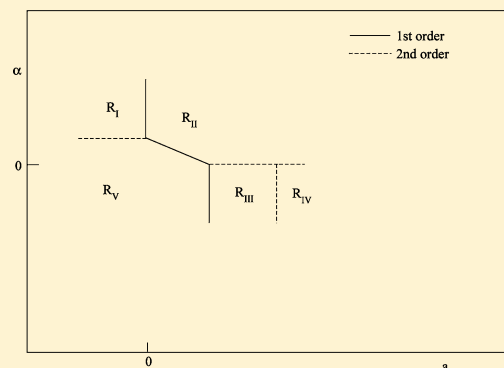


Effect of Gauche Molecular Conformations and Molecular Flexibility on the Rotator Phase Transitions of Alkanes

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ABSTRACT: Experimental studies have shown that the gauche molecular conformations and the chain configurations play an important role in determining the structures and the phase transitions of the different rotator phases of *n*-alkanes. We extend our previous phenomenological theory to describe the effect of gauche defects and molecular flexibility on the various rotator phase transitions of *n*-alkanes. The roles of gauche defects and molecular flexibility are discussed by means of phenomenological theory. The effect of gauche defects and molecular flexibility is to modify the Landau coefficients and to shift the transition lines in the phase diagram. The theoretical predictions are found to be in good qualitative agreement with available experimental results.



INTRODUCTION

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. In alkanes, the rotator phases have been observed for carbon numbers $9 \leq n \leq 40$ interposed, in temperature, between the liquid and fully crystalline phases. Five different rotator phases have been identified by X-ray techniques.^{1–8} In the rotator-I (R_I) phase, the molecules are untilted with respect to the layers, and there is rectangularly distorted hexagonal lattice. The layers are stacked in an ABAB.... bilayer stacking sequence. The rotator-II (R_{II}) phase is usually described as being 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. In the rotator-III (R_{III}) phase, the molecules are tilted in a nonsymmetric azimuthal direction, in between the next nearest-neighbor (NNN) and the nearest-neighbor (NN) directions. The rotator-IV (R_{IV}) phase consists of NNN-tilted molecules and end-to-end layer stacking. The rotator-V (R_V) phase is the same as the R_I phase except that the molecules are tilted toward their NNN. The transitions between the different rotator phases have been extensively studied experimentally by several authors^{5,7,9–12} using calorimetry and X-ray diffraction at room pressure.

The low temperature form of alkane molecules is a straight zigzag chain. Thus the molecules in the low temperature crystalline phase are in all-trans configuration. In the rotator phases, nonplanar conformers begin to play an important role.¹³ The main type of such conformers is that containing the end-gauche modification, or gauche–trans–gauche sequence. The latter gives a kinked shape to the molecule. The main

experimental technique to measure the gauche concentration is by vibrational spectroscopy. Spectroscopic measurements^{14–16} show that there are substantial numbers of chain-end gauche-bond defects in the rotator phases. The number of gauche defects is known to increase with increasing temperature in the rotator phases of longer chain lengths. It is well established that larger head groups on surfactants will cause the molecules to tilt. This mechanism may be responsible for the tilt in the rotator phases. Thus the gauche defects are known to strongly influence the transitions between rotator phases.^{5,7,9} The arrangement of covalent bonds within the chain molecules as well as the weak intermolecular interactions strongly affect the mechanical properties of alkane crystals and rotator phases consisting of chain molecules.

The long chain molecules of *n*-alkanes are characteristic of their high flexibility due to their enormous variety of configuration. Thus the influence of molecular flexibility may be another factor for the various structures of the rotator phases and transitions between them. The dependence of chain length on the rotator phase transitions in *n*-alkanes was observed by several authors.^{5,14} Sirota et al.⁵ measured the change in effective length of the molecules with temperature in the R_V phase where the molecular tilt can change with temperature by the relation $d(T) = l(T) \cos \theta(T)$, where l is an effective length of the molecule, d is the layer spacing, and θ is the tilt angle. The roles of molecular flexibility are very important in the phase transitions in chain molecules.^{17,18} By an orientational phase transition, the flexible molecules usually more or less change their configurations. In a recent work²² we studied the effect of gauche defects and chain flexibility on the R_I – R_V

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transition within phenomenological theory. Wurger^{20,21} proposed a mean-field model to study the conformational defects in alkanes. Liang et al.¹⁹ studied the conformational disorder in crystals of long chain systems in the form of gauche defects using large-scale molecular dynamics simulations. However, there is no particular systematic theoretical work to explain the gauche molecular conformations and molecular flexibility on the different rotator phase transitions.

In this paper, we discuss the effect of gauche defects and molecular flexibility on the different rotator phase transitions. We first construct a Landau free energy expansion for variation in the lattice distortion, tilt, lattice directions, and tilt directions in the different rotator phases of alkanes. This model free energy has been used to describe the phase transitions in the rotator phases.^{22–28} We then examine the gauche defects and the molecular flexibility in the rotator phase transitions that can be favored by this free energy.

THEORY

We developed a Landau theory^{22–28} for transitions among different rotator phases. In this theory we take the tilt angle 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 . The multiplier 2 comes from the fact that the distortion is a symmetric traceless tensor. Then the expansion of the free energy in terms of these two order parameters takes the form

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

where F_0 is the free energy 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^* are the hypothetical second-order transition temperatures. a_0 and α_0 are positive constants. The other coefficients are assumed to be temperature independent. For $\theta = 0$, the free energy (eq 1) describes the first order R_{II} – R_I transition for $b > 0$ and $c > 0$. In this case, the minimum free energy corresponding to the coefficient b occurs at $\omega = 0$ for $b > 0$ and $d = 0$ and at $\omega = \pi/2$ for $b < 0$ and $d = 0$. If b is small, then the next higher order term corresponding to the coefficient d should be taken into account. According to the experimental observations, in the R_I phase, distortion amounts to a compression along the NN bond direction, i.e., $\omega = 0$. The terms corresponding to the coefficients γ and η determine the tilt azimuth δ . For $\gamma < 0$, the only minimum of F is achieved at $\delta = \pi/6 + n\pi/3$ (n is an integer), i.e., for the tilt toward the NNN direction. Since in the R_V phase the tilt occurs toward the NNN direction, eq 1 describes second-order R_I – R_V and R_{II} – R_V transitions for $\beta > 0$ and $\gamma < 0$. The lowest order $\theta\xi$ coupling term gives $\omega = \delta$ for $J > 0$ and $\omega = \delta + \pi/2$ for $J < 0$. Since in the R_V phase $\delta = \omega = 0$, we take $J > 0$. Thus the positive value of J favors the R_V phase over the R_I phases. Physically then, J represents the change in the microscopic interactions that stabilize the R_V phase. Since in the R_{IV} phase tilt occurs toward the NNN direction, we assume $\beta > 0$ and $\gamma < 0$. When γ is small, then the next higher order term corresponding to the

coefficient η is nonzero and important. Then the transition from NN to NNN tilt takes place, with a possible intermediate R_{III} phase in between. The terms corresponding to the coefficients b and d determine the distortion azimuth ω . According to the experimental observations, $\omega = 0$ and $\delta = 0$ for the R_{IV} phase. However, for the R_{III} phase $\omega \neq 0$ and $\delta \neq 0$. Thus the free energy (eq 1) describes the different rotator phase transitions. A very schematic phase diagram of the different rotator phase transitions is depicted in Figure 1.

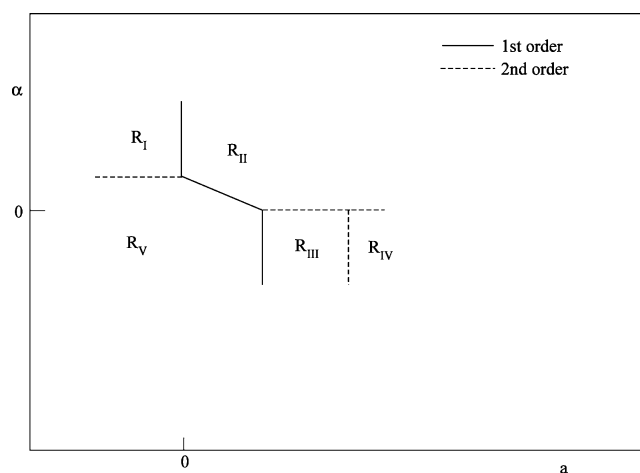


Figure 1. Possible phase diagram describing the rotator phases of *n*-alkanes.

We now consider the effect of gauche defects and molecular flexibility on these rotator phase transitions. Zangi and Rice³⁰ extensively studied the influence of gauche molecular conformations on the phase diagram of a Langmuir monolayer within Landau theory.³¹ They considered the gauche defects as a secondary order parameter. Finally, they observed that the effect of gauche conformations can modify the Landau coefficients and shift the transition lines. The structural phase transitions between the phase sequence R_{II} – R_I – R_V – R_{III} – R_{IV} in alkanes and LS–S–L₂–I–O_v in Langmuir monolayers are similar.^{32,33} We can use this analogy and directly apply the analysis as adopted by Zangi and Rice³⁰ in Langmuir monolayers. In the rotator phases of *n*-alkanes, the molecules are not free to rotate around their long axes. So the directionality of the gauche defects is not correlated with the symmetry of the rotator phases. Thus this quantity should be a scalar. Following Zangi and Rice,³⁰ we define a secondary order parameter, ζ , that is equal to the fraction of gauche conformations of the long chain molecules $\zeta = \langle N_g \rangle / N_d$. Here N_g is the average number of gauche conformations, and N_d is the total number of dihedral angles along the chain. Thus ζ is a scalar-order parameter and has A_1 symmetry. Thus $\zeta = 0$ for the all-trans conformations, and $\zeta \neq 0$ when gauche conformations are present. To consider the effect of molecular flexibility, we define another quantity $\sigma = (l - l_0)/l_0$, where l_0 is the equilibrium value of the length l of a molecule in the absence of tilt angle and distortion. We will now discuss the coupling between the primary and secondary order parameters and the quantity σ for the different rotator phase transitions separately.

R_{II}–R_I TRANSITION

The R_{II}–R_I transition is accompanied by the finite jump of the distortion order parameter. Now the expansion of the free energy including the coupling to gauche conformations order parameter ζ and molecular flexibility σ with the distortion order parameter ξ near the R_{II}–R_I transition is written as

$$F = F_0 + \frac{1}{2}a\xi^2 - \frac{1}{3}b\xi^3 + \frac{1}{4}c\xi^4 + \frac{1}{2}p\zeta^2 + \frac{1}{2}m\sigma^2 + K\zeta\xi + H\sigma\xi + M\zeta\sigma \quad (2)$$

As usual, a and p are temperature-dependent parameters. p is positive in the low-temperature crystal phase (trans conformations) and is negative in the high-temperature rotator phases (gauche conformations). Thus we assume $p = p_0(T - T_2^*)$. p_0 is a positive constant. All other parameters are assumed to be temperature independent. K , H , and M are coupling constants.

The equilibrium value of σ is obtained as

$$\sigma_{\text{eq}} = -\frac{H\xi + M\zeta}{m} \quad (3)$$

Elimination of σ in the free energy (eq 2) yields

$$F = F_0 + \frac{1}{2}a_1\xi^2 - \frac{1}{3}b\xi^3 + \frac{1}{4}c\xi^4 + \frac{1}{2}p_1\zeta^2 + K_1\zeta\xi \quad (4)$$

where $a_1 = a - (H^2)/m$, $p_1 = p - (M^2)/m$, and $K_1 = K - (MH)/m$.

Since the lattice distortion parameter decreases with the chain length and the transition temperature increases with chain length, (σ, ξ) and (σ, ζ) couplings should contribute the positive term in the free energy since $m < 0$. So the R_{II}–R_I transition line shifts to the right side of the coordinate a in the a – α plane in Figure 1.

Now the substitution of the equilibrium value of $\zeta_{\text{eq}} = -(K_1/p_1)\xi$ in eq 4 yields

$$F = F_0 + \frac{1}{2}a^*\xi^2 - \frac{1}{3}b\xi^3 + \frac{1}{4}c\xi^4 \quad (5)$$

with $a^* = a - (H^2/m) - (K_1^2/p_1)$.

The analysis of eq 5 shows that the influence of gauche conformations produces the shift of the transition temperature $T_{\text{I–II}}$. So the R_{II}–R_I transition line further shifts to the right side of the coordinate a in the a – α plane in Figure 1. The lattice distortion parameter decreases with increase of gauche conformations.

To calculate the chain length dependence of the R_{II}–R_I transition temperature, the free energy near the R_{II}–R_I transition can be expressed as

$$F = F_0 + \frac{1}{2}a\xi^2 - \frac{1}{3}b\xi^3 + \frac{1}{4}c\xi^4 \quad (6)$$

where $a = a_2(T - T_1^*(l))$. From the experimental phase diagram⁵ one observes, $T_1^*(l)$ can be portrayed as

$$T_1^*(l) = T_1^0 + u_1(l - l_0)/l_0 + v_1(l - l_0)^2/l_0^2 \quad (7)$$

where l_0 is some specific chain length of the molecules. u_1 and v_1 are positive constants. We assume that the temperature and

chain length region are small so that the nonlinear dependence of the phase transition temperature on chain length is justified.

The chain length dependence of the R_{II}–R_I transition temperature can be expressed as

$$T_{\text{II–I}}(l) = T_1^0 + \frac{2b^2}{9a_0c} + u_1(l - l_0)/l_0 + v_1(l - l_0)^2/l_0^2 \quad (8)$$

The distortion order parameter $\xi(l, T)$ in the R_I phase is given by

$$(\xi - \xi_{\text{II–I}}^+)^2 = (\xi_{\text{II–I}}^+)^2 - \frac{a_0}{c}(T - T_1^0) + \frac{a_0}{c}(u_1(l - l_0)/l_0 + v_1(l - l_0)^2/l_0^2) \quad (9)$$

where $\xi_{\text{II–I}}^+ = b/2c$. When ξ is fixed, eq 9 may be rewritten as

$$T(l) - T_{10}(\xi) = u_1(l - l_0)/l_0 + v_1(l - l_0)^2/l_0^2 \quad (10)$$

where

$$T_{10}(\xi) = T_1^0 - \frac{a}{c}\xi(\xi - 2\xi^+) \quad (11)$$

The jump of the enthalpy density at the transition point is

$$\Delta H_{\text{II–I}} = \frac{2b^2}{9a_0c}T_{\text{II–I}}(l) \quad (12)$$

R_I–R_V AND R_{II}–R_V TRANSITIONS

Assume ξ_0 to be the value of the distortion parameter at the R_I–R_V transition and $F_1(\xi_0)$ is the corresponding free energy at the R_I phase. Now the expansion of the free energy including the coupling to gauche conformations and molecular flexibility order parameters with the tilt angle and distortion order parameter near the R_I–R_V transition is written as

$$F = F_1(\xi_0) + \frac{1}{2}u(\xi - \xi_0)^2 + \frac{1}{2}\alpha\theta^2 + \frac{1}{4}\beta\theta^4 + \frac{1}{2}p\zeta^2 + \frac{1}{2}m\sigma^2 + K\zeta\xi + H\sigma\xi + M\zeta\sigma - J\theta^2\xi + G\theta^2\zeta + L\theta^2\sigma \quad (13)$$

where $u = 1/\chi$, and χ is the response function in the R_I phase. Since here the R_{II}–R_I and R_I–R_V transitions are close, the R_I response function is large at the R_I–R_V transition. G and L are coupling constants.

The equilibrium value of σ can be obtained as

$$\sigma_{\text{eq}} = -\frac{H\xi + M\zeta + L\theta^2}{m} \quad (14)$$

Elimination of σ in the free energy expansion (eq 6) yields

$$F = F_1(\xi_0) + \frac{1}{2}u(\xi - \xi_0)^2 - \frac{H^2}{2m}\xi^2 + \frac{1}{2}\alpha\theta^2 + \frac{1}{4}\beta_1\theta^4 + \frac{1}{2}p_1\zeta^2 + K_1\zeta\xi + G_1\theta^2\zeta - J_1\theta^2\xi \quad (15)$$

where

$$\beta_1 = \beta - \frac{2L^2}{m}$$

$$G_1 = G - \frac{LM}{m}$$

$$J_1 = J + \frac{H^2}{m}$$

One sees the shift of the R_1 – R_V transition line. One can also expect anomalously small coefficients of the fourth-order power of θ for molecules with very “soft” fragments. Thus the coefficient β_1 may change from positive to negative value. Thus the R_1 – R_V transition can be first order for short chain lengths and second order for long chain lengths, which agrees with experimental observations.^{5,7,11,12} The dependence of the chain length on the R_1 – R_V transition in n -alkanes was observed by several authors.^{5,14}

The equilibrium value of ζ can be obtained as

$$\zeta_{\text{eq}} = -\frac{K_1\xi + G_1\theta^2}{p_1} \quad (16)$$

Elimination of ζ in the free energy expansion (eq 8) yields

$$F = F_1(\xi_0) + \frac{1}{2}u(\xi - \xi_0)^2 - \frac{H^2}{2m}\xi^2 - \frac{K_1^2}{2p_1}\xi^2 + \frac{1}{2}\alpha\theta^2 + \frac{1}{4}\beta'\theta^4 - J'\theta^2\xi \quad (17)$$

where

$$\beta' = \beta_1 - \frac{2G_1^2}{p_1}$$

$$J' = J_1 + \frac{G_1K_1}{p_1}$$

Minimization of eq 17 with respect to ξ gives

$$\xi = \frac{1}{u'}(u\xi_0 + J'\theta^2) \quad (18)$$

with $u' = u - (H^2/m) - (K_1^2/p_1)$. Substitution of ξ in eq 17 yields

$$F = F_1(\xi_0) + \frac{1}{2}\alpha^*\theta^2 + \frac{1}{4}\beta^*\theta^4 \quad (19)$$

where,

$$\alpha^* = \alpha - \frac{2J'u\xi_0}{u'} \quad (20)$$

$$\beta^* = \beta' - \frac{2J'^2}{u'} \quad (21)$$

$$F_1(\xi_0) = F_1(\xi_0) + \frac{\xi_0^2}{2u'}(u^2 - 2u + u') \quad (22)$$

Since the gauche conformations, lattice distortion, and tilt angle increase as the area per molecule increases, the coupling between (ζ, ξ) and (ζ, θ) should contribute positive term in free energy. We conclude that $K > 0$ and $G > 0$. From eq 21 we see that for a strong enough coupling constants K and G , β^* can become negative. Thus, if $\beta^* < 0$, eq 19 has a solution for θ . The R_1 – R_V transition is then first order. In this case, a sixth-

order term $\sim\theta^6$ should be added in the free energy (eq 12). For weak coupling constants K and G , β^* remains positive. Then eq 19 has no solution for θ , and the transition is second order. Thus, when $\beta^* > 0$, we have four nonzero-order parameters appearing below a second-order transition, with the tilt angle θ induced by the distortion ξ , molecular flexibility σ , and gauche conformations ζ . Equation 13 shows the shift of the transition temperature. So the new transition line is defined by $\alpha = J'u\xi_0/u'$. What transpires from the above analysis is that the gauche conformations strongly influence the character of the R_1 – R_V transition. The coupling between the gauche conformations and the tilt angle also shifts the R_1 – R_V transition line.

We will now calculate the chain length dependence of the R_1 – R_V transition temperature. We have shown that the R_1 – R_V transition temperature changes with chain length. We start by using the Landau free energy expansion while taking into account the chain length dependence of the R_1 – R_V transition temperature. Then the free energy can be expressed as

$$F = F_1(\xi_0) + \frac{1}{2}u(\xi - \xi_0)^2 + \frac{1}{2}\alpha\theta^2 + \frac{1}{4}\beta\theta^4 + \frac{1}{6}\gamma\theta^6 + H\xi(l - l_0)/l_0 - J\theta^2\xi \quad (23)$$

The sixth-order term γ is added for the stability of the free energy. $\alpha = \alpha_0(T - T_2^*(l))$. We assume a nonlinear form for T_2^*

$$T_2^*(l) = T_2^0 + u_2(l - l_0)/l_0 + v_2(l - l_0)^2/l_0^2 \quad (24)$$

where u_2 and v_2 are constant.

After the elimination of ξ from eq 23, the variation of the tilt angle with chain length and temperature can be expressed as

$$\theta^2(l, T) = -(\beta_1^*/2\gamma) + [(\beta_1^*/2\gamma)^2 - \alpha_1^*/\gamma]^{1/2} \quad (25)$$

where

$$\alpha_1^* = \alpha - \frac{2JH}{u}(l - l_0)/l_0$$

$$\beta_1^* = \beta - \frac{2J^2}{u}$$

For the first-order R_1 – R_V transition, the R_1 – R_V transition temperature is given by

$$T_{1-V}^{\text{tr}} = T_2^0 + \frac{3\beta_1^{*2}}{16\gamma} + \frac{2\xi_0 J}{\alpha_0} + \left(u_2 + \frac{2\xi_0 JH}{\alpha_0 u}\right) \times (l - l_0)/l_0 + v_2(l - l_0)^2/l_0^2 \quad (26)$$

The renormalization of the second-order R_1 – R_V transition temperature can be expressed as

$$T_{1-V}^{\text{C}} = T_2^0 + \frac{2\xi_0 J}{\alpha_0} + \left(u_2 + \frac{2\xi_0 JH}{\alpha_0 u}\right)(l - l_0)/l_0 + v_2(l - l_0)^2/l_0^2 \quad (27)$$

T_{1-V}^{tr} is in the temperature interval between T_{1-V} and T_2^0 . Equation 27 shows that the second-order R_1 – R_V transition temperature increases with the chain length.

Now the minimization of eq 19 over θ becomes

$$F - F_0 = \frac{1}{2}(a - a_2)\xi_1^2 - \frac{\alpha^{*2}}{4\beta^*} \quad (28)$$

with $a_2 = 2b^2/9c$ and $\xi_1 = 2b/3c$.

For the $R_{II}-R_V$ transition line, the right-hand side of eq 28 becomes zero. Hence the second-order $R_{II}-R_V$ transition line can be written as

$$a - a_2 = \frac{\alpha^{*2}}{2\beta^*\xi_1^2} \quad (29)$$

Equation 17 also shows the shift of the $R_{II}-R_V$ transition line on the right side of the coordinate a of the $a-\alpha$ plane.

■ $R_{IV}-R_{III}$ AND $R_{IV}-R_{II}$ TRANSITIONS

We will now discuss the effect of gauche conformations and molecular flexibility on the $R_{IV}-R_{III}$ transition. The R_{III} phase is an intermediate tilt where the tilt azimuth δ varies from 0° to 30° . For the R_{III} phase, we assume $\delta = \omega \neq 0$, as suggested by the experiment. Both in the R_{III} and R_{IV} phases, the distortion ξ is very weak and is induced by a finite coupling to the tilt magnitude θ . Thus the tilt causes an induced distortion $\xi \sim \theta^2$. After substituting $\omega = \delta$ and $\xi \sim \theta^2$ into the free energy (eq 1), the free energy near the $R_{IV}-R_{III}$ transition reads as

$$\begin{aligned} F = F_0 &+ \frac{1}{2}(\alpha + a)\theta^2 + \frac{1}{4}(\beta - 4J)\theta^4 + \frac{1}{4}c\theta^8 \\ &- \frac{1}{6}(\gamma + 2b)\theta^6 \cos 6\delta - \frac{1}{12}(\eta + 2d)\theta^{12} \\ &\times \cos 12\delta + \frac{1}{2}p\zeta^2 + \frac{1}{2}m\sigma^2 + M\sigma\zeta \\ &+ Q\zeta\theta^6 \cos 6\delta + P\sigma\theta^{12} \cos 12\delta \end{aligned} \quad (30)$$

Substitution of $\sigma_{eq} = -[(Pp_1 - M(Q - (MP/m)))/p_1m]\theta^6 \cos 6\delta$ and $\zeta_{eq} = -[(Q - (MP/m))/p_1]\theta^6 \cos 6\delta$ for σ and ζ in eq 18 yields

$$\begin{aligned} F = F_0 &+ \frac{1}{2}(\alpha + a)\theta^2 + \frac{1}{4}(\beta - 4J)\theta^4 + \frac{1}{4}c\theta^8 \\ &- \frac{(P^2p_1 + Q_1^2m)}{4p_1m}\theta^{12} - \frac{1}{6}(\gamma + 2b)\theta^6 \\ &\times \cos 6\delta - \frac{1}{12}\eta^*\theta^{12} \cos 12\delta \end{aligned} \quad (31)$$

where

$$\eta^* = \eta + 2d + \frac{3P^2}{m} + \frac{3Q_1^2}{p_1}$$

$$Q_1 = Q - \frac{MP}{m}$$

Minimization of eq 19 over δ gives

$$\delta = \frac{1}{6} \cos^{-1} \left(\frac{-(\gamma + 2b)}{2\eta^*\theta^6} \right) \quad (32)$$

Thus the coefficient η is renormalized. Since the coefficients m and p are negative, the coefficient η^* can change from positive to negative value. Suppose that $(\eta + 2d)$ is fixed at a negative

value. When $(\gamma + 2b) = 2\eta^*\theta^6$, i.e., for $(\gamma + 2b) > 0$, the only minimum is at $\delta = 0^\circ$. Then the system is in the R_{IV} phase. When $(\gamma + 2b) = -2\eta^*\theta^6$, i.e., for $(\gamma + 2b) < 0$, then the minimum at $\delta = 0^\circ$ passes through 0° to 30° . Since in the R_{III} phase δ changes through 0° to 30° , we have the phase for $(\gamma + 2b) < 0$. We therefore have a second-order transition from the R_{III} phase to the R_{IV} phase at $(\gamma + 2b) = -2\eta^*\theta^6$ as observed for alkanes $28 \leq n \leq 30$. For the positive value of η^* , one observes for the R_{IV} phase $(\gamma + 2b) < 0$ and for the R_{III} phase $(\gamma + 2b) > 0$. Thus the gauche R_{III} conformations and the molecular flexibility are responsible for the NN and NNN neighbors tilt in the R_{IV} and R_{III} phases, respectively.

Experiments show that a second-order tilting transition takes place between R_{II} and R_{IV} phases. Near the $R_{II}-R_{IV}$ transition the free energy reads

$$\begin{aligned} F = F_0 &+ \frac{1}{2}a\xi^2 + \frac{1}{2}\alpha\theta^2 + \frac{1}{4}\beta\theta^4 + \frac{1}{2}p\zeta^2 \\ &+ \frac{1}{2}m\sigma^2 + K\zeta\xi + H\sigma\xi + M\zeta\sigma - J\theta^2\xi \\ &+ G\theta^2\zeta + L\theta^2\sigma \end{aligned} \quad (33)$$

Here the tilt causes an induced distortion $\xi \sim \theta^2$. Similar to the preceding sections, the renormalized free energy reads

$$F = F_0 + \frac{1}{2}\alpha\theta^2 + \frac{1}{4}\beta_1\theta^4 \quad (34)$$

with $\beta_1 = \beta' - (2J^2/a^*)$ and $\alpha = \alpha_0(T - T_C)$

Since the $R_{II}-R_{IV}$ transition is second order, β_1 should be positive. Thus the gauche conformations and the chain flexibility keep the coefficient β_1 positive. Thus $\theta = 0$ in the R_{II} phase for $T > T_C$ and $\theta = [-(\alpha_0/\beta_1)(T - T_C)]^{1/2}$ in the R_{IV} phase for $T < T_C$. Thus the free energy (eq 22) describes the second-order $R_{II}-R_{IV}$ transition.

■ RESULTS AND DISCUSSION

In this section we will compare our theoretical results with the experimental results and previous computer simulations and mean-field theory. For the temperature versus chain length (T vs l) phase diagrams, for the different rotator-rotator phase transitions of n -alkanes, there exists few experiments.^{4,5} All the experimental phase diagrams of T versus l give nonlinear curves. From eq 10, when ξ is fixed, T versus l should be a nonlinear, which agrees well with experiments.^{4,5} In principle, eqs 8–10 are same. Equations 25 and 26 show that the T_{I-V} versus l phase diagram is also nonlinear, which also agrees with experiments. According to eqs 8, 26, and 27, the $R_{II}-R_I$ and R_I-R_V transition temperatures increase with increasing chain length as observed in experiments.^{5,14}

We already pointed out in the previous section that the Landau coefficients decrease with the increase of gauche molecular conformations and chain length. However, these decreasing trends are different for even and odd n -alkanes. This is expected since the jump of the distortion order parameter ξ_{II-I} is higher for the even n -alkanes than for odd n -alkanes.⁷ This can easily be verified by calculating the Landau coefficients a_0, b, c, u_1 , and v_1 for the $R_{II}-R_I$ transition using the relations 8 and 12 and the jump of the distortion order parameter ($\xi_{II-I} = 2b/3c$), with the corresponding experimental data for each chain length. However, we have not repeated the calculations since such calculations are already available in our previous paper.²⁹ In order to check eqs 9 and 25, we see that for fixed T ,

the distortion order parameter ξ and tilt angle θ increases with the chain length, which agrees with experimental results.^{5,7} Again for fixed chain length l , eqs 9 and 25 show that ξ and θ decrease with increase of temperature, which supports the experimental results.⁵ The data ΔH versus l in ref 7 also satisfy our theoretical eq 12. Since both ξ and θ change with temperature, ζ also changes with temperature. Since the R_V phase appears for the longer chain length, the gauche defects play a larger role in longer chain lengths. Equation 16 shows that the gauche defects increase with increasing temperature. This is in complete agreements with experiments.^{13,14} If the alkane molecules in the R_{III} , R_{IV} , and R_V phases support the occurrence of gauche conformations, then it occurs at the expense of the tilting transitions. The bilayer in these three rotator phases can respond to an increase of temperature either by changing the azimuthal angle from NN to NNN or by the presence of gauche conformations.

Molecular dynamics simulations by Liang et al.¹⁹ revealed that the gauche defects depend mainly on temperature and, to some degree, on external constraints. Further it was observed that the chain ends of the long chain molecules have a higher probability for conformational disorder. Within the mean-field theory, Würger^{20,21} showed that the conformational defect locally deforms the crystal and thus costs energy that is proportional to the chain length. This theory predicts the weak variation of the critical temperature with the chain length. Thus both the molecular dynamics simulations¹⁹ and mean-field theory^{20,21} results fairly agree with the present analysis.

What transpires from the above analysis is that the main reason for the first-order character of the R_{II} – R_I and R_I – R_V transitions may be the influence of gauche molecular conformations and the chain flexibility of n -alkanes. In the rotator phases, chains are strongly localized within layers. So the periodicity of the alkanes is nearly equal to the length of an individual stretched chain, which turns the transition first order. Thus we conclude that, although R_{II} – R_I and R_I – R_V transitions are more strongly first order for a shorter chain length and smaller gauche molecular conformations of n -alkanes, the transitions become weakly first order or second order for longer chain lengths and larger gauche molecular conformations. In fact, the flexibility of the molecules forming the R_I phase diminishes the absolute value of the cubic invariant, but it cannot be zero.

In this context we should mention the work of Zangi and Rice,³⁰ who analyzed the same issue for Langmuir monolayers in the mean-field approximation. They included the gauche defects in the Landau free energy function similar to the present work. However, the present analysis differs from the work of Zangi and Rice³⁰ in two ways. First, our model free energy is different from their model free energy. They observed that the gauche defects can only shift the phase transition lines, not the order of the phase transitions, whereas our theory shows that the gauche defects not only shift the transition lines but also change the order of the phase transitions. This holds because there is the temperature dependence in the coefficient p in the free energy expressions (eqs 2 and 13), which was taken as constant in the work of Zangi and Rice.³⁰ Another reason may be the strong coupling between the gauche defects (ζ) and chain flexibility (σ). Second, they did not study the effect of chain flexibility on the Langmuir monolayers phase transitions. However, in the present work we have extensively studied the influence of chain flexibility on the rotator phase transitions.

CONCLUSIONS

We have shown our simple Landau model can explain the main effect of gauche defects and molecular flexibility on the different rotator phase transitions of n -alkanes. The effect of gauche defects in the system of flexible molecules have been investigated by identifying the secondary order parameter which is related to the molecular conformations. This is quite analogous to that for Langmuir monolayers studied by Zangi and Rice.³⁰ The main effect of the gauche defects is to shift the transition lines and, in some cases, the change of the character of the phase transitions. The gauche defects and the molecular flexibility change the Landau coefficients. The effect of gauche defects and molecular flexibility on the tilt angle of the R_{III} , R_{IV} , and R_V phases are discussed.

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