THERMAL CONDUCTIVITY FROM A SIMULATION MONTE CARLO METHOD FOR THE ENSKOG EQUATION

J. M. Montanero,   A. Santos

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

ABSTRACT: We have recently proposed a simulation Monte Carlo method to solve the Enskog equation. The method is inspired on and extends the DSMC method to solve the Boltzmann equation. In this paper we show that our method reproduces the density dependence of the thermal conductivity derived from the Enskog equation. Moreover, the velocity distribution function is seen to agree with the theoretical expression near equilibrium.

1 INTRODUCTION

As is well known, the mathematical complexity of the *nonlinear* Boltzmann equation has limited to a few cases the number of exact solutions[1]. To overcome this problem, two approaches have proved to be especially useful. On the one hand, the detailed Boltzmann collision operator can be modeled with much simpler terms[2], that nonetheless yield realistic results[3]. On the other hand, the Boltzmann equation can be numerically solved in a very efficient way by means of the direct simulation Monte Carlo (DSMC) method[4].

While the Boltzmann equation plays a fundamental role in the description of the dynamics of rarefied gases, its scope cannot be extended to fluids at moderate or high densities. This excludes those phenomena with a characteristic length of the order of or smaller than the range of the interaction potential. As a consequence, dense fluid transport, short wavelength dynamics, kinetics of freezing, crystal elasticity and transport, kinetics of metastable states, or dynamics of amorphous solid states are some of the interesting problems whose solutions lie outside the domain of applicability of the Boltzmann equation. This limitation, however, does not hold for the Enskog equation[5,6]. The Enskog equation can be viewed as an extension of the Boltzmann equation to a *dense* fluid of hard spheres of diameter σ. It introduces two crucial changes in the Boltzmann collision integral: the difference in position $\Delta r = \sigma$ between the centers of a colliding pair of molecules is taken into account, and the collision frequency is increased by a factor χ that accounts for the spatial correlations between the two colliding molecules. The Chapman-Enskog expansion[2] of the Enskog equation yields fluid transport coefficients that are in good agreement with both experimental and simulation values over a wide range of densities. Furthermore, the so-called revised Enskog theory[7] admits the crystal equilibrium state as a stationary solution[8].

Of course, the mathematical intricacy of the Enskog equation is even harder than that of the Boltzmann equation. This explains the fact that only recently the two approaches mentioned above in the context of the Boltzmann equation have succeeded in being extended to the Enskog equation as well. On the one hand, simple kinetic models have been

proposed[9,10] that, while preserving the main physical features of the Enskog equation, re-duce to the familiar Bhatnagar-Gross-Krook kinetic model[2] in the low density limit. On the other hand, a simulation Monte Carlo algorithm based on the DSMC method has been proposed[11] to numerically solve the Enskog equation. The method is applied to shear flow in Ref. [12] and is seen to reproduce the shear viscosity of the Enskog theory, as well as the nonlinear Burnett coefficients associated with normal stresses, over the whole range of fluid densities. A previous attempt[13] is consistent with the equilibrium equation of state for hard spheres but not with the Enskog transport properties.

The objective of this paper is the application of our simulation method to measure the thermal conductivity of a dense system of hard spheres and compare it with the theoretical value derived from the Enskog equation[5,6]. In order to avoid boundary effects, we have considered the homogeneous heat flow state[14], introduced by Evans and Gillan in 1982. In this state, heat flux is induced in a *homogeneous* system by the action of a non-conservative force proportional to a constant vector that mimics the action of a thermal gradient. The paper is organized as follows. In Sec. 2 the Enskog simulation Monte Carlo (ESMC) method is briefly described. The particularization of the Enskog equation and the ESMC method to the homogeneous heat flow state is carried out in Sec. 3. Finally, the results are presented and discussed in Sec. 4.

2 THE ESMC METHOD

The Enskog equation[5-7] reads

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} + \frac{\partial}{\partial \mathbf{v}} \cdot \frac{\mathbf{F}}{m}\right) f(\mathbf{r}, \mathbf{v}, t) = \sigma^2 \int d\mathbf{v}_1 \int d\widehat{\sigma}\, \Theta(\widehat{\sigma} \cdot \mathbf{g})(\widehat{\sigma} \cdot \mathbf{g})$$

$$\times \left[\chi(\mathbf{r}, \mathbf{r} - \sigma) f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r} - \sigma, \mathbf{v}_1', t) - \chi(\mathbf{r}, \mathbf{r} + \sigma) f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r} + \sigma, \mathbf{v}_1, t)\right] , \quad (1)$$

where $f(\mathbf{r}, \mathbf{v}, t)$ is the one-particle distribution function, m is the mass of a particle, $\mathbf{F}$ is an external force (possibly non-conservative), $\widehat{\sigma}$ is a unit vector, $\sigma = \sigma\widehat{\sigma}$, $\Theta(x)$ is the Heaviside function, $\mathbf{g} \equiv \mathbf{v} - \mathbf{v}_1$ is the relative velocity, and the primes on the velocities denote post-collision values: $\mathbf{v}' = \mathbf{v} - (\widehat{\sigma} \cdot \mathbf{g})\widehat{\sigma}$, $\mathbf{v}_1' = \mathbf{v}_1 + (\widehat{\sigma} \cdot \mathbf{g})\widehat{\sigma}$. In the standard Enskog theory[5,6], $\chi(\mathbf{r}, \mathbf{r} + \sigma) = \chi\left(n(\mathbf{r} + \frac{1}{2}\sigma)\right)$, where $\chi(n)$ is the equilibrium pair correlation function at contact corresponding to a *uniform* density n. In the revised Enskog theory[7], $\chi(\mathbf{r}, \mathbf{r} + \sigma)$ is the local equilibrium pair correlation function in a *nonuniform* state. Equation (1) reduces to the Boltzmann equation (for hard spheres) in the low density limit (i.e., $\sigma = 0$, $\chi = 1$). In general, the momentum and heat fluxes have both kinetic and collisional transfer contributions. In particular, the Chapman-Enskog method gives $\mathbf{q} = -\kappa_E(n, T)\nabla T$ for the heat flux, where the thermal conductivity coefficient is given by[6]

$$\kappa_E(n, T) = \frac{1}{\chi(n)} \left[1 + \frac{2\pi}{5} n\sigma^3 \chi(n)\right]^2 \kappa_B(T) + \frac{2}{3} n^2 \sigma^4 \chi(n) \left(\pi k_B^3 T/m\right)^{1/2} , \quad (2)$$

where $\kappa_B(T) = 1.0415 \times \frac{75}{64}(k_B^3 T/m\pi)^{1/2}\sigma^{-2}$ is the Boltzmann thermal conductivity.

The ESMC method to solve Eq. (1) proceeds as follows[11]. A system of N particles in a volume V is split into cells of a size ΔL much smaller than both the mean free path and the hydrodynamic length. The physical number density of cell I is $n_I = \overline{n}(N_I/V_I)(V/N)$, where $\overline{n}$ is the average density, and N_I and V_I are the number of particles and volume,

respectively, of cell I. To update the positions and velocities, a free-streaming stage and a collision stage are decoupled over a time-step Δt much smaller than both the mean free time and the hydrodynamic time. As in the DSMC method[4], in the first stage the particles move independently (under the possible action of an external force) and the boundary conditions are applied. In the collision stage, the following steps are taken for every particle $i = 1, \ldots, N$: (a) a given direction $\widehat{\sigma}_i$ is chosen at random with equal probability; (b) the cell J that contains the point $\mathbf{r}_i + \sigma\widehat{\sigma}_i$ is identified and a *test* particle j belonging to J is chosen at random with equal probability; (c) the collision between particles i and j is accepted with a probability equal to the collision rate times the time-step,

$$\omega_{ij} = \sigma^2 4\pi\Theta(\widehat{\sigma}_i \cdot \mathbf{g}_{ij})(\widehat{\sigma}_i \cdot \mathbf{g}_{ij})\chi(\mathbf{r}_i, \mathbf{r}_i + \sigma\widehat{\sigma}_i)n_J \Delta t , \tag{3}$$

where $\mathbf{g}_{ij} \equiv \mathbf{v}_i - \mathbf{v}_j$; (d) if the collision is accepted, the velocity of particle i is changed to $\mathbf{v}'_i = \mathbf{v}_i - (\widehat{\sigma}_i \cdot \mathbf{g}_{ij})\widehat{\sigma}_i$.

If the density is sufficiently small, the size ΔL of the cells can be taken much larger than σ. Consequently, particle j in step (b) belongs to the same cell as particle i (i.e. $J = I$). In addition, $\chi \to 1$, so that the ESMC method becomes equivalent to Nanbu's scheme[15] of the DSMC method.

3 HOMOGENEOUS HEAT FLOW STATE

As said in the Introduction, the ESMC method described in the previous Section has been validated in the case of shear flow[11,12]. The aim of this paper is to carry out a similar validation in the case of heat flow. In principle, one should place the fluid in a slab and establish a thermal gradient by keeping the two walls at different temperatures[16]. Nevertheless, boundary effects would be unavoidable and could mask the comparison between the measured thermal conductivity and the theoretical value, Eq. (2). Consequently, we have considered a homogeneous method for simulating heat flow[14]. In this method, a fictitious velocity-dependent external field $\mathbf{F}_1 = -\frac{1}{2}(mv^2 - 3k_B T)\epsilon$, where $\epsilon = \epsilon\widehat{\mathbf{x}}$ is a constant vector, is applied. Those particles with a kinetic energy smaller than the average value are accelerated along the x-direction, while the opposite happens to the most energetic particles. As a consequence, a heat flux vector $\mathbf{q} = q_x\widehat{\mathbf{x}}$ is generated in the system, even in the absence of any gradient. Linear response theory proves that the ratio $-q_x/T\epsilon$ in the zero-field limit ($\epsilon \to 0$) is equal to the thermal conductivity coefficient. Thus, ϵ mimics the action of a thermal gradient $\nabla T/T$. The price to be paid is that outside the linear regime close to equilibrium, no physical meaning[17] can be ascribed to the field-dependent nonlinear transport coefficient $-q_x/\epsilon$. The action of the force $\mathbf{F}_1$ produces the absence of conservation of momentum and energy. To compensate for this effect, a force $\mathbf{F}_2 = m(\beta - \alpha\mathbf{v})$ is added, where the parameters β and α are adjusted as to keep the total momentum and energy constant.

A non-trivial problem is how to especialize the Enskog collision term, given by the right-hand side of Eq. (1), to the homogeneous heat flow state. To do so, we exploit the analogy $\epsilon \leftrightarrow \nabla T/T$ and imagine a "virtual" system with a temperature field $T(\mathbf{r}) = T_0 e^{\epsilon \cdot \mathbf{r}}$, T_0 being the homogeneous temperature of our "real" system. The distribution function $f_0(\mathbf{v})$ of the real system would be equal to the distribution function $f(0, \mathbf{v})$ at the reference point $\mathbf{r} = 0$ of the virtual system. Since in the latter all the space dependence must appear through

the temperature, so that the choice of the reference point is completely arbitrary, one has $f(\mathbf{r}, \mathbf{v}) = [T_0/T(\mathbf{r})]^{3/2} f_0(\mathbf{v}_0)$, $\mathbf{v}_0 = [T_0/T(\mathbf{r})]^{1/2}\mathbf{v}$. Thus, insertion into the right-hand side of Eq. (1) with $\mathbf{r} = 0$ yields

$$
\left\{ \frac{\partial}{\partial t} - \frac{\partial}{\partial \mathbf{v}} \cdot \left[\frac{1}{2}\epsilon \left(v^2 - \frac{3k_BT}{m} \right) - \beta + \alpha\mathbf{v} \right] \right\} f(\mathbf{v}, t) = \sigma^2 \chi(n) \int d\mathbf{v}_1 \int d\hat{\sigma}\, \Theta(\hat{\sigma} \cdot \mathbf{g})(\hat{\sigma} \cdot \mathbf{g})
$$

$$
\times \left[f(\mathbf{v}', t) e^{\frac{3}{2}\epsilon \cdot \sigma} f(\mathbf{v}_1' e^{\frac{1}{2}\epsilon \cdot \sigma}, t) - f(\mathbf{v}, t) e^{-\frac{3}{2}\epsilon \cdot \sigma} f(\mathbf{v}_1 e^{-\frac{1}{2}\epsilon \cdot \sigma}, t) \right] , \tag{4}
$$

where the subscript 0 has been removed. Imposing the conservation of momentum and energy, one gets $\beta = (mn)^{-1}\mathsf{P}^c \cdot \epsilon$, where P^c is the collisional part of the pressure tensor, and $\alpha = -(3nk_BT)^{-1}\epsilon \cdot \mathbf{q}$. Notice that $\beta \sim \epsilon$, but $\alpha \sim \epsilon^2$. Thus, the "thermostat" parameter α does not play any role in the linear regime and its inclusion obeys only to computational reasons[14].

It is easy to prove that the solution of Eq. (4) to first order in ϵ coincides with the one obtained from the conventional Chapman-Enskog expansion[5,6]. Let us write

$$
f(\mathbf{v}) = f_{eq}(\mathbf{v}) \left[1 + \mathbf{A}(\mathbf{v}) \cdot \epsilon \right] + \mathcal{O}(\epsilon^2) , \tag{5}
$$

where $f_{eq}(\mathbf{v})$ is the equilibrium distribution function. Substituting into Eq. (4) and neglecting terms of order higher than ϵ, one gets

$$
\left(1 + \frac{2\pi}{5}n\sigma^3\chi \right) \left(\frac{mv^2}{2k_BT} - \frac{5}{2} \right) \mathbf{v} = \sigma^2\chi(n) \int d\mathbf{v}_1 \int d\hat{\sigma}\, \Theta(\hat{\sigma} \cdot \mathbf{g})(\hat{\sigma} \cdot \mathbf{g}) f_{eq}(\mathbf{v}_1)
$$

$$
\times \left[\mathbf{A}(\mathbf{v}) + \mathbf{A}(\mathbf{v}_1) - \mathbf{A}(\mathbf{v}') - \mathbf{A}(\mathbf{v}_1') \right] . \tag{6}
$$

The solution to this integral equation is given approximately by[5]

$$
\mathbf{A}(\mathbf{v}) = 1.0415 \times \frac{15\pi}{16}\tau \left(1 + \frac{2\pi}{5}n\sigma^3\chi \right) \left(\frac{mv^2}{2k_BT} - \frac{5}{2} \right) \mathbf{v} , \tag{7}
$$

where $\tau = (m/k_BT)^{1/2}/2\pi n\sigma^2\chi$ is the mean free time.

The ESMC method is easily adapted to solve Eq. (4). Since the problem is homogeneous, there is no need to store the positions of the particles. In the free-streaming stage, the particles change their velocities under the action of the forces $\mathbf{F}_1$ and $\mathbf{F}_2$. The collision stage proceeds as described in Sec. 2, except that there are no cells and the relative velocity is now $\mathbf{g}_{ij} = \mathbf{v}_i - \mathbf{v}_j e^{\frac{1}{2}\epsilon \cdot \sigma_i}$. This accounts for the fact that particle j in the virtual system is a distance $\sigma_i = \sigma\hat{\sigma}_i$ apart from particle i, so that its velocity is $\mathbf{v}_j e^{\frac{1}{2}\epsilon \cdot \sigma_i}$. The heat flux is obtained as

$$
\mathbf{q} = \frac{mn}{2N}\sum_{i=1}^{N} v_i^2\mathbf{v}_i - \frac{mn\sigma}{4N\Delta t}\sum_{i=1}^{N}(v_i'^2 - v_i^2)\hat{\sigma}_i . \tag{8}
$$

The first term on the right side is the kinetic contribution, while the second term is the collisional contribution.

4 RESULTS AND DISCUSSION

In the simulations, ϵ must be chosen sufficiently small to remain in the linear regime and sufficiently large to provide a good signal-to-noise ratio. We have chosen the value

$\epsilon = 0.177\sigma^{-1}$. The values of the technical parameters are $N = 10^4$, $\Delta t = 0.014\tau$, and the quantities have been averaged over 20 different realizations. The initial condition has been that of equilibrium. Figure 1 shows the time evolution of the heat flux (divided by the stationary Enskog prediction) for $n\sigma^3\chi = 2$ (which corresponds to a density $n\sigma^3 \simeq 0.67$). We
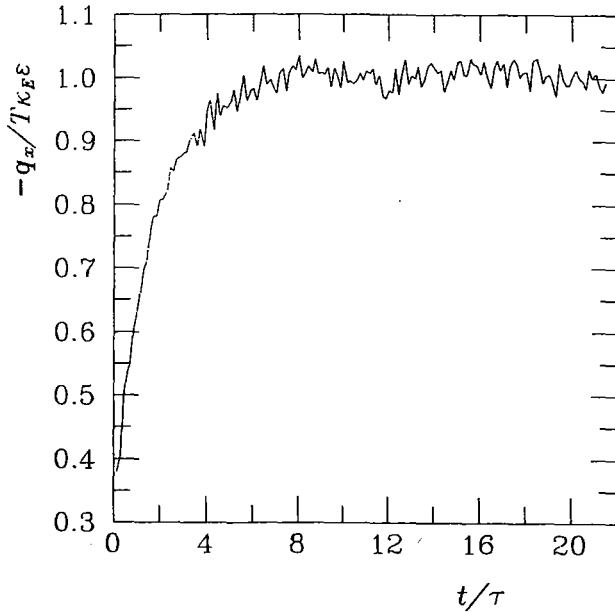

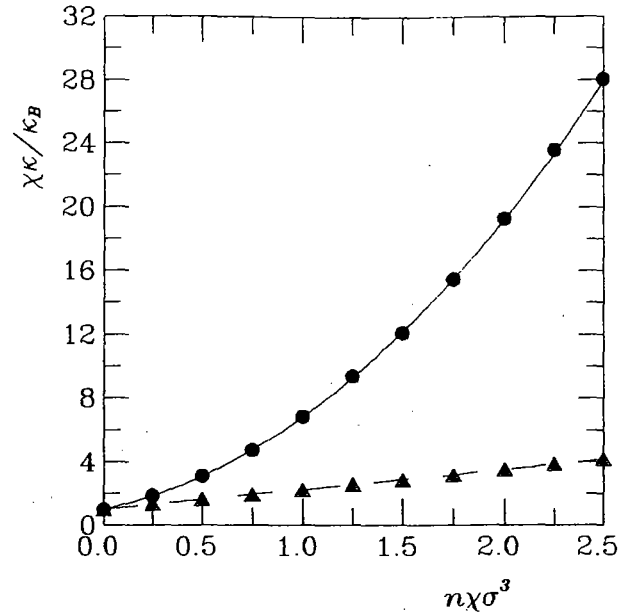Fig. 1 Time evolution of the heat flux for $n\sigma^3\chi = 2$.

Fig. 2 Density dependence of the thermal conductivity.

observe that after a few collisions per particle, the heat flux reaches a stationary value that agrees with the theoretical one. We have performed similar simulations for other densities and have measured the thermal conductivity κ as a time average of the ratio $-q_x/T\epsilon$, once the steady state has been reached ($t > 9\tau$). The results are represented in Fig. 2, where $\kappa/(\chi^{-1}\kappa_B)$ is plotted versus $n\sigma^3\chi$. The circles correspond to the total thermal conductivity, while the triangles correspond to its kinetic part. The agreement with the theoretical Enskog predictions (represented by lines) is excellent.

To make a more stringent test, we have also computed the velocity distribution function. Figure 3 shows the reduced marginal distribution $R_x(\xi_x) = [\int dv_y \int dv_z f(\mathbf{v})]/[\int dv_y \int dv_z f_{eq}(\mathbf{v})]$, where $\xi_x = (m/2k_BT)^{1/2}v_x$, for $n\sigma^3\chi = 2$. The solid line represents the simulation results (with a grid size $\Delta\xi_x = 0.02$) and the dashed line is the theoretical prediction, according to Eqs. (5) and (7). Again, the agreement is extremely good.
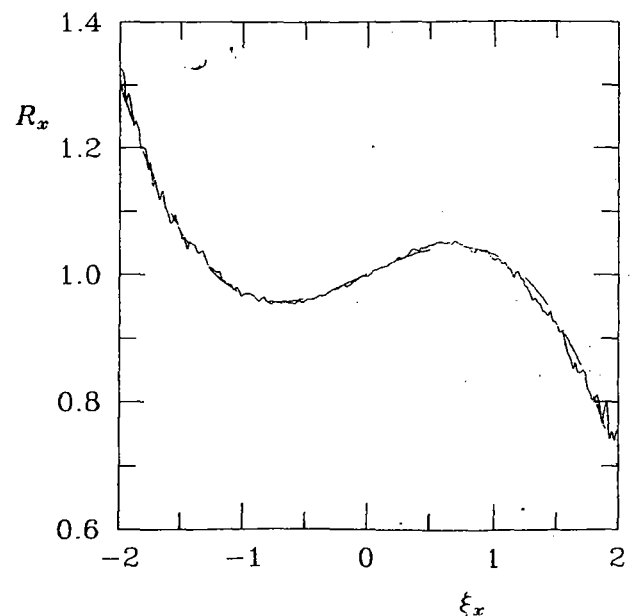

Fig. 3 Marginal velocity distribution function $R_x(\xi_x)$ for $n\sigma^3\chi = 2$.

In summary, the results presented in this paper represent an important validation of our generalization of the DSMC method to deal with the Enskog equation for dense fluids. It opens the possibility to explore many interesting phenomena left out by the Boltzmann equation and that so far were prohibitively difficult to attack with the Enskog equation.

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