PHYSICAL REVIEW B VOLUME 32, NUMBER 6 15 SEPTEMBER 1985

Molecular disorder in even-numbered paraffins

Aldo Craievich
Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro, RJ, Brazil

Jean Doucet
Laboratoire de Physique des Solides, Université Paris-Sud, Orsay, France

Ireno Denicoló
Departamento de Física, Universidade Federal de Santa Catarina, Florianópolis, Brazil

(Received 26 December 1984)

Conformational and displacive molecular defects in even-numbered paraffins C_nH_{2n+2}, with $22 \leq n \leq 28$, are studied as a function of temperature by means of small-angle x-ray diffraction. The amplitude of the molecular longitudinal motion in the rotator phase increases with molecular length, as it was also found to do in previous studies of odd-numbered paraffins. This amplitude is temperature independent in rotator phases of even paraffins with $22 \leq n \leq 26$. The voids between molecular layers in the crystalline phase of even paraffins are narrower than those of odd paraffins. This indicates a closer packing of layers in systems in which molecules are tilted. Structures of the high-temperature hexagonal rotator phases of odd and even paraffins exhibit a minor but significant difference which has been associated with different interactions between molecular ends.

INTRODUCTION

Normal paraffins exhibit solid-solid transitions from crystalline phases at low temperature to disordered phases at high temperature, some degrees below the melting point. The early works of Muller suggest that the transitions are related to rotation of molecular chains about their long axes.[1,2] The atomic structure of the low-temperature "crystalline" phase of odd-numbered paraffins has been determined.[3] More recently the main structure features of the high-temperature "rotator" phases have been established.[4–9] These studies performed by x-ray diffraction techniques show that in crystalline phases the molecules stack together, forming a layered structure with the long molecular axes tilted with respect to the normal to the layer planes. The paraffins with a number of carbon atoms $n < 26$ crystallize in a triclinic lattice. For $n > 26$ the lattice is monoclinic. A coexistence of monoclinic and triclinic phases is observed for $n = 26$. All even-numbered paraffins with $n \geq 22$ present an intermediate phase at temperatures between the crystal and the liquid phase. This mesophase is called a "rotator" phase because of the high degree of orientational disorder of the molecules. The lattices associated with the rotator phase in even paraffins with $n \leq 26$ and $n = 28$ are hexagonal and monoclinic, respectively.

The temperature dependence of the small-angle x-ray diffraction patterns from even-numbered[10] and odd-numbered paraffins[11] showed clear evidence, in the rotator phase, for "rigid-body" longitudinal molecular displacements and conformational intramolecular defects (kinks). The magnitude of molecular disorders in odd paraffins increases both with temperature and molecular length. These disorders present a correlated behavior. The displacement disorder and formation of kink defects are also correlated with the orientational molecular disorder, as has been inferred from previous large-angle[5,6] and small-angle[4,11] x-ray diffraction and neutron-scattering[12] studies. The existence of intramolecular defects in odd-numbered paraffins and the dependence of their concentration on molecular length have been independently determined by spectroscopic techniques.[13,14]

This work is devoted to the study of molecular disorders in even-numbered paraffins with $22 \leq n \leq 28$ by means of the small-angle diffraction technique (long-spacing $00l$ Bragg reflections). These disorders have been studied as functions of temperature and molecular length, and have been compared with a similar previous study of odd-numbered paraffins.[11] Paraffins with $n = 23$ and 25 exhibit two rotator phases at increasing temperatures named rotator I (quasihexagonal) and rotator II (hexagonal).[6] Odd-numbered paraffins with $n = 21$ present only one R_{I} mesophase.[5]

SAMPLES AND METHODS

The samples of paraffins C_nH_{2n+2} with $n = 22$, 24, 26, and 28 were purchased from Fluka with the purity grades 98%, 99%, 99%, and 98%, respectively. The x-ray small-angle diffraction patterns from the various paraffins were obtained by using synchrotron radiation produced by the 1.8 GeV positron-storage ring at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE Université Paris–Sud, Orsay). An elastically bent germanium monochromator was used to obtain a focused monochromatic beam with $\lambda = 1.60$ Å. The cross section of the beam was kept small enough to allow us to consider it as "pointlike" (pinhole collimation). The intensity associated with the low-angle $00l$ Bragg reflection, I_l, was measured by means of an Elphyse position-sensitive detector.

The samples were held at constant temperature within ±0.5 °C during the diffraction experiments by using a specially designed camera heated by a circulating-water device.

The knowledge of the values of the intensities of the $00l$ Bragg reflections extrapolated to zero angle and the decay of these intensities with increasing l allows us to determine structure parameters which are related to the function $\eta(z)$, which represents the projection of the electronic density onto a direction perpendicular to the molecular stacking layers.[10,11] Assuming $\eta(z)$ a constant equal to η_c within the molecule, the difference $\Delta\eta(z)=\eta(z)-\eta_c$ is only nonvanishing in the depleted region between the molecular layers (the interlayer void), as shown in Fig. 1.

Two parameters related to the function $\Delta\eta(z)$ have been determined from the intensities of the $00l$ peaks of the small-angle diffraction patterns. They are (a) the moment of zeroth order κ and (b) the second moment σ^2 of the difference function $\Delta\eta(z)$, which are associated with the electronic density profile in the interlayer voids. These parameters can be directly obtained from the structure factor

$$B(s)=\int \Delta\eta(z)\exp(2\pi i s z)dz$$

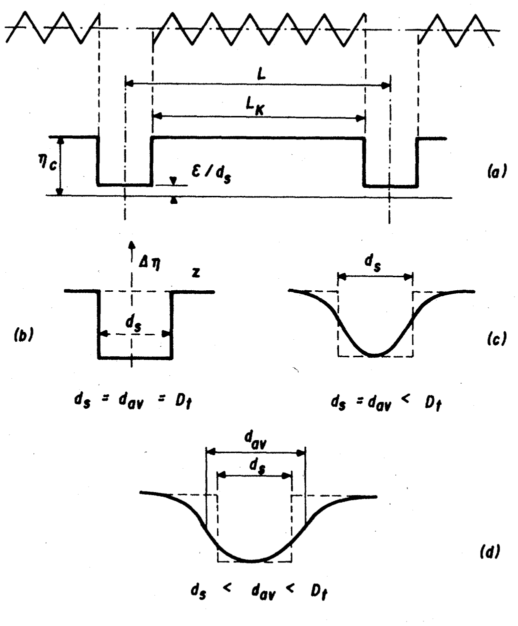

FIG. 1. Schematic profiles of the $\eta(z)$ and $\Delta\eta(z)$ functions. (a) Paraffin molecules and projection of their electronic density onto a direction perpendicular to the stacking planes, $\eta(z)$. The electronic density variations on an atomic scale are not shown since they are not relevant for small-angle diffraction analysis. (b) Difference function $\Delta\eta(z)$ for a perfect layered structure (molecules with neither intramolecular defects nor longitudinal displacements). (c) $\Delta\eta(z)$ associated with a system composed of defect-free molecules with longitudinal displacements. (d) $\Delta\eta(z)$ for a system of molecules with longitudinal displacements and kink defects.

by means of the following expressions:[10]

$$\kappa=B(s\to 0) \tag{1}$$

and

$$\sigma^2=-\frac{1}{8\pi^2}\frac{d^2B^2}{ds^2}(s\to 0)\ , \tag{2}$$

where s represents the modulus of the scattering vector. If the x-ray diffraction intensities at small angles, I_l, are known in an absolute scale, we can obtain B_l directly from

$$B_l=I_l^{1/2}\ . \tag{3}$$

By combining Eqs. (1) and (3) a relationship between the intensity extrapolated towards zero angle, $I(0)$, and the average value of the distance between the ends of consecutive molecules, d_{av}, can be obtained:[10]

$$I(0)=[(\eta_c-\epsilon/d_s)d_{av}]^2\ , \tag{4}$$

where ϵ is the electronic density within the depleted zone (interlayer voids) and $d_s=L-L_K\cos\Psi$, L being the long lattice spacing, L_K the length of the molecules in its more extended conformation [$L_K=n(1.273\ \text{Å})$], and Ψ the molecular tilting angle. The parameter d_{av} is equal to d_s in the case of a perfect crystal.[10]

In order to determine d_{av} for the rotator phases from measurements of x-ray diffraction intensities on a relative scale, we should find the ratio between the intensities $[I(0)]_C$ and $[I(0)]_R$, corresponding to crystal and rotator phases, respectively. This ratio is equal to

$$\frac{[I(0)]_R}{[I(0)]_C}=\frac{[(\eta_c-\epsilon/d_s)d_{av}]_R^2}{[(\eta_c-\epsilon/d_s)d_{av}]_C^2}\ . \tag{5}$$

Since $\eta_c \gg \epsilon/d_s$, $(d_{av})_R$ can be obtained by the approximate expression

$$(d_{av})_R=\left[\frac{[I(0)]_R}{[I(0)]_C}\right]^{1/2}(d_{av})_C\ . \tag{6}$$

The deviation of the d_{av} values determined by means of Eq. (6) from those of Eq. (5) is not grater than 2%. The average parameter $(d_{av})_C$ can be calculated by assuming that the structure of the crystalline phase is defect-free.[11] In this case

$$(d_{av})_C=d_s=(L-L_K\cos\Psi)_C\ . \tag{7}$$

The quotient between the extrapolated intensities is determined from experiments on a relative scale after normalization of the extrapolated intensities to equivalent sample thickness and incident-beam intensity. For the crystalline (orthorhombic) phase of odd-numbered paraffins with $n \leq 25$, the tilting angle is known ($\Psi=0$). Hence the calculation of $(d_{av})_C$ is possible from Eq. (7) and, consequently, Eq. (6) yields $(d_{av})_R$.

Detailed structural data of the crystalline phase of even-numbered paraffins are not available. Consequently, the tilting angle is not known with an accuracy high enough to permit the use of Eq. (7) to determine $(d_{av})_C$. Therefore we have used in this case an alternative procedure. In order to deduce $(d_{av})_C$ for even-numbered paraffins, we determined the ratio of the extrapolated intensities $I(0)$ corresponding to one odd and one even paraffin ($C_{23}H_{48}$ an $C_{24}H_{50}$). The parameter $(d_{av})_{even}$ of the even paraffins was determined by an equation similar to Eq. (6):

$$(d_{av})_{even} = \left[\frac{[I(0)]_{even}}{[I(0)]_{odd}} \right]^{1/2} (d_{av})_{odd} \; . \tag{8}$$

The parameter $(d_{av})_{odd}$ was taken as the average of the d_{av} values corresponding to several odd paraffins with orthorhombic structure.[11]

The extrapolation to zero angle of the low-angle diffraction intensities I_l has been performed by approximating the experimental values of the integrals of the $00l$ diffraction peaks by a fourth-degree polynomial, as described in an earlier paper.[11] Because of the pinhole collimation used in our measurements, the experimental intensities were only corrected for the Lorentz factor and normalized to equivalent sample thickness and intensity of the incident x-ray beam.

In order to determine the second moment σ^2, measurements on an absolute scale are not necessary. It is often useful to determine another parameter $D_t = \sqrt{12}\sigma$, which is equal to d_{av} in case of the absence of molecular defects (perfect crystal).[11] The accuracy of the experimental results is generally not high enough to permit the determination of D_t with reasonable precision for the crystalline phase.[10,11] Therefore the D_t parameter has only been determined here for the rotator phases. From the D_t values it is possible to calculate the mean-square amplitude of the longitudinal displacements of the molecules.[11] Qualitatively, an increase in D_t ($D_t \geq d_{av}$) is associated with an increase in molecular-displacement amplitude. $D_t = d_{av}$ results in cases of absence of longitudinal displacements and intramolecular defects.

EXPERIMENTAL RESULTS

Several diffraction patterns which include the $00l$ reflections from paraffin $C_{24}H_{50}$, at temperatures below and above the crystal-rotator transition, are plotted in Fig. 2. The plots corresponding to several temperatures do not exhibit differences within the domain of stability of each phase. At the transition temperature a sharp increase in intensity of the two lowest-order peaks is observed for each paraffin studied. The diffraction intensities decay more rapidly, for higher orders of reflection, in the rotator phase than in the crystalline phase.

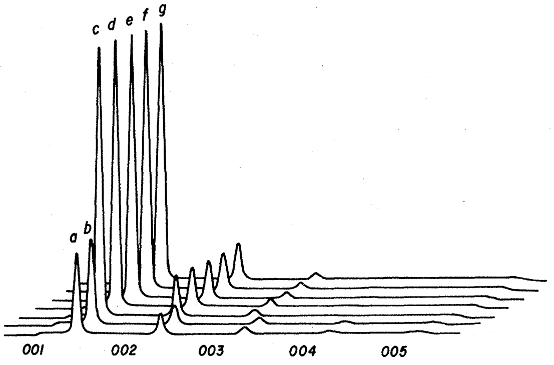

FIG. 2. $00l$ x-ray reflection diagrams corresponding to $C_{24}H_{50}$, at several temperatures: (a) 42.2 °C, (b) 46.0 °C, (c) 49.0 °C, (d) 49.5 °C, (e) 50.0 °C, (f) 50.5 °C, and (g) 51.0 °C.

From the various sets of diffraction patterns corresponding to the different even paraffins, the extrapolated $I(0)$ values have been determined as a function of temperature, as explained in the preceding section.

Substituting in Eq. (8) the experimental value of the ratio $[I(0)]_{24}/[I(0)]_{23}$ and $(d_{av})_{odd} = 1.95$ Å (average value for $19 \leq n \leq 25$), the thickness of the interlayer molecular voids $(d_{av})_{even}$ of the triclinic even paraffins has been estimated. The result was $(d_{av})_{even} = 1.25$ Å, which is significantly lower than that of odd paraffins.

The average thickness of voids, d_{av}, of all even paraffins, is represented in Fig. 3 as a function of temperature. The value $(d_{av})_C$ was assumed to be the same for all the studied even paraffins in the crystalline state. That is a good approximation for $C_{22}H_{46}$, $C_{24}H_{50}$, and $C_{26}H_{54}$ (all having the same triclinic lattice), but it is only a rough estimate for the monoclinic structure of the crystalline phase of $C_{28}H_{58}$. We did not find significant variation in d_{av} within the temperature domain of stability of the rotator phases. Only one experimental value of d_{av} has been determined for the rotator phase of $C_{22}H_{46}$ because of the narrow temperature domain of stability of this phase.

The experimental values of the displacement parameter D_t are also represented in Fig. 3 for the rotator phase of every paraffin. We note that D_t can be considered as temperature independent for $C_{22}H_{46}$, $C_{24}H_{50}$, and $C_{26}H_{54}$. In contrast, the parameter D_t corresponding to $C_{28}H_{58}$ increases with temperature.

DISCUSSION

The discontinuity in the thickness of the interlayer voids at the transition temperature (Fig. 3) is mainly due to the sharp decrease in molecular tilting angle from the

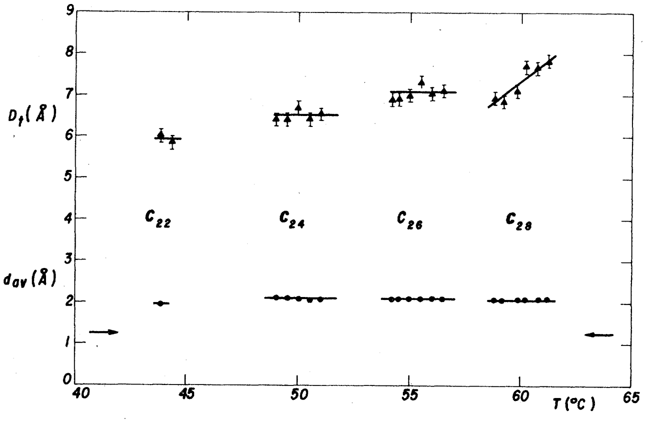

FIG. 3. Disorder parameters of the several even paraffins as functions of temperature (▲, D_t; ●, d_{av}). The arrows indicate the d_s value obtained by use of Eq. (8).

crystalline to the rotator phase. In order to investigate the existence of intramolecular defects, we compared the d_s and d_{av} parameters. The structural parameter d_s, which can be determined from the long spacing L and the length L_K, is equal to 2.30 Å for even paraffins. The mean value d_{av} for rotator phases is approximately equal to 2.10 Å (Fig. 3). These values do not fulfill the condition $d_{av} > d_s$ for the existence of intramolecular (kink) defects.[10,11] Consequently, the present experimental results do not present evidence for the existence of kinks in the even paraffins studied. The unequality $d_s > d_{av}$ of our data may be a consequence of an eventual increase in length of the molecule $[L_K > n(1.273 \text{ Å})]$ in the rotator phase[11] and/or low accuracy of the absolute values of d_s and d_{av} parameters. This may be due to the approximations involved in the calculation of d_{av} [Eq. (8)] and/or the intrinsic low accuracy in the determination of the long spacing L from the angular position of the small-angle $00l$ reflections.

The constancy of D_t for $C_{22}H_{46}$, $C_{24}H_{50}$, and $C_{26}H_{54}$ within the temperature-stability domain of the hexagonal rotator phase implies that the significant variations in longitudinal molecular displacement are associated with major changes in the mean molecular structure which occur at the transition temperature. The singular behavior of $C_{28}H_{58}$, which exhibits a clear variation in D_t within the domain of stability of the monoclinic rotator phase, can be explained as a consequence of a variation in molecular tilting angle.

Average values of the d_{av} parameter are represented in Fig. 4 for the crystalline and rotator phases as a function of the molecular length. This figure also includes the parameter d_{av} corresponding to odd-numbered paraffins. The measured value of $(d_{av})_{\text{even}} = 1.25$ Å for the crystalline phase, which is significantly lower than $(d_{av})_{\text{odd}} = 1.95$ Å, can be easily understood since in crystalline phases of even and odd paraffins the molecules are tilted and nontilted, respectively. The tilting of the molecules in even paraffins allows a closer packing of the molecular ends and, hence, the narrowing of the interlayer voids.

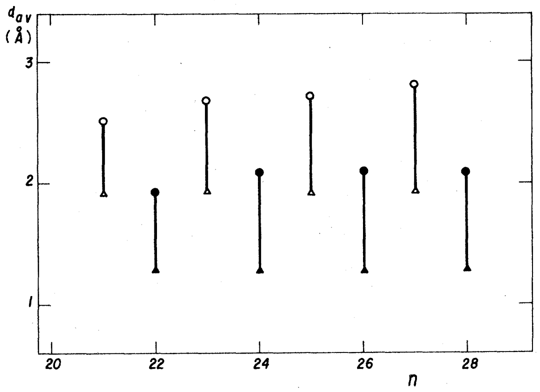

FIG. 4. Average distance d_{av} of even-numbered paraffins corresponding to the crystalline (▲) and rotator (●) phases. The open symbols, corresponding to odd paraffins, have been extracted from Ref. 11 for comparison.

We established from a phase diagram determined in a previous work[15] that the hexagonal rotator-II phase of even paraffins is of the same nature as the rotator II of odd paraffins. In the two phases we have assumed that the molecules are freely rotating around their long axes.[12] The results showed in Fig. 4 evidence a weak but significant structural difference for even and odd paraffins, which may be explained as an effect related to slight variations in interaction between molecular ends. The plot of Fig. 4 suggests that molecules in the rotator phase behave to some extent as in crystalline phases, in the sense that molecule ends interpenetrate more in even than in odd paraffins.

In order to check independently the statement related to the packing differences in rotator phases of even and odd paraffins, we have plotted in Fig. 5 the long lattice spacing L as a function of the molecular length in the rotator-II phase. We can see that the long spacings lie on different straight lines for odd and even paraffins. The lower spacing in even paraffins is consistent with the lower value of d_{av} shown in Fig. 4. We can see that the magnitude of the difference between odd and even paraffins, $\Delta L = 0.2$ Å (Fig. 5), is smaller than $\Delta d_{av} = 0.6$ Å, but this difference may be a consequence of the approximations and experimental errors involved in the determination of d_{av} and d_s, as was pointed out in a preceding paragraph.

Figure 6 represents the average parameter D_t as a function of the molecular length of the paraffins studied. In the same figure we also present the maximum D_t values[11] corresponding to $C_{23}H_{48}$, $C_{25}H_{52}$, and $C_{27}H_{56}$, which are associated with the rotator-II phase for $n=23$ and 25,[6] and with the rotator-IV phase for $n=27$.[9] Since paraf-

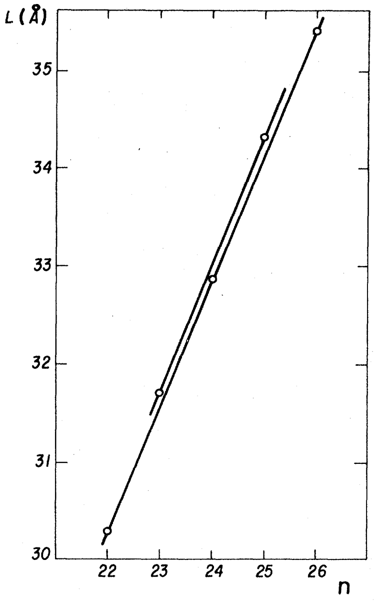

FIG. 5. Long spacing L as a function of molecular length. The plotted parameters have been determined in previous studies (Refs. 5 and 8).

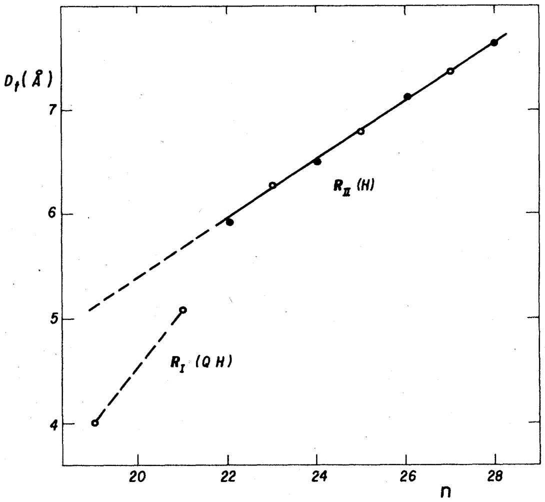

FIG. 6. Disorder D_t parameter corresponding to rotator-I phase for $n=19$ and 21, rotator-II phase for $22 \leq n \leq 26$, and rotator-IV for $n=27$ and 28. The values of odd paraffins are those of Ref. 11. H denotes the hexagonal rotator, QH the quasihexagonal.

fins $C_{19}H_{40}$ and $C_{21}H_{44}$ melt before reaching the free-rotator (R_{II}) phase, their associated D_t values correspond to the quasihexagonal rotator-I phase.[6]

It is apparent in Fig. 6 that the D_t values lie on the same straight line for even and odd paraffins with $n \geq 22$. This suggests that the features of the longitudinal molecular motion are similar in the rotator-II phases of odd and even paraffins. The lower molecular displacement for $C_{19}H_{40}$ and $C_{21}H_{44}$ is expected since the molecular interaction in the quasihexagonal rotator (R_I) phase is stronger than in the free-rotator (R_{II}) phase.

CONCLUSIONS

Several even-numbered paraffins exhibit a layered high-temperature rotator phase in which the molecules are perpendicular ($C_{22}H_{46}$, $C_{24}H_{50}$, and $C_{26}H_{54}$) or tilted ($C_{28}H_{58}$) with respect to the stacking planes. In the rotator phase a displacive disorder has been detected in addition to the previously studied orientational one.

Comparison of the dependence of the thickness of interlayer voids on molecular length for even and odd paraffins (Fig. 4) suggests the existence of two different stacking modes of the molecular extremities according to their evenness. These two stacking modes are not only present in the crystalline phases but also in the rotator phases. This different interlayer correlation does not lead to significant differences in the longitudinal displacements of the molecules, as can be inferred from the data in Fig. 6.

The rather unexpected result concerning the finding of slight but clearly different stacking features in rotator-II phases of odd and even paraffins seems to be conclusive since it has been inferred from two independent measurements (Figs. 4 and 5). This implies that the molecules keep particular features associated with their evenness or oddness even in the hexagonal rotator-II phase. This structural difference suggests that molecules of even paraffins behave like quasifree rotators and not like rigorously free rotators as has been assumed in the past.

The existence of intramolecular (kink) defects, which has been demonstrated for odd-numbered paraffins with $19 \leq n \leq 27$,[11,14] cannot be established from this work for even paraffins with $22 \leq n \leq 28$. This result indicates an evenness dependence of the molecular stability against kink formation. In order to confirm this conclusion, additional experimental studies are required.

---

[1] A. Muller, Proc. R. Soc. London **120**, 455 (1928).

[2] A. Muller, Proc. R. Soc. London, Ser. A **138**, 514 (1932).

[3] A. E. Smith, J. Chem. Phys. **21**, 2229 (1953).

[4] B. Ewen, E. W. Fischer, W. Pieczek, and G. Strobl, J. Chem. Phys. **61**, 5265 (1974).

[5] J. Doucet, I. Denicoló, and A. Craievich, J. Chem. Phys. **75**, 1523 (1981).

[6] J. Doucet, I. Denicoló, A. Craievich, and A. Collet, J. Chem. Phys. **71**, 5125 (1981).

[7] G. Ungar, J. Phys. Chem. **87**, 689 (1983).

[8] I. Denicoló, J. Doucet, and A. Craievich, J. Chem. Phys. **78**, 1465 (1983).

[9] I. Denicoló, J. Doucet, A. Craievich, and C. Germain, J. Chem. Phys. **80**, 1647 (1984).

[10] G. Strobl, B. Ewen, E. Fischer, and W. Piesczek, J. Chem. Phys. **61**, 5257 (1974).

[11] A. Craievich, I. Denicoló, and J. Doucet, Phys. Rev. B **30**, 4782 (1984).

[12] A. Dianoux and J. Doucet, J. Chem. Phys. **81**, 5043 (1984).

[13] G. Zerbi, R. Magni, M. Gussoni, K. H. Moritz, A. Bigotto, and S. Dirlikov, J. Chem. Phys. **75**, 3175 (1981).

[14] M. Maroncelli, S. Ping Qi, H. L. Strauss, and R. G. Snyder, J. Am. Chem. Soc. **104**, 6237 (1982).

[15] I. Denicoló, A. Craievich, and J. Doucet, J. Chem. Phys. **80**, 6200 (1984).