THE BOLTZMANN ENTROPY FOR DENSE FLUIDS NOT IN LOCAL EQUILIBRIUM

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We investigate, via computer simulations, the time evolution of the (Boltzmann) entropy of a dense fluid not in local equilibrium. The macrovariables $M$ describing the system are the (empirical) particle density $f = \{f(x, v)\}$ and the total energy $E$. We find that $S(f_t, E)$ is monotone increasing in time even when its kinetic part is decreasing. We argue that for isolated Hamiltonian systems monotonicity of $S(M_t) = S(M_{X_t})$ should hold generally for “typical” (the overwhelming majority of) initial microstates (phase-points) $X_0$ belonging to the initial macrostate $M_0$, satisfying $M_{X_0} = M_0$. This is a direct consequence of Liouville’s theorem when $M_t$ evolves autonomously.

INTRODUCTION

In 1854 Clausius introduced the notion of the entropy of a macroscopic system (defined up to additive constants) in a state of thermal equilibrium [1]. Not long afterwards Boltzmann gave a microscopic definition of the entropy $S(M)$ of a general macroscopic system in a macrostate defined by values of macrovariables $M$: $M = M_X$ represents suitable “coarse-grained” functions of the system’s microstate, given by a point $X$ in the $2N_d$-dimensional phase space $\Gamma$ for a $d$-dimensional classical system containing $N$ particles. $S(M)$ is (up to constants) equal to the log of the volume $|\Gamma_M|$ of the phase-space region $\Gamma_M$, defined by the macrostate $M$, i.e. containing all phase points (or microstates) giving rise to this macrostate [2]. $S(M)$ agrees with the Clausius entropy for systems in equilibrium when $M = M_{eq}$ is just the total energy $E$, of $N$ particles in a volume $V$. The fact that $|\Gamma_{M_{eq}}|$ is exponential in the number of molecules in the system explains the origin of the second law in the microscopic dynamics: when a constraint is lifted in a system in equilibrium, thereby affording access to a new equilibrium macrostate $M'_{eq}$ of larger entropy per molecule than the original $M_{eq}$, the overwhelming majority of phase points in $\Gamma_{M_{eq}}$ will find themselves eventually in $\Gamma_{M'_{eq}}$, since for a macroscopic system $|\Gamma_{M'_{eq}}|$ is enormously larger than $|\Gamma_{M_{eq}}|$ as well as the volume of the union of all nonequilibrium macrostates without the constraint [2,3].

Boltzmann’s interpretation of entropy naturally extends the second law to nonequilibrium macroscopic systems: a (significant) violation of the second law will not occur provided the microstate $X$ of a physical system prepared in, or evolved into, the macrostate $M$ is typical (or at least not atypical)
of points in $\Gamma_M$ as far as the future evolution of $M$ is concerned. Of course to rigorously prove that $X$ should be (and remain) typical in this sense is difficult. It was pointed out, however, in [4] that a sufficient condition for this is that the evolution of $M_t$ be given by an autonomous deterministic law, i.e. the value of $M$ at any time $t + \tau$ is determined by its value at time $t$, $M_{t+\tau} = \Phi_{\tau}(M_t)$, for $\tau \geq 0$. Such a law implies that, with rare exception, $\phi_{\tau} \Gamma_{M_t} \subset \Gamma_{M_{t+\tau}}$, i.e. the overwhelming majority of phase-points (almost all in suitable limits) $X \in \Gamma_{M_t}$ will, when evolved according to the microscopic evolution law $\phi_{\tau}$, be found in $\Gamma_{M_{t+\tau}}$ for $\tau \geq 0$. It follows then from Liouville’s theorem that (with insignificant error) $S(M_{t+\tau}) \geq S(M_t)$.

The most common example of a deterministic macro-evolution occurs for simple systems in local thermal equilibrium (LTE), described by the macrovariables $M$ representing the locally conserved (particle, momentum and energy) densities. $M_t$ then satisfies deterministic hydrodynamic-type equations, e.g. the Euler or Navier-Stokes equations, and $S(M_t)$, which is given by an integral over the volume $V$ of the equilibrium entropy density, see [5], is then indeed monotone nondecreasing in time.

Such a deterministic evolution is however not necessary for the monotonicity of $S(M_t)$. There is an enormous disparity between the (small) number of possible macrostates (which are always defined with some macroscopic tolerance in terms of a relatively small number of macrovariables) and the large number of microstates corresponding to the possible values of the large number of microvariables (counted say in terms of phase-space cells of volume $\hbar^d N$). Even when $M_0$ does not determine $M_t$, $S(M_{X_0})$ should be nondecreasing to leading order in the size of the system for the overwhelming majority of initial microstates $X_0$; see also [6].

The choice of macrovariables $M$ and the corresponding computation of $S(M)$ suitable for describing systems not in LTE is a daunting task, especially for complex systems such as polymeric fluids, metals with memory, etc. The first and still paradigmatic step in that direction was taken by Boltzmann himself when he computed $S(f)$ for the macrovariables $f = \{f_X(x, \nu)\}$ corresponding to the coarse-grained (empirical) density in the $2d$ dimensional $\mu$-space for a macroscopic system in a microstate $X$ [2], [7]. He found that (up to constants)

$$S(f) = S_{gas}(f) \equiv -k \int_V dV \int_{R^d} d\nu f(x, \nu) \ln f(x, \nu)$$

(1)
We put the subscript “gas” on $S_{\text{gas}}(f)$ to emphasize that $f(x, v)$ can be expected to suffice for the adequate specification of the macrostate away from LTE only for a dilute gas, where interactions between particles make a negligible contribution to the energy of the system. In fact it was for such a dilute gas that Boltzmann derived a deterministic evolution equation for $f$ and proved that the corresponding $f_t$ satisfies the $\mathcal{H}$-theorem, $\frac{d}{dt}S_{\text{gas}}(f_t) \geq 0$, [2], [3], [7]. For dense fluids, specification of $f(x, v)$ is compatible with many different total energies (including infinite ones for hard core interparticle potentials). A simple analysis then shows that the phase points $X$ of a system with specified energy $E$ which is below the maximal energy compatible with $f$ will correspond to an exceedingly small minority of the phase points in $\Gamma_f$, i.e. will be atypical of points in $\Gamma_f$. There is then no reason to expect for such systems that $S_{\text{gas}}(f_{X_t})$ will increase as the system evolves in time according to its energy conserving Hamiltonian dynamics. It is in fact easy to set up in dense fluids initial macrostates $f_0$ such that for $X_0 \in \Gamma_{M_0} S_{\text{gas}}(f_{X_t})$ will typically decrease in time when the fluid goes to equilibrium [8].

It was argued in [4] that if one includes in $M$, in addition to $f$, also the total energy $E$, then the entropy $S(f_t, E)$ should be an increasing function of time, i.e. $S(f_t, E)$ should satisfy an $\mathcal{H}$-theorem for general systems, including dense fluids. It was also noted there that the quantity shown by Resibois [9] to satisfy an $\mathcal{H}$-theorem for $f_t$ evolving via the modified Enskog equation (expected to be accurate for moderately dense hard sphere gases) is in fact the Boltzmann entropy $S(f_t, E)$ for a system of hard spheres.

In this work we use molecular dynamics to investigate the time evolution of $S(f_t, E)$ for dense fluids interacting with Lennard-Jones and other types of pair potentials. We consider in particular situations, such as those in [8], where $S_{\text{gas}}(f_t)$, defined in [11], is expected to decrease. Our simulations, which give a monotone increase of $S(f_t, E)$ when the number of particles in the system is large, support the hypothesis that the time evolution of a typical microstate in $\Gamma_{f,E}$ is indeed such that $S(f_t, E)$ satisfies an $\mathcal{H}$-theorem. We also find evidence that $f_t$ itself evolves in a deterministic way, with different microstates with the same $f_0$ give rise to the same $f_t$, although no equation yielding this evolution is at present known (at least to us) for general dense fluids. This suggests looking for an autonomous equation for $f_t$ (at a given $E$). This is exactly what is done in the heuristic
derivations of the Boltzmann and Enskog equations [10] and is discussed extensively in the literature for various other systems, see [11]. The validity of the Boltzmann equation for dilute gases, i.e. for typical $X_0 \in \Gamma f_0$ in the Boltzmann-Grad limit, was justified rigorously at least for short times, by Lanford [12].

**Formalism:** We consider a system of $N$ particles with unit mass in a box $V$. The microstate is specified by $X = (x_1, v_1, \ldots, x_N, v_N)$ and the dynamics is given by the Hamiltonian

$$H(X) = \frac{1}{2} \sum_{i=1}^{N} v_i^2 + \frac{1}{2} \sum_{i \neq j} \phi(x_i - x_j)$$  \hspace{1cm} (2)

It follows from the structure of the classical phase space $\Gamma$ that $S(f, E)$ can be written, c.f. [4], as

$$S(f, E) = S^{(m)}(f) + S^{(c)}(n, \Phi_{\text{total}}).$$ \hspace{1cm} (3)

Here $S^{(m)} (S^{(c)})$ is the log of the momentum (configuration) space volume corresponding to the macro-state $M = (f, E)$,

$$S^{(m)}(f) = S_{\text{gas}}(f) + k \int_{V} dx n(x) \log n(x)$$ \hspace{1cm} (4)

with $n(x) = \int_{\mathbb{R}} d\nu f(x, \nu)$, the spatial density, and

$$S^{(c)}(n, \Phi_{\text{total}}) = \sup_{\Phi} \int_{V} dx s^{(c)}(n(x), \Phi(x))$$ \hspace{1cm} (5)

where $s^{(c)}(n, \Phi)$ is the configurational entropy density of an equilibrium system with Hamiltonian [2] having particle density $n$ and potential energy density $\Phi$. The sup in eq. (5) is taken over all $\Phi(x)$ such that

$$\int_{V} dx \Phi(x) = \Phi_{\text{total}} = E - \int_{V} dx \int_{\mathbb{R}} d\nu f(x, \nu) \frac{1}{2} \nu^2$$ \hspace{1cm} (6)

Restricting ourselves to spatially uniform systems, $n = N/V$, $f = nh(\nu)$, $\int_{\mathbb{R}} d\nu h(\nu) = 0$, $\Phi = \Phi_{\text{total}}/V$, we find (see eqs. (39)-(41) in [7]) that

$$\frac{d}{dt} S^{(c)}(n, \Phi_{\text{total}}) = \frac{1}{T_\Phi} \frac{d\Phi_{\text{total}}}{dt}$$ \hspace{1cm} (7)

where $T_\Phi$ is the inverse of $\Phi_{eq}(T)$, the potential energy density of the equilibrium system with Hamiltonian [2] at density $n$. 
FIG. 1: Evolution of $S^{(m)}/V$, $\Phi$ and $S/V$ following the initial nonequilibrium state (see text). The particles interact with a cut-off Lennard-Jones potential and $N = 90000$. The total energy and the initial potential energy densities are $\epsilon = 0.6$ and $\Phi = -0.5917...$ respectively.

Simulations: To check whether $S(f_t, E)$ as expressed in eqs. (3) to (7) satisfies an $\mathcal{H}$-theorem for dense fluids we have carried out simulations on a two-dimensional system with density $n = 0.5$ in a periodic box interacting with a cut-off Lennard-Jones potential, $\phi(r) = \bar{\phi}(r) - \bar{\phi}(r_c) - (r - r_c)d\bar{\phi}(r)/dr|_{r=r_c}$ with $\bar{\phi}(r) = 4[r^{-12} - r^{-6}]$ for $r \leq r_c = 2.5$ and $\phi(r) = 0$ otherwise. To obtain $T_\Phi$ in (7) we first computed $\Phi_{eq}(T)$, for such a system. For these simulations, as well as for those described below, we used the Verlet algorithm with time mesh $10^{-4}$.

To carry out the time dependent simulations, we first let the system reach an equilibrium state. We then multiplied the speed of each particle with an appropriate factor to obtain a state with too high a kinetic energy, and let the system evolve freely to its new equilibrium state. This means that the initial $f$ was a Maxwellian with too high a temperature for the total energy—the case considered in [8]. During the consequent evolution the velocity distribution stayed isotropic and we computed $S^{(m)}$, as well as the kinetic and potential energy densities, in time intervals of size 0.001. To compute $S^{(m)}$ we first find the speed distribution by counting the number of particles having their speeds in each of the 50 equal intervals into which we divide the segment $[0, v_{max}]$ where $v_{max}$ is the maximum speed of any particle at time $t$. We then get the configurational entropy $S^{(c)}$ by taking a numerical derivative of $\Phi$ with respect to time and then carrying out a numerical integration of the right side of (7). In Figure 1 we show the time behavior of $S^{(m)}$, $\Phi_{total}$ and $S$ for such a system.

We have carried out similar calculations for the truncated repulsive potential $\phi(r) = \bar{\phi}(r) - \bar{\phi}(r_c)$—
FIG. 2: Evolution of $S^{(m)}/V$, $k$, $\Phi$ and $S/V$ for different size systems $N = 100, 400, 1600, 90000$ and $10^6$. The particles interact with a cut-off $r^{-6}$ potential. The total energy and the initial potential energy densities are $e = 0.7$ and $\Phi = 0.2049$, respectively.

$(r-r_c)d\bar{\phi}(r)/dr|_{r=r_c}$ with $\bar{\phi}(r) = r^{-6}$ for $r \leq r_c = 2.5$ and $\phi(r) = 0$ otherwise. We show the results for different values of $N$ in Fig. 2. The fluctuations for small $N$ are clearly visible: their magnitude, once the system has reached equilibrium, appear to scale as $N^{-1/2}$. There are also finite-size corrections to the equilibrium time averages consistent with those expected from using a micro-canonical ensemble.

We also investigated for this system whether $f_t$ evolves deterministically by comparing $f_t$ for different initial microstates, all having the same $f_0$ and $E$. The results are shown in Figs. 3 and 4. The initial $f_0$ in Fig. 3 is close to a Maxwellian and the subsequent $f_t$ are also close to a Maxwellian with time dependent temperatures. In Fig. 4 the initial $f_0$ is one in which all the particles have the same speed. The evolution of $f_t$ towards a Maxwellian is clearly visible.

**Binary Mixtures:** We also considered the case of a binary system of hard point particles with alternating masses $m_1$ and $m_2$. We used as our macrovariable the total energy $E$ plus the empirical density $f(v)dv$ of particles with velocities in some interval $dv$ (independent of the species) with uniform positional densities $n_1$ and $n_2$ in a box of length $L$. The entropy $S_{(2)}(f, E)$ of this system can be written as a sum:

$$S_{(2)}(f, E) = S_{\text{gas}}(f_1) + S_{\text{gas}}(f_2), \quad E = E_1 + E_2$$

The maximum of $S_{(2)}(f, E)$ is obtained for $f$ a sum of Maxwellians $f_1$ and $f_2$ with the same temperature $T$ determined by the total energy $E = (n_1 + n_2)^1_2kTL$.
FIG. 3: Evolution of $f_t(v)$ during a (B) to (C) process for three different microscopic configurations. The particles interact with a truncated $r^{-6}$ potential and $N = 90000$. The solid lines correspond to the fit of the data to a Maxwellian distribution with the same kinetic energy.

FIG. 4: Evolution of $f_t(v)$ for an initial condition with all particles in a square lattice and equal speeds with random directions for $n = 0.5$, $\epsilon = 0.7$, $\phi(r) = r^{-6}$, and $N = 90000$. Full dots and empty circles are the values of $f_t$ corresponding to two different microscopic states respectively. Gray lines correspond to Maxwellian distributions with temperature $T$ obtained from the kinetic energy of the state.

Starting with an initial microstate for which $S_{\text{gas}}(f_1) > L_{\text{eq}}(n_1, T_1)$, $S_{\text{gas}}(f_2) < L_{\text{eq}}(n_2, T_2)$, we then observed in the simulations that $S_{\text{gas}}(f_1)$ decrease while $S_{(2)}(f, E)$ increase during the evolution towards the equilibrium distributions.

**Concluding remarks:** We have confirmed via computer simulations the monotone increase of the Boltzmann entropy (log of phase space volume) for a dense fluid not in local equilibrium whose macrostate is specified by the empirical density $f$ and energy $E$. Similar results were obtained for a binary system of hard points in $d = 1$. The simulations also show an apparent deterministic
FIG. 5: Evolution of the nonequilibrium entropy $S_{\partial}(f, E)/L$ for a one dimensional system with $N = 10^5$ particles with alternating masses $m_1 = 1$ and $m_2 = (1 + \sqrt{5})/2$. Initially the particles with mass 1 (2) have a maxwellian velocity distribution with temperature $T_1 = 1$ ($T_2 = 5$). $S_{\partial\text{ax}}(f_1)$ is the partial entropy for the $i$-specie.

Evolution of $f_t$ for such systems.

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