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The triple collisions of molecules

Yu.I.Khlopkov^{1,2}, Zay Yar Myo Myint^{*2}, A.Yu.Khlopkov²

¹Central Aerohydrodynamic Institute (TsAGI), Zhukovsky, (RUSSIA)

²Department of Aeromechanics and Flight Engineering, Moscow Institute of Physics and Technology (State University), Zhukovsky, (RUSSIA)

E-mail : zayyarmyomyint@gmail.com

ABSTRACT

The concept of elastic collisions plays an important role in physics, as collisions often have to deal with physical experiment in the field of atomic phenomena. The interaction of particles may be a variety of processes. The process of collision is to change the properties of the particles as a result of interaction. In this paper present the kinetics equations for triple collision of molecules and the results for triple molecular before and after collisions. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Molecular collision;
Kinetics equations;
Boltzmann equations;
Liouville equations.

INTRODUCTION

Basic state of gases determined by interaction of molecules each other and with the boundaries of the solid or liquid bodies. The concept of elastic collisions plays an important role in physics, as collisions often have to deal with physical experiment in the field of atomic phenomena. The interaction of particles may be a variety of processes. The process of collision is to change the properties of the particles as a result of interaction^[1,2]. Conservation laws provide an easy way to set the ratio between the various physical quantities in the collision of particles. In this paper we consider the interaction of molecules with potential for pair and triple elastic collisions of particles.

KINETIC EQUATIONS FOR TRIPLE COLLISIONS OF MOLECULES

Gas properties with noticeable influence of triple

collisions will differ from the usual properties due to the collision of the particles each other and with the solid surface.

In accordance to Gibbs formalism one considers not a single system, but the ensemble of them in $6N$ dimensional, G -space, with system's distributed according to the N -particle distribution function $f(t, \bar{r}_1, \bar{r}_2, \dots, \bar{r}_N, \bar{v}_1, \bar{v}_2, \dots, \bar{v}_N) = f_N$ of which the sense is that of a probability for a system to be in the time moment t at the point $\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N, \bar{v}_1, \bar{v}_2, \dots, \bar{v}_N$ in vicinity of $d\bar{r}_1, \dots, d\bar{r}_N, d\bar{v}_1, \dots, d\bar{v}_N$. We have^[3]

$$dW = f_N d\bar{r}_1 \dots d\bar{r}_N d\bar{v}_1 \dots d\bar{v}_N$$

Such an ensemble is described by the famous Liouville equation:^[3]

$$\frac{\partial f_N}{\partial t} + \sum_{i=1}^N v_i \frac{\partial f_N}{\partial r_i} + \sum_{i \neq j} \sum_{i=1}^N \frac{F_{ij}}{m} \frac{\partial f_N}{\partial v_i} = 0, \quad F_{ij} = -\nabla U_{ij}.$$

And beginning with that moment the Liouville equa-

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tion and all other kinetic equations following from the *Bogoljubov's* chain, including the last link—*Boltzmann* equation—possess the probabilistic nature. And in spite of the fact that *Liouville equation* is simpler than system *dynamical system equation*, it takes into consideration the N -particle collisions of molecules and also remains to be extremely complicated for a practical analysis.

The transition to a less detailed level of description is connected with the further coarsening of system's description with the help of s -particle distribution functions $f_s = \int f_N d\bar{r}_{s+1} \dots d\bar{r}_N d\bar{v}_{s+1} \dots d\bar{v}_N$, which determine the probability of the simultaneous revelation of s particles independently of the state of the remaining $(N-s)$ particles. Following the ideas of *Bogoljubov* one obtains the chain of interconnected equations:

$$\frac{\partial f_s}{\partial t} + \sum_{i=1}^s v_i \frac{\partial f_s}{\partial r_i} + \sum_{i=1}^s \sum_{j=1}^s \frac{F_{ij}}{m} \frac{\partial f_s}{\partial v_i} = - \sum_{i=1}^s (N-s) \frac{\partial}{\partial v_i} \int \frac{F_{ij}}{m} f_{s+1} dr_{s+1} dv_{s+1},$$

For pair molecular collision, it can write

$$\frac{\partial f_2}{\partial t} + \sum_{i=1}^2 v_i \frac{\partial f_2}{\partial r_i} + \sum_{i=1}^2 \sum_{j=1}^2 \frac{F_{ij}}{m} \frac{\partial f_2}{\partial v_i} = - \sum_{i=1}^2 (N-2) \frac{\partial}{\partial v_i} \int \frac{F_{ij}}{m} f_{2+1} dr_{2+1} dv_{2+1}$$

For triple

$$\frac{\partial f_3}{\partial t} + \sum_{i=1}^3 v_i \frac{\partial f_3}{\partial r_i} + \sum_{i=1}^3 \sum_{j=1}^3 \frac{F_{ij}}{m} \frac{\partial f_3}{\partial v_i} = - \sum_{i=1}^3 (N-3) \frac{\partial}{\partial v_i} \int \frac{F_{ij}}{m} f_{3+1} dr_{3+1} dv_{3+1}$$

Now let's see kinetic equation with taking into account triple collision of molecules. The statistical independence of particles before collision, solution of equation is^[4]

$$f_3(t, \tau_1, \tau_2, \tau_3) = f_1(t_0, \tau_{10}) f_1(t_0, \tau_{20}) f_1(t_0, \tau_{30}) .$$

where $\tau_{a0} = \tau_{a0}(t, t_0, \tau_1, \tau_2, \tau_3)$ – coordinate and impulse values which particles at the moment t_0 for that at the time t get into given points τ_1, τ_2, τ_3 of the phase space.

Now, let's move from f_1 to $f = Nf_1$, and find kinetic equation in the form of

$$\frac{\partial f}{\partial t} + \bar{\xi} \nabla f = S_{t_2} f + S_{t_3} f ,$$

$S_{t_2} f(t, \tau_1) = \int \frac{\partial F_{12}}{m} \frac{\partial}{\partial \xi} \{ S_{12} f(t, \tau_1) f(t, \tau_2) \} d\tau_2$ - Integral for pair collisions

$$S_{t_3} f(t, \tau_1) = \frac{1}{N} \int \frac{F_{123}}{m} \frac{\partial}{\partial \xi} \{ R_{123} f(t, \tau_1) f(t, \tau_2) f(t, \tau_3) \} d\tau_2 d\tau_3 \quad -$$

Integral for triple collision

here S_{12} and R_{123} – some operators. Let's consider a few of collision processes taking into account integral. First of all, the operator R_{123} is zero, if at least one of the particles does not interact with the others. The pro-

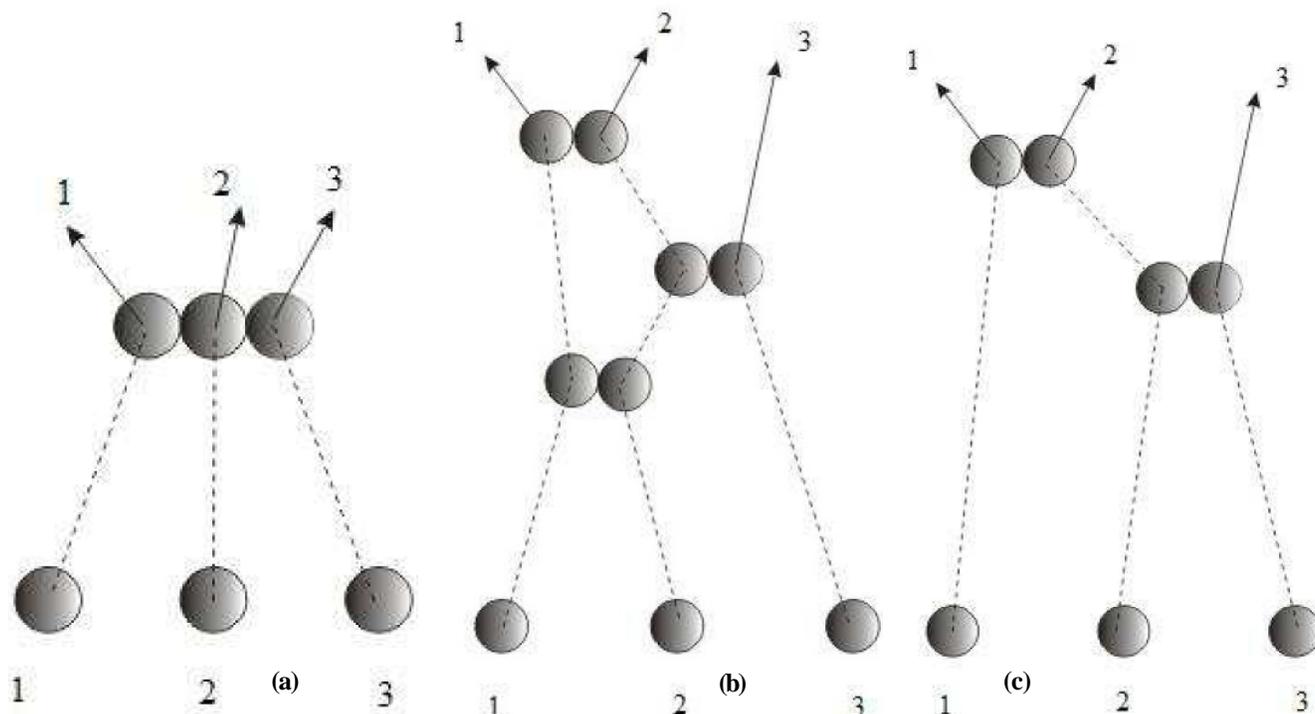


Figure 1 : The basic trajectories of triple collisions of molecules^[4,5]

cess $R_{123} \neq 0$ is not only the triple collisions, but also combination of several pair of molecules. We consider several types of collisions (Figure 1a,b,c).

Let's see the distribution function by modeling the triple collisions of the molecules. The total number of particles $N = 9 \times 10^5$ in vessel. Figures 2-3 show the distribution of the velocity of the molecules before and after collisions. From the graphs, it is clear that the velocity distribution of the molecules before and after collision is the same. Elastic collision is defined as collision in which there is no exchange between the translational

and internal energies.

Triple collisions will occur, after colliding as pair molecular collisions. Although the Lennard-Jones potential and is used in simulations of liquid and solids, strictly speaking, the molecular interaction at high densities is no longer a pair collision.

Generally speaking, at molecular level it is necessary to consider interaction potentials, using electron-nuclear representations. Empirical potential dependences reflect the fact, that attractive forces at large distance and repulsive forces at short distances. This feature is reflected most simply with Lennard-Jones potential^[1]. The sixth power is decrease of potential simulate electro-statistical dipole-dipole and dispersive attraction. The twelfth-power repulsive potential is decreased from reasons of mathematical convenience. At the same time, it models rigid enough reputation

$$U(r) = 4\epsilon \left[\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 \right]$$

when $r = d$ the potential is equal to zero. The value ϵ characterizes the depth of a potential hole of the one electron volt. This feature is most simply reflects Lennard-Jones potential. It's shown that this potential qualitatively can be described the behavior of aerodynamics research.

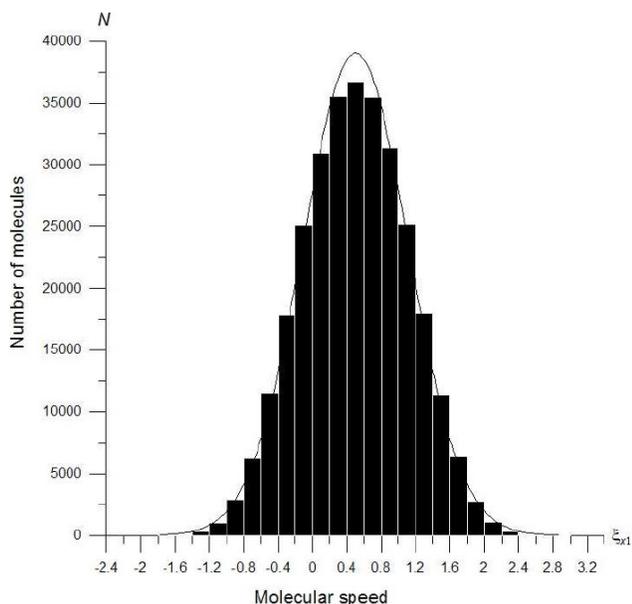


Figure 2 : Velocity distribution function before collisions

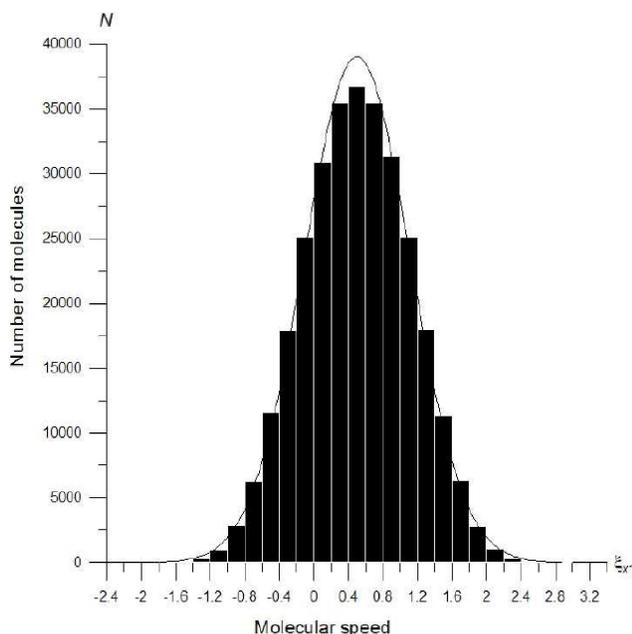


Figure 3 : Velocity distribution function after collisions

CONCLUSIONS

In condensed mediums, to consider the collisions of molecules, the environment affects on the molecules. So, the solid argon contribution to the energy of the triple collisions can reach 10 %^[6]. However, taking into account the triple collisions of molecules computationally too expensive to simulate in rarefied gas dynamics approach^[7].

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REFERENCES

- [1] N.M.Kogan; Rarefied Gas Dynamic, New York, Plenum, (1969).
- [2] G.A.Bird; Molecular Gas Dynamics and the Direct Simulation of Gas Flows, Oxford University Press,

Full Paper

- (1994).
- [3] O.M.Belotserkovskii, Yu.I.Khlopkov; Monte Carlo Methods in Mechanics of Fluid and Gas, World Scientific Publishing Co. New Jersey, London, Singapore, Beijing, Hong Kong, (2010).
- [4] E.M.Lifshitz, L.P.Pitaevskii; Physical Kinetics, Moscow, Fizmatlit, (in Russian), (2002).
- [5] Zay Yar Myo Myint, Kyaw Zin; About the triple molecular collision, Conf.Proc. of MIPT, (in Russian), 156-158 (2009).
- [6] B.M.Axilord, E.Teller; Interaction of the van der Waals' type between three atoms, J.Chem.Phys., **11**, 299-300 (1943).
- [7] Yu.I.Khlopkov, A. Yu.Khlopkov, Zay Yar Myo Myint; Modelling of processes of triple collisions of molecules, International Research and Practical Conference, Science, education and technology: results of 2013, Donetsk, Ukraine, 49-54 (2013).