

Structure and Transformation in Clusters: Computational Experiments¹

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A very brief review of gas-phase electron diffraction and one of its offshoots is given. Parallels are drawn between experimental studies of molecules, including conformational changes, and studies of clusters, including phase changes, calling particular attention to the use of computers as the preferred experimental apparatus. A sketch is presented of what has been learned about matter in transition by the application of computer simulations.

KEY WORDS: Molecular clusters; structure; nucleation; quantum and molecular dynamics computations.

INTRODUCTION

To think of Lev V. Vilkov (LVV) and gas-phase electron diffraction (GED) as twins is entirely fitting, for Lev has been inseparable from GED for all of his professional life [1]. Although the senior author of this paper first practiced GED some years before he met LVV four decades ago, his friendship with him has been more steadfast than with GED for reasons sketched below. Actually, the wave theory of matter and the senior author are twins for they appeared in the same year [2, 3]. The most familiar manifestation of matter waves in chemistry is in the standing electron waves corresponding to atomic and molecular orbitals. The application of these in molecular quantum chemistry is becoming more and more prominent in the programs of LVV and his colleagues [4, 5], again for reasons sketched below.

When research at the University of Michigan left the field of gas-phase electron diffraction studies of molecular structure two decades ago, the emphasis in structural chemistry at the time was on experiment.

Experiments were often interpreted somewhat qualitatively in terms of quantum calculations of varying degrees of rigor. Such interpretations are not to be disparaged for they can often cast a problem into a form that appeals to intuition. Such qualitative and insightful quantum treatments correspond to what Hoffmann has called "portable explanations [6]" that are more satisfying to the bench chemist than rigorous treatments yielding accurate numerical results but little additional enlightenment. Today the tables have all but been turned. Quantitative quantum chemical computations often augment or, in an increasing proportion of structure studies, even replace experimental measurements. This has to do partly with the increasing availability of high-level quantum programs and partly to the skyrocketing advances in computer technology. Structural determinations via the computer are not, in the true sense, theoretical research. They are experimental studies using the computer as the apparatus of choice.

EXPERIMENTAL TRANSITION

The field into which the Michigan GED program evolved, namely a study of nucleation in phase changes, did not initially require a major change in procedure, and it remained for awhile directed toward structures, though

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of large “gas-phase” clusters, not of single molecules. This work followed prior research by the groups at Orsay and Northwestern in generating large molecular clusters in supersonic flow [7], and in probing them with an electron beam. The technique required only modest changes in apparatus from that of GED. What was very different about the Michigan experiments on clusters was the fact that we were chemists, not physicists and gas-dynamacists. Therefore, we studied a great variety of molecular substances, not just a limited number of mostly atomic substances, and the molecular systems led to diverse types of clusters. On the other hand, the simpler substances studied previously had always yielded solid clusters. Moreover, our apparatus had not originally been designed specifically to achieve a certain supersonic performance. Therefore, as it turned out, it allowed a more flexible variation of conditions of observation. This led to the remarkable discovery that some of the clusters we produced could be observed to undergo a change phase during flight in the supersonic beam. By adjusting conditions, we could watch the time evolution of a phase transition on a microsecond time scale, and determine the nucleation rate. Because of the very small size of our particles and the extremely rapid rate of cooling, we were able to observe transitions at far deeper supercoolings than ever studied in prior, conventional investigations of nucleation [8]. More will be said about the consequences of this, below.

ROLE OF COMPUTATION

Our discovery of rates many orders of magnitude higher than heretofore observed encouraged us to study nucleation in computer simulations where even deeper supercooling and higher rates might be explored. It was found that some of the transitions we could study in supersonic beams could also be followed in molecular dynamics (MD) computer simulations of molecular trajectories in clusters [8]. At first, computer simulations were just a valuable complement to our experiments. As time went on, it became harder and harder to keep experimentalists from abandoning experiments and joining the computer simulators. Not only are computers cleaner and less prone to break down than diffraction equipment, but they yield information in full molecular detail. Analogously, high-level quantum calculations can establish not only molecular structure but, in principle, all observable properties of molecules and thus provide more detail than is available from any single experimental technique.

To a greater and greater extent, quantum calculations are displacing experiments. In principle, *ab initio* quantum computations could also treat homogeneous nucleation in large clusters, as well, but the complexity of nucleating systems is so great that the problem is and will remain beyond the reach of fully quantum treatments for a long time to come.

NATURE OF TRANSFORMATIONS

The parallel between research on molecules and clusters goes further. Nucleation research can be regarded, in a sense, as a form of conformational analysis in which the different conformers of clusters are different phases. In conventional structural chemistry there are only a limited number of conformers to monitor, and often all can be studied. This is also true for very small clusters. Even clusters as small as 5 or 10 atoms can exhibit distinct changes between fluxional, liquid-like aggregates and more rigid solid-like entities [9]. Some chemists are content to discuss such changes in terms of melting and freezing, while others regard this loose talk as nothing short of heresy. Such clusters are small enough for the potential surface to be constructed in enough detail to characterize all individual structural forms (conformers) and the pathways between them. They are not large enough, however, for a nucleation barrier to be encountered when a “melt” is solidified by cooling.

As clusters begin to increase in size, the parallel between conformational analysis and the study of structural changes in clusters becomes more and more tenuous. For clusters to serve as useful models for nucleation in bulk systems they must be rather large. How large is large? As clusters increase in size, say beyond some dozens of molecules, the number of distinct configurations becomes so enormous that it is not possible to identify all of them and to determine all the pathways between them. And for large clusters the fluxional form has properties such as heat capacity, density, and self-diffusion, that are so similar to those of the corresponding liquid that it is entirely appropriate to refer to them as liquid. Moreover, the solid-like forms display structures that are readily identified with known crystalline phases. Not to refer to such clusters as crystalline would be pedantic. These bulk-like properties of molecular clusters can be realized when the aggregates contain fewer than 100 molecules [8]. In the case of atomic clusters, a far greater number is required [10]. Therefore, it

is entirely natural to discuss changes from one form of large clusters to another as phase transitions, including melting/freezing, and solid state transformations. Still, since the changes are not perfectly sharp, sometimes taking place over an appreciable range of temperature, they therefore do not obey the conventional signature of first-order transitions.

In our opinion, however, it is ponderous and counterproductive to use circumlocutions to avoid calling the changes phase changes. Even though they look in some respects like second-order phase changes, the parallel with first order changes is too obvious to deny the correspondence. Moreover, due to the complexity of the potential surface, when one structural type (phase) is cooled below the transition temperature (i.e., is supercooled), in general there exists a free energy barrier impeding the transformation. In these cases chance structural fluctuations leading to small pockets of the colder phase (nuclei) are needed to bring about the phase change. When nuclei materialize that are large enough to make further growth spontaneous they are called “critical nuclei.” Nucleation is not, however, generally needed in phase transitions when a substance is heated, as long as the substance has a surface. Since surfaces are more disordered than interiors, even for bulk crystals, and higher temperature phases are progressively more disordered than colder phases, transitions begin at the surface and a special nucleation event is not needed in transitions from colder to warmer phases—unless, by some stratagem, the substance is denied a free surface.

Even though the correspondence between structure and conformational changes in molecules and for phase changes in large clusters breaks down, the increasing use of computer-intensive calculations to augment experiment in each case is a sign of the times.

Central to the University of Michigan program is learning about nucleation in condensed matter. This area is much less developed than the more widely studied area of nucleation in the condensation of vapor into liquid droplets (see, for example, reference 11). Even though the classical nucleation theory (CNT) for freezing was developed a half century ago, mainly by Turnbull and his associates [12], experimental difficulties have been so daunting that a large accumulation of reliable results is not available for theorists to build upon. Although the CNT is semiquantitatively applicable to phase changes at temperatures not far below the freezing point, it is conspicuously imperfect in deeply supercooled systems. It is these systems that were first encountered in the Michigan diffraction laboratory. For example, our measurements

of the nucleation rate in the freezing of submicroscopic water droplets (large molecular clusters) were carried out at far deeper supercooling than in any of the many investigations by conventional means, and the rates we found were astronomically higher [13]. Moreover, when we decided to augment our studies by molecular dynamics simulations of spontaneous phase transitions, rates had to be higher by another 6 to 8 orders of magnitude if we could expect to see anything happen during reasonable CPU times. That meant going to very deep supercoolings, where deficiencies of the CNT become even more acute. How the problem has been approached and what has been found will be described next.

CHARACTER OF COMPUTATIONS

Molecular dynamics (MD) simulations [14] are generally carried out by constructing a preliminary set of coordinates for an aggregate of molecules and allowing individual molecules to move with respect to each other in accordance with Newton’s classical laws of motion. Temperatures are inferred from mean kinetic energies and can be adjusted as desired. It has been shown for molecules appreciably heavier than helium that, in the temperature regime of interest in nucleation studies, quantum corrections are too small to warrant the enormously higher computational costs they would entail [15]. For systems of polyatomic molecules, even classical MD simulations are highly computer-intensive, especially when an ensemble of systems must be studied over a range of temperatures. Therefore, simulations are usually limited to comparatively small numbers of molecules. Until recently this number was commonly hundreds of molecules or fewer. Now, with faster computers available, it can be thousands or more. Still, if it is desired to study properties of bulk matter, periodic boundaries [14] are usually imposed, making molecular coordinates repeat periodically so that, when molecules leave one side of a cell, they re-enter from the opposite side. This construction works quite well for many purposes but, since it denies the system a surface (see above) it can often suppress phase transitions or, in some situations, augment them by false correlations. For this reason the research at Michigan on spontaneous transformations has used clusters with free boundaries instead of imposing periodic boundary conditions. Molecules in the interiors of large clusters behave virtually the same as in the bulk. As will be seen, however, there is a price to pay for this choice of avoiding periodic boundary conditions.

What is needed for MD simulations to be carried out is a realistic potential function describing interactions between molecules. In the treatment of monatomic systems, metals in particular, potentials approximating many-body interactions in a simplified manner are commonly used. In the treatment of systems of polyatomic molecules, however, potential functions are almost always constructed to be pairwise-additive sums over all intermolecular pairs of atoms. Partial charges are frequently employed. Potential parameters are adjusted to yield certain properties of condensed matter. In some studies molecules have been allowed to execute internal motions. Since these motions and the exchange of energy in molecular collisions are treated classically, this type of treatment can lead to errors larger than if molecules had been treated as rigid, especially when molecules are small and not very flexible.

REPRESENTATIVE RESULTS

What sorts of systems have been examined at Michigan and what has been learned will now be sketched briefly. It so happened that some of the first phase transitions observed in ED experiments on supersonic jets of clusters were solid state transitions [8]. For these to take place rapidly meant that the translational reorganization of molecules had to be modest. Molecular reorientations were the primary change. Even so, changes in diffraction patterns were large and easily followed. These cases were, of course, among the first to be studied by computer simulations because extrapolations of nucleation rates based on the CNT forecast that the rates at deeper supercooling would become high enough to be followed in simulations. These predictions proved to be true. Two types of solid state transitions that had been seen experimentally were examined. First, a number of octahedral hexafluorides underwent a transition from bcc to monoclinic when they were cooled. For sulfur- and selenium hexafluoride, this transition was the same as observed in bulk experiments. For tellurium- and the transition metal hexafluorides, however the transition to monoclinic that we saw was not the equilibrium bcc to orthorhombic change occurring in the bulk. The monoclinic product resulted just as it did for the lighter hexafluorides but not because it was thermodynamically favored. It was the kinetics of the process that was responsible. This ability to produce metastable structures by virtue of kinetics turned out to be common at deep supercooling [8].

Another case we studied first in supersonic jets was *t*-butyl chloride [8]. Despite the availability of electron

diffraction patterns of clusters which had transformed from the tetragonal phase to a colder phase, and despite high quality neutron diffraction powder patterns of the same two phases, the crystal structure of the colder phase was unknown. The complex diffraction pattern of the cold phase had eluded analysis. In the MD simulations, the transition took place at roughly the rate expected from extrapolations of the experimental data. Moreover, since the coordinates of the molecules in the colder phase were available in the MD output, the structure of the cold phase was readily deduced. It turned out to be monoclinic, and the coordinates allowed diffraction patterns to be computed and they accorded very well with the observed patterns. So, in this case, the kinetically favored colder phase was the same as the thermodynamically favored phase, and letting the molecules in the simulation decide for themselves how they wanted to pack revealed the unknown structure. Again, the transition consisted mainly of molecular reorientation. The disordered orientation of molecules about their three-fold axes in the tetragonal phase changed to ordered orientations in the monoclinic. Images of the clusters before, during, and after the transition are shown in Fig. 1.

Studies of the freezing of liquid clusters surprised us. The systems we examined were hexafluorides and salts. In earlier Monte Carlo and MD studies of the heating of crystalline clusters it had been found that molecular clusters melted over a range of temperatures [17], a behavior mentioned above and one always seen in prior studies of atomic clusters [9]. What melted first was the surface of the clusters. Surfaces tend to be more disordered than the interior of solid matter, and this has consequences referred to earlier. It seemed natural, then, to expect that when liquid clusters froze, they would tend to freeze in their interiors first because the more freely moving surface molecules are organized more chaotically. What we found, instead, was that nucleation occurs preferentially at or very near the surface [18], as illustrated by typical MD images in Fig. 2. These images show crystalline nuclei forming in liquid clusters of SeF₆. Therefore, clusters do not yield accurate bulk nucleation rates, except by extrapolation to large sizes. Because of the higher surface-to-volume ratio of small clusters and, to some extent because of their higher Laplace pressures, their rates of forming critical nuclei per unit volume tend to be higher.

The property of clusters nucleating at the surface is not limited to molecular substances. Salts exhibit the same site preference [Huang and Bartell, unpublished research]. In other ways salts differ substantially from their molecular counterparts, however, as demonstrated

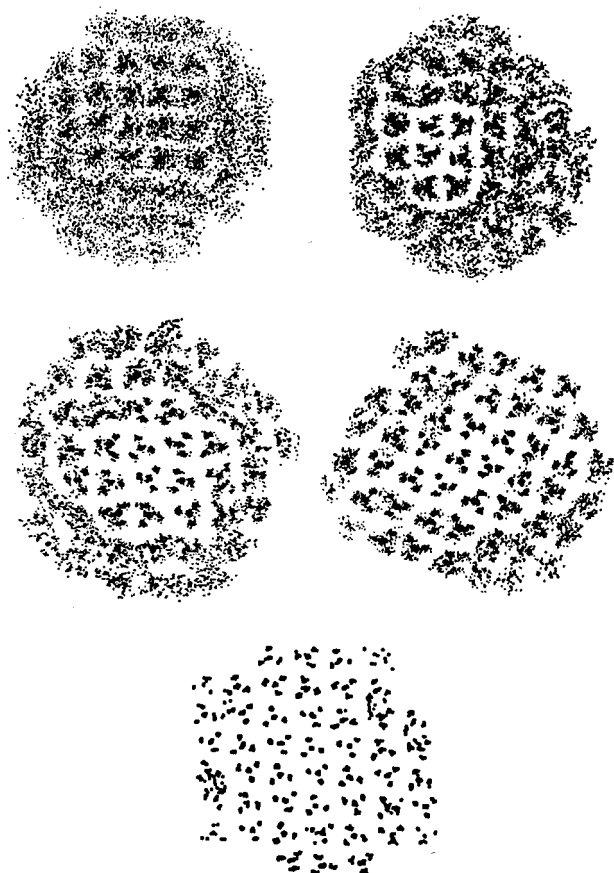


Fig. 1. Images from molecular dynamics simulations of several different 188-molecule clusters of tert-butyl chloride at 120 K at progressively more complete stages of transformation from the tetragonal (upper left) to the monoclinic structure. Direction of viewing, approximately down the C—Cl bonds.

in the computer simulations. When covalently bound molecules are cooled very rapidly, they solidify to a glass. Salts, on the other hand, have such a strong tendency to crystallize [19, 20] that they freeze, even when quenched to low temperatures almost instantaneously in the computer at cooling rates far exceeding any attainable in the laboratory. If quenched to very low temperatures, however, they form polycrystalline masses instead of a single crystal shown. Figure 3 illustrates the strong tendency of even very small clusters of molten sodium chloride to freeze to well faceted single crystals. It also shows the effect of capillary waves in deforming liquid droplets from an ideal spherical shape. In larger drops the deformations are logarithmically slightly larger but relatively less conspicuous.

Another finding was that, at deep supercooling, criti-

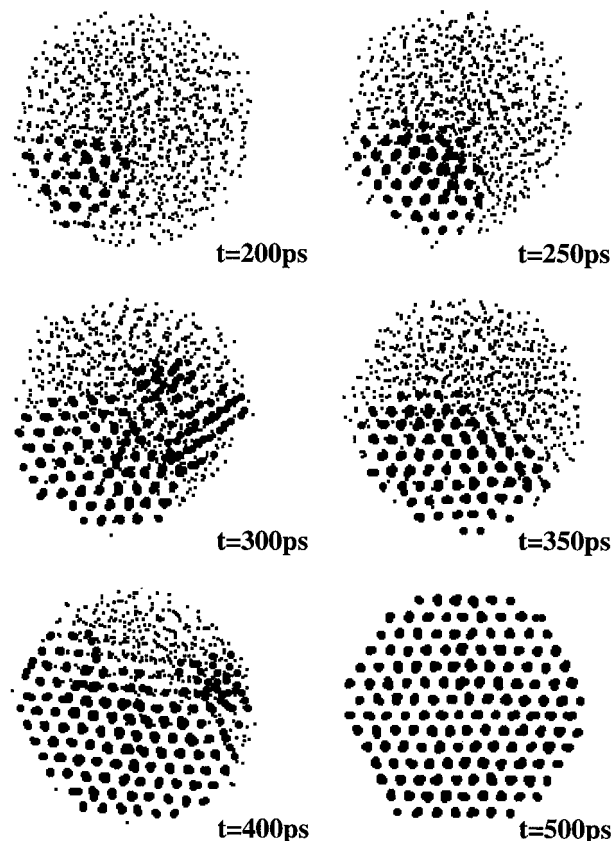


Fig. 2. Projections of centers of mass of core molecules in a single, initially liquid cluster composed of 1722 molecules of SeF_6 , during crystallization. The cluster was supercooled by about 100 K. Heavy dots identify molecules in a nucleus with a “bulk-like” crystalline organization. The fluctuating thin sheets and filaments in the diffuse solid-liquid interface that were identified by “Voronoi analyses” as having a local bcc structure were not highlighted.

cal nuclei are considerably larger and more ramified than implied by the classical theory [18, Huang and Bartell, unpublished research]. Moreover, several kinetic prefactors proposed for nucleation rates are in serious conflict with each other, at least at deep supercooling [21]. We should mention that theoretical density functional (and related) treatments have already overcome some of the shortcomings of the CNT [22–24]. They do not share the simplicity of the CNT of being generally applicable to an arbitrary system without specialized computations, however. What would be helpful is a treatment with a simplicity approaching that of the CNT but with the worst deficiencies corrected. Although we have not arrived at such a formulation, our computational results are making the principal sources of weakness clearer.

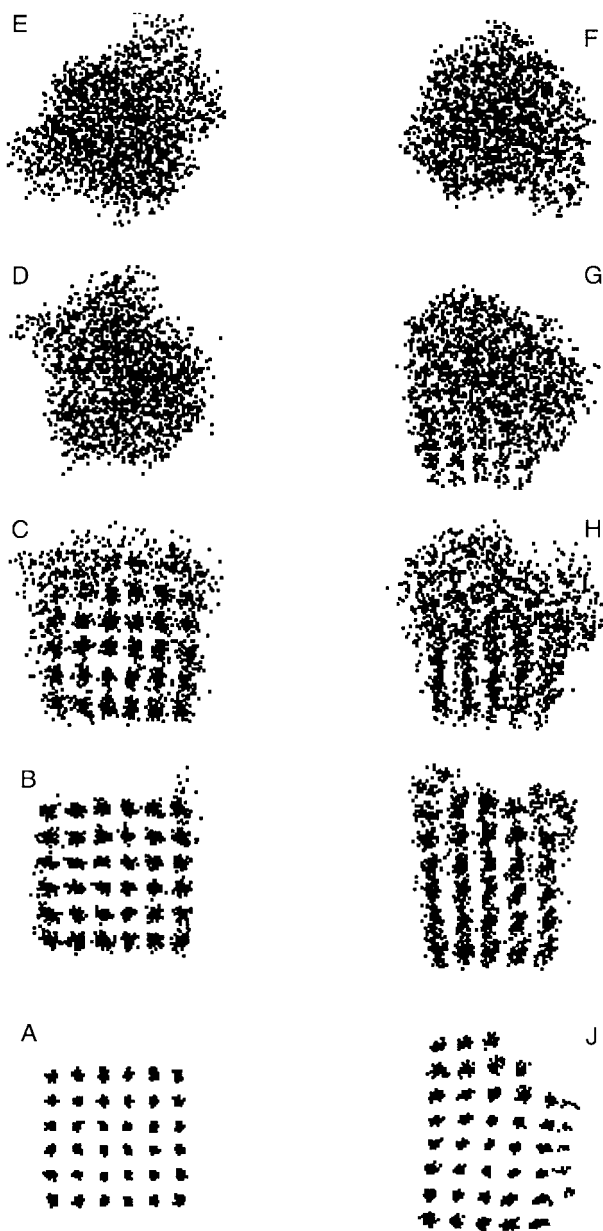


Fig. 3. Left-hand column: Images of a small $(\text{NaCl})_N$ cluster ($N = 108$) at various stages of heating up to and beyond the melting point. (A) 400, (B) 860, (C) 880, (D) 920, and (E) 940 K. **Right-hand column:** Cooling stages of the same cluster beginning with the supercooled liquid at 600 K (F) and showing nucleation and crystal growth at 560 K averaged over the time intervals. (G) 8–16 ps, (H) 17–24 ps, (I) 72–90 ps, followed by cooling to 400 K (J). Lattice directions after the melt nucleated differed from those before melting, but the images of the freezing cluster were rotated for simplicity of viewing the structure. Small clusters melt at much lower temperatures than large ones. Bulk NaCl melts at 1073 K.

CONCLUDING REMARKS

This brief review of the behavior of clusters undergoing phase changes illustrates what can be learned by computer simulation that could not be derived directly from analyses of experimental data. This new-won ability made possible by today's computer science is no longer merely supplementing diffraction analyses of structures of molecules and clusters; it is surging ahead of experiment in important areas.

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