

# Small clusters: between dynamics and thermodynamics

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The relation between equilibrium properties and dynamical properties, and between the two kinds of descriptions, is explored by examining the dynamics of isomerization of argon clusters. The same general subject, from the viewpoint of ergodicity and chaos is examined through the fractal dimension of the trajectory in phase space and the Kolmogorov entropy.

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## 1. Introduction

Small clusters offer a special kind of insight into the structure of matter and into the nature of the theoretical descriptions we impose. On the first aspect, we can use the powerful techniques that have been developed for accurate treatment of atoms and small molecules, extending them to systems much richer in structure and dynamics than the pristine species for which they were first intended. We can address issues long thought to be relevant solely in the province where  $N$ , the number of particles in a system, goes to infinity, yet maintain the control characteristic of the methods for small systems. This is leading us to new insights into how properties of bulk matter evolve from molecular properties, for example how structures of solids evolve from the structures of clusters, and how the electrical conductivity we associate with metals.

The second aspect of what clusters offer, insights into the conceptual foundations of our descriptions, is the main concern of this discussion. In particular, clusters offer such wide ranges of time scales for various kinds of phenomena that we can use them to clarify our notions of equilibrium and dynamical processes, and the relationships between the measurement process and how we think of equilibrium and dynamics. While this may seem more philosophical than scientific when stated in such general terms, the real importance of such considerations is in their application to specific scientific problems, particularly

regarding what we consider significant information about a system and how we interpret it. Here we shall examine two aspects of small clusters relevant to the issue, both dealing with how a cluster explores the space available to it. The first is the question of how the shape of a potential surface governs the way the cluster's structure evolves in time, and how we can infer the most important information about the surface; we shall use  $\text{Ar}_7$  as a principal illustration for this. The second is the question of how the levels of ergodicity and chaos evolve as the energy of a cluster increases. To illustrate this topic, we shall have to restrict ourselves to  $\text{Ar}_3$  at present.

## 2. The dynamics of a cluster

Small clusters can exhibit well-distinguished solid-like and liquid-like forms, although not all clusters need show such sharp distinctions [1]. When the two forms may coexist, they display a dynamic equilibrium in which an ensemble of clusters contains some liquid-like and some solid-like clusters, in a ratio governed by a chemical equilibrium constant, the exponential of the difference between the (temperature dependent) free energies of the two forms. Any individual cluster spends an interval of time in one form, then switches to the other for some time, thus passing back and forth between the two. If the system is ergodic, as we normally expect, then the ratio of the amounts of the

two forms at any instant is, within fluctuations, the same as the ratio of times any one cluster spends in the two forms.

One further phenomenon that small clusters may show is a finite band of temperature and energy within which the solid-like and liquid-like forms coexist [2]. We expect such “finite band coexistence” to be accompanied by sharp but unequal freezing and melting temperatures,  $T_f$  and  $T_m$ . The former is the lower bound for thermodynamic stability of the liquid-like form; the latter is the upper bound for the thermodynamic stability of the solid-like form. Evidence from simulations shows that argon clusters of some but not all sizes can be expected to show such sharp bands of coexistence [2]. Of the  $\text{Ar}_N$  clusters that have been studied by simulation, those that exhibit phase coexistence have  $N=6, 7, 9, 11, 13, 15$  and  $19$ . Those that do not have  $N=8, 14, 17, 20, 22, 26$  and  $33$ . Recent experimental data support the concept, both regarding a sort of surface melting of argon atoms clustered on a single molecule of carbazole [3] and especially of conventional bulk melting of argon clusters containing a single benzene molecule [4]. The latter experiments indicate that  $\text{Ar}_N\text{C}_6\text{H}_6$  clusters exhibit coexistence for all  $N$  from  $17$  through  $24$  under the specific conditions used by Hahn and Whetten.

The first question to address here is why some  $\text{Ar}_N$  clusters do not exhibit a finite band of phase coexistence while others do. Coexistence can be detected in several ways from simulations; the most useful and unambiguous is the appearance, in the history of a molecular dynamics simulation, of a bimodal distribution, either of (short-range) mean temperatures in an isoergic simulation or of (short-range) mean potential energies in an isothermal simulation. So long as the short-range averages are, at least in molecular dynamics (MD), over intervals long enough to include a few vibrations, bimodal distributions indicate two coexisting forms and average properties can be computed by examining separately the contributions to each of the peaks in the distribution. Under such circumstances, we can compute equilibrium properties for each form of the cluster and predict what each form should show in an experiment—for example, what line shapes each might show.

But not all clusters exhibit bimodal distributions; why? One reason that bimodal distributions may not appear is the first that makes us confront what equilibrium means. It may be that the clusters of a particular size pass between the solid and liquid forms faster than the intervals over which we take our short-time averages. In such a case, we would find unimodal distributions of mean temperatures in our simulations and no evidence for anything but gradual softening with energy or temperature. This can be achieved for any

simulation by extending the interval for “short-time” averages until it is significantly longer than the mean time spent in either phase. Likewise, one can test for this phenomenon by reducing the interval for short-time averaging down to as brief as a single vibrational period. In our own simulations, we have most frequently used  $500$  steps of  $10^{-14}$  s each as our averaging interval, about  $3$  breathing vibrations of the Ar clusters. Reducing this to only  $150$  steps did not reveal any bimodal behavior for any of the clusters, e.g.  $N=8$ , which show only unimodal behavior with  $500$ -step averaging [5]. Hence we can rule out this explanation for unimodality of the specific argon clusters mentioned two paragraphs previously.

A second explanation of absence of a sharply bounded band of coexistence is the shape of the potential surface itself. It may be that the potential minima and saddles simply permit a gradually increasing exploration of configuration space as the energy or temperature of the cluster increases. This, at present, seems to be the best explanation of the behavior of  $\text{Ar}_8$ ,  $\text{Ar}_{14}$ , and most of the others in the unimodal club [5].

A third explanation, which is very possibly appropriate for  $\text{Ar}_{33}$ , is that it contains so many atoms that the freezing and melting temperatures are closer than the resolution of any calculations thus far, so that the bimodal region simply has not yet been observed. We guess that as  $N$  gets large,  $T_f$  and  $T_m$  must converge to the same temperature  $T_e$ , the temperature at which the chemical potential is the same in both forms and the equilibrium constant is unity. We know relatively little about how these converge with  $N$ , only that the coexistence range for  $\text{Ar}_{19}$  is about  $12^\circ\text{K}$  and that no bimodality has been seen for  $\text{Ar}_{33}$ . This remains an important aspect of the problem still to be studied.

Two general inferences we can make, particularly from the insight given to us by simulations, are:

- a) that a cluster—or a molecule—is *nonrigid* if it passes among potential wells on a time scale short compared with the time scale of our observations, and
- b) that a cluster is *liquid* if it passes among many potential wells on a time scale roughly comparable with its vibrational frequency within one well.

It will probably be useful to distinguish these two. Of course we create a potential apparent paradox of liquids that are rigid, if we make fast observations, as with electron diffraction, but that is no real paradox because we need only specify the time scale with respect to which the system is rigid. The latter, the characterization of a liquid is extremely important because of what we intuitively want the concept of liquid to be. A liquid is a form of matter characterized by its compliance; one can put one’s finger on ice, but only into water. It is not possible to put one’s finger on water because even with the weakest force, the liquid

complies – unless, of course, the force is applied much faster than the natural compliance time of the liquid, as every beginning diver learns.

Now we turn to the manner in which a cluster passes from one configuration to another. A solid cluster is confined to a single potential well, where it executes nearly harmonic vibrations. A liquid cluster can pass among a wide variety of potential wells which give rise, in general, to permutations of the atoms among the sites within the cluster, at least insofar as that concept has meaning for equilibrium geometries. The liquid cluster may or may not pass through the same potential wells as those that correspond to the solid forms of the cluster. If the cluster has a fixed energy enough above that of the saddles connecting solid-like forms with the liquid-like regions, then only the liquid-like form of the cluster is thermodynamically stable and the cluster may pass through solid-like regions with ease. In the coexistence range, the cluster spends much longer intervals in its solid-like wells than in any of the wells in its liquid-like regions.

This behavior is illustrated by the study of  $\text{Ar}_7$  by Amar and Berry [6], using the quenching method of Stillinger and Weber [7]. The  $\text{Ar}_7$  cluster has four kinds of potential minima, corresponding to geometries of 1) a pentagonal bipyramid, 2), and octahedron with one surface decorated, 3) a tetrahedron with three surfaces decorated, and 4) a “skew” structure which can be considered a tetrahedron with two faces and one edge decorated. The energies of the minima, the number of permutational isomers of each and the barriers [8] between each kind of minimum are given in Table 1.

The total isomerization rate for  $\text{Ar}_7$  increases from  $0.2 \text{ ns}^{-1}$  at an energy of  $-14.4494$ , to  $1.00$  at  $-14.2898$ , to  $2.01$  at  $-14.1739$ , to  $4.48$  at  $-14.0202$ , to  $8.36$  at  $-13.8203$ , to  $26.56$  at  $-13.4352$ , to  $63.7$  at  $-13.0635$ . The isomerization rates give us considerable insight into how long one must look, either with

molecular dynamics simulations or in following experimental heating curves, to see equilibrium frequencies of appearance of different regions of configuration space. The time scale required to see equilibrium distributions of time intervals in each region may be considerably longer, but need not be.

The distributions of residence times are especially revealing regarding solid-liquid coexistence. For energies up to at least  $-13.8203$ , all the durations in structures above the lowest are well below  $200 \text{ ps}$ , while the distribution of times in the pentagonal bipyramid extends into the thousands of ps except for the highest energy, where it extends only a little above  $1000 \text{ ps}$  in the observed runs. This range includes all the energies studied in the coexistence range. At  $-13.0635$ , in the liquid range, the times in the wells around the higher structures extended to about  $40 \text{ ps}$  and for the lowest-energy well, to just over  $200 \text{ ps}$ . In other words, the time scale separability for solid-like and liquid-like regions breaks down when the solid disappears, but it holds when the two forms coexist.

The  $\text{Ar}_7$  cluster was studied with clusters of other sizes by Beck and Berry [5], also using quenching methods [7]. This study concentrated more than that of Ref. 6 on the mechanisms of passage from one well to another and how the geometries affected whether liquid-like regions of configuration space exist at all for particular clusters. For example  $\text{Ar}_{14}$  has no such well-defined liquid-like region. Rather, there are many low-lying minima in a sort of succession of energies like a staircase, so that as the energy increases, the cluster finds a smoothly growing volume of its configuration space to explore.

### 3. Ergodicity and chaos and how they grow

The other path we investigate to see how a cluster explores the space available to it is to quantify two characteristics that indicate the extent of this exploration [9, 10]. The first indicator is the degree of ergodicity, i.e. the degree to which the trajectory of a phase point fills the space energetically available to it. The second is the degree of chaos, the rate at which trajectories initially very close depart from each other. It is important to recognize the difference between these two. For Hamiltonian systems, we know of no connection between them. For dissipative systems, there is only a conjecture that the two are related.

To quantify ergodicity, we use the fractal dimension, precisely the “correlation dimension”, of the trajectory of the phase point describing the cluster’s evolution in phase space. This may be calculated by at least two algorithms; we used that of Grassberger and

**Table 1.** Energies of potential minima, permutational degeneracies and barriers between minima for the cluster  $\text{Ar}_7$ . Energies are in units of the well depth for Lennard-Jones “argon”,  $1.67 \cdot 10^{-21} \text{ J}$ . No additional barriers have been found

Structure	Energy	Permutational degeneracy	Barrier energy [8]
1.	$-16.505$	504	1-2: $-15.44$ 1-3: $-15.03$ 1-4: $-15.02$
2.	$-15.935$	1080	2-2: $-15.10$ 2-3: $-15.32$ 2-4: $-15.28$
3.	$-15.593$	1080	
4.	$-15.533$	5040	

Procaccia<sup>11</sup>. To quantify the degree of chaos we examined the full spectrum of Liapunov exponents as well as the sum of the positive exponents, which has been proven to be equal to the K-entropy [12].

The expectations for these quantities are easy to present, at least qualitatively. The fractal dimension for a perfect set of  $s$  uncoupled harmonic oscillators should be exactly  $s$ , corresponding to the one-dimensional periodic motion of each in its phase space. A cluster of  $N$  particles described in its own internal coordinate system either without rotation or in a rotating system has  $3N-6$  internal vibrational modes and hence that many dimensions, at minimum, for its trajectory in phase space. The largest dimension we might expect is the total dimension of the phase space,  $6N$ , less the number of constraints. There are ten of the latter, three for the position of the center of mass, three for the conserved linear momentum, three for the conserved angular momentum and one for the conservation of energy, ten in all. Hence we expect a maximum dimensionality of  $6N-10$  for the most "ergodic" trajectories. The largest cluster for which we have yet carried out such analyses is  $\text{Ar}_3$ . We therefore expect that the fractal dimension of the trajectory will be near 3 at low energies where the system is much like three harmonic oscillators, and perhaps as high as 8 at high energies.

The Kolmogorov entropy and Liapunov exponents are much more difficult to estimate from qualitative considerations, but we would naively expect them to increase with the energy. In particular, we might expect large increases to accompany melting.

One point must be made here regarding ergodicity and fractal dimension. If a system is ergodic at all, it must, at sufficiently long times, have an integral dimension. However for finite times corresponding to particular separable scales, nonintegral dimensions can be found and have been conjectured to be useful for 2-dimensional systems to characterize the degree of ergodicity attained by the system on that particular time scale. We have found [9, 10] that such separability does occur for  $\text{Ar}_3$  and that the fractal dimension of the trajectory can be computed by the Grassberger-Procaccia algorithm for a wide range of energies. On this basis, we suggest that in general it may be valuable to consider fractal dimensions as characteristics of trajectories which can be associated with particular time scales, and therefore to compute such fractal dimensions over various time scales and corresponding length scales when there are several such scales involved in a problem.

A parallel point regarding the K-entropy and Liapunov exponents is that they can be considered characteristic of particular regions, even to the extent of being local properties of a phase space. This be-

comes important as we examine the energy dependence of the K-entropy of the  $\text{Ar}_3$  cluster.

Now we turn briefly to the properties of  $\text{Ar}_3$  itself. While this cluster does not have enough degrees of freedom or potential minima to exhibit a solid-liquid equilibrium like those of  $\text{Ar}_7$  and  $\text{Ar}_{13}$  it does have one distantly analogous property helpful to us here. The equilibrium geometry of  $\text{Ar}_3$  is an equilateral triangle, so there is only one potential minimum. The linear geometry of this species is a saddle on the energy surface, so there are three equivalent saddles whose energies lie between  $-0.70$  and  $-0.56$ . Below the saddle energy, an  $\text{Ar}_3$  cluster must of course reside in its well, undergoing relatively small-amplitude motions. Above the saddle energy, the cluster may pass through the saddle and return to the well by a large-amplitude motion. In fact, at energies below the saddle, the power spectrum of  $\text{Ar}_3$  has almost no intensity at zero frequency, corresponding to no diffusion; above, the power spectrum has a nonvanishing contribution at zero frequency and diffusion can occur. This change is a sort of phase transition, which it is useful to think of as somewhat solid-to-liquid like.

Table 2 shows the fractal dimensions and K-entropies for  $\text{Ar}_3$  at various energies and equivalent temperatures. The important point to note is that both these characteristic quantities increase monotonically up to the saddle energy and then decrease! The interpretation of this behavior is now clear; it remains to be determined whether  $\text{Ar}_3$  is in any way a model for other, larger clusters. The larger clusters may well be able to pass from one region to another, across saddles, while continuing to increase the dimensionality and K-entropy associated with all their other degrees of freedom. For  $\text{Ar}_3$ , this is not possible, just because of the limited number of degrees of freedom.

The explanation, then, for  $\text{Ar}_3$ , is this. Below the saddle energy, the motion of the cluster within its well becomes more and more ergodic and chaotic as the energy increases. At the saddle energy, the cluster is able to penetrate all the way into the saddle and

**Table 2.** Dimensions ( $D_2$ ) and K-entropies ( $K_2$ ) for  $\text{Ar}_3$  as functions of energy and the corresponding effective temperature. Where two values are given, they correspond to two different scales of correlation. (Taken from Ref. 9)

Energy	Temperature	$D_2$	$K_2$
-0.98	2.12	3.1	—
-0.97	4.15	3.3	1.8
-0.91	10.31	3.5	—
-0.83	18.19	5.9	5.6
-0.70	28.44	2.5, 7.6	4.4, 10.2
-0.56	30.54	2.6, 5.3	4.6, 7.3
-0.47	36.51	6.2	9.0

through, but at the cost of almost all its kinetic energy. This kinetic energy is what enables the trajectories to be ergodic and chaotic in the deep well. In the saddle region, at energies not very far above the saddle energy itself, all the trajectories correspond to slow motions along flow lines across the saddle. Hence the trajectories remain nearly parallel there, and hardly diverge at all. Moreover because the speeds are low in the saddle region, the cluster's phase point spends a long time there. The algorithms used to generate Table 2 produce the time averages of the fractal dimension and K-entropy. As a result the values reflect the rather large contribution to the average of the saddle region.

By separating the trajectories into portions associated with motion in the well from portions associated with the saddle, it has been possible to demonstrate that the reductions in the two indices are indeed due to the two kinds of contributions, from the highly disordered well and the much more ordered saddle.

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