LETTER TO THE EDITOR

Local interpretation of chaotic dynamics in a many-body classical Hamiltonian system

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Abstract. The Kolmogorov entropy of a model Ar_3 cluster converges smoothly to its limiting value when averages are taken over increasingly long segments of a molecular dynamics trajectory. We exploit this convergence and the analytical relation between the local Kolmogorov function and the potential energy surface to obtain a detailed understanding of the classical dynamics of Ar_3. In particular, we are able to explain why the Kolmogorov entropy increases steadily with the total energy and then reaches a plateau. Several generalizations regarding more complex molecular systems are inferred.

Recent studies have focused upon the characterization of dynamical properties of Hamiltonian systems in terms of Liapunov exponents, Kolmogorov entropy (Kolmogorov 1959) and fractal dimensions (Mandelbrot 1983). Sharp and broad peaks in the power spectra of such systems have been related to the distribution of local Liapunov exponents in a Hamiltonian system with only two degrees of freedom (Sepúlveda *et al* 1988). However, the latter approach does not illuminate the results obtained by computer simulations (Beck *et al* 1988) even for a system as simple as Ar_3. Here we construct the Jacobian for the simplest propagator of the motion and consider the convergence of the Kolmogorov entropy. This enables us to explain the variation of the degree of chaos with the total energy in a model Ar_3 cluster.

For a system of N atoms we consider a $2N$-dimensional hypersphere in phase space which evolves into an ellipsoid of constant volume but with principal axes of varying lengths. As time passes, N principal axes continue to grow and N continue to shrink. The average stretching factors for the N lengthening axes are related to the N positive Liapunov coefficients, which are in turn related to the Kolmogorov entropy. We cannot obtain the K entropy from the average stretches occurring at each step of a discretized trajectory, because not all the stretches at any given step actually contribute to the directions which become stretched *in the long run*. Furthermore, local contractions which *do* contribute to these axes would be neglected by such an approximation.

Suppose instead that we break down a discretized trajectory into segments of l time steps. For a trajectory with a total of L time steps there will be L/l such segments, and we can investigate the convergence of the K entropy estimated from the intervals of l time steps. We designate the latter quantities by K^l, and the mean of the L/l values over the trajectory by $\langle K^l \rangle$. According to Pesin's theorem (Pesin 1977) K^l may

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be calculated by accumulating products of the Jacobian over l time steps, diagonalizing to find the eigenvalues and their moduli and finally summing over the logarithms to base 2 of the eigenvalues whose moduli are greater than one. For trajectories that are sufficiently long, K^L converges to the true global K entropy. For a realistic model of an Ar_3 cluster we find that the $\langle K' \rangle$ converge in a regular fashion. This enables us to exploit the analytic relation between K^1 and the underlying potential energy surface to rationalize the variation of the true K entropy with the total energy. First we introduce the approach with a simple example.

Consider a classical system with only one internal degree of freedom, x, and a double-well potential energy function

$$V = 1 - x^2 + x^4. \tag{1}$$

The map according to which this system evolves is given by the discretized equations of motion

$$x(n+1) = x(n) + \frac{p(n)\tau}{m} \qquad p(n+1) = p(n) - V'\tau \tag{2}$$

correct to order τ, the time step, where m is the effective mass and p the conjugate momentum. This map is not accurate or stable enough to be used as a propagator in molecular dynamics simulations (Berendsen and Gunsteren 1986), but this is unimportant in the development of the present theory where τ may be arbitrarily small. The Jacobian, $\mathbf{J}$, for this map is therefore

$$\mathbf{J} = \begin{pmatrix} 1 & \tau/m \\ -2\tau(6x^2 - 1) & 1 \end{pmatrix}. \tag{3}$$

The eigenvalues of $\mathbf{J}$ are

$$\lambda_{\pm} = 1 \pm \tau \left(\frac{1 - 6x^2}{m} \right)^{1/2} \tag{4}$$

and their magnitudes are:

$$\begin{aligned} |\lambda_{\pm}| &= 1 \pm \tau \left(\frac{1 - 6x^2}{m} \right)^{1/2} & |x| < 1/\sqrt{6} \\ |\lambda_{\pm}| &= \left(\frac{1 + \tau^2(1 - 6x^2)}{m} \right)^{1/2} & |x| > 1/\sqrt{6}. \end{aligned} \tag{5}$$

These results are essentially equivalent to the analysis of Brumer and Duff (1976) based on comparing neighbouring trajectories. We write the local Liapunov functions as

$$\begin{aligned} \log_2 |\lambda_{\pm}| &= \pm \frac{\tau}{\ln 2} \left(\frac{1 - 6x^2}{m} \right)^{1/2} + O(\tau^2) & |x| < 1/\sqrt{6} \\ \log_2 |\lambda_{\pm}| &= \frac{\tau^2(6x^2 - 1)}{2m \ln 2} + O(\tau^4) & |x| > 1/\sqrt{6}. \end{aligned} \tag{6}$$

Hence, correct to order τ, the Liapunov functions at a particular point on the potential surface are paired and vanish if $|x| > 1/\sqrt{6}$. This means that K^1 (which is the sum of the positive local Liapunov functions (Pesin 1977)) vanishes to order τ outside the points of inflection of the potential energy, so that all the contributions to $\langle K' \rangle$ must

come from regions where $|x| < 1/\sqrt{6}$. Kosloff and Rice (1981a, b) have previously pointed out that mixing cannot occur in such a one-dimensional system, but this does not affect the methodology of our example.

Now we generalize to a classical system of N particles with masses m_i evolving on a potential energy surface V. The appropriate map is given by the $2N$ coupled discretized equations of motion

$$q_i(n+1) = q_i(n) + \frac{p_i(n)\tau}{m_i} \qquad p_i(n+1) = p_i(n) - \frac{\partial V}{\partial q_i(n)}\tau \qquad (7)$$

where q_i are the Cartesian coordinates and $p_i = m_i \partial q_i / \partial t$ are the conjugate momenta; $i = 1, 2, \ldots, 3N$. The Jacobian for the map is now

$$\mathbf{J} = \begin{pmatrix} \mathbf{I}_{3N} & \mathbf{T}_{3N} \\ -\tau\mathbf{H}_{3N} & \mathbf{I}_{3N} \end{pmatrix} \qquad (8)$$

where $\mathbf{H}_{3N}$ is the $3N \times 3N$ dimensional second derivative matrix of the potential, i.e. the Hessian, and $T_{ij} = \tau\delta_{ij}/m_i$, where δ_{ij} is the Kronecker δ.

Suppose that τ is sufficiently small for equation (7) to provide a reasonable approximation to the time evolution of the trajectory. Then we can solve the determinantal eigenvalue equation for $\mathbf{J}$ as follows (Brumer and Duff 1976):

$$\det(\mathbf{J} - \lambda\mathbf{I}) = 0 \Rightarrow \det(\mathbf{J}' - (\lambda-1)\mathbf{I}) = 0 \qquad \text{where } \mathbf{J}' = \begin{pmatrix} \mathbf{O}_{3N} & \mathbf{T}_{3N} \\ -\tau\mathbf{H}_{3N} & \mathbf{O}_{3N} \end{pmatrix}. \qquad (9)$$

Multiplying by $\mathbf{J}' + (\lambda-1)\mathbf{I}$ reduces the system to two identical blocks, each equivalent to

$$\det\left(\mathbf{H}'_{3N} + \frac{(\lambda-1)^2}{\tau^2}\mathbf{I}_{3N}\right) = 0 \qquad (10)$$

where

$$[\mathbf{H}'_{3N}]_{ij} = \frac{1}{(m_i m_j)^{1/2}} \frac{\partial^2 V}{\partial q_i \partial q_j} \qquad (11)$$

so that $\mathbf{H}'_{3N}$ is the mass-weighted Hessian whose eigenvalues, k_j, are the force constants for the local normal modes of the system. In terms of these force constants the Jacobian eigenvalues are $\lambda_\pm^j = 1 \pm i\tau\sqrt{k_j}$ where $i = \sqrt{-1}$ and $j = 1, 2, \ldots, 3N$. Hence the magnitudes of the eigenvalues are

$$\begin{aligned} |\lambda_\pm^j| &= (1 + \tau^2 k_j)^{1/2} & k_j &> 0 \\ |\lambda_\pm^j| &= 1 \mp \tau|k_j|^{1/2} & k_j &< 0. \end{aligned} \qquad (12)$$

For sufficiently small τ (so that $\tau^2|k_j| < 1$) the local Liapunov functions are

$$\begin{aligned} \log_2|\lambda_\pm^j| &= \frac{\tau^2 k_j}{2\ln 2}(1 - \tfrac{1}{2}\tau^2 k_j + \ldots) & k_j &> 0 \\ \log_2|\lambda_\pm^j| &= \mp\frac{\tau|k_j|^{1/2}}{\ln 2}(1 - \tfrac{1}{2}\tau|k_j|^{1/2} + \ldots) & k_j &< 0. \end{aligned} \qquad (13)$$

Again, correct to order τ, the local Liapunov functions appear as positive and negative pairs, and all the contributions to $\langle K^1\rangle$ come from regions of the potential surface which have negative curvature along one or more local normal coordinates. Here we

assume that there is at least one negative force constant, so that all the contributions from the positive force constants may be neglected. Hence the analysis is inappropriate for model systems whose potentials have curvatures that are positive everywhere. Here the complexity of the molecular model system works to illustrate our method effectively, since negative curvatures are present over practically all the potential energy surface. Furthermore, the region where this assumption breaks down, around the potential minimum, is expected to contribute little to the K entropy. In fact, our analysis also requires that the potential energy function be continuous and twice differentiable in the regions sampled by the trajectories. This excludes stadium models bounded by infinite potential walls.

This single trajectory formulation for K^1 is related to two-trajectory models (Brumer and Duff 1976, Toda 1974, Kosloff and Rice 1981b) which seek a critical lowest energy at which the system first gains access to a region of the potential energy surface with negative curvature. Such an approach does not predict the onset of chaos reliably (Tabor 1981) because the averaged $\langle K^1 \rangle$ is different from the global Kolmogorov entropy, as explained above. The present work, however, shows that the $\langle K^1 \rangle$ converge quite smoothly to the true K entropy in our model Ar_3 cluster, and more extensive calculations suggest that this may be a general property of such systems.

From the validity of the Jacobian iteration (Benettin *et al* 1976, 1980), we expect that $K^\alpha \to K$, the true global K entropy, as $\alpha \to \infty$. We now address the nature of this limit for the dynamics of Ar_3 using the Lennard-Jones pair potential

$$V = 4\varepsilon \sum_{i<j} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \tag{14}$$

where r_{ij} is the distance between atoms i and j, and $\varepsilon = 1.671 \times 10^{-14}$ erg and $\sigma = 3.4$ Å are commonly used for argon. Using this model potential we calculated various $\langle K^1 \rangle$ for a series of molecular dynamics trajectories of length 1 ns (10^5 time steps) and total energies spanning the available range up to the dissociation limit (figure 1). It was, in fact, necessary to use a higher order approximation (correct to order τ^2) for the Jacobian, in order to maintain numerical stability for $\langle K^{2000} \rangle$, as judged by the accuracy of pairing of the eigenvalues. For K^1, however, the results obtained using equation (7) correct to order τ were practically the same as those obtained from diagonalizing the higher order approximation to the full Jacobian (the same is true for our preliminary studies of Ar_7). We also note that there are only two positive Liapunov exponents for this system, along with two negative exponents and 14 zeros (Meyer 1986). All the results were corrected to allow for this; more details will be given elsewhere, along with an analysis which shows that the dynamics are ergodic except at the lowest energies.

We see from figure 1 that the $\langle K^1 \rangle$ appear to converge smoothly to the global Kolmogorov entropy, and follow the same qualitative trends with energy. *Hence $\langle K^1 \rangle$ may be used directly to interpret the energy variation of the global Kolmogorov entropy.* The convergence of the $\langle K^\alpha \rangle$ poses a new challenge to theory; such regular convergence is not a common property of the simple model problems that are often studied. However, results using different model potentials for three- and seven-atom clusters show that these systems can also be treated using the present method, again providing useful insight.

To analyse the results in more detail we have calculated surfaces of K^1 as functions of the unique internal coordinates R_1, R_2 and θ, where R_1 is the separation of atoms 1 and 2, R_2 is the separation of atoms 2 and 3 and θ is the angle $\angle 123$. To produce a surface we freeze one of the coordinates while allowing the other two to vary and
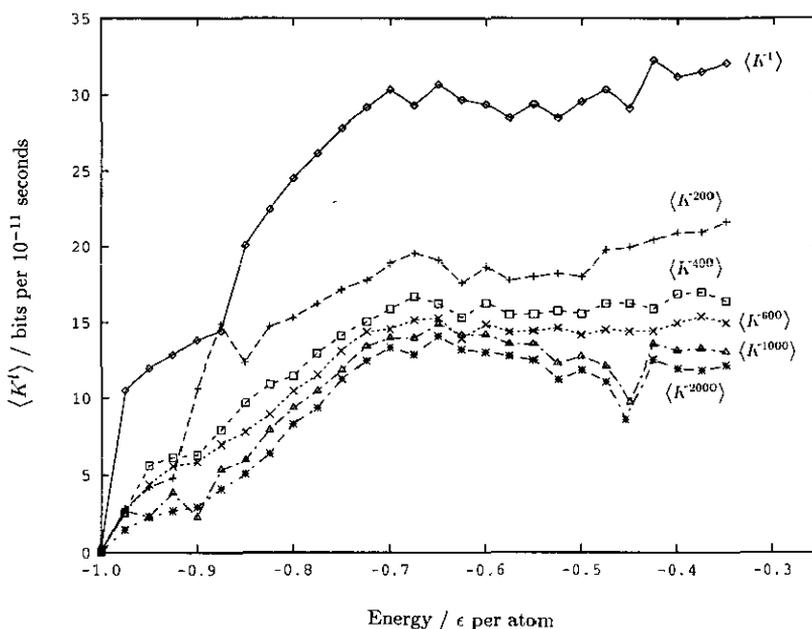
Figure 1. Variation of $\langle K^l \rangle$ with energy calculated from 10^5 step molecular dynamics trajectories with time step 10^{-14} s. $\langle K^{2000} \rangle$ is known to be close to the true K entropy in this system, both from previous work (Beck *et al* 1988) and from new results using alternative algorithms which will be presented in a full report. Above the atomic dissociation energy of -0.3333ε/atom there is a rapid drop in all the $\langle K^l \rangle$.

plot V and K^1 at regular intervals over a two-dimensional grid. The most helpful plots are those with variable $R_1 = R_2 = R$ and θ, and with variable R_1 and R_2 at fixed values of θ (figure 2).

For large atomic separations we expect K^1 to be small, just as we see for the dimer potential. This explains the plateau region in K^1 (figure 2(c)). There is also a valley centred around $\theta = 60°$ which includes the geometry of global minimum energy, the equilateral triangle. This valley corresponds to symmetrical stretching of R_1 and R_2 with θ roughly constant. Only at fairly large separations does this mode cross a point of inflection of the potential energy. We also see that broad and flat regions of the potential energy surface make relatively small contributions to $\langle K^1 \rangle$. There are two aspects to this point. First, the reaction coordinate across a conventional saddle corresponds to a soft, floppy normal mode with a small negative curvature (Murrell and Laidler 1968). Hence, although the saddle region by definition has a negative force constant, the corresponding normal mode is very soft. Second, the kinetic energy is necessarily smallest in the saddle region, so $\langle K^1 \rangle$, being a time average, is biased towards the local values sampled there. This is in accord with our intuitive picture of regular, streaming trajectories passing over the saddle.

When the total energy is low the accessible phase space of the microcanonical ensemble is confined to regions around the bottom of the potential well which contribute little to the average value $\langle K^1 \rangle$. As the total energy of the system increases so does the probability that the phase point samples regions where K^1 is large, and hence the K entropy rises with the total energy. However, when the system has sufficient energy to explore regions of configuration space around the linear geometry, the contributions to the K entropy come increasingly from areas where K^1 is small. The K entropy is
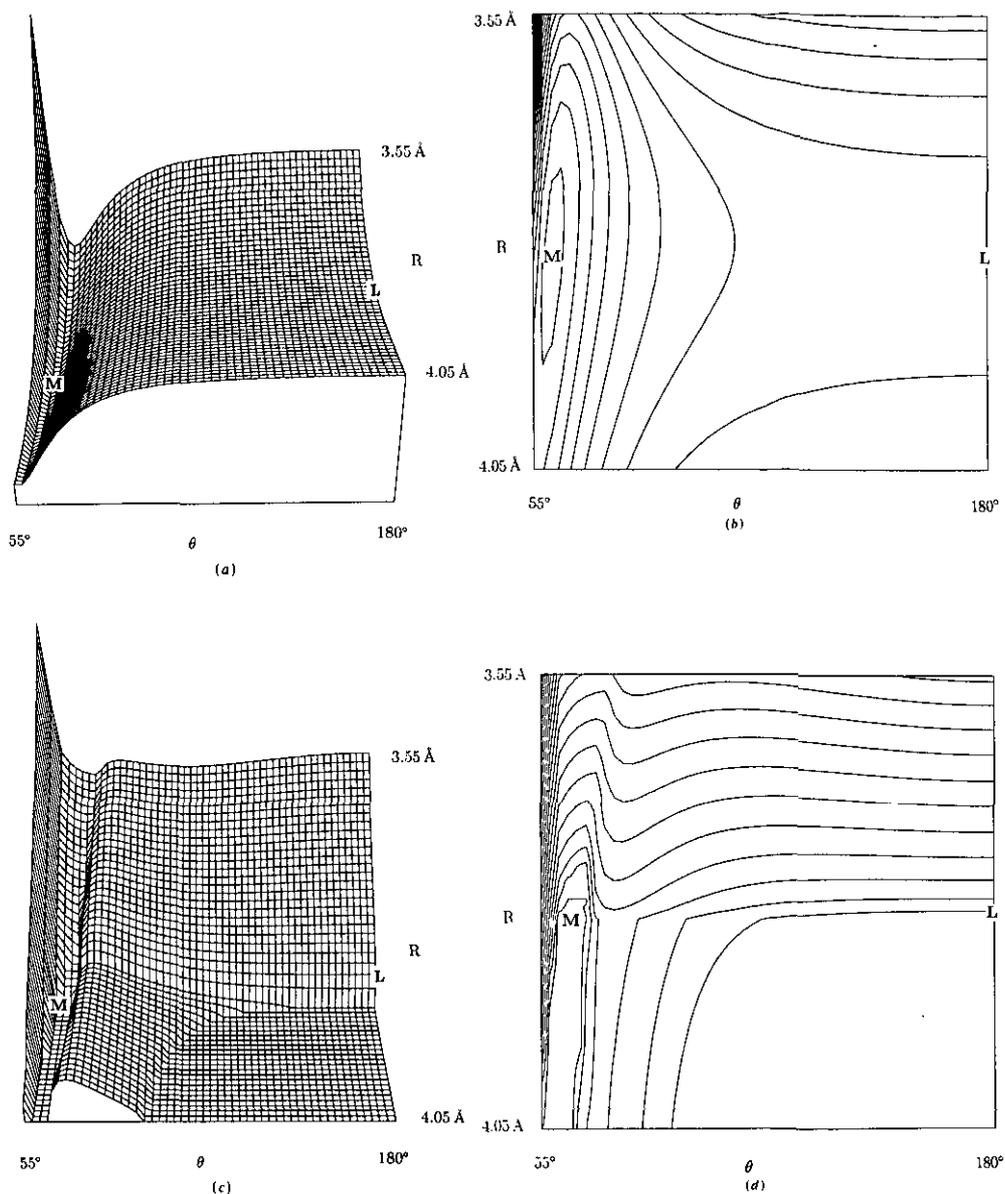
Figure 2. Surfaces and contour plots of K^1 and the potential energy for Ar_3 where $R_1 = R_2 = R$ and θ are the free variables: (a) potential energy surface; (b) potential energy contours; (c) K^1 surface; (d) K^1 contours. The equilateral triangular minimum (M) and the linear saddle point (L) are indicated on all four plots. The minimum and transition state have energy -1.0 and -0.6774ε/atom, respectively.

therefore predicted to rise steadily from zero and peak just before the total energy becomes large enough for the saddle region to be sampled significantly. This is just what is observed for Ar_3.

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