A solution of the Boltzmann equations in the presence of three components and inelastic collisions

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\textbf{A B S T R A C T}

A new algorithm for the solution of the system of three Boltzmann equations for three components in a mixture is developed. Binary collisions between molecules are taken into account assuming that these collisions are elastic or inelastic. The functionality testing of the algorithm is performed using a simple test problem of heat and mass transfer in the mixture of n-dodecane, p-dipropylbenzene and nitrogen between two infinite parallel walls. The mixture of n-dodecane and p-dipropylbenzene is chosen due to the fact that it can approximate realistic Diesel fuels reasonably well. It is concluded that the predictions of the new kinetic algorithm are qualitatively consistent with the predictions of more basic models of the phenomena for which it has been tested. The algorithm is ready for the analysis of a wider range of heat and mass transfer problems in which the contribution of three components in the mixture is essential.

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1. Introduction

The limitations of widely used engineering approaches to modelling evaporation/condensation/heat transfer processes based on the hydrodynamic approximation, even in the case when these processes take place at high pressures, have been discussed in a number of papers (see [1] for a review of the early models and [2] for a review of more recent developments). In a number of papers, including [3–7], the evaporation of n-dodecane C\textsubscript{12}H\textsubscript{26} (an approximation for Diesel fuel) has been studied and a new model has been developed based on a combination of the kinetic and hydrodynamic approaches. In the immediate vicinity of droplet surfaces (up to about one hundred molecular mean free paths), the vapour and ambient gas dynamics have been studied based on the Boltzmann equation (kinetic region), while at larger distances the analysis has been based on the hydrodynamic equations (hydrodynamic region). Mass, momentum and energy fluxes have been conserved at the interface between these regions.

The analysis of [3] was based on the assumption that n-dodecane evaporates into its own vapour (the contribution of air in the kinetic region was ignored). Although this assumption is rather far from most conditions in which fuel droplets evaporate, it allowed the authors of [3] to avoid the numerical solution of the Boltzmann equation and base their analysis on its approximate analytical solution for the mass flux. The authors of [4,5] considered a more realistic problem of n-dodecane evaporation into air and developed a new numerical algorithm for the solution of a system of two Boltzmann equations for n-dodecane and air, taking into account elastic collisions between: n-dodecane molecules; air molecules; and between n-dodecane and air molecules. One of the main limitations of the analysis presented in [4,5] was that the effects of heat transfer in the kinetic region were ignored. The latter was taken into account in a more general model presented in [6].

The approaches of [4–6] were based on the assumption that all collisions between molecules are elastic. A new approach to taking into account the effects of inelastic collisions was developed in [7] and applied to the problem of n-dodecane droplet heating and evaporation in [8].

One of the important limitations of the approaches described in [3–8] is that they have been based on the assumption that Diesel fuel can be approximated by n-dodecane. A more detailed analysis of the composition of Diesel fuel showed that it includes hundreds...
The mathematical model, used in our analysis, is discussed in Section 2. In Section 3 this model is applied to the analysis of three test cases. The main results of the paper are summarised in Section 4.

2. Mathematical models

The evolution of the molecular velocity distribution functions of air \( f_a \) (or any other neutral gas, including nitrogen), n-dodecane \( f_n \) and p-dipropylbenzene \( f_p \) is controlled by the corresponding Boltzmann equations:

\[
\frac{df_a}{dt} + \nabla \cdot (v_a f_a) = J_{an} + J_{an} + J_{ap}, \\
\frac{df_n}{dt} + \nabla \cdot (v_n f_n) = J_{nn} + J_{np} + J_{np}, \\
\frac{df_p}{dt} + \nabla \cdot (v_p f_p) = J_{pn} + J_{nn} + J_{np},
\]

where \( J_{ab} \) (\( a = a, n, p \) and \( b = a, n, p \)) are collision integrals, taking into account the contribution of the collisions between molecules. Triple collisions are ignored.

Explicit expressions for the collision integrals \( J_{ab} \) can be presented as [4]:

\[
J_{ab} = \int_{0}^{\infty} d\mathbf{v}_1 \int_{0}^{\infty} d\mathbf{v}_2 \sin \theta \int_{0}^{2\pi} d\phi \left( f_{a0} f_{b0} - f_{a1} f_{b1} \right) |\mathbf{v}_1 - \mathbf{v}_2|,
\]

where \( \sigma_{ab} = (\sigma_a + \sigma_b)/2 \) and \( \sigma_a \) and \( \sigma_b \) are the corresponding diameters of molecules of air ‘a’, n-dodecane ‘n’ and p-dipropylbenzene ‘p’. \( \theta \) and \( \phi \) are angular coordinates of molecules \( b \) relative to molecules \( a \), superscript ‘0’ indicates the velocities and the distribution functions after collisions, subscript ‘1’ indicates that the function \( f_1 \) is modified under the influence of collisions with molecules of the type \( b \). The first integral on the right hand side of (2) is calculated in the three dimensional velocity space. Expression (2) is the same as that used in [4], where the contribution of only 2 components in the kinetic region was taken into account. This is justified by the fact that triple collisions are ignored.

All collision integrals \( J_{ab} \) are calculated taking into account the contribution of internal degrees of freedom (inelastic collisions) as described in [7]. A degree of freedom is usually defined as a parameter corresponding to each independent variable necessary to describe the energy of a molecule [12]. A mono-atomic molecule has three degrees of freedom corresponding to its translational energies in x, y and z directions. Poly-atomic molecules have additional degrees of freedom corresponding to their rotational and vibrational motions (see [13] for the analysis of degrees of freedom of CO\(_2\) molecules).

The main ideas of the approach used in [7] are summarised below.

Regardless of the nature of the collision between molecules, their centre of mass is not affected by this collision. During the collisions, the energy of each molecule is redistributed between the degrees of freedom, but the total number of degrees of freedom remains the same. If we assume that none of these degrees of freedom is preferable to any of the others we can consider the redistribution of energy between these degrees of freedom during the collision process as random (this follows from the equipartition-of-energy theorem [12]). For each of these degrees of freedom we allocate one dimension in the \( N \)-dimensional space describing all degrees of freedom and consider a sphere in this space with its centre at the origin (where energies of all degrees of freedom are equal to zero) and radius \( r = \sqrt{\sum_{i=1}^{N} E_i} \), where \( E_i \) is the energy of the \( i \)-th degree of freedom. Since \( r^2 \) gives the total energy of the system \( E \), this equation can be considered as an equation for the conservation of energy. The location of the points on the surface of this sphere can be described by an \( N \)-dimensional vector \( \mathbf{X} = (x_1, x_2, \ldots, x_N) \) with the basis \( (\mathbf{e}_1, \mathbf{e}_2, \ldots, \mathbf{e}_N) \) and the norm \( ||\mathbf{X}|| = r = \sqrt{E} \). The redistribution of energy between the degrees of freedom during the collision process can be described in terms of the random rotation of vector \( \mathbf{X} \) in the \( N \)-dimensional space.

The numerical algorithm used in the analysis is based on the method of direct numerical solution of the Boltzmann equation.
Physical and velocity spaces are discretised along with time. Time and physical space are discretised as in conventional structured computational fluid dynamics (CFD) codes. The discretisation of the velocity space is performed similarly to that of the physical space by replacing continuous values of $v$ with a discrete set $\{v^k\}^M$, where $k$ indicates the position of a velocity cell and $M$ is the total number of cells. The numerical solution of the discretised system of equations is performed in two steps. Firstly, molecular displacements are calculated ignoring the effect of collisions ($U'_{ab} = U_{ab} = 0$). Secondly, the collisional relaxation is calculated under the assumption of spatial homogeneity.

### 3. Applications

#### 3.1. Evaporation and condensation from flat walls

Let us consider two parallel walls kept at constant temperatures $T_{w1} = 1$ and $T_{w2} = 1$ as shown in Fig. 1. The distance between the walls $L$ is equal to 10 mean free paths for n-dodecane at the temperature $T_{w2}$. Space between the walls is filled with:

1. a mixture of n-dodecane, p-dipropylbenzene and nitrogen (three component mixture);
2. a mixture of n-dodecane and nitrogen (two component mixture);
3. pure n-dodecane or p-dipropylbenzene (single component).

Initially, molar fractions of all components are assumed to be equal to 1. It is also assumed that the distribution functions of n-dodecane and p-dipropylbenzene at both walls are half-Maxwellian with densities $n_1 = 2$ and $n_2 = 1$, describing evaporated species. N-dodecane and p-dipropylbenzene molecules hitting the walls are removed from the domain (they are condensed), while for nitrogen molecules it is assumed that the flux of incoming molecules is equal to the flux of molecules reflected from the walls.

Note that although, strictly speaking, the above mentioned combination of parameters might not be realistic for practical applications it turned out to be useful for testing the code.

The space grid in the numerical analysis has been taken equal to 0.5 $\ell_n$, and $12 \times 12 \times 12$ velocity grid points have been used.

The predicted distributions of the number density of n-dodecane for three and two component mixtures and one component substance versus the distance from the first plate are shown in Fig. 2 (the distance $x$ is normalised by $\ell_n$). Two cases have been considered: the contribution of internal degrees of freedom (corresponding to rotational and vibrational movements of the constituent molecules) is ignored (a); the numbers of these degrees for n-dodecane and p-dipropylbenzene are equal to 20, while nitrogen has 2 internal degrees of freedom (b). As follows from our previous analysis [7,8], only the first 20 internal degrees of freedom of such complex molecules as n-dodecane contribute to the results predicted by the kinetic calculations (the actual number of internal degrees of freedom of n-dodecane, taking into account translational, rotational and vibrational movements of the constituent molecules, is expected to be much more than 20). It is anticipated that the same conclusion should remain valid for p-dipropylbenzene. This is supported by our analysis presented later in this paper (see Fig. 5).

As follows from Fig. 2, the density distributions for three and two component mixtures are very close. They coincide within the accuracy of plotting when the contribution of internal degrees of freedom is taken into account (see Fig. 2b). Both these distributions differ considerably from the distribution for the one component substance. In all cases the expected concentration jumps near the walls are clearly seen. These jumps are noticeably larger for the one component substance compared with three or two component mixtures. The physical nature of these density jumps has been
widely discussed in the literature, starting with a pioneering monograph [1]. In [14] it was shown that the introduction of these jumps into a conventional CFD code (FLUENT) enables this code to be used for modelling rarefied gases.

The contribution of internal degrees of freedom has little effect on the distribution of number densities of n-dodecane. It leads to an increase in number density jumps for three and two component mixtures and a slight decrease in these jumps for the case of a single component.

The distributions of the number densities of p-dipropylbenzene for a three component mixture and a one component substance are shown in Fig. 3. Comparing Figs. 2 and 3 one can see that the distributions of n-dodecane and p-dipropylbenzene are very close which is related to the closeness of masses and sizes of the corresponding molecules (see Table 1).

The distributions of the number density of nitrogen for three and two component mixtures are shown in Fig. 4. Comparing Fig. 4 with Figs. 2 and 3 one can see that in contrast to n-dodecane and p-dipropylbenzene, the number density of nitrogen increases from the first plate to the second one. This means that nitrogen molecules are expected to move from the region of high concentration of n-dodecane and p-dipropylbenzene to the region of low concentration of these molecules, which is consistent with the corresponding thermodynamics equations for the mixtures. In contrast to the case shown in Fig. 2, the distribution of nitrogen is rather different for three and two component mixtures. Since the number density of nitrogen at the walls is not specified we cannot infer any information about the number density jump in the vicinity of the walls for nitrogen. As in the cases shown in Figs. 2 and 3, the contribution of internal degrees of freedom produces only minor effects on the number density of nitrogen.

The number fluxes of n-dodecane and p-dipropylbenzene for the three component mixture and single components versus the number of internal degrees of freedom $N_{\text{int}}$ are shown in Fig. 5. It is assumed that $N_{\text{int}}$ for n-dodecane and p-dipropylbenzene are equal and $N_{\text{int}}$ for nitrogen is equal to 2, except when $N_{\text{int}}$ for

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical formula</th>
<th>Molar mass (kg/kmol)</th>
<th>Molecular diameter (Å)</th>
</tr>
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<tr>
<td>n-dodecane</td>
<td>C₁₂H₂₆</td>
<td>170.3</td>
<td>7.12</td>
</tr>
<tr>
<td>p-dipropylbenzene</td>
<td>C₁₂H₁₈</td>
<td>162.27</td>
<td>6.73</td>
</tr>
<tr>
<td>nitrogen</td>
<td>N₂</td>
<td>28.97</td>
<td>3.617</td>
</tr>
</tbody>
</table>

Table 1

![Fig. 3. The same as Fig. 2 but for p-dipropylbenzene, taking into account the contributions of three components: n-dodecane, p-dipropylbenzene and nitrogen (thick solid curves) and a single component (p-dipropylbenzene) (dashed curves).](image)

![Fig. 4. The same as Figs. 2 and 3 but for nitrogen, taking into account the contributions of: three components, n-dodecane, p-dipropylbenzene and nitrogen (thick solid curves); and two components, n-dodecane and nitrogen (thin solid curves).](image)
n-dodecane and p-dipropylbenzene are equal to 0. In the latter case \( N_{\text{int}} \) for nitrogen has been taken equal to 0 as well. As one can see from this figure, although the number densities of n-dodecane and p-dipropylbenzene are weak functions of the number of internal degrees of freedom, the dependence of number fluxes of these components on this number is rather strong, at least at \( N_{\text{int}} \leq 20 \). At larger \( N_{\text{int}} \) these fluxes do not depend on \( N_{\text{int}} \), in agreement with our earlier results [7,8]. Mass fluxes of n-dodecane and p-dipropylbenzene are close for the three component mixture, but are noticeably different for the case of single components. Mass fluxes of n-dodecane and p-dipropylbenzene are both much larger for the single components than for the three component mixture as expected.

3.2. Heat conduction between two flat walls

Let us consider the same case as discussed in the previous section, but ignore the effects of evaporation and condensation and assume that \( T_{w1} = 2 \) and \( T_{w2} = 1 \) (see Fig. 1). In this case the processes between the walls will lead to pure heat conduction between them.

The distributions of temperature of n-dodecane for three and two component mixtures and one component substance versus the distance from the first plate are shown in Fig. 6. As in the case shown in Fig. 2, two cases have been considered: the contribution of internal degrees of freedom is ignored (a); the numbers of these degrees for n-dodecane and p-dipropylbenzene are equal to 20, while nitrogen has 2 internal degrees of freedom (b).

As follows from Fig. 6, the n-dodecane temperatures for three and two component mixtures and a single component are reasonably close, especially when the contribution of internal degrees of freedom is ignored (see Fig. 6a). In all cases the expected temperature jumps near the walls are clearly seen. The physical nature of these temperature jumps is similar to that of the density jumps; see [1,14] for details. The contribution of internal degrees of freedom has little effect on the distribution of temperatures of n-dodecane, as in the case of number densities shown in Fig. 2.

The distributions of the temperature of p-dipropylbenzene for the three component mixture and one component substance are shown in Fig. 7. Comparing Figs. 6 and 7 one can see that the distributions of temperature of n-dodecane and p-dipropylbenzene are very close which is related to the closeness of masses and sizes of the corresponding molecules (cf. the corresponding distributions of number densities shown in Figs. 2 and 3).

The distributions of the temperature of nitrogen for three and two component mixtures and a single component are shown in Fig. 8. Note that in contrast to the problem of evaporation and condensation, considered in the previous section, we considered the case when the space between the walls is filled with nitrogen alone. In contrast to the case of the distribution of mass densities, the distribution of temperatures of nitrogen is reasonably close to that of n-dodecane and p-dipropylbenzene. This shows that the system is close to local thermodynamic equilibrium as expected.

The heat fluxes of n-dodecane, p-dipropylbenzene and nitrogen, predicted for the three component mixture, and single components, versus the number of internal degrees of freedom \( N_{\text{int}} \) are shown in Fig. 9. As in the case shown in Fig. 5, it is assumed that \( N_{\text{int}} \) for n-dodecane and p-dipropylbenzene are equal and \( N_{\text{int}} \) for nitrogen is equal to 2, except when \( N_{\text{int}} \) for n-dodecane and p-dipropylbenzene are equal to 0. In the latter case \( N_{\text{int}} \) for nitrogen has been taken equal to 0 as well. As one can see from this figure,
the dependence of heat fluxes of components on \( N_{\text{int}} \) is weaker than in the case of number fluxes (cf. Fig. 5). These heat fluxes remain practically unchanged for \( N_{\text{int}} > 10 \). For the three component mixture the total heat flux between the walls is equal to the sum of the heat fluxes due to individual components. The largest heat flux for single components is predicted for nitrogen which reflects its largest thermal conductivity.

### 3.3. Heat and mass transfer between two flat walls

Let us consider the case when heat and mass transfer between walls take place simultaneously. As in the case of evaporation and condensation considered in Section 3.1, it is assumed that the distribution functions of n-dodecane and p-dipropylbenzene at both walls are half-Maxwellian with densities \( n_1 = 2 \) and \( n_2 = 1 \), describing evaporated species. N-dodecane and p-dipropylbenzene molecules hitting the walls are removed from the domain (they are condensed), while for nitrogen molecules it is assumed that the flux of incoming molecules is equal to the flux of molecules reflected from the walls. Initially, molar fractions of all components are assumed to be equal to 1. In contrast to the case considered in Section 3.1, we took into account the difference between \( T_{w1} \) and \( T_{w2} \) and assumed that \( T_{w1} = 2 \) and \( T_{w2} = 1 \) (see Section 3.2). In all cases we have considered the three component mixture and assumed that \( N_{\text{int}} = 20 \) for n-dodecane and p-dipropylbenzene, and \( N_{\text{int}} = 2 \) for nitrogen.

The spatial distributions of the number densities of n-dodecane and nitrogen, predicted by the models taking into account both heat and mass transfer processes, only heat transfer process (see Section 3.2), and only mass transfer processes (see Section 3.1), are shown in Fig. 10. The plot \( n_n \) versus \( x \) for the case when only mass transfer is taken into account is identical to the corresponding plot shown in Fig. 2b (solid curve). The plot \( n_n \) versus \( x \) for the case when only heat transfer is taken into account is identical to the corresponding plot shown in Fig. 4b (thick solid curve).

As follows from Fig. 10a, the distributions of n-dodecane, predicted by the models taking into account both heat and mass transfer processes and only mass transfer processes are qualitatively similar. Both models predict a decrease in n-dodecane number density with \( x \). This can be attributed to the fact that the rate of evaporation of n-dodecane from the hotter wall is stronger than that from the cooler wall. In the case when only heat transfer is taken into account, the number density of n-dodecane increases with \( x \). This is related to an increase of n-dodecane number density with a decrease in temperature. The number density jumps near the walls, predicted by the model taking into account both heat and mass transfer, are larger than the ones predicted by the model taking into account only the mass transfer process. For all three models the number density of nitrogen increases with \( x \). This is related...
to the fact that nitrogen does not evaporate and its number density decreases with increasing temperature.

The spatial distributions of the temperature of n-dodecane, predicted by the models taking into account both heat and mass transfer processes, only heat transfer process (see Section 3.2), and only mass transfer processes (see Section 3.1), are shown in Fig. 11. The plot $T_n$ versus $x$ for the case when only heat transfer is taken into account is identical to the corresponding plot shown in Fig. 6b (thick solid curve).

As follows from Fig. 11, the distributions of n-dodecane temperature, predicted by the models taking into account both heat and mass transfer processes and only the heat transfer process are qualitatively similar. Both models predict a decrease in n-dodecane temperature with $x$, as expected. The temperature jumps near the walls, predicted by the model taking into account both heat and mass transfer, are larger than the one predicted by the model taking into account only the heat transfer process. For the model taking into account only mass transfer processes, the n-dodecane temperature slowly increases with $x$, which can be related to the corresponding decrease in the n-dodecane number density (see Fig. 10a).

The velocity distribution functions of n-dodecane $f_n(v_x, v_y, v_z = 0)$ at three positions $x (x = 0.25, x = 2.25$ and $x = 4.25)$, predicted by the three component model taking into account both heat and mass transfer processes, are shown in Fig. 12. As can be seen from this figure, at all three positions these functions are close to Maxwellian. An increase in the peak value of this distribution function with $x$ is related to the corresponding decrease in the n-dodecane temperature, as shown in Fig. 11. The models, taking into account the contributions of three components (n-dodecane, p-dipropylbenzene and nitrogen), have been used.

The spatial distributions of the temperature of nitrogen, predicted by the models taking into account both heat and mass transfer processes, only heat transfer process (see Section 3.2), and only mass transfer processes (see Section 3.1), are shown in Fig. 13. The plot of $T_n$ versus $x$ for the case when only heat transfer and only mass transfer are taken into account are qualitatively similar to the
The high nitrogen temperature jump near the walls can be related to the low number density of nitrogen near the walls. Noticeable deviations from the Maxwellian ones. The range of velocities for nitrogen molecules shown in Fig. 14 is wider than in the case of n-dodecane molecules as shown in Fig. 12. This is attributed to the fact that nitrogen molecules are much lighter than n-dodecane molecules. Note that the dispersion of the distribution function, shown in Fig. 14, at $x = 2.25$ is noticeably larger than at other $x$ which leads to increased temperature of nitrogen in the vicinity of this $x$ as shown in Fig. 13. The integrals of $f_n$ over $v_x$, $v_y$ and $v_z$ would give us number densities of nitrogen in the corresponding points $x$ (see thick solid curve in Fig. 10b).

4. Conclusions

A new algorithm for the solution of the system of three Boltzmann equations for three components in a mixture has been developed. Binary (but not triple) collisions between molecules have been taken into account; the collisions have been assumed to be elastic or inelastic and in the latter case they have been analysed based on the model described in [7].

The functionality testing of the model has been performed using three simple test problems of heat and mass transfer in the mixture of n-dodecane, p-dipropylbenzene and nitrogen between two infinite parallel walls. The mixture of n-dodecane and p-dipropylbenzene has been chosen due to the fact that it can approximate realistic Diesel fuels reasonably well [11]. It has been shown that in the case of pure mass transfer the predicted distribution of n-dodecane number density between the walls is almost unaffected by the presence of p-dipropylbenzene, and the effects of internal degrees of freedom on this distribution have been shown to be relatively weak. The distribution of nitrogen between the walls, however, has been shown to be visibly affected by the presence of n-dodecane and p-dipropylbenzene.

In the case of pure mass transfer, the number fluxes of components between walls have been shown to change noticeably with increasing numbers of internal degrees of freedom $N_{int}$ when $N_{int} < 20$, but remain almost unchanged when $N_{int} > 20$. This result is consistent with the one presented in [7] for similar problems but based on the analysis of two component mixtures. In the case of pure heat transfer between the walls the distributions of temperatures of various components between the walls have been shown to be qualitatively similar.

It has been pointed out that the velocity distribution functions of n-dodecane remain almost Maxwellian at various positions between the walls when both heat and mass transfer processes are taken into account. Noticeable deviations from the Maxwellian
distributions have been observed for the corresponding distribution functions of nitrogen.

It is concluded that the predictions of the new kinetic algorithm are qualitatively consistent with the predictions of more basic models of the phenomena for which it has been tested. It is ready for the analysis of a wider range of heat mass transfer problems in which the contribution of three components in the mixture is essential.

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