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# Stochastic models of free-molecular nanopore flows

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### ABSTRACT

In gas transport systems of the nanoscale, fluid–surface interactions become the main forces governing the evolution of the flow state. In ideal nanoscale systems, such as atomically smooth carbon nanotubes, the characteristic lengths reduce to such an extent that the non-equilibrium entrance region comprises a large proportion of the domain. In this regime, the added effective resistance induced by the non-equilibrium entrance region becomes large enough that classical effusion models break down. The mechanisms behind the resistance in this regime are still poorly understood. A stochastic model of interfacial resistance is developed here, which allows for the determination of the effective diffusion coefficient via a novel finite-difference solution. We use this method to model free-molecular gas flow through long nanotubes, showing that such non-equilibrium effects may be present in systems of length scales currently within manufacturing capabilities. Finally, this model is used to discuss gas separation through aligned carbon nanotube arrays, with a focus on the effect of membrane length on the separation of a  $H_2$ –CH<sub>4</sub> mixture.

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### I. INTRODUCTION

As manufacturing technology continues to develop, many engineering fields are beginning to utilize the benefits of constructing components of nanoscale dimension. Examples of such nanoscale technology include rapid molecular sieves using nanoporous media,<sup>1,2</sup> drug delivery using extracellular vesicles combined with engineered nanostructures,<sup>3</sup> and in developing hemodialysis applications.<sup>4</sup> In nanofluidic systems, the corresponding fluid dynamics differ significantly from the continuum and slip models often used in macro- and microscale flows. Here, pronounced regions of non-continuum and non-equilibrium behavior must be taken into account.<sup>5</sup> In sufficiently well-ordered nanoscale materials, such as atomically smooth carbon nanotubes (CNTs), the interfacial resistance due to gas-surface interactions may be far smaller than expected, with flow enhancement exceeding the Knudsen approximation by 2-3 orders of magnitude.<sup>6,7</sup> In finite-length nanoscale systems of this type, as the system length decreases, entrance region effects may become dominant,<sup>6–8</sup> with simulations showing a several order of decrease in magnitude of the effective transport coefficients when compared to infinite-length approximations.9

Over the last 2 decades, thin membranes formed purely of clustered, aligned CNTs have been constructed, allowing for gas separation experiments to be conducted. The first study outlining the synthesis of a multiwalled CNT (MWCNT) membrane was performed by Hinds et al.<sup>10</sup> This study investigated nitrogen transport through the membrane, showing agreement with the Knudsen model of diffusion. Later, Holt *et al.*<sup>11</sup> constructed CNT arrays with average pore size on the order of 2 nm with total membrane thickness between 2 and 3  $\mu$ m. Gas diffusion experiments showed greatly enhanced gas transport, with flow rates exceeding that of the Knudsen model by 2-3 orders of magnitude. Selectivity between gases was also measured, where it was noted that the flow of hydrocarbon gases experienced greater flow enhancement when compared to simple non-hydrocarbon gases, such as H<sub>2</sub>, CO, and CO<sub>2</sub>. This effect was hypothesized to be caused by preferential gas-wall interactions between hydrocarbons and the carbon atoms in the wall of the CNT,<sup>11,12</sup> although this hypothesis remains unconfirmed. Despite this promising flow enhancement, there are still few experimental results measuring transport coefficients across such membranes. Along with a lack of experimental data, there are few theoretical explanations of the origin of excess interfacial resistance in finite-length ordered nanoscale materials. Currently, there exist few works that consider density profiles that are not governed by Knudsen diffusion, with the integral method developed by Clausing,<sup>13</sup> along with corresponding approximate solutions provided by Berman<sup>14</sup> being primary classical works on this topic. To the authors' knowledge, currently, the only theory directly applicable to flows in confined nanomaterials is provided in a very recent publication by Bhatia and Dutta.<sup>15</sup> In this work, the finite-length effects are determined through a kinetic approach, leading to an integral formulation of the dynamics, which agrees well with results determined via equilibrium molecular dynamics simulations.

Generally, the analysis of these systems is conducted via highfidelity simulations including Equilibrium Molecular Dynamics (EMD),<sup>15,16</sup> Direct Simulation Monte Carlo (DSMC),<sup>17</sup> and lattice Boltzmann Methods (LBM).<sup>18</sup> Such analyses are highly numerically expensive for long CNTs and do not directly lead to the fundamental understanding of the effect of this entrance region. Taking this as motivation, this work aims to outline a simple and computationally inexpensive model to aid in the understanding of the underlying mechanics of the involved phenomena. A promising method of theoretical analysis that has risen in popularity recently involves the use of a Fokker-Planck Equation (FPE). This method acts as the stochastic formulation of Boltzmann's transport equation, which is a fundamental governing equation in kinetic theory, often used in non-continuum analyses.<sup>19</sup> The Fokker-Planck model has been investigated as a representation of ion channel transport, with the work of Piasecki et al.20 deriving an approximate analytical solution for transport between two fixed reservoirs with applied current. Melchionna et al.<sup>21</sup> later showed good agreement of this analytic solution with a lattice Fokker-Planck simulation. This model has also seen success when applied to collisional flows, with early work originating with Lebowitz<sup>22</sup> and more recently being developed by Gorji et al.23 and Singh et al.24

Since this equation generally does not admit an analytic solution,<sup>25</sup> we show that, under a suitable scaling, this equation admits a diffusive asymptote and is amenable to a finite difference solution. Here, we derive approximations of the effective transport coefficients, namely, the effective diffusion coefficient and excess interfacial resistance in ordered nanoscale systems. The length dependence of these coefficients is discussed, with the presence of a frictiondominated regime noted as an explanation of the increased interfacial resistance measured in experiments. Finally, this analysis is extended to mixtures of non-interacting gases, allowing for the effect of nanopore length on gas separation to be observed.

### **II. STOCHASTIC COLLISION MODELS**

We investigate a quasi-1D transport model as an approximation of a free-molecular gas flow through a narrow cylindrical nanopore of length *l*, connecting two reservoirs as shown in Fig. 1. We consider the flow fully free-molecular, comprised of a singlespecies gas with molar mass *m* at temperature *T*. We consider the wall of the nanopore to be at this same temperature and to act on the gas molecules with a Maxwell boundary condition.<sup>26</sup> This boundary condition models the probability a particle experiences a diffuse reflection per collision. This fraction is denoted,  $\alpha$ , and models the average momentum loss per collision, as such it is referred to as the Tangential Momentum Accommodation Coefficient (TMAC). The 1D nanopore is modeled as having an effective diameter of d, which is introduced into the model through the effective relaxation time  $\tau$ . This value represents the average time for a sampled particle to encounter the first diffuse collision. We consider the distribution to be in equilibrium within the cross-sectional plane of the pipe and assume that the number of specular collisions, n, between diffuse collisions is sampled from a binomial distribution.<sup>27</sup> We write the relaxation time as

$$\tau = \frac{2d}{3} \frac{2-\alpha}{\alpha} \sqrt{\frac{2m}{\pi k_B T}}.$$
 (1)

A full derivation of the above is present in the Appendix. This relaxation time controls the rate of momentum loss in the system. It is important now to make a comparison of this value with other works, as this  $\tau$  is half the value derived in the work by Bhatia *et al.*<sup>28</sup> The reason behind this difference is due to the assumption of independent flight times from the stochastic framework present in this work and not that of Bhatia, which is performed via an energy analysis. This difference is seen when comparing the Fokker–Planck and Bhatnagar–Gross–Krook (BGK) collision operators in Boltzmann's equation, where to match viscosity between models it is required that  $2\tau_{FP} = \tau_{BGK}$ .<sup>24</sup> We now introduce the distribution function of the particles as  $f(\hat{u}, \hat{x}, \hat{t})$  where we denote, in dimensional coordinates, the velocity as  $\hat{u}$ , position as  $\hat{x} \in [0, l]$  and time as  $\hat{t}$ . With the given relaxation time, we model the evolution of the flow as an Ornstein–Uhlenbeck process

$$d\hat{u} = -\frac{1}{\tau}\hat{u}d\hat{t} + \sqrt{\frac{2}{\tau}}\sigma dW \qquad d\hat{x} = \hat{u}d\hat{t},$$
 (2)

with  $\sigma = \sqrt{k_b T/m}$ . The stochastic term, W, represents a Wiener process with zero mean and unity variance; hence, under an ensemble average, this process obeys  $\langle W(\hat{t}) \rangle = 0$  and  $\langle W(\hat{t})W(\hat{t}') \rangle = \delta(\hat{t} - \hat{t}')$ , where  $\delta$  is the Dirac delta distribution. Taking the scaled variables

$$\hat{u} = \sigma u \qquad \hat{x} = \sigma \tau x \qquad \hat{t} = \tau t$$
 (3)

allows for the system of Stochastic Differential Equations (SDE) to be expressed in dimensionless form as

$$du = -udt + \sqrt{2}dW \qquad dx = udt. \tag{4}$$

This process satisfies a Fokker–Planck equation (often referred to as the Klein–Kramers equation<sup>25</sup> or alternatively the Kramers–Chandrasekhar equation<sup>29</sup>) of the form

$$\frac{\partial f}{\partial t} + u \frac{\partial f}{\partial x} = \frac{\partial u f}{\partial u} + \frac{\partial^2 f}{\partial u^2} = C_{FP}(f), \tag{5}$$

where the differential operator on the right-hand side of Eq. (5) is termed the Fokker–Planck operator and will be denoted  $C_{FP}$ . This operator is linear and admits a system of eigenfunctions given by the Gauss–Hermite functions, defined as

$$\psi_n(u) = He_n(u)g(u), \tag{6}$$

where  $He_n(u)$  is the *n*th Hermite polynomial and g(u) is the standard Gaussian function with unity variance. We note here that each



eigenfunction,  $\psi_n$ , has eigenvalue -n under  $C_{FP}$  and the set of  $\psi_n$  forms a complete basis on the space  $L^2$ . This Fokker–Planck equation rarely admits a closed-form solution, although some non-trivial particular cases have been found.<sup>30</sup>

### A. Diffusion asymptote

Before investigating the complete numerical solution, we wish to investigate the asymptotic behavior of this equation. The outer solution of this equation shows diffusive behavior. To show this, we perform a scaling of  $T = \varepsilon^2 t$  and  $X = \varepsilon x$  for some small scale parameter  $\varepsilon \ll 1$ , leading to

$$\varepsilon^2 \frac{\partial f}{\partial T} + \varepsilon u \frac{\partial f}{\partial X} = C_{FP}(f), \tag{7}$$

where generally this  $\varepsilon$  will be proportional to  $\tau$ . In this analysis, we follow a Chapman–Enskog type procedure,<sup>31</sup> where we first expand the distribution as  $f = f^0 + \varepsilon f^1 + \cdots$ , while enforcing that all moments of u over  $f^n$  are all zero for n > 0. The leading order relations are

$$0 = C_{FP}(f^0), \qquad (8a)$$

$$u\frac{\partial f^0}{\partial X} = C_{FP}(f^1), \qquad (8b)$$

$$\frac{\partial f^0}{\partial T} + u \frac{\partial f^1}{\partial X} = C_{FP}(f^2).$$
(8c)

Since  $C_{FP}$  has a unique eigenfunction  $\psi_0(u)$  corresponding to the eigenvalue 0, we see  $f^0(u, X, T) = g(u)\rho(X, T)$ , with  $\rho$  representing the molar density. Inserting this expression into Eq. (8b), we find

$$C_{FP}(f^1) = \psi_1(u) \frac{\partial \rho}{\partial X}.$$
(9)

Thus,  $f^1$  is defined over only the first spectral term,  $\psi_1$ , as  $\psi_0$  must be neglected due to its non-zero first moment. This term may be written as

$$f^{1}(u, X, T) = -\psi_{1}(u)\frac{\partial\rho}{\partial X}.$$
 (10)

Introducing the forms of  $f^0$  and  $f^1$  into Eq. (8c) leads to

$$g(u)\left[\frac{\partial\rho}{\partial T}-u^2\frac{\partial^2\rho}{\partial X^2}\right]=C_{FP}(f^2).$$
(11)

Integrating this equation over  $u \in \mathbb{R}$  gives

$$\frac{\partial \rho}{\partial T} - \frac{\partial^2 \rho}{\partial X^2} = 0, \qquad (12)$$

where we note that the integral of  $C_{FP}(f)$  over  $u \in \mathbb{R}$  will be zero for any exponentially decaying function f. We see that this expression is exactly the diffusion equation in 1D, with the dimensionless diffusion coefficient of  $D_{\infty} = 1$ . Returning to dimensional coordinates, we find the diffusivity as

$$\hat{D}_{\infty} = \sigma^2 \tau D_{\infty} = \frac{2d}{3} \frac{2-\alpha}{\alpha} \sqrt{\frac{2k_B T}{\pi m}},$$
(13)

which is the expected Smoluchowski diffusion coefficient that would be found in an infinite length nanopore when neglecting any entrance effects. In turn, this coefficient is the limiting case for this analysis as the system length is increased. The prior scaling is often referred to as the "inverse friction expansion,"<sup>25</sup> with the above being a known result in the statistical mechanics community and is seen in standard texts.<sup>19,25</sup> In 3D, including a potential function,  $\Phi(\mathbf{x})$ , the Klein–Kramers equation reads

$$\frac{\partial f}{\partial t} + \mathbf{u} \cdot \nabla_x f = \nabla_u \cdot \left( \left( \mathbf{u} - \nabla_x \Phi \right) f \right) + \nabla_u^2 f.$$
(14)

Consider the appropriate scaling and again expand in terms of some small  $\varepsilon$  to find  $f^0(\mathbf{u}, \mathbf{x}, t) = \rho(\mathbf{x}, t)g(\mathbf{u})$  and the relation

$$\mathbf{u} \cdot \nabla_x f^0 = \nabla_u \cdot \left(\mathbf{u} f^1\right) + \nabla_u^2 f^1 - \nabla_u \cdot \left(f^0 \nabla_x \Phi\right), \qquad (15)$$

which again leads to the expression  $f^1(\mathbf{u}, \mathbf{x}, t) = -\mathbf{u}g(\mathbf{u}) \cdot (\nabla_x \rho - \rho \nabla_x \Phi)$ . Finally, integrating the 2nd order expression over  $\mathbf{u} \in \mathbb{R}^3$  leads to

$$\frac{\partial \rho}{\partial t} - \nabla_x^2 \rho = \nabla_x \cdot (\rho \nabla_x \Phi), \tag{16}$$

which leads to the standard 3D diffusion equation in the absence of a potential function. To further complicate this system, it is noted that

J. Chem. Phys. **158**, 214101 (2023); doi: 10.1063/5.0148289 Published under an exclusive license by AIP Publishing if the normal velocity controlling the mean collision time is a random variable, due to Levy flights, the diffusion equation derived may be fractional in time.<sup>32</sup> The problem of this fractional sub-diffusion will not be investigated here. Neglecting these effects, it is noted<sup>29</sup> that an equivalent formulation of the density transport equation may be derived from comparing the zeroth and first-order moment equations of the Klein–Kramers equation. In 1D in the absence of any potential, we may find

$$\frac{\partial^2 \rho}{\partial^2 t} + \frac{\partial \rho}{\partial t} = \frac{\partial^2 \rho \langle u^2 \rangle}{\partial^2 x},$$
(17)

where here the angled brackets are to be understood to represent the moment over velocity space. This equation considers no parameter straining, but the stress term,  $\langle u^2 \rangle$ , cannot be explicitly determined without an appropriate asymptotic scaling. In the diffusive limit, this stress is constant, and neglecting the higher-order wave behavior, we recover the diffusion equation. We note now that the effective diffusivity arises naturally via the stress tensor present in this equation, as such, in the entrance and exit regions of the flow, we might expect Knudsen-layer behavior to arise as is seen in similar boundary layer analyses.<sup>19</sup>

### **III. NUMERICAL RESULTS AND DISCUSSION**

In this section, we consider the numerical analysis of the 1D free-molecular flow through an idealized carbon nanotube, which connects two reservoirs as seen in Fig. 1. In the chosen dimensionless form, the solution is controlled only by the boundary conditions. For a system defined along the physical coordinates  $\hat{x} \in [0, l]$ , the dimensionless system is defined on  $x \in [0, L]$  where *L* represents the effective scale length, given by  $L = l(\sigma \tau)^{-1}$ . This *L* is the ratio between the "diffusive scale length"  $\sigma \tau$  and the physical scale length *l*. This expression may also be expressed as a scaled aspect ratio of the nanotube, as

$$L = \frac{3}{2} \frac{\alpha}{2 - \alpha} \sqrt{\frac{\pi}{2}} \frac{l}{d}.$$
 (18)

For the physical case corresponding to the flow through a nanopore connecting two reservoirs held at constant densities  $\rho_0$  and  $\rho_L$ , respectively, we consider the elliptic problem with the two half-boundary conditions of the form

$$f(u > 0, 0, t) = \rho_0 g(u) \qquad f(u < 0, L, t) = \rho_L g(u).$$
(19)

For the initial investigation, we choose the most fundamental boundary conditions corresponding to this chosen class, with  $\rho_0 = 1$  and  $\rho_L = 0$ , where it is clear that the corresponding solutions for any given reservoir densities may be recovered via an appropriate scaling. Although we will utilize a numerical model which determines the solution for the entire distribution, the main results that are to be analyzed are the dimensionless molar density and molar flux, which are given by the zeroth and first moments of the distribution, respectively, as

$$\rho(x) = \int_{-\infty}^{\infty} f(u, x) du \qquad j = \int_{-\infty}^{\infty} u f(u, x) du, \qquad (20)$$

where the dimensional form of the molar flux is recovered simply as  $\hat{j} = \sigma j$ . For comparison between individual test cases, we will consider the following scaling:

$$\rho_s(x_s) = \frac{\rho(Lx_s) - \rho(0)}{\rho(L) - \rho(0)} \qquad x_s = \frac{x}{L}.$$
 (21)

From these functions, we may determine an effective diffusion coefficient  $D_{eff}$  by creating a parallel to Fick's law. In the selected coordinates, this is defined

$$D_{eff}(x_s) = -j \left(\frac{\partial \rho_s}{\partial x_s}\right)^{-1}.$$
 (22)

Taking the mean of these profiles across their domains leads to the average effective diffusion coefficient only as a function of L, where

$$\overline{D}_{eff}(L) = \frac{1}{L} \int_0^L D_{eff}(x) dx.$$
(23)

To characterize the membrane flow resistance, we introduce the interfacial resistance as the reciprocal of the diffusivity

$$R = \frac{L}{\overline{D}_{eff}}.$$
 (24)

For the relative interfacial resistance under this scaling, recalling that under these coordinate transforms  $D_{\infty} = 1$ , we simply write

$$\xi = \frac{R - R_{\infty}}{R_{\infty}} = \frac{1}{\overline{D}_{eff}} \, 1, \tag{25}$$

where  $R_{\infty} = L$  is the resistance corresponding to the diffusive asymptotic value of  $D_{\infty} = 1$ .

### A. Finite difference solution

Being an elliptic problem with ill-posed boundary conditions, purely analytical methods likely will not admit a closed-form solution.<sup>25</sup> The Klein-Kramers equation has been solved numerically numerous ways, with common methods using spectral analysis either in terms of the Gauss-Hermite functions<sup>25</sup> or through an alternative basis first derived by Pagani.<sup>33,34</sup> These methods, to the best of the authors' knowledge, have not yet been applied to elliptic boundary problems over finite domains, although the existence and completeness of solutions in the semi-infinite domain has been shown.<sup>35</sup> To solve the system, here a finite difference method is followed. Consider the grid spacing to be generated from the steps of  $\Delta t$ ,  $\Delta x$ , and  $\Delta u$  such that we can write the distribution as  $f(i\Delta t, j\Delta x, k\Delta u) = f_{j,k}^i$ , where  $i \in [0, n_t], j \in [0, n_x]$ , and  $k \in [-n_u, n_u]$ , where we have set maximum bounds on u as  $-n_u \Delta u$  $\leq u_k \leq n_u \Delta u$ . The simplest method is an explicit method, first order in time and space and second order in velocity. This equation belongs to the class of convection-diffusion equations, as such, we must ensure the scheme is upwind for all  $u_k$ . To do this, we use a position-dependent finite difference stencil of the form

$$f_{j,k}^{i+1} = f_{j,k}^{i} - C_{0}u_{k}((1 - \operatorname{sgn}(u_{k}))f_{j+1,k}^{i} + \operatorname{sgn}(u_{k})f_{j,k}^{i})$$
$$- (1 - \operatorname{sgn}(-u_{k}))f_{j-1,k}^{i}) + C_{1}(u_{k+1}f_{j,k+1}^{i})$$
$$- u_{k-1}f_{j,k-1}^{i}) + C_{2}(f_{j,k+1}^{i} - 2f_{j,k}^{i} + f_{j,k-1}^{i}), \qquad (26)$$

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	611	• •		
$\Delta x$	$\Delta u = 0.4$	$\Delta u = 0.2$	$\Delta u = 0.1$	$\Delta u = 0.05$
$1.000 \times 10^{-2}$	0.587 686 26	0.573 509 24	0.570 982 05	0.570 119 34
$5.000 \times 10^{-3}$	0.591 777 89	0.57909547	0.577 302 10	0.57725208
$2.500 \times 10^{-3}$	0.594 238 38	0.583 089 93	0.581 906 48	0.581 156 89
$1.250 \times 10^{-3}$	0.597 067 51	0.586 430 35	0.58457435	0.58459345
$6.250\times10^{-4}$	0.599 542 62	0.589 135 99	0.588 081 29	0.58794705
$3.125\times10^{-4}$	0.589 806 81	0.591 920 68	0.590 778 93	0.590 542 31

**TABLE I.** Effective diffusion value,  $\overline{D}_{eff}$ , for different grid refinement in system with L = 1.

where sgn is the sign function and the following parameters have been introduced:

$$C_0 = \frac{\Delta t}{\Delta x}$$
  $C_1 = \frac{\Delta t}{2\Delta u}$   $C_2 = \frac{\Delta t}{\Delta u^2}$ . (27)

To ensure the stability of this scheme, the time step must obey the following Courant–Friedrichs–Lewy (CFL) condition:

$$\Delta t < \left[\frac{u_{\max}}{\Delta x} + \frac{2}{\Delta u^2} + \frac{1}{2}\right]^{-1}.$$
(28)

To determine the steady-state behavior of this system, a transient simulation is run until convergence is observed. For these simulations, the initial condition used is f(u, x, 0) = (1 - x/L)g(u). To ensure consistency between runs, a grid refinement study was performed. Since each test case considers a different domain size, governed by L, a characteristic length of L = 1 was selected as the sample case for the convergence study. This length was selected as preliminary simulations indicated that the non-ideal effects were most prominent around this length. The steady state of the system was determined once the absolute error between flux measurements, *j*, at 1000 timesteps apart reduced to less than  $1 \times 10^{-3}$ . The convergence of the generated numerical results was measured through the change of  $\overline{D}_{eff}$  for varying grid spacing  $\Delta x$  and  $\Delta u$ . This diffusion term was selected as it is a primary result of this analysis. The dependence of  $D_{eff}$  on the grid spacing is shown in Table I. This output can be seen to be only weakly dependent on the velocity discretization for  $\Delta u \leq 0.1$ , showing a change of less than 0.2% in the  $\overline{D}_{eff}$  value due to refinement from  $\Delta u = 0.1$  to  $\Delta u = 0.05$  for all  $\Delta x$ values considered. Hence,  $\Delta u = 0.1$  was deemed to be sufficient for this study. The range of allowable velocities was set as  $u \in [-10, 10]$ for each case, as this truncation could lead to, at most, errors in the order of the machine precision, due to the exponential nature of the distribution.

For a system with L = 1, a grid spacing of  $\Delta x = 3.125 \times 10^{-4}$ leads only to a change in the  $\overline{D}_{eff}$  value of below 0.5% in comparison with a test run with  $\Delta x = 6.25 \times 10^{-3}$ . Hence, to achieve a balance between accuracy and solution time, a spatial step of  $\Delta x = 6.25 \times 10^{-3}$  was selected. Hence, for every *L* value, the test was run with  $n_x = 1600$  grid points in *x*. To analyze the effect of the effective length parameter on the transport coefficients, the finite difference system is solved for a range of *L* values. The scaled  $\Delta x$  values used in each run are listed in Table II along with the number of steps for convergence,  $n_t$ .

 TABLE II. Parameters for solutions generated by finite difference code at each order of magnitude.

L	$\Delta x$	$Max n_t$	L	$\Delta x$	$\operatorname{Max} n_t$
$ \frac{1 \times 10^{-4}}{1 \times 10^{-3}} \\ 1 \times 10^{-2} \\ 1 \times 10^{-1} \\ 1 \times 10^{0} $	$6.25 \times 10^{-8}  6.25 \times 10^{-7}  6.25 \times 10^{-6}  6.25 \times 10^{-5}  6.25 \times 10^{-4}$	$37 \times 10^{3}$ $36 \times 10^{3}$ $35 \times 10^{3}$ $28 \times 10^{3}$ $34 \times 10^{3}$	$\begin{array}{c} 1 \times 10^{1} \\ 1 \times 10^{2} \\ 1 \times 10^{3} \\ 1 \times 10^{4} \end{array}$	$\begin{array}{c} 6.25\times 10^{-3} \\ 6.25\times 10^{-2} \\ 6.25\times 10^{-1} \\ 6.25\times 10^{0} \end{array}$	$\begin{array}{c} 31 \times 10^{3} \\ 14 \times 10^{3} \\ 3 \times 10^{3} \\ 3 \times 10^{3} \end{array}$

Figure 2 shows the density difference across the reservoir for various values of L. We see that for either very large or small L that the density profiles approach linear trends, this shows the two asymptotic profiles of convective and diffusive dominated behavior, respectively. In the diffusion dominated regime, the linear solution corresponds to the case of Smoluchowski diffusion between two reservoirs, indicating that boundary effects have become negligible on the scale length of the system. The data show the greatest divergence from linear behavior occurs in a transition region of  $L \sim 1$ . This regime change is observed in the mass flux since the flux is position independent and may be expressed as a function of the dimensionless length. Figure 3 shows that in the convective regime  $j \rightarrow 1/\sqrt{2\pi}$  and in the diffusive regime  $j \rightarrow 1/L$ . Figure 4 shows the effect of the dimensionless length on the position-dependent diffusion profile, with systems with  $L \sim 1$  showing highly non-linear profiles due to excess interfacial resistance. The trend for the mean effective diffusion coefficient is shown in Fig. 5. As with the molar flux, two distinct regimes are shown, with the diffusive asymptote of  $\overline{D}_{eff} = 1$  as expected from the prior section, along with a convective asymptote for small L of the form  $\overline{D}_{eff} = 2L$ . Along with this, the equivalent resistance  $\xi$  as a function of *L* is shown in Fig. 6.

These simulations have shown the presence of two asymptotic profiles, with the regime being determined by only the parameter *L*. For  $L \ll 1$ , the rate of momentum decorrelation is of lower order than the mean particle velocity, and as such, the initial momentum of the particles dominates the solution. In this regime, the solution is given by a linear convective profile and the diffusion profile can be seen to asymptote as  $\overline{D}_{eff} \sim L$  as shown in Fig. 5. The other asymptote is that of large *L*, representing the diffusion dominated regime. Due to the overwhelming effect of diffusion, the boundary effects caused by the elliptic boundary conditions cannot propagate a large proportion into the flow, as such the profile is diffusion dominated and for a 1D domain a linear profile is observed.

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This regime asymptotes to the classical Knudsen approximation with  $\overline{D}_{eff} \rightarrow 1.$ 

These calculated trends agree with the recent solutions by Bhatia and Dutta,<sup>15</sup> which include similar derived profiles derived via a separate analytical method, which are validated against EMD simulations. To compare these results to existing literature, we may compare the flux values with the results of the model first derived by Clausing.<sup>13</sup> This model derives an integral expression for the particle flux through small tubes. A comparison with the flux values presented in this work is shown in Fig. 7. As seen in the inset of Fig. 7, there is some error between the two models, of a maximum order of 7% located in the intermediate regime around L = 1. A comparison of a specific density profile can be made against a work by Helmer.<sup>36</sup> In this work, Clausing's integral equation is solved and compared to approximate solutions derived by Berman.<sup>14</sup> Helmer's computational results find a 0.1% difference when compared to Berman's solution. In Helmer's work, the calculated density profile for a system with L = 10 is provided. A comparison between the finite difference solution introduced here and the tabulated data by Helmer is presented in Fig. 8. The inset of Fig. 8 shows that the error between the two methods is significant in the boundary regions, with errors exceeding 20%. This potentially shows that Clausing's integral method underestimates the boundary effects that may be present in systems with *L* close to unity.

These results raise a concern with the use of some previous classical diffusion models, suggesting that with increasing characteristic lengths, boundary effects may be more significant than expected and the effect of excess interfacial resistance must be taken into account for accurate modeling. Section III B outlines the characteristic lengths in real CNTs and applies this methodology to experimental results obtained for gas flows through aligned CNT membranes.



**FIG. 6.** Scaled interfacial resistance profile. Shifted value of  $\xi$  + 1 shown to allow for visualization of the diffusive asymptote.



FIG. 7. Calculated flux compared to the results in Clausing.<sup>13</sup> Inset shows the error between methods.

### B. Comparison with the gas flow through CNTs

Some data for CNTs of finite length are available from numerical works,<sup>79,37</sup> allowing for the comparison of the transport coefficients calculated here with those generated via higher fidelity simulations. It is important to note that very little experimental data for the TMAC in ordered nanoscale systems have been published, with the only suitable data found for comparison with this work being that of Holt *et al.*<sup>11</sup> There are also very few published theories that can predict this value in such materials.<sup>38</sup> In this analysis, the required information defining the CNT required is the aspect ratio of the system and the TMAC of the gas–surface combination. From the previously mentioned simulation studies, the TMAC has been noted to be very small in atomically smooth CNTs when compared to most other materials, with predictions of the order  $\alpha = 0.001.^7$ Here, we consider the flow of both H<sub>2</sub> and CH<sub>4</sub> at 300 K through



**FIG. 8.** Density profile for a system with L = 10 compared with the numerical solution provided by Helmer.<sup>36</sup> Inset figure shows the error between methods.

a (10,10) armchair CNT of length 1  $\mu$ m to align with both the limiting case of the simulations performed by Dutta and Bhatia<sup>6</sup> and the system studied in Holt *et al.*<sup>11</sup> We stress again that there is little available data for TMAC values in nanoscale systems, so we use the numerical value for CH<sub>4</sub> of  $\alpha_{CH4} = 0.001$  as determined by Dutta and Bhatia.<sup>6</sup> For H<sub>2</sub>, we investigate TMAC values within the range  $3\alpha_{CH4} \le \alpha_{H2} \le 6\alpha_{CH4}$  as determined by Bhatia *et al.*<sup>39</sup> via EMD simulation. This gives a considered range for this work of  $0.003 \le \alpha_{H2} \le 0.006$ .

To model the (10,10) armchair CNT, we use geometric parameters of d = 1.35 nm and l = 1000 nm. We note, for such a system with set  $\alpha$  and diameter *d*, the prior analysis may be studied in terms of only physical length *l* in place of the dimensionless length *L* used prior. For nanoscale domains, we can consider the "effective" diameter of the CNT, which may be approximated by the difference between the physical diameter of the CNT and the Lennard-Jones (LJ) diameter for the gas interacting with carbon atoms, which we denote  $\sigma_{LJ}$ . This is a simplifying approximation and acts as one of the simplest methods to include the effect of interatomic potential forces present within the CNT-gas system. This allows for the direct derivation of the relaxation time as shown in the Appendix, which relies on a hard-sphere approximation, leading to a simple expression without the requirement of accounting for the full detail of the inter-atomic potential. Using this approximation, we write the altered expression for effective length as

$$L_{eff} = \frac{3}{2} \frac{\alpha}{2 - \alpha} \sqrt{\frac{\pi}{2}} \frac{l}{d - \sigma_{LJ}}.$$
(29)

For the flow of CH<sub>4</sub> through this CNT we use  $\sigma_{LJ,CH4} = 0.373$  nm to find an effective length parameter of  $L_{eff} = 0.963$ , which is within the transition regime of  $L_{eff} \sim 1$ , implying the presence of sizable excess interfacial resistance. Using the finite difference solution, we find the dimensionless transport coefficients corresponding to this L value as  $\overline{D}_{eff} = 0.580$  and  $\xi = 0.724$ . In physical coordinates, the actual diffusion becomes scaled by the infinite-length value, leading as  $\hat{D}_{eff} = D_{\infty}\overline{D}_{eff} = 13.39 \text{ nm}^2/\text{ s.}$ 

For the flow of H<sub>2</sub>, we set  $\sigma_{LJ,H2} = 0.296$  nm and find the appropriate range of  $L_{eff}$  values for  $0.003 \le \alpha_{H2} \le 0.006$ . This leads, for flow through the same CNT as before, to an effective length parameter range of  $2.680 \le L_{eff} \le 5.367$ , which is larger than the calculated value for methane, due to the increased  $\alpha$  values. This increased value of  $\alpha$  when compared to CH<sub>4</sub> has competing explanations, either being due to the preferential adsorption characteristics between the carbon atoms of the CNT and hydrocarbon molecules<sup>11,12</sup> or due to the increased relative roughness which the smaller H<sub>2</sub> molecule experiences against a CNT wall of equal roughness.<sup>38,40</sup> At these scale lengths, the dimensionless transport coefficients are  $0.795 \le \overline{D}_{eff} \le 0.891$  and  $0.122 \le \xi \le 0.258$  showing near-diffusive behavior.

These results suggest that non-Knudsen effects must be accounted for when analyzing systems with length of the microscale due to excess interfacial resistance. Since this scale length is now within the limits of fabrication technology, future systems utilizing CNT membranes should be aware of these effects. Along with this, it can be seen that the amount of excess interfacial resistance present in a system is affected by species-dependent gas-surface interactions, which are characterized by the TMAC value. Due to this, systems utilizing ordered nanoscale materials for the purpose of gas separation require accurate TMAC values for reliable design. To this end, this paper concludes with a section dedicated to the analysis of a model CNT membrane for the separation of the binary gas mixture.

## C. Notes on multiple species flows: Application to hydrogen separation

Now we consider the effects discussed above on gas mixtures by extending this model to a binary mixture of gases traveling through the same CNT. We note that, in the approximation of freemolecular flow, there are no interactions between particles; hence, each species in a mixture will evolve independently. As such, the model reduces to comparing the flow of two different gases passing through equivalent pipes of length, *l*, and diameter, *d*. Thus, it is clear that the diffusive scale length of each species is unaffected by the presence of other species. The ratio of these lengths may be expressed as

$$\frac{L_2}{L_1} = \frac{2 - \alpha_2}{\alpha_2} \frac{\alpha_1}{2 - \alpha_1} \frac{d - \sigma_{LJ,2}}{d - \sigma_{LJ,1}} = L_{2|1},$$
(30)

where  $\alpha_i$  and  $m_i$  are the TMAC and molecular mass of particles of species *i*. Notably, for similarly sized particles, this expression is only weakly dependent on channel thickness *d* and the primary scaling factor is the ratio of TMAC values. As such, the ratio  $L_{2|1}$  is dependent primarily on the surface-gas properties and is independent of the physical system length. Similarly, the ratio of diffusion coefficients for two species at thermal equilibrium may be expressed

$$\frac{D_1}{D_2} = \frac{2 - \alpha_1}{\alpha_1} \frac{\alpha_2}{2 - \alpha_2} \sqrt{\frac{m_2}{m_1}}.$$
(31)

This expression contains only the parameters m and  $\alpha$ , where for TMAC values of order unity, the standard Knudsen diffusion expressions arise. The interest here exists in systems with scale length ratios differing from 1. We define the selectivity of the gases by the respective mass flux ratio

$$S_{1,2}(L_1, L_2) = \frac{j(L_1)}{j(L_2)}.$$
(32)

From Eq. (30), it can be seen that the dimensional length ratio is independent of system length, as such for a fixed  $L_{2|1}$ , the selectivity can be expressed a single-variable function dependent on only one of the dimensionless lengths,

$$S_{1,2}(L_1) = \frac{j(L_1)}{j(L_1L_{2|1})}.$$
(33)

The behavior of this dimensionless function is shown in Fig. 9. The dimensional selectivity defining the quality of gas separation is a simple scaling of the above formula

$$\hat{S}_{1,2} = \frac{\sigma_1 j_1}{\sigma_2 j_2} = \sqrt{\frac{m_2}{m_1}} S_{1,2}.$$
(34)

Two asymptotic regions may be seen in this system. For a very short CNT, it is clear that the flux difference is simply given by the rate of effusion, such that the selectivity asymptotes toward  $\hat{S}_{1,2} = \sqrt{m_2/m_1}$  as predicted by Graham's law. For systems of large scale length, the diffusive asymptote approaches a scaled version of the Knudsen case, reading

$$\lim_{L_1 \to \infty} \hat{S}_{1,2} = \frac{2 - \alpha_2}{\alpha_2} \frac{\alpha_1}{2 - \alpha_1} \frac{d - \sigma_{LJ,2}}{d - \sigma_{LJ,1}} \sqrt{\frac{m_2}{m_1}}.$$
 (35)

From this analysis, we see a potential application to separation in CH<sub>4</sub>-H<sub>2</sub> mixtures. Due to the dissimilarity of  $\alpha_{H2}$  and  $\alpha_{CH4}$ , this scale length ratio becomes large, with H<sub>2</sub> experiencing far greater relative friction than CH<sub>4</sub> during travel through an equivalent CNT. We can calculate the range of dimensionless length ratios between CH<sub>4</sub> and H<sub>2</sub> as  $0.179 \le L_{H2|CH4} \le 0.359$ . Since this ratio is much less than 1, selectivity rates are expected to be highly length dependent. A comparison of the flux is shown in Fig. 10 for the flow of H<sub>2</sub> and CH<sub>4</sub> through a (10,10) CNT. As system length increases, the volume flux of both species decreases as expected, due to the increased total system friction. In this model, due to the difference in the  $\alpha$  values between the two gases in this system, H<sub>2</sub> experiences a greater rate of flux decrease than CH<sub>4</sub> for increasing *l*. This difference in  $\alpha$  leads to a reversal in the flux ratio of the two gases, and hence, a reduction in molar selectivity. For flow through a (10,10) CNT of length l > 2585 nm, it is seen that a TMAC ratio of  $\alpha_{\rm H2}/\alpha_{\rm CH4}$  = 6 would cause a reversal of gas selectivity. An approximate trend can be determined by taking the asymptotic form of the selectivity, as in Eq. (35), which shows the selectivity reverses as  $l \rightarrow \infty$  when the  $\hat{S}_{1,2} < 1$  is satisfied. Hence, for  $\alpha \rightarrow 0$ , the selectivity reverses when

$$\frac{\alpha_2}{\alpha_1} < \frac{d - \sigma_{LJ,2}}{d - \sigma_{LJ,1}} \sqrt{\frac{m_2}{m_1}}.$$
(36)

Thus, assuming  $\alpha_{CH4}$  and  $\alpha_{H2}$  are very small, a reversal is seen for  $\alpha_{CH4}/\alpha_{H2} > 3.048$ ; hence, the membrane will become selective for methane over hydrogen in sufficiently long systems.

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**FIG. 9.** Effect of varying  $L_{2|1}$  on the molar selectivity of gas 1 in a mixture with gas 2.



FIG. 10. Scaled molar flux of CH<sub>4</sub> against varying physical system length in a (10,10) CNT compared to H<sub>2</sub> with TMAC values within the range 0.003  $\leq \alpha_{H2} \leq 0.006$ .

As stated in the Introduction, very little experimental data for the selectivity ratio through smooth CNT membranes are currently available for comparison. Holt *et al.*<sup>11</sup> measure the molar flux ratio of both H<sub>2</sub> and CH<sub>4</sub> relative to He. From this published data, a hydrogen selectivity of ~2.67 is found in an H2-CH4 mixture, which is notably less than the Knudsen diffusion result of 2.828, which may imply the presence of increased interfacial resistance. The experiments were conducted with CNTs with  $d \sim 2$  nm and  $l \sim 2-3 \mu$ m, which leads in our formulation to dimensionless lengths in the range  $10.73 < L_{H2} < 16.10$  and  $1.93 < L_{CH4} < 2.89$ . As shown in Fig. 11, we can fit the results of this analysis to the experimental results with the ratio within the range  $1.2 \le \alpha_{\rm H2}/\alpha_{\rm CH4} \le 1.3$ , which corresponds to a significantly altered ratio to the 3-6, which was calculated by the works of Bhatia and co-workers.<sup>7,37,39</sup> Clearly, with only a single data point corresponding to the experiment, these results are not reliable and more data would be required to reach valid conclusions. Along



**FIG. 11.** Selectivity of H<sub>2</sub> in a mixture with CH<sub>4</sub> for a TMAC ratio  $\alpha_{H2}/\alpha_{CH4} \in [3, 6]$  as in the simulation works of Bhatia *et al.*<sup>39</sup> with an approximate fit envelope with  $\alpha_{H2}/\alpha_{CH4} \in [1.2, 1.3]$  around the data from Holt *et al.*<sup>11</sup>

with the issues of data reliability, it must be noted that the outlined model is idealized and cannot model the impacts of pore blockages, non-circular pores or excess tortuosity that may be present in manufactured aligned CNT arrays. Even with these outlined issues of reliability, this analysis shows a need for further experimental results for the prediction of the TMAC value in nanoscale materials.

In a prior work by the authors,<sup>38</sup> an expression for predicting the TMAC in nanoscale systems was developed, which only takes the corresponding LJ parameters as inputs. The expression reads

$$\alpha(s) = 1 - (1 - s^2)^{\frac{3}{2}}, \qquad (37)$$

where the roughness parameter is defined as  $\sigma_{LJ,w}/(\sigma_{LJ,g} + \sigma_{LJ,w})$  for LJ diameters of the wall and gas atoms corresponding to the subscripts *w* and *g*, respectively. Taking the LJ diameter of a carbon atom at the wall of the CNT to be  $\sigma_{LJ,C} = 0.34$ , we find  $s_{H2} = 0.5346$  and  $s_{CH4} = 0.4769$ , leading to the estimated ratio of  $\alpha_{H2}/\alpha_{CH4} = 1.231$ , which is a suitable value for the estimated range of 1.2–1.3. This agreement highlights the benefits of the construction of analytical models of nanoscale gas–surface interactions, as well as the current requirement for further experimental and numerical results for TMAC values applicable for use in ordered nanoscale systems.

### **IV. CONCLUSIONS**

This work has investigated the development of a simple mathematical model to investigate the interfacial resistance in nanoscale free-molecular flows. This model can predict the presence of excess interfacial resistance, which is often neglected in fundamental analyses. A finite difference method has been utilized to solve this governing equation and determine results for CNT interfacial resistance, which were compared to values determined through experiment and EMD simulations. The over-prediction of transport coefficients in finite length nanoscale systems was attributed to the increased effect of entrance regions. The effect of this interfacial resistance on the mass flux leads to changes in the selectivity of gases in mixtures, highlighting the potential value of highly ordered CNT arrays for use in gas separation. Some recommendations on the use of ordered CNT array membranes for gas separation have been made, with a note that the lack of reliable TMAC data derived from experiments is a current restriction in the analysis of such systems.

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### AUTHOR DECLARATIONS

### **Conflict of Interest**

The authors have no conflicts to disclose.

### **Author Contributions**

Matthew M. Kratzer: Conceptualization (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Software (lead); Writing – original draft (lead); Writing – review & editing (lead). Suresh K. Bhatia: Conceptualization (supporting); Formal analysis (supporting); Investigation (supporting); Project administration (supporting); Supervision (supporting); Writing – review & editing (supporting). Alexander Y. Klimenko: Conceptualization (supporting); Formal analysis (supporting); Formal analysis (supporting); Funding acquisition (supporting); Investigation (supporting); Methodology (supporting); Supervision (supporting); Writing – review & editing (supporting).

### DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

### APPENDIX: DERIVATION OF RELAXATION TIME

The system of SDEs outlined in Eq. (2) requires a mean relaxation time as an input parameter. This work will use the traditional approach from kinetic theory, by finding the time taken for the average particle to encounter some momentum loss. Here, the coordinate space is considered in cylindrical coordinates, with the time between wall collisions controlled only by the cross-sectional velocities. If the cross-sectional distribution is considered to be at equilibrium, then independence between the cross-sectional and axial distributions may be assumed. The cross-sectional distribution is written in polar coordinates as

$$f(V,\omega,r,\theta) = \frac{2}{\pi^2} \frac{r}{R^2} \frac{V}{\sigma^2} \exp\left[-\frac{V^2}{2\sigma^2}\right]$$
(A1)

for  $r \in [0, R = d/2]$ ,  $\theta \in (\omega, \omega - \pi)$ ,  $V \in (0, \infty)$ , and  $\omega \in [0, \pi]$ . Figure 12 illustrates this coordinate system. It can be seen from geometric arguments that the time taken for a particle to travel from  $(r, \theta)$  to the boundary obeys

$$\Delta t(V,\omega,r,\theta) = r \cos(\theta - \omega) + \frac{\sqrt{R^2 - r^2 \sin^2(\theta - \omega)}}{V}.$$
 (A2)

This leads to the mean first collision time as

$$\begin{split} \langle \Delta t_0 \rangle &= \int_0^\infty \int_{-\pi/2}^{\pi/2} \int_{\omega-\pi}^\omega \int_0^R \Delta t \, f dr d\theta d\omega dV \\ &= \frac{4}{3} \sqrt{\frac{2}{\pi} \frac{R}{\sigma}}. \end{split} \tag{A3}$$

After first reaching a wall, the particle then will travel between wall collisions for the remainder of its trajectory. The distribution at the wall boundary is given as  $f_{wall} = V \sin(\omega) f$ , as such, the time between collisions at the walls is given as

$$\begin{split} \langle \Delta t \rangle &= \int_{0}^{\infty} \int_{-\pi/2}^{\pi/2} \int_{\omega-\pi}^{\omega} \int_{0}^{R} \Delta t f_{wall} dr d\theta d\omega dV \\ &= \frac{8}{3} \sqrt{\frac{2}{\pi}} \frac{R}{\sigma} = 2 \langle \Delta t_{0}. \rangle \end{split} \tag{A4}$$

The total time for a randomly selected particle to encounter the wall is simply

$$t_n = \Delta t_0 + \sum_{i=1}^{n-1} \Delta t_i. \tag{A5}$$

Assuming the collision times to be independent, this leads to the simple average time of

$$\langle t_n \rangle = \left(n - \frac{1}{2}\right) \langle \Delta t \rangle.$$
 (A6)

The probability that a particle experiences its first diffuse collision at the nth collision is taken to be a geometric distribution of the form



 $\ensuremath{\text{FIG. 12}}$  Illustration of chosen particle coordinate system within a CNT cross section.

J. Chem. Phys. **158**, 214101 (2023); doi: 10.1063/5.0148289 Published under an exclusive license by AIP Publishing  $P(n) = \alpha(1 - \alpha)^{n-1}$ . The average time for the first diffuse collision to occur is then given by the appropriate averages of Eq. (A5),

$$\tau = \sum_{n=1}^{\infty} P(n) \langle t_n \rangle$$
  
=  $\sum_{n=1}^{\infty} \alpha (1-\alpha)^{n-1} \left( n - \frac{1}{2} \right)$   
=  $\frac{2-\alpha}{2\alpha} \frac{8}{3} \sqrt{\frac{2}{\pi}} \frac{R}{\sigma} = \frac{2d}{3} \frac{2-\alpha}{\alpha} \sqrt{\frac{2m}{\pi k_B T}}.$  (A7)

This value of  $\tau$  leads to equivalent diffusion rates at the corrected Knudsen result determined by Smoluchowski by determining free-molecular diffusion rates.<sup>41–43</sup>

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