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CHEMICAL REACTIONS, HEAT EXCHANGE AND FAST PARTICLES

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We give results of a numerical and analytical study of the effect of the "tails" of the distribution function, i.e., the solution of the model Bkhatnagar—Gross—Krook equation, on the rate of a high-threshold reaction and on the heat flux.

It is known that many chemical reactions have a high energy barrier and take place in collisions of molecules whose velocities of motion are much larger than the average thermal velocity. The validity of the Chapman—Enskog solution of the Boltzmann equation which is the basis for the Euler equation, Navier—Stokes equation, etc., is limited by the conditions $k = l_0/L \ll 1$, $mc^2 \sim 2 \varkappa T$ (see, e.g., [1, 2]). Taking into account large energies of translational motion of the particles requires that one gives up the familiar concepts about the properties of kinetic equations for $k \ll 1$. In particular, the molecular distribution function f of molecules which interact with potential $U_{ij} = B_{ij} r^{1-s}$, $s > 2$, differs considerably from the Maxwell distribution f_0, and is nonlocal for $c > c^* = c_T k^{-\beta/2}$, $\beta = (s-1)/(s+1)$. It is important to note for a further investigation that in the last estimate, the Knudsen number is determined from the scale of change of the gas parameters (e.g., its temperature) by a magnitude.

Thus, one can expect that in spatially inhomogeneous flows, the rate constant of a high-threshold reaction will differ considerably from the equilibrium value [2]. In addition, the increase of k reduces the region in the space of molecular velocities where the difference between f and f_0 is small, and where the Chapman—Enskog solution is valid. This in turn is reflected in the increase of the direct effect of the "tail" properties of the distribution functions on the gas dynamics.

The direct effect here means the effect of the deviation of f from the Chapman—Enskog solution on the reaction rate, heat flux, stress tensor, etc., which are calculated from f. We note that the effect can also be indirect. For example, because of the change in the description of the kinetics of high-threshold reactions, the solution will give different concentration fields of the components and, as a result, different values of the transfer coefficients. This phenomenon will not be considered here. In this work we use the example of heat exchange between two infinite parallel plates at temperature T_{1w} and $T_{2w} > T_{1w}$ in the

TABLE 1. Comparison of the Analytical and Numerical Solutions

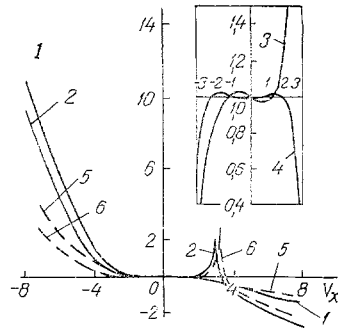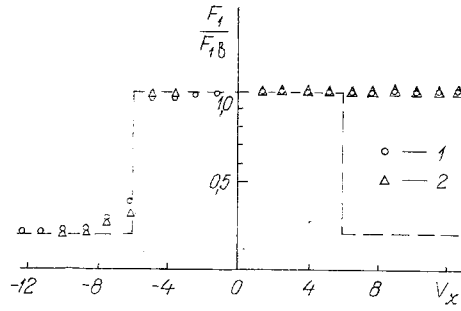| V_x		2,5	5,0	7,5	10	12,5
$x_1 = 0,265$	$\Phi^{(+)}_{1,num}$	0,882	0,364	0,142	0,0655	0,0347
$k = 0,0245$	$\Phi^{(+)}_{1,an}$	0,888	0,369	0,143	0,0659	0,0348

Fig. 1   Fig. 2

Fig. 1. Deviation of the Maxwell and Navier—Stokes distribution functions for $k = 0.0245$: 1) $\log F_1/F_{01}$; 2) $\log F_1/|F_{1NS}|$; 3) F_{01}/F_1; 4) F_{1NS}/F_1 for $x_1 = 0.265$; 5) $\log F_1/F_{01}$; 6) $\log F_1/|F_{1NS}|$ for $x_1 = 0.171$.

Fig. 2. Nonlocal form of the distribution function for $V_x < 0$, $k = 0.0245$: 1) $x_1 = 0.27$; 2) 0.71.

situation when the heat-conduction coefficient λ is proportional to T, to consider the following problems:

1) Properties of the distribution function (solution of the model Bkhatnagar—Cross—Krook (BGK) equation) for large velocities of translational motion of the molecules.

b) The effect of these properties on the Chapman—Enskog result for the rate of a high-threshold reaction and the heat flux.

The choice of the heat-conduction problem for the BGK equation is made for two reasons: firstly, because of the simple formulation and availability of proven methods for the solution. Second, the Chapman—Enskog result for the heat flux in the case of a planar heat flux in a molecular gas with $\lambda \sim T$ contains only one Navier—Stokes term [3].

The model BGK equation is [4]

$$c_x \frac{\partial f}{\partial x} = An(f_0 - f), \quad f_0 = n(m/2\pi\varkappa T)^{3/2} \exp(-mc^2/2\varkappa T).$$

Before the solution, we introduce dimensionless variables ($f = n_* c_T^{-3} F$, $n_* L = \int\limits_0^L n dx$, $c_T = (2\varkappa T_{1W}/m)^{1/2}$, $\eta = n/n_*$, $x = Lx_1$, $s = \int\limits_0^{x_1} \eta dz$, $c = c_T V$) and average over the velocity components V_y and V_z with weights 1 and $V_\perp^2 = V_y^2 + V_z^2$ ($F_1 = \int F d\mathbf{V}_\perp$, $F_2 = \int F V_\perp^2 d\mathbf{V}_\perp$). As a result, we obtain the equations

$$kV_x \frac{\partial F_i}{\partial s} = F_{0i} - F_i, \quad F_{0i} = \eta\tau^{a_i} \pi^{-1/2} \exp(-V_x^2/\tau), \tag{1}$$

where $\tau = T/T_{1W}$, $k = c_T(An_*L)^{-1}$, $a_1 = -0.5$, $a_2 = 0.5$. The coordinate $s = 0$ corresponds to the plate with temperature $\tau_{1W} = 1$.

The heat flux Q, density, and temperature can be expressed in terms of F_i as follows:

$$Q = \int \frac{mc^2}{2} c_x f dc = n_*\varkappa T_{1w} c_T q, \quad q = \int\limits_{-\infty}^{+\infty} (V_x^3 F_1 + V_x F_2) dV_x,$$

$$\eta = \int\limits_{-\infty}^{+\infty} F_1 dV_x, \quad \frac{3}{2}\eta\tau = \int\limits_{-\infty}^{+\infty} (V_x^2 F_1 + F_2) dV_x.$$

The reflection of the molecules from the films will be assumed diffusive at the temperature of the surface. Equations (1) were solved numerically by the method developed in [5].
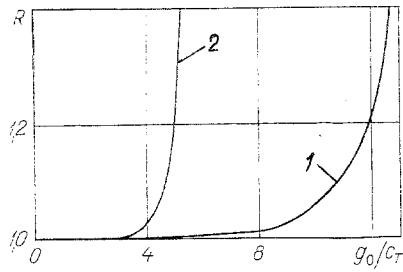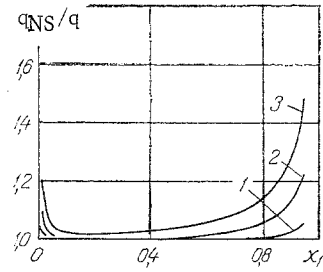
Fig. 3

Fig. 4

Fig. 3. The effect of the deviation from the Maxwell distribution function on the chemical reaction rate: 1) $x_1 = 0.36$; 2) 0.17; $k = 0.0245$.

Fig. 4. The deviation from the Chapman—Enskog result for the heat flux: 1) $k = 0.008$; 2) 0.033; 3) 0.67.

Properties of the Distribution Functions F_i

for Large Velocities of Molecules

Assuming that $k \ll 1$ and $V_x = 0$ (1), outside the Knudsen layers one can construct an approximate solution of Eqs. (1) with error $O(k^2)$,

$$F_i = F_{i0} - kV_x \frac{\partial F_{i0}}{\partial x} + \cdots = F_{i0}\left[1 - kV_x\left(\frac{V_x^2}{\tau} + a_i - 1\right)\frac{d\ln\tau}{ds} + \cdots\right], \tag{2}$$

which corresponds to the solution of Eqs. (1) by the Chapman—Enskog method in the Navier—Stokes approximation. For $|V_x| \sim k^{-1/3}$, this solution loses its accuracy. In addition, for $V_x = V_{x0}$, $1 \simeq (kV_{x0}^3/\tau^2)d\tau/ds$ the function F_i, defined by expressions (2), changes sign.

All this indicates that the region of validity of (2) is limited to velocities for which $kV_x^3 \ll 1$ [1, 2]. However, for a finite temperature difference and not too small k, the velocity $v_{x0} = V_{x0}\tau^{-1/2}$ (the quantity $v = c(m/2\varkappa T)^{1/2}$ determines the contribution of molecules with velocities of order c to the macroscopic quantities) is not very large. For $k = 1/30$ and $\tau_{2w} = 4$ at a point where $\tau = 2.5$, we have $v_{x0} = 2.7$. Therefore, for an accurate discussion of the heat exchange in these conditions it is in general necessary to refrain from an unconditional use of the solution (2).

Using this remark we shall construct the solution of Eqs. (1) under the sole assumption that k is small. By writing F_i in the form of a product $F_i = F_{i0}\Phi_i$, we obtain for Φ_i the equation

$$kV_x \frac{\partial\Phi_i}{\partial s} + A_i\Phi_i = 1, \quad A_i = 1 + kV_x\left[\frac{d\ln\eta}{ds} + \left(\frac{V_x^2}{\tau} + a_i\right)\frac{d\ln\tau}{ds}\right], \tag{3}$$

whose solution will be written in the integral form

$$\Phi_i^{(+)} = \Phi_{iw1}\exp\left(-\int_0^s \frac{A_i d\sigma}{kV_x}\right) + \frac{1}{kV_x}\int_0^s \exp\left(-\int_\sigma^s \frac{A_i dz}{kV_x}\right)d\sigma, \quad V_x \geqslant 0, \tag{4}$$

$$\Phi_i^{(-)} = \Phi_{iw2}\exp\left(-\int_1^s \frac{A_i d\sigma}{kV_x}\right) - \frac{1}{kV_x}\int_s^1 \exp\left(\int_s^\sigma \frac{A_i dz}{kV_x}\right)d\sigma, \quad V_x < 0. \tag{5}$$

Outside the Knudsen layers,

$$A_i = A_i^* = 1 + kV_x(V_x^2/\tau + a_i - 1)d\ln\tau/ds + \cdots \tag{6}$$

Using (6), it follows from (4) that in the internal points of the flow, the influence of the "cold" surface on $\Phi_i^{(+)}$ is exponentially small, and for $\Phi_i^{(+)}$ we have the following expression which is valid uniformly for all $V_x > 0$:

$$\Phi_i^{(+)} = \frac{1}{A_i^*} + \frac{kV_x}{A_i^{*3}}\frac{dA_i^*}{ds} + 3\frac{k^2 V_x^2}{A_i^{*5}}\left(\frac{dA_i^*}{ds}\right)^2 - \frac{k^2 V_x^2}{A_i^{*4}}\frac{d^2 A_i^*}{ds^2} + O(k^2). \tag{7}$$

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It can be shown that this expression is nothing else but an expansion of $\Phi_i^{(+)}$ in powers of $k^{2/3}$. A comparison of the solution, whose error is $O(k^{4/3})$ and which is given by the first two terms from the right in (7), with the numerical solution gives a good agreement (see Table 1). The expansion of (7) for $V_x = 0$ (1) leads to the familiar Chapman—Enskog solution.

The description of the functions $\Phi_i^{(-)}$ is more difficult. To facilitate the discussion below, we note that outside the Knudsen layers and for sufficiently large magnitudes of the velocities $V_x < 0$ the quantity $A_i^*(s, V_x)$ falls with decreasing s. Therefore, in the velocity region $V_{xi}^{(1)} < V_x < 0$, where $V_{xi}^{(1)} \simeq O(k^{-1/3})$ is determined from the condition $A_i^*(s, V_{xi}^{(1)}$ (s)) $= 0$, the functions $\Phi_i^{(-)}(s, V_x)$ are local and are given by the expansions (7). In this region, $A_i^*(\sigma, V_x) > 0$ for $s \le \sigma$.

For $V_x < V_{xi}^{(1)}$, the functions $\Phi_i^{(-)}(s, V_x)$ become nonlocal. The main contribution to the second term from the right in (5) comes here from the neighborhood of the point s_0, where $A_i^*(s_0, V_x) = 0$, $s < s_0$. In this case, using estimates by the saddle-point method, we find for $\Phi_i^{(-)}$

$$\Phi_i^{(-)} \simeq - \frac{1}{kV_x} \exp \left(\int_s^{s_0} \frac{A_i^* \, dz}{kV_x} \right) \sqrt{- \frac{2kV_x \pi}{A_{i0}^{*\prime}}} \gg 1, \quad A_{i0}^{*\prime} = \left(\frac{dA_i^*}{ds} \right)_{s=s_0}, \tag{8}$$

and hence we have for $F_i^{(-)}$

$$F_i^{(-)}(s, V_x) = F_{i0}(s_0, V_x) \sqrt{- \frac{4\pi}{A_{i0}^{*\prime} kV_x}} \exp \left(\frac{s_0 - s}{kV_x} \right) \gg F_{i0}(s, V_x).$$

The region of applicability of (8) in the molecular velocity space is bounded by the velocity $V_{xi}^{(2)}$ for which the maximum of the function $W_i(\sigma) = - \int_s^\sigma A_i dz$ coincides with $\sigma = 1$. For $V_x < V_{xi}^{(2)}(s)$, we obtain from (5)

$$\Phi_i^{(-)}(s, V_x) = (\Phi_{iwz} + H_i) \exp \left(\int_s^1 A_i d\sigma / kV_x \right) \gg 1,$$

where $H_i = - (1/kV_x) \int_s^1 \exp \left(- \int_\sigma^1 A_i dz / kV_x \right) d\sigma > 0$ and $H_i \sim 1$. A simplification of H_i is hindered by a logarithmic singularity of A_i for $s \to 1$.

The form of F_1 is shown in Fig. 1 on the example of a calculation of the distribution function of molecular velocities at several points between the plates. We note the sharp increase of $\Phi_1^{(-)}$ with increasing absolute value of the velocity, and a sufficiently fast decrease of $\Phi_1^{(+)}$ with increasing v_x. It is clear that this agrees with expressions (7) and (8). It is significant that, in contrast with the Chapman—Enskog solution, $\Phi_1^{(+)}$ is here always positive.

The nonlocal form of $\Phi_1^{(-)}$ and local form of $\Phi_1^{(+)}$ at large absolute values of V_x are shown in Fig. 2 by a comparison of the theoretical data on the distribution function for diffusely reflecting plates (unperturbed solution), and also when the distribution function of molecules reflected from the surface has the form

$$f_{w per} = n_r (m/2\pi\varkappa T_r)^{3/2} \exp (- mc^2/2\varkappa T_r) \{ 1 + 5\chi [(V_x - V_w) \operatorname{sgn} V_x] \},$$

where $\chi(z)$ is the Heaviside function equal to zero for $z < 0$, and to unity for $z \ge 0$. The quantity n_r is found from the condition of no through flow. For the reasons of nonlocality for $V \sim k^{-1/3}$ when the range $l(V) = l_0 V \sim l_0 k^{-1/3} \sim L k^{2/3} \ll L$, see [1, 2].

Contribution of the Deviation from the Chapman—Enskog

Solution to Macroscopic Quantities

The effect of the strong perturbation of f_0 for $V \gg 1$ on the kinetics of high-threshold reactions in the present case is shown in Fig. 3, which gives the results of the calculation of the ratio R of the true rate of the model reaction to the local equilibrium value

$$R = \int f_1 f_2 g_{12} d\sigma_{12}^R \, d\mathbf{c}_1 d\mathbf{c}_2 [\int f_{10} f_{20} g_{12} d\sigma_{12}^R d\mathbf{c}_1 d\mathbf{c}_2]^{-1}.$$

Here $g_{12} d\sigma_{12}^R = \chi(g_{12,x} - g_0) U_0 b\, db$, $\mathbf{g}_{12} = \mathbf{c}_1 - \mathbf{c}_2$ is the relative velocity; χ, Heaviside step function; b, impact parameter of the collision, $b < b_0 = \text{const}$; and U_0, characteristic velocity. The functions $f_1(\mathbf{c}_1)$ and $f_2(\mathbf{c}_2)$ used here were the solutions of the model equation constructed earlier. This is possible if the chemical reaction has no effect on the form of f for $c \gtrsim g_0/2$ because of the smallness of the inelastic collision cross section. The increase of R for large values of the ratio $g_0/c_T = g_0(m/2\varkappa T)^{1/2}$ can be explained by the large magnitude of Φ_1 for negative values V_x, $|V_x| \gg 1$.

The equation of the BGK model is considerably simpler than the Boltzmann equation. The properties of f for $V \gg 1$ and their implications are, therefore, studied more easily by using the model equation. However, these solutions cannot be used a priori to obtain exact results on the perturbation of the equilibrium kinetics of high-threshold reactions in spatially non-uniform flow, but only for qualitative estimates. This is because the true distribution function (the solution of the Boltzmann equation) is considerably distorted at high velocities of molecules. This fact was clarified in the study of the effect of the tail properties of f on the heat exchange.

It was noted above that the Chapman—Enskog expression for the heat flux in the case of planar heat exchange in a gas with $\lambda \sim T$ contains only one Navier—Stokes term $(-\lambda dT/dx)$ [3]. Figure 4 shows the results of the calculation of the ratio $(-\lambda dT/dx)/Q$, where $\lambda = 2.5 \varkappa^2 T/Am$ is the thermal conductivity for the BGK model, and the gas temperature in λ and dT/dx is obtained by a numerical solution of Eqs. (1) for $\tau_{2W} = 4$.

It is seen from the data that the deviation from the Navier—Stokes (or Chapman—Enskog) results for the heat flux is due here mainly to the properties of the flow in the Knudsen layers near the plates, rather than to a deviation from the Chapman—Enskog solution for f outside the Knudsen layers. Indeed, in this case the deviation of $(-\lambda dT/dx)/Q$ from unity would be larger near the cold plate because of the large values of the local temperature gradient. A possible explanation is given below.

The fact that the BGK model equation for $f(\mathbf{x}, \mathbf{c})$ does not contain molecular velocities of directions other than $\mathbf{c}$ (which makes it possible to reduce the original equation to closed equations for the function $F_1(x, c_x)$) is, unfortunately, the reason for the strong distortion of the properties of the true distribution function at large molecular velocities. Indeed, this property of the BGK model leads to the fact that in the present one-dimensional formulation, the quantity V_* (the "limit" of large deviation from f_0) is given by the condition

$$L_x(V_*) = L/V_*^2 \sim l_x(V_*) = l_0 V_* \cos \vartheta, \tag{9}$$

where $L_x(V)$ is the scale of the variation of f_0 in the direction of x for $c \sim c_T V$, and ϑ is the angle between $\mathbf{c}$ and the x axis. It follows from (9) that V_* depends appreciably on the direction of $\mathbf{c}$

$$V_* \sim k^{-1/3} \cos^{-1/3} \vartheta. \tag{10}$$

When using the Boltzmann equation, the perturbation which occurs in some direction $\mathbf{c}$ is transferred to the whole spectrum of directions of motion of the molecules. As a result, an estimate for V_* loses the angular dependence, and the region in the velocity space where the difference between f and f_0 is small reduces considerably, particularly for finite angles between $\mathbf{c}$ and the x axis. This increases the effect of a strong perturbation of f_0 for $V \gg 1$ on the heat flux (since the main contribution to Q comes from particles with these directions of motion).

We estimate the reduced effect of the tails on Q when the Boltzmann equation is replaced by the BGK model. According to [1, 2], in the case of Boltzmann equation for $V_* \sim k^{-1/3}$, the effect of tails on Q is determined by the estimate $\delta Q \sim p_* c_T k^{-4/3} \exp(-k^{-2/3})$, $p_* = n_* \varkappa T_{1W}$. According to (10) or because $q = Q/p_* c_T = \int (V_x^3 F_1 + V_x F_2) dV_x$, for the BGK model $\delta Q_M \sim p_* c_T k^{-2/3} \exp(-k^{-2/3})$, which is only $O(k^{2/3})$ of δQ.

At the same time, an asymptotic estimate of the contribution of the distribution function at the cold plate to Q gives, for $s \gg k$, the expression

$$\delta Q_{w1} \sim \frac{n_{r1} \varkappa T_{1w} c_T}{\sqrt{\pi}} \int_0^\infty V_x^3 \exp\left(-V_x^2 - \frac{s}{V_x}\right) dV_x \simeq \frac{n_{r1} p_* c_T s}{2\sqrt{3}\,k} \exp\left(-\frac{3 s^{2/3}}{2^{2/3} k^{2/3}}\right).$$

Hence it follows that the effect of the edge of the flow field on the heat flux is in the present case larger than the effect of the tails of the distribution function. This is also confirmed by the character of the change of the ratio $(-\lambda dT/dx)/Q$ near the cold plate. The presence of δQ_{W1} lead to an effective increase of the thermal conductivity of gas, and to a local increase of the temperature gradient near the wall.

We note that, in general, a more complex geometry (e.g., cylindrical) rather than planar does not remove this property of the BGK model. The limit (10) is exceeded here only for velocities of molecules which satisfy the inequality $V \gtrsim V_{**} = r^{1/4}k^{-1/2}$, where r is the distance from the axis of the coaxial cylinders divided by L. The velocity V_{**} is comparable with $k^{-1/3}$ for $r \sim k^{2/3}$. In other words, in order to estimate the realistic effect of the tails of the distribution function on the heat exchange using the BGK model, it is necessary to consider, for example, the heat exchange between coaxial cylinders when the radius of the smaller cylinder does not exceed $l_0^{2/3}L^{1/3}$ of the range at velocity $V \sim k^{-1/3}$. However, the heat transfer phenomenon is here more complex on account of a number of factors which have no relation to the problem in hand. Therefore, the analysis of the effect of the tails of the distribution function on the heat exchange should therefore be carried out using the solution of the exact Boltzmann equation, and the model BGK equations should be used only for the estimate of the contribution of the perturbation of f_0 for $V \gg 1$ to the kinetics of the high-threshold reactions.

NOTATION

Here c_T is the characteristic thermal velocity of molecules; m, their mass; $\varkappa$, Boltzmann constant; n_*, average numerical density of the molecules; $l_0 = c_T/An_*$, mean free path of the molecules; L, separation between plates; and $k = l_0/L$, Knudsen number.

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