

***H*-Theorem for the Hard-Sphere Gas**

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The approach to equilibrium of the hard-sphere gas is discussed from the master-equation point of view. An *H*-theorem is established, which is valid for arbitrary initial conditions.

KEY WORDS: Master equation; hard-sphere gas; nonlinear thermodynamics; symmetry breaking; Liapunov function.

1. INTRODUCTION

The demonstration of an approach to equilibrium and an *H*-theorem for large dynamical systems has remained an open problem since Boltzmann's work. It has proved very difficult to extend Boltzmann's ideas beyond the case of a dilute gas. Moreover, serious difficulties arise at the conceptual level: Even for a dilute gas, Boltzmann's statistical definition of entropy applies only to certain initial conditions and a particular form of the collision operator.^(1,2) Recent computer as well as spin echo experiments in dipolar coupled systems illustrate clearly the difficulties in Boltzmann's derivation. Indeed, they display situations for which a kinetic equation of the Boltzmann type is not valid.

Recently, a reformulation of statistical mechanics has been developed by Prigogine *et al.*⁽¹⁻⁴⁾ They have shown the way to construct a more general microscopic model of entropy, which displays the expected monotonic approach to equilibrium even in non-Boltzmann situations, such as experiments involving "negative time evolution." More precisely, they have pointed out that if we expect the second law of thermodynamics to be valid whatever the initial state of the system, entropy has obviously to depend in

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general on all dynamical variables of the problem.⁽⁴⁾ It is only in special cases, such as near local equilibrium conditions, that entropy may be expressed in terms of reduced distribution functions or even in terms of macroscopic quantities alone as in thermodynamics.^(5,6)

Let us summarize briefly some aspects of the principle of symmetry breaking as a dissipativity condition.^(1,5) Take the Liouville equation

$$(\partial/\partial t)\rho = -iL\rho \quad (1)$$

for the distribution function. If $-L$ is substituted for L and $-t$ for t , the equation remains unchanged. Thus it is “ Lt ” invariant. On the contrary, kinetic equations derived from Eq. (1), such as the Boltzmann equation, are not “ Lt ” invariant. The origin of this symmetry breaking is due to an explicit consideration of causality, which leads, for a system for which the operator L has a continuous spectrum, to the need for analytical continuation of the resolvent $(L - z)^{-1}$ associated with Eq. (1). The analytical continuation leads in turn to the appearance of even terms in L in the evolution equations. These even terms Φ^e break the “ Lt ” symmetry and play a central role in the so-called dissipativity condition given by $\Phi^e \neq 0$. It is the clarification of this mechanism that is the distinctive feature of this approach.

The object of this paper is to study a model of a gas of hard spheres in the light of this theory. In a previous paper⁽⁷⁾ we established an H -theorem for the Enskog kinetic equation. The validity of this theorem is shown to be limited to the range of linear thermodynamics of irreversible processes. For far-from-equilibrium states we have demonstrated the impossibility of expressing an H -theorem in terms of reduced distribution functions.

We know from the work of Enskog the importance of this model.⁽⁸⁾ He was the first to predict the density dependence of the transport properties of a dense gas from his kinetic equation, which has the form

$$\begin{aligned} \frac{\partial}{\partial t} f + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} f &= \sigma^2 \iint d\mathbf{v}_2 d\mathbf{k} \mathbf{g}_{12} \cdot \mathbf{k} \\ &\times [Y(\mathbf{r}_1 + \frac{1}{2}\sigma\mathbf{k})f'(\mathbf{r}_1)f'(\mathbf{r}_1 + \sigma\mathbf{k}) \\ &- Y(\mathbf{r}_1 - \frac{1}{2}\sigma\mathbf{k})f(\mathbf{r}_1)f(\mathbf{r}_1 - \sigma\mathbf{k})] \end{aligned} \quad (2)$$

where $f(\mathbf{r}_1) \equiv f(\mathbf{v}_1, \mathbf{r}_1; t)$; $f(\mathbf{r}_1 + \sigma\mathbf{k}) \equiv f(\mathbf{v}_2, \mathbf{r}_1 + \sigma\mathbf{k}; t)$ is the one-particle distribution function; and $f'(\mathbf{r}_1) = f(\mathbf{v}_1', \mathbf{r}_1; t)$, with \mathbf{v}_1' denoting the velocities of the two molecules before collision. The diameter of the molecules is σ and $\mathbf{g}_{12} = \mathbf{v}_2 - \mathbf{v}_1$ is the relative velocity; \mathbf{k} is the unit vector along the apse line joining the centers of the two molecules at the instant of contact. The factor Y expresses the increase in the probability of a collision, and has the value of the equilibrium radial distribution function at the position of impact in a molecular collision.^(9,10) Despite its simplicity, transport properties obtained

from Enskog's equation compare favorably with those derived from the more rigorously based equation of Choh and Uhlenbeck.^(11,12)

The approach to equilibrium of the hard-sphere model described by the Enskog equation remains an open problem, and no *H*-theorem, one of the great successes of the Boltzmann equation, has been established to our knowledge beyond the linear range of irreversible processes.⁽⁷⁾

In Section 2, following a similar procedure as that employed by Kac to derive the Boltzmann equation,⁽¹³⁾ we propose a master equation, which for a classical system of hard spheres generates the Enskog equation.⁽¹⁴⁾ Then we show how the symmetry breaking as a dissipative condition is displayed. A generalized *H*-theorem valid for the complete system is established in Section 3, whatever the initial state of the system. In the conclusions (Section 4), we discuss the Boltzmann form of the *H*-theorem. We show the necessity of a more general definition of entropy out of equilibrium for more complex systems than dilute gases.

2. MASTER EQUATION FOR THE HARD-SPHERE GAS

Consider an assembly of N identical particles as hard spheres of diameter σ enclosed in a volume v . The evolution of such a system is mainly governed by the dynamics of binary elastic collisions.⁽¹⁴⁾ A kinetic equation of this system [cf. Eq. (2)] has been derived by Enskog using intuitive arguments. The Enskog theory can also be approached by studying an appropriate master equation.

Denote by $\mathbf{V} = \mathbf{v}^N = \mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_N$ the velocities of the N molecules and by $\mathbf{R} = \mathbf{r}^N$ their positions and combine them into a $6N$ -dimensional master vector

$$(\mathbf{R}, \mathbf{V}) = (\mathbf{v}_1, \mathbf{r}_1; \mathbf{v}_2, \mathbf{r}_2; \dots; \mathbf{v}_N, \mathbf{r}_N) \quad (3)$$

Consider now the process in which a collision occurs between the i th and j th particles ($i < j$). Let the direction from the center of i to j be \mathbf{k} . Then \mathbf{V} changes into $A_{ij}(\mathbf{k})\mathbf{V}$, where

$$A_{ij}(\mathbf{k})\mathbf{V} = (\mathbf{v}_1, \dots, \mathbf{v}_i + (\mathbf{v}_j - \mathbf{v}_i) \cdot \mathbf{k}\mathbf{k}, \dots, \mathbf{v}_j - (\mathbf{v}_j - \mathbf{v}_i) \cdot \mathbf{k}\mathbf{k}, \dots, \mathbf{v}_N) \quad (4)$$

More generally, the action of the operator $A_{ij}(\mathbf{k})$ on a function $F(\mathbf{V})$ is such that

$$A_{ij}(\mathbf{k})F(\mathbf{V}) = F(A_{ij}(\mathbf{k})\mathbf{V}) \quad (5)$$

The analysis of the binary collision expansion of such a model has been made by Ernst *et al.*⁽¹⁴⁾ and they have obtained a pseudo-Liouville equation. We will recover their result using a master equation approach. In effect for a

gas at ordinary pressure a master equation approach to Boltzmann's theory for a monatomic and spatially homogeneous gas has been given by Kac.⁽¹³⁾ The probability per unit time of a collision such that particles i and j lie in a volume $dr_i dr_j$ and their velocities lie in a range $dv_i dv_j$ and \mathbf{k} lies in $d\mathbf{k}$ is assumed to be of the form ψ_{ij} . At time $t = 0$, we start with a distribution of N molecules given by the density $\rho(\mathbf{V}, 0)$ and the distribution will evolve in time according to the equation

$$\frac{\partial}{\partial t} \rho(\mathbf{V}; t) = \sum_{i < j} \int d\mathbf{k} \psi_{ij} [\rho(A_{ij}(\mathbf{k})\mathbf{V}; t) - \rho(\mathbf{V}; t)] \quad (6)$$

This equation requires correction when the gas is dense. Indeed, for a dilute gas the mean free path of a molecule is large compared to the molecular dimensions. However, this ratio is much reduced if the gas is dense. Consequently, an additional mechanism to the collision process, describing transfer of momentum and energy over the distance separating the centers of the two colliding molecules, becomes important. To take this effect into account we have to specify the position of the colliding particles. If the particle i is at \mathbf{r}_i , the particle j must be at $\mathbf{r}_j = \mathbf{r}_i - \sigma\mathbf{k}$, where \mathbf{k} is the direction of the centers of the particles (i, j) which will collide at $\mathbf{r}_i - \frac{1}{2}\sigma\mathbf{k}$. Thus on the right-hand side of Eq. (6) this effect will appear by the introduction of a function $\delta(\mathbf{r}_{ij} + \sigma\mathbf{k})$ associated with $\rho(\mathbf{V}, \mathbf{R}; t)$; $\delta(\mathbf{r})$ is a three-dimensional Dirac δ -function. In the inverse collision process the center of the molecule i lies in a volume dr_i and the velocities of the two molecules after collision lie in the range $dv_i dv_j$ while the direction of the line of centers is $-\mathbf{k}$, where \mathbf{k} lies in $d\mathbf{k}$, so as above, $\rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{R}; t)$ in Eq. (6) must be replaced by $\delta(\mathbf{r}_{ij} - \sigma\mathbf{k}) \times \rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{R}; t)$. In such a collision the center of the second molecule is at $\mathbf{r}_j = \mathbf{r}_i + \sigma\mathbf{k}$, while the two molecules actually touch at $\mathbf{r}_i + \frac{1}{2}\sigma\mathbf{k}$.

In these collisions $\sigma^2 d\mathbf{k}$ denotes a surface element on the sphere, or radius σ and center i , on which j must lie at the collision. Hence for a gas at ordinary pressure the probability per unit time of a collision such that i lies in a volume dr_i , the velocities of the two molecules lie in range $dv_i dv_j$, and \mathbf{k} lies in $d\mathbf{k}$ can be given in a more explicit form, which is actually the same as in the Enskog equation (2). Thus the master equation for a nonuniform dense gas is

$$\begin{aligned} & \frac{\partial}{\partial t} \rho(\mathbf{V}, \mathbf{R}; t) + \mathbf{V} \cdot \frac{\partial}{\partial \mathbf{R}} \rho(\mathbf{V}, \mathbf{R}; t) \\ & = \sigma^2 \sum_{i < j} \int d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} [\delta(\mathbf{r}_{ij} - \sigma\mathbf{k}) A_{ij}(\mathbf{k}) - \delta(\mathbf{r}_{ij} + \sigma\mathbf{k})] \rho(\mathbf{V}, \mathbf{R}; t) \quad (7) \end{aligned}$$

with $\mathbf{g}_{ij} = \mathbf{v}_j - \mathbf{v}_i$ the relative velocity.

Introducing the collision operator O defined by

$$O = \sigma^2 \sum_{i < j} \int d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} [A_{ij}(\mathbf{k}) \delta(\mathbf{r}_{ij} - \sigma\mathbf{k}) - \delta(\mathbf{r}_{ij} + \sigma\mathbf{k})] \quad (8)$$

we may write Eq. (7) as

$$\frac{\partial}{\partial t} \rho(\mathbf{V}, \mathbf{R}; t) + \mathbf{V} \cdot \frac{\partial}{\partial \mathbf{R}} \rho(\mathbf{V}, \mathbf{R}; t) = O\rho(\mathbf{V}, \mathbf{R}; t) \quad (9)$$

To derive from the master equation, Eq. (7), the Enskog kinetic equation we have to make some assumptions, as Enskog does in his theory for dense gases. In equilibrium the pair-distribution function f_2^0 is related to the one-particle distribution function f^0 by

$$f_2^0(\mathbf{v}_1, \mathbf{v}_2, \mathbf{r}_1, \mathbf{r}_2 = \mathbf{r}_1 + \sigma\mathbf{k}) = Y(\sigma\mathbf{k})f^0(\mathbf{v}_1, \mathbf{r}_1)f^0(\mathbf{v}_2, \mathbf{r}_1 + \sigma\mathbf{k}) \quad (10)$$

where $Y(\sigma\mathbf{k})$ is the equilibrium radial distribution function at a separation $\sigma\mathbf{k}$. This equilibrium radial distribution function is independent of the velocities and depends only on the relative distance $|\mathbf{r}_{12}| = \sigma$ at a collision. We assume, as Enskog did, that this relationship is valid even when the system is not in equilibrium^(9,10):

$$f_2(\mathbf{v}_1, \mathbf{v}_2, \mathbf{r}_1, \mathbf{r}_2 = \mathbf{r}_1 + \sigma\mathbf{k}; t) = Y(\sigma; n(\mathbf{R}_{12}))f(\mathbf{v}_1, \mathbf{r}_1; t) \quad (11)$$

where $Y(\sigma; n(\mathbf{R}_{12}))$ is now the equilibrium value of the pair distribution function for $|\mathbf{r}_{12}| = \sigma$, evaluated as a function of the local density $n(\mathbf{r})$ at position $\mathbf{R}_{12} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ of contact between the two colliding spheres.

3. GENERALIZED *H*-THEOREM

To study the approach to equilibrium of a system of hard spheres, the evolution of which is described by the master equation (9), it will be convenient to decompose the collision operator O into two new operators. We define through inversion of the velocities an operator symmetric in velocities, which we denote by O^S , and another O^A antisymmetric in the velocities. They are such that $O \equiv O^S + O^A$ and explicitly take the form

$$\begin{aligned} O^S = & \frac{1}{2}\sigma^2 \sum_{i < j} \int_{\mathbf{g}_{ij} \cdot \mathbf{k} > 0} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} [A_{ij}(\mathbf{k}) - 1] \delta(\mathbf{r}_{ij} - \sigma\mathbf{k}) \\ & + \frac{1}{2}\sigma^2 \sum_{i < j} \int_{\mathbf{g}_{ij} \cdot \mathbf{k} > 0} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} [A_{ij}(\mathbf{k}) - 1] \delta(\mathbf{r}_{ij} + \sigma\mathbf{k}) \end{aligned} \quad (12)$$

and

$$\begin{aligned} O^A = & \frac{1}{2}\sigma^2 \sum_{i < j} \int_{\mathbf{g}_{ij} \cdot \mathbf{k} > 0} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} [A_{ij}(\mathbf{k}) + 1] \delta(\mathbf{r}_{ij} - \sigma\mathbf{k}) \\ & - \frac{1}{2}\sigma^2 \sum_{i < j} \int_{\mathbf{g}_{ij} \cdot \mathbf{k} > 0} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} [A_{ij}(\mathbf{k}) + 1] \delta(\mathbf{r}_{ij} + \sigma\mathbf{k}) \end{aligned} \quad (13)$$

The master equation (9) is then written in the form

$$\frac{\partial}{\partial t} \rho(\mathbf{V}, \mathbf{R}; t) + \mathbf{V} \cdot \frac{\partial}{\partial \mathbf{R}} \rho(\mathbf{V}, \mathbf{R}; t) = (O^S + O^A) \rho(\mathbf{V}, \mathbf{R}; t) \quad (14)$$

In the following $\mathbf{g}_{ij} \cdot \mathbf{k}$ will be assumed to be > 0 , unless otherwise stated.

It has been established and recently demonstrated on different models^(1,15,16) that the general evolution of dynamical dissipative systems may be characterized in terms of a Liapunov function Ω , namely

$$\Omega = \iint d\mathbf{V} d\mathbf{R} \rho^2(\mathbf{V}, \mathbf{R}; t) \quad (15)$$

Then from the evolution equation (14) we obtain

$$\begin{aligned} \frac{1}{2} \frac{\partial}{\partial t} \Omega &= - \iint d\mathbf{V} d\mathbf{R} \rho(\mathbf{V}, \mathbf{R}; t) \mathbf{V} \cdot \frac{\partial}{\partial \mathbf{R}} \rho(\mathbf{V}, \mathbf{R}; t) \\ &+ \iint d\mathbf{V} d\mathbf{R} \rho(\mathbf{V}, \mathbf{R}; t) (O^S + O^A) \rho(\mathbf{V}, \mathbf{R}; t) \end{aligned} \quad (16)$$

Consider first the contribution of the symmetric collision operator O^S which is given by

$$\begin{aligned} &\iint d\mathbf{V} d\mathbf{R} \rho(\mathbf{V}, \mathbf{R}; t) O^S \rho(\mathbf{V}, \mathbf{R}; t) \\ &= \frac{1}{2} \sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^{N-1} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \rho(\mathbf{V}, \mathbf{r}_{ij} = \sigma \mathbf{k}; t) \\ &\quad \times [\rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{r}_{ij} = \sigma \mathbf{k}; t) - \rho(\mathbf{V}, \mathbf{r}_{ij} = \sigma \mathbf{k}; t)] \\ &+ \frac{1}{2} \sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^{N-1} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \rho(\mathbf{V}, \mathbf{r}_{ij} = -\sigma \mathbf{k}; t) \\ &\quad \times [\rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{r}_{ij} = -\sigma \mathbf{k}; t) - \rho(\mathbf{V}, \mathbf{r}_{ij} = -\sigma \mathbf{k}; t)] \end{aligned} \quad (17)$$

But the operator $A_{ij}(\mathbf{k})$ is orthogonal acting on the velocity space V ; hence we have the following relation:

$$\begin{aligned} &\sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^{N-1} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \rho^2(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{r}_{ij} = \sigma \mathbf{k}; t) \\ &= \sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^{N-1} \mathbf{g}_{ij} \cdot \mathbf{k} \rho^2(\mathbf{V}, \mathbf{r}_{ij} = -\sigma \mathbf{k}; t) \end{aligned} \quad (18)$$

Introducing this relation into Eq. (17), we obtain

$$\begin{aligned}
 & \iint d\mathbf{V} d\mathbf{R} \rho(\mathbf{V}, \mathbf{R}; t) O^S \rho(\mathbf{V}, \mathbf{R}; t) \\
 &= -\frac{1}{4}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^{N-1} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \\
 & \quad \times [\rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t) - \rho(\mathbf{V}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t)]^2 \\
 & - \frac{1}{4}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^{N-1} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \\
 & \quad \times [\rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{r}_{ij} = -\sigma\mathbf{k}; t) - \rho(\mathbf{V}, \mathbf{r}_{ij} = -\sigma\mathbf{k}; t)]^2 \quad (19)
 \end{aligned}$$

and hence

$$\iint d\mathbf{V} d\mathbf{R} \rho(\mathbf{V}, \mathbf{R}; t) O^S \rho(\mathbf{V}, \mathbf{R}; t) \leq 0 \quad (20)$$

If we consider a gas at rest in a smooth vessel, the first term on the right-hand side of Eq. (16) gives no contribution. In effect the components of the velocity of the particules along the normal of any element dS of the surface of the vessel are exactly reversed, since the vessel is smooth. The contributions at the point of contact of the hard spheres will be eliminated in the same manner as for the third contribution, which is given below.

The third contribution on the right-hand side of Eq. (16), that is, of the antisymmetric part O^A of the collision operator, is

$$\begin{aligned}
 & \iint d\mathbf{V} d\mathbf{R} \rho(\mathbf{V}, \mathbf{R}; t) O^A \rho(\mathbf{V}, \mathbf{R}; t) \\
 &= \frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^{N-1} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \rho(\mathbf{V}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t) \\
 & \quad \times [\rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t) + \rho(\mathbf{V}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t)] \\
 & - \frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^{N-1} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \rho(\mathbf{V}, \mathbf{r}_{ij} = -\sigma\mathbf{k}; t) \\
 & \quad \times [\rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{r}_{ij} = -\sigma\mathbf{k}; t) + \rho(\mathbf{V}, \mathbf{r}_{ij} = -\sigma\mathbf{k}; t)] \quad (21)
 \end{aligned}$$

Considering the inverse collision, this expression is simplified to

$$\begin{aligned}
 & \iint d\mathbf{V} d\mathbf{R} \rho(\mathbf{V}, \mathbf{R}; t) O^A \rho(\mathbf{V}, \mathbf{R}; t) \\
 &= \frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^{N-1} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \rho^2(\mathbf{V}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t) \\
 & - \frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^{N-1} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \rho^2(\mathbf{V}, \mathbf{r}_{ij} = -\sigma\mathbf{k}; t) \\
 &= \frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^{N-1} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \rho^2(\mathbf{V}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t) \quad (22)
 \end{aligned}$$

$$0 \leq \mathbf{g}_{ij} \cdot \mathbf{k} \leq 0$$

On transformation by Green's theorem, this is equal to

$$\frac{1}{2} \sum_{i < j} \iint d\mathbf{V} d\mathbf{r}^N \mathbf{g}_{ij} \cdot \frac{\partial}{\partial \mathbf{r}_{ij}} \rho^2(\mathbf{V}, \mathbf{r}^N; t) \quad (23)$$

with $|\mathbf{r}_{ij}| \geq \sigma$. The coordinates are transformed to relative and center-of-mass coordinates by means of the relations

$$\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i; \quad \mathbf{R}_{ij} = \frac{1}{2}(\mathbf{r}_i + \mathbf{r}_j); \quad \mathbf{g}_{ij} = \mathbf{v}_j - \mathbf{v}_i; \quad \mathbf{G}_{ij} = \frac{1}{2}(\mathbf{v}_i + \mathbf{v}_j) \quad (24)$$

Then, after introduction of the relations (24), the expression (23) becomes

$$\begin{aligned} & \frac{1}{2} \sum_{i < j} \iint d\mathbf{v}^{N-2} d\mathbf{G}_{ij} d\mathbf{g}_{ij} d\mathbf{R}_{ij} d\mathbf{r}_{ij} \cdot \mathbf{g}_{ij} \cdot \frac{\partial}{\partial \mathbf{r}_{ij}} \rho^2(\mathbf{v}^{N-2}, \mathbf{G}_{ij}, \mathbf{g}_{ij}, \mathbf{R}_{ij}, \mathbf{r}_{ij}; t) \\ &= \frac{1}{2} \sigma^2 \sum_{i < j} \iint_{0 \leq \mathbf{g}_{ij} \cdot \mathbf{k} \leq 0} d\mathbf{v}^{N-2} d\mathbf{G}_{ij} d\mathbf{g}_{ij} d\mathbf{R}_{ij} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \\ & \quad \times \rho^2(\mathbf{v}^{N-2}, \mathbf{G}_{ij}, \mathbf{g}_{ij}, \mathbf{R}_{ij}, \mathbf{r}_{ij} = \sigma \mathbf{k}; t) \\ & \quad \quad \quad 0 \leq \mathbf{g}_{ij} \cdot \mathbf{k} \leq 0 \end{aligned} \quad (25)$$

Since the collisions are elastic near the element $\sigma^2 d\mathbf{k}$ of surface, the \mathbf{k} components of relative velocity $\mathbf{g}_{ij} \cdot \mathbf{k}$ of the particles i and j are exactly reversed whatever the center-of-mass velocity \mathbf{G}_{ij} and their orthogonal components to \mathbf{k} , $\mathbf{g}_{ij\perp}$, are unaltered. Hence we have directly

$$\iint d\mathbf{V} d\mathbf{R} \rho(\mathbf{V}, \mathbf{R}; t) O^A \rho(\mathbf{V}, \mathbf{R}; t) = 0 \quad (26)$$

Thus, taking into account the property of Eq. (19) of the symmetric operator O^S , we get

$$(\partial/\partial t)\Omega \leq 0 \quad (27)$$

To establish a connection between the above dynamical formulation and thermodynamics, one needs to find a functional of $\rho(\mathbf{V}, \mathbf{R}; t)$ which has all the properties of the thermodynamic entropy. In fact, for the stochastic-type model considered here, we have two candidates for an H -functional.^(1,19)

The generalized H -functional which has been proposed for Markovian or non-Markovian processes leads, for requirement of additivity for independent systems, to the definition

$$H - H_{\text{eq}} = \frac{1}{2} \ln(\Omega/\Omega_{\text{eq}}) \quad (28)$$

where the index "eq" indicates the equilibrium value of the quantity. The numerical factor is chosen in such a way as to recover the results of linear nonequilibrium thermodynamics. We obtain directly from Eq. (27) the result

$$(\partial/\partial t)H = \frac{1}{2} \Omega^{-1} (\partial/\partial t)\Omega \leq 0 \quad (29)$$

whatever the initial conditions. The system is driven to the equilibrium state for which the functional *H* reaches its minimum value. In this state we get from Eq. (19) that the distribution function will satisfy the conditions

$$\rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t) = \rho(\mathbf{V}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t) \quad \forall i, j \quad (30)$$

For a hard-sphere gas the equilibrium distribution function can be written as $\{\exp(-\beta H_0)W$, where H_0 is the kinetic part of the Hamiltonian, and $W = \prod_{ij} W(|\mathbf{r}_{ij}| = \sigma)$ is a product of step functions that are equal to one for nonoverlapping configurations and vanish for overlapping ones.

4. DISCUSSION AND CONCLUDING REMARKS

In this simple model there are other Liapunov functions that could be used as well for the statistical definition for the entropy. Indeed it has been pointed out that this seems to be a general property of Markov processes. In particular, we can use instead of (28)

$$H_B = \int d\mathbf{V} d\mathbf{R} \rho \log \rho \quad (31)$$

The decrease in time of the H_B -functional defined in Eq. (31) is directly obtained from the alternative expressions given in the appendix. They look like the manipulations of the Boltzmann collision operator for such a problem. It will be shown in a similar manner as in Section 3 that the anti-symmetric operator gives no contribution, recalling that

$$\begin{aligned} \rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t) &= \rho(\mathbf{G}, \mathbf{g}'_{ij} \cdot \mathbf{k}, \mathbf{g}'_{ij\perp}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t) \\ &= \rho(\mathbf{G}, -\mathbf{g}_{ij} \cdot \mathbf{k}, \mathbf{g}_{ij\perp}, \mathbf{r}_{ij} = \sigma\mathbf{k}; t) \end{aligned} \quad (32)$$

The equilibrium conditions obtained from the decrease of H_B are the same as in the study of the evolution of the generalized *H*-theorem.

The H_B quantity defined in Eq. (31) is obviously related to the fact that with the molecular chaos assumption, this expression leads to the Boltzmann functional for the one-particle distribution function. But as it has been discussed by Prigogine and Henin, the molecular chaos assumption is very restrictive.⁽¹⁵⁾ It corresponds to a very particular preparation of the system. Then even if one can derive an *H*-theorem from Eq. (31) under this rather strong condition, one should not expect it to be valid in more complex systems than dilute gases or weakly coupled systems.⁽¹⁶⁾

As we know, the fundamental problem of the theory of irreversibility is to describe the mechanism by which a dynamic system is driven to equilibrium. This includes the evolution of all reduced distribution functions and all correlations. Therefore a description in terms of the one-particle distribution function will in general not be possible, as we have shown in Ref. 3. The

results obtained demonstrate the necessity of a general definition of entropy in terms of the N -particle distribution function when one wants to describe the approach to equilibrium, whatever the initial conditions, in systems more complex than dilute gases.⁽¹⁵⁾

APPENDIX

Consider the molecular property $\varphi(\mathbf{V}, \mathbf{R}; t)$ and the integral expression

$$A = \frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{R} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \varphi(\mathbf{V}, \mathbf{R}; t) \rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{R}; t) \delta(\mathbf{r}_{ij} - \sigma\mathbf{k}) \quad (\text{A.1})$$

Because of the dynamical reversibility, this expression evaluated for direct encounters specified by $(\mathbf{v}_i, \mathbf{v}_j, \mathbf{k})$ is equivalent to a summation over all possible inverse encounters specified by $(\mathbf{v}'_i, \mathbf{v}'_j, -\mathbf{k})$. Hence the integral given by Eq. (A.1) becomes equal to [given that $A_{ij}(\mathbf{k})(\mathbf{v}_i, \mathbf{v}_j) = (\mathbf{v}'_i, \mathbf{v}'_j)$]

$$A = -\frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{R} d\mathbf{k} \mathbf{g}'_{ij} \cdot \mathbf{k} \varphi(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{R}; t) \times \rho(\mathbf{V}, \mathbf{R}; t) \delta(\mathbf{r}_{ij} + \sigma\mathbf{k}), \quad -\mathbf{g}'_{ij} \cdot \mathbf{k} > 0 \quad (\text{A.2})$$

But we know from the dynamics of a binary encounter that $\mathbf{g}_{ij} \cdot \mathbf{k} = -\mathbf{g}'_{ij} \cdot \mathbf{k}$. Then Eq. (A.2) is written as

$$A = \frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{R} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \varphi(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{R}; t) \rho(\mathbf{V}, \mathbf{R}; t) \delta(\mathbf{r}_{ij} + \sigma\mathbf{k}) \quad (\text{A.3})$$

Using the same arguments, the following quantity, denoted by B , is transformed in a straightforward manner into

$$\begin{aligned} B &= \frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{R} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \varphi(\mathbf{V}, \mathbf{R}; t) \rho(\mathbf{V}, \mathbf{R}; t) \delta(\mathbf{r}_{ij} - \sigma\mathbf{k}) \\ &= \frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{R} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \varphi(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{R}; t) \\ &\quad \times \rho(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{R}; t) \delta(\mathbf{r}_{ij} - \sigma\mathbf{k}) \end{aligned} \quad (\text{A.4})$$

Consider now the expression

$$\frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{R} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \varphi(\mathbf{V}, \mathbf{R}; t) [A_{ij}(\mathbf{k}) - 1] \rho(\mathbf{V}, \mathbf{R}; t) \delta(\mathbf{r}_{ij} - \sigma\mathbf{k}) \quad (\text{A.5})$$

From the alternative expressions of A and B given by (A.3) and (A.4) we have immediately a new form of (A.5) in terms of $\varphi(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{R}; t)$, that is,

$$\begin{aligned} &-\frac{1}{2}\sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{R} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} \varphi(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{R}; t) [A_{ij}(\mathbf{k}) - 1] \\ &\quad \times \rho(\mathbf{V}, \mathbf{R}; t) \delta(\mathbf{r}_{ij} + \sigma\mathbf{k}) \end{aligned} \quad (\text{A.6})$$

The equivalence of (A.5) and (A.6) with the similar ones obtained by changing \mathbf{k} to $-\mathbf{k}$ gives an interesting expression for the collisional integral. We obtain from the symmetric part of the collision operator

$$\begin{aligned} & \iint d\mathbf{V} d\mathbf{R} \varphi(\mathbf{V}, \mathbf{R}; t) O^S \rho(\mathbf{V}, \mathbf{R}; t) \\ &= \frac{1}{2} \sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{R} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} [\varphi(\mathbf{V}, \mathbf{R}; t) - \varphi(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{R}; t)] \\ & \quad \times [A_{ij}(\mathbf{k}) - 1] \rho(\mathbf{V}, \mathbf{R}; t) \delta(\mathbf{r}_{ij} - \sigma \mathbf{k}) \\ &+ \frac{1}{2} \sigma^2 \sum_{i < j} \iint d\mathbf{V} d\mathbf{R} d\mathbf{k} \mathbf{g}_{ij} \cdot \mathbf{k} [\varphi(\mathbf{V}, \mathbf{R}; t) - \varphi(A_{ij}(\mathbf{k})\mathbf{V}, \mathbf{R}; t)] \\ & \quad \times [A_{ij}(\mathbf{k}) - 1] \rho(\mathbf{V}, \mathbf{R}; t) \delta(\mathbf{r}_{ij} + \sigma \mathbf{k}) \end{aligned} \quad (\text{A.7})$$

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