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Clusters: A laboratory for studying chaos and ergodicity

Concezione Amitrano and R. Stephen Berry

Department of Chemistry and the James Franck Institute
The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, USA

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Abstract. The dynamics of clusters are revealed, in part, by the extent and nature of their chaotic and ergodic behavior. Conversely, small clusters offer opportunities to study the origins and evolution of chaotic and ergodic behavior. This investigation uses, as a probe, the time evolution of the distribution of sample values of the largest Liapunov exponent λ_{max}. Two kinds of clusters are examined, Ar_3 and Ar_7. The distributions $g(\lambda_{max}, E)$ allow inference of dynamical characteristics such as dwell times in the various potential minima and durations and frequencies of saddle crossings.

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1. Introduction

Among the many subjects for which clusters are particularly appropriate vehicles, the study of chaos and ergodicity is particularly tantalizing. It is natural to use clusters to go beyond the very simple systems which have, until recently, been the objects of most investigations into chaos and ergodicity. (There are exceptions, of course; Liapunov spectra of some clusters have been determined [1].) Here, we concentrate on one particular problem within that subject, the time evolution of ergodicity, the extent to which a system's trajectory fills the phase space allowed to it by energy, momentum and angular momentum conservation. We show how it is possible to infer from data regarding Liapunov exponents, strictly measures of chaos rather than of ergodicity, how the extent of ergodicity expands with time, and then discuss what can be learned about the particle dynamics from this evolution. A preliminary report of this work [2] laid out the approach, based on the analysis of the three-particle cluster bound by pairwise Lennard-Jones forces; we shall refer to these and their larger counterparts as if they were argon clusters.

Evaluating Liapunov exponents requires taking the long-time limit of the time average of the logarithm of the ratio of the distance of two trajectories at time t and their distance at time 0. For Hamiltonian systems, this can be found by propagating the Jacobian $\delta\mathbf{F}/\delta\mathbf{x}$ of the time evolution $\mathbf{F}[\mathbf{x}(t)] = d\mathbf{x}/dt$ of infinitesimal displacements $\delta\mathbf{x}(t)$ of the system in phase space. Naturally this procedure is carried out in practice by propagating the Jacobian for n finite intervals and then taking the nth root of this product of n succesive values of the Jacobian along the trajectory. One then finds the eigenvalues of the resulting matrix, attempting to reach converged values of the averages of those sample values that approximate the exponents governing the growth of $\delta\mathbf{x}(t)$. There are at least two procedures for carrying out the calculations, which have been compared recently [3], in the context of small clusters; the better-known is the method of Benettin et al. [4, 5].

2. The argon trimer

Here, we describe how to use the distributions of sample values as probes, not of chaos but of ergodicity. The first application of this approach [2], the examination, at several energies, of evolution of ergodicity in Ar_3, showed that the distributions of sample values of the largest Liapunov exponent for this system are indicators of ergodicity, apart from their implications regarding chaos. In particular, the shapes of the distributions as functions of the length or duration of path over which the exponents are estimated, at each of a series of energies, change qualitatively, to show that there is a clear separation of time scales in the dynamics of the argon trimer.

We used path lengths of 2^j steps, with $j = 7, 8, 9, 10, 11, 12$ and 13. Since $2^{13} = 8192$, and we had previously demonstrated that our simulations only begin to lose their mechanical reversibility between 5000 and 10000 steps, we can be comfortable that the dynamics are fairly well represented even on the longest trajectories. Using a set of averaging lengths that differ by factors of two enabled us to use only a few very long runs that we could subdivide into two, four, ... segments. The total numbers of time steps in each simulation were 10^9–10^{10}, corresponding to times of 10^{-5}–10^{-4} s. Thus the total number of sample values ranged from ca. 10^6 for the shortest trajectories to 10^5 for the longest.

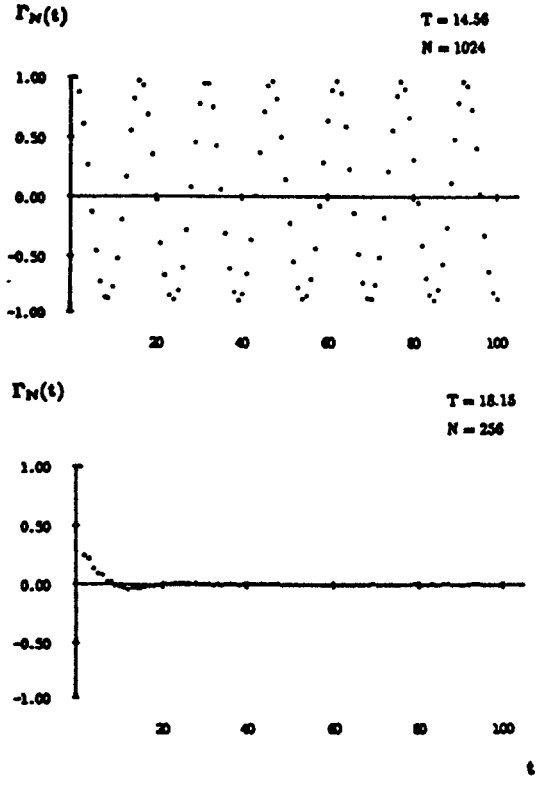

Fig. 1. Autocorrelation functions for the largest Liapunov exponent of Ar_3 at mean temperatures of 14.56 (upper) and 18.15 K (lower). The upper figure is based on 1024 steps and the lower, on only 256, showing the persistence of correlations at the lower temperature and the rapidity of their disappearance at the higher temperature.

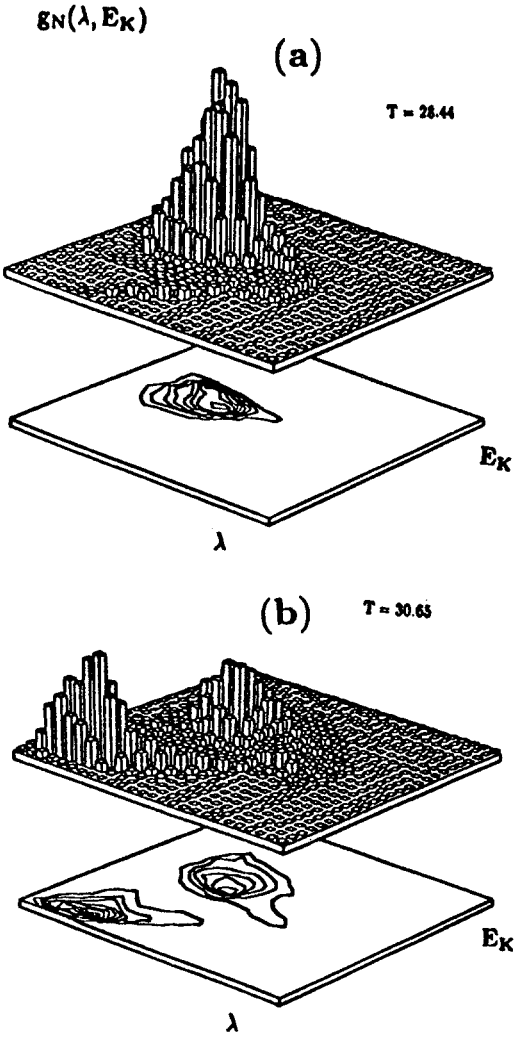

Fig. 2. The joint distribution of largest Liapunov exponents for Ar_3 at two energies, corresponding to (a) 28.44 and (b) 30.65 K. The Liapunov exponent values are on the left axis and the short-time mean kinetic energies, on the right. The bimodality of (b) is apparent.

At very low energies, e.g. approximately $-\epsilon$ per atom where $-\epsilon$ is the energy of two LJ atoms at their equilibrium distance, the distributions of sample Liapunov exponents are extremely sensitive to initial conditions, for all the trajectory lengths we considered. At about -0.85ϵ/atom, the distributions are quantitatively but not qualitatively sensitive to initial conditions: distributions based on trajectories of the same length but different initial conditions look similar but have different second moments. Furthermore the time autocorrelation functions of the largest Liapunov exponents are $\Gamma_N(t) = \langle(\lambda_N(t) - \langle\lambda_N(t)\rangle)(\lambda_N(0) - \langle\lambda_N(0)\rangle)\rangle/(\lambda_N(0) - \langle\lambda_N(0)\rangle)^2$. If the dynamics were chaotic, $\Gamma_N(t)$ would average to zero in some energy-dependent, relatively short decay time. The brackets indicate averages over the many segments of trajectory. As Fig. 1a shows, at a low energy of $-0.91\ \epsilon$/atom, corresponding to a mean vibrational temperature of 14.56 K, $\Gamma_N(t)$ is clearly periodic, while at an energy of $-0.83\ \epsilon$/atom, corresponding to 18.15 K, the autocorrelation function decays rapidly, as Fig. 1b shows.

The sample largest Liapunov exponents have simple, unimodal distributions for temperatures of 28.44 K and below, whatever the averaging trajectory length. However at energies corresponding to 30.65 K and even 36.71 K, the distributions are bimodal for short trajectories. At the lower of these temperatures, the bimodality appears for trajectories up to 1024 steps but not 2048; at the higher temperature, bimodality occurs only for 256 steps. However at both these temperatures, the asymptotic value of the largest Liapunov exponent is reached only after at least 10^4 steps. This bimodality for Ar_3 is clearly associated with the bimodality in the short-time average kinetic energies or temperatures, which in turn are the consequence of part of the population being in the deep wells and part, in the flat saddle regions [2, 3, 6]. To see this bimodality and its association with the local "temperature", it is useful to examine the distributions $g_N(\lambda_{max}, E_K)$ of λ_{max}, the largest Liapunov exponents, as functions of both the value of the exponent λ_{max} and the short-term, mean kinetic energy E_K. The distributions $g_N(\lambda_{max}, E_K)$ of λ_{max} are shown in Fig. 2, for two total energies, corresponding to 28.44 K in the unimodal (solid) region and 30.65 K in the bimodal region.

The standard deviations of the Liapunov exponent distributions have been used also as diagnostics [7] on the basis that large standard deviations imply that there are regions of

phase space that are heavily weighted and that give rise to rapid changes. In the extreme, one encounters such things as the bimodal distributions we report here. The standard deviations for 128-step averages are large and increase only slightly with the clusters energy; they diminish, as one expects, with increasing trajectory length, by about an order of magnitude from 128-step averages to 8192-step averages.

3. The Ar_7 cluster

The seven-atom argon or Lennard-Jones cluster has four locally stable structures [8]. It is the smallest system known to show well-defined, persistent solid-like and liquid-like forms [9, 10]. The joint distribution functions $g_N(\lambda_{max}, E_K)$ for Ar_7 are shown in Fig. 3 for three energies, -0.341, -0.300 and -0.265×10^{-13} erg/atom, respectively (ϵ is -1.67×10^{-14} erg/atom), for trajectories of 256 steps. The bi- or multimodality is not as well resolved for this cluster as for Ar_3, because its potential surface is more complicated. Nevertheless the distribution is clearly not unimodal in the intermediate energy shown here. As with Ar_3, bimodality occurs for short trajectories, at intermediate energies.

4. Conclusions

The bimodality reported here is characteristic of populations exploring different regions of the same allowed phase space. The transformation from bimodality to unimodality is a signature of the passage from limited, nonergodic behavior to ergodic behavior and full exploration of all regions of the phase space by all trajectories. The rather sharp transition from one shape to the other, as a function of the length or duration of trajectory, implies that the two kinds of behavior can be identified with the two sides of a time scale separation, below which the system is nonergodic and above which, it can probably be considered ergodic.

One question remains to be answered about the ergodicity: for times longer than the scale separation time, do the trajectories truly fill the phase space in which they are embedded? What are the fractal dimensions of the trajectories of the 7-particle cluster and, at least for long trajectories, of the 3-particle cluster? These have been determined for short trajectories for Ar_3; they are less than their infinite-time limiting values, the dimension of the full phase space [6]. However evaluating fractal dimensions of trajectories in several dimensions does not yet have an economical solution.

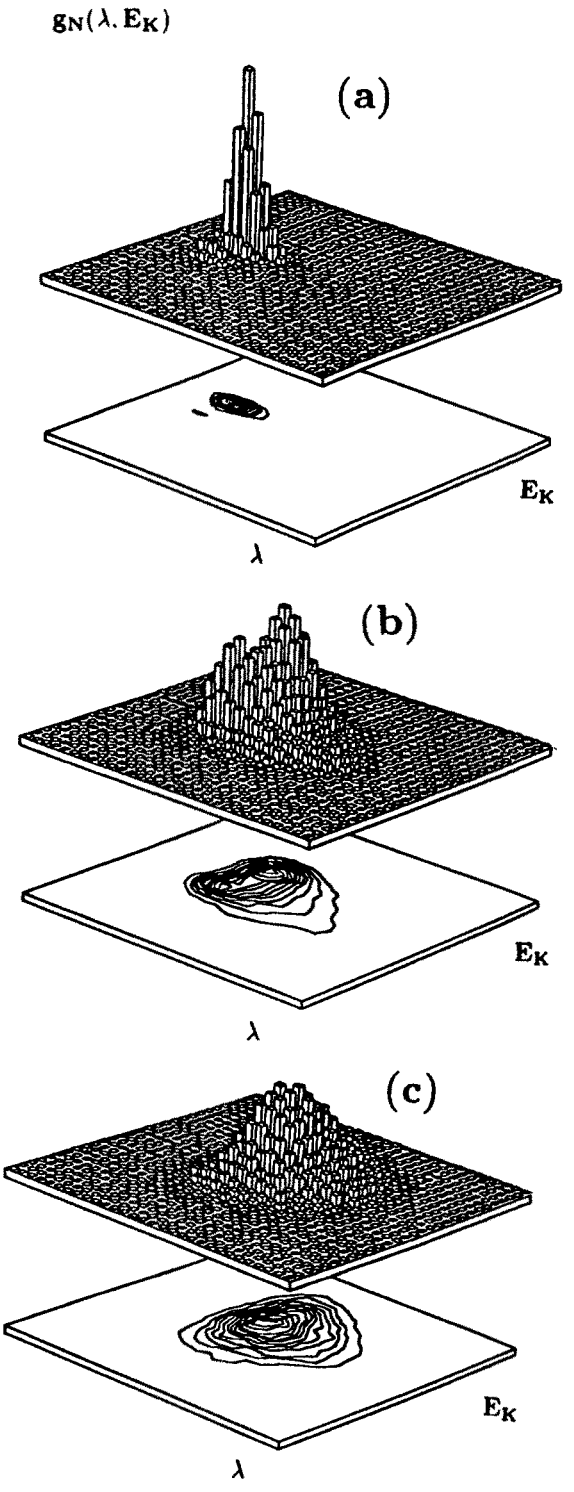

Fig. 3. Joint distributions for the frequency of the largest Liapunov exponent for Ar_7 at three energies, as specified in the text. The distribution in (b) shows bimodality, less well resolved than for Ar_3.

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