Freezing and Melting of Metallic and Salt-Like Clusters

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ABSTRACT

Simulations have been carried out of small clusters of KCl and of Cu, by means of classical, isoergic molecular dynamics, in order to study the stability of coexistence of phase-like forms. To study Cu clusters, it was necessary to generate relatively reliable but efficient potentials, which was done by iterating efficient embedded-atom potentials against comparisons with more reliable but much less efficient density functional potentials. Born-Mayer-Rittner potentials without polarization were used for KCl. Both solid-liquid and solid-soft solid transitions were found. No sharp bimodal temperature distributions were found for coexisting Cu$_{13}$ solid-like and liquid-like clusters, but the highly asymmetric temperature distributions actually found would not preclude such coexistence.

INTRODUCTION

Clusters offer a tantalizing potential for creating new materials and new reactions, as recognized by this session of the Conference. But to realize that potential, we shall have to understand and control the species we make. This means that one of our important tasks is learning the forms clusters may assume, and then finding how these forms differ in their behavior. Some examples illustrate the issues. One is the prediction from several early simulation studies that clusters at least of rare gas atoms, may exhibit solid-like and liquid-like forms (1). Another is the evidence that clusters of a given size may have several locally stable geometric forms, and that what these forms are depends on the number $N$ of particles comprising the cluster (1–3). A third is the observed differences (4) in reactivity of clusters of similar but not identical size.

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presumably reflecting how the forms of clusters depend on $N$. Here, we focus on the nature of the solid-like and liquid-like forms of clusters, and of the equilibrium between them. To do this, we emphasize results originating in general arguments regarding densities of states, but which are derived by simulations, largely by molecular dynamics (MD) methods. The discussion following is a progress report on the extension of our own earlier work $(1,2)$ on rare gas clusters to high-temperature materials, notably to alkali halides and metals.

To carry out simulations by molecular dynamics, one must have an effective potential energy function, a surface, for the system one is describing. In the case of alkali halides, rather good potentials are available $(5,6)$, based on Born-Mayer-like interactions, representing polarizable ions with rather hard-core, short-range repulsions in addition to the long-range attractive forces. Representing clusters of metal atoms is a different kind of problem. It has been very difficult to obtain accurate representations of their potentials in terms of pair potentials, even when supplemented by single-particle, density-dependent terms. Most attempts to construct effective potentials for metal clusters have fallen back onto quantum mechanical solutions of the electronic Schroedinger equation at some level of approximation. This might be a simple spherical shell model, or an elaborate multiconfiguration calculation, but the approaches have been largely through the electronic structure. The consequence has been that only a very few molecular dynamics calculations have been done for metal clusters $(7,8)$; most of the calculations have been restricted to the regions around the (often presumed) lowest minima on the potential surface. We have taken a pragmatic approach, not so ambitious as the elaborate scheme of Car and Parinello $(9)$ nor as simple and economical as that of Sawada and Sugano $(8)$, but an intermediate way that passes back and forth in a series of iterations between dynamics done with simple potentials and more accurate calculations done in very restricted regions of the surface. The next section describes how the potential for the copper cluster was derived and also what potentials were chosen for the alkali halides. The third section describes the results of our preliminary simulations of alkali halide clusters and compares these results with the earlier results of others. The fourth section describes the results of our simulations of copper clusters of several sizes and compares those with analogous simulations of argon clusters. The final section summarizes the results and makes some general inferences.

THE POTENTIALS

For the alkali halides, we have used the potentials of Welch et al. $(6)$. These were chosen in preference to those of Brumer and Karplus $(5)$ in large part because we wish to compare our results with those of other simulations, most of which have used those of $(6)$.

For the copper clusters, we used Cu$_6$ as the basis for selecting parameters of the potential and larger clusters for verifying those param-
eters. To fix the potential, we iterated between two methods, the embedded atom (10,11) (EA) and the discrete variational (DVM) version (12,13) of the Xα method, a local-density formalism that has been applied previously to the determination of structures and binding energies of copper clusters (14). The EA potential is a sum of two-body terms and effective many-body terms that are represented by charge-density-dependent one-body terms. The first trial values of the parameters of the EA potential were taken from a prior computation of bulk copper (11) and molecular dynamics calculations were carried out with that EA potential. The molecular dynamics simulation was used at that stage to find first approximations to all the potential minima and saddles, the latter by the method of “slowest slides” introduced recently (15). Then DVM calculations were carried out in the vicinity of the lowest potential minimum, a regular octahedron, particularly along the direction of the symmetric stretching mode of the cluster. The results of these calculations were next used as the energy curve to which a second, refined set of EA parameters was fit. The Cu–Cu potential based on these parameters was then used to determine the minima of the potentials for Cu₆, Cu₈, and Cu₉. Two minima and a saddle were found for Cu₆, with energies, respectively, of −3.00, −2.970 and −2.969 eV/atom. Previously, dynamics of 6 and 7-atom metal clusters had been simulated (8) with the Gupta potential, a sum of exponentials.

The results were structures very close in geometry to the minimum-energy structures for Cu₆ and Cu₉ found by the DVM (no DVM calculation was done for Cu₇), and the energies around the minima were also as well represented for the larger clusters by the refined EA potential as was the shape of the Cu₆ surface. Further refinements are planned, based on geometries at the saddles found with EA functions and the energies at those saddles found by the DVM.

THE SIMULATED ALKALI HALIDE CLUSTERS

Previously, extensive simulations have been done to determine structures of alkali halide clusters (3,16). These gave results showing strong variation of equilibrium geometry with the number of alkali halide ion pairs in the cluster, and decided exceptional stability for those numbers from which cubic or rectangular parallelepiped structures can be made. Simulations done to probe dynamics were done for NaCl (3); these showed that some sizes exhibit transitions like solid-solid, softening transitions, and at higher energies, melting like that seen (1) for Al₁₃. One example, (NaCl)₁₀₈ at an energy equivalent to 811 K, was quoted as showing liquid behavior on one side and solid behavior on the other. This last situation is especially interesting for us because it appears to exemplify a liquid that does not wet its corresponding solid.

We felt that the dynamics of alkali halides other than NaCl needed to be examined, partly to get a sense of the generality of the conclusions drawn in (3), partly to probe further into the wetting-nonwetting ques-
tion and partly to lay the groundwork for other studies that deal with sintering. Here we report some of our first findings for KCl clusters, specifically (KCl)$_4$ and (KCl)$_5$. These were chosen because the former has as a lowest-energy form a "cube" with one ion at each corner, whereas the latter has no such magic-number geometry.

The easiest way to see the outcomes of the simulations is to look first at the caloric curves of $\langle T \rangle$ vs E, then at the distribution functions of short-time (500-step) averages of $\langle T \rangle$, and then at the properties of the cluster that account for the effective temperatures and their distributions. The caloric curve for (KCl)$_4$, Fig. 1, based on the effective temperature average over an entire long run appears at first sight to be qualitatively like that of the argon trimer (17). There is a low-temperature region in which the slope, the heat capacity at a constant pressure of zero, is a straight line and the cluster is solid-like. There is a high-temperature region, also with a nearly constant slope but displaced to higher energies than the solid-like region. Between them is a region of negative slope connecting the two extreme regions. The intermediate region of E and $\langle T \rangle$ for some clusters, such as Ar$_2$ and Ar$_{13}$, is the domain of coexisting solid-like and liquid-like clusters (1). (In those two examples, the slope of the caloric curve is everywhere positive, but for Ar$_3$ it is negative there.)

For (KCl)$_4$, the region linking the lowest and next-lowest branches of the caloric curve is a region of two coexisting solid-like forms of this cluster. This becomes clear when one constructs the curves of the mean square displacement of an ion as function of time, as shown in Fig. 2. The diffusion process simply does not carry an ion everywhere in the cluster when the energy of the cluster is of order $-2.92$ eV per ion or $-23.4$ eV; on a time scale of about $10^{-12}$ s, the mean square displacement is only about 3 Å$^2$ and at longer times, this curve oscillates around a value that seems constant on the picosecond time scale. At an energy slightly higher, $-2.83$ eV per ion, the mean square displacement reaches a level value of about 20 bohr$^2$ in a picosecond; this corresponds to traversal of the entire cluster and to liquid-like behavior. The process associated with the "transition" at about $-2.95$ eV/ion is the opening of an isomerism between the lowest-energy structure, Fig. 3a, and other structures, including the rectangular form, Fig. 3b, and the sort of octagon, Fig. 3c. The cohesive energies of these structures are $-24.97$, $-24.50$, and $-24.53$ eV, respectively. A fourth structure was reported (3) for (NaCl)$_4$ but has not been seen for (KCl)$_4$ in this work. These structures are, of course, the geometric forms of the (KCl)$_4$ cluster at the minimum energies of the potential wells on the effective energy surface; the clusters vibrate within these wells and pass among them, spending virtually no time in the geometries of the minima.

It seems that the saddles separating the "octagon" structure and the other two, the "cube" and the "rectangle," are all relatively low. If one of the minima were separated from the others by high saddles, isoergic simulations based on increasing the energy in steps from the lowest-energy structure could reach regions in which some basins allowed on
Fig. 1. The caloric curve for (KCl)_4 based on molecular dynamics (MD) simulations for clusters at constant energy. The smooth, continuous curve is based on long-time averaging of the kinetic energy to fix the mean temperature. The two terminating branches are based on the short-time average temperatures within each peak of the temperature distribution in the region of energy where it is bimodal.

The basis of total energy would be unreachable by any classical path. For such cases, caloric curves based on isothermal simulations would be expected to differ from those based on isoergic simulations carried out as ours were. However, whether this occurs with any alkali halide cluster will be answered only when the corresponding saddles have been identified. If there are "puddles" on the potential surface, one might think it possible to use several different initial points for the isoergic simulations in order to develop caloric curves from microcanonical ensembles or Hamiltonian systems that are equivalent to the curves developed from canonical ensembles. However, there is a difficulty in doing this: One does not know without a detailed analysis of the available volumes of the phase space in the unconnected regions how to weight their contributions.

The distributions of mean kinetic energies, that is, of mean temperatures, for (KCl)_4 for several energies are shown in Fig. 4. At low energies, these are unimodal and at very low energies, not at all like Gaussian distributions (a), but become Gaussian (b), and then unsymmetrical and then bimodal (c) at temperatures in the region of coexisting isomers. At still higher temperatures, the curves become Gaussian again (d). In contrast to some of the argon clusters, this cluster does not show bimodality between solid and liquid forms, but between regular and less regular, soft solid structures. It seems likely that the clusters are so non-rigid in the energy range of coexisting solid-like isomers that the small increment required to make such clusters liquid-like is enough to facilitate frequent passages among all the wells so that only the liquid form is seen at the higher temperatures.
Fig. 2. The mean square displacements of the K$^+$ (solid curve) and Cl$^-$ (dotted curve) ions of (KCl)$_4$ at energies of $-2.92$ and $-2.73$ eV per ion or total energies of $-23.36$ and $-21.84$ eV, corresponding to temperatures of approximately 800 and 1200K, respectively. One unit on the time scale is one time step, $3 \times 10^{-15}$ s.
Fig. 3. Structures of the stable forms of $(\text{KCl})_4$ found in these simulations. The energies of the cluster in these forms are $-24.97$, $-24.53$, and $-24.50$ eV for the "cube," "octagon," and "rectangle," (a), (b), and (c).

One diagnostic used for clusters is $\delta$, the root-mean-square nearest neighbor distance. As Fig. 5 shows, this quantity seems to satisfy the Lindemann criterion very nicely, staying well under 10% of the interionic spacing for low energies at which the cluster is a "cube," and rising rapidly to about 10% in the transition region. However, the rise starts well below the energy at which the liquid appears, at the energy of appearance of the "rectangular" isomer. In other words, this criterion may sometimes be weaker or more ambiguous in its meaning than has been supposed.

The $(\text{KCl})_5$ cluster is rather different from its $(\text{KCl})_4$ homologue. The lowest-energy structures are shown in Fig. 6; their energies are, respectively, $-31.25$ and $-31.12$ eV, considerably closer than the lowest two minima of the tetramer. The calorific curve of $(\text{KCl})_5$ is shown in Fig. 7; this shows two regions of nonconstant slope, the lower around $-2.96$ eV/ion and the upper, around $-2.71$ eV/ion. Even as low as $-3.0$ eV/ion, the distribution of temperatures is bimodal and remains so for most of the range up to about $-2.85$, about halfway between the two wiggly parts of the calorific curve. The curves of mean square displacement of an ion as a function of time, Fig. 8, shows how this cluster exhibits solid-like rigidity at an energy of $-3.01$ eV/ion, softness and slow diffusion at $-2.95$, and, like $(\text{KCl})_4$ illustrated by the higher-energy curves of Fig. 2, two distinct time scales at $-2.91$ and $-2.85$ eV/ion. For the pentamer, these occur with fast motion on a distance scale of about 2.2 Å and time scale of about 400 time steps of $3 \times 10^{-15}$ s, and slow diffusive motion on longer distance and time scales. At about $-2.85$ eV/ion or even lower energies, the cluster seems to be liquid-like. The interruption in the calorific curve at about $-2.71$ eV/ion is associated with vaporization.
Fig. 4. Distributions of mean kinetic energies for (KCl)$_4$ at energies of $-3.09$, $-2.99$, $-2.94$, and $-2.884$ eV per ion, or totals of $24.7$, $23.9$, $23.5$, and $23.07$ eV for (a), (b), (c), and (d), respectively.

COPPER CLUSTERS

We report here on simulations of Cu$_7$ and Cu$_{13}$. The results from simulations based on the once-iterated embedded atom potentials developed for Cu$_6$ are strikingly like those of the corresponding argon clusters based on Lennard Jones 6-12 potentials. The reason is that the seven-particle cluster is the smallest that seems to show unambiguous liquid-like behavior, as least for Lennard-Jones clusters, and the thirteen-particle cluster is the paradigm and most-studied small cluster, therefore most suited for comparison of different potentials.
Fig. 5. The mean displacement $\delta$ from equilibrium of the ions in (KCl)$_4$ as functions of temperature. The step corresponds closely to illustrating the Lindemann criterion of 10% as the value of $\delta$ at the solid-liquid transition—except that the new phase is not liquid-like at the energy of the threshold.

At this stage, Cu$_7$ was studied for its structures and potential surface; Cu$_{13}$ was studied primarily for dynamics. Like Ar$_7$ and the hypothetical metal simulated by Sawada and Sugano (8) the Cu$_7$ cluster has four kinds of potential minima, of which the lowest has the D$_{5h}$ symmetry and structure of a pentagonal bipyramid. The order of the next states is also that of Ar$_7$ and the Gupta-potential 7-cluster. The next-to-lowest equilibrium geometry is that of an octahedron with one face capped, giving the structure C$_{3v}$ symmetry. The third structure has symmetry C$_{3v}$, a trigonal tetrahedron, and the highest has only C$_2$ symmetry. These are all shown in Fig. 9. The energies of these structures are $-3.05$, $-3.03$, $-3.014$, and 3.011 eV/atom.

Dynamics were carried out for the Cu$_{13}$ cluster over a range of temperatures. The geometry of minimum energy is, like the Lennard-Jones cluster, an icosahedron. The caloric curve for this cluster is shown in Fig. 10. Like Ar$_{13}$, the curve has a long, solid-like region at low energies and a liquid-like region at higher energies, and the two are separated by a transition region that is flatter but still monotonically increasing. The melting transition occurs in the region of 650 K, about half the bulk melting temperature of 1351 K.

The geometry of the lowest-energy form of Cu$_{13}$ is the regular icosahedron shown in Fig. 11a. Its energy is $-3.285$ eV/atom or $-42.71$ eV total. The next-lowest structures are those of Fig. 11b, c, and d, with one atom removed from the octahedral shell and placed on a face of the
Fig. 6. Two views of each of the two lowest-energy structures of (KCl)$_5$.

Fig. 7. The caloric curve for the (KCl)$_5$ cluster from about $-3.0$ to $-2.6$ eV/atom, showing two "unstable" regions. The one at higher energy is associated with vaporization; that at lower energy is associated with the onset of a solid–solid interconversion.

icosahedron. There are three geometrically distinct kinds of such faces and all three are shown. The energies are almost identical: the lowest of these, Fig. 11b, is $-3.233$ eV/atom or $-42.03$ eV total; the energies of the next two are equal, $-3.232$ eV/atom in our simulation. (The significance of all the figures is only in how close the energies are.) These are the same as the lowest-energy geometries (2) of Ar$_{13}$.

The solid-like and liquid-like character of the low-energy and high-energy forms of the cluster are exhibited by the mean square displacements of the atoms. Two examples are shown in Fig. 12, for energies corresponding to 627 and 711K. The curve for 627 K is essentially a
Fig. 8. Four curves of the mean square displacement of an ion in (KCl)$_5$ at four different energies; from bottom to top, -3.02, -2.96, -2.92, and -2.86 eV/ion. Note the two distinct slopes in the two upper curves, corresponding to fast local processes and slow diffusive processes.

Fig. 9. The structures of the four locally stable forms of the Cu$_7$ cluster based on the once-iterated embedded-atom potential. The lowest-energy structure is a pentagonal bipyramid. The next has $C_{3v}$ symmetry, corresponding to an octahedron with one capped face, the cap being the top atom in (b); the third also has $C_{3v}$ symmetry and the highest, $C_2$. The next-highest corresponds to a tetrahedron with three capped faces, or a trigonal bipyramid with two capped faces.

horizontal line with small fluctuations around a mean of approximately 0.005 Å (2). The corresponding diffusion coefficient is zero. At the higher temperature of 711 K, the mean square displacement slopes, in the mean, upward, exhibiting an average slope of $6.4 \times 10^{-6}$ cm$^2$/s. The root-mean-square nearest neighbor distance $\delta$ is shown in Fig. 13. This function rises somewhat more gradually with mean temperature than its counterpart for Ar$_{13}$, but liquid-like behavior does set in where $\delta$ reaches about 10%, the Lindemann criterion value.
The final set of data we present here consists of the distributions of short-term-mean temperatures for Cu$_{13}$ at various energies, Fig. 14. At low temperatures, we see a phenomenon that should not be surprising but has apparently not been reported for simulations previously. This is a sharp cutoff at high temperatures, i.e., at high kinetic energy, that is presumably associated with the restricted vibrations available to the cluster at low energies. The cluster's vibrations can carry it up only to a maximum kinetic energy equal to its total energy, and the dynamics in this cluster seem to concentrate the clusters probable position into the region not far from that deepest part of the potential surface. Furthermore, whereas the distributions for higher energies, in particular in the transition region, are very asymmetric, the Cu$_{13}$ cluster as we have simulated it has not displayed a bimodal distribution of temperatures. This result is sufficiently different from what was expected, based on the example of Ar$_{13}$, that it will be investigated further.

**SUMMARY AND FUTURE ISSUES**

Simulations of salt-like and metal clusters show softening, solid-like to solid-like changes with two or more forms coexisting over ranges of temperature, like chemical isomers, in addition to solid–liquid transformations. The changes seem to be less sharp for these substances than for
Fig. 11. The four lowest-energy geometries of Cu$_{13}$. The atoms are shown as inequivalent only to clarify the geometric relationships. The central atom of the icosahedron of (a) is shaded there and its counterpart is similarly shaded in the other three figures. The lowest atom of (a) is the most darkly shaded; the other three figures are arranged so that the lowest icosahedral site in these figures is vacant. In (b), (c), and (d), the atom which occupied that lowest site in the most stable structure occupies each of the three kinds of surface faces available to the promoted atom.

Fig. 12. Two curves of mean square displacement of a Cu atom in Cu$_{13}$. The lower, nearly horizontal curve is drawn for an energy corresponding to a mean temperature of 627 K; the upper, dotted curve is drawn for 711 K.
Fig. 13. The rms fluctuation of the nearest-neighbor distance of "bond length" for Cu$_{13}$, as a function of temperature.

rare-gas (Lennard-Jones) clusters, perhaps because of the longer ranges and softer character of the potentials of salts and metals.

Questions that remain to be studied even for small clusters of metals and salts are the establishment of the saddles as well as of the minima on their potential surfaces and the connection of that information to the "phase coexistence" phenomenon in such clusters. How sharp are the limits of stability for any one form? What are the time scales for passage from one phase-like region of the potential surface to another?

Going beyond these questions of phase stability and coexistence, we can turn to questions of whether clusters of metals or salts can be used to construct phases of bulk matter unavailable by conventional mass processing, and of whether cluster reactivity can be distinguished from and related to bulk heterogeneous reactions. In particular, the study of reactions of clusters will have to confront the question of whether heats of reaction can be trapped in clusters and transform clusters from one phase to another during a sequence of reactions. If this can occur, and we see no reason why it should not, the reactivity of clusters becomes a more complicated matter that has sometimes been supposed, but offers a rich new range of possibilities for control of reactions with clusters.

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Fig. 14. Distributions of short-time-average temperatures for Cu$_{13}$ at energies of (a) $-2.948$ eV/atom, (b) $-2.938$ eV/atom, and (c) $-2.888$ eV/atom. The first is essentially solid, the third liquid and the second, a mixture of the two.
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