

Evidence for a Pronounced Local Orientational Order in the High Temperature Phase of C₆₀

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The rotational dynamics in the high temperature phase of C₆₀ has been investigated experimentally by means of diffuse x-ray and quasielastic neutron scattering on a single crystal and theoretically by molecular dynamics simulations. Our results provide evidence for pronounced local orientational order with a correlation length $\zeta \sim 40 \text{ \AA}$ at $T = 265 \text{ K}$. The local order seems to be driven by the same nearest neighbor interaction which leads to long range order below T_s but does not possess the symmetry of the low T structure.

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As solid C₆₀ is composed of nearly spherical molecules on a fcc lattice, one may expect that the orientational potential is very soft. It was therefore not surprising that early experiments indicated that the molecules are spinning freely at room temperature: Bragg scattering could be very well described by approximating the C₆₀ molecule by a hollow sphere [1], and the quasielastic neutron scattering observed on a powder sample could be described by a model in which each molecule undergoes rotational diffusion which is uncorrelated with the motion of adjacent molecules [2]. Orientational ordering was found to set in abruptly at $T_s \approx 258 \text{ K}$ [1], but later a variety of experimental techniques indicated that the rotation is not fully free also above T_s . From synchrotron x-ray [3] and neutron [4,5] Bragg diffraction, it was concluded that the atomic density on a C₆₀ sphere at 300 K is nonuniform. The correlation time τ_{NMR} of the rotational dynamics, as determined by NMR measurements, yielded an activated behavior not only in the low temperature phase but also in the high temperature one [6]. X-ray diffuse scattering experiments [7,8] showed that the scattering is not only radially but also *azimuthally* anisotropic.

The experimental results of Refs. [3–8] provide clear evidence that the rotational motion is hindered to some extent. Chow *et al.* [3] discussed the nonuniform atomic density on a C₆₀ sphere in terms of an effective potential that a single C₆₀ molecule sees in the cubic field of its neighbors. In this paper we report results which cannot be understood on the basis of a single molecule effective potential, but point to the importance of intermolecular correlations. The experimental results were obtained by diffuse x-ray and diffuse neutron scattering experiments on single crystals. In particular, the diffuse neutron scattering intensity patterns, observed with a narrow energy window, show very sharp features indicative of a pronounced local order with a correlation length of several tens of angstroms.

The basic features of the observed scattering law were successfully reproduced from structures generated by molecular dynamics calculations. This allowed us to analyze the intermolecular correlations which are at the origin of the observed diffuse scattering peaks. A preliminary account of this work has been given in Ref. [9].

The single crystals were grown from the vapor phase using a double-temperature-gradient technique [10]. X-ray precession photographs of the (111) scattering plane were taken with Mo K_α radiation at room temperature. The neutron measurements were performed on the 2T-triple-axis spectrometer located at the ORPHEE reactor, Saclay, with horizontally and vertically focusing pyrolytic graphite crystals as the monochromator and analyzer. The sample had a volume of $V \approx 5 \text{ mm}^3$ and was clamped between two thin strips of vanadium. The incoherent scattering from the vanadium in the neutron beam was not negligible but rather easy to correct for, as it was nearly Q and temperature independent. Survey measurements were carried out with a final energy $E_F = 29 \text{ meV}$ ($\Delta E = 2.1 \text{ meV FWHM}$), which allowed us to cover a region in momentum space $Q \leq 6.9 \text{ \AA}^{-1}$. Selected areas in reciprocal space were investigated with $E_F = 13.4 \text{ meV}$ giving a better energy resolution ($\Delta E = 0.7 \text{ meV FWHM}$). The Q resolution was sufficient in all cases to discriminate the diffuse scattering from Bragg scattering, apart from relatively small areas in reciprocal space. The temperature was varied between $T = 10$ and 310 K . The results obtained for $T < T_s$ will be published elsewhere [9,11], and only some selected low temperature data will be shown here for the sake of comparison.

The x-ray diffuse scattering photographs showed well-defined peaks, which indicates that the structure is far from complete rotational disorder. The peaks were found along the [110] direction or close to it. Details will be published in a separate publication [12]. Subsequent measurements using quasielastic neutron scattering revealed

even sharper peaks in the diffuse scattering patterns, especially when using a narrow energy window. Typical raw data are depicted in Fig. 1 (upper panel). Sharp peaks were observed not only in radial scans, but also in azimuthal ones. An example is shown in the inset of Fig. 1. Further results summarizing a systematic investigation of a particular area of the $(1\bar{1}0)$ scattering plane are shown in Fig. 2(b). In other areas of the $(1\bar{1}0)$ scattering plane, distinct peaks were observed as well, although not as sharp as those seen in Figs. 1 and 2.

Energy scans revealed that peaks and valleys in the diffuse intensity pattern are correlated with minima and maxima in the quasielastic linewidth (examples are shown in Fig. 3). This explains why the fine structure in the intensity pattern becomes less pronounced when going from a narrow energy window to a larger one and finally to an infinite one (the x-ray case).

We note that the Q dependence of both the diffuse scattering intensity and the quasielastic linewidth observed in

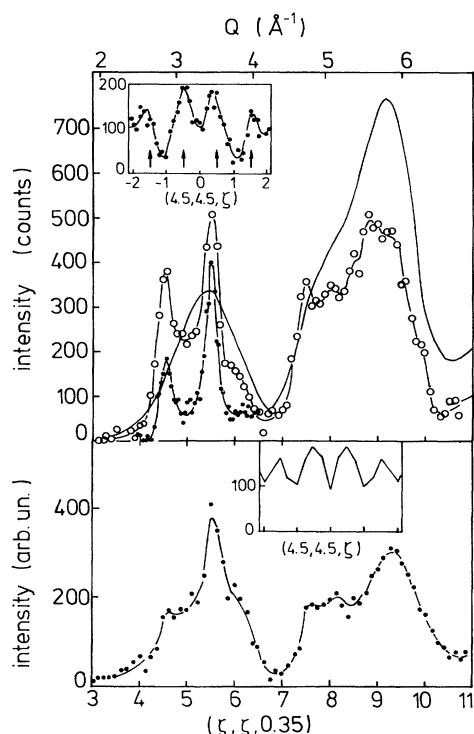


FIG. 1. Upper panel: Diffuse scattering intensity along the line $(\zeta, \zeta, 0.35)$ as observed by neutron scattering. (All indices refer to a cubic lattice with $a_0 = 14.16 \text{ \AA}$). The points refer to measurements using different energy windows (circles: $\Delta E = 2.1 \text{ meV}$, full points: $\Delta E = 0.7 \text{ meV}$ FWHM). The full line shows the calculated energy integrated intensity distribution for uncorrelated rotational diffusion after Ref. [17]. Scaling of the three curves is arbitrary. The inset shows a high resolution measurement in the transverse direction. The arrows correspond to $2a_0$ fcc superlattice spot positions. Lower panel: results calculated from the MD simulation described in the text.

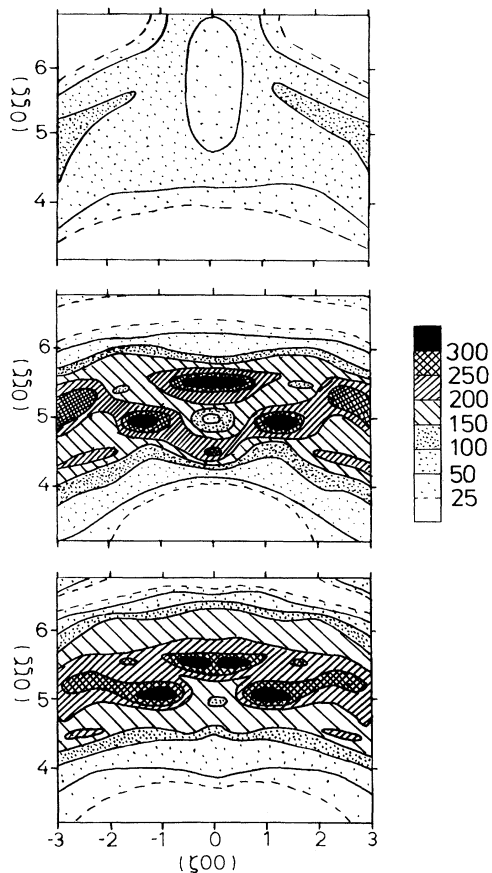


FIG. 2. Diffuse scattering intensity patterns in a special area of the $(1\bar{1}0)$ scattering plane, (above) as observed in experiment at $T = 250 \text{ K}$ (middle) as observed in experiment at $T = 265 \text{ K}$, and (below) as deduced from molecular dynamics simulations. Bragg scattering contributions were omitted in the patterns and the diffuse scattering intensities at the Bragg peak positions interpolated from neighboring points. The energy window was $\Delta E = 2.1 \text{ meV}$ (FWHM).

our experiment are fully compatible with the powder data of Neumann *et al.* [2]. It is the direction dependence of the quantities under discussion which shows the inadequacy of a model where each molecule undergoes rotational diffusion with no correlation between the motions of adjacent molecules.

The observation of rather sharp peaks in the diffuse scattering with a small width in energy (pseudo-Bragg peaks) implies a pronounced local orientational order. From the width in Q of the peaks we estimate the correlation length (as defined by $Z\pi/\Delta Q$) $T = 265 \text{ K}$ to be $\zeta \sim 40 \text{ \AA}$, which is four times the nearest intermolecular distance. One might think that the peaks indicate the appearance of embryos of the low T phase, but we emphasize that the positions of the diffuse peaks shown in Figs. 1 and 2 do not agree with the positions of the fcc-forbidden simple cubic

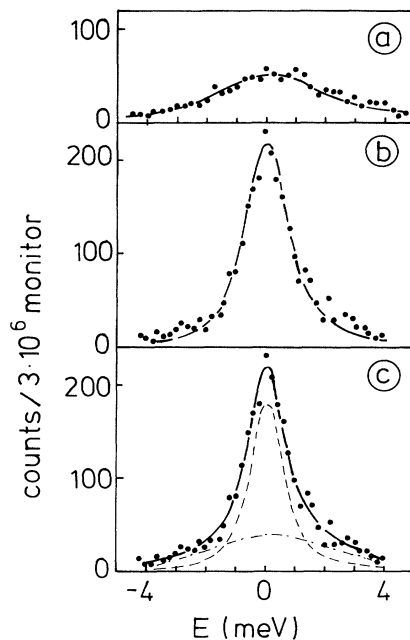


FIG. 3. Energy scans performed at (a) $Q = (0.3, 5, 5)$ and at (b), (c) $Q = (0.3, 5.5, 5.5)$. The full lines are the result of a fit using a relaxation ansatz for the scattering law $S(E) = A[1 - \exp(-E/kT)]E\Gamma/(E^2 + \Gamma^2)$ and folding it with the experimental resolution ($\Delta E = 0.7$ meV, FWHM). In (c) the full line was obtained as the sum of a narrow component (dashed line) and of a broad component having the width as in (a) (dash-dotted line).

(sc) spots of the low T phase and therefore cannot be associated with critical scattering. Critical scattering at the sc spot positions was indeed observed, but in agreement with Blaschko *et al.* [13], only in a very narrow temperature region above T_s ($\leq T_s + 2$ K). On the other hand, measurements performed in fine temperature steps in the close vicinity of the phase transition showed no indication for a divergent behavior of the intensity of the peaks to be seen in Fig. 1. Measurements in a large temperature range $260 < T \leq 310$ K revealed that the peak amplitudes decrease and the peak widths in Q and E increase significantly with increasing temperature, but the peaks remain remarkably well defined at $T = 310$ K, the highest temperature probed in our experiment. The somewhat puzzling conclusion from these observations is that the local order is not a precursor phenomenon of the low T phase.

Well-defined, although relative, broad diffuse scattering peaks have been observed also below T_s . As has been shown in Refs. [9,11], these peaks can be very well explained on the basis of the two-state model of David *et al.* [14]. As the diffuse scattering pattern observed above T_s is very different from that observed below T_s (an example is shown in Fig. 2), this corroborates

our conclusion that there is some fundamental difference between the local structures above and below T_s .

In order to understand the origin and the nature of the local orientational order, we performed a molecular dynamics (MD) simulations based on the split-bond charge model [15,16], developed to explain the external vibrations of the low T phase. The simulations were carried out on macrocells of 256 molecules with periodic boundary conditions. The molecules were assumed to be rigid, and the Newton-Euler equations of motion were integrated with a time step of 0.02 ps for 240 ps. The temperature was chosen so high as to destroy the orientational order of the starting structure within the first 40 ps. As 40 ps is a very short interval, the orientational melting temperature came out unrealistically high, i.e., $T = 900$ K. The diffuse scattering pattern was then evaluated from the structures generated after 140 ps and 240 ps, respectively, by calculating the superlattice intensities arising from the disorder in the macrocell. This procedure has been proven as very satisfactory to simulate the diffuse scattering pattern of the low T phase [9,11]. In order to take the finite energy resolution ΔE into account, the intensities were averaged over a time $\tau \sim \hbar/\Delta E$. The experimental momentum resolution in the vertical direction was accounted for by including superlattice points, above and below the scattering plane, in the evaluation.

As can be seen from Figs. 1 and 2, the basic features of the observed diffuse scattering pattern are well reproduced by the simulation. In particular, the simulations reproduce the observation of diffuse scattering peaks at $(h + \frac{1}{2}, k + \frac{1}{2}, l + \frac{1}{2})$ positions. The fact that the calculated peaks are broader than seen in experiment is presumably due to the rather high temperature assumed in the MD calculations. Further calculations for a lower temperature are planned, which require, however, a larger computational effort as the evolution in time of the structure slows down. We note that the computational effort needed to obtain the results presented in this paper was already very large (several hundred hours of CPU time on the parallel computer, ANUPAM, developed at the Bhabha Atomic Research Centre).

The good agreement between calculated and observed intensity patterns indicates that the structures generated via the MD calculations are realistic. In order to learn what distinguishes these structures from a full orientational disorder, we calculated various pair correlation functions $g_{ij}(r)$ for different sites on the C_{60} molecule, whereby only intermolecular correlations were taken into account. We focussed on the distance range $2.3 \text{ \AA} < r \leq 3.5 \text{ \AA}$, as this covers the range of the closest intermolecular contacts. The calculations were performed for the following sites: atom positions, centers of single and double bonds, and centers of pentagons and hexagons. For an easy comparison of the various $g_{ij}(r)$ functions, all the sites were shifted onto the surface of the molecules.

Those pair correlation functions, which markedly differ from the corresponding functions for complete orientational disorder, are plotted in Fig. 4. For the sake of clarity, we plotted only the excess values from the average of all the $g_{ij}(r)$ calculated. What comes out very clearly from Fig. 4 is that double bonds tend to face pentagons and, to a lesser extent, also hexagons of adjacent molecules, as in the low temperature phase. Concurrently, double bonds tend to avoid double bonds, and in particular pentagon-pentagon contacts seem to be very unfavorable.

The correlations just mentioned support the idea that the driving force for the intermolecular correlations is the same that leads to long-range order below T_s , and so the question arises as to why the symmetry of the locally ordered structures above T_s is different from that of the low T structure. From simplified models based

on a few discrete orientations, we learned that the locally ordered structures are frustrated, and that the frustration is induced by preferred orientations different from the discrete orientations of the low T phase. So far, we can only partly answer the question of which orientations are involved. A good candidate is an orientation which is obtained by a 45° rotation from the so-called standard orientation around one of the (100) axes. However, further orientations are probably involved, too.

In conclusion, we have shown that pronounced orientational correlations persist well above the sc-to-fcc phase transition of solid C_{60} , and that these correlations can be understood from the same intermolecular potential which explains the external vibrations of the sc phase.

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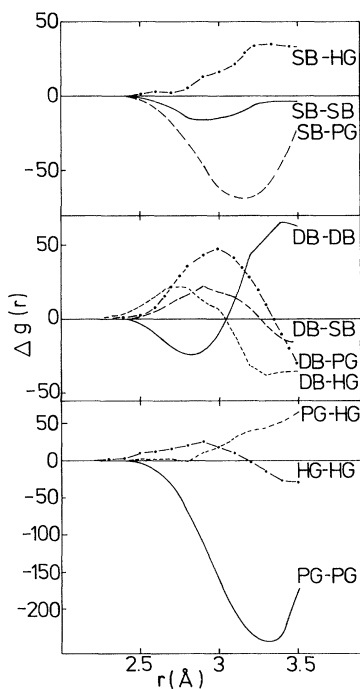


FIG. 4. The pair correlation functions corresponding to various pairs of sites on the surface of neighboring molecules. In order to emphasize preferred correlations, the excess values of the correlation from its average over all the pairs of sites is plotted. DB: double bond center, SB: single bond center, PG: pentagon center, and HG: hexagon center. Only those functions are plotted which strongly deviate from the average.

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