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## PHASES, PHASE CHANGES, AND THE THERMODYNAMICS OF SMALL SYSTEMS

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### Abstract

The thermodynamics of small systems seems strange, even bizarre, at first encounter, especially if one's thinking is locked to the concepts traditionally presented in texts and courses on thermodynamics of conventional bulk systems. Perhaps the most striking aspect shows itself in the thermodynamics of phase changes. Atomic and molecular clusters exhibit a variety of phase-like forms and phase changes that differ from those of bulk matter. It is possible to relate some – but not all – of these to corresponding phases and phase transitions of bulk matter. Clusters are attractive vehicles for studying phases and phase changes because they are susceptible to the analytic and computational methods applicable to small systems. Moreover they open the way to study size dependence of phase characteristics, even to quite large systems. Among the properties that distinguish phases and phase changes of small systems are bands of temperature and pressure within which two *or more* phase-like forms may coexist – not just curves of coexistence. This coexistence is dynamic, like that of coexisting chemical isomers. Moreover clusters may exhibit phase-like forms that do not exist for bulk matter. These properties of existence and coexistence are the consequence of the small differences between the free energies of clusters in different phase-like forms. Theory predicts that the bands of coexistence should have sharp boundaries, due to the disappearance of local stability of each phase-like form, implying that, in the bulk limit, the two branches of the spinodals should have sharp limits of temperature and pressure. One necessary condition that a species of cluster exhibit a particular phase is that such clusters must reside in the corresponding region of configuration and phase space long enough to establish equilibrium-like properties characteristic of that phase.

### 1. Introduction

Finite systems, especially small finite systems on the scale of atomic and molecular clusters, exhibit some of the solid-like and liquid-like behavior of bulk solids and

liquids. However they also show some dramatic differences in thermodynamic behavior from bulk matter, differences that can give us important insights into both small and large systems. Because we can treat small systems in considerable detail, and study how they approach the many-particle limit as they grow, we can use them to give us those new insights, especially into the phases and phase transitions of bulk matter. However small systems have many interesting phase-like properties that do not extend to bulk matter, properties that have been recognized but, for the most part, not yet exploited. This discussion will explore the thermodynamics and especially the phase-like properties of finite systems in terms of which properties extend simply to bulk matter and which are specific to small systems. It will also point out areas where further research is waiting to be done.

The phase-like properties of clusters and nanoscale particles lend themselves to study by simulation and by analytic theory. It has long been recognized that small particles have properties different from their bulk counterparts. The melting points were probably the first properties to be so identified, albeit by very crude and uncertain experiments [1]. Until now, a number of experimental studies have demonstrated specific phase-like forms of these species [2-8], but very little has come from the laboratory to elucidate the nature of the equilibrium or the transitions between these forms [9-14]. Optical excitation has recently proved to be a powerful tool for probing phase changes. Observations of the differences in optical response of sodium clusters [11] opened this approach. Then the same group selected charged sodium clusters of a single size, thermalized these clusters and then photodissociated the clusters, using the fragmentation pattern as a measure of the internal energy of the equilibrated clusters. A sharp increase in the fraction of small-cluster fragments was taken as a signal of melting [12]. They then carried out similar experiments with clusters of various sizes, and determined that there is no apparent regularity in the size dependence of the appearance temperature of a liquid phase [15]. Another approach that has made it possible to study phase changes experimentally is microcalorimetry; by allowing very small particles on surfaces to act as their own bolometers, Allen and coworkers have been able to determine heats of fusion, e.g. of large clusters of tin atoms [16]. The relevant experimental methods have included electron diffraction, which probes structure directly, and bolometric, spectroscopic and mass-spectroscopic studies, such as the intensity distributions of mass peaks generated by photoionization and photodissociation.

The theoretical background of this subject has been reviewed, and this Chapter is based in considerable part on one of the most recent of these reviews [17], somewhat updated.

The first fundamental concept one must grasp to understand the thermodynamics of small systems and especially the description of their phase-like behavior is the idea that thermodynamic equilibrium of clusters and nanoscale particles must be the dynamic equilibrium of an ensemble. One may consider a single, isolated particle as being in a kind of equilibrium state that traces a path through its phase space. Although such a state may truly be a stable mechanical state of an isolated dynamical system, the path of the system may be very intricate, most likely aperiodic and, because clusters and nanoscale particles are complicated dynamical systems, probably chaotic

and ergodic. Such systems typically have no *separable* internal modes of motion, and hence lend themselves to descriptions involving some kind of averaging. Because they are presumably ergodic, such a description could emerge from the long time history of a single system, or from the instantaneous state of an ensemble of many, many such systems.

As in all of statistical thermodynamics, the ensemble of choice depends on the conditions of interest: microcanonical, for a constant-energy system; canonical for a constant-temperature system; grand-canonical for a system at constant chemical potential; isobaric, for a system at constant pressure, and so on. Histories of single systems based on computer simulations often yield desired information, dynamical as well as equilibrium, regarding changes of phase or about the phases of clusters themselves. The crucial condition for this is simply that the simulation be long enough to show the long-time average distribution of all the accessible regions of the system's phase space. Such histories come typically from molecular dynamics (MD) simulations, numerical solutions of the equations of Newton's Second Law if the simulations are classical, of the time-dependent Schrödinger (or quantum-mechanical Liouville) equation if the simulations are quantum-mechanical. The dynamical information from MD is limited, because computer-induced, random errors destroy the mechanical reversibility of the integration. In practice, such simulations retain full reversibility for 500 to 10,000 time steps with usual degrees of precision, and lose at least one or two significant figures with each doubling of the length of the trajectory. This means that very slow processes cannot be reproduced reliably with MD simulations as we now carry them out. Nevertheless MD simulations do reveal short-time, high-frequency dynamics. Long MD simulations should be thought of as stochastic models retaining short-time correlations.

The alternative approach to simulation is through Monte Carlo methods, which explore the system's phase space but use no dynamics to link one step to the next. This is therefore a way to sample an ensemble at an instant, the alternative to a time history and equally valid, for any ergodic system. But because they use no dynamics, Monte Carlo methods also yield no dynamics. Both methods have been useful, molecular dynamics perhaps a bit more because it gives both dynamical and thermodynamical information.

"Phase transitions in small systems are gradual, not sharp." This is a commonplace that still sometimes appears in discussions of clusters and nanoparticles. In one sense this is correct [18]. However these changes have a kind of precision and sharpness of their own, which we find when we explore their nature in a bit of detail. To make our language precise, we shall refer to the changes of phase exhibited by bulk matter as "phase transitions", and their analogues for finite systems, as closely as they come, as "phase changes". The reason is that the changes of phase for small systems are not the same as the phase transitions of bulk systems. We shall see the emergence of bulk transitions from the phase changes of small systems. The phase changes of small systems cannot be classified according to the traditional "order" in the Ehrenfest pattern of cataloguing. In this characterization, the order of a phase transition is that of the lowest derivative of the energy or entropy to vanish at the point of the transition.

Moreover, as we shall see, the Gibbs Phase Rule loses its meaning because the distinction between "phase" and "component" becomes unclear for small systems.

Another important distinction between the phases of bulk matter and the phase-like forms of clusters and nanoparticles is that there are many varieties of phase-like forms of clusters that do not persist in the limit of very large systems. Table I lists a menagerie of such forms, with examples or possible examples.

TABLE I. A Menagerie of Phase-Like Forms that Clusters May Exhibit

Phase-like form	Example
solid	any cluster but $\text{He}_n$ , at low enough $T$
soft solid (or "fluxional cluster")	6-particle metal clusters [19]; $\text{Au}_{55}$ [20]
liquid	$\text{Ar}_7$ [21, 22]
surface-melted	$\text{Ar}_{55}$ [23-25]
core-melted	possibly $\text{Ga}_n$ or $(\text{H}_2\text{O})_n$ [24b]
glassy or amorphous	$\text{Ar}_n$ or mixed rare-gas clusters; $(\text{KCl})_n$ [26]
"restricted liquid"	$\text{Li}_8$ [27]

We begin by examining the simplest, best-studied forms of clusters, the solid-like and liquid-like forms, and the passages between these forms. This will inform us regarding the way a first-order transition occurs, and about limits on metastability and the spinodals of bulk matter. Then we go on to the more exotic phase-like forms of clusters and to the question of coexistence of these forms. We conclude by pointing out some of the most challenging open questions.

## 2. Solid and Liquid Clusters and Their Equilibria

### 2.1. SOLID-LIKE AND LIQUID-LIKE FORMS OF CLUSTERS

At sufficiently low temperatures or energies, all clusters with the exception of those of helium and possibly of hydrogen molecules behave like solids. Their component atoms or molecules undergo nearly-harmonic, small-amplitude vibrations around the equilibrium sites to which they are bound. In simulations, the Lindemann criterion [28], that the relative root-mean-square deviation of nearest-neighbor or interparticle distances be less than about 0.1, is satisfied [21,29]. Very little diffusion occurs; the mean square displacement of the particles with time is nearly zero [21]. The velocity auto-correlation functions have no very-low-frequency components, meaning that there are

no very soft, diffusive modes of motion in these clusters [21]. Many clusters exhibit well-ordered geometries, but many of these are not geometries consistent with periodic lattices. For example many kinds of atomic clusters have solid-like structures based on icosahedra. Clusters of no more than a few thousand rare-gas atoms generally take on variations of icosahedral geometries in the lowest-energy or global-minimum structures on their potential surfaces, although there are a few sizes for which the global minima are close-packed; much larger clusters have close-packed, lattice-based structures. The precise way this change occurs as the number of component atoms increases is not yet understood, but how it happens and at what size depend on the range of the interatomic forces [30]. There is sound experimental evidence for such structures [4,8,31-35]. Simulated cold clusters show pair distribution functions with the sharp peaks of successive shells of neighbors, like an ordered solid, and angular distributions likewise are characteristic of solid-like structures. For example icosahedral clusters show angular distributions with negligible amplitude at  $90^\circ$ , an angle that simply does not occur for triples of neighbors in that structure [36].

At higher temperatures, many kinds of clusters show liquid-like behavior in simulations [21]. The particles exhibit mean square displacements that increase linearly as functions of time, corresponding to well-defined diffusion coefficients, until the displacements reach the linear dimension of the cluster. The Lindemann criterion parameter is typically well above 0.10 for warm enough clusters. The velocity autocorrelation function has a significant contribution from very-low-frequency modes, which are the soft modes of a liquid; these show clearly in the Fourier transforms. The pair distribution function and the angular distribution function have the broad form characteristic of liquids. Experimentally, a few instances of liquid clusters have been identified [37]. Simulations first revealed such forms [22,26,38-41] and implied one of the conditions for such liquid-like forms to be recognizable forms of clusters: the liquid had to persist long enough for the system to establish at least vibrational equilibrium in that form. Many of these same simulation studies indicated that clusters of certain sizes, e.g.  $\text{Ar}_7$  (the smallest of the Lennard-Jones clusters to show this),  $\text{Ar}_{13}$  and  $\text{Ar}_{19}$ , all modeled by pairwise Lennard-Jones potentials, and others such as  $\text{Au}_6$  (now the smallest to show solid-liquid equilibrium),  $\text{Au}_7$ ,  $\text{Au}_{13}$  [42], and other gold clusters, all modeled with Gupta potentials [43], can exhibit well-defined dynamic equilibrium between their solid and liquid forms. The same was confirmed and shown for  $\text{Ar}_{55}$  soon after [25].

Some aspects of the dynamic equilibrium in those simulations led to the speculation by Briant and Burton [22] that the solid-liquid change might even be a first-order transition. This was puzzling, since dogma had it that first-order transitions are properties only of bulk matter and cannot occur in small systems.

Certain clusters exhibit, in some range of energy or temperature, a floppiness or fluxional character that allows them to explore only a limited set of potential minima, and not become liquid in the sense of exploring their entire potential energy surface. One is the 6-particle cluster modeled by the Gupta potential, a system studied by Sawada and Sugano [44]; they have also examined other metal clusters in this manner [20]. The tetramers and pentamers of alkali halides exhibit such behavior; they have a kind of nonrigid, planar, phase-like form which can pass readily between open rings

and "ladders" or rectangles [45,46]. Still another exotic phase-like form of cluster is the very flexible  $\text{Li}_8$  species, which has a region of its potential surface in which it is extremely flexible and liquid-like, with the one qualification that one atom, at the center of the cluster, cannot participate in the permutational motions that mix all the other seven and make them liquid-like [27]. We call this kind of system, in which most but not all the component particles are mobile, a "restricted liquid".

## 2.2. EQUILIBRIUM OF SOLID AND LIQUID CLUSTERS

We may think of the solid-like cluster as an ordinary, near-rigid molecule with small-amplitude vibrations, and the liquid-like cluster as a sort of nonrigid, fluxional molecule. From this perspective, it is natural to construct a quantum-statistical model to infer and rationalize the temperatures at which these two forms may coexist [47,48]. This requires making a model based on the postulate that there is at least some temperature at which the two forms are both locally stable, in this sense: the free energy, expressed as a function of temperature, pressure (or density), and a nonrigidity parameter that serves like an order parameter, has two minima as a function of the nonrigidity parameter at some temperature and pressure. This condition, plus the dynamic condition of long-enough persistence of each phase, are sufficient to describe coexistence of the solid and liquid forms of the cluster. The next step in the logic implies that if such coexistence occurs at all for clusters, it occurs not at a single point or along a single curve in the space of two such variables as pressure and temperature; coexistence of solid and liquid clusters, if it occurs, occurs within a *band* of the space of thermodynamic variables of the system [17,21,47,49,50].

The reasons for this are straightforward. To begin, the densities of states of solid and liquid forms can be represented as functions of a nonrigidity or order parameter  $\gamma$ , at any given temperature. We choose the scale of  $\gamma$  so that when its value is zero or near that, the system is rigid and solid-like, and when the system is very nonrigid and liquid-like,  $\gamma$  approaches an upper limit of 1. The density of solid-like states is invariably higher at low temperatures. This means that the free energy of the solid is lower, at low temperatures, than that of the liquid and is a monotonically increasing function of the extent of nonrigidity at those low temperatures. The only minimum in  $F(T,\gamma)$  occurs for some small value of  $\gamma$ , the nonrigidity parameter, in the solid-like range. However the density of liquid-like states rises considerably faster with  $T$  than that of the solid clusters. As the temperature increases, the greater density of states for nonrigid systems, i.e. for large  $\gamma$ , reduces the free energy for nonrigid forms of the cluster, relative to more rigid forms; the free energy  $F(T,\gamma)$  becomes less strongly monotonic and, eventually at a sufficiently high temperature  $T_f$ , develops a point of zero slope, i.e.

$$\left[ \frac{\partial F(T,\gamma)}{\partial \gamma} \right]_{T_f} = 0$$

at some value of  $\gamma$ . We call  $T_f$  the freezing limit, because below this temperature the only stable form of the system is solid. At temperatures above  $T_f$ ,  $F(T, \gamma)$  has two minima, one in the solid-like range and one in the liquid-like range of  $\gamma$ . But as the temperature continues to increase and the density of states of the liquid-like form becomes larger and larger with respect to that of the solid-like form, the curve of  $F(T, \gamma)$  as a function of  $\gamma$  continues to tip, more and more, toward the liquid-like side until the system reaches a temperature  $T_m$  at which the minimum in  $F(T, \gamma)$  near the solid-like end of the scale turns into just a flat spot, a point of zero slope. We call  $T_m$  the melting limit, because only the liquid form is stable at temperatures above  $T_m$ . At those higher temperatures (and we neglect evaporation in this discussion),  $F(T, \gamma)$  has only a single minimum, and that is in the liquid-like region. This is illustrated in Figure 1.

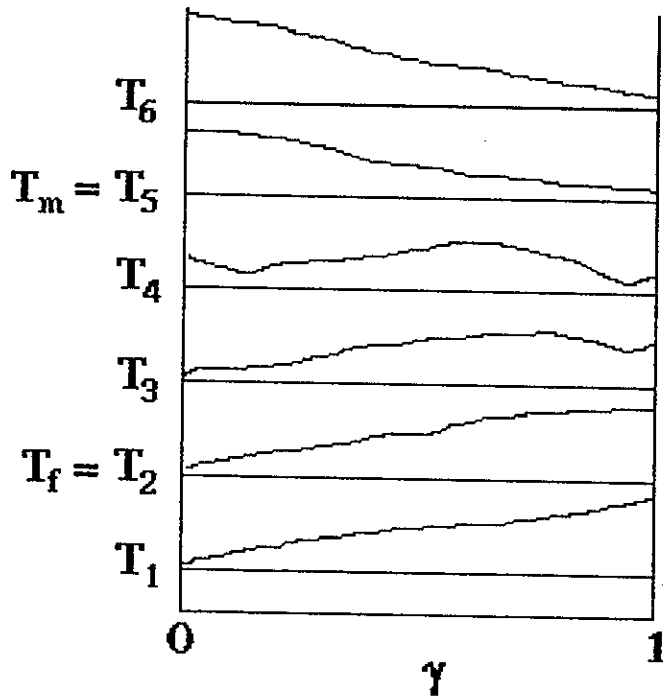


Figure 1. The free energy  $F(T, \gamma)$  as a function of the nonrigidity parameter  $\gamma$ , for six temperatures, increasing from  $T_1$  through  $T_6$ . Below  $T_2$ ,  $F(T, \gamma)$  has only one minimum near  $\gamma = 0$ , in the solid-like end of the scale. At  $T_2 = T_f$ ,  $F(T, \gamma)$  develops a point of zero slope near the nonrigid limit, i.e. near  $\gamma = 1$ . Between  $T_2 = T_f$  and  $T_5 = T_m$ ,  $F(T, \gamma)$  has two minima, that for lower  $\gamma$  corresponding to a locally stable solid-like form and that for the higher  $\gamma$ , to a locally stable liquid. At  $T_5 = T_m$ , the free energy has only one minimum and one other point of zero slope and zero second derivative, as a function of  $\gamma$ . Above  $T_5 = T_m$ , the free energy has only one minimum, corresponding to the one stable form.

This argument implies that between the lower limit  $T_f$  and the upper limit  $T_m$ , the solid and liquid forms of the cluster may coexist, all at the single pressure for which the curves were constructed. Hence at each pressure there must be a range of temperature within which the free energy has two minima, therefore two locally stable forms, therefore two coexisting forms. The relative amounts of these two forms is fixed by a traditional chemical equilibrium constant,

$$K_{eq} = \exp[-\Delta F(T, \gamma) / kT].$$

The argument also implies that  $K_{eq}$  should have two discontinuities, one at  $T_f$  and another at  $T_m$ , for each pressure. However the relative amounts of solid and liquid, fixed as the ratio  $K_{eq}$ , vary smoothly between these limits, with the ratio of liquid to solid increasing with temperature  $T$  [21,47]. The analytic argument has been well supported by simulations, both constant-energy and constant-temperature, and by simulations based on both molecular dynamics and Monte Carlo methods [19-21, 44,49-54]. One characteristic signature is a bimodal form for the distributions of various properties. One used frequently as such an index is the distribution of (short-term) mean kinetic energies, i.e. of mean vibrational temperatures, in isoergic dynamic simulations of the cluster's evolution. Likewise, another such signature is a bimodal distribution of total energies and potential energies in isothermal molecular dynamics simulations, if the conditions of temperature and pressure correspond to the range of coexistence. Outside the coexistence range, the distributions are unimodal. The ratio of the fraction of the time the cluster spends as a solid to that spent as a liquid is just the equilibrium constant  $K_{eq}$ , so long as the system is ergodic. (This equivalence, of time average for a single system with the corresponding instantaneous ensemble average, is precisely one definition of the property of ergodicity.)

The relation linking the phase change between solid and liquid clusters and the first-order solid-liquid phase transition of bulk matter now becomes apparent from this argument. To see this relation, it is easier to think in terms of a transformation of  $K_{eq}$ , specifically the equilibrium distribution function

$$D_{eq} = (K_{eq} - 1) / (K_{eq} + 1),$$

than of  $K_{eq}$  itself. The reason is that  $K_{eq}$  varies from zero to infinity, with the value 1 when the amounts of solid and liquid are equal, while the function  $D_{eq}$  varies between  $-1$  if the system is all solid and  $+1$  if it is all liquid. At low temperatures, below  $T_f$ ,  $D_{eq}$  is a constant  $-1$ ; at  $T_f$ , it shows a discontinuity, and rises to some finite value greater than  $-1$ . Between  $T_f$  and  $T_m$ ,  $D_{eq}$  rises monotonically and smoothly, presumably going through zero and up from negative to positive values. Then, at  $T_m$ , it has another discontinuity, and rises to its high-temperature limit of  $+1$ . At the temperature where  $D_{eq} = 0$ , the equilibrium constant is 1, the amounts of solid and liquid are equal (or the times are the same that each system spends in each phase), so the free energies of the solid and liquid forms are equal at that point. We can call the temperature at which this occurs  $T_{eq}$ , since it is the counterpart of the equilibrium or melting temperature of a bulk system.



Thus, between the two limiting temperatures,  $T_f$  and  $T_m$ , solid and liquid clusters coexist in a canonical ensemble; alternatively, a single cluster, at constant temperature, passes back and forth between solid-like and liquid-like forms, so long as that temperature lies between  $T_f$  and  $T_m$ . As we shall see in the context of finite analogues of second-order transitions, it is possible that a phase-like form of a cluster might be stable and present in detectable quantities, yet, under no conditions, have a chemical potential equal to or lower than that of any other phase-like form.

If the cluster is small, then the discontinuities in  $D_{eq}$  are detectably large and the transition from negative to positive values is gradual. As the cluster gets larger, the magnitudes of the discontinuities at  $T_f$  and  $T_m$  decrease, the sigmoidal curve of  $D_{eq}$  becomes steeper and more abrupt, and the values of  $D_{eq}$  remain close to  $-1$  and  $+1$  until  $D_{eq}$  comes close to  $T_{eq}$ , the value of  $T$  at which  $D_{eq} = 0$ , where almost all its change in value occurs. In other words, the discontinuities get smaller and smaller and the continuous change of equilibrium constant becomes sharper and sharper. There is still an open question of whether fluctuations destabilize the undercooled liquid or superheated solid so much that the discontinuities in  $D_{eq}$  are observable [55]. If the cluster approaches macroscopic size, the discontinuities are immeasurably small and the continuous change of  $D_{eq}$  from very near  $-1$  to very near  $+1$  takes place so abruptly that it is in effect discontinuous at  $T_{eq}$ ! That is how a first-order melting and freezing transition emerges from its counterpart in small systems. Figure 2 illustrates the behavior of  $D_{eq}$  schematically for three sizes of clusters; the figure is drawn to show all three clusters with the same  $T_{eq}$ , but this is only done here to emphasize the evolution of the shape of  $D_{eq}$  with the number of particles,  $N$ . In reality,  $T_{eq}$  can be expected to vary with  $N$ .

A variety of *sufficient* conditions were found in which clusters can coexist in solid and liquid phase-like forms, both in simulations [22,39,41,48,49,52a,54,56] and analytically [47a,57]. The analytic results follow from a model in which the nonrigidity is expressed by a free energy which is a polynomial function of the density of defects. The model is phenomenological insofar as the exact nature of the defects need not be specified. From this, a statistical theory, quantum or classical, leads to the sufficient condition that the free energy has two minima within some finite range of temperature. Furthermore, provided the defects either attract each other or lower the vibrational frequencies of the cluster, the interval between the two minima persists as  $N$  becomes infinite. In other words, clusters of substances whose free energy has such a dependence on defects have solid and liquid forms whose phase changes merge smoothly into conventional first-order phase transitions as the clusters grow to become bulk matter.

More recently, *necessary* conditions were also found for the coexistence of solid and liquid (or any other two dense, phase-like) forms of clusters [58-60]. These conditions are expressed as the requirements to assure that the distribution of short-time mean temperatures of a microcanonical ensemble, or the distribution of short-time mean free energies of a canonical ensemble have a bimodal distribution. Two sets of necessary conditions are that there be three points of inflection in the canonical distribution (for bistability in a microcanonical ensemble) or in the grand canonical distribution (for bistability in a canonical ensemble), respectively. The next Section addresses

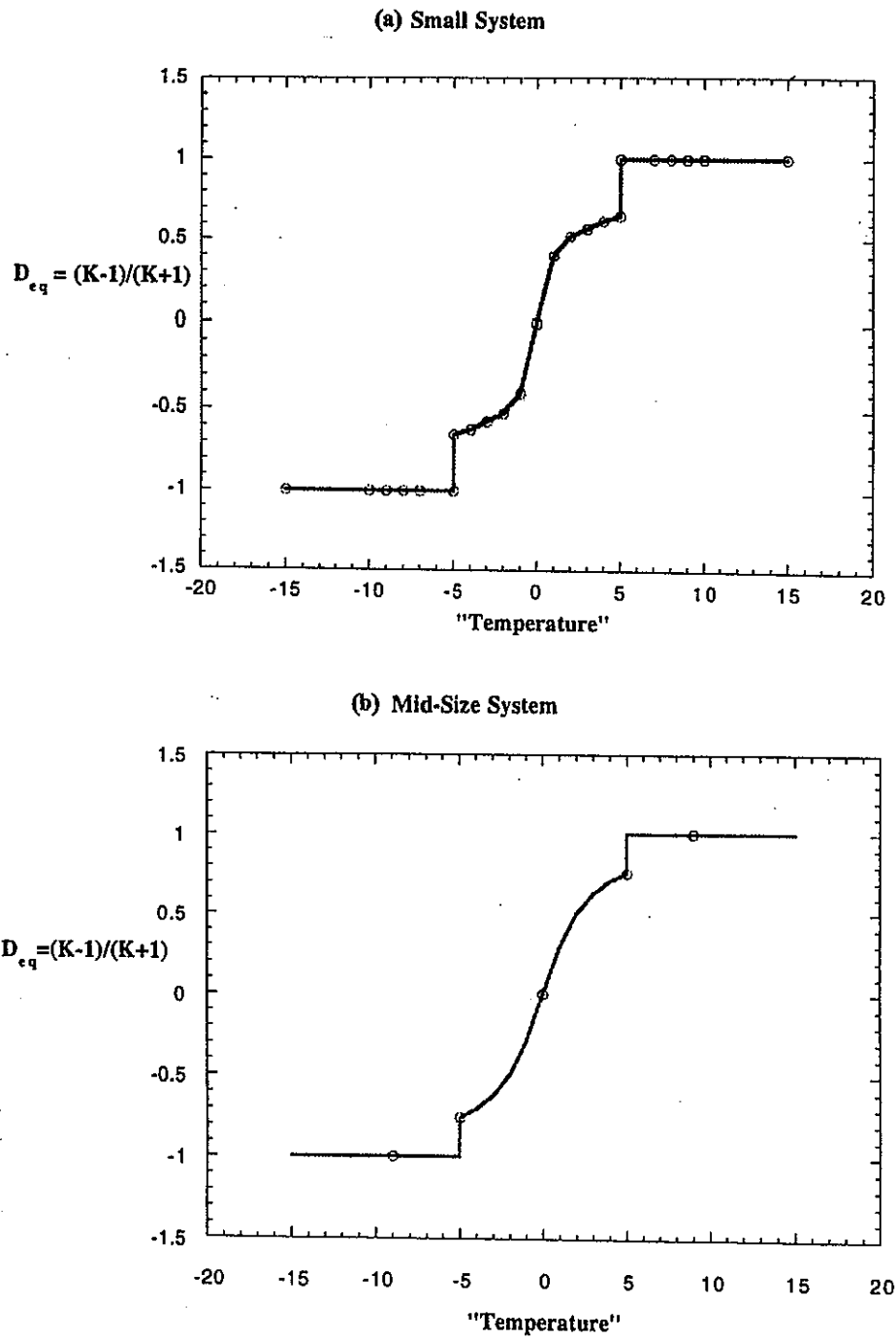


Figure 2. Schematic curves of  $D_{eq}$  for a) a small cluster, b) a cluster of intermediate size, and c) (see next page) a large cluster.

(c) Large System

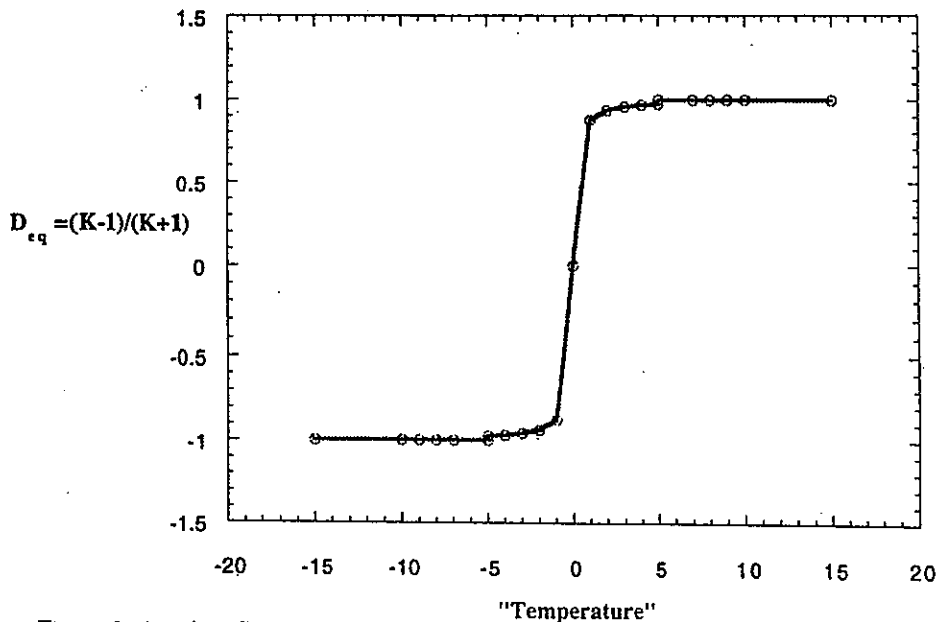


Figure 2. (continued)

the question of what is meant by a "short-time mean" temperature or free energy.

One intriguing aspect of phase coexistence of clusters appears in the caloric curves, the representations of the mean temperature as a function of energy, for an isoergic system, or of the mean energy as a function of temperature for an isothermal system. The slope of a curve of  $T$  vs.  $E$ , subject to constraints, is of course the heat capacity of the system under the conditions of those constraints. Such curves have been constructed for many years [22]. These typically are nearly linear in the regions of single phases but in the coexistence regions may be flat or even, in the case of curves based on microcanonical distributions, have negative slope [61]. It is not difficult to understand how the heat capacity for a *constant-energy* system might be negative in a region in which solid and liquid are in equilibrium. If the density of nonrigid, liquid-like states is very high but lies in a region of high potential energy, while the solid corresponds to a deep, narrow minimum with a low density of states, and we use either the mean kinetic energy or the derivative of energy with respect to entropy at constant volume as the measure of effective temperature for our system, then raising the energy just a little could easily lead to a large increase in population of high-potential-energy, low-kinetic-energy states, and hence to a drop in the mean effective temperature. This does not in any way negate the traditional condition that heat capacities for systems at well-defined temperatures can only have positive values.

The s-shapes of caloric curves as found from molecular dynamics simulations, at least for  $Ar_{13}$  and  $Ar_{55}$ , match caloric curves based on model partition functions.

The agreement is quantitative if those partition functions include the anharmonic contributions to the potential surface [62]. However even a simpler model shows the essential characteristics [63]. It seems that a region of negative slope, corresponding to a region of negative heat capacity, is sufficient for coexistence of two phases of clusters. However it is not *necessary* for the caloric curve to have a region of negative slope in order to have dynamic bistability; an outstanding example is the Ar<sub>13</sub> cluster [60].

With relatively simple analytic models, it is possible to estimate the binding energies and the configurational entropies of clusters of different structures [63,64]. Because the vibrational contributions to the entropies are almost the same for different solid structures, one can use the binding energies and configurational entropies to compute the free energy differences and relative stabilities of different solid phases or structures of clusters of moderate size. For example, it was possible to compute the phase equilibrium between icosahedral and face-centered cubic (fcc) forms of a 923-atom cluster of particles bound by pairwise Morse interactions [64].

### 2.3. TIME SCALES AND PHASES OF SMALL SYSTEMS

The possibility of observing solid-like and liquid-like clusters depends, as we have seen, on the individual clusters spending time intervals in one phase-like form long enough to establish equilibrium-like properties characteristic of that phase. This requires that the mean time spent in each phase be long relative not only to the vibrational period of the components, but also to the time required for the system to establish a well-defined mean-square displacement  $\langle d^2(t) \rangle$  of its particles, which is equivalent to the requirement that it must establish a well-defined diffusion coefficient  $D$  since these are directly related:

$$D = (1/6)[d\langle d^2(t) \rangle / dt]$$

in three dimensions.

The system must also establish a stable velocity autocorrelation function for a time long enough for that autocorrelation function to have a stable Fourier transform, which means that the distribution of vibrational frequencies must be stable. Clusters even as small as Ar<sub>7</sub> do exhibit this behavior. However many other small clusters, such as Ar<sub>12</sub> and Ar<sub>14</sub>, do not; they pass between solid-like and liquid-like forms too frequently to establish such properties for purposes, for example, of infrared spectroscopy. In their infrared or Raman spectra, a canonical ensemble of Ar<sub>7</sub>, Ar<sub>13</sub> or Ar<sub>19</sub> would look like a collection of solid particles at low temperatures, like a collection of liquid particles at high temperatures (but below temperatures at which the particles would vaporize within the time scale of the observation), and at intermediate temperatures, like a mixture of solid and liquid particles. By contrast, a similar ensemble of clusters of Ar<sub>12</sub>, Ar<sub>14</sub>, or Ar<sub>17</sub> would look like a collection of slush balls at those intermediate temperatures. If the probe were very much slower than infrared spectroscopy, for example if it were a radio-frequency probe or some other means requiring microseconds or milliseconds, then the observer would see the long-time average behavior – on that time scale – of all the clusters in the ensemble, and would therefore interpret

the behavior of the clusters as slush-like, whatever the size of the clusters. This is because the time scale for residence in solid-like and liquid-like forms for  $\text{Ar}_7$ ,  $\text{Ar}_{13}$  and  $\text{Ar}_{19}$  is of order 50–500 ps, long relative to vibrational line widths but very short compared with times for absorption or emission of a radio-frequency photon.

What we mean by “equilibrium” of these clusters depends on the time scale we intend for their description. On a short time scale, they exhibit traditional, distinguishable phases, but on a long time scale, they transform smoothly from solid through slush to liquid. This is an illustration of how the study of small systems opens our perception of some of the tacit, hidden assumptions of familiar subjects, in this case thermodynamics. It is precisely because the time scales of the dynamics of clusters fall into ranges we can span with our experimental methods that we become sensitized to these fundamental ideas. There are many situations in which we rely on separations of time scales to allow ourselves to describe a system in thermodynamic terms when we are assuming that only some restricted subset of the degrees of freedom are participating in the equilibration. Such hidden assumptions lurk even in some of the most elementary-seeming concepts of thermodynamics, but there, they are easy to overlook because the readily-ignorable time scales do not force us to confront them. For example the notion of a “reversible adiabatic process” would be an oxymoron, were it not possible to separate the time scale for its internal thermal equilibration from the much longer time scale for loss of heat to the surroundings [65]. Making such assumptions and using theoretical concepts this way is perfectly valid, provided we use our science responsibly, and make ourselves aware of such tacit assumptions.

Time scales are not only important for distinguishing what we mean by a “state” and “equilibrium”. They are also important because what we can extract from a simulation may depend on the time scales of the computation as well as of the dynamics it seeks to simulate. At the short-time end of the scale, it is important to ask whether or not the results one seeks require accurate representation of the vibrations. If so, then the time steps must be significantly shorter than the vibrational period. This is an obvious conclusion. Speeding up a molecular dynamics computation by using long time steps can be hazardous, if one intends to extract dynamical information. Yet it is at the long end of the time scale that inferences are more likely to be misled. For example one may in principle infer from isothermal molecular dynamics simulations the free energy differences between two forms of a cluster in dynamic equilibrium. If the system is ergodic, then, as we said previously, the equilibrium constant is the ratio of the times spent in the two forms. However the duration of a simulation long enough to provide a stable value for that ratio may be very long indeed, compared with most current simulations. Moreover it is also important for molecular dynamics to recognize another time scale mentioned previously, which is associated not with the system but with the computation: this is the time scale over which the computation remains mechanically reversible. Typically, this is about 5,000 to 10,000 time steps. Reversing dynamics calculations longer than these typically reveals a loss of significant figures if one tries to recover the initial conditions. This means that long molecular dynamics calculations are not really following reversible, Hamiltonian dynamics, even though they may remain isoergic to within very narrow limits. Rather, they become a kind of slowly-randomized on-shell or isoergic walk with strong correlations for short times

but none for very long times. (The duration of the interval of validity for time reversal only doubles, approximately, if the number of significant figures doubles. This is a clear symptom that the roundoff errors of the simulation are making the trajectories chaotic.)

#### 2.4. PHASE RULE, MAXWELL CONSTRUCTION AND PHASE DIAGRAMS

The behavior of solid-liquid equilibrium of clusters seems at first sight to contradict the Phase Rule for the number of stable phases  $p$ , for a system with  $c$  components and  $n$  degrees of freedom,  $n = c - p + 2$ , and the Maxwell construction argument against any second phase existing except along the binodal and the "equal-area" tie-line. In a sense this is correct, but for a reason that makes the behavior of clusters fall outside the realm in which these two traditional ideas apply. The Maxwell construction argues that between the binodal and the spinodal, only the phase of lower mean chemical potential  $\mu$  can be stable. For bulk systems, this is quite true, because the free energy  $N\mu$  of the less stable phase would be enormously higher, effectively infinitely higher, than the free energy of the more stable phase. Clusters, by contrast with bulk matter, have values of  $N$  small enough that if the free energy of the less stable form is not very much higher than that of the more stable form, then the ratio

$$K_{eq} = \exp[-\Delta F(T,\gamma) / kT]$$

is still large enough even near the spinodal that both forms may be present in detectable amounts in an ensemble or in the time history of a single system, if it is in the coexistence region. In other words, the thermodynamically unfavored phase is not necessarily so very unfavored if the number of particles  $N$  is not enormous.

We use the Phase Rule when we implicitly distinguish phases from components in chemical equilibrium by tacitly supposing that the free energy difference between phases is effectively  $\pm\infty$  at all points where it is not zero, while the free energy difference between components may take on any value. Hence if our systems are clusters and not bulk matter, the former supposition does not apply, and the distinction between phases and components is lost – so the Phase Rule is irrelevant to ensembles or time histories of clusters.

The difference between phases and components in bulk systems can be expressed in a way that emphasizes why the Gibbs phase rule properly describes phase equilibria but equilibrium constants describe the equilibria of components. This description also shows why clusters and nanoscale particles differ from bulk matter. It is simply that only a small number of particles, typically the number of atoms in a molecule, that determines the free energy of the molecule, but all the particles of the system participate *and interact* in its phase transitions. Hence for bulk systems, the relevant  $N$  for a component may be of order 10 or 1000, or perhaps even 100,000 for a polymer, but for a phase transition, the relevant  $N$ , the number of interacting particles whose interactions produce the transition, is typically of order  $10^{20}$  or more. In clus-

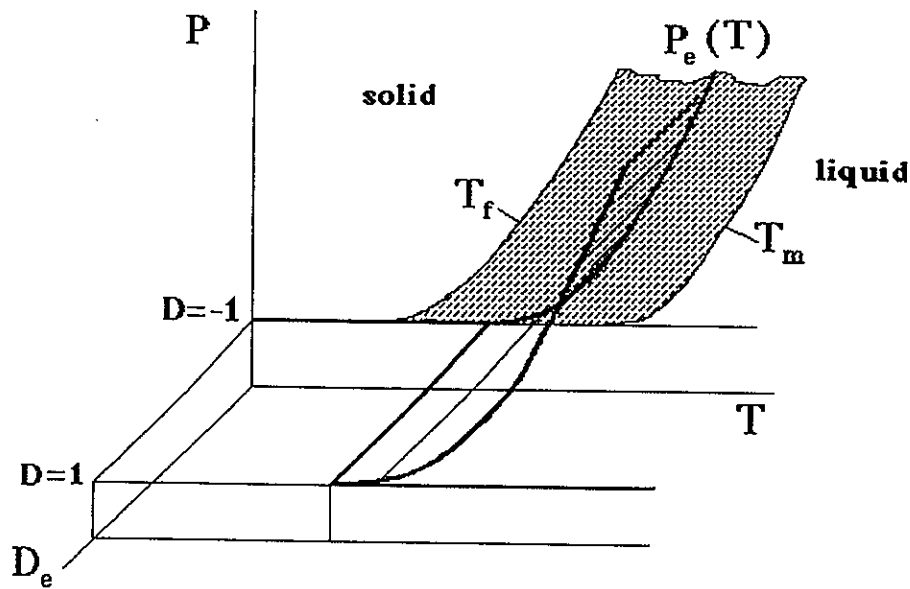
ters, however, the total number of particles in each "system" or cluster is comparable to the number of atoms comprising a molecule.

Thus far, the discussion has neglected effects of pressure on the behavior of clusters; we have discussed only simulations at constant pressure, usually either not specified or zero. Of course pressures may vary, and with them, the temperature dependence of free energy relationships. The full phase behavior of clusters may be simulated [66] by using the Nosé method [67] or now, the stochastic method [68] to maintain constant temperature and the Andersen method [69] to keep the simulated system isobaric. The results show how the distribution  $D_{\text{eq}}$  between solid and liquid forms changes with pressure as well as with temperature. Furthermore these results give us enough insight to construct phase diagrams for clusters and nanoparticles that are somewhat different from – and extensions of – conventional phase diagrams [66]. In particular, the phase diagram for a cluster requires, in addition to the traditional thermodynamic variables such as pressure  $p$  and temperature  $T$ , an additional variable which we most naturally choose to be  $D_{\text{eq}}$ , the distribution function introduced previously. The phase diagram for solid-liquid equilibrium of a *bulk* system in this representation contains no more information than that in a conventional plot of vapor pressure vs. temperature; off the curve along which  $\mu_{\text{vap}} = \mu_{\text{liq}}$  the system is either all solid with  $D_{\text{eq}} = -1$  (at low temperatures) or all liquid with  $D_{\text{eq}} = +1$  (at high temperatures) and the transition between these two values of  $D_{\text{eq}}$  is so abrupt that it appears to be a discontinuity. The phase diagram thus consists of a half-plane with  $D_{\text{eq}} = -1$  and a half-plane with  $D_{\text{eq}} = +1$ , and the two are separated along the curve of the equilibrium vapor pressure.

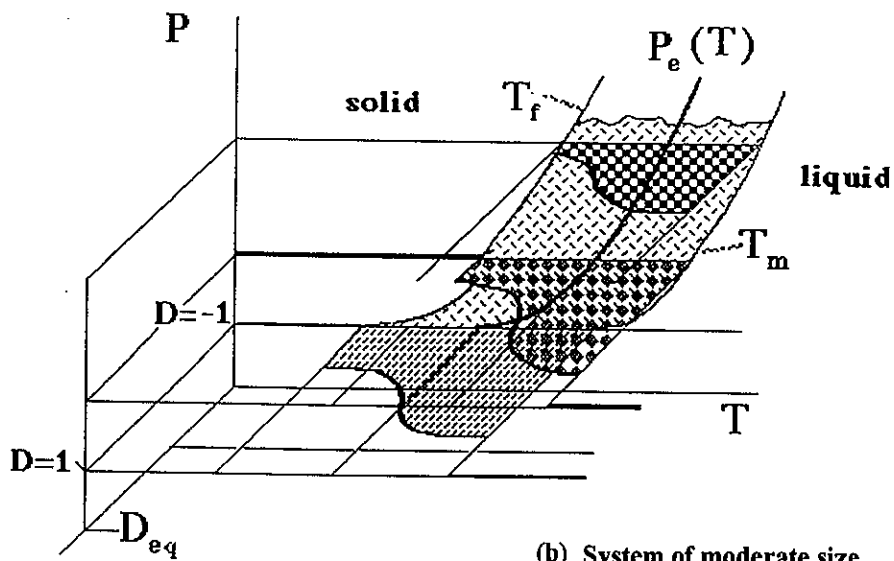
A small cluster presents a much richer diagram. In the solid-liquid phase diagram of the small cluster, there are indeed discontinuities in  $D_{\text{eq}}$ , but not at  $p(T_{\text{eq}})$ . These discontinuities occur where  $D_{\text{eq}}$  is truly discontinuous, along the curves of  $p(T_f)$  and  $p(T_m)$ . These discontinuities separate, respectively, a half-plane where  $D_{\text{eq}} = -1$  from a curved surface that joins that plane at the lowest fractional values of  $D_{\text{eq}}$ , and then, that curved surface at the highest fractional values of  $D_{\text{eq}}$  with the half-plane where  $D_{\text{eq}} = +1$ . The new information in such a diagram is in the curved surface between the two half-planes. Figure 3 shows schematic representations of the two cases just described. As yet, no such diagram has been presented for any real system, although there have been steps toward such a construction [60,66,70].

## 2.5. LIMITS OF METASTABILITY OF BULK PHASES

This line of reasoning has one important implication for bulk matter, specifically for the spinodal and for the metastable superheated solid and undercooled or supercooled liquid. The logic based on the densities of states of solid and liquid forms of finite systems implied the existence of the limiting temperatures  $T_f$ , below which the liquid has no local stability, and  $T_m$ , above which the solid has no local stability. We also reviewed conditions for the coexistence of two free energy minima, each responsible for the stability of one phase, and for the persistence of two such minima as  $N$  grows arbitrarily large. If a system with very large  $N$  is not at its  $T_{\text{eq}}$ , then what is the role of the higher-energy minimum of the free energy  $F(T,\gamma)$ ? To see this, suppose we cool an



(a) Large system



(b) System of moderate size

Figure 3. Schematic phase diagrams for solid-liquid equilibrium of finite systems: a) a large system, and b) a system of moderate size, e.g.  $N$  of about 20 or 100. The three axes correspond to pressure  $p$  (vertical), temperature  $T$  (horizontal, in the plane of this surface), and  $D_{eq}$ , the distribution (projecting horizontally out of the plane of this surface).



ensemble of very large liquid systems and, instead of allowing the ensemble to come to thermodynamic equilibrium, we keep all of it in the vicinity of its local, liquid-like minimum, as an ensemble of undercooled liquid systems. This local stability can be maintained at temperatures below  $T_{eq}$  just so long as the local minimum in the free energy  $F(T, \gamma)$  is there. If that minimum disappears, then so does local stability. Hence the liquid branch of the spinodal exists down only to the temperature  $T_f$ , and the solid branch of the spinodal, up only to the temperature  $T_m$ . There are limits to the temperatures, then, beyond which metastable solid and liquid phases cannot exist. In other words, at any pressure, there are temperature limits to the two branches of a family of spinodal curves.

### 3. "Surface-Melted" Clusters and Coexistence of Multiple Phases

Surface melting of rare-gas clusters seemed plausible to Briant and Burton [22], when they carried out molecular dynamics simulations of small systems, and appeared unambiguously in the simulations of the 55-atom Lennard-Jones cluster by Nauchitel and Pertsin [25]. It is now well established in simulations of metal clusters as well, with various representations of the potential [71]. A softening, sometimes called "premelting", occurs in somewhat smaller clusters, e.g. of Ni [72], at temperatures a bit below that at which homogeneous liquid appears. This however is probably not simply related to surface-melting, for reasons that will become clear in the next paragraph. The inference that the surface is liquid and the core, solid comes from standard diagnostics – diffusion coefficient, velocity autocorrelation function and pair distribution function, for example – with the particles comprising the cluster kept in separate categories, corresponding to the layers of the cluster. Furthermore snapshots of clusters with liquid surfaces show unstructured, amorphous outer layers and ordered, polyhedral or crystalline cores. Typically, in these snapshots, a few atoms float in the region just outside the outer layer of the cluster. Lennard-Jones clusters of about 45 or more particles display this behavior within bands of temperature beginning just below and somewhat narrower than the bands of liquid-solid coexistence.

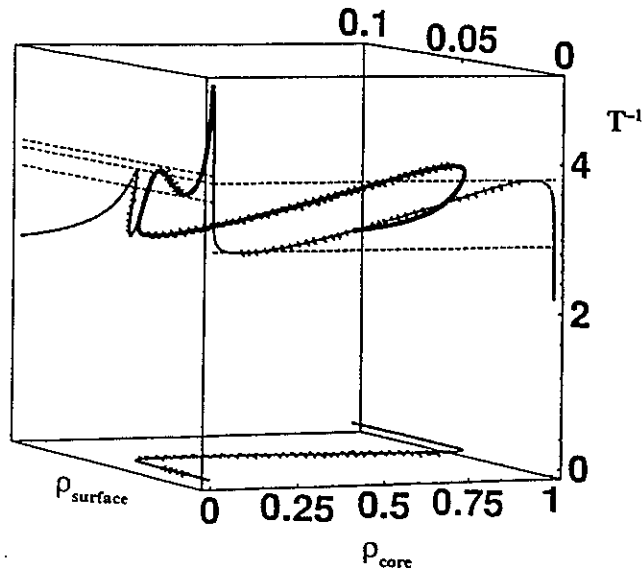
The surface-melted cluster was assumed to have a polyhedral core and an amorphous, swarm-like liquid coat – until animations revealed something quite different [23]. Animations constructed from dynamics simulations of such clusters as  $Ar_{147}$  (or, more precisely, the Lennard-Jones cluster "LJ<sub>147</sub>") show that in the "surface-melted" state, a) the cores are indeed solid-like polyhedra in this range of sizes, b) most of the particles of the outer layer execute large-amplitude, highly anharmonic, complex oscillations, and c) a few particles, about 1 in 30 of those in the outer layer, have come out of the surface and float relatively freely around the cluster's surface. These "floaters" carry the large-amplitude, low-frequency motion and contribute the values of the numerical diagnostics that imply that the surface is liquid-like. The other particles that remain in the surface, undergoing large-amplitude vibrations, move in a highly collective manner, oscillating around a well-defined polyhedral equilibrium structure. In other words, the surface-melted state, while so distinct and self-organized that it behaves as much like a distinct phase as do the normal solid and liquid forms, is not at

all like a conventional liquid coating a conventional solid. This is especially significant in the context of nanoparticles because it implies that the "melted surface" of the cluster in the surface-melted, phase-like form *does not provide nuclei to initiate normal, homogeneous melting*. This in turn implies that the standard argument, that materials whose liquids wet their solid forms cannot be superheated, is not applicable to clusters, and therefore that clusters may, at least in some cases, be superheated. This may be useful in the fabrication and annealing of nanoscale particles.

Lennard-Jones clusters of about 45 or more atoms simulated at constant energy indeed exhibit bimodal and multimodal distributions of short-time-average mean kinetic energies (times long with respect to the vibrational period, short with respect to dwell times in a given phase-like form) – that is, of mean vibrational temperatures; in isothermal simulations, they show bimodal or multimodal distributions of short-time-average or even of instantaneous potential or total energy [24]. The plateaus in these bimodal and multimodal distributions are not all of the same kind. Just above the lowest temperatures where the distributions are unimodal and the clusters are solid, the bimodal distributions correspond to clusters that are sometimes solids and sometimes in their surface-melted phase. At still higher temperatures the distributions become trimodal, then bimodal again, and finally, at the highest temperatures before evaporation dominates the simulations, unimodal. In the trimodal region, the three plateaus correspond to solid, surface-melted and homogeneously-melted phases. The bimodal region above that is the region of dynamic coexistence of surface-melted and liquid phases, and the high-temperature, unimodal region is that of the homogeneous liquid.

We can express the partition function of such clusters in terms of contributions from their cores, from their surfaces and from their floaters, and include the floater-surface and surface-core interactions. These contributions can be expressed in terms of parameters reflecting the energy required to produce defects and floaters [24]. With such partition functions, we can search for the limits of the conditions of stability of each phase-like form, just as with the solid-liquid equilibrium. It is convenient to study the results in the form of a kind of phase diagram, such as that in Figure 4. This figure was constructed with parameters that made it correspond to the diagram found from molecular dynamics simulations of  $Ar_{55}$  and  $Ar_{147}$ . It reveals a region of two-phase equilibrium of the solid and surface-melted forms, a region of equilibrium of three phases, solid, surface-melted and liquid, a region of two-phase equilibrium of surface-melted cluster and liquid, and a region in which only the liquid is stable.

Not all plausible diagrams of this type have precisely these regions of stability or mutual stability. It is possible to have non-overlapping regions of bistability, for example [24]. There need not be a tristable region, although the Lennard-Jones system does show one. In fact, with suitable and plausible parameters, this theoretical framework predicts that there could be substances that could have, instead of a surface-melted phase, a core-melted or frozen-surface phase. Naturally one condition for such behavior is that the liquid be denser than the solid. The likely candidate clusters for a frozen-surface phase are those of gallium, indium and even water. Clusters in this state would be much like ice cubes that have not yet frozen through, but have liquid centers.



*Figure 4.* A type of phase diagram for a cluster indicating regions of stability and coexistence for three phase-like forms: solid, surface-melted and liquid. The vertical axis measures  $T^{-1}$ , and the two horizontal axes, the densities  $\rho_{\text{surface}}$  and  $\rho_{\text{core}}$ , of defects in the surface and core, respectively. The heavy curve is the curve of stability, like that of a van der Waals gas in a pressure-volume plot. The lighter curves are its projection onto the three planes of the graph. Wherever the curve's slope is downward, the system is stable; where it slopes up, the system fails to satisfy a local stability condition. The regions of unstable equilibrium are cross-hatched. Each downward branch corresponds to a stable phase, whose limits are the points where the curve's direction reverses. Thus, in this figure, the solid is stable from the lowest temperatures (highest part of the heavy curve) in the region where there are very few defects in the surface or the core; the surface-melted form is stable only over a finite band of temperature because the curve reverses its direction twice, in the vicinity of very low densities of bulk defects but moderately high densities of surface defects; and the homogeneous liquid is stable in the region of high densities of surface and bulk defects.

#### 4. Small-System Analogues of Second-Order Transitions

We turn now to the question of what the finite-system analogue of a second-order phase transition would be [73]. Typical examples are some solid-solid structural transitions and many transitions of magnetic ordering. The true second-order transition of bulk matter has only a single stable minimum with respect to the order parameter, at any temperature. The value of the order parameter at which the free energy is a minimum changes with the system's temperature, and this value moves from a region in which one phase is stable to a region in which the other phase is stable. A precise analogue of this second-order transition for finite systems would presumably be one

that has only a single minimum with respect to the order parameter, for all sizes of clusters. This would be the most obvious formal counterpart.

But there is another possibility: the system might have two minima for very small or even moderate-size systems, but these minima might converge to a single, common, stable value as  $N$  grows very large. This can indeed happen if the defects repel each other, or if they raise the frequencies of the normal modes of the cluster.

It turns out that both possibilities occur, and that there are two kinds of second-order transitions, one from each of the two conditions. One type arises from a single minimum for all  $N$ , and the other, from the coalescence of two minima in the free energy for small  $N$ , as the cluster grows large. This has been studied in the context of structural transitions of molecular clusters, specifically clusters of octahedral molecules such as  $\text{SF}_6$  and  $\text{TeF}_6$  [73].

The second case, of two converging minima, raises a subsidiary question, of whether the convergence occurs at some finite  $N$  or only as  $N$  goes to infinity. Still another, related possibility is that the two minima approach but do not quite merge for very large  $N$ . This case is clearly a prototype for a weak first-order transition, associated with a very small but nonzero latent heat.

The hexafluorides show two solid-solid transitions that seem, in the bulk limit, to be second-order. The higher-temperature transitions take the clusters from tetragonal to monoclinic structures, and from completely orientationally-disordered arrays to partially-ordered structures. The lower-temperature transition takes a system from a partially-ordered monoclinic structure to one that is completely ordered, orientationally. The upper transition shows dynamic coexistence and bimodality for clusters of order 100 to 300 molecules, while the lower-temperature transition shows only a single phase at any given temperature, indicating that the free energy has only a single minimum as a function of the order parameter.

## 5. Some Unsolved and Open Questions

Most of the discussion thus far has dealt with phases and phase changes that are now moderately well understood. However the study of phase-like forms of clusters and nanoparticles can hardly be said to be complete. We have already pointed out that the role of fluctuations in metastable, superheated or undercooled systems is still uncertain, at least with regard to whether they would mask the discontinuities of the distribution  $D_{\text{eq}}$ . There are some others that deserve mention.

In small systems, for which multiple phase coexistence is possible, an intermediate phase may appear as an intermediate between the high- and low-temperature forms and yet, under no conditions, be the most stable phase. If this occurs, the intermediate phase would be found in clusters but not in bulk matter, where its free energy would everywhere be above that of one or another phase. Such a case may occur in clusters of  $\text{TeF}_6$ , which exhibit an intermediate, monoclinic phase between two others found both in clusters and bulk  $\text{TeF}_6$  [73a,b].

One other open issue deserves mention. It appears from still-unpublished results that clusters may exhibit solid-liquid critical points. The conditions for this to

occur are entirely consistent with the finite, nonperiodic nature of the cluster. The stability condition for two phases is, in effect, the condition that the change of entropic contribution to the free energy difference of the phases be matched by the change in energy or enthalpy. If this condition is met at two points then two phases are in equilibrium. This can be put in terms of two curves that cross at a point. If the two crossing points were to become a single tangent point, that tangent point would be a limit, beyond which the two phases could no longer be distinguished as equilibrium forms of the substance. In short, the point of tangency would be the critical point. It appears at present that there is no logical barrier to the existence of such a point for clusters.

It is even possible to argue that there might be solid-liquid critical points for some bulk systems, on the following grounds. The traditional argument that they cannot exist for bulk systems is the symmetry ground, that there can be no continuous transition from the discrete symmetry of the crystalline solid to the continuous translational and rotational symmetry of the amorphous liquid. However as the temperature of a solid increases, so does the density of its defects, so that establishing the translational symmetry of a hot solid requires averaging over successively longer lengths to establish that average discrete translational symmetry. Likewise, as the pressure increases on a liquid, it becomes more and more ordered. This requires averaging over longer and longer lengths as the pressure increases, in order to establish the continuous translational symmetry of the liquid. If these lengths increase only slowly with  $N$ , then the symmetry arguments will be valid. However if they increase rapidly enough, or if they were even to diverge as temperature or pressure increase, then the symmetry argument would be inapplicable and there could perfectly well be a solid-liquid critical point for a macroscopic system.

## 6. Summary

The phase-like behavior of small clusters leads us not only to a rich variety of new phenomena such as "phases" that do not exist as such in bulk matter, but also to deepened insights into thermodynamics of materials. The solid-liquid equilibria of ensembles of clusters reveal, through the finite bands of their coexistence regions, the basis of the sharp coexistence curves of bulk solids and liquids, and of the limits of metastability. The coexistence of multiple phase-like forms of clusters and nanoparticles clarifies some of the limits on concepts of "phase" and "component", on the Phase Rule, and on the Maxwell construction normally used to explain the "tie-line" of the solid-liquid phase diagram, with its discontinuities of slope.

Furthermore, in attempting to elucidate the phase-like behavior of clusters, we are forced to reexamine the role of time scales in the thermodynamic interpretation of phenomena when it is possible to make observations on different time scales. Concepts assumed without scrutiny in the context of bulk matter become elusive, requiring care and precision, when we confront them in the context of systems so small that different time scales do not necessarily separate neatly. Careful consideration of time scales is important not only conceptually but technically as well, especially when we deal with molecular dynamics simulations.

Clusters may exhibit coexistence of more than two phases over finite bands of temperature and pressure. This is because, as with solid-liquid equilibria, the various phase-like forms differ from one another by relatively small amounts of free energy, so that detectable amounts of several forms may be present under conditions in which they have nonzero differences in their chemical potentials. Among these forms are not only solid and liquid, but also surface-melted and possibly core-melted (frozen-shell) clusters. This is an example of a situation in which "phase" and "component" cannot be separated.

Clusters have led us to recognize that there can be two kinds of second-order phase transitions of bulk matter, depending on whether their small-system counterparts have only a single minimum in the free energy at every temperature, or two minima in a range of temperatures, minima which converge in some way as the number of particles comprising the cluster increases.

Open questions remain, such as the nature of the transition from polyhedral to lattice-based structures that occurs in those clusters, such as the Lennard-Jones, which are polyhedral for small sizes but close-packed in the bulk crystal. Still another is the question of the structures and phases of molecular clusters, of the extent to which these take on the structures of their bulk counterparts even at small sizes, and of what kinds of phase transitions they may show – clearly an issue closely related to that of the second-order transitions. Finally, the phase behavior of clusters is a subject in which theory and simulation have far outpaced experiment; we can hope that recognition of these ideas will serve as stimuli for new laboratory studies of the phase behavior of clusters and nanoparticles.

### Acknowledgments

The author would like to express his debt to his many coworkers whose efforts have made it possible to bring this subject to its present level. The research described here that was carried out at The University of Chicago has been supported by Grants from the National Science Foundation.

### References

1. (a) Pawlow, P. (1909) *Z. Phys. Chem.* **65**, 1-35. (b) Pawlow, P. (1909) *Z. Phys. Chem.* **65**, 545-548.
2. Bartell, L.S. (1992) *J. Phys. Chem.* **96**, 108-111.
3. Bartell, L.S. and Dibble, T.S. (1991) *Z. Phys. D* **20**, 255-257.
4. Bartell, L.S., Sharkey, L.R., and Shi, X. (1988) *J. Am. Chem. Soc.* **110**, 7006-7013.
5. Buck, U., Schmidt, B., and Siebers, J.G. (1993) *J. Chem. Phys.* **99**, 9428-9437.

6. Goldstein, A.N., Colvin, V.L., and Alivisatos, A.P. (1991) *Mater. Res. Soc. Symp. Proc.* **206**, 271-274.
7. Martin, T.P., Näher, U., Schaber, H., and Zimmermann, U. (1994) *J. Chem. Phys.* **100**, 2322-2324.
8. (a) Valente, E.J. and Bartell, L.S. (1984) *J. Chem. Phys.* **80**, 1451-1457. (b) Valente, E.J. and Bartell, L.S. (1984) *J. Chem. Phys.* **80**, 1458-1461.
9. (a) Bartell, L.S. and Chen, J. (1992) *J. Phys. Chem.* **96**, 8801-8808. (b) Bartell, L.S. and Dibble, T.S. (1991) *J. Phys. Chem.* **95**, 1159-1167. (c) Dibble, T.S. and Bartell, L.S. (1992) *J. Phys. Chem.* **96**, 2317-2322.
10. Torchet, G., de Feraudy, M.-F., and Raoult, B. (1995) *J. Chem. Phys.* **103**, 3074-3083.
11. Ellert, C., Schmidt, M., Schmitt, C., Reiners, T., and Haberland, H. (1995) *Phys. Rev. Lett.* **75**, 1731-1734.
12. Schmidt, M., Kusche, R., Kronmüller, W., von Issendorff, B., and Haberland, H. (1997) *Phys. Rev. Lett.* **79**, 99-102.
13. Hudgins, R.R., Dugourd, P., Tenenbaum, J.M., and Jarrold, M.F. (1997) *Phys. Rev. Lett.* **78**, 4213-4216.
14. Bachels, T., Güntherodt, H.-J., and Schäfer, R. (2000) *Phys. Rev. Lett.* **85**, 1250-1253.
15. (a) Schmidt, M., Kusche, R., von Issendorff, B., and Haberland, H. (1998) *Nature* **393**, 238-240. (b) Kusche, R., Hippler, T., Schmidt, M., von Issendorff, B., and Haberland, H. (1999) *Eur. Phys. J. D* **9**, 1-4.
16. (a) Lai, S.L., Guo, J.Y., Petrova, V., Ramanath, G., and Allen, L.H. (1996) *Phys. Rev. Lett.* **77**, 99-102. (b) Lai, S.L., Ramanath, G., Allen, L.H., and Infante, P. (1997) *Appl. Phys. Lett.* **70**, 43-45. (c) Efremov, M.Yu., Schiettekatte, F., Zhang, M., Olson, E.A., Kwan, A.T., Berry, R.S., and Allen, L.H. (2000) *Phys. Rev. Lett.* **85**, 3560-3563.
17. Berry, R.S. (1999) Phases and Phase Changes of Small Systems, in Jellinek, J. (ed.), *Theory of Atomic and Molecular Clusters: With a Glimpse at Experiments*, Springer, Berlin, pp. 1-26.
18. (a) Hill, T.L. (1963) *The Thermodynamics of Small Systems*, Part 1, Benjamin, New York. (b) Hill, T.L. (1964) *The Thermodynamics of Small Systems*, Part 2, Benjamin, New York.
19. Sawada, S. and Sugano, S. (1989) *Z. Phys. D* **12**, 189-191.
20. Sawada, S. and Sugano, S. (1992) *Z. Phys. D* **24**, 377-384.
21. Berry, R.S., Beck, T.L., Davis, H.L., and Jellinek, J. (1988) Solid-Liquid Phase Behavior in Microclusters, in Prigogine, I. and Rice, S.A. (eds.), *Evolution of Size Effects in Chemical Dynamics*, Part 2, Wiley, New York, pp. 75-138.
22. Briant, C.L. and Burton, J.J. (1975) *J. Chem. Phys.* **63**, 2045-2058.

23. (a) Cheng, H.-P. and Berry, R.S. (1991) *Mater. Res. Soc. Symp. Proc.* **206**, 241-252. (b) Cheng, H.-P. and Berry, R.S. (1992) *Phys. Rev. A* **45**, 7969-7980.
24. (a) Kunz, R.E. and Berry, R.S. (1993) *Phys. Rev. Lett.* **71**, 3987-3990. (b) Kunz, R.E. and Berry, R.S. (1994) *Phys. Rev. E* **49**, 1895-1908.
25. Nauchitel, V.V. and Pertsin, A.J. (1980) *Mol. Phys.* **40**, 1341-1355.
26. Amini, M. and Hockney, R.W. (1979) *J. Non-Cryst. Sol.* **31**, 447-452.
27. Jellinek, J., Bonačić-Koutecký, V., Fantucci, P., and Wiechert, M. (1994) *J. Chem. Phys.* **101**, 10092-10100.
28. (a) Lindemann, F.A. (1910) *Phys. Z.* **11**, 609-612. (b) Lindemann, F.A. (1912) *Engineering* **94**, 515.
29. Zhou, Y., Karplus, M., Ball, K.D., and Berry, R.S. (2001) Submitted.
30. (a) Doye, J.P.K., Wales, D.J., and Berry, R.S. (1995) *J. Chem. Phys.* **103**, 4234-4249. (b) Wales, D.J. and Doye, J.P.K. (1995) *J. Chem. Phys.* **103**, 3061-3070.
31. Bartell, L.S. (1986) *Chem. Rev.* **86**, 491-505.
32. (a) Farges, J., de Feraudy, M.-F., Raoult, B., and Torchet, G. (1983) *J. Chem. Phys.* **78**, 5067-5080. (b) Farges, J., de Feraudy, M.-F., Raoult, B., and Torchet, G. (1986) *J. Chem. Phys.* **84**, 3491-3501.
33. Lee, J.W. and Stein, G.D. (1987) *J. Phys. Chem.* **91**, 2450-2457.
34. Raoult, B., Farges, J., de Feraudy, M.-F., and Torchet, G. (1989) *Philos. Mag. B* **60**, 881-906.
35. (a) Torchet, G., de Feraudy, M.-F., Raoult, B., Farges, J., Fuchs, A.H., and Pawley, G.S. (1990) *J. Chem. Phys.* **92**, 6768-6774. (b) Torchet, G., Farges, J., de Feraudy, M.-F., and Raoult, B. (1990) Electron Diffraction Studies of Clusters Produced in a Free Jet Expansion, in Scoles, G. (ed.), *The Chemical Physics of Atomic and Molecular Clusters*, Proceedings International School of Physics "Enrico Fermi", Vol. 107, North-Holland, Amsterdam, pp. 513-542.
36. Quirke, N. and Sheng, P. (1984) *Chem. Phys. Lett.* **110**, 63-66.
37. Bartell, L.S., Harsanyi, L., and Valente, E.J. (1989) *J. Phys. Chem.* **93**, 6201-6205.
38. (a) Cotterill, R.M.J., Damgaard Kristensen, W., Martin, J.W., Peterson, L.B., and Jensen, E.J. (1973) *Comput. Phys. Commun.* **5**, 28-31. (b) Cotterill, R.M.J. (1975) *Philos. Mag.* **32**, 1283-1288. (c) Damgaard Kristensen, W., Jensen, E.J., and Cotterill, R.M.J. (1974) *J. Chem. Phys.* **60**, 4161-4169.
39. (a) Eters, R.D. and Kaelberer, J. (1975) *Phys. Rev. A* **11**, 1068-1079. (b) Eters, R.D. and Kaelberer, J. (1977) *J. Chem. Phys.* **66**, 5112-5116. (c) Kaelberer, J.B. and Eters, R.D. (1977) *J. Chem. Phys.* **66**, 3233-3239.
40. Lee, J.K., Barker, J.A., and Abraham, F.F. (1973) *J. Chem. Phys.* **58**, 3166-3180.
41. McGinty, D.J. (1973) *J. Chem. Phys.* **58**, 4733-4742.



42. Garzón, I.L. and Jellinek, J. (1991) *Z. Phys. D* **20**, 235-238.
43. (a) Jellinek, J. and Garzón, I.L. (1991) *Z. Phys. D* **20**, 239-242. (b) Garzón, I.L. and Jellinek, J. (1993) *Z. Phys. D* **26**, 316-318.
44. Sawada, S. (1987) Dynamics of Transition-Metal Clusters, in Sugano, S., Nishina, Y., and Ohnishi, S. (eds.), *Microclusters*, Springer Series in Materials Science, Vol. 4, Springer, Berlin, pp. 211-217.
45. Luo, J., Landman, U., and Jortner, J. (1987) Isomerization and Melting of Small Alkali-Halide Clusters, in Jena, P., Rao, B.K., and Khanna, S.N. (eds.), *Physics and Chemistry of Small Clusters*, NATO ASI Series, Ser. B, Vol. 158, Plenum Press, New York, pp. 201-206.
46. Rose, J.P. and Berry, R.S. (1992) *J. Chem. Phys.* **96**, 517-538.
47. (a) Berry, R.S., Jellinek, J., and Natanson, G. (1984) *Phys. Rev. A* **30**, 919-931. (b) Berry, R.S., Jellinek, J., and Natanson, G. (1984) *Chem. Phys. Lett.* **107**, 227-230.
48. Jellinek, J., Beck, T.L., and Berry, R.S. (1986) *J. Chem. Phys.* **84**, 2783-2794.
49. (a) Beck, T.L. and Berry, R.S. (1988) *J. Chem. Phys.* **88**, 3910-3922. (b) Beck, T.L., Jellinek, J., and Berry, R.S. (1987) *J. Chem. Phys.* **87**, 545-554. (c) Beck, T.L., Leitner, D.M., and Berry, R.S. (1988) *J. Chem. Phys.* **89**, 1681-1694.
50. (a) Davis, H.L., Beck, T.L., Braier, P.A., and Berry, R.S. (1988) Time Scale Considerations in the Characterization of Melting and Freezing in Microclusters, in Long, G.J. and Grandjean, F. (eds.), *The Time Domain in Surface and Structural Dynamics*, NATO ASI Series, Ser. C, Vol. 228, Kluwer, Dordrecht, pp. 535-549. (b) Davis, H.L., Jellinek, J., and Berry, R.S. (1987) *J. Chem. Phys.* **86**, 6456-6464.
51. Amar, F.G. and Berry, R.S. (1986) *J. Chem. Phys.* **85**, 5943-5954.
52. (a) Blaisten-Barojas, E. and Levesque, D. (1986) *Phys. Rev. B* **34**, 3910-3916. (b) Blaisten-Barojas, E. and Levesque, D. (1987) A Molecular Dynamics Study of Silicon Clusters, in Jena, P., Rao, B.K., and Khanna, S.N. (eds.), *Physics and Chemistry of Small Clusters*, NATO ASI Series, Ser. B, Vol. 158, Plenum Press, New York, pp. 157-168.
53. Garzón, I.L., Borja, M.A., and Blaisten-Barojas, E. (1989) *Phys. Rev. B* **40**, 4749-4759.
54. Honeycutt, J.D. and Andersen, H.C. (1987) *J. Phys. Chem.* **91**, 4950-4963.
55. (a) Fisher, M.E. and Privman, V. (1985). *Phys. Rev. B* **32**, 447-464. (b) Fisher, M.E. and Privman, V. (1986) *Commun. Math. Phys.* **103**, 527-548. (c) Privman, V. and Fisher, M.E. (1983) *J. Stat. Phys.* **33**, 385-417.
56. Etters, R.D., Danilowicz, R., and Kaelberer, J. (1977) *J. Chem. Phys.* **67**, 4145-4148.
57. Wales, D.J. and Berry, R.S. (1990) *J. Chem. Phys.* **92**, 4473-4482.
58. Wales, D.J. and Berry, R.S. (1994) *Phys. Rev. Lett.* **73**, 2875-2878.

59. Lynden-Bell, R.M. and Wales, D.J. (1994) *J. Chem. Phys.* **101**, 1460-1476.
60. Doye, J.P.K. and Wales, D.J. (1995) *J. Chem. Phys.* **102**, 9673-9688.
61. Labastie, P. and Whetten, R.L. (1990) *Phys. Rev. Lett.* **65**, 1567-1570.
62. Doye, J.P.K. and Wales, D.J. (1995) *J. Chem. Phys.* **102**, 9659-9672.
63. Berry, R.S. and Smirnov, B.M. (2001) *J. Chem. Phys.* **114**, 6816-6823.
64. Berry, R.S. and Smirnov, B.M. (2000) *J. Chem. Phys.* **113**, 728-737.
65. Woods, L.C. (1975) *Thermodynamics of Fluid Systems*, Clarendon Press, Oxford.
66. Cheng, H.-P., Li, X., Whetten, R.L., and Berry, R.S. (1992) *Phys. Rev. A* **46**, 791-800.
67. (a) Nosé, S. (1984) *Mol. Phys.* **52**, 255-268. (b) Nosé, S. (1984) *J. Chem. Phys.* **81**, 511-519. (c) Nosé, S. (1991) *Prog. Theor. Phys. (Suppl.)* **103**, 1-46.
68. (a) Kast, S.M., Nicklas, K., Bär, H.-J., and Brickmann, J. (1994) *J. Chem. Phys.* **100**, 566-576. (b) Kast, S.M. and Brickmann, J. (1996) *J. Chem. Phys.* **104**, 3732-3741. (c) Sholl, D.S. and Fichthorn, K.A. (1997) *J. Chem. Phys.* **106**, 1646-1647.
69. Andersen, H.C. (1980) *J. Chem. Phys.* **72**, 2384-2393.
70. Vekhter, B. and Berry, R.S. (1997) *J. Chem. Phys.* **106**, 6456-6459.
71. (a) Jellinek, J. and Guvenc, Z.B. (1995) Structure, Melting, and Reactivity of Nickel Clusters from Numerical Simulations, in Farrugia, L.J. (ed.), *The Synergy Between Dynamics and Reactivity at Clusters and Surfaces*, NATO ASI Series, Ser. C, Vol. 465, Kluwer, Dordrecht, pp. 217-240. (b) Jellinek, J. (1996) Theoretical Dynamical Studies of Metal Clusters and Cluster-Ligand Systems, in Russo, N. and Salahub, D.R. (eds.), *Metal-Ligand Interactions: Structure and Reactivity*, NATO ASI Series, Ser. C, Vol. 474, Kluwer, Dordrecht, pp. 325-360.
72. Garzón, I.L. and Jellinek, J. (1992) Melting of Nickel Clusters, in Jena, P., Khanna, S.N., and Rao, B.K. (eds.), *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, Vol. 1, NATO ASI Series, Ser. C, Vol. 374, Kluwer, Dordrecht, pp. 405-410.
73. (a) Proykova, A. and Berry, R.S. (1997) *Z. Phys. D* **40**, 215-220. (b) Proykova, A., Radev, R., Li, F.-Y., and Berry, R.S. (1999) *J. Chem. Phys.* **110**, 3887-3896. (c) Proykova, A., Pisov, S., and Berry, R.S. (2001) *J. Chem. Phys.*, in press.