Statistical simulation of the transport coefficients of the rarefied gases

V Ya Rudyak and E V Lezhnev
Novosibirsk State University of Architecture and Civil Engineering, 113, Lenin-gradskaya St., Novosibirsk, 630008, Russia

E-mail: lionlev@yandex.ru

Abstract. The algorithm for computation of the transport coefficients of rarefied gas is suggested. It is based on stochastic modeling of phase trajectories considered molecular systems. The Lennard-Jones intermolecular interaction potential is used. The number of operations is proportional to the number of used molecules. Naturally in this algorithm the conservation laws are performed. The efficiency of the algorithm is demonstrated by the calculation of the viscosity coefficients of several noble gases (argon, neon, xenon, krypton) and polyatomic gases (nitrogen, carbon dioxide, methane and oxygen). It was shown that the algorithm accuracy of the order of 1-2% can be obtained by using a relatively small number of molecules. The accuracy dependence on the number of used molecules, statistics (the number of the used phase trajectories) and the calculation time were analyzed.

1. Introduction
In connection with the appearance and development of computers it was possible to use them directly for modeling the properties of matter. In particular, the molecular dynamics (MD) method had been appeared. In this case the computer was used as a special tool for solving a large number of equations of motion of the molecules. However, in addition, it was also necessary to develop the special technique by means of which the data obtained (coordinates and momenta of the molecules) would be transformed into pressure, stress, transport coefficients, and so on. The nonequilibrium statistical mechanics solved this methodological problem. Firstly, in the theory of linear reaction, an idea about the connection between the transport coefficients and the time evolution of equilibrium fluctuations was formulated. Later a complete set of fluctuation-dissipation theorems connecting all transfer coefficients with correlation functions of corresponding dynamical variables was formulated [1, 2].

However MD method can not be applied for transport processes modeling of rarefied gas (we have to use a huge number of molecules). On the other hand, systematic studies of the ideology and results of the MD method have shown that it does not provide true phase trajectories of molecular systems (see [2–4]). Adequate results of MD simulations can be obtained only by averaging the corresponding dynamical variables over an ensemble of independent phase trajectories. As a result, MD simulation is a very computer-intensive process. In this connection, there appeared the idea of creating an algorithm in which the phase trajectories of the considered molecular system would not have been calculated deterministically. The aim of this paper is the realization of this idea to model the transport coefficient of rarefied gases. Ideology of this approach has been formulated in our papers [5–7] for the hard spheres system. In the present paper an algorithm is generalized for modeling the transport coefficients of rarefied gases with real intermolecular interaction potentials. The cut-off Lennard-Jones potential is...
used; this allows us to introduce the concept of the mean free path for molecules and the average frequency of collisions of molecules. Using this frequency the pair interactions of the molecules are fulfilled that lead to changing their velocities. In this case, a pair of molecules for a collision is chosen randomly, regardless of their mutual position and velocities. Thus the phase trajectories of the molecular system are modeled stochastically. However, conservation laws in the process of collision of molecules must be fulfilled. An ensemble of such independent phase trajectories is created and the transport coefficients determined by the Green-Kubo formulas are obtained by averaging over the ensemble of these trajectories.

With the help of this approach, a systematic modeling the self-diffusion, diffusion and viscosity coefficients of different gases were carried out. The noble gases, nitrogen, carbon dioxide, methane and oxygen and their mixtures were considered. It is shown that with a relatively small number of molecules it is possible to achieve accuracy comparable with the experimental one. The effect of the number of molecules and the number of used independent phase trajectories on the accuracy of calculation is studied. The simulation accuracy can be substantially increased by eliminating so named repeated collisions in the calculation cell.

2. Algorithm of the molecular collision simulation
In rarefied gas only binary collisions of molecules takes place and the molecules themselves are material points. The spatiotemporal scales of the order of the time of the molecules interaction and their size are indistinguishable. This implies that the intermolecular interaction does not contribute to the transport coefficients and the equation of state. Such contributions appear only in the next approximation for density [8]. For this reason, the transport coefficients of a dilute gas are only functions of the velocities of molecules. Therefore, to model the dilute gas dynamics, it is sufficient to consider its evolution in the space of velocities. The second important fact is that transport coefficients are calculated using the equilibrium distribution function and it is sufficient to study the dynamics of the system in local equilibrium. The transport coefficients are defined by the equilibrium correlation functions.

The interactions of the gas molecules are described by the Lennard-Jones potential

\[
U(r) = \begin{cases} 
4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} - U_c & \text{for } r \leq r_c \\
0 & \text{for } r > r_c
\end{cases}
\]

(1)

Here \( \sigma \) is the effective radius of the molecule, \( \varepsilon \) is the maximum value of the attraction energy, and \( r_c \) is the potential cut-off radius.

Since the gas is rarefied, it suffices to consider the evolution of the system only in the velocity space. At the initial time, the velocities of the molecules \( v_i \) are distributed according to the Maxwell distribution at a given temperature \( T \). Simulation of the gas dynamics starts with generating a list of velocities of the molecules at the initial time \( t \). Molecules are introduced in the list in a random order. Changing the order of the particles in the list, we will obtain different phase trajectories (this, of course, is not the only method for obtaining independent phase trajectories). Thus, at time \( t \), the molecules have velocities \( (v_1, v_2, ..., v_N) \). It is necessary to obtain the values of the molecule velocities at successive times in the simulation interval \( (t, t_\tau) \). We select the time interval \( \tau_1 = \sigma/v_{\text{max}}, \) where \( v_{\text{max}} \) is the maximum magnitude of the velocity of the molecules in the system at the given time. The generation of the list for the time \( t + \tau_1 \) starts with a consideration of molecule 1. To determine whether a molecule interact with any other molecule in time \( \tau_1 \), a random number uniformly distributed in the interval \( (0, 1) \) is generated. If, in time \( \tau_1 \), it is less than the average probability of collision \( P_{\tau_1} = 4\tau_1 m^2 \sqrt{\pi kT/m} \) (see [9]), then molecule \( j \) with which molecule 1 collides is randomly selected from the remaining \( (N - 1) \) molecules. Here \( n = N/V \) is the numerical density of the gas and \( V \) is the
volume of the simulation cell. As a result, the velocities of the colliding molecules change according to the laws of elastic collision

$$\mathbf{v'}_i = \mathbf{v}_i + (\mathbf{v}_{ij} \cdot \mathbf{e}) \mathbf{e}, \quad \mathbf{v'}_j = \mathbf{v}_j + (\mathbf{v}_{ij} \cdot \mathbf{e}) \mathbf{e},$$

where $\mathbf{v}_{ij} = (\mathbf{v}_j - \mathbf{v}_i)$ is the vector of relative velocity and $\mathbf{e}$ is the unit vector from centre of molecule $j$ to molecule 1. The actual mechanisms of the molecules interaction is described in detailed in paper [10].

If the generated number is greater than the average probability of collision, molecule 1 does not collide in the time interval $t_1$ and its velocity does not change. If it collides, the velocities of molecules 1 and $j$ in the initial list change. The remaining molecules are treated similarly. As a result, a new list of the velocities of the molecules $(\mathbf{v'}_1, \mathbf{v'}_2, ..., \mathbf{v'}_N)$ is generated.

After the generation of the list for the time $(t + t_1)$, the next time interval is selected as $t_2 = \sigma / \nu_{\text{max}}$, where $\nu_{\text{max}}$ is the maximum magnitude of the velocity of the molecules of the system at the time $(t + t_1)$ and the procedure is repeated. This procedure is repeated until the given simulation time $t_s$ equal to $t_s = t_1 + t_2 + t_3 + ... + t_N$ is reached. The calculation result is the full set of the velocities of all the molecules of the simulated system at successive times.

The algorithm input parameters are initial coordinates and velocities of the molecules, their masses, the gas density and its temperature, the number of molecules in the system, and parameters of the intermolecular interaction potential. On the other hand, the output parameters are the velocities of all molecules at successive moments of the time.

3. Transport coefficients modeling

The algorithm described was created to calculate the transport coefficients of the rarefied gas. These coefficients were calculated using fluctuation–dissipation theorems that relate transport coefficients to the evolution of the corresponding correlation functions. In the literature, these relations are called the Green–Kubo formulas [1, 2]. The identity these formulas with the relations obtained in kinetic theory of gases was proofed in papers [11, 12]. Using these formulas the coefficients of self-diffusion, diffusion and viscosity were calculated.

The self-diffusion coefficient $D$ is the integral on the autocorrelation velocity function (ACVF) $\chi$ of the modeled system

$$D = \frac{1}{3} \int_0^{t_p} \chi(0, \tau) d\tau,$$

where $t_p$ is so named plateau time of the calculation of the integral (2) [13]. ACVF is calculated over all molecules velocities at

$$\chi(0, t) = \frac{1}{N_l} \sum_{i=1}^{N_l} \sum_{j=0}^{t-1} [\mathbf{v}_i(0) \cdot \mathbf{v}(j\Delta t)].$$

Here $t = l \Delta t$, $l$ is the number of the time steps where ACVF was calculated, $\Delta t$ is the integration step, $l$ is the number of the independent phase trajectories.

The diffusion coefficient is described by the formula similar (2). The accuracy of the suggested algorithm is illustrated below on the example of the viscosity coefficient calculation. This coefficient is described by the following Green–Kubo formula

$$\eta = \frac{1}{\rho k T} \int_0^{t_p} \left\langle \sigma_{xy}(0) \sigma_{xy}(\tau) \right\rangle d\tau,$$
where \( k \) is the Boltzmann constant. The components of the total momentum flux tensor in relation (4) are calculated as

\[
\sigma_{y\sigma}(t) = \frac{1}{3!} \sum_j \sum_i \sum_{\Delta t} m[v'_i(j\Delta t)v'_j(j\Delta t)].
\]  

(5)

As the kinetic theory predicts, the correlation function \( \sigma(0,\tau) \) (5), which describes the correlations of the stress tensor, decays at times of the order of the mean free time (see figure 1). The viscosity coefficient (4) is the function of the time. Its evolution is presented in figure 2. The value of the viscosity coefficient is equal to the plateau value [13] that achieved during 5–10 mean free times (see figure 2).

Table 1 provides a comparison of the simulated and experimental [14] data of the viscosity coefficients for several gases at a temperature of 273 K and atmospheric pressure. The calculation was performed for 3200 molecules using an ensemble of one thousand independent phase trajectories. In calculations the following parameters of the Lennard-Jones potential (1) are used: \( \sigma = 0.3822 \text{ nm}, \quad \varepsilon / k = 137 \text{ K for CH}_4, \quad \sigma = 0.359 \text{ nm}, \quad \varepsilon / k = 110 \text{ K for CO}_2, \quad \sigma = 0.4484 \text{ nm}, \quad \varepsilon / k = 189 \text{ K for CO}, \quad \sigma = 0.3433 \text{ nm}, \quad \varepsilon / k = 113 \text{ K for O}_2, \quad \sigma = 0.311 \text{ nm}, \quad \varepsilon / k = 116 \text{ K for Ar}, \quad \sigma = 0.351 \text{ nm}, \quad \varepsilon / k = 190 \text{ K for Kr}, \quad \sigma = 0.178 \text{ nm}, \quad \varepsilon / k = 35.7 \text{ K for Ne and \sigma = 0.386, \varepsilon / k = 190 for Xe} [15]. Here simulated values of the viscosity coefficient \( \eta \) are given in the first line, and corresponding experimental values of \( \eta_e \) in the second. In the third line the relative error is presented. The agreement of the simulated and experimental data is very well for noble gases and for CH\(_4\) and O\(_2\). These data were obtained practically with the accuracy of their measurements. However the agreement between the experimental and calculated data for CO and CO\(_2\) is worse. In this case it is necessary to use more particles in the cell for simulation or more phase trajectories for averaging (see conclusion).

|       | CH\(_4\) | CO | CO\(_2\) | O\(_2\) | Ar | Kr | Ne | Xe |
|-------|----------|----|---------|--------|----|----|----|----|
| \( \eta \cdot 10^6 \text{(Pa·s)} \) (simulated) | 10.48    | 15.95 | 13.0   | 18.91 | 22.25 | 25.87 | 32.28 | 23.78 |
| \( \eta_e \cdot 10^6 \text{(Pa·s)} \) (experimental) | 10.37    | 16.6  | 13.8   | 19.3  | 22.7 | 25.5 | 31.7 | 23.3 |
| \( \Delta \), % | 1.06 | 3.94 | 5.84 | 2.02 | 1.97 | 1.46 | 1.84 | 2.05 |
4. Discussion and conclusion

In this paper it is shown that the proposed stochastic simulation algorithm is quite suitable for modeling transport coefficients of rarefied gases. As an example, the calculation of the viscosity coefficients for noble and polyatomic gases was considered. It is shown that in the case of polyatomic molecules, the Lennard-Jones potential can be used and satisfactory results obtained. Certainly, strictly speaking this potential is applicable for spherical molecules. Therefore the simulated data for methane are better than for carbon dioxide or carbon monoxide (see Table 1). In the last cases we need to use a larger number of molecules for simulation.

The question naturally arises whether precision can be improved by increasing the number of molecules or the number of trajectories. Table 2 shows the results of calculating the coefficient of viscosity for different numbers of particles and molecules for carbon monoxide. Relatively good results were obtained only for 12800 molecules.

The accuracy of the simulation depends also on the number of trajectories used. As the number of trajectories decreases, the accuracy of calculating the viscosity coefficient deteriorates. However, the accuracy depends not only on the number of particles and trajectories, but also on other parameters: the time to reach the plate value, the choice of the time step $\tau_i$, the accuracy of calculating the potential parameters. In the case of a rarefied gas the plateau value occurs over a time on the order of the free time, and the time step $\tau_i$ is chosen in such a way that it is much smaller than the mean free time.

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Table 2. Dependence the relative error on the number of molecules (N) and phase trajectories (l) for calculation of CO viscosity.

| N       | η·10^6 Pa·s | l  | η·10^6 (Pa·s) | Δ, % |
|---------|-------------|----|---------------|------|
|         | (simulated) |    | (experimental)|      |
| 3200    | 15.95       | 250| 15.34         | 3.94 |
| 6400    | 16.1        | 500| 15.5          | 3.03 |
| 12800   | 16.19       | 1000| 15.95        | 2.47 |

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