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Phase transitions of *n*-alkane systems

Part 1 *Calculation of heats of transition of the order-disorder phase transition of pure paraffins*

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McClure's theory of the rotational phase transition of long chain *n*-alkane crystals is extended in the light of recent experimental results. Good agreement is achieved between calculated and experimental heats of transition if the molecular motion for $C_{21}H_{44}$ and shorter molecules is different from that for $C_{23}H_{48}$ and longer molecules. Translational motion along the molecular axis only occurs for the latter materials. The possibility of the occurrence of molecular defects is discussed.

1. Introduction

The nature of the first order phase transition, which occurs just below the melting point, of long chain *n*-alkanes containing an odd number of carbon atoms has been investigated by many authors. The transition is from an ordered to a disordered phase and two possible mechanisms have been proposed. Mueller [1] suggested a rotational motion of the molecules about their long axes to explain his observation of an hexagonal, or an approach to hexagonal structure in the upper phase. On the basis of N.M.R.† spectra Andrew [2] proposed that the rotation of the molecules was co-operative, like a set of meshed gears. This model was used by McClure [3] as the basis of a microscopic theory of the transition energies of $nC_{21}H_{44}$ and $nC_{29}H_{60}$ on the basis of the X-ray data of Mazee [4] and Mueller [5]. An alternative model was put forward by Pechold and Blasenbrey [6, 7]; they interpreted measurements of the dynamic mechanical properties in terms of a transition caused by interchain kink defect motion.

Barnes [8] has studied the transition in powdered samples of $nC_{19}H_{40}$ by quasi-elastic neutron scattering. He fitted his data using a model in which the molecules made random rotational jumps about their long axes. However, recent neutron scattering experiments [9] on a well orientated sample of $nC_{23}H_{48}$, a unique *c*-axis direction, have shown the occurrence of molecular motion both along and about the *c*-axis. This suggests that the molecular motion in the upper phase is more complex than has been assumed previously. Indeed McClure found that plots of heats of transition per CH_2 unit and of heats of fusion per CH_2 unit as a function of molecular length are linear for the series $C_{23}H_{48}$ to $C_{29}H_{60}$. However, at $C_{21}H_{44}$ there is an abrupt change in the slope of the plots with irregular behaviour for shorter molecular lengths. Thus, there are grounds for supposing that the nature of the transition is different in short chain paraffins, with 21 or less carbon atoms, from that in long chain paraffins, with 23 or more carbon atoms.

This idea receives further support from the recent study of Pieszek, Strobl, and Fischer *et al.* [10–12] of an extremely pure sample of $C_{33}H_{68}$. They observed three solid state phase transitions. N.M.R. and X-ray structural studies suggested that in modification A($T < 54.5°$ C) there is little molecular motion, only small amplitude oscillations of the molecules about their long axes. In modification B($54.5° < T < 65.5°$ C) co-operative 180° rotational jumps occur about the long molecular axis leading to a loss of long range order of the plane of the carbon molecular backbone but retaining short range order. In the second high temperature phase C($65.5° < T < 68°$ C) screw

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†N.M.R. = Nuclear magnetic resonance.

motions, involving coupled rotational jumps about and translational jumps along the long molecular axis, occur. Finally, in the highest temperature phase D($T > 68°$ C) the motion becomes highly disordered with intrachain defects, which can diffuse along the chains, superimposed on the rotational and translational motion.

Recently the phase transition of the *n*-paraffins has been treated from a statistical thermodynamical viewpoint by Ishinabe [13] and Baur [14–17]. Ishinabe considers fluctuations in molecular orientation angle in the Bragg–Williams approximation while Baur treats the model of Pechold and Blasenbrey in the same approximation and also in a quasi-chemical approximation. Both workers predict the existence of a co-operative phase transition despite the differences in the microscopic processes considered. In view of the more detailed account of molecular motion in a microscopic theory in this paper we present an extension of McClure's approach taking into account the new experimental results.

2. Theoretical model

McClure [3] has considered in detail the calculation of heats of transition for *n*-alkane crystals in terms of the intermolecular forces. Two such forces are assumed; firstly a Van de Waals attraction between CH_2 groups described by a potential function $U(R) = -A/R^6$, and secondly a hydrogen–hydrogen repulsion. Repulsive forces between the carbon atoms were neglected due to shielding. Calculations of theoretical vibrational spectra show this assumption to be substantially correct [18–20]. With chains disposed according to the structure of the ordered phase determined by Smith [21], as shown in Fig. 1, the attractive energy can be calculated.

We calculate the total attractive potential for the interaction of the reference molecule with fifty nearest neighbours. A correction for more distant molecules, identical with that used by Salem [22], was applied.

The repulsive energy is dependent on the form of the potential function of the hydrogen–hydrogen interaction. McClure employed two potential functions, the A.L.M., derived from molecular scattering experiments [23] and the Mueller function, derived by fitting vibrational force constants for *n* alkanes [24]. We have used these and also that due to Williams [25] having the form

$$U(R) = 1729 \exp\left[-3.74R\right] \text{ kcal mol}^{-1} \quad (1)$$

derived by computer fitting the structural potential minimum of numerous saturated hydrocarbons. This function should in principle be more accurate than the former two functions in view of the much larger amount of input data used in its derivation.

As shown in Fig. 1, the CH_2 groups lie in discs normal to the long axis of the molecules. If τ is the vector joining the centres of any two hydrogen atoms in different molecules, then

$$\tau = \mathbf{r}_2 - \mathbf{r}_1 + \mathbf{s} + \mathbf{z};\ |\mathbf{r}_1| = |\mathbf{r}_2| = r$$

$$\tau^2 = 4r^2 \sin\frac{(\alpha_1-\alpha_2)}{2} + s^2 + z^2 - 4sr$$

$$\sin\frac{(\alpha_1+\alpha_2)}{2}\sin\frac{(\alpha_1-\alpha_2)}{2} \quad (2)$$

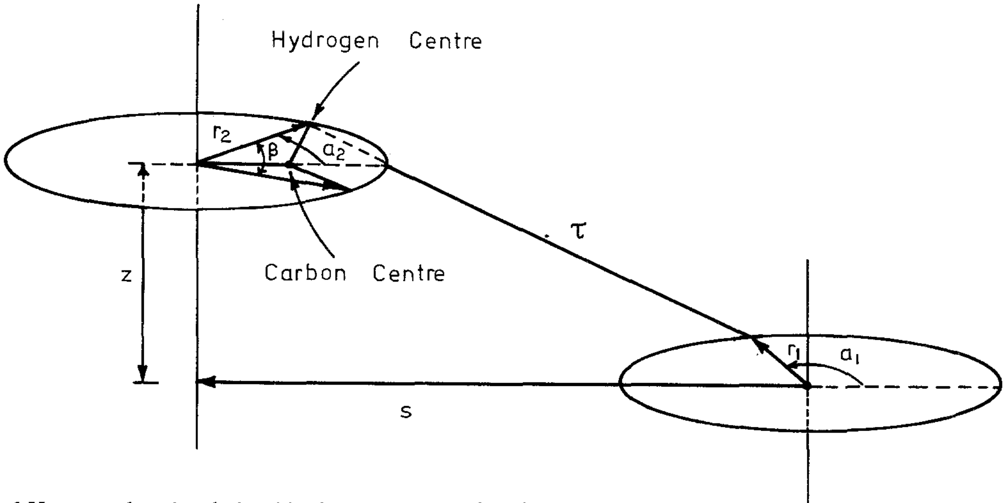

Figure 1 Vector and angle relationships between interacting chains.

The calculation of the repulsive energy is restricted to the six nearest neighbour molecules and the seven nearest CH_2 discs, given by $z = 0$, $\pm\lambda$, $\pm 2\lambda$ and $\pm 3\lambda$, in each case of these molecules which are taken to be infinitely long cylinders. λ is the projection on to the c-axis of the C–C bond and s the separation of the molecules.

In the low temperature phase, McClure assumed the molecules to be stationary. The repulsive energy of a single CH_2 unit on the reference molecule and a single neighbouring molecule is:

$$U(\tau) = \sum_{i=1}^{4} U_i(0) + 2 \sum_{z=\lambda}^{3\lambda} \sum_{i=1}^{4} U_i(z) \qquad (3)$$

where i labels the four hydrogen pair interactions between CH_2 units. The total repulsive energy $U(\tau)$ total, is obtained by summing $U(\tau)$ over the six nearest neighbours.

In the disordered phase, McClure imposed two conditions on his model. First that the molecules will execute complete rotations so that the repulsive energy of the whole system is a minimum and secondly that the rotational environments for all molecules randomly chosen are identical. McClure used the model of Andrew [2] of meshed rotation as shown in Fig. 2, where chains I and II rotate symmetrically and I and III antisymmetrically. If the symmetry of these relative motions is interchanged, the repulsive energy is doubled, violating the first condition.

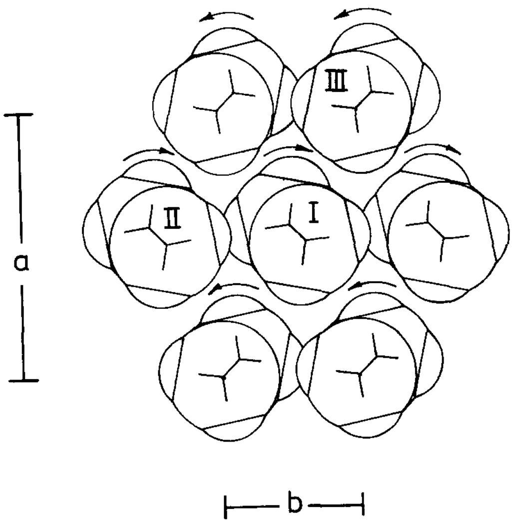

Figure 2 Drawing of an hexagonally packed array of chains as viewed in the a–b plane. This packing arrangement would correspond to a state at or near the melting point.

For such correlated motion, the angular rotation vectors of any two nearest neighbour molecules at any time t can be expressed in terms of their initial positions, α_1^0 and α_2^0, and phase functions dependent on time:

$$\alpha_i(t) = \alpha_i^0 \pm \delta_i(t) \qquad (4)$$

Subsequently the average repulsive potential reduces to the form (assuming correlated motion),

$$\langle U[\alpha_i(z), z]\rangle_i = \frac{1}{2\pi} \int_{\alpha_i^0}^{\alpha_i^0 + 2\pi} U[\alpha_i(z), z] \, d\alpha_i \qquad (5)$$

for the ith disc pair. The total repulsive energy then has the same form as Equation 3 with $U_i(z)$ replaced by $\langle U[\alpha_i(z), z]\rangle_i$.

The energy of transition is given by the energy differences calculated for the pre and post transition cases. The energy values calculated are not absolute, their difference will correspond to the true transition energy.

3. Calculated heats of transition

Heats of transition were calculated for the simple model described above and for more complex models, which attempted to give a more realistic description of the molecular motion in the upper phase. The additional features we have considered are (a) variation in relative phase of molecules in the coherent rotational motion, (b) translational motion along the long molecular axis and (c) the possibility of kinking of the molecules. The calculations were performed on an ICL 1900 series computer for paraffins from $C_{21}H_{44}$ to $C_{29}H_{60}$. Lattice parameters for zone refined samples of these paraffins were measured below and above the main transition [26]. There is evidence of multiple transitions in some of these paraffins, as reported for $C_{33}H_{68}$. However, the values for heats of transition given by Schaerer *et al.* [27] and Broadhurst [28] are for less pure samples, which show a single transition. Therefore we have assumed that the molecular disorder occurs at a single transition and not in stages. For purposes of comparison we have included calculations based on Mazee's lattice parameters for $C_{21}H_{44}$ and Meuller's parameters for $C_{29}H_{60}$, though the latter was almost certainly an impure sample.

3.1. Calculations with rotational motion only

The calculated values of heats of transition for a coherent rotation, McClure's model, are listed in

TABLE I Heats of transition (ΔH in kcal mol^{-1} CH$_2$) for an upper phase with rotational motion only.

Material	ΔH only	ΔH + ALM	ΔH + MUEL	ΔH + WILL	ΔH Experimental
$C_{19}H_{40}$	0.196	0.218	0.398	0.342	0.174
$C_{21}H_{44}$	0.193	0.211	0.367	0.321	0.176
$C_{21}H_{44}$ (Mazee)	0.223	0.229	0.390	0.338	0.176
$C_{23}H_{48}$	0.215	0.213	0.350	0.307	0.226
$C_{25}H_{52}$	0.224	0.199	0.224	0.249	0.250
$C_{29}H_{60}$	0.280	0.224	0.281	0.254	0.260
$C_{29}H_{60}$ (Mueller)	0.211	0.199	0.300	0.268	0.260

Table I. It is clear that while the experimental values for heats of transition increase with molecular length, the values calculated for the three different hydrogen–hydrogen repulsive potentials all decrease. Indeed a much better fit to the experimental data is obtained if the repulsive term is neglected. This is obviously not physically justified and the discrepancy between experimental and calculated values reflects the inadequacy of the simple rotational model.

The model uses phases of the coherently rotating molecules determined by the initial molecular orientations. This is not necessarily the least energy configuration in the disordered phase. Thus, the relative phases were varied to seek a minimum energy configuration. The attractive energy remains constant and for the symmetric molecules (I and II) the repulsive energy is at a minimum, since the planes of the molecular backbones are parallel. However, most of the repulsive energy results from the interaction of molecules rotating antisymmetrically (I and III). This energy is a function of ϕ', i.e. $\alpha_1^0 + \alpha_2^0$, so that ϕ' was varied until a minimum was obtained. The dephasing angle was found to vary from -25° for materials retaining an orthorhombic structure to -15° for those attaining a hexagonal structure, see Table II. With these new values of the phase angle, the calculated heats of transition are as listed in Table III. The agreement with the experimental values is now much better; the trend with molecular length is correct but not quite large enough. An attempt to obtain a new repulsive potential function to fit the experimental data on the basis of this model failed to produce significantly better agreement [26]. Thus, as suggested in the introduction, account must be taken of the possibility of different molecular motion for short and long molecules.

TABLE II Relative angles of antisymmetrically rotating molecules for a minimum repulsive energy in the upper phase

Material	$\Delta\phi'$–min°
$C_{19}H_{40}$	-25°
$C_{21}H_{44}$	-25°
$C_{21}H_{44}$ (Mazee)	-25°
$C_{23}H_{48}$	-25°
$C_{25}H_{52}$	-20°
$C_{29}H_{60}$	-15°
$C_{29}H_{60}$ (Mueller)	-20°

3.2. Calculations with translational motion

Evidence for the occurrence of translational as well as rotational molecular motion in the upper phase was outlined in the introduction. The translational motion may be correlated with the rotational motion (a screw motion), or uncorrelated We calculated the repulsive energy for the latter case, allowing single translations of 2.55 Å, i.e. one repeat distance of the carbon molecular backbone. This corresponds to a jump from one molecular energy minimum to the next, neglecting end effects. Such neglect seems reasonable in view

TABLE III Heats of transition (ΔH in kcal mol^{-1} CH$_2$) using minimum values of the repulsive energy

Material	ΔH + ALM	ΔH + MUEL	ΔH + WILL	ΔH Experimental
$C_{19}H_{40}$	0.157	0.185	0.172	0.174
$C_{21}H_{44}$	0.157	0.182	0.170	0.176
$C_{21}H_{44}$ (Mazee)	0.175	0.198	0.183	0.176
$C_{23}H_{48}$	0.166	0.189	0.174	0.226
$C_{25}H_{52}$	0.173	0.194	0.177	0.250
$C_{29}H_{60}$	0.209	0.237	0.212	0.260
$C_{29}H_{60}$ (Mueller)	0.163	0.183	0.168	0.260

TABLE IV Heats of transition (ΔH in kcal mol^{-1} CH2) for both molecular rotation and translation in the upper phase

Material	ΔH + ALM	ΔH + MUEL	ΔH + WILL	ΔH Experimental
$C_{19}H_{40}$	0.263	0.247	0.244	0.174
$C_{21}H_{44}$	0.258	0.240	0.238	0.176
$C_{21}H_{44}$ (Mazee)	0.280	0.258	0.253	0.176
$C_{23}H_{48}$	0.265	0.242	0.238	0.226
$C_{25}H_{52}$	0.266	0.228	0.226	0.250
$C_{29}H_{60}$	0.299	0.265	0.252	0.260
$C_{29}H_{60}$ (Mueller)	0.261	0.227	0.225	0.260

of the observation of partly irregular chain stacking in the upper phase [10].

In terms of the model described in Section 2 the translational repulsive energy is calculated by keeping α_1 and α_2 constant and allowing z to vary so that for the ith hydrogen–hydrogen disc pair,

$$\langle U[z, z', \alpha_1, \alpha_2]_{\text{trans}}\rangle_i = \frac{1}{\lambda}\int_0^{\lambda} U[z, z', \alpha_1, \alpha_2]\,\mathrm{d}z' \qquad (12)$$

Then for the ith pair and a neighbouring molecule,

$$\langle U(\tau)\rangle_{\text{trans}} = \sum_{i=1}^{4} \langle U[0, z', \alpha_1, \alpha_2]_{\text{trans}}\rangle_i + 2\sum_{z=\lambda}^{3}\sum_{i=1}^{4} \langle U[z, z', \alpha_1 \alpha_2]_{\text{trans}}\rangle_i \qquad (13)$$

The total is found by summing $\langle U(\tau)\rangle_{\text{trans}}$ over the six nearest neighbours. This energy was calculated for different initial orientations of the molecule in steps of 20°, to allow for the molecular rotation, and an average found. The results are given in Table IV. Agreement with the experimental values is now good for the longer molecules but poor for the shorter molecules. Comparison with Table III, a similar calculation without translation, shows that the reverse is then true. This reinforces the idea that different molecular motions occur for different molecular lengths.

TABLE V Differences between calculated heats of transition with minimum repulsive energy and the experimental values ($\Delta(\Delta H)$) in kcal mol^{-1} CH$_2$)

Material	$\Delta(\Delta H)$ ALM	$\Delta(\Delta H)$ MUEL	$\Delta(\Delta H)$ WILL
$C_{19}H_{40}$	0.32	−0.21	0.04
$C_{21}H_{44}$	0.40	−0.12	0.12
$C_{21}H_{44}$ (Mazee)	−0.02	−0.46	−0.14
$C_{23}H_{48}$	1.38	0.85	1.20
$C_{25}H_{52}$	1.92	1.40	1.82
$C_{29}H_{60}$	1.48	0.67	1.39
$C_{29}H_{60}$ (Mueller)	2.82	2.24	2.66

3.3. The possibility of molecular kinking

The possibility of the occurrence of molecular defects (kinks) in the upper phase can be investigated by a comparison of the calculated and experimental values given in Table III. Subtracting the calculated values from the experimental values gives the results listed in Table V. Various molecular defects can occur [6, 7] but the most probable is a $2g1$ kink, which involves the chain being divided into two parallel sections joined by the two gauche bonds separated by one trans bond of the kink. This defect has the lowest energy possible and fits relatively easily into the crystal structure of the disordered phase. A $2g1$ kink introduces an excess energy of 1 to 1.5 kcal mol^{-1} over that of an all trans molecular structure. Thus, it is clear that for chain lengths greater than $C_{21}H_{44}$ there is sufficient energy difference to allow the introduction of kinks but not for $C_{21}H_{44}$ or shorter. Molecular kinking will obviously compete with translational motion for longer chains so the actual kink density will be less than one per molecule, as implied by Table V. Furthermore, there will be some reduction of rotational energy since the kinked chains have a much greater radius of motion and energy considerations preclude the existence of a large number of rotating kinked chains.

4. Discussion

The possibility of molecular motion in the lower phase has not been taken into consideration in these calculations. Such librational motion was originally proposed by Andrew [2], however Barnes [8] found no quasi-elastic broadening below the transition. Our measurements on $C_{23}H_{48}$ show no appreciable line broadening but there is a small residual line broadening which is almost independent of scattering angle. This may, indeed, be due to small angle librations of the molecules, but should not, however, affect our results, since the motion in the upper phase will have similar librational motion superposed on the hindered rotational and translational motions. Thus, as stated earlier, though the total energies do not have the correct absolute values, their difference does correspond to the experimental heat of transition.

The question of multiple transitions is complex. We have evidence of such behaviour in some of our materials and the data on $C_{33}H_{68}$ is impressive [10–12]. However, the effects of impurities are not clear since Schaerer *et al.* [27] report multiple transitions in $C_{27}H_{56}$ and $C_{36}H_{74}$ samples which were impure, and only single transitions in $C_{25}H_{52}$ and $C_{29}H_{60}$ which were claimed to be purer. They also found a transition for 99.9% pure $C_{20}H_{42}$ with an appreciable heat of transition. We have also observed the occurrence of a transition in $C_{20}H_{42}$ samples if the purity is less than 99.9%. Unfortunately in the work on $C_{33}H_{68}$, the purity is not stated explicitly, though the method of preparation suggests a high purity since only $C_{22}H_{46}$ or $C_{44}H_{90}$ are expected to occur and can easily be separated.

We have calculated the heats of transitions for $C_{33}H_{68}$ for the various transitions using the X-ray data and models of molecular motion of Piesezek *et al.* [10–12]. For the first transition the energy difference between 45° librations and 180° librations was found to be much less than the experimental value of 0.015 kcal mol^{-1} CH_2 for all three choices of hydrogen–hydrogen repulsion potential. This suggests that the model of 180° rotational jumps is correct, though this motion is less amenable to calculation and we were not able to confirm this directly. Combining a rotational motion and a translational one, which is equivalent to combining the next two independent transitions, gives a total energy change of 0.238 kcal mol^{-1} CH_2 for the Williams potential function. This agrees will with the combined experimental values of 0.248 kcal mol^{-1} CH_2. Thus we find good agreement of our calculations and the experimental values, which further supports the molecular models proposed previously and the idea that the multiple transitions are a property of a pure paraffin of this molecular length.

We can find further support for the occurrence of different molecular motions in the upper phase for short and long molecules in our X-ray measurements. The 0 0 *l* lines which depend on the long axis spacing of the molecular units become diffuse above the transition. However a *c*-axis repeat value can be determined for $C_{19}H_{40}$ and $C_{21}H_{44}$ even just below the melting point. This is not so for the longer molecules, where there is obviously more disorder along the *c*-axis. Changes of the other lattice dimensions in the upper phase suggest an increasing degree of disorder as the melting point is reached. Thus we conclude that for $C_{21}H_{44}$ and shorter molecules the molecular motion in the disordered phase is predominantly a hindered rotation. However, for $C_{23}H_{48}$ and longer molecules the upper phase motion consists of hindered rotation and translation with the very probable occurrence of some molecular defects.

It is interesting to relate this work to the high pressure observations of a chain extended polyethylene phase by Bassett [29]. Using X-ray diffraction he observed a hexagonal phase above 230° C at a pressure of 5 kbars. This is the opposite to the observations of Wuerflinger and Schneider [30], who found for the *n*-alkanes the solid state transition disappears above a few kbars pressure. Here the pressure compresses the crystal and prevents the onset of molecular rotation by increasing the potential barriers for such motion. Thus the mechanism for the occurrence of the chain extended hexagonal phase of polyethylene must be essentially different from that in the *n*-alkanes. The X-ray data of Bassett suggests that there is considerable disorder in the polyethylene before the hexagonal phase is reached. This is presumably due to large amplitude torsional motions, since chain folding would preclude rotation. The occurrence of molecular defects is uncertain since it is favoured by the high temperature but is hindered by the high pressure. Defects may be present in the chain fold region, however, and at a high enough temperature and pressure the molecular motion in this region becomes sufficient to allow translation of the molecule to a chain extended form. There would then be voids left in the structure allowing much greater molecular motion in the chains and the occurrence of a disordered hexagonal phase.

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