

Monte Carlo simulation of the Boltzmann equation in the colour conductivity problem for general repulsive potentials

By C. MARÍN, J. M. MONTANERO and V. GARZÓ

Departamento de Física, Universidad de Extremadura, E-06071 Badajoz, Spain

(Received 15 September 1995; revised version accepted 13 February 1996)

The homogeneous colour conductivity problem for a binary mixture in the low-density regime is studied by means of the direct Monte Carlo simulation method. This method is used to solve the Boltzmann equation for three different repulsive $r^{-\mu}$ potentials: Maxwell molecules ($\mu = 4$), 'soft' spheres ($\mu = 12$), and hard spheres ($\mu \rightarrow \infty$). The main transport properties and the velocity distribution functions are computed as functions of the field strength and the parameters characterizing the mixture. In the case of Maxwell molecules, the results are compared with those derived from an *exact* solution of the Boltzmann equation, showing fairly good agreement over a wide range of field strengths. Beyond the Maxwell interaction, the effect of the interaction potential on the properties of the system is analysed.

1. Introduction

Nonlinear transport phenomena generated by the action of an external force in a homogeneous system is a very interesting problem from theoretical and computer simulation points of view. One of the best known of such phenomena is the so-called colour conductivity problem [1], in which the system is a binary mixture where particles of different species possess different 'colour charges'. Under the action of a constant external field, particles of different charges are accelerated along opposite directions so that mutual diffusion is produced in the absence of concentration gradients. The ratio between the mass flux and the colour field defines the colour conductivity coefficient, which is the most relevant transport coefficient of the problem. In the zero-field limit, this coefficient reduces to the mutual diffusion coefficient. This equivalence was the original motivation for introducing the colour field algorithm in molecular dynamics simulations [1, 2].

Beyond the scope of the linear regime, an interesting problem is to analyse the nonlinear response of the system to arbitrary values of the field strength. Since the external field (non-equilibrium parameter of the problem) can take large values in this state, one expects that deviations from linear laws can be observed. In the context of the Boltzmann equation, an exact solution for a binary mixture of mechanically different particles subjected to an external colour field has been found recently [3]. Explicit expressions for the mass and momentum fluxes have been obtained as functions of the colour field and the parameters of the mixture, namely, the mass ratio, the concentration ratio, and the interaction constant ratios. Due to the mathematical difficulties embodied in the Boltzmann collision integral, the results were restricted to the particular case of Maxwell molecules, i.e., particles interacting through repulsive forces inversely proportional to the fifth power of the distance. Nevertheless, it is evident that the above description cannot be regarded as general, since the model of

Maxwell molecules is not generally a very realistic representation of intermolecular interactions.

In this paper we extend our previous solution [3] to other repulsive interaction models. Unfortunately, this objective cannot be overcome analytically using the Boltzmann equation. One possibility would be to replace the exact Boltzmann collision kernel by approximate kinetic models that retain its essential features. Here, however, we want to consider the details of the Boltzmann collision term and, for this reason, we numerically solve the Boltzmann equation by means of the direct simulation Monte Carlo (DSMC) method [4]. Although the colour problem has been studied by molecular dynamics in dense fluids [1, 2], to the best of our knowledge the DSMC method has not been applied so far to the colour problem. Furthermore, and from a computational point of view, the DSMC method is more efficient than the molecular dynamics method for dilute gases. The reliability of the Monte Carlo algorithm for studying transport phenomena in far from equilibrium situations has been shown recently in the case of uniform shear flow [5–7].

The goal of this paper is to evaluate the effect of the interaction potential on the main transport properties of the mixture and on the velocity distribution functions. To this end, three representative repulsive potentials of the form $r^{-\mu}$ are considered: Maxwell molecules ($\mu = 4$), ‘soft’ spheres ($\mu = 12$), and hard spheres ($\mu \rightarrow \infty$). The r^{-12} model can be seen as an intermediate case between the two extreme cases of Maxwell molecules and hard spheres. In addition, and as a validation test of the simulation method, a comparison with the exact results obtained for Maxwell molecules for the mass flux, the partial temperature and the pressure tensor is carried out.

The plan of the paper is as follows. In section 2 we describe the colour conductivity problem in a binary mixture and give a brief summary of the results derived from the Boltzmann equation for Maxwell molecules. Section 3 is concerned with the simulation results obtained for the interaction models considered. Two different systems are simulated for each interaction model. The results are illustrated and compared with those derived for Maxwell molecules [3]. Finally, we close the paper in section 4 with some concluding remarks.

2. Description of the colour conductivity problem

Let us assume that in a binary mixture of mechanically different particles we assign ‘colour charges’ to particles of different species. Particles of each colour are accelerated along opposite directions when a constant external force is applied. Consequently, mass fluxes are generated across the system in a spatially homogeneous state. This is the main aspect of the colour conductivity problem. The colour force \mathbf{F}_i ($i = 1, 2$) is given by

$$\mathbf{F}_i = -k_B T \boldsymbol{\epsilon}_i, \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature of the mixture, and $\boldsymbol{\epsilon}_i = \boldsymbol{\epsilon}_i \hat{\mathbf{x}}$ is a constant vector that mimics the role played by a chemical potential gradient in a typical diffusion problem. In this problem the field strength is the only non-equilibrium parameter so that it measures the departure of the system from equilibrium. Since the colour force does work on the mixture, an additional external force must be introduced to achieve a steady state. Hamilton’s principle of least action

provides the simplest choice [8], namely, a drag force of the form $-\alpha m_i \mathbf{v}$, where m_i is the mass of a particle of species i and α is a thermostat parameter identical for both species. This type of thermostat force is usually employed in computer simulations [9].

For a low-density binary mixture, all the information on the properties of the system is contained in the velocity distribution functions f_i . They obey the set of two coupled Boltzmann equations [10]. When a steady homogeneous state has been reached, the corresponding Boltzmann equations in the colour problem are

$$-\frac{k_B T}{m_1} \boldsymbol{\epsilon}_1 \cdot \frac{\partial}{\partial \mathbf{v}} f_1 - \alpha \frac{\partial}{\partial \mathbf{v}} \cdot (\mathbf{v} f_1) = J_{11}[f_1, f_1] + J_{12}[f_1, f_2], \quad (2)$$

$$-\frac{k_B T}{m_2} \boldsymbol{\epsilon}_2 \cdot \frac{\partial}{\partial \mathbf{v}} f_2 - \alpha \frac{\partial}{\partial \mathbf{v}} \cdot (\mathbf{v} f_2) = J_{22}[f_2, f_2] + J_{21}[f_2, f_1], \quad (3)$$

where $J_{ij}[f_i, f_j]$ is the Boltzmann collision term which in standard notation is given by [10]

$$J_{ij}[f_i, f_j] = \int d\mathbf{v}_1 \int d\Omega |\mathbf{v} - \mathbf{v}_1| \sigma_{ij}(\mathbf{v} - \mathbf{v}_1, \theta) [f_i(\mathbf{v}) f_j(\mathbf{v}_1) - f_i(\mathbf{v}_1) f_j(\mathbf{v})], \quad (4)$$

σ_{ij} being the cross-section of collisions i - j . This quantity contains all the dependence on the potential model considered.

Conservation of total momentum (taken to be zero) and energy yields, respectively,

$$n_1 \boldsymbol{\epsilon}_1 + n_2 \boldsymbol{\epsilon}_2 = \mathbf{0}, \quad (5)$$

and

$$\alpha = -\frac{\rho}{3nm_1\rho_2} \boldsymbol{\epsilon}_1 \cdot \mathbf{j}_1 = -\frac{\rho}{3nm_2\rho_1} \boldsymbol{\epsilon}_2 \cdot \mathbf{j}_2, \quad (6)$$

where

$$n_i = \int d\mathbf{v} f_i \quad (7)$$

is the number density of species i , $n = n_1 + n_2$ is the total number density, $\rho = \rho_1 + \rho_2 = n_1 m_1 + n_2 m_2$ is the total mass density, and

$$\mathbf{j}_i \equiv \rho_i \mathbf{u}_i = \int d\mathbf{v} m_i \mathbf{v} f_i \quad (8)$$

is the mass flux of species i . Equation (5) implies that the colour forces acting on the two species are not independent, while equation (6) couples α with the relevant fluxes of the problem. The mass flux defines the nonlinear colour conductivity coefficient σ through the law

$$\mathbf{j}_i = -\frac{m_1 m_2 n}{\rho} \sigma n_i \boldsymbol{\epsilon}_i, \quad (9)$$

which is the main transport coefficient of the problem. According to the original motivation of the colour field method in molecular dynamics simulations [2], σ reduces to the conventional mutual diffusion coefficient D [10] in the zero-field limit. Beyond the linear regime σ depends on the field strength.

In terms of f_i we also define the pressure tensor of species i as

$$\mathbf{P}_i = \int d\mathbf{v} m_i (\mathbf{v} - \mathbf{u}_i) (\mathbf{v} - \mathbf{u}_i) f_i \quad (10)$$

and the heat flux of species i as

$$\mathbf{q}_i = \int d\mathbf{v} \frac{m_i}{2} (\mathbf{v} - \mathbf{u}_i)^2 (\mathbf{v} - \mathbf{u}_i) f_i. \quad (11)$$

The two quantities measure the contribution of each species to total momentum and energy fluxes, respectively. Furthermore, it is also interesting to introduce a partial temperature T_i for species i through

$$\frac{3}{2} n_i k_B T_i = \int d\mathbf{v} \frac{m_i}{2} (\mathbf{v} - \mathbf{u}_i)^2 f_i, \quad (12)$$

which is related to the mean kinetic energy of each species. The temperature of the mixture T (which is the relevant one at a hydrodynamic level) is

$$n k_B T = \sum_{i=1}^2 (n_i k_B T_i + \frac{1}{3} \rho_i u_i^2). \quad (13)$$

The hierarchy of moments of equations (2) and (3) can be solved exactly if one restricts oneself to Maxwell molecules (particles interacting via the potential, $\varphi_{ij} = \kappa_{ij} r^{-4}$). In particular, the reduced colour conductivity coefficient $\sigma^* = \sigma/D$ is [3]

$$\sigma^*(\epsilon^*) = \epsilon^{*-2} [(1 + 2\epsilon^{*2})^{1/2} - 1], \quad (14)$$

where ϵ^* is a reduced field strength. Expression (14) indicates that, in terms of convenient reduced units, the colour conductivity is a function only of the colour field. All the dependence on the ratios of mass, concentration, and force constants has been scaled out. This general character disappears for other quantities, such as the partial temperature or the pressure tensor. Their explicit expressions can be found in [3].

As stated in the introduction, no analytical solution of the Boltzmann equation is available in the colour problem when the particles interact via a potential other than the Maxwell interaction. Even in the case of Maxwell molecules, the distribution functions f_i are not known. In order to tackle the problem we use a numerical approach based on a Monte Carlo method. This will be the goal of the next section.

3. Simulation results

From a numerical point of view, the DSMC method [4] is the most convenient algorithm to study non-equilibrium phenomena in rarefied gases. It was devised to mimic the dynamics involved in the Boltzmann collision term. In the simulation, one has to deal with N particles in each one of \mathcal{N} realizations of the stochastic process associated to the Boltzmann equation. As a consequence, the results are averaged over an ensemble of $N \times \mathcal{N}$ members. In the method, the free motion and the collisions are uncoupled over a time step Δt which is small compared with the mean free time. In the free motion stage, all the molecules are displaced according to their velocity components. In the collision stage, a number of collisional pairs are chosen at random. Each pair is accepted or rejected according to a probability that depends on the relative velocity and the potential model considered. If the collision is accepted, the post-collision relative velocity is chosen at random, taking into account the scattering law. This process is repeated until an adequate set of collisions, according to the time step Δt , is considered. Further details of the method can be found in Bird's monograph [4].

We have used Bird's scheme to simulate the colour conductivity problem in a binary mixture. As the problem is homogeneous, it is necessary neither to store the coordinates of the particles nor to split the system into cells. In order to evaluate the transport properties, specific interaction models must be considered. We are interested in the case of repulsive potentials of the form $\varphi_{ij} = \kappa_{ij} r^{-\mu}$. Specifically, we consider three representative cases of this kind of potential: Maxwell molecules ($\mu = 4$), soft spheres ($\mu = 12$), and hard spheres ($\mu \rightarrow \infty$). The cases $\mu = 4$ and $\mu \rightarrow \infty$ are limit cases in the above family of potentials, while the r^{-12} potential is an illustrative example of an intermediate case. The combination of the three cases may allow us to predict the general influence of repulsive potentials on the properties of the system. In addition, the Maxwell interaction will be used to check the degree of reliability of the simulation results.

In the following we will focus on the transport properties of species 1. The properties of species 2 can be obtained by changing adequately the roles of both species. In this case, we taken an effective mean free path and an effective mean collision time for collisions 1-1 as units of length and time, respectively. In addition, to compare the results obtained from the three interaction models, the force constant ratios (for Maxwell molecules and soft spheres) and the diameter ratios (for hard spheres) are chosen to give the same equilibrium collision frequencies. This implies that

$$\frac{\kappa_{ij}}{\kappa_{11}} = \left(\frac{d_{ij}}{d_1}\right)^\mu, \quad (15)$$

where $d_{ij} = (d_i + d_j)/2$, and d_i is the diameter of sphere i .

We are interested in computing the main transport properties as well as the velocity distribution function in a steady state. For this reason a thermostat force is introduced. Here, the thermostat parameter $\alpha(t)$ is chosen as the one that keeps the temperature T constant at any time. When the steady state has been achieved (long time limit), α will be given exactly by equation (6). On the other hand, and to carry out a detailed comparison with the exact solution obtained in [3], a convenient reduced field strength ϵ^* must be introduced. To parallel the results derived in the Maxwell case, we take

$$\epsilon^* = \left(\frac{2 k_B T m_1 m_2 n_1}{3 \tau^2 \rho m_2}\right)^{1/2} \epsilon_1, \quad (16)$$

where the effective collision frequency τ is defined by

$$\tau = \frac{k_B T}{nD}, \quad (17)$$

D being the mutual diffusion coefficient of a binary mixture with general repulsive intermolecular forces [10]. This choice guarantees that the reduced colour conductivity coefficient $\sigma^* = \sigma/D$ tends to the universal value $\sqrt{2}|\epsilon^*|^{-1}$ in the limit of large field strengths. The fact that σ^* reaches the same saturation value for all the interaction models is not surprising, since the system behaves as a collisionless gas when $\epsilon^* \rightarrow \infty$ [3].

In our simulations we have typically taken a total number of particles $N = N_1 + N_2 = 5000$, a number of replicas $\mathcal{N} = 100$, and a time step $\Delta t = 3 \times 10^{-3}$. Furthermore,

Table 1. Simulation values of some quantities for $n_1/n_2 = 4$ and $m_1/m_2 = 1/3$ in the cases of Maxwell molecules ($\mu = 4$), soft spheres ($\mu = 12$) and hard spheres ($\mu = \infty$). We also include the exact solution values for Maxwell molecules. The statistical error is indicated in parentheses, in units of the last digit.

μ	$e^* = 0.125$	0.25	0.5	0.75	1	1.25	1.5	
4	σ^*	0.99230	0.97056	0.89897	0.81375	0.73205	0.65984	0.59787
	T_1^*	0.99142	0.96731	0.88923	0.79853	0.71347	0.63962	0.57707
	$P_{1,yy}^*$	0.98938	0.95972	0.86554	0.75979	0.66431	0.58430	0.51864
4	σ^*	0.993(5)	0.971(5)	0.900(2)	0.817(0)	0.733(1)	0.661(3)	0.598(6)
	T_1^*	0.9913(5)	0.9669(4)	0.8891(3)	0.7977(3)	0.7134(4)	0.6391(5)	0.5753(7)
	$P_{1,yy}^*$	0.991(1)	0.957(4)	0.864(1)	0.761(8)	0.662(5)	0.584(6)	0.517(7)
	q_1^*	-0.027(6)	-0.062(0)	-0.036(5)	0.027(1)	0.0966(3)	0.1456(1)	0.1803(0)
	σ^*	0.993(4)	0.972(7)	0.892(0)	0.8026(0)	0.7186(6)	0.6451(1)	0.5839(7)
	T_1^*	0.9800(5)	0.9678(4)	0.8937(2)	0.8084(4)	0.7297(1)	0.6613(4)	0.6027(4)
12	T_1^*	0.9863(6)	0.9558(8)	0.8538(5)	0.7407(2)	0.642(3)	0.561(8)	0.4965(4)
	$P_{1,yy}^*$	0.0191(0)	0.0539(0)	0.2563(8)	0.266(2)	0.349(5)	0.4057(9)	0.4416(4)
	q_1^*	0.990(3)	0.966(5)	0.876(6)	0.782(7)	0.700(6)	0.628(4)	0.566(1)
	σ^*	0.98046(0)	0.958(0)	0.8881(8)	0.8105(7)	0.7370(1)	0.67326(1)	0.6181(0)
∞	T_1^*	0.975(2)	0.939(0)	0.822(4)	0.707(2)	0.605(0)	0.5238(0)	0.458(4)
	$P_{1,yy}^*$							
	q_1^*	0.0076(3)	0.0234(2)	0.088(4)	0.165(0)	0.231(9)	0.305(0)	0.324(5)

Table 2. Simulation values of some quantities for $n_1/n_2 = 4$ and $m_1/m_2 = 3$ in the cases of Maxwell molecules ($\mu = 4$), soft spheres ($\mu = 12$) and hard spheres ($\mu = \infty$). We also include the exact solution values for Maxwell molecules. The statistical error is indicated in parentheses, in units of the last digit.

μ		$\epsilon^* = 0.125$	0.25	0.5	0.75	1	1.25	1.5
		Exact results						
4	σ^*	0.99230	0.97056	0.89897	0.81375	0.73205	0.65984	0.59787
	T_1^*	0.97445	0.90707	0.72571	0.56625	0.45058	0.36896	0.31020
	$P_{1,yy}^*$	0.97168	0.89746	0.70108	0.53298	0.41431	0.33263	0.27510
		Simulation results						
4	σ^*	0.993(5)	0.975(2)	0.904(8)	0.8163(0)	0.7351(6)	0.6631(0)	0.6009(4)
	T_1^*	0.9750(1)	0.9072(4)	0.7243(0)	0.5650(4)	0.4485(5)	0.3661(8)	0.3072(3)
	$P_{1,yy}^*$	0.9721(8)	0.897(2)	0.7009(8)	0.5335(2)	0.4124(6)	0.3308(7)	0.2731(6)
	q_1^*	0.0078(8)	0.0562(3)	0.1922(3)	0.2629(1)	0.2752(4)	0.2617(4)	0.2426(3)
12	σ^*	0.982(1)	0.911(2)	0.794(0)	0.6993(7)	0.6280(1)	0.5697(5)	0.5205(6)
	T_1^*	0.974(2)	0.9160(6)	0.7768(3)	0.6541(3)	0.5526(6)	0.4722(5)	0.4098(9)
	$P_{1,yy}^*$	0.9688(4)	0.9002(0)	0.7353(6)	0.5929(8)	0.4807(4)	0.3976(7)	0.3342(0)
	q_1^*	0.0122(2)	0.0642(4)	0.2747(0)	0.324(8)	0.371(2)	0.3786(8)	0.3706(7)
∞	σ^*	0.995(0)	0.898(3)	0.754(8)	0.659(2)	0.5879(4)	0.5330(9)	0.4881(1)
	T_1^*	0.9734(6)	0.9183(0)	0.7953(3)	0.6852(7)	0.5935(3)	0.517(7)	0.4556(8)
	$P_{1,yy}^*$	0.9674(1)	0.894(2)	0.7332(9)	0.5963(1)	0.4891(0)	0.408(0)	0.345(4)
	q_1^*	0.0145(1)	0.0775(8)	0.2543(6)	0.3732(9)	0.4343(0)	0.4545(2)	0.4513(5)

an angular cut-off $\chi = 0.8^\circ$ has been introduced for Maxwell molecules and $\chi = 0.6^\circ$ for soft spheres. All these technical values have been seen to reproduce well the exact results of Maxwell molecules. It is expected that the reliability of the method increases as the number N of particles increases. The study of the influence of the simulation parameters on the convergence rate is an interesting subject in itself, although such an analysis lies beyond the scope of the present paper. This question has been recently studied in [6] in the case of uniform shear flow for a single gas of Maxwell molecules.

With respect to the choice of the force constants κ_{ij} , and for illustrative purposes, we take $d_2 = 2d_1$, so that according to equation (15) $\kappa_{12}/\kappa_{11} = (3/2)^4$, and $\kappa_{22}/\kappa_{11} = 2^4$ for Maxwell molecules while $\kappa_{12}/\kappa_{11} = (3/2)^{12}$ and $\kappa_{22}/\kappa_{11} = 2^{12}$ in the case of soft spheres. We have considered the field strengths $\epsilon^* = 0.125, 0.25, 0.5, 0.75, 1, 1.25$, and 1.5 . We have simulated mixtures with a concentration ratio $n_1/n_2 = 4$ and two values of the mass ratio: $m_1/m_2 = 1/3$ and $m_1/m_2 = 3$. The properties of the system with $n_1/n_2 = 1/4$ can be inferred by changing 1 to 2.

In tables 1 (for $m_1/m_2 = 1/3$) and 2 (for $m_1/m_2 = 3$) we display the values of the reduced colour conductivity coefficient σ^* (which is the main transport coefficient of the problem), the partial temperature ratio $T_1^* = T_1/T$, the reduced normal element of the pressure tensor $P_{1,yy}^* \equiv P_{1,yy}/n_1 k_B T$, and the reduced heat flux vector $q_1^* \equiv (2/\rho_1)(m_1/2k_B T)^{3/2} q_1$. At a given value of the field strength, we include the values corresponding to the three interaction models studied and also the analytical solution in the Maxwell case.

Figure 1 shows σ^* as a function of ϵ^* . In the case of Maxwell molecules, we see that the simulation data reproduce fairly well the exact solution. For this interaction model, and according to the results presented in tables 1 and 2, σ^* is a function of ϵ^* that is independent of the parameters of the mixture. Beyond the Maxwell model, this independence disappears. As seen in figure 1, the influence of the interaction potential

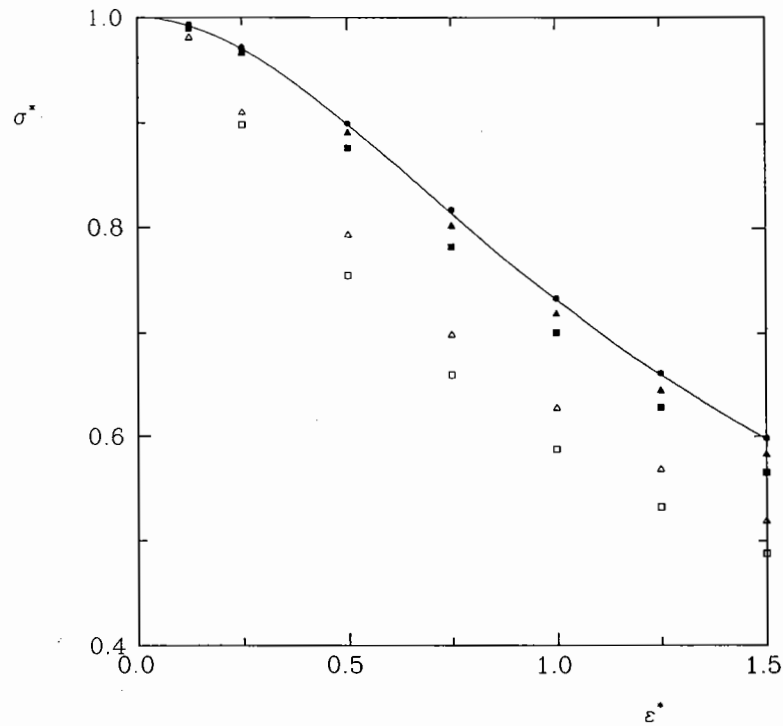


Figure 1. Plot of the reduced colour conductivity coefficient $\sigma^*(\epsilon^*)$ for the concentration ratio $n_1/n_2 = 4$ and for two values of the mass ratio: $m_1/m_2 = 1/3$ (filled symbols) and $m_1/m_2 = 3$ (open symbols). The simulation data are represented by circles (Maxwell molecules), triangles (soft spheres), and squares (hard spheres) while the solid curve corresponds to the exact result obtained for Maxwell molecules.

becomes more noticeable as the field strength increases, very specially when the particles of the defect species are lighter than the particles of the excess species. We also observe that, for a given value of ϵ^* , σ^* monotonically increases as the intermolecular repulsion becomes softer, whatever the mass ratio. All the curves collapse into the universal value $\sqrt{2}|\epsilon^*|^{-1}$ in the limit of large field strengths.

In figure 2 we plot the partial temperature T_1^* . In contrast to σ^* , T_1^* depends on the parameters of the mixture, even in the case of Maxwell molecules. According to the results derived in [3], T_1^* is not in general a monotonic function of ϵ^* although for the simulations performed here it always decreases as the field strength increases. With respect to the influence of the inverse power law, we seen again that it is more sensitive when the excess particles are heavier than the defect particles. In contrast to what happens for σ^* , T_1^* increases with increasing interaction parameter μ for a given ϵ^* . The reduced normal element $P_{1,yy}^*$ of the pressure tensor measures the transport of momentum across the system along a direction orthogonal to the external field. Its dependence on the field strength is shown in figure 3. We observe that, at a given value of ϵ^* , $P_{1,yy}^*$ monotonically decreases as the interaction parameter μ increases when $m_1/m_2 = 1/3$, and the opposite occurs for $m_1/m_2 = 3$.

A knowledge of the velocity of all the particles allows one to construct the velocity distribution function $f_1(\mathbf{v})$. This quantity contains all the information for the colour problem. In addition, no explicit expression for the distribution function is known in

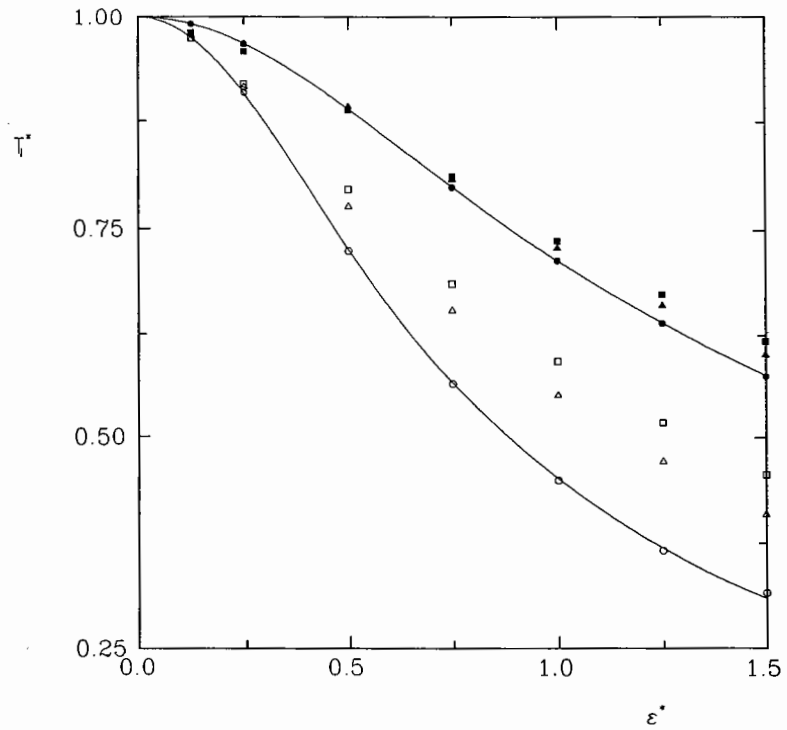


Figure 2. Plot of the reduced partial temperature $T_1^* = T_1/T$ as a function of ϵ^* for the same cases as in figure 1. Symbols as for figure 1.

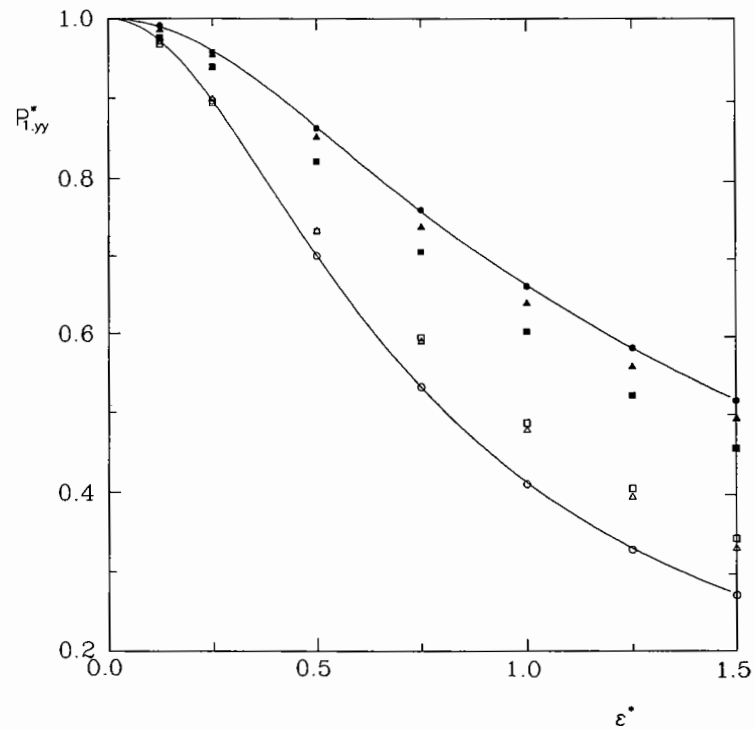


Figure 3. As for figure 1 but for the reduced normal element of the pressure tensor $P_{1,yy}^*$.

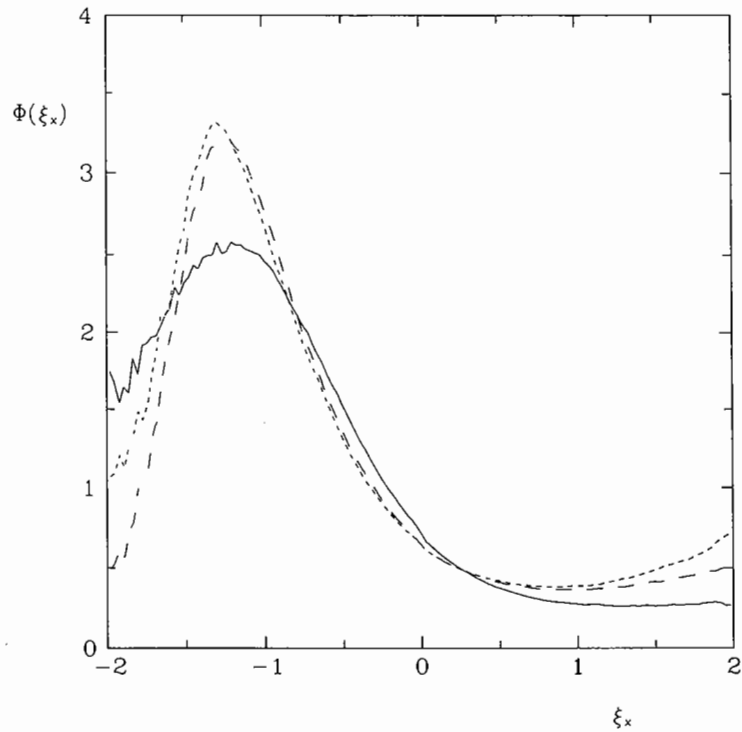


Figure 4. Reduced distribution function $\Phi(\xi_x)$ obtained from simulation results for $n_1/n_2 = 4$, $m_1/m_2 = 1/3$ and $\epsilon^* = 1$, in the cases of Maxwell molecules (—), soft spheres (---), and hard spheres (-.-).

the context of the Boltzmann equation, even in the particular case of Maxwell molecules. Since $f_1(\mathbf{v})$ depends on the three velocity components, for the sake of illustration, we consider the reduced distribution

$$\Phi(\xi_x) = \pi^{1/2} e^{\xi_x^2} \int_{-\infty}^{+\infty} d\xi_y \int_{-\infty}^{+\infty} d\xi_z \Psi_1(\xi), \quad (18)$$

where $\xi \equiv (m_1/2k_B T)^{1/2} \mathbf{v}$, and $\Psi_1(\xi) \equiv (1/n_1) (2k_B T/m_1)^{-3/2} f_1(\mathbf{v})$. This distribution measures the distortion from equilibrium ($\Phi(\xi_x) = 1$) resulting from the fact that the system is far from equilibrium. The behaviour of $\Phi(\xi_x)$ is shown in figures 4 and 5 for $\epsilon^* = 1$ and the mixtures previously considered. In both systems we observe in general a distortion from equilibrium. A comparison of the three interaction models indicates that the velocity distribution function is rather sensitive to the repulsive intermolecular law in a far from equilibrium state. Although the qualitative behaviour of all the potentials is similar, important differences appear, especially in the high-velocity region. This is not surprising as one expects that influence of the potential law to become significant as one goes up in the degree of the moments, which are the relevant ones in the region of high velocities. With respect to the dependence on the mass ratio, it is evident that the effect of the power law is much more noticeable when the defect particles are lighter than the excess particles. In this situation there exist important discrepancies not only in the region of high velocities but also in the location and the value of the maximum. Anyway, in general, the predictions of the soft

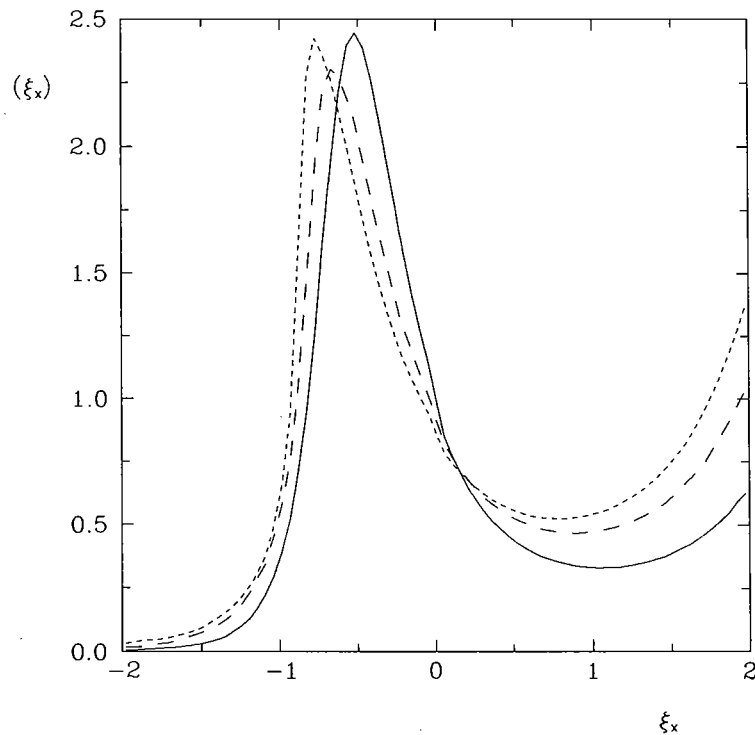


Figure 5. As for figure 4, but for $m_1/m_2 = 3$.

sphere model are between the two extreme cases of Maxwell molecules and hard spheres. This monotonic behaviour is in agreement with the results derived for the first moments.

4. Conclusion

In this paper, we have analysed the colour conductivity problem for a binary mixture in the low density regime. The system is subjected to an external force that produces mutual diffusion in the absence of concentration gradients. As a consequence, the physical situation corresponds to a non-equilibrium homogeneous steady state. The only non-equilibrium parameter is the field strength, which can take values arbitrarily large. The main transport coefficient is the colour conductivity coefficient. It is defined as the ratio of the mass flux to the colour field strength. Recently, an exact solution of the colour conductivity problem has been derived in the case of Maxwell molecules [3]. In this paper we extend our previous analysis to stronger interaction models. For this purpose we use a Monte Carlo simulation method due to Bird [4], which has been devised to capture the dynamics involved in the Boltzmann collision term. We have computed the main transport properties and the velocity distribution functions for three different $r^{-\mu}$ potentials: Maxwell molecules ($\mu = 4$), 'soft' spheres ($\mu = 12$), and hard spheres ($\mu \rightarrow \infty$).

Concerning the influence of the potential model, discussed at length in section 3, the following conclusions may be drawn. Beyond the Maxwell interaction, the reduced colour conductivity coefficient σ^* happens to be a function of the parameters of the mixture as well as of the reduced field strength e^* . This conclusion contrasts with the results obtained for Maxwell molecules, where σ^* is a function only of e^* . The colour

conductivity coefficient decreases as the field strength increases, so that the mass transport is inhibited by the colour field whatever the interaction model. Further, the influence of the potential model becomes more significant as the mass of the defect particles is smaller than that of the excess species. With respect to the temperature ratio T_1^* , and in contrast to what happens for σ^* , at a given value of the field strength it decreases as the intermolecular repulsion becomes softer. The influence of the interaction parameter μ on the normal element of the pressure tensor is not monotonic, and depends on the mass ratio considered. Even though all the fluxes are defined with respect to a frame moving with species velocity, we have verified that other choices for the reference frame of the fluxes (for instance, laboratory frame) do not alter the general dependence of the transport properties on the parameters of the problem. Finally, the simulation data show that the velocity distribution function is strongly distorted from equilibrium as well as being affected appreciably by the inverse power law.

Although the results obtained in this work have been restricted to three different interaction potentials, we believe that our predictions can be extrapolated to other repulsive interaction potentials. This expectation is based on the general monotonic dependence with the interaction parameter observed in the simulation. On the other hand, note that the choice of the reduced field strength ϵ^* may affect the conclusions about the influence of the interaction model. It is clear that in a mixture there are several possibilities for ϵ^* . Since the mixture behaves as a collisionless gas in the limit of large field strengths, we take ϵ^* under the condition that the reduced conductivity coefficient $\sigma^*(\epsilon^*)$ tends to a 'universal' value (independent of the potential law) when $\epsilon^* \rightarrow \infty$. In this sense, our choice seems to be the most natural. In terms of this reduced field strength, and in contrast to what happens for a single gas in other non-equilibrium situations [5, 11], we observe that the transport properties are sensitive to the interaction potential so that the quantitative predictions previously made from the exact description for Maxwell molecules cannot be extended to other interaction potentials.

As a final comment, we should like to point out that the comparison between exact and simulation results for the colour conductivity coefficient, the temperature ratio, and the normal element of the pressure tensor show good agreement when the simulation parameters are chosen properly. This comparison may be considered as a stringent test of the DSMC method for binary mixtures in far from equilibrium situations.

We are grateful to Andrés Santos for suggestions for the improvement of the manuscript. This research has been supported partially by the Dirección General de Investigación Científica y Técnica (Spain) through grant no. PB94-1021 and by the Junta de Extremadura (Fondo Social Europeo) through grant no EIA94-39. The research of C.M. and J.M.M. has been supported by Ministerio de Educación y Ciencia (Spain) through predoctoral fellowships.

References

- [1] EVANS, D. J., HOOVER, W. G., FAILOR, B., MORAN, B., and LADD, A. J. C., 1983, *Phys. Rev. A*, **28**, 1016; EVANS, D. J., LYNDALL-BELL, R. M., and MORRIS, G. P., 1989, *Molec. Phys.*, **67**, 209.
- [2] EVANS, D. J., and CUMMINGS, P. T., 1991, *Molec. Phys.*, **72**, 893; SARMAN, S., and EVANS, D. J., 1992, *Phys. Rev. A*, **45**, 2370.

- [3] MARÍN, C., GARZÓ, V., and SANTOS, A., 1994, *J. statist. Phys.*, **75**, 797.
- [4] BIRD, G. A., 1994, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows* (Oxford University Press).
- [5] GÓMEZ ORDÓÑEZ, J., BREY, J. J., and SANTOS, A., 1989, *Phys. Rev. A*, **39**, 3038; 1990, *Phys. Rev. A*, **41**, 810.
- [6] MONTANERO, J. M., and SANTOS, A., 1995, *Rarefied Gas Dynamics*, edited by J. Harvey and R. G. Lord (Oxford University Press).
- [7] CERCIGNANI, C., and CORTESSE, S., 1994, *J. statist. Phys.*, **75**, 817.
- [8] HOOVER, W. G., 1995, *Phys. Lett. A*, **204**, 133.
- [9] EVANS, D. J., and MORRIS, G. P., 1990, *Statistical Mechanics of Nonequilibrium Liquids* (Academic Press, London).
- [10] CHAPMAN, S., and COWLING, T. G., 1970, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press).
- [11] MONTANERO, J. M., ALAOU, M., SANTOS, A., and GARZÓ, V., 1994, *Phys. Rev. E*, **49**, 367.