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Simple Landau Model of the Liquid-R_{II}-R_I Rotator Phases of Alkanes

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ABSTRACT

Simple Landau free energy function is presented to describe the Liquid-R_{II}-R_I phase sequence of alkanes and transitions between them. The order parameters necessary to describe these rotator phase transitions are identified. We present a mean-field description of the Liquid-R_{II} and Liquid-R_I transitions. General arguments are presented for the topology of the phase diagram in the vicinity of the Liquid-R_{II}-R_I triple point. Within this model the Liquid-R_{II} and Liquid-R_I transitions are found to be always strongly first order. Calculations based on this model agree qualitatively with experiments.

1. Introduction

During the last two decades much progress has taken place in the field of rotator phases. Rotator phases are among the most interesting condensed states of matter exhibited by normal alkanes (C_nH_{2n+2}), alcohols, and other hydrocarbon chain systems consisting of layered structures with three dimensional crystalline order of the center of mass, but no long range orientational order of the molecules about their long axes. Rotator phases have a number of unique and unusual properties which include surface crystallization, anomalous heat capacity, negative thermal compressibilities and unusually high thermal expansions. Five different rotator phases had been identified. The rotator-II (R_{II}) phase is usually described as composed of molecules that are untilted with respect to the layers that are packed in a hexagonal lattice. The layers are stacked in an ABCABC... trilayer stacking sequence. This phase is also referred to as the rhombohedral phase. In the rotator-I (R_I) phase the molecules are also untilted with respect to the layers and there is a rectangularly distorted hexagonal lattice. The layers are stacked in an ABAB... bilayer stacking sequence. This phase is referred to as the face-centered-orthorhombic (FCO) phase. In shorter chain lengths the phase sequence was reported to be Liquid-R_{II}-R_I-Crystal.

A large number of experimental studies [1-10] are devoted to describe the structure and the phase transitions of the rotator phases. According to the X-ray scattering study by Sirota *et al.* [3], the R_{II}-R_I transition is first order

with jump of the distortion order parameter and sharp peak on the heat capacity data [4]. The binary mixtures of normal alkanes [11-14] also shows a first order character of the R_{II}-R_I transition. Sirota *et al.* [15] carried out a high pressure study on the R_{II}-R_I transition and confirmed the first order character of the R_{II}-R_I transition. Zammit *et al.* [7,8] studied the IL-R_{II} and R_{II}-R_I transitions in pure and binary mixtures of alkanes. Over the IL-R_{II} transition, they observed the single peak in both the specific heat and latent heat in the pure material, splits into two features at different temperatures. This indicates the first order character of the IL-R_{II} transition. They also confirmed the first order character of the R_{II}-R_I transitions. The presence of the thermal hysteresis at these transitions indicates the first order character of the transition.

Theoretical studies of the R_{II}-R_I transition follow two main lines. The first approach consists of Monte Carlo and molecular dynamics simulations [16-22] which confirms the first order character of the Liquid-R_{II} (IL-R_{II}) and R_{II}-R_I transitions. The second approach is pursued by Wurger [23] and Mukherjee [24-34]. Wurger [23] developed a microscopic model for the pair interaction of hydrocarbon chains and discussed the detailed structure of the R_I and R_{II} phases in terms of a molecular-field approximation. In a series of paper Mukherjee [24-26] discussed R_{II}-R_I phase transition within Landau phenomenological approach and discussed in detail the various aspect of this transition including the elastic properties.

To the best of the author's knowledge, there is so far no detailed theoretical studies on the IL-R_{II}-R_I phase sequence and the transitions between them. The purpose of the present paper is to investigate the IL-R_{II}-R_I phase

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sequence and the transitions between them within Landau theory. We define a new order parameter to describe the IL-R_{II} and IL-R_I phase transitions.

2. Model

Order Parameters

The R_I phase differs from the R_{II} phase only in the distortion of the hexagonal lattice. Following [5,35] we define the lattice distortion parameter $\xi = \left(a^2 - b^2\right)/\left(a^2 + b^2\right)$, where a and b are the major and minor axes of an ellipse draws through the six nearest neighbors. The distortion ξ is defined with respect to a plane whose normal is parallel to the long molecular axes. $\xi = 0$ for the R_{II} phase. Thus we take ξ as an order parameter for the R_{II}-R_I transition.

Now to define the order parameter of the IL-R_{II} or IL-R_I transitions. The low temperature crystal phase of *n*-alkanes is found to exist in layered structures. In these cases the molecules stay in some layer stacking and the probability that a single molecule is present (partially) in two simultaneous layers is almost zero. When the temperature rises further the stacking breaks, *i.e.* the molecules start occupying positions which are shared by more than one layer stacking. We may choose to represent alternate layer sequences with suffixes $1, 2, 3, \cdots, j$ etc. The bilayer stacking can be represented as $A_1 A_2 A_1 A_2 A_1 A_2 \cdots$ and the trilayer stacking can be represented as $A_1 A_2 A_3 A_1 A_2 A_3 A_1 A_2 A_3 \cdots$ We represent the probability of the k-th molecule of the system to occupy any of the j-th layer sequence as $P_k\left(A_j\right)$. For bilayer the only feasible cases are $P_k\left(A_1\right)$ and $P_k\left(A_2\right)$, one of which is 1 and the other being 0 in perfect layer ordering. Now we define a correlation factor β_k for the k-th molecule in a N-layer stacking as

$$\beta_k = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} P_k\left(A_i\right) P_k\left(A_j\right) \qquad (1)$$

This is clearly 0 in ordered layer phase and non-zero in other phases with lower or higher order.

The rotator phases of n-alkanes are found to exist in bilayer and trilayer structures. If we consider the correlation factor for the highest possible layer structure in the alkanes, *i.e.* trilayer we find that for the k-th molecule

$$\beta_k = P_k\left(A_1\right) P_k\left(A_2\right) + P_k\left(A_2\right) P_k\left(A_3\right) + P_k\left(A_3\right) P_k\left(A_1\right) \quad (2)$$

It is 0 (or almost zero) in R_{II} and R_I phases which in nature are bilayer and trilayer respectively. β_k does have a finite value in the liquid phase which can be calculated. In isotropic liquid phase the probability density of the k-th molecule is constant everywhere in space. So,

$$P_k\left(A_1\right) = P_k\left(A_2\right) = P_k\left(A_3\right) = \frac{\left(V_{\text{layer}}\right)\left(\dfrac{N_{\text{layer}}}{3}\right)}{V_{\text{total}}},$$

N_{layer} is the total number of layers. Hence β_k can be expressed as

$$\beta_k = \frac{1}{3}\left(\frac{V_{\text{layer}}}{V_{\text{total}}}\right)^2 N_{\text{layer}}^2 = C\left(\text{say}\right) \qquad (3)$$

Thus β_k is independent of k. Hence we define the correlation order parameter η as

$$\eta = \frac{1}{C}\left(C - \bar{\beta}\right) \qquad (4)$$

Here the average correlation factor is calculated for all molecules together.

Thus η is 0 is the isotropic liquid phase and has a value >0 in the R_I and R_{II} phases.

3. Free Energy

Thus we take ξ and η as two order parameters involved in the R_I-R_{II}, IL-R_{II} and IL-R_I phase transitions. For simplicity we neglect the weak interlayer interaction between the stacking layers in different rotator phases so that the problem becomes two dimensional. The distortion is a two component order parameter; its components are expressed the distortion amplitude ξ and the azimuthal angle 2ω. The multiplier 2 comes from the fact that the distortion is a symmetric traceless tensor. Since the the free energy is a scalar quantity, negative and positive ξ and η result in inequivalent structures, causing the Landau free energy expansion contain ξ^3 and η^3 terms, thus resulting in a first order transition. Expanding the total free energy in terms of the above mentioned order parameters yields

$$F = F_0 + \frac{1}{2}\alpha\eta^2 - \frac{1}{3}\beta\eta^3 + \frac{1}{4}\gamma\eta^4 + \frac{1}{2}a\xi^2$$
$$- \frac{1}{3}b\xi^3\cos6\omega + \frac{1}{4}c\xi^4 + H\eta\xi \qquad (5)$$

where F_0 is free energy of the isotropic liquid phase. The coefficients a and α are assumed to vary strongly with an external parameter. For $\eta = 0$, free energy (5) describe a first order R_I-R_{II} transition for $b > 0$ and $c > 0$. In this case the minimum free energy occurs at $\omega = 0$, for $b > 0$ and at $\omega = \pi/3$ for $b < 0$. According to the experimental observations, in the R_I phase, $\omega = 0$. H is the coupling constant. β, γ, b, c and H are chosen positive.

The material parameters a and α can be assumed as $a = a_0\left(T - T_1^*\left(l\right)\right)$ and $\alpha = \alpha_0\left(T - T_2^*\left(l\right)\right)$. T_1^* and T_2^* are virtual transition temperatures. a_0 and α_0 are constants.

From the experimental phase diagrams [3] one observes, $T_1^*\left(l\right)$ and $T_2^*\left(l\right)$ can be portrayed as

$$T_1^*\left(l\right) = T_1^0 + u\left(l - l_0\right)/l_0 \text{ and } T_2^*\left(l\right) = T_2^0 + v\left(l - l_0\right)/l_0,$$

where l_0 is some specific chain length of the molecules. u and v are positive constants.

Minimization of Equation (5) with respect to ξ and η yields the following phases:

1) Isotropic liquid (IL) phase: $\eta = 0$, $\xi = 0$.
This phase exists for $\alpha > 0$ and $a > 0$.
2) R_{II} phase: $\eta \neq 0$, $\xi = 0$.
The R_{II} phase exists when $\alpha < 0$ and $a > 0$.
3) R_I phase: $\eta \neq 0$, $\xi \neq 0$.
The R_I phase exists for $\alpha < 0$ and $a < 0$.

Thus it is clear from the solutions that three types of transition are possible: 1) IL-R_{II}; 2) IL-R_I; 3) R_{II}-R_I.

The sufficient condition for the R_I phase to be stable are

$$\frac{\partial^2 F}{\partial \xi^2} = a - 2b\xi + 3c\xi^2 > 0 \qquad (6)$$

$$\frac{\partial^2 F}{\partial \eta^2} = \alpha - 2\beta\eta + 3\gamma\eta^2 > 0 \qquad (7)$$

$$\frac{\partial^2 F}{\partial \xi^2} \cdot \frac{\partial^2 G}{\partial \xi^2} - \left(\frac{\partial^2 F}{\partial \xi \partial \eta}\right)^2 = a\alpha - H^2 + a\eta(3\gamma\eta - 2\beta)$$
$$+ \alpha\xi(3c\xi - 2b) + 2b\eta\xi(2\beta - 3\gamma\eta) \qquad (8)$$
$$+ 3c\eta\xi(3\gamma\eta\xi - 2\beta\xi) > 0$$

These three conditions determine the stability of the R_I phase explicitly. The sufficient condition for the stability of the R_{II} phase reads

$$\frac{\partial^2 F}{\partial \eta^2} = \alpha - 2\beta\eta + 3\gamma\eta^2 > 0 \qquad (9)$$

For the IL phase the stability conditions are $\alpha > 0$ and $a > 0$.

By lowering the temperature from the isotropic liquid phase, the R_{II} and R_I phases can appear sequentially or in partial sequence. The R_{II} and R_I phases can arise either directly from the IL phase along the curves IL-R_{II} and IL-R_I or along the curve R_{II}-R_I. In the spirit of Landau theory all the phase transitions IL-R_{II}, IL-R_I and R_{II}-R_I are first order because of the cubic invariant in the free energy expansion. If all the phase transitions involved are first order ones, then one can observe the IL-R_{II}-R_I triple point as observed in experiment [3].

The conditions for the first order R_{II}-R_I transition can be obtained as

$$F_I(\xi) = 0, F_I'(\xi) = 0, F_I''(\xi) \geq 0 \qquad (10)$$

The conditions for the first order IL-R_I transition are given by

$$F_I(\xi, \eta) = 0, F_I'(\xi, \eta) = 0, F_I''(\xi, \eta) \geq 0 \quad (11)$$

The conditions for the first order IL-R_{II} transition read

$$F_{II}(\eta) = 0, F_{II}'(\eta) = 0, F_{II}''(\eta) \geq 0 \qquad (12)$$

Solving (10)-(12) simultaneously will determine the various phase transition lines. **Figure 1** shows a typical phase diagram for the IL-R_I, IL-R_{II} and R_{II}-R_I phase transitions. As can be seen from the **Figure 1**, the R_{II} and R_I phases arise from the isotropic phase along the curves IL-R_{II} and IL-R_I or along the curve R_{II}-R_I respectively. The IL-R_{II} and IL-R_I transitions are first order because of the cubic invariant in the free energy expansion. The line of the R_{II}-R_I transition starts at the IL-R_{II}-R_I triple point as shown in **Figure 1**. When the temperature of the IL-R_{II} and of R_{II}-R_I transitions coincide, a triple point appears.
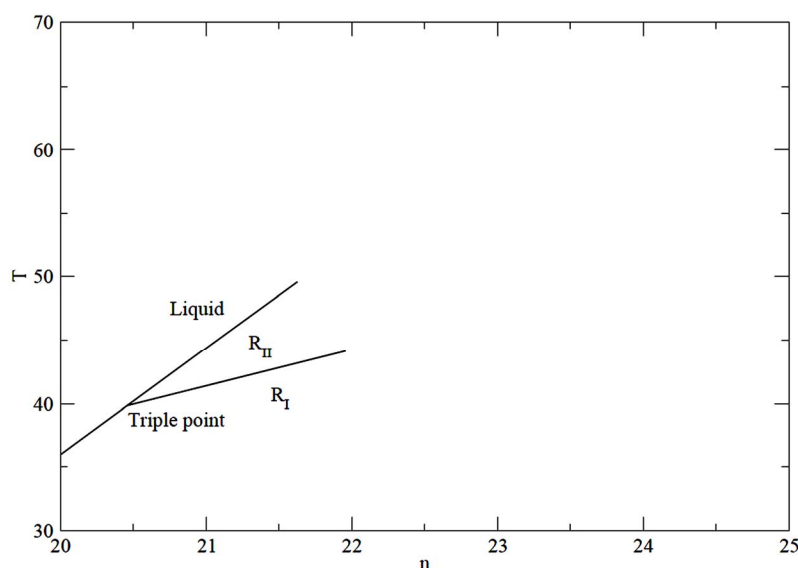

Figure 1. Possible chain length (n)-temperature (T) phase diagram in the vicinity of the Liquid-R_{II}-R_I triple point. $n = (l - l_0)/l_0$.

The region of the R_I phase shrinks and finally disappears when the IL-R_{II} transition takes place. In experimental studies [3], alkanes C20-C27 show such a IL-R_{II} transition via triple point. Thus the above analysis of the IL-R_{II}-R_I triple point agrees well with the experimental observations [3]. Thus there is always a direct IL-R_{II} transition is possible within the framework of our model free energy (6) satisfying the above stability conditions. Of course the IL-R_I transition could proceed before the IL-R_{II} the transition temperature $T_{IL\text{-}R_{II}}$ is reached. To prevent this, $T_{IL\text{-}R_{II}}$ has to be larger than the IL-R_I transition temperature $T_{IL\text{-}R_I}$. Thus we have always $T_{IL\text{-}R_{II}} > T_{IL\text{-}R_I}$. The cubic coefficient β in the free energy (5) yields a first order IL-R_{II} transition at

$$T_{IL\text{-}R_{II}} = T_2^* + 2\beta^2/9\alpha_0\gamma$$

with an order parameter jump $\Delta\eta = 2\beta/3\gamma$ and a latent heat of $\Delta H = \left(2\alpha_0\beta^2 T_{IL\text{-}R_{II}}/9\gamma^2\right)$. The so-called temperature hysteresis is related to the existence of metastable states within a certain temperature range. The above analysis qualitatively agrees with experimental observations[3,4,7,8].

4. Conclusion

A simple model free energy has been constructed to describe the IL-R_{II}-R_I phase sequence and transitions between them. The order parameters are identified for different phase transitions. The model predicts the first order character of the IL-R_{II}, IL-R_I and R_{II}-R_I transitions and IL-R_{II}-R_I triple point in the T-n phase diagram. The proposed interpretation of the IL-R_{II} transition allow us to explain the various types of phase behavior observed experimentally. These results are in qualitative agreement with all experiments reported so far.

5. Acknowledgements

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