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# Clusters of Atoms and Molecules

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## 2.8 Melting and Freezing of Clusters: How They Happen and What They Mean

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### 2.8.1 Introduction: The “Phases” of Clusters

Clusters, of even as few as seven atoms, may exhibit characteristics we associate with distinct, solid-like and liquid-like forms of matter [1]. Understanding how these forms behave at a microscopic level, how we identify them and characterize them, and what we can learn from them about phase changes more generally are the topics of this chapter.

The first issue to address is what “liquid” and “solid” should mean in the context of clusters. What is a liquid-like cluster or a solid-like cluster? What observable or calculable properties characterize liquid-like and solid-like forms? We take a first clue from the *compliance* of bulk liquids and the contrasting stiffness of solids. Bulk liquids, inelastic as they are, respond to even very small forces, deforming and conforming as the forces demand. Solids are, of course, stiff and elastic up to fairly high limits, beyond which they deform permanently or fracture. The compliance of liquids implies that they have some “soft modes” of motion, that is, some vibration-like modes whose natural frequencies are very low compared with those of typical lattice vibrations, e.g. lower than  $10^{12} \text{ s}^{-1}$  [2, 3]. This is not to say that liquids have no high-frequency modes; indeed, all the spectral evidence indicates that liquids have many modes with frequencies comparable to those of solids, but in addition have some of much lower frequencies. The characteristic deformability of liquids also implies that liquids can change their geometric forms easily. Translating both of these to apply to the world of small clusters, we can expect the vibrational spectrum of a liquid cluster to have a significant density of states at frequencies well below typical frequencies of solid-like clusters, and to be capable of passing readily – on the time scale of the periods of the soft modes – from the well around one minimum on the cluster’s potential surface to the wells around other minima. In other words, the liquid cluster should have some slow, large-amplitude modes of motion so that it can relatively readily rearrange, isomerize and explore its potential surface.

Another kind of structural characteristic that should distinguish solid clusters from liquids are their radial and angular correlation functions. Solids, specifically crystals, show peaks in radial (pair) correlation functions corresponding to the mean nearest-neighbor distance and to successive second-nearest

and further-removed neighbors. Liquids show broader nearest-neighbor peaks and rarely any well-defined peaks corresponding to more distant atoms or molecules. The same criterion should distinguish solid from liquid clusters, with the one ramification that clusters may have polyhedral as well as lattice-based geometries and still be solid-like [4–6]. The angular correlation function, being a three-body property rather than a two-body, is less frequently used than the radial or pair function [7, 8]. However it too is a useful diagnostic. Not only are maxima at particular angles sometimes helpful in identifying a geometry or ruling one out; minima, corresponding to nonappearance of certain angles, are strong indicators of solid-like behavior and in many cases of one structure rather than another. The appearance of a low minimum at  $90^\circ$  in the angular distribution functions of cold  $\text{Ar}_{13}$  and  $\text{Ar}_{55}$  indicate solid-like icosahedral structures; the face-centered cubic (fcc) close-packed geometry is ruled out because it has successive nearest neighbors forming  $90^\circ$  angles. More energetic  $\text{Ar}_{13}$  and  $\text{Ar}_{55}$  clusters have angular distribution functions with significant probabilities at  $90^\circ$  (but still this is a minimum) indicating some kind of breakdown of structural rigidity.

The adjacency matrix, showing which atoms are next to which others, has been used to distinguish stiff solids, soft solids and liquids [9]. Another related characteristic which naive intuition suggests might be an important property to distinguish liquids from solids is the ease with which identical atoms or molecules can permute positions with one another [10]. Indeed, the establishment of permutational equivalence of identical particles is a *sufficient* condition for liquid-like behavior. However the time scale required to achieve permutational equivalence may be far longer than is relevant for experimental or computational tests of “phase”, so we should not require attainment of permutational equivalence as a necessary condition for liquid-like behavior. However we may wish at least to demonstrate that feasible paths are open to establish that equivalence. Alternatively, if only the atoms of certain sites of a cluster seem able to permute with one another, we may wish to denote such a situation as “surface melting” or some other appropriate, restricted behavior.

Clusters may but need not exhibit clear solid-like or liquid-like behavior [1]. They may, instead, in a range of temperature or energy that is in some sense “intermediate”, be slush-like, with properties that fall between those of solids and liquids. Clusters of almost all substances are solid-like at low energies or temperatures and clusters of many substances are liquid-like at higher energies or temperatures. Between, a cluster may be slush-like or may exhibit clearly defined, observable, coexisting solid and liquid forms, like chemical isomers [11]. Both kinds of behavior seem to occur; at issue is what factors determine which kind of behavior a given cluster follows. Another issue is whether the solid or especially the more energized liquid can be relatively stable toward evaporation, at least enough so to be observed in experiments or simulations.

At present, our ideas concerning the “phases” of clusters come from theory and simulation. Important experimental results consistent with the theory and simulations have been obtained but as yet they cannot be called definitive or

unambiguous demonstrations of the theory-based ideas. Historically, the first indications of distinguishable solid-like and especially liquid-like forms were obtained from simulations [3, 12–17]. The general theory of the thermodynamics of small systems has been well established some time ago [18] but the specifics that explain how real systems behave, and how their thermodynamic and dynamic behavior are related to each other and to the potential surface and energy levels of the cluster, have emerged more recently, stimulated in part by the simulations. Then, in part because of the new challenges stirred by theoretical advances, many more simulations have now been done. The picture is still far from complete but many of the main aspects of the subject now seem clear. Here, we describe the theory and the simulations, and what we learn from them of the freezing and melting of clusters, and of the implications of the behavior of clusters for phase stability and metastability of bulk matter.

In the next section we develop the theory from the viewpoint of its logical structure insofar as that can now be done, rather than from its historical evolution. We begin with a few comments regarding that evolution in order to illuminate some of the conceptual and technical difficulties. The third section addresses the use of simulations for studying clusters and particularly for studying their phase behavior. The final section treats the implications for phase equilibrium of bulk matter.

## 2.8.2 Theoretical Basis

The theory of phase equilibrium of clusters is really a balancing act between thermodynamics and dynamics, in which time scales become an overarching concern [19]. The very meaning of “equilibrium” comes under scrutiny in a way one very, very rarely encounters with conventional phase or chemical equilibrium. The reason is that the time scales for clusters to attain dynamic equilibrium are sometimes just the time scales characteristic of some of the experiments best suited for studying clusters, so that “what you get is what you look for.” But before we explore the ramifications of time scales, let us examine the problem in what seem like static terms.

We begin our discourse on the thermodynamics of clusters with a description in terms of the Helmholtz free energy of a cluster in a canonical (isothermal) ensemble of clusters, all of a specific size,  $F_N(T)$ . This description is appropriate for the clusters of  $N$  particles, which we shall call  $N$ -clusters, under conditions of some but certainly not all experiments. That is, in some experiments, the size distribution becomes constant – “frozen in” – but the clusters are still in thermal equilibrium with a heat bath of surrounding atoms. This may occur with jets of carrier gas seeded with the species of interest, producing molecular beams of the clusters. By contrast, in jet experiments with little or no carrier, the clusters may, as a result of evaporative cooling without collisions, attain a distribution of energies far from a thermal distribution [20]. A canonical distribution is hardly

appropriate for such a system; instead, one must describe the system in terms of an "evaporative ensemble". At an opposite extreme, in a static cell clusters of each size may not only approach thermal equilibrium distributions of energy; the entire sample may approach an equilibrium distribution of cluster sizes, so that the description of clusters of any given size must be described by a grand canonical ensemble, in which both energy and mass may be exchanged with the surroundings [21]. But with any of these descriptions, we can assume that the internal vibrational modes of the individual clusters are coupled strongly enough that we can define a mean internal temperature based on the mean kinetic energy of the atoms within the cluster. Moreover the reasoning we present can be extended readily, at least to evaporative ensembles and, with a little modification to allow for evaporation and condensation, to grand canonical ensembles.

Now we return to the Helmholtz free energy and to its connection to the quantum statistics of a system. The canonical partition function,  $Q(T) = \sum_j g_j e^{-E_j/kT}$ , is related to  $F_N(T)$ :  $Q(T) = e^{-F_N(T)/kT}$ . Furthermore all the other thermodynamic functions can be derived from  $Q(T)$  by taking suitable derivatives. In other words, knowledge of the canonical partition function is sufficient to tell us all the equilibrium properties of the system of fixed mass number  $N$  at temperature  $T$ . For example if we know the vibrational and rotational energy levels  $E_j$  of a solid-like  $N$ -cluster and the degeneracies  $g_j$  of those levels, we can compute the free energy of that cluster.

In fact, if we have a reasonable approximation for those vibrational and rotational energies and degeneracies, we can compute rather reliable free energies and other thermodynamic properties simply because the thermodynamic properties are essentially weighted *average* values of negative exponentials of the energies, in units of the average kinetic energy. That is, we do better in estimating thermodynamic quantities than in estimating the individual energy levels and degeneracies, provided we represent their general pattern correctly.

But we are interested not in the solid alone or the liquid alone but in the comparison of the stabilities of the two. To make this comparison we must evaluate free energies for both forms. This means we need models for both, from which their free energies can be estimated. It looks at this point like two simple models are all we need. This would be correct if we could assume that both the solid and liquid forms are stable at whatever temperature interests us. This is a terribly strong assumption, too strong to be acceptable, although making it, one can go on to rationalize the results of the early simulations from rather simple quantum statistics [22]. Instead of making that assumption, we can take a much sounder step by asking, "Within a context consistent with our (presumed) models for solid and liquid clusters, what are necessary and sufficient conditions for the solid and liquid to both be stable?" This is a very productive question because it leads us to new physical insight [23].

The stability of a form of matter can always be expressed in terms of the existence of a minimum in a thermodynamic potential, such as a free energy, suitable for the constraints on the system of interest. This is an easy statement to

make, but it avoids a vital but subtle problem: with respect to what quantity is the thermodynamic potential a minimum? In the present case, we suppose that the system may be characterized by a parameter indicating the degree of nonrigidity of the system, a parameter that acts much like an order parameter in the Landau theory of second-order phase transitions. At least two ways have been used to define this nonrigidity parameter, one a phenomenological quantity, the ratio of two spectroscopic frequencies and the other, a quantity based in the microscopic structure of the substance, the density of defects in the material when it is quenched to the geometry of lowest energy in its current potential well. The former, the ratio of the energy of the lowest rotational transition to the lowest transition with no rotational excitation, is a slight generalization of a parameter that had been used previously to characterize the degree of nonrigidity in triatomic molecules [24]. The latter is an adaptation of a quantity central to the Stillinger-Weber version of the defect model for liquid structure and melting [25]. Used in our context, both give the same result when both yield results, and the microscopic parameter leads to additional results [26].

Both ways of defining the extent of nonrigidity can be associated with ideal, extreme models at the rigid, solid-like and nonrigid, liquid-like ends of a scale. Calling  $\gamma$  the nonrigidity parameter and setting  $\gamma = 0$  at the rigid end of the scale and  $\gamma = 1$  at the nonrigid end (so the density of defects is defined on a relative scale), we construct the patterns of energy levels and degeneracies, i.e. the densities of states, for the two limiting cases. By introducing this parameter, we make the energies  $E_j$ , the partition functions and the free energies into functions of  $\gamma$ . Explicitly, we now write  $F(T, \gamma)$  for the free energy;  $T$  is a physical variable, and  $\gamma$  is a parameter that allows us to tune the extent of nonrigidity of the system, in principle by varying the Hamiltonian in a suitable, continuous manner. We shall use this dependence of  $F$  on  $\gamma$  shortly.

Using the phenomenological parameterization, it is natural to choose for the solid either a very general, phenomenological model such as the Einstein or Debye crystal whose density of states is well known and derivable from the model Hamiltonian, or a reasonably realistic Hamiltonian such as a harmonic model based on diagonalizing the harmonic Hamiltonian representing small-amplitude oscillations around an assumed equilibrium structure. The Einstein model, with all the vibrational frequencies the same and independent of cluster size, is too crude to represent the solid-like clusters adequately, but almost any more refined model, even an Einstein model with a size-dependent single frequency for the lattice vibrations, seems adequate for describing the qualitative aspects of the phase equilibrium of clusters [22].

A suitable corresponding choice of a phenomenological model for the liquid is the *Gartenhaus-Schwartz* model [27], in which the interactions are identical, harmonic attractive forces between every pair of particles. This model, developed for nuclei, leads to a spectrum of equally spaced levels with the degeneracies of the totally symmetric representations of the unitary group  $SU(3N - 3)$  for a cluster of  $N$  identical particles. This model supposes that there is so much empty space in the cluster that all the significant encounters between

particles occur outside the radius of any hard-core repulsion, yet close enough that the attractions are strong. It is not particularly realistic, but that is irrelevant because we need not require the free energy to have its liquid-like minimum at the extreme limit.

The microscopic model based on the density of defects yields results for the solid essentially identical to those of the accurate derivation described above because they really describe the same situation [26]. The defect model for the liquid introduces, in addition to the solid-like modes, a configurational entropy and a set of energy terms in the Hamiltonian. The precise form of these terms depends on one's choice of detailed model. For example one may assume that the defects are independent of one another and of the vibrational modes of the host, or that the defects interact with each other or with the host modes, presumably to lower their frequencies.

For both kinds of model, the outcome is similar: the density of states of the solid-like cluster is the lower at the low end of the energy scale, but at higher energies, the density of states of the liquid-like cluster becomes the larger. Consequently if we connect the limiting cases, rigid and nonrigid, in a correlation diagram, all the energy levels at the low end of the energy scale slope upward from the rigid limit to the nonrigid, but the energy levels high on the energy scale must slope downward from the rigid limit to the nonrigid [28]. This is because every state appearing at one limit must also appear at the other, and, apart from avoided crossings forced by Ehrenfest's adiabatic theorem, the connections can be made in order from bottom up. An example of such a correlation diagram is shown in Fig. 1, for a cluster of five argon atoms [22]. The vertical scale is exaggerated by a factor of about 5 for the rotational level spacings of the rigid limit in order to make them visible.

Now it is time to follow the implications of the energy level patterns for the free energy [23]. At low temperatures, with only the low-energy levels populated, the free energy of the solid cluster is lower than that of the corresponding liquid; in fact, at low enough temperatures, because of the upward slope of the low-lying energy levels, the free energy must be a monotonic, increasing function of  $\gamma$ . However as the temperature increases, usually lowering the free energy of solid, liquid and everything between, the free energy near the nonrigid end of the scale decreases slower with  $T$  than that near the rigid end, because of the larger contribution to  $T\Delta S$  of the many available levels of the nonrigid form. This makes the curve of  $F(T, \gamma)$ , for  $T$  above the lowest range, droop at the nonrigid end of the scale of  $\gamma$ . At some temperature,  $F(T, \gamma)$  develops a flat spot at or near the nonrigid limit, a point of

$$\frac{\partial F(T, \gamma)}{\partial \gamma} = 0 ;$$

we call this temperature  $T_f$ , the "freezing temperature", because the solid is the only thermodynamically stable form at temperatures below  $T_f$ . Above this temperature,  $F(T, \gamma)$  has two minima, one near the rigid end of the scale of  $\gamma$  and another near the nonrigid end. Each minimum corresponds to a locally stable

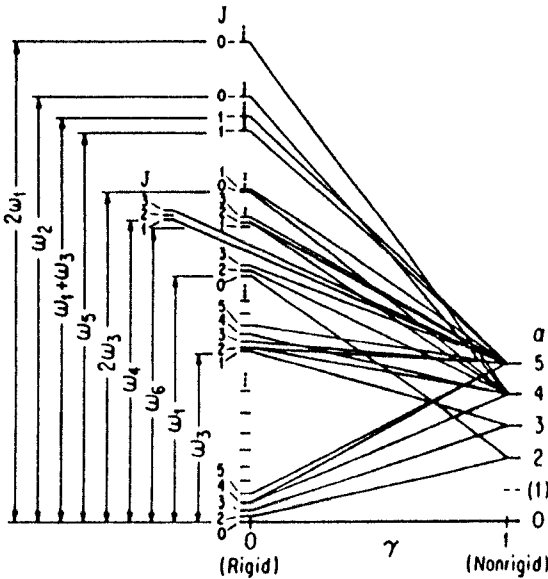


Fig. 1. A correlation diagram for the rotation-vibration levels of  $\text{Ar}_3$  in which the horizontal scale is the degree of nonrigidity,  $\gamma$ . No promotional energy is assumed necessary to achieve the liquid-like form, which is a far stronger assumption than necessary. Nevertheless the qualitative form of the diagram, with upward-sloping levels at the bottom of the scale and downward-sloping levels at higher energies, carries the essentials for describing the phase equilibrium of solid and liquid clusters

form, analogous to chemical isomers. If a collection of  $N$ -clusters is in thermal equilibrium, the solid and liquid forms are both present at any temperature for which  $F(T, \gamma)$  has two minima on the  $\gamma$  scale, and the ratio

$$\frac{(\text{liquid})}{(\text{solid})} \equiv K_{\text{eq}} = e^{(-\Delta F/kT)},$$

where  $\Delta F = F_{\text{liq}} - F_{\text{sol}}$ . The two forms coexist in a dynamic equilibrium; each cluster is either solid-like or liquid-like at any instant, but over time, passes back and forth between the two forms. At a temperature we can call  $T_{\text{eq}}$ , the free energies of the two forms are equal and the equilibrium ratio is unity. At temperatures below this but above  $T_f$ , the solid predominates. At temperatures above  $T_{\text{eq}}$  the liquid predominates. In fact, as the temperature increases, the curve of  $F(T, \gamma)$  tips more and more toward the nonrigid end, until a temperature  $T_m$  is reached which has

$$\frac{\partial F(T, \gamma)}{\partial \gamma} = 0$$

near or at the rigid limit. Above  $T_m$ , only the liquid-like form is stable, and the



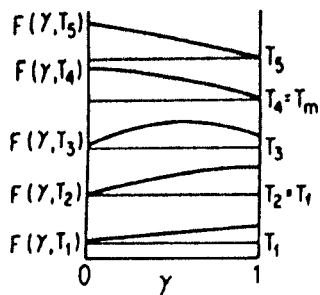


Fig. 2. A schematic representation of the free energy  $F(T, \gamma)$  as a function of the nonrigidity parameter  $\gamma$  for several temperatures, from very low to high enough that the only stable form is liquid

curve of  $F(T, \gamma)$  is monotonic and decreasing with  $\gamma$ . Figure 2 shows the free energy as a function of  $\gamma$  for several different temperatures including  $T_f$  and  $T_m$ .

The picture that has emerged here is one in which clusters may have sharp freezing temperatures, below which only their solid forms are stable, and sharp melting temperatures, above which only their liquid forms are stable, but the *freezing temperature and melting temperature are not the same!* Moreover this description has separated the freezing and melting temperatures logically; they need not be the same, when expressed in these terms. The equilibrium constant has two discontinuities, at the limits of thermodynamic stability of each "phase".

This description would be adequate if a) all clusters had distinct liquid-like and solid-like forms and b) all clusters spent long enough intervals in their solid-like and liquid-like forms to establish well-defined, observable equilibrium properties characteristic of each phase. In reality, only some clusters meet both these conditions [11, 29]. Some clusters, such as  $Ar_7$ ,  $Ar_{13}$ ,  $Ar_{15}$  and  $Ar_{19}$ , do meet both conditions. Others, such as  $Ar_8$  and  $Ar_{14}$ , have potential surfaces with wells forming heavily-worn staircases, successions of wells with not very high barriers between one and the next, so these clusters do not have well-defined solid-like and liquid-like regions of their potential surfaces. Others, possibly  $Ar_{17}$ , pass back and forth between "phases" too rapidly to exhibit well-defined solid and liquid forms and, instead, display average properties that make such clusters seem slush-like. Figure 3 illustrates three kinds of potential surface, of which only the first kind gives rise to the phase equilibrium described above.

The matter of time scale is crucial here [19]: does the cluster pass from one "phase" to another at a rate fast or slow relative to the time required to establish well-defined properties of a single phase, and is this time long or short compared with the time we require to observe the "phase"? We cannot answer this question from thermodynamic arguments; we must turn to dynamics to address it. But notice that we have made a subtle twist to what we are calling "equilibrium". If the observation time is long relative to the time required to establish the dynamic equilibrium of the two "phases", then "equilibrium" means we observe a single kind of species with properties that are the average over both "phases"; if the observation time is short relative to the mean interval spent in a single phase and to the time required to establish stable, phase-like properties,

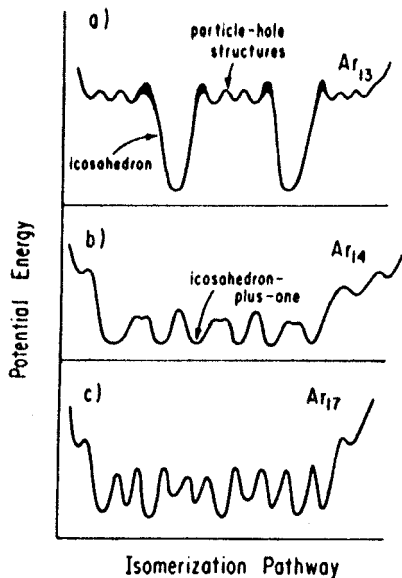


Fig. 3. Schematic cross sections of the potential energy surfaces for three kinds of argon cluster. Only the first kind, here illustrated by  $\text{Ar}_{13}$ , gives rise to separately observable solid-like and liquid-like phases and to sharp but unequal freezing and melting temperatures

then "equilibrium" means a mixture of two forms whose concentrations are in a characteristic, fixed ratio at each temperature. In other words, what we mean by "equilibrium" depends on how we observe the system.

### 2.8.3 Simulations and Experiments

Experiments to distinguish liquid and solid clusters have relied on two kinds of information: spectral line widths and electron diffraction data. The spectral analyses have been carried out thus far with argon clusters containing a single foreign molecule that acts like a probe. In one set of experiments, *Bösiger* and *Leutwyler* [30] used carbazole, a large, flat, disc-like molecule as the probe. They found a range of low-energy conditions in which the visible spectrum of carbazole with several Ar atoms attached appears sharp but shifted from the spectrum of pure carbazole. At higher energies, the carbazole bands become broader, which was interpreted as due to the availability of low-frequency modes of motion for liquid-like argons attached to the carbazole by weak van der Waals forces.

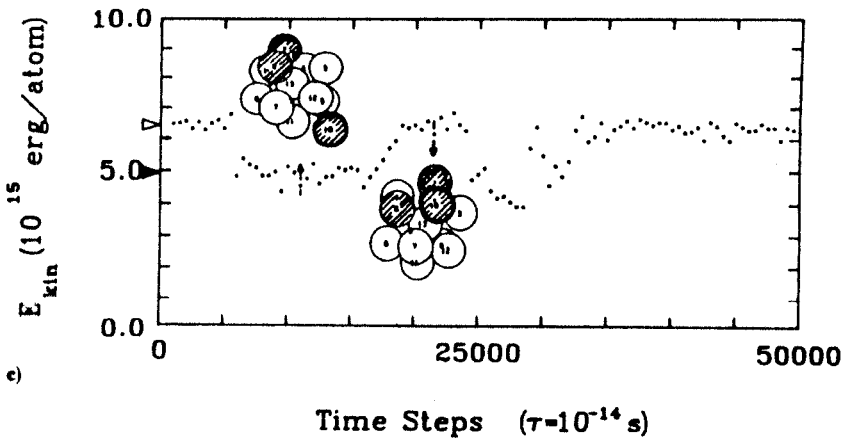
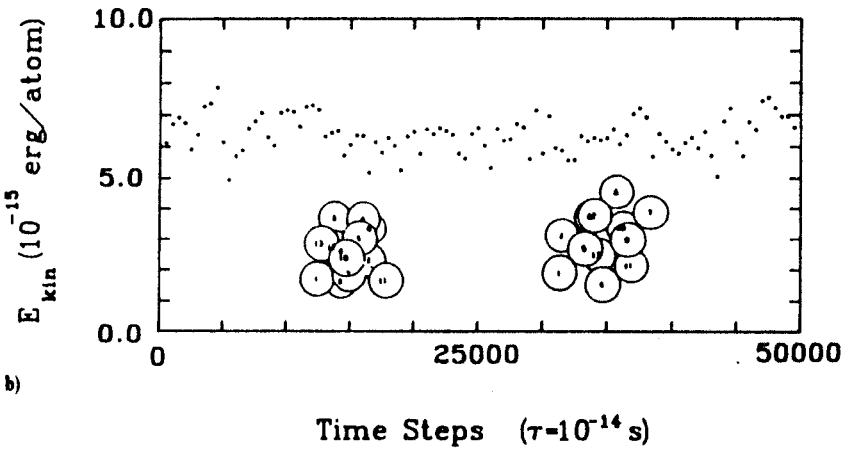
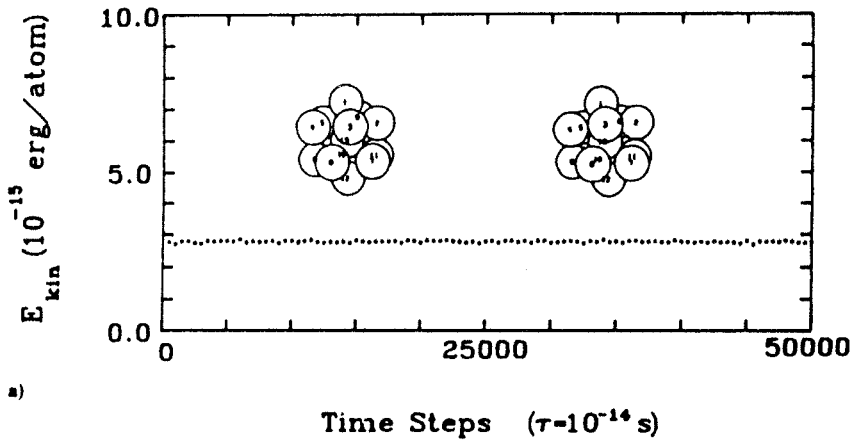
Other spectroscopic experiments were done by *Gough*, *Knight* and *Scoles* [31] with sulfur hexafluoride in argon and by *Hahn* and *Whetten* [32], with benzene in argon. The former were based on interpretation of the shift and width of vibrational bands of the  $\text{SF}_6$  and the latter, on an electronic transition of benzene, again on the frequency shifts and widths of the transition in clusters of

various sizes. At a fixed temperature in both of these experiments, the small clusters show broad bands which were interpreted as due to liquid-like behavior and the large clusters showed sharp bands, attributed to solid clusters. Clusters of intermediate size showed complex bands consisting of sharp, solid-like bands and broader, liquid-like bands. This was interpreted to support the idea of coexisting solid-like and liquid-like clusters of a given size. However both sets of experiments were reinterpreted – the infrared by Eichenauer and LeRoy [33] and the ultraviolet by Adams and Strat [34] and by Fried and Mukamel [35] – to indicate not two phases but two sets of sites for the impurity molecules, one kind in the interior of the cluster and the other, on the surface. Other experiments, using fragmentation patterns of ionized clusters [36], were interpreted to imply that clusters may exhibit both solid-like and liquid-like forms. This interpretation has not been challenged or replaced.

Electron diffraction experiments have concentrated primarily on structural studies. However *Bartell* and coworkers have seen sharply peaked and more diffuse, broadly peaked patterns for carbon tetrachloride and then for other species, which they have interpreted as due to solid and liquid clusters [6]. Which appears in a given experiment depends on the conditions in the source from which the clusters come. Coexistence of these two forms has yet to be proven.

Until more experiments can be done which test the coexistence and sharp limits of existence of solid and liquid phases of clusters, simulations can be carried out to explore and test some aspects of the issue. Two kinds of simulations have dominated the research on phase changes in clusters. Some have been carried out by *Monte Carlo* (MC) methods [7, 15–18] and others, by molecular dynamics (MD) [3, 8–14, 19, 37], which is simply successive solution of the equations of motion from an assumed potential of interaction among the particles. Both MC and MD calculations may be carried out at constant energy or at constant temperature. However MC has been used far more for isothermal (constant-T) systems and MD, for constant-E systems because these correspond to time-invariant Hamiltonians and conservative systems. However it is possible to carry out MD calculations that give the same values for all equilibrium properties as a canonical ensemble gives. This method, introduced by *Nosé* [38], involves adding to the Hamiltonian one degree of freedom more than is found for the physical system. The “phantom” degree of freedom, if suitably chosen, acts like a heat bath, exchanging energy with all the physical variables. The entire system maintains a constant energy but the energy of the set of physical variables fluctuates just like an isothermal system. This procedure can be carried out with many different choices of the extra degree of freedom, but until now, only the choice made by *Nosé* has been exploited [39].

Fig. 4. Time histories of short-term average kinetic energies or vibrational temperatures for clusters of  $\text{Ar}_{13}$ : a) a cold solid; b) a warm liquid; c) within the coexistence range of energies, with both solid and liquid behavior for the same cluster, as it passes between the two forms as time proceeds



The simplest way to use simulations is to follow the time sequence of the mean kinetic energy of the atoms in a cluster held at constant energy. This is, in effect, a vibrational temperature. One carries out the averaging over enough steps of the integration in time to cover a few periods of vibration but not so long that many different regions of the potential surface are explored during the averaging interval. For argon clusters, a time step of  $10^{-14}$  s<sup>-1</sup> is suitable for most work and an averaging interval of 500 steps works out well. For systems with stronger forces, such as clusters of KCl, one must use a shorter time step.

A time history of a cluster of Ar<sub>13</sub> at low energy is shown in Fig. 4a [37]; the temperature is nearly constant and low. In fact the mean temperatures for this system form a sharp Gaussian distribution. At a slightly higher temperature, one sees a slightly broadened distribution of short-term mean kinetic energies, and an occasional dip corresponding to passage from one potential well to another, that is, from one permutational isomer to another. At considerably higher energies, one sees a broad distribution. Furthermore the solid clusters all have approximately the geometry of the icosahedron, while the broad distribution of Fig. 4b is associated with what seems an amorphous structure, i.e. that of a liquid. Between the energy at which the cluster looks liquid and the lower energy at which it seems solid, one sees for many clusters a bimodal pattern of mean temperatures, a sharper distribution corresponding to a hot solid and a broader distribution corresponding to a cold liquid. Recall that these refer to simulations at constant energy, so the two parts of the distribution correspond to a high-potential energy region of liquid behavior and a deep-potential region in which the cluster has a high mean kinetic energy and temperature. Figure 4c shows an example of this.

The distribution of mean temperatures may be constructed in either of two ways. The mean temperatures may be collected into "bins" and the number in each bin plotted [11, 37], or the mean temperatures may simply be sequenced and a curve constructed by augmenting the ordinate one unit with each new incidence of a temperature as one goes up the temperature scale of the abscissa [40]. The former is, in principle, the derivative of the cumulative distribution constructed in the second method. The former is susceptible to errors of making the bins too large so that small peaks and shoulders in the distribution get overlooked. The latter may give false impressions of shoulders or small maxima because of noise in the data.

The passage back and forth between liquid and solid occurs only within a limited energy range, consistent with the predicted sharp limits on the stability of liquid and solid. However simulations cannot of course tell whether these limits are truly *sharp*. They can only give us an indication of bounds on the region within which the two phases may coexist.

To establish well-defined short-term temperatures requires only about  $5 \times 10^{-12}$  s<sup>-1</sup> or 500 time steps. To establish a stable distribution and mean of the short-term mean temperatures requires about 10,000 time steps. In the energy range within which both phases may coexist, one may be able to see

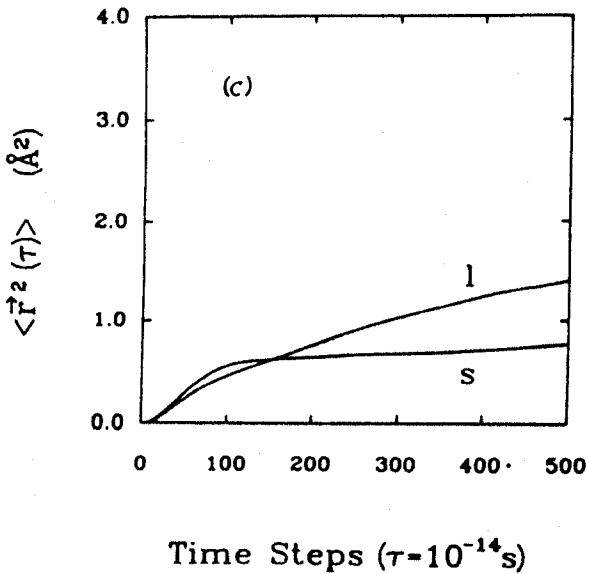
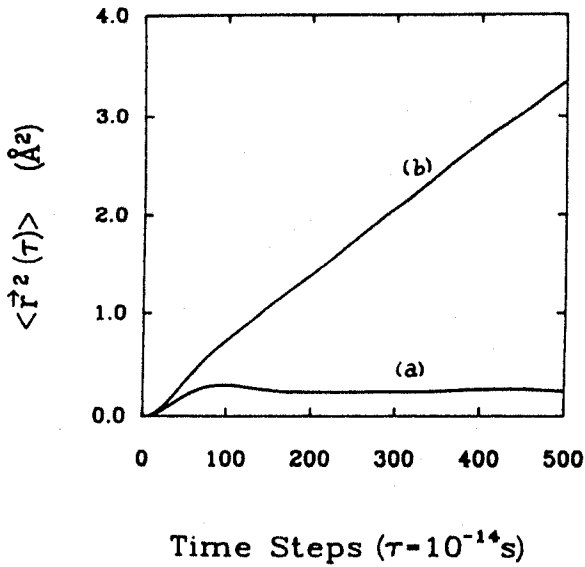


Fig. 5. Mean square displacements for  $\text{Ar}_{13}$ , as functions of time: a) a cold solid as in Fig. 4a; b) a warm liquid, as in Fig. 4b; c) the mean square displacements for the coexistence region with the data for the two peaks in the distribution plotted separately

passage from one to another "phase" within perhaps 50,000 time steps or less. However to determine the equilibrium ratio of liquid to solid as the ratio of times spent by one cluster as liquid divided by the corresponding time spent as solid, i.e. to use the ergodic hypothesis, we require as many as 1-3 million time steps. Fortunately such long runs are now entirely feasible on modern computers.

Other diagnostics are also very useful and sometimes very enlightening. The mean square displacement as a function of time,  $\langle r^2(t) \rangle$  is one of these. Its slope is six times the diffusion coefficient. Clusters at low energies show  $\langle r^2(t) \rangle$  that are essentially horizontal, meaning that there is no diffusion. At higher energies, the cluster takes on the slope and diffusion coefficient of a liquid. In the region in which the temperature distribution is bimodal, the mean square displacements for each mode in the distribution can be computed. What one finds is a very warm solid with only very slow diffusion and a significantly cooler liquid with significant diffusion and a diffusion constant compatible with that of the bulk liquid. Of course all the mean square displacements reach a constant upper limit at the distance corresponding to the diameter of the cluster.

The radial and angular distributions have been used as diagnostics of simulations. The angular distributions in particular, as mentioned previously, give helpful indications about what structures the solid form may have [7, 8].

A common and helpful characteristic for distinguishing liquid-like behavior from solid-like is the root-mean-square deviation of the nearest-neighbor distance from its mean. It had been suggested by Lindemann that this quantity should show a sharp increase when the liquid forms, and that this should follow a slow increase with temperature up to a value of about 10 should jump. This criterion, shown in Fig. 6, is well supported.

The caloric curve of  $\langle T(E) \rangle$  vs. energy for a constant-energy simulation or  $\langle E(T) \rangle$  vs. temperature for a constant-temperature simulation is another useful way to extract information about phase equilibria from simulations and the data they generate [8, 11, 14, 37]. A smooth curve without inflection is a good indicator for a continuous transition from solid-like to liquid-like; a caloric curve with a flat spot such as that in Fig. 7, or even an S-like wiggle indicates equilibrium between two phases. However the presence of an inflection or wiggle only indicates phase equilibrium without disclosing what phases are involved.

That not all clusters show coexistence of well-marked phases emerges also from the simulations. Some, such as  $\text{Ar}_{14}$ , simply have no bimodal distribution of temperatures. Others, such as  $\text{Ar}_{17}$ , appear to have ready passage between solid and liquid. In either case, the clusters must act like slush, rather than like distinguishable liquid and solid phases. And still others, notably metal clusters and clusters of salt molecules, show "phases" much like soft solids, in which the cluster may pass among several structures without large displacements that permute atoms among all the equivalent sites. For example  $\text{Cu}_6$  has a regular octahedral geometry in its configuration of lowest energy [9] (if the Jahn-Teller distortion, due to orbital degeneracy, is neglected); there are thirty of these

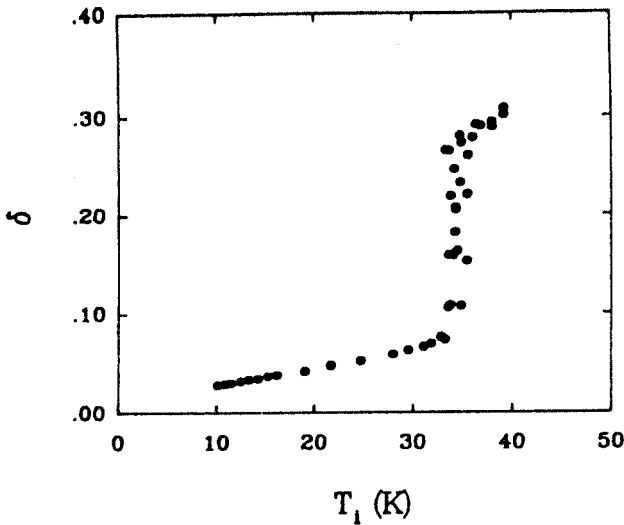


Fig. 6. The behavior of the root-mean-square variation in the nearest-neighbor distance as a function of temperature; the example is  $\text{Ar}_{13}$  but the sharp jump is a very generally found phenomenon

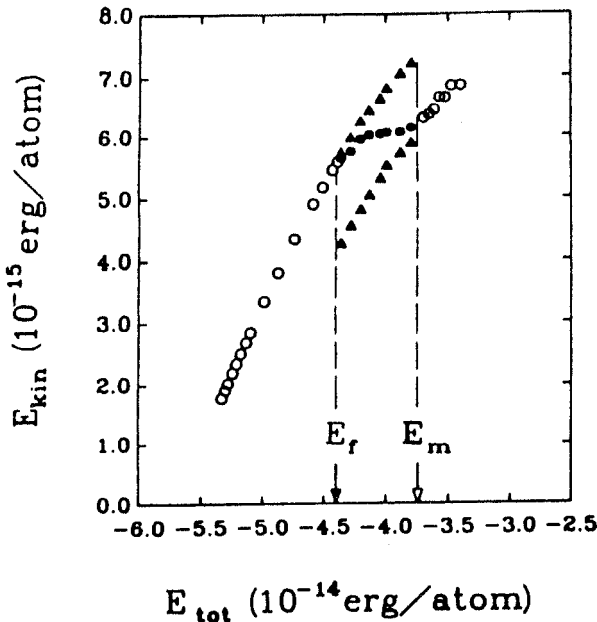


Fig. 7. A typical caloric curve of  $\langle T(E) \rangle$  vs.  $E$ , in this case for  $\text{Ar}_{13}$ : circles represent averaging over the entire distribution of temperatures, while triangles represent averaging only within a single peak in the bimodal distribution of temperatures, in the range where bimodality occurs



octahedra that are permutationally distinct. And each octahedron can be distorted to another structure that corresponds to a local minimum on the potential surface well above the octahedron in energy; around each of the thirty octahedra, there are twelve of these distorted structures. Within a restricted range of energies a  $\text{Cu}_6$  cluster may pass among the twelve distorted octahedra and the regular octahedron from which they are derived, without passing to any other octahedron or related distorted structure. This situation is a kind of soft solid behavior, which *Sawada* and *Sugano* [9] called the "fluctuating state." At higher energies, the cluster can pass among all the stable structures and permute all the atoms among all the sites, but in the energy range of the "fluctuating state" no such permutational equivalence can be established.

The connection between these various kinds of behavior and the potential surface or the energy levels of the cluster is a subject still very much in development. It is clear that if the cluster has one kind of deep, narrow potential well and a high, rolling region separated from the deep well by a moderate or high barrier, then the cluster must exhibit the two-phase coexistence described in the previous section. If the potential has a series of wells at successively higher energies, all separated by low barriers, like a staircase, then the behavior is slush-like and no clearly defined coexistence region will be found. A set of quantum-statistical models, based on constructed densities of states, were analyzed by *Bixon* and *Jortner* [41] to probe the coexistence question in terms of the two diagnostics of a) the number of maxima in the distribution of mean temperatures and b) the form of the caloric curve of mean temperature vs. energy.

## 2.8.4 Implications for Bulk Matter

The phase equilibrium behavior of clusters seems to produce a paradox for the phase equilibrium of bulk matter, but in fact if we follow carefully how this equilibrium depends on  $N$ , we can gain several insights into the behavior of bulk matter [26]. There are two things to question: first, why are the freezing and melting transitions the same sharp transition for bulk matter? Second, what becomes of the discontinuities at  $T_f$  and  $T_m$  as  $N$  becomes arbitrarily large? The first question was answered many years ago but we get a little new insight by answering it in the present context. The second is a new challenge whose answer tells us something about metastable, supercooled bulk matter.

The reason that freezing and melting occur at the same temperature for bulk matter is apparent when we write the free energy and the equilibrium constant with  $N$  explicit [18]. The free energy difference,  $\Delta F_N = N \times \Delta\mu_N$  where  $\Delta\mu_N$  is the difference in the mean chemical potentials of the liquid and solid clusters of  $N$  particles. The equilibrium constant

$$K = e^{-\Delta F_N/kT} = e^{-N\Delta\mu_N/kT}$$

which is dominated by the behavior of  $N\Delta\mu_N$ . The chemical potential difference  $\Delta\mu_N$  changes from positive to negative as the temperature increases through  $T_{eq}$  where  $\Delta\mu_N = 0$ . This makes  $K$  swing from a small number to a large number. If  $N$  is relatively small, then the change of  $K$  from less than 1 to greater than 1 is gradual. If, on the other hand,  $N$  is large, for example  $10^{10}$ , then  $K$  swings from very near zero to very, very large within a tiny interval of  $T$ . To see this, we can best use not  $K$  but  $\mathcal{X} = (K - 1)/(K + 1)$ , equivalent to [(liquid) - (solid)]/(total amount), which varies from  $-1$  at low temperatures where the clusters are all solid to  $+1$  at high temperatures where the clusters are all liquid. The quantity  $\mathcal{X}$  has discontinuities at  $T_f$  and  $T_m$  just as  $K$  does, but it is easier to display. Figure 8 shows how  $\mathcal{X}$  behaves for two values of  $N$ .

The result is that for large  $N$ ,  $\mathcal{X}$  switches continuously from a value very near  $-1$  through 0 to a value very near  $+1$  within an immeasurably small interval of temperature, so  $\mathcal{X}$  and  $K$  look discontinuous at  $T_{eq}$ . The discontinuity associated with the first-order melting/freezing transition is thus a consequence of large  $N$ , and for any finite system  $\mathcal{X}$  is, strictly speaking, continuous. Furthermore the local stability of each phase persists on both sides of  $T_{eq}$ . This means that a theory of the first-order melting and freezing transition must not be one in which one phase changes from unstable to stable while the other does the reverse at  $T_{eq}$ . The local stability prevents such behavior.

Now how about the other question? What happens to  $\Delta T_c \equiv T_m - T_f$  as  $N$  becomes very large? To answer this, we return to the defect model of *Stillinger* and *Weber* [25], which gives us a way to write and differentiate  $\Delta F(T, \gamma)$  for any

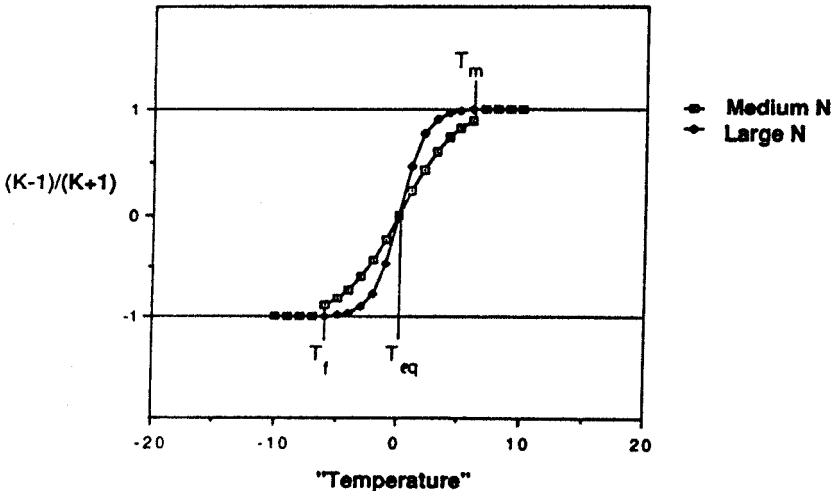


Fig. 8. Two schematic curves of  $\mathcal{X}$ , the more gradually sloping curve for moderate  $N$  and the steeper curve for larger  $N$ . Note that the discontinuities at  $T_f$  and  $T_m$  are visible for moderate  $N$  but not for larger  $N$ .

$\gamma$ . The details of this calculation are given elsewhere [40]; here we merely cite the conclusions.

If the defects do not interact with each other or with the lattice vibrations, then  $\Delta T_c$  goes to zero as  $N$  becomes large. However if the defects attract each other or if, as is most usual, the defects lower the energy of the lattice modes, then  $\Delta T_c$  remains finite as  $N$  becomes arbitrarily large. The local stability of the thermodynamically unfavored phase persists beyond  $T_{eq}$ . However if  $N$  is large, this local stability cannot be seen in a system in equilibrium because  $\mathcal{X}$  is too near  $-1$  or  $+1$ . Moreover the discontinuities at  $T_f$  and  $T_m$  cannot be seen because they are too small.

There is a way to observe the persistence of local stability, namely by preventing a system being cooled from coming to chemical and phase equilibrium. If a liquid is cooled below  $T_{eq}$  and no solid has been formed, one can cool that liquid further still. In fact the liquid can be cooled as low as  $T_f$ . Below that temperature, there is no locally stable liquid, whatever the size of the system. In other words, this analysis has shown that there is a sharp limit to supercooling of pure liquids, and that the locus of lowest temperatures for which the liquid branch of the  $p$ - $V$  curve has negative slope, the so-called spinodal curve, has a sharp lower bound. This is an answer to a question that has been raised since the spinodal was recognized from the equation of state of van der Waals.

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## References

1. For a recent review of this topic, see R.S. Berry, T.L. Beck, H.L. Davis, J. Jellinek.: In: *Evolution of Size Effects in Chemical Dynamics*, Part 2, Advances in Chemical Physics, Vol. LXX 1988, p. 75 (Wiley, New York)
2. J.M. Dickey, A. Paskin: *Phys. Rev.* **188**, 1407 (1969); *ibid. Phys. Rev. B* **1**, 851 (1970)
3. W. Damgaard Kristensen, E.J. Jensen, Martin, R.M. Cotterill: *J. Chem. Phys.* **60**, 4161 (1973)
4. J. Farges, M.F. de Feraudy, B. Raoult, G. Torchet: *J. Chem. Phys.* **59**, 3454 (1973); *ibid.* **78**, 5067 (1983); *ibid.* **84**, 3491 (1986); *ibid.* In: *Physics and Chemistry of Small Clusters*, P. Jena, B.K. Rao, S.N. Khanna (eds.), p. 15. (Plenum, New York); B. Raoult, J. Farges, M.F. de Feraudy, G. Torchet: *Z. Phys. D* **12**, 85, 93 (1989)
5. B.G. De Boer, G.D. Stein: *Surf. Sci.* **106**, 84 (1981)
6. E.J. Valente, L.S. Bartell: *J. Chem. Phys.* **80**, 1451, 1458 (1984); L.S. Bartell: *Chem. Rev.* **86**, 491 (1986); Y.Z. Barshad, L.S. Bartell: In: *Physics and Chemistry of Small Clusters*, P. Jena, B.K. Rao, S.N. Khanna (eds.), p. 31. (New York, Plenum, 1987); L.S. Bartell, L. Harsanyi, E.J. Valente: In: *Physics and Chemistry of Small Clusters*, P. Jena, B.K. Rao, S.N. Khanna (eds.), p. 37. (Plenum, New York, 1987)

7. N. Quirke, P. Sheng: *Chem. Phys. Lett.* **110**, 63 (1984)
8. H.L. Davis, J. Jellinek, R.S. Berry: *J. Chem. Phys.* **86**, 6456 (1987)
9. S. Sawada, S. Sugano: *Z. Phys. D* **12**, 189 (1989); S. Sawada: In: *Microclusters*, S. Sugano, Y. Nishina, S. Ohnishi (eds.) (Springer, New York, 1987)
10. F. Amar, R.S. Berry: *J. Chem. Phys.* **85**, 5943 (1986)
11. T.L. Beck, J. Jellinek, R.S. Berry: *J. Chem. Phys.* **87**, 545 (1987)
12. D.J. McGinty: *J. Chem. Phys.* **58**, 4733 (1973)
13. R.M. Cotterill, W. Damgaard Kristensen, J.W. Martin, L.B. Peterson, E.J. Jensen: *Comput. Phys. Comm.* **5**, 28 (1973)
14. C.L. Briant, J.J. Burton: *Nature* **243**, 100 (1973); *ibid. J. Chem. Phys.* **63**, 2045 (1975)
15. J.K. Lee, J.A. Barker, F.F. Abraham: *J. Chem. Phys.* **58**, 3166 (1973)
16. R.D. Etters, J.B. Kaelberer: *Phys. Rev. A* **11**, 1068 (1975); *ibid. J. Chem. Phys.* **66**, 5112 (1977); J.B. Kaelberer, R.D. Etters: *J. Chem. Phys.* **66**, 3233 (1977); R.D. Etters, R. Danilowicz, J. Dugan: *J. Chem. Phys.* **67**, 1570 (1977); R.D. Etters, R. Danilowicz, J.B. Kaelberer: *J. Chem. Phys.* **67**, 4145 (1977); R.D. Etters, R. Danilowicz: *J. Chem. Phys.* **71**, 4767 (1979)
17. V.V. Nauchitel, A.J. Pertsin: *Mol. Phys.* **40**, 1341 (1980)
18. T.L. Hill: *Thermodynamics of Small Systems*. New York: Benjamin Part 1, 1963; Part 2, 1964
19. R.S. Berry: In: *Large Finite Systems*, J. Jortner, A. Pullman, B. Pullman (eds.) (Riedel, Amsterdam, 1987); T.L. Beck, R.S. Berry: *J. Chem. Phys.* **88**, 3910 (1988); H.L. Davis, T.L. Beck, P.A. Braier, R.S. Berry: In: *The Time Domain in Surface and Structural Dynamics*, G.J. Long, F. Grandjean (eds.) (Kluwer, New York, 1988); R.S. Berry: *Z. Phys. D* **12**, 161 (1989)
20. C.E. Klots: *J. Phys. Chem.* **92**, 5864 (1988)
21. H. Reiss, P. Mirabel, R.L. Whetten: *J. Phys. Chem.* **92**, 7241 (1988)
22. G. Natanson, F. Amar, R.S. Berry: *J. Chem. Phys.* **78**, 399 (1983)
23. R.S. Berry, J. Jellinek, G. Natanson: *Chem. Phys. Lett.* **107**, 227 (1984); *ibid. Phys. Rev. A* **30**, 919 (1984)
24. K. Yamada, M. Winnewisser: *Z. Naturforsch. A* **31**, 134 (1976)
25. F.H. Stillinger, T.A. Weber: *J. Chem. Phys.* **81**, 5095 (1984)
26. R.S. Berry, D.J. Wales: *Phys. Rev. Lett.* **63**, 1156 (1989); D.J. Wales, R.S. Berry: *J. Chem. Phys.* **92**, 4473 (1990)
27. S. Gartenhaus, C. Schwartz: *Phys. Rev.* **108**, 482 (1957)
28. M.E. Kellman, R.S. Berry: *Chem. Phys. Lett.* **42**, 327 (1976); F. Amar, M.E. Kellman, R.S. Berry: *J. Chem. Phys.* **70**, 1973 (1979); M.E. Kellman, F. Amar, R.S. Berry: *J. Chem. Phys.* **73**, 2387 (1980); G.S. Ezra, R.S. Berry: *J. Chem. Phys.* **76**, 3679 (1980)
29. J.D. Honeycutt, H.C. Andersen: *J. Phys. Chem.* **91**, 4950 (1987)
30. J. Bösigler, S. Leutwyler: *Phys. Rev. Lett.* **59**, 1895 (1987)
31. T.E. Gough, D.G. Knight, G. Scoles: *Chem. Phys. Lett.* **97**, 155 (1983)
32. M.Y. Hahn, R.L. Whetten: *Phys. Rev. Lett.* **61**, 1190 (1988)
33. D. Eichenauer, R.J. LeRoy: *Phys. Rev. Lett.* **57**, 2920 (1986); *ibid. J. Chem. Phys.* **88**, 2898 (1988)
34. J.E. Adams, R.M. Stratt: *J. Chem. Phys.* **93**, 1358 (1990)
35. L.E. Fried, S. Mukamel: *Phys. Rev. Lett.* **66**, 2340 (1991)
36. A.J. Stace: *Chem. Phys. Lett.* **99**, 470 (1983)
37. J. Jellinek, T.L. Beck, R.S. Berry: *J. Chem. Phys.* **84**, 2783 (1986)
38. S. Nosé: *J. Chem. Phys.* **91**, 511 (1984); *ibid. Mol. Phys.* **52**, 244 (1984)
39. J. Jellinek: *J. Phys. Chem.* **92**, 3163 (1988); J. Jellinek, R.S. Berry: *Phys. Rev. A* **38**, 3069 (1988)
40. D.J. Wales, R.S. Berry: *J. Chem. Phys.* **92**, 4283 (1990); *ibid.* **92**, 4473 (1990)
41. M. Bixon, J. Jortner: *J. Chem. Phys.* **91**, 1631 (1989)