Kolmogorov-Sinai Entropy of the Dilute Wet Granular Gas

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We present an analytical expression for the Kolmogorov-Sinai entropy of a wet granular gas. The influence of the liquid is modeled by a hysteretic interaction force. For the dilute limit (two-particle collisions only), we find a simple expression accounting for the contribution of both the scattering states and the bound states in arbitrary dimensions. It is shown that the system is significantly more chaotic than a gas of (dry) hard spheres, as reflected by a pronounced increase of the Kolmogorov-Sinai entropy.

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While equilibrium statistical mechanics is an established field of classical physics, the search for general principles governing the nonequilibrium has never stopped. In recent times, promising new concepts have been put forward, which concern fluctuations in driven many-particle systems [1–6]. In particular, the fluctuation theorems formulated by Evans, Cohen, Morriss, and Gallavotti [1–3] provide a direct link between fluctuations in the entropy flux of a driven system and the geometry of its trajectory in phase space. More precisely, the formulation of Evans *et al.* [4] states that

$$\frac{p(\bar{J}_\tau = A)}{p(\bar{J}_\tau = -A)} = \exp(\beta V F_e A \tau), \tag{1}$$

where $p(\bar{J}_\tau = A)$ gives the probability for the average entropy flux, projected on the direction of the applied field $\mathbf{F}_e$, to be equal to A when averaging over the time τ. The system volume is V, while β is the reciprocal temperature $1/k_B T$. The entropy flux is positive if it follows the applied field. Thus, the nonzero probability $p(\bar{J}_\tau = -A)$ represents an extension of the second law of thermodynamics including fluctuations for a finite time.

Equation (1) is a very interesting achievement and has already inspired a lot of further work. In particular, it is desirable to devise well-defined nonequilibrium model systems which allow one to verify this prediction. As a fairly accessible example, granular systems [7–9] have attracted interest recently as paradigmatic models for tests of the fluctuation theorem as stated in Eq. (1) [10,11]. Their particularity is that impacts between grains are inelastic, as usually described by the so-called restitution coefficient ϵ. This is defined by $\epsilon = |\mathbf{p}_\mathrm{f}|/|\mathbf{p}_\mathrm{i}|$, where $\mathbf{p}_\mathrm{i}$ and $\mathbf{p}_\mathrm{f}$ are the relative momenta before and after impact, respectively. As opposed to the standard hard spheres gas, a granular gas is thus a dissipative system, and Eq. (1) may be legitimately applied. This has been done in a few cases, corroborating many aspects of (1) with great success [10,11]. However, it may be viewed as a disadvantage of these systems that the dissipation is ''hidden'' in the inelastic collisions and is not accessible as a physical process.

A completely different situation is encountered with wet granular gases. Here the dissipation is due mainly to the formation and rupture of liquid capillary bridges between adjacent spheres. This is strong enough to account for the dramatic mechanical differences between dry and wet sand [12]. It was recently shown that the main physical properties of these systems may be successfully modeled by hard spheres interacting via hysteretic capillary forces, with the impacts themselves being assumed elastic [12,13]. As a result, the total energy of the system is a continuous function of time.

In order to apply the fluctuation theorem to a wet granular system, one needs information about its Lyapunov spectrum. In particular, the sum of all positive Lyapunov exponents (LE) plays an important role in the course of derivation of (1). Recently, sums of all positive LE have been computed for systems of hard disks and spheres without interaction [14–16]. Provided the system is closed and sufficiently chaotic, which we will henceforth assume, the sum of all positive LE is identical to the Kolmogorov-Sinai entropy (KSE) [17]. In the present Letter, we present expressions for the KSE of wet granular systems. Our analytical treatment is a generalization of the approach suggested in Ref. [14], with the liquid bridge force taken into account.

Our model system consists of N equally sized hard spheres (''grains'') with diameter σ and mass m. In the real system, the presence of a liquid leads to the formation of a capillary bridge whenever two grains touch each other. As long as this bridge is present, it exerts an attractive force which is proportional to the size of the grain and to the surface tension of the liquid [18]. Its most important feature is that it withstands a certain separation of the surfaces it connects and pinches off only when the latter exceeds a critical value. As a consequence, there is a hysteresis in the interaction force, which therefore is nonconservative. Figure 1 shows the force characteristic we use in this Letter (extended capillary model [12]), which is closely inspired by known force laws of wet granular materials [18,19]. When two particles undergo a complete collision, a fixed amount of energy E_loss is lost, which corresponds to

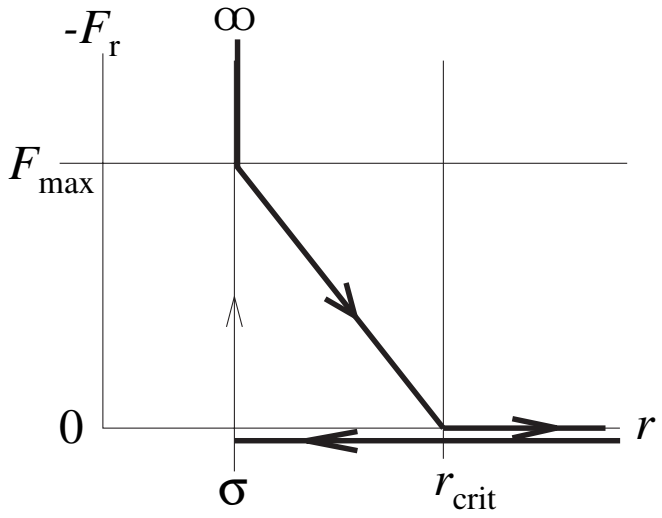

FIG. 1. The (attractive) force exerted by a liquid capillary bridge between two spheres. Its hysteretic character gives rise to dissipation within the system. Its form is a slight idealization of the experimentally determined force characteristic [18].

the area of the hysteresis loop. This contrasts sharply with common models assuming a constant coefficient of restitution. We define a corresponding velocity by $E_{\mathrm{loss}} = m v_{\mathrm{loss}}^2/4$. The effective restitution coefficient of the capillary model is a function of the initial energy or velocity: $\epsilon(E_{\mathrm{i}}) = \sqrt{1 - (E_{\mathrm{loss}}/E_{\mathrm{i}})}$ or $\epsilon(v_{\mathrm{i}}) = \sqrt{1 - (v_{\mathrm{loss}}/v_{\mathrm{i}})^2}$. In what follows, we refer to an impact as the point in time when two spheres touch. This is preceded by a drift interval, in which both collision partners move free of force. The time interval $[t_{\mathrm{i}}, t_{\mathrm{f}}]$, which starts at the beginning of the drift interval and ends when the liquid bridge between them ruptures, will be called a collision cycle.

Let us denote by v_{crit} the modulus of the critical relative velocity $\vec{v}_{\mathrm{i}} = \vec{v}_1 - \vec{v}_2$, which discerns whether the particles will form a bound state or scatter. For the head-on collisions (impact parameter $b = 0$), $v_{\mathrm{crit}} = v_{\mathrm{loss}}$; otherwise, $v_{\mathrm{crit}} > v_{\mathrm{loss}}$, since there is an additional energy in the rotary motion. In the latter case, one can find the critical impact parameter which depends on the initial relative velocity and separates sticking and scattering events.

If the modulus of the initial relative velocity v_{i} is smaller than v_{crit}, the particles stick together, and the collision cycle is not terminated until a third particle bumps into the bound two-particle system. In this case, the interaction time is of the order of ν^{-1}, where ν is the mean collision frequency of one particle. The total collision rate of the system is $N\nu/2$ (each collision involves two particles).

We should note here that, while our system is dissipative, we intend to use a method developed for equilibrium dynamics, with a fixed velocity distribution and constant temperature. We therefore consider the system on a time scale during which the temperature can be considered constant, but the number of collisions is large enough to see the influence of the liquid bridge force on the KSE, as well as to perform proper averaging procedure (see below). This is possible if $E_{\mathrm{loss}}/T \ll 1$, where T is the granular temperature, defined as the average kinetic energy per degree of freedom. We thus consider only temperatures well above condensation. This also prevents us from having to discuss effects due to the formation of larger clusters.

To judge the chaotic behavior of the system, one studies its sensitivity to the initial conditions. Evolution of their perturbation can be characterized by the LE, which give the rate of exponential divergence (contraction) of trajectories in the phase space. Further, one can say that a deterministic system is chaotic if its KSE per unit time is positive [20]. Let $\vec{R} = (\vec{r}_1 + \vec{r}_2)/2$ and $\vec{V} = (\vec{v}_1 + \vec{v}_2)/2$ denote the center of mass position and velocity, respectively, of the two impact partners, as well as $\vec{r} = \vec{r}_1 - \vec{r}_2$ and $\vec{v} = \vec{v}_1 - \vec{v}_2$ their spatial separation and relative velocity, respectively. Since in the dilute system the free drift time is large compared to the interaction time, the deviations in velocity space are amplified much stronger than those in real space [14]. We thus conjecture the velocity space to coincide (approximately) with the unstable manifold of the system. Consequently, we consider the KSE to be given by the logarithmic volume growth rate in velocity space.

The next step is to compute the matrix M that transforms initial velocity deviations from a specific point in the 4D phase space $(\vec{R}, \vec{r}, \vec{V}, \vec{v})$ of the two-particle system

$$\begin{pmatrix} \delta\vec{V}_{\mathrm{i}} \\ \delta\vec{v}_{\mathrm{i}} \end{pmatrix}$$

at the beginning of the collision cycle to the final deviations

$$\begin{pmatrix} \delta\vec{V}_{\mathrm{f}} \\ \delta\vec{v}_{\mathrm{f}} \end{pmatrix} = M \begin{pmatrix} \delta\vec{V}_{\mathrm{i}} \\ \delta\vec{v}_{\mathrm{i}} \end{pmatrix} \tag{2}$$

at the end of the collision cycle. Thus, we use the following expression for the KSE h_{KS} as a starting point:

$$h_{\mathrm{KS}} = \lim_{s\to\infty} \frac{1}{t(s)} \ln \left| \det \prod_{i=1}^{s} M_i \right|, \tag{3}$$

where M_i is the deviation matrix of the ith collision cycle and $t(s)$ is the time elapsed after s collisions. This limit exists by virtue of Oseledec's multiplicative ergodic theorem [17,21]. Although there will frequently be pair interactions overlapping in time, there is no ordering problem when writing down the total deviations as a product of collision cycles, because the coexisting liquid bridge interactions affect disjoint pairs, and deviation matrices of these pairs commute. Then the expression (3) can be simplified dramatically (see also [14]):

$$\frac{h_{\mathrm{KS}}}{N} = \frac{\nu}{2} \langle \ln |\det M| \rangle.$$

The angle brackets $\langle \ldots \rangle$ denote averaging over the full

two-particle phase space only. Because of the possible formation of bound states, there are two types of scattering matrices, splitting the expression above into two terms:

$$\frac{h_{\mathrm{KS}}}{N} = \frac{\nu}{2}[\langle \ln|\det M_{\mathrm{b}}|\rangle_{v_{\mathrm{i}}<v_{\mathrm{crit}}} + \langle \ln|\det M_{\mathrm{s}}|\rangle_{v_{\mathrm{i}}>v_{\mathrm{crit}}}]. \quad (4)$$

Next we have to determine the matrices M_{b} and M_{s}. After a lengthy but straightforward calculation, we arrive at the surprisingly simple result

$$|\det M| = \left(1 - x_{\mathrm{i}}\frac{\partial\vartheta}{\partial b}\right)\left(1 - \frac{v_{\mathrm{loss}}^2}{v_{\mathrm{i}}^2}\theta(v_{\mathrm{i}} - v_{\mathrm{crit}})\right)^{(D/2)-1} \times \left(1 + \frac{x_{\mathrm{i}}}{b}\sin\vartheta\right)^{D-2}, \quad (5)$$

which depends only on the initial relative velocity v_{i}, scattering angle ϑ, impact parameter b, and x_{i}—the distance traveled to the collision along the direction of the relative velocity, which is approximately equal to the initial distance between colliding particles at $t = t_{\mathrm{i}}$. D is the dimensionality of the problem. Quite remarkably, Eq. (5) is valid for both the scattering and the bound case. The only difference is the actual value of the scattering angle and final velocities. The step function θ indicates that a bound state is terminated by a third particle and a new collision cycle restarts with the same velocity distributions. In the limit $v_{\mathrm{loss}} \to 0$, we recover the result for ideal hard spheres [14].

Let us discuss what contributes to the KSE and why it is different for the wet granular case. We are considering the dilute gas limit $n\sigma^D \ll 1$, and the result for the KSE is intrinsically presented in the form of an expansion with respect to this small parameter (see below). In formula (5), unity in the first parentheses can be safely neglected. The initial distance between particles is of the order of the mean free path and, thus, inversely proportional to the density of particles. This gives the leading term in the expansion of the KSE at low densities, which is known for the dry case. The derivative of the scattering angle with respect to the impact parameter in the scattering regime gives the correction to the next order, but for the bound state the situation is different. The scattering angle (and its derivative) grows linearly with time because of the rotation and bouncing of two particles in a cluster until a third particle breaks it. This time is again of the order of the mean free path divided by the center of mass velocity. Therefore, this term in bound collisions contributes to the leading one in the expression for the KSE.

To finally obtain the KSE, we take the average of the logarithm of (5) over all possible impact parameters, relative velocities, and initial distances between colliding particles. For the velocities, we chose a Maxwellian distribution. For the initial distances, it turns out that their probability distribution is not a simple exponential, as for the free path of the particle, but has the form:

$$\frac{v_1 + v_2}{v_{\mathrm{i}} l} e^{-x_{\mathrm{i}}((v_1+v_2)/(v_{\mathrm{i}} l))}, \quad (6)$$

where $l = (2\sqrt{2}\sigma n)^{-1}$ in 2D and $l = (\sqrt{2}\pi\sigma^2 n)^{-1}$ in 3D is the mean free path. After averaging with the velocity distributions in 2D, for example, this yields an expectation value $\langle x_{\mathrm{i}}\rangle \approx 0.71 l$ for the initial distance. Using the conventional assumption of molecular chaos (i.e., the relative positions of two particles are uncorrelated), we arrive at

$$\langle \ldots \rangle = \left(\frac{m}{2\pi T}\right)^D \int_{\mathbb{R}^D} d^D v_1 \int_{\mathbb{R}^D} d^D v_2 \frac{v_1 + v_2}{v_{\mathrm{i}}} \int_0^\sigma \frac{db^{D-1}}{\sigma^{D-1}} \times \int_0^\infty \frac{dx_{\mathrm{i}}}{l} e^{-(m/2T)(v_1^2+v_2^2)-(x_{\mathrm{i}}/l)(v_1+v_2)/(v_{\mathrm{i}})} \ldots$$

for the averaging integral, which is to be applied to Eq. (4). In terms of the natural length scales of the problem, l and σ, we obtain

$$\frac{h_{\mathrm{KS}}}{N} = \frac{\nu}{2}\Big\{(D-1)\ln\frac{l}{\sigma} + \left\langle \ln\left(\sigma\left|\frac{\partial\vartheta_{\mathrm{b}}}{\partial b}\right|\right)\right\rangle_{v_{\mathrm{i}}<v_{\mathrm{crit}}} + \left\langle \ln\left[\frac{x_{\mathrm{i}}}{l}\left(\frac{\sigma}{l}\cos\vartheta + \frac{x_{\mathrm{i}}}{l}\frac{\sigma}{b}\sin\vartheta\right)^{D-2}\right]\right\rangle + \left\langle \ln\left[\sigma\left|\frac{\partial\vartheta_{\mathrm{s}}}{\partial b}\right|\left(1 - \frac{v_{\mathrm{loss}}^2}{v_{\mathrm{i}}^2}\right)^{(D/2)-1}\right]\right\rangle_{v_{\mathrm{i}}>v_{\mathrm{crit}}}\Big\}.$$

The first term, as in the dry case, gives the leading and dominating term of the expansion with respect to small density: $-\ln n\sigma^D$. The second one is a correction due to the sticking collision. The scattering angle for the bound state can be estimated from the angular momentum conservation $\vartheta_{\mathrm{b}} \sim \mathrm{const} + t_3 b v_{\mathrm{i}}/\sigma^2$ and is proportional to the interaction time t_3. It is equal to the mean free path of the particle with higher cross section $3\sigma/2$ and doubled mass, divided by the center of mass velocity. Therefore, it gives the correction $(-\ln n\sigma^2)\langle 1\rangle_{v_{\mathrm{i}}<v_{\mathrm{crit}}}$, proportional to the sticking probability.

Finally, the general expression for the KSE of the wet granular gas is (see Fig. 2 cf. [14])

$$\frac{h_{\mathrm{KS}}}{N} = -\nu A \ln n\sigma^D + \nu B + \mathcal{O}(n\sigma^D),$$

where A is the sum of the dry limit value $(D-1)/2$ and the sticking probability:

$$A = \frac{D-1}{2} + \frac{2^{-D}}{\Gamma(\frac{D}{2})}\left(\frac{m}{T}\right)^{D/2}\int_0^\sigma \frac{db^{D-1}}{\sigma^{D-1}} \times \int_0^{v_{\mathrm{crit}}(b)} dv v^{D-1} e^{-(m/4T)v^2}.$$

The general expression for B in arbitrary dimension is enormously complicated. We present here the result for $D = 2$, which reads

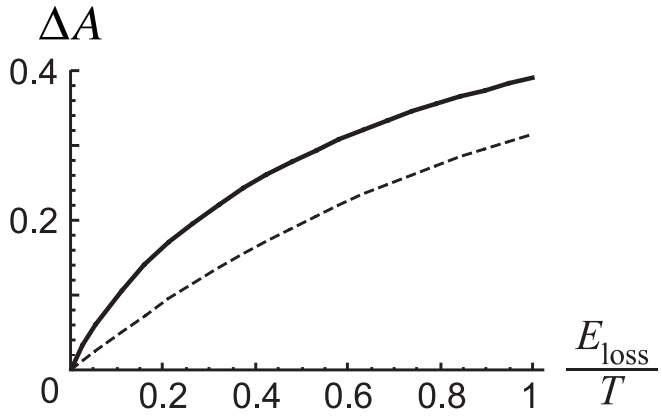

FIG. 2. The increase of the leading term coefficient $A = (D-1)/2 + \Delta A$ in the KSE due to the liquid bridge interaction for two (solid line) and three (dashed line) dimensions.

$$B = \frac{1}{2}\Big[-\frac{3}{2}\ln 2 + \left\langle \ln\left(\frac{x_i}{l}\right)\right\rangle - \ln 3\sqrt{3}\langle 1\rangle_{v_i<v_{crit}} + \left\langle \ln\frac{v_i}{V_i}\right\rangle_{v_i<v_{crit}} + \left\langle \ln\left(\sigma\left|\frac{\partial \vartheta_s}{\partial b}\right|\right)\right\rangle_{v_i>v_{crit}}\Big].$$

The analytical expression for the coefficient A is the central result of the present Letter. We can see that the leading term of the KSE immediately reacts on the humidity even for a small water content, which is indicated by the strictly positive slope of the corresponding curves in Fig. 2 in the applicability region $E_{loss}/T \ll 1$. The dry limit of the coefficient B gives the value -0.52 for $D = 2$. It is lower than the theoretical and numerical results of Ref. [14], which are 0.1045 and 0.679, respectively. One of the reasons for that is the different definition of the collision cycle. The accurate calculation of B is a separate and complicated problem [16], but, as it gives the next order correction to the KSE, its careful analysis was out of the focus of this Letter.

In conclusion, we have shown that the presence of a liquid in a granular gas significantly enhances the KSE of this system and that analytic expressions for it can be written down. We should point out that the details of the force characteristic due to the liquid bridges are of minor importance. Other force laws, such as a constant but hysteretic force [13], lead to similar results. The leading term in the expansion of the KSE with respect to density ($n\sigma^D \ll 1$) is greatly influenced by the existence of bound states. They are not present in the standard granular systems, in which dissipation comes about via the restitution coefficient. Finally, it should be mentioned that relations between the Lyapunov spectrum of microscopic dynamics and macroscopic properties such as viscosity and heat conductivity have been established within the last years for several systems, in most detail for the Lorentz gas [20]. We hope that our results on the KSE of the wet granular gas might help to develop analogous relations for dissipative systems such as wet granular gases as well.

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