

Studies on Tilted and Untilted Rotator Phases of Long Chain Alkanes

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Abstract

Long chain hydrocarbon molecules show significantly similar thermal properties and phase sequences. These chain alkanes (C_nH_{2n+2} from $n=20$ to 33 and above) exhibit different rotator phases depending on their chain lengths. The phase behaviour of these rotator phases has been studied both experimentally and theoretically. All these rotator phases correspond to different orderings and dynamic behaviours caused by the intermolecular interaction field coupled with thermal agitation. A unified description of all probable phase sequence irrespective of chain lengths and the reason behind the generation of tilt in relatively longer chain alkanes is presented. We calculate the Fourier transform of the approximate atom to atom potential and thereby construct the free energy density. We obtain all theoretical phase sequences in terms of structural order parameters. We compare these phase sequences with those obtained from Landau mean-field theory and find explicit chain length dependence with molecular tilt within Landau theory framework as well. The theoretical predictions conform with existing experimental studies.

Keywords

Rotator Phases, Alkanes, Phase Transitions

1. Introduction

Almost all normal alkanes show characteristic of thermal properties which follow a common phase sequence order from low temperature crystalline (X) phase to higher temperature partly ordered rotator phases. Rotator phases are defined as the phases where long range orientational ordering is lost but translational ordering is retained. Different rotator phases have been identified corresponding to difference in molecular arrangements like rotator-I (R_I) phase, rotator-II (R_{II}) phase, rotator-III (R_{III}) phase, rotator-IV (R_{IV}) phase and rotator-V (R_V) phase [1-4].

In the R_I phase the molecules are untilted with respect to the layers and there is rectangularly distorted hexagonal lattice. The R_{II} phase is usually described as composed of molecules that are also untilted with respect to the layers that are packed in a hexagonal lattice. The Rotator-III (R_{III}) phase is triclinic, with molecules tilted in a non-symmetric azimuthal direction, in between the NNN and the nearest-neighbour (NN) directions. Rotator-IV (R_{IV}) phase is

monoclinic, with NNN-tilted molecules and end-to-end layer stacking. Finally, the R_V phase is the same as the R_I phase except that the molecules are tilted towards their next nearest neighbour (NNN).

The study of these rotator phases has been performed extensively over the last few years mostly because of its importance as a basic building block of a vast range of biomolecules of both biological and commercial importance [1-10]. While the experimental study through various spectroscopy and calorimetric techniques completely exposed the inherent structural order of these molecules in different temperature, the theoretical explanation mostly followed the track of mean-field approach [11-15]. However, none of these studies put any light on the chain length driven restriction of observable phase sequences. In smaller chain alkanes the phase sequence is liquid- R_{II} - R_I -X but in longer chains ($> C_{27}$) the normal phase sequence is liquid- R_{IV} - R_V -X. The tilted phases appear in relatively longer chain alkanes. So far all the theoretical studies on rotator phases have been kept confined in two dimensional modelling [11] and Landau theory [12-15]. Wurger [11] used Buckingham type potential

approximation to describe the molecular field in 2D array of rotator phases. This model gave qualitatively correct fit to the experimental data obtained so far. However, no information regarding of tilt could be obtained due to the two dimensional nature of the field. In general abstraction the molecular field for tilted systems can be compared to external magnetic field in Heisenberg ferromagnetic system, where the field corresponds to the orientation of molecules.

The molecular field in the assembly of rotator molecules comes from the potential of intermolecular C-C, H-H and H-C interaction pairs with C-C interaction being the chief contributor. While all these van-der Waals potential depend on their relative distances due to the rotational degree of freedom in rotator crystals it is convenient to consider each sp^3 H-C-H as a single source of interaction. Then the potential depends on intermolecular C-C distance and azimuthal orientation of the molecules. This could be possible because the H-C-H bonds do not have any internal rotational degree of freedom with respect to molecular axis. This approximation is not valid in cases of poly-alkanes. Naturally we see different phase sequence in them. In this paper the potential of a single carbon molecule on sight due to all the other molecules follows few approximations. First the molecular potential field is considered to be of the form

$$V(r) = Ar^{-6} + Be^{-Cr}$$

Where A, B and C are constants. We approximate the molecular field in the form where we consider the other nearest neighbour molecules as constituted of large number of hypothetical van-der Waals interaction sources. Each H-C-H site on one chain is assumed to interact with these continuum type of molecules. This continuous approximate molecular modelling can incorporate the ignored interaction of molecules beyond the nearest neighbour distances also. With suitable constants A, B and C logically this is always a permitted approximation since the distance dependence of the molecular potential is kept the same. The effect of nearest neighbour molecules is only taken into account. The total potential energy of a single molecule thus becomes the summation of potential of all its H-C-H sites. It is evident that the approximation of nearest neighbour count is valid for atoms near the center of mass only. So we consider the centered molecular potential only and expand the molecular potential of other interaction sites in terms of Taylor expansion and sum over. Fourier expansion of the constants

$$V_c^{ij} = \sum(-A_{ij} r^{-6} + B_{ij} e^{-Cr}) \frac{\epsilon \Delta x}{l_0} = \frac{\epsilon}{l_0} \int dx (-A_{ij} r^{-6} + B_{ij} e^{-Cr}) P(x) \quad (1)$$

where $P(x)$ is the probability density. For a finer model, we consider linear probability density $P(x)$ along molecular chain.

Consideration of the central molecule enables us to limit the integration within the nearest neighbours only. Beyond which the field is considered too weak to be effective. Tilt angle is defined as the angle between long axis and the

A and B in terms of rotational pair angle variable gives us the insight to relevant azimuthal couplings in terms of molecular geometry.

We sort out the observable order parameters from the potential expressions under mean-field approximation and find out the relation between chain lengths and tilt order parameters. The structured parameter depended phase sequences are studied. In the first part of the paper, the pair potential model and order parameters are explained and the phase sequences are derived. The dependence between block radius l and critical molecular chain length is studied with molecular chain length. These studies are compared with the experimental results.

2. Theory

2.1. Potential Model

As indicated above, the only time dependent portion of our potential model is the relative azimuthal angle between two molecules. Since the atoms within the molecules are assumed to have no internal rotational degree of freedom, this corresponds to a planar interaction model. Before doing this two dimensional approximation, we calculate the long chain interaction potential of single H-C-H site which is situated at the molecular center of mass. For odd chain molecules there will be exactly one site of this kind, for even chains there will be two sites equally close to the center of mass. The potential of H-C-H sites adjacent to the central site will be related with an analytic power series with an approximation of near equivalence.

We take the central atom of the j -th molecule and consider its potential energy due to the interaction of the molecule of the k -th molecule which is its nearest neighbour. The k -th molecule is considered as it is constituted of large number of point molecules along its molecular axis proposed earlier. We consider an infinitesimal portion Δx on a locally defined x of the k -th molecules with distance vector obeying the relation $r = r_0 + x$, where r is the vector distance between center of mass of the j -th molecule and the position x far from the molecular center of mass of the k -th molecule have the vector distance r_0 .

If the hypothetical number density of molecules along the k -th chain is ϵ and l_0 be the chain length, the total molecular potential of central molecule can be read as

molecular axis. If θ_j is the scalar tilt angle of the j -th molecule then it is evident that

$$r^2 = r_0^2 - 2r_0 x \sin \theta_j + x^2 \quad (2)$$

So the potential becomes

$$V_c^{ij} = \frac{\epsilon}{l_0} \int dx \left[-A_{ij} (r_0^2 - 2r_0 x \sin \theta_j + x^2)^{-3} + B_{ij} e^{-C \sqrt{(r_0^2 - 2r_0 x \sin \theta_j + x^2)}} \right] P(x) = \frac{\epsilon}{l_0} \int dx [I_1(r_0, \sin \theta_j) A_{ij} + I_2(r_0, \sin \theta_j) B_{ij}] P(x) \quad (3)$$

If φ_i and φ_j be the azimuthal angle of the i -th and j -th molecules in the lattice plane, then we incorporate the azimuthal dependency of the constants A_{ij} and B_{ij} in terms of double Fourier series expansion

$$A_{ij} = \sum_{n,m} A_{nm}^{ij} e^{in\varphi_i + im\varphi_j} \quad (4)$$

$$B_{ij} = \sum_{n,m} B_{nm}^{ij} e^{in\varphi_i + im\varphi_j} \quad (5)$$

Here azimuthal order parameter is defined as $\langle e^{in\varphi} \rangle$. The integral functions can also be represented in terms of Taylor expansion of $\sin \theta_j$ around $I_1(R_0, 0)$ and $I_2(R_0, 0)$ in the form

$$I_1(r_0, \sin \theta_j) = \sum_n C_1^n(r_0) \sin^n \theta_j \quad (6)$$

$$I_2(r_0, \sin \theta_j) = \sum_n C_2^n(r_0) \sin^n \theta_j \quad (7)$$

$$E_{\{\varphi\}} = \sum_i (E_i^0 / 2) (1 - \cos 3\varphi_i) + \sum_{k,l} [B_{kl} \exp(-Cr_{kl}) - A_{kl} r_{kl}^{-6}] \quad (9)$$

The first sum in Eq. (9) includes all bonds subject to rotation; the second sum includes all atom pairs k, l whose distance of separation r_{kl} depends on one or more of the φ . The terms in the second sum describe the repulsions between non-bonded atom pairs. The terms of the both sums are determined by the set of rotation angles $\{\varphi\}$. A_{kl} and B_{kl} are constants characteristic of the atom pairs. The conformational energies of n-alkanes chains can be calculated from Eq. (9).

2.2. Landau Model

We will now construct the Landau free energy in terms

$$F = F_0 + \frac{1}{2} \alpha \theta^2 + \frac{1}{4} \beta \theta^4 - \frac{1}{6} \gamma \theta^6 \cos 6\delta - \frac{1}{12} \eta \theta^{12} \cos 12\delta + \frac{1}{2} a \xi^2 - \frac{1}{3} b \xi^3 \cos 6\omega + \frac{1}{4} c \xi^4 - \frac{1}{6} d \xi^6 \cos 12\omega - J \theta^2 \xi \cos 2(\delta - \omega) + f_1 + f_2 \quad (10)$$

where f_1 and f_2 are the stress energy and stress energy shared along the chain respectively. The stress energy shared along the chain can be calculated by defining the order parameter $\mu = \frac{(l-l_0)}{l}$. Here l_0 is the original length and l is the layer width. The length width can be expressed as

$$F = F_0 + \frac{1}{2} \alpha \theta^2 + \frac{1}{4} \beta \theta^4 - \frac{1}{6} \gamma \theta^6 \cos 6\delta - \frac{1}{12} \eta \theta^{12} \cos 12\delta + \frac{1}{2} a \xi^2 - \frac{1}{3} b \xi^3 \cos 6\omega + \frac{1}{4} c \xi^4 - \frac{1}{6} d \xi^6 \cos 12\omega - J \theta^2 \xi \cos 2(\delta - \omega) + \frac{1}{2} m \mu^2 + H \mu \xi + L \theta^2 \mu + P \mu \theta^{12} \cos 12\delta + f_1 \quad (12)$$

Where F_0 is free energy density of the R_{II} phase. As usual in the Landau theory, we assume $a = a_0(T - T_1^*)$ and $\alpha = \alpha_0(T - T_2^*)$. T_1^* and T_2^* hypothetical second order transition temperatures. All other coefficients are assumed to be positive and temperature independent. In our previous paper [13] we extensively studied the chain length dependence of the rotator phase sequence using the free energy density (12) excluding the stress energy. Minimization of Eq. (12) with respect to θ, ξ, ω , and δ yields five rotator phases: $R_I, R_{II}, R_{III}, R_{IV}$ and R_V . So the above free energy density describes the $R_{II} - R_I, R_I - R_V, R_{II} - R_V, R_{IV} - R_{III}$ and $R_{IV} - R_{II}$ phase transitions which conform with experimental studies [1-5].

Here tilt order parameter is defined as $\langle \sin^n \theta \rangle$. The potential for the far system can be expressed as

$$V = \sum m V_c^{ij} + V_{layering} \quad (8)$$

where m represents the number of H-C-H sites. For non-layered cases all sites over carbon long chain have exactly the same potential. For layered cases the molecules situated closer to the chain acquires slightly more potential which we have termed as $V_{layering}$. For the rotator cases there are directly two types of $V_{layering}$, $V_{layering}$ for bilayer and trilayer. Our model may ignore it as a constant since layer configuration doesn't change over $X-R_I-R_{II}$ or $X-R_{IV}-R_{III}$ phase changes.

The intramolecular energy associated with the configuration specified by the set of rotation angles φ is given by [16-18]

of chain length potential. Similar to our previous paper [12], we define the tilt and lattice distortion as two primary order parameters. The tilt angle and the lattice distortion are described by two-component order parameters. The tilt components can be expressed through a polar tilt angle θ and the tilt azimuth δ . The distortion components are expressed through the distortion amplitude ξ and the azimuth 2ω .

Then the Landau free energy density can be written as [12].

$$l = \frac{1}{4} \sum e^{-E(l)/k_B T} l \quad (11)$$

where $E(l)$ is defined in Eq. (9). Then the free energy density (10) can be rewritten as

3. Conclusion

We have defined the chain length dependence of the tilt angle and azimuthal angle. The reason behind the generation of tilt in relatively longer chain alkanes is discussed. We calculate the Fourier transform of the approximate atom to atom potential and thereby construct the Landau free energy density. A unified description of all rotator phase sequence irrespective of chain length is discussed.

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