Kinetic Flows with Chemical Reactions and Nonequilibrium Structures

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Abstract: Simulations of flows on the basis of kinetic equations for mixtures with chemical reactions are performed. The Nonuniform Relaxation Problems (NRP) are formulated and solved. Unified Flow Solver (UFS) is used for 1D and 2D NRP. The nonequilibrium kinetics provides results outside the traditional theory of macroscopic phenomena based on the Navier-Stokes equations. Nonequilibrium flows with different properties in relaxation zones are described. Complex processes including model anabolic and catabolic chemical reactions are also considered.

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1. Introduction

Numerous potential applications of flows with chemical reactions require new kinetic models and methods to describe complicated nonequilibrium phenomena. Consideration of nonequilibrium flows in spatial relaxation regions by means of the Boltzmann equation revealed interesting nonclassical features, see [1], possible experimental tests were discussed in [2]. In the present paper we expand field of the study of these structures with the help of more complex and realistic kinetic equations for mixtures with chemical reactions [3-6]. We can mention some references concerning reactive Boltzmann [7-10] and reactive BGK [11-13]. The methods of kinetic theory [14-15] are used. The apparatus in detail principally differs from the theory of the nonequilibrium thermodynamics [16] which can describe processes only near to equilibrium states and which are based on phenomenological relations between the gradients of macroscopic quantities and the gradients of appropriate values. The importance of these new types of problems, namely, Nonuniform Relaxation Problems (NRP), can be explained as follows: if the boundary distribution is equilibrium, then there is no spatial structure. The nonequilibrium boundary condition results in the nonuniform flow, i.e. the nonequilibrium velocity distribution is transformed into spatial nonuniformity. Previous solutions of NRP for various cases confirmed that nonclassical transfer properties can be demonstrated in the relaxation zones for monatomic simple gases, for mixtures of simple gases and for molecular gases, see [17, 18, 1, 2]. In the present paper we consider new solutions of NRP for media with chemical reactions. Solutions for 1D and 2D flows are obtained. Note that the use of model kinetic equations allows us to describe, in principle, different media (not only gas but also liquid).

Recently specific kinetic phenomena, e.g. thermal creep, thermophoresis etc., have been discussed, see [19], and these effects can be used in applications. As a rule, the mentioned effects are connected with transfer processes caused by gradients of some macroscopic values. It is known that transport of dissipative values is not directly connected with the appropriate gradients for nonequilibrium
distributions. For instance, the temperature gradient can equal zero but the heat flux (treated as the appropriate moment of the distribution function) in the same coordinate point is not equal to zero if the distribution function is nonequilibrium. The anomalous transfer for NRP under some boundary conditions in several simulations is confirmed.

2. NRP for Kinetic Equations with Chemical Reactions

The general purpose of this study is to construct and investigate complex flux structures with nonequilibrium states. The system of Boltzmann equations for mixture taking into account chemical reactions are written in the form for the distribution function \( f^i(x, \xi, t) \) of \( i \)-th species

\[
\frac{\partial f^i}{\partial t} + \left( \xi \cdot \frac{\partial f^i}{\partial x} \right) = I^i, \quad (i = 1 \ldots N),
\]

where \( N \) is the number of species, \( x = (x, y, z) \) is the coordinate vector, \( \xi = (\xi_x, \xi_y, \xi_z) \) is the vector of molecular velocity. The collision term \( I^i \) may be split into two parts (the nontranslational degrees of freedom are neglected)

\[
I^i = I^i_{el} + J^i_{chem},
\]

Where \( I^i_{el} = \sum_{j=k}^{N} \bar{I}(f^i, f^j) \) is an elastic collision operator for the binary interaction and \( J^i_{chem} \) is a chemical collision term considering additional transfer of mass and energy of the chemical bond in each microscopic chemical interaction.

The global macroscopic parameters of the mixture (number density \( n \), density \( \rho \), velocity \( u \), stress tensor components \( P_{kl} \), pressure \( p \), nonequilibrium stress tensor components \( p_{kl} \) and heat flux \( q \)) are defined by macroscopic parameters of \( i \)-th species, number density

\[
n^i = \int f^i d\xi,
\]

velocity

\[
u^i = \int \xi f^i d\xi / n^i,
\]

partial stress tensor components, pressure and nonequilibrium stress tensor components

\[
P_{kl}^i = m^i \int C_k C_l f^i d\xi, \quad p^i = \frac{1}{3} \left( P_{xx}^i + P_{yy}^i + P_{zz}^i \right), \quad p_{kl}^i = P_{kl}^i - \delta_{kl} p^i,
\]

partial heat flux

\[
q^i = \frac{1}{2} m^i \int C(C) \xi f^i d\xi.
\]

Here \( m^i \) is the mass of the \( i \)-th species, \( C = \xi - u \), the formulas for the mixture velocity \( u \) and other macroscopic parameters are given below:

\[
n = \sum_{i=1}^{N} n^i, \quad \rho = \sum_{i=1}^{N} m^i n^i, \quad u = \sum_{i=1}^{N} m^i n^i u^i / \rho, \quad P_{kl} = \sum_{i=1}^{N} P_{kl}^i, \quad p_{kl} = \sum_{i=1}^{N} p_{kl}^i \quad \text{and} \quad q = \sum_{i=1}^{N} q^i.
\]
The temperature of the mixture is defined as

\[ \frac{3}{2} n kT = \sum_{i=1}^{N} m_i \frac{(C)^2}{2} f'_i d\xi. \]

Here \( k \) is the Boltzmann constant.

The system of the Boltzmann equations for a mixture with chemical reactions (1) might be numerically integrated by the method proposed e.g. in [20], but numerical methods for direct solving the generalized Boltzmann equation are rather time-consuming. Instead, we use the method [3-6] which is based on the solution of BGK-type model equations, collision integrals are replaced by one model relaxation term accounting for any type of interactions of species \( i \) with all other species. We consider a four-component mixture of interacting species \( A_i \), \( i=1,...,4 \), undergoing a reversible bimolecular chemical reaction

\[ A^1 + A^2 \rightleftharpoons A^3 + A^4, \]

where \( A \) with a superscript denotes the appropriate component. The model equations have the following form

\[ \frac{\partial f^i}{\partial t} + \left( \xi_i, \frac{\partial f^i}{\partial \xi} \right) = Q^i (f) = \nu_i (M_i - f^i), \quad i=1, \ldots, 4, \quad (2) \]

where \( M_i \) is local Maxwellian depending on five disposable parameters \( n_i \), three components of vector \( u_i \) and \( T_i \):

\[ M_i (\xi) = n_i \left( \frac{m_i}{2kT_i} \right)^{3/2} \exp \left( -\frac{m_i (\xi - u_i)^2}{2kT_i} \right), \quad i=1, \ldots, 4. \]

The above auxiliary fields \( n_i, u_i \) and \( T_i \) are determined in such a way that exact exchange rates for mass, momentum and energy of each species are correctly reproduced. We consider the chemical bond energies \( E \), with the energy jump

\[ \Delta E = -\sum_{i=1}^{4} \lambda^i E^i = E^1 + E^4 - E^2 - E^3, \]

where \( \lambda^i \) is a component of the string of the stoichiometric coefficients \((1,1,-1,-1)\). Species may always be ordered in such a way that the sign of \( \Delta E \) is positive so that we will stick to such option, without any loss of generality. The chemical collision term takes into account the mass transfer (with \( m^1+m^2=m^3+m^4=M \)). The collision equilibria are identified as the seven parameter family of local Maxwellians: three components of common velocity, common temperature and three of four number densities because number densities are linked by the law of mass action

\[ \frac{n_1 n_3}{n_2 n_4} = \left( \frac{m_1 m_3}{m_2 m_4} \right)^{3/2} \exp(\Delta E / kT). \]

From the kinetic equation we get seven exact, non-closed, macroscopic conservation equations. The appropriate equations enable us to recover the correct macroscopic conservation equations for the model equations. Collision frequencies are rewritten from the appropriate tables in \[5\]. The use of the disposable parameters in Eq. (2) leads to changing densities of components in a process of a chemical reaction. The exchange rate derived from Eq. (2) is as follows

\[ \int Q^i (f) d\xi = \nu_i (n_i - n_i') \quad i=1, \ldots, 4. \]
The analogous expressions for other moments are written in a similar way (see [5]). It is worth to mention that the authors of the approach [3-6] have constructed the BGK chemical model in such a way that it corresponds to the BGK-model for the simple monatomic gas, so the Prandtl number equals unity. We use this BGK chemical model nevertheless for chemical reactions because of simplicity and possible perspectives of this crude approach. So we associate the BGK model with the ordinary (for this model) the Prandtl number $Pr = 1$. The development of the model approach (e.g. of S-model type) or generalization of the Boltzmann equation could correct the Prandtl number.

NRP is a time independent problem with nonequilibrium boundary conditions. Formulation of 1D NRP is presented in [1]. For 2D NRP for a steady case the following boundary conditions are accepted:

$$f_i(x = 0, y, \xi) = \begin{cases} F_i(\xi), & |y| < y_0 \\ 0, & |y| > y_0 \end{cases} \forall \xi : y_0 > 0, i = 1,...,4.$$  

where $F_i(\xi)$ is the nonequilibrium distribution functions, $y_0$ is a half of the width of the slit. Zero conditions are accepted in the other boundaries of computational domain in $(x, y)$ because a positive supersonic flow velocity is sufficiently large.

Transport equations for NRP can differ principally from the ordinary equations of transfer nonequilibrium stress and heat flux in the framework of the Navier-Stokes theory (see [17, 18]). In [1, 2] more complex transport equations have been written for mixtures of simple and molecular gases. For mixtures with chemical reactions we study behaviour of the moments by numerical simulations.

We note that hydrodynamic equations in the closed form can be derived analytically by expansion in a powers of small parameter for NRP from kinetic theory. For simple 1D situations such equations were deduced in [17, 18], of course this system of macroscopic equations differs from the Navier-Stokes equations. Simple analytical solutions of these equations were constructed in [17, 18]. For more complex 1D problems in particular for mixtures with chemical reactions the analogous equations can be derived, although this task is complicated. For 2D case the derivation of a such closed system is problematical.

### 3. Results of Simulations

All numerical simulations have been carried out with the Unified Flow Solver (UFS) [21], in which the direct solver of the model kinetic equations with chemical reactions [3-6] has been implemented recently. We simulate the NRP for 3 chemically reacting mixtures. Note that all reactions are models but the 1st and the 3rd one can correspond (by masses) to real interactions. The first case corresponds to the reaction

$$\text{NO} + \text{CO}_2 = \text{NO}_2 + \text{CO}.$$  

The masses are as follows: $m^1 = 1.0$, $m^2 = 1.4667$, $m^3 = 1.5332$, $m^4 = 0.9335$. For the second one (the pure model case) $m^1 = 1.0$, $m^2 = 1.5$, $m^3 = 1.9$, $m^4 = 0.6$. For the third case the masses are as follows: $m^1 = 2.2$, $m^2 = 0.9$, $m^3 = 1.5$, $m^4 = 1.6$. For all cases of reactions the ratios of masses of components are taken into account. The 3rd reaction is expected to model some features of the real and important chemical reaction, namely, the reaction of photosynthesis. In this process, plants use the energy of the sunlight to convert carbon dioxide and water into glucose and oxygen

$$6\text{CO}_2 + 6\text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2.$$  

In our crude kinetic model we consider the model addition of energy (energy jump) and the masses proportional to real masses of the components of this chemical reaction. We consider reactions with different values of the energy jump $\Delta E$.

For all simulations the nonuniform boundary condition for each component of the gas was set as a sum of 2 Maxwell functions with different mean velocities.
To nondimensionalize the kinetic equation we use values that are specific to the problems under consideration. The gas temperature, masses and concentration of particles are normalized to \( T_{\text{ref}} \), \( m_{\text{ref}} \), \( n_{\text{ref}} \) correspondingly. Velocities are referenced to the thermal velocity \( \nu_T = \sqrt{2kT_{\text{ref}}/m_{\text{ref}}} \) and collision frequency is normalized to a model value \( \nu_{\text{ref}} \). The characteristic length in physical space \( L \) is set to a particle mean free path \( \lambda = \nu_T/\nu_{\text{ref}} \) in 1D problem and to \( 2l \) in 2D problem, where \( l \) is the slit width. Energy \( E \), pressure and heat flux are normalized to \( kT_{\text{ref}} \), \( n_{\text{ref}}kT_{\text{ref}} \) and \( m_{\text{ref}}n_{\text{ref}}\nu_T^3 \). The frequency of chemical interactions is chosen to be much smaller than the frequencies of elastic collisions (slow chemistry) and these dimensionless values are taken from [3].

Figure 1. 1D NRP. a) Profiles of mean velocities of four components for the 3rd case, \( \Delta E=0.5 \) (an index \( i \) numerates numbers of components); b) profiles of the heat flux of four components. The 2nd case, \( \Delta E=2.5 \). (\( x \) is normalized to characteristic mean free path of a molecule).

In Figure 1a) profiles of mean velocity of the different components for the 3rd case are shown (the energy jump in plots is noted as \( \Delta E \) and equals 0.5). One can see that downstream all velocity components tend to the same equilibrium value. In Figure 1b) profiles of heat flux component for the 2nd case (\( \Delta E=2.5 \)) are demonstrated.

In Figure 2 the behaviour of temperature and heat flux, which is complex due to the redistribution of the chemical energy between the components (for the 2nd case, \( \Delta E=2.5 \)) is shown. One can see that there is a region (\( x<8 \)) for which the anomalous heat transfer takes place, namely, here the heat flux and the temperature gradient are positive. In the right plot of Figure 2 it is shown that temperature reaches equilibrium (where the gradient tends to zero) at large distances from the nonequilibrium boundary.

Figure 2. 1D NRP. Heat flux (left) and temperature profile (in different scales) for the 2nd case.

In Figure 3 profiles of mean velocity and a component of nonequilibrium viscous stress tensor are presented. The anomalous behaviour is recognized, until \( x=10 \) the velocity gradients are positive and values of the appropriate stress tensor components are also positive. One can see a slow relaxation region for \( \nu_i \) due to the character of the chemical reaction relaxation.
The anomalous behavior of heat flux can be connected with simple competition of heat conduction and diffusion processes and strong mass diffusion due to chemical reactions can change the sign of the heat flux. The considered effects including anomalous correspondence between stress and velocity gradient are discussed by other authors, see, e.g. [10]. Nevertheless it should be emphasized that in contrast to the ordinary case of deriving the macroscopic equations (the Navier-Stokes equations) from the kinetic equation at small Knudsen number the situation in a flow for spatial relaxation is principally different. Knudsen number is of the order of unity and the Chapman-Enskog method fails. For this supersonic flow (NRP) one can derive the other macroscopic equations with the anomalous transport relationships. This is the case for mixtures of simple gases as well as for mixtures of gases with chemical reactions. We have to note that in NRP there are “anomalous terms itself”, namely e.g. the heat flux has the same signs with the temperature gradient. Such equations for a mixture of simple gases are deduced in [22] In [22, 23] it has been shown that if velocities of components are close and therefore diffusion terms are neglected the anomalous character of transfer equations remains due to the mentioned relations.

The structure can change their form with varying the outer (external) conditions. So besides increasing (or decreasing) the density in the spatial nonuniform relaxation from the nonequilibrium state to equilibrium one, the density can change their value after changing the temperature for this equilibrium state. We simulate this complex process for the 3rd case of the of the reaction for consideration of the 3rd component which can be associated with “glucose”. The first part of this process is a synthesis (anabolic reaction) – the left plot in Figure 4, the second part of this process is a degradation (catabolic reaction) – the right plot in Figure 4. The second part is obtained by changing the temperature for the boundary distribution function. One can see the combined structure (of course without details of the real mechanism) according to notion of general schematic processes in a green leaf. This simple simulation reflex some features of real processes which are intrinsic for biological systems.

The structures can change their form in the process of changing some conditions. Results of simulations of 2D flows are presented in Figure 5. The mean velocity of the boundary nonequilibrium...
condition influences the form and length of the structure. For a greater boundary velocity the length (distance between the left boundary and the same contour lines) of the nonuniform structure is greater.

Figure 5. 2D NRP. Density contours for the 4th component (3rd case, $\Delta E=4.5$) with two different boundary conditions (dashed lines are related to a greater boundary velocity).

Figure 6. 2D NRP. Profiles of nonequilibrium stress tensor component $p_{xx}$ (left) and velocity component $u_x$ (right). Crosssections of surface plots with constant $y$ are presented, the range for $y$ is from 0 to 1 increasing downwards on both plots, the 3rd case, $\Delta E=0.5$.

In Figure 6 results of 2D simulations from the point of view of discussing of transport properties for 2D NRP for the 3rd case of the reaction are presented. One can see some zones with anomalous transfer properties, here the mean velocity gradient and the stress tensor component are positive (in Figure 6 higher lines on both plots correspond to lower values of $y$ coordinate).

4. Concluding Remarks

In the present paper we simulate characteristics of nonequilibrium spatial structures. We suggest that, using this kinetic approach it may be possible to describe some features of natural objects. Note, e.g., that if a velocity of the flux equals to zero then there is no spatial structure and the distribution at any point is equilibrium.

In future works the attention is to be paid to the nonequilibrium generalization of entropy $S$ (- $H$-function), which plays an important role in the kinetic theory. In contrast with the traditional nonequilibrium thermodynamics, entropy is not a function of parameters at equilibrium. Principles of description of open systems are general, namely both for kinetic theory and for irreversible thermodynamics we have the following equation for entropy.

$$dS = dS_{(inner)} + dS_{(outer)}.$$  

where $dS$ is the full change of the entropy in the open system under consideration, $dS_{(inner)}$ is the entropy change due to the inner processes (only positive according to the second law of the thermodynamics, i.e. $dS_{(inner)}>0$, $dS_{(outer)}$ is the entropy change due to interaction with the environment (for the kinetic theory the mentioned inequality is valid according to the H-theorem).
The distribution of nonequilibrium entropy in an open system can be adequately described only by the kinetic theory. Using results from [18, 2] one can demonstrate the difference between the global entropy in the equilibrium and the nonequilibrium entropy. The integral value of this difference determines the value of the system negentropy. We emphasize that there is a difference between near equilibrium and nonequilibrium descriptions. This fact maybe is not surprising but one should calculate this difference in future studies and use this value as an instrument for the evaluation of complexity of the open system.

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**References**


