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ANALYSIS OF LOCAL FREE VOLUME IN LAMELLAR CRYSTALS : AN AID FOR UNDERSTANDING RADICAL MOBILITY IN SOLIDS

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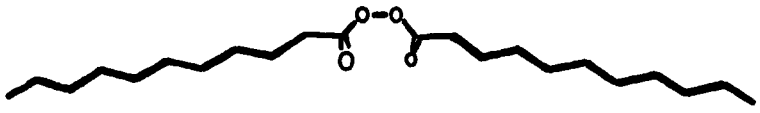
Abstract In crystals with two short axes it is easy to partition free volume into local components by plotting a profile of the free areas of planes parallel to the plane defined by the short axes. Local free volume is used to analyze radical motion in bis-undecanoyl peroxide. It is relevant to melting-point alternation in long-chain compounds and to packing in a lipid bilayer.

INTRODUCTION

In solids, as in fluids, free volume should be important in determining molecular mobility and reactivity. For either phase one may estimate molar free volumes by comparing experimental densities with molecular volumes, which can be calculated by a method such as group additivity.[1] In many cases, especially for large molecules and rigid media, one might suppose that local free volume near some particular portion of the molecule should have more influence over mobility and reactivity than overall molar free volume does. For crystalline solids of known structure it should be possible to test this hypothesis. The present paper describes a preliminary approach toward dissecting free volume into local components in order to understand how a particular crystal lattice accomodates the stress generated by a solid-state reaction.

Using X-ray diffraction and radical-pair EPR spectros-

copy of single-crystals Segmuller has recently demonstrated that n-decyl radicals, generated as a pair by partial photolysis of crystalline bis-undecanoyl peroxide (UP), behave



UP

"nontopochemically" by recoiling from one another in two distinct steps before they come together again and react.[2] The dominant motion consists of a rotational translation in which each CH_2 group of one radical replaces its neighbor down the zig-zag chain. This type of screw motion has been proposed for relaxation in polyethylene,[3] although its importance in n-alkanes has been disputed.[4] Hollingsworth has used FTIR to confirm that the screw motion in UP is driven by relaxation of compressive stress on the CO_2 molecules, which are generated together with the radicals by peroxide photolysis.[5]

It seemed at first surprising that the best way to accomodate stress is for an entire radical to shift longitudinally rather than for the first few carbons to shift laterally.[6] Crystals of long-chain compounds are typically much less compressible along the chain axis than perpendicular to it.[7] In polyethylene the compressibility difference is 70-fold.[8] When longitudinal motion occurs in UP, the environment must somehow make room for the terminal methyl group, since the n-decyl chain is not likely to shorten appreciably. Figure 1 shows that longitudinal motion in UP can be accomodated in part by lateral compression of the next layer of molecules, but the question remains why this motion should be preferred over lateral motion of a part of the radical. We suspected that unusually low packing density near

the methyl terminus favored the screw motion. The remainder of this paper explains what aroused this suspicion and how we tested it quantitatively.

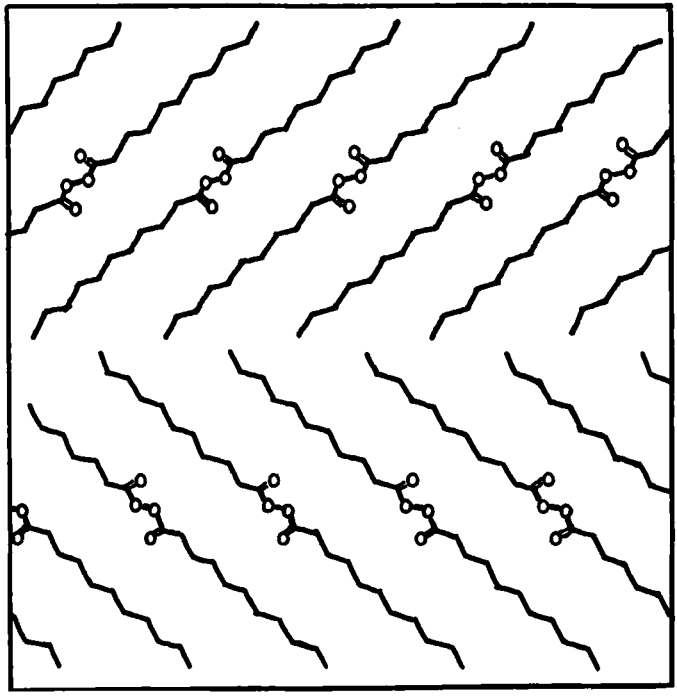


Figure 1. Layer structure of UP viewed along the a axis (7.421 Å). The b axis (8.036 Å) points right; the c axis (39.99 Å), up. C-centering of space group $C222_1$ offsets the next level nearer the viewer by half a b spacing to the right.

MELTING POINT ALTERNATION IN LAMELLAR CRYSTALS

Most long-chain compounds crystallize with molecules arranged side-by-side to give two-dimensional sheets, which stack so that molecules in adjacent sheets meet through their terminal groups.[9] More than a century ago Baeyer noted the alternation in melting point which differentiates odd from even members

of so many homologous series.[10] Some fifty years later Malkin realized that alternation occurs only for lamellar crystals where the long molecular axes are not perpendicular to the interface between sheets.[11] He proposed that forces within the sheets should be a smooth function of chain length, so that alternation must arise from differing interactions between terminal groups of adjacent lamellae. In 1956 von Sydow noted that the tilt of the zig-zag backbone of crystalline fatty acids makes the terminal C-C bonds roughly parallel to the interface in the even (high-melting) acids, while in the odd acids they are roughly perpendicular.[9] The alternation of melting points and of many other properties should provide important information about nonbonded interactions and their anisotropy, but it has received little systematic attention, perhaps because so few three-dimensional crystal structures have been determined for long-chain compounds.

Of course all symmetrical diacyl peroxides from fatty acids have an even number of atoms in the long chain, but still there is an alternation of melting points between molecules with twice an even number and those with twice an odd number (see Figure 2).[12] This is hardly surprising, since the fatty acids, which show alternation, crystallize as dimers. UP is a member of the low-melting series of peroxides, and X-ray diffraction showed that its terminal C-C bonds are roughly perpendicular to the interface, as in the low-melting fatty acids. This made us suspect that packing between adjacent lamellae is inefficient, and that excess free volume at the interface may help accomodate the longitudinal radical motion observed by Segmuller. Furthermore carbonyl branching in the middle of the UP molecule might decrease free volume near the radical centers and hinder lateral motion. It is presumably to reduce such congestion that the molecules

incline so far from being perpendicular to the interface. Figure 1 shows how tilting offsets the peroxide bulges.

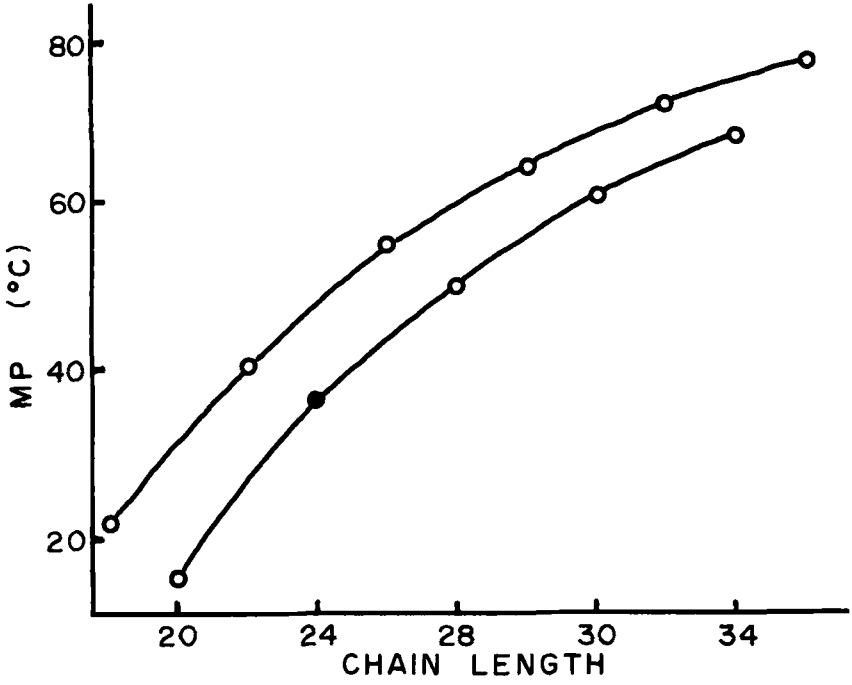


Figure 2. Melting points for symmetrical diacyl peroxides of fatty acids (Ref. 12). Chain length includes the peroxy oxygens. UP is the filled point in the 4n series.

FREE AREA ANALYSIS OF LAMELLAR STRUCTURES

Molar free volume is easy to define once one has decided on a scheme for estimating molecular volume, but local free volume is more difficult, since one must also define "local". A perfectly general approach to this problem would be to plot the radial distribution of free area about each atom of interest. That is, to consider a set of spheres centered on some atom (or any other point), and plot, as a function of radius, the fraction of spherical surface which is not within van der Waals distance of any atom. For all atoms in a crys-

tal such curves would converge to the same overall fractional free volume at large distance, but the short-range behavior should show local free volumes characteristic of each atom.

For long-chain compounds which crystallize in unit cells with two short axes, there is an easier method. One can choose a set of planes parallel to the plane defined by the two short axes and plot the fractional free area of the planes as a function of their positions in the third direction. Since the repeat distance on these planes is short, the free area does not need to be evaluated over more than one unit cell. The free area on planes in other directions would take longer to evaluate and would not permit the same local interpretation.

Evaluating the cross-sectional area of a molecule is difficult because of single and multiple overlaps among its atoms. We wrote a program for the Apple II+ computer which drew filled circles on the high-resolution (280 x 190) graphics screen to represent the intersection of a plane with the van der Waals spheres of all atoms. A subroutine then counted the number of pixels within the boundaries of a unit cell which were illuminated. From this number it was easy to reckon the cross-sectional area of the molecule corrected for overlap. Figure 3 shows two such planes for polyethylene.[13] Remarkably enough there is less free area on the plane which bisects the C-C bonds and avoids atom centers than on the plane which passes through the nuclei of the CH_2 groups. This is because atoms from adjacent layers consume very little area on the latter plane.

Of course calculated free area depends on the choice of van der Waals radii, but for comparative purposes a single set of reasonable values should suffice. We chose radii of 1.8 Å for carbon and oxygen and 1.35 Å for hydrogen.

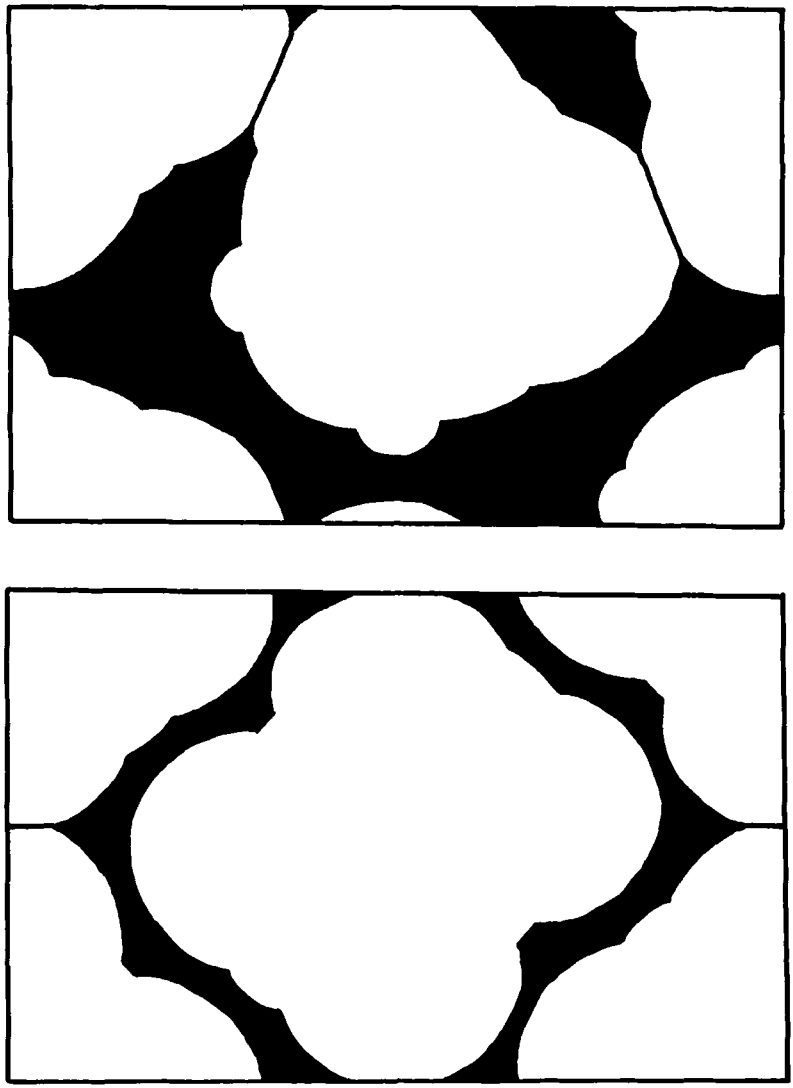


Figure 3. Cross sections of crystalline polyethylene perpendicular to the long molecular axis. The top section passes through atomic centers and has 24% unoccupied area (shaded); the lower section, midway between atoms, has 11%.

A more serious problem is that x-ray atomic coordinates for long-chain compounds are often unreliable because of low crystal quality. Appreciable differences in atom-atom distances could cause large differences in the intramolecular overlap of van der Waals spheres and thus in calculated free areas. We minimized this problem by adjusting atomic positions toward 1.53 Å C-C distances and 112° C-C-C angles[14] and then recalculating hydrogen positions with C-H distances of 1.08 Å and H-C-H angles of 109.5°.

APPLICATION TO RADICAL MOTION IN BIS-UNDECANOYL PEROXIDE

To appreciate the significance of free-volume distribution in UP it is useful first to examine several hydrocarbons in the high-melting series. Figures 4-6 are free-area plots for polyethylene, n-octane, and n-octadecane.[15] Circles show the position of carbon atoms. In polyethylene free area varies from 11% to 24% and averages about 16%. For both alkanes the amount of free area along most of the chain is similar to that in polyethylene, but there is extra free area at the interface between layers. It is hardly surprising that the roughly cylindrical centers of chains pack more efficiently than their roughly hemispherical ends. It is more noteworthy that at the terminal carbon atom the free area has already fallen into the range characteristic of polyethylene.

Figure 7 is an analogous plot for UP. In this case atoms near the middle of the hydrocarbon chain pack about as densely as those of polyethylene. There is very little free volume near the carbonyl branching, but the two terminal carbons fall in a region with nearly twice the free area of polyethylene. It seems obvious that the n-decyl radicals should relax by longitudinal motion into a region of low density rather than by lateral motion into a region of high density.

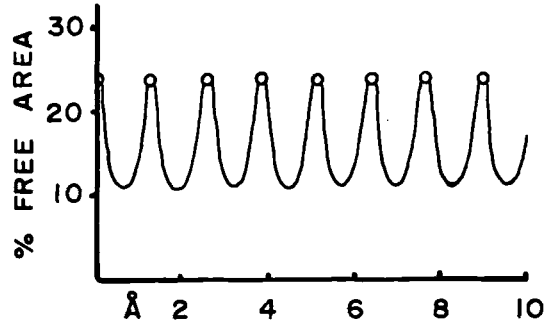


Figure 4. Cross-sectional free area of polyethylene as a function of distance along the molecular axis from an arbitrary carbon. Circles show atomic positions.

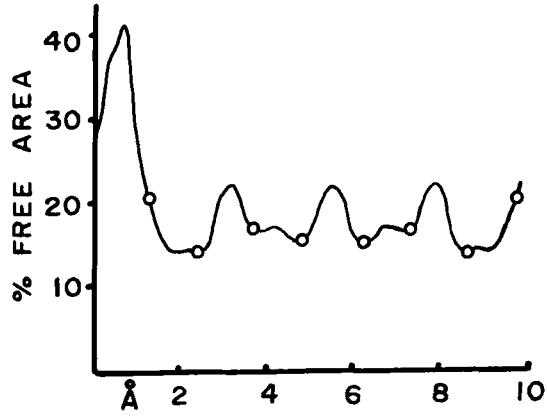


Figure 5. Cross-sectional free area of n-octane as a function of distance from the interface between molecular layers.

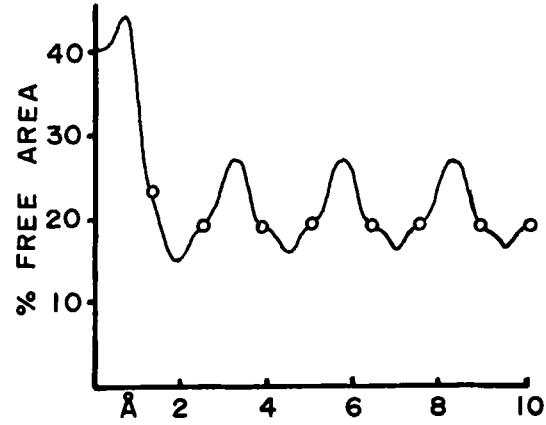


Figure 6. Analogue of Figure 5 for n-octadecane.

Figure 7. Analogue of Figure 5 for UP. Open circles are saturated carbons; filled circles, oxygens; the half-filled circle is carbonyl carbon.

Comparing Figure 7 with Figures 4-6 shows that the overall molar free volume of crystalline UP is much less informative than its distribution is.

OTHER APPLICATIONS

There are many striking phenomena which depend on interlamellar properties in general and on odd-even alternation in particular. These include vibrational spectra of hydrocarbons,[16] radical stability in irradiated fatty acid amides,[17] and formation of different radiolysis products in hydrocarbons of different chain-length parity.[18] There is a recent report of strict alternation in the nature of radicals formed by radiolysis of the n-alkanes from C_{10} through C_{25}.[19] All of these problems should profit from free-volume analysis, although in many cases crystallographic data are lacking.

The interlamellar structure of lipid bilayers has substantial biological implications. Since X-ray structural data are available for the phospholipid 1,2-dilauroylphosphatidyl-

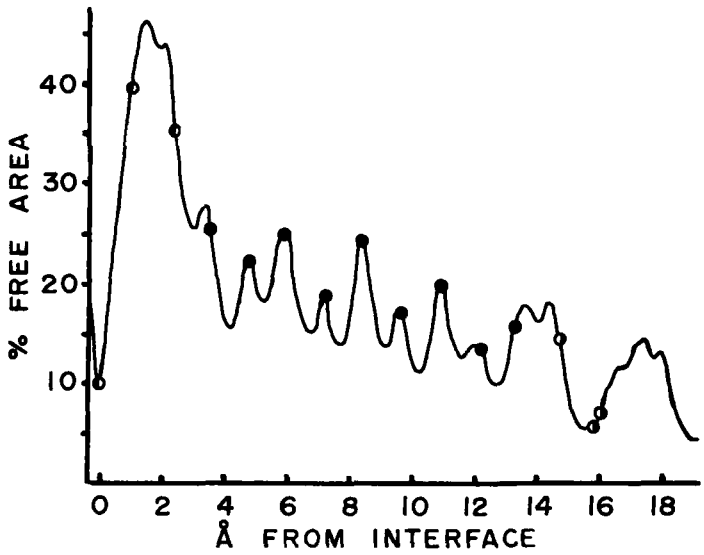


Figure 8. Free area profile of a lipid. Circles shaded on the left show carbon positions of the straight 12-carbon chain; those shaded on the right, of the bent chain. Filled circles are positions of both chains. Positions of other atoms in the polar region at the right are not indicated.

ethanolamine,[20] we have plotted its free volume distribution in Figure 8. The profile is qualitatively similar to that of UP. The region near the polar head group is very densely packed, while a region of low density extends to 3 Å from the interface. Free volume right at the interface is unusually low because chain ends from adjacent layers interdigitate slightly. Isotropic thermal parameters for atoms in this structure may not be experimentally significant, but it is notable that they correlate better with local free volume than they do with distance from the methyl terminus.

ACKNOWLEDGEMENTS

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