

H-Theorem for the (Modified) Nonlinear Enskog Equation

P. Resibois¹

Received May 19, 1978; revised September 5, 1978

We construct an H -function suitable for a system of dense hard spheres satisfying the (modified) nonlinear Enskog equation and we show that $\partial_t H \leq 0$. The equality sign holds only when the system has reached absolute equilibrium, in which case $S = -k_B H$ becomes the exact equilibrium entropy of the hard-sphere fluid.

KEY WORDS : Enskog equation ; entropy ; hard-sphere fluid ; H -theorem ; kinetic theory.

1. INTRODUCTION

Despite its phenomenological character, the Enskog equation⁽¹⁻³⁾ is very successful in describing transport phenomena in dense fluids.⁽⁴⁾

This equation, governing the time evolution of the one-particle distribution function (df) $f_1(\mathbf{r}_1, \mathbf{v}_1; t)$, is written

$$\partial_t f_1 + \mathbf{v}_1 \cdot \partial f_1 / \partial \mathbf{r}_1 = J^E(f_1, f_1) \quad (1)$$

where the collision operator J^E is defined by

$$\begin{aligned} J^E(f_1, f_1) = & a^2 \int d\mathbf{v}_2 \int d^2\epsilon (\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) \\ & \times [g_2(\mathbf{r}_1, \mathbf{r}_1 - a_+ \boldsymbol{\epsilon} | n(t)) f_1(\mathbf{r}_1, \mathbf{v}_1'; t) f_1(\mathbf{r}_1 - a\boldsymbol{\epsilon}, \mathbf{v}_2'; t) \\ & - g_2(\mathbf{r}_1, \mathbf{r}_1 + a_+ \boldsymbol{\epsilon} | n(t)) f_1(\mathbf{r}_1, \mathbf{v}_1; t) f_1(\mathbf{r}_1 + a\boldsymbol{\epsilon}, \mathbf{v}_2; t)] \quad (2) \end{aligned}$$

Here, a denotes the hard-sphere diameter (a_+ means $a + |\eta|$ with $|\eta| \rightarrow 0$), $\boldsymbol{\epsilon}$ is a unit vector, and $\Theta(x)$ is the Heaviside function; moreover, \mathbf{v}_1' and \mathbf{v}_2' are the velocities after the collision:

$$\mathbf{v}_1' = \mathbf{v}_1 - \boldsymbol{\epsilon}(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}), \quad \mathbf{v}_2' = \mathbf{v}_2 + \boldsymbol{\epsilon}(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) \quad (3)$$

¹ Faculté des Sciences, Université Libre de Bruxelles, Brussels, Belgium.

($\mathbf{v}_{12} = \mathbf{v}_1 - \mathbf{v}_2$); finally, g_2 , a functional² of the local density $n(\mathbf{r}; t) = \int d\mathbf{v} f_1(\mathbf{r}, \mathbf{v}; t)$, is defined below.

Two features of this equation make it very different from the Boltzmann equation:^(2,3) (a) The centers of particles 1 and 2 are separated by a distance a at collision; this leads to the mechanism of *collisional transfer*. For example, at collision, the momentum $\Delta\mathbf{p} = m(\mathbf{v}_1' - \mathbf{v}_1)$ exchanged between the molecules is instantaneously transferred from the center of one molecule to the center of the other. (b) Although the dynamics of the collisions corresponds to two-body events, the frequency of these collisions differs from the dilute gas value by the factor g_2 .

In his original intuitive argument, Enskog took for g_2 a quantity which, in modern language, can be identified with the equilibrium pair correlation function, calculated for the local density at point $(\mathbf{r}_1 + \mathbf{r}_2)/2$. More recent investigations⁽⁵⁻⁷⁾ have shown, however, that this prescription has to be slightly modified (leading then to the so-called "modified" Enskog equation) in order to have a consistent theory; such work leads to a microscopic expression for g_2 from the single approximation that, at any time, the only correlations in the system are due to the excluded volume between the spheres; in particular, no correlations between velocities are retained. The mathematical aspects of this approach are discussed in detail in Section 2.

While Boltzmann's H -theorem lies at the very basis of the kinetic theory of dilute gases—in particular, in justifying the local equilibrium assumption underlying the Chapman–Enskog method⁽²⁾—no such theorem has been proved as yet for the Enskog theory. For example, such a careful text as that of Chapman and Cowling⁽²⁾ merely notices that, for a spatially *uniform* system, the Enskog equation drives the velocity distribution function toward the Maxwellian (because, in this case, J^E only differs from the Boltzmann collision operator by the constant factor g_2); these authors then immediately limit themselves to distribution functions differing only slightly from local equilibrium. Whether the Enskog equation drives an *arbitrary* initial df toward absolute equilibrium remained an open question: the aim of this paper is to settle this point in the affirmative, at least for the *modified* Enskog theory.

The remainder of this paper is organized as follows: as already mentioned, Section 2 is devoted to the precise formulation of the modified Enskog theory. In Section 3, we define a functional of the one-particle df , $S = S(f_1(t))$, which at equilibrium reduces to the exact entropy of the hard-sphere fluid; we then prove the following H -theorem (assuming, for simplicity, periodic boundary conditions):

$$dS/dt \geq 0 \quad (4)$$

² The quantity $f(\mathbf{r}_1)$, depending functionally on $g(\mathbf{r}; t)$ for all \mathbf{r} , is often written $f(\mathbf{r}_1|g(t))$.

Under rather mild mathematical conditions, we also show that S tends toward a stationary value, and that f_1 is then the absolute equilibrium df over the whole system.

A few questions raised by our approach are briefly discussed in Section 4.

2. THE MODIFIED ENSKOG EQUATION (MEE)

In this section, we present a derivation of the MEE, with the help of one single approximation made, for all times, on the N -particle time-dependent distribution function.

A convenient starting point is the first BBGKY hierarchy equation:⁽³⁾

$$\partial_t f_1 + \mathbf{v}_1 \cdot \partial f_1 / \partial \mathbf{r}_1 = \int d\mathbf{r}_2 d\mathbf{v}_2 K_{12} f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2; t) \quad (5)$$

where, in the case of hard spheres, the operator K_{12} is defined by

$$K_{12} = a^2 \int d^2\epsilon (\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) [\delta(\mathbf{r}_{12} - a_+ \boldsymbol{\epsilon}) b_\epsilon - \delta(\mathbf{r}_{12} + a_+ \boldsymbol{\epsilon})] \quad (6)$$

Here b_ϵ is the following displacement operator in the velocity space of particles 1 and 2:

$$b_\epsilon f(\mathbf{v}_1, \mathbf{v}_2) \equiv f(\mathbf{v}_1', \mathbf{v}_2') \quad (7)$$

Of course, the whole problem is to close Eq. (5) by finding a functional relationship expressing f_2 in terms of f_1 . Though this can be done *formally* by a variety of methods (see the examples of Ref. 3), one has in general to use some approximation in order to get *explicit* compact expressions.

The approximation made in deriving the MEE is based on two wishes: (a) to take into account explicitly the excluded volume effect due to the finite diameter of the hard spheres; (b) to keep as much as possible of the original Boltzmann *stosszahlansatz*, which, in the dilute gas limit, says that $f_2 = f_1 f_1$, before collision at least.

A convenient way to cast these properties into a mathematical framework is to assume that, at all times, *the reduced df of the system can be calculated from the following grand canonical df :*

$$\rho_N = \frac{1}{N!} \prod_{i>j=1}^N \Theta_{ij} \prod_{i=1}^N W_i(t) / \Xi(t), \quad N = 0, 1, 2, \dots \quad (8)$$

with

$$\Xi(t) = \sum_{N=0}^{\infty} \frac{1}{N!} \int d\Gamma^N \prod_{i>j=1}^N \Theta_{ij} \prod_{i=1}^N W_i(t) \quad (9)$$

In these equations, we have introduced the notations

$$\begin{aligned}\Theta_{ij} &= \Theta(r_{ij} - a), & r_{ij} &= |\mathbf{r}_i - \mathbf{r}_j| \\ W_i(t) &= W(\mathbf{r}_i, \mathbf{v}_i; t) \\ d\Gamma^{N-n} &= d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N d\mathbf{v}_{n+1} \cdots d\mathbf{v}_N\end{aligned}\quad (10)$$

The reduced n -particle df

$$f_n(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{v}_1, \dots, \mathbf{v}_n; t) = \sum_{N=n}^{\infty} \frac{N!}{(N-n)!} \int d\Gamma^{N-n} \rho_N \quad (11)$$

are thus all expressible in terms of $W(\mathbf{r}, \mathbf{v}; t)$. Yet, to be meaningful, we still need to define this latter function precisely; this is done by considering Eq. (11) for $n = 1$ as providing the *definition* of W :

$$f_1(\mathbf{r}_1, \mathbf{v}_1; t) \equiv f_1(\mathbf{r}_1 | W(t)) \quad (12)$$

We assume that this expression can be inverted to express W as a functional of f_1 [see also the remarks after Eq. (14)].

Before showing how this formalism leads to the MEE, we make a few remarks:

(a) The form proposed in Eq. (8) is not new. In the canonical ensemble, a similar assumption was explicitly used by Lebowitz *et al.*^(5,6) to derive the *linearized* form of the MEE; these authors also showed that this approximation leads to the exact short-time behavior for the velocity autocorrelation function. Again in the canonical formalism, Van Beijeren and Ernst⁽⁷⁾ proposed an approximation similar to Eq. (8) to derive the nonlinear MEE; extending their calculation to mixtures, they showed that this MEE was superior to the original Enskog equation, because it leads to transport coefficients consistent with the Onsager relations.

(b) Two reasons caused us to prefer to working in the grand canonical formalism. First, it is clear that in the canonical formalism, where we should take instead of Eq. (8)

$$\rho_N^{\text{can}} = \frac{\prod_{i>j=1}^N \Theta_{ij} \prod_{i=1}^N W_i(t)}{\int d\Gamma^N \prod_{i>j=1}^N \Theta_{ij} \prod_{i=1}^N W_i(t)} \quad (N \text{ fixed}) \quad (13)$$

the function W enters with the same power in the numerator and in the denominator; in this case, Eq. (12) can at best determine W up to a constant. This constant has then to be fixed by an extra condition, which is not obvious to guess.³

³ Yet, to establish the global H -theorem discussed here, this extra condition only plays a minor role, and the canonical formalism can be used, as we have done in a preliminary work.⁽⁸⁾

Second, the statistical mechanics of the *nonuniform* system described by Eq. (8) is fairly well understood; indeed, disregarding the dependence on time, Eq. (8) shares a great many similarities with the *equilibrium* grand canonical distribution of hard spheres in an external field $V(\mathbf{r})$. We need merely keep in mind the correspondence rule⁴

$$W(\mathbf{r}, \mathbf{v}; t) \rightleftharpoons z \{ \exp[-V(\mathbf{r})/k_B T] \} \varphi^{\text{eq}}(\mathbf{v}) \tag{14}$$

(where z is the fugacity and φ^{eq} is the Maxwellian) for us to be able to borrow many interesting results from the literature (in particular, see the remarkable review of Ref. 9). The analogy is even more striking if we limit ourselves to the spatial part:

$$z_1(\mathbf{r}; t) \equiv \int d\mathbf{v} W(\mathbf{r}, \mathbf{v}; t) \rightleftharpoons z \exp[-V(\mathbf{r})/k_B T] \tag{15}$$

Let us illustrate this point by an example. We define the quantity

$$b_n(\mathbf{r}_1, \dots, \mathbf{r}_n | z_1(t)) = \left[\sum_{N=n}^{\infty} \frac{1}{(N-n)!} \int d\Gamma^{N-n} \prod_{i>j=1}^N \Theta_{ij} \prod_{i=1}^N W_i \right] / \Xi(t) \tag{16}$$

where, in the notation, we have explicitly taken into account that b_n depends on W only through its velocity integral. We can then rewrite Eq. (12) as

$$f_1(\mathbf{r}_1, \mathbf{v}_1; t) = W(\mathbf{r}_1, \mathbf{v}_1; t) b_1(\mathbf{r}_1 | z_1(t)) \tag{17}$$

and, by integrating over \mathbf{v}_1 , we find that z_1 is determined by the local density through the implicit relation

$$n(\mathbf{r}_1; t) = z_1(\mathbf{r}_1; t) b_1(\mathbf{r}_1 | z_1(t)) \tag{18}$$

Formally, this equation is precisely the same as the expansion of the local equilibrium density in terms of $z_1 \rightarrow z \exp[-V(r)/k_B T]$: in the frame of the Mayer cluster expansion at least, we know that this relation can be inverted⁽⁹⁾ and this guarantees the existence of z_1 [and therefore of $W(\mathbf{r}, \mathbf{v}; t)$] for any arbitrary density $n(\mathbf{r}; t)$ [and therefore for any $f_1(\mathbf{r}, \mathbf{v}; t)$]. Moreover, we are also taught that

$$\ln \frac{n(\mathbf{r}; t)}{z_1(\mathbf{r}; t)} = \text{“real number”} \tag{19}$$

[see, for example, Eq. (5.6) of Ref. 9], where the “real number” is defined in terms of a series of graphs (the precise definition of which is irrelevant for our present purpose): hence $z_1(\mathbf{r}; t)$ is a positive function for any given (positive) density profile $n(\mathbf{r}; t)$. An immediate consequence of this and of Eqs. (16) and (17) is that $W(\mathbf{r}, \mathbf{v}; t) \geq 0$ provided $f_1(\mathbf{r}, \mathbf{v}; t) \geq 0$: this property is crucial, as it ensures that the approximate ρ_N of Eq. (8) can indeed be interpreted as a probability density.

⁴ “Fugacity” functions like W were first introduced into nonequilibrium statistical mechanics by E. Cohen and co-workers (see Ref. 3b and references quoted there).

(c) Of course, except at equilibrium [where $W = z\varphi^{\text{eq}}(v)$], Eq. (8) is an approximation and can, at best, be exact at one single instant. Yet, it is precisely the crucial assumption of the Enskog theory that the velocity correlations—which are unavoidably present—always remain small and can be neglected. It is not the purpose of this paper to discuss this approximation.

The derivation of the MEE from our basic assumption (8) is very direct. Taking Eq. (11) for $n = 2$, we get

$$f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2; t) = W(\mathbf{r}_1, \mathbf{v}_1; t)W(\mathbf{r}_2, \mathbf{v}_2; t)b_2(\mathbf{r}_1, \mathbf{r}_2|z_1(t)) \quad (20)$$

and combining this expression with Eq. (17), we arrive at the desired closure relation:

$$f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2; t) = g_2(\mathbf{r}_1, \mathbf{r}_2|n(t))f_1(\mathbf{r}_1, \mathbf{v}_1; t)f_1(\mathbf{r}_2, \mathbf{v}_2; t) \quad (21)$$

where g_2 is defined by⁵

$$g_2(\mathbf{r}_1, \mathbf{r}_2|n(t)) = \frac{b_2[\mathbf{r}_1, \mathbf{r}_2|z_1(\cdot|n(t))]}{b_1[\mathbf{r}_1|z_1(\cdot|n(t))]b_1[\mathbf{r}_2|z_1(\cdot|n(t))]} \quad (22)$$

This is formally written as a functional of the density because of the implicit equation (18), i.e.,

$$z_1(\mathbf{r}; t) = z_1(\mathbf{r}|n(t)) \quad (23)$$

Using the remarks made after Eq. (14), it is easily verified that, at equilibrium, g_2 reduces to the familiar pair correlation function; more generally, one can show that Eq. (22) coincides with the definition of the function $\bar{\chi}$ used by Van Beijeren and Ernst.⁽⁷⁾ Let us recall that these authors have shown that their $\bar{\chi}$ [hence g_2 , as defined in (22)] differs from the original Enskog choice to second order in the gradients of the density for a simple gas (and to first order in a mixture): the results derived in the next section, and obtained by using (22), will thus apply to the MEE only, and not to the original Enskog equation.

As a matter of fact, this MEE [i.e., Eqs. (1), (2), (22)] is immediately obtained within our formalism by inserting (21) into (5).

Before closing this section, we mention three properties which we shall use later.

First, let us calculate the variation of $\ln \Xi(t)$ in an infinitesimal variation of $W(\mathbf{r}, \mathbf{v}; t)$. It immediately follows from the definitions (8), (9), and (15) that

$$\begin{aligned} \delta \ln \Xi(t) &= \int d\mathbf{r}_1 d\mathbf{v}_1 b_1(\mathbf{r}_1|z_1(t)) \delta W(\mathbf{r}_1, \mathbf{v}_1; t) \\ &= \int d\mathbf{r}_1 b_1(\mathbf{r}_1|z_1(t)) \delta z_1(\mathbf{r}_1; t) \end{aligned} \quad (24)$$

⁵ The discussion after (19) shows that the b_n , and therefore g_2 , are positive-definite quantities.

Second, let us differentiate b_1 with respect to \mathbf{r}_1 . Using the property

$$\frac{\partial}{\partial \mathbf{r}_1} \Theta_{12} = \frac{\mathbf{r}_{12}}{a} \delta(r_{12} - a)$$

we get from the definition (16)

$$\frac{\partial b_1(\mathbf{r}_1|z_1)}{\partial \mathbf{r}_1} = \int d\mathbf{r}_2 \frac{\mathbf{r}_{12}}{a} \delta(r_{12} - a) b_2(\mathbf{r}_1, \mathbf{r}_2|z_1) z_1(\mathbf{r}_2; t) \quad (25a)$$

Dividing both sides by $b_1(\mathbf{r}_1|z_1)$ and using the definition (22) for g_2 , we rewrite this as

$$\frac{\partial \ln b_1(\mathbf{r}_1|z_1)}{\partial \mathbf{r}_1} = \int d\mathbf{r}_2 \frac{\mathbf{r}_{12}}{a} \delta(r_{12} - a) g_2(\mathbf{r}_1, \mathbf{r}_2|n(t)) n(\mathbf{r}_2; t) \quad (25b)$$

which is the first equation of a hierarchy which imitates, for our particular nonequilibrium ensemble, the well-known equilibrium hierarchy for hard spheres (see, for example, Ref. 5).

Finally, we notice that if z_1 is independent of the spatial coordinate \mathbf{r} , b_1 is then spatially uniform by translation invariance; from (18), we learn that the density n is also constant throughout the system.

3. THE *H*-THEOREM

We have a few guides to help us in finding an entropy function S (or the corresponding *H*-function: $H = -S/k_B$) appropriate for studying the MEE:

(a) In the dilute gas limit, the MEE becomes the Boltzmann equation, and S should then reduce to the well-known $-k_B \int d\mathbf{r} d\mathbf{v} f_1(\ln f_1 - 1)$, possibly apart from a constant.

(b) In a spatially homogeneous system, the Enskog collision operator differs from the Boltzmann operator by the constant factor $g_2(r_{12} = a|n)$ only; therefore S should again reduce to Boltzmann's entropy in this case.

(c) More important is the fact that the local equilibrium properties calculated from the MEE are *exactly* those of the hard-sphere gas. (This point is stressed in particular in Refs. 3a and 4b.) For example, the local equilibrium energy density—of purely kinetic origin—is given by

$$e(\mathbf{r}; t) = 3n(\mathbf{r}; t)k_B T(\mathbf{r}; t)/2 \quad (26)$$

Similarly, one can show that the pressure that appears in the Navier-Stokes equation as derived from the MEE is again the exact formula:

$$p(\mathbf{r}; t) = n(\mathbf{r}; t)k_B T(\mathbf{r}; t)[1 + \frac{2}{3}\pi a^3 n(\mathbf{r}; t)g_2(a|n(t))] \quad (27)$$

As these two thermodynamic properties calculated with the MEE take the

correct value for the dense hard-sphere gas, it is tempting to conjecture that the same should hold true for all such properties, in particular, for the entropy.

(d) As the MEE describes the time evolution of f_1 only, our definition of entropy, if it is to be of any use at all, should be a functional of f_1 and of no other time-dependent quantity.

A suggestion which satisfies the above requirements is the often mis-treated formula⁶

$$H(t) = \sum_{N=0}^{\infty} \int d\Gamma^N \rho_N(t) \ln[N! \rho_N(t)] \quad (28)$$

where ρ_N is the *approximate* N -particle df (8), and of course not the exact solution of the Liouville equation, for which (28) would remain constant.

Let us rewrite (28) more explicitly:

$$H(t) = \frac{1}{\Xi(t)} \left\{ \sum_N \frac{1}{N!} \int d\Gamma^N \prod_{i>j=1}^N \Theta_{ij} \prod_{i=1}^N W_i(t) \right. \\ \left. \times \ln \left[\prod_{i>j=1}^N \Theta_{ij} \prod_{i=1}^N W_i(t) \right] \right\} - \ln \Xi(t) \quad (29)$$

Interpreting $\Theta_{ij} \ln \Theta_{ij}$ as zero for $r_{ij} < a$, we get, with the help of (11), (15), and (17),

$$H(t) = H^k(t) + H^v(t) \quad (30)$$

where the kinetic part H^k is

$$H^k(t) = \int d\mathbf{r}_1 d\mathbf{v}_1 f_1(\mathbf{r}_1, \mathbf{v}_1; t) [\ln f_1(\mathbf{r}_1, \mathbf{v}_1; t) - 1] \quad (31)$$

and the potential part H^v is

$$H^v(t) = -\ln \Xi(t) + \int d\mathbf{r}_1 n(\mathbf{r}_1; t) \{1 - \ln b_1[\mathbf{r}_1 | z_1(\cdot | n(t))]\} \quad (32)$$

With H written as (30)–(32), it is an easy task to verify that all the conditions (a)–(d) are satisfied. As a hint, let us simply point out that $\Xi(t)$ depends on time through $z_1(\mathbf{r} | n(t))$, which, in a homogeneous system, is independent of \mathbf{r} and t , while in the dilute gas limit, it reduces to $n(\mathbf{r}; t)$.

To derive our H -theorem, let us first consider the time derivative of H^k . We have

$$\partial_t H^k(t) = \int d\mathbf{r}_1 d\mathbf{v}_1 (\ln f_1) J^E(f_1, f_1) \quad (33)$$

⁶ The factor $N!$, which appears for the classical grand ensemble, is discussed, for example, in Ref. 10.

where the term coming from free flow,

$$\int d\mathbf{r}_1 d\mathbf{v}_1 (\ln f_1) \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} f_1 = - \int d\mathbf{r}_1 d\mathbf{v}_1 \mathbf{v}_1 \cdot \frac{\partial f_1}{\partial \mathbf{r}_1} \tag{34}$$

has been set equal to zero. Indeed, we consider here a system satisfying *periodic* conditions at the boundaries: this will keep us from having to enter into the delicate analysis of the physically realistic conditions that f_1 has to satisfy at the walls; even in the dilute gas limit (see the excellent discussion of Refs. 3b and 11), these conditions are not simple, but we may hope they have little bearing on the irreversible processes which occur in the bulk of the system.⁷

With the help of (2), we rewrite (33) as

$$\begin{aligned} \partial_t H^k(t) = a^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{v}_1 d\mathbf{v}_2 \int d^2\epsilon [\ln f_1(\mathbf{r}_1, \mathbf{v}_1; t)] \\ \times (\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) g_2(\mathbf{r}_1, \mathbf{r}_2 | n(t)) [\delta(\mathbf{r}_{12} - a_+ \boldsymbol{\epsilon}) f_1(\mathbf{r}_1, \mathbf{v}_1'; t) \\ \times f_1(\mathbf{r}_2, \mathbf{v}_2'; t) - \delta(\mathbf{r}_{12} + a_+ \boldsymbol{\epsilon}) f_1(\mathbf{r}_1, \mathbf{v}_1; t) f_1(\mathbf{r}_2, \mathbf{v}_2; t)] \end{aligned} \tag{35}$$

which we then submit to two standard manipulations:

(a) In the term involving $\delta(\mathbf{r}_{12} - a_+ \boldsymbol{\epsilon})$, we use $\mathbf{v}_1', \mathbf{v}_2'$, and $\boldsymbol{\epsilon}' = -\boldsymbol{\epsilon}$ as new integration variables. The Jacobian of this transformation is unity and we obtain readily

$$\begin{aligned} \partial_t H^k(t) = -a^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{v}_1 d\mathbf{v}_2 \int d^2\epsilon \left[\ln \frac{f_1(\mathbf{r}_1, \mathbf{v}_1; t)}{f_1(\mathbf{r}_1, \mathbf{v}_1'; t)} \right] (\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) \\ \times g_2(\mathbf{r}_1, \mathbf{r}_2 | n(t)) \delta(\mathbf{r}_{12} + a_+ \boldsymbol{\epsilon}) f_1(\mathbf{r}_1, \mathbf{v}_1; t) f_1(\mathbf{r}_2, \mathbf{v}_2; t) \end{aligned} \tag{36}$$

(b) In (36), we exchange the variables $\mathbf{r}_1, \mathbf{v}_1 \rightleftharpoons \mathbf{r}_2, \mathbf{v}_2$ and, at the same time, we use $\boldsymbol{\epsilon}' = -\boldsymbol{\epsilon}$ as a new integration variable. Taking half the sum of this new expression with (36), we arrive at

$$\begin{aligned} \partial_t H^k(t) = -\frac{1}{2} a^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{v}_1 d\mathbf{v}_2 \int d^2\epsilon \left[\ln \frac{f_1(\mathbf{r}_1, \mathbf{v}_1; t) f_1(\mathbf{r}_2, \mathbf{v}_2; t)}{f_1(\mathbf{r}_1, \mathbf{v}_1'; t) f_1(\mathbf{r}_2, \mathbf{v}_2'; t)} \right] \\ \times (\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) g_2(\mathbf{r}_1, \mathbf{r}_2 | n(t)) \delta(\mathbf{r}_{12} + a_+ \boldsymbol{\epsilon}) \\ \times f_1(\mathbf{r}_1, \mathbf{v}_1; t) f_1(\mathbf{r}_2, \mathbf{v}_2; t) \end{aligned} \tag{37}$$

The crucial inequality which allows us to proceed is

$$x(\ln x - \ln y) \geq x - y \quad (x, y > 0) \tag{38}$$

with the equality sign holding only when $x = y$; the use of (38) in non-equilibrium statistical mechanics goes back to Gibbs.⁽¹²⁾

⁷ Our point of view can be confirmed by verifying that, in the dilute gas limit, our artificial periodic conditions lead to results similar to more realistic treatments of the walls.

We obtain (keeping in mind that g_2 and $\epsilon \cdot \mathbf{v}_{12}$ are positive)

$$\begin{aligned} \partial_t H^k(t) &\leq \frac{1}{2} a^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{v}_1 d\mathbf{v}_2 \int d^2\epsilon (\epsilon \cdot \mathbf{v}_{12}) \Theta(\epsilon \cdot \mathbf{v}_{12}) \\ &\quad \times [f_1(\mathbf{r}_1, \mathbf{v}_1'; t) f_1(\mathbf{r}_2, \mathbf{v}_2'; t) - f_1(\mathbf{r}_1, \mathbf{v}_1; t) f_1(\mathbf{r}_2, \mathbf{v}_2; t)] \\ &\quad \times g_2(\mathbf{r}_1, \mathbf{r}_2 | n(t)) \delta(\mathbf{r}_{12} + a_+ \epsilon) \end{aligned} \quad (39)$$

Using again the change of variables $\mathbf{v}_1', \mathbf{v}_2' \rightleftharpoons \mathbf{v}_1, \mathbf{v}_2$ and performing the integral over ϵ with the help of the Dirac delta function, we arrive at the following formula:

$$\partial_t H^k(t) \leq I(t) \quad (40)$$

with

$$\begin{aligned} I(t) &= \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\mathbf{r}_{12}}{a} \delta(r_{12} - a_+) g_2(\mathbf{r}_1, \mathbf{r}_2 | n(t)) \\ &\quad \times \left[\int d\mathbf{v}_1 \mathbf{v}_1 f_1(\mathbf{r}_1, \mathbf{v}_1; t) \right] n(\mathbf{r}_2; t) \end{aligned} \quad (41)$$

where the symmetry between particles 1 and 2 has also been exploited.

The potential term H^k is easier to treat; from Eqs. (24) and (32), we get immediately

$$\begin{aligned} \partial_t H^k(t) &= - \int d\mathbf{r}_1 \left\{ b_1(\mathbf{r}_1 | z_1(t)) \partial_t z_1(\mathbf{r}_1; t) - \partial_t n(\mathbf{r}_1; t) + \partial_t n(\mathbf{r}_1; t) \right. \\ &\quad \left. \times \left[\ln b_1(\mathbf{r}_1 | z_1(t)) \right] + \frac{n(\mathbf{r}_1; t)}{b_1(\mathbf{r}_1; t)} \partial_t b_1(\mathbf{r}_1 | z_1(t)) \right\} \end{aligned} \quad (42)$$

From (18), we immediately check that all the terms in the integrand cancel except the one involving $\ln b_1$. As, moreover, the density $n(\mathbf{r}_1; t)$ satisfies the continuity equation

$$\partial_t n(\mathbf{r}_1; t) = - \frac{\partial}{\partial \mathbf{r}_1} \cdot \int d\mathbf{v}_1 \mathbf{v}_1 f_1(\mathbf{r}_1, \mathbf{v}_1; t) \quad (43)$$

we obtain, after an integration by parts,

$$\partial_t H^v(t) = - \int d\mathbf{r}_1 \frac{1}{b_1(\mathbf{r}_1 | z_1(t))} \frac{\partial}{\partial \mathbf{r}_1} b_1(\mathbf{r}_1 | z_1(t)) \left[\int d\mathbf{v}_1 \mathbf{v}_1 f_1(\mathbf{r}_1, \mathbf{v}_1; t) \right] \quad (44)$$

From Eqs. (25b) and (41), we find, then,

$$\partial_t H^v(t) = -I(t) \quad (45)$$

and, combining (30), (40), and (45), we arrive at the announced H -theorem⁸

$$\partial_t H(t) \leq 0 \quad (46)$$

⁸ The fact that exactly the same function $I(t)$ appears in our inequality for $\partial_t H^k(t)$ and in $\partial_t H^v(t)$ is not true when the original Enskog equation is used instead of the MEE.

It remains to prove that the function H reaches a stationary value and that, when $\partial_t H = 0$, the one-particle df is the absolute Maxwellian. Concerning the first of these two statements, we merely have to repeat the assumptions made in discussing the Boltzmann equation:⁽³⁾ the finiteness of the total number of particles

$$\int d\mathbf{r}_1 d\mathbf{v}_1 f_1(\mathbf{r}_1, \mathbf{v}_1; t) < \infty \quad (47)$$

and of the total energy⁹

$$\int d\mathbf{r}_1 d\mathbf{v}_1 \frac{1}{2} m v_1^2 f_1(\mathbf{r}_1, \mathbf{v}_1; t) < \infty \quad (48)$$

ensures that $H^k(t)$ is bounded from below. Moreover, it is easy to verify that the potential part H^v , which depends on the local density only, is also bounded. Therefore, H has to reach a stationary value; from (37) and (38), this happens only if

$$\ln f_1(\mathbf{r}_1, \mathbf{v}_1) + \ln f_1(\mathbf{r}_1 + a\boldsymbol{\epsilon}, \mathbf{v}_2) = \ln f_1(\mathbf{r}_1, \mathbf{v}_1') + \ln f_1(\mathbf{r}_1 + a\boldsymbol{\epsilon}, \mathbf{v}_2') \quad (49)$$

for all $\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2$, and $\boldsymbol{\epsilon}$ such that

$$(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) > 0 \quad (50)$$

Yet, this latter condition can be forgotten. To show this, we take Eq. (49), at given $\boldsymbol{\epsilon}$, for values of \mathbf{v}_1 and \mathbf{v}_2 respectively equal to $\mathbf{v}_1' = \mathbf{v}_1 - \boldsymbol{\epsilon}(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12})$ and $\mathbf{v}_2' = \mathbf{v}_2 + \boldsymbol{\epsilon}(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12})$. With $(\mathbf{v}_i)' = \mathbf{v}_i$ ($i = 1, 2$), we see that Eq. (49) remains unchanged while (50) becomes

$$(\boldsymbol{\epsilon} \cdot \mathbf{v}'_{12}) = -(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) > 0 \quad (51)$$

which establishes our point.

To proceed, it is convenient to define the Fourier transform of $\ln f_1$:

$$\Phi_{\mathbf{k}}(\mathbf{v}_1) = \int d\mathbf{r}_1 [\exp(i\mathbf{k} \cdot \mathbf{r}_1)] \ln f_1(\mathbf{r}_1, \mathbf{v}_1) \quad (52)$$

The wave number \mathbf{k} takes the discrete values

$$\mathbf{k} = 2\pi\mathbf{n}/L, \quad \mathbf{n} = (n_x, n_y, n_z), \text{ integers} \quad (53)$$

where, to simplify, we suppose that our system is enclosed in a cubic vessel of side L .

⁹ With our periodic conditions, both the number of particles and the energy inside the system are conserved in time: therefore, (47)–(48) have only to be imposed at $t = 0$. Let us, moreover, stress that our whole calculation, including the definition of H itself, makes sense for a large but *finite* volume Ω only (see also Section 4).

For any \mathbf{v}_1 , \mathbf{v}_2 , \mathbf{k} , and $\boldsymbol{\epsilon}$, Eq. (49) leads to

$$\Phi_{\mathbf{k}}(\mathbf{v}_1) + \Phi_{\mathbf{k}}(\mathbf{v}_2) \exp(-i\mathbf{a}\mathbf{k}\cdot\boldsymbol{\epsilon}) = \Phi_{\mathbf{k}}(\mathbf{v}_1') + \Phi_{\mathbf{k}}(\mathbf{v}_2') \exp(-i\mathbf{a}\mathbf{k}\cdot\boldsymbol{\epsilon}) \quad (54)$$

We then take the same equation for the value $\bar{\boldsymbol{\epsilon}} \equiv -\boldsymbol{\epsilon}$ [noticing that $\mathbf{v}_i'(\bar{\boldsymbol{\epsilon}}) = \mathbf{v}_i'(\boldsymbol{\epsilon})$] and we both subtract and add this result to (54). We arrive at the two following conditions; for any \mathbf{v}_1 , \mathbf{v}_2 , \mathbf{k} , and $\boldsymbol{\epsilon}$

$$\sin(\mathbf{a}\mathbf{k}\cdot\boldsymbol{\epsilon})[\Phi_{\mathbf{k}}(\mathbf{v}_2) - \Phi_{\mathbf{k}}(\mathbf{v}_2')] = 0 \quad (55a)$$

$$[\Phi_{\mathbf{k}}(\mathbf{v}_1) - \Phi_{\mathbf{k}}(\mathbf{v}_1')] = \cos(\mathbf{a}\mathbf{k}\cdot\boldsymbol{\epsilon})[\Phi_{\mathbf{k}}(\mathbf{v}_2) - \Phi_{\mathbf{k}}(\mathbf{v}_2')] \quad (55b)$$

Suppose first that $\mathbf{k} \neq 0$; provided that

$$\mathbf{a}\mathbf{k}\cdot\boldsymbol{\epsilon} = (2\pi a/L)\mathbf{n}\cdot\boldsymbol{\epsilon} \neq \pi m, \quad m \text{ any integer} \quad (56)$$

Eq. (55a) is equivalent to

$$\Phi_{\mathbf{k}}(\mathbf{v}_2) = \Phi_{\mathbf{k}}(\mathbf{v}_2'), \quad \mathbf{k} \neq 0 \quad (57)$$

Moreover, $\boldsymbol{\epsilon}$ is a continuous variable (subject to the constraint $\epsilon_x^2 + \epsilon_y^2 + \epsilon_z^2 = 1$) and the set of $\boldsymbol{\epsilon}$ satisfying $\mathbf{a}\mathbf{k}\cdot\boldsymbol{\epsilon} = \pi m$ is, for fixed \mathbf{k} , of zero measure compared to the total allowed domain of $\boldsymbol{\epsilon}$. Therefore, if we assume that the one-particle df $f_1(\mathbf{r}, \mathbf{v}; t)$ [or $\Phi_{\mathbf{k}}(\mathbf{v}; t)$] is a continuous function of \mathbf{v} , we may forget the restriction (56) and use Eq. (57) for any \mathbf{v}_2 and $\boldsymbol{\epsilon}$; the solution of this equation is simply

$$\Phi_{\mathbf{k}}(\mathbf{v}_2) = \alpha_{\mathbf{k}}, \quad \mathbf{k} \neq 0 \quad (58)$$

where $\alpha_{\mathbf{k}}$ is a constant independent of \mathbf{v}_2 .¹⁰

In the case $\mathbf{k} = 0$, Eq. (55a) is of no use, but Eq. (55b) then reduces to the familiar condition characterizing the collision invariants of the Boltzmann equation;⁽³⁾ we have

$$\Phi_0(\mathbf{v}) = \alpha_0 + \boldsymbol{\beta}\cdot\mathbf{v} + \gamma v^2 \quad (59)$$

where α_0 , $\boldsymbol{\beta}$, and γ are absolute constants. Combining (58) with (59) and going back to configurational space, we find

$$\ln f_1 = \sum_{\mathbf{k}} \alpha_{\mathbf{k}} \exp(-i\mathbf{k}\cdot\mathbf{r}) + \boldsymbol{\beta}\cdot\mathbf{v} + \gamma v^2 \quad (60)$$

or

$$f_1 = \frac{n(\mathbf{r}) \exp[-m(\mathbf{v} - \mathbf{u})^2/2k_B T]}{(2\pi k_B T/m)^{3/2}} \quad (61)$$

¹⁰ The formal proof of this rather obvious result follows the line used to show that 1 is the only collision invariant of the Boltzmann-Lorentz operator (see Ref. 3 and the references quoted there).

where $n(\mathbf{r})$, \mathbf{u} , and T are related in the usual manner^(2,3) to α_k , β , and γ and have an obvious interpretation: they respectively represent the density, the velocity, and the temperature of the fluid.

Let us stress that Eq. (61) is very different from the local equilibrium solution of the Boltzmann collision term: \mathbf{u} and T are absolute constants over the whole system. This important feature can be traced back to the mechanism of collisional transfer: this latter allows the different points of the system to exchange momentum and energy through collisions. In fact, we even have the stronger result, which we prove presently, that the only density $n(\mathbf{r})$ such that Eq. (61) describes a stationary solution of the MEE is also a constant.

To see this, we insert Eq. (61) into (1), (2); to get a time-independent solution of the MEE, we need to have

$$\begin{aligned} & \mathbf{v}_1 \varphi^{\text{eq}}(|\mathbf{v}_1 - \mathbf{u}|) \cdot \frac{\partial n(\mathbf{r}_1)}{\partial \mathbf{r}_1} \\ &= a^2 \int d\mathbf{v}_2 \int d^2\epsilon (\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\epsilon} \cdot \mathbf{v}_{12}) [g_2(\mathbf{r}_1, \mathbf{r}_1 - a_+ \boldsymbol{\epsilon} | n) n(\mathbf{r}_1) n(\mathbf{r}_1 - a\boldsymbol{\epsilon}) \\ & \quad - g_2(\mathbf{r}_1, \mathbf{r}_1 + a_+ \boldsymbol{\epsilon} | n) n(\mathbf{r}_1) n(\mathbf{r}_1 + a\boldsymbol{\epsilon})] \varphi^{\text{eq}}(|\mathbf{v}_1 - \mathbf{u}|) \varphi^{\text{eq}}(|\mathbf{v}_2 - \mathbf{u}|) \end{aligned} \quad (62)$$

with

$$\varphi^{\text{eq}}(v) = (m/2\pi k_B T)^{3/2} \exp(-mv^2/2k_B T) \quad (63)$$

Using standard manipulations for hard-sphere collisions,^(2,3) we can perform the integration over \mathbf{v}_2 on the right-hand side of (62). Comparing the result with the right-hand side of Eq. (25b), we can readily verify that condition (62) on the density $n(\mathbf{r}_1)$ can also be written

$$\frac{\partial \ln n(\mathbf{r}_1)}{\partial \mathbf{r}_1} = \frac{\partial \ln b_1(\mathbf{r}_1)}{\partial \mathbf{r}_1} \quad (64)$$

Integrating this equation, we see from (18) that $z_1 = n(\mathbf{r}_1)/b_1(\mathbf{r}_1|z_1)$ is independent of \mathbf{r}_1 ; as we demonstrated in the final paragraph of Section 2, this implies that the density is constant throughout the system:

$$n(\mathbf{r}) = n \quad (\text{independent of } \mathbf{r}) \quad (65)$$

Finally, we have seen in Eq. (61) that our periodic conditions allow for an arbitrary constant fluid velocity \mathbf{u} ; however, as this velocity is conserved in time, we best imitate a system with realistic boundaries by choosing $\mathbf{u} = 0$.

In this way, our H -theorem guarantees that the MEE drives the system toward the absolute Maxwellian:

$$f_1 = n\varphi^{eq}(v_1) \quad (66)$$

(for periodic boundary conditions at least).

4. DISCUSSION

Despite the approximate character of the MEE, the proof of an H -theorem for this kinetic equation is important because it is the first explicit demonstration of the approach to equilibrium of the one-particle df in a strongly interacting system. From this point of view, the MEE seems to offer a definite advantage over the density expansion of the (formally exact) generalized kinetic equation, where, except for the lowest order Boltzmann term, no equivalent property has been found (see Ref. 3 and references quoted there). Let us repeat also that our calculation says nothing about the original Enskog equation [from which the MEE differs to order $(\partial/\partial\mathbf{r})^2$ is a simple gas]; yet, the fact that this original Enskog approximation suffers from serious inconsistencies (like the violation of the Onsager relations for mixtures) makes it improbable that it obeys an H -theorem in general.

Clearly, from a rigorous point of view, our calculation—at least in its present stage—tells us very little on how the irreversibility of observable (reduced) properties can possibly emerge from the reversible equations of motion for the whole system: the MEE is based on an ad hoc assumption, which, despite its success, cannot be made mathematically rigorous in any limit. Yet, it is very remarkable that there exists an H -function, depending on f_1 only, such that $\partial_t H \leq 0$, with the equality sign holding at absolute equilibrium only. Glancing backward at the coherence of the whole calculation, we cannot believe that this fact is fortuitous, and therefore it should open the way to a deeper understanding of strongly coupled systems.

Yet, we should not hide the enormous difficulties that are circumvented with the approximate MEE. Let us cite just a few of them:

- (a) What replaces the excluded volume effect when the forces are smooth?
- (b) What should be done with the non-Markovian effects which are ineluctable consequences of the velocity correlations between the particles? (See, for example, Ref. 3a.)
- (c) What happens when the strict thermodynamic limit ($N \rightarrow \infty$, $\Omega \rightarrow \infty$, $N/\Omega = n$ finite) is taken?

Concerning this last point, the attentive reader will have already noticed a paradoxical situation: while it is generally believed that irreversibility is a property of systems with infinitely many degrees of freedom, we have proved here a *global* H -theorem, i.e., a property applying to the whole system: this

system is large but necessarily *finite* (otherwise, we find, for example, difficulties when talking about boundary conditions). Of course, from our phenomenological point of view, we may ignore this difficulty (we have merely neglected terms of “order $1/N$ ”), but it is not easy to be more rigorous, except perhaps by generalizing our approach to a *local* point of view (see below).¹¹

Another difficulty is that, beyond the macroscopic regime where non-equilibrium thermodynamics holds, nothing forces us to a unique definition of entropy: any “Liapounov function” displaying the irreversible kinetic behavior is a priori valuable. For example, Prigogine and co-workers have investigated Liapounov functions at the level of the *N-body* formal master equations:⁽¹⁵⁾ due to this difference in point of view, it is very difficult to compare their approach with the present calculation. We also cite an attempt by Hubert⁽¹⁶⁾ to prove an *H*-theorem for the (original) Enskog equation, but, except in the thermodynamic regime where no surprise was expected,¹² he was not able to get any conclusive result.¹³ Nevertheless, the present attempt is extremely pleasing because it generalizes, in the most natural way, Boltzmann’s original ideas.

To give a hint of other possible extensions of our work, let us recall that the second postulate of thermodynamics can be written (see, for example, Ref. 20)

$$dS_{\Omega}/dt = d_e S_{\Omega}/dt + d_i S_{\Omega}/dt \tag{67}$$

$$d_i S_{\Omega}/dt \geq 0 \tag{68}$$

The total entropy variation dS_{Ω}/dt of an open system of volume Ω is the sum of an entropy exchange with the external world $d_e S_{\Omega}/dt$ and of an entropy production $d_i S_{\Omega}/dt$ which is semipositive definite.

In order to provide a microscopic content to these equations for a system described by the MEE, we have used periodic boundary conditions: thus, there is no accessible “external world.” Any entropy flow at the walls is automatically reinjected into the system and therefore $d_e S_{\Omega}/dt = 0$. In some sense, we have a model of “pure” irreversible behavior. It is hard to believe that more realistic boundary conditions could destroy our *H*-theorem;

¹¹ Such a difficulty can be avoided with the Boltzmann equation if, instead of the usual thermodynamic limit $N \rightarrow \infty, \Omega \rightarrow \infty, N/\Omega = n$ finite, we adopt the so-called Grad limit $a \rightarrow 0, n \rightarrow \infty, (a^2 n)$ finite and Ω *finite*.^(11,13,14) As the covolume effects are of order $(a^3 n)$, this limit is of no use here.

¹² The macroscopic physics of a strongly interacting system is that of a dilute gas, except for the value of the transport coefficients.

¹³ In passing, we also cite a master-equation attempt by Hubert⁽¹⁸⁾ to describe the hard-sphere gas: this work will be discussed elsewhere.⁽¹⁹⁾

nevertheless, we have here an obvious question to answer in a precise fashion, probably along the lines used for the Boltzmann equation.^(3b,11)

A second point is that Eqs. (67)–(68) can also be postulated for any part of a macroscopic system, leading to a more *local* formulation. In other words, taking a subvolume V delimited by a surface Σ inside Ω , the existence of an entropy density $s(\mathbf{r}; t)$ is postulated such that

$$\frac{dS_V}{dt} = \int_V d\mathbf{r} \frac{ds(\mathbf{r}; t)}{dt} \quad (69)$$

with Eqs. (67) and (68) still holding with the subscript V replacing Ω . Yet, it is clear that $d_e S_V/dt$, though it describes the exchange of entropy from the inside to the outside of Σ , *cannot* generally be written as the surface integral

$$-\int_{\Sigma} d\mathbf{\Sigma} \cdot \mathbf{J}_s \quad (70)$$

where J_s would depend on the points on Σ only. For example, in our microscopic MEE model again, we immediately see that [due to collisional transfer and whatever the precise definition adopted for $s(\mathbf{r}; t|f_1)$] ($d_e S_V/dt$) should depend on the one-particle df_1 over a region of width of order a around Σ . Only when we further assume that f_1 is slowly varying in space should (70) become a legitimate expression for the entropy exchange, leading then to the familiar local formula⁽²⁰⁾

$$ds(\mathbf{r}; t)/dt + \nabla \cdot \mathbf{J}_s(\mathbf{r}; t) = \sigma(\mathbf{r}; t) \quad (71)$$

$$\sigma(\mathbf{r}; t) \geq 0 \quad (72)$$

(σ is the local entropy production). If we go one step further, and assume that our system is close to local equilibrium, then we should recover the Gibbs relation.⁽¹⁷⁾

Preliminary investigations show that such a local approach can indeed be justified microscopically for the MEE, by combining the present formalism with a definition for local entropy along classical lines (see, for example, Ref. 20). The technical aspects of the problem are, however, rather involved and will be discussed in a separate publication.

Finally, in an analysis previous to the present work, we studied the approach to equilibrium as described by the *linearized* MEE. Of course, from the more general point of view described here, this much simpler problem finds an automatic solution. It suffices to write

$$f_1(\mathbf{r}, \mathbf{v}; t) = n\varphi^{\text{eq}}(v) + \delta f_1(\mathbf{r}, \mathbf{v}; t) \quad (73)$$

and to expand all our formulas to leading nontrivial order in δf_1 in order to show that this linearized MEE also satisfies an H -theorem. Yet, an independent

proof of this theorem reveals a series of interesting properties, which can be useful in other contexts; for this reason, the linearized MEE is discussed independently in a separate publication.⁽¹⁹⁾

ACKNOWLEDGMENT

We thank Dr. M. Baus for interesting remarks about some aspects of this work.

REFERENCES

1. D. Enskog, *Kungl. Sv. Vetenskapsakad. Handb.* 63, No. 4 (1922).
2. S. Chapman and T. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge Univ. Press, Cambridge, 1935).
3. (a) P. Résibois and M. De Leener, *Classical Kinetic Theory of Fluids* (Wiley-Interscience, New York, 1977); (b) J. Dorfman and H. Van Beijeren, in *Statistical Mechanics, Part B*, B. Berne, ed. (Plenum Press, New York, 1977).
4. (a) H. Hanley, R. MacCarthy, and E. Cohen, *Physica* 60:322 (1972); (b) J. Piasecki, in *Fundamental Problems in Statistical Mechanics*, E. Cohen, ed. (Polish Academy of Sciences, Warsaw, 1978); (c) P. Résibois, in *Fundamental Problems in Statistical Mechanics*, E. Cohen, ed. (Polish Academy of Sciences, Warsaw, 1978).
5. J. Lebowitz, J. Percus, and J. Sykes, *Phys. Rev.* 188:487 (1967).
6. J. Sykes, *J. Stat. Phys.* 8:279 (1973).
7. H. Van Beijeren and M. Ernst, *Physica* 68:437 (1973); 70:225 (1973).
8. P. Résibois, *Phys. Rev. Lett.*, 40: 1409 (1978).
9. G. Stell, in *The Equilibrium Theory of Classical Fluids*, H. Frisch and J. Lebowitz, eds. (Benjamin, New York, 1964).
10. D. Ter Haar, *Statistical Mechanics* (Constable, London, 1954).
11. C. Cercignani, *Theory and Application of the Boltzmann Equation* (Scottish Academic Press, Edinburgh, 1975).
12. W. Gibbs, *Elementary Principles of Statistical Mechanics* (reprinted by Dover, New York, 1960).
13. H. Grad, in *Handbuch der Physik*, S. Flügge, ed. (Springer-Verlag, Berlin, 1958), Vol. 12.
14. O. Lanford III, in *Proceedings of the Int. Conf. on Dynamical Systems in Math. Phys.*, Rennes 1975 (Soc. Math. de France, Paris, 1976).
15. I. Prigogine, C. George, F. Henin, and L. Rosenfeld, *Chemica Scripta* 4:5 (1973).
16. D. Hubert, *Phys. Chem. Liq.* 6:71 (1977).
17. (a) I. Prigogine, *Physica* 15:272 (1949); (b) G. Nicolis, J. Wallenborn, and M. Velarde, *Physica* 43:475 (1968).
18. D. Hubert, *J. Stat. Phys.* 15:73 (1976); *Physica* 83A:548 (1976).
19. P. Résibois, *Physica* 94A: 1 (1978).
20. P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations* (Wiley-Interscience, New York, 1971).
21. (a) R. Nettleton and M. Green, *J. Chem. Phys.* 29:1365 (1958); (b) Y. Yvon, *Les Corrélations et l'Entropie* (Dunod, Paris, 1966).