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On the Entropy of Nonequilibrium States

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A definition originally proposed by H. S. Green is used to calculate the entropy of nonequilibrium steady states. This definition provides a well-defined coarse graining of the entropy. Although the dimension of the phase space accessible to nonequilibrium steady states is less than the ostensible dimension of that space, the Green entropy is computed from within the accessible phase space, thereby avoiding the divergences inherent in the fine-grained entropy. It is shown that the Green entropy is a maximum at equilibrium and that away from equilibrium, the thermodynamic temperature computed from the Green entropy is different from the kinetic temperature.

KEY WORDS: Nonequilibrium states; entropy; kinetic temperature.

1. INTRODUCTION

Since the foundation of statistical mechanics there has been a continuing debate over the microscopic formulation of the entropy for nonequilibrium states. Gibbs$^{(1)}$ noted that for any Hamiltonian system, even one subject to an external field, the entropy S, defined as it is in equilibrium statistical mechanics,

$$S(t) \equiv \frac{-k_B}{N!} \int d\Gamma\, f(\Gamma, t) \ln(f(\Gamma, t)) \tag{1}$$

is a constant of the motion. Gibbs recognized this difficulty and partially resolved the problem by computing a coarse-grained entropy, which he showed satisfied a generalized H-theorem.$^{(1)}$ In the years since no one has been able to show that as the characteristic lengths for the coarse graining

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tend to zero, the coarse-grained entropy tends to a limit which is different from the fine-grained value. Neither, as far as I know, has anyone succeeded in deriving a useful connection between the coarse-grained entropy and irreversible thermodynamics.

Recently simulation-inspired studies of nonequilibrium steady states have only compounded the difficulties. In 1985, I showed$^{(2)}$ that for systems subject to a dissipative external field F_e and thermostatted using any of the time-reversible thermostats used in computer simulations, the fine-grained entropy diverges to $-\infty$ at long time and that the rate of change of the system entropy in a nonequilibrium steady state is

$$\dot{S} = -3Nk_B\langle\alpha(t)\rangle \tag{2}$$

where α is related to the rate at which internal energy H_0 is removed from the system by the thermostat and to the peculiar kinetic energy of the system K,

$$\alpha = -\dot{H}_0^{\text{them}}/(2K) \tag{3}$$

The dissipative flux is defined by the adiabatic derivative of the internal energy as $(dH_0/dt)^{\text{ad}} \equiv -JF_e$. In a steady state $\langle\alpha\rangle$ is equal to $LF_e^2/(2\langle K\rangle)$, where L is the transport coefficient defined by the constitutive relation $J \equiv -L(F_e)F_e$. In accord with the second law of thermodynamics, L is always observed to be positive and therefore, by Eq. (2), the entropy decreases linearly in time without limit. This occurs in the linear regime close to equilibrium, where $\lim(F_e \to 0)\, L(F_e) = L(0)$, and in the nonlinear regime far from equilibrium.

This is not in accord with intuition or linear irreversible thermodynamics. Close to equilibrium we expect that the system entropy is constant and equal to its equilibrium value. This is after all the postulate of *local thermodynamic equilibrium*. For nonequilibrium steady states, far from equilibrium we expect that the N-particle distribution function will tend to a time independent steady-state distribution f_{ss} and that the steady-state entropy for systems far from equilibrium should be given by Eq. (1) evaluated for f_{ss}. The reason for expecting the steady-state nonequilibrium distribution function to converge to a time-independent function f_{ss} is that for steady states, all the moments of the distribution and all phase averages taken with respect to the steady state distribution are, by definition, time independent. It is important to keep in mind, however, that not all thermostatted nonequilibrium systems are *steady*-state systems.

Recent numerical studies of small nonequilibrium systems have gone some way toward explaining the entropy divergence in nonequilibrium steady states. Beginning with simulations of thermostatted systems of just two particles subject to a dissipative external field, Moran *et al.*⁽³⁾ and Morris⁽⁴⁾ have produced convincing evidence that $f_{ss}(\Gamma)$ is singular and fractal. In extending their simulations to 8- and 32-particle systems, there appears to be no reason to doubt that this fractal nature persists in the large-system limit.⁽⁵⁾ Furthermore, they⁽⁴⁾ have shown that the dimension of the phase space which is accessible to nonequilibrium steady states is less than the ostensible dimension of the full phase space ($2dN$ for N-particle systems in d Cartesian dimensions).

This was implicit in my earlier work⁽²⁾ when I showed that the streaming density of the phase space distribution function increases at a constant average rate in the steady state,

$$\frac{1}{f}\frac{df}{dt} \equiv \Lambda = dN\alpha \tag{4}$$

I called Λ the phase space compression factor. Figure 1 is a graph of the configurational phase space for a two-particle system under shear. We see

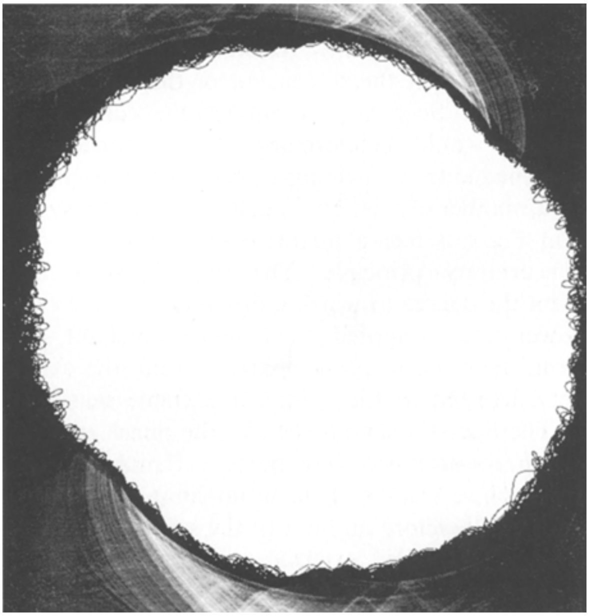

Fig. 1. The pair distribution function for the two-particle soft-disk fluid at a reduced strain rate of 1.250, a total kinetic energy of 0.25, and a density of 0.4. The run length is 20 million timesteps. One can clearly see the filamentary structure characteristic of a fractal distribution. This distribution is extremely sensitive to applied conditions. The volume of accessible phase space for this system is less than the ostensible dimension 3.

that the steady-state distribution function has contracted onto a strange attractor of dimension lower than three. The structure is extremely filamentary and is exquisitely sensitive to the precise values of the density, strain rate, etc., but is entirely independent of the initial starting point in phase space. The sensitivity of this distribution function to applied conditions is evidenced by the fact that the location of the filaments changes appreciably when the calculation is performed in single rather than double-precision arithmetic.

Since the dimension of the accessible phase space decreases to less than the ostensible $2dN$ dimensions, the volume of the accessible phase space as measured from the ostensible space is zero (e.g., the three-dimensional volume of the surface of a three-sphere is zero.) The entropy of a system is proportional to the logarithm of the accessible phase volume. Since that volume as determined from the ostensible phase space is zero, the entropy will diverge to negative infinity. These simple observations explain the divergence of entropy as computed in the ostensible space. Presumably the thermodynamic entropy should be arrived at by integrating (1) over the accessible phase space only. This would remove the apparent divergence. However, the determination of the topology of the phase space which is accessible to nonequilibrium steady states is exceedingly complex. Even the dimension of the accessible space is only known approximately. Such a program for the calculation of the nonequilibrium entropy would therefore appear quite hopeless.

The fine-grained entropy as computed from the ostensible phase space dimension has a number of further difficulties. First, if a system such as the one depicted in Fig. 1 is meant no represent argon, it is violation of the Heisenberg uncertainty principle. The uncertainty principle puts an absolute limit on the degree to which a distribution function can be fractal. There is a lower limit, imposed by Planck's constant, to the scale of features that can be found in phase space. Second, the extreme sensitivity of the filaments depicted in Fig. 1 implies extreme sensitivity to external perturbations. The finer the length scale of the phase space structures, the more sensitive those structures will be to external perturbations. If the distribution function is fractal, there is no limit to the smallness of the space structures and therefore no limit to the sensitivity of the full distribution function to uncontrolled external perturbations. In an experiment, averaging over an ensemble of possible external fluctuations would of course "wash out" the fine structure below a critical length scale. The precise cutoff value would be determined by the amplitude and spectrum of the external fluctuations. This "washing out" of fine structure provides an Ansatz for the computation of the entropy of nonequilibrium steady states.

In this paper I will describe a systematic method for computing the coarse-grained entropy of nonequilibrium steady states. The coarse graining is introduced by decomposing the Gibbs entropy (1) into terms arising from the partial distribution functions involving correlations of successive numbers of particles. I test the expansion at equilibrium and find that for densities less than $\sim 75\%$ of the freezing density, the singlet and pair contributions to the entropy appear to be accurate to more than $\sim 90\%$. If the expansion is carried out to order N, then for an N-particle system the results will be identical to the fine-grained Gibbs entropy. Away from equilibrium the expansion will consist of a series of finite terms until the dimension of the partial distribution function exceeds the dimension of the accessible phase space. Once this occurs, all succeeding terms will be infinite. The method yields finite terms below this dimension because all the lower-dimensional integrals are carried out in the accessible phase space.

I will show that away from equilibrium the method yields a finite entropy which is observed to be less than that of the equilibrium state characterized by the same density and internal energy. Away from equilibrium the thermodynamic temperature is *not* given by the equipartition kinetic value. Neither is the thermodynamic pressure given by the average diagonal element of the pressure tensor. The thermodynamic pressure is instead, within statistical uncertainties, equal to the smallest eigenvalue of the pressure tensor. Thus, the thermodynamic pressure could be related to the *minimum* work required to cause a virtual density change.

2. GREEN'S EXPANSION FOR THE ENTROPY

In 1952, Green[(6)] used Kirkwoods's factorization[(7)] of the N-particle distribution function to write an expansion for the entropy. We define z-functions in an infinite hierarchy,

$$\begin{aligned}
&\ln f_1^{(i)} \equiv z_1^{(i)} \\
&\ln f_2^{(ij)} \equiv z_2^{(ij)} + z_1^{(i)} + z_1^{(j)} \\
&\ln f_3^{(ijk)} \equiv z_3^{(ijk)} + z_2^{(jk)} + z_2^{(ki)} + z_2^{(ij)} + z_1^{(i)} + z_1^{(j)} + z_1^{(k)} \\
&\qquad\vdots
\end{aligned} \tag{5}$$

The various f-functions are the partial 1, 2, 3,...-body distribution functions. Green showed that Gibbs' fine-grained entropy can be written as an infinite series,

$$S = -k_B \left\{ \frac{1}{1!} \int d\Gamma_1 \, f_1 z_1 + \frac{1}{2!} \iint d\Gamma_1 \, d\Gamma_2 \, f_2 z_2 + \cdots \right\} \tag{6}$$

Using Eq. (5), one can easily show that the entropy per particle is given by the series

$$\frac{S}{N} = -\frac{k_B}{\rho}\int d\mathbf{p}_1 f_1(\mathbf{p}_1)\ln f_1(\mathbf{p}_1) - \frac{k_B}{2N}\iint d\Gamma_1\, d\Gamma_2\, f_2(\Gamma_1, \Gamma_2)\ln\left(\frac{f_2^{(2)}}{f_1^{(1)} f_1^{(2)}}\right) + \cdots \tag{7}$$

In deriving this equation, we have assumed that the fluid is homogeneous. This enabled a spatial integration to be performed in the first term. This equation is valid away from equilibrium. Using the fact that a equilibrium the two-body distribution function factors into a product of kinetic and configurational parts for two-dimensional fluids, we find that Eq. (7) reduces at equilibrium to

$$\frac{S}{N} = 1 - k_B \ln\left(\frac{\rho}{2\pi m k_B T}\right) - \frac{k_B \rho}{2}\int d\mathbf{r}_{12}\, g(r_{12})\ln g(r_{12}) + \cdots \tag{8}$$

where $g(r_{12})$ is the equilibrium radial distribution function. Equation (8) has been tested using experimental radial distribution function data by Wallace.(8) He found that in liquid sodium at 7 K above the melting temperature that the Green expansion for the entropy, terminated at the pair level, was accurate to within estimated statistical uncertainties of 2%. As far as I know, the Green expansion has never been tested against computer simulation data either at or away from equilibrium.

I used a simulation of 32 soft disk to test Eq. (8) truncated at the pair level. The soft-disk intermolecular potential function $\phi(r) = \varepsilon(\sigma/r)^{12}$ was used. All units were expressed in dimensionless from by expressing all quantities in terms of the potential parameters σ, ε, and the particle mass m. The potential was trincated at a reduced separation $r^* = r/\sigma = 1.5$. Table I shows some of the equilibrium data gathered for the soft-disk fluid. All units are expressed in reduced form. Each state point was generated from a 10 million-timestep simulation run using a reduced timestep of 0.002. The energy per particle is denoted e, and the total one- and two-body entropy per particle is denoted by s. The entropy was calculated by forming histograms for both $g(\mathbf{r})$ and $f(\mathbf{p})$. These numerical approximations to the distribution functions were then integrated numerically. The radial distribution function was calculated over the minimum image cell to include exactly the long-ranged contributions arising from the fact that the integral of $g(r) - 1$ is related to the compressibility in the well-known fashion.(9) The equipartition temperature corrected for $O(1/N)$ factors is denoted T_k. The thermodynamic temperature T_{th} was calculated from

Table I. Equilibrium Modurate Density Data[a]

ρ	e	s	T_k	T_{th}
0.6	1.921	3.200		
0.6	2.134	3.341	1.552	1.614
0.6	2.347	3.464		
0.625	1.921	3.034		
0.625	2.134	3.176	1.499	1.500
0.625	2.347	3.318		
0.65	1.921	2.889		
0.65	2.134	3.044	1.445	1.454
0.65	2.347	3.182		
0.675	1.921	2.754		
0.675	2.134	2.919	1.306	1.374
0.675	2.347	3.064		
0.7	1.921	2.889		
0.7	2.134	3.044	1.326	1.291
0.7	2.347	3.182		

[a] The uncertainties in the entropies are ±0.005.

Eq. (8) using the thermodynamic relation $T_{\text{th}} = (\partial e/\partial s)_V$. For each separate density the three state points were used to form a simple finite difference approximation for the midpoint derivative.

I did not use the analytical expression for the kinetic contribution to the entropy, but rather this contribution was calculated from simulation data by histogramming the observed particle velocities and numerically integrating the single-particle contribution. This numerical estimate for the kinetic contribution to the entropy was then compared to the theoretical expression (basically the Boltzmann H-function) and agreement was observed within the estimated statistical uncertainties.

By using the entropies calculated at $\rho = 0.6$, 0.7 to form a finite difference approximation to the derivative $\partial s/\partial \rho^{-1}$, one can compare the pressure calculated from the relation $p = T(\partial S/\partial V)_E$ with the virial expression calculated directly from the simulation. The virial pressure at $e = 2.134$, $\rho = 0.65$, is 3.85, whereas the pressure calculated exclusively by numerical differentiation of the entropy is 3.72 ± 0.15. The largest source of error in these calculations is likely to be in the finite difference approximation for the various partial derivatives.

3. THE NONEQUILIBRIUM ENTROPY

Away from equilibrium the main difficulty in using even the first two terms in Eq. (7) is the dimensionality of the required histograms. The nonequilibrium pair distribution function does *not* factorize into a product of kinetic and configurational parts. One has to deal with the full function of six variables for a translationally invariant two-dimensional fluid. It may be possible to expand this distribution in an appropriate set of orthogonal polynomials. In this work I decided to reduce the density to $\rho \sim 0.1$, where the configurational contributions to the entropy can largely be ignored. I evaluated the entropy of the same system of 32 soft disk as above, but now the system was subject to an isoenergetic shear flow. The equations of motion used were the SLLOD equations of motion, which are known to be exact for low-Reynolds-number shear flows,(9)

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i + \mathbf{i}\gamma y_i \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{i}\gamma p_{yi} - \alpha \mathbf{p}_i \end{aligned} \tag{9}$$

In these equations $\gamma = \partial u_x/\partial y$ is the strain rate and the momenta $\mathbf{p}_i$ are peculiar with respect to the stable low-Reynolds-number streaming velocity profile. The term $\alpha \mathbf{p}_i$ is the Gaussian thermostat. In this simulation it was used to maintain a constant thermodynamic internal energy $H_0 \equiv \sum p^2/2m + \Phi$. The internal energy is a constant of the motion if the multiplier α takes the form(10)

$$\alpha = -\frac{P_{xy}\gamma V}{\sum (p_i^2/m)} \tag{10}$$

where P_{xy} is the xy element of the pressure tensor. These equations combined with Lees–Edwards shearing periodic boundary conditions(11) enable us to simulate isoenergetic shear flow.(12)

To check the validity of the assumption that at these low densities the configurational parts of the entropy may be ignored, I performed some checks on the equilibrium thermodynamic properties of this system. Table II shows the thermodynamic temperature computed using a finite difference approximation to the derivative $\partial e/\partial s$ ($e = H_0/N$, $s = S/N$). It also shows the kinetic temperature computed using the equipartition expression. At equilibrium, the data at a reduced density of 0.1 predict a thermodynamic temperature which is in statistical agreement with the kinetic temperature, 2.12 ± 0.04 as against 2.17, respectively. The equilibrium data at $e = 2.134$, $\rho = 0.1$, give a thermodynamic pressure of 0.22, in reasonably good agreement with the virial pressure (including both kinetic and configurational components) of 0.24. The disagreement between the thermodynamic and the kinetic expressions for both the temperature and the pressure arises from two causes: first, at this low density, we are ignoring the configurational contributions to the entropy, and second, we are approximating the required partial differentials by centered, finite difference expressions.

Figure 2 shows the analogue of Fig. 1 for a 32-particle system under shear. The nonequilibrium pair distribution function is free of the singularities apparent in the two-particle system. It is smooth because for one- and two-particle distributions in systems of many particles, one averages over all possible positions and momenta for the other $N-2$ particles. This averaging "washes out" all the fine structure. These distributions, even at very high strain rates, are *not* fractal. If the Green expansion converges rapidly, we will clearly arrive at a finite value for the entropy.

Table II gives the computed kinetic contribution to the entropy as a function of energy, density, and strain rate. At low densities the increased mean free paths of particles relative to the corresponding situation in dense fluids means that considerably longer simulation runs are required to achieve an accuracy comparable to that for dense fluids. The data given in Table II are taken from 15 million-timestep simulation runs. Away from equilibrium the strain rate tends to increase the "mixing" of trajectories in phase space, so that the errors actually decrease as the strain rate is increased.

Fig. 2. The pair distribution function for the 32-particle soft-disk fluid at a relatively high reduced strain rate of 2.0. The reduced density and total energy per particle are 0.1 and 1.921, respectively. The run length is 24 million timesteps. The distribution is, as far as can be told from the simulation data, completely smooth. In spite of the high anisotropy of this distribution, the configurational contriduction to the system entropy is only about 0.4%.

For a given energy and density, the entropy is observed to be a monotonic *decreasing* function of the strain rate. As expected from thermodynamics, the equilibrium state has the maximum entropy. Although there is no generally agreed upon framework for thermodynamics far from equilibrium, it is clear that the entropy can be written as a function $S = S(N, V, E, \gamma)$. *Defining* T_{th} as $(\partial E/\partial S)_{V,\gamma}$, p_{th} as $T(\partial S/\partial V)_{E,\gamma}$ and ζ_{th} as $-T(\partial S/\partial \gamma)_{E,V}$, we can write

$$dE = T_{\text{th}}\, dS - p_{\text{th}}\, dV + \zeta_{\text{th}}\, d\gamma \tag{11}$$

Some years ago Evans and Hanley(13) proposed Eq. (11) as a generalized Gibbs relation; however, at that time there was no way of directly computing the entropy or any of the free energies. This forced Evans and Hanley to postulate that the thermodynamic temperature was equal to the equipartition or kinetic temperature $T_k \equiv 2K/(dNk_B)$ for systems in d dimensions. For reasons of convenience the kinetic temperature has been universally used by computer simulators in studies of nonequilibrium systems.(14)

Evans and Hanley(13) observed that away from equilibrium, although the pressure tensor is anisotropic, the thermodynamic pressure must be independent of the manner in which a virtual volume change is performed. The thermodynamic pressure must therefore be a scalar. They assumed that the thermodynamic pressure would be equal to "the simplest scalar invariant of the pressure tensor" that was also consistent with equilibrium thermodynamics. In two-dimensional systems they assumed $p = (P_{xx} + P_{yy})/2$.

Since we can now calculate the coarse-grained Gibbs entropy directly, we can check the correctness of these postulates. We only assume that the internal energy is given by the sum of the peculiar kinetic energy and the potential energy, that we know the system volume and strain rate, and that the thermodynamic entropy is equal to the coarse-grained Gibbs entropy, which at low densities can be approximated by the first term of Eq. (7). Table II shows a comparison of kinetic and thermodynamic temperatures for the 32-particle soft-disk system.

As has been known for some time,(10) $(\partial T_k/\partial \gamma)_{V,E}$ is negative, leading to a decrease in the kinetic temperature with increasing strain rate. For this low-density system the effect is far smaller than has been seen for moderately dense systems.(10) At a density of 0.1 the kinetic temperature drops by 0.3% as the shear rate is increased to unity. The precision of the kinetic temperature for these runs is about 0.01%. The thermodynamic temperature also decreases as the strain rate is increased, but in a far more dramatic fashion. It decreases by 10% over the same range of strain rates. The results clearly show that away from equilibrium the thermodynamic

Table II. Low-Density Data[a]

ρ	γ	e	s	T_k	T_{th}
0.075	0.0	2.134	6.213		
0.1	0.0	1.921	5.812		
0.1	0.0	2.134	5.917(27)	2.175	2.12(6)
0.1	0.0	2.346	6.013		
0.125	0.0	2.134	5.686		
0.075	0.5	1.921	5.744		
0.075	0.5	2.134	5.852	2.190	2.088
0.075	0.5	2.347	5.948		
0.1	0.5	1.921	5.539		
0.1	0.5	2.134	5.653	2.171	2.048
0.1	0.5	2.346	5.747		
0.125	0.5	1.921	5.369		
0.125	0.5	2.134	5.478	2.153	2.088
0.125	0.5	2.347	5.573		
0.075	1.0	1.921	5.380		
0.075	1.0	2.134	5.499	2.188	1.902
0.075	1.0	2.347	5.604		
0.1	1.0	1.921	5.275		
0.1	1.0	2.134	5.392	2.169	1.963
0.1	1.0	2.346	5.492		
0.125	1.0	1.921	5.157		
0.125	1.0	2.134	5.267	2.149	2.019
0.125	1.0	2.347	5.368		

[a] Away from equilibrium the uncertainties in the entropy are ± 0.005.

Table III. Nonequilibrium Pressure[a]

γ	p_{th}	p_{tr}	p_1	p_2
0.0	0.215(7)	0.244	0.244	0.244
0.5	0.145	0.245	0.361	0.130
1.0	0.085	0.247	0.397	0.096

[a] $e = 2.134$, $\rho = 0.1$.

temperature is smaller than the kinetic or equipartition temperature. As the strain rate increases, the discrepancy grows larger.

Using the simulation data at $e = 2.134$, one can estimate the thermodynamic pressure as a function of strain rate. Table III shows the finite difference approximation for the thermodynamic pressure p_{th}, the "hydrostatic pressure" $p_{\mathrm{tr}} = (P_{xx} + P_{yy})/2$, and the largest and smallest eigenvalues of the pressure tensor p_1 and p_2, respectively. As expected, the hydrostatic pressure increases with shear rate. This effect is very slight at these low densities. This effect is known as shear dilatancy. The thermodynamic pressure shows a much larger effect, but in *decreases* as the strain rate is increased. In an effort to give a mechanical interpretation to the thermodynamic pressure, I calculated the two eigenvalues of the pressure tensor. Away from equilibrium, the diagonal elements of the pressure tensor differ from one another and from their equilibrium values; these are termed normal stress effects. The eigenvalues are influenced by all the elements of the pressure tensor, including the shear stress. One of the eigenvalues increases with strain rate, while the other decreases, and within statistical uncertainties the latter is equal to the thermodynamic pressure.

I conjecture that the thermodynamic pressure is equal to the minimum eigenvalue of the pressure tensor, $p_{\mathrm{th}} = p_2$. This relation is exact at equi-

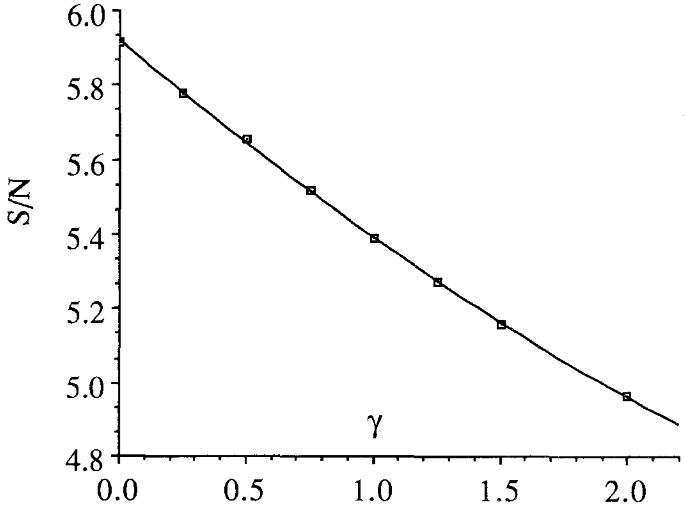

Fig. 3. The kinetic contribution to the system entropy as a function of strain rate. The system density is 0.1 and the energy per particle is 2.134. Within the accuracy of the data the entropy is essentially a linear function of strain rate. The derivative of entropy with respect to strain rate gives ζ/T. The ζ is positive, but decreases with strain rate, mostly due to the decrease in the thermodynamic temperature with increasing strain rate.

librium and is in accord with the numerical results. It is also clear that if the entropy is related to the minimum reversible work required to accomplish a virtual volume change in a nonequilibrium steady-state system, then $p_2\,dV$ is the minimum pV work that is possible. If one imagines carrying out a virtual volume change by moving walls inclined at arbitrary angles with respect to the shear plane, then the minimum virtual pV work (minimized over all possible inclinations of the walls) will be $p_2\,dV$.

Figure 3 shows the kinetic contribution to the entropy as a function of strain rate for the 32-particle system at an energy $e = 2.134$ and a density $\rho = 0.1$. The entropy seems to be a linear function of strain rate for the range of strain rates covered by the simulations. Combining these results with those from Table II allows us to compute ζ_{th} as a function of strain rate. For $\gamma = 0.0$, 0.5, and 1.0 one finds that $\zeta_{\text{th}}/N = 1.22$, 1.08, and 0.91, respectively. Most of the decrease in ζ is due to the decrease in the thermodynamic temperature with increasing strain rate. I have assumed that asymptotically s is linear in strain rate as the strain rate tends to zero. It is always possible that at strain rates which are too small for us simulate, this linear dependence gives way to a quadratic variation. This would not be inconsistent with the present observations and would lead to $\zeta = 0$, at equilibrium.

4. CONCLUSION

Although these calculations are restricted to the low-density gas regime, the results suggest that a sensible definition for the nonequilibrium entropy can be given. The definition based on Eq. (7) avoids the divergences inherent in the fine-grained entropy due to the contraction of the nonequilibrium phase space. At low densities the present entropy reduces to the Boltzmann entropy given by the Boltzmann H-function. The present entropy is, for states of a specified energy and density, a maximum at equilibrium.

Defining a temperature on the basis of this entropy indicates that far from equilibrium there is no reason to expect that the equipartition or kinetic temperature is equal to the thermodynamic temperature. Similarly, there seems to be no reason to expect that the average of the diagonal elements of the pressure tensor will be equal to the thermodynamic pressure far from equilibrium. The concept of minimum reversible virtual work, together with the present numerical results, suggests that the thermodynamic pressure is instead equal to the minimum eigenvalue of the pressure tensor.

One can form an exact fluctuation expression for our nonequilibrium entropy. In the low-density regime one can use the exact transient time correlation function formalism⁽¹⁶⁾ to show that the single-particle velocity distribution is related to transient correlations of the equilibrium stress, $-P_{xy}(0)$ and the transient probability that at a time s, a particle had a momentum $\mathbf{p}$:

$$f_{\text{ss}}(\mathbf{p}) = f_{\text{eq}}(p)\left[1 - \beta\gamma V \int_0^\infty ds\, P_{xy}(0)\, f(s; \mathbf{p})\right] \tag{12}$$

In this equation f_{SS} is the steady-state single-particle distribution function. It is equal to the limit as $s \to \infty$ of $f(s; \mathbf{p})$. Here f_{eq} is the initial equilibrium Maxwell–Boltzmann distribution with Boltzmann factor $\beta = 1/k_{\text{B}}T$ [note: $f(s=0; \mathbf{p}) = f_{\text{eq}}$]. Equation (12) may be substituted into the first term of (7) to give an exact expression for the low-density entropy. It can then be used to compute various interrelationships between entropy derivatives.

In future work I plan to examine whether the entropy as defined here is a local maximum in nonequilibrium steady states. If this can be satisfactorily demonstrated, one will have for the first time a fundamental basis for a generalized thermodynamics of steady states far from equilibrium.

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