Thermal transport in gases via homogeneous nonequilibrium molecular dynamics

Werner Loose
Institut für Theoretische Physik, Technische Universität Berlin, PN 7-1, D-1000 Berlin 12, West Germany
(Received 12 April 1989)

Thermal transport in gases is investigated by nonequilibrium molecular-dynamics computer simulations. A homogeneous driving force generates a heat flux in the absence of a temperature gradient. It is uniquely derived from a moment-method analysis of the Boltzmann equation by requiring an identical linear response as would result from a temperature gradient. The algorithm is shown to be identical to the Evans-Gillan method if in the latter only kinetic terms are retained in the equations of motion. The validity of this peculiar approach in the linear regime is demonstrated by simulation results for the heat conductivity and the distorted velocity distribution function. In the nonlinear regime, however, the external force leads to an unphysical divergence of the heat conductivity. The accompanying kinetic theory analysis and other recent related work confirm the long-standing presumption that the Evans-Gillan algorithm gives an incorrect nonlinear response.

I. INTRODUCTION

Nonequilibrium molecular-dynamics computer simulations (NEMD) are widely used to investigate the linear and nonlinear transport properties of fluids. In the pioneering work of Ashurst and Hoover[1] the simulation aimed at a great resemblance to the corresponding laboratory experiments: velocity and temperature gradients were induced by walls. Due to the usually small system size, a considerable dependence on the number of particles was observed, and definite conclusions about the bulk properties were impeded by the effects of the boundaries. For the plane shear flow the periodic-boundary conditions can be adjusted to allow for simulations of quasi-infinite systems.[2] Meanwhile, several well-probed homogeneous algorithms for the shear flow problem are at hand. Their validity in the nonlinear flow regime has been established by means of nonlinear response theory for transient phenomena[3] and by comparing the steady-state response of a sheared gas with predictions of the Boltzmann equation.[4,5] The thermal transport appears to be more intricate. Although a corresponding homogeneous algorithm has been derived independently by Evans[6] and Gillan,[7] its validity beyond the linear regime could not be proved. In the present approach the outstanding position of the kinetic theory of gases in statistical mechanics is used to elucidate the problems inherent in a homogeneous heat flux simulation. The article proceeds as follows.

In Sec. II the kinetic theory based on the Boltzmann equation with inclusion of an external (velocity-dependent) force is introduced. A moment-method approach for its solution is briefly sketched. The transport relaxation equations are linearized in Sec. III where the external force is constructed to exactly mimic a temperature gradient. It is *uniquely* derived by requiring an identical linear response as would result from a temperature gradient. Not surprisingly, the external force is shown to be equivalent to the Evans-Gillan force if only kinetic terms are retained in the latter. The formalism of Sec. II is applied to predict the nonlinear response to this force and to compare the nonlinear coupling behavior with the corresponding coupling which would result in the presence of a temperature gradient. These predictions are confirmed by the simulation results presented in Sec. IV. In the linear regime the (macroscopic) transport coefficient as well as the (microscopic) velocity distribution function are shown to be identical as in a laboratory experiment where the same heat flux is generated by a thermal gradient. In the nonlinear regime, however, the external driving force leads to an unphysical divergence of the heat conductivity which contradicts recent exact kinetic theory results[8] as well as observations made in other computer simulations for the heat flux of a gas between parallel plates.[9] The conclusions are summarized in Sec. V.

II. KINETIC THEORY

A moment-method approach is used for the kinetic-theory analysis based on the Boltzmann equation. In general, moment methods consist of an expansion of the one-particle distribution function with respect to a complete set of functions. In the present case, Sonine polynomials in conjunction with Cartesian irreducible tensors are employed to describe the deviation from the *local* equilibrium distribution. The method was introduced by Waldman[10] (for small deviations from a *global* equilibrium) and turned out to be particularly useful for the case of a streaming gas far from equilibrium.[5,11]

In regard of earlier presentations of the method[11,12] only a brief sketch is given here, mainly to introduce the notation. In addition, the discussion is restricted to the case of a homogeneous heat flux, generated either by a temperature gradient or a homogeneous driving force $\mathbf{K}$, which will be specified in the following section.

It is useful to introduce a characteristic thermal speed $c_0(\mathbf{r},t)$ and a dimensionless velocity $\mathbf{V}(\mathbf{r},t)$ by

$$c_0 \equiv \sqrt{k_B T/m} \quad \text{and} \quad \sqrt{2} c_0 \mathbf{V} \equiv \mathbf{c} \ . \tag{1}$$

The local character of these quantities is due to a possible space and time dependence of the temperature field $T(\mathbf{r},t)$. The particle velocity and mass are denoted by $\mathbf{c}$ and m, respectively, and k_B is Boltzmann's constant.

The deviation of the nonequilibrium velocity distribution function $F(\mathbf{r},\mathbf{V},t)$ from a local Maxwellian distribution $F_M(V^2)$ is expressed by a function $\Phi(\mathbf{r},\mathbf{V},t)$,

$$F(\mathbf{r},\mathbf{V},t)=F_M(V^2)[1+\Phi(\mathbf{r},\mathbf{V},t)] \ . \tag{2}$$

In the present notation the (normalized) Maxwellian distribution simply reads as

$$F_M(V^2)=\pi^{-3/2}\exp(-V^2) \ . \tag{3}$$

Insertion of the ansatz (2) in the Boltzmann equation leads to an equation for the quantity Φ,

$$\frac{d}{dt}(F_M\Phi)+\sqrt{2}c_0\mathbf{V}\cdot\nabla(F_M\Phi)+\frac{1}{\sqrt{2}mc_0}\frac{\partial}{\partial\mathbf{V}}\cdot(\mathbf{K}F_M\Phi)+F_M\omega(\Phi)+F_M\tilde{\omega}(\Phi,\Phi)$$
$$=-\frac{d}{dt}F_M-\sqrt{2}c_0\mathbf{V}\cdot\nabla F_M-\frac{1}{\sqrt{2}mc_0}\frac{\partial}{\partial\mathbf{V}}\cdot(\mathbf{K}F_M) \ . \tag{4}$$

The linear and the quadratic part of the collision operator are denoted by ω and $\tilde{\omega}$, respectively.[12] The function Φ is now expressed in terms of the basis functions,

$$\Phi(\mathbf{r},\mathbf{V},t)=\sum_{l=0}^{\infty}\sum_{r=1}^{\infty}{}'a^{(r)}_{\mu_1\cdots\mu_l}(\mathbf{r},t)\phi^r_{\mu_1\cdots\mu_l}(\mathbf{V})\equiv\sum_i{}'a^i\phi^i \ . \tag{5}$$

The summation is restricted (as indicated by the prime) to those functions ϕ^i which characterize the deviation from a local equilibrium distribution. Some examples were given in Ref. 11. The last relation in (5) introduces a useful shorthand. One should keep in mind, however, that the i stands for a whole set of indices, indicating the tensorial rank and the order of the respective expansion function.

The ϕ^i are orthogonal with respect to an integration with the Maxwellian distribution

$$\delta^{ij}=\langle\phi^i\phi^j\rangle=\int F_M(V^2)\phi^i\phi^j d^3V \ . \tag{6}$$

Consequently, using (2) and (5) one readily obtains

$$a^i=\langle\phi^i\Phi\rangle=\int F_M(V^2)\Phi\phi^i d^3V=\int F(\mathbf{V})\phi^i d^3V\equiv\langle\langle\phi^i\rangle\rangle \ . \tag{7}$$

Hence, the *moments* a^i are just the nonequilibrium averages of the corresponding expansion functions. Two expansion functions, ϕ^2_μ and $\phi^1_{\mu\nu}$, deserve special attention as their moments are proportional to the heat flux and the friction pressure, viz.

$$Q_\mu\equiv a^{(2)}_\mu=\left\langle\!\!\left\langle\left[\frac{4}{5}\right]^{1/2}(V^2-\tfrac{5}{2})V_\mu\right\rangle\!\!\right\rangle=\left[\frac{2}{5}\right]^{1/2}\frac{1}{c_0p_0}q_\mu \ , \tag{8}$$

$$\pi_{\mu\nu}\equiv a^{(1)}_{\mu\nu}=\langle\langle\sqrt{2}\{V_\mu V_\nu\}^0\rangle\rangle=\frac{1}{\sqrt{2}p_o}\{P_{\mu\nu}\}^0 \ . \tag{9}$$

The symmetric traceless part of a tensor is denoted by $\{\cdots\}^0$. The ideal-gas pressure is $p_0=nk_BT$ and the symbols Q_μ and $\pi_{\mu\nu}$ are introduced as a reminder of the special meaning of these moments. Similarly, the first two scalar and the first vectorial expansion functions are related to the density, temperature, and streaming velocity, respectively. However, these quantities determine the local equilibrium distribution and must not occur in the expansion (5).

The transport relaxation equations (equations of transfer) for the moments a^i result from a multiplication of (4) with ϕ^i and subsequent integration. For stationary states one obtains

$$\sum_j\left[\sqrt{2}c_0\langle\phi^i\phi^jV_\mu\rangle\nabla_\mu+\frac{c_0}{\sqrt{2}}\left\langle\phi^jV_\mu\left[3+V_\nu\frac{\partial}{\partial V_\nu}\right]\phi^i\right\rangle\frac{1}{T}(\nabla_\mu T)-\frac{1}{\sqrt{2}mc_0}\left\langle\phi^jK_\mu\frac{\partial}{\partial V_\mu}\phi^i\right\rangle\right.$$
$$\left.+\langle\phi^j\omega(\phi^i)\rangle+\sum_k\langle\phi^j\tilde{\omega}(\phi^i,\phi^k)\rangle a^k\right]a^j=-\left[\frac{5}{2}\right]^{1/2}c_0\frac{1}{T}(\nabla_\mu T)\langle\phi^i\phi^2_\mu\rangle+\frac{1}{\sqrt{2}mc_0}\left\langle K_\mu\frac{\partial}{\partial V_\mu}\phi^i\right\rangle \ . \tag{10}$$

Where differential operators act on F_M in (4), partial integrations were performed such that the resulting integrals are simply local equilibrium averages which are denoted by brackets, cf Eq. (6). Implicit use has been made of the usual constant-pressure assumption and of the resulting identity $-\nabla(\ln n)=\nabla(\ln T)$. The first term in (10) can be disregarded for the present case as for a homogeneous heat flux the moments, characterizing the

deviation from local equilibrium, are homogeneous too. Except for the matrix elements of the linearized collision operator all remaining terms on the left-hand side of (10) lead to nonlinearities in the driving term ∇T (or $\mathbf{K}$). The right-hand side is linear in these quantities and, due to the orthogonality (6) of the expansion functions, contributes for selected moments only. In the absence of an external force linearization of (10) leads to

$$\omega_1^{22} Q_\mu = -\left[\frac{5}{2}\right]^{1/2} c_0 \frac{1}{T}(\nabla_\mu T) , \tag{11}$$

where ω_1^{22} stands for the matrix element $\langle \phi_\lambda^2 \omega(\phi_\lambda^2)\rangle$. Nondiagonal matrix elements are neglected. The standard form of the heat conductivity[10,13] is rediscovered with the use of (8),

$$\lambda = \frac{5}{2}\frac{k_B}{m}\frac{p_0}{\omega_1^{22}} . \tag{12}$$

Before the consequences of the nonlinearities in (10) are investigated in detail, a homogeneous force $\mathbf{K}$ is formally constructed to mimic a temperature gradient.

III. HEAT FLUX VIA EXTERNAL FORCE

In a first step the *linearized* transport relaxation equations are used to construct a driving force $\mathbf{K}$ such that it generates exactly the same linear response as would result from a temperature gradient. This approach can be expected to lead to a kinetic theory analog of the force derived independently by Evans[6] and Gillan[7] by means of linear-response theory. In addition, the left-hand side of (10) allows to compare the nonlinear coupling behavior, which will be dealt with in the second part of this section.

A. Linear regime

A homogeneous driving force $\mathbf{K}$ which induces a heat flux in a stationary, constant-temperature NEMD simulation has to fulfill the following requirements.

(i) No net momentum must be produced; the momentum balance equation thus leads to

$$\langle\langle K_\mu \rangle\rangle \equiv 0 . \tag{13}$$

(ii) The constant-temperature constraint and the energy balance equation demand[5]

$$\langle\langle K_\mu V_\mu \rangle\rangle = 0 . \tag{14}$$

(iii) The driving terms on the right-hand side of (10) must be identical in the equation for the heat flux,

$$-\left[\frac{5}{2}\right]^{1/2} c_0 \frac{1}{T}(\nabla_\nu T) = \frac{1}{\sqrt{2}mc_0}\left\langle K_\mu \frac{\partial}{\partial V_\mu}\phi_\nu^2 \right\rangle . \tag{15}$$

(iv) Finally, for all other moments the right-hand side of (10) must vanish,

$$\left\langle K_\mu \frac{\partial}{\partial V_\mu}\phi^i \right\rangle = 0, \text{ for } \phi^i \notin \{\phi^1, \phi^2, \phi_\nu^1, \phi_\nu^2\} . \tag{16}$$

Similar to (5) a general ansatz for K_μ is made,

$$K_\mu = \sum_{l=0}^{\infty}\sum_{r=1}^{\infty} A^{(r)}_{\mu\nu_1\cdots\nu_l}\phi^r_{\nu_1\cdots\nu_l}(\mathbf{V}) . \tag{17}$$

However, here the summation extends over all expansion functions and, in fact, those which had to be excluded in (5) for physical reasons are essential for the following. They are

$$\phi^1 = 1, \quad \phi^2 = \left[\frac{2}{3}\right]^{1/2}(V^2 - \tfrac{3}{2}), \quad \phi_\mu^1 = V_\mu . \tag{18}$$

Insertion of the ansatz (17) in (13) immediately leads to the conclusion that only the last two functions in (18) are relevant. Their averages vanish and the remaining coefficients $A^{(r)}_{\mu\ldots}$ are restricted by

$$A^{(1)}_\mu + \sum_{l=0}^{\infty}{\sum_{r=1}^{\infty}}' A^{(r)}_{\mu\nu_1\cdots\nu_l} a^{(r)}_{\nu_1\cdots\nu_l} = 0 . \tag{19}$$

This identity must hold irrespectively of the nonequilibrium state, determined by the moments a^i, cf Eq. (5). Hence all coefficients $A^{(r)}_{\mu\ldots}$ in (19) must be zero and (17) simply reduces to

$$K_\mu = A^{(2)}_\mu \phi^2 + A^{(1)}_{\mu\nu}\phi^1_\nu . \tag{20}$$

Further restrictions for the matrix $A^{(1)}_{\mu\nu}$ are next derived from the orthogonality requirement (16). Using (6) and partial integration it is rewritten as

$$\left\langle \left[2K_\mu V_\mu - \frac{\partial K_\mu}{\partial V_\mu}\right]\phi^i \right\rangle = 0 ,$$
$$\text{for } \phi^i \notin \{\phi^1, \phi^2, \phi_\nu^1, \phi_\nu^2\} . \tag{21}$$

Insertion of (20) and use of the explicit form of the expansion functions [Eqs. (9) and (18)] leads to

$$2K_\mu V_\mu - \frac{\partial K_\mu}{\partial V_\mu} = \left[\frac{10}{3}\right]^{1/2} A^{(2)}_\mu \phi_\mu^2 + \left[\frac{4}{3}\right]^{1/2} A^{(1)}_{\mu\mu}\phi^2 + 2\{A^{(1)}_{\mu\nu}\}^0 \phi^1_{\mu\nu} . \tag{22}$$

The last term in (22) would generate a friction pressure, cf. Eq. (9), consequently, $\{A^{(1)}_{\mu\nu}\}^0 = 0$ and only the trace $A^{(1)}_{\lambda\lambda}$ is of relevance. Note, (22) allows no conclusions about an antisymmetric part of $A^{(1)}_{\mu\nu}$. For the heat-flux problem, however, there is only *one* significant direction. Consequently, $A^{(1)}_{\mu\nu}$ is dyadic and hence *per se* symmetric.

The remaining coefficients, $A^{(2)}_\mu$ and $A^{(1)}_{\lambda\lambda}$, are now determined by the final two requirements. The constant-temperature constraint (14) reduces to

$$A^{(1)}_{\lambda\lambda} = 2\left[\frac{5}{6}\right]^{1/2} A^{(2)}_\mu Q_\mu , \tag{23}$$

where the relations [(2), (5)–(7)] have been used. $A^{(2)}_\mu$ is determined by the last constraint (15),

$$A^{(2)}_\mu = -\left[\frac{3}{2}\right]^{1/2} mc_0^2 \frac{1}{T}(\nabla_\mu T) . \tag{24}$$

In order to avoid confusion it is preferable to introduce a different symbol for the field strength which was constructed to mimic a temperature gradient

$$g_\mu \equiv \frac{1}{T}(\nabla_\mu T) \ . \tag{25}$$

With the two remaining coefficients [(23) and (24)] and the explicit form of the relevant expansion functions (18), one ends up with

$$K_\mu = -mc_0^2(V^2 - \tfrac{3}{2})g_\mu - \beta V_\mu \ , \tag{26}$$

$$\beta \equiv -\frac{2}{3}\left[\frac{5}{4}\right]^{1/2} mc_0^2 \, g_\mu Q_\mu > 0 \ . \tag{27}$$

The conclusion about the sign of β is drawn in view of Eq. (11) which, due to the requirement (15) holds equally well when $\nabla_\mu(\ln T)$ is replaced by the field strength g_μ.

It is certainly worthwhile to compare this result with the equations of motion derived by Evans[6] and Gillan[7] by means of linear-response theory. As for small perturbations, the thermostating multiplier β is not relevant only the first term in (26) is considered. Using the definition (1) it can be rewritten as $(\frac{1}{2}mc^2 - \frac{3}{2}k_B T)g_\mu$. The first part clearly is the (kinetic) energy of a particle while the second part can be either interpreted as the average (kinetic) energy or as $k_B T$ minus the (kinetic part of the) enthalpy. The latter distinction, which is, of course, trivial for the ideal-gas case, corresponds to the subtle difference between the equations of motion of Evans and Gillan which has attained some attention in the past.[14] In the present case, where only the kinetic contributions to these quantities are relevant, the two algorithms are identical. It should be mentioned, however, that the Evans-Gillan driving force involves an additional contribution, solely attributed to the potential interaction between the particles which, of course, is beyond the scope of kinetic gas theory.

The thermostating multiplier β (27) is relevant for nonequilibrium molecular-dynamics simulations of a stationary heat flux and an explicit form for the Evans algorithm is given in Ref. 15. To identify (27) with the kinetic part of Evans's equation, β has to be multiplied by $(\sqrt{2}mc_0)$ to get the correct dimension, cf. Eq. (1). If the (dimensionless) heat flux Q_λ is written as a nonequilibrium average of ϕ_λ^2 [Eqs. (7) and (8)], one readily obtains

$$-\sqrt{2}mc_0\beta = \frac{1}{3mk_B T}\langle\langle(\tfrac{1}{2}mc^2 - \tfrac{5}{2}k_B T)mc_\lambda\rangle\rangle g_\lambda \ . \tag{28}$$

The second part in parentheses could be identified with the average enthalpy as well as with the average energy of a particle because, as $\langle\langle c_\lambda \rangle\rangle = 0$, an additive constant does not alter the result of this nonequilibrium average. The denominator is $3mk_B T = \langle\langle (m\mathbf{c})^2 \rangle\rangle$ and if these averages are to be evaluated as N-particle averages one gets

$$-\sqrt{2}mc_0\beta = \sum_{i=1}^{N}(E^i - E)\mathbf{g}\cdot\mathbf{p}^i \Big/ \left[\sum_{i=1}^{N}\mathbf{p}^i\cdot\mathbf{p}^i\right] \ , \tag{29}$$

which is indeed the results of Evans[15] if all potential contributions are neglected; $\mathbf{p}^i$ is the momentum of a particle i and E^i its (kinetic) energy, E the average (kinetic) energy per particle.[16]

The inhomogeneous driving mechanism as expressed by the velocity-dependent force $\mathbf{K}$ (26) can be interpreted as follows: Depending on their energy relative to the average energy, the particles experience the driving force $\mathbf{K}$ in a way that "cold" particles are accelerated in the direction of $\mathbf{g}$ and "hot" particles in the opposite direction. The magnitude of the acceleration depends on the deviation from the average energy and is consequently varying. Its time average vanishes which prevents a spatial separation of hot and cold particles, i.e., the temperature and density fields are homogeneous. However, a flux is induced which is, in the linear approximation, identical to the heat flux generated by a temperature gradient. This "Fourier demon" does work on the system which is extracted by the drag term $-\beta V_\mu$ in Eq. (26).

To summarize this section, an external driving force was *uniquely* derived from the Boltzmann equation by requiring an identical linear response as would result from a thermal gradient. It was found to be identical with the forces derived by Evans and Gillan if in these all potential contributions are neglected. So far, however, it is only in the linear regime that the quotient of the resulting fluxes (here Q_λ) and the driving field $(-g_\lambda)$ can be identified with the heat conductivity. The present approach allows us to analyze the nonlinear response too and, hence, provides means to probe the validity of this relation even in the nonlinear regime.

B. Nonlinear regime

The two "experiments" to be compared are as follows: First, the usual setup where a homogeneous heat flux is generated by a temperature gradient between two plates which are sufficiently separated to neglect boundary effects. No external forces shall disturb this standard textbook example. Second, the "demoniacal" driving force constructed in Sec. III A is used to generate a homogeneous heat flux in the absence of a temperature gradient.

For the first case the transport relaxation equations for the moments a^i (10) reduce to

$$\sum_j \left[\frac{c_0}{\sqrt{2}}\left\langle\phi^j V_\mu\left[3 + V_\nu\frac{\partial}{\partial V_\nu}\right]\phi^i\right\rangle\frac{1}{T}(\nabla_\mu T) + \omega^{ij} + \sum_k \tilde{\omega}^{j,ik}a^k\right]a^j = -\left[\frac{5}{2}\right]^{1/2} c_0\frac{1}{T}(\nabla_\mu T)\langle\phi^i\phi_\mu^2\rangle \ , \tag{30}$$

while for the latter they now read as

$$\sum_j \left[\frac{c_0}{\sqrt{2}} \left\langle \phi^j (V^2 - \tfrac{3}{2}) \frac{\partial}{\partial V_\mu} \phi^i \right\rangle g_\mu - \frac{c_0}{\sqrt{2}} \tfrac{2}{3} \left[\frac{5}{4} \right]^{1/2} \left\langle \phi^j V_\mu \frac{\partial}{\partial V_\mu} \phi^i \right\rangle g_\lambda Q_\lambda + \omega^{ij} + \sum_k \tilde{\omega}^{j,ik} a^k \right] a^j = - \left[\frac{5}{2} \right]^{1/2} c_0 g_\mu \langle \phi^i \phi_\mu^2 \rangle \ . \tag{31}$$

Two obvious abbreviations for the collision matrix elements have been introduced and in (31) explicit use has been made of the results and constraints of Sec. III A. The nonlinear response is determined by the coupling of the expansion functions on the left-hand side of (30) and (31). In order to make use of the orthonormalization (6) of the expansion functions, the action of the multiplication and differentiation operators on the functions ϕ^i is to be investigated. This can be done using general relations for the Sonine polynomials.[17] For scalar expansion functions ϕ^r $(r > 2)$, e.g., one obtains,

$$V_\mu \left[3 + V_\nu \frac{\partial}{\partial V_\nu} \right] \phi^r = \left[\frac{1}{6} \right]^{1/2} (2r+1)\sqrt{2r+1}\,\phi_\mu^r + \left[\frac{1}{3} \right]^{1/2} 4r\sqrt{r-1}\,\phi_\mu^{r-1} + \left[\frac{2}{3} \right]^{1/2} \sqrt{(r-2)(r-1)(2r-1)}\,\phi_\mu^{r-2} \ , \tag{32}$$

$$(V^2 - \tfrac{3}{2}) \frac{\partial}{\partial V_\mu} \phi^r = \left[\frac{1}{6} \right]^{1/2} 2(r-1)\sqrt{2r+1}\,\phi_\mu^r + \left[\frac{1}{3} \right]^{1/2} (4r-6)\sqrt{r-1}\,\phi_\mu^{r-1} + \left[\frac{2}{3} \right]^{1/2} \sqrt{(r-2)(r-1)(2r-1)}\,\phi_\mu^{r-2} \ , \tag{33}$$

$$V_\mu \frac{\partial}{\partial V_\mu} \phi^r = 2(r-1)\phi^r + \sqrt{2(r-1)(2r-1)}\,\phi^{r-1} \ . \tag{34}$$

The similarities in (32) and (33) are striking. These equations determine the coupling of vectorial to scalar moments which, obviously, differs slightly for the two situations. In general, these operators couple tensors of rank l to tensors of rank $l \pm 1$. For the external-force case an additional coupling term occurs which couples tensors of equal rank only, and can thus be conceived as a modification of the matrix elements of the linear collision operator.[11] It stems from the constant-temperature constraint of the simulation and has no counterpart in the thermal-gradient case. For vectorial and tensorial expansion functions similar relations can be derived which lead to the conclusion that the nonlinear coupling behavior on the left-hand side of the Boltzmann equation ("streaming term") is quantitatively different for the two driving mechanisms, although the qualitative similarities are striking.

At this point one is tempted to continue the parallel evaluation of the transport relaxation equations in order to arrive at a detailed quantitative comparison of the two methods. However, the field strengths which are applied in the simulations correspond to significant variations over the length scale of a few molecular diameters. These go along with density inhomogeneities and restrict the applicability of the present analysis. The temperature dependence of the collision matrix elements is certainly significant for the nonlinear heat flow problem between parallel plates. In addition, the restriction to homogeneous moments is a crude simplification which is, in general, not consistent with the constant pressure assumption. Corresponding modifications are beyond the scope of this article; instead, recent exact results for the nonlinear heat flow problem between parallel plates[8] are utilized for a final comparison with the results of a moment-method solution for the force-driven heat flux. In this case even the temperature and density fields are homogeneous such that the present description is complete.

For a further evaluation of the transport relaxation equations the coupling behavior for the vectorial and tensorial expansion functions for the external force case are needed; they are for vectorial functions ϕ_λ^r $(r > 1)$

$$(V^2 - \tfrac{3}{2}) \frac{\partial}{\partial V_\mu} \phi_\lambda^r = \delta_{\mu\lambda} \left[\left[\frac{1}{3} \right]^{1/2} (2r+1)\sqrt{r}\,\phi^{r+1} + \left[\frac{2}{3} \right]^{1/2} 2(r-1)\sqrt{2r+1}\,\phi^r + \left[\frac{1}{3} \right]^{1/2} \sqrt{(r-1)(2r+1)(2r-1)}\,\phi^{r-1} \right]$$
$$+ \left[\frac{4}{5} \right]^{1/2} (r-1)\sqrt{2r+3}\,\phi_{\mu\lambda}^r + \left[\frac{2}{5} \right]^{1/2} (4r-4)\sqrt{r-1}\,\phi_{\mu\lambda}^{r-1} + \left[\frac{4}{5} \right]^{1/2} \sqrt{(r-2)(r-1)(2r+1)}\,\phi_{\mu\lambda}^{r-2} \ , \tag{35}$$

$$V_\mu \frac{\partial}{\partial V_\mu} \phi_\lambda^r = (2r-1)\phi_\lambda^r + \sqrt{2(r-1)(2r+1)}\,\phi_\lambda^{r-1} \ . \tag{36}$$

And for tensorial functions $\phi_{\lambda\kappa}^r$,

$$(V^2-\tfrac{3}{2})\frac{\partial}{\partial V_\mu}\phi^r_{\lambda\kappa}=\Delta^{(2)}_{\lambda\kappa,\sigma\mu}\left[\left[\frac{2}{5}\right]^{1/2}(2r+3)\sqrt{r}\,\phi^{r+1}_\sigma+\left[\frac{4}{5}\right]^{1/2}(2r-1)\sqrt{2r+3}\phi^r_\sigma\right.$$
$$\left.+\left[\frac{2}{5}\right]^{1/2}\sqrt{(r-1)(2r+1)(2r+3)}\phi^{r-1}_\sigma\right]$$
$$+\left[\frac{6}{7}\right]^{1/2}(r-1)\sqrt{2r+5}\phi^r_{\mu\lambda\kappa}+2\left[\frac{3}{7}\right]^{1/2}(2r-1)\sqrt{r-1}\phi^{r-1}_{\mu\lambda\kappa}$$
$$+\left[\frac{6}{7}\right]^{1/2}\sqrt{(r-2)(r-1)(2r+3)}\phi^{r-2}_{\mu\lambda\kappa}\,, \tag{37}$$

$$V_\mu\frac{\partial}{\partial V_\mu}\phi^r_{\lambda\kappa}=2r\phi^r_{\lambda\kappa}+\sqrt{2(r-1)(2r+3)}\phi^{r-1}_{\lambda\kappa}\,, \tag{38}$$

where $\Delta^{(2)}_{\lambda\kappa,\sigma\mu}$ is the isotropic tensor of rank 4,[18]

$$\Delta^{(2)}_{\lambda\kappa,\sigma\mu}\equiv\tfrac{1}{2}(\delta_{\lambda\sigma}\delta_{\kappa\mu}+\delta_{\lambda\mu}\delta_{\kappa\sigma})-\tfrac{1}{3}\delta_{\lambda\kappa}\delta_{\sigma\mu}\,. \tag{39}$$

Before the general coupling scenario in (31) is addressed, some remarks on the collision matrix elements are appropriate. While the linear part ω^{ij} couples tensors of equal rank only, the quadratic part $\tilde{\omega}^{j,ik}$ exhibits a much more complicated coupling behavior which would severly obstruct the following analysis. Henceforth, however, the quadratic part will be neglected. This is justified by results of earlier studies on the non-Newtonian viscosity coefficients.[11,12] It was clearly demonstrated that the effect of the quadratic collision operator on the transport coefficient is completely negligible while only selected higher moments are slightly modified. Similar remarks hold for the nondiagonal elements of the linearized collision operator.[11] But, as they are easily incorporated in the present formalism, they need not be neglected.

For the present problem $(\omega^{22}_1)^{-1}$, cf. Eqs. (11) and (12), provides a characteristic relaxation time τ. It is inversely proportional to the density and is used to define a reduced (dimensionless) field strength G_μ,

$$\tau\equiv(\omega^{22}_1)^{-1},\quad G_\mu\equiv\left[\frac{5}{2}\right]^{1/2}c_0\tau g_\mu\,. \tag{40}$$

Let the heat flux be in z direction (e^z_μ being the corresponding unit vector),

$$G_\mu\equiv Ge^z_\mu,\ Q_\mu\equiv Qe^z_\mu\,. \tag{41}$$

Then, in the linear regime, cf. Eqs. (11) and (25), the (reduced) heat conductivity simply reads $-Q/G=1$. Nonlinear corrections to Fourier's law would involve the dimensionless quantity G rather than the field strength itself.

Finally, note that for the present pure heat flux problem all vectorial and (irreducible) tensorial moments have one relevant component only,

$$a^{(r)}_\mu\equiv a^{(r)}_z e^z_\mu,\quad a^{(r)}_{\mu\nu}\equiv a^{(r)}_0\left[\frac{3}{2}\right]^{1/2}\{e^z_\mu e^z_\mu\}^0\,. \tag{42}$$

The factor $\sqrt{3/2}$ has been chosen to be consistent with the notation in Ref. 11. With these definitions it is straightforward to select the relevant moments and to solve the transport relaxation equations in this finite moment approximation.

The selection of the moments is done in view of the coupling behavior in Eq. (31). It was found above to be dominated by the first term while the relatively simple coupling of the second term can be treated as a modification of the matrix elements for the linearized collision operator. Some qualitative features of the complex system of equations can best be described by looking at a simplified version where only "dominating" terms are retained. They are

$$a^{(r)}\approx -G(C^{r,r}_{01}a^{(r)}_z+C^{r,r-1}_{01}a^{(r-1)}_z$$
$$+C^{r,r-2}_{01}a^{(r-2)}_z)\,, \tag{43}$$

$$a^{(r)}_z\approx -G\delta^{r2}-G(C^{r,r+1}_{10}a^{(r+1)}+C^{r,r}_{10}a^{(r)}$$
$$+C^{r,r-1}_{10}a^{(r-1)}+C^{r,r}_{12}a^{(r)}_0$$
$$+C^{r,r-1}_{12}a^{(r-1)}_0+C^{r,r-2}_{12}a^{(r-2)}_0)\,, \tag{44}$$

$$a^{(r)}_0\approx -G(C^{r,r+1}_{21}a^{(r+1)}_z+C^{r,r}_{21}a^{(r)}_z$$
$$+C^{r,r-1}_{21}a^{(r-1)}_z+\cdots)\,. \tag{45}$$

The ellipsis in (45) stands for the coupling to tensorial moments of rank 3 which need not to be considered for the present purpose. The coefficients $C^{r,s}_{ll'}$ are determined by the relations (33), (35), and (37). Two properties of these relations are important: all coefficients are positive and tensors of rank l couple to tensors of rank $l'=l\pm1$ only. Each coupling involves a multiplication with the driving field G. The coupling scenario with increasing field strength can now be described as follows. The heat flux $Q=a^{(2)}_z$ is the only moment which is linear in G. It is negative and couples to the scalar moments $a^{(3)},a^{(4)}$ as well as to the tensorial moments $\pi_0,a^{(2)}_0,a^{(3)}_0$. Hence these moments have a positive leading term proportional G^2. Some of them, viz. $a^{(3)}$, $\pi_0,a^{(2)}_0$, in turn, lead to additional negative contributions proportional G^3 to the heat flux, cf. Eq. (44). In addition, of course, other vectorial and tensorial moments of third rank are driven by a similar coupling. Their leading term is negative and proportional to G^3. These odd ranked tensorial moments lead to positive contributions proportional G^4 to the tensorial

moments of even rank, and so on. Consequently, if the heat flux is expanded in powers of G, only odd powers occur and all coefficients are negative. This can be generalized to all moments of odd tensor rank and the corresponding statement for moments of even tensor rank is obvious. Hence all moments are monotonic functions of the temperature gradient and diverge. This coupling scenario differs drastically from the shear flow case where especially the feedback of higher moments on the linear terms was found to be almost negligible.[5,11]

Of course, the reasoning was not rigorous insofar as only apparently dominating coupling terms were considered. These trends, however, can be substantiated by quantitative results of a finite moment approximation. To obtain the heat flux in a precision of order G^4 the moments $a^{(2)}$, π_0, and $a_0^{(2)}$ were above found to be relevant. They are supplemented by all other moments with a leading term proportional to G^2, viz. $a^{(4)}$ and $a_0^{(3)}$; $a_z^{(3)}$ is included to account for the nondiagonal coupling via the collision matrix and (35). All collision matrix elements for the selected moments can be found in the literature[11,19,20] and the coefficients are obtained from the general relations [Eqs. (33)–(38)]. One ends up with a nonlinear system of seven equations which can be solved by a recursion scheme. The method has been successfully applied in Ref. 11 and shall not be repeated here. In the present case, however, solutions can only be obtained for a limited range of field strengths. They are used for a comparison with the results of NEMD simulations to be introduced in Sec. IV. In the present context it is interesting to note that the NEMD algorithm fails as well for field strengths above a certain threshold.

IV. NONEQUILIBRIUM MOLECULAR DYNAMICS

The simulations were performed for a gas interacting via the Lennard-Jones potential

$$\Phi=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], \tag{46}$$

which is "cutoff" at $r=2.5\sigma$. As usual, the energy parameter ε, the "particle diameter" σ, and the mass m are used to define reduced units. The results are for $T=2.75\varepsilon/k_B$ and $n=0.02\sigma^{-3}$ which corresponds to an argon gas at 330 K and 2.4 MPa. The mean free path is 16σ and field strengths ranging from $g=0.002\sigma^{-1}$ to $g=0.016\sigma^{-1}$ were applied. With the identification (25) these would correspond to temperature gradients of about 1–5 K/σ for an argon gas which is far beyond the capability of laboratory facilities. Nevertheless, the results for $g\lesssim 0.005\sigma^{-1}$ will be shown to be in accordance with predictions of the linearized kinetic theory.

The following equations of motion for the 128 particles are solved by a predictor-corrector method[2] with a time step of $\Delta t=0.005\sigma\sqrt{m/\varepsilon}$,

$$m\ddot{\mathbf{r}}_i=\sum_{j=1}^{N}\mathbf{F}_{ij}-mc_0^2(V_i^2-\tfrac{3}{2})g\mathbf{e}^z-\beta\mathbf{V}_i\ , \tag{47}$$

$$\beta=-\tfrac{2}{3}mc_0^2g\frac{1}{N}\sum_{i=1}^{N}[(V_i^2-\tfrac{5}{2})V_{i_z}]\ , \tag{48}$$

cf. Eqs. (26) and (27). Note, an N-particle average is employed to evaluate the heat flux (8) in the equation for β.

Although the external force was derived by requiring a constant temperature, only the total energy is constant while the temperature is found to fluctuate by less than 2% around its prescribed value. This is due to the interaction via the pair-force $\mathbf{F}_{ij}$ and, hence, beyond the capability of the ideal-gas analysis. However, the work done on the system is purely kinetic and compensated by the thermostating multiplier β.

A related remark concerns the relatively low density. For the chosen state the characteristic relaxation time $\tau(38)$ is 7.5 $\sigma\sqrt{m/\varepsilon}$ or 1500 time steps. This sets the time scale for the regression of fluctuations and makes the phase-space sampling rather inefficient. However, considerable density effects were observed for higher densities which contrasts the gas phase simulations of the shear flow at the density $n=0.1\sigma^{-3}$ (Refs. 5 and 11) where the potential contribution to the pressure tensor was found to be negligible. In the present case only the kinetic contribution to the heat flux is driven by the external force and one would not expect to observe a noticeable potential contribution to the heat flux which, in the present notation, reads as[6,21]

$$Q^{\mathrm{pot}}=\frac{1}{V}\sum_i\mathbf{V}_iE_i^{\mathrm{pot}}+\tfrac{1}{2}\sum_{i\neq j}\sum\mathbf{V}_i\cdot\mathbf{F}_{ij}\mathbf{r}_{ij}\ ; \tag{49}$$

E_i^{pot} stands for the potential energy of particle i and $\mathbf{r}_{ij}\equiv\mathbf{r}_i-\mathbf{r}_j$. This quantity was monitored in some exploratory simulations for (reduced) densities ranging from $n=0.01$–0.1. A surprising empirical rule was found for the relation of the potential and kinetic contributions to the heat flux: $Q^{\mathrm{pot}}/Q^{\mathrm{kin}}\approx n$, i.e., for $n=0.1$, $Q^{\mathrm{pot}}/Q^{\mathrm{kin}}\approx 10\%$. In contradistinction to the shear flow case a considerable cross coupling between kinetic and potential effects is observed which, in light of the apparently different nonlinear behavior of dense fluids,[15] deserves more attention in the future.

A. Transport coefficient

The results for the heat flux are displayed in Fig. 1 and are compared with results of the seven-moment solution of the Boltzmann equation introduced in Sec. III B. The heat flux, defined in Eq. (8), is evaluated as an N-particle average. It is preaveraged in each run with 100 000 time steps by accumulating values in intervals of 200 time steps. Thirty-two runs were performed for each field strength and the averages and standard deviations of a final averaging over all 32 runs are displayed in the figure. The central processing unit (CPU) time used for each state point amounts to 5 h on a Cray Research XMP-24.

Reasonable accordance between kinetic theory and simulation results is found. This is confirmed by similar plots for the other six moments, which are evaluated analogously according to Eq. (7). Apparent deviations from Fourier's law are observed for $G>0.1$. It has already been mentioned that both the kinetic theory analysis and the simulation fail for field strengths above a certain threshold. The reproducible breakdown of the simulation for $g=0.018\sigma^{-1}$ is a consequence of an align-

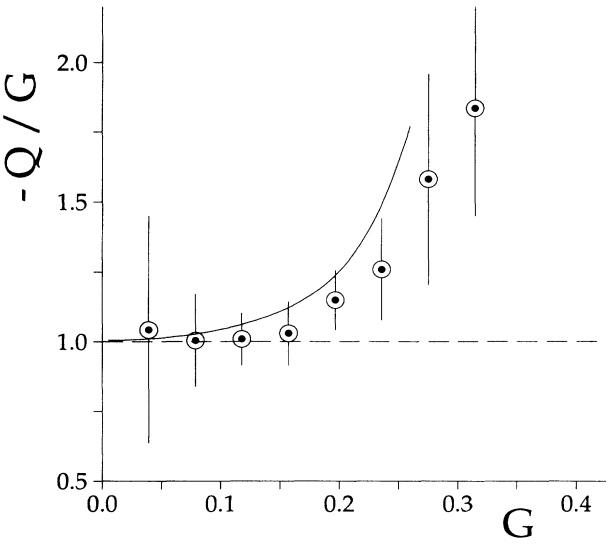

FIG. 1. Heat flux divided by the strength of the external field which mimics thermal gradient. The results of the simulations are compared with a seven-moment solution of the Boltzmann equation. Apparent deviations from Fourier's law (dashed line) are observed (see text).

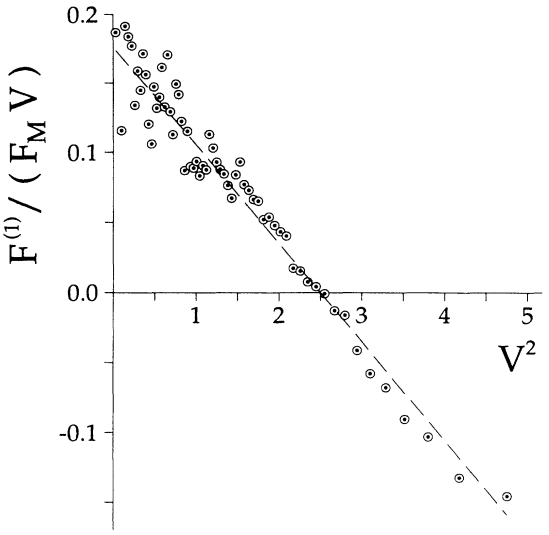

FIG. 2. The distribution function $F^{(1)}$ divided by the Maxwellian distribution and the speed V [see Eq. (51)]. It is compared to the result of the linearized Boltzmann equation (dashed line).

ment of the particle motion in the direction of the applied force which reduces the collision rate. Between the rare collisions the constant acceleration leads to huge velocities for some of the particles while others, due to the constant-temperature constraint, appeared to be "frozen." The simulation is terminated by a "catastrophic" collision between members of these groups. The scenario leads to an increasing statistical uncertainty with increasing applied field. The alignment of the particle motion in z direction is manifested by a normal pressure difference, expressed by the moment π_0, cf. Eq. (9), and is in accordance with the kinetic theory analysis.

B. Velocity distribution function

The two lowest gradients considered (corresponding to $g=0.002\sigma^{-1}$ and $g=0.004\sigma^{-1}$) can be associated with the linear regime and can thus be used for a comparison with laboratory experiments of temperature-driven heat flow. A very sensitive comparison is based on the velocity-distribution function. Although experimentally difficult, Doppler broadening techniques have successfully been applied for a direct measurement of the velocity distribution function of a heat-conducting (polyatomic dilute) gas.[22] Corresponding results for a streaming gas were first obtained by NEMD.[23] The method introduced in Ref. 23 can be easily employed for the present case of a homogeneous force-driven heat flux.

First, the directional dependence of the nonequilibrium velocity distribution is taken into account,

$$F(\mathbf{V})=F_S(V^2)+F^{(1)}(V^2)\hat{V}_z+\cdots\ , \tag{50}$$

where the ellipsis stands for contributions of higher tensor rank and $\hat{V}_z$ stands for the z component of the unit vector $\hat{V}$. In the linear regime the only relevant moment in the ansatz (2,5) is the heat flux, hence the scalar part $F_S(V^2)$ reduces to the local Maxwellian $F_M(V^2)$ and, cf. Eq. (8),

$$F^{(1)}(V^2)\approx F_M(V^2)Q\left[\frac{4}{5}\right]^{1/2}(V^2-\tfrac{5}{2})V\ . \tag{51}$$

Note, the function $F^{(1)}(V^2)$ contains the full information on the velocity distribution for the specified directional dependence, while the right-hand side on (51) is a kinetic theory approximation. The quality of this approximation can be tested by a direct evaluation of $F^{(1)}(V^2)$ via the NEMD simulation. It is obtained as an N-particle average of $\sum_i \hat{V}_z\delta(V-V_i)$. Details can be found elsewhere.[11,23] In Fig. 2 the quantity $F^{(1)}/(F_M V)$ is plotted for $g=0.004\sigma^{-1}$ and compared to results of the linearized Boltzmann equation (dashed line), cf. Eqs. (11) and (51). Excellent agreement is found. The graphical representation is chosen in close analogy to Ref. 22.

V. CONCLUDING REMARKS

A kinetic theory analysis based on the Boltzmann equation has been employed to elucidate the relevance of the homogeneous Evans-Gillan algorithm for the simulation of thermal transport. The uniquely derived external force which mimics a temperature gradient in the linear regime led to an unphysical nonlinear response which contradicts recent theoretical[8] and (computer) "experimental"[9] results. The uniqueness indicates the limitations of homogeneous algorithms for the simulation of nonlinear transport. The failure of an algorithm based on Gauss's principle of least constraint has already been es-

tablished.[24] In this respect the present results support the current tendency "back to the roots" of NEMD, viz. to the boundary-driven simulations as pioneered by Ashurst and Hoover.[1] Due to the increasing computing power of modern vector computers the systems can be made large enough to be able to distinguish between bulk and boundary effects. It is interesting to note that the kinetic theory of gases is quite often used to establish newly developed simulation techniques.[4,9,25,26] Reference 4 also contains a first remark about the discrepancy of the normal stresses obtained from the Evans-Gillan algorithm and the Chapman-Cowling analysis.[19]

However, the Evans-Gillan scheme provides an efficient tool to study *linear* thermal bulk properties. It has successfully been applied in conjunction with the difference method.[27] Even in the gas phase additional investigations seem to be promising. For polyatomic gases the node of the velocity distribution function as displayed in Fig. 2 is shifted due to additional contributions in the Sonine polynomial which are attributed to the rotational and vibrational energies.[22] The experiments confirmed a rapid convergence of the Sonine expansion which was *a priori* not obvious. Supplementary NEMD simulations for polyatomic model gases could promote a deeper understanding of, e.g., the relative importance of the intramolecular potential which could easily be varied.

And even in the nonlinear regime the Evans-Gillan method, if applied with care, has some merits. The present study provides insight in the respective relevance of the magnitude of the driving field and the accompanying inhomogeneities. The computer simulation as well as the kinetic theory analysis excluded the latter and led to an apparently unphysical divergence of the "heat conductivity." It has been pointed out that the nonlinear coupling via the streaming term of the Boltzmann equation is qualitatively equal for the force- and the gradient-driven case. It is concluded that the spatial variations of the density and temperature fields are essential because they compensate for the effect of large driving fields (temperature gradient or external force).

In general, the homogeneous "computer experiments" are easier to analyze theoretically. A generalization of the present moment method approach for (strongly) inhomogeneous nonlinear transport phenomena would, if feasible, further complicate the formalism and obstruct a more physical interpretation of the results. Other methods, based on the Bhatnagar-Gross-Krook (BGK) collision model[8] appear to be more promising in this respect. However, the successful treatment of the nonlinear shear flow problem[5,11] inspires one to employ the same methods to study the nonlinear coupling between the two fundamental transport processes. Although restricted to be linear in the temperature gradient some progress can be expected concerning the influence of the normal pressure differences on the heat flux. These were not taken into account in earlier treatments of the nonlinear transport processes in gases.[28,29]

ACKNOWLEDGMENTS

This work originates from the Nato Advanced Study Institute on "Computer Simulation of Fluids, Polymers, and Solids," in Bath, England. Thanks are due to the organizers and to the lecturers (among these the two "inventors" of the Evans-Gillan method) and participants for many stimulating discussions. The advice of Professor S. Hess during the preparative stage of this paper is gratefully acknowledged as well as a grant of the "Studienstiftung des deutschen Volkes."

[1] W. T. Ashurst and W. G. Hoover, Phys. Rev. A **11**, 658 (1975).

[2] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987); W. G. Hoover, Annu. Rev. Phys. Chem. **34**, 103 (1983); D. J. Evans and G. P. Morriss, Comput. Phys. Rep. **1**, 297 (1984).

[3] D. J. Evans and G. P. Morriss, Phys. Rev. A **30**, 1528 (1984).

[4] A. J. C. Ladd and W. G. Hoover, J. Stat. Phys. **38**, 973 (1985).

[5] W. Loose, Phys. Lett. A **128**, 39 (1988).

[6] D. J. Evans, Phys. Lett. **91A**, 457 (1982).

[7] M. J. Gillan and M. Dixon, J. Phys. C **16**, 869 (1983).

[8] A. Santos, J. J. Brey, C. S. Kim, and J. W. Dufty, Phys. Rev. A **39**, 320 (1989); A. Santos, J. J. Brey, and V. Garzó, *ibid.* **34**, 5047 (1986).

[9] P.-J. Clause and M. Mareschal, Phys. Rev. A **38**, 4241 (1988).

[10] L. Waldmann, in *Transporterscheinungen in Gasen von mittlerem Druck,* Vol. 12 of *Handbuch der Physik,* edited by S. Flügge (Springer-Verlag, Berlin, 1959), p. 295.

[11] W. Loose and S. Hess, Phys. Rev. A **37**, 2099 (1988).

[12] N. Herdegen and S. Hess, Physica A **115**, 281 (1982).

[13] J. R. Dorfman and H. van Beijeren, in *Statistical Mechanics B,* edited by B. J. Berne, (Plenum, New York, 1977), p. 65.

[14] D. MacGowan and D. J. Evans, Phys. Lett. A **117**, 414 (1986).

[15] D. J. Evans, Phys. Rev. A **34**, 1449 (1986).

[16] Note, in Ref. 15 the formula for the thermostating multiplier is slightly misprinted. The correct form is easily obtained by inserting the equations of motion in $(d/dt)\sum_i \mathbf{p}^i \cdot \mathbf{p}^i = 0$.

[17] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980), Eqs. 8.971.

[18] S. Hess and W. Köhler, *Formeln zur Tensorrechnung* (Palm & Enke, Erlangen, 1980).

[19] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, England, 1939).

[20] H. Vestner and L. Waldmann, Z. Naturforsch. **32a**, 667 (1977).

[21] J. H. Irving and J. G. Kirkwood, J. Chem. Phys. **18**, 817 (1950).

[22] B. S. Douma, H. F. P. Knapp, and J. J. M. Beenakker, Chem. Phys. Lett. **74**, 421 (1980).

[23] W. Loose and S. Hess, Phys. Rev. Lett. **58**, 2443 (1987).

[24] W. G. Hoover, B. Moran, and J. M. Haile, J. Stat. Phys. **37**, 109 (1984).

[25] M. Mareschal, W. Kestemont, F. Baras, E. Clementi, and G. Nicolis, Phys. Rev. A **35**, 3883 (1987).

[26] D. K. Bhattacharya and G. C. Lie, Phys. Rev. Lett. **62**, 897 (1989).

[27] C. Massobrio and G. Ciccotti, Phys. Rev. A **30**, 3191 (1984).

[28] J. J. Brey, A. Santos, J. W. Dufty, Phys. Rev. A **36**, 2842 (1987).

[29] D. K. Bhattacharya and B. C. Eu, Phys. Rev. A **35**, 821 (1984).