Molecular Dynamics Simulation of Flow in Pores

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Abstract. The gaseous flow in nano-scale pores is of wide interest for many today’s industrial applications, e.g. in microelectronics, nano-mechanical devices (Knudsen compressor) and reaction and adsorption at porous surfaces. This can be seen from a variety of papers of recent RGD Symposia. Furthermore it is possible to separate gases by porous membranes. Although the fundamental problem of all these applications is same, namely the important role of the gas-surface interaction in such small structures, we will primarily concentrate on the separation of different gas species by porous membranes. These membranes are typically very robust (temperature, chemical resistance) because they are made from ceramics which offers new application fields. Porous flow can roughly be divided in several flow regimes by the Knudsen number: From viscous flow to Knudsen diffusion to surface diffusion and up to capillary condensation. A Molecular Dynamics (MD) model for the gas as well as the surface is formulated to investigate the interaction of gas atoms or molecules with internal degrees of freedom and the pore. The MD method seems to be well suited to study these phenomena because it can deal with the high density and the many-body-interactions, which occur during the multilayer adsorption and condensation at the surface, although it is clear that it is limited to a small physical space because of its high computational consumption.

I INTRODUCTION

Gas separation by porous membranes is known since long times (Graham 1829; Knudsen 1911), although nowadays almost only dense membranes, which are usually made of organic materials, are used for membrane based separation tasks because of their better selectivity. Next to the resistance, selectivity is one of the key properties of a membrane and it is defined for a binary mixture as

\[ \alpha_{12} = \frac{y_1 x_2}{y_2 x_1} \]

while \( x_i \) is the upstream and \( y_i \) the downstream mol fraction and \( x_1 + x_2 = 1 \) and \( y_1 + y_2 = 1 \). Usually \( \alpha_{12} \) is based on the better permeating component, i.e. it is larger then unity. Nevertheless porous membranes are still interesting because they can be made from ceramics and glasses, which offers high resistance against heat and aggressive chemical environments, while organic materials are rather limited (max 250 °C). So they can be integrated directly into chemical reactors to continuously separate the products to bypass the limitations of the thermodynamical equilibrium. The flow in pores is governed by different mechanisms. These different regimes can be distinguished by the Knudsen number

\[ Kn = \frac{\lambda}{D}, \quad \lambda = \frac{1}{\sqrt{2\pi r_0^2 n}} \]

defined as the ratio of the mean free path \( \lambda \) of a hard-sphere molecule and the pore diameter \( D \). With increasing Knudsen number the regimes are as follows: In large pores laminar flow occurs, which must be avoided because no separation takes place. In smaller pores Knudsen diffusion is the main transportation mechanism. Here the gas flows of the different components is independent from each other, because the number of gas-gas collisions is small compared to gas-surface collisions. When the up- and downstream pressure are same, the flux \([7]\) \( \dot{n}_i \) is

\[ \dot{n}_i = \pi D^2 \frac{\bar{V}_i}{k_B T} \frac{\Delta p_i}{1 + \frac{3}{8} \frac{T}{D}}, \quad \bar{V}_i = \frac{\sqrt{8k_B T}}{\pi M_i} \].

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Periodic boundary

Source

3D Model

1D Model

Sink

**FIGURE 1.** Sketch of simulation area

Usually the length of the pore is much larger than the radius, so that Eq. 3 simplifies to

\[
\dot{n}_i = -\frac{\bar{V}_i D}{3 k_B T} \Delta p_i \quad L.
\]  

The highest selectivity is reached when the downstream pressure is negligible, this leads to an ideal separation factor \( \alpha_{12;id} \), which only depends on the mass of the components

\[
\alpha_{12;id} = \sqrt{\frac{M_1}{M_2}}.
\]  

If the interaction between the gas molecules and the pore walls is strong enough, the gas is adsorbed at the surface wall and transported by surface diffusion. If one component is condensable, capillary condensation might occur, i.e. a liquid drop of this component blocks the pore for the other component. This gives very high selectivity. If the length of the pore is negligible, countereffusion can be seen, which leads to Graham’s law

\[
\frac{\dot{n}_1}{\dot{n}_2} = \sqrt{\frac{M_2}{M_1}}
\]  

when the up- and downstream pressure is same (isobaric counterdiffusion). If the pore diameter is reduced to the size of the permeating gas components, molecular sieving might occur, i.e. the species are separated just by their size. All these mechanisms can occur at the same time and hinder or enhance each other. While in this simulation only one pore of a certain diameter is used in a real membrane the poresize varies about an average; the standard deviation of this distribution should be narrow for best separation results.

**II MOLECULAR DYNAMICS MODEL**

The molecular dynamics (MD) model consists mainly of two regions: The gas-phase, which is further divided in an upstream and downstream part, and the bulk material of the membrane (Fig. 1). The length-scale in these two domains is usually very different: In the lattice it is determined by the binding length of the potential and in the gas phase by the mean free path \( \lambda \) (see Eq. 2). So usually the bulk material is much more dense then the gas, i.e. much more atoms have to be simulated for the surface than for the gas and an effective model for the surface has to be chosen. In this work the surface is simulated by an heat bath method based on the Langevin differential equation as described earlier [2].

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The pore itself is modeled by a three dimensional lattice, either by Lennard-Jones-interactions between all atoms within a cutoff distance (2.5 Å, platinum) or by a harmonic lattice with nearest and next nearest neighbour interactions (graphite). The formentioned model omits some binding energy for each lattice atom, i.e. energy caused by interactions with the atoms outside the cut-off radius and the binding energy between the atoms and lattice atoms which are even outside the simulated area. These energies are calculated once before the simulation and are given to the lattice atoms by interaction with the heat-bath particles, to virtually form an infinite lattice. This procedure results in a weak coupling to the heat bath at the inner pore walls and increasing influence to the outer regions. The coupling energy for a pore from platinum is shown in Fig. 2.

To reduce the computational cost, in the outside regions only a one dimensional model of the surface is used, similar to the soft cube model, but with added features of the same heat bath method described above, so that both surface areas are kept at the presetted temperature. These particles are only allowed to move in the direction perpendicular to the surface. Figure 3 shows a calculated potential energy surface (PES) between a platinum surface and one nitrogen atom (of a molecule) for an energy corresponding to the potential well depth of the interaction potential $e_{PL-N}$ and Fig. 4 shows the PES of $e_{C-N}$ for the graphite - nitrogen system: No differences can be seen between 1D and 3D model. Furthermore it can be seen, that the PES for platinum - nitrogen is very rough with deep "valleys" between the platinum atoms whereas the carbon surface is very smooth. To test the properties of the 1D model the energy distribution of an adsorbed layer is calculated $(T_{surf} = 200K; T_{gas} = 500K)$. Figure 5 shows the number density, the rotational energy and the kinetic energy of the adsorbed layer: There are only minor differences between the 1D and 3D model area. The number density shows two adsorbed layers; (the first one one the first gridline and the second one on the third gridline from the surface. Kinetic and rotational energy show little higher values in the 1D than in the 3D area, i.e. the heat transfer in the 1D region is slower.

At the moment only pores of (nearly) circular shape are investigated, but any shape can be used easily, because the configuration is filled step by step by searching for the next neighbours of existing molecules. Afterwards the parameters of the heat bath are calculated automatically as described above. As gas species several monatomic gases ($He, Ar, Kr$) and diatomic species ($N_2, O_2$) were chosen. The diatomic molecules were treated as rigid rotators and quaternions were used for describing their rotational motion to avoid the singularity of the Euler angles [1]. In the source and sink region molecules are inserted randomly according...
to the equilibrium distribution function of the preset temperature and pressure up- and downstream of the membrane respectively. Furthermore molecules are removed from the simulation, after crossing the outer border of the sink, while for the side walls of the source a periodic boundary and for the backside a specular reflection is choosen. Usually the distance of the source to the surface is about 20 times the mean free path. In the downstream region the mean free path is longer, so the distance is only about 10 times the path, because
else the simulation region would become very large.

For the time integration either an embedded Runge-Kutta (RK) Method of 5th order with stepsize-control [3] or a Leap-Frog (LF) method is used, which is modified for the integration of the rotational motion [1]. The speed of both integrations is approximately the same for the same precision (energy conservation); the RK method needs six force evaluations per step, but this is compensated by a larger step size. The main drawback of the RK method is the memory requirements for the intermediate steps, so that for larger systems only the LF method can be used. The carbon lattice requires a much smaller stepsize, because the frequency of the lattice vibrations is much higher, which can already be seen by the Debye Temperature which is 10 times higher for carbon than for platinum ($\omega_{Pt} = 240K, \omega_{C} = 2230K$). The indices of interacting atoms are stored in a neighbour-list, which is updated from time to time, i.e. every 50 steps for LF and about every 10 steps for RK integration. Afterwards this list is sorted and the interactions are grouped into vectors, so that inside of one vector the force calculations, which are responsible for approx. 90% of the computational time, are independent from each other and can be fully vectorized on the available Fujitsu Vector-Computer (NWT).

Typically about 80 vectors are created for the lattice, 250 vectors for interactions between gas and 3D-surface and 200 for interaction between gas and 1D-surface, rather independent from the size of the simulation area, but slightly increasing with thick adsorbate layers.

Following sources for the potentials were used and the cross potentials, which are not explicitly mentioned, are estimated by the Lorentz-Berthelot mixing rules: $Pt - Pt$, $Pt - N_2$ [2]; $C - C$ (harmonic lattice), $N_2 - C$, $O_2 - C$ [12]; $O_2 - O_2$ [6]; $N_2 - N_2$ [9]; $He - He$, $Ar - Ar$, $Kr - Kr$, $C - C$ (for gas-surface-interaction) [10].

### III SAMPLE CALCULATIONS

Figures 6 - 9 show the effusion of a gas mixture (helium/argon, 50/50, 10MPa) through a pore (diameter 55 Å, length 43 Å) of graphite or platinum into vacuum. Helium can neither be adsorbed by graphite or platinum, while argon is trapped at the platinum surface, as can be seen by the number of argon atoms inside the pore. The temperature of the whole system is either 500 K or 1000 K. First all simulations are performed until the number of atoms inside the pore is constant, after that we start counting the molecules passing through the pore. Figure 8 is one example of the beginning of a simulation and Fig. 9 the corresponding counting (for the other cases the starting is not shown). The lines in the diagrams are for Knudsen diffusion calculated by Eq. 3 when the downstream pressure is negligible, although it is clear that the diameter and the length of such a small pore cannot be determined ambiguously. Figure 6 shows a good agreement between simulation and expected Knudsen flux ($\dot{n}_{Ar} = 0.68/timeunit(TU)^1, \dot{n}_{He} = 2.1/TU$). In Fig. 7 the temperature is halved, i.e. the gas density doubles and the Knudsen flux rates should increase by a factor of $\sqrt{2}$. The density inside the pore is roughly doubled for both species, but the fraction of argon is slightly higher than helium, i.e. argon seems to be adsorbed at the wall. The flux of argon ($\dot{n}_{Ar} = 1.1/TU$) increases even more than expected, while the helium flux ($\dot{n}_{He} = 2.4/TU$) is much lower than the Knudsen value. This might be caused by the adsorption of argon or a stronger interaction between the species because of the increased density and reduced Knudsen number. Figure 9 shows the same situation for a platinum pore: Here many argon atoms are trapped and the flux of argon ($\dot{n}_{Ar} = 1.6/TU$) is much higher than in the graphite pore (Fig. 7) and higher than for Knudsen flow, while the helium flux ($\dot{n}_{He} = 2.62/TU$) is slightly higher than in the graphite pore but still below the Knudsen value. The flux rates are quite close to each other so that separation is reduced.

Figures 10 & 12 and Figs. 11 & 13 show similar simulations (dia. 50 Å, length 43 Å, 500K, 10MPa) for nitrogen-argon (50/50) and nitrogen-helium (50/50), respectively. The masses of nitrogen and argon are not too different, which results in similar Knudsen flux rates. Indeed in the graphite pore the simulation shows quite similar flux rates ($\dot{n}_{N_2} = 1.3/TU, \dot{n}_{Ar} = 1.1/TU$), both a little bit higher than the expected values (Fig. 10). But in the platinum pore (Fig. 12), where argon is adsorbed much more than nitrogen, although nitrogen can be trapped by platinum as was shown in Fig. 5, the argon flux ($\dot{n}_{Ar} = 1.6/TU$) is increased and becomes even stronger than the nitrogen flux ($\dot{n}_{N_2} = 1.1/TU$), i.e. the ratio is reverse compared to pure Knudsen diffusion. Because of the large mass ratio, helium and nitrogen have very different Knudsen fluxes, but Fig. 11 shows, that the nitrogen flux ($\dot{n}_{N_2} = 1.5/TU$) is increased by the adsorption at the graphite pore walls, while the helium flux ($\dot{n}_{He} = 2.6/TU$) is reduced compared to the Knudsen value, because the diameter of the pore for helium is reduced by the adsorbed layer of nitrogen at the walls. The nitrogen flux ($\dot{n}_{N_2} = 1.8/TU$) in the

\[1) \ \frac{TU}{s} = 7.13 \cdot 10^{-13}s\]
platinum pore is even much stronger, because of the surface diffusion, whereas the helium flux ($\dot{n}_{He} = 2.6/TU$) is same as in the graphite pore.

**IV CONCLUSION**

A molecular dynamics model of porous flow was developed: Two lattice materials (graphite, platinum) and gas atoms as well as molecules with rotational degrees of freedom can be simulated. The model was used to calculate the effusion of gas mixtures into vacuum. The results show a strong influence of the gas-surface interaction on the flux rates, which do not follow the Knudsen flux rate when adsorption in the pore occurs. In Knudsen flow lighter molecules travel faster than heavier ones, which gives the separation effect. At least for the gas molecules investigated here, heavier molecules have also stronger interaction potentials with the surface and these components build adsorbate layers inside the pore and surface diffusion of this component occurs which enlarges the flux for the heavier component so that the separation effect of the Knudsen flow is reduced or even inverted. The presented simulations used very short pores and simulations with longer pores (220 Å) are going to be performed now.

The lattice is going to be extended to other materials and models. Silicon and graphite lattices can be simulated by the Brenner-potential, which is a three body potential. Furthermore ionic crystals, which are very important as membrane materials, are going to be implemented, but here special simulation techniques are necessary, to handle the long range coulomb forces, i.e. Ewald summation or multipole methods. Ionic crystals are made from different species which give rough and ordered structures on the surface [4].
A Knudsen compressor using the thermal transpiration effect in pores with a diameter of 200Å was investigated by Vargo and Muntz [11] experimentally and theoretically. It seems to be possible to extend the present MD model to such pore diameters because all computations in the present work were done on one PC (PII 500-Dual) and two α-Workstations (Compaq XP1000) within only 3 weeks and the memory requirement was about 60 MB. But the experimentally length ratios \( L/D > 100 \) cannot be treated by the MD method, because the surface would require a number of atoms in the order of \( 10^6 \).

Recently experiments were published influencing the flow of molecules with internal degrees of freedom in pores by magnetic fields by Hermans [4]. Levdansky [5] investigated the pumping of gases in pores by exciting internal degrees of freedom by laserlight. Sone [8] reported the flux of a rarefied gas without average temperature and pressure gradients. These effects are going to be included in the molecular dynamics model to further investigate the influence of the internal degrees of freedom and the results are going to be compared with the published experimental results.

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