Direct stochastic molecular modelling of transport processes in gases

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Abstract. The stochastic molecular modeling method (SMM) of transport processes in rarefied gases developed by the authors is systematically discussed in this paper. It is shown that, it is possible to simulate the transport coefficients of rarefied gas with high accuracy, using a relatively small number of molecules. The data of modeling the thermal conductivity coefficient are presented for the first time. The second part of the paper is devoted to the generalization of the SMM method for modeling transport processes in confined conditions. To describe the dynamics of molecules in this case, the splitting of their evolution by processes is used: first, the movement of molecules in the configuration space is simulated, and then their dynamics in the velocity space is imitated. Anisotropy of viscosity and thermal conductivity in nanochannels has been established. The interaction of gas molecules with walls is described by specular or specular-diffuse reflection laws. Gas viscosity can be either greater than in the bulk or less, depending on the law of gas interaction with the channel walls.

Keywords: molecular modeling; rarefied gas; transport coefficients; nanochannel.

1. Introduction
Most of the actually occurring flows of gases and liquids can be described within the framework of continuum mechanics. However, the application of the corresponding equations requires knowledge of the transport coefficients. The transport coefficients have the molecular nature. Therefore these coefficients can be derived from first principles only. A consistent theory of transport processes has been developed only for a rarefied gas on the basis of the Boltzmann kinetic theory. One of its main achievements is the derivation of explicit formulas for the transport coefficients [1, 2]. However, the calculating these coefficients requires solving a system of integral equations, which is not an easy task.

A constructive kinetic theory cannot be created for a dense gas and liquid in principle. Despite of this fact, a consistent theory of transport processes by methods of nonequilibrium statistical mechanics has been developed. However, the calculation of the transport coefficients comes up against a well-known problem, a regular method for solving the dynamic many-body problem does not exist. The situation is even more complicated when it is necessary to find the transport
coefficients of nanofluids or other complex fluids. In these cases, the only alternative to the experimental determination of the transport coefficients is their direct numerical molecular modeling. This idea is implemented in the molecular dynamics method \[3, 4\]. However, its limitations are well known. This method manages to simulate systems of a small number of molecules and at relatively short times. It is practically inapplicable for modeling the properties of a rarefied gas up to now.

In recent years, a new important field of application for molecular modeling has opened up: the description of the transport processes and fluid flows in nanochannels and nanoporous media. Here, the measurement of transport coefficients is generally impossible, as a rule. Therefore, it is extremely important to create a method that would retain the main advantage of the molecular dynamics method – the transport properties calculation, based on processing the phase variables of the system under consideration (coordinates and velocities of all its particles), on the one hand, and would be much more economical and effective, on the other. This work was devoted to the development of such a method, which was called the method of stochastic molecular modeling (SMM). A rarefied gas in bulk and in nanochannels is considered here.

2. SMM method for rarefied gases in the bulk

The molecular dynamics method has extremely successfully used to solve a variety of problems in physics, mechanics, chemistry, and biology. However, it is known that it does not give true phase trajectories \[4-6\]. Adequate data on observables are obtained only by averaging over a large number of independent phase trajectories of the modeled system. That stimulated the idea of the SMM method constructing, where the phase trajectories of the system were simulated stochastically. The easiest way to implement this idea was for a rarefied gas. That was due to two circumstances. First, the molecules interaction in such gas does not contribute to the transport coefficients and the equation of state \[7\]. In particular, it means that all fluctuation-dissipation theorems (FDT) \[4, 8\], that determine these coefficients, contain correlation functions that depend only on the velocities of molecules. For this reason, the transport coefficients depend only on the velocities of the molecules, and it is necessary to have only information about the evolution of molecules in the velocity space for their calculation. An important circumstance is that the corresponding correlation functions are calculated by means of the equilibrium Maxwellian distribution function. This means that it is necessary to simulate the equilibrium state of gas molecules in order to calculate the transport coefficients. The equivalence of FDTs to the formulas of the gases kinetic theory for calculating the transport coefficients \[1\] was proved in \[9, 10\] (see also \[4\]).

The second circumstance is determined by the fact that only pair collisions of molecules take place in a rarefied gas. Since the momenta of molecules change only in the process of their collisions, it is not difficult to determine the probability of each molecule collision in a given time interval using the kinetic theory \[1\]. Then, if the collision should occur, randomly find a molecule, which this collision is realized with.

This idea was implemented in our papers \[11-13\]. The SMM method allows using any interparticle interaction potentials. In this paper the Lennard-Jones potential was used. The corresponding algorithm is quite simple. First, the initial state of the simulated gas is created. In order to do this, \( N \) molecules with a given density \( n \) are evenly distributed in a given volume of modeling. Molecular velocities are plotted according to the Maxwellian distribution function. Thus, at initial moment of time \( t \), the molecules have velocities \( (v_1, v_2, \ldots v_N) \). Then the time interval \( \tau_s \) is determined, where the dynamics of the system will be studied. This time interval is divided into steps of duration \( \tau_i = \sigma/v_{i,max} \), where \( \sigma \) is the effective size of molecules, and \( v_{i,max} \) is the maximum value of the molecules velocity at a given time step.

Next step is the imitation of the molecules collisions. In rarefied gas the probability of molecule \( i \) collision with any other in time \( \tau_i \) is calculated on the basis of the kinetic theory, \( P_{ci} = 4\pi n \sigma^2 \sqrt{n kT/m} \) \[1\], here \( T \) is the gas temperature, \( k \) is Boltzmann constant and \( m \) is the molecule mass. For each molecule, the probability of its collision is sequentially played out.
collision should occur, the molecule \( j \) is randomly selected from the remaining \((N - 1)\) molecules. Then the velocities of the molecules \( i \) and \( j \) are changed in accordance with the conservation laws. This procedure is performed for all \( N \) at each time step.

It is shown in the papers [11-13] that the described algorithm permit to simulate with high accuracy the diffusion and viscosity of rarefied gases. However, the possibility of modeling the most complex transport coefficient, the thermal conductivity coefficient, has not yet been considered. It is determined by the following FDT [4, 14]

\[
\lambda = \frac{k}{3VT^2} \int_0^{T_p} (j(0) \cdot j(t)) dt = \frac{k}{3VT^2} \int_0^{T_p} \chi(0, t) dt, j(t) = 0.5 \sum_i m_i v_i v_i^2(t). \tag{1}
\]

Here \( V \) is volume, \( v_{ij} \) is the vector of the relative velocity of molecules \( i \) and \( j \).

The correlation functions must exponentially decay in a rarefied gas [4]. This is also confirmed by the data of calculations using SMM, presented in Fig. 1a. Here is a calculation of the correlation function normalized to the initial values for xenon at a temperature of 300 K and atmospheric pressure, the time is normalized to the mean free path time of xenon molecules. The decay of the correlation function occurs over several free path times.

\[
\lambda, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}
\]

Figure 1. Evolution of normalized correlation function of xenon heat flux (a) and corresponding thermal conductivity coefficient (b).

The exponential decay of the correlation function means a fairly fast approach to the plateau value of the thermal conductivity coefficient. Fig. 1b illustrates this fact, reaching the plateau value occurs in 8–10 times of free path of molecules. This plateau value actually determines the experimentally measurable value of the thermal conductivity coefficient.

The accuracy of this method was investigated by calculating various transport coefficients for both monatomic and polyatomic gases. It was shown that in all cases it increased with an increase in both the number of particles \( N \) used and the number of phase trajectories \( l \), which were taken for the averaged results. The relative error turned out to be of the order of \( \Delta \sim 1/\sqrt{Nl} \). In particular, therefore, the number of molecules can be "exchanged" for the number of trajectories to achieve a given accuracy.

Calculation of the thermal conductivity coefficient requires more resources in comparison with other transport coefficients. However, the error in determining the thermal conductivity coefficient turns out to be less than one percent (averaging was carried out over 1000 phase trajectories) even for polyatomic gases, using 6400 molecules in the calculations. Thus, the relative calculation error for oxygen was 0.93%, and it was 0.67% for methane (the error was determined by comparison with experimental data [15]).

3. SMM algorithm for nanochannels
The SMM method, described in the previous part, simulates only the dynamics of molecules in the velocity space. In confined conditions, let us speak about channels for the sake of definiteness, it is
necessary to take into account the interaction of gas molecules with the channel walls. For this reason, despite the fact that rarefied gas is simulated, the transport coefficients of which depend only on the molecules velocities, it is now necessary to simulate the evolution of the considered system not only in the velocity space, but also in the configuration space. The most important element of modeling such a system is the interaction of its molecules with the boundary. Below the interaction of molecules with the channel walls is described using specular or specular-diffuse reflection laws. This approach is usually used to solve various problems of the rarefied gas dynamics [16, 17]. In the case of specular reflection, the molecule velocity component does not change along the surface, but the normal velocity component changes a sign. In the case of diffuse reflection, the reflected molecule velocity is played out according to the Maxwell distribution function with a given temperature. This temperature must correspond to the channel wall’s temperature, which may differ from the gas temperature in the general case. In specular-diffuse reflection, the fraction of molecules \( \theta \) interacts with the wall diffusely, and \((1-\theta)\) is specular, where \( \theta \) is so-called accommodation coefficient.

In confined conditions (particular in nanochannels) at initial moment of time, the coordinates \( \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N \) and velocities \( \boldsymbol{v}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{v}_N \) of all molecules considered are determined. The simulation of each molecule dynamics is split into processes. First, the position of molecule \( i \) is determined, it shifts in the configuration space in accordance with its velocity: \( \boldsymbol{r}'_i = \boldsymbol{r}_i + \boldsymbol{v}_i \tau_n \) during the time step \( n \). If a fluid molecule reaches the wall, then its further interaction with the wall is realized, while the velocity of this molecule changes. The velocity of the reflected molecule is determined in accordance with the law of interaction with the wall adopted in this particular calculation: specular, diffuse, or specular-diffuse.

If molecule \( i \) does not reach the wall, its collision with other gas molecules is played out. This procedure is realized by the same way as in the bulk (see previous section). The described procedure is repeated until the specified computation time \( \tau_s \), which is equal to: \( \tau_s = \tau_1 + \tau_2 + \cdots + \tau_k \). The result of the calculation is a complete set of coordinates and velocities of all modeled system molecules at successive times.

The SMM method [11–13] has proven itself well in modeling the transport coefficients of rarefied gases and their mixtures both, monoatomic, and also polyatomic. In all cases, the simulation accuracy was assessed by comparison with known experimental data. This accuracy was quite high even using a relatively small number of molecules, and it could be enhanced by increasing the number of molecules or independent phase trajectories used. In the case of flow in nanochannels, there are no reliable experimental data on measuring the transport coefficients. In this paper, we use the modeling of the self-diffusion coefficient \( D \) of rarefied argon at atmospheric pressure and a temperature of 273 K in order to test the SMM algorithm. Testing is possible, since the value of the self-diffusion coefficient along the channel must correspond to its value in the bulk.

The self-diffusion coefficient was calculated on the basis of FDT [4, 8, 14], which connected the self-diffusion coefficient \( D \) with the velocity autocorrelation function (VACF) \( \chi \) of the simulated gas molecules by the following relation

\[
D = \frac{1}{3} \frac{\tau}{\tau_0} \chi(0, t) dt, \quad \chi_{vv}(t) = \frac{1}{Nt} \sum_{i=1}^{N} \sum_{\alpha=1}^{l} [\boldsymbol{v}_i(t) \cdot \boldsymbol{v}_i(t + \Delta t)],
\]

(2)

here \( l \) is the number of phase trajectories, which were used to calculate the VACF and \( \Delta t \) is time integration step.

Diffusion along the channel should occur in the same way as in the bulk, since in this direction the channel is unlimited. Indeed, the VACF of gas molecules decays exponentially along the channel. The relaxation time is of the order of the molecules free path time. On the other hand, diffusion in the channel is anisotropic. The interaction of molecules with the channel walls leads to the appearance of a negative branch of the VACF. The depth of this negative tail depends on the channel height. It increases with decreasing the channel height.
Like the VACF, the self-diffusion coefficient \( (2) \) is a function of time. Under the normal conditions (in the bulk), the actual experimentally measured value of the diffusion coefficient is obtained only when function \( (2) \) reaches the plateau value. The time for reaching plateau value corresponds to the decay time of the VACF. The evolution of the argon self-diffusion coefficient along the channel, calculated using formula \( (2) \), is shown in Fig. 2a. Coefficient \( (2) \) along the channel reaches a plateau value during 15–20 free path times of the molecules. On the contrary, the evolution of the self-diffusion coefficient across the channel (see Fig. 2b) is much more complicated: first, some growth is observed, and then it decreases monotonically and tends to zero. Moreover, this happens quite quickly, the corresponding time will be determined by the channel height.

![Figure 2. Evolution of the self-diffusion coefficient along a) and across b) the channel.](image)

The isotropy absence of the molecules self-diffusion coefficient in nanochannel, described above, is quite expected. So, the SMM method gives a qualitatively physically quite reasonable result. However, its use requires a clear understanding, on the one hand, the accuracy of the calculation of the transport coefficients. On the other, it is necessary to understand how effective this algorithm is, in particular, how many molecules in a cell should be used to achieve acceptable accuracy, what should be its minimum possible size, etc. Some of the posed questions can be answered fairly accurately. It is clear that the simulation accuracy will depend on the channel length. As an example of studying this dependence in Table 1, the data of calculating argon self-diffusion coefficient in a channel with a square cross section of 10 nm\(^2\) under normal conditions were compared. In this Table, the second row shows the calculated value of the self-diffusion coefficient, and the last one shows the relative error in comparison with the experimental value [15]. The channel length \( L \) varies from 311 to 9952 nm (i.e., approximately from 0.3 to 100 μm). In the latter case, one could already expect that the self-diffusion coefficient would be close to the corresponding value in the bulk. It really turned out to be like that. The experimental value of the self-diffusion coefficient in the bulk is 0.156 sm\(^2\)/s [15], and the simulation accuracy at the maximum channel length turned out to be about one percent.

| \( L \), nm | 311 | 622 | 933 | 9952 |
|---|---|---|---|---|
| \( D \), sm\(^2\)/s | 0.192 | 0.175 | 0.168 | 0.158 |
| \( \Delta \), % | 22.95 | 12.36 | 7.46 | 1.23 |

Table 1. Accuracy of the self-diffusion coefficient calculation for different channel lengths \( L \).

| \( l \) | 100 | 200 | 500 | 1000 | 10000 |
|---|---|---|---|---|---|
| \( D \), sm\(^2\)/s | 0.1674 | 0.1633 | 0.1627 | 0.1623 | 0.1601 |
| \( \Delta \), % | 7.28 | 4.69 | 4.3 | 4.04 | 2.57 |

Table 2. Dependence of simulation accuracy on \( l \).
It is clear that, in the general case, the accuracy should essentially depend on the number of independent phase trajectories \( l \) used for averaging in stochastic modeling of phase trajectories. To study the effect of the phase trajectories number used let us consider again the self-diffusion in a square channel with a cross section of \( 777.5 \text{ nm}^2 \) and a length of 15 nm only. The number of phase trajectories varied from 100 to 10000. The corresponding data are given in Table 2. The result is quite obvious. The simulation data significantly improve with an increase in the number of ensemble members of the phase trajectories used for averaging.

4. Anisotropy of the gas viscosity in nanochannels

The anisotropy of molecules diffusion is a natural consequence of the anisotropy of nanochannel geometry (its length is much greater than the height and width). In an unrestricted environment, the root-mean-square movement of molecules grows in proportion to time. On the other hand, this distance cannot be greater than the characteristic size of the system in a limited environment. On the contrary, viscosity is usually understood as some universal characteristic of a given fluid. However, viscosity is a redistribution of momentum in a system from a molecular kinetic point of view. In confined conditions, for example, in a nanochannel, the most important factor in the redistribution of the momentum of gas molecules is their interaction with the boundaries of the system. Anisotropy also naturally arises here: the redistribution of the momentum along and across the channel should be different. This means that the viscosity must also be anisotropic.

In order, to verify this, let us consider modeling the viscosity of argon in nanochannels with a square cross section. The modeling cell was selected in the form of a rectangular parallelepiped as it had been before. The viscosity coefficient is calculated using the Green–Kubo formula

\[
\eta = \frac{1}{3VkT} \int_0^\tau \langle \sigma(0) : \sigma(t) \rangle dt, \quad \sigma(t) = \frac{1}{N_i \sum_{j=1}^l \sum_{m=1}^M m[v_i(j\Delta t)v_i(j\Delta t)]}.
\]  

The viscosity coefficient \( \eta \) of rarefied argon was simulated at atmospheric pressure and a temperature of 273 K. The channel had a square cross section, its height varied from 6.22 to 500 nm. The viscosity coefficient was averaged over a thousand independent phase trajectories, each of which was calculated for about 1 nanosecond.

![Figure 3](image)

**Figure 3.** Evolution of the normalized correlation function a) and the viscosity coefficient b) of argon along (solid line) and across (dashed line) of nanochannel.

The viscosity coefficient (3) is determined by the integral of the corresponding correlation function. The evolution of this correlation function \( \chi_n \) normalized to the initial values along and across the channel is shown in Fig. 3a. The correlation function across the channel has a characteristic negative tail caused by the molecules interaction with the wall. In this example (in Fig.
3), the interaction with the wall was described by a specular law, and the channel height was 15.55 nm. The presence of a negative tail led to the fact that the contribution to the viscosity coefficient of molecules across the channel was almost twenty times smaller than along. The corresponding values of the viscosity coefficients are shown in Fig. 3b. Thus, the total gas viscosity coefficient in the channel was almost three times lower than in the bulk.

The law of gas molecules interaction with the wall will essentially change the momentum transfer in the system. Changing the accommodation coefficient of the channel walls (their material) one may transform the viscosity of the gas in channel. The value of the viscosity coefficient across the channel for purely diffuse reflection of molecules from the wall is almost 50% higher than along, and the total coefficient of viscosity is almost three times higher than in the bulk. The gas viscosity coefficient changes more than six times, when the accommodation coefficient changes from zero to unity. The excess of the total viscosity naturally depends on the height of the channel.

5. Conclusion
This work is devoted to the development of the SMM method for modeling transport processes in rarefied gases. This method is quite simple and reproducible by almost any user. Its performance was previously demonstrated by the example of calculating the coefficients of self-diffusion, diffusion and viscosity of both, monoatomic and polyatomic gases [11-13]. This method is shown to be successfully applied to simulate the thermal conductivity coefficient in this work.

The study of the gas viscosity in nanochannel shows that the processes of momentum transfer, and hence the viscosity in such channels, are anisotropic. The average gas viscosity in a channel can be controlled by varying the wall material. Real channels usually have roughness. Their presence will significantly affect the gas flow character. In particular, the presence of roughness leads to an increase in the channel surface area. This means that anisotropy of momentum transfer in gas in such channels will be more pronounced than in a channel with smooth walls. Therefore, the presence of roughness can lead to both, an increase in viscosity or a decrease in it. The similar effect may have place when the nano-structuring of the channel walls.

It is shown that the anisotropy of momentum transfer increases with decreasing depth of the Lennard-Jones potential well and with an increase in the characteristic size of molecules. The latter one is generally a rather important factor in confined conditions, since the numerical density of the gas will significantly change at given pressure and temperature. Indeed, the characteristic volume of molecules, such as neon and xenon, differs by more than three times.

Anisotropy is characteristic of all transport processes in nanochannels. The presence of such anisotropy will significantly change the thermal conductivity of the gas. It is important to note that, with a specular law of reflection from the walls, the thermal conductivity of the gas in the channel will be lower than the corresponding value in the volume.

The main conclusion that follows from the obtained modeling data is that both, the viscosity and the thermal conductivity of gases in nanochannels are a property of the entire system “gas + channel walls”, and not just only gas. This was consistent with the conclusions, obtained by the methods of nonequilibrium statistical mechanics, where generalized fluctuation-dissipation theorems were derived that described transport processes in confined conditions [18,19].

Finally, it is important to have an answer to the question when the processes of momentum transfer become practically isotropic. Our calculations show that viscosity anisotropy can be observed not only in nano, but also in microchannels with character size of the order of certain micrometers.

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