PHYSICAL REVIEW B VOLUME 27, NUMBER 5 1 MARCH 1983

# Dislocation melting in *n*-paraffin homologs

D. T. Vigren
*Theoretische Physik, Universität des Saarlandes,*
*D-6600 Saarbrücken, Federal Republic of Germany*
(Received 10 August 1982; revised manuscript received 23 November 1982)

A formula for the melting temperature of *n*-paraffin homologs as a function of polymer chain length is derived in a simple model of dislocation catastrophe. The salient features of the melting curve can be understood as a consequence of the gradual transition with increasing chain length from a melting process dominated by dislocations which bridge the paraffin chain lamellae, to one in which nonbridging loops play the principal role.

Low-temperature paraffin crystallizes in a stacked layer structure. Each lamella of thickness ~100 Å is composed of extended linear chains of $CH_2$ units, having methane terminal groups, that are oriented perpendicular to the lamellar planes in an orthorhombic array. The carbon atoms of a single chain are arranged in a low-angle planar zigzag structure, the zigzag planes of neighboring chains being orthogonal.[1] Near the melting point of many paraffin systems the zigzag planes become randomly oriented, perpendicular to the plane of the lamella, and the chains order hexagonally.[2] In Fig. 1(a) a single chain of carbon atoms is shown in the planar zigzag structure. The hydrogen atoms of the $CH_2$ unit are not shown for simplicity. In Fig. 1(b) the top view of a lamella is shown near and below the melting point. The chain ends are indicated schematically as circles, ordered hexagonally, whereas the arrows give the orientation of the zigzag planes, and are disordered. The detailed structure of the crystalline defects in this "rotator phase" which is a precursor to melting has been discussed in detail elsewhere.[3] In the present paper the zigzag structure of the polymers will be ignored and they will be represented simply as flexible rods without internal structure.

The solid curve in Fig. 2 shows the observed dependence of the melting temperature $T_m$ on the number $M$ of $CH_2$ units in a polymer chain.[4] The curve shown is for homologs with an odd number of units. The melting curve for even homologs has the same general features with a different initial slope. Since the chains are presumably extended,[1,2] $M$ will be proportional to the lamellar thickness.

A reasonable fit to $T_m(M)$ has been obtained for $44 \leq M \leq 100$ with the formula[5]:

$$T_m = T_m^* \left[ \frac{M-a}{M-b} \right] , \tag{1}$$

where $T_m^* = 419.6$ K and $a$ and $b$ are, respectively, the end-group heat and entropy of melting. Outside this range of $M$, the calculated value is much too high for long chains, and much too small for short chains.[4] In fact Eq. (1) fails badly at small $M$ where $T_m(M)$ is observed to decrease rapidly. A logarithmic correction to Eq. (1) has been proposed[6] which accounts for the loss of order between weakly coupled terminal groups of polymers in neighboring lamellae during the melting process. However, this correction also fails to describe the melting curve for smaller values of $M$.

At low temperatures the polymers within a lamella may be thought of as a stack of rigid rods. Thus the only allowed structural defects are *straight* edge—type dislocations which bridge the lamella, and the melting transition is exactly analogous to the smectic-*B* to smectic-*A* transition in liquid crystals. There, the hexagonal order in a platelet of rods disappears during the transition, but the layered structure persists into the high-temperature phase. Such a system was treated theoretically by Huberman *et al.*,[7] using a two-dimensional model in which the density of point dislocations increases catastrophically at $T_m$.

For temperatures above 200 K the thermal activation of polymer kinks becomes possible through rotational conformations of the gauche type.[8] Thus one expects the stiff polymer description to break down when chains become long enough to produce kink defects before melting takes place. From Fig. 2 this occurs when $M \gtrsim 10$. Even for the longest chain systems, polymer conformations with more than one kink are highly improbable.[1,2] In spite of this, local aggregates of polymer jogs should be generated rather easily, due to the strong steric constraint imposed on next neighbors in the close-packed structure. Such jog aggregates may be viewed as lateral screw-type dislocation segments.[1,4] These can connect

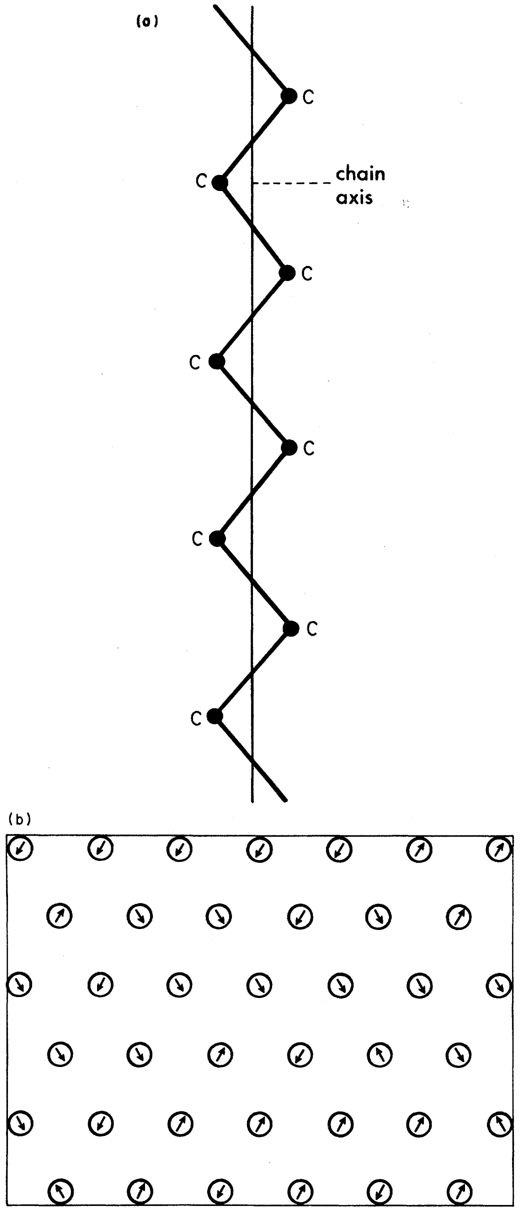

FIG. 1. (a) Single-chain polymer of paraffin, composed of $CH_2$ units. The carbon atoms form a planar zigzag structure (plane of the figure). The hydrogen atoms are not shown. (b) Top view of a paraffin lamella near the melting point. The chain ends are indicated schematically by circles which are hexagonally ordered. The chain axes are perpendicular to the figure plane, and the arrows (randomly ordered) give the orientation of the respective zigzag planes.

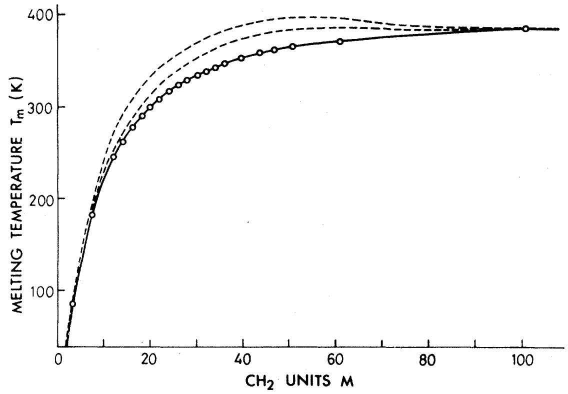

FIG. 2. Melting curve of odd paraffin homologs as a function of lamellar thickness. The solid line is drawn through the experimental points. The dashed curves are predictions of the dislocation catastrophe model.

with edge-type segments that run parallel to the chain axis, to form square loops. A loop which makes contact with both lamellar surfaces forms what I term a "bridging loop" whereas an "open loop" begins and ends on the same surface. Examples of bridging and open loops are given in Fig. 3.

In Ref. 3 a melting theory of paraffin is presented which assumes that only relatively straight bridging loops are responsible for melting. In this paper it is suggested that laterally spread bridging loops as well as nonbridging loops may become increasingly important in the longer chain systems. In fact, it will be shown within a simple theory of dislocation screening that the gross features of the melting curve can be understood as a transition from bridging to nonbriding loop dominated melting statistics.

Assuming that a dislocation catastrophe is responsible for paraffin melting$^{9-11}$ one expects that $T_m$ should depend in an essential way on the lamellar thickness in short chain systems, since only relatively straight bridging loops can form. On the other hand, for thicker lamellae, shorter nonbridging

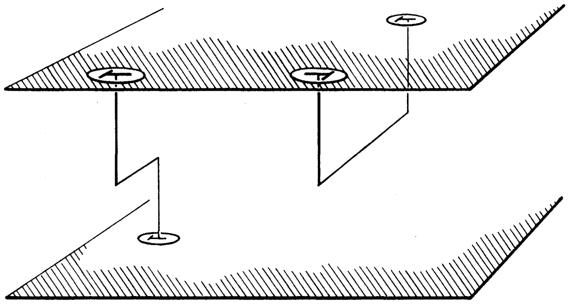

FIG. 3. Examples of bridging and open dislocation loops in a paraffin lamella. The upper and lower lamellar surfaces are cross hatched, and the orientation of the edge dislocation segments are indicated within the circles. The horizontal segments are of the screw type, and are formed through polymer kinking. For clarity the polymers are not shown.

loops become more favorable, both energetically and entropically, so that $T_m$ is expected to become insensitive to the lamellar thickness.

To demonstrate this effect quantitatively I consider only conservative defect motions, so that the dislocation slip systems can be defined by a unit vector normal to the lamellar surface and any one of six Burgers vectors within this surface, that are allowed by the hexagonal symmetry. Since the dislocations will be assumed independent, I look for the dislocation catastrophe in a single slip system in which $n_D$ loops are considered to be disposed upon a square lattice. Since it will be presumed that closed loops play only a minor role in the experimental range of $M$, I take $n_D = n_B + n_0$, where $n_B$ and $n_0$ are, respectively, the number of bridging and open loops in the slip system under consideration.

The columns of the square lattice coincide with the positions of $N_0$ polymers in the perfect crystal. The rows are labeled by the integers $\{k = 1, \ldots, M\}$, and the $i$th dislocation loop is represented as a random walk of $N_i$ steps. Neglecting excluded volume effects, the first steps may be chosen in $W_s$ ways:

$$W_s = N_0![n_B!n_0!(N_0 - n_B - n_0)!]^{-1} . \tag{2}$$

Then within the independent-dislocation approximation the total partition function may be written as

$$Z(M) = W_s[z_0(M)]^{n_0}[z_B(M)]^{n_B} , \tag{3}$$

where $\{z_i; i = 0, B\}$ are the *single*-loop partition functions. Then the total free energy per polymer is given by

$$\begin{aligned} F(M) &\equiv -(N_0\beta)^{-1}\ln Z(M) \\ &= \beta^{-1}\left[(1-\rho_0-\rho_B)\ln(1-\rho_0-\rho_B) \right. \\ &\quad \left. + \sum_{i=0,B} \rho_i \ln(\rho_i/z_i)\right] , \end{aligned} \tag{4}$$

where $\beta \equiv (k_BT)^{-1}$ and $\rho_i \equiv n_i/N_0$.

To calculate $z_0$ and $z_B$ I adapt the transfer-matrix method[12] to the paraffin system. A probability vector $\vec{P}(N) \equiv \{P(k,N); k = 1, \ldots, M\}$ may be defined, whose $k$th component represents the probability that a walk, which begins in the first row, ends in the $k$th row after $N$ steps. The vectors $\vec{P}(N)$ and $\vec{P}(N-1)$ are related by the transfer matrix $W$,

$$\vec{P}(N) = W\vec{P}(N-1) \equiv [W]^N\vec{P}(0) , \tag{5a}$$

where

$$W(p_h,p_u,p_d) \equiv \begin{bmatrix} p_h & p_u & 0\cdots & 0 & 0 & 0 \\ p_d & p_h & p_u\cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0\cdots & p_d & p_h & p_u \\ 0 & 0 & 0\cdots & 0 & p_d & p_h \end{bmatrix} , \tag{5b}$$

with the convention $\vec{P}(0) \equiv (1,0,\ldots,0)$. The quantities $p_h$, $p_u$, and $p_d$ are the probabilities for a *single* horizontal, upward, and downward step, respectively. For example, Eq. (5a) yields

$$\vec{P}(1) = \begin{bmatrix} p_h \\ p_d \\ 0 \\ \vdots \\ 0 \end{bmatrix} , \tag{5c}$$

$$\vec{P}(2) = \begin{bmatrix} p_h^2 + p_dp_u \\ p_hp_d + p_dp_h \\ p_d^2 \\ 0 \\ \vdots \\ 0 \end{bmatrix} , \tag{5d}$$

$$\vec{P}(3) = \begin{bmatrix} p_h^3 + p_dp_up_h + p_hp_dp_u + p_dp_hp_u \\ p_dp_h^2 + p_dp_up_d + p_h^2p_d + p_hp_dp_h + p_d^2p_u \\ p_hp_d^2 + p_d^2p_h + p_d^2p_h \\ p_d^3 \\ 0 \\ \vdots \\ 0 \end{bmatrix} , \tag{5e}$$

etc. I choose

$$p_h \equiv \xi^{-1}e^{-\beta\epsilon_h} , \tag{6a}$$

$$p_v \equiv p_d \equiv p_u \equiv (2\xi)^{-1}e^{-\beta\epsilon_v} , \tag{6b}$$

where $\xi \equiv e^{-\beta\epsilon_h} + e^{-\beta\epsilon_v}$ and $(\epsilon_h, \epsilon_v)$ is the energy associated with the creation of one-step unit of (screw, edge) dislocation. This choice ensures that $p_h + p_u + p_d = 1$, and reduces to the usual result[12] when all paths are energetically equivalent.

Multiplying the first row of $W$ by $e^{\theta_1}$ and the last row by $e^{\theta_M}$ Eq. (5a) gives the probability of a *bridge* after $N+1$ steps as

$$P(M,N+1) = \sum_{k=0}^{N+1} \sum_{l=0}^{N+1-(M-1)} p_{k,l}(M,N+1)e^{(k\theta_1 + l\theta_M)} , \tag{7}$$

where $(k,l)$ is the number of times the random walk has entered into the (upper, lower) lamellar surfaces, and $p_{k,l}$ is a sum of $(N+1)$-fold products of $p_u$, $p_d$, and $p_h$ [see Eqs. (5c)–(5e)].

Since we are only interested in bridges which span the lamella once, the required probability for such bridges is

$$P_B(M,N+1) \equiv p_{0,1}(M,N+1) \ . \tag{8}$$

Similarly the probability of an open loop after $N+1$ step is

$$P(1,N+1) = \sum_{k=0}^{N+1} \sum_{l=0}^{N+1-(M-1)} p_{k,l}(1,N+1) e^{(k\theta_1 + l\theta_M)} \tag{9}$$

so that the probability of forming a *simple* open loop (i.e., without bridging the lamella) is

$$P_0(1,N+1) = p_{1,0}(1,N+1) \ . \tag{10}$$

In view of Eqs. (5) and (6) the single-loop partition functions may be written as

$$z_0 = \sum_{N=1}^{\infty} (2\xi)^{N+1} P_0(1,N+1) \ , \tag{11a}$$

$$z_B = \sum_{N=1}^{\infty} (2\xi)^{N+1} P_B(M,N+1) \ , \tag{11b}$$

where $M > 1$ is assumed.

In Eqs. (11) a factor $(2)^{N_h}$ was introduced, $N_h$ being the number of horizontal steps taken on the $(N+1)$-step path, since the method of counting does not distinguish between left and right steps. The sums begin with $N=1$, since at least two steps are necessary for an open loop and for bridges with $M > 1$.

The expressions which appear on the right-hand side of Eq. (11) have been calculated[12] and reduce to the following expressions in the present model:

$$z_0 = e^{-\beta\epsilon_v^0} \sinh[(M-2)\phi_0] \{\sinh[(M-1)\phi_0]\}^{-1} \ , \tag{12a}$$

$$z_B = e^{-\beta\epsilon_v^B} \sinh\phi_B \{\sinh[(M-1)\phi_B]\}^{-1} \ , \tag{12b}$$

where $\phi_i$ is given through

$$\cosh\phi_i \equiv \tfrac{1}{2} e^{\beta\epsilon_v^i} (1 - 2e^{-\beta\epsilon_h^i}) \ . \tag{12c}$$

For simplicity I approximate the dislocation step energies as[13]:

$$\epsilon_{v,h}^B = \epsilon_c - A_B \ln(\rho_B + \rho_0) \ , \tag{13a}$$

$$\epsilon_{v,h}^0 = \epsilon_c - A_0 \ln(\rho_B + \rho_0) \ . \tag{13b}$$

In writing Eqs. (13) it is assumed that the logarithmic divergence of the average strain energy associated with a unit length of dislocation is cut off by the mean distance between dislocation lines, and that the *average* energy may be different depending upon whether the unit length of dislocation is participating in a bridge or an open loop. Furthermore, it should be stressed that although the system is assumed to contain a low density of dislocations, these are by no means isolated from one another so that a high degree of loop interpenetration exists, thus justifying the logarithmic cutoffs in Eq. (13).

Finally I have associated a single-core energy $\epsilon_c$ to horizontal and vertical steps. Although the physical mechanism is different for the two defect types, the core energies are a result of nonlinear strains and are not well known. At any rate the introduction of different core energy parameters is not expected to alter in any essential way the results presented in this paper. (It will be seen that the melting temperature is independent of core energy in the present model.)

Upon substitution of Eqs. (12) and (13) in Eq. (4), and assuming that $\epsilon_{v,h}^i \gg k_B T$, the following expression for the free energy per polymer is obtained:

$$\begin{aligned} F = {} & [(M-1)\rho_B + 2\rho_0]\epsilon_c - [(M-1)A_B\rho_B + 2A_0\rho_0]\ln(\rho_B + \rho_0) \\ & + k_B T(1-\rho_B-\rho_0)\ln(1-\rho_B-\rho_0) + k_B T[\rho_B \ln\rho_B + \rho_0 \ln\rho_0] \end{aligned} \tag{14}$$

with $M > 1$.

In the solid state $\rho_B \ll 1$ and $\rho_0 \ll 1$, and, as was discussed above, $\rho_B \gg \rho_0$ for small $M$, whereas $\rho_B \ll \rho_0$ for large $M$. For simplicity I take:

$$\rho_B \equiv \rho e^{-\gamma M} \ , \tag{15a}$$

$$\rho_0 \equiv \rho(1 - e^{-\gamma M}) \ , \tag{15b}$$

where $\rho \ll 1$ is some average $M$-independent dislocation density, and $\gamma$ characterizes the transition from bridging to open-loop dominated melting statistics.

Substitution of Eqs. (15) into Eq. (14) yields

$$F = A\rho + B\rho \ln\rho + k_B T(1-\rho)\ln(1-\rho) \ , \tag{16a}$$

where

$$\begin{aligned} A(M,T) \equiv {} & [(M-3)e^{-\gamma M} + 2]\epsilon_c \\ & + k_B T[(1-e^{-\gamma M})\ln(1-e^{-\gamma M}) \\ & - \gamma M e^{-\gamma M}] \ , \end{aligned} \tag{16b}$$

$$B(M,T) \equiv k_BT - \{[(M-1)A_B - 2A_0]e^{-\gamma M} + 2A_0\} \,, \tag{16c}$$

with $M > 1$.

Equation (16) can be considered to be the three-dimensional (3D) generalization of the free energy, used in Ref. 7 to describe the smectic-*B* to smectic-*A* transition in an essentially 2D liquid-crystal platelet. In fact Eqs. (16) reduce identically to the expression given in Ref. 7 for the case $M = 2 \ll \gamma^{-1}$.

Minimizing Eq. (16a) with respect to $\rho$ under the condition that $\rho \ll 1$ one obtains

$$\rho = \exp\left[\frac{k_BT - A(M,T) - B(M,T)}{B(M,T)}\right] . \tag{17}$$

Melting occurs at a temperature $T_m$ at which the condition $\rho \ll 1$ can no longer be met; that is, when

$$B(M,T<T_m)<0, \quad B(M,T>T_m)>0 \,, \tag{18}$$

and

$$[A(M,T)+B(M,T)] < k_BT \tag{19}$$

for all $T$. Using Eqs. (16b) and (16c), one obtains

$$k_BT_m \equiv 2A_0 + [(M-1)A_B - 2A_0]e^{-\gamma M} \tag{20}$$

if the following subsidiary condition is met:

$$\left[\frac{\epsilon_c}{k_BT}\right] < [\gamma M e^{-\gamma M} - (1-e^{-\gamma M})\ln(1-e^{-\gamma M}) + 1] \times [(M-3)e^{-\gamma M}+2]^{-1} \,. \tag{21}$$

For $M \ll \gamma^{-1}$ and $M > 1$ the linear stiff-polymer behavior is obtained, $T_m \approx A_B k_B^{-1}(M-1)$ with $\epsilon_c < A_B$. For $M \gg \gamma^{-1}$ the constant 3D behavior results are $T_m = 2A_0 k_B^{-1}$ with $\epsilon_c < A_0$.

The upper dashed curve of Fig. 2 is calculated using Eq. (20) with $A_0 k_B^{-1} = 194$ K, $A_B k_B^{-1} = 10$ K, and $\gamma = 0.066$, corresponding to $M_0 \equiv \gamma^{-1} = 15$; the lower dashed curve is calculated with $A_0 k_B^{-1} = 194$ K, $A_B k_B^{-1} = 4$ K, and $\gamma = 0.080$, corresponding to $M = 13$. The large difference between $A_B$ and $A_0$ is difficult to justify physically, and may be a result of the simplifications introduced through Eqs. (15), which allow only a single parameter $\gamma$. The weak maximum appearing in the theoretical curves may also be an artifact of this parametrization. It was felt, however, that the descriptive level of this work did not warrant the introduction of more parameters in Eqs. (15) or a more accurate expression for the dislocation line energy than Eqs. (13).

The results shown in Fig. 2 demonstrate that the general features of the melting curve can be understood as resulting from a transition from bridging to nonbridging loop dominated melting statistics with increasing lamellar thickness. The description suffers, however, from the way in which dislocation screening is handled in Eqs. (13). In fact the present treatment, as well as that of Ref. 7, presumes a low density of independent dislocation bridges rather than closely bound pairs[10,11] as being the defects of the solid state for $M \ll M_0$. This together with the crude treatment of screening leads to the prediction of a first-order transition, without the distinguishing feature of nonconservative dislocation motion which is a necessary added input to the more elaborate melting theories.[10,11]

The author wishes to thank Professor A. Holz and Dr. J. Naghizadeh for many useful discussions. This work was supported in part by NATO Research Grant No. 028.82 and in part by the Deutsche Forschungsgemeinschaft Sonderforschungsbereich 130.

---

[1] B. Wunderlich, *Macromolecular Physics 1* (Academic, New York, 1973).

[2] G. Strobl, Phys. Blätter 33, 550 (1977).

[3] A. Holz, J. Naghizadeh, and D. T. Vigren, Phys. Rev. B 27, 512 (1983).

[4] B. Wunderlich, *Macromolecular Physics 3* (Academic, New York, 1980).

[5] M. G. Broadhurst, J. Chem. Phys. 36, 2578 (1962).

[6] P. J. Flory and A. Vrig. J. Am. Chem. Soc. 85, 3548 (1963).

[7] B. A. Huberman, D. M. Lublin, and S. Doniach, Solid State Commun. 17, 485 (1975).

[8] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969).

[9] D. Kuhlmann-Wilsdorf, Phys. Rev. 140, 1599 (1965).

[10] J. M. Kosterlitz and D. J. Thouless, J. Phys. C 6, 1181 (1973).

[11] A. Holz and J. F. N. Medeiros, Phys. Rev. B 17, 1161 (1978).

[12] E. A. Di Marzio and R. J. Rubin, J. Chem. Phys. 55, 4318 (1971).

[13] F. R. N. Nabarro, *Theory of Crystal Dislocations* (Oxford University Press, London, 1967), p. 688.