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Maximal Lyapunov exponent in small atomic clusters

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We study small clusters of atomic argon, Ar_7, Ar_{13}, and Ar_{55}, in the temperature range where they undergo a transition from a solidlike phase to a liquidlike phase. The signature of the phase transition is clearly seen as a dramatic increase in the largest Lyapunov exponent as the cluster "melts."

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I. INTRODUCTION

Molecular dynamics (MD) simulations of small Lennard-Jones clusters have given evidence for a transition from solid phase to a liquid phase as the energy is increased [1]. A variety of studies [2–4] have examined the dynamical behavior as a function of the internal energy or temperature, and observe that finite clusters of different sizes exhibit dynamical coexistence of the solid and liquid phases over a range of energy [5,6]. This leads to distinct and unequal melting and freezing temperatures, in contrast to the behavior of bulk matter, for which the freezing and melting temperatures coincide.

In this paper we study the dynamics of small clusters of rare-gas atoms as a function of the average kinetic energy or temperature, and examine the variation of the maximal Lyapunov exponent (MLE): the MLE increases dramatically as the system makes a transition from a solidlike to a liquidlike phase, and this offers a characterization of the phase transition.

There has been considerable work on such dynamical indicators, most notably by Berry and co-workers [1,4,7–11], who have looked in detail at a variety of quantities, including [7,9] the Kolmogorov-Sinai (KS) entropy, i.e., the *sum* of all the positive Lyapunov exponents. This quantity increases monotonically and smoothly with temperature or energy as the phase changes; however, detailed information can be obtained regarding the underlying potential-energy surface [9]. Other work that has looked for the connection between phase transitions and the Lyapunov exponent is by Butera and Caravati [12], who found a discontinuity in the slope of the MLE at the temperature of the phase transition in a system of planar rotors. Related work by Posch and Hoover [13] has examined the entire spectrum of exponents, and suggests that the positive Lyapunov exponents are power-law distributed, with different scaling exponents in solid and liquid phases.

Our observation is that the signature of the phase change is most clearly seen in the largest Lyapunov exponent alone. For realistic atomic and molecular systems, this quantity is simpler to compute than the corresponding KS entropy.

In studying clusters it is usual [2] to examine a caloric curve as a function of the temperature. The caloric curve exhibits low and high energy regions and the onset of phase change is marked by a change in slope. A more striking depiction of the change in phase as a function of the temperature is provided by examination of the rms bond length (or Lindemann index) δ. This quantity, when plotted against temperature, shows a relatively sharp change at the phase transition. Our results show that the MLE exhibits a variation analogous to δ as the temperature is varied.

In order to probe the microscopic origins of such behavior, we examine the classical density of states. The sudden increase in the MLE should be correlated with a change in entropy implying a sudden increase in the accessible phase space. The increase in the density of states as clusters melt has been demonstrated previously [14] through finite-temperature Monte Carlo simulations which act essentially as probes of the configurational density of states. A sharp, steplike increase in the density of states in the solid-liquid coexistence regime arises from a bimodal potential-energy distribution. Thus at low temperature (in the solid state) the potential-energy distribution looks like a single Gaussian with a small width—the system is basically confined to the global potential minimum, and the peak is sharp. With increasing temperature, the cluster has access to more and more configurations; when the cluster gains access to a large number of high energy minima, the distribution broadens, and furthermore, becomes bimodal—with one Gaussian for the solidlike minima, and one for the liquidlike. We have carried out constant temperature Monte Carlo simulations for Ar_7 and Ar_{13}, and make comparison with

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existing data [14] for Ar_{55}. We present a detailed study of the MLE over a range of energies and observe a direct correlation between the energy range where the distribution of the density of states is bimodal and the abrupt increase in the MLE.

This paper is organized as follows. In the next section we briefly give details of the systems studied and the computational methods used in the molecular dynamics and Monte Carlo simulations. In Sec. III, results are presented for the largest Lyapunov exponent as a function of the internal energy. The classical configurational density of states is estimated from potential-energy distributions at several temperatures and the above connections are verified. Our conclusions are summarized in Sec. IV.

II. METHODOLOGY

A. Molecular dynamics

The interatomic potential between neutral rare-gas atoms is taken to be the usual Lennard-Jones potential of the form

$$V(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}], \tag{2.1}$$

where r_{ij} is the distance between the atoms i and j, and $-\epsilon$ is the minimum of the potential at a distance $2^{1/6}\sigma$, σ being the unit of the length. The dynamics of the cluster is studied using standard MD techniques [15]. The classical equations of motion are integrated by the velocity Verlet algorithm; all the quantities are expressed in scaled form, time, and distances by $(m\sigma^2/48\epsilon)^{1/2}$ and σ, respectively. We choose ϵ and σ appropriate to argon [16]: $m = 6.633\,82 \times 10^{-26}$ kg is the Ar mass, $\sigma = 0.3405$ nm, and $\epsilon = 119.8$ K. The time step used is 0.01 in reduced units (3.125 fs) which ensures that the total energy is conserved to within 0.01%.

In this paper we have studied clusters of sizes of 7, 13, and 55; these systems have been previously studied [4,11,17–21] extensively from several points of view. Our calculations were carried out for zero total linear and angular momentum [4], and the clusters were equilibrated for 3×10^5 MD steps. The average energy can be adjusted as desired by a process of adiabatic heating (or cooling), wherein the velocities are scaled by a factor slightly exceeding (or less than) 1, for a limited time interval at a sufficiently slow rate [2]. This is particularly useful in probing the coexistence region, when the cluster wanders erratically between solid and liquid configurations [22].

B. Monte Carlo simulations

Classical Monte Carlo simulations were carried out using the Metropolis algorithm as follows. Clusters were restricted to a spherical cavity [3,14] using a confining potential of the form

$$V_c = \epsilon \sum_i [|\mathbf{R}_i - \mathbf{R}_{\text{c.m.}}|/R_c]^{20}, \tag{2.2}$$

where $\mathbf{R}_i$ and $\mathbf{R}_{\text{c.m.}}$ are the position vectors of the ith atom and the center of mass of the cluster, respectively, and R_c is the cut off radius. The effect of the confining potential, in particular the choice of R_c, is significant once cluster evaporation sets in [23]. However, in the coexistence regime studied here, evaporation was verified to be negligible by careful inspection of the density profiles generated from the simulations. A cut off value of $R_c = 4\sigma$ was used for both Ar_7 and Ar_{13}.

Results from the microcanonical MD simulations and the canonical ensemble MC simulations are connected by the total density of states function. The density of states can be constructed from constant temperature canonical ensemble simulations using the multiple histogram method [14,24]. The total density of states is a convolution of the kinetic and potential (or configurational) density of states. For an N-atom cluster, the kinetic energy density of states at kinetic energy K is given by $U(K) = CK^{0.5(3N-6)-1}$ where C is a constant for a given particle mass and system volume [25]. While the density of states was calculated, it was found that the actual finite-temperature potential-energy distributions were more useful from our point of view, as discussed in Sec. IIIB.

III. RESULTS

We first discuss the results from molecular dynamics simulations at constant energy. The average temperature T of the system is given by

$$T = \frac{2E}{(3N-6)k_B}, \tag{3.1}$$

where N is the number of atoms, $k_B = 1.381 \times 10^{-23}$ erg/K is the Boltzmann constant, and E is the kinetic energy, suitably averaged over the entire trajectory. The root mean square bond length fluctuation is defined by

$$\delta = \frac{2}{N(N-1)} \sum_{i<j} \frac{\sqrt{\langle r_{ij}^2\rangle - \langle r_{ij}\rangle^2}}{r_{ij}}, \tag{3.2}$$

which is a sensitive quantity for detecting a change in phase. In Eq. (3.2) above, $\langle\ \rangle$ implies an average over the entire trajectory. *Melting* of the cluster is indicated by the increase in δ above 0.1, and occurs at different temperatures for different clusters. In the transition regime, owing to dynamical coexistence [7,22] these small clusters fluctuate back and forth between solidlike and liquidlike states, giving rise to fluctuations in the value of δ. Figure 1 shows the kinetic energy of an Ar_{13} cluster as a function of time for three different values of the total energy. In Figs. 1(a) and 1(b) where the total energy corresponds to the solid or the liquid state the system clearly has a mean kinetic energy and hence a temperature. But in Fig. 1(c), where the total energy lies in the transition region, the system wanders between high- and low-kinetic energy configurations and it is only possible to define an average temperature. Since the total energy is held constant, the high kinetic energy (or the low po-

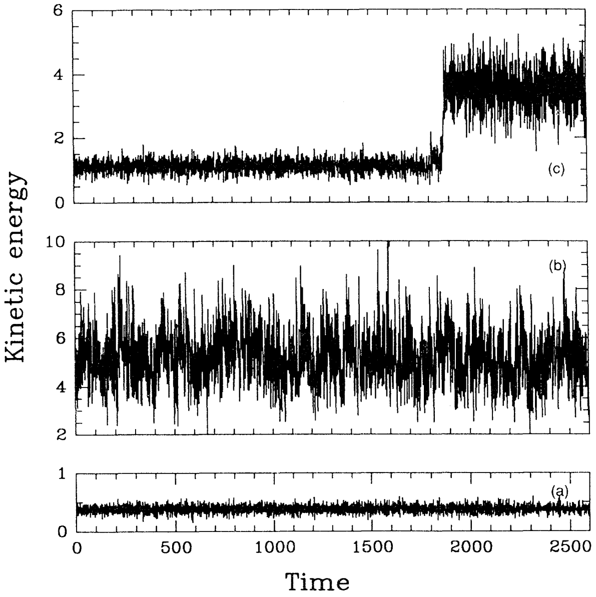

FIG. 1. Kinetic-energy fluctuations in a cluster of Ar_{13} in (a) the *solid* state, energy equal to -0.48, $T = 2.78$ K, $\Delta = 0.015$; (b) *liquid*, energy equal to -0.35, $T = 37.8$ K, $\delta = 0.308$; and (c) a state of dynamical coexistence, energy equal to -0.46, $\delta = 0.098$. Units of energy are 10^{-13} erg/atom.

tential energy) corresponds to the solidlike state whereas the low kinetic energy (or the high potential energy) corresponds to the liquidlike state.

A. Maximal Lyapunov exponent

Local stability properties of trajectories are estimated by computing the average rate of exponential divergence of two nearby trajectories. For an N-atom cluster, since the system is conservative and Hamiltonian, there can be up to $3N - 7$ positive Lyapunov exponents [26], and we calculate the largest of these, defined by

$$\lambda = \lim_{T\to\infty} \lim_{d(0)\to 0} \frac{1}{T} \ln \frac{d(T)}{d(0)}, \tag{3.3}$$

where $d(0)$ is the initial distance between the two trajectories and $d(t)$ the separation at time t. For chaotic dynamics, $\lambda > 0$.

We use the tangent space method [27] to calculate the MLE from the final portion of 3×10^5 MD step trajectories. As the total energy increases, 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 is globally chaotic. Thus the MLE, which is either zero (or small) for energies below the transition temperature, becomes significantly larger. Interestingly, this change in MLE occurs at the same total energy when $\delta \approx 0.1$, which is the usual Lindemann criterion for bulk melting. The variation of the Lyapunov exponent with energy is shown in Fig. 2. For the larger clusters, Ar_{13} and Ar_{55}, the change in the MLE at the melting transition is sharp. In the smaller cluster, however, there is only a discontinuity in the slope as the energy increases (cf. Butera and Caravati [12]). In even smaller clusters such as Ar_3, the MLE increases uniformly with temperature, and there is no explicit signature of a phase transition. It should be noted that Ar_7 is the smallest cluster that can be considered to show any evidence of a change in "phase" with temperature [17]. A comparison with previously published results [4,6,21] for Ar_N clusters shows that the behavior of the MLE with cluster energy (in microcanonical simulations) closely parallels the behavior of the Lindemann index.

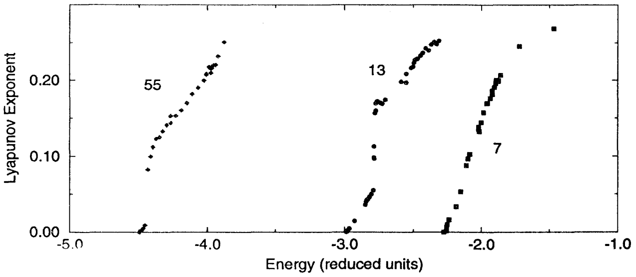

FIG. 2. Variation of the largest Lyapunov exponent λ, with internal energy (units are ϵ per atom) for clusters of different sizes. The dependence of the MLE on the temperature also shows similar behavior.

B. Finite-temperature simulations

The magnitude of the maximal Lyapunov exponent may be correlated with the volume of phase space available to the system, which suggests that a significant change in the energy density of states should occur at approximately the energy at which the isoergic MD simulations show a sharp rise in the Lyapunov exponent. As has also been noted earlier [14], a distinct, step-like increase in the configurational density of states in the cluster solid-liquid coexistence regime is reflected in the bimodal character of potential-energy (PE) distributions obtained from canonical Monte Carlo (MC) simulations for the phase coexistence temperatures. In this section, we accordingly examine the potential-energy distributions for Ar_7, Ar_{13}, and Ar_{55} and correlate them with the energy at which the MLE shows a steep rise.

For Ar_{13}, the caloric curve [21] is essentially flat below $T \approx 35$ K corresponding to constant average kinetic energy $\langle K \rangle$. Consequently one can assume the kinetic-energy density of states in this region to remain approximately constant and consider only the potential energy or configurational distribution of states. To within reasonable accuracy, the total kinetic energy for the 13-atom cluster is found to be 4.83ϵ, and the corresponding values of the energy of freezing, E_f and the energy of melting E_m to be -34.7ϵ (-2.6ϵ/atom) and -29.2ϵ (-2.2 ϵ/atom), respectively. From Fig. 2, it may be seen that this is exactly the region in which the MLE for Ar_{13} shows a dramatic rise. The corresponding range of potential energies that is pertinent for the cluster coexistence region lies between -39.5ϵ and -34ϵ, which, again, is precisely the region in which the Monte Carlo distribution shows a shouldering, i.e., evidence of bimodality (see Fig. 3). The bimodality is particularly marked at temperatures of 33.5 and 35.2 K.

The caloric curve for Ar_7 does not show a distinct region of constant temperature but merely an inflection point at a temperature of approximately 20 K and a total energy of approximately -13.2ϵ. At this value of total energy, corresponding to -1.9ϵ/atom, the curve of MLE versus total energy shows a knee. This value of total energy corresponds to a potential energy of -14.4ϵ. This is again the region in which the potential-energy distributions at constant temperature (noticeably at 20.1 and 23.5) show a distinct broadening and shift, indicative of an increase in the density of states curve. Although the distributions themselves broaden, there is no evidence of bimodality in the manner of Ar_{13}. (See Fig. 3.) This is also in keeping with the fact that the MLE for Ar_7 does not show a sharp increase as the cluster melts, but only has a "knee."

We have not computed PE distributions for Ar_{55} since results have been published for this system [14]: the total density of states curve shows a region of positive curvature (leading to a very pronounced bimodal character) centered at approximately -240ϵ (-4.4 ϵ/atom). This correlates very well (see Fig. 2) with the energy at which the MLE for Ar_{55} rises dramatically. (Note that the results in Ref. [14] are for the total energy density of states; in the phase coexistence region, the kinetic energy will be approximately constant and the bimodality will reflect changes in the configurational density of states.)

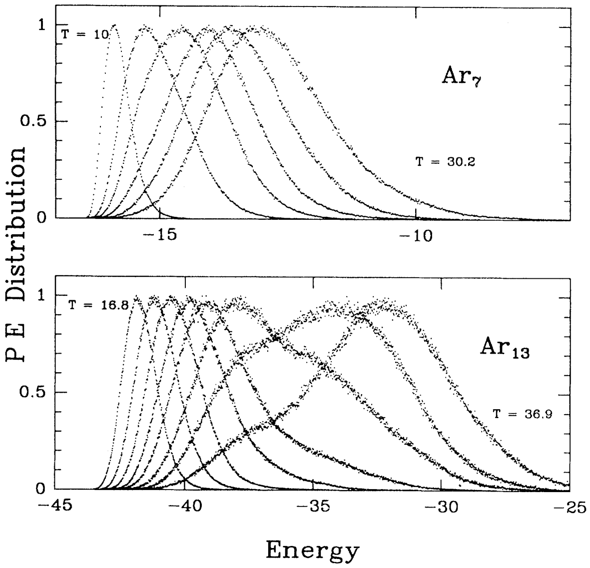

FIG. 3. Potential-energy distributions at different temperatures for the clusters, from classical Monte Carlo simulations. For Ar_7, the temperatures are, from left to right, $T = 10$, 13.4, 16.8 20.1, 23.5, 26.8, and 30.2 K, while for Ar_{13}, they are $T = 16.8$, 20.1, 23.5, 26.8, 30.2, 33.5, 35.2, and 36.9 K. Similar distributions for Ar_{55} have been published earlier by Labastie and Whetten [14].

To summarize, the rise in the MLE is strongly correlated with the bimodality and a sharp increase in the configurational density of states for the cluster sizes examined in this work. Although the discussion above has been in terms of the internal energy of the clusters, similar observations and conclusions hold if one considers the behavior of the MLE as a function of the average kinetic energy or temperature.

IV. CONCLUSION

In the present work we have focused on the variation of the maximal Lyapunov exponent, which examines the "chaoticity" of the system as a function of internal energy or temperature in small atomic clusters.

The MLE is found to be positive at all energies, indicating that motion at all temperatures is chaotic for systems of this size and complexity. However, the striking feature is that there is a dramatic increase in the Lyapunov exponent (paralleling the behavior of δ), in the phase transition region, which indicates that the MLE should prove to be an unambiguous characteristic of phase transformations in clusters and larger systems, when such a phase transition is accompanied by sufficient change in entropy. In fact, the derivative of the MLE with temperature behaves very much like the specific heat at phase transition; this provides a direct connection, in some sense, between the classical dynamics and the thermodynamics.

It is not *a priori* obvious why the increase in internal energy or temperature must lead to an increase in the Lyapunov exponent— we have conjectured that this abrupt increase in the MLE corresponds to an increase in the available phase space and consequently in the local rate of divergence of trajectories [27]. In the solid phase, the cluster vibrates mainly around the global minimum and explores confined regions in the phase space. The Lyapunov exponent does not increase significantly as the energy (or temperature) is increased, until several higher energy minima become accessible. This opening up of phase space is reflected in the sharp rise in the MLE. When the frequency of passage between these potential wells increases, the cluster melts. With further increase in energy the time spent in a particular well becomes comparable to the time taken for the interwell passage: the system is essentially in the liquid state, and the value of the largest Lyapunov exponent is considerably larger than it is in the solid or the coexistence phase and changes gradually with temperature.

Support for this picture is obtained by examining the potential-energy distributions generated from canonical ensemble Monte Carlo simulations. These provide a clear indication (particularly in the case of larger clusters Ar_{13} and Ar_{55}) of a bimodal distribution in the phase coexistence region, indicative of a sharp rise in the density of states.

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