

# Orientational order–disorder phase transitions in plastic molecular clusters: Projection of three-dimensional distributions onto a two-dimensional surface

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In addition to the traditional methods of identification of order–disorder transformations in nanoscale clusters containing highly symmetrical molecules, we have developed a simple projection method to recognize such transformations. The three-dimensional orientation distributions of the molecules are projected onto a two-dimensional spherical surface without any loss of information. We have applied the method in the analysis of the phase changes of clusters containing up to 180 tellurium hexafluoride molecules. The molecular configurations are generated by constant energy molecular dynamics simulations of the thermal history of free clusters. We observe two successive transitions as the clusters cool from their melting point. The projection method clearly reveals the mechanism of the structural transformations in the studied clusters: the orientation order of the molecular axes at low temperatures is accompanied by lattice distortion. © 1998 American Institute of Physics. [S0021-9606(98)50433-3]

## I. INTRODUCTION

Orientationally disordered phases are common characteristics of the phase diagrams of molecular systems.<sup>1</sup> Experiments and computer simulations illustrate the difference in the behavior of free atomic and molecular clusters. Electron diffraction experiments<sup>2</sup> have shown that small argon clusters adopt the bulk cubic structure when they consist of more than a few thousand atoms. Neutron and electron diffraction<sup>3</sup> have shown that the clusters of SF<sub>6</sub>, SeF<sub>6</sub>, and TeF<sub>6</sub> pack in a crystalline structure when they are much smaller—only a few tens of molecules. The development of experimental methods to investigate small clusters makes it possible to test the predictions of computer models<sup>4,5</sup> and analytical theories.<sup>6</sup> One attraction to study clusters is its role as a tool to understand bulk properties: more and more, we have also realized that they deserve study as unique objects in nature. Some phase diagrams of clusters show metastable structures that have never been detected in bulk.<sup>3</sup> Apparently, at least some of these structures arise from vibrational–rotational coupling in structural transformations induced by temperature changes of clusters.<sup>7,8</sup>

Our interest in clusters of the form AF<sub>6</sub> is their potentiality as vehicles for a search for analogs in small systems of continuous transitions. It is well known that quasispherical molecules build plastic materials characterized by orientational disorder at elevated temperatures. They undergo either second order or fluctuation-induced first-order transitions<sup>9</sup> to more ordered phases as they cool. The latter transitions take place when the correlation length exceeds a limit at which

fluctuations in the order parameter make a discontinuous transition energetically favorable. The cluster's finite size obviously limits the correlation length to the linear size of the cluster. Furthermore, the surface of the free cluster breaks the symmetry of the crystalline structure that can be assumed in the bulk material. Many years ago, the following question was posed.<sup>10</sup> Do symmetry-breaking fields restore continuous phase transitions in systems with fluctuation-induced first-order transitions? This question has been approached by Jensen,<sup>11</sup> who studied phase transitions in magnetic materials with order parameters of dimension  $n \geq 4$  with the help of Monte Carlo simulations and renormalization group calculations. The crucial result is that for  $n = 6$  a finite value of symmetry-breaking stress is required to destroy the first-order phase transitions. A continuous transition replaces the first-order transition in that case.

There are similarities between the plastic crystals and paramagnetic materials, although the forces in the plastic substances are more complex. In addition to the question about the role of the surface in the phase transitions, many others should be answered in order to understand the mechanism of the transformations in finite plastic systems. For example, do plastic clusters present an instructive example of crossover from first-order to continuous transitions? Do they form domains of differently oriented molecules? If “yes,” how does the collective reorientation of the molecules take place?

We have used clusters of TeF<sub>6</sub> as we did before<sup>7,8,12</sup> to study the ordering process in finite plastic clusters by follow-

ing the molecular trajectories computed by isoenergetic molecular dynamics.

In this paper we describe the diagnostic method that we have developed to analyze the spatial distributions of the molecular orientations.<sup>8</sup> In Sec. II we give details of computations. Section III shows how the method is implemented in the analysis of the structural transformations in a 137-molecule cluster. A discussion of the method's application completes the paper.

## II. COMPUTATIONAL PROCEDURE

### A. Model for the cluster and potential

The procedure used for arranging clusters of rigid octahedral molecules and computing molecular trajectories is described in detail elsewhere.<sup>7,8</sup> The molecules are not rigid bodies in any sense: they consist of atoms interacting via intra- and intermolecular forces, but the forces acting within molecules are at least an order of magnitude greater than those acting between the molecules. In the case of relatively rigid, structured molecules, it is reasonable to neglect the very rapid intramolecular motions.

The intermolecular potential is a sum of an atom-atom Lennard-Jones term and a Coulomb term.<sup>7</sup> Initially, the simulated cluster was arranged in a base-centered cubic lattice at elevated temperatures but below the melting point.<sup>7</sup> The classical equations of motion for a cluster of  $N$  molecules interacting via this potential are written in Hamiltonian form. The center-of-mass trajectories are the solutions of a set of  $6N$  first-order differential equations, integrated with the velocity Verlet algorithm.<sup>13</sup> Successive decreases and increases of the temperature yield data sufficient to construct constant-pressure sections of the phase diagrams of the clusters.

The cluster is thermalized at each particular temperature using the velocity scaling algorithm:

$$\sum_i 0.5m_i[\mathbf{v}_i^*(t + \Delta T/2)]^2 = s^2 \sum_i 0.5m_i[\mathbf{v}_i(t + \Delta t/2)]^2 = 6Nk_B T. \quad (1)$$

This velocity scaling proves to give the correct canonical distribution in the coordinate space with accuracy of order  $\Delta t$ , provided the scaling is carried out in every time step during the thermalization.<sup>14</sup> The time step  $\Delta t = 10$  fs is chosen to keep the total energy constant during the run. After the thermalization is switched off, the system's equilibration is monitored by recording instantaneous values of the potential and kinetic energy during this period. These are taken every 0.1 ps, in order to avoid collecting correlated values of the quantities. Adequate equilibration is especially important when the initial configuration is a lattice with one type of symmetry and at the state point of interest the cluster has another symmetry.

In our computations, the orientation of the molecules relative to the cluster's center of mass in the space-fixed system is defined by the four quaternions suggested by Evans;<sup>15</sup> these solve the problem of divergence in the orientation equations for the three Euler angles when transforming

between the space and the body system. The orientation of the rigid molecule specifies the relation between an axis system fixed in the space and one fixed with respect to the body. We have chosen the body system of each molecule to have its origin at the center of mass of that molecule so the inertial tensor is diagonal. Any unit vector  $\mathbf{e}$  can be expressed in terms of components in the body ( $\mathbf{e}^b$ ) or space ( $\mathbf{e}^s$ ) coordinate system. Conversions from the body-fixed to space-fixed systems are expressed by the equation<sup>16</sup>

$$\mathbf{e}^b = \hat{A} \mathbf{e}^s, \quad (2)$$

where  $\hat{A}$  denotes the rotational matrix expressed in terms of quaternions.

The quaternions of each molecule are recorded during the simulations of molecular trajectories. These quaternions are used to project the three-dimensional orientational distributions. The quaternion is a set of four scalar quantities  $q_0, q_1, q_2, q_3$ , which are subject to the constraint  $\sum_{i=0}^3 q_i^2 = 1$ .

### B. Projection procedure

We propose a novel method for representing the molecular orientation in order to study its time dependence and to compute the density of molecules oriented in a given direction. There is a theorem<sup>17</sup> that states that a three-dimensional rotational manifold cannot be mapped onto a two-dimensional Euclidean manifold. However, if one selects a spherical surface, then it is possible to project the three-dimensional (3-D) manifold onto this 2-D surface without losing any information.

Let us note that the orientation of molecules with octahedral or higher symmetry can be completely represented in  $\frac{1}{8}$ th of the surface of a unit sphere. For molecules of a lower symmetry, this simplification is not valid.

In a rigid octahedral molecule  $AF_6$ , the six fluorine atoms are at the vertices of an octahedron and the A atom is at the center. The orientation of the molecule at any instant is defined by the three orthogonal F-A-F directions in the body frame. At a given temperature these three directions differ from one configuration to another. Snapshots reveal the instantaneous orientation of the molecules in the cluster. If we project many successive configurations, we can follow the time evolution of the cluster.

The projection of a configuration is performed in steps.

- (1) A unit vector  $\mathbf{e}$  from the body system is converted in the space system with the following equation:  $\mathbf{e}^s = \hat{A}^T \mathbf{e}^b$ , where  $\hat{A}^T$  is the transpose matrix of  $\hat{A}$ . In the case of octahedral molecules, the unit vector coincides with the axis of symmetry.
- (2) The vector located either in the octant  $(x, y, z)$  or in the octant  $(-x, -y, -z)$  is taken as the unit vector of the projection. When it is in the first octant, it is not changed in the further calculations. If the projected vector belongs to the complementary octant  $(-x, -y, -z)$ , then

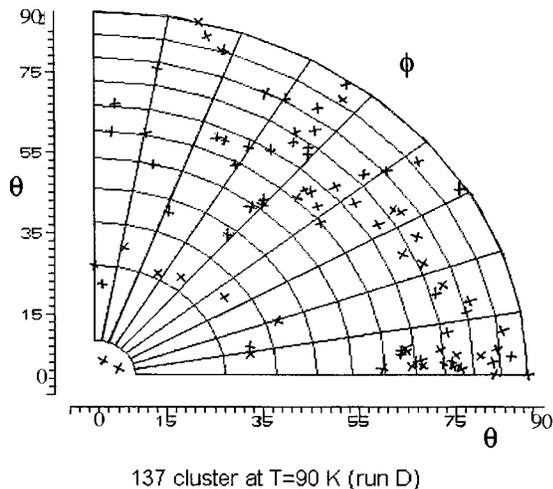


FIG. 1. The 137-molecule cluster above its upper solid–solid transition temperature. The orientational and vibrational temperatures are equal, at 90 K.

it is rotated with the help of the matrix

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

- (3) Two of the Euler angles  $\{\theta, \phi\}$  are determined by the position of this vector. In order to keep the information about the third angle, we use the second unit vector of the body system. Its relative orientation with respect to the first (in the space system) determines the third angle  $\psi$ . This last angle is taken as modulo  $\pi/2$  due to the molecular symmetry. In such a way we obtain the condition that  $(\theta, \phi, \psi) \subset [0, \pi/2]$ .

The Euler angles  $(\theta, \phi, \psi)$  are plotted onto the two-dimensional spherical surface in the following way: the angle  $\theta$  increases as the usual polar angle and the angle  $\phi$

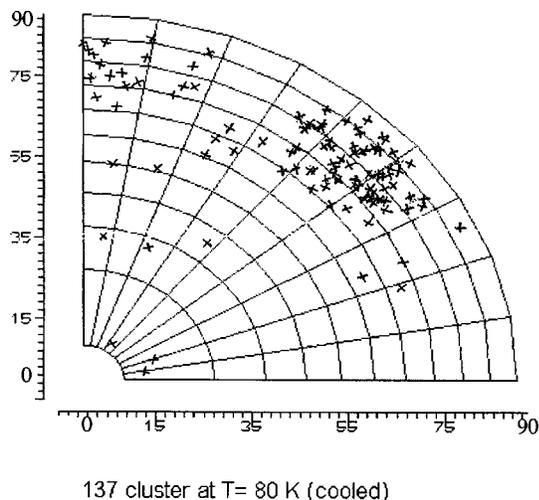


FIG. 2. The 137-molecule cluster just below the first structural transition, at 80 K: most of the molecules have one of their symmetry axes oriented in a common direction.

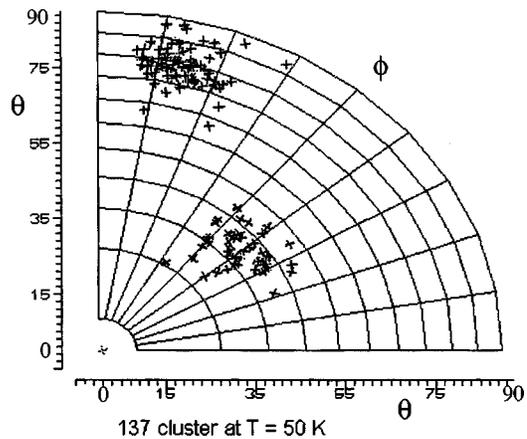


FIG. 3. The 137-molecule cluster at a temperature of 50 K, below the second, lower-temperature transition.

increases along the radial axis. Thus, we obtain a point with coordinates  $(\theta, \phi)$ . In this point we draw a cross that is oriented at an angle  $\psi$  with respect to the  $(\theta, \phi)$  radius vector of the point.

If the symmetry of the molecules is taken into account in the projection procedure, then the points having coordinates  $(\theta, \phi, \psi)$ ,  $(\theta \pm \pi/2, \phi, \psi)$ ,  $(\theta, \phi \pm \pi/2, \psi)$ ; and  $(\theta - \pi/2, \phi - \pi/2, \psi)$  coincide. Care should be taken in the case of  $(\theta, \phi)$  equal to  $(0, \pi/2)$ .

This method makes it possible to follow the dynamics of each molecule during phase transformations when cluster is cooling or heating when the projections are used for animation.

The static projection is useful to determine the orientational distribution. This is done very easily with the help of a special net that covers the spherical surface. Each cell of this net has the same area. Hence, the numbers of molecules in these cells correspond to the normalized orientational distribution.

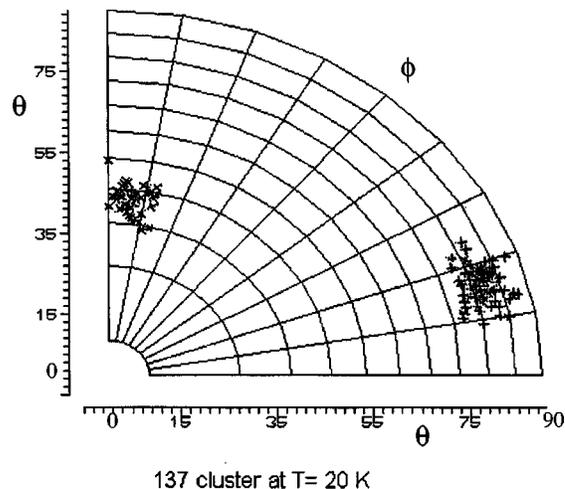


FIG. 4. The 137-molecule cluster at 20 K. The molecules are oriented in the two preferred orientations.

### III. APPLICATION TO THE ORDER-DISORDER TRANSFORMATIONS OF TeF<sub>6</sub> CLUSTERS

Figures 1–4 demonstrate how the method reveals the behavior of a 137-molecule cluster in the temperature range of its various solid phases. The cluster is cooled from 180 K in steps of 10 K. The snapshots were taken 50 ps after the kinetic-energy rescaling was switched off.

Figure 1 corresponds to the disordered solid phase observed at temperatures above the upper transition temperature. The orientations of the molecules are uniformly distributed. When the cluster is cooled below 85 K (the estimated transition temperature for a cluster of this size), most of the molecules align one of their symmetry axes. The alignment is seen as a high-density region on the surface. Careful inspection of the crosses in this region shows that the other two axes of the molecules are still disordered. Figure 3 is a snapshot of the cluster at 50 K—below the second transition. The two groups of crosses correspond to the preferred orientations of the molecules in the ordered phase. The denser group, around (75°, 80°), shows a strong tendency to orient the third angle as well, but the orientation of the third angle is more random in the smaller group.

The analyses of these groups at different times and the same temperature give the mean reorientation period of a molecule. At the transition temperature, it was found to be about 420 ps; that is about 200 times longer than the libration period. This slow process makes it extremely difficult to judge whether these clusters exhibit the coexistence of different phases.<sup>18</sup>

### IV. SUMMARY

The method developed here provides a means to represent the distribution of orientations in three dimensions of the molecules in a cluster or small sample, e.g., of a con-

densed phase or partly oriented beam. The specific system used to illustrate the method requires only one quadrant because of its high symmetry, but the method can be used for molecules of arbitrary symmetry. Following the evolution of the orientations of the molecules reveals the mechanism of their ordering process in plastic clusters. It is clearly seen that the metastable phase seen at about 85 K corresponds to a partial alignment of the molecular axes of symmetry.

### ACKNOWLEDGMENTS

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