

Disorder at the Bilayer Interface in the Pseudohexagonal Rotator Phase of Solid *n*-Alkanes

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Molecular-dynamics calculations are used to characterize the structure and dynamics of the two solid bilayer phases of the *n*-alkane tricosane ($C_{23}H_{48}$). In the crystalline orthorhombic phase at 38°C , chains undergo translational, rotational, and torsional motions, but are otherwise essentially all-*trans* and perfectly ordered with a herringbone packing. By contrast, at 42°C , in the pseudohexagonal (rotator) phase, there is a dramatic increase in longitudinal chain motion, each chain now has four possible orientations, and a significant number of conformational defects develop, predominantly at the chain ends.

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The nature of the interface within molecular bilayers is not only of intrinsic interest but may, indirectly (i.e., through refinement of intermolecular force models) be of relevance to the understanding of both real and model biomembranes,¹ micelles,² and Langmuir-Blodgett films.³ The simplest example of a bilayer system that is stable *around room temperature* is provided by the odd-chain-length normal (*n*-) alkanes (C_mH_{2m+2}) with *m* ranging from 19 to 25.

The complexity of the phase diagrams exhibited by these long-chain molecules near their respective melting points has only become apparent in recent years. Stable solid phases have been identified that contain both conformational and orientational disorder.^{4,5} Moreover, the number and character of these phases vary with the molecular chain length.⁵ Elegant experiments based on diffraction⁶ and spectroscopic techniques,⁴ plus calorimetric and NMR studies,⁷ have established that when the crystalline phase transforms to the pseudohexagonal rotator phase, longitudinal diffusive motion of the chains increases dramatically and a significant concentration of conformational defects is generated, predominantly in the vicinity of the bilayer interface.⁴

We have used constant-volume molecular-dynamics calculations to study the structure and dynamics of the C_{23} *n*-alkane compound (tricosane) in both the crystalline and pseudohexagonal rotator phases close to the phase-transition temperature of 40°C . The aim is to characterize further the nature of the bilayer interface, and the differences between these solid phases, making use of a microscopic model based on flexible (semirigid) chains and atom-atom intermolecular potentials.⁸ We find that the model yields a stable crystalline phase with all-*trans* chains. In the rotator phase, each molecule is

undergoing rotational jumps between four possible sites. These jumps are *independent* of enhanced chain longitudinal translational motion. A variety of intramolecular defects occur, predominantly near the chain ends, but these cause relatively little roughening of the bilayer interface. The most common defects are the so-called end-gauche defects and kinks.⁴ In one example, we observed kink formation at the center of a chain and its subsequent migration down the chain backbone towards the bilayer interface. These findings complement experimental studies,⁴⁻⁶ and give a microscopic picture of a stable, but highly disordered, bilayer system. The four-site orientational distribution function that we obtain for the bilayer phase confirms the structure inferred from an analysis of the x-ray and calorimetric data.⁵

In the crystalline phase, *n*-alkane chains adopt their all-*trans* most elongated conformation and pack in a lamellar bilayer structure. Within each layer the molecular longitudinal axes are mutually parallel and the planar zigzag chains have two possible orientations; thus there are four molecules in the unit cell. The experimental lattice constants for crystalline tricosane are $a = 7.47 \text{ \AA}$, $b = 4.98 \text{ \AA}$, and $c = 62.40 \text{ \AA}$.⁹ However, around 40°C , this crystalline phase transforms to a pseudohexagonal rotator phase with $a = 8.00 \text{ \AA}$, $b = 4.85 \text{ \AA}$, and $c = 63.22 \text{ \AA}$; this is sometimes referred to as the R_I or face-centered orthorhombic (fco) phase.^{5,6} Just below its melting point, 46°C , tricosane undergoes a further transformation to a rhombohedral (R_{II}) structure,⁵ but, because this is a trilayer structure, it will not concern us here.

Molecular-dynamics calculations have been carried out on periodically replicated bilayer systems arranged as 3×5 unit cells in the (*a*,*b*) plane. The sample con-

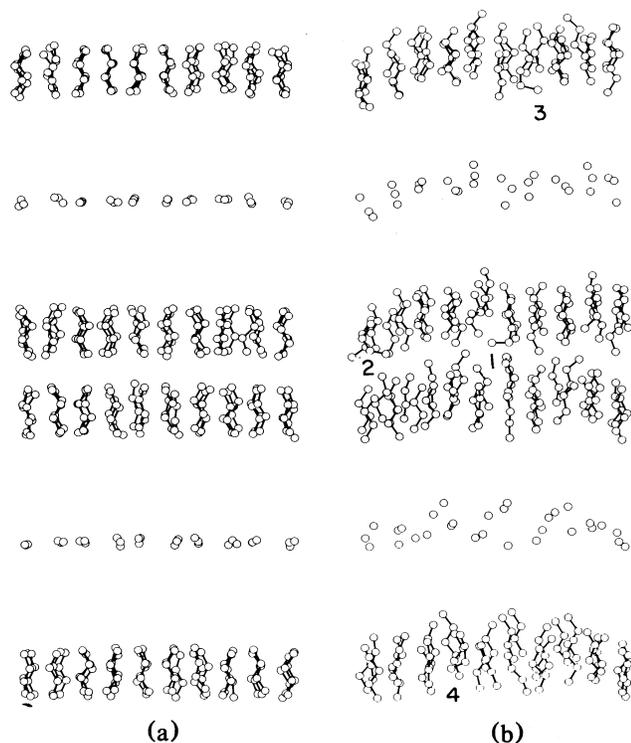


FIG. 1. Instantaneous configurations of the bilayer systems viewed down the a axis: (a) the crystalline orthorhombic phase at 38°C , (b) the pseudo-hexagonal phase at 42°C . For clarity, no H atoms and only the terminal plus the central C atoms are indicated. The disorder at the interface is dominated by longitudinal diffusion of the chains as is clearly indicated by the enhanced fluctuations in the position of the central C atom in case (b).

tained only one unit cell in the c direction so that the total system consisted of 60 chains (4260 atoms). Because of the boundary conditions there are two distinct interfaces. This was the largest system that could be conveniently studied with our available computing resources. The intermolecular interactions were of the atom-atom type and included C-C, C-H, and H-H contributions, truncated at around 8 \AA . The chains were partially rigid in the sense that the H atoms follow the chain backbone, but are otherwise constrained to prevent the wagging, twisting, and scissoring motions of the methylene groups as well as the C-H stretching. The intramolecular potential consists of bending and torsional terms plus methylene-methylene group interactions starting from fourth neighbors. This potential model was used recently to study a monolayer of infinitely long, flexible chains.⁸ In the present work we have added a torsional potential for the terminal methyl groups with a barrier height of 12 kJ/mol .¹⁰ The equations of motion were solved with use of standard methods.¹¹

The crystalline phase was brought to equilibrium at

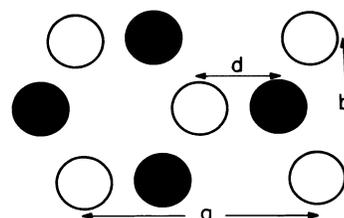


FIG. 2. A view down the c axis of an idealized bilayer system; d indicates the relative displacement of the two layers.

the desired temperature (3°C) by a constant-temperature technique¹¹ and the phase-space trajectories were followed for 8 ps with a time step of 3.3 fs. A typical instantaneous configuration viewed down the crystal a axis is shown in Fig. 1(a). The crystal was very stable and the bilayer interface well defined, there being only modest longitudinal displacements of the chains, even though the temperature is very close to the melting point.

An analogous, but somewhat longer (19 ps), simulation was performed for the pseudo-hexagonal phase at 42°C ; the experimental a and b lattice constants were used, but c was held at 62.40 \AA rather than the experimental value of 63.22 \AA .⁵ This modest compression was induced so that we could compare the crystalline and rotator phases at a constant bilayer thickness. We began with all-*trans* chains oriented parallel to the (b,c) plane and the chain centers of mass located as suggested by experiment, i.e., with d , the relative displacement along the a axis, equal to $\frac{1}{2}a$ (Fig. 2).⁵ This configuration, which is consistent with the x-ray structure ($Fm\bar{3}m$), immediately disordered; each chain rotated to adopt one of four possible orientations, located at $\pm 45^\circ$ and $\pm 135^\circ$ with respect to the crystal b axis. We therefore carried out the long calculation starting from a configuration in which all-*trans* chains were randomly distributed among these four possible sites. We note that this initial configuration is compatible with the $Fm\bar{3}m$ structure inferred from x-ray data⁵ and is almost certainly also compatible with NMR data taken on deuterated samples of the n -alkane $\text{C}_{19}\text{H}_{40}$ in its pseudo-hexagonal rotator phase.⁷ This structure is similar to the four-site orientational distribution found in molecular-dynamics⁸ and Monte Carlo¹² studies on the rotator phases of n -alkane monolayers.

An instantaneous configuration of the bilayer rotator phase is shown in Fig. 1(b). Although the temperature is only 4°C higher than in the crystalline phase, and the cross-sectional area per chain differs by only 6%, it is immediately evident there is now considerable disorder present. However, the system was stable as judged by the ease with which the temperature was controlled at its desired value and by the fact that the calculated internal stress-tensor components were all small (i.e., less than about 1 kbar). Other quantities, which will be discussed

below, were also stable throughout the run.

It is worthwhile to comment on the relative lateral positions of the two monolayers which comprise the periodically replicated bilayer system. Figure 2 shows the centers of mass of an idealized bilayer system as viewed down the c axis. In the crystalline phase, the measured⁹ relative displacement parameter is $d=b/3=2.5$ Å, whereas in the pseudohexagonal rotator phase it is $d=b/2=4.0$ Å. While the simulations agreed with the latter value, the calculated relative displacement for the crystalline phase was $d=3.3$ Å. We note also that in the crystalline phase the longitudinal chain axes are all parallel to the c axis, whereas in the rotator phase the chains have a mean canting angle of about 6° . Methyl-group rotation is active in both phases but is roughly twice as frequent in the rotator phase.

We now turn to a discussion of the rotational disorder. In the crystalline phase one rotational defect appeared and subsequently disappeared over a period of about 200 time steps but, apart from this isolated event, the system remained fully ordered. This behavior contrasts strongly with that found in the rotator phase where the four-site orientational distribution appeared to be quite stable (Fig. 3). The mean residence time between jumps was estimated to be about 13 ps which compares favorably with estimates based on neutron measurements.¹³

Even though the simulations were carried out at essentially the same temperature, the much larger dispersion in the positions of the chain centers of mass in Fig. 1(b) compared with that in Fig. 1(a) indicates the presence of enhanced longitudinal chain displacements in the rotator phase. The root mean square chain displacement along the c axis is calculated to be 1.2 Å, which compares rather well with the value 1.7 Å estimated from small-angle

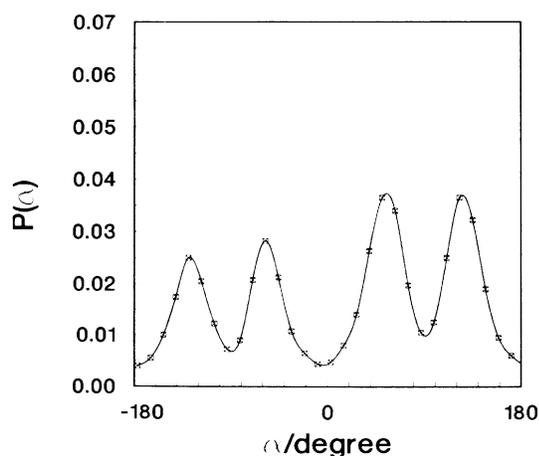


FIG. 3. Orientational probability distribution for chains in the rotator phase. Differences in peak intensities are a consequence of poor statistics (on average each chain has made only about 2 jumps in the total molecular-dynamics run).

x-ray diffraction data.⁶

Figure 1(b) also indicates the presence of intramolecular defects in the rotator phase. The presence of a *gauche* defect, two of which are clearly evident, will cause a chain to shorten by about 1.1 Å. On average, we find about 6% of the chain ends to have *gauche* defects, a concentration which implies that the average chain length will shorten by $2 \times 0.06 \times 1.1 \text{ Å} = 0.13 \text{ Å}$. The actual mean end-to-end chain length in the rotator phase was found to be shortened by about 0.30 Å, which is a considerably larger value than can be attributed solely to the presence of *gauche* defects. It is likely therefore that the chains are shortened predominantly via torsional motions.

Figure 4 compares the calculated percentage of *gauche* defects at various positions along the n -alkane chain backbone with that measured experimentally on a closely related system ($C_{21}H_{44}$).⁴ Both the calculations and the experiments suggest an exponential growth of defects towards the chain ends, but the calculated number of defects seems to be too few, possibly because of inadequacies in the assumed form of the chain intramolecular potential.⁸

It seems natural to imagine that the bilayer interface is the most hospitable place for the birth of intramolecular defects; however, on one occasion we observed the spontaneous formation of a defect in the middle of a chain! This defect then proceeded to migrate along the chain. Such an observation suggests that the birth and death of intramolecular defects might profitably be modeled with use of theories of soliton dynamics.

In summary, we have used molecular-dynamics calculations to study the nature of the disorder present in the bilayer rotator phase of n -alkanes. We find that the dominant effect is due to longitudinal motion of the chains. Although intramolecular defects are present in

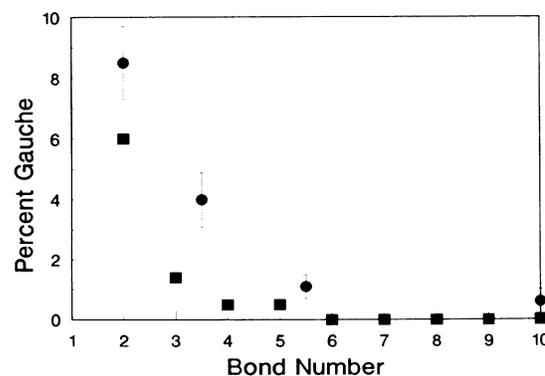


FIG. 4. Percentage of *gauche* defects along the chain backbone. The circles are experimental values taken from Ref. 4 the squares are the molecular-dynamics results with errors at least comparable to those of experiment.

abundance, and occur mainly at the bilayer interface, they have a relatively modest effect on the structure. These findings are in complete accord with inferences based on spectroscopic studies⁴ and small-angle x-ray diffraction.⁶ A prediction emerges from our calculations; it is that the pseudo-hexagonal rotator phase has a four-site orientational distribution function. It would be of interest to know whether or not this finding is supported by new experimental data.

Finally, our successful modeling of the bilayer interface required explicit inclusion of intermolecular interactions between hydrogen atoms. In previous attempts to model related membrane and micelle systems, such interactions have often been omitted.¹⁴ It remains to be seen whether or not this simplification was indeed justifiable for these more complicated systems.

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