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Entropy and Irreversibility in a Dilute Gas of Hard Disks

J. Orban[1,2] and A. Bellemans[1,2]

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The partition of the canonical entropy (invariant of motion) into a thermodynamic part S_{th} and a nonthermodynamic one S_{nonth}, respectively increasing and decreasing functions of time for a system approaching equilibrium, was proposed by Prigogine and co-workers. This viewpoint is critically examined in the special case of an initially uncorrelated gas of hard disks. Both S_{th} and the leading term of S_{nonth} are evaluated for finite assemblies of 400, 1600, and 6400 disks, by the method of molecular dynamics. There is good evidence that, in the limit of an infinite system, the Prigogine scheme is verified.

KEY WORDS: entropy; irreversibility; method of molecular dynamics; gas of hard disks; *H*-function of Boltzmann.

1. INTRODUCTION

Consider a classical monatomic fluid of N molecules, characterized by their positions $\mathbf{r}^{(N)}$ and velocities $\mathbf{v}^{(N)}$, and let f_N be the density function of this system in phase space, normalized to unity

$$\int f_N(\mathbf{r}^{(N)}, \mathbf{v}^{(N)}; t)\, d\mathbf{r}^{(N)}\, d\mathbf{v}^{(N)} = 1$$

The *canonical* entropy, defined in terms of f_N, is given by

$$S_{\text{can}}/k = -\int f_N \ln f_N \, d\mathbf{r}^{(N)}\, d\mathbf{v}^{(N)} \tag{1}$$

apart from an additive constant.

The entropy function so defined is strictly an invariant of the motion of the system, as a consequence of Liouville's theorem, $df_N/dt = 0$, and therefore is in contradiction with the thermodynamic definition of entropy, which states that, for an isolated system, this function increases monotonically with time.

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[1] Center for Statistical Mechanics and Thermodynamics, University of Texas, Austin.

[2] On leave of absence from the University of Brussels, Belgium.

The resolution of this paradox, according to Prigogine and co-workers (see Ref. 1), is to be found in the fact that the *thermodynamic* entropy, hereafter denoted as S_{th}, is a function distinct from S_{can} (except for a system at thermodynamic equilibrium, for which f_N would be given exactly by the Boltzmann distribution; only in this particular situation do we have the equality $S_{\text{th}} = S_{\text{can}}$). Indeed, S_{th} is an experimentally measurable quantity, and, as such, must be defined in terms of *observables* only, i.e., reduced distribution functions relative to small subsets of molecules, and not in terms of f_N, which obviously is unaccessible experimentally. Following this viewpoint, S_{th} is only a part of S_{can}, which may, accordingly, be rewritten as

$$S_{\text{can}} = S_{\text{th}} + S_{\text{nonth}} \tag{2}$$

In this scheme, the *nonthermodynamic* entropy S_{nonth} must decrease with time, exactly at the same rate as S_{th} increases, in order to insure the steadiness of S_{can}.

Actually, the increase of S_{th} with time constitutes a problem in itself because of the mechanical reversibility (paradox of Loschmidt). Indeed, if we find a system with such positions and velocities that S_{th} increases, then, by reversing all velocities, we can (in principle, at least) design a system where S_{th} decreases. This difficulty was carefully analyzed by Prigogine and Résibois(2) and Balescu,(3) who pointed out the role of the initial correlations existing in the system: according to these, the evolution may be *kinetic* (increase of S_{th}) or *antikinetic* (decrease of S_{th}).[3] They also showed that the spontaneous correlations which are progressively created by molecular interactions in an initially uncorrelated system determine a kinetic evolution (S_{th} increases) persisting for a duration of the order of Poincaré's time, i.e., much larger than any time interval corresponding to an experiment.

If we now start from an initially uncorrelated system, collisional processes will create intricate correlations between positions and velocities after a short time interval. As the time proceeds, the low-order distribution functions, as well as the thermodynamic entropy, approach their equilibrium values; in the meantime, correlations involving higher and higher distribution functions are created through collisions, giving rise to a decrease of S_{nonth}.

The purpose of this paper is to illustrate this behavior of entropy in the case of a dilute gas by the method of *molecular dynamics*[4] (simulation on a computer) which, for finite systems, provides us with a complete knowledge of all positions and velocities at any instant, and consequently allows the computation of both S_{th} and S_{nonth}. For the sake of simplicity, we shall work on a two-dimensional gas of hard disks.

2. FORMULATION OF S_{th} AND S_{nonth} FOR A DILUTE GAS OF HARD DISKS

Consider a highly dilute gas, so that, from the macroscopic point of view, the one-molecule distribution function $f_1(\mathbf{r}, \mathbf{v}; t)$, defined as

$$f_1 = \int f_N \, d\mathbf{r}^{(N-1)} \, d\mathbf{v}^{(N-1)} \tag{3}$$

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[3] These two kinds of behavior have been reproduced on a computer for a dilute gas of hard disks.(4)

[4] The method was initiated by Alder and Wainwright.(5)

is the only relevant function for describing the system. Its thermodynamic entropy is therefore identified to the H-function of Boltzmann with reversed sign, i.e.,

$$S_{\text{th}}/Nk = -\int f_1 \ln f_1 \, d\mathbf{r} \, d\mathbf{v} \tag{4}$$

Note that f_1 and all other reduced distribution functions to be introduced later on are normalized to unity.

The nonthermodynamic entropy is defined as the remainder between S_{can} and S_{th}, i.e.,

$$S_{\text{nonth}}/Nk = -(1/N) \int f_N \ln f_N \, d\mathbf{r}^{(N)} \, d\mathbf{v}^{(N)} + \int f_1 \ln f_1 \, d\mathbf{r} \, d\mathbf{v} \tag{5}$$

Following Prigogine, we decompose $\ln f_N$ into a sum of terms involving lower-order distribution functions $f_1, f_2, f_3, \ldots$ in the following way

$$\begin{aligned} \ln f_N = {} & \sum_i \ln f_1(\mathbf{i}) + \sum\sum_{i<j} \ln[f_2(\mathbf{i}, \mathbf{j})/f_1(\mathbf{i}) f_1(\mathbf{j})] \\ & + \sum\sum\sum_{i<j<k} \ln[f_3(\mathbf{i}, \mathbf{j}, \mathbf{k}) f_1(\mathbf{i}) f_1(\mathbf{j}) f_1(\mathbf{k})/f_2(\mathbf{i}, \mathbf{j}) f_2(\mathbf{i}, \mathbf{k}) f_2(\mathbf{j}, \mathbf{k})] \\ & + \cdots \end{aligned} \tag{6}$$

where $\mathbf{i}$ stands for the position and velocity of molecule i. We then get, from (5) and (6),

$$S_{\text{nonth}}/Nk = -K_2 - K_3 - K_4 - \cdots \tag{7}$$

where

$$K_2 = \frac{N-1}{2} \int f_2(\mathbf{1}, \mathbf{2}) \ln \frac{f_2(\mathbf{1}, \mathbf{2})}{f_1(\mathbf{1}) f_1(\mathbf{2})} \, d(\mathbf{1}) \, d(\mathbf{2}) \tag{8}$$

and higher K_n are given by similar formulas.

Let us now apply (8) to a two-dimensional gas of hard disks with diameter D. The pair distribution function $f_2(\mathbf{1}, \mathbf{2})$ vanishes for $r_{12} < D$. On the other hand, for $r_{12} > D$, the correlation

$$[f_2(\mathbf{1}, \mathbf{2}) - f_1(\mathbf{1}) f_1(\mathbf{2})]/f_1(\mathbf{1}) f_1(\mathbf{2})$$

is expected to remain small compared to unity, because of the low density of the system. Hence, expanding the logarithmic term of (8) up to the second order, we get

$$\begin{aligned} K_2 \approx {} & \tfrac{1}{2}(N-1) \int_{r_{12}>D} [f_2(\mathbf{1}, \mathbf{2}) - f_1(\mathbf{1}) f_1(\mathbf{2})] \, d(\mathbf{1}) \, d(\mathbf{2}) \\ & + \tfrac{1}{4}(N-1) \int_{r_{12}>D} \{[f_2(\mathbf{1}, \mathbf{2}) - f_1(\mathbf{1}) f_1(\mathbf{2})]^2/[f_1(\mathbf{1}) f_1(\mathbf{2})]\} \, d(\mathbf{1}) \, d(\mathbf{2}) \end{aligned}$$

For a spatially homogeneous gas, the first term is simply equal to $\pi D^2/V$, where V is the volume of the system. This constant term will be conventionally dropped, so that K_2 will subsequently be defined as

$$K_2 \approx \tfrac{1}{4}N \int_{r_{12}>D} [f_2(\mathbf{1},\mathbf{2}) - f_1(\mathbf{1})f_1(\mathbf{2})]^2/[f_1(\mathbf{1})f_1(\mathbf{2})]\, d(\mathbf{1})\, d(\mathbf{2}) \qquad (9)$$

This expression, which is positive-definite, becomes negligibly small both for an uncorrelated system [i.e., $f_2(\mathbf{1},\mathbf{2}) \approx f_1(\mathbf{1})f_1(\mathbf{2})$] and for a dilute system at equilibrium. This, however, does not imply that this term remains negligible in all circumstances. On the contrary, if we start at time 0 from a totally uncorrelated system, we expect, after a while, the appearance of complicated correlations between pairs of molecules on account of two-body collisions, so that K_2 will increase and become significantly different from zero. As the time proceeds, correlations involving larger and larger sets of molecules will appear in the system. In the meantime, the pair correlations initially created will progressively decrease to reach ultimately their equilibrium value, which is nearly zero for a dilute gas. This means that K_2 is expected to pass through a maximum and then to decrease again to a vanishingly small value.

As K_3, K_4,... are defined by integrals similar to (9), their behavior as functions of time will be qualitatively the same as for K_2. However, the time scales will obviously be different. Roughly speaking, if τ is the mean free time between collisions, then K_2 should reach its maximum value around $t = \tau$ and fall back again to zero for $t \approx 2\tau$; similarly, K_3, which is associated with triplet correlations and is zero at $t = 0$, should go through a maximum at $t \approx 2\tau$ and return to zero near $t \approx 3\tau$, and so on.

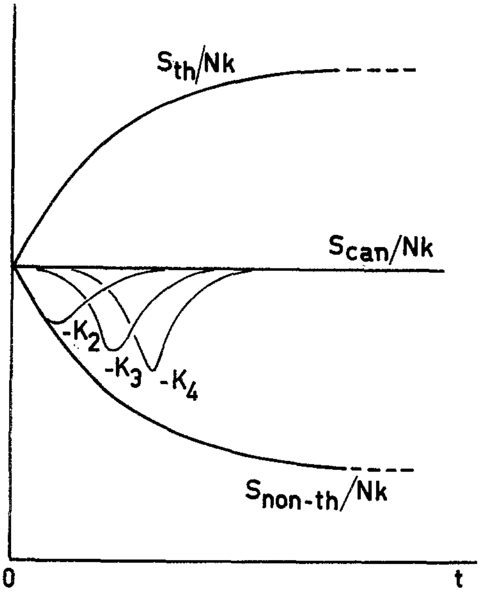

Fig. 1. Schematic representation of the expected behavior of K_2, K_3, K_4,..., S_{th}, and S_{nonth} versus time.

In the meantime, of course, the singlet distribution function f_1 approaches its equilibrium value, and S_{th} increases regularly with time. The corresponding decrease of S_{nonth}, ensuring the invariance of S_{can}, results from the accumulation of $K_2, K_3, K_4, \ldots$ as shown schematically in Fig. 1 (for a system which is totally uncorrelated at time 0). Each K_n component of S_{nonth} starts from a zero value, increases and passes through a maximum as the time proceeds, then decays, and eventually reaches a very small equilibrium value. The sum of *all* K_n is, nevertheless, finite and such that, at any instant, the constancy of $S_{\text{can}} = S_{\text{th}} + S_{\text{nonth}}$ is ensured.

3. NUMERICAL COMPUTATIONS OF f_1, f_2, S_{th}, AND K_2 FOR FINITE ASSEMBLIES OF HARD DISKS

The purpose of this paper is to see how far the picture of the preceding section corresponds to the actual behavior of the system. We therefore study the evolution of various finite assemblies of hard disks ($N = 400$, 1600, and 6400) on a computer,[5] starting from an initially uncorrelated state and calculating f_1, f_2, S_{th}, and K_2 at regular time intervals.

The dynamics of a system of hard disks can be described very simply; it has been done many times in the literature, so that we shall not expound it here (see, e.g., Ref. 6). Let us only mention that we place the N molecules in a square box with periodic boundaries. For definiteness, let us take both the diameter D and the mean square velocity $\langle v^2 \rangle$ of the disks as unity. It then follows that, for a density $\rho = N/V$, the pressure p, the mean free path, and the mean collision frequency of a molecule (in the limit $\rho \to 0$) are given by

$$p/\rho kT = 1 + (\pi/2)\,\rho, \qquad \langle l \rangle = 1/(\rho\sqrt{8}), \qquad \langle \nu \rangle = \rho \langle v \rangle \sqrt{8}$$

where the mean velocity $\langle v \rangle$ equals $\frac{1}{2}\sqrt{\pi}$. We choose $\rho = 0.04$, so that the gas is nearly perfect ($p/\rho kT \approx 1.063$). This gives

$$\langle l \rangle \approx 8.84, \qquad \langle \nu \rangle \approx 0.1002$$

Note that, for the three cases considered, $N = 400$, 1600, and 6400, the side of the box equals 100, 200, and 400 respectively, and is always much larger than $\langle l \rangle$.

The initial state is chosen as follows: (a) All velocities have the same absolute value ($v = 1$), but are randomly oriented, so that $\langle \mathbf{v} \rangle = 0$. (b) The molecules are distributed at random in the box, apart from the fact that the distance between any pair is greater than 1.[6] Under these conditions, the system is homogeneous, isotropic, and totally uncorrelated at time 0. As the time proceeds, correlations appear and the

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[5] The present research was started at the University of Brussels on an IBM 7040 (16K). All calculations reported here were made on the CDC 6600 of the University of Texas, Austin.

[6] In this way, the radial distribution function is (on the average) equal to one for $r_{12} > 1$ and K_2 is effectively equal to zero initially.

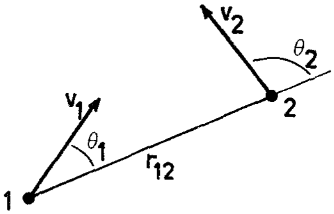

Fig. 2. Definition of the variables r_{12}, v_1, v_2, θ_1, and θ_2 determining f_2 for a homogeneous isotropic system.

velocity distribution is progressively driven to the Maxwellian form, but the system remains homogeneous and isotropic, so that f_1 and f_2 may be written as follows

$$f_1(\mathbf{r}, \mathbf{v}; t) = (1/V)\, \varphi_1(v; t)$$

$$f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2; t) = (1/V^2)\, \varphi_2(r_{12}, v_1, v_2, \theta_1, \theta_2; t)$$

(For the definition of the angles θ_1 and θ_2, see Fig. 2.)

The evaluation of φ_1 and S_{th} is rather straightforward, and a fairly good picture of the evolution of S_{th} toward equilibrium is already obtained with a few hundred disks. However, the situation is much less favorable for φ_2, which involves five molecular variables, r_{12}, v_1, v_2, θ_1, and θ_2. A reasonably good sampling of φ_2 requires several thousands of disks at least, which is close to the limit of the possibilities of the computers presently available. A supplementary difficulty comes from the fact that K_2 is actually a *fluctuation* and therefore depends critically on N. At equilibrium and for infinite N, it follows from (10) that K_2 is zero for a highly dilute system. For N finite, however, K_2 differs significantly from zero, varying probably as N^{-1}.

On account of this, an immediate verification of the anticipated behavior of Fig. 1 (strictly valid for $N \to \infty$) is out of question. We give plots of S_{th} and K_2 in Fig. 3 for $N = 400$, 1600, and 6400. The results are totally inconclusive in the two first cases, but we nevertheless give them, in order to see the evolution of K_2 with N. For $N = 6400$, K_2 roughly accounts for the expected behavior. Note that, near equilibrium, K_2 fluctuates around 2.0, 0.5, and 0.15 for $N = 400$, 1600, and 6400 respectively, and is indeed approximately inversely proportional to N.

The maximum of K_2 is rather unexpectedly located around $t \approx 2$ or 3 (while, from the simple arguments of Section 2, it should occur around $t \approx 10$).

4. CONCLUSIONS

The numerical results for K_2 quoted in the preceding section are certainly not as significant as one might hope. Nevertheless, from the data of Fig. 3, it seems almost certain that K_2 approaches the expected behavior of Fig. 1 in the limit $N \to \infty$, thereby supporting the mechanism proposed by Prigogine *et al.* on theoretical grounds for compensating the increase of S_{th}. Unfortunately extensions of the present calculations to larger N values and to higher-order terms (K_3, K_4,...) appear practically

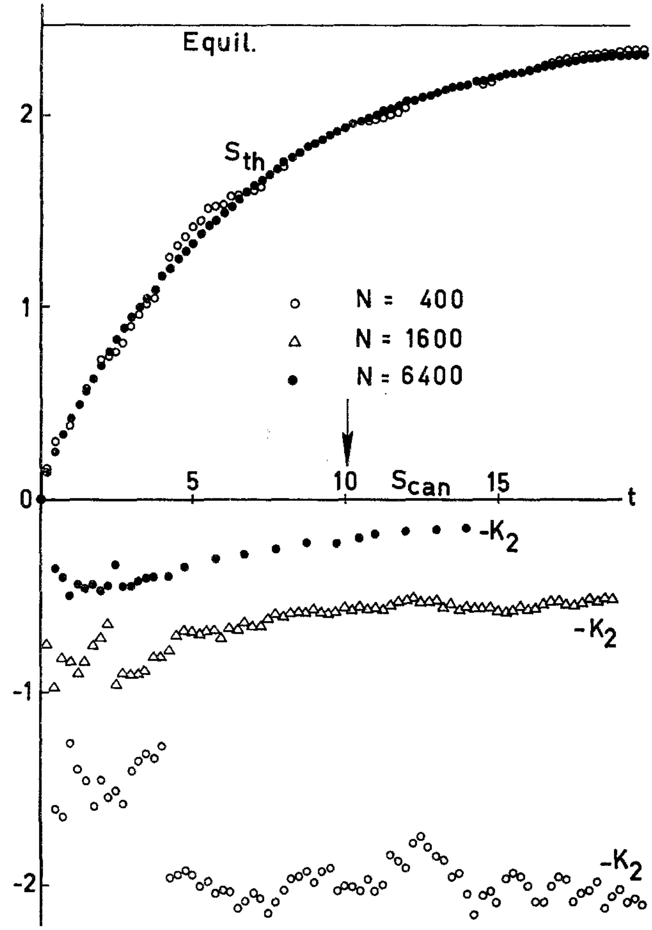

Fig. 3. Variation of S_{th} and K_2 with time for $N = 400$, 1600, and 6400. (S_{th} is not shown for $N = 1600$, as the curve is very close to the 6400 one.) At $t = 0$, S is conventionally put equal to zero. (The vertical arrow indicates the mean free time between collisions.)

untractable for the time being, so that the kind of "proof" presented here is necessarily incomplete.[7]

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[7] Obviously, the wiggles in the various K_2 curves could be eliminated by averaging over a number of similar runs. The main problem here, however, is to increase N as much as possible in order to approach the thermodynamic limit.

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