

Knudsen Diffusivity of a Hard Sphere in a Rough Slit Pore

Gaurav Arya, Hsueh-Chia Chang, and Edward J. Maginn

Department of Chemical Engineering, University of Notre Dame, Notre Dame, Indiana 46556, USA
(Received 30 January 2003; published 10 July 2003)

An analytic theory for the Knudsen self-diffusivity D_s of hard spheres in an atomically rough slit-shaped pore is presented which quantitatively matches simulation results. The theory assumes that, due to chaotic molecular trajectories caused by surface morphology, collisions of gas molecules with the wall are partly diffuse and partly specular, the relative magnitude of each depending upon the magnitude of the tangential momentum accommodation coefficient f . The theory thus represents a universal Knudsen fluctuation-dissipation correlation between longitudinal momentum loss and diffusivity that can simplify efforts to estimate D_s . It is also found that D_s , computed using Maxwell's theory of slip, in which collisions with the walls are assumed to be purely diffuse or specular, overpredicts the simulated D_s by a large margin.

DOI: 10.1103/PhysRevLett.91.026102

PACS numbers: 68.43.Jk, 05.20.Dd, 83.10.Rs, 83.50.Rp

Studying the diffusion of gases within nanopores is an area of intense research due to the practical importance of diffusion in the areas of catalysis and separations, as well as the emerging interest in diffusion in carbon nanotubes [1,2]. The quantity of interest is the self-diffusivity $D_{s,x}$ of a gas molecule along a longitudinal direction x of a pore or a slit, as given by

$$D_{s,x} = \lim_{t \rightarrow \infty} \frac{\langle (\Delta x)^2 \rangle}{2t}. \quad (1)$$

In the large Knudsen number limit, i.e., the rarefied gas state, which is the regime of interest here, the self-diffusivity and a closely related collective property known as the transport diffusivity become equivalent [3]. Hence, $D_{s,x}$ alone adequately quantifies diffusion. In this regime, collisions between gas molecules are extremely rare and do not contribute to $D_{s,x}$. Wall collisions therefore supply the stochastic driving force necessary for the diffusive process. In Maxwell's classical theory of slip [4], two uncorrelated random variables are often associated with this key wall collision event—a Maxwell-Boltzmann (MB) distribution of molecular velocity for the incident molecule and a two-state distribution of the x -momentum loss at the walls. The tangential momentum accommodation coefficient f is defined for the second distribution, and it represents the fraction of gas collisions that reflect diffusely with the wall. The remaining collisions are considered to be specular. Therefore, one expects D_s to be impacted by the magnitude of f , which has been strongly linked to the atomic roughness of a defect-free wall [5].

Almost a century ago, Knudsen derived the classic expression for the Knudsen diffusivity of a gas within a cylindrical pore, assuming that all the gas-wall collisions are diffuse [6]. Later, Smoluchowski generalized Knudsen's result using Maxwell's model of purely diffuse or specular collisions to cases when only a fraction f of the collisions are diffuse [7]. The latter study has thereby considered the effect of varying degrees of wall rough-

ness on the self-diffusivity. In both studies, the diffuse collisions have been assumed to follow the cosine distribution in the reflected angle [4,8]. Recently, Malek and Coppens [9] have considered the impact of large-scale fractal roughness on the diffusivity of gases within pores, without explicitly relating the roughness to the factor f . It was observed that the roughness of the wall has a significant impact on the self-diffusivity of the sorbate.

Previous work on diffusion in nanopores [5,10,11] has shown that the thermalization time of the sorbate molecule with the surrounding lattice is often much larger than the collision time for the case of weakly adsorbing molecules with kinetic diameters much less than half the pore width. For these situations, lattice vibrations are relatively unimportant and little stochastic thermal force exists during each wall collision event. Instead, the stochastic forcing is due to the chaotic Hamiltonian and deterministic trajectory of the constant-energy molecule in the pore [10]. Each collision involves a different incident angle and strikes the surface at a different position. Insofar as the surface is not smooth, the incident and reflected angles are different simply because the molecule strikes the surface atom at a point with an oblique tangent plane. This mechanism implies that each collision is never purely diffuse or specular, as assumed in the classical theory of Maxwell [4]. Instead, a fraction of x momentum is lost for each collision, and this fraction depends upon the incident angle and the strike position. This implies that a new f can be defined that represents the average fraction of momentum loss for each collision. As such, details of the collision dynamics are unnecessary and only certain statistical moments are required to evaluate Eq. (1). We modify Smoluchowski's model here by reformulating Maxwell's collision model to obtain the correct dependence of $D_{s,x}$ on the coefficient f in this weakly coupled regime.

Consider the diffusion of hard spheres in a slit-shaped pore with a square lattice structure extending to infinity in the x and z directions (Fig. 1). Since the lattice is

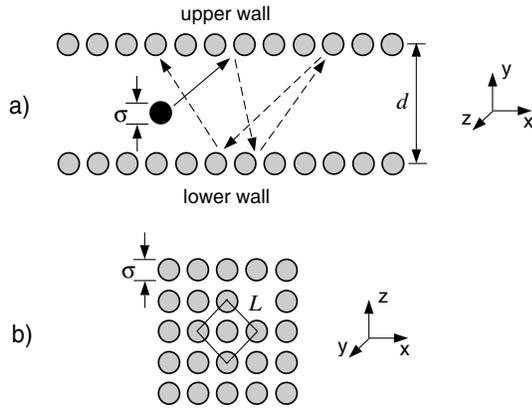


FIG. 1. Schematic of (a) hard-sphere gas molecule diffusing in a Knudsen-like fashion in a rough slit-pore, (b) pore wall structure modeled as a square lattice of hard spheres.

assumed to be defect free, the roughness of the wall is on the order of atomic dimensions. A more macroscopic roughness as treated by Malek and Coppens [9] will only serve to magnify f , but may be treated in a similar fashion. The tangential velocity component in the x direction is v_x , while the normal velocity is v_y . The time between successive wall collisions is the “collision time” τ . Consider now the trajectory of a gas molecule undergoing $N + 1$ successive collisions with the walls thereby generating N different collision times, τ_n , and x -direction path lengths, $\Delta x_n = v_{x,n} \tau_n$ for $n = 1, \dots, N$. The self-diffusivity $D_{s,x}$ in Eq. (1) is therefore given by

$$D_{s,x} = \lim_{N \rightarrow \infty} \frac{\left\langle \left(\sum_{n=1}^N v_{x,n} \tau_n \right)^2 \right\rangle}{2 \left\langle \sum_{n=1}^N \tau_n \right\rangle}. \quad (2)$$

Knudsen model.—The tangential velocities of the incident and reflected molecules for all collisions are uncorrelated with each other when $f = 1$, thereby implying that $\langle v_{x,n} v_{x,m} \rangle = 0$ for $n \neq m$. In addition, $v_{x,n}^2$ and τ_n^2 can be assumed to be uncorrelated, whereupon Eq. (2) may be simplified to

$$D_{s,x}|_{f=1} (\equiv D_K) = \frac{\langle v_x^2 \rangle \langle \tau^2 \rangle}{2 \langle \tau \rangle}. \quad (3)$$

The mean and the mean-square collision times in the above expression may be estimated as $d_{\text{eff}} \langle v_y^{-1} \rangle$ and $d_{\text{eff}}^2 \langle v_y^{-2} \rangle$, respectively, where d_{eff} is the effective or available distance between the pore walls, given by

$$d_{\text{eff}} = d - \frac{16}{L^2} \int_0^{L/2\sqrt{2}} \int_0^{L/2\sqrt{2}} \sqrt{\sigma^2 - (x^2 + z^2)} dx dz, \quad (4)$$

where σ , d , and L are parameters related to the gas species and the wall crystal as shown in Fig. 1. Note that the ensemble averages $\langle v_y^{-1} \rangle$ and $\langle v_y^{-2} \rangle$ are performed with respect to the number of collisions. The integration

prefactor and limits in the above equation are dependent upon the lattice being examined and may be appropriately modified for a different type of lattice. If the transverse velocity of the colliding molecules v_y is given by a MB distribution [5], then

$$\langle \tau \rangle = \alpha d_{\text{eff}} \sqrt{\frac{m}{k_B T}}, \quad \alpha = \frac{\int_{\epsilon}^{\infty} e^{-x} / \sqrt{2x} dx}{\int_{\epsilon}^{\infty} e^{-x} dx} = \sqrt{\frac{\pi}{2}}, \quad (5)$$

$$\langle \tau^2 \rangle = \beta d_{\text{eff}}^2 \left(\frac{m}{k_B T} \right), \quad \beta = \frac{\int_{\epsilon}^{\infty} e^{-x} / 2x dx}{\int_{\epsilon}^{\infty} e^{-x} dx} = -\frac{\ln \epsilon}{2}, \quad (6)$$

in the limit of $\epsilon = mv_c^2/2k_B T \rightarrow 0$, where v_c is a cutoff velocity described below. Using the fact that v_x is also MB distributed, i.e., $\langle v_x^2 \rangle = k_B T/m$, along with Eqs. (3), (5), and (6), we obtain the final estimate of the Knudsen model self-diffusivity in terms of the pore width, temperature and mass of the gas molecule

$$D_K = -d_{\text{eff}} \sqrt{\frac{k_B T}{8\pi m}} \ln \epsilon. \quad (7)$$

The above expression for D_K agrees with the expression derived by Knudsen for a cylindrical pore of radius R when the cutoff parameter is set as $\ln \epsilon = -16R/3d_{\text{eff}}$. Note that a MB distribution is used to represent molecular velocities due to the fact that the velocity distribution of a number of *noninteracting* hard-sphere molecules with *arbitrarily* chosen initial velocities, when simulated for long periods of time within a slit-pore (refer to Fig. 1), gradually approaches a MB distribution.

The cutoff parameter ϵ arises because the Boltzmann integral in $\langle \tau^2 \rangle$ diverges due to the lower-bound of zero transverse velocity (infinite collision time), so unlike the case of a cylinder which has a natural geometrical cutoff, a cutoff transverse velocity $v_y > v_c$ must be introduced. A plethora of physical mechanisms can be responsible for such a cutoff. The probability of gas-gas collision is not entirely zero for large but finite Knudsen numbers, and the cutoff would correspond to the mean free path of the sorbate molecules. Another need for a cutoff arises due to finite pore length scales. For example, a real system is bounded in both the *lateral* directions. In such cases, cutoffs corresponding to the pore width for finite aspect ratios and/or the pore lengths are required. Curvature along the length of the pore also gives rise to additional length-scale cutoffs. Finally, a cutoff may arise due to energetic interactions between the gas molecules and the pore walls, whereby molecules with small v_y would be unable to escape from the pore surface and undergo multiple collisions with the wall [5]. Fortunately, the weak logarithmic dependence on the cutoff ϵ implies that it does not affect the leading-order scalings with respect to other system parameters, as will be shown shortly.

Smoluchowski model.—In this model we invoke Maxwell’s assumption that all gas collisions with the

wall are either purely diffuse or purely specular, depending upon the magnitude of the coefficient f . Note that the probabilities a molecule randomizes its tangential velocity after times of $\langle\tau\rangle$, $2\langle\tau\rangle$, $3\langle\tau\rangle \cdots n\langle\tau\rangle$ are given by f , $f(1-f)$, $f(1-f)^2 \cdots f(1-f)^{n-1}$, respectively. Hence, the mean time a molecule takes to randomize its tangential velocity, referred to as an effective collision time, $\langle\tau\rangle_{\text{eff}}$, is calculated by summing up the product of various randomization times and their probabilities. The effective mean-square collision time $\langle\tau^2\rangle_{\text{eff}}$ may be calculated in a similar fashion.

$$\begin{aligned}\langle\tau\rangle_{\text{eff}} &= \langle\tau\rangle f \sum_{n=1}^{\infty} n(1-f)^{n-1} = \langle\tau\rangle/f^2, \\ \langle\tau^2\rangle_{\text{eff}} &= \langle\tau^2\rangle f \sum_{n=1}^{\infty} n^2(1-f)^{n-1} = \langle\tau^2\rangle(2-f)/f^3.\end{aligned}\quad (8)$$

Using the above effective collision times in Eq. (3) in place of $\langle\tau\rangle$ and $\langle\tau^2\rangle$, we obtain the dependence of $D_{s,x}$ on f for the Smoluchowski model

$$D_{s,x} (\equiv D_S) = D_K \left(\frac{2-f}{f} \right). \quad (9)$$

The above analysis shows that the self-diffusivity of a Knudsen gas goes to infinity when the walls become perfectly smooth, i.e., when f approaches zero, while it approaches a lower limit given by Eq. (7) when the walls become infinitely rough.

Extended Smoluchowski model.—As mentioned before, collisions on a weakly adsorbing wall, as represented by hard spheres here, are purely deterministic in nature. This means that the angle of reflection of a gas molecule upon the collision is highly dependent on the incident angle and its point of impact at the surface atoms. Consequently, each collision is not simply diffuse or specular, but is rather a combination of both.

Consider a gas molecule incident upon the wall with a tangential velocity v_{inc} which is MB distributed at temperature T . Let a fraction $(1-f)$ of this incident velocity be retained in its reflected velocity v_{ref} of the gas mole-

cule. This therefore represents the specular component of each collision. Next, a random velocity kv_g is added to the existing specular velocity to model the diffuse component of the collision due to lattice roughness and molecular chaos. The term v_g is sampled from an appropriate distribution described later, while k is a constant which depends on f . This rule may therefore be summarized as

$$v_{\text{ref}} = (1-f)v_{\text{inc}} + kv_g. \quad (10)$$

Let us now consider a number of gas molecules with velocities distributed in a MB fashion at temperature T within a pore. At steady state or global thermodynamic equilibrium, where the distribution of molecular velocities is invariant, it follows via a self-consistency argument that the distribution of v_{ref} should be identical to v_{inc} . This necessitates that both v_{ref} and v_g be distributed in a MB fashion at the same temperature T , and that $k = \sqrt{f(2-f)}$. The validity of Eq. (10) has been verified using hard-sphere scattering simulations similar to those used in an earlier paper [5]. In short, each deterministic collision, *in an averaged sense*, retains a fraction $(1-f)$ of its incident velocity and is also scattered to an extent in a MB fashion, the magnitude of which being determined by the value of k .

We next apply Eq. (10) to N successive collisions starting with a MB distributed tangential velocity given by $v_{x,1}$. The tangential velocities $v_{x,2} \cdots v_{x,N}$ between the collisions are therefore given by

$$\begin{aligned}v_{x,2} &= (1-f)v_{x,1} + kv_{g,1}, \\ v_{x,3} &= (1-f)^2v_{x,1} + (1-f)kv_{g,1} + kv_{g,2}, \\ &\vdots \\ v_{x,N} &= (1-f)^{N-1}v_{x,1} + k \sum_{m=1}^{N-1} (1-f)^{N-m-1}v_{g,m},\end{aligned}\quad (11)$$

where $v_{g,i}$ is the MB distributed velocity added to each specular component of the incident velocity upon collision. The self-diffusivity $D_{s,x}$ from Eq. (2) may then be written as

$$D_{s,x} = \lim_{N \rightarrow \infty} \frac{1}{2 \left\langle \sum_{n=1}^N \tau_n \right\rangle} \left\langle \left[v_{x,1} \sum_{n=1}^N (1-f)^{n-1} \tau_n + k \sum_{n=1}^{N-1} v_{g,n} \sum_{m=n+1}^N (1-f)^{m-n-1} \tau_m \right]^2 \right\rangle. \quad (12)$$

The above expression may be simplified further by using the fact that $\langle v_{x,1} v_{g,i} \rangle = 0$ for all i ; $\langle v_{g,i} v_{g,j} \rangle = 0$ and $\langle \tau_i \tau_j \rangle = \langle \tau \rangle^2$ for all $i \neq j$; $\langle v_{x,1}^2 \rangle = \langle v_{g,i}^2 \rangle = \langle v_x^2 \rangle$ for all i , and taking the limit to $N \rightarrow \infty$, to obtain

$$D_{s,x} = \frac{\langle v_x^2 \rangle \langle \tau^2 \rangle}{2 \langle \tau \rangle} \left[1 + 2 \frac{\langle \tau \rangle^2 (1-f)}{\langle \tau^2 \rangle f} \right]. \quad (13)$$

Equation (13) may be simplified using Eqs. (3), (5), and (6) to give

$$D_{s,x} = D_K \left[1 - \frac{2\pi(1-f)}{\ln \epsilon f} \right]. \quad (14)$$

Equation (14) is the main result we seek. It represents an extension of the Smoluchowski model given by Eq. (9) to take into account the scattering mechanism described by Eq. (10). Note that the two models become identical only in the case where $\langle \tau \rangle^2 = \langle \tau^2 \rangle$, which would not generally be the case for realistic velocity distributions. To test Eqs. (7), (9), and (14), we conducted hard-sphere

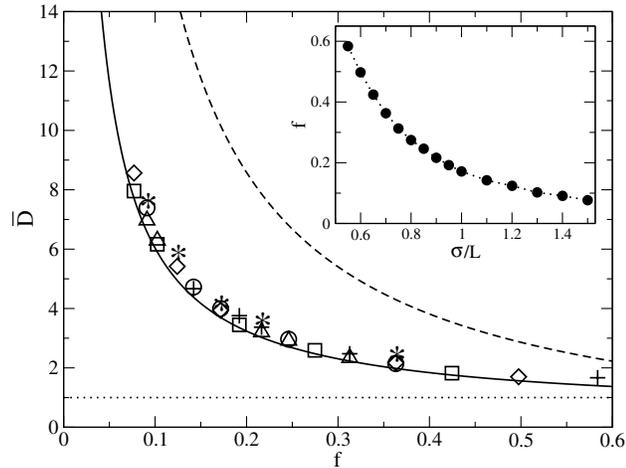


FIG. 2. Dimensionless self-diffusivity \bar{D} of a hard sphere as a function of f . The dotted, dashed, and solid lines represent predictions from Knudsen, Smoluchowski, and our extended Smoluchowski model, respectively, while the open symbols represent simulation results at different roughness (characterized by the ratio σ/L), temperatures and effective pore widths [\square (200 K, 30 Å), \circ (400 K, 20 Å), \diamond (300 K, 20 Å), \triangle (300 K, 30 Å), $+$ (200 K, 10 Å), and $*$ (400 K, 30 Å)]. The inset shows the computed values of f as a function of the roughness σ/L . The dotted line in the inset is meant to guide the eye.

dynamics simulations of the system depicted in Fig. 1. The initial velocity distribution was chosen identical to that used in the model, with a small cutoff of $\epsilon = 8 \times 10^{-6}$. This cutoff would ideally correspond to a large Knudsen number of about 300 for $d_{\text{eff}} = 16$ Å, $m = 16$ amu, and $T = 300$ K, if interactions between gas molecules were accounted. The self-diffusivity was computed from the mean-square displacement using Eq. (1). The effective separation d_{eff} was varied from 10 to 30 Å while the temperature was varied from 200 to 400 K (see Fig. 2). The simulations were conducted at different values of wall roughness, σ/L , and therefore different values of f . The accommodation coefficients at these different values of roughness were computed using a molecular simulation scattering technique [5] with results shown in the inset of Fig. 2.

The reduced self-diffusivity $\bar{D} = D_{s,x}/D_K$ computed from the simulations versus f is shown in Fig. 2, along with the predictions from the three models. The Knudsen model as represented by Eq. (7) does not capture the dependence of \bar{D} on f at all. While both the Smoluchowski and the extended Smoluchowski models diverge as f^{-1} in the smooth wall limit ($f \rightarrow 0$), they do so with different coefficients. Indeed, the divergence of $D_{s,x}$ at small f has been proposed to explain abnormally high self-diffusivity estimates in recent carbon nanotube simulations [12]. The self-diffusivities from the two models also approach the infinitely rough wall limit $\bar{D} = 1$

differently. There is hence a considerable discrepancy between the two theories. The extended Smoluchowski model [Eq. (14)] quantitatively matches the exact simulation results, while the original Smoluchowski model [Eq. (9)] only qualitatively agrees with the simulations. This indicates that the partitioning of collisions into specular and diffusive components due to the surface morphology must be introduced for each collision as in Eq. (10), and not in the ensemble average probability as in the Maxwell/Smoluchowski model. Once the intercollision statistics are captured in D_K of our extended model, the self-diffusivity estimate reduces to the determination of our new accommodation coefficient f as a function of pore geometry and surface morphology. This can be done through an examination of the collision operator or via a single collision scattering simulation [5]. Solution of the full Boltzmann equation is unnecessary as are molecular dynamics simulations involving many collisions. Even realistic cutoff mechanisms, which require a long time to simulate, can easily be introduced with a specific ϵ . The general fluctuation-dissipation correlation for longitudinal Knudsen momentum loss and diffusivity in Eq. (14) should thus provide a basis for predicting the self-diffusivity $D_{s,x}$ of a confined gas in nanopores with respect to the pore width, temperature, mass, and the surface roughness.

This work was partially supported by a NSF XYZ-on-a-chip grant (CTS99-80745) and the Donors of The Petroleum Research Fund, administered by the ACS. Computational resources were provided by a grant from NSF (DMR00 79647). G. A. acknowledges the Center for Applied Mathematics at Notre Dame for support.

-
- [1] S. M. Auerbach, *Int. Rev. Phys. Chem.* **19**, 155 (2000).
 - [2] V.P. Sokhan, D. Nicholson, and N. Quirke, *J. Chem. Phys.* **117**, 8531 (2002).
 - [3] G. Arya, H.-C. Chang, and E. J. Maginn, *J. Chem. Phys.* **115**, 8112 (2001).
 - [4] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1938).
 - [5] G. Arya, H.-C. Chang, and E. J. Maginn, *Molecular Simulation* (to be published).
 - [6] M. Knudsen, *Ann. Phys. (Leipzig)* **28**, 75 (1909).
 - [7] M. Smoluchowski, *Ann. Phys. (Leipzig)* **33**, 1559 (1910).
 - [8] M. Knudsen, *The Kinetic Theory of Gases* (Methuen & Co. Ltd., London, 1934).
 - [9] K. Malek and M.-O. Coppens, *Phys. Rev. Lett.* **87**, 125505 (2001).
 - [10] D. I. Kopelevich and H.-C. Chang, *J. Chem. Phys.* **114**, 3776 (2001); *Phys. Rev. Lett.* **83**, 1590 (1999).
 - [11] E. J. Maginn, A. T. Bell, and D. N. Theodorou, *J. Phys. Chem.* **97**, 4173 (1993).
 - [12] A. I. Skoulidas, D. M. Ackerman, J. K. Johnson, and D. S. Sholl, *Phys. Rev. Lett.* **89**, 185901 (2002).