Stochastic method for modeling of the rarefied gas transport coefficients

V Ya Rudyak\(^1\) and E V Lezhnev\(^2\)

\(^1\) Doctor of Physics and Mathematics, Professor, Honored Worker of Higher School of Russia, member of the MAS HS, member of the American Nano Society, Head of the Department of Theoretical Mechanics NGASU (Sibstrin), Novosibirsk State University of Civil Engineering, 113, Leningradskaya Str. Novosibirsk, 630008, Russia

E-mail: valery.rudyak@mail.ru

\(^2\) Ph.D., assistant professor of higher mathematics NSTU Novosibirsk State Technical University, 20, Av. K. Marks, Novosibirsk, 630073, Russia

E-mail: lionlev@yandex.ru

Abstract. In this paper, we propose an algorithm for computation of the transport coefficients of rarefied gas, which is based on stochastic modeling of phase trajectories considered molecular system. The hard spheres 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 and diffusion coefficients of several noble gases (argon, neon, xenon, krypton). 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 (number of the used phase trajectories) and calculation time was analyzed.

1. Introduction

Transport processes in gases and liquids are due to the complex processes of energy, momentum, and mass transfer in physical space. Information on the corresponding transport coefficients is mainly obtained experimentally, although in rarefied gases, this can be done using the kinetic theory of gases [1, 2]. For dense gases and liquids, the transfer coefficients can be modeled by molecular dynamics simulations. However, to obtain sufficient calculation accuracy even in the simplest cases, it is necessary to use tens of thousands of molecules, which requires very long computation time [3].

For rarefied gases, the molecular dynamics method cannot be used to model transport coefficients because it is necessary to model very large number of particles. The using of the kinetic theory is also not a trivial task (one should be able to calculate the so-called $\Omega$-integrals, and, to obtain sufficient accuracy, it is necessary to perform the rather long and cumbersome procedure of solving the corresponding integral equations, etc.). The procedure of modeling transport coefficients could be significantly accelerated by developing a method for simulating the dynamics of molecular systems. In...
this connection it should be noted that the molecular dynamics method does not give real phase trajectories of the considered molecular system. Then, using a sufficiently large number of simulated trajectories of the initial molecular system, one can expect to obtain satisfactory data on its average characteristics such as transport coefficients (note that the same is done in molecular dynamics simulations too). The purpose of this study is to develop a simulation method suitable for modeling transport processes in rarefied and moderately dense gases. In this work, the proposed algorithm was implemented for a system of molecules in the form of hard spheres.

2. Algorithm for simulating the dynamics of molecules

For the simulation of the dynamics of a molecular system to be reasonable, it is necessary to satisfy certain conditions. In particular, in the construction of any algorithm, the conservation laws must hold. The most time-consuming process in modeling the real dynamics of a molecular system is the implementation of the free movement of the molecules and their collisions. In molecular dynamics simulations of collisions, one has to perform $N^2$ operations ($N$ is the number of molecules in the system). In the present algorithm, the collision process is assumed to occur randomly. Molecules of the simulated gas are placed in a simulation box which is a rectangular parallelepiped (or cube). Periodic boundary conditions are used to simulate the gas in the bulk. As a result, along with the main box, the evolution of all the copies surrounding it is taken into account. Initially, the molecules are distributed uniformly over the simulation volume in accordance with the predetermined number density. The velocities of the molecules are distributed according to the Maxwell distribution at a given temperature $T$,

$$f_M(v_i) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m|v_i|^2}{2kT}\right),$$

but so that the total momentum of the system of molecules is equal to zero. Here $m$ and $v_i$ are the mass and velocity of the molecule $i$, respectively. The created system is not equilibrium in general case. To reach the equilibrium state it is carried out the preliminary calculation after that the velocity distribution of the modeling molecules is the Maxwell’s one (1).

Simulation of the dynamics of a rarefied gas starts with compiling a list of molecules. At the initial time $t$, all the molecules are listed in a random order. Then, the time interval $\tau = d/v_{\text{max}}$ is chosen, where $v_{\text{max}}$ is the maximum absolute value of the velocity of molecules of the system at the given time and $d$ is the diameter of the molecule. Generation of the list for the time $\tau + t$ begins with a consideration of molecule 1. Since, in general, to calculate the transport coefficients of a rarefied gas, it is sufficient to know only the velocities of the molecules, the evolution in the physical space may not be considered (for dense gases, it should be considered). Therefore we can actually consider a spatially homogeneous system and investigate only the dynamics of change in the velocities of the molecules.

Thus, at time $t$, the molecules have velocities $(v_1, v_2, ..., v_N)$. To determine whether molecule 1 collides with another molecule in the time interval $\tau$, a random number uniformly distributed in the interval $(0;1)$ is generated. If it is less than the average probability of collision $P_{\text{coll}} = \frac{4\pi nd^2\sqrt{\pi kT}}{m}$ (see [1]) in the time interval $\tau$, then molecule $j$ which collides with molecule 1 is randomly chosen 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

$$v_i' = v_i + (v_{ij} \cdot e)e, \quad v_j' = v_j + (v_{ji} \cdot e)e,$$

where $v_{ij} = (v_j - v_i)$ is the vector of relative velocity and $e$ is the unit vector from centre of molecule $j$ to molecule 1.
If the generated number is greater than the average probability of collision, molecule 1 does not collide in the time interval $\tau_1$ 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 $(v_1, v_2, ..., v_N)$ is generated.

After the generation of the list at the time $(t + \tau_1)$, the next time interval $\tau_2 = d / v_{\text{max}}$ is chosen, where $v_{\text{max}}$ is the maximum absolute value of the velocity of molecules of the system at the time $(t + \tau_1)$ and the procedure is repeated. This procedure is repeated within the given computation time period $t_s$, which is equal to $t_s = \tau_1 + \tau_2 + \tau_3 + ... + \tau_k$. The result of the computation is the full set of the velocity coordinates of all the molecules of the simulated system at successive times.

3. Modeling of transport coefficients

The described algorithm is applied to model the transport processes in rarefied gas. In particular, using this algorithm it may be calculated the transport coefficients. In this paper the viscosity and self-diffusion coefficients were calculated. The transport coefficients of the molecular system considered are calculated using fluctuation-dissipation theorems, which relate transport coefficients to the evolution of the corresponding correlation functions. In the literature, these relations are called the Green-Kubo formulas [4].

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

$$D = \frac{1}{3} \int_0^{t_p} \chi(0, \tau) d\tau,$$  \hspace{1cm} (2)

where $t_p$ is so named plateau time of the calculation of the integral (2) [3]. ACVF is calculated over all molecules velocities at

$$\chi(0, \tau) = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=0}^{l} [v_i(0) \cdot v_j(\Delta \tau)].$$ \hspace{1cm} (3)

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

For the rarefied gas ACVF decays exponentially. The corresponding relaxation time is of the order of mean free path time, however the plateau values of the transport coefficients (the values after which they change little over time) are reached at times which are about an order of magnitude larger (25–30 of mean free path time). Comparison of the modeling and experimental data for a few inert gases (argon, neon, and krypton) shows their high accuracy (see Table 1). For example, in the simulation using an ensemble of 3200 molecules and one thousand independent phase trajectories, the accuracy of the self-diffusion coefficient was around 1–2%, which is within the experimental error.

Table 1. Comparison of simulation data of the self-diffusion coefficient $D$ with the experimental data $D_e$ [5].

|     | Ar | Kr | Ne | Xe |
|-----|----|----|----|----|
| $D$, cm$^2$/c | 0.158 | 0.081 | 0.456 | 0.049 |
| $D_e$, cm$^2$/c | 0.156 | 0.08 | 0.452 | 0.048 |
| $\Delta$, % | 1.2 | 1.2 | 0.9 | 2.1 |

The viscosity coefficient is calculated by means of the following formula
\[ \eta = \frac{1}{V k T} \int_0^T \left\langle \sigma_{xy}(0) \sigma_{xy}(t) \right\rangle \, dt, \quad \sigma_{xy}(t) = \frac{1}{3} \sum_{l=1}^{N} \sum_{i=j}^{N} m \left[ v_i^j (t \Delta) v_j^i (t \Delta) \right]. \]

The correlation of the stress tensor \( \sigma_{xy} \) decays exponentially too. The comparison of the calculated and experimental data of the viscosity coefficient \( \eta \) with the experimental value \( \eta_e \) is presented in Table 2. Here the following effective diameters \( d \) were used, for Ar \( d = 0.366 \), for Kr \( d = 0.42 \), for Ne \( d = 0.26 \), for Xe \( d = 0.494 \) nm [6]. The obtained accuracy of the determination of the viscosity coefficient is rather high.

Table 2. Comparison of simulation data of the viscosity coefficient with the experimental data \( D_e \) [5].

|        | Ar  | Kr  | Ne  | Xe  |
|--------|-----|-----|-----|-----|
| \( \eta \cdot 10^{-6} \), Pa\cdot s | 22.51 | 25.6 | 31.9 | 23.4 |
| \( \eta_e \cdot 10^{-6} \), Pa\cdot s | 22.7 | 25.5 | 31.7 | 23.3 |
| \( \Delta, \% \) | 0.8 | 0.4 | 0.6 | 0.4 |

4. Conclusions

Thus, it is shown that the proposed stochastic simulation algorithm is quite suitable for modeling transport processes in rarefied gases. It is much more cost-effective than the molecular dynamics method. The computation time is found to increase linearly with the number of molecules used.

The accuracy of the simulation is depended, of course, on the number of the molecules used. The high accuracy is realized beginning from determine number of particles. As a rule the number of needed particles should be of the order of a few thousands. It is connected with the appearance in the system so named repeated collisions (see [7, 8]). In rarefied gas such collisions are absent. We developed the special procedure to exclude these collisions. In this case the needed number of particles is reduced in times.

Another important factor that determines the accuracy of the simulation is the number of ensemble members over which the averaging is performed. Test calculations have shown that the accuracy of the calculations is \( \Delta \sim 1/\sqrt{l} \), where \( l \) is the number of ensemble members over which the averaging is performed.

Acknowledgments

This work was supported by the Russian Science Foundation (grant No. 14-19-00312).

5. References

[1] Chapman S and Cowling T G 1990 The Mathematical Theory of Non-Uniform Gases (Cambridge: Cambridge University Press) p 457
[2] Ferziger J H and Kaper H G 1972 Mathematical Theory of Transport Processes in Gases (Amsterda-London: North-Holland Publishing Company) p 550
[3] Rudyak V Ya, Belkin A A, Ivanov D A and Egorov V V 2008 High Temperature 46 30
[4] Zubarev D N 1974 Nonequilibrium Statistical Thermodynamics (New York: Consultants Bureau) p 412
[5] Physical Values. Handbook 1991 Eds Grigoriev I S and Meilikhova E Z (Moscow: Energoatomizdat) p 1234
[6] Bird G A 1976 Molecular Gas Dynamics (Oxford: Clarendon Press) p 297
[7] Gimelshtein S F and Rudyak V Ya 1991 Soviet Technical-Physics Letters 17(19) 74
[8] Rudyak V Ya 1991 Fluid Dynamics 26 p 909