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Computer Simulation of Size Effect from Orientationally Disordered Molecular Crystals: Monoclinic Dibromodiethyldimethylbenzene

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Abstract

Size-effect distortions have been computed in a pair of orientationally disordered isomers of dibromodiethyldimethylbenzene using Monte Carlo simulation. Net forces/torques were computed for each molecule and the direction of movement was determined using variational methods. The sampling was carried out both in sequential and in a random manner. Effects of lattice size, interaction radius and boundary conditions have been investigated. In the lowest-energy configuration, typical centre-of-mass displacements were in the range 0·25-0·30 Å. Average molecular librations, represented in terms of Eulerian angles, were in the range 0-4°. The φ and ψ components however had large r.m.s. values (~10°). Basic results and trends were unaffected by the lattice size and the interaction radius (6-15 Å). However, the r.m.s. values of the angles came down considerably for fixed boundaries. The influence of temperature on size effect has also been investigated.

1. Introduction

In recent publications (Welberry, Jones & Epstein, 1982; Epstein & Welberry, 1983; Welberry & Siripitayananon, 1986, 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. Although the most recent of these studies involved quantitative fitting of calculated three-dimensional-disorder diffuse-scattering distributions to the observed data, no account was taken of thermal diffuse scattering nor the molecular equivalent of the size-effect distortions that are found to be important in alloys (Warren, Averbach & Roberts, 1951). In a more recent paper (Khanna & Welberry, 1987) general diffraction equations for diffuse scattering from molecular crystals, taking account of these additional effects, were developed, and a basic analysis scheme for separating the various components of the diffuse scattering was outlined. This work showed that the analysis for molecular crystals is considerably more complex than the analogous analysis for alloys because of several factors: the slowly varying and essentially spherical atomic scattering factors f_A *etc.* applicable to the alloy case must be replaced by molecular scattering factors, which are rapidly varying complex functions in the reciprocal space; alloys also tend to be relatively simple structures with high symmetry whereas molecular crystals are generally of low (*e.g.* monoclinic) symmetry; perhaps most importantly, molecular crystals often contain different sublattices upon which the molecules have a different (symmetry-related) orientation.

Before embarking on an analysis of the diffuse scattering from a real sample, we decided, in order to obtain some feeling for the relative magnitudes of the various effects likely to be encountered in practice, to undertake a computational study using semi-empirical potential-energy calculations (see *e.g.* Kitaigorodsky, 1973; Ramdas & Thomas, 1978) on the previously reported dibromodiethyldimethylbenzene system [BEMB1 and BEMB2 (Fig. 1); see Welberry & Siripitayananon (1986, 1987)]. Both BEMB1 and BEMB2 are monoclinic with two molecules per unit cell. Their lattice parameters are:

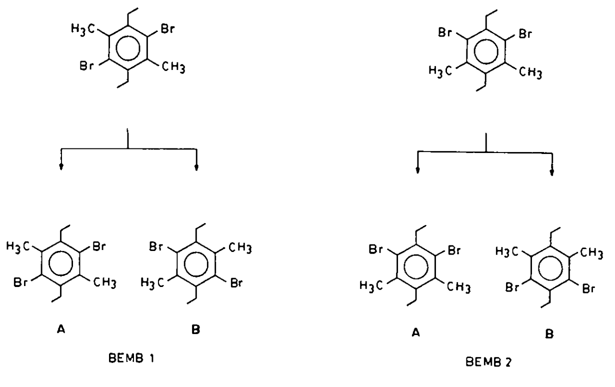

Fig. 1. Molecular structures of two isomers BEMB1 and BEMB2 which possess static orientational disorder. Two possible orientations, *A* and *B*, are shown in the figure.

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BEMB1 $a = 9{\cdot}084$, $b = 4{\cdot}459$, $c = 17{\cdot}940$ Å, $\beta = 122{\cdot}82°$; BEMB2 $a = 9{\cdot}086$, $b = 4{\cdot}442$, $c = 17{\cdot}969$ Å, $\beta = 122{\cdot}62°$. The disorder in these isostructural compounds arises because the molecules are able to take up either of two different orientations in each molecular site (see Fig. 1). The crystal-structure determination (Wood, Welberry & Puza, 1984) revealed that to a good first approximation only the methyl and bromine atomic sites are disordered and the remaining diethylbenzene fragment of the molecule remains well ordered. However, as for the alloy case, although the average molecular fragment appears ordered, small local distortions which may occur could have a significant effect on the scattering. The aim of the present work was to investigate the effects analogous to the size-effect distortions in alloys, by setting up a potential-energy model system of BEMB1 or BEMB2 molecules and allowing relaxation of the individual molecular positions from the previously assumed average values obtained from the crystal-structure determinations.

2. Force distributions

The source of size effect in disordered molecular crystals is slightly different from that in binary alloys. In alloys, the atomic displacements from the average lattice sites are caused by the unequal size of the constituent atoms. The disordered arrangement of the atoms relaxes in such a way that the smaller atoms move closer together and the larger ones further apart. To a good approximation, it can be imagined that the forces producing these distortions act along the lines of centres for each pair of neighbouring atoms, with the resulting distortions reflecting the simplicity of this form. For molecular crystals, the analogous situation is more complex. Even if we confine our attention to the case where the two molecules are in fact the same molecule in two orientations, the actual size of the two is the same, but the detailed shape presented to the environment is different. Each molecule is therefore subject to a complex force field resulting from the different atomic contacts with the occupants of the neighbouring sites.

Semi-empirical atom–atom potentials of the Buckingham 6-exp type or the Lennard-Jones 6-12 type (Kitaigorodsky, 1973; Williams, 1976; Ramdas & Thomas, 1978) can be used to compute these interatomic forces. The force is central in nature and is directed along the interatomic contact. It can be either repulsive or attractive depending on the contact distance and the nature of the atoms involved in the interaction. Depending on the contact distances involved, there may be a number of distinct forces acting on an atom of the molecule leading to a net force. Similarly there will be other net forces on other atoms of the molecule. These forces cannot be simply added up to get the effective force on the molecule. To cause the displacement of the molecule as a whole, one requires the total force directed towards the centre of mass (CM) of the molecule. So the net force acting on each atom has to be decomposed into two components: one directed towards the CM, and the other perpendicular to it. The perpendicular component will result in a torque with a tendency to rotate the molecule. The vectorial summation of the contributions from all atoms of the molecule results in a net effective force and net torque on the molecule. These forces may or may not be directed along the well defined crystallographic directions. For the present simulation we assume that the molecule itself is not flexible and its internal degrees of freedom are not being considered.

Table 1. *Non-bonded potentials for the various atomic interactions*: $V = Ar^{-6} + B\exp(-Cr)$; *the potential for* $CH_3 \cdots CH_3$ *is of the* 6-12 *type*; $V = -Ar^{-6} + Br^{-12}$

Interaction type	A (kJ mol^{-1} Å^6)	B (kJ mol^{-1})	C (Å^{-1})
$C \cdots C$	1993	$1{\cdot}58 \times 10^5$	3·513
$Br \cdots Br$	14023	$6{\cdot}78 \times 10^5$	3·250
$CH_3 \cdots CH_3$	21219	$5{\cdot}304 \times 10^7$	(kJ mol^{-1} Å^{12})

To minimize the computational task we have used an intermolecular potential with as simple a form as possible consistent with the need to describe the essential features of the disorder problem. We define the lattice energy, E, per molecule as

$$E = N_0^{-1} \sum_{N=1}^{N_0} \sum_m \sum_{n=1}^{12} V_{nm}(r, N), \tag{1}$$

where V_{nm} is the interaction between an atomic group n of a central molecule N and the m atomic groups of the neighbouring molecules which are within a specified interaction range. The parameters for V_{nm} are given in Table 1. r represents the interaction distance. The summation over N is over all molecules in the lattice and the summation over n runs from 1 to 12 (six C atoms, two Br atoms, two methyl groups and two ethyl groups). Although the ethyl group in the free molecule is able to rotate about the ring-methylene bond, for the present work the conformation has been assumed rigidly fixed with the plane of the ethyl groups normal to the plane of the benzene ring. For simplicity, the methyl group was approximated by a single Lennard-Jones 6-12 potential as given by Dashevsky (1966), and furthermore the ethyl group was approximated by a combination of two such methyl potentials, one at the site of the methylene C atom and the second at the position of the terminal methyl group. For consistency, the potentials for C–C and Br–Br were also taken from Dashevsky (1966).

3. Computational procedure

The most commonly used method to compute size-effect distortions in disordered systems is Monte Carlo simulation (Beeler, 1970). The method was most effective in a recent study of the effects of multisite correlations on the size-effect distortions in a simple model alloy (Welberry, 1985). In this method, an atom is chosen at random and is given a small random shift. The energy of the lattice is computed before and after the displacement. If the energy of the system is lowered by the shift then the shift is accepted, otherwise it is rejected. The procedure is repeated many times until the minimum-energy configuration is reached. The advantage of the Monte Carlo technique is that it is considerably easier to implement than a complete energy-minimization scheme involving calculation of first and second derivatives of the intermolecular potential as used for the single-site-defect problem. However, preliminary attempts to use the Monte Carlo procedure indicated that for our molecular crystal systems the method was most inefficient. It was found that a very large percentage of the random shifts to the CM and orientational parameters were rejected, despite the fact that each molecule was evidently still subject to significant residual forces and torques.

As a result of these considerations we decided to adapt some aspects of variational methods (Beeler, 1970) to the Monte Carlo simulation scheme. In the variational method, each atom is treated in succession, one at a time, and moved to a position of zero extrapolated force. Here a force f and its gradient is computed at the current position of the atom. A zero force position is then estimated by linear extrapolation and the atom is moved to its new position. The process is repeated until each atom experiences a negligible force. In our simulation, a molecule was evaluated by the procedure outlined in § 2. The molecule was then given a small displacement in the direction of the force and a small rotation about an axis passing through its CM whose direction was determined by the net torque on the molecule. Basic steps of Monte Carlo simulation for energy minimization were then carried out. By this means, exploration of much of the parameter space, which had previously led to rejected configurations, was avoided, and the system now proceeded smoothly to a lower-energy state. Iteration was continued for ~30–40 cycles, where one cycle was defined as the number of individual steps required for each molecule to be considered once on average. The size of the random shift employed in each cycle was adjusted periodically to maintain an acceptance/rejection ratio close to unity. Lattice size, interaction radius and temperature were used as parameters and their effect on the size-effect distortions was investigated. We also looked at the role played by the boundary conditions.

Table 2. *The size-effect distortions as a function of interaction radius*

These changes in lattice energy, centre-of-mass displacement and molecular librations were computed for a 12×12×12 lattice of BEMB2 using periodic boundary conditions.

Interaction radius	$R=5{\cdot}0$ Å	$R=7{\cdot}5$ Å	$R=10{\cdot}0$ Å	$R=15{\cdot}0$ Å
Initial E (kJ mol^{-1})	−88·228	−137·837	−144·337	146·355
Final E (kJ mol^{-1})	−91·213	−135·806	−146·456	148·377
$\Delta E/E$(%)	3·27	−1·47	1·45	1·36
u	0·263	0·261	0·267	0·267
U_x	0·144	0·133	0·152	0·155
U_y	0·385	0·381	0·384	0·384
U_z (in Å)	0·195	0·203	0·208	0·206
θ Mean	−0·196	−0·203	−0·209	−0·209
R.m.s. dev.	0·314	0·338	0·35	0·352
φ Mean	3·52	3·23	3·13	3·169
R.m.s. dev.	11·867	11·68	11·25	11·12
ψ Mean	−3·43	−3·14	−3·04	−3·08
R.m.s. dev. (in degrees)	11·82	11·58	11·14	11·01

Table 3. *Effect of the boundary conditions on the size effect in BEMB*1 *and BEMB*2

The interaction radius was chosen to be 15 Å.

	BEMB1		BEMB2	
	Rigid walls	Periodic boundary conditions	Rigid walls	Periodic boundary conditions
Initial E (kJ mol^{-1})	−148·09	−139·80	−146·74	146·383
Final E (kJ mol^{-1})	−149·30	−140·76	−149·76	148·405
$\Delta E/E$(%)	0·8	0·69	2·05	1·38
u	0·2285	0·2052	0·2703	0·267
U_x	0·0527	0·08	0·0546	0·155
U_y	0·3920	0·3376	0·3702	0·384
U_z (in Å)	0·0140	0·0768	0·2814	0·206
θ Mean	−0·149	−0·087	−0·206	−0·209
R.m.s. dev.	0·734	0·54	0·294	0·352
φ Mean	2·18	4·10	2·46	3·169
R.m.s. dev.	2·29	19·12	2·40	11·12
ψ Mean	−2·15	−4·04	−1·52	−3·08
R.m.s. dev. (in degrees)	2·35	19·04	2·569	11·01

4. Results and discussion

Preliminary results for a 12 × 12 × 12 lattice of BEMB1 and BEMB2 are given in Tables 2–5. Following the procedure used to represent thermal vibrations of molecules (Willis & Pryor, 1975), the static displacements of molecules were represented by two terms: the translational displacement u of the centre of mass and the librational movement of the molecule as a whole. The mean-square CM displacement is expressed in terms of the symmetric matrix U whose elements are defined as: $U_{ij}=\langle u_i u_j \rangle$, where $\langle \ldots \rangle$

Table 4. *Effect of temperature on the size effect in BEMB1*

The simulation was carried out with periodic boundary conditions and for $R = 15$ Å.

	$KT = 0{\cdot}01$	$KT = 0{\cdot}05$	$KT = 0{\cdot}1$
Initial E (kJ mol^{-1})	−139·80	−139·80	−139·80
Final E (kJ mol^{-1})	−140·30	−140·408	−127·249
$\Delta E/E$(%)	0·36	0·44	−8·97
u	0·207	0·208	0·224
U_x	0·083	0·087	0·002
U_y	0·341	0·341	0·389
U_z	0·075	0·076	0·001
(in Å)			
θ Mean	−0·108	−0·112	−0·023
R.m.s. dev.	0·57	0·564	0·097
φ Mean	5·40	5·43	9·098
R.m.s dev.	6·37	6·68	19·95
ψ Mean	−5·33	−5·58	−8·867
R.m.s dev	6·39	6·514	20·19
(in degrees)			

Table 5. *Effect of temperature on the size effect in BEMB2*

The simulation was carried out with periodic boundary conditions and for $R = 15{\cdot}0$ Å.

	$KT = 0{\cdot}01$	$KT = 0{\cdot}05$	$KT = 0{\cdot}1$
Initial E (kJ mol^{-1})	−146·45	−146·45	−146·45
Final E (kJ mol^{-1})	−145·37	145·349	145·28
$\Delta E/E$(%)	−0·7	−0·77	−0·8
u	0·224	0·224	0·224
U_x	0·002	0·002	0·002
U_y	0·388	0·388	0·388
U_z	0·001	0·001	0·001
(in Å)			
θ Mean	−0·09	−0·019	−0·018
R.m.s. dev.	0·252	0·104	0·105
φ Mean	3·87	4·36	4·62
R.m.s. dev.	12·45	16·25	16·28
ψ Mean	−3·76	−4·20	−4·457
R.m.s. dev.	12·47	16·294	16·543
(in degrees)			

indicates the space average with $U_i = \langle U_{ii}^2 \rangle^{1/2}$, $u = \langle (1/3 \sum U_{ii})^2 \rangle^{1/2}$. The librational movement is represented in terms of the mean and the r.m.s. values of the Eulerian angles φ, θ and ψ. The statistical accuracy of the displacements was checked by carrying out the computation with different initial random states. The numbers were accurate within ±5%. The molecular configuration was chosen to be random.

4.1. *Effect of interaction radius*

For calculating the lattice energy (equation 1), one has to compute the lattice sums r^{-6} and $\exp(-Cr)$ between the atomic pairs of different molecules. In Fig. 2(a), lattice energy mol^{-1} has been plotted as a function of interaction radius (R) for both BEMB1 and BEMB2. Since the dispersion energy and the repulsive energy of atoms quickly decrease with distance, it may be sufficient to use distances up to 15 Å for summation. In Fig. 2(b) we have plotted number of atomic pairs [m in (1)] involved in the summation as a function of interaction radius. The steady increase in m with interaction range results in a sharp increase in computation time. In Table 2, we have listed the size-effect distortions as a function of the interaction radius in BEMB2. It is to be noted that even though energy values change considerably as a function of R, the results for CM displacement and molecular libration show a very slight variation beyond 7·5 Å. Similar results were obtained for BEMB1. It appears that for a rough estimate of size effect, even summations up to 7·5 Å will be quite adequate.

4.2. *Effect of boundary conditions*

In Table 3, we have listed the simulation results for BEMB1 and BEMB2 using fixed boundaries and

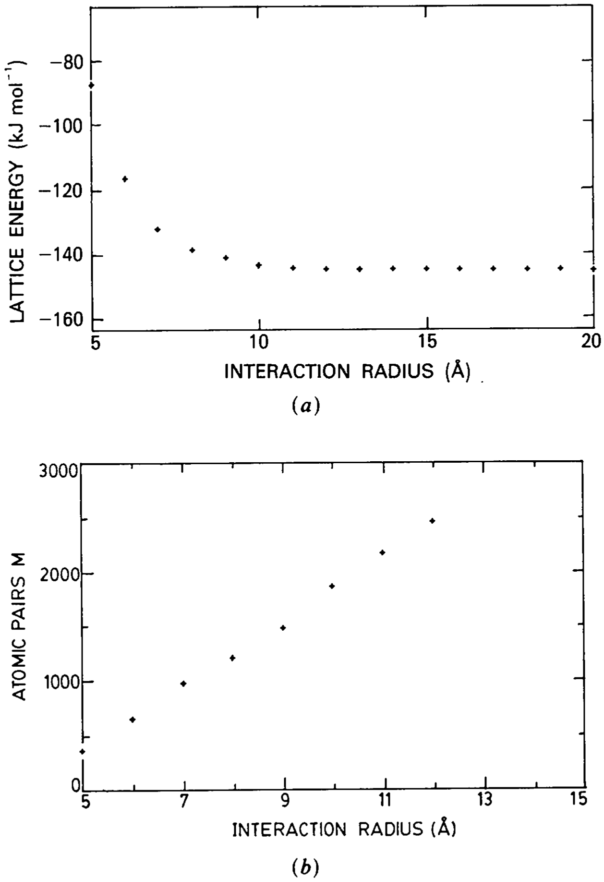

Fig. 2. (a) Lattice energy of BEMB2 as a function of the interaction radius. (b) Interaction pairs m for BEMB2 as a function of interaction radius.

periodic boundary conditions. The differences in the two cases are only marginal except for the r.m.s. values of the Eulerian angles φ and ψ. The r.m.s. values are considerably larger for a system with periodic boundaries whereas the rigid walls appear to constrain the librational movement of the molecules. In order to contain the computation time, the lattice size is rather small in the present simulation. Periodic boundary conditions are to be preferred over fixed boundaries so as to minimize the effects due to small lattice size.

4.3. *Effect of temperature*

During the energy-minimization process, it is quite probable that the system may get locked in a local minimum and the results may not be a true representation of the lowest-energy configuration. The temperature of the system was increased slightly so that the effects of local minima, if any, could be minimized. The energy change $\Delta E = E(X') - E(X)$ resulting from a configuration change $X - X'$ was computed. The transition probability (Binder, 1981)

$$W = \exp(-\Delta E/KT)/[1+\exp(-\Delta E/KT)] \qquad (2)$$

was then compared to a random number η, chosen uniformly from the interval (0, 1). If $W > \eta$, the transition (relaxation) is performed, otherwise the old configuration is retained. This algorithm is known to lead to thermal equilibrium distribution. KT was used as a parameter in units of energy and the results for $KT = 0{\cdot}01$, $0{\cdot}05$, $0{\cdot}1$ are presented in Tables 4 and 5. It is to be noted that there is a very slight change in energy with temperature. Even the centre-of-mass displacements and the mean values of Eulerian angles of libration are not affected much by temperature. Only r.m.s. deviations of angles appear to have increased considerably indicating a large scatter in the libration data.

Concluding remarks

From the preceding sections we observe that the size-effect distortions are quite small in both BEMB1 and BEMB2. The distortion magnitude is strongly dependent on the atomic contact distances and the nature of interacting atoms. These results are at best of a preliminary nature and give order-of-magnitude estimates. For a more detailed study, better interaction potentials and bigger lattice sizes are necessary. However, the basic computational formalisms are now ready for a theoretical calculation of diffuse scattering from disordered molecular crystals. The analysis of diffuse scattering data from molecular crystals has been semiquantitative so far. The computer programs developed for the present study will help to put the data analysis on a better quantitative footing.

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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

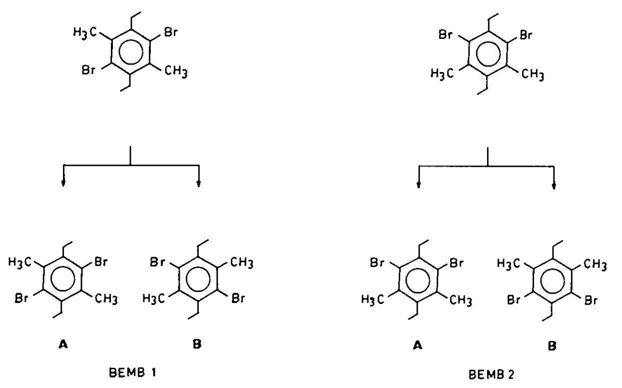

Fig. 1. Molecular structures of two isomers BEMB1 and BEMB2 which possess static orientational disorder. Two possible orientations, *A* and *B*, are shown.

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