## **Boltzmann Entropy for Dense Fluids Not in Local Equilibrium**

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Using computer simulations, we investigate 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  $f = \{f(\underline{x}, \underline{v})\}$  and the total energy E. We find that  $S(f_t, E)$  is a 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 consequence of Liouville's theorem when  $M_t$  evolves according to an autonomous deterministic law.

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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 the values of a set of macrovariables  $M: M = M_X$ represents suitable "coarse-grained" functions of the system's microstate, given by a point X in the 2Nddimensional 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. Agreement here means that  $V^{-1}S(E)$  coincides when  $N \to \infty$ , and  $E/N \rightarrow e$ ,  $N/V \rightarrow n$ , with the corresponding Clausius equilibrium entropy density  $s_{eq}(n, e)$ . The fact that  $|\Gamma_{M_{\infty}}|$  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  $M_{\rm eq}$ , the overwhelming majority of phase points in  $\Gamma_{M_{\mathrm{eq}}}$  will find themselves eventually in  $\Gamma_{M'_{\mathrm{eq}}}$ , since for a macroscopic system  $|\Gamma_{M'_{\mathrm{eq}}}|$  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, i.e., a decrease of entropy by a macroscopic amount, will not occur provided the microstate X (of a physical system prepared in, or evolved into, the macrostate M) is typical 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 if the evolution of  $M_t$  is given by an autonomous deterministic law, i.e.,

the value of M at any time  $t+\tau$  is determined by its value  $M_t$  at time t alone,  $M_{t+\tau}=\Phi_{\tau}(M_t)$ , for  $\tau\geq 0$ , then  $S(\Phi_{\tau}(M))$  must obey an  $\mathcal{H}$  theorem:  $S(M_{t+\tau})\geq S(M_t)$ . Having such a deterministic law means 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  $\tau\geq 0$ . Thus, if any purported evolution law for  $M_t$  violates this inequality, that law cannot be consistent with the microscopic evolution of typical X in  $\Gamma_M$  (see below).

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The most common example of a deterministic macroevolution occurs for simple systems in local thermal equilibrium (LTE), described by the macrovariables Mrepresenting 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 microscopic volume). Even when  $M_0$  does not determine  $M_t$ ,  $S(M_{X_t})$  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  $f = \{f_X(\underline{x}, \underline{v})\}$  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)

$$S(f) = S_{gas}(f) \equiv -k \int_{V} d\underline{x} \int_{R^d} d\underline{v} f(\underline{x}, \underline{v}) \ln f(\underline{x}, \underline{v}). \quad (1)$$

We put the subscript "gas" on  $S_{gas}(f)$  to emphasize that  $f(\underline{x}, \underline{v})$  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,  $\frac{d}{dt}S_{\mathrm{gas}}(f_t) \geq 0$ [2,3,7]. For dense fluids, specification of  $f(\underline{x}, \underline{v})$  is compatible with many different total energies (including infinite ones for hard core interparticle potentials). A simple analysis then shows that  $\Gamma_f$  will consist mostly of phase points X whose total energy is close to the maximum possible value  $E_{\text{max}}$  consistent with f; e.g., in a system with hard cores typical X in  $\Gamma_f$  will have some cores overlap, and so the energy will be infinite. This means 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  $\Gamma_f$ . For such systems there is then no reason to expect that  $S_{\rm gas}(f_{X_t})$  will increase as the system evolves in time according to its energy conserving Hamiltonian dynamics. For dense fluids it is, in fact, easy to set up initial macrostates  $H_0 = f_0$ , E with  $E \subset E_{\text{max}}$  such that for typical  $X_0 \in \Gamma_{M_0}$ ,  $S_{\text{gas}}(f_{X_t})$  will decrease in time when the fluid goes to equilibrium [8]. Of course, for many initial  $f_0$  and E,  $S_{eq}(f)$  may still increase. This is what happened in [9].

It was argued in [4] that if one includes in M both f and 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. The original Enskog equation does not give a monotone increase of  $S(f_t, E)$  and is therefore incorrect.

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  $S_{\rm gas}(f_t)$ , defined in (1), 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  $f_0$  giving 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  $X = (\underline{x}_1, \underline{v}_1, \dots, \underline{x}_N, \underline{v}_N)$  and the dynamics is given by the Hamiltonian

$$H(X) = \frac{1}{2} \sum_{i=1}^{N} \underline{v}_i^2 + \frac{1}{2} \sum_{i \neq j} \phi(\underline{x}_i - \underline{x}_j).$$
 (2)

In [4] it was shown that S(f, E) can be written as

$$S(f, E) = k \ln |\Gamma_{f, E}| = S^{(m)}(f) + S^{(c)}(n, \Phi_{\text{total}}).$$
 (3)

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

$$S^{(m)}(f) = S_{gas}(f) + k \int_{V} d\underline{x} n(\underline{x}) \ln n(\underline{x})$$
 (4)

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

$$S^{(c)}(n, \Phi_{\text{tot}}) = \sup_{\Phi} \int_{V} d\underline{x} s^{(c)}(n(\underline{x}), \Phi(\underline{x})), \tag{5}$$

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

$$\int_{V} d\underline{x} \Phi(\underline{x}) = \Phi_{\text{total}} = E - \int_{V} d\underline{x} \int_{R^{d}} d\underline{v} f_{t}(\underline{x}, \underline{v}) \frac{1}{2} \underline{v}^{2}. \quad (6)$$

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

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

where  $T_{\Phi}$  is the inverse of  $\Phi_{\rm eq}(T)$ , the potential energy density of the equilibrium system with Hamiltonian (2) at density n.

Simulations.—To check whether  $S(f_r,E)$  as expressed in Eqs. (3)–(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 cutoff 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  $\Phi_{\rm eq}(T)$ , for such a system. For these simulations, as well as for those

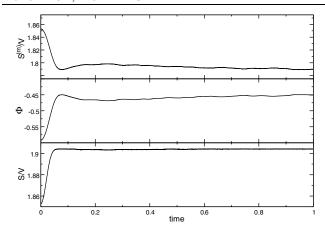


FIG. 1. Evolution of  $S^{(m)}/V$ ,  $\Phi$ , and S/V following the initial nonequilibrium state. The particles interact with a cutoff Lennard-Jones potential and  $N=90\,000$ . The energy density and the initial potential energy density are e=0.6 and  $\Phi=-0.5917\ldots$ 

described below, we used the velocity-Verlet algorithm with time mesh  $10^{-4}$  [13].

To carry out the time dependent simulations, we started with all particles on a square lattice with each particle having the same speed and random velocity directions and let the system evolve to 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 relative to its potential energy and let the system evolve 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

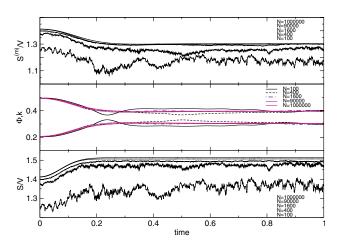


FIG. 2 (color online). Evolution of  $S^{(m)}/V$ , k,  $\Phi$ , and S/V for different size systems  $N=100,400,1600,90\,000$ , and  $10^6$ . The particles interact with a cutoff  $r^{-6}$  potential. The energy density and the initial potential energy density are e=0.7 and  $\Phi=0.2049$ .

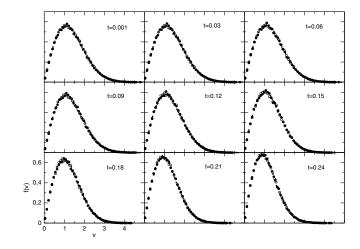


FIG. 3. Evolution of  $f_t(v)$  for three different initial microscopic configurations. With  $f_0$  and E the particles interact with a truncated  $r^{-6}$  potential and  $N = 90\,000$ .

speed distribution by counting the number of particles having their speeds in each of the 50 equal intervals into which we divide the segment  $[0, v_{\text{max}}]$  where  $v_{\text{max}}$  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 Fig. 1 we show the time behavior of  $S^{(m)}$ ,  $\Phi_{\text{total}}$ , and S for such a system.

We have carried out similar calculations for the truncated repulsive potential  $\phi(r) = \bar{\phi}(r) - \bar{\phi}(r_c) - (r - r_c) d\bar{\phi}(r)/dr|_{r=r_c}$  with  $\bar{\phi}(r) = r^{-6}$  for  $r \le r_c = 2.5$  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 magnitudes, once the system has reached equilibrium, appear to scale as  $N^{-1/2}$ . There

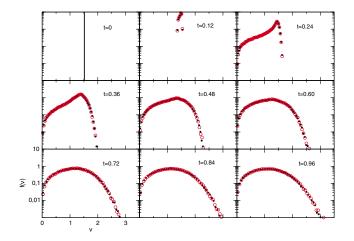


FIG. 4 (color online). Evolution of  $f_t(v)$  for an initial condition with all particles in a square lattice and equal speeds with random directions for  $n=0.5, e=0.7, \bar{\phi}(r)=r^{-6}$ , and  $N=90\,000$ . Full dots and empty circles are the values of  $f_t$  corresponding to two different microscopic states, respectively.

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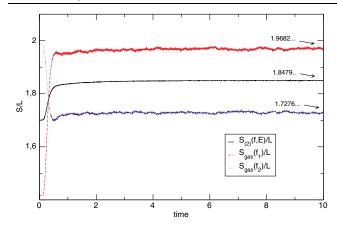


FIG. 5 (color online). Evolution of the nonequilibrium entropy  $S_{(2)}[f,E]/L$  for a one-dimensional system with  $N=10^5$  particles with alternating masses  $m_1=1$  and  $m_2=(1+\sqrt{5})/2$ . Initially the particles with mass  $m_1$  ( $m_2$ ) have a Maxwellian velocity distribution with temperature  $T_1=1$  ( $T_2=5$ ).  $S_{\rm gas}(f_i)$  is the partial entropy for the ith species.

are also finite-size corrections to the equilibrium time averages consistent with those expected from using a microcanonical ensemble.

For this system we also investigated 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  $f_t$  is towards a Maxwellian.

Binary Mixtures.—We also simulated a onedimensional binary system of hard point particles with masses alternately  $m_1$  and  $m_2$  [14]. 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  $S_{(2)}(f, E) =$  $\max\{S_{\text{gas}}(f_1) + S_{\text{gas}}(f_2)\}\$ , where  $f_i$  is the distribution corresponding to species i and the maximum is taken subject to the constraint  $f = f_1 + f_2$ ,  $E = E_1 + E_2$ ,  $E_i =$  $\frac{1}{2}m_i \int v_i^2 f_i dv$ . Starting with an initial microstate for which  $S_{\text{gas}}(f_1) > Ls_{\text{eq}}(n_1, T_1), \quad S_{\text{gas}}(f_2) < Ls_{\text{eq}}(n_2, T_2),$ we then observed in the simulations that  $S_{gas}(f_1)$  decreases while  $S_{(2)}(f, E)$  increases during the evolution towards the equilibrium distributions given by Maxwellians  $f_i$  with the same temperature; see Fig. 5.

In conclusion, using computer simulations we have confirmed 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 evolution of  $f_t$  for such systems.

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