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Thermodynamic second law in irreversible processes of chaotic few-body systems

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Irreversible processes of few hard-ball (N) mechanical systems are investigated numerically and compared with the theoretical results of quasistatic processes. The thermodynamic second law is valid for $N \geqslant 2$ for both equilibrium and nonequilibrium systems if the average ensemble of the large number of identical systems is taken.

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The problem of ergodicity for low-dimensional chaotic systems has attracted continual interest in the several recent decades. The fundamental significance of this problem is that it builds up a bridge from mechanics to statistical physics [1–6]. Very recently, the investigation in this regard has focused on exploring the statistical properties and thermodynamic quantities of few-body ergodic chaotic systems, and on examining the thermodynamic second-law (TSL) in equilibrium states [7,8]. However, to our knowledge, a problem of great importance for statistical physics and thermodynamics, the TSL in irreversible processes of purely mechanical few-body systems, has never been studied. In this Rapid Communication we focus our attention on studying the TSL in irreversible processes of few-body chaotic systems. By numerical investigations, we find that the TSL is valid in these cases if fluctuations, which are inevitable for few-body systems, can be eliminated by ensemble average.

We consider a physical system, the motion of N identical and distinguishable classical hard balls of radius r and mass m in a box [a rectangle in two-dimensional (2D) space or a cuboid in three-dimensional (3D) case]. The balls interact elastically with each other and with the boundaries of the box. The Hamiltonian reads $H=\Sigma_{i=1}^{N} p_i^2/2m$, $p_i^2=p_{ix}^2+p_{iy}^2$ and $p_i^2=p_{ix}^2+p_{iy}^2+p_{iz}^2$ for 2D and 3D motions, respectively. It is emphasized that these systems are practically important and realistic. They are well-known as gas systems for $N \geqslant 1$, and as typical chaotic and ergodic systems in few-body ($N \geqslant 2$) cases [9–13]. Therefore, various statistical and thermodynamic quantities can be computed analytically in equilibrium. Before considering irreversible processes, we first study the behavior of entropy for N-particle systems in equilibrium case. For instance, in 2D two-body cases we can give explicit expression of entropy as

$$
\begin{aligned}
S_2(2) &= \ln Z_2(2) + \text{const} \\
&= 2\ln E + \ln\Big[{L_1}^2 {L_2}^2 - \pi(2r)^2 L_1 L_2 + \frac{4}{3}(L_1+L_2) \\
&\quad \times (2r)^3 + \left(\pi - \frac{11}{3}\right)(2r)^4 \Big] + \text{const}, \qquad (1)
\end{aligned}
$$

where E is the energy of the system, L_1+2r and L_2+2r are the lengths of two edges of the rectangle.

For 2D systems with large N and for 3D systems with $N \geqslant 2$, the expression of entropy becomes tedious (though no principal difficulty exists for computations). However, because of ergodicity it is easy to analytically predict the general form of the entropies for arbitrary N-particle systems. For the 2D case with N particles, we have

$$S_N(2) = N \ln E + \ln f(L_1, L_2, N, r) + \text{const}, \qquad (2a)$$

$$E = A f^{1/N} e^{S_N(2)/N}. \qquad (2b)$$

In 3D case we have

$$S_N(3) = \frac{3}{2} N \ln E + \ln g(L_1, L_2, L_3, N, r) + \text{const}, \qquad (3a)$$

$$E = B g^{2/(3N)} e^{2S_N(3)/(3N)}, \qquad (3b)$$

where the constants A and B and functions f and g can be easily determined numerically in a certain equilibrium process, i.e., in an adiabatic process.

For investigating irreversible (nonequilibrium) processes, we move the right boundary of the system L_1 as $L_1(t) = L_{10} - ut$ with all other boundaries of the system fixed. Then after each collision between a particle and the moving wall, the particle's velocity is reset to

$$\overline{v_\parallel} = v_\parallel, \quad \overline{v_\perp} = -v_\perp - 2u, \qquad (4)$$

where v and $\overline{v}$ are the velocities of the given particle before and after the collision, respectively; $v_\perp$ and $\overline{v_\perp}$ are the velocity components perpendicular to the wall in the collision, while $v_\parallel$ and $\overline{v_\parallel}$ are the parallel ones.

First, we let $u \to 0$, i.e., we deal with the quasistatic (reversible, or equilibrium) adiabatic process. All solid lines in Fig. 1(a) are numerical simulations of quasistatic compression processes (for $N=2$ and $u=0.05 \ll 1$) for three different entropy values, and squares, circles, and triangles are theoretical predictions of the equal-entropy curves of Eq. (1) for the corresponding entropies, respectively. The numerical experiments fit the analytic results perfectly. For large N we do not have full analytical forms of the entropy. However, all the equal-entropy curves can be drawn semianalytically according to Eq. (2). In Fig. 1(b) we perform a quasistatic

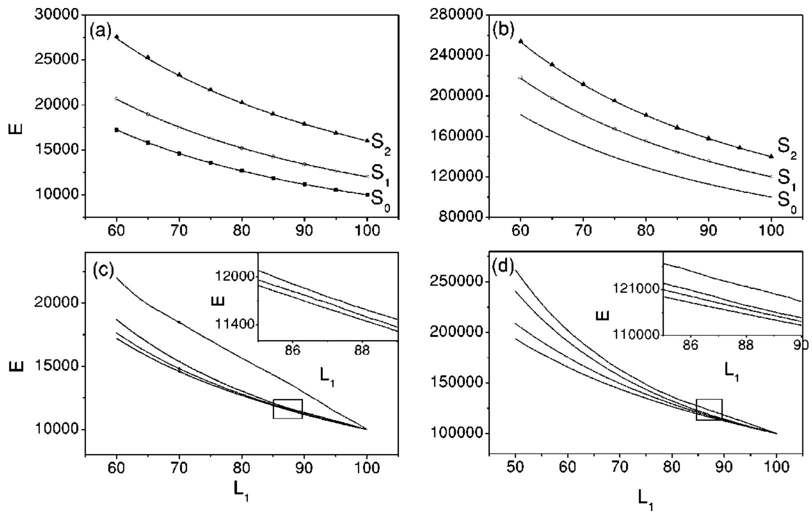

FIG. 1. $L_2=100$. (a) $r=10$. Equal-entropy curves in E-L_1 plane for the 2D-two-body system for different entropies. The squares, circles, and triangles represent the theoretical predictions, and the solid curves plot the numerical quasistatic adiabatic compression processes, with $u=0.05$. The initial energy of S_0 curve is 1×10^4 and $S_1=S_0+0.4463$, $S_2=S_0+0.9400$. (b) $r=5$. The initial energy of the S_0 curve is 1×10^5, and $S_1=S_0+3.6464$, $S_2=S_0+6.7294$. Equal-entropy curves for the 2D system with 20 balls. All solid curves S_0-S_2 are drawn by quasistatic adiabatic compressing $(u=0.1)$. Circles and triangles are predicted from the curve S_0 and the formula from Eq. (2) for the corresponding entropies as $E_i(L,S)=E(L,S_0)e^{S_i-S_0}$, $i=1,2$. (c) $r=10$. Different lines represent compression processes of the 2D-two-body system for various u from a given pair of $(E,L_1)(u=0.05,\ 2,\ 10,$ and 50 for different lines from the lowest one). The inset is the blowout of the blocked part of the figure. (d) The same as (c) with $r=5$, $N=20$ ($u=0.1,\ 1,\ 5,$ and 20 for different lines from the lowest one).

compression process for $N=20$ to draw an equal-entropy curve (curve S_0) numerically. Then, starting from the curve S_0, we compute all equal-entropy curves for different S's according to the analytic form of Eq. (2). For instance, the circles and triangles in Fig. 1(b) represent the equal-entropy curves for $S_1=S_0+3.6464$, $S_2=S_0+6.7294$, respectively, which are theoretically predicted from curve S_0 and Eq. (2). Then we numerically perform the quasistatic compression processes and plot all these equal-entropy curves S_1 and S_2 in Fig. 1(b) by solid curves. We find again that the predictions (circles and triangles) coincide with numerical results (solid curves) very well.

At finite u the process becomes irreversible. Let us denote the energy increase in a process by $\Delta E=E(t)-E(t_0)$. According to the TSL, we expect $\Delta E_i>\Delta E_e$, where ΔE_i and ΔE_e are the energy increases in irreversible and quasistatic processes, respectively, for the same volume change [i.e., for the same $\Delta L=L(t)-L(t_0)$]. In Figs. 1(c) and 1(d) we plot the E-L_1 curves of the adiabatic compression processes of 2D systems for various u's for $N=2$ and $N=20$, respectively. In these figures, an average of 10^5 numerical data from different initial conditions is used for each plot, and at $L=L_0$ we run the system for long time before $t=0$ to ensure that the initial ensembles are prepared in equilibrium when each reversible or irreversible processes started.

Two features are clearly shown in Figs. 1(c) and (d). First, all curves for $u>0$ are above the corresponding equal-entropy curves (the lowest line). Second, a curve with larger u is always above the curves with smaller u. There isn't any intersection between these curves. These features strongly suggest that entropy production in irreversible processes must be positive, and stronger irreversible processes have larger entropy production rates (note, for any given L_1, larger E corresponds to larger entropy when equilibrium is reached). All these observations fully agree with the TSL in both equilibrium and nonequilibrium processes, though the systems have only two particles.

By irreversible process, we mean that the state in the process is in nonequilibrium. However, for a few-body (e.g., two-body) system, how can one distinguish equilibrium and nonequilibrium states, since any state of a given system must be strongly nonequilibrium? A clear answer to this problem can be found by using the ensemble statistical distribution. Let us consider the three states indicated by dots in Fig. 1(c). In Fig. 2(a) we plot the theoretical prediction of equilibrium probability distribution $P(v)$ versus absolute velocity $v=\sqrt{v_x^2+v_y^2}$ by the solid line, and plot the ensemble distribution for the adiabatic quasistatic compression process by dots (the lowest dot in Fig. 1(c), 60 000 samples are used for the probability computation). It is found that the dots follow the theoretical curve satisfactorily, then the equilibrium state is indeed realized in the quasistatic process. In Figs. 2(b) and 2(c) we do the same as Fig. 2(a), with the two upper dots in Figs. 1(c) computed. It is obvious that the probability distributions for finite u's deviate from equilibrium distribution considerably, and larger u produces stronger deviation and then indicates stronger irreversibility.

In all the above simulations of irreversible processes, we applied the ensemble average of a large number of identical systems to make the curves smooth. For the small ensemble, fluctuations become inevitable. A detailed study of fluctuations is extremely useful for understanding the nature of the TSL in few-body systems. In Fig. 3 we consider the 2D-two-body system, and compress our system from L_1+2r to $L_1/2+2r$ for various u, and then plot ΔS versus u, where ΔS is the entropy difference between the final state and the ini-

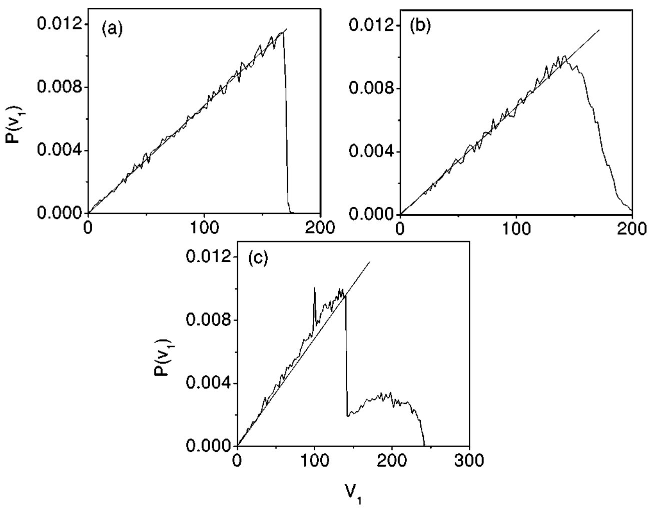

FIG. 2. (a) Plots: the velocity distribution of a given particle $P(v_1)$ ($v_1 = \sqrt{v_{1x}^2 + v_{1y}^2}$) for adiabatic compressing at the lowest dot in Fig. 1(c). 60 000 runs have been taken for computing the probability. The straight line shows the theoretical prediction of the equilibrium probability distribution for the given (E, L_1). (b), (c) The same as (a) with the dots in the $u = 2$, and $u = 50$ curves, respectively, in Fig. 1(c) being considered.

tial state. In Fig. 3(a) we average the results by $M = 5$ runs and large fluctuations are observed. We observe that the TSL can be broken for many plots, i.e., ΔS can be negative after these adiabatic compressions, and ΔS's for a larger u can be smaller than those for a smaller u. In Figs. 3(b) and 3(c), we do the same as Fig. 3(a) by averaging more runs. As the number of averaging runs M increases, the fluctuations become increasingly weaker and the number of events breaking the TSL becomes less. In Fig. 3(d) all plots obey the second law as 2000 averaging runs are taken.

By increasing the number of particles of the system, we can effectively reduce fluctuations. In Figs. 4(a)-4(c) we do

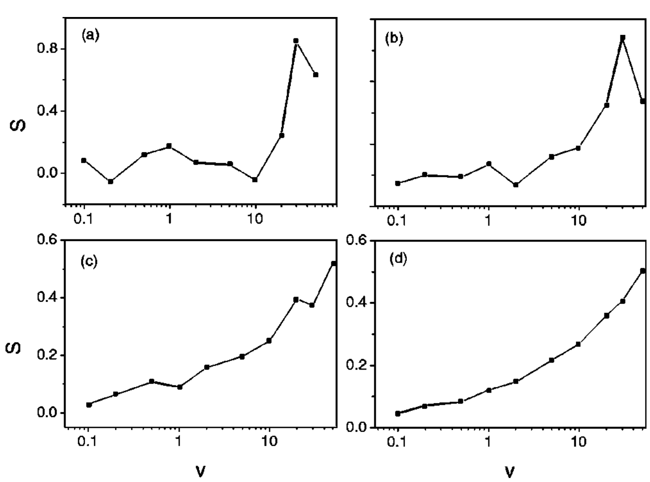

FIG. 3. $r = 10$, $L_2 = 100$. Entropy increases during the adiabatic compressing processes of the 2D-two-body system vs u. (a) Average of $M = 5$ runs is taken. (b), (c), and (d) The same as (a) with $M = 50$, 500, and 2000 are taken, respectively. In (d) the TSL is valid without exception.

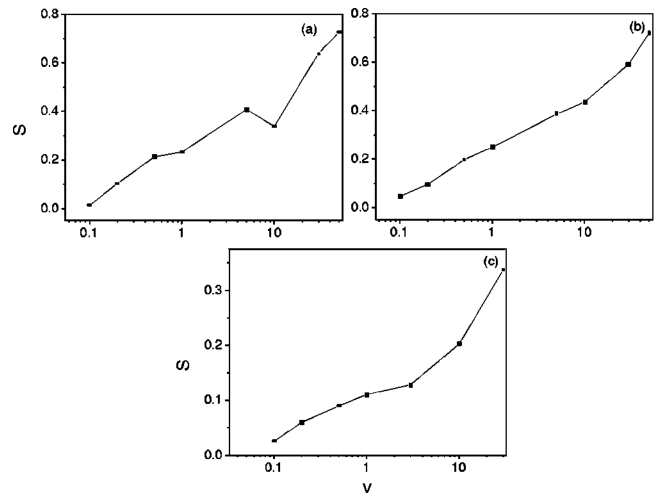

FIG. 4. $L_2 = 100$. (a), (b) The same as Fig. 3 with $N = 20$, $r = 5$. (a) $M = 5$ (b) $M = 20$. (c) The same as Fig. 3 with $N = 500$, $r = 1.6$, and $M = 1$.

the same as Figs. 3 with N replaced by $N = 20$ [(a) and (b)], and $N = 500$ [(c)], respectively. In Fig. 4(a) we apply $M = 5$. Though some events can still fluctuate to break the TSL, the number of these events is considerably reduced in comparison with $N = 2$ for the same M. As $M = 20$, we can already eliminate the event breaking TSL in $N = 20$ case [Fig. 4(b)]. For sufficiently large N ($N = 500$ in our case), we can observe that all the plots of a single system can perfectly follow the TSL [see Fig. 4(c)] in our precision, then self-averaging plays role for such a large number of particles.

In all the above discussions, we considered systems that are ergodic and chaotic for static boundaries. We have shown that the TSL is valid for both reversible and irreversible processes. It is emphasized that any ergodic system must satisfy the TSL in a reversible process, whether chaotic or nonchaotic, but it is interesting to point out that a nonchaotic system ergodic in the static vessel may not satisfy the TSL in irreversible processes. Let us consider a one-particle system in a 1D system of length L_0, where the particle moves freely in the space and collides with the two boundaries elastically (note, the radius of the particle is now an irrelevant parameter). This system is obviously ergodic while nonchaotic. In this case, the entropy of the equilibrium state $S_1(1) = \ln 2\sqrt{2E/m}L + \text{const}$, and for the quasistatic adiabatic compression, the energy of the system is $E = E_0 L_0^2/L^2$. Then the entropy of the system during the compression is $S_1(1) = \ln 2\sqrt{2E_0 L_0^2/m}$, which keeps constant following the TSL. In Fig. 5, we numerically compute adiabatic quasistatic compression the same as Figs. 1(c) and 1(d), starting from an ensemble of uniform distribution in the space, and obtain the E-L curve S_0, which coincides with the analytic results perfectly. The TSL is thus valid indeed for a reversible process even though the system is nonchaotic. The E-L curve for finite u can also analytically calculated. Here we will not give the explicit form, which is a bit complicated, rather we present the results of numerical computation of some adiabatic compressions in Fig. 5, where the E-L curves of $u = 10$ and $u = 20$ are presented by dash-dot line and dot line.

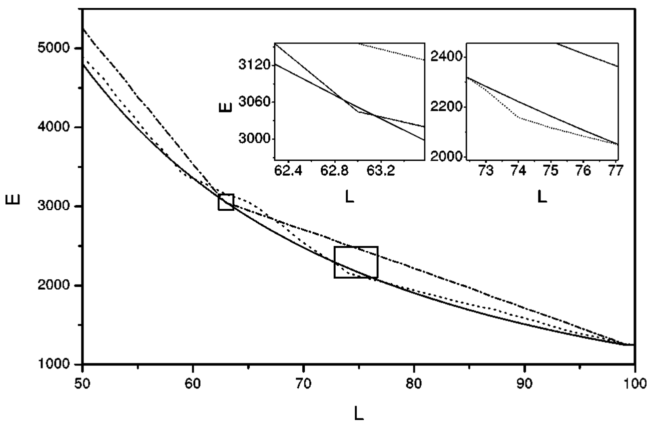

FIG. 5. The same as Fig. 1(c) with 1D and the one-particle system is considered. $L_0=100$, $E_0=2500$. The curve S_0 (the solid line in the figure) represents a quasistatic process, which is an equal-entropy curve for the ergodic system; dash-dot line and dot line are the curves of $u=10$ and $u=20$, respectively. Violation of the TSL is clearly seen for the curves of finite u's.

We find that, ΔE_i's are not always greater than ΔE_e's, thus the TSL is violated. Moreover, ΔE_i for larger u can be smaller than that of smaller u, which is also against the TSL. Though we cannot tell the precise conditions for the validity of the TSL in few-body systems, it is definitely known from Fig. 5 that ergodic and nonchaotic systems satisfying the TSL in reversible processes may not obey the TSL in irreversible processes.

In conclusion, we find that the TSL is valid in irreversible processes of chaotic ergodic few-hard-ball systems. This validity is disregarding the number of particles of the system. As the number of particles of the system is small, an average ensemble of many identical systems is necessary for eliminating fluctuations and explaining the TSL. By increasing the number of particles of the system, we can considerably reduce fluctuations. For the thermodynamic limit $N\to\infty$, we can surely anticipate negligibly small fluctuations and the validity of the TSL in the conventional sense, i.e., validity for a single system. Therefore a bridge from the TSL for chaotic few-body mechanical systems to that for usual thermodynamic system in irreversible processes is clearly built up for our systems. We have checked the above conclusions by considering both 2D and 3D systems and by varying the number and the radius r of particles, and also by changing u from positive to negative, etc., in all numerical experiments the TSL is definitely valid. We were able to check the TSL in purely mechanical (no thermo-reservoir is involved) few-body systems in irreversible processes (i.e., for the inequality of the TSL).

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