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Dynamical signatures of 'phase transitions': Chaos in finite clusters

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Abstract. Finite clusters of atoms or molecules, typically composed of about 50 particles (and often as few as 13 or even less) have proved to be useful prototypes of systems undergoing phase transitions. Analogues of the solid–liquid melting transition, surface melting, structural phase transitions and the glass transition have been observed in cluster systems. The methods of nonlinear dynamics can be applied to systems of this size, and these have helped elucidate the nature of the microscopic dynamics, which, as a function of internal energy (or 'temperature') can be in a solidlike, liquidlike, or even gaseous state. The Lyapunov exponents show a characteristic behaviour as a function of energy, and provide a reliable signature of the solid–liquid melting phase transition. The behaviour of such indices at other phase transitions has only partially been explored. These and related applications are reviewed in the present article.

Keywords. Clusters; chaos; phase transitions; Lyapunov exponents.

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1. Introduction

One major impetus for research in the dynamics of nonintegrable systems has been the hope of understanding the basis for the effectiveness of statistical mechanical ideas in the description of systems with several degrees of freedom [1]. On the one hand, while the ergodic hypothesis is presumed to be valid for generic many-body Hamiltonians, it is difficult to prove for any particular system since a realistic dynamical picture of a multi-particle system is not easy to obtain owing to the extremely large number of degrees of freedom. On the other hand, the application of ideas of statistical mechanics to few-body systems is fraught with difficulty.

A regime where some progress can be made has been provided in recent years by cluster systems, namely aggregates of atoms or molecules consisting of typically between 10 and 1000 particles [2]. These systems are small enough that the explicit dynamics can be followed for reasonably long times. They are also large enough for it to be possible to characterise them as having a well-defined temperature or being in a particular state of matter. Indeed, in recent years, a major interest in cluster studies is the elucidation of simple phase transformations [3,4]. The study of the dynamics at these phase transformations is the subject of this article.

Clusters, being intermediate in size between molecules and bulk matter, have physical and chemical properties which can sometimes be very different from the properties of a

bulk sample of the same material. Technological interest in clusters thus obtains from the practical possibility of engineering materials with desired physical characteristics [2, 5, 7, 8].

Theoretical studies of the dynamics of cluster systems are usually carried out using classical molecular dynamics (CMD) techniques. The connection between the microscopic dynamics and thermodynamics or statistical mechanics can be explored in some detail by studying clusters of increasing size or varying other parameters of the system such as particle mass or the interaction potential. These studies also play an important role in clarifying the spread of ergodic behavior in many-body systems.

In the context of nonlinear studies, finite clusters are important as they provide useful examples of micro- and mesoscopic systems where the methods of nonlinear dynamics (which were essentially developed with low-dimensional systems in mind) can find application. For a N-particle cluster, the number of freedoms is $3N$, which is quite large for even the smallest ($N \approx 7$) systems studied in this context. Given the highly nonlinear nature of the interparticle interaction, the motion is unlikely to be globally regular at finite temperatures. Thus, chaotic dynamics may provide the basic mechanism for inducing statistical behavior in cluster systems by facilitating the rapid mixing among modes and consequent redistribution of vibrational energy. In general, stochastic trajectories are presumed to be the main cause for giving rise to statistical behavior, when the ergodic hypothesis, namely that the time averages are identical to the phase space averages, is expected to hold. This statistical description is manifest in the measured values and the distributions of different quantities [9–11].

With regard to simple phase transitions, it is now well-established that although the numbers of atoms or molecules present is small compared to bulk material ($\sim 10^{23}$), clusters can exhibit structural isomerization [12–15] and related phenomena. Small clusters go from a solid-like phase to a liquid-like phase as the temperature or total internal energy is increased [16]. In bulk matter, the temperature at which the solid melts, T_m, is same as the temperature at which the corresponding liquid freezes, T_f. However, T_m and T_f can be different in finite clusters [17], when there can be dynamical coexistence [18, 19] of both of these phases in the intermediate temperature regime (between T_f and T_m) when clusters start melting. This phenomenon is distinct from the phase change in bulk matter, and has been experimentally verified; extensive molecular dynamics and Monte Carlo simulations [16] also support this picture. Cluster systems can show yet another form of coexistence in surface melting where atoms in the cluster core are at a lower effective temperature and are in a solid state, while atoms on the surface are in a liquid-like state and show much greater diffusivity [13, 20]. At temperatures below the melting transitions, there can also be structural phase transitions [21]. In addition, the so-called glass transition can also be mimicked by cluster systems [22].

The methods and techniques of nonlinear dynamics of relevance to the study of atomic clusters are reviewed in this article. These include the computation of Lyapunov exponents, in particular the largest (maximal) one which has been found to be a reliable phase-space indicator of cluster phase change, the Kolmogorov (K-) entropy, short time distributions of local K-entropy and Lyapunov exponents and Lyapunov spectra. These prove invaluable in understanding phase transitions since there are few available reliable measures for exploring the process of phase change in finite systems.

In the next section we briefly describe the classical methodology of cluster simulations, and define the Lyapunov exponents and the K-entropy. We then discuss the connection between phase transformations (solid-to-liquid) and the maximal Lyapunov exponent (MLE). This is followed by a review of some of the other techniques that have been applied in cluster dynamical studies. We conclude in § 5 with a summary.

2. Cluster dynamics, Lyapunov exponents and the Kolmogorov entropy

The simulation of clusters is usually performed through Monte Carlo (MC) methods, or through molecular dynamics (MD) [23], namely the integration of the relevant Hamilton's or Newton's equations of motion. MD simulations can be carried out either at constant energy, when the microcanonical ensemble obtains, or at constant temperature, with the use of thermostats, in which case the canonical ensemble results. For dynamical studies the most relevant are the MD methods although some progress is being made in the extraction of dynamical information from equilibrium MC simulations [24].

Details of the molecular dynamics simulations of N-particle systems have been extensively documented [23], and the computational methodology of integrating Newton's equation of motion has been developed in considerable detail. Since a cluster is an isolated group of particles, the boundary conditions are simpler to incorporate than in bulk or liquid-state simulations. The interaction between particles is normally taken to be composed of pair-potentials, so that the total potential energy $\mathcal{V}$ for a configuration $\mathrm{R} \equiv r_1, r_2, \ldots, r_N$ is

$$\mathcal{V}(\mathcal{R}) = \sum_{i<j}^{N} V(r_{ij}) \tag{1}$$

where r_i is the position of the i th particle and $r_{ij} \equiv |r_i - r_j|$ is the distance between particles i and j. The pair-potential $V(r)$ is usually taken to be of a simple analytic form, such as the Lennard-Jones (for rare-gas systems), Yukawa (for nuclear systems) or Gupta (for metallic clusters) [25–28]. The total potential energy, $\mathcal{V}$, is an extremely complicated function of the configuration $\mathbf{R}$. Finding the ground state, namely the global minimum, is a tricky problem, although for small enough clusters, this and the lowest few local minima (corresponding to isomers) can be located by several techniques.

The dynamics follows Newton's equations, which are (m_i is the mass of the ith particle)

$$m_i \ddot{\mathbf{r}}_i = -\frac{\partial \mathcal{V}}{\partial \mathbf{r}_i} \quad i = 1, 2, \ldots, N \tag{2}$$

The total energy, namely the Hamiltonian $\mathcal{H} = \mathcal{T} + \mathcal{V}$, where $\mathcal{T} = \sum \frac{1}{2} m_i \dot{\mathbf{r}}_i^2$, is conserved, as are all the components of the total momentum and the angular momentum, giving a total of 7 constants of the motion. At any given total energy, the 'temperature' of the cluster is defined through the average kinetic energy as

$$T = \frac{2\langle \mathcal{T} \rangle}{(3N-6)k_b} \tag{3}$$

k_b being the Boltzmann constant and $\langle\ \rangle$ denoting an average over the entire trajectory.

The spectrum of Lyapunov exponents of a given dynamical system characterizes the dynamical instability of the orbits. An N-freedom hamiltonian system has $2N$ Lyapunov exponents, $\lambda_1, \ldots, \lambda_{2N}$ which are defined by the eigenvalue spectrum of the squared Jacobi matrix [29]

$$J(t) = \frac{\partial(\mathbf{p}(t), \mathbf{r}(t))}{\partial(\mathbf{p}(0), \mathbf{r}(0))},$$
$$(\mathbf{p}_i \equiv m\dot{\mathbf{r}}_i \quad \text{and} \quad \mathbf{p} \equiv \mathbf{p}_1 \cdots \mathbf{p}_N) \tag{4}$$

in the asymptotic limit i.e.,

$$\{e^{2\lambda_1 \tau}, \ldots, e^{2\lambda_{2N}\tau}\} = \text{eigenvalue spectrum of } J^T(\tau)J(\tau) \text{ as } \tau \to \infty \tag{5}$$

Therefore, for a N-particle system in three dimensions there are $6N$ Lyapunov exponents, which come in matching positive-negative pairs as a consequence of Liouville's theorem [30]. They are independent of initial condition $(\mathbf{r}(0), \mathbf{p}(0))$ for ergodic Hamiltonians, and further, if there are L independent constants of motion then $2L$ of the exponents vanish. Hence for a cluster system of N particles there will be $3N - 7$ positive Lyapunov exponents. From Pesin's theorem [31] the sum of these equals the Kolmogorov entropy, which measures the rate of loss of information in a chaotic system. Standard techniques to compute the entire spectrum of Lyapunov exponents have been devised, and these can be further simplified to get only the largest one, the MLE [32, 33]. If the distance between two trajectories at time $t = 0$ is $\mathrm{d}(0)$, and the distance at time t is $\mathrm{d}(t)$, then

$$\lambda_1 = \lim_{t\to\infty} \lim_{d(0)\to 0} \frac{1}{t} \log \frac{\mathrm{d}(t)}{\mathrm{d}(0)} \tag{6}$$

The actual computation of the MLE uses the above definition, but calculates the rate of increase of distance in tangent space [32].

3. Phase transitions and Lyapunov exponents

The behaviour of the MLE at a phase transition was first studied by Butera and Caravati [34] who simulated the planar O(2) Heisenberg model of interacting planar rotors on a lattice in $2d$ as a function of temperature. They noted that the MLE had a distinct bend or 'knee' at the temperature of the Kosterlitz-Thouless transition.

In subsequent studies, Posch and Hoover [35] studied Lyapunov spectra for monoatomic system in two and three spatial dimensions, both solid and liquid states using a repulisive potential. Their results show that the partial spectrum of positive Lyapunov exponents, λ_n, are well approximated by a power law $\lambda_n = \alpha n^\beta$ with $\beta \approx \frac{1}{3}$ for solid-like states and $\beta \approx 1$ for the liquidlike states. Hinde *et al* [36] examined the entire Lyapunov exponent spectra in 7 atom rare-gas cluster and observed the linear dependence of λ_n with distinct slopes in solidlike and liquidlike states.

The idea that the MLE could be an indicator of phase changes was further investigated by Nayak *et al* [37], who examined the melting of rare-gas clusters by using classical molecular dynamics techniques. Simulations of atomic clusters, using the Lennard-Jones

pair potential for cluster sizes of 7, 13 and 55 showed that the MLE has a characteristic dependence at the temperature of the solid-liquid melting transition.

Studies of finite clusters have explored this transition for several years, and the usual manner in which melting is detected is by computing the Lindemann index, namely the average rms fluctuation of the atoms about their equilibrium positions,

$$\delta = \frac{2}{N(N-1)} \sum_{i<j} \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}}{r_{ij}}, \tag{7}$$

i indexing the various atoms, r_{ij} the interparticle distances and $\langle\ \rangle$ implying an average over a MD trajectory. The Lindemann criterion [38, 39] for bulk melting is that δ is larger than 0.1, and has its origin in empirical observations on the characteristic distances between atoms, as estimated from the amplitude of vibrations, which is greater in the liquid state as compared to the solid. This criterion is used even for the study of small systems and is known to correlate well with other indicators of melting such as diffusivity.

A striking result of the dynamical studies [37] was that the change in the largest Lyapunov exponent occurs at the same total energy when $\delta \approx 0.1$, namely, when the Lindemann criterion for melting was satisfied. At melting, the cluster goes from fairly rigid to nonrigid configurations, and is hence able to access a larger volume of the phase space. As a result, larger nonlinearities become important and the motion becomes globally chaotic. Thus the MLE, which is either zero (or small) for energies below the transition temperature, increases significantly at the transition (figure 1). For clusters such as Ar_{13}, the change in the MLE at the melting transition is large, whereas in smaller clusters such as Ar_7, there is only a discontinuity in the slope as the energy increases. In even smaller clusters such as Ar_3, the MLE increases uniformly with temperature, and there is no explicit signature of a phase transition (Ar_7 is the smallest cluster that can be considered to show any evidence of a change in "phase" with temperature [40]). Comparison with previously published results [18, 41, 42] for various cluster sizes shows that the behaviour of the MLE with energy or temperature closely parallels the behaviour of the Lindemann index.

The magnitude of the MLE may be correlated with the volume of phase space available to the system, which also increases significantly at a phase transition. Such increase of phase-space volume apparently accelerates the divergence of nearby trajectories, and this appears to be a generic feature of nonlinear systems. Since the sum of positive Lyapunov exponents is the Kolmogorov entropy, it is not surprising that the MLE should reflect the large increase in entropy at a phase transition. This connection has been explored to some extent–see e.g. refs. [34, 40, 43]. One also therefore expects that the energy density of states should increase sharply at approximately the energy at which the isoergic MD simulations show a sharp rise in the Lyapunov exponent. This has indeed been noted earlier [44], as an increase in the configurational density of states in the cluster solid-liquid coexistence regime, which in turn is reflected in a bimodal character of PE distributions obtained from canonical Monte Carlo simulations for the phase coexistence temperatures. (The density of states can be constructed from constant temperature canonical ensemble simulations using multiple histogram method; see [37] for details.) Although the discussion above is in terms of the internal energy of the clusters, similar

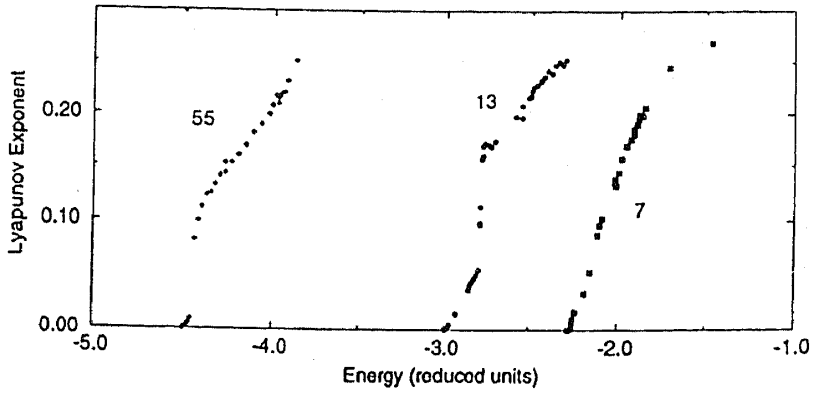


Figure 1. Variation of the largest Lyapunov exponent, λ_1, with internal energy (units are ϵ per atom) for Lennard–Jones clusters of various sizes. The dependence of MLE on the temperature also shows similar behavior.

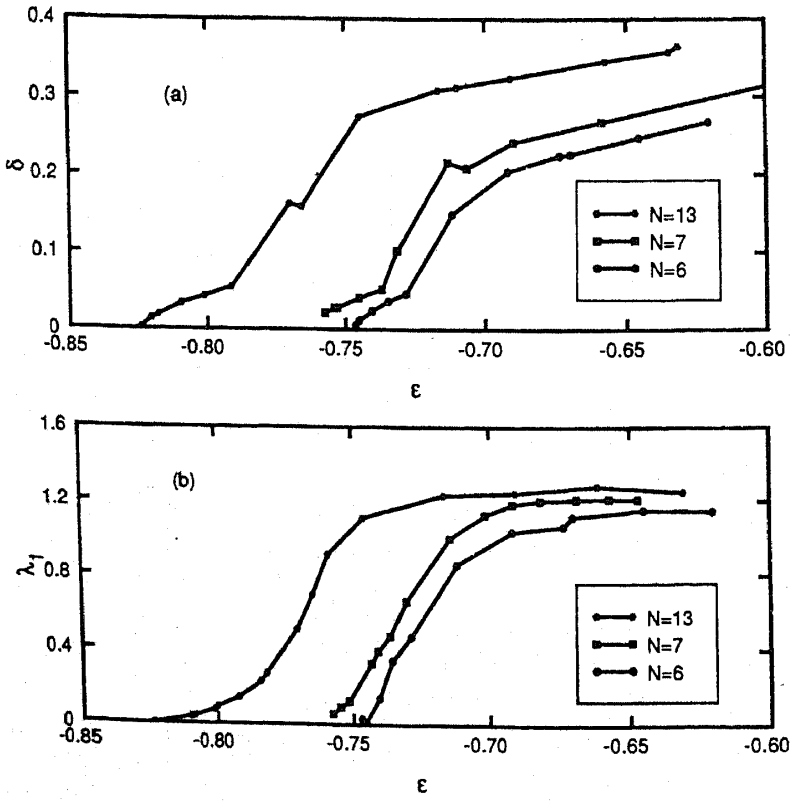


Figure 2. (a) Variation of Lindemann index with energy per particle (in reduced units) for Gupta$_N$ clusters for $N = 6, 7, 13$. (b) Variation of maximal Lyapunov exponent with energy per particle (in reduced units) for Gupta$_N$ clusters for $N = 6, 7, 13$.

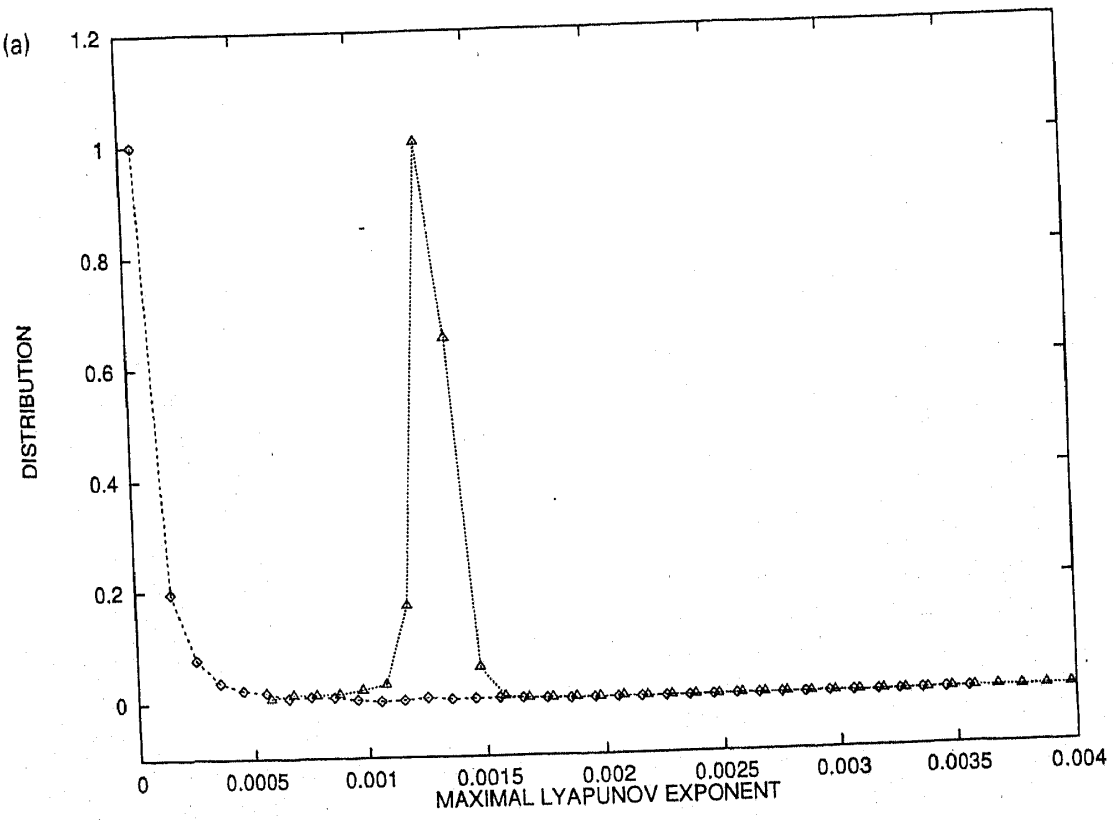
observations and conclusions hold if one considers the behaviour of the MLE as a function of the average kinetic energy or temperature.

At the melting transition, both the Lindemann index and the Lyapunov exponent give identical information about the change in phase of the cluster. At other transitions, when a

'phase transition' is not as well defined, it is often difficult to find a reliable indicator of phase change. Take, for example, the putative glass-like transition that has been seen in small clusters, an example of which is provided by Ar_{19} [22]. The global behavior of the MLE has been examined [45] as a function of average kinetic energy or temperature for Ar_{19}, starting from different configurations corresponding to the global minimum, local minima and saddles in the potential energy hypersurface. The radial function which is commonly used in bulk studies proves unreliable in detecting phase change, while the MLE can be shown to characterise the instability in a precise manner, both in bulk materials as well as in finite clusters [45].

The generality (and perhaps universality) of these observations needs to be investigated in detail. Mehra and Ramaswamy [46] have studied melting in transition-metal clusters using the Gupta potential. In these systems there is no regime of solid-liquid coexistence, but there can be a fluctuating state where the cluster continuously moves between two structures with zero diffusion coefficient. Simulations of 6, 7, and 13 atom clusters have shown parallel behavior: no discontinuities were observed in the MLE, but a marked discontinuity in the slope near T_m was noted (figure 2).

In other recent work on the dynamics at phase transitions, Bonasera *et al* [47] have reported CMD simulations near the critical point for the liquid-gas transition. They study a system of 100 nucleons interacting through a pairwise Yukawa potential, as well as a liquid helium droplet containing about 800 He^4 atoms interacting via the Slater-Kirkwood potential and claim that the MLE has a peak at T_c and can be fitted near the



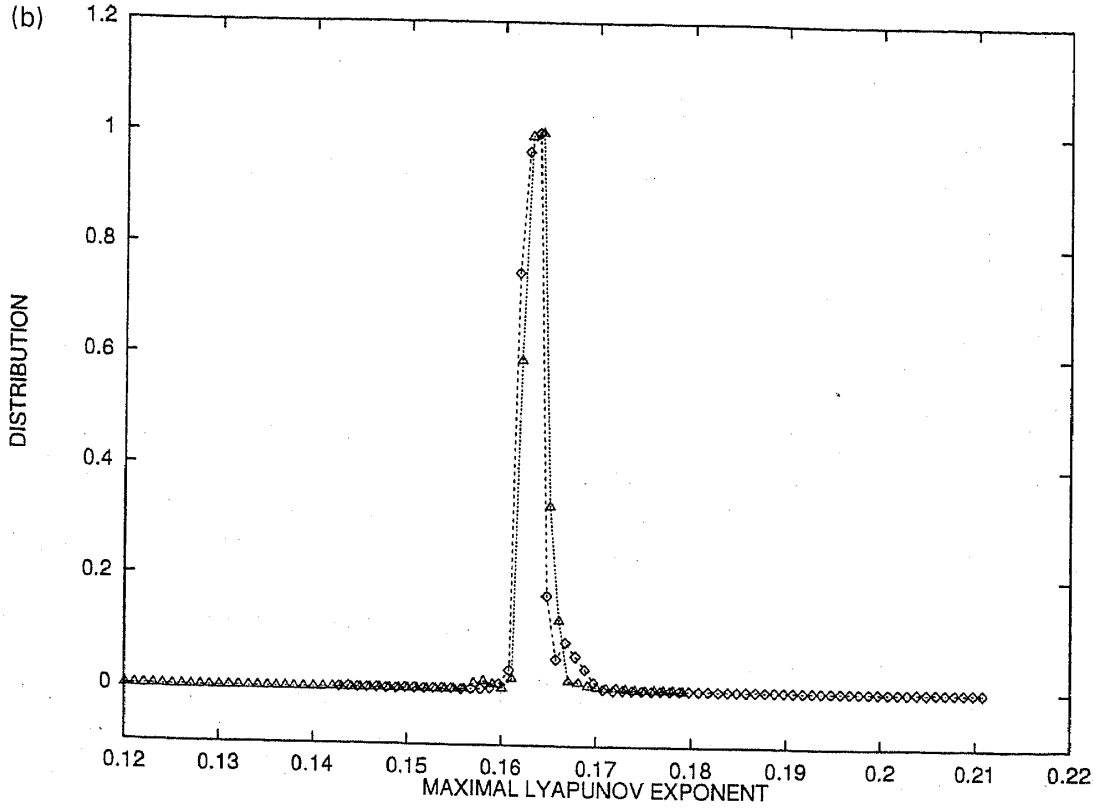


Figure 3. (a) Probability distribution of the maximal Lyapunov exponent for Ar_3. The two different symbols correspond to two different initial conditions. The distributions differ markedly and is a signature of non-ergodicity at low temperatures. See the text for details. (b) Probability distribution of MLE for Ar_3 for two different initial conditions at $E = -0.156 \times 10^{-13}$ erg/atom, $T = 32.3$ K. The distributions collapse on each other indicating that the system has attained ergodicity.

critical temperature with a power law

$$\lambda \sim |T - T_c|^{\omega}$$

with exponent $\omega = 0.15$ (in both the systems). It is not clear if this observation is on solid ground since, as has been pointed out by Nayak *et al* [47], the numerical fit to data is rather poor and the error bars in the data itself is unacceptably large. At continuous phase transitions though, the MLE shows characteristic and distinctive behaviour. Apart from the study of Butera and Caravati, there is recent work by Yamaguchi [10] who has studied a globally coupled Hamiltonian lattice which undergoes a continuous phase transition as energy per particle is increased. There is apparently a peak in the MLE at T_c although the model is integrable both in zero-energy and high-energy limits. It appears that at continuous phase transitions the Lyapunov exponent has a maximum value, while for first-order transitions MLE typically displays a sigmoidal curve. Welding these disparate observations into a coherent whole and giving a satisfactory explanation of the phenomena is currently a major theoretical challenge.

The general features of the behaviour of the MLE at phase transitions can be verified by studying simpler systems where the same behaviour occurs. Simple dissipative dynamical systems show so-called 'crises' [48], where the phase space volume changes

discontinuously with the change in a system parameter. Crises (which also occur in conservative systems [49]) can be of several types. For attractor widening crises [50] where the volume increases by an order of magnitude or more, the MLE changes abruptly at the crisis point, increasing as a power law. For attractor merging crises when the phase space volume doubles, the variation of the MLE with parameter is "knee"-like, i.e. there is a change in the slope of the MLE. Interestingly, both these behaviours have been seen in the case of phase change in finite system (c.f. the cases of Ar_{13} and Ar_7), as well as in phase transitions in other systems.

Calculations of entire spectrum of Lyapunov exponents have also been made [36, 46, 51]. For the study of complex systems this is indeed important, but calculating them through the standard methods such as the tangent space technique can be computationally intensive. New methods proposed [52, 53] can circumvent this bottleneck. Lyapunov spectra characterize the short-time behaviour of correlation functions, and are related to the entire set of relaxation times in the system [54] although this has been established only for simple low-dimensional systems. For high-dimensional systems, in the limit $N \rightarrow \infty$, the existence of a smooth distribution λ_n, $n = i, \ldots, N$ has been numerically verified [55]. In the highly chaotic regime the function λ_n is linear [56], and this has been verified for Ar clusters (see figure 3(a)). In other systems, such as metallic clusters (using the Gupta potential) the results differ: the Lyapunov spectra for 6, 7 and 13 particle metal clusters have been calculated, and λ_n is found to be a nonlinear function of n [50] (figure 3(b)). The behaviour of Lyapunov spectra at phase transitions needs to be investigated.

4. Local K-entropy and local Lyapunov exponents

Global dynamical indicators are useful, but they are also somewhat limited in that they do not provide details about local dynamics—whether motion within a particular region is more or less chaotic. They also do not give any indication of the time-dependence of phenomena such as the spread of ergodicity. This information is provided by local indicators of the dynamics, namely the short time distributions of the K-entropy and the Lyapunov exponent. Berry and coworkers, in a series of papers [11, 36, 57], related the local K-entropy information to the topology of the cluster potential energy surface (PES). The local K-entropy is finite-time analogue of the global entropy, and is obtained by dividing a long trajectory into several parts of duration $N\Delta t$ and calculating the entropy for each time segment separately. From this the probability distribution of entropies is obtained, which can then be compared with the distribution of potential energy averaged over same duration $N\Delta t$.

A direct way to characterize the structure of a PES is to catalogue its various minima and saddles through steepest gradient and quenching techniques. This can be done for small clusters but as the number of minima and saddles increases exponentially with size, it is a formidable task to list all of these. The geometric features of a saddle can be determined by calculating the average curvature from the eigenvalues of the instantaneous Hessian matrix, namely the instantaneous normal mode spectra [24]. The analysis of clusters in saddle regions is important in understanding phenomena such as isomerization and solid-liquid transition.

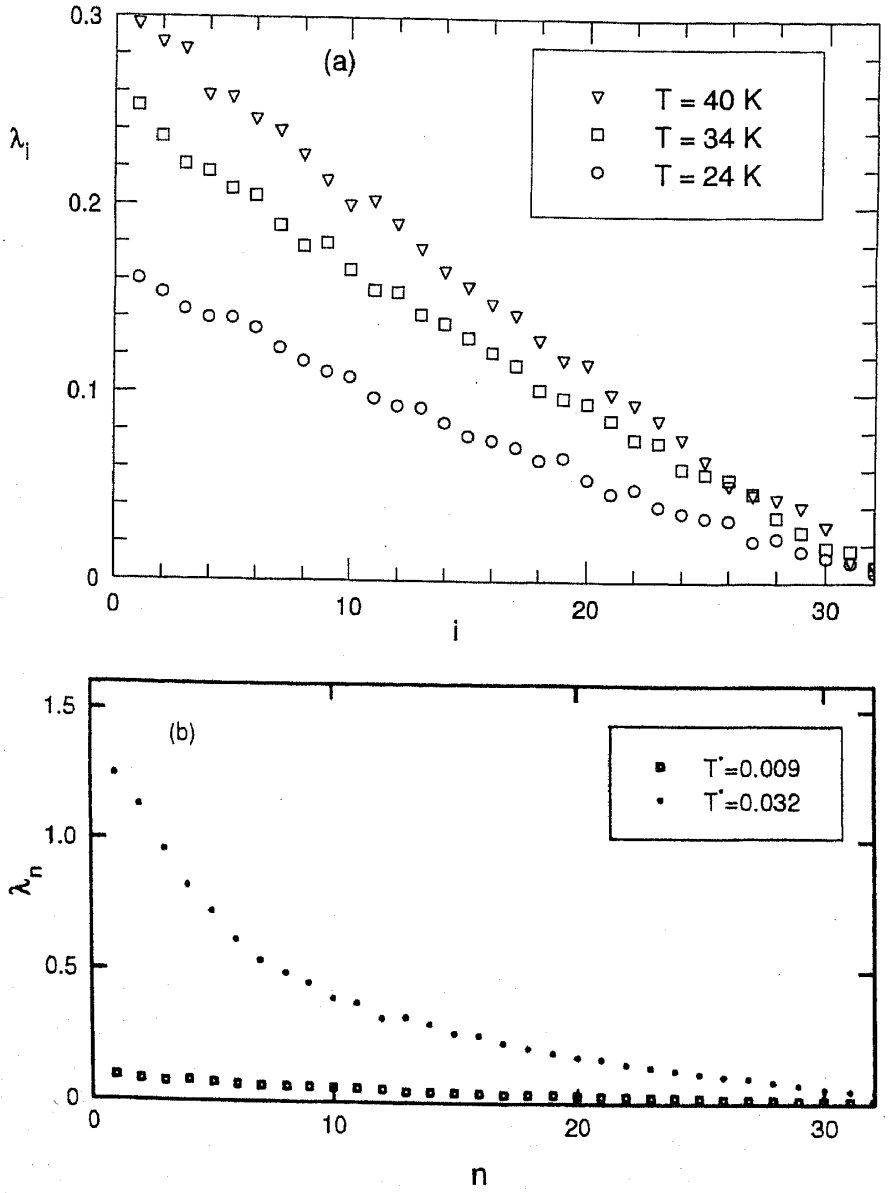


Figure 4. (**a**) Lyapunov spectra for Ar_{13} at three temperatures (1) 24 K (solid phase), (2) 34 K (coexistance phase) and (3) 40 K (liquid phase). (**b**) Lyapunov spectra for $Gupta_{13}$ at reduced temperatures (1) $T^* = 0.009$ (solid) and (2) $T^* = 0.032$ (liquid). Only the 32 positive exponents are shown.

In Ar_3 and Ar_4 clusters, which have rather flat saddles, the local K-entropy was found [11, 36, 57] to be significantly smaller in the saddle region as compared to other regions of the PES. This was attributed to an increase in the degree of quasiperiodicity near the saddle arising from a partial decoupling of the cluster's vibrational modes (as measured by the total vibrational coupling). In Ar_5 on the other hand, the local K-entropy in saddle regions was comparable to that in the well while for Ar_6 and Ar_7 saddle entropy was intermediate between entropies of the two wells which are connected by that saddle. All these clusters have relatively steep saddles, which suggests that the 'regularizing' effect of a saddle depends on the shape of PES near the saddle, especially the flatness of the

saddle along the isomerization or reaction path. This behaviour is size-dependent: in larger clusters the influence of a particular saddle is reduced as the system will not spend much time on a sharp saddle.

In systems where the topography of the potential energy surface is very complicated, ergodicity cannot be guaranteed at all energies or temperatures. This can be seen by examining the distribution of finite-time or local Lyapunov exponents which are defined in the same manner as the local K-entropy, by dividing a long trajectory into segments of length $N\delta t$. Amitrano and Berry [57, 58] calculated the probability distribution of the largest local Lyapunov exponent for Ar_3 at different values of energy for various time intervals, and related these distributions to the evolution of ergodicity. At low energies ($T = 18\,\mathrm{K}$) in the argon trimer, the shape of the distribution depends on the initial conditions for any time interval: the system does not exhibit ergodicity even on long time scales. At intermediate energies ($T = 28\,\mathrm{K}$) the system is found to be ergodic: different initial conditions gave similar unimodal distributions but with different second moments. At energies high enough to allow saddle crossing ($T = 31\,\mathrm{K}$) the distributions are bimodal up to a particular time interval, and unimodal for longer times, showing a time scale separation between the intra–well and inter–well motions. At still higher energy ($T = 37\,\mathrm{K}$) one has true ergodic behavior with unimodal distributions even for shortest trajectory segments. Figure 3(a) is the probability distribution of MLE for Ar_3 at $E = -0.156 \times 10^{-13}$ erg/atom, $T = 7.41\,\mathrm{K}$ for two different initial conditions, the trajectories being of 10^8 MD time steps. The distributions shows no sign of convergence, indicating the non-ergodic nature of the system at that temperature. In contrast, the probability distributions of MLE at a higher energy $E = -0.089 \times 10^{-13}$ erg/atom, $T = 32.3\,\mathrm{K}$ (see figure 3(b)) for two different initial conditions collapse on each other indicating the system has attained ergodic behavior. These observations at the microscopic level are significant particularly in the context of transition from non-ergodic to ergodic behavior in small finite systems. Similarly, at $T = 14\,\mathrm{K}$ the autocorrelation function of the local Lyapunov function is oscillatory, while it rapidly decays to zero for $T \geq 18\,\mathrm{K}$. Qualitatively similar results hold for Ar_7. A general theory of these phenomena has not yet been given, and it is not a simple matter to extend these calculations to larger cluster sizes.

5. Discussion and summary

Finite cluster systems may provide one regime where the methods of dynamical systems and statistical mechanics can simultaneously be applied. Given the highly nonlinear character of the typical cluster dynamical system, it is not surprising that chaotic motion is both so widespread and that it plays such an important role. For small clusters, although the number of freedoms is not too large, it is possible to focus on particular features of interest—such as the K-entropy or the Lyapunov exponents—and explore the dynamics of how statistical behaviour such as ergodicity develops in such systems.

There are, however, dynamical regimes of interest when the motion of clusters becomes simple. For example, at very low energies above the global minimum, the cluster, like many hamiltonian systems, can be expected to be nearly integrable. In a recent study of Ar_{13} clusters, Salian *et al* [59] examined the dynamics of collective

excitations by exciting the monopole mode, namely that mode of oscillation where the particles execute radial motion only, as a function of temperature. Below a threshold, which they determined to be $T_s = 7.2$ K, this mode does not decay for long times. Above T_s, the time dependence of the amplitude variation could be accurately modeled by a damped harmonic oscillator, while below T_s, the monopole mode is periodic or quasiperiodic. This suggests [59] that as long as the cluster is confined to the global minimum in the PES, the monopole mode does not decay. When the temperature is high enough for the system to come out of this well, the nearby local minima, which correspond to rearrangement of one or a few particles act as decay channels, akin to single–particle excitations in nuclei [60]. The MLE in this temperature range has also been studied [61]: below T_s, the MLE is essentially zero, and although in the so-called 'solid' state, the MLE becomes positive only above T_s. Thus the survival of the symmetric monopole mode is intimately connected to the onset of globally chaotic motions in the dynamics.

A major focus of this article has been on the appropriateness of using the Lyapunov exponents as indicators of phase change since this focuses on a property of the phase space behaviour of the system. The dynamics of the solid-liquid melting transition, the liquid-gas transition, and the glass transition in finite systems have been studied using this quantity. For phase transitions where order parameters based on other criteria can be ambiguous (as for example the glass transition), the MLE may be able to provide the clearest signature of the transition.

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