

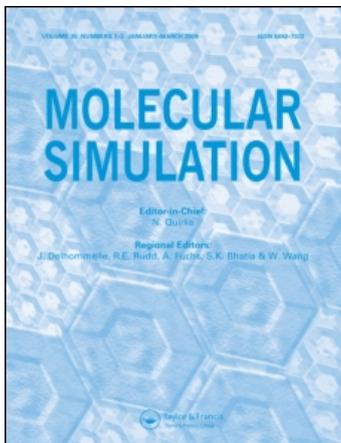
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Fluid transport in nanospaces

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We review recent progress in the transport of a fluid phase through spaces of simple geometry (parallel sided slits or cylinders) in which the confining walls restrict the fluid phase to a few molecular widths in at least one dimension. We emphasise the fact that in such spaces, the contingent solid phase plays a major role in creating strong non-uniformity in directions normal to the confining surface, even at very low fluid densities and ambient temperatures. Furthermore, the adsorbent field of the solid distorts molecular trajectories from linear and is a major factor in determining the extent to which momentum tangential to the surface is re-allocated in the collision process.

The first part of the review surveys briefly the contributions that can be made from computer simulation, and the nature of some theoretical constructs relating to the problem; we focus, in particular on the theoretical advances that have been made in Queensland over the last few years.

Following this we turn attention to progress in understanding the molecular scattering process at the point of normal momentum reversal at the surface and the theoretical and experimental developments relating to the intriguing possibility of 'superfast' flow in carbon nanotubes.

Keywords: adsorbate; transport; nanopores; momentum accommodation

1. Introduction

Fluids confined within spaces of only a few molecular widths have unique properties. These originate from the influence of the confining walls, which affect the dynamics of, and confer structure on, the molecularly thick layers within their vicinity. Much is known about this structuring from numerous adsorption studies, and its essential character of non-uniformity normal to the adsorbent wall has been thoroughly investigated in simulations of adsorbates trapped in pore spaces. Non-uniformity parallel to the wall due to adsorbent forces can also occur, though this is usually of secondary importance except at low temperatures, where phenomena such as the commensurate and incommensurate structures of adsorbates with the hexagons of a graphitic surface have received extensive discussion in the past [1]. Non-uniformity is of course a feature of a fluid flowing under a driving chemical potential gradient and enters the title of Chapman and Cowling's classical book [2]. Here we use it exclusively to refer to the non-uniformity in density normal to the adsorbent wall that is found at equilibrium.

Figure 1 shows some typical single particle distribution functions for a variety of temperatures and pore widths for a spherical model of methane confined by model pores consisting of planar parallel walls (slit pores). More complicated geometries and different adsorbate species exhibit similar features, though the details depend

in subtle ways on temperature, intermolecular forces, and the molecular structure of the adsorbate and adsorbent *inter alia*. Descriptions such as the Langmuir model, in which the molecules are either on the surface or in the gas phase, do not describe adsorption correctly in pores of this size unless the temperature is very low or the adsorption force is very large (chemisorption).

In the examples illustrated, it can be seen that the fluid tends to become more uniform in density within 3 or 4 molecular layers of the wall surface and the influence of non-uniformity on the transport properties of the fluid becomes less important in spaces of large enough width. In addition to the effects of non-uniformity, the ratio of molecule-wall to molecule–molecule collisions increases as the width of the confining space decreases. Collision is a clear cut concept for hard sphere fluids, but when the attractive and repulsive intermolecular forces, operative in real fluids, are involved, collision with another atom can only be defined in terms of the closest approach to that atom. This will be given further consideration below. The important point to note here is that molecule-wall events assume a far greater significance for the dynamics of fluids in highly confined fluids than they do for fluids in broader channels. Even recent treatments quite often ignore the important effects of adsorption densification and non-uniformity in nanosystems [3,4] or adopt simplistic adsorption models which do not capture the continuous nature of the real density distribution [5].

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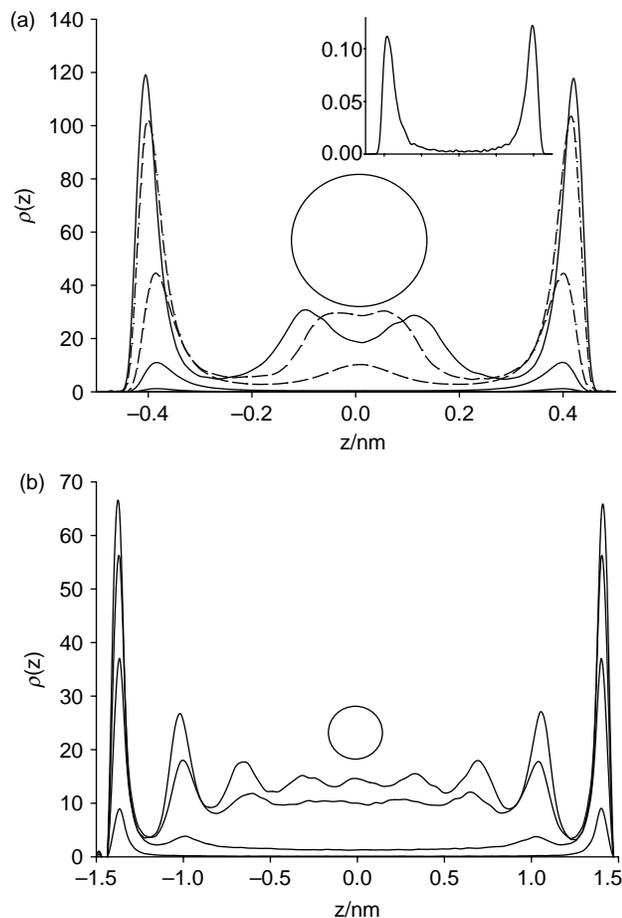


Figure 1. (a) Density distribution inside a parallel sided slit pore. The adsorbate is a spherical model for methane at 298 K. The pore walls are structureless graphite separated by a distance of 1.5 nm between the C-centres of the outer graphene layers. The mean and (external phase) densities of the confined fluid (nm^{-3}) are, from bottom to top [0.0142 (0.00102); 0.142 (0.0105); 1.367 (0.1015); 6.447 (1.0149) and 9.89 (10.15)]. The inset shows the distributions at the lowest density. The circle is approximately the hard sphere diameter of a molecule. (b) As Figure 1(a) for a slit pore width of 3.5 nm. The mean densities and external phase densities of the confined fluid (nm^{-3}) are, from bottom to top [0.57 (0.10); 3.26 (1.01); 10.00 (10.49); 12.88 (10.0) and 14.49 (10.13)].

The unique and intriguing nature of fluids in confined spaces has attracted much attention, increasingly so in the last decade as interest in nanotechnology has grown and as new materials such as carbon nanotubes have become available. A recent review predominantly of diffusion in zeolites and MOFs (metal organic frameworks) [6] has covered many aspects of these materials, and a very comprehensive review of carbon nanotubes up to 2003 [7] appeared in 2004. Fluid flow in nanotubes and nanopipes, mainly emphasising the experimental and practical challenges of producing nanofluidic devices, has been surveyed recently by Whitby and Quirke [8].

Many possible applications for such devices have been foreseen, primarily related to their potential as separative membranes and the remarkable transport efficiency of some materials. The analogy with porous channels that are ubiquitous in natural contexts has not escaped notice [9]. Here, we shall focus on spaces of simple structure such as slits or cylinders with emphasis on simulation and theoretical models, placing particular emphasis on the wall fluid friction effects.

A number of phenomenological approaches to transport phenomena through membranes, and several alternatives to forging links between phenomenological coefficients and molecular properties, have been proposed. The essential content of these theories is that an observable measure of transport such as flux or permeability is related to a driving force. Flux can refer to either the mass of molecules or to the number of molecules of a given species passing a unit area in unit time. Here, we envisage a simple experiment in which the flow is measured in a single direction and the membrane has a simple geometry as previously mentioned. Furthermore, although temperature gradients can drive molecular fluxes, we restrict our discussion to isothermal conditions.

There is no consensus about notation amongst the many publications in this subject area. We use J_i to denote the number flux of a species i , and $\bar{\rho}_i = N_i/V$ to denote its number density. The mass density is then simply $m_i\rho_i$. The chemical potential of species i is μ_i , defined in the sense that $\sum N_i\mu_i$ is a contribution to the internal energy in an open system. In the interests of a cleaner notation the driving force $d\mu_i/dz$ in the direction of flow (z) will be written $\nabla\mu_i$ although the generality implied is redundant in the present context. We need to keep in mind that in the systems of interest here, density will be a function of location in space $\rho_i(\mathbf{r})$ as already discussed above.

The mean density can be written as an integral over the local density distribution

$$\bar{\rho} = \frac{1}{V} \int d\mathbf{r} \rho(\mathbf{r}),$$

and the mean molecular flux of a component i is

$$J_i = u_i \bar{\rho}_i,$$

in which the streaming velocity in the direction z of species i is given in terms of the molecular velocity components of that species:

$$u_i = \frac{1}{N_i} \sum_j v_{ij}. \quad (1)$$

The irreversible thermodynamic formulation of the z -components of a multicomponent flux can now be

written very simply as

$$J_i = -L_{ii}\nabla\mu_i - \sum_{j \neq i} L_{ij}\nabla\mu_j. \quad (2)$$

The only constraint is that the cross-phenomenological coefficients should be equal if the Onsager reciprocal relations are to be respected. The more formidable task is to be able to unwrap the phenomenological coefficients in terms of quantities accessible from simulation and open to interpretation in terms of molecular theory.

An invaluable link with simulation is provided by Green-Kubo theory with the aid of which, the phenomenological coefficients can be expressed as a correlation of the axial streaming velocity components which can be easily collected in a standard EMD simulation.

$$L_{ij} = \frac{N_i N_j}{s k_B T V} \int_0^\infty \langle \mathbf{u}_i(0) \cdot \mathbf{u}_j(t) \rangle dt, \quad (3)$$

here s is a factor that depends on the dimensionality of the system ($= 1$ for cylindrical pores, 2 for slit pores, and 3 in a general 3D case).

The mean correlation of the streaming velocity decays to zero at long times. For a single component, Equation (2) can be re-expressed in terms of the collective diffusion coefficient, D_o :

$$J = -L\nabla\mu = -\frac{D_o \bar{\rho}}{k_B T} \nabla\mu = -D_o \left[\frac{\partial \ln f}{\partial \ln \bar{\rho}} \right] \nabla \bar{\rho}, \quad (4)$$

where the term in the square brackets in the last equation is the Darken factor relating fugacity f to the mean fluid density. Combining Equation (4) with Equation (3), leads to the Green-Kubo expression for D_o :

$$D_o = \frac{N}{s} \int_0^\infty \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle dt, \quad (5)$$

This equation can be further broken down into self- and cross-diffusion parts with the aid of Equation (1). For example in a cylinder ($s = 1$), we can write,

$$D_o = D_s + D_\xi. \quad (6)$$

In which the self-diffusion term, corresponding to the movement of a tracer molecule through the fluid, is

$$D_s = \frac{1}{N} \int_0^\infty \sum_i \langle v_i(0)v_i(t) \rangle dt, \quad (7)$$

and the cross-term that accounts for interactions between

distinct molecules, is

$$D_\xi = \frac{2}{N} \int_0^\infty \sum_i \sum_{j \neq i} \langle v_i(0)v_j(t) \rangle dt. \quad (8)$$

At sufficiently low density of the adsorbate, the distinct term becomes negligible, and all the flux can be accounted for by the self-diffusion term. Typically, D_s tends towards a constant limit at low density denoted here by D_o^{LD} (Figure 2).

Flux can also be calculated by more direct methods, either by imposing an external force on each molecule in non-equilibrium MD calculations, or by setting up a driving gradient in chemical potential, as in dual control molecular dynamics DCVMD [10,11]. Comparative studies have demonstrated that, even though very large driving forces have to be employed in these more direct methods, they give the same results as EMD within error limits both for very small (zeolitic) pores [12] and for pore sizes in the ‘mesopore’ size range [13]

2. Theory

Three fundamental approaches to transport phenomena can be singled out:

- (1) The Liouville equations that are essentially a statement of Newtonian principles applied to non-equilibrium fluid phenomena and assert that distribution functions are constant along the trajectories of the system. They were developed, particularly by Kirkwood and co-workers in the 40’s and 50’s, to describe fluid flow.
- (2) The Boltzmann equation, initially developed by Chapman, Enskog and Cowling [2] which like the Liouville equations expresses the change, away from equilibrium in the Maxwellian velocity distributions,

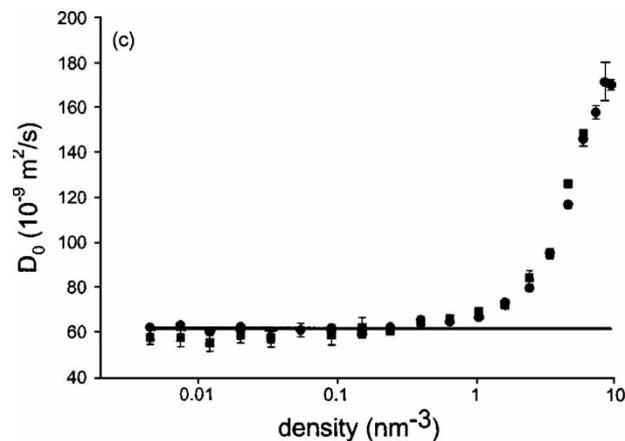


Figure 2. Density dependence of the transport diffusion coefficient at 298 K, for methane transport in carbon slit pores of width 2.0 nm. Circles are data from EMD simulations; squares from NEMD simulations. (From [40]).

but includes terms accounting for binary molecular collision processes.

- (3) The Navier–Stokes equations, central to the continuum view of fluids, which use the stress balances on a fluid element and which incorporate shear and bulk viscosities as phenomenological coefficients.

One might perhaps add irreversible thermodynamics; though in a sense the very general relations between fluxes and driving forces in this formulation can be regarded as simply a route to the identification of relevant phenomenological coefficients appearing in Equation (2) above, with the important constraint that cross coefficients are governed by the Onsager reciprocal relations. Interrelationships between the above three formulations have been thoroughly explored in the past [14].

A recent comprehensive review by Kerkhof and Geboers [15] has drawn attention to the inadequacy of most existing theories in accounting for quite elementary and long-standing observations in experimental studies of transport phenomena. Their particular focus was on flow of fluid mixtures and they gave a new derivation for mixture transport based on a rigorous analysis of the Boltzmann equation that follows the classical Chapman–Enskog method, but which differs from this in using mass velocities of individual components in place of the mass velocity of the mixture as a whole. This type of procedure was originally proposed by Snell et al. [16] in their re-analysis of the Bearman–Kirkwood equations [17]. The velocity profile model of Kerkhof and co-workers [18] is successful in describing results of experiments of Remick and Geankoplis [19], and resolves inconsistencies in the treatment of the Stefan tube, but has not been extended to nanospaces where non-uniformity is important.

A rigorous theory for non-uniform fluids that starts from the Liouville equations, and that includes non-uniformity, has been developed [20,21], and has been applied to the calculation of self-diffusion coefficients in a zeroth order approximation [22] and non uniform viscosities [23–25]. The theory uses the division of potential functions into hard sphere and attractive components that has been fruitful in perturbation theory of liquids and in the density functional theory for non-uniform fluids, but it has not been fully developed as a tractable theory for the transport of confined fluids; possibly because of the very formidable expressions that emerge. A further limitation of this theory is that the crucial molecule-wall interactions are introduced through distribution functions that embody details of wall scattering but for which there is no independent account.

Moving molecules are subject to resistances due to frequent collisions; in highly confined spaces, it needs to be appreciated that both intermolecular and molecule-wall collisions will contribute to the frictional resistance. This can be most clearly recognised when the fluid is a gas

phase in channels with cross-sections many times larger than molecular diameters and the flux can be expressed as a sum of viscous and slip contributions. The latter accounts for the non-zero streaming velocity of the gas at the channel wall, and in the limit of infinite dilution (no intermolecular collisions) the permeability ($Jl/\Delta p$) for a single component gas is the classical Knudsen diffusion coefficient. The original experiments of Knudsen for gas flow in capillaries of cylindrical cross-section can be fitted quite well by an equation that represents the viscous and diffusion components of flow separately [26]

$$\frac{Jl}{\Delta p} = D_K \left(\frac{1 + \frac{\pi R}{4\lambda}}{1 + \frac{R}{\lambda}} \right) + \frac{R^2 \bar{p}}{8\eta}, \quad (9)$$

where R/λ , the ratio of capillary radius to mean free path, is the inverse of the Knudsen number, \bar{p} is the mean pressure, and D_K is the Knudsen diffusion coefficient ($2R\bar{v}/3$).

A similar division into viscous and wall friction components can be proposed for highly confined fluids whatever their density; in this spirit the dusty gas model of Mason and co-workers [27] was extended to fluid phases, for a single component, their equation for the flux of a single component can be written in the form

$$J = - \left(D_o^{\text{LD}} + \frac{\bar{\rho} k_B T B_o}{\eta} \right) \left[\frac{\partial \ln f}{\partial \ln \bar{\rho}} \right] \nabla \bar{\rho}, \quad (10)$$

in which the coefficient D_o in Equation (4) is given a more explicit form in terms of the low density diffusion coefficient, the fluid viscosity and a geometric factor B_o .

However, this expression implies some kind of averaging of the phenomenological coefficients (represented by the diffusion and viscosity coefficients here) over the non uniform density, if it is to be applied to nanospaces. This kind of approach was extended by Mason and Viehland [28] to mixture transport who obtained the classical Stefan–Maxwell equations, starting from the Bearman–Kirkwood theory [17], and identified the solid matrix as one of the mixture components (a procedure from which the ‘dust’ of the dusty gas originates). The Stefan–Maxwell equations do not include a viscous term, but Mason and co-workers gave arguments to include a viscous flow component of the flux as an extra term. Kerkhof et al. [29,30] have pointed to internal contradictions in the dusty gas model, in that it leads to a zero mass-averaged velocity for isobaric transport in a capillary. They criticised the arbitrary nature of the additional viscous term on the grounds that this cannot be justified from first principles.

The Navier–Stokes approach to flow in systems that are non-uniform due to adsorption forces, has been thoroughly explored by Evans and co-workers [31,32]. They re-examined the expressions first given by Kirkwood

[33,34], in which the pressure tensor in a non-uniform fluid was developed as a Taylor series expansion. By exploiting the properties of reciprocal space they were able to examine various simulation techniques that can accurately and efficiently determine the density dependent pressure tensor and thus the variation of viscosity with density across a slit pore. Examples of the variation of viscosity obtained by integration of the energy continuity equation are shown in Figure 3 for two different pore widths. An alternative route to the calculation of non-uniform viscosity profiles from simulation, presented in this work (the method of planes) has also been extended to cylinders [35].

Earlier, a method for calculating the viscosity and diffusion in non-uniform fluids had been proposed by Davis and co-workers, based on the principle of local averaging of the density (LADM) over the range of a hard sphere molecular diameter [36,37], and the method has been shown to have a rigorous foundation in statistical mechanics [20]. However, as discussed by Bhatia and Nicholson [13,38], their development assumed that pressure, rather than chemical potential remains constant over the pore cross-section which is not consistent with the

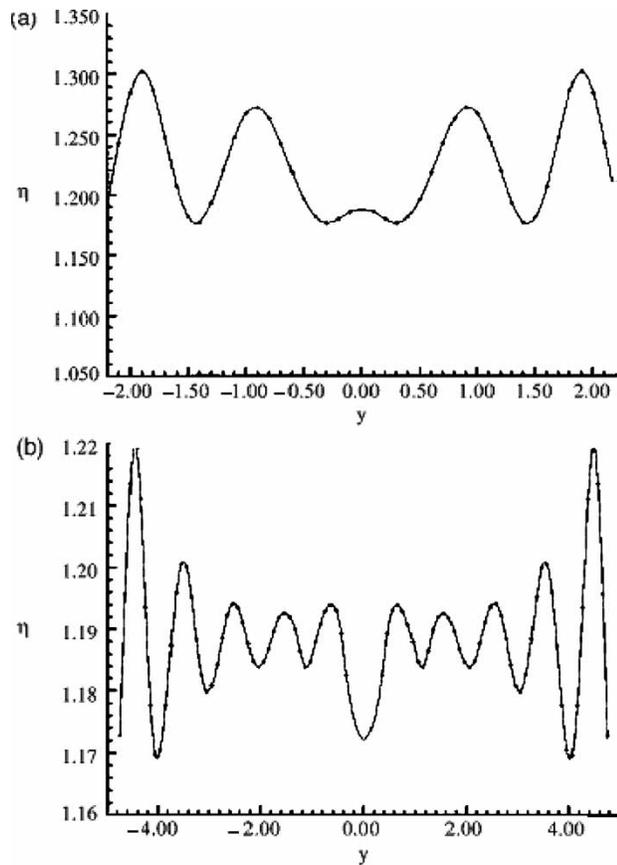


Figure 3. Viscosity variation across a slit for an Anderson, Chandler Weeks fluid. The slit walls were composed of fcc fixed atoms, at a reduced temperature of 0.722. The pore widths (in reduced units) were (a) 5.1 and (b) 10.2. (From [32]).

Gibbs–Duhem relation:

$$\sum_i \rho_i d\mu_i = dp. \quad (11)$$

A general treatment that incorporates the LADM formulation for viscosity and that includes a kinetic term that accounts for wall effects, has been developed [13,38–43] starting from the Navier–Stokes equation. In the original derivation for cylindrical pores [13,38], this equation, written for a density- (and thus position-) dependent viscosity, was integrated with a frictional boundary condition at the wall in place of the customary zero slip assumption. As already emphasised, the location of the solid wall needs particular attention when nano-spaces are under consideration. The minimum of the adsorbent–adsorbate potential function r_o (corresponding to the position of the maximum in the single particle distribution function) was taken to be an appropriate choice, since clearly (Figure 1) the molecular density falls rapidly to zero beyond this radius; it was therefore assumed that wall friction at this position, where the axial streaming velocity is u_o (the slip velocity) and the adsorbate density is ρ_o , can be attributed to a coefficient k . The wall momentum at r_o is then balanced by the fluid (viscous) momentum

$$k\rho_o u_o = -\eta \frac{du}{dr}. \quad (12)$$

Use of this boundary condition in the solution of the Navier–Stokes equation, yields an expression for the axial streaming velocity profile at a position r in the cylinder

$$u(r) = u_o - \nabla\mu \int_r^{r_o} \frac{dr'}{r' \eta(\bar{\rho}(r'))} \int_0^{r'} r'' \rho(r'') dr'', \quad (13)$$

where it has been stressed that the viscosity is a function of a local coarse grained density, obtained by integration over the hard sphere radius, $\sigma/2$, of the fluid atoms:

$$\bar{\rho}(r) = \frac{6}{\pi\sigma^3} \int_{|r'| < \sigma/2} \rho(r+r') dr'. \quad (14)$$

The mean flux in the axial direction (z) then follows from a radial averaging of $u(r)\rho(r)$ giving the axial number flux J as

$$J = -\frac{2}{r_p^2} \left\{ \frac{1}{kr_o\rho_o} \left(\int_0^{r_o} r\rho(r) dr \right)^2 + \int_0^{r_o} \frac{dr}{r\eta(\bar{\rho}(r))} \left(\int_0^r r'\rho(r') dr' \right)^2 \right\} \nabla\mu. \quad (15)$$

Here r_p is the pore radius, as measured from the cylinder axis to the position of the atom centres in the first layer of the adsorbent. The two components of this equation clearly identify with the slip and viscous terms in Equation (10)

above and therefore provide a simple route to averaging the position (density) dependent properties of the system.

Further developments and refinements of this theory have been made, and tested by comparison with molecular dynamics simulations. An important subsequent development has been to replace the original wall friction-related diffusion term by one based on an oscillator model [39–43].

The essential content of the latter model is a treatment for transport at the molecular flow limit (i.e. in the absence of any fluid–fluid intermolecular interactions). In this limit the molecular trajectories are subject solely to the force field due to the adsorbent wall and can be described by Newtonian equations of motion. For example in a cylindrical pore with wall potential $\phi(r)$, the Hamiltonian is [41]

$$H = \phi(r) + \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} + \frac{p_z^2}{2m} - zF, \quad (16)$$

where p_q are components of the q -momentum vector, and F is an external axial driving force. The radial momentum of a molecule has zeros at the positions r_1, r_2 where the molecule reverses its radial direction in the external (adsorbent) field and its profile from a position r as a function of position r' , can be obtained by integrating the equations of motion to give

$$p_r^2(r', r, p_r, p_\theta) = 2m[\phi(r) - \phi(r')] + \frac{p_\theta^2}{r^2} \left[1 - \left(\frac{r}{r'} \right)^2 \right] + p_r^2(r), \quad (17)$$

$p_r(r', r, p_r, p_\theta)$ is real inside the range $[r_1, r_2]$ and imaginary elsewhere.

Integration of the reciprocal of $p_r(r', r, p_r, p_\theta)$ over the range where it is real then gives the time for one oscillation:

$$\tau(r, p_r, p_\theta) = 2m \int_{r_1}^{r_2} \frac{dr'}{p_r(r', r, p_r, p_\theta)}, \quad (18)$$

where the factor of 2 accounts for a full oscillation.

From Equation (4) the steady state axial velocity component of a streaming fluid is

$$u = -\frac{D_o^{\text{LD}}}{k_B T} \nabla \mu, \quad (19)$$

where the superscript implies that the equation is now specifically applied to molecular streaming and takes no account of intermolecular collisions and $-\nabla \mu$ is the driving force that maintains the steady state (as noted above this may alternatively be a ‘gravitational’ force in an NEMD simulation). The force can be equated with the average momentum change, $m u / \langle \tau \rangle$, with $\langle \tau \rangle$ calculated from a Boltzmann weighted average of τ in Equation (18) and the diffusion coefficient at low density

is then obtained as

$$D_o^{\text{LD}} = \frac{k_B T}{m} \langle \tau \rangle. \quad (20)$$

In the limit where the molecules reflect diffusely from a hard wall ($\phi = 0$) these equations lead to the well-known Knudsen diffusion result for D_K in Equation (9). An equivalent treatment has also been developed for slit pores, [39,40] although in this case there is no finite ‘hard wall’ limit. The horizontal line in Figure 2 is calculated from the oscillator model for slit pores [40] and shows excellent agreement with simulation at the low density limit, for diffusion.

In the oscillator model theory, the first term in the braces in Equation (15) for the flux, is replaced by $k_B T D_o^{\text{LD}} / \bar{\rho}$. A test of the two theories against computer simulation data, and including the viscosity contribution, is shown in Figure 4.

It needs to be stressed here that all these tests against simulation have made use of a somewhat arbitrary diffuse wall reflection condition in which molecules that reverse their velocities normal to the wall at a position beyond the potential minimum, lose all memory of their incident velocity parallel to the wall, in other words the parallel velocity components are randomised when wall reflection events occur. This accords precisely with the principles underlying the theory outlined above, but takes no account of the detailed atomic structure of the wall. It should be noted that even in the absence of any persistence of parallel molecular velocity components, there is still a non-zero wall slip term.

3. Role of the solid surface

In the treatment described above, molecules moving beyond r_o (in a cylindrical pore) in a positive r direction are within the ‘slip’ zone, and will eventually reflect from the repulsive cores of the surface atoms.

Interest in how the solid surface affects transport phenomena dates back almost a century, from the time of Knudsen’s original experiments on the flow of rarefied gases through glass capillaries [44]. Knudsen found that his results were consistent with the hypothesis that the direction of reflection of a molecule from the wall was independent of its direction of incidence (the cosine reflection law). He offered two possible explanations: (i) that molecules entered, and subsequently emerged from, a dense adsorbed layer at the surface or (ii) that the gas atoms encountered a complex atomic structure at the glass surface from which they emerged only after several disorienting collisions. Clearly neither of these situations can exist within the nanospaces discussed here, and the question of what actually happens when a molecule reflects from the atoms of a solid surface becomes one of considerable

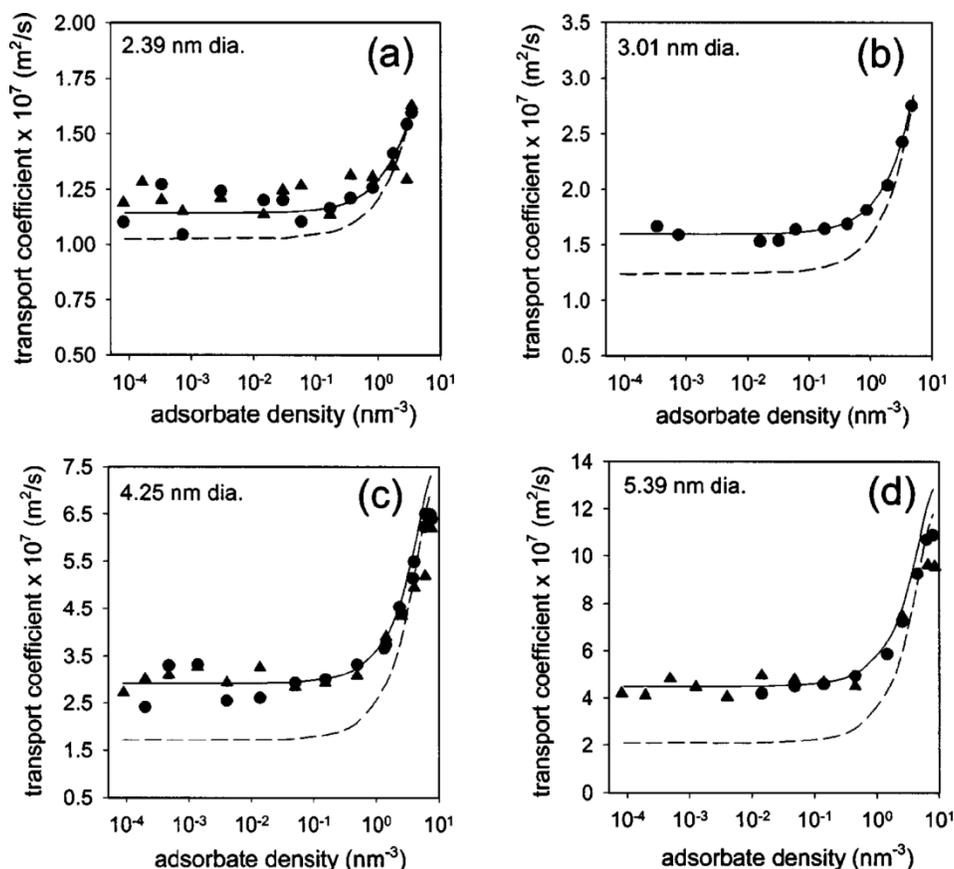


Figure 4. Variation of the transport coefficient with density for a spherical methane model in model cylindrical silica mesopores at 450 K (From [41]). The full lines are calculated using Equation (20) in the slip contribution and the broken lines from the earlier theory (Equation (15)). The points are from NEMD simulation (circles) and EMD simulation (triangles) respectively.

importance, since the extent of the momentum exchange between fluid and surface is intimately related to the frictional resistance. Nevertheless, as explained in the previous section, the Knudsen assumption (whatever its status in real systems) has been invaluable in helping to clarify ideas about transport in highly confined spaces.

A more generalised approach to surface reflection was initiated by Maxwell [45] and discussed by Smoluchowski [46] with the introduction of the tangential momentum accommodation coefficient (TMAC). In Maxwell's interpretation the incident (u_i) and reflected (u_r) components of the streaming velocity parallel to the wall may differ; though the latter is not necessarily zero as it would be for cosine law reflection; the tangential momentum accommodation coefficient is defined by:

$$\alpha = \frac{u_i - u_r}{u_i}.$$

Smoluchowski showed (see also Jepps et al. [40]) that if a fraction α of the collisions is diffuse and the remainder

specular, then the diffusion flux (or diffusion coefficient) should be multiplied by a factor $(2 - \alpha)/\alpha$.

In the spirit of the kinetic theory that underlies the original Knudsen experiments, hard sphere models for surface reflection might be thought to be a reasonable representation of the near surface reflection processes. This surmise also gains support from the success of perturbation theory in equilibrium studies in which the interaction potential is split into short range repulsive and long range attractive parts and in consideration of the single particle distribution functions shown in Figure 1, from which it is clear that the fluid is highly rarefied in a region beyond the potential minimum. A simple hard sphere model of this type demonstrates clearly how values of α may be < 1.0 in reflections from a real atomic surface. Figure 5(a) illustrates a ballistic collision process between a molecule and a surface in which the tangential momentum of the incident molecule is conserved in a frame oriented with the reflection plane normal to the direction of incidence, but is modified in the direction of streaming parallel to the plane of the solid surface. Detailed analysis [47] of such collision processes shows

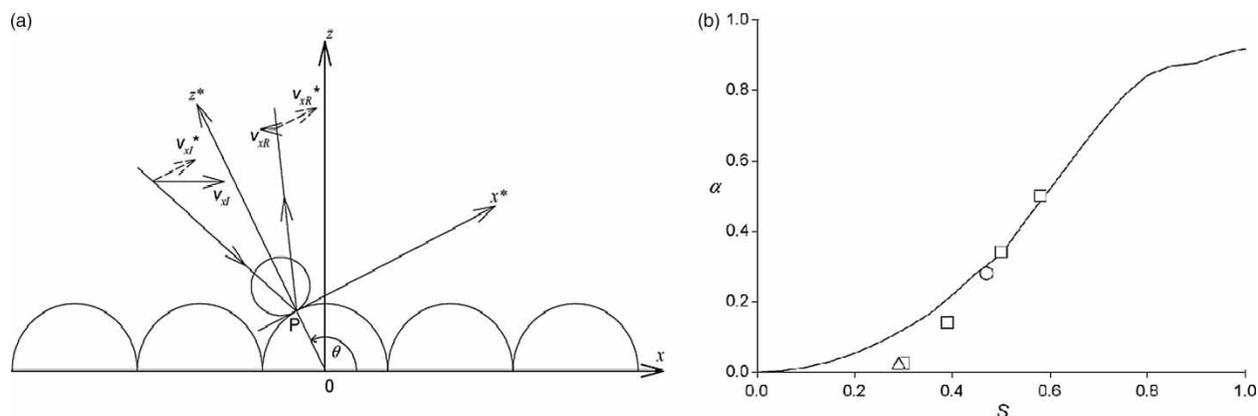


Figure 5. (a) Incident and reflected velocity components in a 2D reflection of a hard sphere from a hard sphere surface. Here, the x -axis is tangential to the direction of flow and x^* is tangential to the two atoms at the point of contact; v_{xI} and v_{xR} are components of the incident and reflected velocity in the flow direction; v_{zI} and v_{zR} are the same. (b) Calculations for a ‘ballistic’ model for hard sphere reflection from a 2D hard sphere surface (full line). The square points are taken from the infinite temperature limit of data from Ref. [61]. The circle from data in [65], and triangle is for the graphene surface in [64]; $S = \sigma_s/(\sigma_f + \sigma_s)$, depends on the relative size of fluid and hard sphere atoms. (From [42]).

that a ‘ballistic’ α depends on the relative sizes of the fluid and solid atoms as shown in (Figure 5(b)), where comparisons are made with other estimates of α , to be discussed below.

Ballistic models have also been analysed for more exotic surfaces [48]. These models also highlight the way in which momentum is modified at each collision, and that although both gain and loss can occur, the overall effect is a gradual decay of incident momentum over a number of collisions such that after that multiple collisions α will always approach the cosine law value of unity. In the classical kinetic theory situation of flow of a rarefied gas, this has been shown to result in α values close to unity after a number of wall reversal events [49]. At higher densities, a reflected molecule will tend to re-enter the fluid stream; that is to be projected past the minimum position of the adsorbate-wall potential where molecular density is highest and therefore to undergo momentum exchange with other flowing molecules. This of course is precisely the mechanism underlying viscous flow and lends support to the argument for treating flux contributions from either side of the potential energy minimum as being determined by different mechanisms.

Several studies of scattering from surfaces, both experimental and theoretical have appeared [50–56] and studies that specifically use simulation of molecular trajectories to examine reflection from roughened [57–59] or atomically detailed surfaces [60–62]

Arya et al. [61] used molecular dynamics simulations to follow the trajectories of non-colliding molecules reflecting from a model atomic surface (in a similar manner to an earlier investigation [60]). Their surface was a 101 plane of an fcc crystal, and they made a very extensive examination of atom size, temperature and potential field effects (for wall fluid atom potential well

depths of ε) on the momentum change experienced by atoms projected to the surface from a zero potential region, and subsequently captured in a zero-potential region after reflection at a distance of three molecular sizes from the surface. In this respect, their investigation resembled experimental studies using beams [50,51,53,54]. They found that when the surface atom size was more than 1.5 times the lattice spacing, α is decreased to a value well below 0.1, and approached unity when this size ratio was below 0.5 with ε/k_B of 100 K and for a number of temperatures. They also observed that $\alpha > 0.8$ when $\varepsilon/k_B T$ exceeds 1.0, even for quite smooth surfaces.

A difficulty with methods that capture reflected molecules at a distance from the surface is that not all the observed momentum exchange can be attributed to the actual surface reversal event since both the incident and the departing molecules travel through the potential field from the solid and consequently their trajectories can be modified in different ways depending on the details of the surface event at reflection. Thus, if α is to refer solely to reflections in the zone beyond the potential minimum, its value should exclude these effects. Indeed, as already mentioned above, the trajectories of molecules moving away from the wall through the potential minimum are more likely to collide with fluid phase molecules than with surface atoms.

Both the ballistic methods and the more realistic treatments that include the effects of the potential field strongly suggest that the Smoluchowski model, where each collision is either perfectly specular or totally diffuse, does not accord with a real physical process. Thus, although a meaning can be given to the idea of a perfectly specular reflection (tangential momentum is conserved), totally diffuse reflection is clearly a collective property.

It follows that the factor of $(2 - \alpha)/\alpha$ as a multiplier to the diffusion coefficient, although it satisfies momentum balance, may not faithfully represent the effects of momentum accommodation. This question was addressed by Arya et al. [62] who analysed a hard sphere model for reflection in slit pores in which each collision loses some fraction of its momentum. They derived a modified factor

$$1 - \frac{2\pi}{\ln \varepsilon} \left(\frac{1 - \alpha}{\alpha} \right),$$

to replace the Smoluchowski factor of $(2 - \alpha)/\alpha$. In this the term $\ln(\varepsilon)$ is related to the square of a cutoff velocity, necessary because in slit pores infinitely long trajectories parallel to the pore walls are a possibility, so there is no finite limiting value for the diffusion coefficient in the (intermolecular) collision free limit at infinite dilution. In cylinders of course this can never happen, and transport at infinite dilution converges to the well known Knudsen diffusion limit as shown from the oscillator model in the limit $\phi = 0$.

The sequence of the true surface event can be captured in a procedure developed by Sokhan et al. [63–66]. In their NEMD simulations of the flow of dense methane at ambient temperatures through carbon slits and cylindrical nanotubes, they collected temporal distributions zeroed at the time of collision. Their nanotubes were modelled as discrete carbon atoms and both rigid and vibrating structures were considered. A surface collision was defined as the time step at which momentum normal to the wall is reversed and data were collected over NEMD runs of around 1 ns in length. Ensemble averages of the temporal distributions are equivalent to the change in tangential streaming velocity over the collision event and exhibit a characteristic profile.

Shortly before the collision the axial streaming velocity (u) increases as molecules are accelerated into the potential field; there is then a sudden drop in u at the collision followed by a gradual increase as molecules rejoin the fluid stream (Figure 6). Sokhan et al. took the decrease in u at the surface divided by the incident streaming velocity as the relative loss in u as the tangential momentum accommodation coefficient α . They also studied a ‘Lennard–Jones’ surface composed of methane sized atoms, and found that this generated much larger α values than the C-surfaces although still below the diffuse reflection value of unity.

A surprising conclusion to emerge from this work was that α in carbon nanotubes and graphitic slit pores was very much less than unity. Inclusion of surface vibrations in the modelling did not greatly increase these very small α values as noted also by Arya et al. [61]. Some results from these calculation are summarised in Table 1.

About the same time that this work appeared, Skoulidas et al. [67] carried out simulations of methane and hydrogen transport in C-nanotubes and in silicalite and reported

diffusion coefficients that were orders of magnitude higher for the former. Other studies followed [68,69] that supported the main conclusions of these investigations. However, later simulations [70] in which only the self-diffusion coefficient was calculated suggested that, when surface atom vibrations are taken into account, much, if not all, of the ‘superfast’ quality of nanotubes is lost; in contradiction to these results and studies by Arya et al. [61] and by Sokhan et al. [63,64] in which surface atom vibrations were included (Table 1). Subsequent simulation studies by the Pittsburgh group [71] demonstrated that although self-diffusion coefficients may be substantially reduced by surface vibrations compared to a rigid lattice, the transport diffusion coefficients are not greatly affected, and that flow at high densities is still much in excess of that expected at diffusely reflecting surfaces.

Other approaches to obtaining an estimate of α from simulation data have been explored. Sokhan and Quirke [65] used the exponential time decay of the collective streaming velocity correlation for the fluid as a whole (of mass M) moving with respect to the confining solid. This can be deduced from the Langevin equation, analysis of which [65] leads to:

$$\langle u(0) \cdot u(t) \rangle = \frac{k_B T}{M} \exp(-t/\tau_R).$$

Sokhan and Quirke argued that the characteristic relaxation time τ_R , for N fluid particles, is related to the wall collision frequency ν and to α by

$$\alpha = \frac{N}{\nu \tau_R},$$

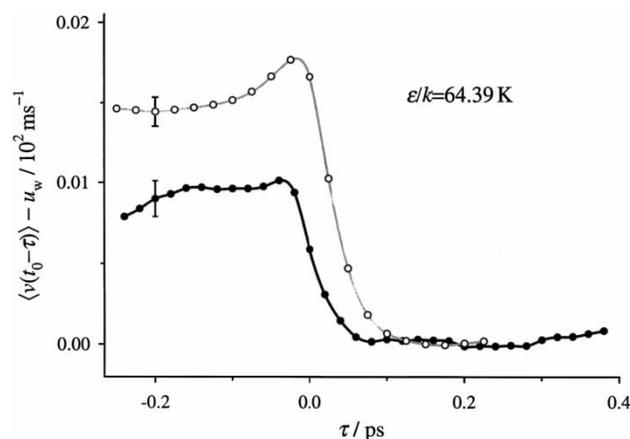


Figure 6. Temporal velocity profiles collected from NEMD simulations of spherical methane at a mean density of $0.61\sigma^3$ at 298 K in carbon slit pores of width 7.1 nm ε/k is the Lorentz mean of the fluid and wall potential parameters. The ordinate axis is the mean value of the axial molecular streaming velocities at the time of collision relative to the mean axial streaming velocity component at the wall. Filled circles are for a rigid wall; open circles for a wall of vibrating C-atoms. (From [63]).

Table 1. Values of α calculated from temporal distributions.

Adsorbent	Diameter or width/nm)	Methane density $\rho\sigma^3$	α	References
Rigid Gr slit pore	7.1	0.61	0.013	[63]
Flexible Gr slit pore	7.1	0.61	0.023	[63]
Rigid (10, 10) nanotube	1.357	0.61	0.0012	[64]
Flexible (10, 10) nanotube	1.357	0.61	0.0011	[64]
Rigid (20, 20) nanotube	2.714	0.61	0.0039	[64]
Flexible (20, 20) nanotube	2.714	0.61	0.0035	[64]
Rigid L–J slit pore	4.1	0.047	0.265	[65]
Rigid L–J slit pore	4.1	0.234	0.252	[65]
Rigid L–J slit pore	4.1	0.468	0.261	[65]
Rigid L–J slit pore	4.1	0.709	0.407	[65]

and thus α can be obtained directly from the decay of the streaming velocity correlation. Results for α , determined by this method, were in excellent agreement with those from temporal distributions. At very high densities a strong density dependence was noted which was attributed to deeper penetration of the adsorbate fluid into repulsive regions of the wall potential (Table 1). Bhatia et al. [72] used the oscillator model at very low density in conjunction with simulations of transport of methane and hydrogen in rigid C-nanotubes to calculate α using the Smoluchowski factor, and found good agreement with the results of Sokhan et al. [64] suggesting that any discrepancy between the Smoluchowski model and one in which momentum alteration at each collision is incorporated may be of only minor consequence. Moreover, this theory enables the relative contributions to the flux from diffusive and viscous contributions to be resolved; the latter was found to be a very small fraction of the total in these superfast conditions, being less than 1% for methane and only 4% for hydrogen. These extremely low values contrast with the much larger viscous contributions that would be found for diffusely reflecting walls.

In 2004 a group led by Hinds [73] succeeded in fabricating a membrane penetrated by C-nanotubes, and the following year reported results for transport of water, ethanol and hydrocarbon fluids; all of which showed ‘superfast’ transport [74]. Similar results for different fluids in an independently fabricated C-nanotube membrane were published shortly afterwards [9,75,76]. At the present time it seems clear that C-nanotubes do have extraordinary transport properties that can be directly attributed to the very low surface friction with adjacent fluids. Porous carbon materials on the other hand do not appear to show any extraordinary behaviour [77] presumably because the random orientations of the internal surfaces produce the overall effect of a roughened surface.

The foregoing discussion shows that the surface interaction with a fluid flowing through a highly confined space is more complicated than a purely ballistic effect due to hard sphere reflections. Not only can surface vibrations

play a part, but the remarkable differences in α between planar slit pores, cylindrical geometry and between cylinders of different radius, show that the shape of the potential function (which of course varies with pore size) also has a role to play. A related observation of diffusion coefficient enhancement in pores of small dimensions was reported some time ago by Derouane [78,79] and subsequently followed in some detail by Yashonath and co-workers [80–85] who proposed the name ‘levitation effect’. In their work molecular dynamics simulations of self-diffusion through a zeolite window between two open cages were performed. The diffusing atoms were Lennard–Jones species, and their size could be arbitrarily varied. It was found that diffusion was considerably enhanced when a certain critical ratio of atom size to window size was reached. Similar effects occur at a critical size ratio in other geometries [86]. The enhancement in diffusion coefficient due to the levitation effect is not as spectacular as that observed by comparing graphitic surfaces with zeolites, but probably contributes to the overall transport properties of nanotubes. Further progress in understanding this phenomenon was made when it was demonstrated that the oscillator model could give a quantitative account of the simulation data [87] in showing that the frequency of wall collisions of diffusing particles decreases at the critical pore size where the fluid–wall potential energy becomes flattened and the oscillation amplitude lengthens. Furthermore, the oscillator model theory predicts that the effect is temperature dependent and disappears at high temperatures when the ratio of kinetic energy to the solid–fluid interaction energy is large. As in the earlier studies referred to above this work applied a diffuse reflection surface condition, so it may be concluded that the two phenomena, of low tangential momentum accommodation and levitation, although they may act in concert are entirely separate in origin.

4. Conclusions

The fascination with transport in narrow spaces dates back more than 100 years and reflects the recognition that

confined fluids behave anomalously compared to bulk materials. The largely academic interest in this subject area has now intersected the exciting new fields of nanotechnology and nanoengineering. Computer simulation has played a vital role in making progress in understanding the physics of fluids in confined spaces. In part this is because the construction of exactly characterisable nanoporous materials is fraught with practical problems, and partly because simulations permit the invention of fantasy systems in which certain aspects of reality can be suppressed. Examples in the present review include the extensive use of simplified geometries, of the diffuse surface reflection condition and of the facility to vary molecule to window size in an arbitrary way in studies of levitation. Nevertheless it needs to be stressed that experiment is the only true arbiter of theoretical constructs; the fact that a theory fits simulation data does not mean that the problem is completely solved. This is a particularly prevalent problem in the context of transport in nano-systems where the neglect of strong density variations contradicts a huge body of knowledge from adsorption experiments.

Although computer simulation has achieved many advances, it is important to develop theories that underpin results from simulation. At the present time it seems likely that the formidable challenges of a fully rigorous theory will prevent further useful progress from this front. However, more ad hoc approaches based on sound physical principles have yielded promising results; up to now these theories and many of the simulations have been restricted to structureless molecules. Simulations of equilibrium adsorption have shown that rotational constraints imposed by confinement can produce interesting effects, for example in selectivity between different components [88].

The importance of the specific structure of the solid surface for the transport of highly confined fluids has been highlighted by both theoretical and experimental investigations; carbon nanotubes may turn out to be unique materials in this respect, and there remain uncertainties about their transport properties, however at the present time there appears to be the possibility for future applications in the field of nanotechnology, and incentive to investigate related materials.

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