Revisiting Maxwell-Smoluchowski theory: low surface roughness in straight channels

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Abstract

The Maxwell-Smoluchowski (MS) theory of gas diffusion is revisited here in the context of gas transport in straight channels in the Knudsen regime of large mean free path. This classical theory is based on a phenomenological model of gas-surface interaction that posits that a fraction $\vartheta$ of molecular collisions with the channel surface consists of diffuse collisions, i.e., the direction of post-collision velocities is distributed according to the Knudsen Cosine Law, and a fraction $1 - \vartheta$ undergoes specular reflection. From this assumption one obtains the value $D = \frac{2}{1 - \vartheta} D_K$ for the self-diffusivity constant, where $D_K$ is a reference value corresponding to $\vartheta = 1$. In this paper we show that $\vartheta$ can be expressed in terms of micro- and macro-geometric parameters for a model consisting of hard spheres colliding elastically against a rigid surface with prescribed microgeometry.

Our refinement of the MS theory is based on the observation that the classical surface scattering operator associated to the microgeometry has a canonical velocity space diffusion approximation by a generalized Legendre differential operator whose spectral theory is known explicitly. More specifically, starting from an explicit description of the effective channel surface microgeometry—a concept which incorporates both the actual surface microgeometry and the molecular radius—and using this operator approximation, we show that $\vartheta$ can be resolved into easily obtained geometric parameters, $\vartheta = \lambda h / C$, having the following interpretation: $C$ is a macroscopic parameter determined by the shape of the channel cross-section; $h$ is a parameter that precisely captures the degree of roughness of the effective microgeometry, and $\lambda$ is a parameter that characterizes the overall curvature of the surface microgeometry independent of $h$. Thus $\vartheta$ is resolved as the quotient of microscopic ($\lambda h$) over macroscopic ($C$) signature parameters of the channel geometry. The identity $\vartheta = \lambda h / C$ holds up to higher order terms in the roughness parameter $h$, so our main result better applies to well polished, or low roughness, surfaces.

1 INTRODUCTION

The study of diffusion of low-pressure gases through long channels has been a topic of scientific interest, for its theoretical and practical importance, since the classical work on kinetic-molecular theory by M. Knudsen over a century ago. Applications to porous media systems and nano scale

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units are at the mainstream of contemporary engineering and technology in areas such as chemical, biochemical, and environmental engineering, production of batteries and semiconductors. In all such systems, a channel can be identified as the key unit for transport through the given media. The transport process depends on the structural properties of the channel surface captured by a measure of surface irregularity generally referred to as surface roughness.

Understanding and modeling the transport process in channels taking into account surface roughness is critical for creating new technologies. Obtaining highly polished, very low roughness silicon wafers is a major concern in the development of semiconductor devices [13]. Regarding porous systems, the traditional experimental methods of measurements of surface roughness, both through contact and non-contact methods (optical and spectroscopic methods), are not applicable. This is why the development of a theoretical framework for the precise characterization of surface roughness based on exit flow measurements is a topic of current interest. This paper is a contribution towards such characterization in situations where the nano scale units of transport are straight channels whose surface roughness is relatively low.

1.1 The classical theory

We recall that in the large Knudsen number limit, when the mean free path is greater than the channel diameter, gas-surface interactions predominate over collisions between gas molecules; thus the geometric characteristics of the channel surface become an important factor influencing the speed of transport. This influence is often captured phenomenologically through the introduction of a tangential momentum accommodation coefficient. A popular phenomenological model, due to Maxwell and Smoluchowski, is based on the assumption that all collisions of gas molecules with the channel surface are either purely diffusive or purely specular, with a fraction $\vartheta$ of the collisions being diffuse. We refer to $\vartheta$ as the Maxwell-Smoluchowski parameter. From this assumption one obtains the value

\begin{equation}
\mathcal{D} = \frac{2}{\vartheta} \mathcal{D}_K
\end{equation}

for the constant of self-diffusivity, in which $\mathcal{D}_K$ is the diffusivity obtained under the assumption that, at each collision, the post-collision velocity is independent of the pre-collision velocity and satisfies the so-called Knudsen cosine law distribution, given explicitly in Equation (7). See [2] for a detailed theoretical discussion and further elaboration on the Maxwell-Smoluchowski model for two-dimensional channels. See also [18], for example, for a reference on how the tangential momentum accommodation coefficient is measured experimentally for various materials and gas species in long tubes.

1.2 The surface scattering operator and self-diffusivity

A more fundamental description of surface-molecule interaction can be obtained by introducing a Markov (classical scattering) operator $P$, which gives the probability distribution of molecular post-collision velocities conditional on the pre-collision velocity. See, for example, [5] for a general description of $P$—a self-adjoint operator on an appropriate Hilbert space—for explicit mathematical interaction models.
All the relevant surface-molecule properties that can affect diffusivity pertain to the spectrum of $P$. As shown in [4], one has

$$D = \left( \int_0^{\frac{2\pi}{2}} \frac{\partial}{\partial \vartheta} d\mu(\vartheta) \right) D_K$$

where $\mu$ is a certain measure derived from the spectral resolution of $P$. Although conceptually useful, the practical value of this formula is not ideal since a detailed determination of $\mu$ from an explicit molecule-surface interaction model is often not easy to obtain.

Given the usefulness of the Maxwell-Smoluchowski phenomenological model, it is natural to ask whether it is possible to identify specific surface characteristics making up the single model parameter $\vartheta$ in Equation (1). It turns out that a useful estimation of the quantity $\eta = D/D_K$ (the expression in parentheses in Equation (2)) and further qualitative understanding of $\vartheta$ can be achieved when the surface-molecule interaction is relatively weak; that is to say, when the surface exhibits low roughness. Since we are here mostly concerned with geometric characteristics of the surface affecting diffusivity, we assume that collisions are elastic and no energy is exchanged between surface and molecules, in which case weak scattering should be understood in the sense that the channel surface has a relatively high degree of polish, or is fairly flat.

1.3 Signature geometric parameters of the channel

Such an estimation of $\eta$ requires in the first place a precise characterization of what is to be understood by roughness. One of the main contributions of this paper is to provide a mathematical characterization of roughness that precisely connects the details of surface-molecule interaction and $\eta$ under conditions of relatively weak interaction. This is captured by the geometric parameter $h$ defined below. Since the term ‘roughness’ is already widely used and our $h$ is very specific, we will refer to it here instead as the flatness parameter. (Small values of $h$ correspond to low roughness.) The main observation of this paper is as follows. An analysis of the operator $P$ based on approximating it by a diffusion operator in velocity space, which will be detailed shortly, reveals that a small set of parameters enters into the description of $\vartheta$ (as defined in Equation (1)). These parameters, which will be defined mathematically later in the paper, are:

- The flatness parameter $h$: an overall measure of how flat, or polished, the surface is.
- The shape parameters $\lambda_1, \lambda_2$. These are a measure of mean surface curvature not affected by the flatness per se, as will be better explained below. When $\lambda_1 = \lambda_2$, we say that the surface microgeometry is isotropic. The assumption of isotropic microgeometry will be made throughout this paper and we write $\lambda = \lambda_1 = \lambda_2$. Our main result, the determination of $D$ in terms of channel geometric parameters, can still be stated in the non-isotropic case except that the self-diffusivity constant would then depend on the direction tangent to the surface in which it is measured. For simplicity of presentation we do not consider this more general case here.
- The macroscopic parameter $C$. This parameter accounts for the shape of the channel cross-section, but not on its size proper. It may take different values for channels with, say, a circular versus a square cross-section, but does not depend on the radius of the circle or the side length of the square.
As will be seen, $h, \lambda_1$ and $\lambda_2$ are obtained relatively easily from an explicit description of the surface micro-relief. $C$ will be given in the form of a power series in Theorem 2. An approximate value for circular channels is $C_{circle} \approx 0.68$. (See Figure 2.) Our analysis of $P$ in the weak scattering limit, under the assumption of isotropic scattering, shows that

$$\vartheta = \hbar \lambda / C,$$

where we write $\lambda$ for the common value of $\lambda_1$ and $\lambda_2$. See Equation (4) and, for a precise mathematical statement, Theorem 2 near the end of the paper.

Thus the horizontal plane parallel to the surface at $F$.

For example, the surface indicated on the left-hand side of Figure 1,

1.4 Effective microstructure

Before elaborating on this factorization of $\vartheta$ result, it is important to note that diffusivity is affected by both the actual surface relief and the shape and size of the gas molecules. Thus when we speak of the surface microgeometry we have in mind this combined surface-molecule geometry. This point is illustrated in Figure 1 for a simple geometry consisting of packed spheres of radius $r_s$. When probed by spherical molecules of radius $r_m$, the effective radius of curvature associated to the surface is $r_s + r_m$. Thus, as far as diffusivity is concerned, the same surface should be considered flatter (or less rough) for larger gas molecules. We call this effective geometry the billiard geometry.

![Figure 1: The effective microgeometry of the channel surface depends on the size of the gas molecule. To the simple surface relief on the left one associates the effective, or billiard geometry, on right, which is the locus of centers of the spherical gas molecule. In this example, the microgeometry is periodic; a tile or cell of this periodic relief is highlighted on the right.](image)

The analytical approach we explore here applies to much more general situations that allow for non-periodic microgeometries and thermal interaction, but for the sake of making the main ideas most transparent we restrict attention to the setting of rigid and periodic structures. This general approach is based on approximating $P - I$, where $I$ is the identity operator, by a differential operator $L$ which we have called in [7] MB (Maxwell-Boltzmann)-Laplacian. Under the assumptions of the present paper regarding the surface-molecule interaction, i.e., that we have elastic collisions against a rigid surface with no thermal interactions and that diffusivity is
isotropic, the MB-Laplacian turns out to be a generalized Legendre operator in dimension 2, whose spectral theory is well-understood. As the spectral theory of more general MB-Laplacians becomes better understood, it will be possible to undertake a similarly detailed analysis of more general situations than discussed in this paper.

1.5 Definition of the roughness/flatness parameter \( h \)

The precise definition of low roughness will be given in terms of what we have called in \( 3 \) the flatness parameter \( h \), defined as follows. Let us assume that the surface relief in a billiard cell (see Figure 1) is represented by the graph of a function \( f \) as shown in Figure 2. Then \( h \) is the maximum value of the square length of the gradient of \( f \):

\[
(3) \quad h = \max_{x \in O} |\nabla_x f|^2,
\]

where the maximum is taken over the points \( x \) in a rectangle parallel to the opening of the cell, denoted by \( O \) in Figure 2.

We should emphasize here the distinction between our flatness coefficient \( h \) and the standard measure of roughness used today in industry. The most common parameter used to specify surface texture is the average roughness. It is defined as the average deviation of a surface relief from its mean height. More precisely, let \( f_0 \) denote the function whose graph defines the physical surface relief, as opposed to \( f \), which represents the effective microgeometry. In Figure 1 \( f_0 \) defines the surface on the left-hand side (the part of the spheres packing surface that is exposed to gas molecules collisions) and \( f \) the one on the right. Then surface roughness may be defined, in the setting of periodic microstructures, as

\[
Ra = \frac{1}{A} \int_{O} |f_0(x, y)| \, dx \, dy
\]

where \( O \) is a rectangular unit of the horizontal plane containing a surface cell, as in Figure 2 and \( A \) is the area of the rectangle. Our definition of \( h \), on the other hand, applies to the
effective microgeometry that characterizes the combined surface-molecule system. Note that
the standard measure of roughness has physical unit of distance while our $h$ is scale-invariant. It (as
well as $\lambda$; see the next subsection) may be regarded as a dimensionless measure of the curvature
of the effective geometry rather than the actual geometry’s deviation from mean height as in
the standard definition. The flatness parameter $h$ is meant to capture a property of the surface
that is directly relevant to gas diffusion considerations.

1.6 The shape matrix $\Lambda$ and the factorization of $\vartheta$

For small values of $h$—corresponding to well-polished, or relatively flat, surfaces—, all
the geometric parameters characteristic of the surface microstructure having relevance for the
diffusion process are contained (in dimension 3) in $h$ itself and in a real, symmetric 2 by 2
matrix $\Lambda$ also obtained from the cell-defining function $f$. (See Figure 2.) In order to define $\Lambda$, let us first introduce a matrix $A$ as follows: for any vector $u$ in the plane tangent to the channel
surface at a given point (we should think of $u$ as the tangential component of a post-collision
velocity at that point) we set

$$Au := \frac{1}{\text{Area}(O)} \int_O \langle \mathbf{n}(x), u \rangle \mathbf{n}(x) \, dx.$$ 

Here $\mathbf{n}$ is the tangential component of the unit normal vector to the graph of $f$, shown in Figure
2 and $\langle \mathbf{n}(x), u \rangle$ is ordinary dot product. We then define

$$\Lambda := \lim_{h \to 0} A/h$$

when the limit exists. We will call $\Lambda$ the average curvature matrix (for small $h$) and its eigenvalues
$\lambda_1, \lambda_2$ the shape parameters.

We say that the diffusion is isotropic if $\Lambda$ is a scalar matrix. Notice that this is a condition on
the microstructure and not, naturally, on the transport at the scale of the channel. Let $\lambda$ be its
single eigenvalue. Then our main remark is that $\lambda h/C$ provides the appropriate replacement for
the Maxwell-Smoluchowski parameter $\vartheta$. More precisely, our central result is that

$$\eta = 2 - \vartheta + O(h^{1/2}), \quad \vartheta = \frac{\lambda h}{C}.$$ 

We describe below how $h$ and $\lambda$ are computed. The value of $C$ is given later in the paper in
series expansion form using generalized Legendre functions.

As an example, consider $f_\epsilon(x) = \epsilon f(x)$, defined over $O = [-c_1, c_1] \times [-c_2, c_2]$. For $\epsilon$ small,

$$\mathbf{n}(x) = -\epsilon \text{grad}_x f + O(\epsilon^3), \quad h = \epsilon^2 \max |\text{grad}_x f|^2.$$ 

Then the entries of $\Lambda$ are

$$\Lambda_{ij} = \frac{1}{\max |\text{grad}_x f|^2} \int_{-c_1}^{c_1} \int_{-c_2}^{c_2} \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} \, dx_1 \, dx_2.$$ 

For a more explicit example, consider the model shown in Figure 1. Let $r_s$ be the radius of
the spheres making up the surface and $r_m$ the radius of the gas molecules. Then, disregarding
terms of 4th order in \( r_s/(r_s + r_m) \), one easily computes

\[
\lambda h \approx \frac{1}{3} \left( \frac{r_s}{r_s + r_m} \right)^2.
\]

See Section 4 for details. Thus, insofar as diffusivity is concerned, roughness is lower when the same channel is transporting gas with larger molecular diameter.

### 1.7 The Method of Diffusion Approximation in Velocity Space

This topic was developed in greater detail, in dimension 2, in [3]. In the present paper, we explain the necessary modifications needed for the more realistic 3-dimensional context. The central theoretical ideas are contained in Theorems 1 and 2. The essential point is that, for relatively weak scattering, the Markov chain generated by \( P \), which we now denote by \( P_h \) to make explicit the dependence on the flatness parameter, can be approximated by a diffusion process in velocity space (not to be confused with the actual gas diffusion in the channel). The generator of the diffusion process is the MB-Laplacian \( \mathcal{L} \), a differential operator which is related to \( P_h \) according to

\[
P_h \approx I + h\mathcal{L}
\]

in the precise sense of Theorem 1. One then obtains \( \eta \) via the solution of a Markov-Poisson equation by expanding the solution in terms of the eigenfunctions of \( \mathcal{L} \). In the isotropic case, \( \mathcal{L} \) has the form

\[
\mathcal{L}\Psi(u) = 2\lambda \text{div} \left( (\rho^2 - |u|^2) \text{grad}\Psi(u) \right).
\]

This leads to the conclusion of Theorem 2, which is the paper’s main result. The proof of Theorem 2 is similar to that of the corresponding result in dimension 2 from [3] and is not presented here. The main difference is that in dimension 2 one is dealing with the standard Legendre (ordinary differential) operator, whereas here the spectral theory of the above partial differential operator is needed instead.

It is important to observe that our use of the generalized Legendre differential operator and its eigenfunctions is not at all arbitrary. It is dictated by the remarkable fact that such operator arises naturally in the diffusion approximation of the Markov operator \( P \). Thus, the overall logic in our approach can be summarized as follows: as already noted (Equation 2), \( \eta = D/D_K \) is fully specified by the spectrum of \( P \); for small \( h \), \( P \) is well approximated by \( \mathcal{L} \) up to a multiplicative constant, as in Equation 3. The spectral theory of \( \mathcal{L} \) is known explicitly, thus yielding an effective method for obtaining \( \eta \). From this analysis results Equation 4.

When the channel surface microstructure is not rigid but contains moving parts, \( \mathcal{L} \) is a partial differential operator that generates a positive recurrent diffusion in velocity space whose stationary probability is the surface Maxwellian (which contains, in particular, Knudsen’s cosine law) at a given temperature as discussed in detail and in great generality in [7]. Our approach to determine diffusivity for weak surface-molecule interactions applies to this more general case, except that the spectral theory for the general MB-Laplacian (needed for Theorem 2) is still to be developed.

In the following sections, we describe our methods and results in greater mathematical detail.
2 Random billiards and the surface operator $P$

The surface microgeometry and Knudsen diffusivity are naturally mediated by a classical scattering operator, here denoted by $P$. For much of what we show in this paper, we may allow the microgeometry to be very general, although it will greatly simplify the discussion to assume that it is periodic. The channel surface is then considered to be tiled by identical elements that we call billiard cells. A representative cell is imagined to be contained in a rectangular region, as in Figure 3, that has one face open to the interior of the channel (the opening) and four faces on which we impose periodic conditions.

2.1 Definition of the surface operator

Since we regard these cells to be very small relative to the diameter of the channel, it makes sense to characterize a molecule-surface collision as a scattering event given as follows: when a gas molecule impinges on the surface, its post-collision velocity $V(r,v)$ is a function of the incoming velocity $v$ and of a point $r$ on the opening of the cell which we regard as being random, uniformly distributed on the cell opening. (See [8] for more details.) Let us denote the opening by $O$. The event that the post-collision velocity lies in a set $S$ of 3-dimensional vectors will then have the probability

$\text{Prob}(V \text{ lies in } S \mid \text{ pre-collision velocity is } v) = \frac{1}{\text{Area}(O)} \int_{O} \mathbb{1}_{S}(V(r,v)) \, dr = \mathbb{E}_{v}[\mathbb{1}_{S}(V)].$

Here $\mathbb{1}_{S}$ is the indicator function of $S$ which, by definition, takes on the value 1 in $S$ and 0 outside $S$, and $\mathbb{E}_{v}$ indicates conditional expectation given the pre-collision velocity $v$. Using more general test functions $f(V)$, we define the classical scattering operator $P$ (or Markov transition operator) associated with the microgeometry as

$(Pf)(v) = \mathbb{E}_{v}[f(V)].$

All the geometric properties of the surface that are relevant to diffusion are contained in $P$. It is the surface’s scattering signature. Given $r$ and $v$, $V(r,v)$ is the result of the deterministic motion involving one or more billiard-like, specular collisions in the billiard cell. The random nature of $V$ is due to the randomness of the point of incidence $r$ in the opening of the billiard cell. Notice how the random flight in the cylindrical channel is then obtained in this surface model by combining two essentially independent steps: one step is the free flight between two consecutive molecule-surface collisions and the other is the determination of the post-collision velocity as a random function of the pre-collision velocity. The latter step does not require knowing the exact position at which the molecule hits the surface.

2.2 General properties of the surface operator

As has been described elsewhere (for example, [4, 5, 6]), the operator $P$ has many nice properties, a few of which we summarize here:

- **Knudsen cosine law.** The probability distribution

$\, d\mu = \frac{1}{2\pi} \cos \varphi \, d\Omega$


Figure 3: The post-collision velocity $V$ is a function of the pre-collision velocity $v$ and the random variable $r$ describing the position on the opening of the billiard cell.

on solid angles, where $\varphi$ is the angle a post-collision velocity makes with the normal vector to the channel surface, is stationary under the Markov chain defined by $P$, irrespective of the given microgeometry.

- **Self-adjointness of $P$.** On the Hilbert space of functions $f(V)$ that are square integrable with respect to the Knudsen cosine distribution $\mu$, $P$ is a bounded self-adjoint operator. Its spectrum is real and is contained in the closed interval $[-1, 1]$.

- **Spectrum.** The spectrum of $P$ (real and often discrete) is thus a signature of the microgeometry. It fully determines diffusivity. (See [9] for many examples. See also [4], where the integral formula 2 over the spectrum of $P$ is obtained for the diffusivity.) Of special importance is the spectral gap $\gamma$, defined as the gap between the top eigenvalue 1 and the rest of the spectrum of $P$. This quantity has a pronounced effect on diffusivity, as will be further noted in this paper.

This model of microstructure can be extended to allow for moving parts and surface potentials. In this more general situation, the stationary probability distribution on velocity space is the (boundary) Maxwell-Boltzmann distribution at a given temperature, expressed in terms of the variance of velocities of the moving parts of the surface microstructure. This contains the Knudsen cosine law as the distribution of scattering directions. (See [4, 5, 7].)

3 Random flight in a cylindrical channel

We summarize in this section some results about diffusion, mostly special cases of theorems proved in [4], that are needed for the present paper. We assume for concreteness that the channel cross-section is circular. Different cross-sections correspond to different displacement functions, denoted $X$ below. All the other elements of the analysis remain unchanged.
Figure 4: On the left is the definition of the moving frame \((\tau, e, \nu)\) on the channel surface. Pre- and post-collision velocities, \(v\) and \(V\), lie on (the surface of) a sphere of radius \(\rho = |v|\). It is convenient to represent velocities by their orthogonal projections \(\tau\) and \(\nu\) to the disc \(D_\rho\) of radius \(\rho\) perpendicular to \(\nu\). On the right is the definition of the displacement function \(X = (q - p) \cdot e\) where \(q = p + tv\) is the next point of collision, \(t\) is the time between collisions, and \(u\) is the projection of \(v\) to the disc of radius \(\rho\) perpendicular to \(\nu\).

3.1 The Markov Chain of Scattered Velocities and Random Flight

The remarks of Section 6 can be expressed in the language of Markov chains. Let \(V_1, V_2, V_3, \ldots\) be the sequence of post-collision velocities of a tagged gas molecule as it undergoes random flight in the cylindrical channel of radius \(R\). This sequence of random variables constitutes a Markov chain with transition operator \(P\). In the stationary regime, even though \(V_i\) and \(V_{i+1}\) can be strongly correlated, these random variables satisfy the cosine distribution of directions regardless of the given microstructure. Given \(V_i\), the distribution of \(V_{i+j}\) converges to the cosine law at an exponential rate as \(j\) increases. This rate of relaxation, which is dominated by the spectral gap \(\gamma\), is a key factor influencing diffusivity. The mathematical details in dimension 2 are developed in [3].

As the speed \(\rho = |V_i|\) does not change during the process due to the assumption that collisions are elastic, \(V_i\) is determined by its orthogonal projection \(\nu_i\) to the disc \(D_\rho\) of radius \(\rho\):

\[ V_i = \left( \nu_i, \sqrt{\rho^2 - |\nu_i|^2} \right). \]

It is not difficult to show that having the cosine law for the stationary probability distribution of the process \(V_i\) is equivalent to the process \(\nu_i\) having the uniform distribution on \(D_\rho\) for its stationary probability distribution.

We introduce the orthonormal moving frame \((\tau, e, \nu)\) on the surface of the cylindrical channel defined in Figure 4. At any given point, \(\tau\) is the unit vector tangent to the circle cross-section, \(e\) is the unit length vector pointing along the axis of the cylinder, and \(\nu\) is the unit vector normal to the cylinder surface, pointing in. If \(P_1, P_2, \ldots\) are the collision points with the channel surface of a random flight trajectory, where \(i\) indicates the flight step, we write

\[ \tau_i = \tau(P_i), \quad e_i = e(P_i) = e \quad \text{(constant)}, \quad \nu_i = \nu(P_i). \]

We now describe the mathematical model of the random flight in a cylindrical channel. Each step of the random flight is determined as follows.
Let \( P_i \) be the point on the channel wall at the moment \( t_i \), where \( i \) indicates the present collision step of the random flight. At this step, let \( V_i \) be the post-collision velocity.

The time \( t_{i+1} = t_i + T_i \) of the next collision is obtained from

\[
T_i = 2R \frac{V_i \cdot \nu_i}{(V_i \cdot \nu_i)^2 + (V_i \cdot \tau_i)^2}.
\]

The next collision point is \( P_{i+1} = P_i + T_i V_i \) and the displacement along the axis of the channel accounted for by this segment of random flight is \( X_i = (V_i \cdot e) T_i \).

Finally, the post-collision velocity \( V_{i+1} \) is obtained as follows: Given \( V_i \) and a random point \( r \) in \( O \) uniformly distributed, we obtain \( V_{i+1} = V(r, V_i) \), as indicated in Section 2, for a given choice of microstructure.

The total displacement after \( n \) steps of the random flight is then \( S_n = X_0 + \cdots + X_{n-1} \).

Introducing the displacement \( X(p, v) \) and the free-flight time \( T(p, v) \) functions

\[
X(p, v) = 2R \frac{(v \cdot \nu)(v \cdot e)}{(v \cdot \nu)^2 + (v \cdot \tau)^2}, \quad T(p, v) = 2R \frac{v \cdot \nu}{(v \cdot \nu)^2 + (v \cdot \tau)^2},
\]

where \( \tau, e, \nu \) are evaluated at \( p \), let us write \( X_i = X(P_i, V_i) \) and \( T_i = T(P_i, V_i) \). It is clear that, relative to the stationary probability distribution, \( X \) has mean 0. A simple integral calculation gives the variance of \( X \) and mean value of \( T \):

\[
E[X^2] = \frac{4}{3} R^2, \quad E[T] = \frac{2R}{\rho}.
\]

### 3.2 Channel Diffusion as Limit of the Random Flight Process

The diffusion process arises from the random flight model through an application of a Central Limit Theorem. In this regard, the facts we need for this paper will be taken from [4]. A concrete way to think about the CLT in the present context comes by the consideration of the following idealized experiment. Keeping in mind that one quantity that can be effectively measured is the time that molecules undergoing random flight take to escape from a finite length channel, let the channel be a cylinder of radius \( R \) and total length \( 2L \), and let \( \tau(R, L, \rho) \) be the mean exit time (where the random flight is defined for some choice of microstructure with Markov operator \( P \)), assuming starting point at the middle of the channel and random initial velocity (with speed \( \rho \)). The CLT (as in [4]) implies the asymptotic expression for large \( L \):

\[
\tau(R, L, \rho) \sim L^2 \frac{\mathcal{D}}{\mathcal{D}_K}
\]

where \( \mathcal{D} \) is the constant of self-diffusivity. A simple dimensional analysis argument shows that \( \mathcal{D} = C_p R \rho \), where \( C_p \) is a constant, depending only on the microstructure, obtained by taking the limit for large \( a \) of the dimensionless quantity \( a^2/F(a) \), where \( F(L/R) = (\rho/R) \tau(L, R, \rho) \).

A standard way to express \( \mathcal{D} \) is through the relation \( \mathcal{D} = \eta \mathcal{D}_K \), where \( \mathcal{D}_K \) (K standing for Knudsen) is the diffusivity obtained under the assumption that the velocity process is
independent and identically (cosine law) distributed. One finds by an application of the standard CLT:

\[ D_K = \frac{2}{3} R \rho. \]  

We give now a formula for \( D \) for a given choice of \( P \). As already noted, \( P \) is a self-adjoint operator on the Hilbert space \( \mathcal{H} \) of square integrable (complex-valued) functions on \( D_\rho \) with inner product

\[ \langle f, g \rangle = \int_{D_\rho} f(u) g(u) du. \]

(Recall that the cosine law on the hemisphere of radius \( \rho \) corresponds to the uniform probability distribution on \( D_\rho \).) The norm derived from this inner product will be denoted \( \| f \| = \sqrt{\langle f, f \rangle} \).

The spectral theorem for self-adjoint operators provides a projection-valued measure \( \Pi(d\lambda) \) on the spectrum of \( P \), a closed subset of the real line. Combining \( \Pi \) with the displacement function \( X \) (which is square-integrable due to its finite variance; here, the fact that the channel is a cylinder is being used; this would not be the case for diffusion between two parallel plates) one obtains a finite measure on the spectrum:

\[ \Pi_X(d\lambda) = \| X \|^{-2} \langle X, \Pi(d\lambda) X \rangle. \]

We can now state a fundamental formula showing that the information about the microstructure of the channel surface relevant to diffusion properties is contained in the spectrum of \( P \):

\[ \eta = \int_{-1}^{1} \frac{1 + \lambda}{1 - \lambda} \Pi_X(d\lambda), \]

recalling that \( D = \eta D_K \). (This is a reformulation of the integral in Equation (2).) The argument used in [4] to derive (8) actually shows the following:

\[ \eta = 1 + 2 \| X \|^{-2} \langle X, P(I - P)^{-1} X \rangle. \]

Note that \( \| X \| = (2/\sqrt{3}) R \) as seen above. Equation (9) together with a canonical approximation of \( P \) by a generalized Legendre differential operator, discussed in the next section, are the key ingredients for the main results of the present paper.

To understand how this equation can be used to find \( \eta \), let us introduce the function \( Y = (I - P)^{-1} X \), which is a solution of the Markov-Poisson equation

\[ LY = -X, \]

in which \( L = P - I \) may be called the Laplacian associated to \( P \). As will be seen next, when the channel surface has low roughness (i.e., it is a well-polished surface, defined mathematically by the small valued of the flatness parameter \( h \)), \( L \) is well-approximated by a differential operator \( \mathcal{L} \) for which the solution to the equation \( \mathcal{L} Y = -X \) can be effectively obtained. Here \( \mathcal{L} \) is a generalized Legendre operator, which we describe in the next section.
4 The shape matrix $\Lambda$ and the generalized Legendre operator $L$

We specialize here a key remark made in much greater generality in [7]. When surface roughness is small (well-polished surfaces), it will be seen that all the micro-geometric parameters influencing diffusivity (assuming isotropic diffusion) are summarized by $h$ and a matrix $\Lambda$, which we call the shape matrix. For sufficiently flat billiard microgeometries we may assume that the surface in a billiard cell is the graph of a function $f$, that is, points $r$ on the surface take the form $r = (x, f(x))$, where $x$ may be regarded as a point in the cell opening $O$ (or, in fact, any vertical translate of $O$; see Figure 2). For any given $x$ let $n(x)$ be the unit length perpendicular vector to the surface at $(x, f(x))$ and let $\tilde{n}(x)$ be the orthogonal projection of $n(x)$ to the plane of $O$. Since $n(x)$ lies in the direction of the gradient of $F(x, y) = y - f(x)$, and denoting by $e = (0, 0, 1)$ the unit vector in the direction of the $y$-axis (see Figure 2), we have

$$n(x) = \frac{e - \nabla_x f}{\sqrt{1 + |\nabla_x f|^2}}, \quad \tilde{n}(x) = -\frac{\nabla_x f}{\sqrt{1 + |\nabla_x f|^2}}.$$

Recall that the maximum value of $|\nabla_x f|^2$ over the points $x$ in $O$ is the flatness parameter $h$ of the surface defined by $f$. Also recall that $\Lambda$ is obtained from the 2 by 2 matrix $A$ via the limit $\Lambda := \lim_{h \to 0} A/h$, and that $A$ acts on vectors $u$ in the plane perpendicular to $e = (0, 0, 1)$ as $Au := \frac{1}{\text{Area}(O)} \int_O \langle \tilde{n}(x), u \rangle \tilde{n}(x) \, dx$.

The flatter the surface the smaller is $Au$, in such a way that, in typical cases, we should expect $Au$ to be of the order of the flatness parameter $h$, justifying the definition of $\Lambda$.

4.1 Example of computation of microparameters $\lambda$ and $h$

Let us consider a couple of representative examples. We write $x = (x_1, x_2)$. Suppose $O$ is the rectangle such that $|x_1| \leq c_1$ and $|x_2| \leq c_2$ for positive numbers $c_1, c_2$. Let $a_1, a_2, b$ be also positive, $\epsilon$ a small number, and set

$$f_\epsilon(x) = \frac{b}{\epsilon} \left\{ \sqrt{1 - \left( \frac{\epsilon x_1}{a_1} \right)^2} - \sqrt{1 - \left( \frac{\epsilon x_2}{a_2} \right)^2} \right\}.$$

The graph of $f_\epsilon$ is a piece of ellipsoid over $O$ whose principal axes are proportional to $1/\epsilon$. Straightforward calculation gives

$$h = b^2 \left( \frac{c_1^2}{a_1^4} + \frac{c_2^2}{a_2^4} \right) \epsilon^2 + O(\epsilon^4)$$

and

$$A/h = \frac{1}{3} \begin{pmatrix} \epsilon \frac{c_1^2}{a_1^2} & \epsilon \frac{c_2^2}{a_2^2} & 0 \\ \epsilon \frac{c_1^2}{a_1^2} & \epsilon \frac{c_2^2}{a_2^2} & \epsilon \frac{c_2^2}{a_2^2} \\ 0 & \epsilon \frac{c_2^2}{a_2^2} & \epsilon \frac{c_2^2}{a_2^2} \end{pmatrix}^{-1} + O(\epsilon^2).$$
We record for later use the isotropic case, in which
\[ Ψ \left( \frac{c^2}{a_1^2} + \frac{c^2}{a_2^2} \right)^{-1} \text{ for } i = 1, 2. \]

We record for later use the isotropic case, in which
\[ a := a_1 = a_2, \quad c := c_1 = c_2, \quad λ_1 = λ_2 = 1/6, \quad h = 2 \left( \frac{b}{a} \right)^2 \left( \frac{c}{a} \right)^2 c^2 + O(ε^4). \]

For the special case of the example of Figure 1, let \( r_s \) be the radius of the spheres that constitute the surface and \( r_m \) the radius of the gas molecules. Then \( ε = r_s/(r_s + r_m) \) and \( a_1 = a_2 = b = c_1 = c_2 = r_s \) and we have
\[ λh ≈ \frac{1}{3} \left( \frac{r_s}{r_s + r_m} \right)^2, \]

disregarding terms of 4th order in \( r_s/(r_s + r_m) \).

4.2 The generalized Legendre operator

The interest in \( Λ \) is that it appears as a matrix of coefficients for a differential operator \( L \) that we now define, which generalizes the well-known Legendre differential operator in dimension 1. This generalized Legendre operator will appear in the approximation of the Markov operator \( P \) for small \( h \) microstructures. \( L \) will act on functions of the molecular velocity \( v \). Since molecular speed, \( ρ \), does not change during the random flight inside the channel under the assumption that collisions are elastic, we may identify the space of velocities at any point on the surface of the channel with the sphere of radius \( ρ \). Rather than use \( v \) itself, it is convenient to represent velocities by their orthogonal projection to the disc \( D_ρ \) of radius \( ρ \) perpendicular to the unit normal vector \( ν \) to the surface of the channel as indicated in Figure 1. Representing the orthogonal projection of a velocity \( v \) by \( \overline{v} \), we wish to define a differential operator on functions \( Ψ(\overline{v}) \) for \( \overline{v} \) in \( D_ρ \).

We can now define
\[ (LΨ)(\overline{v}) = -4(\text{grad}_{v}Ψ, Λ\overline{v}) + 2\left( ρ - |\overline{v}|^2 \right) \text{Tr}(Λ\text{Hess}_vΨ). \]

Here \( \text{grad} \) and \( \text{Hess} \) are the two-dimensional gradient and Hessian. A simpler expression results by using coordinates on the plane adapted to an orthonormal basis of eigenvectors of the symmetric matrix \( Λ \). Writing \( u = \overline{v} = u_1e_1 + u_2e_2 \), where \( Λe_i = λ_ie_i \), then one easily shows that
\[ \frac{1}{2}(LΨ)(u) = λ_1 \frac{∂}{∂u_1} \left( (ρ^2 - |u|^2) \frac{∂Ψ}{∂u_1} \right) + λ_2 \frac{∂}{∂u_2} \left( (ρ^2 - |u|^2) \frac{∂Ψ}{∂u_2} \right). \]

In this paper we restrict attention to isotropic diffusion, mainly because an explicit spectral theory of \( L \) does not seem to be available to the best of our knowledge. This amounts to assuming that \( Λ \) is a scalar matrix of the form \( λI \) where \( I \) is the identity. In this case
\[ (AΨ)(u) := \frac{1}{2λ}(LΨ)(u) = \text{div} \left( (ρ^2 - |u|^2) \text{grad}Ψ(u) \right). \]
Note that the only parameters associated to the billiard microstructure are then \( \lambda \) and \( h \). Without loss of generality, we set \( \rho = 1 \). The disc of radius 1 will be written \( D \) instead of \( D_1 \). The spectral theory of \( A \), just as that of its one-dimensional counterpart, is available although not widely known. See [12, 15]. We summarize the main facts in the next proposition.

**Proposition 1 (Spectral theory of \( A \)).** The eigenvalues of \( A \) are given by

\[
\lambda_{k\ell} = (2\ell + 1)(2\ell + 2k + 1), \quad k, \ell = 0, 1, 2, \ldots
\]

where the multiplicity of \( \lambda_{k\ell} \) is 1 when \( k = 0 \) and 2 when \( k \geq 1 \). For each \( k, \ell \) and \( j = \pm 1 \), the corresponding eigenfunctions are given by

\[
\phi_{k\ell j}(u) = F(-\ell, \ell + k + 1; k + 1; |u|^2)H_{kj}(u),
\]

where \( F \) is the classical hypergeometric function and \( H_{kj}(u) = |u|^k e^{ijk\theta} \), with \( \theta \) being the polar angle of \( u \in D \).

Note that \( \{H_{kj}\} \) is the basis of the space of harmonic homogeneous polynomials of degree \( k \). The explicit form of \( F \) (traditionally written \( _2F_1 \)) is

\[
F(-\ell, \ell + k + 1; k + 1; s) = \sum_{n=0}^{\ell} (-1)^n \frac{\ell+n}{n} \binom{\ell+k+n}{n} s^n.
\]

5 Differential approximation of the shape operator \( P \) and self-diffusivity

We can now state the key fact we need that relates the Markov operator \( P \) and the differential operator \( L \). The result quoted here was established in much greater generality in [7], although the observation that this relation can be used to approximate Knudsen self-diffusivity was not made there.

**5.1 The operator approximation result**

**Theorem 1.** Let \((f_h)\) be a family of piecewise smooth functions defined on \( O \) with associated average curvature matrix \( \Lambda \), where \( h > 0 \) is the flatness parameter. Let \((P_h)\) be the corresponding family of Markov transition operators. Then for any function \( \Psi \) on \( D \) having continuous derivatives to order at least 3,

\[
P_h \Psi(u) - \Psi(u) = hL\Psi(u) + O(h^{3/2})
\]

holds for each \( u \) such that every initial condition with velocity \( v \) having projection \( \overline{v} = u \) results in a trajectory that collides only once with the boundary surface of the cell. Here \( L \) is the generalized Legendre operator associated to \( \Lambda \).

Using the basis \( \{\phi_{k\ell j}\} \) of eigenfunctions for \( L \), we are able to construct solutions of the Markov-Poisson equation \((P_h - I)Y = X\). In analogy with Theorem 4 of [3] we are thus able to
give an approximation formula for $\eta$ in the present 3-dimensional setting based on Equation (9). Roughly, we have $\eta \approx 1 + 2|X|^{-2}(X,Y)$ where $Y$ is now solution to $hLY = -X$ or $2\lambda hAY = -X$.

This analysis leads to the following 3-dimensional counterpart (proved similarly) to Theorem 8 of [3]. It is the main result of the present paper.

5.2 The factorization of the Maxwell-Smoluchowski parameter $\vartheta$

**Theorem 2.** Let $(P_h)_{h>0}$ be a family of random billiard transition operators for a family of billiard cells satisfying the geometric assumptions of Theorem 1. Then

$$\eta = \frac{2 - \vartheta}{\vartheta} + O(h^{1/2})$$

where $\vartheta = \lambda h/C$ and

$$C = \frac{1}{2} \sum_{j=-1}^{1} \sum_{k,\ell=0}^{\infty} \frac{\langle \phi_{kj\ell}, X \rangle^2}{\lambda_{k\ell} \|\phi_{kj\ell}\|^2}$$

only depends on the macrogeometry of the cylinder channel. (In fact, only on the shape of the cross-section of the channel, up to scale. Thus, for a circular cross-section of radius $R$, $C$ is simply a number independent of $R$.) Here $X = X/\|X\|$.

Figure 5: Approximation of the macroscopic constant $C$ for a circular straight channel. The value $C \approx 0.685$ was obtained by truncating the triple iterated infinite series for $k,\ell \leq 35$. More precisely, for each $j \in \{-1,+1\}$, $k,\ell \in \{0,1,\ldots,35\}$ the terms $A_{kj\ell}$ in the sum are calculated and for each $\ell$ the sum $B_{\ell}$ of the $A_{kj\ell}$ over $j$ and $k$ are obtained. The plot shows the values of $\sum_{n=1}^{n} B_{\ell}$ for $n = 1,\ldots,35$. Further details about the calculation of $A_{kj\ell}$ are given in the body of this article. See Theorem 2.

A few words are in order regarding the determination of $C$. The terms of the infinite sum in Equation (10) involve the eigenfunctions $\phi_{kj\ell}$ and eigenvalues $\lambda_{k\ell}$ of the operator $A$ (related to $L$).
given in Proposition 1. The inner product \( \langle \cdot, \cdot \rangle \) and norm \( \| \cdot \| \) in Equation 10 are the standard operations in the Hilbert space of square integrable functions on the disc \( D_\rho \) indicated in Figure 4. \( X \) is the displacement function between two consecutive scattering events of the random flight inside the cylindrical channel, as shown in the same figure. Thus the quantities \( \| X \|, \| \phi_{k\ell j} \| \) and \( \langle \phi_{k\ell j}, X \rangle \) require evaluating integrals over \( D_\rho \). We used MATLAB for the approximate evaluation of \( C_{\text{circle}} \) as indicated in Figure 5.

6 Conclusions

We revisit and refine the classical Maxwell-Smoluchowski theory of gas-diffusion in channels. This refinement consists of a new method for the computation of the tangential momentum accommodation coefficient \( \eta \) of self-diffusivity of gases in straight channels, in the large Knudsen number regime, based on an explicit description of the channel surface microgeometry. It is assumed that the molecule-surface interaction is modeled by elastic collisions of hard spheres against a rigid surface. The main conclusion is that, for surfaces having a high degree of polish, or low roughness, as measured by a geometric parameter \( h \) which we have called flatness, \( \eta \) can be expressed as follows: \( \eta = (2 - \vartheta)/\vartheta \) and \( \vartheta = \lambda h/C \). All the quantities involved can be calculated from first principles given an explicit mathematical description of the surface microgeometry and the shape of the cross-section of the straight channel. Here \( C \) is a scale-independent constant that depends only on this cross-section. For example, for a circular channel this number is approximately 0.68 and is independent of the channel diameter. The flatness parameter \( h \), as already noted, gives the overall level of surface polish so that low values of \( h \) imply a low degree of surface ‘roughness’—a widely used term that is given precise mathematical meaning in our work through the analytic definition of \( h \). And the shape parameter \( \lambda \) is a measure of surface curvature independent of \( h \). Both \( \lambda \) and \( h \) are easily obtained from the mathematical model of the surface microgeometry whereas \( C \) is given by an infinite series as indicated in Theorem 2.

For the simple example of Figure 4 consisting of a planar packing of spheres of radius \( r_s \) and spherical gas molecules of radius \( r_m \), we have

\[ \lambda = \frac{1}{6}, \quad h = 2\epsilon^2 + O(\epsilon^4), \quad \epsilon = \frac{r_s}{r_s + r_m}, \quad C_{\text{circle}} \approx 0.685 \]

so the Maxwell-Smoluchowski parameter is

\[ \vartheta \approx 0.49 \left( \frac{r_s}{r_s + r_m} \right)^2. \]

The accommodation coefficient \( \eta \) then becomes, for low roughness (up to higher orders in \( h \)),

\[ \eta = \frac{2C}{\lambda h} - 1 \approx 4.10 \left( 1 + \frac{r_m}{r_s} \right)^2 - 1. \]

This rather simple model can be a guide to an important factor determining \( \vartheta \) and \( \eta \). Taking \( r_s \) as a proxy for the scale of surface irregularities, the squared quotient in this expression is close to 1 when the size of the gas molecules is significantly smaller than \( r_s \); it is approximately 1/4 when \( r_m \) and \( r_s \) are comparable in value, and it can be very small when \( r_m \) is significantly
larger than \( r_s \). Notice that \( \eta \) changes by an order of magnitude (\( \approx 11.6 \)) as \( r_m/r_s \) varies from 0 to 2. It is important to note, however, that our approximation is not assured for small values of the ratio \( r_m/r_s \) since the flatness parameter \( h \) grows larger than 1 as this ratio of radii becomes less than approximately 0.4. Taking as a physical example the diffusion of argon in carbon nanotubes, we have the following very crude estimate: \( r_s \) may be taken to be the radius of carbon, approximately 0.1 nm, and \( r_m \) the radius of argon molecule, which is approximately 0.18 nm. In this case \( r_m/r_s \) is approximately 1.85 and \( h \) is approximately 0.25, giving \( \mathcal{D} \approx 32\mathcal{D}_K \). This large value should be compared with experimental results in [10] for airflow through carbon nanotube membranes, in which flow enhancements \( \mathcal{D}/\mathcal{D}_K \) between 16 and 120 are observed. We expect that our values for \( \vartheta \) and \( \eta \) as given by the above formulas are sufficiently accurate to be useful in this situation, although more detailed work is needed to effectively implement such a case study.

Our method for obtaining \( \vartheta \) is based on an approximation of the classical scattering operator, \( P \), that represents the gas-surface interaction by a diffusion operator in velocity space, which we call Maxwell-Boltzmann (MB) Laplacian. In the present work, the MB-Laplacian is a generalized Legendre differential operator. This approximation method has much greater validity than demonstrated here. For more refined models of gas-surface interactions that allow for energy exchange, the associated MB-Laplacian is also known due to our earlier work [7], but their spectral theory is not presently well understood. Further progress on this mathematical topic will allow for greatly extending the applicability of the analysis developed here.

REFERENCES


