) The transport diffusivities for various molecular mass at constant Lennard-Jones parameters σ_{ff} and ϵ_{ff}. (b) Transport diffusivities scaled with respect to molecular mass. The transport diffusivity scaled with respect to the minimum value is plotted in the inset. The lines are from the theory and symbols from molecular dynamics simulations.

While we have investigated the levitation effect at low densities, molecular dynamics simulations[25] have shown this to occur also at higher densities where fluid−fluid interactions are important and affect self-diffusivity. The persistence of this effect even at higher densities would indicate that clustering behavior, reported for the single file region by Sholl and Lee,[26] has negligible influence on the existence of the levitation effect. The above theory of levitation effect, based on oscillator model, should also be applicable to real systems, such as ALPO's that have cylindrical pores. In prior work with this model from this laboratory[27,28] a maximum in the diffusivity of methane with respect to pore size was observed for carbon slit pores, indicating the applicability of the approach, and for the levitation effect, also for carbons. In principle, the effect may also exist for carbon nanotubes; however, the nearly specular reflection in this case requires knowledge of the Maxwell coefficient.[29] Further, at the small pore sizes at which the levitation effect occurs, the transport is largely in the ballistic regime, which complicates the analysis of simulation results, and leads to non-Fickian behavior. Finally, We note that the levitation effect should also apply to light molecules such as H_2 even in the presence of quantum effects, which is significant at lower temperatures. The quantum effects can be incorporated in the oscillator model theory calculations using the Feynman−Hibbs variational approach, as discussed elsewhere.[30]

4. Conclusions

In conclusion, we have provided an explanation of the floating molecule or levitation effect of different molecules in nanopores of varying diameter, based on our oscillator model theory. The calculations show that the levitation effect exists for all molecules when the pore dimensions become comparable to the molecular dimensions, provided the temperature is sufficiently low. The anomalous peak occurs in the region where the solid−fluid potential energy profile undergoes a transition from a double minimum to a single minimum, which is in agreement with the concept of Derouane and co-workers. The oscillator model theory explains the increase in transport diffusivity when this crossover occurs as arising from reduction in frequency of wall collision. The intensity of the anomalous peak decreases as the temperature is increased and vanishes at high temperature, which is in agreement with earlier simulation results. In this regard, the kinetic energy is found to play an important role in determining the position and intensity of the maximum in the diffusivity with pore diameter. The effect of interaction strength is exactly opposite to that of temperature and both of them are correlated to each other, and it is the ratio $k_B T/\epsilon_{fs}$ that determines the occurrence of the floating molecule or levitation effect. The transport diffusivity is found to scale with the ratio of kinetic energy to the solid−fluid interaction strength. It is shown that mass does not affect the existence of the levitation effect and also there exists a scaling of the transport diffusivities with respect to mass. The oscillator model theory is successful in providing physical explanations to all of the above features.

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