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A Simple Lennard-Jones Model for Computer Simulation of Conformational Disorder in Molecular Crystals

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A simple generalized model is proposed to describe the phenomenon of conformational disordering in molecular crystals. The model represents a classical two-dimensional system of "conformationally flexible" particles interacting through a modified, orientation- and conformation-dependent Lennard-Jones potential. Monte Carlo simulation of the phase behavior of the model system shows that the model is quite adequate to describe all essential features inherent in the transitions to the conformationally disordered state.

Keywords: CONDIS transition, 2 dim-LJ system, internal degree of freedom

1. INTRODUCTION

Polymorphic transitions to the conformationally disordered (CONDIS) crystal state represent a widely occurring phenomenon in organic molecular crystals, particularly in crystalline polymers. According to Wunderlich,[1] CONDIS crystals are classified with mesophases, as also are plastic and liquid crystals. The CONDIS state is typical of crystals composed of flexible molecules, capable of taking several distinct stable conformations. At low temperatures, the molecules are crystallized into a completely ordered packing of identical conformers. (Usually, this is the most energetically favorable conformer, although it is not necessary from the theoretical point of view). With increasing temperature, the conformational degrees of freedom are liberated, and the other, higher-energy conformers appear. In the CONDIS state, the system represents a dynamic mixture of different conformers; it loses the conformational order, while still retains a translational and orientational long-range order in the arrangement of "conformationally averaged" molecules.

Crystallographically, a CONDIS crystal can be defined as a crystal in which symmetrically equivalent lattice sites are occupied by conformationally distinct molecules. (By comparison, in plastic crystals, crystallographically equivalent positions are occupied by orientationally distinct molecules in the same conformation.)

The available experimental data show that the ordered crystal—CONDIS crystal transitions usually involve an increase in volume. A rise in crystal symmetry is also typical. (For example, the CONDIS transition in the polyethylene (PE) crystal is accompanied by the change in symmetry from the orthorhombic to hexagonal one corresponding to the close packing of cylinders.) When a CONDIS crystal melts, the distribution of its constituent molecules over conformations remains practically unchanged, i.e., the concentration of "defective" conformers in the resulting melt is practically the same as in the original crystal.[2] For this reason, CONDIS crystals are sometimes referred to as "defect-saturated."

An obvious way of simulating a CONDIS transition would be to consider a particular molecular crystal (say, PE), to describe the intra- and intermolecular interactions with an appropriate atomistic forcefield,[3] and to resort to the powerful molecular dynamics (MD) or Monte Carlo (MC) techniques to simulate the behavior of the crystal as a function of temperature. Such an obvious approach, however, involves a serious problem associated with the "pseudo-non-ergodicity"[4] of the relevant configurational space. As far as the crystal state is concerned, the ordered and CONDIS states in the configurational space may well be separated by high energy barriers, so that it will be practically impossible to reach the CONDIS state using MD or MC chains of a finite length. This is particularly true of atomistic models because of the extremely high dimensionality of the relevant configurational space. Our preliminary MC experiments with atomistic models of PE showed that at densities corresponding to the solid state it is indeed impossible to leave the "pocket" of the configurational space corresponding to the ordered starting configurations.

The only published attempt at computer simulation of a CONDIS transition is the one undertaken by Sumpter *et al.*[5] for the PE crystal. The temperature behavior of the crystal was investigated using the MD method and an atomistic forcefield. The systems considered involved up to 37 mobile PE chains, and the trajectories generated were up to 30 ps. As the temperature was increased, the authors[5] did observe the appearance of conformational defects in the PE chains. However, despite a tremendous computational effort and a comparatively large size of the model system, no cooperative phenomena were detected and no changes in the molecular packing and crystal symmetry were reported. It seems that the simulation of the cooperative phenomena would require much larger systems and much longer times, provided, of course, that the ergodic problems could be overcome at all.

In view of the computational difficulties involved in simulation of the CONDIS state using atomistic forcefields, a need arises for simplified semiquantitative models, which would reflect only the dominant properties of the systems exhibiting the CONDIS state. In this work we propose such a simplified model and investigate its temperature behavior to see whether it is capable of simulating a CONDIS transition.

2. MODEL

To construct a simple generalized model for simulating the CONDIS state, let us first analyze what are the dominant features necessarily present in the crystals

experiencing CONDIS transitions. As any molecular crystal, a CONDIS crystal represents a system of particles interacting via a certain intermolecular potential. The distinguishing feature of CONDIS crystals is that their constituent molecules are necessarily flexible and can assume at least two stable conformations. The flexibility means that each molecule has at least one internal degree of freedom, whose variation affects both the intramolecular energy and the form of the intermolecular interaction potential. The existence of stable conformers implies, in its turn, that the dependence of the intramolecular energy on the internal degree of freedom must involve at least two minima separated by a barrier.

In constructing our model, it is reasonable to take, as the starting point, a two-dimensional Lennard-Jones (LJ) system, which is known to be capable of simulating the most general phenomena in the phase behavior of the matter (such as crystallization, melting, and evaporation). With polymers, the use of the two-dimensional representation is justified by the fact that the conformation-induced changes in the arrangement of the chains occur mostly in the planes perpendicular to the chain axes, while the phenomena occurring in the third dimension, such as the chain shortening, seem to be of minor importance. In a sense, the two-dimensional representation of a CONDIS transition may be regarded as a simulation of the situation that occurs in polymeric CONDIS crystals in the planes perpendicular to the axes.

To adapt the LJ system to our particular case, let us assume that each particle i in the system has an internal or "conformational" degree of freedom, ξ_i, which varies in the range from 0 to 1. Let us also ascribe a "conformational energy" $V(\xi_i)$ to each particle i. The particular dependence used in this work for $V(\xi_i)$ is shown in Figure 1. This is a fifth-order power dependence,

$$V = A_5\xi^5 + A_4\xi^4 + A_3\xi^3 + A_2\xi^2, \tag{1}$$

with minima at $\xi = 0$ and 1, and a maximum at $\xi = 0.5$. The coefficients of the polynomial are chosen so that the energy difference ΔE and the barrier B are equal to some prescribed values. (The additional constraints needed to determine all the four unknown coefficients in Equation (1) are $dV/d\xi = 0$ at $\xi = 0.5$ and 1). So, ΔE and B are two first parameters of the model.

The next step is to make the shape of the initially symmetrical LJ potential,

$$\varphi_{ij} = \varepsilon_{ij}[(\delta_{ij}/\delta_{ij}^0)^{-12} - 2(\delta_{ij}/\delta_{ij}^0)^{-6}], \tag{2}$$

dependent on the mutual orientation and conformations of the interacting molecules. This can be accomplished by incorporating an orientational and conformational dependence in the equilibrium distance δ_{ij}^0 and depth ε_{ij} of the potential. For the equilibrium distance, this is done by writing δ_{ij}^0 in the form of the geometrical mean[3]

$$\delta_{ij}^0 = [(2\rho_i^0)(2\rho_j^0)]^{1/2} \tag{3}$$

and then assuming that the equilibrium molecular radii, ρ_i^0 and ρ_j^0, depend on the conformation and mutual orientation of the interacting molecules.

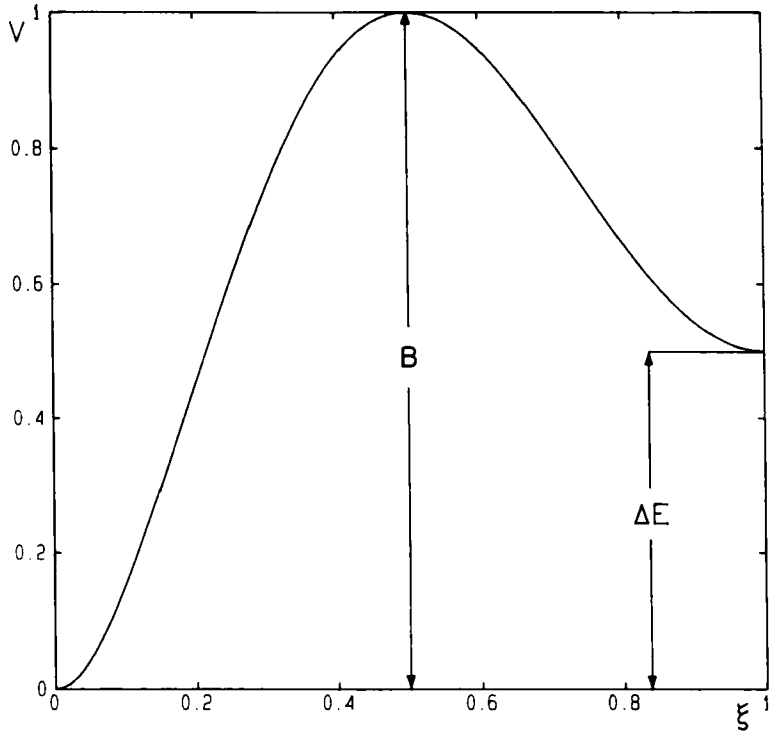

FIGURE 1 The dependence of the intramolecular energy V on the conformational parameter ξ.

The angular dependence for ρ^0 is chosen such that $\rho^0(\theta)$ forms an ellipsis around the molecular center (see Figure 2 for the definition of θ). The shape of the ellipsis depends on the relevant conformational parameter ξ in such a way that at $\xi = 0$ the ellipsis degenerates to a circle, and then, with increasing ξ, the ellipsis becomes more and more extended until it reaches a certain limiting allowable ellipticity characterized by a constant $\Gamma < 1$. As a measure of ellipticity, it is convenient to use parameter γ which varies from Γ to 1 and defines the short and long radii of the ellipsis, r and R (see Figure 2), by the relations

$$r = R_0\gamma, \qquad R = R_0/\gamma, \qquad \gamma = (r/R)^{1/2}, \tag{4}$$

where R_0 is a constant.

The explicit relationship between γ and ξ may then be set to be

$$\gamma = 1 - (1 - \Gamma)\xi. \tag{5}$$

That is, at $\xi = 0$, $\gamma = 1$ and $r = R = R_0$, so that the ellipsis degenerates to a circle of radius R_0; at $\xi = 1$, $\gamma = \Gamma$ and $(r/R)^{1/2} = \Gamma$, so that ellipsis has the greatest

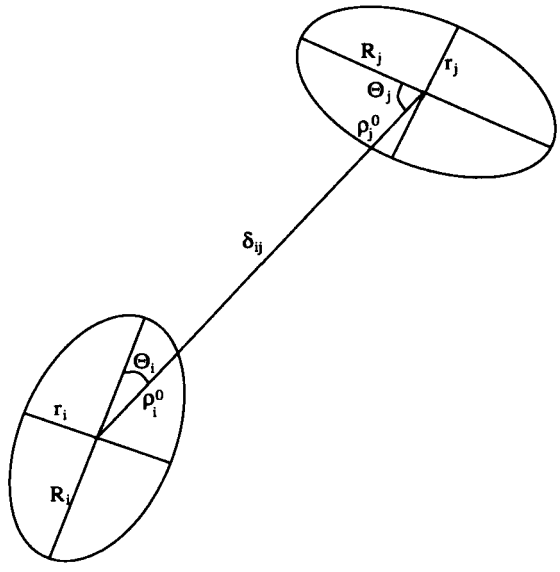

FIGURE 2 The definition of the geometrical parameters of the interaction potential φ.

allowed extension. It is noteworthy that with the above definitions, any variation in ξ leaves the ellipsis' area unchanged,

$$\pi Rr = \pi R_0^2, \tag{6}$$

and equal to the area of a circle of radius R_0 (hereinafter, the "equivalent circle").

With the above definitions, the analytical expression for ρ^0 can be readily shown to be

$$(\rho^0)^2 = R_0^2\gamma^2/[\cos^2\theta(\gamma^4 - 1) + 1] \tag{7}$$

so that

$$\begin{aligned}(\delta_{ij}^0)^2 &= \frac{4\,R_0^2\gamma_i\gamma_j}{[\cos^2\theta_i(\gamma_i^4 - 1) + 1]^{1/2}[\cos^2\theta_j(\gamma_j^4 - 1) + 1]^{1/2}} \\ &= D_0^2\alpha,\end{aligned} \tag{8}$$

where α contains all the angular and conformational dependence, and $D_0 = 2R_0$, the diameter of the equivalent circle or the equilibrium separation between the centers of two circles. It is reasonable to take D_0 as the unit of distance and to measure all distances in the model system in terms of D_0.

For the potential depth ε_{ij}, the angular and conformational dependence is reasonable to take in the form

$$\varepsilon_{ij} = \varepsilon_0 R_0^2/\rho_i^0\rho_j^0 = \varepsilon_0/\alpha. \tag{9}$$

That is, if one approaches the ellipsis on its wide side, the potential minimum is deep, and it is shallow in the case of the narrow side. This reflects the fact that the interaction potential of two organic molecules is roughly proportional to the size of each molecule in the direction of interaction. With the above choice, $\varepsilon_{ij} = \varepsilon_0$ if both interacting molecules are in the circular conformation. If they are ellipses with the largest allowable ellipticity, then $\varepsilon_{ij} = \varepsilon_0 \Gamma^2$ for the linear configuration (the weakest interaction), $\varepsilon_{ij} = \varepsilon_0/\Gamma^2$ for the parallel configuration (the strongest interaction), and $\varepsilon_{ij} = \varepsilon_0$ for the perpendicular (T-shaped) configuration. As with D_0, it is reasonable to take ε_0 as the unit of energy.

Substituting (8) and (9) into (2) and assuming D_0 and ε_0 equal to unity, we obtain the final form of the interaction potential[6]

$$\varphi_{ij} = \alpha^5 \delta_{ij}^{-12} - 2\alpha^2 \delta_{ij}^{-6}. \tag{10}$$

To summarize, the generalized model suggested in this section represents a classical two-dimensional system of LJ particles, each possessing one internal or conformational degree of freedom ξ ranging from 0 to 1. Associated with this degree of freedom is an internal or conformational energy $V(\xi)$ characterized by two minima at the two limiting values of ξ. The intermolecular interaction potential gradually changes its symmetry from circular to elliptical on variation of ξ from 0 to 1. Altogether, the model involves three parameters: ΔE, the energy difference between the circular and elliptical and conformers; B, the barrier separating the internal energy minima; and Γ, the square root of the lowest allowable ratio of the short and long ellipsis' radii. The latter parameter, Γ, characterizes the extent of the geometrical changes occurring on going from one conformer to the other. So, all the three parameters have a clear physical meaning and can be related, in a more or less straightforward way, to the properties of a real molecule. (In essence, the model involves only two significant parameters, ΔE and Γ, because the barrier B does not appear to be very important in calculations of the equilibrium structure and properties).

3. MONTE CARLO TECHNIQUE

The technique used was a standard NVT-ensemble technique[4] involving periodic boundary conditions and a cyclic procedure for molecular displacements. For the number of particles in the periodic box, N, several discrete values were tried between 36 and 336. Most calculations were conducted with $N = 36$. In the high- and mid-density regions, the effect of increasing the number of particles was negligible: an $N = 36$ system showed practically the same structure and thermodynamic properties as a system containing as many as 336 particles. The size of the system became, however, important in the solid-liquid transition region. Here small systems tended to exaggerate the stability of the solid state because of an extra periodicity imposed upon the system by the periodic boundary conditions. This extra periodicity was not so important for the ordered crystal—CONDIS crystal transitions because the system did not lose its translational symmetry.

A typical MC chain involved $3 \cdot 10^5$ cycles, that is $N\, 3 \cdot 10^5 = 10^7$ to 10^8 random configurations. The first $1 \cdot 10^5$ cycles were only used to bring the system to a more or less equilibrium state and were not included in the averaging. Each trial configuration of the model system was generated by changing the translational, orientational, and conformational coordinates of a particle at a time. The maximum single step displacements for the orientational and conformational degrees of freedom were chosen so as to results in the same linear shift of the ellipses end, as produced by the maximum translational displacement. This latter was chosen so as to give the usual 50:50 acceptance ratio for the accepted and rejected moves.

The structure and phase state of the system were analyzed using the following distribution functions:

$\rho(\delta)$ the radial distribution function, i.e., the probability of finding a molecule at a distance δ from another molecule.

$a(z)$ the angular distribution of a molecule's nearest neighbors. To calculate $a(z)$ during the MC run, an arbitrary molecule was selected and its six closest neighbors were found. Then the molecule at the center was joined by straight lines with its neighbors to give six virtual bonds. One arbitrary bond was taken as a reference one and the angles z between this bond and the other five were calculated and averaged over the chain.

$c(\theta)$ the angular correlation function characterizing the distribution of mutual orientations of neighboring molecules. To calculate $c(\theta)$, an arbitrary molecule and its six neighbors were selected. Then the angles formed by the long molecular axes of the center molecule and the neighboring ones were calculated and averaged over the chain. Each contribution from molecules i and j was given a weight $\xi_i\xi_j$, so that the contribution was the greater, the more elliptical were the molecules.

$o(z)$ the orientational distribution of molecules, defined as the probability density of finding a molecule whose long axis forms an angle z with the x-axis of the periodic box. On calculating $o(z)$, each contribution from molecule i was given a weight ξ_i.

$p(\xi)$ the distribution of molecules over conformations, i.e., the probability density of finding a molecule with a conformational parameter equal to ξ.

Considering the problem of non-ergodicity,[4] which might well arise as far as the solid state was concerned, much attention was given to check if the equilibrium structure and thermodynamic quantities resulting from MC calculations depend on the starting configuration used to initiate the random walk. In doubtful cases, the results were recalculated using different starting configurations. The set of starting configurations used included a hexagonal close packing of circles with a random orientation of the molecular axes, and three distinct regular packings of ellipses with $\xi = 1$. Also used as a starting configuration was a packing of ellipses ($\xi = 1$) corresponding to the minimum static potential energy. A fragment of this packing is depicted in Figure 3. The unit cell of the minimum energy structure contains three symmetrically independent molecules, whose long axes form angles 0, 120, and $-120°$ with the x-axis. An essential feature of the structure is that the centers of the two molecules inside the unit cell do not coincide with the centers of the

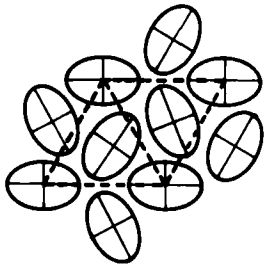

FIGURE 3 A fragment of the structure corresponding to the minimum energy packing of ellipses with $\gamma = \Gamma$.

respective triangles (see Figure 3), so that the structure does not possess a hexagonal symmetry even with respect to the molecular centers.

RESULTS AND DISCUSSION

In our studies of the equilibrium structure and phase behavior of the model system, the barrier B was fixed at $B = 1$, while ΔE and Γ^2 were varied in the ranges -1 to $+1$ and 0.58 to 1, respectively. The temperature range studied was from 0.1 to 1 (hereinafter, the temperature is expressed in dimensionless reduced units as kT/ε_0). The range of volumes V was typically from 0.7 to 1.2, when expressed in reduced units as the actual specific volume related to the specific volume of the hexagonal close packing of circles. (In two dimensions, V is an area, but we will refer to it as a "volume" to retain correspondence to the conventional thermodynamic nomenclature). Formally, our analysis represented a four-dimensional problem, since it involved a total of four variable parameters: V, T, ΔE, and Γ. In this work we discuss some selected cross sections through the four-dimensional parameter space, which best illustrate the basic properties of our model system.

Figure 4 shows the calculated pressure-volume isotherm (i.e., the equation of state) for $\Delta E = -0.1$, $\Gamma^2 = 0.64$, and $T = 0.5$. Also shown is the volume dependence of the ensemble average $\langle\xi\rangle$ 100, which characterizes the equilibrium composition of the system in terms of the average percentage of ellipses. It is seen that the equation of state comprises three well defined branches. A typical configuration of particles in the high-density branch is shown in Figure 5. By comparing with Figure 3, one can see that this is essentially the lowest energy configuration slightly disturbed by thermal motion. The deviation from the hexagonal symmetry shows itself as a satellite in the first peak of the radial distribution function $\rho(\delta)$, which is presented in Figure 6 together with the other distribution functions. Similar satellites, resulting from the deviation from the exact hexagonal symmetry, are seen in the angular distribution $a(z)$. From the conformational distribution $p(\xi)$, one can see that most molecules in the system are ellipses. The averaged conformational parameter $\langle\xi\rangle$ in the high-density range is about 0.9; so, the molecules strongly prefer the elliptical conformation.

With decreasing density, the percentage of ellipses first slightly decreases and then, at a volume of about 0.81, there occurs a drop in $\langle\xi\rangle$ (see Figure 4): nearly

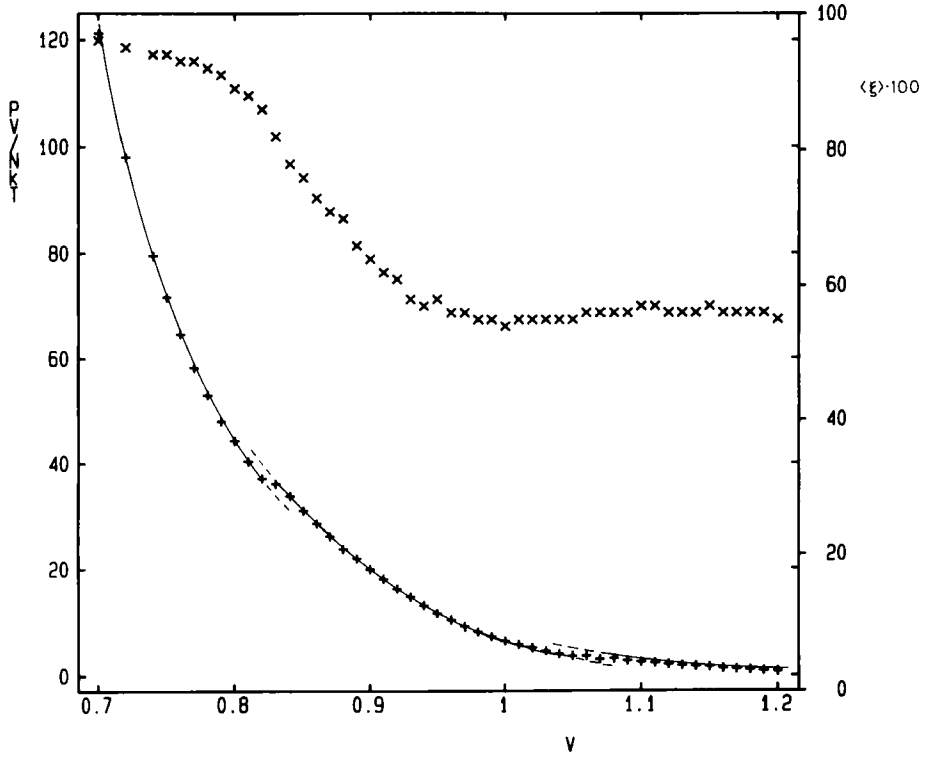

FIGURE 4 The equation of state (+) and average conformational parameter $\langle \xi \rangle$ (×) for $\Delta E = -0.1$, $\Gamma^2 = 0.64$, and $T = 0.5$.

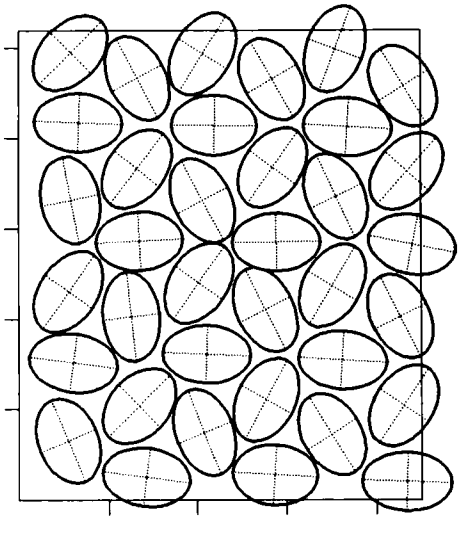

FIGURE 5 A typical snapshot from the structure of the high-density phase.

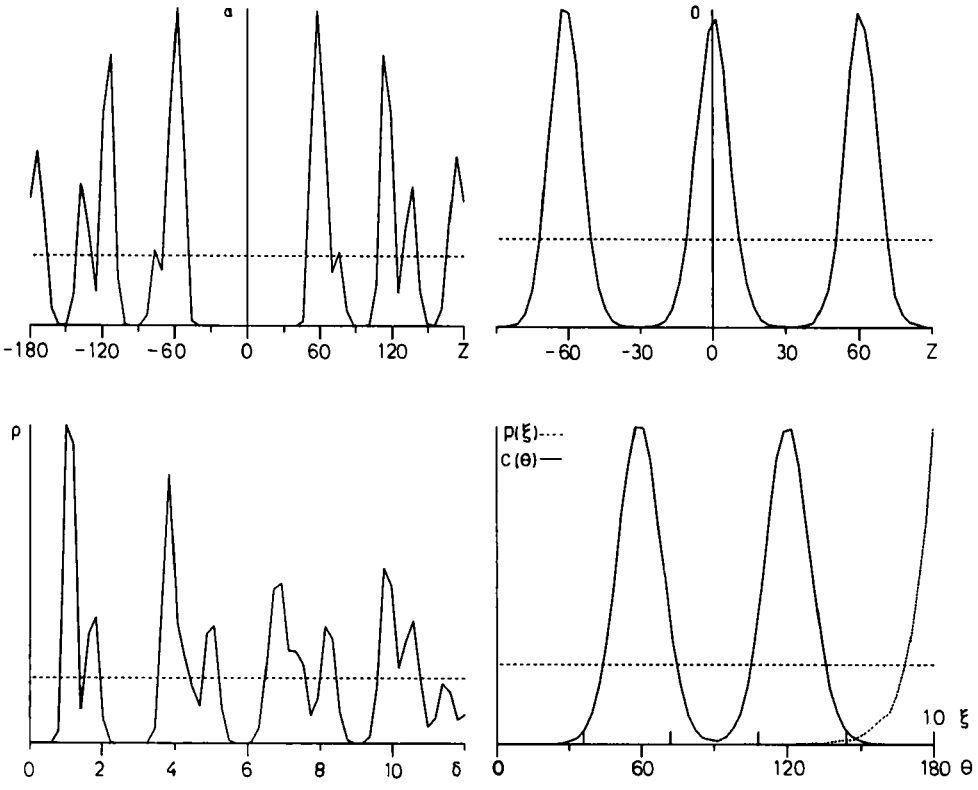

FIGURE 6 The distribution functions of the high-density phase ($V = 0.72$))

a half of the particles convert to circles. Turning to the equation of state, one can see that this drop corresponds to the transition from the high-density branch to the next, mid-density one. The kink in the PV curve, observed in the translational region, indicates to a rise in volume.

A typical mid-density configuration shown in Figure 7 represents a mixture of ellipses and circles. As follows from the presence of zero-density gaps in $\rho(\delta)$ (Figure 8), the system remains solid. Moreover, even some orientational order in the arrangement of the ellipses still exists, as it is seen from the presence of three well-defined peaks in $o(z)$. At the same time, the characteristic satellites in $\rho(\delta)$ and $a(z)$ disappear, and the most preferable orientations of ellipses near 0, 120, and $-120°$ are occupied at random. As a result, the lattice of "averaged molecules," as it could be seen in an x-ray diffusion experiment, assumes an ideal hexagonal symmetry. The sites in this hexagonal lattice are occupied, with nearly equal probabilities, by different conformers: circles and ellipses.

Thus the behavior of our model system shows all essential features inherent in the CONDIS transitions:

(1) The transition is induced by the appearance of conformationally distinct particles in the system;
(2) The system retains translational and orientational order;

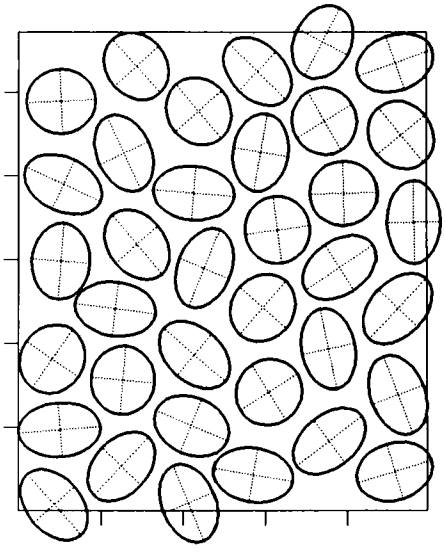

FIGURE 7 A typical snapshot from the structure of the mid-density (CONDIS) phase.

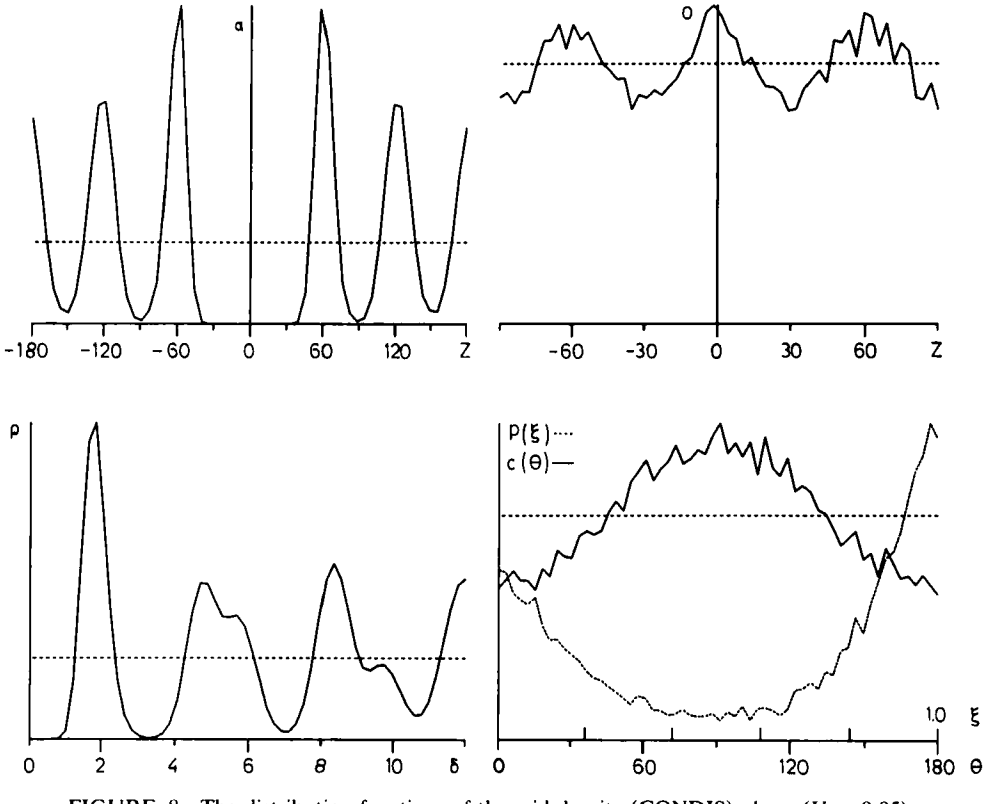

FIGURE 8 The distribution functions of the mid-density (CONDIS) phase (V = 0.95).

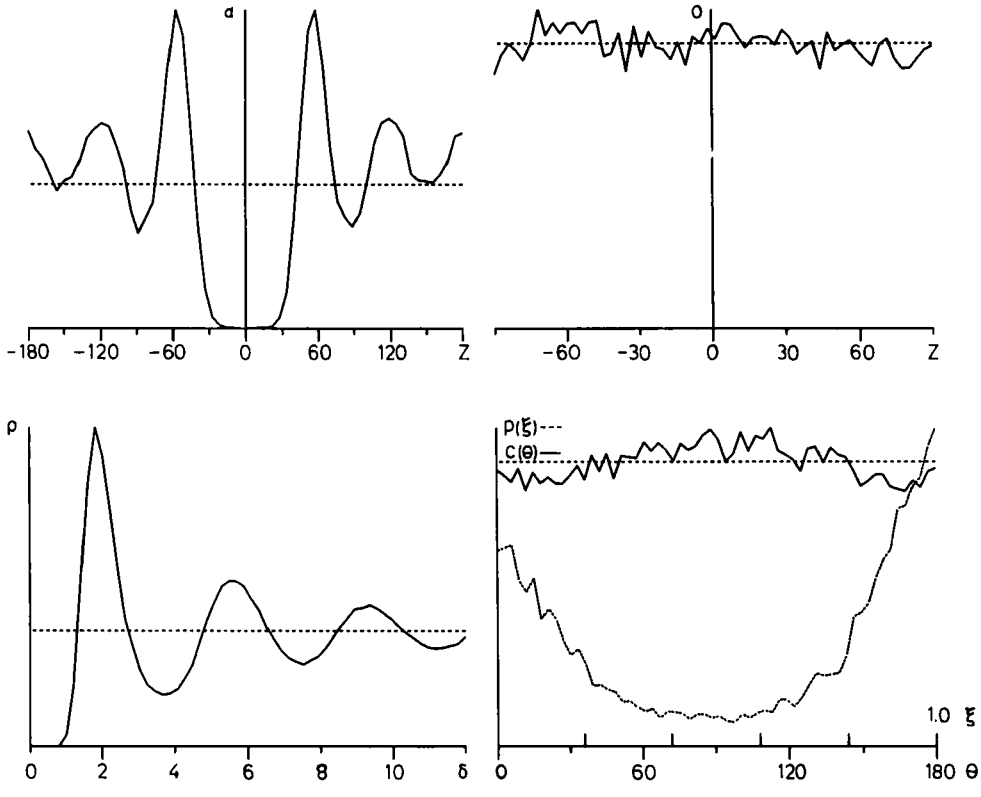

FIGURE 9 The distribution functions of the low-density (liquid) phase ($V = 1.16$).

(3) The transition involves a rise in crystal symmetry;
(4) The transition is accompanied by an increase in volume;
(5) The resulting crystal phase is conformationally disordered, inasmuch as the crystallography equivalent lattice sites in this structure are occupied by distinct conformers.

It is useful to give a simplified qualitative analysis of the driving forces behind the observed CONDIS transition. From the viewpoint of the static potential energy, a regular packing of ellipses is obviously preferable over a common packing of ellipses and circles together. This preference should be particularly strong in the high-density region, in which a common packing of ellipses and circles should necessarily involve intermolecular overlaps and repulsions because of irregularities in the packing. That is why we observe only ellipses in the high-density region.

The conformational energy, too, favors a system of pure ellipses, because in our particular case the parameter ΔE is assumed to be negative.

The only contribution to the free energy, which promotes the appearance of circles is the entropy. This is quite clear because the entropy should favor a mixture of distinct conformers even for combinatorial reasons alone.

With decreasing density, the difference in the potential packing energy between the system of ellipses and a mixture of ellipses and circles should obviously decrease

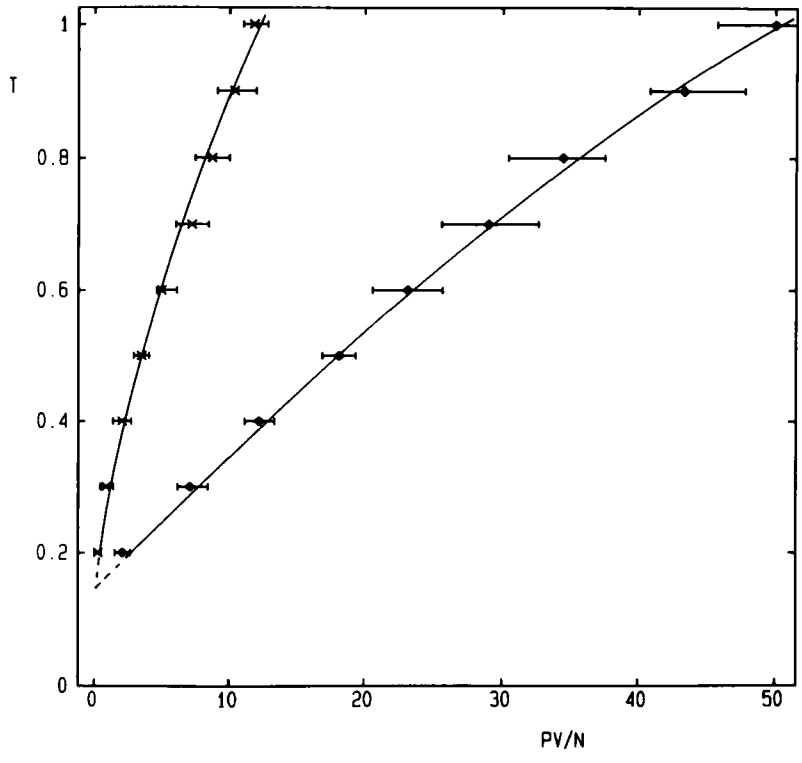

FIGURE 10 The phase diagram of the model system for $\Delta E = -0.1$, $\Gamma^2 = 0.64$.

because of relaxation of the unfavorable contacts in the lattice of the mixed system. As a result, the role of entropy increases and the mixed CONDIS system becomes more favorable.

Turning to the low-density branch of the equation of state, one can see from Figure 9 that the zero-density gaps in $\rho(\delta)$ and $a(z)$ are filled in, so that the distribution functions become typical of liquids. No preferential orientation of molecules can be seen from $o(z)$. Thus, the low-density branch in the equation of state can be associated with the liquid state. Comparing the conformational distribution functions $p(\xi)$ in Figures 8, 9 and looking at the behavior of $\langle\xi\rangle$ in Figure 6, one can also see that the melting has practically no effect on the distribution of molecules over conformations. This is again in agreement with experimental evidence.[2]

The temperature-pressure behavior of the model system can be seen from the phase diagram presented in Figure 10. With increasing pressure, the CONDIS transition temperature increases, as it is usually observed with real systems. The melting point also rises, and at a higher rate. The latter fact suggests that the two relevant phase boundaries should intersect one another at some T_t, so that below T_t the model system will exhibit a straightforward transition from an ordered crystal to melt. Unfortunately, for the particular set of model parameters ΔE and Γ, the expected T_t refers to too low temperatures, at which the MC method fails because of the ergodic problems.

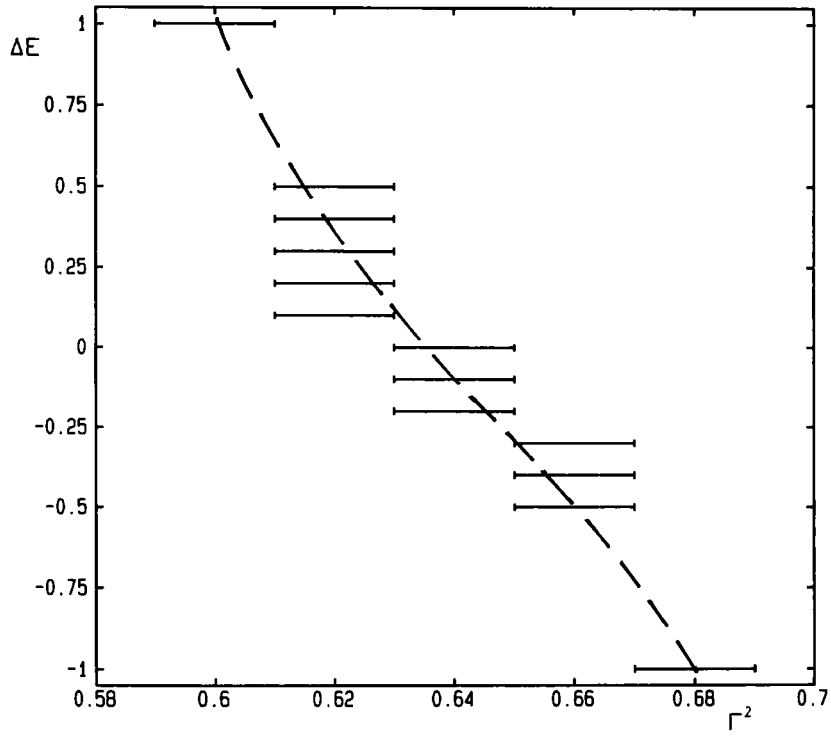

FIGURE 11 The phase behavior of the system as a function of ΔE and Γ^2 at $T = 0.4$.

An important advantage of our generalized model over a structure-related model is that it allows continuous variation in the model parameters to be made. In doing so, one can relate the phase behavior of the system to its inherent properties and, eventually, understand the factors responsible for the CONDIS transition.

Figure 11 gives an idea of the dependence of the phase behavior of the system on the model parameters ΔE and Γ at $T = 0.4$. The broken line through the bars separates a two-transition region, in which the melting is necessarily preceded by a CONDIS transition, from a single-transition region, in which the ordered crystal goes into the melt in a straightforward way. The width of the bars reflects the uncertainty involved in location of the corresponding separation points.

Let us fix Γ^2 at some selected value, say 0.64, and analyze the phase behavior of the system as a function of ΔE, starting from the already discussed value $\Delta E = -0.1$. When ΔE goes to positive values, the phase behavior remains the same. Moreover, the kinks in the equation of state become more pronounced (see Figure 12 for $\Delta E = 0.5$). The ordered crystal-CONDIS crystal transition occurs at lower volumes and becomes sharper. The reason is obvious: aside from the entropic preference, there appears an additional factor, the conformational preference of circles ($\Delta E > 0$), which promotes the formation of a mixed system. (Properly speaking, the case of a positive ΔE is somewhat artificial, because the new conformers appearing in real CONDIS crystals are usually higher-energy ones.)

By contrast, when ΔE is set to be more and more negative, the CONDIS tran-

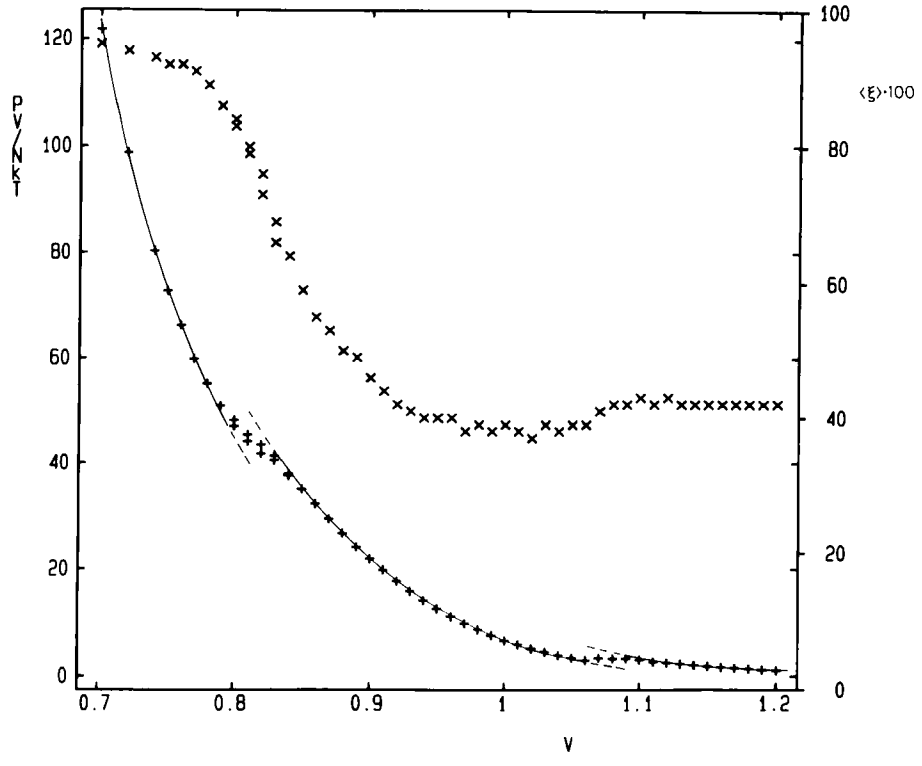

FIGURE 12 The equation of state (+) and average conformational parameter ⟨ξ⟩ (×) for $\Delta E = 0.5$, $\Gamma^2 = 0.64$, and $T = 0.5$.

sition becomes less and less clearly defined and, eventually, disappears at all. Starting from $\Delta E = -0.3$ the ordered crystal goes into the melt in a straightforward way. Again, the reason is clear: with large negative ΔE, the energetic preference for ellipses is so great that it cannot be compensated for by the entropy increase due to the conformational disordering alone. As a result, the crystal remains ordered and melts before it could experience a CONDIS transition.

Thus, the analysis of the effect of ΔE on the phase behavior of the model system shows that the difference in conformational energy between possible molecular conformers of a substance should not be too large for the substance to undergo a CONDIS transition. This correlates well with the experience that different conformers observed in real CONDIS crystals are generally close in energy.

As seen from Figure 11, the effect of Γ on the phase behavior of the system is opposite to the above-discussed effect of ΔE: an increase in Γ is equivalent to a decrease in ΔE, so that the CONDIS region in the phase diagram disappears when Γ becomes too small. This means, again in agreement with the experimental experience, that the changes in molecule geometry, involved in a CONDIS transition, should not be too large for the transition to occur.

To conclude, despite the extreme simplicity of the suggested generalized model, it is capable of simulating the most important phenomena involved in CONDIS transitions. Moreover, the model provides quantitative estimates for the changes

in molecular geometry and conformational energy, that are critical for the existence of the CONDIS state. These estimates appear to be of great utility in interpreting the phase behavior of real CONDIS systems. Although the model was used within the framework of the MC method, it can be employed in MD calculations as well, to study the general aspects of dynamic phenomena involved in CONDIS transitions.

References

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