Wall Mediated Transport in Confined Spaces: Exact Theory for Low Density

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We present a theory for the transport of molecules adsorbed in slit and cylindrical nanopores at low density, considering the axial momentum gain of molecules oscillating between diffuse wall reflections. Good agreement with molecular dynamics simulations is obtained over a wide range of pore sizes, including the regime of single-file diffusion where fluid-fluid interactions are shown to have a negligible effect on the collective transport coefficient. We show that dispersive fluid-wall interactions considerably attenuate transport compared to classical hard sphere theory.

The problem of transport in small pores and confined spaces is one of long-standing interest, which is now receiving renewed attention due to its importance to applications of new nanomaterials being vigorously developed. Nevertheless, despite a long history dating back to the classical work of Knudsen [1], our understanding of the subject is still relatively rudimentary with no successful theory except for certain limiting situations. Classical nonequilibrium thermodynamic models [2,3] based on purely viscous flow are increasingly inaccurate at low densities and in molecularly sized pores where the relevant field quantities are ill-defined. Further, recent simulation and modeling studies in our laboratory [4,5] have confirmed that under such conditions momentum exchange processes associated with molecular collisions at the pore walls lead to finite surface slip that is not captured in the classical models. Such mechanisms are not unknown, and historically have received attention [1,6,7] using kinetic theory. However, these classical works have considered noninteracting systems, and the associated Knudsen diffusivity is applicable under such conditions. While it is unclear how these results apply to real interacting systems, it is common to interpret transport in this way, while introducing an empirical activated diffusion in micropores [8].

The development of transport theories incorporating more realistic interactions in small pores has long been a goal of subsequent workers; however success has been limited, with mechanical models involving many body interactions fast becoming intractable [9,10]. While these latter works have predominantly focused on intermolecular interactions and highlighted the mathematical complexities involved, our studies have shown [4,5] that, at least at low densities, it is not the intermolecular interactions in the pore fluid but the surface interactions that govern the transport. Interpretation of equilibrium and nonequilibrium molecular dynamics (EMD and NEMD, respectively) simulations revealed that the surface interactions lead to a weakly density dependent friction factor at the pore wall that influences the surface slip, and which

is approximately consistent with kinetic theory estimates. Here we build on these initial studies and develop an exact theory for the low-density transport coefficient in slit-shaped and cylindrical nanopores, considering the axial momentum gain during oscillatory motion between diffuse wall reflections. The theory is validated against MD simulations, and it is found that the wall potential field, neglected in the classical developments, considerably attenuates the transport in small pores. Furthermore, the range of conditions corresponding to the "low-density region" is quite broad, so that many industrial applications take place close enough to this limit for the model to be of practical interest. The low-density limit diffusion coefficient can also be used in the estimation of the transport mobility in single-file diffusion processes.

The transport theory we present models fluid molecules being forced along a pore of a microporous solid. Consider a system of fluid molecules adsorbed into a slit pore, at temperature T. We describe the slit pore in Cartesian coordinates, with the pore walls normal to the x axis and the pore axis lying in the z direction. The pore-fluid interaction is represented by a potential $V(x)$, symmetric about the pore center. Such a potential precludes the exchange of z momentum between molecules and the pore, which is an essential part of the transport dynamics. We therefore introduce a further boundary condition — the average z momentum of a molecule is zero whenever a fluid molecule "reflects" off a wall. Such reflections occur when $\dot{x} = 0$; and there is no potential minimum between the molecule and the pore wall. This boundary condition represents a diffuse reflection [11]. Details of the treatment of the y momentum on reflection are unimportant for the theory.

The mechanism driving the diffusion is an external force field of magnitude F in the positive z direction, applied to each molecule. In such a system, the transport diffusion coefficient D_0 is given by

$$D_0 = J k_B T / \rho F = \langle v_z \rangle k_B T / F, \qquad (1)$$

where J is the flux through the pore, ρ is the number

density of fluid molecules, $\langle v_z \rangle$ is the average axial velocity, and k_B is Boltzmann's constant. We therefore seek to determine $\langle v_z \rangle$ via the model.

At low densities, fluid molecules rarely interact with one another, and the dynamics of a molecule will be dominated by its interaction with the pore. This dynamics can be determined from the Hamiltonian

$$H_S = V(x) - Fz + p_x^2/2m + p_y^2/2m + p_z^2/2m.$$

We define

$$E_x = V(x) + p_x^2/2m, \qquad E_y = p_y^2/2m,$$

$$E_z = -Fz + p_z^2/2m,$$

noting that they are constant between reflections, and that E_x is constant throughout. The motion in the x direction will therefore be periodic. Molecules will either oscillate in one side of the pore, or across both sides if they have sufficient energy. We assume that the pore is centered at $x = 0$. We define x_- and x_+ as the bounds of the oscillation in the side of the pore where $x > 0$, for molecules not crossing the center. For molecules that do cross the center, we set x_+ to the upper bound of the oscillation, and $x_- = 0$. A molecule passes through each $x \in (x_-, x_+)$ twice between wall collisions — once at a time t_x after a reflection, and later at time t_x before a reflection. In a symmetric pore, the period between successive reflections, τ, will be a continuous function of E_x, and therefore the average z momentum of a molecule at $x \in (x_-, x_+)$ will be $\{Ft_x + F[\tau(E_x) - t_x]\}/2 = F\tau(E_x)/2$. Considering a canonical distribution of energies, Eq. (1) yields

$$D_0 = \frac{k_B T}{F} \langle v_z \rangle$$

$$= \frac{k_B T}{2m} \frac{\int_{-\infty}^{\infty} \int_0^{\infty} \tau(x, p_x) e^{-E_x(x,p_x)/k_B T} dx\, dp_x}{\int_{-\infty}^{\infty} \int_0^{\infty} e^{-E_x(x,p_x)/k_B T} dx\, dp_x}. \qquad (2)$$

The expression for E_x leads to

$$\tau(x, p_x) = \sqrt{2m} \int_{x_-(x,p_x)}^{x_+(x,p_x)} [E_x(x, p_x) - V(x^*)]^{-1/2} dx^*.$$

We note here an early numerical treatment of molecular trajectories [12] that instead averages the product of path length and velocity in estimating the flux.

We derive a similar expression for D_0 in a cylindrical pore. Using cylindrical polar coordinates, the pore has walls at radius R, and axis in the z direction. An external force acts together with the solid-fluid interaction potential $V(r)$, and the average z momentum is zeroed at reflections. A key difference originates from the cylindrical pore Hamiltonian

$$H_C = V(r) - Fz + p_r^2/2m + p_\theta^2/2mr^2 + p_z^2/2m,$$

in which the r and θ components cannot be separated.

Consequently, we can only separate H_C into two parts:

$$E_r = V(r) + p_r^2/2m + p_\theta^2/2mr^2, \qquad E_z = -Fz + p_z^2/2m.$$

The expression for D_0 is now obtained as

$$D_0 = \frac{k_B T}{2m}$$

$$\times \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \tau(r, p_r, p_\theta) e^{-E_r(r,p_r,p_\theta)/k_B T} dr\, dp_r\, dp_\theta}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} e^{-E_r(r,p_r,p_\theta)/k_B T} dr\, dp_r\, dp_\theta}, \qquad (3)$$

with $\tau(r, p_r, p_\theta)$ given by

$$\tau(r, p_r, p_\theta) = \sqrt{2m} \int_{r_-(r,p_r,p_\theta)}^{r_+(r,p_r,p_\theta)} [E_r(r, p_r, p_\theta) - V(r^*)$$
$$- p_\theta^2/2mr^{*2}]^{-1/2} dr^*,$$

and where $r_\pm(r, p_r, p_\theta)$ denote the bounds of oscillation. Sidestepping algebraic details, we note that the above expression for the transport diffusion coefficient collapses to the Knudsen result, when $V(r) = 0$ in the pore space.

Equations (2) and (3) have been solved here to obtain estimates of the low-density transport diffusion coefficient for methane adsorption in carbon slit pores and silica cylindrical pores. The slit pore walls were represented using the Steele 10-4-3 potential [13], with 12-6 Lennard-Jones (LJ) parameters defined via the Lorentz-Berthelot combining rules (where $\varepsilon_f/k_B = 148.1$ K, $\sigma_f = 0.381$ nm for methane and $\varepsilon_s/k_B = 28.0$ K, $\sigma_s = 0.340$ nm for carbon). The silica cylindrical pore walls were considered infinitely thick and comprised of close-packed LJ sites having [4,5] $\varepsilon_s/k_B = 290$ K, $\sigma_s = 0.29$ nm. The solid-fluid interaction was determined by summing the (LJ) interactions between pore atoms and a methane molecule at various radii.

Values of D_0 determined from the model, using these potentials, are plotted in Figs. 1 and 2. For the slit pore calculations (Fig. 1) the temperature was 298 K, and pore widths (center-to-center distance between opposing carbon planes) ranged from 0.6 to 2.0 nm. For the cylindrical pore (Fig. 2), the temperature was 450 K, with pore diameters (center-to-center) ranging from 0.7 to 5 nm. To validate the model, we have performed NEMD simulations modeling the systems at low density (no greater than 0.1 nm^{-3}). The solid-fluid interaction potentials in the simulations were identical to those used in the model, with reflections between molecules and the pore wall treated using diffuse boundary conditions [11]. Fluid-fluid interactions were determined using a LJ potential, cut off at 1.5 nm. The force field acceleration was chosen in the range 0.002–0.02 nm ps^{-2}, which afforded linear response behavior. To maintain constant temperature, a Gaussian thermostat [14] was applied. The length of the pores was selected to ensure that at least 500 molecules were contained in the simulation cell, and each simulation lasted 10^7 steps. The value of D_0 was obtained from
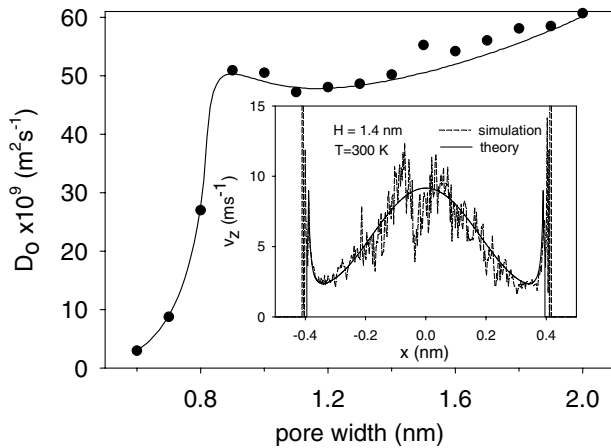
FIG. 1.   Variation of transport coefficient with slit width for the adsorption of methane at 300 K in carbon slit pores. The line corresponds to the model predictions and symbols to simulation data. The inset shows a comparison of the velocity profiles predicted by the model and generated by the simulation, for a pore of 1.4 nm width.

Eq. (1) and the values are depicted as the symbols in Figs. 1 and 2. While showing excellent agreement with the simulation results in these figures, the theory is computationally faster by 2 to 3 orders of magnitude and avoids the statistical variation inherent to simulations, making it a very attractive alternative.

Depicted as the dash-dotted line in Fig. 2 is the Knudsen result for the variation of transport coefficient with pore diameter, showing considerable overprediction
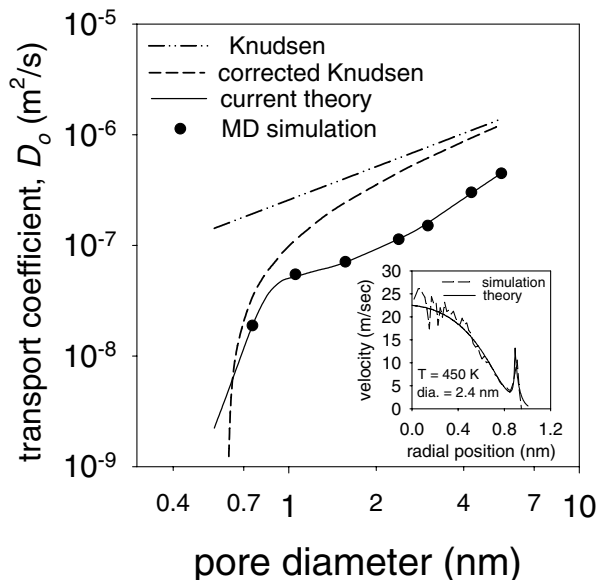

FIG. 2.   Variation of transport coefficient with pore diameter for the adsorption of methane at 450 K in cylindrical silica pores. The inset shows a comparison of the streaming velocity profiles predicted by the model and generated by the simulation, for a 2.4 nm diameter pore.

(even by orders of magnitude) by this classical theory considering only hard sphere interactions. Clearly, dispersive interactions considerably attenuate the transport, as they reduce the period of oscillation. The dashed curve in Fig. 2 depicts a corrected Knudsen coefficient, in which the pore radius is reduced by $0.92\sigma_{fs}$ to approximate the radius at the potential minimum, showing that the excluded region accounts for most of the overprediction in pores smaller than about 1 nm diameter. Also shown in the insets of Figs. 1 and 2 are comparisons of the velocity profiles generated from NEMD and from the model. In both cases, the model's prediction for the velocity profile across the pore is supported by the simulation results.

While ignoring fluid-fluid interactions, the model is applicable at all densities where the time spent by molecules in interacting with each other is small compared to that between such interactions. For example, consider a monolayer in a slit pore. If the mean separation is taken as that on a hexatic lattice, $d = \sqrt{4/\rho H \sqrt{3}}$, the intermolecular interaction time can be estimated as $\Delta t = 0.76\sqrt{m/k_B T \rho H}$, where a mean approach velocity of $2\sqrt{k_B T/m}$ (twice the mean thermal velocity) is assumed. For a 0.8 nm pore at $\rho = 0.1$ nm^{-3} and $T = 298$ K, we obtain $\Delta t = 6.8 \times 10^{-12}$ sec, while the oscillation period $\langle \tau \rangle = 3.6 \times 10^{-13}$ sec [based on Eq. (1) and the value of D_0]. Thus, a molecule oscillates about 20 times between intermolecular collisions, and the model is expected to be accurate at this density which corresponds to a bulk pressure of about 4 bars.

The above theory offers an attractive first-principles option for the accurate prediction of transport coefficients in nanopores, overcoming the empiricism in existing approaches [8]. As the momenta of different molecules are uncorrelated in a smooth pore in the absence of fluid-solid interactions, the self and transport diffusivities are identical and are determined from the present theory. As discussed above, this transport diffusivity is constant over a range of densities of practical importance under supercritical conditions. This holds even for single-file diffusion, as shown in Fig. 3 for methane transport at 450 K in a 0.75 nm diameter silica pore, in which only one layer can be accommodated. It is evident that this transport diffusivity, obtained using NEMD as well as EMD (where we used the autocorrelation of the streaming velocity [4,5]), is constant at the low-density value predicted remarkably well by the theory. The density variation of the transport coefficient is predominantly due to viscous effects [4,5], which are absent in single-file diffusion where particle crossings are rare. For the single component case, it is easily seen that intermolecular "collisions" cannot affect the collective transport coefficient in true single-file diffusion, where they do not affect the center of mass motion or lateral oscillation period. Consequently, the transport diffusivity
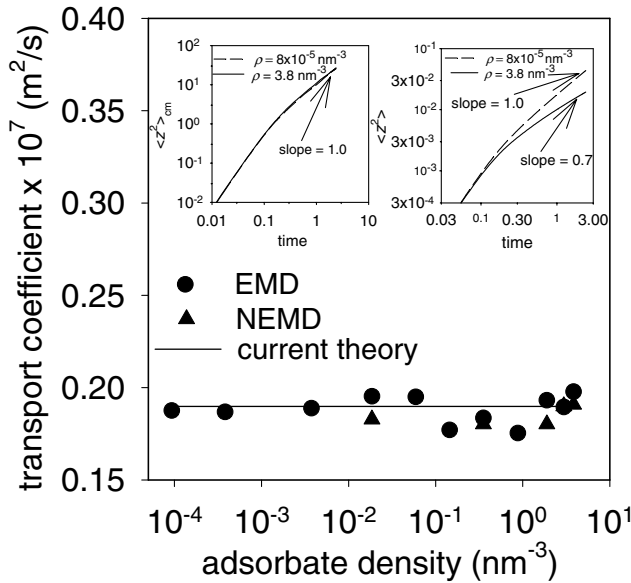
FIG. 3. Variation of transport coefficient with density for the adsorption of methane at 450 K in a 0.75 nm diameter cylindrical silica pore. The left inset depicts the temporal variation of the mean squared displacement of the center of mass and the right that for a single particle, at a low as well as a high density.

will be independent of density, which is confirmed by Fig. 3. On the other hand, it is known [15,16] that self-diffusion is nonclassical with mean squared displacement $\langle z^2 \rangle \propto \sqrt{t}$ when intermolecular collisions dominate. The classical nature of the transport diffusivity is evident in the inset of Fig. 3, illustrating linearity of the mean squared displacement of the center of mass, $\langle z^2 \rangle_{cm}$, with time, obtained using EMD, at low (8×10^{-5} nm^{-3}) and high (3.84 nm^{-3}) density. However, for $\langle z^2 \rangle$ the slope is unity at the low density and approaches 0.7 at the high density, indicating transition to nonclassical behavior when intermolecular interactions become important. Thus, the value of the present theory in predicting the diffusivity pertinent to actual transport is clearly evident.

In summary, a first-principles theory is developed that determines the transport coefficient of an LJ fluid in a nanopore under the action of the fluid-wall potential. The theory is presented here using the diffuse reflection boundary condition, and in the hard sphere limit yields the classical Knudsen result. Nevertheless, the theory is easily extended to accommodate other boundary conditions, such as only partially diffuse reflection, which may indeed be more realistic for some cases such as the methane-nanotube system where a smooth energy landscape leading to predominantly specular reflection has been noted using atomistic models [17,18]. In addition, rough surfaces and potentials more complex than one-dimensional as used here may also be considered, albeit with added computational burden. Indeed, more complex potentials and pore topologies may yield behavior different from that noted here, e.g., concentration dependence of single-file transport diffusivity in networked pore systems such as in silicalite observed for some gases but not others [19]. In future work we hope to address such problems.

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