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SUPEREQUILIBRIUM INCREASE OF A CHEMICAL TRANSFORMATION IN THE DETONATION FRONT AND OTHER EFFECTS IN DETONATION WAVE INITIATED BY A SHOCK WAVE

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ABSTRACT

The Monte Carlo non-stationary method of statistical simulation (MCNMSS) (another name DSMC) was used in calculations. Non-stationary case of forming a detonation wave in the shock tube was considered. It was supposed that chemical reaction $A+M \rightarrow B+M$ ($M=A, B$ and C) took place. The ratio of molecular masses of gases A , B and C was:20:20:1. Different thresholds of the reaction were considered. For the case of low reaction thresholds, velocity of detonation wave was higher than Chapman-Jouguet velocity. A quasi-stationary region of the flow inside product beside the front with unchangeable values of parameters took place. Increase of the reaction threshold led to disappearance of the quasi-stationary region and a rise of something like to an expansion wave with peaks of parameters of flow at the leading edge of the detonation wave. The meanings of these parameters remain constant with time. Velocity of detonation wave became appreciably lower than Chapman-Jouguet velocity. Farther increase of the reaction threshold led to disappearance of detonation. The reactions $A+B \rightarrow B+B$ and $A+C \rightarrow B+C$ were very important for initiation of detonation

Keywords: detonation wave, shock tube, threshold of the reaction

INTRODUCTION

The Monte Carlo non-stationary method of statistical simulation (MCNMSS) (another name DSMC) with variable weight factors (see Genich *et al.*, 1992, Kulikov and Serikov, 1993, Kulikov, 1999) was used in calculations. The idea of the method was proposed by G. A. Bird (1976). The method takes into account all the details of mass and heat- transfer automatically. Development of computers permits now to simulate by MCNMSS a gas processes in which a local mean free path of molecules (l) is much less than a local character size of this process (L) except a small region where $l \sim L$. Detonation in the shock tube is one of a such processes. Numerical study of a process of forming a detonation wave in the gas on the molecular process level gives a lot of useful information. Simulation of a stationary detonation front was

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accomplished in (Anderson and Long, 2003, O'Conner *et al.*, 2005) for the case of low initial temperature. Interesting attempt of simulation of non-stationary detonation for 1D and 2D cases were undertaken in (Walenta and Teodorczyk, 2005) But, a taken large size of the spatial cell can lead to false results. Work of Kulikov and Ternovaia (2007) presents results of non-stationary detonation simulation when detonation was initiated by shock wave. In this case the chemical reaction from works of Anderson and Long (2003), O'Conner *et al* (2005) was taken. More real case was considered in presented work.

STATEMENT OF PROBLEM

Non-stationary case of forming a detonation wave in the shock tube was considered. Simulation was carried out in the one-dimensional coordinate space and in the three-dimensional velocity space. At an initial moment, the low-pressure channel (LPC) of a shock tube was filled with a gas *A*. And the high-pressure chamber (HPC) was filled with a gas *C*. Cross-sections of HPC and LPC and initial temperatures of gases *A* and *C* were the same (T_1). At the beginning of the simulation the ratio of pressures in HPC and in LPC was equal to 100. The simulation started after removing a diaphragm between these parts of the shock tube. It was supposed that chemical reaction $A+M \rightarrow B+M$ ($M=A, B$ and C) took place. The ratio of molecular masses (m_i) of gases *A*, *B* and *C* was:20:20:1. This is analogue to the case of internal molecular energy release.

The energy release in reaction Q was equal to $50 kT_1$ (k is the Boltzmann constant). This is a half of energy release in complex chemical process $H_2+0.5O_2 \rightarrow H_2O$ if T_1 is equal to room temperature. It was supposed that a collision of two particles leads to the reaction if the total energy of their relative motion is higher than the threshold of the reaction. All considered molecules were treated as hard spheres with equal diameters (d) without internal structure. Particles reflected elastically from walls at boundaries of the simulation region.

METHOD OF SIMULATION

Used method (MCNMSS) employs weight factors (see Genich *et al.*, 1992, Kulikov, 1999 and scheme 2 in Kulikov and Serikov, 1993). In order to the size of spatial cell (Dx) did not exceed l in the gas, the value of spatial cell in HPC was 20 times smaller than the value of that in LPC at the beginning. During the simulation, that part LPC where molecules have entered from HPC, got new cells the value of which was 20 times smaller than the value of old sells. The initial average number of model particles per cell (N) was equal to 360 both in LPC and in HPC, initial $Dx = 0.15$ in LPC. Here and bellow distance is normalized to mean free path in LPC at the initial moment (l_1). The time of splitting of collision and displacement stages was $\Delta t = 0.04$. Here and bellow time is normalized to the ratio l_1/u , where u is the most probable thermal velocity of molecules of component *C* at the beginning. The initial average number of model particles per cell was equal to 360 both in LPC and HPC.

Parallel calculations were carried out by means of a multi-processor computer. Domain decomposition of a simulation region was performed (see Kulikov and Ternovaia, 2004). The modeled region spreads from 0 to 5631.75 Boundary between LPC and HPC was placed at $x=4882.5$. And 200 processors were used. Standard Message Passage Interface (MPI) was used to communicate data between processors (see Snir. *et al.*, 1998).

RESULTS

In considered case mass of reagent m_A is equal to mass of product $m_B=m$. And there is the Hugoniot analytical relation:

$$p_2/p_1 = (4 + 2Q/kT_1 - n_1/n_2)/(4 n_1/n_2 - 1).$$

Here, indices 1 and 2 refer to parameters ahead of and behind a wave, p_i is a pressure and n_i is a numerical density of a gas. This formula is from (Anderson and Long, 2003). It is easy to obtain from this analytical expression of the Chapman-Jouguet condition. If we denote $z=2Q/kT_1$ then we obtain this expression

$$n_1/n_2 = \{[2(z+5) - (4z^2 + 15z)^{1/2}]/10\}.$$

Expression for velocity of detonation D_* in this case is

$$D_*/u = \{(m_c/m)[(T_2/T_1) - (n_1/n_2)]/[2(n_1/n_2)(1 - (n_1/n_2))]\}^{0.5}$$

It gives the following parameters of the Chapman-Jouguet condition for our case: $n_2/n_1=1.59$, $p_2/p_1=68.28$, $T_2/T_1=42.91$, $D_*=2.12$. Here and below velocities are normalized to u .

Figs 1-5 show the results obtained at the moment of time 2047.15 for the thresholds of the reaction (Q_{AB}) which was equal to $26kT_1$.

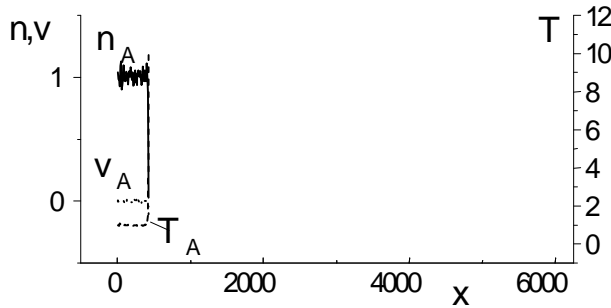


Fig. 1. Results for $Q_{AB}=26kT_1$.

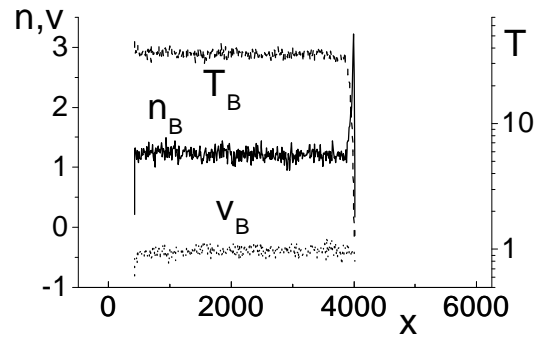


Fig.2. Results for $Q_{AB}=26kT_1$.

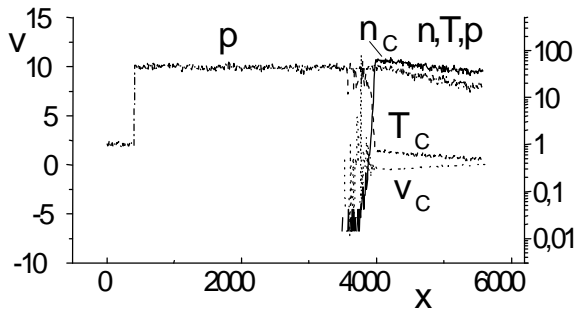


Fig.3. Results for $Q_{AB}=26kT_1$.

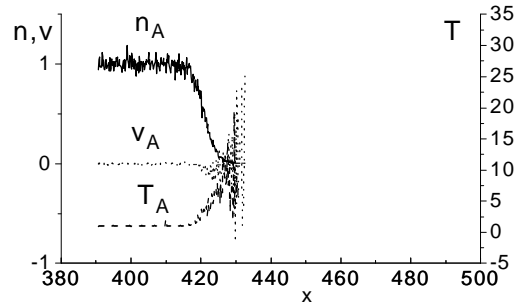


Fig.4. Detailed structure of the front for $Q_{AB}=26kT_1$

Figs 1-3 show the profiles of the concentration (n), kinetic temperature (T), longitudinal velocity (v)

for reagent (Fig.1), product (Fig.2) and gas C (Fig.3). Fig.3 also shows the profiles of total pressure (p). Here and below n , T and p are normalized by corresponding initial values for reagent. One can see a forming a quasi-stationary region of the flow inside product beside front. Parameters of the flow remains unchanged in the region: $n_2/n_1 \approx 1.25$, $p_2/p_1 \approx 48$ $T_2/T_1 \approx 37$, being approximately 20, 30 and 6% lower than those characteristics of the Chapman-Jouguet point; at the same time, the mean detonation velocity is 1% higher, $D=2.14$. This is a case of weak detonation. One can see penetration of small amount of gas C into product B.

The results which were presented in figs 1-3 are sampled via spatial intervals approximately $9l_1$. But the size of spatial cell is equal to $0.15l_1$. Figs 4-5 show detailed structure of detonation front and present meaning of parameters in each cell.

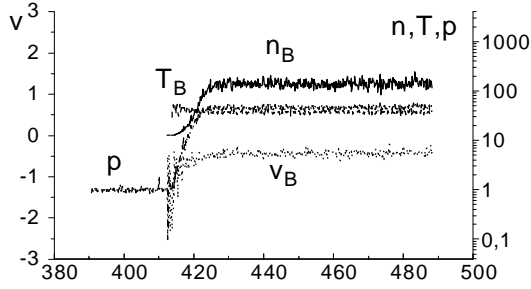


Fig.5. Detailed structure of the front for $Q_{AB}=26kT_1$.

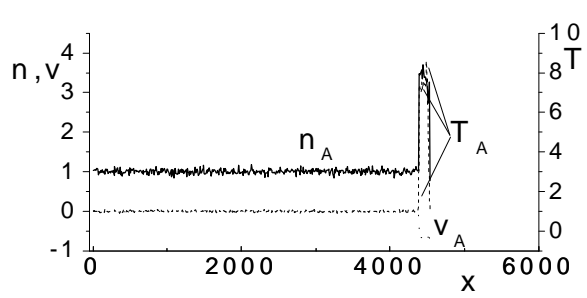


Fig.6. Results for reagent at the moment 531.65 ($Q_{AB}=130kT_1$).

One can see monotony of profiles of all parameters and considerable difference of T_A and T_B . This difference indicates high translational non-equilibrium. Similar difference of T_A and T_B was obtained by O'Conner *et al.* (2005). Zeldovich-Von Neuman-Doering (ZND) pressure profile with peak is absent. It should be noted stationarity of the front structure.

An analytical evaluation of top values of the time of decrease of initial reagent concentration by 1/8 (Dt_c) was made. Equilibrium velocity distribution of molecules, absence of relative motion of components and invariability of temperatures were assumed. It was also supposed that $T_1=1$, $k=0.5$, $T_A=1.6$, $T_B=45$ (see Figs 4-5). One can show that relative velocity distribution of pairs of molecules A and B looks like equilibrium with effective temperature $T_{AB} = (m_A T_A + m_B T_B)/(m_A + m_B) = (T_A + T_B)/2 = 23.3$.

Evolution of concentration of reagent A follows to equation:

$$dn_A/dt = -k_A (n_A)^2 - k_B n_A (n_A^1 - n_A)$$

Here n_A^1 is initial n_A , k_A and k_B are rate constants, expressions for which are easy to obtain from (Bird, 1976) (see formulas 4.2 and 12.2) remembering that a collision of two particles leads to the reaction if the total energy of their relative motion is higher than the threshold of the reaction.

$$k_i = m_e d^2 (16kT p / m/2)^{0.5} (Q_{AB}/kT + 1) \exp(-Q_{AB}/kT).$$

According to normalization $d = 0.0968$.

Final expression is:

$$(1/b_2) \ln[n_A / (b_1 n_A + b_2)]|_1^2 = -t|_1^2.$$

Here $b_1 = k_A - k_B$, $b_2 = k_B n_A^l$.

This leads to $Dt_C=7.5$. One can obtain from Fig. 5 that evaluation of the time of decrease of initial reagent concentration by 1/8 as a result of simulation (Dt_S) is equal to 4, so, $Dt_C/Dt_S \approx 2$. One can suppose from this result deviation of relative velocity distribution from Maxwell profile. If to suppose complete equilibrium ($T_A=T_B$) then $Dt_C/Dt_S \approx 55$. So translational non-equilibrium increase the rate of chemical reaction in the leading part of detonation front.

Next, simulations was carried out for $Q_{AB}=130 kT_1$. Figs 6-8 show the results obtained at the moment of time 531.65. Shock wave and aborning detonation wave are seen clear in Figs 6, 7.

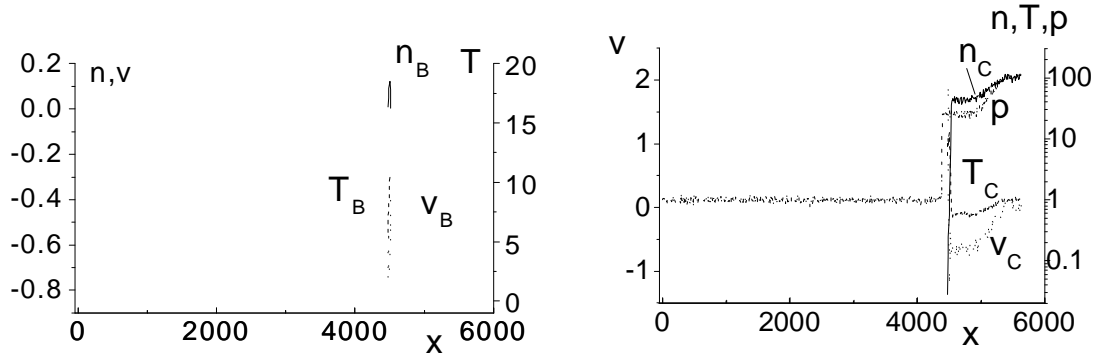


Fig.7. Results for product at the moment 531.6 ($Q_{AB}=130kT_1$)

Fig.8. Results for gas C at the moment 531.65 ($Q_{AB}=130kT_1$)

Figs 9-13 show the results obtained at the moment of time 2710.75. One can see a developed detonation.

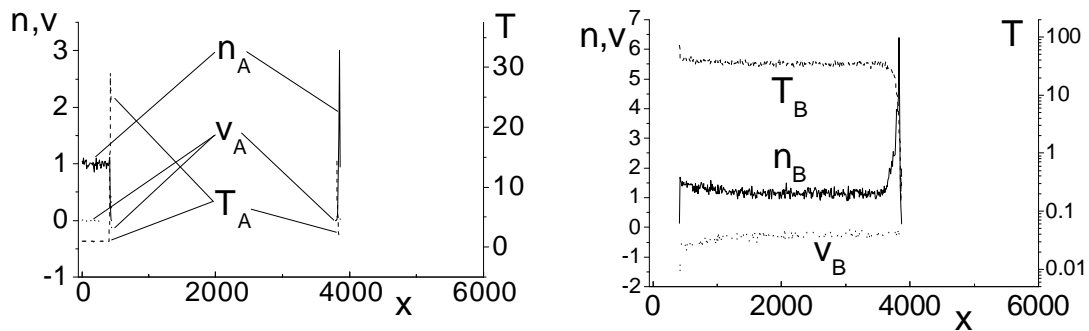


Fig.9. Results for reagent at the moment 2710.75 ($Q_{AB}=130kT_1$).

Fig.10. Results for product at the moment 2710.75 ($Q_{AB}=130kT_1$).

The residue of reagent is revealed near $x=3850$ (Fig.9). The increase of Q_{AB} has led to the disappearance of the quasi-stationary region in the leading part of detonation wave (compare Figs 2 and 10). Instead the region one can see something like an expansion wave (see profile of v_B in Fig. 10). The obtained maximum values of parameters are: $n_2/n_1 \approx 1.5$, $p_2/p_1 \approx 55$, $T_2/T_1 \approx 40$. The mean value of D 1.85 is essentially lower than Chapman-Jouguet velocity (by 13%). It should be noted a peak of n_B in the end of the product placement region which was and in the case of $Q_{AB}=26 kT_1$.

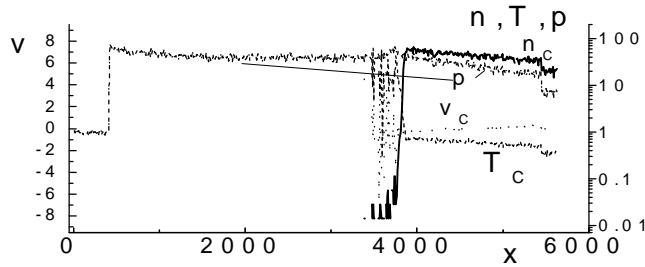


Fig.11. Results for gas C at the moment 2710.75 ($Q_{AB}=130kT_1$).

Figs 12, 13 show detailed structure of detonation front and present values of parameters in each cell.

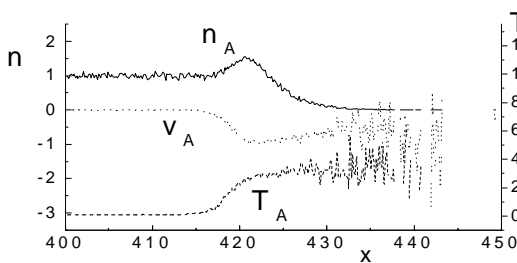


Fig. 12. Detailed structure of the front for reagent at the moment 2710.75 ($Q_{AB}=130kT_1$).

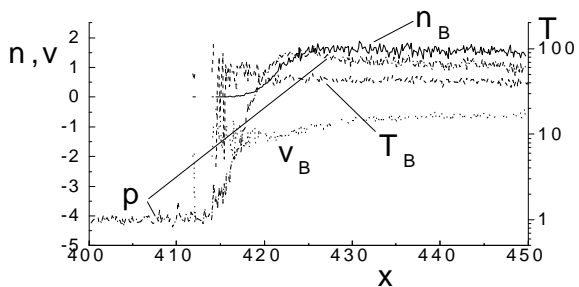


Fig. 13. Detailed structure of the front for product at the moment 2710.75 ($Q_{AB}=130kT_1$).

Stationarity of the detonation front structure is revealed and in this case. A monotony of profiles of n_A is absent. Considerable difference of T_A and T_B persist and in this case. The pressure profile is differed considerably from ZND profile as in the case for $Q_{AB}=26kT_1$. A correct evaluation of Dt_C/Dt_S isn't possible in the case for $Q_{AB}=130kT_1$ according to non-monotony of profiles of n_A . But due to the difference of T_A and T_B , translational non-equilibrium must increase the rate of chemical reaction in the detonation front.

Simulation was carried out also for $Q_{AB}=130kT_1$ without taken into account reaction $A+B \rightarrow B+B$. It was supposed that reactions $A+A \rightarrow B+A$ and $A+C \rightarrow B+C$ took place only. In this case, simulation was continued up to 5976.7. And detonation wasn't obtained. A burning took place in this case and burning wave was behind shock wave.

Besides, simulation was carried out for $Q_{AB}=130kT_1$ without taken into account reaction $A+C \rightarrow B+C$. It was supposed that reactions $A+A \rightarrow B+A$ and $A+B \rightarrow B+B$ took place only. In this case, simulation was continued up to 4724.65. Detonation wasn't obtained also. Only a little amount of reagent was converted in product. So interaction of of reagent with gas C from HPC is very important for initiation of detonation. This fact isn't evident in advance.

Next, simulation was carried out for $Q_{AB}=150kT_1$. All reactions were taken into account. In this case, simulation was continued up to 5030.75. And detonation wasn't obtained. A burning took place in this case and burning wave was behind shock wave.

CONCLUSION

Velocity of detonation wave is higher than D^* when $Q_{AB}=26kT_1$. And one can see a quasi-stationary region of the flow inside product beside front with unchangeable values of parameters. Increase of the reaction threshold leads to disappearance of the quasi-stationary region and a rise of something like to an

expansion wave with peaks of parameters of flow at the leading edge of the detonation wave. The meanings of these parameters are time-constant with accuracy of statistical dispersion of results. Velocity of detonation wave becomes appreciably lower than D^* . Farther increase of the reaction threshold ($Q_{AB} \geq 150kT_I$) leads to disappearance of detonation.

After formation of the front, its structure and values of parameters don't changed during time of simulation with accuracy of statistical dispersion of results. The pressure profile is differed considerably from Zeldovich-Von Neuman-Doering profile. Due to the difference of T_A and T_B , translational non-equilibrium increases the rate of chemical reaction in the detonation front.

The reactions $A+B \rightarrow B+B$ and $A+C \rightarrow B+C$ are very important for initiation of detonation.

We believe that importance of the reaction with B as second body for initiation of detonation and the difference of T_A and T_B will be found also in 3D simulation.

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APPENDIX I.

Let us consider a mixture of two components A and B with different temperatures T_A and T_B . The gases remain motionless relatively each other.

Rate constant of chemical interaction of these components is (see in book of Bird (1976), section 4.3)

$$k_B = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} gS(g) \frac{(m_A m_B)^{3/2}}{(2pk)^3 (T_A T_B)^{3/2}} \exp[-m_A c_A^2 / (2kT_A) - m_B c_B^2 / (2kT_B)] dc_A dc_B. \quad (1)$$

Here, m_i is mass, \mathbf{c}_i – velocity of molecule of component i , $S(g)$ is cross-section of chemical interaction for considered case. Relative velocity of molecules g is equal to $|\mathbf{c}_A - \mathbf{c}_B|$. Let us use more convenient variables:

$$\begin{aligned}\mathbf{g} &= \mathbf{c}_A - \mathbf{c}_B; \\ \mathbf{c}_m &= (m_A \mathbf{c}_A + m_B \mathbf{c}_B) / (m_A + m_B).\end{aligned}\tag{2}$$

It is well known that Jacobian of this transformation (see, for example, section 4.3 in book of Bird (1976))

$$\partial(\mathbf{c}_A, \mathbf{c}_B) / \partial(\mathbf{g}, \mathbf{c}_m) = 1.$$

It is easy to obtain from equation (2):

$$\begin{aligned}\mathbf{c}_A &= \mathbf{c}_m + m_B / (m_A + m_B) \mathbf{g}; \\ \mathbf{c}_B &= \mathbf{c}_m - m_A / (m_A + m_B) \mathbf{g}.\end{aligned}\tag{3}$$

After using (3), equation (1) is transformed into:

$$k_B = \int_{-\infty}^{+\infty} \left\{ \int_{-\infty}^{+\infty} g S(g) f(g, \mathbf{c}_m) \exp[-m_r c_m g \cos(q) \left(\frac{1}{T_A} - \frac{1}{T_B}\right) / k] d\mathbf{c}_m \right\} dg,$$

where $m_r = m_A m_B / (m_A + m_B)$,

$$\begin{aligned}f(g, \mathbf{c}_m) &= p \exp\left[-\frac{c_m^2}{2k} \left(\frac{m_A}{T_A} + \frac{m_B}{T_B}\right) - \frac{m_r g^2}{2k} \left(\frac{m_B}{m_A + m_B} \frac{1}{T_A} + \frac{m_A}{m_A + m_B} \frac{1}{T_B}\right)\right], \\ p &= \frac{(m_A m_B)^{3/2}}{(2pk)^3 (T_A T_B)^{3/2}},\end{aligned}$$

$\cos(\theta)$ is an angle between vectors \mathbf{g} and \mathbf{c}_m .

Then we use a frame of reference in which axis “z” coincides with vector \mathbf{g} , integrate over φ and θ for \mathbf{c}_m and use obtained results: $\int_0^{2p} dj = 2p$ and

$$\int_0^p \sin q \exp(-qc_m \cos q) dq = [\exp(qc_m) - \exp(-qc_m)] / q,$$

where $q = m_r g \left(\frac{1}{T_A} - \frac{1}{T_B}\right) / k$. As a result, we obtain:

$$k_B = \int_{-\infty}^{+\infty} g S(g) h(g) \frac{1}{q} \left\{ \int_0^{+\infty} c_m [\exp(-rc_m^2 + qc_m) - \exp(-rc_m^2 - qc_m)] dc_m \right\} dg, \quad (4)$$

where $r = (m_A T_A + m_B T_B) / (2k)$, $h = 2p \exp[-\frac{m_r^2 g^2}{2k} (\frac{1}{m_A T_A} + \frac{1}{m_B T_B})]$. Integration in figure brackets of (4) gives:

$$\int_0^{+\infty} c_m [\exp(-rc_m^2 + qc_m) - \exp(-rc_m^2 - qc_m)] / q dc_m = q \pi^{1/2} \exp[q^2 / (4r)] / (2r^{3/2}). \quad (5)$$

If we take into account expression (5), make integration over φ and θ in (4) using for \mathbf{g} a spherical frame of reference and execute several transformations we obtain:

$$k_B = \int_0^{+\infty} g S(g) g^2 \frac{4(m_r)^{3/2}}{p^{1/2} (2kT_{AB})^{3/2}} \exp[-m_r g^2 / (2kT_{AB})] dg,$$

where $T_{AB} = (m_A T_B + m_B T_A) / (m_A + m_B)$. It is clear that distribution G_{AB} of relative velocities g for pairs containing one molecule of component A and one molecule of component B is:

$$G_{AB} = g^2 \frac{4(m_r)^{3/2}}{p^{1/2} (2kT_{AB})^{3/2}} \exp[-m_r g^2 / (2kT_{AB})]. \quad (6)$$

It is easy to see that in the case of equality of temperatures G_{AB} becomes usual equilibrium distribution (see, for example, formula (4.33) in book of Bird (1976)). In the case of equality of molecular masses $T_{AB} = (T_A + T_B) / 2$.

APPENDIX II. NOTATION

The following symbols were used:...

- c velocity of molecule
- c module of molecular velocity
- c_m velocity of center masses of pair molecules
- c_m velocity module of center masses of pair of molecules
- D velocity of detonation
- D^* velocity of classical Chapman-Jouguet detonation
- \mathbf{g} relative velocity of molecules
- g module of relative velocity of molecules
- d diameter of molecule
- k Boltzmann constant
- k_A rate constants of chemical interaction reactant with reactant
- k_B rate constants of chemical interaction reactant with product
- m mass of molecule
- n numerical density
- p pressure of mixture

Q energy release in reaction
 Q_{AB} thresholds of the reaction
 T temperature
 t time
 T_{AB} effective temperature of chemical interaction reactant with product
 T_w temperature of hot flat end
 v longitudinal velocity of component
 Δt splitting time
 Δx size of cell
 l mean free path of molecules

Subscripts

1 ahead of the front
 2 behind the front
 A for reactant
 B for product

Superscripts

1 ahead of the front