

Phase coexistence in clusters: An “experimental” isobar and an elementary model

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This work examines the temperature dependence of the coexistence ratios of phaselike forms of atomic clusters of two kinds, a homogeneous cluster bound by pairwise Lennard–Jones forces that simulates Ar_{55} , and a binary, ionic cluster simulating $(\text{KCl})_{32}$. Two methods have been used: isothermal molecular dynamics and a simple analytical model based on highly simplified densities of states. The phase behavior of the alkali halide cluster is well represented by a two-level density of states, a nondegenerate lower level, and a highly degenerate upper level. The phase behavior of the argon cluster needs an intermediate level of moderate degeneracy to reproduce the three-phase behavior of the simulations. © 1997 American Institute of Physics. [S0021-9606(97)50615-5]

It is well known that simulated clusters can undergo transitions between solidlike (*S*) and liquidlike (*L*) forms, changing their mean vibrational temperature in isoergic molecular dynamics simulations, or their mean internal energy in isothermal simulations. The dynamical coexistence of solid and liquid phaselike forms in equilibrium, or even of more than two such forms, within sharp bands of energy or temperature, has been investigated both analytically and numerically. (For recent reviews, see Refs. 1 and 2.) This work determines, from simulations, the equilibrium ratios of amounts of coexisting phases of two model clusters, i.e., the equilibrium constants, and how these ratios depend on temperature. That is, we quantify the coexistence curve of two specific clusters along one isobar; the work does not yet achieve the construction of a full phase diagram. (Such diagrams have been sketched qualitatively in the past.³) Then we interpret these results in terms of simple statistical–thermodynamic models, slight variants of the Bixon–Jortner model.⁴

The two model systems we have chosen are $(\text{KCl})_{32}$ and Ar_{55} . The first has a staircase potential and readily goes into a crystalline, rocksalt structure on cooling. The Ar_{55} cluster is an example that has a sawtooth potential,⁵ and is a glass former. The phase coexistence of the KCl cluster has been reported by Rose and Berry,^{6,7} and of the argon cluster, by various authors.^{2,8,9}

Phase coexistence in clusters, the number of coexisting phases, and the occurrence of a solid–liquid transition, are related to the peculiarities of the density of states $\rho_0(E)$, and in large part to the density of states just of the local minima on that surface, $\rho_0(E_m)$. Both these densities can be found numerically, in principle. To do this exhaustively becomes impractical for systems of more than about 15 particles; there are perhaps 500 000 geometrically distinct local minima for Ar_{19} , and the number increases exponentially with *N*, the number of atoms in the cluster. Hence, for larger clusters, we use statistical sampling or simple analytic models to determine densities of states and thermodynamic properties, such

as free energies and equilibrium ratios of coexisting phase-like forms.

To investigate the ranges of phase coexistence and the temperature dependence of the equilibrium concentration ratios, we have performed molecular dynamics (MD) simulations of the isothermal evolution of the clusters from different configurations. These were done with both Nosé–Hoover (extended-system)^{10–13} and stochastic^{14,15} algorithms, averaging the results over many runs. The effective pressure was zero and uncontrolled, but no evaporative events were observed, so pressure was essentially irrelevant. We have used the same pairwise potential and parameters for $(\text{KCl})_{32}$ most often used for KCl;^{6,7} for the Ar_{55} cluster, the potential and its parameters are those previously used for this cluster.^{8,9} The results are based on the assumption that both systems are ergodic; the agreement of the results from the two altogether different methods of simulation is strong support for the validity of that assumption. (The time scales required for the simulations to display ergodicity may, however, be so long that in the lowest reaches of the coexistence range, below 33 K for Ar_{55} for example, the molecular dynamics model might not explore the full, available phase space.)

At low temperatures, both clusters are of course solidlike. In temperature ranges around ~ 730 – 760 K for $(\text{KCl})_{32}$ and ~ 40 K for Ar_{55} , dynamic solid–liquid phase coexistence occurs. (Note that for small finite systems such as these clusters, solid–liquid coexistence occurs within *bands* of temperature and pressure, not along the coexistence curves familiar for bulk phase equilibria.^{1–3}) At still higher temperatures, the MD simulations show that the clusters are mainly in high-potential-energy regions, and spend only very brief intervals in the vicinity of any individual minimum. By contrast, in the intermediate temperature ranges, these clusters jump between the phaselike forms, spending times longer, relative to their vibrational periods and even to the times for thermal equilibration (equipartition) of their vibrational energies, in the solidlike and liquidlike regions of their configuration spaces. Examples of typical runs are given in Fig. 1. While we have observed coexistence of only two

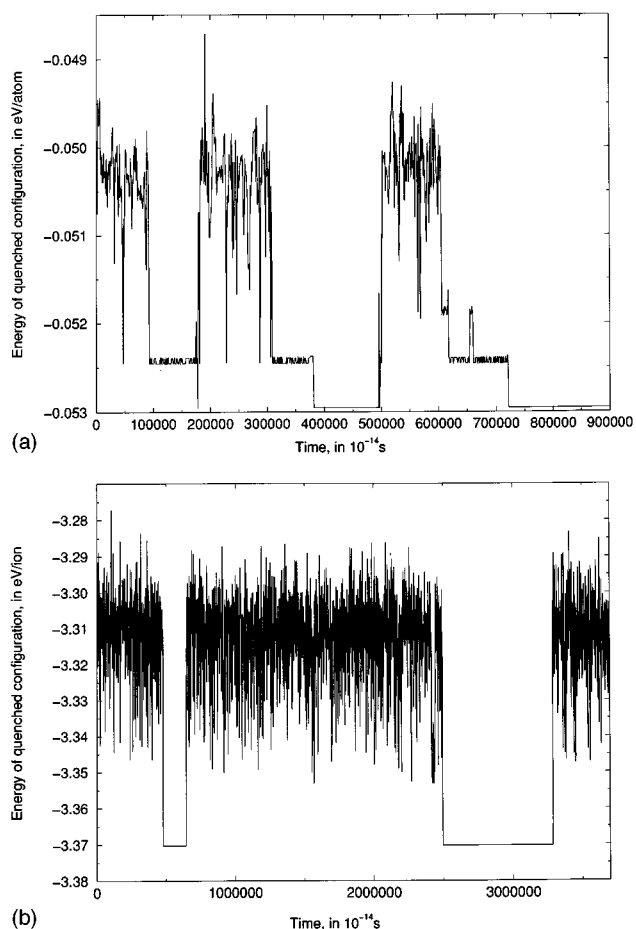


FIG. 1. Illustration of the phase-coexistence phenomenon in the two clusters (a) Ar_{55} at 35.9 K, and (b) $(\text{KCl})_{32}$ at 740 K, as revealed by the time dependences of the energies of their quenched configurations, i.e., of the configurations around which they are vibrating at each sampling instant. These patterns are similar in appearance to those of the temporal behavior of short-time mean potential or total energies, but the information in these curves is rather different, insofar as it shows the range of fluctuations of energies of the local minima around which the system is oscillating, at each instant of quenching.

phases for $(\text{KCl})_{32}$, crystallike and liquidlike, the simulations show at least three phaselike forms of Ar_{55} , consistent with the results of Kunz and Berry.^{8,9} Figures 2 and 3 illustrate the temperature dependence of occupation of different phases in the coexistence range of temperatures, for the two systems.

The configurational energy spectra of clusters, especially of those corresponding to “magic numbers,” typically exhibit a gap between the ground level, such as the symmetrical configurations of the global minima in the examples studied here, and a quasicontinuum of higher-energy configurations corresponding to the liquidlike structures. Between these and inside the gap, there may be states related structurally to the global minimum, states that may have “defects” in solidlike configurations. In some systems, intermediate states may be considered as surface-melted forms.^{8,9,16–18}

The global minimum of Ar_{55} has an icosahedral structure with energy -5.296×10^{-2} eV/atom. The lowest excited configurations correspond to structures with a single hole at a

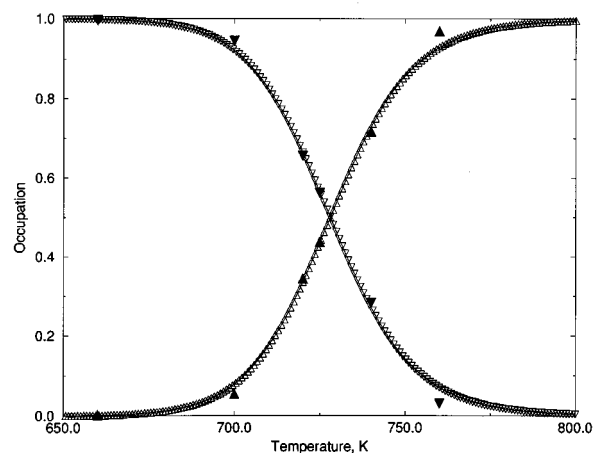


FIG. 2. Temperature dependence of the phase occupancies at coexistence for $(\text{KCl})_{32}$, from simulations (large triangles) and from the two-level analytic model (small, open triangles). The parameters for the model are $\ln(N_1)=61.2$ and $d_1=6.10 \times 10^{-2}$ eV/ion. The steep, rising curve is, of course, that for the liquid and the falling curve, for the solid.

vertex of the outer icosahedral shell and a popped-out atom or floater outside this shell. The energies of such structures depend on the position of the floater on the shell and on the hole–floater distance; however, this dependence is weak. These energies are in the narrow range from -5.245 to -5.238×10^{-2} eV/atom. Configurations with an edge hole have higher energies, around -5.195×10^{-2} eV/atom, depending upon the position of the floater. In the same energy range, there are also structures with two vortex holes, from about -5.205 to -5.185×10^{-2} eV/atom, and high-symmetry D_{5h} structures, e.g., at -5.202 . In our runs, we have found an apparently new D_{5h} structure different from those previously reported.¹⁹ The next higher-energy excited structures are associated with greater numbers of holes and floaters, and their energy range is much wider.

The time sequence of Fig. 1 reveals the existence of an intermediate (-5.245) phase, in addition to solidlike and liquidlike forms, and indicates, to a smaller extent, another (-5.200) phase as well. The first of these has been recognized as the so-called surface-melted form, which, although it has many liquidlike characteristics, is not really an amorphous fluid surrounding a solid.¹⁷ There is no evidence of any other phases with energies between -5.200 and the lower bound, approximately -5.090 , of the liquid-state manifold.

The $(\text{KCl})_{32}$ cluster has a $4 \times 4 \times 4$ rocksalt structure at its global minimum. Its long-range, Born–Mayer potential, in contrast to the Lennard–Jones potential of argon clusters, gives rise to relatively low-lying excited configurations obtained by displacement of ordered small subunits consisting of several, usually no less than four, ions. Invariably, these structures consist of rocksalt-structure blocks, so that their energies fall in a narrow range around -3.35 eV/ion. Partially rocksalt structures, with amorphous regions, have higher energies, filling the range up to the liquidlike manifold with energy -3.31 eV/ion. As Fig. 1 shows, the (-3.35)

partially amorphous configurations do not give rise to a separate phaselike form as the surface-melted states of Ar_{55} do, but merge smoothly into the fully amorphous structures that comprise the overwhelming majority of local minima for this system.⁷

Both $(\text{KCl})_{32}$ and Ar_{55} show a rapid (approximately exponential) increase of $\rho_0(E_m)$ with E_m , as is expected from general considerations.^{7,9} This suggests that we try to describe the situation with a very simple ‘‘two-level’’ model, based on a nondegenerate ground state plus a N_1 -fold-degenerate excited state separated from the ground state by the energy gap d .⁴ The ground state corresponds to the crystallike structure while the excited, highly degenerate level represents the set of amorphous, ‘‘liquidlike’’ configurations. The population or occupation number of the excited state is given by the expression

$$n_1(T) = N_1 \cdot \exp(-d/kT) / [1 + N_1 \cdot \exp(-d/kT)], \quad (1)$$

which becomes equal to n_0 , the occupation number of the ground state, at the temperature at which the degeneracy of the excited state just compensates for its Boltzmann factor,

$$kT_e = d / \ln(N_1). \quad (2)$$

At large enough N_1 (see below), the change from most of the population being in the ground state to most being in the upper level occurs within a rather small temperature range. In this case, T_e can be considered as the temperature of a solid–liquid transition. The results of molecular dynamics simulations give the transition temperature of 730 K for $(\text{KCl})_{32}$ and 36.4 K for Ar_{55} . From Fig. 1 we see that the liquidlike energies that determine the value of d lie in the range $[-3.305; -3.315]$ – $[-5.000; -5.025]$, respectively. (While the energies of the solidlike phase and the intermediate phase can be found rather accurately from the MD runs, there is some uncertainty about the energy of the liquidlike state, due to the large width of the corresponding quasicon- tinuum of states.) With these values, it follows from Eq. (2) that

$$\ln[N_1(\text{KCl})] = [57-66], \quad \text{and} \quad \ln[N_1(\text{Ar})] = [47-53]. \quad (3)$$

If the total number of locally stable states of a cluster increases as $\exp(N)$, where N is the number of particles comprising the cluster, then we should expect values for $\ln(N_1)$ of 64 for $(\text{KCl})_{32}$ and 55 for Ar_{55} . These values are reassuringly close to those given by Eq. (3), thus, illustrating that the two-level model may, at very least, be a useful guide for estimating values. For example, if we suppose that the solid–liquid transition happens when N_1 changes from 0.1 to 0.9, the model gives for the range of the transition

$$dT/T_e = 2 \cdot \ln 9 / \ln(N_1), \quad (4)$$

also in good agreement with the results of numerical simulations, both in the value and in the dependence upon N_1 , a little greater for Ar_{55} than for $(\text{KCl})_{32}$.

The three-phase coexistence observed in Ar_{55} can be considered in the same model by adding one more intermediate, ‘‘surface-melted’’ level at the energy d_{sm} of -5.24

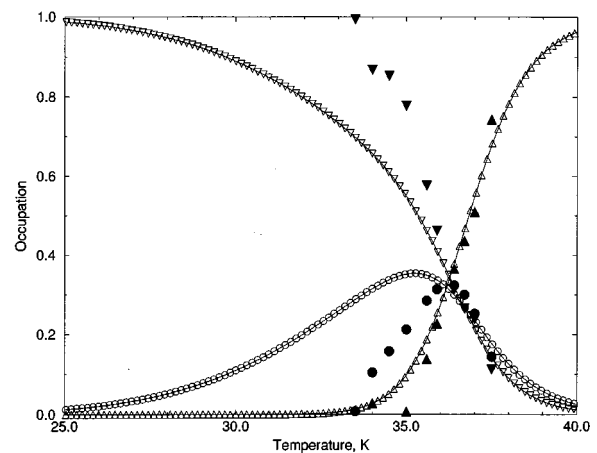


FIG. 3. Relative populations of the three phaselike forms of Ar_{55} , from simulations (large, black triangles for solid and liquid; black circles for the surface-melted form) and from the three-level model (small, open triangles for solid and liquid; small, open circles for the surface-melted form) for phase coexistence. The simulations could only be carried out between approximately 33.5 and 37.5 K; this is because below 33.5 K, the processes are too slow for molecular dynamics and the amount of liquid is too small to be detected, while above 37.5 K, particles evaporate rapidly from the liquid clusters. The steep, rising curve corresponds to the liquid, the falling curve to the solid, and the intermediate curve, to the surface-melted form. The parameters for the model are $\ln(N_1)=49.7$, $\ln(N_{sm})=8.9$, $d_1=2.84 \times 10^{-3}$ eV/atom, and $d_{sm}=0.51 \times 10^{-3}$ eV/atom.

$\times 10^{-3}$ eV/atom and degeneracy N_{sm} . Surface melting in Ar_{55} is related to the peak in the cluster’s density of states at this energy, which seems to be associated with surface-melted states.^{8,9,17,20} Two consecutive transitions, solid to surface melted and then surface melted to liquid, at the temperatures given by

$$kT_{sm} = d_{sm} / \ln(N_{sm}), \quad (5)$$

and

$$kT_{sl} = (d_1 - d_{sm}) / \ln(N_1 / N_{sm}), \quad (6)$$

can occur if the d ’s and N ’s have values such that $T_{sl} > T_{sm}$. If values of the d s and N s give $T_{sm} > T_{sl}$, then in this model, the intermediate state does not show itself at all when $T < T_{sl}$. And finally, if $T_{sm} \approx T_{sl}$, three-phase coexistence occurs. For this to happen with this model, the relation

$$N_{sm} = (N_1)^f, \quad f = d_{sm} / d_1, \quad (7)$$

should be fulfilled. For Ar_{55} , $d_{sm} \approx 0.0005$, so from Eq. (7) with d_1 from the above given range one has $\ln(N_{sm}) \sim 9$. Figure 3 shows the temperature dependence of the occupancies of the states for these values of the parameters. Thus, this ratio of N_{sm} to N_1 leads, indeed, to three-phase coexistence. If one uses this value with the above values of N_1 and d_1 , then Eq. (6) gives T_{sl} close to 36.4 K, demonstrating that the model with a few intermediate states corresponding to peaks in the actual density of states is satisfactory for rationalizing multistate coexistence. In the full treatment, three-phase coexistence is possible throughout a band of temperature and pressure, provided the parameters of the system are suitable, as they seem to be for Lennard-Jones clusters, according to

simulations.^{8,9} A similar model in which a core-melted state replaces the surface-melted state will rationalize the core-melted clusters postulated in Refs. 8 and 9.

One may try to estimate N_{sm} from microscopic considerations. If the surface-melted state corresponds to configurations with one atom promoted out of the surface to a site or region in the next outer shell,^{8,9} then this atom can reside on any of 20 triangle faces, and there are four possible places for it on each of the faces, so there should be about 80 places above the surface where the promoted atom can find a local potential minimum. The promoted atom can be any of twelve isosahedron vortex atoms, so the total number of such configurations is equal to $12 \times 80 = 960$. Molecular dynamics simulations illustrate that there is an "exchange" between the floater and the outer shell, thus, all the atoms of the outer shell participate in floating. Taking this into account increases the effective number of configurations to 3360, a value between $\exp(8)$ and $\exp(9)$, close to the value found above.

The $(KCl)_{32}$ cluster differs from the Ar_{55} cluster, insofar as a third phaselike form, the "surface-melted," occurs in the argon cluster but not the alkali halide. In $(KCl)_{32}$, there is no evidence for any peak in the density of states between the global minimum and the smoothly rising region of the amorphous structures primarily responsible for the properties of the liquid; the quasicontinuum of excited configurations starts at an energy of about -3.35 eV/ion and rises monotonically into the liquidlike range that begins at about -3.31 eV/atom.⁶

By contrast, Ar_{55} has a double peak in the corresponding energy range of its density of locally stable states.²¹ This appears to be due, at least partly, to the difference in the nature of the configurations of the intermediate states, and partly to the energies at which they occur. The intermediate-energy configurations of the Lennard-Jones cluster correspond to single-particle-hole-excitation states in the lower-energy peak, and, in the next-higher-energy peak, to double-particle-hole excitations and to some collective rearrangements of the entire cluster that preserve moderately high symmetry. In the alkali halide cluster, the intermediate states correspond to configurations that are amorphous "on one side," and crystalline, rocksaltlike on the other, largely as a consequence of the molten salts not wetting their parent solids. Hence, the intermediate-energy alkali halide states simply spread fairly smoothly over a wide energy band from -3.35 eV/ion up into the liquid region. Furthermore, if we were to use this number to define a parameter d_{sm} for the KCl cluster to estimate the density of intermediate states, the ratio d_{sm}/d_1 would be about twice the value of that ratio in the Ar cluster. The value of $\ln(N_{sm})$ would then have to be

about 21 if there were to be a detectable third form, an unreasonably large value.

One can try to predict from this primitive model how the coexistence criteria depend upon the cluster size. The value of d_{sm} must be roughly equal to the energy needed for removal of an atom from the outer shell. This should not depend in a sensitive way on the cluster size for clusters with Lennard-Jones or similar pairwise potentials, provided the clusters are large enough that the populations of cluster faces dominate those of the edge and vertex sites. Surface melting only occurs with clusters of about 50 atoms or more, which makes the lower limit for surface melting just a bit small to meet the criterion for the weak size dependence of d_{sm} . In this range, roughly 50–100 particles, d_{sm} can be estimated explicitly by counting the numbers of different kinds of sites on the surface. The ratio of density of states for surface-melted and liquidlike configurations drops to favor the latter as cluster size increases. It follows from these considerations that in clusters larger than Ar_{55} , the solid-liquid transition becomes increasingly likely to engulf three-phase coexistence, as N grows.

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- ¹R. S. Berry, in *Clusters of Atoms and Molecules*, edited by H. Haberland (Springer-Verlag, Berlin, 1994), p. 187.
- ²R. S. Berry, in *Large Clusters of Atoms and Molecules*, edited by T. P. Martin (Kluwer, Dordrecht, 1996), p. 281.
- ³H.-P. Cheng, X. Li, R. L. Whetten, and R. S. Berry, *Phys. Rev. A* **46**, 791 (1992).
- ⁴M. Bixon and J. Jortner, *J. Chem. Phys.* **91**, 1631 (1989).
- ⁵K. D. Ball, R. S. Berry, A. Proykova, R. E. Kunz, and D. J. Wales, *Science* **271**, 963 (1996).
- ⁶J. P. Rose and R. S. Berry, *J. Chem. Phys.* **98**, 3246 (1993).
- ⁷J. P. Rose and R. S. Berry, *J. Chem. Phys.* **98**, 3262 (1993).
- ⁸R. E. Kunz and R. S. Berry, *Phys. Rev. Lett.* **71**, 3987 (1993).
- ⁹R. E. Kunz and R. S. Berry, *Phys. Rev. E* **49**, 1895 (1994).
- ¹⁰S. Nosé, *Mol. Phys.* **52**, 255 (1984).
- ¹¹S. Nosé, *J. Chem. Phys.* **81**, 511 (1984).
- ¹²S. Nosé, *Prog. Theor. Phys. Suppl.* **103**, 1 (1991).
- ¹³W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
- ¹⁴S. M. Kast, L. Nicklas, H.-J. Bär, and J. Brickmann, *J. Chem. Phys.* **100**, 566 (1994).
- ¹⁵S. M. Kast and J. Brickmann, *J. Chem. Phys.* **104**, 3732 (1996).
- ¹⁶H.-P. Cheng and R. S. Berry, in *Proceedings of the Symposium on Clusters and Cluster-Assembled Materials*, edited by R. Averbach (Materials Research Society, Pittsburgh, 1991), Vol. 206, p. 241.
- ¹⁷H.-P. Cheng and R. S. Berry, *Phys. Rev. A* **45**, 7969 (1992).
- ¹⁸F. Calvo and P. Labastie, *Chem. Phys. Lett.* **258**, 233 (1996).
- ¹⁹D. J. Wales, *J. Chem. Phys.* **101**, 3750 (1994).
- ²⁰V. V. Nauchitel and A. J. Pertsin, *Mol. Phys.* **40**, 1341 (1980).
- ²¹R. M. Lynden-Bell and D. J. Wales, *J. Chem. Phys.* **101**, 1460 (1994).