Analogues in clusters of second-order transitions?

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Abstract. The question of existence and nature of a finite-system analogue of a second-order phase transition in molecular clusters is discussed. By means of constant-energy molecular dynamics, we have simulated the phase transitions of various free clusters of $TeF_6$6 during cooling and heating. Structural changes have been recognized by changes of slope of the caloric curve and by the distributions of the molecular axes of symmetry. The structure seen at about 160 K is an orientationally disordered phase. It transforms in two steps to an orientationally ordered structure as cluster cools: 1) an intermediate structure with partial alignment of the molecular axes of symmetry is formed at about 80 K; 2) almost all molecules align their axes of symmetry. We interpret the appearance of the intermediate phase to be a result of an ordering-displacement coupling. In addition, a size-dependent Coriolis force has been identified as another cause generating a metastable phase. As the number N of molecules in a cluster increases, this force decreases as $1/N$. We associate the hysteresis of the caloric curve with the finite-size effects and critical slowing down, typical of second order transitions.

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1 Introduction

Although small clusters do not show traditional first-order phase transitions, clusters which exhibit persistent solid-like and liquid-like forms display a dynamic "solid-liquid" phase equilibrium that becomes a first-order phase transition as N, the number of particles in the cluster, grows very large. This phenomenon is now reasonably well understood [1]. The question is still open, however, regarding the existence and the nature of a finite-system analogue of a second-order phase transition.

Molecular substances exhibit a rich diversity of structures and dynamics because of the anisotropy of their intermolecular potentials. If the molecules are somewhat globular, and generally in the case of ionic molecules, it is common to observe orientationally disordered phases known as plastic crystals. Such substances undergo either second-order or weakly first-order transitions to more orientationally ordered phases as the temperature is lowered [2]. Although the behavior of these systems is similar to paramagnetic material with molecules positioned in a lattice structure, the intermolecular interactions are more complex than those of Ising or Heisenberg type, due to the orientational dependence of the former.

Tellurium hexafluoride TeF_6, an octahedral molecule, provides a highly symmetrical example for which extensive experimental and theoretical data are available [3]. Crystals of TeF_6 have been found in several different structures: body-centered cubic, monoclinic (below 100 K), and orthorhombic (around 40 K). The monoclinic structure is observed only in clusters, while the others are found both in clusters and bulk [3]. The monoclinic phase has a lower symmetry than that of orthorhombic phase. Its appearance only in clusters might be explained by the kinetics, [2], i.e. it could be a truly metastable phase, but it might be a signal of specific finite-size effects. The last possibility motivated our study because phases that are only metastable in the bulk limit may exhibit perfectly valid, *dynamic* stability for finite systems, because their free energies may, while higher than those of their most stable counterparts, still be low enough to sustain readily observable concentrations in equilibrium ensembles of clusters.

Computer simulation of orientationally disordered phases by molecular dynamics based on realistic intermolecular potentials has proved to be a powerful complement to experiments [2]. We have carried out a series of constant-energy MD simulations of free TeF_6 clusters of various sizes. The results of simulations indicate small latent heats and hysteresis in the caloric curves of the clusters. The hysteresis effect diminishes as the number N of molecules in the cluster increases. This indicates that the effect is associated with the critical slowing down near second-order transitions [4]. The latent heat is zero in the continuous transitions in the infinite limit only. Finite-size effects [5] make it practically impossible to determine if the latent heat goes to zero as N grows large but remains finite.

In the computed data, different structures have been recognized by the changes of the slope of the caloric curve, and

by the changes of the spatial distribution of the molecular axes of symmetry. An animation program, written by Feng-Yin Li in the programming language GL for an IBM RISC computer, was used to monitor the structural changes [6]. The structure seen at high temperatures, about 160 K, is an orientationally disordered phase, for all the clusters. It transforms in two steps to an orientationally ordered structure as cluster cools. In the first step, an intermediate structure with partial alignment of the molecular axes of symmetry is formed at about 80 K; in the second, almost all molecules align their axes of symmetry. We interpret the appearance of the intermediate phase to be a result of the *ordering-displacement* (*orientational-vibrational*) couplings. In addition, a size-dependent Coriolis force has been recognized as another causative factor for generating a metastable phase. As N increases, this force decreases as $1/N$. The Coriolis force appears in small clusters due to the alignment of the molecular axes during the phase transitions and the clusters rotate as a whole in order to preserve the total angular momentum (Sect. 3).

2 Computational procedure

Molecular dynamics computations were carried out on free clusters of TeF_6 of various sizes $(51, 81, 89, 129, 137$ molecules in the cluster). The potential of the system is a sum of a pairwise-additive atom-atom intermolecular (Lennard-Jones) and Coulomb potentials:

$$U(r) = \sum_{i<j}^{N_a} u(r_{ij}) = \sum_{i<j}^{Na} 4\varepsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r_{ij})^{12}$$
$$-(\sigma_{\alpha\beta}/r_{ij})^6] + q_{i\alpha}q_{i\beta}/r_{ij} \tag{1}$$

where $N_a = 7N$ is the number of the atoms in a cluster of N molecules of TeF_6, the indices α, β denote either fluorine or tellurium atoms, $q_{i\alpha}$ are small charges ($\approx -0.1e$ for F and $\approx +0.6e$ for Te), and r_{ij} is the distance between the atoms. No cutoffs are applied to the potential functions. The parameters for the Lennard-Jones potential are taken from [3]. The numerical integration of the coupled equations of motion is carried out by the velocity Verlet algorithm [7]. It is time-reversible for about 5000 time steps if the system is away from the transition region and the total energy is easily conserved to one part in 10^{-5}, even for relatively large time steps -10^{-14} fs.

The calculated contribution of the electrostatic energy to the Lennard-Jones potential is particularly small – less than 0.2% – for high temperatures ($T > 100$ K). For the transition temperatures, $T \in (70–90$ K), it is around 4% of the total energy E_{tot} and contributes to the increase of the correlation length during the phase changes.

The clusters were initially arranged as spherically as possible in a bcc structure that was seen in the high temperature region. The axes of symmetry of TeF_66 were randomly oriented with respect to the space frame having its origin in the cluster center of mass. The lattice constant minimizing the static potential changed a little with $N – 6.18$ A for 51 molecules, 6.25 A for 137 molecules.

The total energy of the system was calculated from:

$$E = U(r) + 0.5\sum_{i=1}^{N}[m_i\bar{\nu}_i^2 + I\bar{\omega}_i^2] \tag{2}$$

where $U(r)$ is from (1), m_i is the molecular mass ($241.6 \times 1.6710^{-27}$ kg), $\bar{\nu}_i$ is the linear velocity of the molecular center of mass, $I = 4.1510^{-45}$ kg·m² is the tensor of inertia of one molecule defined in a coordinate system fixed in the molecular center of mass (body frame) where $I = I_{11} = I_{22} = I_{33}$, and $\bar{\omega}_i$ is the angular velocity of the i-th molecule in the body frame.

The desired temperature of the clusters was obtained by the velocity scaling technique [8]: the linear and angular velocities of each molecule were scaled until the average temperature was within ± 2 K of the desired value. The scaling factor s is determined from the relation

$$\sum_i \frac{1}{2}m_i\left(\bar{\nu}_i^*(t+\Delta t/2)\right)^2 = s^2\sum_i \frac{1}{2}m_i\bar{\nu}_i(t+\Delta t/2)^2$$
$$= \frac{3}{2}k_BT6(N-1), \tag{3}$$

where $\bar{\nu}_i^*(t+\Delta t/2)$ is the scaled velocity. This scaling procedure is very convenient and gives the correct canonical distribution in the coordinate space with accuracy of order Δt if the scaling is carried out in every time step in the bath (thermal equilibration). The thermal equilibration stage lasted 10 ps to 100 ps depending on the cluster size, on the rate of cooling or heating, and on the temperature. The closer the temperature was to that of transition, the longer was the thermal equilibration time. After the first stage (in the 'bath') the velocity scaling was switched off and the simulations were performed at a constant total energy for 50–100 ps at temperatures well away from the transition. The run time was longer (up to nanoseconds) in the transition region due to the long relaxation time.

The structural changes were monitored by the specially developed animation program [6]. Input files for this were the coordinates and quaternions of every molecule in the cluster that were recorded during the MD run. Four different windows were seen simultaneously on the screen. The first showed a 3D-image of the cluster as a whole. The next showed the mean squared displacement (MSD) of the molecules belonging to a specific shell in the cluster. The MSD were calculated from:

$$\langle r^2(t)\rangle_j = \frac{1}{N_j}\sum_{i=1}^{N_j}[r_i(t_0+t) - r_i(t_0)]^2 \tag{4}$$

where N_j is the number of the molecules in the j-th shell. The shell radii (for the movie) correspond to the positions of the first, second, etc. neighbors in the bcc structure.

The third window showed the projection of the z-axis of every molecule onto the space frame, while the fourth window showed the displacement of the molecules.

3 Results

On heating above 120 K the molecules belonging to the different shells mixed, as in a fluid. Above 180 K, some of the molecules evaporated after a stage of surface melting. On cooling below the transition temperature, about 80–90 K for
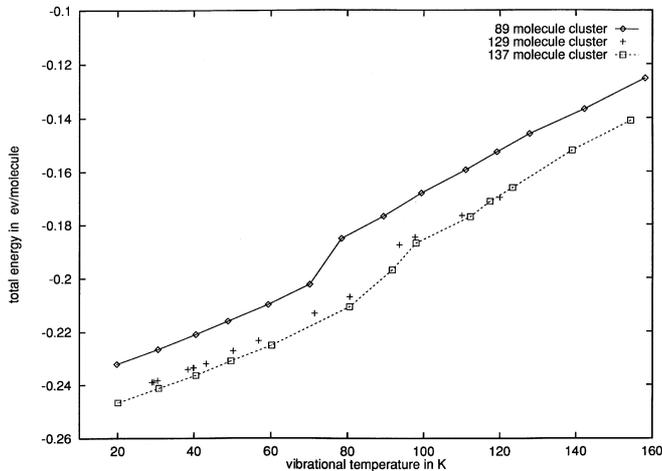
Fig. 1. The caloric curve $E\left(\langle T_{\mathrm{vib}}\rangle\right)$ for TeF$_6$ clusters of different sizes on cooling. The vibrational kinetic temperature is defined as $T_{\mathrm{vib}} = 2\langle E_{\mathrm{vib}}\rangle/3(N-1)k_{\mathrm{B}}$, where N is the number of molecules in the cluster, $\langle E_{\mathrm{vib}}\rangle$ is the average kinetic energy of the vibrational motion of the molecular center of masses, k_{B} is the Boltzmann constant
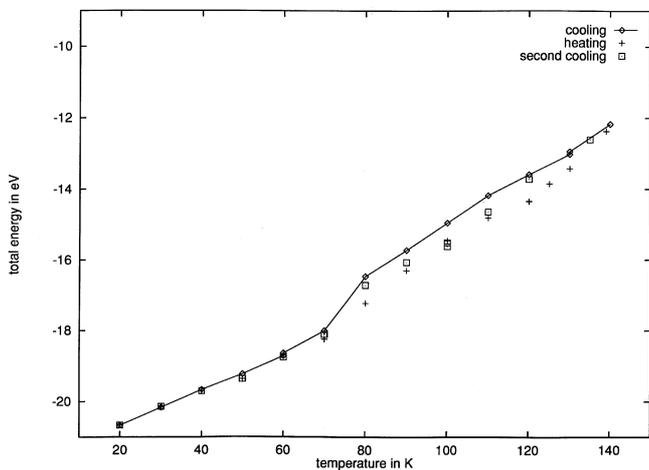

Fig. 2. The total energy, (2), of the 89-cluster is presented for different temperatures. Changes of the slope of the curve indicate a phase transition. The thermal history of the system controls the transition as it is seen from different behavior on cooling and heating

the studied cluster sizes, the molecules formed well distinguishable layers. In the vicinity of this transition, most of the molecules had grouped around two orientations in the space, having one axis properly aligned; this is discussed below (Figs. 4, 5).

What emerges from the simulations is the confirmation that structural phase transformation can be observed in a small molecular cluster that preferentially adopts the bulk structure. This is not the case for small atomic clusters. Figure 1 shows the caloric curve $E(T_{\mathrm{vib}})$ for 89, 129, and 137 molecule clusters. The jump at the transiton temperature, about 80–90 K, smooths for the larger clusters. This is an indication that the transition might be second-order [4]. In general, it is very difficult to prove that a phase transition is of a specific kind. The best one can do is to analyze as many properties as possible in the neighborhood of the phase transition [9].

To investigate whether the cluster memorizes its own thermal history and the influence of the temperature change rate, we have calculated the total energy of the 89- molecule cluster as a function of the temperature in a repeated cycle of cooling and heating (Fig. 2). The data presented in Fig. 2 were generated with thermal steps of 10 K. The system shows a reproducible pattern of behavior on heating, which differs from those for cooling, which show small variations. This implies that the apparent behavior of the phase transition can be controlled by the thermal preparation of the cluster, if it is done by insufficiently slow cooling.

The mean radial displacement computed from (4) shows that the energy of the lattice vibrations is much less than the energy of the jump in Fig. 3. However, the spontaneous re-orientation of some of the molecules (at least 65 %) changes the specific heat of the system, which reveals itself as a change in slope of the caloric curve. We shall see below that there are two possible orientations of the molecules. Orientational ordering motion couples [10] to the lattice vibrations and the result is distortion of the lattice structures [11].

From previous analysis [2, 3, 6] is known that the molecules librate at low temperatures. This is seen from the negative part of the angular velocity correlation functions [12]. In order to see how the transition influences the libration of the cluster we plot the magnitude of the total angular velocity $\bar{\omega}^s$ as a function of time in Fig. 3. The velocity $\bar{\omega}^s$ is calculated from $\bar{\omega}^s = \sum_{i=1}^{N} \bar{\omega}_i^s$, where $\bar{\omega}_i^s$ is the angular velocity of the i-th molecule in the space frame. The conversion between the space frame and the body frame is performed as follows:

$$\bar{\omega}^s = \hat{A}\bar{\omega}^b \tag{5}$$

where $\hat{A}$ is the rotational matrix expressed in terms of quaternions [12] and $\bar{\omega}^b$ is the angular velocity in the body frame.

The amplitude of the oscillations of the angular velocity depends on the temperature of the cluster and changes in time as well. The plots in Fig. 3a,b show the magnitude $|\bar{\omega}^s|$ and the z-component of the total angular velocity after 800 ps of evolution of the cluster at different temperatures. During that interval, not presented in the figure, the cluster was cooled in steps of 10 K from 160 K to 80 K. This last temperature was kept during the next 300 ps. The rapid decrease of the projected velocity at 1000 ps (the cluster was still at 80 K) signals a beginning of a phase transformation (the arrow in the figure). At that moment, the z-component (Fig. 3b) is almost zero. The amplitude of the oscillations increases in the next 100 ps (Fig. 3a,b) which testifies an alignment of the vectors of the angular velocity and coherent libration. The cluster is orientationally ordered. Further, another decrease of the angular velocity at 1400 ps denotes a beginning of another transformation. At this time the cluster temperature was about 40 K. The caloric curves (Fig. 1) do not show peculiarities at this temperature but the heat capacity calculated from fluctuation theory[13] should diverge; for these finite clusters, it shows a maximum. We are tempted to conclude that the magnitude of the total angular velocity might be more sensitive to the phase transitions than is the caloric curve.

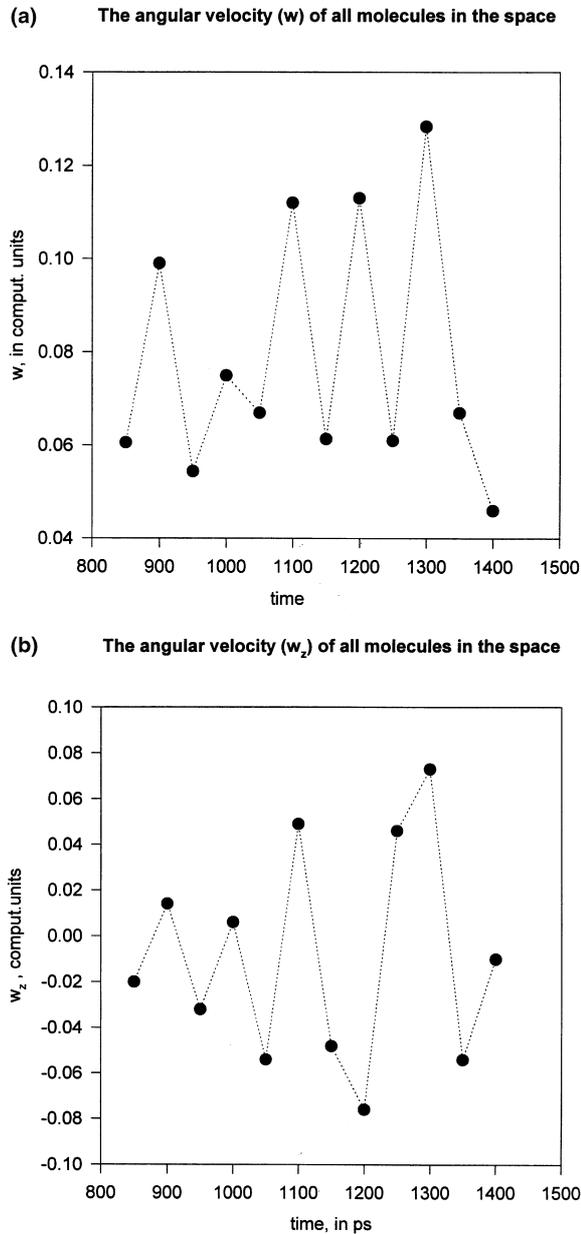The alignment of the vectors of the molecular libration detected during the phase transition implies a rotation Ω of

(a) The angular velocity (w) of all molecules in the space

(b) The angular velocity (w_z) of all molecules in the space

Fig. 3a,b. The angular velocity and its z-component of the molecules projected onto the space frame are shown as functions of time during cooling of the cluster. The magnitude oscillates between two values due to the libration of the molecules. **a** The magnitude of the angular velocity; **b** the z-component of the angular momentum in the space frame

the cluster as a whole due to the conservation of the total angular momentum of the system considered as composition of the set of molecules and the cluster as a whole:

$$\bar{L}_{\text{system}} = \text{const} = \bar{L}_{\text{cluster}} + \sum_{i=1}^{N} I\bar{\omega}_i^s \,, \tag{6}$$

where $\bar{L}_{\text{cluster}} = \hat{I}_{\text{cluster}}\Omega$ is the angular momentum of the cluster considered as a rigid body. The second term in (6) is the internal angular momentum of the system. Hence, depends only on the change of the magnitude of the total angular velocity, $\sum_{i=1}^{N} I\bar{\omega}_i^s$ if the tensor of inertia of the cluster $\hat{I}_{\text{cluster}}$ is approximately constant. We have mentioned already

that the molecule vibrate a little bit, hence no important redistribution of the cluster mass is expected. That is why we can assume that $\hat{I}_{\text{cluster}}$ is constant during the cluster evolution for a fixed N. The tensor $\hat{I}_{\text{cluster}}$ increases linearly with N. Thus the velocity Ω (6) approaches zero as $1/N$.

For small N, the overall rotation of the clusters induces a Coriolis force. The Coriolis force (fictitious) acts on every molecule with a mass m and a velocity $\bar{\nu} - 2m[\bar{\Omega}, \bar{\nu}]$. The effect of this action is a distortion of the molecular trajectory from that of a nonrotating cluster. We expect that one observable result of this effect will be a distortion of the diffraction patterns that is greater for smaller than for larger clusters. The influence of the Coriolis force disappears as $1/N$.

The effect we have found in molecular clusters can be seen in another class of small systems, although the reason for its appearance might be completely different. This possibly analogous phenomenon in the macroscopic world is the Einstein-de Haas effect: a ferromagnetic, very light sample rotates if it is surrounded by a magnetic field switching off and on. The cause of the rotation is the alignment of the internal magnetic moments of the constituent electrons. The rotation of the sample indicates the cooperative behavior of the electrons in addition to demonstrating the quantum nature of the magnetic moment. Obviously, correlated molecular interactions in orientational order-disorder phase transitions which cause alignment of the molecular axes are results of cooperative motion of the molecules. Let us emphasize that the alignment during the phase transition is more complicated than it is in a magnetic system.

The influence of an induced Coriolis force is observed in other finite-size systems as well, namely in atomic nuclei [15, 16] produced in heavy-ion reactions. The final nuclear state is highly excited, with a large angular momentum. As a result of the nuclear rotation, the spins of the constituent nucleons align along the rotational axes. In a sense, this is the reverse of the effect we have observed.

To find a quantitative description to supplement the qualitative representation of the angular velocity distribution, we have developed [14] a method for projecting the 3-dimensional distributions onto a 2-dimensional spherical (φ, θ) surface, in which the third of the Euler angles (ψ) is plotted as an 'oriented' cross. In such a way the 2-dimensional distributions contain the complete orientational information. A mesh covering the surface contains cells of equal area. The method is particularly efficient for the case of highly symmetrical molecules, for which it suffices to work in 1/8 of the space and yet retrieve the complete information. We apply the method to analyze the orientational distributions of the molecular axes of symmetry for a cluster of 89 TeF_6 molecules as functions of temperature.

Figure 4a confirms that the molecules are completely orientationally disordered at temperatures above the transition. On cooling, the cluster transforms to a more ordered phase at about 80 K, and at 70 most of the molecules have already aligned at least one of their rotational axes. The overall rotation of the cluster can be inferred from Fig. 5a,b.

From the equations of motion of the two spots observed in (φ, θ)-plane, one estimates the angular velocity $|\bar{\Omega}| = (d\theta/dt, d\varphi/dt, d\psi/dt)$. The frequencies of the cluster

(a)

89 cluster at T=120 K
almost isotropic distribution
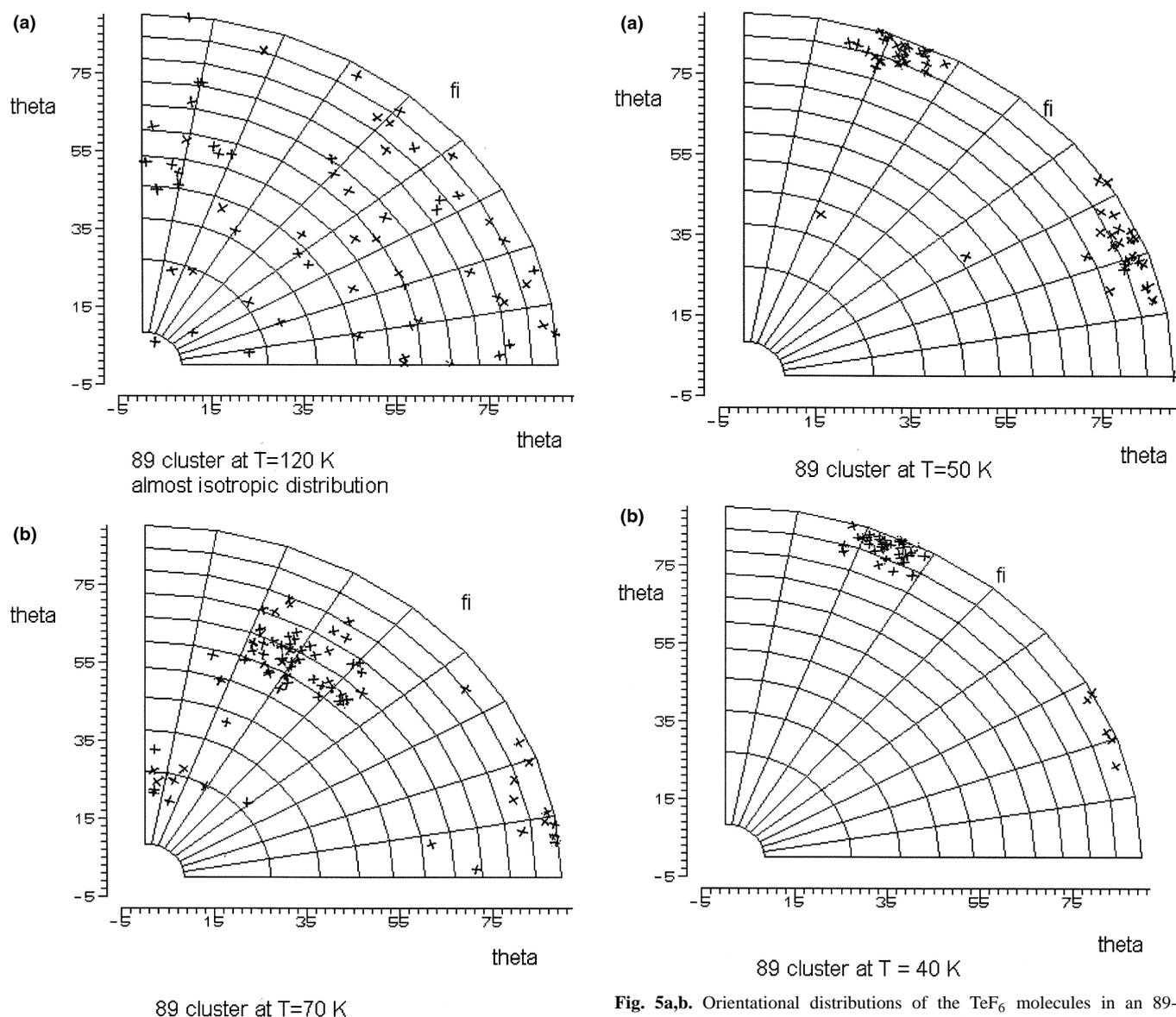
(b)

89 cluster at T=70 K

Fig. 4a,b. Distributions of the orientation of the molecular axes of an 89-molecule cluster: **a** Isotropic orientational distribution of the molecular axes of symmetry at $T = 120$ K (above the transition) in 2D spherical surface $\{\varphi, \theta\}$; the third Euler angle ψ is plotted as an oriented cross. **b** The distribution at $T = 70$ K (below the transition at 80 K); most of the molecules have already aligned their rotational axes. Note that the molecules forming a spot in a specific (φ, θ) orientation might have different orientations in the third direction, ψ

rotation $(d\psi/dt)$ and nutation $(d\theta/dt)$, and the molecular libration projected into the space $(\bar{\omega}^s)$ are size-dependent. The frequencies due to the Coriolis force $(d\psi/dt)$ and $(d\theta/dt)$ go to zero as $1/N$, while the libration frequency $(\bar{\omega}^s)$ depends on the surface contribution, $N^{-2/3}$.

4 Discussion

The investigation of the structural phase transitions in small clusters of tellurium hexafluoride indicates that they can be considered as a precursor of the second order phase changes in bulk. A result of phase changes in a finite molecular clus-

(a)

89 cluster at T=50 K

(b)

89 cluster at T = 40 K

Fig. 5a,b. Orientational distributions of the TeF$_6$ molecules in an 89-molecule cluster at low temperatures. **a** At $T = 50$ K, equal population of the two orientations is seen as it is expected for large clusters. A comparison with the distribution at $T = 70$ K indicates a rotation of the cluster as a whole along the z-axes. **b** At $T = 40$ K a different population of the two orientations appears, due to a new structural transformation

ter is a spontaneous alignment of the rotational axes of the molecules in the cluster. The alignment causes a rotation of the cluster as a whole because of the conservation of angular momentum of the system composed of the cluster as whole and the set of molecules. The rotation of the cluster as a whole modulates the spectrum of the density of states. It is necessary to estimate its angular velocity in order to compute the magnitude of the Cotiols force and to estimate the actual distortions of the lattice. The Coriolis force vanishes as $1/N$ and is not important for large clusters. Small molecular clusters are those which present a variety of interesting effects during phase transition.

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