Mixing, Lyapunov instability, and the approach to equilibrium in a hard-sphere gas

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We present maximum Lyapunov exponents λ_1 and related Kolmogorov-Sinai entropies h_{KS} for a gas of hard spheres at various densities. The time scales defined by λ_1 and h_{KS} are compared with the collision time, the decay time of typical autocorrelation functions, and the relaxation time of a one-particle distribution. At low densities the Lyapunov time $\tau_\lambda \equiv 1/\lambda_1$ is much smaller than the collision time τ_c, whereas at high densities we find $\tau_\lambda \gg \tau_c$. We discuss consequences for kinetic theory and numerical simulations. The mixing properties in phase space are investigated for the two-dimensional Lorentz gas. It is numerically verified that the Kolmogorov-Sinai time $\tau_{KS} \equiv 1/h_{KS}$ is the characteristic time for this relaxation process. [S1063-651X(97)50301-1]

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Mixing in phase space is a necessary condition for the relaxation of a nonequilibrium state towards equilibrium and therefore for statistical mechanics to apply [1]. Due to the exponential instability characterized by a positive Kolmogorov-Sinai entropy h_{KS}, a number of initially close phase points are eventually uniformly distributed over the energy surface. The characteristic time for this mixing process in phase space is the Kolmogorov-Sinai time $\tau_{KS} = 1/h_{KS}$ [2,3]. In order to relate this time to the typical relaxation time of a nonequilibrium state and to decay times of equilibrium autocorrelation functions, we performed a series of relaxation experiments on a hard sphere gas. Such experiments were pioneered by Alder and Wainwright in 1958 [4], and repeated by several authors since then [5,6].

Consider a system of N identical smooth hard spheres with diameter σ and mass m prepared with velocities equal in magnitude but pointing in random directions. We monitor the time evolution of this nonequilibrium state by computing the reduced single-particle distribution $f(p,t)$ of the magnitude $p = |\mathbf{p}|$ of the momenta. $f(p,t)$ is obtained as an average over 1000 runs with different initial conditions. Starting from the δ distribution at time $t=0$, $f(p,t)$ converges towards the equilibrium Maxwell-Boltzmann distribution $f_0(p)$. To describe the relaxation of this nonequilibrium state we use

$$H(t) = \int_0^\infty f(p,t) \ln f(p,t)\, dp, \tag{1}$$

which is similar to Boltzmann's H function. However, Boltzmann's original H function involves the full one-particle distribution function $f(\mathbf{p},\mathbf{q},t)$.

Figure 1 shows $\Delta H \equiv H(t) - H_0$ as a function of t/τ_c for 108 hard spheres at different densities $\rho \equiv N/V$ ranging from $\rho = 0.0001\sigma^{-3}$ to $\rho = 1\sigma^{-3}$, where τ_c is the mean time between collisions of an individual particle. $H(t)$ converges monotonically towards its equilibrium value H_0. For all densities $\Delta H(t/\tau_c)$ has a universal behavior. Thus, at all densities, the collision time τ_c, which is also the decay time of a typical autocorrelation function, can be regarded as the relaxation time of this system.

We now turn to the question of how this relaxation rate is related to the maximum Lyapunov exponent and the Kolmogorov-Sinai entropy per particle. Krylov [2,3] envisioned that a little phase volume $\Delta\Gamma_0$ after a time t will be spread over a region with a volume $\Delta\Gamma_t = \Delta\Gamma_0 \exp(h_{KS} t)$. Thus, after a time

$$t_0 = \frac{1}{h_{KS}} \ln \frac{1}{\Delta\Gamma_0} \tag{2}$$

$\Delta\Gamma_t$ is of order 1, and the initial phase droplet is spread over the whole phase space. Therefore, one might expect typical relaxation times to be proportional to $1/h_{KS}$. It will be shown in the following that this is not the case for the relaxation of the nonequilibrium state described above.

Figure 2 shows the maximum Lyapunov exponent λ_1, the Kolmogorov-Sinai entropy per particle h_{KS}/N and the collision rate $\nu \equiv 1/\tau_c$ as a function of ν over a wide range of densities for 108 hard spheres in a cubic simulation box with periodic boundary conditions. λ_1, h_{KS}, and ν are all measured in units of $(K/m\sigma^2 N)^{1/2}$, where K is the total kinetic energy of the system. The Lyapunov exponents and the Kolomogorov-Sinai entropy are computed with a recently developed variant of the standard algorithm of Benettin [7–9].

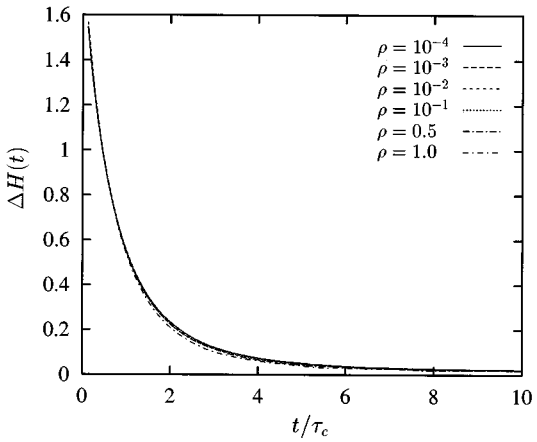

FIG. 1. $H(t) - H_0$ as a function of t/τ_c for a 108-sphere system. The densities range from $\rho = 10^{-4}\sigma^{-3}$ to $1\sigma^{-3}$. Each curve is obtained by averaging over 1000 runs with different initial conditions.

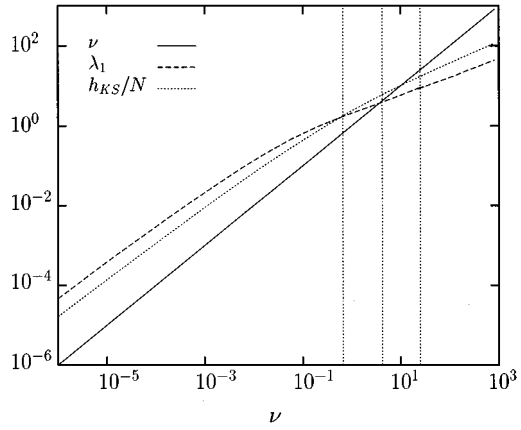

FIG. 2. ν, λ_1, and h_{KS}/N as a function of the collision rate for the 108-particle system. The vertical dotted lines denote the densities $\rho=0.1\sigma^{-3}$, $0.4\sigma^{-3}$, and $1\sigma^{-3}$. All quantities are given in units of $(K/m\sigma^2N)^{1/2}$.

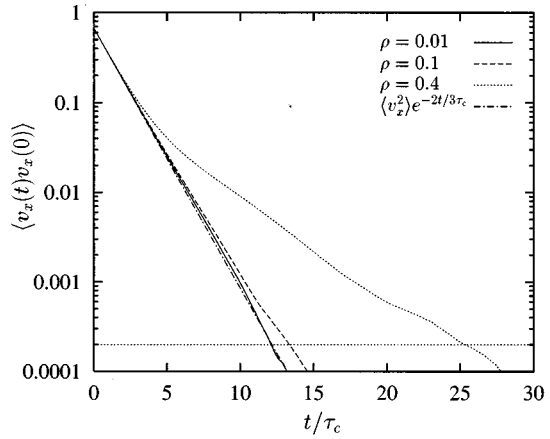

FIG. 3. Velocity autocorrelation function of the 108-particle system as a function of t/τ_c for the densities $\rho=0.01\sigma^{-3}$, $0.1\sigma^{-3}$, and $0.4\sigma^{-3}$. The horizontal dotted line denotes the numerical noise level. The autocorrelation functions are given in units of K/Nm.

The most striking feature of these curves is a crossover between λ_1 and ν in the region of intermediate densities. At high densities both λ_1 and h_{KS}/N are smaller than ν, whereas at low densities λ_1 and h_{KS}/N are much larger than ν. In the low-density limit the collision time τ_c is inversely proportional to the density ρ, the maximum Lyapunov exponent λ_1 is proportional to $|\rho\log\rho|$, and the ratio of Lyapunov to collision times becomes

$$\frac{\tau_\lambda}{\tau_c}\propto\frac{1}{|\log\rho|}. \tag{3}$$

Hence, τ_λ can become arbitrarily small with respect to the collision time. The same is true for $\tau_{KS}=1/h_{KS}$ [9]. For high densities we found [9] that the maximum Lyapunov exponent is proportional to ν^b with $b\approx0.46$, and

$$\frac{\tau_\lambda}{\tau_c}\propto\frac{\nu}{\nu^b}\approx\nu^{0.54}. \tag{4}$$

Thus, we find the two limits

$$\lim_{\rho\to0}\frac{\tau_\lambda}{\tau_c}=0,\quad \lim_{\rho\to\rho_{cp}}\frac{\tau_\lambda}{\tau_c}=\infty, \tag{5}$$

where ρ_{cp} is the density of close packing. Although a positive Kolmogorov-Sinai entropy is crucial for the relaxation of a nonequilibrium state, it follows from Eq. (5) that neither λ_1 nor h_{KS} can be regarded as the rate with which the system evolves towards equilibrium.

The Lyapunov time τ_λ is a measure for the time the system needs to forget its past. Correspondingly, h_{KS} measures the rate at which information is produced. If τ_λ and τ_{KS} are much smaller than the average collision time, subsequent collisions are uncorrelated and the assumption of molecular chaos is valid. Thus, $\tau_\lambda\ll\tau_c$ marks the range of validity of lowest-order kinetic theory (disregarding correlated collisions).

As a check of this idea we calculated the velocity autocorrelation function $c(t)\equiv\langle v_x(0)v_x(t)\rangle$ for different densities and considered its deviation from exponential behavior. In Fig. 3 $c(t)$ is shown for the densities $\rho=0.01\sigma^{-3}$, $0.1\sigma^{-3}$, and $0.4\sigma^{-3}$, specially marked by the vertical lines in Fig. 2, as a function of t/τ_c. The respective ratios of the Lyapunov time to the collision time are $\tau_\lambda/\tau_c=0.12,0.38$, and 1.07. For comparison, the Enskog-form of the velocity autocorrelation function, $c(t)=\langle v_x^2\rangle e^{-2t/3\tau_c}$ [10], is shown too. The horizontal dotted line denotes the numerical noise level $\sqrt{2\tau_v/3Nt_{run}}$, where $\tau_v=\int_0^\infty\langle v_x(t)v_x(0)\rangle dt/\langle v_x^2\rangle$, and t_{run} is the total simulation time [11]. For $\rho=0.01\sigma^{-3}$ and $0.1\sigma^{-3}$ the deviation from exponential behavior is small. For $\rho=0.4\sigma^{-3}$, for which $\tau_\lambda/\tau_c=1.07$, $c(t)$ has a long-time tail and is exponential only for short times. Thus, $c(t)$ is purely exponential only if $\tau_\lambda\ll\tau_c$, which means that the velocity of a particle is completely decorrelated before it collides again. On the other hand, if $\tau_\lambda\geqslant\tau_c$, correlations persist over many collisions and long-time tails appear.

Next we address the question whether the Lyapunov instability limits the time for which autocorrelation functions can be accurately computed. Consider again the velocity autocorrelation function $c(t)$. An initial error ϵ_0, due to an inaccuracy of the integration algorithm or to computer roundoff, is amplified after a time t to $\epsilon_t\sim\epsilon_0\exp(\lambda_1 t)$. It is tempting to assume that $c(t)$ becomes unreliable if ϵ_t becomes of order one. For a typical roundoff error $\epsilon_0\approx10^{-15}$ with 64-bit floating point numbers [12] this happens after $t\sim35/\lambda_1$. In Fig. 4 we show $c(t)$ as a function of t/τ_λ. Again the horizontal dotted line marks the numerical noise level. For $\rho=0.1\sigma^{-3}$ and $0.4\sigma^{-3}$ $c(t)$ decreases below the noise level before the critical time $t\sim35/\lambda$ is reached. However, no indication of the Lyapunov instability is observed for $\rho=0.01\sigma^{-3}$, even for times much longer than $35/\lambda$. To understand this behavior we note that in the dilute gas the collision times of an individual particle are distributed exponentially and very long straight paths are possible [13]. Over the whole free path the velocities of the particles are completely correlated and are not affected by the Lyapunov in-

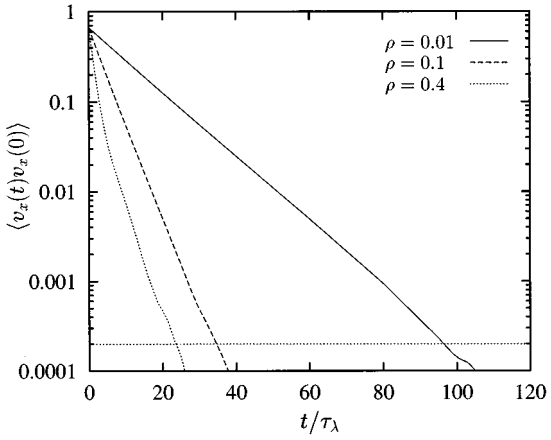

FIG. 4. Velocity autocorrelation function of the 108-particle system as a function of t/τ_λ for the densities $\rho=0.01\sigma^{-3}$, $0.1\sigma^{-3}$, and $0.4\sigma^{-3}$. The horizontal dotted line denotes the numerical noise level. The autocorrelation functions are given in units of K/Nm.

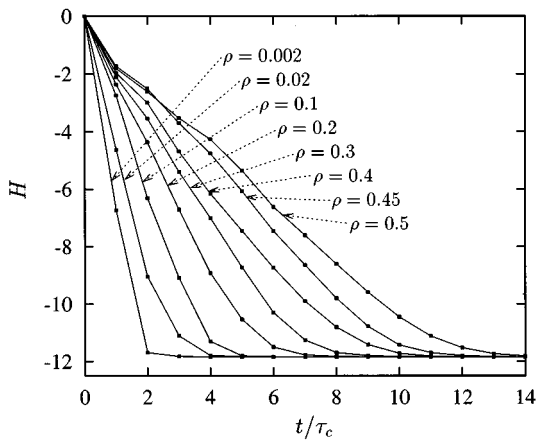

FIG. 5. H function for the two-dimensional Lorentz gas as a function of t/τ_c at various densities.

stability of the system, because the only source of chaos are the elastic hard collisions. After time t a certain fraction of the particles have not yet collided again and their velocities are still completely correlated with their initial velocities. These particles contribute to the nonvanishing value of $c(t)$ even if $t \gg \tau_\lambda$. *Hence, τ_λ does not limit the time for which $c(t)$ can be accurately computed for systems with hard interactions.*

So far we have considered the relaxation of a *nonequilibrium single-body distribution* of a many-body system towards equilibrium. What is the relevant relaxation time for a *many-body distribution* $f(\{\mathbf{p}_i\},\{\mathbf{q}_i\},t)$ or, equivalently, the mixing time in phase space? The numerical answer to this problem is far beyond present techniques, but we may address it for an essentially two-body problem, the two-dimensional Lorentz gas [14,16]. This model consists of a point particle moving in an infinite array of hard circular scatterers located on the sites of a triangular lattice. Periodic boundaries restrict the problem to one hexagonal basis cell of the lattice. The wandering particle moves with constant kinetic energy on straight lines and is elastically reflected at collisions with the scatterer. This model is equivalent to a two-particle system with periodic boundaries. The planar Lorentz gas is both ergodic and mixing due to the dispersing effect of the convex scatterer, and the constant-energy surface is three dimensional.

We reduce the dimension of the phase space further by introducing the two-dimensional Poincaré plane of the collision points $(\alpha,\sin\beta)$ [15]. α is the angle between the positive x axis and the collision point on the surface of the scatterer, and β is the angle of the incoming momentum with the normal vector at the collision point. The motion of the system generates a Poincaré map of the $(\alpha,\sin\beta)$ plane onto itself mapping one collision point into the next.

We use this representation to perform a numerical relaxation experiment. First, we define a coarse graining of the phase space by dividing the Poincaré plane into N boxes of equal size. Next one of the boxes is chosen at random and n phase points are uniformly distributed in the box. We follow this set of points from one collision to the next. Due to the Lyapunov instability of the system the points initially located in one of the small boxes are spread more and more over the whole plane. We monitor the time evolution of the initial distribution by computing the function

$$H_k=\sum_{i=1}^{N} f_i \ln f_i , \tag{6}$$

where the sum is over all boxes, and $f_i \equiv n_i/n$. n_i is the number of phase points in the ith box. At every collision the integer k is incremented by one. Thus, k defines a discrete time $t=k\tau_c$, where τ_c is the mean time between collisions. Initially all phase points are in one box and $H(0)=0$. If the system is equilibrated, all boxes contain an approximately equal number of points and $H(\infty)=-\ln N$. In Fig. 5 we show H as a function of $k=t/\tau_c$ for different densities ranging from $\rho=0.002R^{-3}$ to $0.5R^{-3}$, where R is the radius of the scatterers. The Poincaré plane was divided into 400×400 rectangular boxes, and 6.4×10^5 phase points were followed in time. The results for H are averaged over 80 different initial conditions. We compute also the Lyapunov exponents and the Kolmogorov-Sinai entropy for this system [16]. Since there is only one positive Lyapunov exponent λ_1, the Kolmogorov-Sinai entropy is equal to λ_1.

The time constants for the decay of the H functions, plotted in Fig. 5 as a function of t/τ_c, differ vastly with density. This indicates that τ_c is not relevant for this experiment. If, however, H is plotted as a function of t/τ_{KS}, where τ_{KS} is the Kolmogorov-Sinai time, all curves for different densities become very similar. This is shown in Fig. 6. It follows that the Kolmogorov-Sinai time determines the time scale for the relaxation of the full many body distribution and, hence, for the mixing in phase space.

According to Krylov the number N_t of boxes occupied by the phase points initially concentrated in one single box grows exponentially with time $t=k\tau_c$,

$$N_t=\exp(h_{KS}t). \tag{7}$$

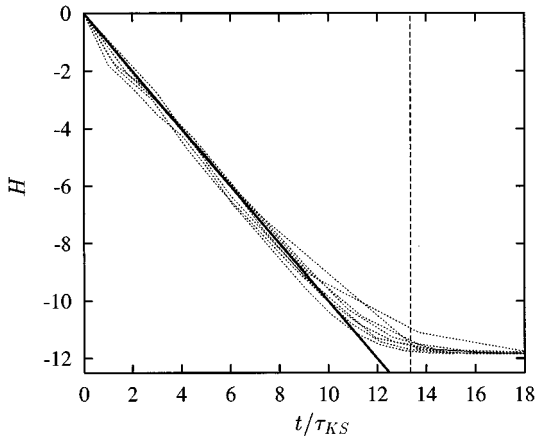

FIG. 6. H function for the two-dimensional Lorentz gas as a function of t/τ_{KS} at various densities. The full line denotes the linear decay according to the Krylov picture. The coarse-grained relaxation time is indicated by the vertical broken line.

If we assume that the n phase points at time t are distributed uniformly over the N_t boxes, it follows that $f_i = 1/N_t$ for the occupied boxes, and

$$H(t) = -h_{KS}t. \tag{8}$$

This relation is shown by the thick solid line in Fig 6. Obviously, the relaxation process comes to an end if the phase points cover the whole Poincaré plane. According to Eq. (7) this happens for times $t > \overline{\tau} \equiv 1/h_{KS}\ln N$, or, equivalently, $t/\tau_{KS} = \ln N$. This time $\overline{\tau}$, which is the coarse-grained relaxation time of the full many-body distribution, is indicated by the vertical broken line in Fig. 6. $H(t)$ deviates from the linear decay (8) if t exceeds $\overline{\tau}$. Shortly after, $H(t)$ reaches its equilibrium value. These results are in excellent agreement with the Krylov picture of the mixing process in phase space.

Our simulation results for hard sphere systems demonstrate that the relaxation of the one-body distribution function (or its moments) and the mixing in phase space occur with different time scales. In the first case the relevant relaxation time is given by the collision time τ_c in agreement with kinetic theory. In the second case the Kolmogorov-Sinai entropy determines the characteristic time scale.

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