

Statistical method for modeling Knudsen diffusion in nanopores

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This paper presents a statistical method for the calculation of gaseous flux and diffusion coefficients through a Knudsen-regime cylindrical nanopore. A general integral formula for the flux is derived in terms of collision frequency, molecular density, and a scattering path length probability distribution. Under appropriate steady-state assumptions, the general formula simplifies to Fick's first law, from which an expression for the diffusion coefficient is derived. The model is shown to be dimensionally consistent with the Einstein relation. The conditions for agreement with Fick's second law are investigated. Using a model probability distribution the model leads to an expression for the diffusion coefficient for a pore of finite length. This result is shown to compare favorably with a classic formula from the literature.

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I. INTRODUCTION

Effectively engineered nanomaterial technologies require theoretical determination of processes which result from nanoscale interactions between molecules. Nanofluidic transport is dominant in many emerging technologies that have worldwide implications, e.g., water filtration and carbon dioxide sequestration. Diffusion through microporous membranes with precisely tuned material qualities and structure is essential to how a membrane can operate. Molecular transport at small scales is the primary mechanism for the selective diffusion processes seen in semipermeable fuel cell membranes and gas separation devices [1]. Carbon nanotubes, [2,3] zeolites, [4,5], silicon nanochannels, [6] and block copolymers [7] are all materials currently being investigated to fabricate these types of membranes. There is even evidence of separation membranes being fabricated via three-dimensional printing techniques which would introduce the precise structural control essential for nanotechnologies [8].

In an effort to expand the knowledge base for the flow of gases in confined spaces we report here on a model that can be used to compute the flux and a Fickian diffusion coefficient for gaseous flow through cylindrical nanopores in the highly rarefied, free molecular flow regime. First, a brief introduction to current ideas in the theory of bulk gaseous diffusion and gaseous diffusion in confined spaces is given.

Diffusion mechanics are analogous to Fourier's law of heat conduction, where transport of heat is proportional to the temperature heat gradient. In the same way, a phenomenological description of gaseous diffusion is defined by

$$J = -D \frac{\partial n}{\partial z}, \quad (1)$$

also known as Fick's first law, where J is molecular flux, D the diffusivity or self-diffusion coefficient for a gaseous particle.

$n = n(z, t)$ is the molecular concentration as a function of position z and time t . Here J and D refer to a lone gaseous species, which will continue to be the case throughout the entirety of this report. In time-dependent systems, applying conservation of mass naturally leads into Fick's second law:

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial z^2}, \quad (2)$$

which is sometimes called the diffusion equation.

It can also be shown that $D = \langle z(t)^2 \rangle / 2t$, which is often referred to as the Einstein relation, where $\langle z(t)^2 \rangle$ is the mean displacement squared, as a function of elapsed time. The self-diffusivity of the a gaseous species can alternatively be calculated using kinetic theory where $D = \frac{1}{3} \lambda \bar{v}$ [9]. The factors λ and \bar{v} are the familiar expressions for mean-free path and mean speed, respectively:

$$\lambda = \frac{k_b T}{\sqrt{2P\pi} d_i^2}, \quad (3)$$

$$\bar{v} = \sqrt{\frac{8k_b T}{\pi m}}, \quad (4)$$

where k_b is the Boltzmann constant, P is the gas pressure, T is the temperature, d_i is the effective diameter of the gas particle, and m is particle mass (Ref. [9], pp. 873, 869).

In porous membranes, the diffusivity is often modified to take into account the effects of membrane design and structure. If the diffusion coefficient for a gaseous particle within a single pore is given by D_i , then the effective diffusivity, D_{eff} , for the membrane is computed as

$$D_{\text{eff}} = \frac{\epsilon}{\tau} D_i, \quad (5)$$

where porosity, ϵ , is the fraction of membrane surface area containing pores and the tortuosity factor, τ , is a unitless parameter that accounts for the twisting and turning of otherwise straight pores. $\tau \geq 1$ where $\tau = 1$ for a pore without geometric disorder, for example, a uniformly cylindrical pore with circular cross section [10].

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It is useful to consider the *Knudsen number*, K_n . Let d be the pore diameter, then $K_n = \lambda/d$ [11]. *Knudsen diffusion* describes the transport of molecular particles through a pore of exceptionally narrow diameter, i.e., for $K_n \gg 1$, for the highly rarefied situation where intermolecular collisions can be neglected and all momentum transfer processes occur at the pore wall. In Knudsen's original analysis for flow within this regime, the physical mechanism of particle-wall interaction is concealed by assuming purely diffuse reflections for pores of infinite length. The diffusion coefficient under these conditions is [12,13]

$$D_k = \frac{1}{3}\bar{v}d. \quad (6)$$

When $K_n \sim 1$ intermolecular collisions near the pore center transfer momentum away from diffusing molecules, reducing the overall diffusivity, the so-called *transition regime*. Diffusivity can be computed in this regime by using the Bosanquet approximation [14]:

$$\frac{1}{D_t} = \frac{1}{D} + \frac{1}{D_k}, \quad (7)$$

where D is the bulk gas phase diffusion coefficient and D_t is the transition regime diffusion coefficient. As K_n decreases further, other diffusion contributions arise from viscous or *Poiseuille* flow and surface flow, which combine additively with the transition diffusion coefficient to form a bulk diffusivity, D_b , which can be approximated by

$$D_b = D_t + K \left(\frac{1-\epsilon}{\epsilon} \right) D_s + D_p, \quad (8)$$

where K is a dimensionless absorption equilibrium constant and D_s is surface flow diffusivity [15]. Viscous diffusivity is defined by Poiseuille flow as $D_p = Pd_i^2/32\eta$ where η is the viscosity.

Modeling and simulation of free-molecular mass transport through confined spaces have experienced few milestones since the original analysis of Knudsen, Pollard, and Present proposed a model that predicted Knudsen diffusivity for a pore of finite length which converges to the Knudsen result for infinite pores [13]. More recently, the research group of Bhatia, Nicholson, and co-workers have made additional progress [16–18]. The theory put forth by this group considers the motion of a fluid molecule in a cylindrical pore driven by a chemical potential gradient under the influence of a Lennard-Jones potential field originating from the pore wall. The diffusion coefficient D_{to} is calculated using the mean oscillation time $\langle t \rangle$ in seconds, extracted from simulation trajectories as

$$D_{to} = \frac{k_b T}{m} \langle t \rangle. \quad (9)$$

Accommodation of viscous contributions is accomplished by superimposing a surface diffusivity term, calculated using simulated density profiles. Other recent modeling innovations include the direct simulation Monte Carlo method and the test particle method [19].

In this report an alternative method is presented whereby the flux and a Fickian diffusion coefficient for Knudsen diffusion, within cylindrical nanopores of circular cross section,

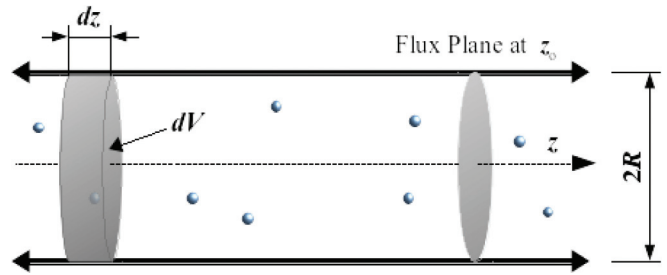


FIG. 1. Diffusing particles within a cylindrical nanopore of perfect circular cross section of infinite length where a coordinate system, a differential volume, and a flux plane are depicted.

can be estimated. Rather than using conservation of momentum or mean times between collisions the theory makes use of a probability distribution for axial scattering path lengths. Under certain simplifying assumptions the model is shown to be consistent with Fick's first law, and the Einstein relation for any finite probability distribution function that vanishes at $+\infty$. Conditions for agreement with Fick's second law are determined. To further demonstrate the method, an exponential distribution function is employed and an expression for the Knudsen diffusion coefficient is arrived at for a pore of finite length. This formula is shown to have similar behavior to that of a classic result from the literature.

II. THEORY

Consider a single cylindrical nanopore with perfect circular cross section of infinite length through which gas molecules are diffusing at constant temperature in the Knudsen regime. As depicted in Fig. 1, an axial coordinate z is positioned within the nanopore of radius R , and a flux evaluation plane is placed at an arbitrary location z_0 which may or may not be at the origin for the coordinate system, $z = 0$. A differential disk of thickness dz is placed within the nanopore at an arbitrary coordinate z . In the Knudsen regime, a differential volume will almost certainly contain no particles, except for instances where a particle transits through. The differential volume is implicitly monitored for a sufficient amount of time, where sufficient is defined as long enough to accurately capture the number of particles contained at that location, but short enough such that the transient changes of the macroscopic diffusion remain negligible over the time interval.

The infinitesimal number of particles, dN within dV is calculated by multiplying dV by particle number density $n(z, t)$:

$$dN = \pi R^2 dz n(z, t). \quad (10)$$

Each dV within the pore has some number of particles that uniquely originated from that location, enumerated by identifying how many particles undergo a collision with the wall; for example, see Fig. 2. Each particle is characteristic of the location of the last wall collision, a location unique for each particle.

We begin by assuming that all particles in the system have the same translational energy E . For example, this could be the mean energy from the kinetic theory of gases: $(1/2)m\bar{v}^2$. Effects for a distribution of energies will be considered later.

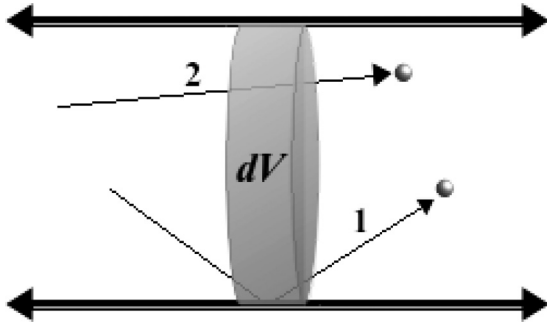


FIG. 2. Particles traveling in relation to dV over a small time interval within a pore of infinite length. Trajectory 1 constitutes a particle that is unique and characteristic to dV due to its collision with the wall, while 2 does not.

The rate at which particles collide with the wall is computed by multiplying the number of particles, Eq. (10), by the mean collision rate for a single particle, denoted by ξ . Define df as the particle-wall collision rate infinitesimal for particles contained in dV , computed by

$$df(z, t, E) = \xi dN, \quad (11)$$

which is equivalent to the rate of particles exiting the volume.

A particle originating from dV will contribute to flux through the plane if it travels so that its next collision is at the flux plane or at any location farther beyond the plane. For example, the solid trajectory lines in Fig. 3 illustrate possible paths for a particle originating from dV that contribute to the flux. Each potential trajectory can be assigned a probability of occurrence, from which a probability distribution function (PDF) can be assembled [which, e.g., could be calculated from molecular dynamics (MD) simulations]. To do this, the particular interaction conditions between the gaseous molecule and the pore wall would need to be considered. In this work no attempt is made to generate a PDF for a specific gas-pore system, so the details of the molecule and pore wall interaction are not discussed. However, the required properties of the PDF that allow the model to be consistent with known laws of diffusion are determined.

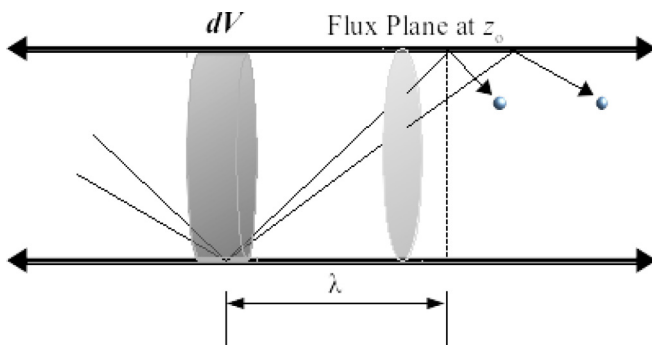


FIG. 3. Identification of potential intercollision trajectories within a pore of infinite length. Axial intercollision distance is denoted by λ , and solid lines represent possible trajectories originating from dV where the particle successfully contributes to flux through the flux plane.

The probability of a particle traveling an intercollisional axial distance λ is expressed by a PDF: $P_l(\lambda)d\lambda$. Here λ should not be confused with the symbol's previous use in Eq. (3) for the gas phase mean-free path. However, as illustrated in Fig. 3, a contribution to flux is satisfied not only by a particle traveling to the flux plane, but also to any location beyond the plane. Therefore, the more relevant quantity is a cumulative sum of probabilities, i.e., a cumulative distribution function (CDF). Since the PDF is dependent on the relative location of dV and the flux plane (i.e., the PDF may not be symmetric), the formal definition of the CDF, C , must be a piecewise function that reflects that dependency. For the flux plane at z_o we have

$$C(z, z_o) = \begin{cases} \text{if } z \geq z_o & \int_{\lambda=z-z_o}^{\infty} P_l(\lambda) d\lambda \\ \text{if } z \leq z_o & \int_{-\infty}^{\lambda=z-z_o} P_l(\lambda) d\lambda \end{cases}, \quad (12)$$

where we have used the notation $C = C(z, z_o)$ to denote that C has its origin at $z = z_o$ the flux plane, unlike the density $n(z, t)$ with its origin at $z = 0$.

Let $d\dot{N}$ denote the particle contribution rate infinitesimal from dV to the flux plane, calculated by multiplying the wall collision rate with the CDF: $d\dot{N} = df(z, t)C(z)$. The total particle contribution rates for the rightward and leftward directions can be obtained by appropriately integrating $d\dot{N}$ over the length of the nanopore. For example, the rightward progressing particle contribution rate would be computed by $\dot{N}_R = \int_{-\infty}^{z_o} d\dot{N}$, and the analogous integration from z_o to infinity is done to compute \dot{N}_L :

$$\dot{N}_R = \pi R^2 \xi \int_{-\infty}^{z_o} n(z, t) C(z, z_o) dz, \quad (13)$$

$$\dot{N}_L = \pi R^2 \xi \int_{z_o}^{\infty} n(z, t) C(z, z_o) dz. \quad (14)$$

Net particle flux J is defined traditionally as $J(z_o, t) = (\dot{N}_R - \dot{N}_L)/\pi R^2$. Replacing z by $2z_o - z$ in the above expression for \dot{N}_R , and using a known property of definite integrals, we can combine the two integrals into one. The resulting equation for net flux is then

$$J(z_o, t) = \xi \int_{z_o}^{\infty} [n(2z_o - z, t) C(2z_o - z, z_o) - n(z, t) C(z, z_o)] dz, \quad (15)$$

where J is the time-dependent net particle flux at z_o for constant ξ .

It is desirable to consider Eq. (15) for particles of different translational energies. Letting $\xi = \xi(E)$ and $C = C(z, t, E)$ and multiplying the right side of Eq. (15) by $f(E)dE$, where $f(E)$ is a normalized energy distribution function, we get

$$dJ(z, t, E) = \xi(E) f(E) dE \int_{z_o}^{\infty} [n(2z_o - z, t) C(2z_o - z, z_o, E) - n(z, t) C(z, z_o, E)] dz. \quad (16)$$

The total flux across all translational energies is then

$$J(z_o, t) = \int_0^{\infty} \left\{ \xi(E) f(E) \int_{z_o}^{\infty} [n(2z_o - z, t) C(2z_o - z, z_o, E) - n(z, t) C(z, z_o, E)] dz \right\} dE. \quad (17)$$

To use Eq. (17) the collision frequency and the PDF would need to be estimated analytically or via simulation. Then, the number density and translational energy distribution would be specified. A straightforward integration of Eq. (17) would then provide flux, from which diffusivity can easily be calculated. However, certain simplifications allow Eq. (17) to be cast into a more manageable form, though with loss of generality. The process of making these simplifications sheds light on the physical significance of the formula, enables comparison to existing more restrictive theory, and reveals that for the steady-state case a diffusion coefficient can be directly computed given a PDF and collision frequency.

III. SIMPLIFICATION

A. Symmetric PDF

The shape of the PDF will depend on the geometry of the pore wall and the particle-wall interaction. However, the evaluation of Eq. (15) is simplified by considering a pore of uniform geometry and particle-wall interaction. Symmetry of the PDF implies mathematical evenness, so $P_l(\lambda, E) d\lambda = P_l(-\lambda, E) d\lambda$. Using this simplification, Eq. (12) reduces to

$$C(z, z_o) = \int_{\lambda=|z-z_o|}^{\infty} P_l(\lambda) d\lambda, \quad (18)$$

which is now used in the simplification of Eq. (15). Replacing z with $2z_o - z$ in Eq. (18) demonstrates that $C(2z_o - z, z, E) = C(z, z_o, E)$, and the subsequent flux formula of Eq. (15) can be written as

$$J(z_o, t) = \xi \int_{z_o}^{\infty} [n(2z_o - z, t) - n(z, t)] C(z, z_o) dz. \quad (19)$$

B. Steady-state diffusion

Many important diffusion problems occur under conditions of steady state. Assuming time-independent conditions and a uniform translational energy distribution Eq. (15) is simplified to

$$J(z_o) = \xi \int_{z_o}^{\infty} [n(2z_o - z) - n(z)] C(z, z_o) dz, \quad (20)$$

where $J(z_o)$ is the flux at any location z_o in the pore.

Equation (20) can be used to shed light upon the nature of n during steady-state conditions. During steady-state conditions the molecular flux through the plane will be the same at all locations within the pore. Flux is equated for two arbitrary locations within the pore: $z = 0$ and $z = z_o$. Using these two locations in the integral of Eq. (20) and equating leads to

$$\begin{aligned} & \int_0^{\infty} [n(-z) - n(z)] C(z, 0) dz \\ &= \int_{z_o}^{\infty} [n(2z_o - z) - n(z)] C(z, z_o) dz. \end{aligned} \quad (21)$$

By shifting the coordinate z in the functions on the right of Eq. (21) by z_o it becomes possible to match the limits of the integrals and thus equate the integrands. This leads to $n(-z) - n(z) = n(z_o - z) - n(z_o + z)$, and thus in this case $C(z, 0) = C(z + z_o, z_o)$. A Taylor series expansion is performed on all four terms: $n(-z)$ and $n(z)$ are expanded about 0. $n(z_o - z)$

and $n(z_o + z)$ are expanded about z_o . Grouping like terms and simplifying results in

$$\begin{aligned} & \left[\frac{dn}{dz} \Big|_0 z - \frac{dn}{dz} \Big|_{2z_o} (z - z_o) \right] + \left[\frac{d^3n}{dz^3} \Big|_0 \frac{z^3}{3!} - \frac{d^3n}{dz^3} \Big|_{2z_o} \frac{(z - z_o)^3}{3!} \right] \\ & + \left[\frac{d^5n}{dz^5} \Big|_0 \frac{z^5}{5!} - \frac{d^5n}{dz^5} \Big|_{2z_o} \frac{(z - z_o)^5}{5!} \right] + \dots = 0. \end{aligned} \quad (22)$$

For Eq. (22) to be true, all pairs of derivatives must vanish for any choice of z_o location, necessitating constant value derivatives. If any higher order derivatives are nonzero constants, then lower order derivatives will no longer be constants. Therefore all higher order derivatives must be zero, and to avoid the trivial solution, the first-order derivative is assigned a nonzero constant, i.e., $dn/dz = \text{constant}$. Thus, for steady-state flow through a pore the number density will be linear: $n(z) = \frac{dn}{dz} z + n_o$, where n_o will be a constant defined by the number density at the flux plane. Entering this expression for $n(z)$ into Eq. (20), setting the flux plane location to $z_o = 0$ and letting $C(z, 0) = C(z)$, yields

$$J = -2\xi \frac{dn}{dz} \int_0^{\infty} z C(z) dz, \quad (23)$$

which computes steady-state particle flux by assuming a symmetric PDF and uniform translational energy. In other words, given the flux plane at $z_o = 0$ along with a symmetric PDF, one is only required to integrate the PDF over all positive space and multiply by two as seen by Eq. (23). Therefore, the steady-state and particle-independent energy expression for the CDF is then

$$C(z) = \int_{|z|}^{\infty} P_l(\lambda) d\lambda. \quad (24)$$

Additionally, by inserting the energy-dependent form of ξ and C , along with an energy distribution $f(E) dE$ into Eq. (23), one can then get a steady-state flux or diffusion coefficient over all translational energies of the distribution.

IV. ANALYTICAL VALIDATION OF FLUX FORMULA

A. Agreement with Fick's first law

Analytical validation is performed by examining the mathematical behavior of the formula under simplifying assumptions and observing if the results are in accord with existing theory and expectations. In this section conditions for agreement between Eq. (23) and Fick's first law and the Einstein relation will be discussed. We will show that any CDF, that is finite for z over $[z_o, \infty)$ and vanishing at $+\infty$ will permit agreement between Eq. (23) and Fick's first law. This implies that the PDF must be finite over the same interval. Additionally, a CDF that yields agreement between the model and Fick's second law is determined in the subsequent section.

Continuing here as in the previous section with $z_o = 0$ and upon inspection of Eq. (23) it is seen that a flux is written in terms of a constant multiplied by a density gradient. This constant is then the Fickian diffusion coefficient D_{new} . Using

Eq. (24) in (23) this constant is then

$$D_{\text{new}} = 2\xi \int_0^\infty z \left[\int_{|z|}^\infty P_l(\lambda) d\lambda \right] dz, \quad (25)$$

so that Eq. (23) can be written as $J = -D_{\text{new}} \frac{dn}{dz}$, i.e., Fick's first law.

Equation (25) is also in dimensional agreement with the Einstein relation. The equation relating the diffusion coefficient to the square of mean spatial displacement is generally known as Einstein's relation. The one-dimensional result, for a particle located at the origin at time zero, is

$$D = \frac{\frac{1}{t} \langle z^2(t) \rangle}{2}. \quad (26)$$

Finite P_l integrates to $C(z)$ and Eq. (25) becomes

$$D_{\text{new}} = 2\xi \int_0^\infty z C(z) dz. \quad (27)$$

ξ in Eq. (27) has dimensions inverse time while the integral has dimensions distance squared so that Eq. (25) is dimensionally consistent with the Einstein relation for any finite PDF. This can be shown more directly for a specific case. To do this we consider the following PDF:

$$P_l = ae^{-a\lambda}, \quad (28)$$

where a is a constant. Using Eq. (24) this leads to the corresponding expression for the CDF:

$$C_{E_o}(z) = e^{-az}. \quad (29)$$

Using this in Eq. (27) leads to

$$D_{\text{new}} = \frac{2\xi}{a^2}. \quad (30)$$

From Eq. (26) the factor $\langle z^2(t) \rangle$ is the average displacement squared, which is similar in physical meaning to $1/a^2$ as defined by Eq. (28). The factors ξ and $1/t$ also have corresponding units.

B. Agreement with Fick's second law

We now investigate under what conditions the integral equation of Eq. (19) obeys Fick's second law. For convenience we study the flux J as a function of the flux plane position z_o and time t . Here it will be shown that the CDF is a function of position and time during the non-steady-state period. Equation (19) is again

$$J(z_o, t) = \xi \int_{z_o}^\infty [n(2z_o - z, t) - n(z, t)] C(z, z_o) dz, \quad (31)$$

We examine the time-dependent behavior of J and n where the initial density is given by a step function. That is, $n = n_o$, where n_o is a positive constant, for $z < 0$ and $n = 0$ for $z \geq 0$ for z over the interval $(-\infty, \infty)$. In this case the unique solution for Fick's second law is given by

$$n(z, t) = \frac{1}{2\sqrt{\pi Dt}} \int_{-\infty}^\infty \exp\left[-\frac{(z-\zeta)^2}{4Dt}\right] n(\zeta, 0) d\zeta, \quad (32)$$

for $t > 0$, where D was determined from the steady-state situation and $n(\zeta, 0)$ is the initial condition for $n(z, t)$ [20].

Computing Eq. (32) for this case yields

$$n(z, t) = \frac{n_o}{2} \operatorname{erfc}\left[\frac{z}{2\sqrt{Dt}}\right]. \quad (33)$$

Inserting into Eq. (31) leads to

$$J(z_o, t) = \frac{\xi n_o}{2} \int_{z_o}^\infty \left(\operatorname{erfc}\left[\frac{2z_o - z}{2\sqrt{Dt}}\right] - \operatorname{erfc}\left[\frac{z}{2\sqrt{Dt}}\right] \right) \times C(z, z_o) dz. \quad (34)$$

Now by using Eq. (33) in Fick's first law, i.e., Eq. (1), the flux can be computed and written in terms of z_o :

$$J(z_o, t) = \frac{n_o}{2} \sqrt{\frac{D}{\pi t}} \exp\left[-\frac{z_o^2}{4Dt}\right]. \quad (35)$$

Equating (34) and (35) leads to

$$\begin{aligned} \frac{n_o}{2} \sqrt{\frac{D}{\pi t}} \exp\left[-\frac{z_o^2}{4Dt}\right] \\ = \frac{\xi n_o}{2} \int_{z_o}^\infty \left(\operatorname{erfc}\left[\frac{2z_o - z}{2\sqrt{Dt}}\right] - \operatorname{erfc}\left[\frac{z}{2\sqrt{Dt}}\right] \right) C(z, z_o) dz, \end{aligned} \quad (36)$$

A possible solution for Eq. (36) is when $C = C(z, z_o, t)$, that is C is a function of position, relative to the flux plane, and time. Therefore, the following is a solution:

$$C(z, z_o, t) = \frac{(z - z_o) \exp\left[-\frac{(z - z_o)^2}{4Dt}\right]}{\beta \left(\operatorname{erfc}\left[\frac{2z_o - z}{2\sqrt{Dt}}\right] - \operatorname{erfc}\left[\frac{z}{2\sqrt{Dt}}\right] \right)}, \quad (37)$$

where β is a factor that does not involve z . Using Eq. (37) in (36) gives

$$\frac{n_o}{2} \sqrt{\frac{D}{\pi t}} \exp\left[-\frac{z_o^2}{4Dt}\right] = \frac{\xi n_o}{2\beta} \int_{z_o}^\infty (z - z_o) \exp\left[-\frac{(z - z_o)^2}{4Dt}\right] dz. \quad (38)$$

The integral on the right side of Eq. (38) yields $2Dt$. We have an equality when β is of a particular form and has dimensions of distance. Since we require the PDF to be normalized, it must be that $C = 1$ as $z \rightarrow z_o$ thus leading to $\beta = (\sqrt{\pi Dt}/2) \exp[z_o^2/4Dt]$. This implies that Eq. (38) is true when $\xi = 1/4t$.

It is interesting to consider certain attributes of the function C given by Eq. (37). C in the form of Eq. (37) has a bell curve shape. Its origin is a function of the flux plane location; however, its width is also a function of the flux plane location. This has the effect of causing the width of the bell curve to decrease when the flux plane is moved to regions with lower flux at a particular time. CDF curves for an example case are sketched in Fig. 4 for three different flux plane locations. Thus we can see one of the principle features of the steady-state PDF: Knudsen diffusivity differences, for different gaseous species within identical pores of equivalent density profile, are accounted for by each having a unique PDF. In other words, as the flux decreases, the probability spectrum becomes dominated by shorter scattering path lengths, and in turn the diffusion coefficient determined by Eq. (25) decreases. As time increases, the bell curve of Eq. (37) spreads out. Finally as $t \rightarrow \infty$, $C \rightarrow 1$ for all z .

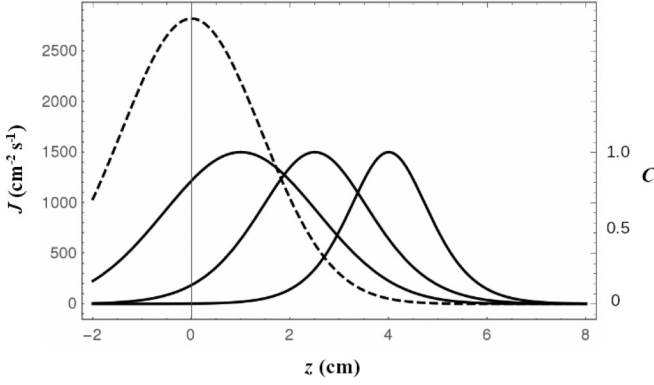


FIG. 4. CDF curves for three different flux plane locations at a fixed time given the initial condition of a density step function as discussed in this section. Flux is given by the dashed curve. Parameters were set to $D = 1.0$ (cm²/s), $t = 1.0$ s, and $n_o = 1.0 \times 10^4$ cm⁻³. Locations of the flux plane are $z_o = 1.0$ cm, 2.5 cm, and 4.0 cm.

One might expect that the steady-state case of Eq. (25) would be the most commonly considered situation. Here any CDF, with the properties mentioned in Sec. IV 1, used within Eq. (23) would be mathematically consistent with Fick’s first law and give a finite result for J . In the next section a convenient PDF, with the required mathematical properties, is used derive a formula for the Knudsen diffusion coefficient within a pore of finite length.

V. APPLICATION

Though the true PDF is unknown, and would need to be estimated via simulation or analytic methods, we can examine the validity of the model further by utilizing a model distribution function that has convenient mathematical properties. The study of Eq. (25) is then continued in this section using an exponential PDF. In addition to its favorable mathematical properties, this type of distribution is known to describe the distribution of mean-free path lengths between scattering in bulk gases [21]. Using this distribution function an expression for the Knudsen diffusion coefficient is arrived at for a cylindrical pore of circular cross section of finite length. It is then shown that this result is in general agreement with a classic formula derived by Pollard and Present for highly rarefied gaseous flow through a cylindrical pore of finite length [13].

Let the length of the pore be l and the diameter be d . Let the normalized distribution function for axial path lengths that contribute to flux through the flux plane be given by

$$P_l(\lambda) = ae^{-a\lambda}, \tag{39}$$

where a is a constant that will be shown to depend upon the pore diameter d . Here the axial distance along the pore will be given by z . The flux plane is set at the center of the pore, i.e., $z_o = 0$. Therefore $n = z(dn/dz) + n_o$ with n_o being the density at the flux plane. We let the collision frequency be approximated as \bar{v}/d . Equation (25) can then be written as

$$D_{\text{new}} = \frac{2\bar{v}}{d} \int_0^{l/2} z \left(\int_z^\infty ae^{-a\lambda} d\lambda \right) dz. \tag{40}$$

The infinite limit is retained in the inner integral for simplicity assuming that the distribution function is negligible for $\lambda > l/2$. On computing the integrals in Eq. (40) and rearranging, the result is

$$D_{\text{new}} = \frac{2\bar{v}}{a^2 d} [1 - e^{-al/2}(l + al/2)]. \tag{41}$$

A value for a is arrived at by considering D_{new} for the pore of infinite length. One finds that $\lim_{l \rightarrow \infty} D_{\text{new}} = 2\bar{v}/a^2 d$. This is equated to the Knudsen result of Eq. (6), which leads to $a = \sqrt{6}/d$, so that the final formula for D_{new} is

$$D_{\text{new}} = \frac{1}{3} \bar{v} d \left[1 - e^{-\frac{\sqrt{6}l}{2d}} \left(1 + \frac{\sqrt{6}l}{2d} \right) \right]. \tag{42}$$

Equation (42) is now compared to another well-known result from the literature for a gas diffusing under the same conditions in a cylindrical pore of finite length and diameter d . Pollard and Present give [13]

$$D_{PP} = \frac{1}{3} \bar{v} d \left[1 - \frac{3d}{4l} \right]. \tag{43}$$

We can show the similarity of Eqs. (42) and (43) by rearranging and factoring Eq. (42) to get

$$D_{\text{new}} = \frac{1}{3} \bar{v} d \left\{ 1 - \frac{3d}{4l} \left[\left(\frac{4l}{3d} + \frac{4\sqrt{6}l^2}{6d^2} \right) e^{-\frac{\sqrt{6}l}{2d}} \right] \right\}. \tag{44}$$

The expression in square brackets of Eq. (44) can be thought of as a positive factor of less than one by which the correction term in the Pollard and Present formula is adjusted. For example, when $l = d$ this factor is ~ 0.85 .

The behavior of these formulas can be further studied by considering plots as l varies for a fixed diameter d . This is depicted in Fig. 5. Both Eqs. (42) and (43) converge to the Knudsen result as $l \rightarrow \infty$. Additionally, the formulas both give decreasing values for D as l gets small.

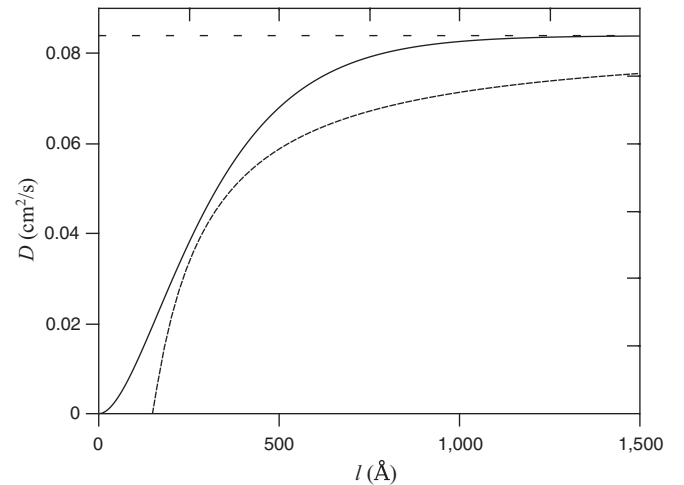


FIG. 5. Estimated Knudsen diffusion coefficients vs pore length l for a fixed diameter of 200 Å for He at 300 K. Value from the Knudsen formula, Eq. (6), (D_k), is the horizontal dashed line. Equation (43), (D_{PP}), is the lower dashed curve. Equation (42), (D_{new}), is shown by the solid curve.

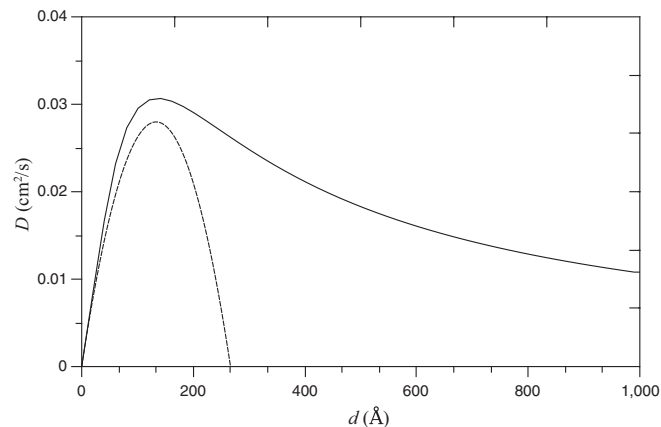


FIG. 6. Estimated Knudsen diffusion coefficients vs pore diameter d for a fixed length of 200 Å for He at 300 K. Equation (42), (D_{PP}), is the lower dashed curve. Equation (43), (D_{new}), is shown by the solid curve.

The behavior of each formula as d varies for fixed l is depicted in Fig. 6. As expected, both go to zero as d gets small. Also, both expressions show a maximum in D at $d \sim l/2$, and Eq. (43) gives D falling to zero when $d \sim l$, while Eq. (42) shows that $D \rightarrow 0$ as $d \rightarrow \infty$.

It is unknown to the authors which of Eq. (42) or (43) would provide the best match for experimental data in the region where $l \sim d$. Reports for diffusion coefficients of lone gaseous species in nanopores known to the authors [6,22,23] are all for cases when $l \gg d$ and thus in the region where both expressions converge to the Knudsen result of Eq. (6). Additional experimental work on very thin porous membranes is thus encouraged.

VI. CONCLUSION

In this report a model is presented whereby flux and a diffusion coefficient can be computed for Knudsen diffusion in a cylindrical pore. The method utilizes a probability distribution for particle-scattering axial path lengths. Using a simplified version of the model it is demonstrated how it is consistent with Fick's first law and the Einstein relation for a certain class of distribution functions. The CDF that allows the model to agree with Fick's second law was determined, thus revealing that as the flux decreases the CDF becomes dominated by shorter path lengths. A model for the probability distribution is employed, and a formula for the diffusion coefficient for a pore of finite length was determined. We study how the resulting formula behaves for different pore diameters and lengths. The expression is shown to exhibit behavior similar to that of a well-known formula from the literature for Knudsen diffusion in pores of finite length. Having verified that the theory leads to results which are consistent with classical laws of diffusion and other well-established relations, there are now opportunities for future work. Using MD or analytical methods one could directly compute the PDF and collision frequency for a particular pore and gaseous species at a mean energy or over a particular energy spectrum. Another possibility is to write the PDF as an unknown function parameterized in terms of the physical properties of the system. Then, given a known diffusion coefficient, one could adjust parameters until Eq. (25) yields the known value.

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