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Melting of normal paraffin hydrocarbons

UMA KAPUR, V. D. GUPTA† and CHAMAN MEHROTRA‡
Physics Department, Indian Institute of Technology, Kanpur, India
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Abstract. The theory of diffuse transition is applied to study melting of short-chain hydrocarbons. An adjustable nucleation parameter reported earlier for polyethylene is used. Experimental data of Flory and Vrij are utilized.

In an earlier communication (Gupta and Gupta 1967a) in this journal one of the authors (V.D.G.) has reported an application of the theory of the Ising model to a study of dimensional changes during melting in polyethylene. It was based on the cell model for diffuse transition and essentially involved writing the Ising matrix in terms of segment pair partition functions which are either in the amorphous (denoted by r) or in the crystalline region (denoted by h). The boundary between the crystalline and amorphous states, that is the first h segment in a sequence of h states is denoted by a k state. f_r, f_h and f_k are the corresponding segment partition functions of the three states. Taking into account the nearest-neighbour interaction the basic matrix for the problem is

$$M = \begin{array}{c|ccc} & r & k & h \\ \hline r & f_r^{\frac{1}{2}} f_r^{\frac{1}{2}} & f_r^{\frac{1}{2}} f_k^{\frac{1}{2}} & 0 \\ k & f_r^{\frac{1}{2}} f_k^{\frac{1}{2}} & 0 & f_k^{\frac{1}{2}} f_h^{\frac{1}{2}} \\ h & f_h^{\frac{1}{2}} f_r^{\frac{1}{2}} & 0 & f_h^{\frac{1}{2}} f_h^{\frac{1}{2}} \end{array} \qquad (1)$$

Previously, approximate results for fractional crystallinity and average sequence lengths in the amorphous and crystalline regions have been reported in polyethylene (Gupta and Gupta 1967b) and other biopolymers (Tobolsky and Gupta 1963). In this communication we derive results which are valid for an arbitrary and finite value of N—the number of segments in the chain. This enables us to study the melting phenomenon in normal paraffin hydrocarbons.

The eigenvalues of M are given by

$$\begin{aligned} \lambda_1 &= \tfrac{1}{2}[(f_r+f_h)+\{(f_r-f_h)^2+4f_rf_h\}^{1/2}] \\ \lambda_2 &= \tfrac{1}{2}[(f_r+f_h)-\{(f_r-f_h)^2+4f_rf_h\}^{1/2}] \qquad (2) \\ \lambda_3 &= 0. \end{aligned}$$

The matrix T which diagonalizes M is given below

$$T = \left|\begin{array}{ccc} 1 & 1 & 1 \\ \left(\dfrac{\lambda_1-f_r}{f_r^{\frac{1}{2}} f_k^{\frac{1}{2}}}\right) & \left(\dfrac{\lambda_2-f_r}{f_r^{\frac{1}{2}} f_k^{\frac{1}{2}}}\right) & \left(-f_r^{\frac{1}{2}} f_k^{-\frac{1}{2}}\right) \\ \left(\dfrac{f_h^{\frac{1}{2}} f_r^{\frac{1}{2}}}{\lambda_1-f_h}\right) & \left(\dfrac{f_h^{\frac{1}{2}} f_r^{\frac{1}{2}}}{\lambda_2-f_h}\right) & \left(-f_r^{\frac{1}{2}} f_h^{-\frac{1}{2}}\right) \end{array}\right. \qquad (3)$$

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† Present address: Physics Department, Lucknow University, Lucknow, India.
‡ Institute of Advanced Studies, Meerut University, Meerut.

Similarly T^{-1} can be written as

$$T^{-1} = \left|\begin{matrix} C_1 & \left(\dfrac{C_1 f_r^{\frac{1}{2}} f_k^{\frac{1}{2}}}{\lambda_1}\right) & \left(\dfrac{C_1 f_r^{\frac{1}{2}} f_k f_h^{\frac{1}{2}}}{\lambda_1(\lambda_1 - f_h)}\right) \\ C_2 & \left(\dfrac{C_2 f_r^{\frac{1}{2}} f_k^{\frac{1}{2}}}{\lambda_2}\right) & \left(\dfrac{C_2 f_r^{\frac{1}{2}} f_k f_h^{\frac{1}{2}}}{\lambda_2(\lambda_2 - f_h)}\right) \\ 0 & (C_3) & \left(-C_3 f_k^{\frac{1}{2}} f_h^{-\frac{1}{2}}\right) \end{matrix}\right.$$

where

$$C_1 = \frac{\lambda_1 - f_h}{\lambda_1 - \lambda_2} \qquad C_2 = \frac{\lambda_2 - f_h}{\lambda_2 - \lambda_1}$$

and

$$C_3 = \frac{1}{\left(f_r^{\frac{1}{2}} f_k^{\frac{1}{2}} f_h^{-1} - f_r^{\frac{1}{2}} f_k^{-\frac{1}{2}}\right)}.$$

Let the first segment be assumed in the amorphous phase (Gauch configuration). Its contribution to the partition function is given by

$$U = (f_r^{\frac{1}{2}}, 0, 0). \tag{4}$$

The way the matrix M is constructed, the configurations ending with r, k or h have to be multiplied by $f_r^{\frac{1}{2}}, f_k^{\frac{1}{2}}, f_h^{\frac{1}{2}}$ respectively before their contribution is summed to give the partition function. For this purpose we define a column matrix U^+ given by

$$U^+ = \begin{pmatrix} f_r^{\frac{1}{2}} \\ f_k^{\frac{1}{2}} \\ f_h^{\frac{1}{2}} \end{pmatrix}.$$

Now the partition function is given by

$$Z = UM^{N-1}U^+ = UTT^{-1}M^{N-1}TT^{-1}U^+ \tag{5}$$

$$UT = (f_r^{\frac{1}{2}}, f_r^{\frac{1}{2}}, f_r^{\frac{1}{2}})$$

$$T^{-1}U^+ = \begin{pmatrix} C_1 f_r^{-\frac{1}{2}} \lambda_1 \\ C_2 f_r^{-\frac{1}{2}} \lambda_2 \\ 0 \end{pmatrix}$$

and

$$T^{-1}MT^{N-1} = \left|\begin{matrix} \lambda_1^{N-1} & 0 & 0 \\ 0 & \lambda_2^{N-1} & 0 \\ 0 & 0 & 0 \end{matrix}\right..$$

The partition function Z now becomes

$$Z = UT[T^{-1}MT]^{N-1}T^{-1}U^{+}$$

$$= (f_r^{\frac{1}{2}}, f_r^{\frac{1}{2}}, f_r^{\frac{1}{2}}) \begin{vmatrix} \lambda_1^{N-1} & 0 & 0 \\ 0 & \lambda_2^{N-1} & 0 \\ 0 & 0 & 0 \end{vmatrix} \begin{pmatrix} C_1\lambda_1 f_r^{-\frac{1}{2}} \\ C_2\lambda_2 f_r^{-\frac{1}{2}} \\ 0 \end{pmatrix}$$

or

$$Z = C_1\lambda_1^N + C_2\lambda_2^N$$

$$= Z_1 + Z_2 \qquad \text{(say)}.$$

We denote the number of r segments, k segments and h segments (exclusive of k segments) by n_r, n_k and n_h^*. These values are given by

$$\frac{n_r}{N} = \frac{1}{N}\frac{\partial \ln Z}{\partial \ln f_r}$$

$$= \frac{f_r}{Z}\left(\frac{Z_1}{\lambda_1}\frac{\partial\lambda_1}{\partial f_r} + \frac{Z_2}{\lambda_2}\frac{\partial\lambda_2}{\partial f_r}\right) + \frac{f_r}{NZ}\left[\frac{Z_1\partial \ln C_1}{\partial f_r} + \frac{Z_2\partial \ln C_2}{\partial f_r}\right] \tag{6}$$

$$\frac{n_k}{N} = \frac{f_k}{Z}\left(\frac{Z_1}{\lambda_1}\frac{\partial\lambda_1}{\partial f_k} + \frac{Z_2}{\lambda_2}\frac{\partial\lambda_2}{\partial f_k}\right) + \frac{f_k}{NZ}\left(\frac{Z_1\partial \ln C_1}{\partial f_k} + \frac{Z_2\partial \ln C_2}{\partial f_k}\right) \tag{7}$$

and

$$\frac{n_h}{N} = \frac{f_h}{Z}\left(\frac{Z_1}{\lambda_1}\frac{\partial\lambda_1}{\partial f_h} + \frac{Z_2}{\lambda_2}\frac{\partial\lambda_2}{\partial f_h}\right) + \frac{f_h}{NZ}\left(Z_1\frac{\partial \ln C_1}{\partial f_h} + Z_2\frac{\partial \ln C_2}{\partial f_h}\right). \tag{8}$$

These expressions reduce to the following, writing $f_h/f_r = Y$, $f_k/f_r = \sigma$, $(\lambda_1 - \lambda_2)/f_r = P$, and $A = \{(f_r - f_h)^2 + 4f_k f_r\}^{-1/2})$,

$$\frac{n_r}{N} = \frac{1}{2} + \frac{(1-Y)}{2P}(2A-1) + \frac{(1+Y)}{2P^2N}\{(2A-1)P-1+Y\} \tag{9}$$

$$\frac{n_k}{N} = -\sigma\frac{(1+Y+P)}{2P(Y-\sigma)} + \frac{A\sigma(1+Y)}{(Y-\sigma)P} - \frac{(1-Y)}{2NP^2}\{(2A-1)P-1+Y\} \tag{10}$$

$$\frac{n_h^*}{N} = \frac{Y}{P}\left(\frac{1-Y+P}{1+Y-P}\right) - \frac{AY(1-Y+2\sigma)}{P(Y-\sigma)} - \frac{Y}{NP^2}\{(2A-1)P-1+Y\}. \tag{11}$$

It can be immediately checked that

$$\frac{n_r}{N} + \frac{n_k}{N} + \frac{n_h^*}{N} = 1.$$

In as much as we use segment partition functions, these quantities can be interpreted in the following manner:

$$f_r = g_r$$

$$f_h = g_h \exp\left(\frac{\Delta H_f}{RT}\right) \tag{12}$$

$$f_k = \epsilon.$$

g_r is the statistical weight of an r segment, g_h is the statistical weight of an h segment and ΔH_f is the heat of fusion from the crystalline to amorphous state. The partition function f_k of the k segments which represent the boundary between amorphous and crystalline regions is taken to be temperature-independent and very small, to represent the difficulty of entering such a boundary region.

In the above equations, g_h, g_r and ϵ are assumed to be constants, and ΔH_f is the heat of fusion per mole of segments. For N large at the fusion point, $f_h = f_r$. The temperature of fusion and the entropy of fusion are therefore given by

$$T_f = \frac{\Delta H_f}{R} \ln\left(\frac{g_r}{g_h}\right) = \frac{\Delta H_f}{\Delta S_f}.$$

$$\Delta S_f = R \ln\left(\frac{g_r}{g_h}\right)$$

Hence we can write

$$\begin{aligned} Y = \frac{f_h}{f_r} &= \frac{g_h}{g_r} \exp\left(\frac{\Delta H_f}{RT}\right) \\ &= \exp\left(\frac{\Delta H_f - \Delta S_f T}{RT}\right) \\ &= \exp\left(\frac{\Delta H_f}{TT_fR}(T_f - T)\right) = e^X \end{aligned} \tag{13}$$

where

$$X = \frac{\Delta H_f}{TT_fR}(T_f - T)$$

and

$$\sigma = \frac{f_k}{f_r} = \frac{\epsilon}{g_r}.$$

The number of amorphous sequences $\bar{r}$ and that of helical sequences $\bar{h}$ are given by

$$\bar{r} = \frac{n_r}{n_k}$$

and

$$\bar{h} = \frac{n_h^* + n_k}{n_k}$$

also defining fractional crystallinity Q we have

$$Q = 1 - \frac{n_r}{n}$$

or

$$\frac{n_r}{n} = (1 - Q). \tag{14}$$

Now the density d of a macromolecule with large N can be written as $d = QC + (1-Q)A$, where C and A are partial densities of the crystalline and amorphous parts. At sufficiently high temperature $Q = 0$ and $A = d_0$, the density of the amorphous part. Hence the expression for density in terms of C and A_0 is

$$d = QC + (1-Q)d_0. \tag{15}$$

Discussion

Normal paraffins for odd $N \geqslant 9$ and for $N \geqslant 44$ exist in the orthorhombic crystalline form. Transition from the orthorhombic to the hexagonal form precedes melting for odd n in the range $11 \leqslant N \leqslant 43$ and for even N, $34 \leqslant N \leqslant 42$. Flory and Vrij (1963) have recently reported the melting points and enthalpies of fusion for $N = 15$, 19, 25, 29, 30 and 43. We have made use of their data in obtaining the melting curves (Q against T). The nucleation parameter f_k/f_r is adjusted to give the correct melting point; these are shown in figure 1. The dependence of transition curves on σ values is also shown and as expected it gets sharper for smaller values. For $N = 30$, Seyer *et al.* (1944) have reported the variation of density with temperature. To compare it with our calculations we use $d_0 = 0{\cdot}779$ (Flory *et al.* 1964). Q against T curves combined with relation (15) enable us to calculate density as a function of temperature. The experimental results and theoretical calculations are shown in figure 2.

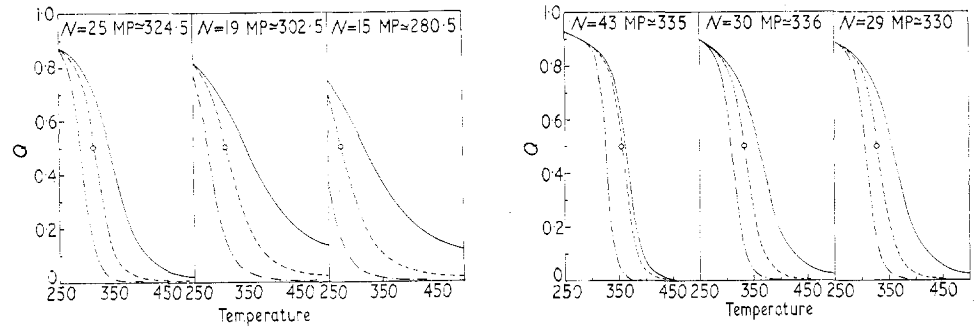

Figure 1. Crystallinity against temperature curves for different values of chain lengths. Full line $\sigma = 10^{-3}$; broken line $\sigma = 10^{-4}$; chain line $\sigma = 10^{-5}$.

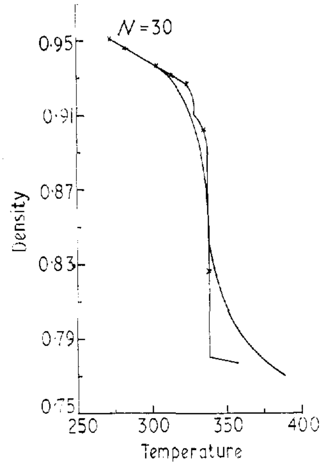

Figure 2. Experimental and theoretical density against temperature curves for $N = 30$. Experimental points are shown as crosses.

Because of the equivalence of the crystal structures for polyethylene and n-paraffin hydrocarbons and the virtual identity of their unit cell dimensions, it is expected that the limiting melting point for the n paraffin hydrocarbon series must be coincident with the melting point for linear polyethylene of infinite chain length.

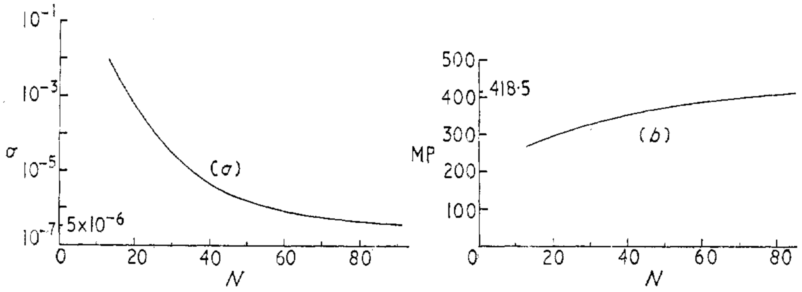

Figure 3. (*a*) Variation of σ with chain length. (*b*) Variation of melting point with chain length.

This is supported by calculations shown in figure 3(*b*). The value of the nucleation parameter f_k/f_r also asymptotically approaches the value 5×10^{-6} which yields correct results for polyethylene (Gupta and Gupta 1967a).

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