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A Computer Simulation Study of Local Arrangements in Disordered Molecular Crystals

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Abstract

Local molecular arrangements have been generated with the help of Monte Carlo computer simulation using experimentally measured short-range-order parameters in two isostructural (monoclinic) isomers of dibromodimethyldiethylbenzene. The computer program was based on the GC concept of Gehlen & Cohen [*Phys. Rev. A* (1965), **139**, 844-855] modified for use with molecular crystals. It is seen that the atomic contact distances play an important role and the first nine short-range-order parameters were required to obtain a reliable picture of the structure of the disordered molecular crystal. Microstructures for the two isomers were found to be very similar.

1. Introduction

In recent publications (Welberry, Jones & Epstein, 1982; Epstein & Welberry, 1983; Welberry & Siripitayananon, 1986, 1987; Khanna & Welberry, 1987) we have described our interest in the study of disordered molecular crystals and the development of methods for recording and analysing diffuse X-ray scattering data. Recently we have also carried out a computer simulation study of molecular size effect in two isomers of dibromodiethyldimethylbenzene (BEMB1 and BEMB2) (Khanna & Welberry, 1990). The average crystal structures of both these compounds were reported by Wood, Welberry & Puza (1984). These compounds were found to be isostructural (monoclinic) but were disordered. The disorder arose because each molecule was able to take up either of the two different orientations at each molecular site (see Fig. 1). The methyl and the bromine atomic sites are disordered while the remaining diethylbenzene fragment of the molecule remains well ordered. In this paper we present a computer simulation study of the microstructure associated with the local order in BEMB1 and BEMB2.

From the diffuse scattering experiment one obtains the information about the pair correlation function α_{lmn} for all intermolecular vectors within a given neighbourhood of a particular molecule. α_{lmn} is defined as $(1-P_{lmn}/m_B)$ or $(1-P_{lmn}/m_A)$ where P_{lmn} is the conditional probability of finding a B-type molecule at a site lmn provided there is an A-type molecule at the local origin. m_A and m_B are the fractional site occupancies. It is not easy to visualize the microstructural details from the observed order parameter. For binary alloys, there have been many attempts (Gehlen & Cohen, 1965; Williams, 1976; Gragg, 1970) to generate the local microstructure from a set of order parameters using a digital computer. Though the resulting structure is not unique, there has been considerable empirical evidence (Gragg, Bardhan & Cohen, 1971) indicating it to be a very good statistical representation. In this paper, we have extended the basic features of binary alloy computer simulation to disordered molecular crystals.

2. Local molecular arrangements

The computer program used here is based on the GC concept (Gehlen & Cohen, 1965) modified for use with molecular crystals. We first point out the basic differences between the cubic binary alloys, for which the GC-type simulation has been conventionally used, and disordered molecular crystals. There are two types of distances to be considered for molecular crystals: one from the centre of mass (CM) of one

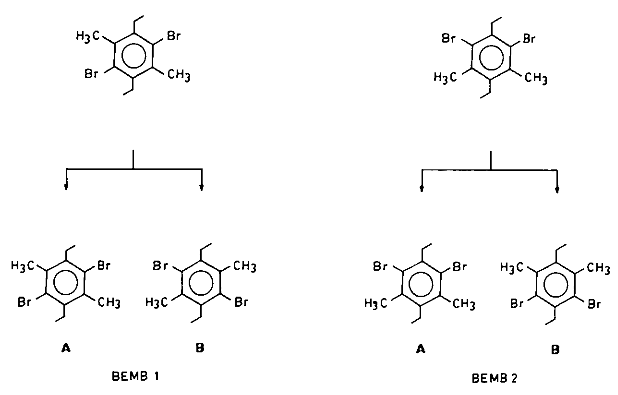

Fig. 1. Molecular structures of two isomers BEMB1 and BEMB2 which possess static orientational disorder. Two possible orientations, *A* and *B*, are shown.

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molecule to that of another, the second one the contact distance between the atoms of one molecule and those of the neighbouring molecules. The first type of vector involves the intermolecular lattice vectors whereas the second type involves the position vectors of various atoms constituting the molecule. The atomic contact distances play an important role in determining the pair correlation functions. The basic assumption of GC simulation, that order parameters are related and that the lower-order ones constrain the values that higher-order parameters can assume (Cowley, 1950), has to be applied very carefully to molecular crystals. While three to six α's suffice for binary alloys, for molecular crystals one should use all those lower-order α's for which the atomic contact distances are within the significant interaction range. No general statement about the requisite α's can be made for molecular crystals and each case has to be determined individually. Once this aspect has been properly accounted for, the molecules may be treated as point objects at their lattice position as far as the simulation is concerned.

The two components of a disordered molecular crystal can be either two different molecules or the same molecule in different (two or more) orientations. While the first case is similar to that of binary alloys, there is only one type of molecule in the second case. However, for the purpose of simulation, two different orientations with their well defined concentrations can be treated as two distinct species. Thirdly, the binary alloys normally tend to have a high-symmetry crystal structure and most of the GC-type simulation programs have been written for cubic crystals (Gragg, 1970; Williams, 1976; Epperson, 1979). Molecular crystals, in general, have a low-symmetry crystal structure, *e.g.* monoclinic. The basic concept of GC simulation is, however, very general and does not place stringent restrictions on the symmetry of the lattice as long as the neighbour positions and the coordination numbers are properly accounted for.

3. The computational procedure

The main idea is to generate a large model representing the molecular structure consistent with the pair probabilities α_{lmn}. Monoclinic models having two molecules per unit cell with ten cells on an edge were used. Periodic boundary conditions were used to minimize the surface effects. A storage location was allocated to each lattice site. As the models were assumed to have only two types of molecules (or two different orientations), the molecules of one kind were represented by a one and those of another kind by a zero. The input data were as follows:

(*a*) The occupancy of each lattice site as determined by a random initial state. Gehlen & Cohen considered an initially ordered state also. For molecular crystals, there may be more than one ordered state depending on the energetics. For the time being we restrict our attention to an initial random state.

(*b*) The initial number of 1-type molecules (m_{11} or m_{01}) in $1, \ldots, n$ neighbouring shells around each molecule. The number n has to be chosen specifically for each molecular crystal.

(*c*) The initial and the final number of $(1, 0)$ pairs in each shell, *i.e.* $(1, 0)^i_k$ and $(1, 0)^f_k$ with $k = 1, \ldots, n$. These numbers are machine computed for the initial state and for the final state; they are obtained from

$$(1, 0)^f_k = (1 - \alpha_k) m_1 m_0 C_k N \qquad (1)$$

where the α's are the pair correlation functions. m_1 and m_0 are respectively the concentrations of 1- and 0-type molecules. C_k is the coordination number of the kth shell and N is the total number of molecules in the crystal.

The program first selects two lattice sites at random, one corresponding to a 1 molecule and the second one to a 0 molecule. The selection of these sites was done by using the GC method. The criteria for possible interchange was the following: If $(1, 0)^1_k$ represents the total number of $(1, 0)$ pairs before the jump, the same quantity after the jump, $(1, 0)^2_k$, can be written as

$$(1, 0)^2_k = (1, 0)^1_k + 2[(m_{11})_k - (m_{01})_k + \delta] \qquad (2)$$

where $(m_{11})_k$ and $(m_{01})_k$ are, respectively, the number of 1 molecules around the 1 and 0 molecule to be interchanged. δ is unity if the sites are kth neighbours and zero otherwise. $(1, 0)^2_k$ was computed for k $(1, \ldots, n)$ shells. In the GC procedure, the interchange is made only if each of the $(1, 0)^2_k$ was closer to $(1, 0)^f_k$ than $(1, 0)^1_k$. We found this criterion computationally very slow. We used the following criterion instead for a possible interchange:

$$\sum_{k=1}^{n} |(1, 0)^2_k - (1, 0)^f_k| < \sum_{k=1}^{n} |(1, 0)^1_k - (1, 0)^f_k|. \qquad (3)$$

If the selected 0 molecule did not satisfy this criterion, the scanning was continued until a suitable 0 molecule was found. If the time taken to find a suitable 0 molecule was excessive, then the procedure was restarted with a new random 1 molecule. The program was stopped when

$$\sum_{k=1}^{n} |(1, 0)^2_k - (1, 0)^f_k| \leq 5. \qquad (4)$$

At this stage, the computed α's matched very well with the experimentally observed ones.

Table 1. *Simulation results for BEMB*1

The correlation coefficients are with respect to the central molecule located at (55501); see Welberry & Siripitayananon (1986) for details.

Correlation coefficient (site)	Experimental value	Simulation results for 2000 molecules Initial state Random			Ordered
		$n=5$	$n=9$	$n=11$	$n=11$
α_1(56501)	0·029	0·029	0·029	0·029	0·029
α_2(57501)	0·007	0·007	0·007	0·007	0·007
α_3(66502)	−0·208	−0·207	−0·207	−0·207	−0·207
α_4(65501)	−0·141	−0·139	−0·141	−0·141	−0·140
α_5(56502)	0·0	0·0	0·0	0·001	0·000
α_6(64501)	0·089	0·934	0·089	0·089	0·089
α_7(66501)	0·023	−0·052	0·023	0·023	0·023
α_8(67502)	0·013	−0·008	0·013	0·014	0·130
α_9(57502)	−0·009	0·019	−0·009	−0·009	−0·009
α_{10}(63501)	0·041	0·030	−0·020	0·041	0·041
α_{11}(67501)	−0·025	−0·032	−0·014	−0·025	−0·025
Number of jumps		878	878	900	2338
$\sum_{k=1}^{n} \lvert(1,0)_k^i-(1,0)_k^f\rvert_{\text{initial state}}$			2616		25 546

Table 2. *Simulation results for BEMB*2

Correlation coefficient (site)	Experimental value	Simulation results for 2000 molecules Initial state Random			Ordered
		$n=5$	$n=9$	$n=11$	$n=11$
α_1(56501)	−0·102	−0·102	−0·102	−0·102	−0·101
α_2(57501)	0·068	0·068	0·068	0·068	0·068
α_3(66502)	0·139	0·139	0·139	0·138	0·139
α_4(65501)	0·214	0·214	0·214	0·214	0·214
α_5(56502)	0·084	0·084	0·084	0·084	0·084
α_6(64501)	−0·121	−0·034	−0·120	−0·120	−0·122
α_7(66501)	−0·103	0·018	−0·102	−0·102	−0·102
α_8(67502)	−0·039	0·0	−0·038	−0·038	−0·069
α_9(57502)	−0·035	0·011	−0·035	−0·034	−0·035
α_{10}(63501)	−0·009	0·034	0·010	−0·008	−0·09
α_{11}(67501)	0·017	0·002	0·004	0·018	0·019
Number of jumps		800	800	800	1810
$\sum_{k=1}^{n} \lvert(1,0)_k^i-(1,0)_k^f\rvert_{\text{initial state}}$			2738		26 393

4. Results and discussion

The experimental data for BEMB1 taken recently by Welberry & Siripitayananon (1986) together with the computer simulation results are shown in Table 1. There are some interesting observations. For binary alloys, in general, the first few α's are the most significant ones and the rest are quite small. α's generally decrease in magnitude with increasing distance (Gragg, Bardhan & Cohen, 1971). In the case of BEMB1, α_3, α_4 and α_6 are the most important correlation parameters and there is no well defined decrease with the increasing shell number. This is due to the role played by atomic contact distance. From the point of view of interatomic interactions (Kitaigorodsky, 1973), the contact distances up to seven neighbouring shells are important in BEMB1 (Siripitayananon, 1985). So any simulation must include α_k's up to seven neighbouring shells and perhaps a few additional α_k's can be included to improve the fit. The results in Table 1 indicate that the agreement between the experimental and the computed α_k's is very good for n having a value of 9 and 11 respectively. Computer simulation results for BEMB2 are given in Table 2. The experimental data were taken from Welberry & Siripitayananon (1987). The simulation results for BEMB2 are very similar to those from BEMB1.

It is not certain *a priori* that the configurations generated by this procedure are unique and represent the actual microstructure corresponding to a given set of α_k's. In order to show that the configuration was indeed representative of the actual molecular arrangement, we compared the two final configurations having the same α_k's but generated from two different initial states (a random and a completely ordered state). Depending on energetics there can be more than one ordered state for molecular crystals. For the present simulation, we considered an ordered state with all molecules in one sublattice pointing in

Table 3. *BEMB*1: *Set* I (II): *number of* 1(0) *molecules having* $n(1)[n(0)]$ *molecules in the kth neighbouring shell*

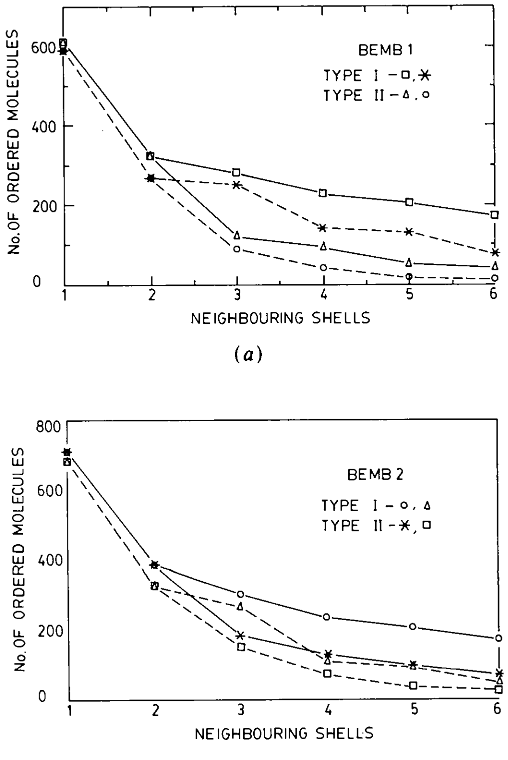
	Initial random state					Ordered initial state				
$k\backslash n$	0	1	2	3	4	0	1	2	3	4
Set I										
1	193	475	277			210	425	202		
2	251	434	260			267	364	202		
3	135	309	329	148	24	183	266	255	114	19
4	229	501	215			241	402	194		
5	57	220	358	237	73	148	194	278	156	61
6	136	422	387			97	369	371		
Set II										
1	200	450	405			192	464	507		
2	229	445	381			233	425	505		
3	125	264	338	259	69	117	268	314	256	208
4	231	476	348			238	399	526		
5	69	239	322	199	226	62	244	347	239	271
6	72	519	464			71	416	676		

Table 4. *BEMB*2: *Set* I (II): *number of* 1(0) *molecules having* $n(1)$ $[n(0)]$ *molecules in the kth neighbouring shell*

	Initial random state					Ordered initial state				
$k\backslash n$	0	1	2	3	4	0	1	2	3	4
Set I										
1	277	418	177			277	414	155		
2	212	445	215			220	393	233		
3	42	181	351	234	64	78	153	318	235	62
4	99	440	333			116	417	313		
5	42	168	361	238	63	89	182	291	219	65
6	178	420	274			165	396	285		
Set II										
1	253	460	415			274	420	430		
2	194	477	457			202	423	529		
3	15	140	375	443	155	22	149	349	385	249
4	94	462	572			116	401	637		
5	25	181	330	340	252	36	199	330	317	272
6	112	548	468			124	469	561		

one direction while the molecules in the second sublattice pointed in the opposite direction. The end results are quite similar (see Tables 1 and 2). It appears that the microstructure corresponding to the experimental α_k's is much closer to a random system than to an ordered state as indicated by the number of jumps required to reach the final state and the initial number of $\sum_{k=1}^{n}(1,0)_k^f-(1,0)_k^i$. In Tables 3 and 4, we have tabulated the distribution of 1(0) atoms having a given number of 1(0) atoms in the kth-neighbour shell. The results from the two initial configurations are in good agreement for both BEMB1 and BEMB2. These results indicate that the simulated configuration must be a good statistical representation of the actual molecular structure and not just a picture of one possible arrangement.

We next look at the ordered regions in the computer-generated structures. The definition of order is somewhat arbitrary and will be specified in each case. We discuss two kinds of ordered arrangements labelled as I and II. In type I order, all molecules have the same orientation, *i.e.* the ordered region has either only A-type or B-type molecules. In type II order, all the molecules in one sublattice have one orientation (A or B) while all the molecules in the second sublattice have the opposite orientation. There can be other types of ordered arrangements also. Looking at the clusters extending out to six neighbouring shells, two sets of I and II for different initial conditions were considered. The definition of an ordered A (or B) molecule was the following: In a type I arrangement, an A-type molecule was ordered if there were two A molecules in the first shell, two A molecules in the second shell, two to four A molecules in the third shell, one or two A molecules in the fourth shell, two to four A molecules in the fifth shell and one to two A molecules in the sixth shell. In a type II arrangement, there were B-type molecules in the third and the fifth shell. In Figs. 2(a) and (b) we show the number of ordered molecules as the order extends from the first to the sixth neighbouring shell. In both BEMB1 and BEMB2 type I order is predominant compared with the type II arrangement. Also, the simulated configuration from an initially ordered state has a slightly larger number of ordered molecules. For the present set of



(a)

(b)

Fig. 2. Number of ordered molecules (a) BE.MB1 and (b) BEMB2 as a function of neighbouring shells. The solid curves are for an ordered initial state and the broken curves are for a random initial state.

α_K's, the whole configuration can be described as a random matrix in which small ordered regions are distributed.

In conclusion, we note that the computer simulation of microstructure in disordered molecular crystals is very similar to that for binary alloys. These computations are expected to aid the theoretical calculation of diffuse scattering and will help in putting the data analysis on a better quantitative footing.

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The Simulation of Condensed Phases in Cyclohexane Clusters

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Abstract

An extensive molecular dynamics study has been made as a prediction of possible structural phase changes in cyclohexane-d_{12}, using highly parallel computers. Clusters of 128 molecules and larger are simulated, giving results for zero-pressure conditions. Intermolecular interaction is modelled by 6-exp atom-atom potentials relating all non-bonded C and D atoms of rigid chair-form molecules. The system forms the natural low-temperature structure (phase II, space group $C2/c$), and on heating a transition is observed at 65 ± 10 K to a new rhombohedral phase (space group $R\bar{3}m$). This phase has not been found experimentally, but there is a natural unidentified metastable phase at ambient pressure and another unidentified phase under pressure. This new simulated phase persists to a further transition at 175 ± 15 K, above which there is no apparent molecular orientational ordering and the structure agrees well with the known f.c.c. plastic crystalline phase I. At 200 ± 15 K the plastic phase melts, and the liquid drop does not sublime, again in agreement with experiment. The analysis for the ordering in the clusters is done with the aid of equal area orientational and translational 'dot plots', radial distribution functions and powder diffraction patterns. Future bulk molecular dynamics simulations are suggested as a function of pressure, with the possible inclusion of the internal molecular distortion potential function.

1. Introduction

The development of molecular dynamics (MD) to model condensed systems goes back to the early work of Rahman (1964) and before. Considerable progress has since been made in the understanding of real systems through MD models, as evidenced by the work reported by Allen & Tildesley (1987), Tildesley (1987) and others. The use of MD to study the solid phases of matter is particularly appropriate for those systems whose phases are not highly ordered and crystalline. For the ordered systems, straightforward lattice-dynamical calculations give a good representation of the system behaviour, as reviewed by Pawley (1986); this is especially useful for those molecular systems where comparison with experiment is possible. For the more disordered systems one cannot use

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