

## X-ray diffuse scattering by cyclohexanol in the plastic phase: A theoretical model including orientational and translational molecular correlations

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X-ray diffuse scattering from the plastic phase of cyclohexanol has been recorded on photographic films by the Burger precession method. We present a new theoretical model to calculate x-ray diffusion intensity including orientational and translational molecular correlations. We calculate the dielectric correlation factor  $g$  ( $g=1.176$ , which agrees with the experimental value  $g=1.33$ ). We define an orientational correlation matrix which allows us to calculate  $g$ . The computed x-ray diffusion intensity describes qualitatively the experimental intensity variations. In the theoretical model the strong hard-core repulsions are responsible for the orientational correlations (we neglect the electric dipole and H-bond interactions, but they may be included in a more general model). Translational correlations are described by a simple model including phonons and orientational-translational coupling.

### I. INTRODUCTION

Descamps and Coulon<sup>1-4</sup> have calculated the diffuse scattering of neutrons and x rays from the plastic phases of different compounds by the weak-graph method (which includes molecular orientational correlations coming from steric hindrance). Furthermore, they used a closed-form evaluation of the static susceptibility  $X(\mathbf{q})$  with the Bethe-level approximation.<sup>4,5</sup> In plastic adamantane derivatives,<sup>6</sup> Descamps used a mean-field treatment of the hard-core repulsions.

In this work we do not discuss the validity of all these models, but we present a new theory which seems to be more rigorous for describing molecular orientational correlations arising from steric hindrance (and including translational correlations). We calculate molecular orientational correlations using a set of computed microcrystals with random orientational configurations (but sterically compatible). The model is applied to cyclohexanol in its plastic phase.

X-ray diffusion has been recorded on photographic films by the Burger precession method. We hoped to test also the model on succinonitrile which has been studied by Descamps with the weak-graph method.<sup>2,7</sup> However, when we computed our steric hindrance compatibility matrix (described in Sec. II for cyclohexanol) we observed that the x-ray structure of succinonitrile  $I_{m3m}$  ( $Z=2$ ) seemed to be incorrect. Fontaine<sup>8</sup> described this structure used by Descamps,<sup>7</sup> but we find that it lead to a steric incompatibility: There is an overlap of the Van der Waals envelopes of the molecules located at neighboring origins always greater than 0.8 Å when a nitrogen atom is between the origins. Note that this structure has also been applied with the weak-graph method<sup>9</sup> to determine the dielectric correlation factor  $g$  from Kirkwood theory of the polar dielectric.<sup>10</sup> In our model we also determine the Kirkwood dielectric correlation factor  $g$ .

We are interested in cyclohexanol because we have shown<sup>11,12</sup> that it is a good model to study the glass tran-

sition. The plastic phase  $I$  may be easily supercooled and gives a glassy crystal phase  $I'_g$ . Note that our theory for the plastic phase may be applied to the glassy crystal to calculate the x-ray diffusion scattering and the orientational molecular correlations.

### II. THEORY

The theoretical model will be presented for the case of cyclohexanol in the plastic phase. It may be easily generalized to all other cases of plastic crystals (and glassy crystals) where the orientational correlations of the molecules are observed for short distances (for example, one or two intermolecular distances). In the case of long-range orientational correlations the model is not valid. We also include translational correlations associated with phonons. (It is clear that vibrational states are not described by simple models because there is orientational disorder.)

We suppose that orientational correlations of molecules are governed by strong hard-core repulsions. (The van der Waals envelopes of the molecules must not overlap more than a short distance.) In the case of cyclohexanol we calculated that electronic energy of molecular dipoles may be neglected for the orientational correlations. However, in the cases of other molecules it may be important and the model may be generalized with electric dipole and H-bond interactions. The structure of cyclohexanol in its plastic phase has been determined:<sup>12</sup> It is a face-centered-cubic crystal ( $Z=4$ ); with orientational disorder, the molecules are in equatorial or axial configuration  $(\frac{1}{2}, \frac{1}{2})$ , and for each molecule on a site there are 48 orientational configurations which may be deduced from the position 1 (or 49) by the 48 symmetry operations of the crystal  $F_{m3m}$ . The rotation center of the molecule is fixed with the structure.

#### A. General expression for x-ray diffuse scattering

The x-ray diffuse scattering intensity  $I(\mathbf{q})$  may be written as the sum of different terms:

$$I(\mathbf{q}) = I_B(\mathbf{q}) + I_{\text{WC}}(\mathbf{q}) + \Delta I_{\text{OC}}(\mathbf{q}) + \Delta I_{\text{TC}}(\mathbf{q}) + I_{\text{Compton}}(\mathbf{q}). \quad (1)$$

We discuss the different terms in detail.

(a)  $I_B(\mathbf{q})$  is the Bragg intensity:

$$I_B(\mathbf{q}) = |\langle F \rangle_T|^2 \sum_{p=1}^M e^{i\mathbf{q} \cdot \mathbf{R}_p}, \quad (2)$$

$$I_B(\mathbf{q}) = |\langle F \rangle_T|^2 \sum_{\mathbf{K}} \delta(\mathbf{q} - \mathbf{K}), \quad (3)$$

where  $M$  is the number of molecules in the crystal and  $\mathbf{K}$  is any reciprocal-lattice vector. The factor  $|\langle F \rangle_T|^2$  is the square of the mean value of the molecular structure factor at temperature  $T$ . There are  $48 \times 2 = 96$  states for one site (the molecule is equatorial or axial):

$$\langle F \rangle_T = \sum_{m=1}^{96} F_m(\mathbf{q}) e^{-q^2 \Delta r_B^2 / 2}. \quad (4)$$

$F_m$  is the molecular structure factor of the molecule.  $\Delta r_B$  is determined with the structure of the crystal (isotropic approximation) and

$$q^2 \Delta r_B^2 \simeq \langle (\mathbf{q} \cdot \Delta \mathbf{r}_{im})^2 \rangle. \quad (5)$$

The average is taken over atoms  $i$ , states  $m$ , and thermal disorder  $\Delta \mathbf{r}_{im}$ .

(b)  $I_{\text{WC}}(\mathbf{q})$  is the computed x-ray diffusion intensity without orientational and translational molecular correlations:

$$I_{\text{WC}}(\mathbf{q}) = \langle |F|_T^2 \rangle - |\langle F \rangle_T|^2, \quad (6)$$

$$\langle |F|_T^2 \rangle = \sum_{m=1}^{96} F_m^* F_m e^{-q^2 (\Delta r_B^2 - \Delta r_A^2)}, \quad (7)$$

with

$$q^2 \Delta r_A^2 \simeq \langle (\mathbf{q} \cdot \Delta \mathbf{r}_{im})(\mathbf{q} \cdot \Delta \mathbf{r}_{jm}) \rangle. \quad (8)$$

The average is taken over atoms  $i$  and  $j$  of the same molecules ( $i \neq j$ ), the states  $m$ , and thermal disorder.  $\Delta r_B$  is known [see item (a)], and  $\Delta r_A$  is estimated.

(c)  $\Delta I_{\text{OC}} + \Delta I_{\text{TC}}$  gives the effect of orientational and translational correlations:

$$\Delta I_{\text{OC}} + \Delta I_{\text{TC}} = \sum_{p=2}^M \langle F_m^* F_{m+p} \rangle e^{i\mathbf{q} \cdot \mathbf{R}_p} e^{-q^2 (\Delta r_B^2 - \epsilon_p \Delta r_p^2)} - |\langle F \rangle_T|^2 \sum_{p=2}^M e^{i\mathbf{q} \cdot \mathbf{R}_p}. \quad (9)$$

The average  $\langle F_m^* F_{m+p} \rangle$  is taken over all the configurations in the crystal. For practical reasons we will use a set of computed microcrystals with random orientational disorder (the orientational correlations results in steric hindrance). This point is developed in Sec. III. Thermal disorder, translational correlations of molecules, and rotation-translation coupling are simply described by the factor

$$e^{-q^2 (\Delta r_B^2 - \epsilon_p \Delta r_p^2)}, \quad (10)$$

where

$$\epsilon_p \Delta r_p^2 q^2 = \langle (\mathbf{q} \cdot \Delta \mathbf{r}_{im})(\mathbf{q} \cdot \Delta \mathbf{r}_{j,m+p}) \rangle. \quad (11)$$

$\epsilon_p = \pm 1$  is the sign of the average and the average is taken over  $i, j, m$  and thermal disorder. The correlations appear for molecules located at origins separated by a vector  $\mathbf{R}_p$  of the lattice. (The lattice used is the lattice with one molecule per cell.)

We may separate orientational correlation effects from translational correlation effects in the following way:

$$\Delta I_{\text{OC}}(\mathbf{q}) = \sum_{p=2}^M \langle F_m^* F_{m+p} \rangle e^{i\mathbf{q} \cdot \mathbf{R}_p} e^{-q^2 \Delta r_B^2} - |\langle F \rangle_T|^2 \sum_{p=2}^M e^{i\mathbf{q} \cdot \mathbf{R}_p} \quad (12)$$

and

$$\Delta I_{\text{TC}}(\mathbf{q}) = \sum_{p=2}^M \epsilon_p q^2 \Delta r_p^2 |\langle F \rangle_T|^2 e^{i\mathbf{q} \cdot \mathbf{R}_p}. \quad (13)$$

This results from the fact that

$$e^{-q^2 \Delta r_B^2} \langle F_m F_{m+p} \rangle \simeq |\langle F \rangle_T|^2. \quad (14)$$

For practical reasons we include in Eq. (13) orientational-translational coupling. Note that in Eq. (12) the orientational correlations vanish for  $|\mathbf{R}_p| > R_0$ , a critical radius. Then the summation over  $p$  is limited to  $P_S \ll M$ .  $M$  is the number of molecules in the crystal.  $P_S$  is also smaller than the number  $M_C$  of molecules in the computed microcrystals.

(d)  $I_{\text{Compton}}(\mathbf{q})$  is the well-known Compton incoherent intensity which is easily computed.

## B. Microcrystals computed with random orientational disorder

In Eq. (12) the average  $\langle F_m^* F_{m+p} \rangle$  will be determined using a set of computed microcrystals with random orientational disorder. Orientational correlations result from steric hindrance and when the number  $N_C$  of microcrystals is of the order of  $2000 \times 48 = 96000$ , we observe a convergence of the orientational correlations.

### 1. Steric hindrance compatibility matrix

When we determined the structure of cyclohexanol we used a steric hindrance compatibility matrix. To study intermolecular contacts, every molecular orientation has to be taken into account. Each lattice site thus corresponds to 96 orientational states (48 for equatorial and 48 for axial) which are the same for every site. Each molecule is surrounded by 12 neighboring ones (lying at the same distance  $a(\sqrt{2}/2)$ ). So we have to describe how any one of the same 96 orientational states of one central site interacts with any one of the same 96 states of the neighboring site of the  $(\frac{1}{2}, \frac{1}{2}, 0)$  type. Obviously, the interactions between a central molecule and any neighboring one can be deduced through a rotation from the interactions between other such couple. Then it will be sufficient to study the contacts between a central molecule and its neighbors lying at  $(\frac{1}{2}, \frac{1}{2}, 0)$ .  $96 \times 96$  orientational states

couples are to be studied.

Instead of describing the detailed intermolecular contacts, which would have been cumbersome, we chose to build a  $96 \times 96$  matrix in which the value of the elements  $A(m_1, m_2)$  defines steric compatibility between a molecule in orientational state  $m_1$  at  $(0,0,0)$  and a molecule in orientational state  $m_2$  at  $(\frac{1}{2}, \frac{1}{2}, 0)$ .  $A(m_1, m_2) = 1$  if the two states are sterically compatible, and 0 when they are not. Any two cyclohexanol molecules are considered as sterically noncompatible when any distance between two atoms belonging to each molecule is shorter than the sum of the Van der Waals radii of the two atoms minus a given distance, which should take intermolecular interaction and motion into account. The van der Waals radii for carbon, oxygen, and hydrogen were taken as 1.8, 1.4, and 1.2, respectively. We define  $\alpha$ , the radii of the number of compatible orientational state which couples to the total number ( $96 \times 96$ ).  $\alpha$  is of the order of 0.7 for  $\epsilon = 0.1$  Å.

## 2. Computed microcrystals with random orientational states of molecules

We compute a set of microcrystals with random orientational states of molecules using the steric hindrance compatibility matrix. There are  $M_c = 55$  molecules per crystal. The central molecule is chosen in state 1 or 49. The states of the remaining molecules are defined by a random function but we require the system to be completely sterically compatible.

Each molecule is taken in a random state  $n$  from 1 to 96 and we program the computer to determine if the state is sterically compatible. If not, we try the state  $n + 1$ ; if in one site there is not a compatibility state we build another crystal.

A crystal is composed of molecules at sites of the following type:

- (0,0,0) central molecule,
- $(\frac{1}{2}, \frac{1}{2}, 0)$  shell  $n^r$  1,
- (1,0,0) shell  $n^r$  2,
- $(1, \frac{1}{2}, \frac{1}{2})$  shell  $n^r$  3,
- (1,1,0) shell  $n^r$  4.

When a microcrystal is computed, the 48 symmetries of the crystal give 48 equivalent microcrystals. The number of computed microcrystals is  $N_c = 4000 \times 48 = 192\,000$ . When we compute the x-ray diffuse scattering intensity, the orientational correlations, the orientational correlations appear in Eq. (11), which becomes

$$\Delta I_{OC}(\mathbf{q}) = \sum_{e=1}^{48} \sum_{n=1}^N \sum_{p=2}^{P_s} f_1^*(n,e) f_p(n,e) \lambda_p e^{i\mathbf{q} \cdot \mathbf{R}_p} - |\langle F \rangle_T|^2 \sum_{p=2}^{P_s} e^{i\mathbf{q} \cdot \mathbf{R}_p}, \quad (15)$$

where  $\lambda_p$  is a normalization factor:

$$\lambda_p = \frac{1}{(48)^2} \frac{P}{N}. \quad (16)$$

$N = 2000$  is the number of initial microcrystals and  $P$  is the number of molecules on the shell corresponding to  $p$ .

The summation over  $e = 1$  to 48 gives symmetric equivalent microcrystals for given  $n$ .

## C. Orientational correlations

### 1. Convergence of the orientational correlations in the model of the microcrystals

A simple method to observe the convergence of the orientational correlations in the microcrystals is to compute  $\Delta I_{OC}(\mathbf{q})$  in Eq. (15) and to observe that the term  $\Delta I_{OC}(\mathbf{q})$  is well stabilized for  $N$  greater than 2000 or less for the first and the second shells. This has been verified for  $N = 2000$  to 4000. Another method to observe the convergence of the orientational correlations is to define an orientational correlations matrix  $M_{s,c,N'}$ , where  $s$  is a shell (1 to 4),  $c$  is a conformer coefficient, and  $N'$  is the number of microcrystals. We consider the central molecule 1 and a molecule 2 on the shell  $s$ . If 1 and 2 are equatorial, then  $c = 1$ ; if 1 is equatorial and 2 axial, then  $c = 2$ ; if 1 is axial and 2 equatorial, then  $c = 3$ ; if 1 and 2 are axial molecules, then  $c = 4$ . The central molecule is in state 1 or 49. Consider the central molecule 1 and a molecule 2 of the shell  $s$  at position  $p$ . If  $\mu_1^0$  and  $\mu_2^0$  are unit vectors of the molecules, the scalar products are

$$\mu_1 \cdot \mu_2 = \mu_1^0 O_{s,p,n,c} \mu_2^0. \quad (17)$$

$O$  is a symmetry matrix which defines the orientational state of the molecule 2. It is clear that the average  $\langle \mu_1 \cdot \mu_2 \rangle_{s,c}$  over all the molecules 2 of the shell  $s$  and all the  $N'$  microcrystals (for given  $c$ ) is an orientational correlations term:

$$\langle \mu_i \cdot \mu_j \rangle_{s,c} = \mu_i^0 \cdot \langle O_{s,p,n,c} \rangle \mu_j^0. \quad (18)$$

This correlation term shows that

$$M_{s,c,N'} = \langle O_{s,p,n,c} \rangle \quad (19)$$

is effectively an orientational correlation matrix independent of the unit vectors  $\mu_1^0, \mu_2^0$ . We must now show that this orientational correlation matrix converges for  $N'$  greater than 1000. This is verified by the following arguments:  $M_{s,c,N'}$  is stabilized for  $N'$  greater than 1000. It is verified by the fact that for  $N' = 1000$  to 2000 the elements  $m_{ij}$  of the matrix are stabilized and the Euclidian norm is constant. It is difficult to define a rigorous convergence criterion, but the fact that the diffuse x-ray term  $\Delta I_{OC}(\mathbf{q})$  is constant for  $N = 2N' = 2000$  to 4000 is evidence that for the diffusion model the convergence is verified to a very good approximation. The convergence has been verified for the two first shells of the microcrystals. For the third shell the Euclidean norm of the matrix vanishes and the orientational correlations are considered to be negligible.

### 2. Kirkwood dielectric correlation factor $g$

It is well known that in liquid or plastic phases of molecules having a permanent electric dipole the static dielectric constant  $\epsilon$  may be calculated with the Kirkwood dielectric correlation factor  $g$ :

TABLE I. Fractional atomic coordinates ( $\times 10^5$ ) for the structural model of cyclohexanol phase I at 275 K.

Equatorial			
C	1064	-742	16227
C	2373	-16803	9447
C	9741	-15864	-6380
C	-138	-5917	-16824
C	-1446	10144	-10045
C	-8814	9205	5782
H	8786	-23261	16230
H	-7976	-21382	8539
H	-20089	-11285	-5471
H	10591	-26292	-10782
H	4645	-5308	-27101
H	-10487	-10496	-17733
H	8902	14723	-9136
H	-7860	16602	-16827
H	-9664	19633	10185
H	-19163	4625	4874
H	11413	3837	17135
O	-5777	-1614	30921
Axial			
C	-3899	660	18720
C	-1900	-13124	8154
C	+4444	-7793	-7240
C	-6686	3558	-14513
C	-8685	17342	-3947
C	-15029	12011	11448
H	5326	-20494	12877
H	-11948	-18164	6566
H	14492	-2753	-5653
H	5742	-16742	-14101
H	-2567	7019	-24509
H	-16734	-1482	-16101
H	1363	22383	-2359
H	-15911	24713	-8670
H	-16327	20961	18308
H	-25077	6971	9860
H	-8017	-2801	28716
O	10469	7867	20990

$$\epsilon - \epsilon_\infty = \frac{4\pi}{V} \frac{3\epsilon}{2\epsilon + \epsilon_\infty} \left[ \frac{\epsilon_\infty + 2}{3} \right] \frac{Ng}{3kT} \langle \mu_V^2 \rangle, \quad (20)$$

where  $\mu_V$  is the permanent dipole moment in the molecule in the gas phase. The Kirkwood dielectric correlation factor  $g$  is defined by

$$g = \frac{\sum_{\gamma=1}^N \mu_1 \cdot \mu_\gamma}{\sum_{\gamma=1}^N \langle \mu_V^2 \rangle}. \quad (21)$$

The sum is realized for the molecules  $\gamma$  around a molecule 1. In the case of cyclohexanol the dipole moment of the molecule is not completely defined because in the C-O-H system O-H may take any orientation around C-O. How-

ever, if we take  $\mu_V = 1.688$  D the projection  $\mu_\Delta$  of  $\mu_V$  on the direction C-O is  $\mu_\Delta = 1.588$  D. If we neglect the correlations of position of the O-H around C-O, Eq. (21) becomes

$$g = 1 + \sum_{\gamma=2}^N \frac{\mu_{\Delta 1} \cdot \mu_{\Delta j}}{\mu_\Delta^2} \left( \frac{\mu_\Delta}{\mu_V} \right)^2 \quad (22)$$

with

$$\left( \frac{\mu_\Delta}{\mu_V} \right)^2 = 0.8854. \quad (23)$$

We have verified that the crystal structure gives relative positions of neighboring molecules such as

$$\frac{\mu_V^2}{\Delta r^3} < kT. \quad (24)$$

$\Delta r$  is the distance between the dipoles of the molecules. The relation (24) has been verified for more than 98% of the configurations. This allows us to suppose that strong hard-core repulsions are predominant for the configurations. However, we are not completely sure that hydrogen bonds may be neglected for this problem. A more general model might consider the bimolecular configurations in order to describe the electric dipole and H-bond interactions (the compatibility matrix must be considered with an energy probability matrix).

The Kirkwood dielectric correlation factor  $g$  is calculated with Eqs. (18), (19), (22), and (23). The number of microcrystals used is  $N = 4000$  ( $N' = 2000$ ) which gives well-defined correlation matrices  $M_{s,c,N'}$ . We find  $g = 0.619$  with two shells of molecules in the microcrystal. This value does not agree with the experimental value  $g = 1.33$  found by Reinisch<sup>13</sup> with dielectric measurements. However, when we published our structure of cyclohexanol,<sup>12</sup> we gave results of one solution but (inside the precision of the results) there was another solution which was equivalent in relation with validity criterion. This indetermination results from the fact that only 10 Bragg spots were taken into account. So in this work we

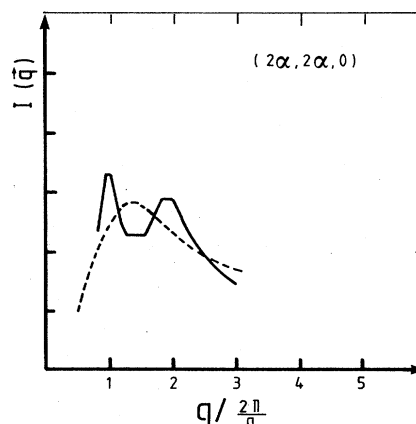


FIG. 1. Diffusion intensity in the direction  $q = (2\alpha, 2\alpha, 0)2\pi/a$ . —, experimental; ---, computed without orientational and translational molecular correlations.

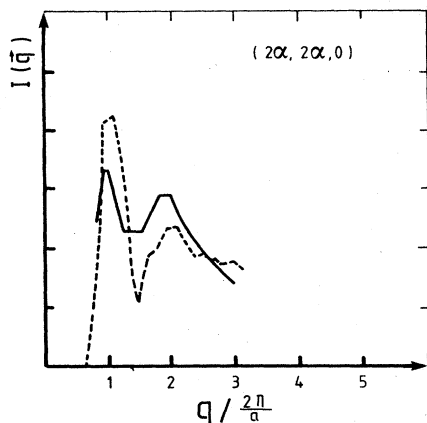


FIG. 2. Diffuse intensity in the directions  $\mathbf{q}=(2\alpha, 2\alpha, 0)2\pi/a$ . —, experimental; ---, computed intensity with orientational and translational molecular correlations.

have computed the two solutions, and the second gives a computed dielectric correlation factor  $g=1.176$  which agrees quite well with the experimental value ( $g=1.33$ ). Furthermore, when we computed the x-ray diffuse scattering  $I(\mathbf{q})$ , only the second unpublished structure agreed with experimental  $I(\mathbf{q})$ . In Table I we give the nonpublished structure of cyclohexanol.

### III. COMPUTED X-RAY DIFFUSION INTENSITY

We compute the x-ray diffusion intensity  $I(q)$  for different trajectories in reciprocal space:

- $\mathbf{q}=(2, 2, 0)(2\pi/a)$ ,
- $\mathbf{q}=(4, 2, 0)(2\pi/a)$ ,
- $\mathbf{q}=(4, 2, 2)(2\pi/a)$ , and
- $|\mathbf{q}|=4\pi/a$  circle in  $(1, 0, 0)$  plane.

Experimentally we know that Bragg spot (200) is surrounded by a strong diffusion area. The same strong diffusion appears in the computed trajectory (d). In the cases (a), (b), and (c), the computed intensity (without Bragg spots) is not exactly the same as the experimental intensity but it is a good qualitative description for the experimental diffusion. For example Fig. (2) gives  $I(\mathbf{q})$  for the case (a). If we neglect the orientational and translational correlations (Fig. 1), the x-ray computed diffusion  $I_{\text{WC}}(\mathbf{q})+I_{\text{Compton}}(\mathbf{q})$  is completely incorrect (compared to the experimental diffusion intensity).

The orientational correlation term  $\Delta I_{\text{OC}}(\mathbf{q})$  is not sufficient to find a good agreement with experimental data and

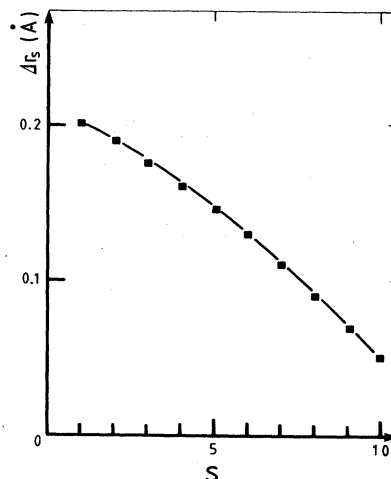


FIG. 3. Variation of  $\Delta r_s$  with  $s$  (number of the shell).

we must include the translational correlation term  $\Delta I_{\text{TC}}(\mathbf{q})$ . In Eq. (13) we consider  $\epsilon_p \Delta r_p^2 = \epsilon_s \Delta r_s^2$ , where  $s$  is the shell corresponding to  $p$ . We cannot find a model for  $\epsilon_s \Delta r_s^2$  because translational correlations come from unknown vibrational states (orientational disorder gives not simple phonons). So we choose a simple model of simple decrease of  $\Delta r_s$  with  $s$  (Fig. 3) and  $\epsilon_s = +1$ . We find that the computed  $I(\mathbf{q})$  is strongly dependent on the decrease of  $\Delta r_s$ .  $\Delta r_A = 0.25 \text{ \AA}$  and  $\Delta r_B = 0.433 \text{ \AA}$  (from x-ray structure). The fact that x-ray computed diffusion is not very close to the experimental one (but agree only qualitatively with it) may arise from the fact that the parameters  $\Delta r_A, \Delta r_B, \Delta r_s$  are introduced in simple isotropic models which may be developed with more rigorous methods. But these methods lead to complexity related to the case of cyclohexanol. In more simple cases we may introduce librational parameters and other more rigorous methods.

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