

***Ab initio* simulation of transport phenomena in rarefied gases**

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Ab initio potentials are implemented into the direct simulation Monte Carlo (DSMC) method. Such an implementation allows us to model transport phenomena in rarefied gases without any fitting parameter of intermolecular collisions usually extracted from experimental data. Applying the method proposed by Sharipov and Strapasson [*Phys. Fluids* **24**, 011703 (2012)], the use of *ab initio* potentials in the DSMC requires the same computational efforts as the widely used potentials such as hard spheres, variable hard sphere, variable soft spheres, etc. At the same time, the *ab initio* potentials provide more reliable results than any other one. As an example, the transport coefficients of a binary mixture He-Ar, viz., viscosity, thermal conductivity, and thermal diffusion factor, have been calculated for several values of the mole fraction.

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I. INTRODUCTION

Intermolecular potentials are an essential part of rarefied gas dynamics and kinetic theory of gases. The most simple and widely used potential is the hard sphere model which does not contain the attractive force. This model provides the viscosity and heat conductivity proportional to the square root of gas temperature. Since such a dependence is not confirmed by experimental data, many other models were proposed, e.g., Lennard-Jones and Stockmayer potentials, which provide more physical dependence of the transport coefficient on the gas temperature. The detailed information about the potentials can be found in many books on kinetic theory of gases; see, e.g., Refs. [1–4]. These potentials were successfully implemented into a numerical solution of the Boltzmann equation [5,6] and into the direct simulation Monte Carlo (DSMC) method [7,8]. All these potentials have one or more adjustable parameters extracted from experimental data. It would be attractive to construct a theory *ab initio*, i.e., when all quantities are calculated without any experimental information, but calculations are based on the primary principles.

At present, a technique to calculate *ab initio* potentials is well elaborated and the corresponding data for monatomic gases and their mixtures can be found in the open literature; see, e.g., [9–13]. The data on diatomic gases are still restricted by the potential energy curve for one molecule; see, e.g., Refs. [14,15]. We hope that *ab initio* potentials for interaction between two diatomic molecules will appear soon. An implementation of these potentials into rarefied gas dynamics will make this theory independent of any experimental data. Since the Boltzmann equation can be solved for any potential [5,6] and the DSMC method [4] can be applied with an arbitrary potential [7], the implementation of the *ab initio* potential became possible.

The aim of the present work is to show how to implement the *ab initio* potentials into the DSMC method. As an example, the transport coefficients such as viscosity, heat conductivity, and thermal diffusion factor are calculated. Since the influence of the potential on the transport phenomena in mixtures

is stronger than in a single gas [16,17], we are going to consider a binary mixture of helium and argon. The transport coefficient values will be compared with those reported in Refs. [11,13,18,19]. The paper by Kestin *et al.* [18] reports expressions and values of the transport coefficients deduced from the Chapman-Enskog theory [2,3] of gases. The Ω integrals being a part of the expressions were interpolated using experimental data so that their method can be called semiempirical. The authors of Ref. [18] estimated the following uncertainties of the coefficients for the mixture He-Ar: viscosity $\pm 0.4\%$, heat conductivity $\pm 0.7\%$, and the thermal diffusion factor $\pm 3\%$. The authors of Ref. [19] reported numerical results of viscosity and thermal conductivity for mixtures also based on the Chapman-Enskog theory [2,3]. The Ω integrals were calculated using the *ab initio* potential given in Ref. [9]. The authors of Ref. [19] did not estimate the uncertainty of their results, but a deviation of their values from other results reaches a few percent. The papers [11,13] contain similar results but only for single gases helium and argon. The uncertainty of these data is $\pm 0.02\%$. The DSMC method employed here cannot provide so high an accuracy, but our target is the uncertainty of 0.5%, which is enough to check the reliability of our results.

II. POTENTIAL

As an example, we consider a mixture of helium with argon at the temperature 300 K. In this case, the potentials calculated in Ref. [9] can be applied, which read

$$U(r) = E_h \left[A e^{-a_1 R - a_2 R^2} - \sum_{n=3}^8 \frac{C_{2n}}{R^{2n}} \left(1 - e^{-bR} \sum_{k=0}^{2n} \frac{(bR)^k}{k!} \right) \right],$$

$$R = \frac{r}{a_0}, \quad (1)$$

where $E_h = 4.359\,744\,17 \times 10^{-18}$ J is the Hartree energy, $a_0 = 5.291\,772\,109\,2 \times 10^{-11}$ m is the Bohr radius. The potential parameters A , a_1 , a_2 , and b are taken from the last columns of Tables III, IX, and XIII of Ref. [9]. The coefficients C_n are taken from the corresponding Tables in Ref. [9]. The values of all parameters of the potentials are summarized in Table I. Moreover, the distance r_0 corresponding to the zero

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TABLE I. Parameters for the *ab initio* potential given by Eq. (1), Ref. [9].

	He-He	Ar-Ar	He-Ar
A	6.62002	82.9493	23.1693
a_1	1.88553	1.45485	1.63329
a_2	0.0639819	0.0379929	0.0462008
b	1.85822	1.62365	1.63719
C_6	1.46098	63.7520	9.38701
C_8	14.1179	1556.46	165.522
C_{10}	183.691	49437.9	3797.16
C_{12}	3.26527×10^3	2.07289×10^6	1.16518×10^5
C_{14}	7.64399×10^4	1.105297×10^8	4.66258×10^6
C_{16}	2.27472×10^6	7.24772×10^9	2.36861×10^8
r_0/a_0	5.0066	6.3745	5.8921
ϵ/k_B (K)	10.6312	139.5325	29.7296

potential, i.e., $U(r_0) = 0$, and the well depth of the potentials, i.e., $\epsilon = -\min\{U\}$, are given in Table I.

III. DEFINITIONS

A chemical composition of mixture is characterized by the mole fraction defined as

$$C = n_1/(n_1 + n_2), \quad (2)$$

where n_1 and n_2 are number densities of species. The viscosity μ is defined via the Newton law which in the particular case $u_y = u_y(x)$ and $u_x = u_z = 0$ reads as

$$P_{xy} = -\mu(\partial u_y/\partial x), \quad (3)$$

where P_{xy} is the shear stress and u_y is the bulk velocity of mixture. The heat conductivity is defined via the Fourier law. In a particular case when all species of mixture are at rest and the temperature $T(x)$ depends only on the x coordinate, this law reads

$$q_x = -\kappa(\partial T/\partial x), \quad (4)$$

where q_x is the x component of the heat flux. If a mixture being at rest is subject to a temperature gradient $\partial T/\partial x$, then a mole fraction gradient is established, which is related to the temperature gradient as

$$(\partial C/\partial x) = -(k_T/T)(\partial T/\partial x), \quad (5)$$

where k_T is the thermodiffusion ratio coefficient. Instead of this coefficient one often works in terms of the thermal diffusion factor defined as

$$\alpha_T = k_T/[C(1 - C)]. \quad (6)$$

We are going to calculate the transport coefficients μ , κ , and α_T of the mixture He-Ar by the DSMC method [4] applying the *ab initio* potential (1).

IV. METHOD OF SOLUTION

In order to calculate the transport coefficients, a one-dimensional problem is solved. Let us consider a mixture confined between two infinite parallel plates fixed at $x = \pm H/2$. For our purpose, the equilibrium pressure p_0 value

does not matter, but it must be sufficiently large to guarantee the hydrodynamic regime, i.e., the rarefaction parameter

$$\delta = p_0 H / (\mu v_0), \quad v_0 = \sqrt{2k_B T_0 / m} \quad (7)$$

must be high. Here v_0 is the characteristic molecular speed and $m = C m_1 + (1 - C) m_2$ is the mean molecular mass. In the calculations, the rarefaction parameter was larger than 40. To reach this value, the calculations were carried out for $H = 1$ m and for the pressure p_0 varied from 0.5 to 1 Pa by varying the mole fraction from $C = 0$ (single Ar) to $C = 1$ (single He).

The DSMC method for an arbitrary potential applied to a single gas is described in our previous paper [7]. Here, only the differences for a mixture will be described. To apply a potential like that given by Eq. (1), it should be cut off, i.e., a maximum impact parameter $b_{M,\alpha\beta}$ when a collision between species α and β happens must be assumed. Then the total cross section will be given as $\sigma_{\alpha\beta} = \pi b_{M,\alpha\beta}^2$. Following the no time counter method [4], the number of pairs to be tested for collisions is given as

$$N_{\text{coll}} = N_\alpha(N_\alpha - 1)F_n\sigma_{\alpha\alpha}g_{m,\alpha\alpha}\Delta t/(2V_c), \quad \alpha = 1, 2 \quad (8)$$

for an interaction between the same species, and

$$N_{\text{coll}} = N_\alpha N_\beta F_n \sigma_{\alpha\beta} g_{m,\alpha\beta} \Delta t / V_c, \quad \alpha \neq \beta \quad (9)$$

for an interaction between the different species. Here, N_α and N_β are numbers of model particles of species α and β in a cell, F_n is the representation of model particle, $g_{m,\alpha\beta}$ is the maximum relative velocity between molecules of species α and β , Δt is the time increment, and V_c is the cell volume. Among N_{coll} of randomly chosen pairs, those satisfying the condition $g_{\alpha\beta}/g_{m,\alpha\beta} > R_n$ are selected for collision, where $g_{\alpha\beta}$ is the relative velocity of this pair and R_n is the random number varying from 0 to 1.

Once a pair of particles is selected for collision, their velocities are changed according to the classical theory of binary collision; see Chap. 2 of Ref. [4]. The deflection angle χ determining the direction of the relative velocity $\mathbf{g}_{\alpha\beta}$ after a collision depends on the dimensionless kinetic energy of collision defined as

$$E_{\alpha\beta} = \frac{m_\alpha m_\beta g_{\alpha\beta}^2}{2(m_\alpha + m_\beta)\epsilon_{\alpha\beta}}, \quad (10)$$

where $\epsilon_{\alpha\beta}$ is given in Table I for each kind of collisions. Since the calculation of the deflection angle χ for a binary collision needs significant computational effort, it is precalculated and stored in computer memory as was proposed in Ref. [7]. The regularly distributed values of the energy are considered, i.e.,

$$E_{j,\alpha\beta} = (j - 0.5) \frac{E_{m,\alpha\beta}}{N_E}, \quad (11)$$

where $1 \leq j \leq N_E$, $E_{m,\alpha\beta}$ is the maximum energy for a $\alpha - \beta$ collision and N_E is an integer. The impact parameter values $b_{i,\alpha\beta}$ are distributed as

$$b_{1,\alpha\beta} = \frac{b_{M,\alpha\beta}}{\sqrt{2N_b}}, \quad b_{i,\alpha\beta} = \sqrt{b_{i-1,\alpha\beta}^2 + \frac{b_{M,\alpha\beta}^2}{N_b}}, \quad (12)$$

where $2 \leq i \leq N_b$, $b_{M,\alpha\beta}$ is the impact parameter cutoff and N_b is an integer. To choose the deflection angle χ_{ij} of a pair

selected for a collision the following rules are used:

$$i = N_b R_n + 1, \quad j = \frac{E_{\alpha\beta}}{E_{m,\alpha\beta}} N_E + 1, \quad (13)$$

where R_n is a random number and $E_{\alpha\beta}$ is the dimensionless energy of this pair.

For a binary mixture, three matrices of the deflection angle χ_{ij} are calculated for the three kinds of collisions, i.e., He-He, Ar-Ar, and He-Ar, applying the potential (1) with the data given in Table I and using the following parameters: $E_{m,\alpha\beta} = 600$, $N_E = 600$, $b_M = 3r_0$, $N_b = 900$. The values of r_0 are given in Table I for each kind of collisions. It was verified that the fraction of collisions having the energy $E_{\alpha\beta} > E_{m,\alpha\beta}$ is about 10^{-8} . Further increases of E_{\max} and $b_{M,\alpha\beta}$ do not change the results within 0.5%.

To calculate the viscosity coefficients, the mixture is perturbed by a motion of the plates, i.e., the plate at $x = -H/2$ moves with a speed $U_w/2$ in the y direction, while the other plate moves in the opposite direction with the same speed. The temperatures of the plates are kept constant and equal to T_0 . The speed of the plate should be small enough in order to maintain the equilibrium temperature in the middle between the plates. An analysis showed that the speed $U_w = 0.2v_0$ does not affect the temperature within 0.2%. According to the definition (3), to calculate the viscosity coefficient the shear stress $P_{\alpha\beta}$ and the bulk velocity gradient $\partial u_y/\partial x$ are needed. The shear stress P_{xy} is calculated for each cell during the simulation of the free motion of model particles, i.e., the momentum of all particles crossing a cell is counted and summed. The velocity gradient was calculated in the middle of the gap for the range $-0.25H \leq x \leq 0.25H$. This range does not include the Knudsen layers near the plates. To reduce the statistical scattering of the viscosity up to the desirable uncertainty 0.5% the number of samples was 10^5 .

To calculate the heat conductivity coefficients, the mixture is perturbed by a temperature deviations of the plates, i.e., the plate at $x = -H/2$ is maintained at a temperature $T_0 + \Delta T/2$, while the other plate is maintained at a temperature $T_0 - \Delta T/2$. The temperature difference ΔT should be small enough in order to avoid a nonlinear term contribution into the heat flux q_x . An analysis showed that the temperature difference $\Delta T = 0.2T_0$ satisfies this condition. The heat conductivity was extracted from Eq. (4). The heat flux q_x is calculated for each cell during the simulation of the free motion, i.e., the energy of all particles crossing a cell is counted and summed. The temperature gradient is calculated in the range $-0.25H \leq x \leq 0.25H$ excluding the Knudsen layer. The thermal diffusion factor α_T is calculated from Eqs. (5) and (6). In this case only the gradients of the mole fraction and of the temperature are needed which are calculated also in the range $-0.25H \leq x \leq 0.25H$. The number of samples 5×10^4 guarantees the statistical scattering of the heat conductivity and thermal diffusion factor less than 0.5%.

In calculations of both viscosity and heat conductivity, the gap between plates was divided in 400 cells. The number of model particles was 40 000, i.e., about one hundred per cell. The time increment was $\Delta t = 0.002H/v_0$. Test calculations with larger numbers of cells and particles and with a smaller time increment showed that the above given values guarantee the numerical error less than 0.5%.

TABLE II. Viscosity μ of mixture He-Ar vs mole fraction C .

C	μ ($\mu\text{Pa s}$)			$\Delta\mu/\mu$ (%)			
	DSMC	[11,13]	[18]	[19]	[11,13]	[18]	[19]
0.	22.68	22.669	22.83	22.772	0.05	0.7	0.4
0.25	23.22		23.33	23.169		0.5	0.2
0.5	23.53		23.67	23.420		0.6	0.5
0.75	23.18		23.30	23.057		0.5	0.5
1.	19.91	19.910	20.04	20.172	<0.02	0.7	1.3

V. RESULTS

The calculations were carried out for the mole fraction C equal to 0, 0.25, 0.5, 0.75, and 1 at the temperature 300 K. The values of the viscosity μ and heat conductivity κ are reported in the second columns of Tables II and III, respectively. The results of Refs. [11,13] and Refs. [18] and [19] are given in the third, fourth, and fifth columns of these tables, respectively. The deviations of the values obtained in the present work from those reported in the previously published papers are given in the sixth, seventh, and eighth columns. First, the comparison with the most exact results Refs. [11,13] available in the literature shows that the viscosity was calculated with the quite high accuracy, i.e., 0.05%. The accuracy of the heat conductivity is slightly worse but it is still high 0.2%, i.e., it is within the planned uncertainty 0.5%. If one compares the results obtained in Refs. [11,13] with those reported in Ref. [18] for single gases He and Ar, one concludes that the uncertainty 0.3% of the viscosity declared in Ref. [18] is not confirmed, but the uncertainty of both viscosity and heat conductivity is 0.7%. Thus, if we compare the present results with those reported by Kestin *et al.* [18], we conclude that they are in agreement with the results of Ref. [18] within the accuracy 0.7%. The deviation of the present data on the viscosity from the results by Song *et al.* [19] is within our numerical error 0.5% for all values of the mole fraction except $C = 1$. The disagreement of the present results on the heat conductivity with those reported in Ref. [19] is significant and reaches 2.5%. Since the results by Song *et al.* diverges significantly with those reported in Refs. [11,13,18], we conclude that their uncertainty is about 2.5%.

The thermal diffusion factor α_T has not been calculated for the *ab initio* potential previously. Thus, the *ab initio* results on this quantity presented in Table IV are reported. They are compared only against data reported in Ref. [18] obtained by the semiempirical method with the uncertainty 3%. It can be

TABLE III. Heat conductivity κ of mixture He-Ar vs mole fraction C .

C	κ (mW/m K)			$\Delta\kappa/\kappa$ (%)			
	DSMC	[11,13]	[18]	[19]	[11,13]	[18]	[19]
0.0	17.74	17.709	17.83	17.789	0.2	0.5	0.3
0.25	32.60		32.71	31.797		0.3	2.5
0.5	54.34		54.36	52.976		0.04	2.5
0.75	89.63		89.28	88.284		0.4	1.5
1.0	155.52	155.66	156.66	157.71	0.1	0.7	1.4

TABLE IV. Thermal diffusion factor α_T of mixture He-Ar vs mole fraction C .

C	α_T		$\Delta\alpha_T/\alpha_T$ (%)
	DSMC	[18]	
0.25	0.3222	0.3144	2.4
0.5	0.3849	0.3865	0.4
0.75	0.4887	0.5026	2.8

seen that the present results are in agreement with those reported in Ref. [18] within the accuracy of 3% declared in that paper.

VI. CONCLUSION

The *ab initio* potential has been implemented into the direct simulation Monte Carlo method. Such an implementation allows us to calculate gas flows at any rarefaction *ab initio*, i.e., no parameter usually extracted from experimental data is needed. The implementation of the *ab initio* potential requires practically the same computational effort as an application

of the widely used molecular models such as hard spheres, variable hard sphere, variable soft sphere, etc. Thus, if *ab initio* potentials for a specific gas or for a specific mixture are known, the other models of potential can be dispensed.

As an example of the implementation, the viscosity, heat conductivity, and thermal diffusion factor were calculated with the uncertainty of 0.5% for a helium-argon mixture. The viscosity and heat conductivity were calculated with a higher accuracy than that in the previously published paper [19] based on the Chapman-Enskog method applying the same potential. The values of the thermal diffusion factor have been calculated on the basis of the *ab initio* potential. The reported numerical results can be used for verification of model kinetic equations and new methods to solve the Boltzmann equation. In the future, the benchmark problems for rarefied gas dynamics formulated in Ref. [20] will be solved by the method elaborated in the present work.

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