A Deterministic Entropy Based on the Instantaneous Phase Space Volume

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A deterministic entropic measure is derived for the time evolution of Newtonian N-particle systems based on the volume of the instantaneously occupied phase space (IOPS). This measure is found as a natural extension of Boltzmann's entropy. The instantaneous arrangement of the particles is exploited in the form of spatial correlations. The new entropy is a bridge between the time-dependent Boltzmann entropy, formulated on the basis of densities in the one-particle phase space, and the static Gibbs entropy which uses densities in the full phase space. We apply the new concept in a molecular dynamics simulation (MDS) using an exactly time reversible "discrete Newtonian equation of motion" recently derived from the fundamental principle of least action in discretized space-time. The simulation therefore is consistent with micro-time-reversibility. Entropy becomes an exact momentary observable in both time directions in fulfillment of a dream of Boltzmann.

1. Introduction

In the Cartesian tradition one is willing to work on a consistent description of the physical world. Boltzmann certainly did so. Nevertheless, he claimed that it will take centuries to fully understand the micro-macro-transition. We agree. Looking at the endless list of controversial contributions to this field of research within the century which has passed since Boltzmann made this remark, we would like to think that this is how everybody else feels. In contrast to Boltzmann's original deterministic entropy concept (best known under the name H-function), the Gibbsian ensemble statistics has been fruitful only as a static concept up till now. Microscopic applications of Gibbs' concept are restricted to equilibrium situations. Jaynes' "maximum entropy formalism" is an attempt to approximate a time-dependent entropy by introducing the fiction of time-dependent macro constraints, which allows one to retain the ensemble concept for intermediate steps of the entropy evolution as "momentary equilibria" [1]. His information theoretical approach led to the now well-established "maximum entropy method" used for the reconstruction of incomplete or noisy time series which uses constraints from macroscopic pre-knowledge on the system on hand [2]. A further drawback of the Gibbs ensemble formalism is that it formally presupposes ergodicity which is rarely found in realistic systems [3].

Encouraged by René Descartes we make a kind of "tabula rasa" and look at that what we have on hand "here and now". Both, a prospective and a retrospective view are of a cumulative nature. They presuppose that one knows already what happened or is going to happen in a certain time interval which must not be too small to be representative. Since we are today able to check our theories by creating an artificial universe in the computer, we can try to implement a "here-and-now" (hic et nunc) physics: it consists of N identical particles with a repulsive $\frac{1}{r}$-potential as a two-dimensional molecular dynamics simulation (MDS). Is it possible to have an instantaneous entropy?

MDS of N-particle-systems are well-suited for investigations into the entropic behavior of conservative dynamical systems. Because of the Newtonian nature one is able to perform "experiments" on the microscopic level which allow one to make assertions about the way micro-entities give rise to macroscopic observables. Boltzmann's H-function, frequently computed in MDS [4], is an example for a (scalar) function of the microstates. It is the velocity part of the so-called Boltzmann entropy

$$S_B = -k \int_\gamma f_\gamma \ln f_\gamma \, d\gamma, \tag{1}$$

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where f_γ is the density in the one-particle phase space γ and k Boltzmann's constant. Intuitively, the density f_γ is constituted by the cloud of points which one gets throught the projection of the phase space coordinates onto a one-particle subspace. To compute S_B in an MDS, one usually generates a histogram of the positions and momenta of the N particles to get an approximation for the density f. This could be done at every instant of time; i. e., S_B actually is a deterministic entropy. It is nevertheless not very accurate.

The Gibbs entropy

$$S_G = -k \int_\Gamma f_\Gamma \ln f_\Gamma \, d\Gamma, \tag{2}$$

in contrast, uses the density f_Γ in the full phase space Γ. In Γ the N-particle-system is represented by one point at every instant of time. To speak of a density makes sense only if one either waits long enough until the trajectory fills out the phase space more or less densely (at different locations in phase space) or if it is interpreted using (fictitious) ensembles.

In an isolated thermodynamical system, the entropy is according to Boltzmann and Gibbs connected to the phase space volume Ω by

$$S = k \ln \Omega. \tag{3}$$

Up until now, the concept of phase-space volume has always been a (quasi) static one; i. e., (3) presupposes equilibrium. Jaynes' above mentioned information-theoretical approach uses an observer-dependent reference class of macro observables. The entropy thereby becomes "anthropomorphic". Being anthropomorphic is – according to Jaynes – a constitutive part of the nature of entropy [5].

In the following we propose a deterministic variant to (3). Essentially, we introduce the new concept of the "instantaneously occupied phase space" (IOPS). The concept of IOPS enables one to describe transient behavior. It is a fully deterministic concept. The resulting entropy becomes a symmetric function of the microstates. Hence, if the particle momentums are all reversed at a certain instant of time, which correspondes to an allowed microstate, the entropy may decrease for a short period of time. This troubling fact deserves to be briefly discussed (Section 2). For convenience and the sake of consistency, we use an exactly time reversible MDS algorithm to integrate the equation of motion of the particles. A brief review of this algorithm and a description of the N-particle system are given in Section 3. Then, we introduce the concept of IOPS from a "local" viewpoint in Section 4. We show that the resulting entropy converges to Boltzmann's entropy (1) and can in this sense be regarded equivalent to the histogram approximation to (1). The insufficiency of this entropy formula, when dealing with fairly low-dimensional systems, is demonstrated. This provides the motivation to introduce in Sect. 5 a derivation of a generalized "global" entropy formula. This formula is then applied to an MDS of a 100-particle system. It is markedly improved. Finally we discuss our results in Sect. 6 and give an outlook on further studies.

2. Time symmetric vs. time asymmetric entropies

If one assumes given the time reversible Newtonian equations as a correct description of a microscopic dynamics, it follows that an entropy constructed as a symmetric scalar function of the microstates necessarily decreases in time after a reversal of all momentums when it was increasing in the forward direction. This means that the increasing or decreasing behavior of the entropy depends on the initial state of the system. Boltzmann's H-function, frequently computed in MDS [4, 6], is of that type. The question is whether such a function could be called an entropy at all.

Actually, some authors prefer to regard any entropy as increasing by definition independently of the direction of time [7, 8]. In 1980 J. Hurley tried to give a "resolution of the time-asymmetry paradox" [9]. He looked at the phase space trajectory of a many particle system as a solution of the corresponding Newtonian equations, valid from the initial time t_0 to infinity and also from t_0 to minus infinity. We assume given an initial state such that all particles are at rest (all momentums equal to zero) in a state of mutual repulsion. Then we leave the system alone. The interactions accelerate the particles in both directions of time. The two half trajectories are identical in configuration space. The entropy produced than clearly increases in both directions of time. Hurley's results can than be put into the following form: If one now arbitrarily picks a point on the finished trajectory and looks at a short segment lying to the left and to the right of that point, one finds qualitatively the same behavior with very high probability as it was found above for the extremal initial state of zero momentums. That is, one is close to a "U-turn"

with both ends showing the same entropy increase, almost everywhere. A transient decreasing entropy occurs only in those extremely rare cases where the trajectorial segment in question came in from a far away loop. This is Hurley's principle of the "bezoar". Note that the lump of hair found in the stomach of a cow (bezoar) shows virtually the same behavior if one tries to pick a random point on it. Hence almost always, the entropy increases in both directions of time.

If one now tries to apply this argumentation to complex systems like biological ones, the earth or even the whole universe, one wonders how such a long past history of continually increasing entropy could be possible as we believe it to exist [10]. Many scientists therefore prefer a time-asymmetric entropic desription of such systems [11, 12]. They either introduce non-Newtonian equations of motion on the microscopic level or time-asymmetric entropies, or both. The concept of broken ergodicities, for example, formally leads to equations of motion that have non-integer (fractional) time derivatives [13]. Such equations are the formal implication of a treatment of phase space flows with semigroup features. Petrosky and Prigogine [11, 12] also use semigroup features of phase space flows. They, therefore, give up the concept of trajectories for the description of thermodynamical systems. Even quantum systems are amenable to being described in this fashion [12]. The dependency of the sign of the entropic behavior on the initial state can be avoided by introducing the concept of the "absence of pre-collisional correlations" for all initial states [7].

In spite of the time-asymmetric concepts briefly outlined above, Lebowitz [3], as already mentioned, as well as other authors [6, 14] are predicting a renaissance of classical Boltzmannian concepts. When working on such a philosophically charged subject, one can hardly avoid to get between the lines. As we argued in [15] by means of a Gedankenexperiment there is some putative evidence for a time reversible structure of the universe. On the other hand we think that Boltzmann's concepts need to be improved as we will show in the following. Nevertheless we stick with the symmetric nature of the entropy because we start out from the classical MDS paradigm. A second excuse for our confidence in the new entropy formula could be seen to lie in the fact that it is not confined to reversible systems. It can also be applied to dissipative macroscopic systems of high dimensionality including experimental time series of different origins (work in preparation).

Specifically a generalized H-function will be presented. It confirmes a most recent result by Vollmer *et al.* which was obtained on the basis of a so-called multibaker map [16] which is of interest also under both time and space symmetric conditions (work in preparation). We close the section by reiterating the confession of Petrosky and Prigogine offered at the end of their 1994 paper:

"In summary we believe that our approach avoids the usual dichotomy between what is microscopic and time reversible, and what is macroscopic and time irreversible. In this sense we hope that we have contributed to the elucidation of the research program started more than one century ago by Boltzmann and Planck."

3. An N-Particle-System in Two Dimensions

We now prepare to set up an artificial universe by means of a fully deterministic Newtonian MDS using a digital computer. A first step to do this in a consistent way has been obtained recently. Nadler et al. [17] proposed a variant of Verlet's algorithm which was derived from the fundamental physical principle of least action, applied to discretized space and time. A precondition for an exactly time reversible algorithm is use of an integer arithmetic. Levesque and Verlet [6] first applied an algorithm of this type to compute Boltzmann's H-function in a simulation of a many-particle Lennard-Jones gas. A computationally generated dissipation due to round-off errors [18] was thereby avoided. Levesque and Verlet were able to exactly retrace the system trajectory. The same finding was made independently in [19] where a few-particle system was used for the demonstration.

Application of the action principle to discretized space and time, combined with the use of integer arithmetic, leads to a modified form of Verlet's algorithm as used by Levesque and Verlet. The force term is replaced by a difference-quotient of the potentials. This allows for an unequivocal definition of the rounding term in the equation. Moreover and more importantly, a criterion is provided which tells one whether the trajectory is still physical.

Concretely, we assume as given a discretization of time and space: $t = t_i + k\Delta t$, and $q = q_0 + x\Delta q$, respectively, with $k, x \in \mathbb{Z}$. Then the discretized path, $q(t)$, of a Hamiltonian system is represented by an

integer sequence $\{x_k\}$. Given a potential $V(q(t))$, the discrete Newtonian equation of motion reads

$$x_{k+1} = 2x_k - x_{k-1} - \mathrm{ROUND}\Big(\Delta t^2 \frac{V(q_0 + (x_k + 1)\Delta q) - V(q_0 + (x_k - 1)\Delta q)}{2\Delta q^2}\Big). \tag{4}$$

Hereby the ROUND-function, unlike the INT or TRUNC-function, represents the closest integer value to its floating-point argument. One sees that two antecedents are used to calculate the next point. As long as each triple (x_{k-1}, x_k, x_{k+1}) obeys the inequality

$$\begin{aligned}&\Big\{x_{k+1} - 2x_k + x_{k-1} + 1 + (\Delta t)^2 \frac{V(q_0 + x_k\Delta q) - V(q_0 + (x_k - 1))\Delta q)}{(\Delta q)^2}\Big\}\\ &\cdot\Big\{x_{k+1} - 2x_k + x_{k-1} - 1 + (\Delta t)^2 \frac{V(q_0 + (x_k + 1)\Delta q) - V(q_0 + x_k\Delta q)}{(\Delta q)^2}\Big\} < 0,\end{aligned} \tag{5}$$

the action principle, underlying the derivation of (4), is fulfilled. Otherwise the computed trajectory ceases to be physical because the action principle is violated [17]. Existence and uniqueness of (4) as a variational solution to the action principle is assured, as shown in [17].

Next, we apply the algorithm of (4) to an N-particle MDS with unit-mass particles. The potential is in this case a sum of distance-dependent pair-potentials, so that the Hamiltonian reads

$$H(t) = \sum_{i=1}^{N} \frac{1}{2}\boldsymbol{p}(t)^2 + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} u(r_{ij}t). \tag{6}$$

The Coulomb-like pair potentials $u(r_{ij})$ are defined as $u(r_{ij}) = \frac{\varepsilon}{r_{ij}(t)}$, with r_{ij} the distance between particles i and j, ε being a small constant (e. g., 0.005). The motions of the particles are bounded, confined to the square [–1, 1]×[–1, 1]. The boundary condition of an infinite potential outside the square completes the Hamiltonian.

We subdivide the square into equal-size cells with side lenght Δq. To each cell, an integer is assigned. Implementation of the algorithm of (4) is particularly straightforward when the reflections at the walls are approximated by the following scheme: The next point, defined as $\big(\tilde{x}_i^{(1)}(t+\Delta t), \tilde{x}_i^{(2)}(t+\Delta t)\big)$, is retained if and only if it lies inside the square, otherwise its mirror image, with respect to the wall, is chosen. In other words, the same thing reads

$$\tilde{x}_i^{(1)}(t + \Delta t) = 2x_i^{(1)}(t) - x_i^{(1)}(t - \Delta t) - \mathrm{ROUND}\left[\frac{(\Delta t)^2}{2(\Delta q)^3}\tilde{V}\right], \tag{7a}$$

$$\begin{aligned}\tilde{V} = &\sum_{\substack{j=1 \\ j\neq i}}^{N} \left\{\frac{\varepsilon}{\sqrt{(x_i^{(1)}(t) + 1 - x_j^{(1)}(t))^2 + (x_i^{(2)}(t) - x_j^{(2)}(t))^2}}\right\}\\ &- \sum_{\substack{j=1 \\ j\neq i}}^{N} \left\{\frac{\varepsilon}{\sqrt{(x_i^{(1)}(t) - 1 - x_j^{(1)}(t))^2 + (x_i^{(2)}(t) - x_j^{(2)}(t))^2}}\right\},\end{aligned}$$

$$x_i^{(1)}(t + \Delta t) = \begin{cases} \tilde{x}_i^{(1)}(t + \Delta t) & \text{if} \quad -\dfrac{1}{\Delta q} \leq \tilde{x}_i^{(1)}(t + \Delta t) \leq \dfrac{1}{\Delta q},\\ \dfrac{1}{\Delta q} - (\tilde{x}_i^{(1)}(t + \Delta t) - \dfrac{1}{\Delta q}) & \text{if} \quad \tilde{x}_i^{(1)}(t + \Delta t) > \dfrac{1}{\Delta q},\\ -\dfrac{1}{\Delta q} - (\tilde{x}_i^{(1)}(t + \Delta t) + \dfrac{1}{\Delta q}) & \text{otherwise.}\end{cases} \tag{7b}$$

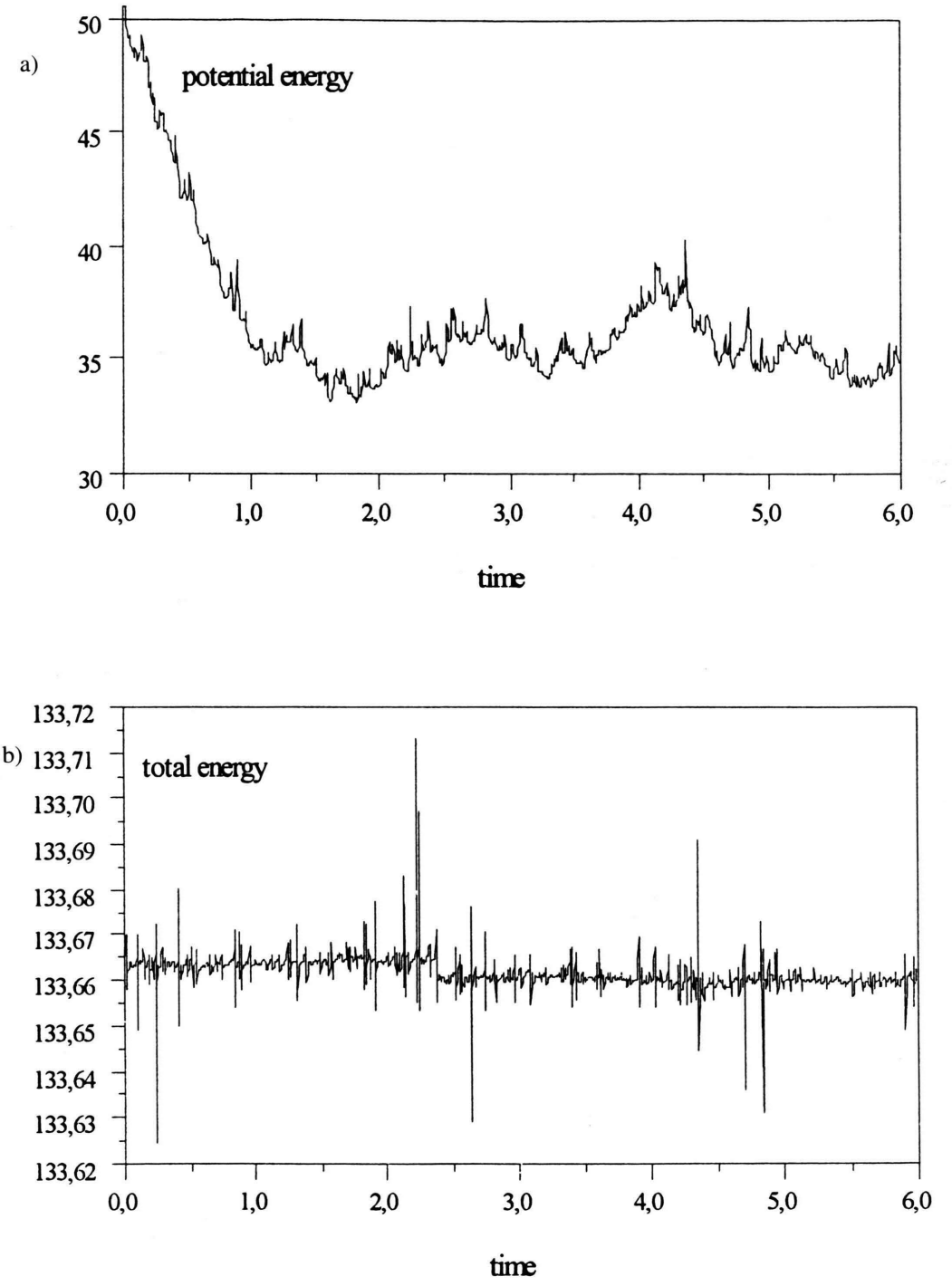

Fig. 1. a) Time series of the potential energy of a 100-particle-MDS of a 2D gas, described by (6), that expands from the right half of the volume into the whole volume. After about one time unit, relaxation has taken place. b) Time series of the total energy of the 100-particle-MDS. One sees that the total energy shows no secular drift and the fluctuations are very small.

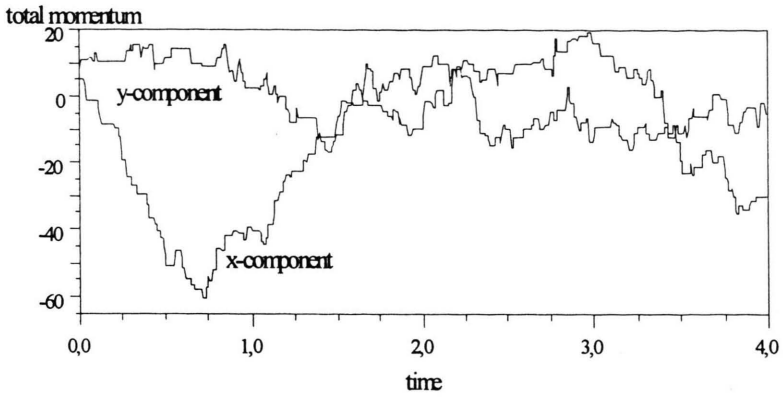

Fig. 2. Time series of the two components of the total momentum in the 100-particle MDS of Figure 1. Until relaxation is completed, there is a dominantly negative x-component present. This fact mirrors the diffusion of the gas from the right half of the volume into the whole available volume.

The corresponding equations for the second component, $x_i^{(2)}$, are generated analogously. This yields all $2N$ positional components.

We now start the simulation with a set of equi-distributed initial positions $\{x_i^{(j)}(0), i = 1, ..., N; j = 1, 2\}$ of the $N = 100$ particles in the right half of the square. A second set of initial positions, $\{x_i^{(j)}(-\Delta t), i = 1, ..., N; j = 1, 2\}$, is randomly generated by the addition of normally distributed replacements. The two sets taken together yield the initial velocities, i. e. the two antecedents needs to continue with the calculation. Note that in generating the second set, the standard normal variates (mean = 0, variance = 1) were divided by 20,000. The time steps and the spacings are chosen to be $\Delta t = 0.00005$ and $\Delta q = 2^{-50}$, respectively.

Figure 1 shows a time series of the potential energy, (a), and the total energy, (b). It can be seen that the total energy is well conserved even though a relaxation takes place, as one sees from the behavior of the potential energy. The value of the temporal mean of the total energy was $\langle E(t) \rangle = 133.662$. Figure 2 confirmes the presence of relaxation in the behavior of one component of total momentum. For the duration of about one time unit, the x-component is strongly negative, which reflects the ongoing extension of the gas from the right half of the volume into the total available space.

To sum up, there is no secular drift in total energy and the fluctuations are minor. Therefore, the system on hand is highly appropriate for the – next-following – investigation of a deterministic entropy concept. By the way, the "physicality-condition", (5), was computed throughout the whole simulation without being violated at any time.

4. The IOPS Concept from a "Local" Viewpoint

In order to derive an approximation to Boltzmann's entropy (1), which uses given microstates without introducing an artificial binning, we start with the definition of the "free space" of a particle in the "one-particle phase space". We stick with our two-dimensional MDS example, an extension to three dimensions is straighforward.

The distances of a given particle i to a second one j in position and momentum space, in the respective coordinate directions, are given by

$$\begin{aligned} &\Delta x_{ij} = |x_i - x_j|, \Delta y_{ij} = |y_i - y_j|, \\ &\Delta p_{x_{ij}} = |p_{x_i} - p_{x_j}|, \Delta p_{y_{ij}} = |p_{y_i} - p_{y_j}|. \end{aligned} \tag{8}$$

The maximum distances in the position space are given by the side length of the square to which the motion is confined, i. e., $\Delta x_{\max} = \Delta y_{\max} = 2$. In the momentum space, the distances are restricted by the total energy of the system, which leads to $\Delta p_{x_{\max}} = \Delta p_{y_{\max}} = 2\sqrt{2E}$. in our 2-dimensional example. Now we introduce the radius r_i which defines

the "free space" of particle i:

$$r_i = \min_{j \neq i} \left\{ \left[\left(\frac{\Delta x_{ij}}{\Delta x_{\max}} \right)^2 + \left(\frac{\Delta y_{ij}}{\Delta y_{\max}} \right)^2 + \left(\frac{\Delta p_{x_{ij}}}{\Delta p_{x,\max}} \right)^2 + \left(\frac{\Delta p_{y_{ij}}}{\Delta p_{y,\max}} \right)^2 \right]^{1/2} \right\}. \quad (9)$$

Radius r_i is a dimensionless number, due to the normalization (division) of each component by the respective maximum distance. Equation (9) defines the radius of the largest possible 4-D hypersphere which just does not contain a neighbouring particle. To be specific, this hypersphere in 4-dimensional one-particle phase space has the volume

$$\omega_i = \frac{1}{2}\pi^2 r_i^4. \quad (10)$$

The geometric mean of all these partial volumes of the phase space is given by

$$\omega = \sqrt[N]{\prod_{i=1}^{N} \omega_i}. \quad (11)$$

The total "occupied phase space volume" can therefore be defined as

$$\Omega = N\omega, \quad (12)$$

because we approximate the sum of the individual hyperspheres by N times the mean.

With respect to Boltzmann's entropy, in the form (3), we now use Ω to create an entropy formula by taking the logarithm of Ω:

$$S = k \ln \Omega = k \left[\ln \left(\frac{1}{2}\pi^2 \right) + \ln N + \frac{1}{N} \sum_{i=1}^{N} \ln \left(r_i^4 \right) \right]. \quad (13)$$

In order to show that the derived entropy formula (13) tends to the Boltzmann entropy also in the form of (1), we trivially augment the terms of (13) to obtain

$$S = k \left(\frac{1}{N} \sum_{i=1}^{N} \ln \left(\frac{1}{2}\pi^2 \right) + \frac{1}{N} \sum_{i=1}^{N} \ln N + \frac{1}{N} \sum_{i=1}^{N} \ln \left(r_i^4 \right) \right). \quad (14)$$

We can now combine the sums to get

$$S = k \left(\frac{1}{N} \sum_{i=1}^{N} \ln \left[\frac{1}{2}\pi^2 N r_i^4 \right] \right). \quad (15)$$

In this representation, the entropy thus turns out to be the mean of the logarithms of the free spaces of the particles. The reciprocal of the free space of particle i (i. e., the argument in the logarithm of (15)) represents the local density f_γ in the vicinity of the state point of the particle in question in one-particle phase space. The logarithm thereby suffers a sign change. If we now refer to the law of large numbers (c f. [20] or any other statistics textbook), we finally recover Boltzmann's entropy in the form of (1).

The new entropy formula (13) deals with a monomolecular system so far. It is possible, however, to extend (13) to the more general case of several participating species which may react according to a given chemical reaction scheme. If J denotes the number of species and N_j represents the number of particles of species j (with $j = 1, \ldots, J$), then the augmented form corresponding to (13) reads

$$S(t) = k \left[\sum_{j=1}^{J(t)} \left(\ln N_j(t) + \frac{1}{N_j(t)} \sum_{i=1}^{N_j(t)} \ln (\omega_i) \right) \right]. \quad (16)$$

For a given chemical reaction system, the number N_j of particles is a function of time, $N_j(t)$, as explicitely contained in (16). The number of participating species, J, can in principle become a function of time as well; which is mentioned here for the sake of future studies only. In this paper, we restrict our attention to non-chemical MDS.

We turn to computing the entropy of (13) in a dimensionless manner (with $k = 1$) in the MDS which was simulated in the previous section. The mean of the total energy, $\langle E \rangle = 133.662$, is used to compute the maximum distance in the momentum space to obtain the denominator in (9). The result of the ensuing calculation accompanying the simulation is shown in Figure 3. The fluctuations are large when compared to the mean increase of the entropy itself. This is perhaps not astonishing since only 100 particles are involved.

A second shortcoming of the "local" entropy, (13), is the fact that certain global structures are not recognized. For example, two well-separated particle clusters lead to a similar entropy as if the clusters were

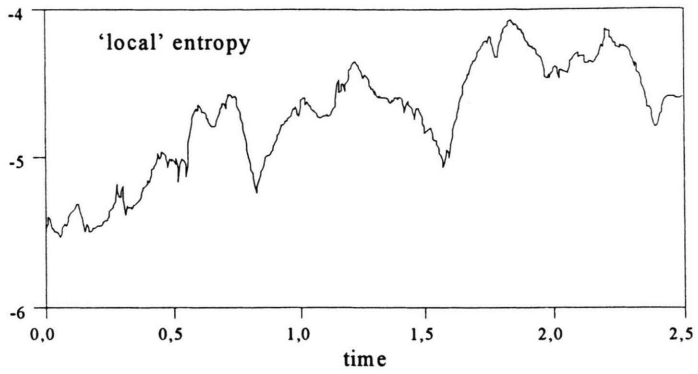

Fig. 3. Time series of the "local" entropy (13) for the same gas as in Figure 1. Note the fairly large fluctuations for the rather low-dimensional system in question.

not separated. The global arrangement is thus not sufficiently taken into account.

Because of these two shortcomings and in view of the fact that the IOPS concept has not yet been taken into explicit regard, in the following an improved deterministic entropy concept will be presented.

5. The IOPS Concept from a Global Viewpoint

We again pay attention to the global arrangement of the particles. On the basis of the distances described by (8), radii of a given particle i with respect to all $N-1$ other particles j are given by

$$r_{ij} = \left\{ \left[\left(\frac{\Delta x_{ij}}{\Delta x_{\max}} \right)^2 + \left(\frac{\Delta y_{ij}}{\Delta y_{\max}} \right)^2 + \left(\frac{\Delta p_{x_{ij}}}{\Delta p_{x,\max}} \right)^2 + \left(\frac{\Delta p_{y_{ij}}}{\Delta p_{y,\max}} \right)^2 \right]^{1/2} \right\}. \tag{17}$$

This equation differs from (9) in one important respect. Instead of taking the minimum of all distances in one-particle phase space, as was done in (9), we here go into the full phase space Γ. To this end, we use the distance in one-particle phase space, described by (17), to define the "free volume" available to particle i in Γ. We first form the product over the $N-1$ 4-dimensional hyperspheres:

$$v_i = \prod_{\substack{j=1 \\ j \neq i}}^{N} \frac{1}{2}\pi^2 r_{ij}^4. \tag{18}$$

This yields a volume in a $4(N-1)$-dimensional space. Secondly, we return to the one-particle phase space in the following way. The geometric mean over the "distances" v_i of the reference particle i to the $N-1$ particles j is given by

$$\omega_i = \sqrt[N]{v_i} = \sqrt[N]{\prod_{\substack{j=1 \\ j \neq i}}^{N} \frac{1}{2}\pi^2 r_{ij}^4}. \tag{19}$$

Equation (19) once more corresponds to a volume in the one-particle phase space, formed through a kind of a projection of a volume in the (almost) total phase space. In contrast to the "local" viewpoint adopted previously with (10), (19) contains information about the global arrangement of the particles as well.

In formal analogy to what we did in the local context of the previous section, we again take the geometric mean over all partial volumes ω_i:

$$\omega = \sqrt[N]{\prod_{i=1}^{N} \omega_i}. \tag{20}$$

It represents an instantaneously valid "generalized diameter" of phase space. As before, the total occupied volume in the one-particle phase space becomes

$$\Omega = N\omega = N \sqrt[N]{\prod_{i=1}^{N} \sqrt[N]{\prod_{\substack{j=1 \\ j \neq i}}^{N} \frac{1}{2}\pi^2 r_{ij}^4}}. \tag{21}$$

Logarithmizing, we arrive at the following new entropy in analogy to (3):

$$S = k \left\{ \ln N + \frac{1}{N^2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \ln \left(\frac{1}{2}\pi^2 r_{ij}^4 \right) \right\}. \tag{22}$$

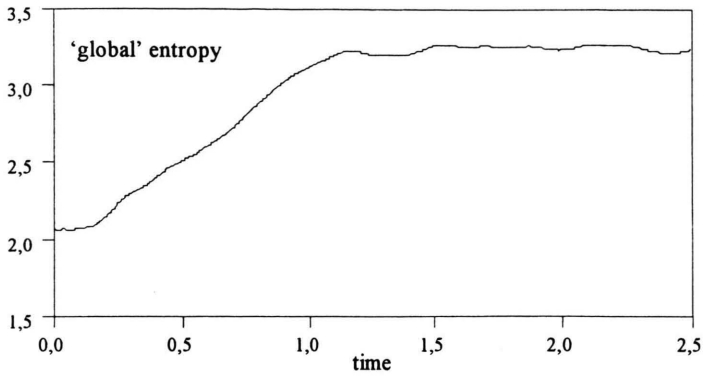

Fig. 4. Time series of the "global" entropy (21) for the same gas. In contrast to the "local" entropy (Fig. 3) the fluctuations are now minor.

This is our main result. An extension to multi-species systems, as discussed above for the "local" entropy, Eq. (16), can be obtained in complete analogy for (21).

Equation (21) has the formal structure of a correlation function. The global arrangement of the particles is therefore taken into full regard. One is reminded of a so-called correlation dimension in nonlinear analysis, cf. [21].

Let us apply the new formula to the above MDS. The time series of the global entropy (21) is shown in Figure 4. One sees that the fluctuations are much smaller than in Figure 3. The incorporation of the global arrangement of the particles achieved by the global entropy (21) is apparently responsible for the damping of the fluctuations observed. Formula (21) does turn out to be especially useful for low-dimensional MDS-systems.

Note, that the differences ΔS between the initial value of the entropy and the final value, in both figures, Fig. 3 and Fig. 4, are about unity. This difference appears plausible. In an ideal gas, one would expect ΔS to be $\ln 2 \approx 0.693$. This is due to the doubling of the volume on the one hand, and to the absence of smooth pair potentials on the other. Nevertheless, the absolute values of the "local" and the "global" entropy are different. This difference can easily be explained. A first reason seems to lie in the arbitrary choice of the geometric shape of the "free spaces" defined by (9) and (17). Since the two tilings overlap differently, they generate different scaling factors for the resulting phase space volumes. In Fig. 3, total phase space is less than unity, which explains the negative value of the local entropy. In Fig. 4, the total phase space volume is greater than unity. Nevertheless, these differences can be removed by getting rid of the overlaps. Note that in the global entropy, the maximum phase space volume is "overrated" by a factor of N. This raises the logarithm by 10; the real difference between Fig. 3 and Fig. 4 is about 7. A more detailed discussion is in preparation.

6. Discussion

A deterministic entropy has been derived. Specifically, the concept of an instantaneously occupied phase space volume has been introduced and employed in two ways, first more approximately ("local" entropy formula), then more rigorously ("global" entropy formula). Thereby, Boltzmann's entropy, $S = k \ln \Omega$, which is based on the phase space volume Ω could be given a new time-dependent interpretation.

The new entropy allows for a completely "system-based" estimation of how far a given system is momentarily away from thermal equlibrium. The instantaneous time-dependent entropy does not require any observer-specific decisions to be made, like those introduced by Jaynes in his more macroscopic constraint-based "maximum entropy formalism".

A relative drawback from a practical numerical point of view regarding S_{glob} deserves to be mentioned. While other Newtonian MDS can be kept growing with less than N^2 in terms of numerical operations required as a function of N, since interactions with more distant particles can be skipped, the present algorithm requires the calculation of all pair distances. This reduces the maximum attainable N in a machine-dependent manner (currently, an $N \approx 10{,}000$ would still be accessible for fast relaxing systems).

An idea of Hoover [22] may nervertheless allow for an effective reduction in CPU time. An "available space" can be defined for a fictitious particle to be added [22]. That is, Hoover looks not at the "occupied phase space volume" but at its complement,

the "unoccupied" volume. In this way, a measure of the "work" required to insert another particle is defined. This idea may save computation time because "many-body-state-counting" is reduced to estimating the probability of being allowed to with impunity insert an additional particle. Thus, looking at Hoover's unoccupied volume during the simulation may eventually reduce computation time.

A second asset of Hoover's idea is the implied link to a measurable macro observable. The new measurable work – a kind of energy, $(\partial A/\partial N)_{V,T}$, termed "excess chemical potential" by Hoover – plays a similar role as a macro observable, as entropy itself does. So far, Hoover's method is confined to one-particle phase space. However, there is a chance that it can be "globalized", too.

We feel tempted to add another speculation. The new entropy formula could prove useful also for the description of the transient behavior of purely macroscopic systems – like a set of coupled dissipative oscillators. In such "synergetic" systems with many equal units [23], one can also hope to profit from the many-unit character of the problem. In this way, the "IOPS-concept" becomes a candidate for an "entropic measure" for such systems. The evolutionary and transient character of chemical and biological systems can perhaps be investigated more systematically in this fashion.

To conclude, a new fundamental tool in dealing with dissipative structures – such as galaxies, star clusters, flames and living systems like neurons and brains [24] – appears to be available: An instantaneous time-dependent entropy. For the first time, the "pulse" of these systems can be felt continuously, so to speak, when they are simulated without approximations, that is, from reversible first principles.

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