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Molecular Dynamics Study of a Crystalline Cluster Undergoing a Second-Order Transition. An Inchoate Model of Acetylene

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To extend our molecular dynamics studies of nucleation in molecular clusters undergoing phase changes, we selected the acetylene system whose clusters had already been examined experimentally in supersonic flow. Because molecular dynamics simulations based on the several existing model potential functions were incapable of accounting for the structure of the low-temperature orthorhombic phase, a new interaction potential was developed which successfully yielded the correct molecular packing at low temperatures as well as the cubic structure observed at high temperatures. The results obtained in heating and cooling runs for the model system were unlike any seen in our prior simulations. There was no nucleation barrier inhibiting the passage from the cubic to the orthorhombic phase on cooling, nor were there discernible volume or enthalpy changes in the transformation. In clusters of several hundred molecules the apparently second-order or continuous transition was spread over a much wider range of temperatures than had been seen in first-order transitions in previous simulations. Although the results provide an instructive example of an unusual type of transformation, they do not appear to correspond to the transition observed experimentally for pure, bulk acetylene.

Introduction

A variety of solid state and freezing transitions have been observed in large molecular clusters as they cool in supersonic flow.[1] Several of these transitions have also been seen to occur spontaneously in molecular dynamics (MD) simulations of cooling clusters.[2−7] Clusters are particularly convenient systems for MD simulations of phase transitions because clusters avoid the severe limitations imposed by periodic boundary conditions. In both the experimental and computational research it is possible to determine rates of genuinely homogeneous nucleation, a notoriously difficult phenomenon to achieve, verify, and characterize by more conventional techniques. In the MD simulations, in particular, it is possible to observe directly the formation of critical nuclei, the key but elusive entities of nucleation theory. Because an entirely satisfactory theory has yet to be formulated, it seemed worthwhile to continue studies of nucleation by MD techniques. Previous results had been for substances composed of spherical top and symmetric top molecules. So far, no transitions of linear molecules have been reported in MD investigations of clusters even though phase changes have been seen in experiments on clusters of acetylene[8] and (the quasilinear) dimethylacetylene.[9] Indeed, clusters of the latter substance froze to an unknown phase giving an anomalous diffraction pattern. It seemed possible that MD simulations might help to determine the solid structure because such simulations had previously resolved the unknown structure to which *tert*-butyl chloride transformed when cooled.[10] When attempts to devise a potential function capable of reproducing the known phases of dimethylacetylene were unsuccessful, it was decided to investigate acetylene itself.

As will be discussed presently, the several potential functions already proposed for acetylene gave inadequate accounts of the material in MD simulations. Therefore, an alternative potential function was sought. When a simple one was found that did yield a stable orthorhombic phase of approximately the correct structure in simulations at low temperatures and correctly reproduced the packing of the stable cubic phase at warmer temperatures, it was decided to investigate the nucleation phenomenon responsible for the transition from cubic to orthorhombic as warm clusters were cooled. Our prior modeling of nucleation in solid state phase transitions had suggested that the qualitative behavior of clusters did not depend sensitively upon the exact values of the potential parameters applied as long as the potential function was sufficiently realistic to reproduce the essential structural aspects of the phases involved. The present results pour cold water on this generalization.

We point out at once that the results we obtained do not correspond to what is believed to be the behavior of the real substance, despite the fact that the model accounted fairly well for the structures at high and low temperatures. Even though our computations yielded a transition entirely different in character from that of true acetylene, the results are so striking and unlike anything our simulations have shown before that they offer an instructive example. Therefore, we report an account of the molecular behavior taking place in what appears to be a second-order or continuous phase transition more like Ehrenfest's textbook classification[11] than like the continuous lambda transitions found in nature.[12]

Thermodynamic Properties

Because pure acetylene is a hazardous material, its thermodynamic properties are not known with precision. It has two crystalline phases, orthorhombic below 133 K and cubic. Cubic acetylene sublimes at 189.6 K and melts at 191.7 K under a pressure of about 1.2 atm.[13] Its heat of sublimation is reported to be 23.0 kJ/mol,[13] and despite several conflicting values reported, its heat of vaporization appears to be about 16.6 kJ/mol,[14] making the entropy of fusion of the plastically crystalline material approximately 4 R. As far as we are aware, the heat of transition from the orthorhombic to the cubic phase has not been measured.

Crystal Structures

The low-temperature phase is orthorhombic, space group *Acam*, $Z = 4$, with lattice constants at 4.2 K of $a = 6.193$, $b = 6.005$, and $c = 5.551$ Å.[15] The high-temperature phase is cubic,

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space group *Pa*3, $Z = 4$, with $a = 6.091$ Å at 141 K.[16] In the orthorhombic phase, molecules lie in layers parallel to the 001 plane with orientations nearly parallel to the *ab* diagonals, giving rise to interwoven chains of T configurations. In the cubic phase, the molecules are oriented along the body diagonals of the cube.

Intermolecular Potential Functions

Several model interaction potentials for acetylene have been proposed in the literature, all of which were based to some extent upon the multipole moments found in an *ab initio* quantum study of the monomer by Amos and Williams.[17] Hirshfeld and Mirsky (HM) constructed a model field with exp-6−1 atom−atom interactions,[18] adjusting the Coulomb terms to reproduce approximately the electric moments of Amos and Williams (0.312*e* on hydrogen, −0.312*e* on carbon, C≡C length of 1.207 Å, and C−H length of 1.059 Å). Lattice energy calculations gave a somewhat lower cubic cell constant (5.65 Å) and a somewhat higher heat of sublimation (25.9 kJ/mol) than observed. Molecular dynamics computations by Klein and McDonald[19] incorporating the HM field yielded lattice frequencies that were too high. Calculations of phonon dispersion curves by Gamba and Bonadeo[20] (GB) showed that the HM field applied to the orthorhombic phase led to imaginary frequencies. Molecular dynamics computations carried out in the present investigation confirmed that the HM field does not yield a stable orthorhombic phase.

Filippini, Gramaccioli, and Simonetta[21] (FGS) tried a number of existing semiempirical atom−atom potentials to compute some of the properties of the cubic and orthorhombic phases. They found that Williams' exp-6−1[22] and Lifson's 9−6−1[23] potentials, which account very well for properties of many solid hydrocarbons, account poorly for the solid phases of acetylene. One of the disagreements found was that the calculated lattice vibrational frequencies were much higher than the experimental frequencies unless parameters were modified to reduce the calculated sublimation energy to about half the reported experimental value. The selected parameters included atomic charges only about half those implied by the *ab initio* electric moments. Another problem for the FGS potential parameters was that they were unable to account for the observed orthorhombic phase. Basing their conjecture on the fact that prior treatments of organic solids with similar interaction potentials had given good results, FGS suggested that the trouble might well lie in inaccuracies in the reported determinations of the sublimation energy and orthorhombic crystal structure.

Klein and McDonald[19] applied both the HM and the FGS model fields in their molecular dynamics simulations of the liquid and cubic phases of acetylene. They found discrepancies in calculated properties of the cubic phase of the sort commented upon by the previous authors and echoed the call for more reliable experimental data. They did not report on the othorhombic phase.

In a study overlooked by us until after completion of our molecular dynamics computations, Gamba and Bonadeo[20] reported calculations of phonon dispersion curves of solid acetylene. When they used atom−atom Buckingham functions augmented by electric moments similar to those tried by HM and FGS, they encountered the same discrepancies as those noted previously. They discovered, however, that if they distributed four dipoles along the molecular axis in such a way as to retain the quadrupole and hexadecapole moments but to double the 2^6 multipole moment, the main troubles encountered before vanished. No longer did computations with the experimental orthorhombic phase give imaginary frequencies indicative of negative force constants serving to destabilize the observed packing. Gamba and Bonadeo likened the situation to that for the crystal structures of the halogens, examples for which simple atom−atom exp-6−1 potential functions are also unable to account for the observed structures. Our opinion is that the principal problem encountered in the HM and FGS comparisons with experiment is *not* that the experimental results are unreliable but that the model potential functions, themselves, are deficient.

TABLE 1: Lennard-Jones Parameters for Intermolecular Potential Function for Acetylene[a]

atom pair	H−H	C−C	C−H
σ, Å	1.4	3.4	2.1817
ϵ, kJ/mol	0.10	0.35	0.1870

[a] For charge distribution, see text.

The above discussion of the historical background of the problem, however germane it may be to the ultimate resolution of the modeling of crystalline acetylene, is somewhat beside the point of the present treatment. As mentioned in the Introduction, the value of our approach is not in its reproduction of the properties of solid acetylene (though it does yield the correct packing for both the low- and high-temperature structures) but rather as an example of a type of transition not heretofore encountered in MD simulations of clusters.

Present Model. As pointed out by Gamba and Bonadeo, the problem of modeling the orthorhombic structure of acetylene may be closely analogous to that of modeling the crystal structures of Cl_2 and related substances. Simple atom−atom models are inadequate. Various authors have attributed the specific interactions needed to explain the molecular packing to charge-transfer or donor−acceptor forces,[24] to higher multipole forces,[25,20] or to aspherical atoms.[26] Recent work by Price[26] calling attention to the latter factor has been particularly persuasive. Therefore, when our initial attempts to model orthorhombic acetylene failed in the same way as those of HM and FGS, we tested the simplest aspherical model for carbon atoms imaginable, that of placing a pseudoatom at the center of the triple bond. Before assigning LJ parameters to this site, we simply gave it the charge normally allocated to the carbons, a charge of such magnitude (0.54*e*) as to give moments of 6.76 D Å and 17.64 D Å^3, reproducing, approximately, the 2^2 and 2^4 electric moments of Amos and Williams. This gave a 2^6 moment similar to that of the HM model, but only half that of the successful GB model. Nevertheless, when the model yielded the correct molecular orientations for the orthorhombic phase in potential energy minimizations, we decided to go ahead with MD simulations to explore the consequences.

Carbon−carbon and carbon−hydrogen bond lengths were taken to be 1.21 and 1.01 Å, respectively, the latter distance being shorter than the internuclear distance in order to incorporate the "foreshortening" found by Williams[27] to correct approximately for the nonspherical charge distribution of electrons around a hydrogen atom in a C−H bond. The remaining intermolecular interactions in the present model were pairwise additive atom−atom Lennard-Jones functions whose parameters are listed in Table 1. It seemed necessary to make the hydrogen atoms smaller than usual to achieve the desired molecular orientations in the low-temperature phase.

Lattice Energy Minimization

Lattice energy minimization calculations were carried out on the cubic and the orthorhombic phases using the Williams MPA96 program.[28] The cubic cell volume was found to be 150.80 Å^3 with a lattice constant $a = 5.3228$ Å. The converged lattice energy was −33.03 kJ/mol, out of which −25.39 kJ/mol came from the Coulombic part. For the orthorhombic phase, the model yielded a cell volume of 158.61 Å^3 with $a = 5.2281$, $b = 5.2847$, and $c = 5.7408$ Å. The lattice energy per molecule was −34.33 kJ/mol, of which the Coulombic contribution was −28.98 kJ/mol. Cell dimensions and energies can be seen to be in only very crude agreement with experiment.

MD Simulations

Simulations were performed at constant energy on clusters containing 137, 217, and 435 molecules of acetylene. In view of the cluster's free boundaries, the systems corresponded essentially to (NPH) ensembles. Approximately spherical clusters were carved out of a lattice with the ideal orthorhombic molecular packing. Appropriate quarternions were generated to match the orientations of the molecules observed in the bulk crystal. Linear and angular velocities were set to zero to start with. Newton's equations of motion were solved numerically using the fifth-order predictor−corrector algorithm. An integration timestep of 3 fs was found to yield good energy conservation. Equilibration in a heat bath, during both heating and cooling stages, was carried out for 4000 time steps with velocities rescaled at each step. Velocity scaling was then switched off, and constant energy MD trajectories were followed for another 4000 time steps. Thermodynamic averages such as potential energy, temperature, total energy, etc., were accumulated, and coordinates, quarternions, center-of-mass velocities, etc., of all the molecules were saved every 20 steps during the constant energy period. The bath temperature was increased by 10 K every 8000 steps (half of which were in the heat bath). Runs were continued until the molecules started to evaporate from the cluster. Subsequently, cooling runs were initiated with clusters containing 139, 217, and 429 molecules, each carved from an ideal cubic lattice of acetylene. Each of these clusters was then cooled from 160 to 20 K in steps of 10 K. The rate of cooling was the same as the rate of heating, that is, 10 K per 8000 steps.

Clusters were found to rotate because of nonconservation of angular momentum during velocity rescaling. This spurious rotation was nulled out using a standard Gauss−Newton least-squares procedure described elsewhere.[29] Autocorrelation analyses of configurational energies were carried out to establish the effective number of statistically independent configurations. Various diagonostic tests were applied to monitor the structural changes. For example, the temperature dependence of the configurational energy was followed, and images of the molecular arrangements were examined using the proprietary software MACSPIN. Pawley projections[30] of molecular orientations were studied. Specific heats of the individual clusters were calculated via the NPH ensemble fluctuation formula[31] as well as from the slopes of the caloric curves. These analyses showed that the caloric data yielded substantially more precise results. Error analyses are sketched briefly in the Appendix.

Results

Figure 1 verifies that the present model correctly reproduces the molecular orientations in the low-temperature orthorhombic phase. Figure 2 displays the caloric curves during the heating and cooling of the 217-molecule cluster. Although the initial structures of the heating and cooling runs were prepared quite differently, the two caloric curves are almost identical. Despite the fact that the structure changed from orthorhombic to cubic, and vice versa, the curves are essentially smooth and devoid of inflection points and hysteresis of the type always seen in our prior MD simulations of clusters undergoing a phase change.

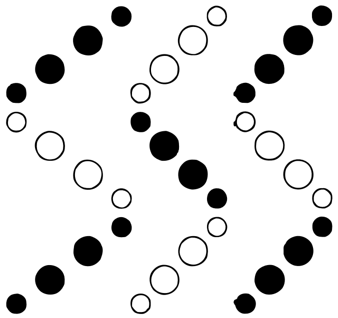

Figure 1. View down the c axis of the low-temperature orthorhombic unit cell derived from the lattice energy minimization calculations using the present potential model. The large and small circles represent the carbon and hydrogen atoms, respectively. The full circles correspond to molecules at $z = 0$ and the open ones to $z = c/2$. Molecular orientations agree closely with those observed in ref 15 but cannot be accounted for by the HM or FGS model fields.

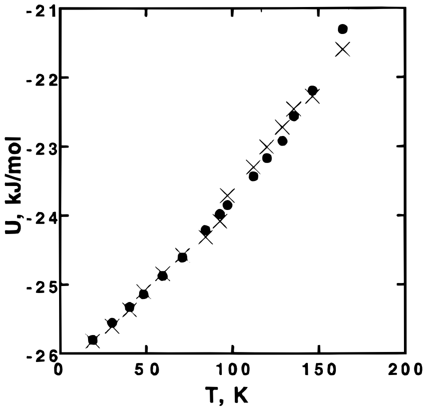

Figure 2. Configurational energy per molecule vs temperature for the 217-molecule cluster during heating (filled circles) and cooling (crosses) stages. Despite the fact that the starting configurations of the heating (and cooling) runs were nearly spherical clusters of the ideal orthorhombic (and cubic) phases and, hence, were different, the curves agree closely.

In previous runs on crystalline clusters it has been found that surface molecules tend to be appreciably more disordered than molecules in the core, whereas core molecules behave very nearly like those of the bulk. For a cluster of N molecules, we consider the fraction

$$F = 3(4\pi/3N)^{1/3}(1 - 0.5(4\pi/3N)^{1/3})^2$$

of the molecules to lie in surface. In Figures 3 and 4 are shown MACSPIN images of the core of the 217-cluster during heating and cooling, viewed along the a axis. At 20 K, the image corresponded to the orthorhombic structure. As the cluster was heated the amplitudes of the out-of-plane molecular displacements increased markedly, but the cluster retained its character up to about 100 K. At 110 K, the visual appearance of the cluster began to approach that of the cubic phase. Although the core remained cubic until 170 K, the cluster surface had begun to melt. Molecules began to evaporate at 190 K. Images at various stages of cooling indicate that the cluster remained cubic until about 110 K and then began to change to orthorhombic at 100 K. Figures 5 and 6 are Pawley projections of the core molecules of the 217-molecule cluster during heating and cooling viewed along the a axis. These dot plots confirm that the most characteristic aspect of the structural change occurs between 100 and 110 K but that the overall change is continuous over a wide temperature range. Orientational disorder in both phases is evident in the dot plots at all temperatures. For an ideal orthorhombic crystal there would be just two highly

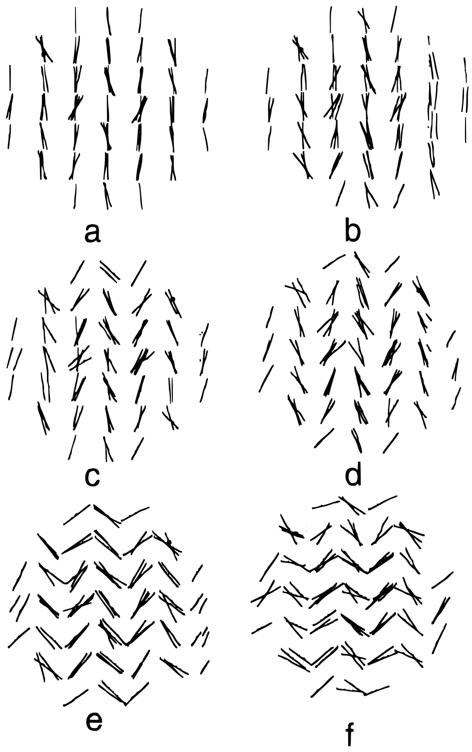

Figure 3. View down the *a* axis of the core of the 217-molecule cluster at various stages of the heating runs: (a) 20, (b) 60, (c) 100, (d) 110, (e) 140, and (f) 160 K. Images were generated from the last step of the MD runs after nulling out the rotation of the cluster. Out-of-plane excursions of molecules increase markedly as the cluster is warmed.

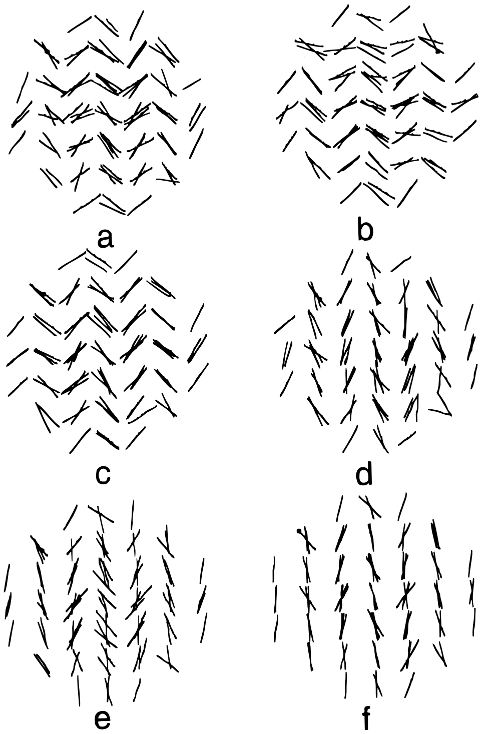

Figure 4. Images corresponding to those of Figure 3 but for cooling runs: (a) 160, (b) 140, (c) 110, (d) 100, (e) 60, and (f) 20 K.

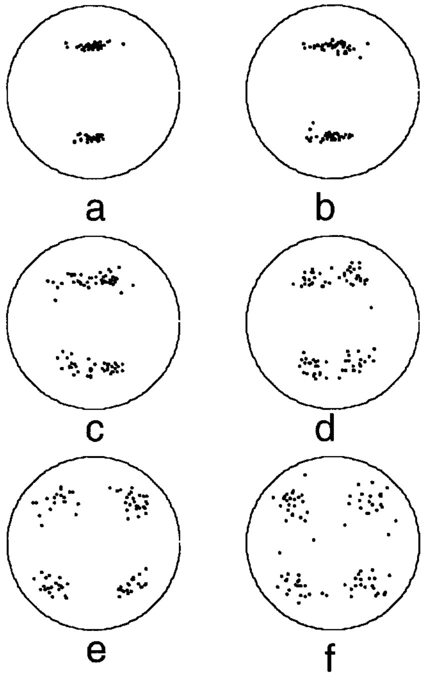

Figure 5. Pawley projections of bond directions in the core of the 217-molecule cluster during heating stages: (a) 20, (b) 60, (c) 100, (d) 110, (e) 140, and (f) 160 K. Orientational disorder is persistent at all temperatures.

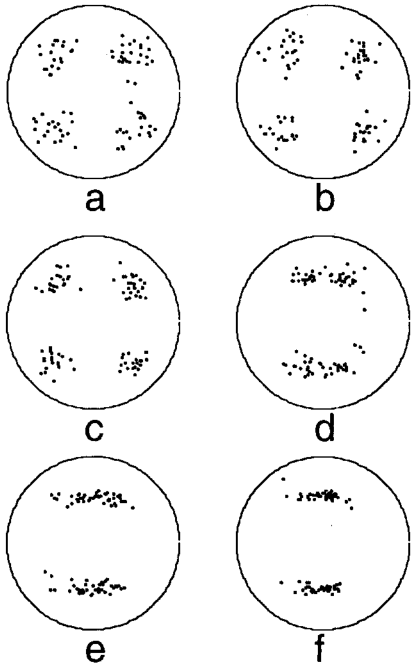

Figure 6. Pawley projections corresponding to those of Figure 5 but for cooling runs. (a) 160, (b) 140, (c) 110, (d) 100, (e) 60, and (f) 20 K.

localized areas of dots in the plot, but thermal motions in the clusters broaden these to elongated patches instead. The orientation of the patches shows that out-of-plane displacements are of much greater amplitude than the in-plane motions. Clearly, the softening of the out-of-plane force constant is the leading factor promoting the phase change. In Figure 7 are plotted the temperature variations of the cell constants during heating. Orthorhombic lattice constants converge to the single cubic constant upon heating. Figure 8 shows heat capacities for clusters containing 137, 217, and 435 molecules. These reveal little evidence, beyond the statistical noise, of a localized jump corresponding to an enthalpy difference between the phases. The upsweep at the higher temperatures signals the onset of surface melting.

Discussion

It is well understood that clusters composed of limited numbers of molecules cannot undergo abrupt transitions with

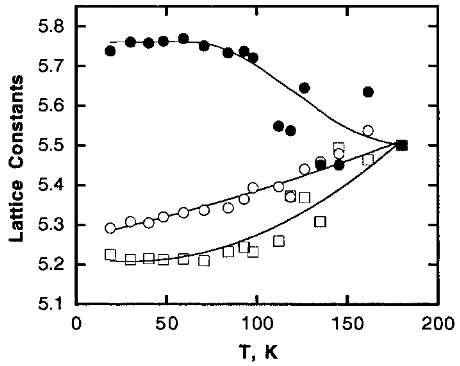

Figure 7. Temperature dependence of the lattice constants *a* (squares), *b* (open circles), and *c* (filled circles). Continuous lines are simply to guide the eye through the region of fluctuations.

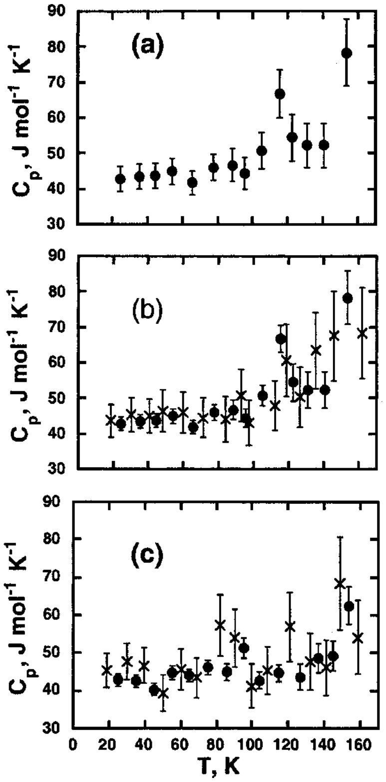

Figure 8. Heat capacities of the clusters calculated from the slopes of the caloric curves (filled circles) and from fluctuations in the potential energy (crosses) during heating stages. Error bars correspond to 2σ. The kinetic energy contribution to the heat capacity $(5N - 6)R/2N$ was added in each case to obtain the total heat capacity for the system of *N* rigid molecules. (a) 137-molecule cluster, (b) 217-molecule cluster, and (c) 435-molecule cluster.

sharp transition temperatures even if the structural changes involved correspond convincingly to those of first-order phase changes of the same substance in the bulk. Although the transitions in clusters take place over a range of temperatures, the thermal signatures are nevertheless readily recognizable, and many diagnostic tools exist to characterize the transitions. As a matter of taste, some thermodynamicists prefer not to consider small clusters as having definite phases or as undergoing first-order phase transitions. Nevertheless, to avoid tedious circumlocutions in the following, we shall simply speak of the phaselike structures of molecular clusters as phases and make inferences about transitions more on the basis of analogy with bulk structures than on sharpness of changes in thermodynamic properties.

The most striking result of the present simulations is the continuous, reversible passage between the cubic and the orthorhombic structures, structures which correspond to distinct phases in the real compound. Our simulations show that there is no discernible nucleation barrier separating the orthorhombic from the cubic. In all of our prior simulations of phase changes in clusters undergoing cooling, a nucleation barrier had made it its presence felt by requiring significant supercooling in order to overcome the barrier. An analogous barrier has not appeared in heating runs because the somewhat disordered cluster surface has always contained large enough pockets of precursors of the higher temperature phase to obviate the need for nucleation events. This makes heating runs quite reproducible whereas cooling runs, with the element of chance involved in the formation of a critical nucleus, are not reproducible. Hence, a greater or smaller degree of hysteresis in caloric curves had always characterized our previous phase changes. No such behavior was seen in the present runs.

In all published MC and MD runs on systems of atomic and molecular clusters undergoing transitions, the caloric curves have exhibited conspicuous inflection points corresponding to a shift in enthalpy from one structure to another. No clear evidence of an enthalpy difference between the two structures was apparent in the present caloric curves. Even so, in the region over which the structural changes are most conspicuous, fluctuations in the configurational energy in the present runs seem to be slightly elevated as if the structures differ in energy by a minor amount, but this is more or less within the statistical noise.

In our prior studies of clusters in transition as they were cooled, a region of the new phase could be seen growing in the old phase. An interface between the two phases was present. By contrast, in the present simulation, the entire cluster changed continuously, and there was no evidence of the coexistence of two distinct phases. None of the foregoing justifies a description of the transition as first order, however liberally the meaning is interpreted.

Ehrenfest[11] classified a transition as first order if the first derivatives of the free energy with respect to temperature and pressure (i.e., volume, entropy, and enthalpy) were discontinuous and second order if these quantities were continuous but the second derivatives (e.g., heat capacity) were not. Higher-order transitions were postulated. Experience has indicated that transitions with continuous volumes and entropies are associated with critical points for which higher derivatives tend to diverge rather than simply being discontinuous.[32,12] Superconducting transitions are an exception.[12] Because of the resemblance of the divergent heat capacities to the 11th Greek letter, such transitions became known as lambda transitions, and they are commonly called “continuous”, rather than second-order transitions. Typical examples of such phase changes are found among the perovskites which can undergo transitions in which orthorhombic lattices merge to tetragonal, then to cubic, continuously as the temperature is increased. Therefore, volumes and enthalpies vary continuously. Several of these have been modeled by constant pressure MD simulations[33−35] with periodic boundary conditions. Although the heat capacities of the real systems do exhibit the lambda shape,[36] this aspect of the simulations was not discussed. In the one case we are aware of in which configurational energies were reported, no evidence of the lambda behavior was evident, and hence, the transformation appeared to correspond to a second-order transition with little change in heat capacity.[35] In this respect, the change resembled that of the present simulations.

In the present simulations the orthorhombic lattice constants *a*, *b*, and *c* converge to the cubic constant, making the volume change continuous. That and the lack of a detectable enthalpy change would seem to qualify the structural change as a continuous change, second-order rather than a lambda transition in the loose sense we are using for clusters. On the other hand, not even the heat capacity undergoes enough of a change in the region of the transition to make it closely resemble the Ehrenfest definition. We do not want to belabor fine distinctions here. What seems to be the case is that the structural change in our model acetylene has the earmarks of a second-order transition with thermal properties smeared out by virtue of the smallness of the clusters examined. Continuous transitions in the bulk take place at a sharply defined temperature.

That the nominally first-order transitions of clusters are spread over a range of temperatures can be understood semiquantitatively on the basis of the capillary model, as exemplified by the treatment of Riess, Mirabel, and Whetten.[37] Such an approach seriously underestimates the range, however, mainly because the capillary approximation neglects effects of the thickness of the interface between the phases.[2] In the case of second-order transitions where there is no interfacial free energy, the capillary model does not apply, and no alternative is readily available. The present results suggest that the range of temperatures over which such a transition takes place in a cluster is considerably greater than that for first-order transitions.

The question remains as to whether the qualitative behavior of the model acetylene mimics that of the real material in any sense besides the structural characteristics at high and low temperatures. The answer appears to be negative. Crystals of cubic acetylene shatter upon cooling through the 133 K transition temperature, and the lattice frequencies change discontinuously.[38,39] Therefore it is almost certain that the real substance, unlike the model, undergoes a first-order transition. We conclude that our original goal has failed to be met. What was found, instead, is a model system with remarkable properties providing an enlightening example of a higher-order transition.

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Appendix

Statistical errors in heat capacities derived from fluctuations in the potential energy for an NPH ensemble were calculated from the following relation:

$$\sigma_{C_p} = (2/n_e)^{1/2} C_p \qquad \text{(A1)}$$

where n_e is the effective number of statistically uncorrelated saved MD dumps at a given temperature. To take correlation into account we assume that

$$n_\mathrm{e} \approx n_\mathrm{T}/\{S[2 - \exp(-S/6)]\} \qquad \text{(A2)}$$

where S is the sum of the autocorrelation coefficients over the correlated region of the dumps and n_T is the total number of MD dumps. This rough approximation gives the correct limits for moderately correlated data ($S \gg 1$, treated by Allen and Tildesley[40]) and for uncorrelated data ($S = 1$).

Statistical errors in heat capacities derived from the slopes of the caloric curves were taken to be

$$\sigma_{C_u} = \sigma\left(\frac{U_2 - U_1}{T_2 - T_1}\right) \approx \left(1 + \frac{C_u}{2.5R}\right)\frac{\sqrt{2}\sigma_u}{\Delta T} \qquad \text{(A3)}$$

in view of the negative correlation between potential energy U and kinetic energy (and, hence, T), where C_u is the contribution to the heat capacity from configurational energy.

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