If we choose the origin of our molecule-fixed coordinate system at $\mathbf{R}_{cm}$, then we can eliminate q_* since $\mathbf{R}_{cm} = 0$ implies $\mathbf{P}_*(t) = 0$ and $\mathbf{A}_*(t) = 0$. Thus we may define $\mathbf{P}_0 = \mathbf{P}_{**}$, $\mathbf{A}_0 = \mathbf{A}_{**}$, $q_0 = q_{**}$, and $v_0(s) = v_{**}(s)$. In addition, eq A.4 tells us that when we sit at the center of mass, the net force felt by the polymer is zero. This implies that the normal mode expansion in eq 4.11 cannot represent the translational degrees of freedom.

Rotation. The total angular momentum of the polymer can be written as the sum of the angular momenta of all of its segments

$$\mathbf{L}(t) = \frac{\rho}{L} \int_{-L/2}^{L/2} ds \ \mathbf{r}(s,t) \times \dot{\mathbf{r}}(s,t) \qquad (A.5)$$

and the total stochastic torque is similarly

$$\mathbf{T}(t) = \frac{1}{L} \int_{-L/2}^{L/2} ds \ \mathbf{r}(s,t) \times \mathbf{A}(s,t) \qquad (A.6)$$

Now note that

$$\int_{-L/2}^{L/2} ds \ \mathbf{r}(s,t) \times \frac{\partial^4 \mathbf{r}(s,t)}{\partial s^4} = \sum_{l=0}^{\infty} \lambda_l \mathbf{P}_l \times \mathbf{P}_l = 0 \quad (A.7)$$

This implies that the bending force does not directly contribute to the torque equation. Substituting the bending equation into the torque integral and using eq A.6 and A.7, we obtain

$$\mathbf{T}(t) = \frac{d}{dt}\mathbf{L}(t) + \frac{\zeta}{\rho}\mathbf{L}(t) \qquad (A.8)$$

which is the expected torque in a viscous medium. If we substitute the normal mode expansion (eq 4.11) into the above relation, we get

$$\mathbf{T}(t) = \frac{1}{L}\left[\rho \frac{d}{dt}\sum_{l=0}^{\infty}\mathbf{P}_l \times \dot{\mathbf{P}}_l + \zeta\sum_{l=0}^{\infty}\mathbf{P}_l \times \dot{\mathbf{P}}_l \right] \quad (A.9)$$

Thus, a given mode will contribute angular momentum if the cross product $\mathbf{P}_l \times \dot{\mathbf{P}}_l$ does not vanish. It is easy to see that every nonzero mode is double degenerate in space because the oscillations can occur in two perpendicular

planes. These two degenerate modes can be combined to give a "pseudorotation" around the elongation axis of the molecule and give an effective parallel axis rotation to the polymer. It is just these rotations that we have considered as averaging out our polymer structure into an effective cylindrically symmetric body.

Rotations of the elongation axis, however, cannot be reproduced by the above mechanism. Thus the major conclusion is that perpendicular rotations, or tumbling of the elongation axis, are independent dynamical variables that cannot be expressed by the bending dynamics.

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Statistical Thermodynamic Theory for the Melting of *n*-Alkanes from Their Rotator Phases[†]

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ABSTRACT: Most liquid *n*-alkanes comprised of 9–43 carbons freeze to an equilibrium "rotator" phase a few degrees above the temperatures at which they fully crystallize. We develop statistical mechanical theory to account for the thermodynamic properties of melting from this rotator phase. Chain configurations are taken into account through the rotational isomeric state approximation. Volume-dependent interactions are approximated through adaptation of a classical equation of state for liquid alkanes. The anisotropy of the short-range repulsive forces, which must be the principal source of ordering in alkanes, is taken into account through appropriate modification of a chain pair potential. We also present a critical study of available experimental data. With a minimum of free parameters, the theory predicts enthalpies, volume changes, and temperatures of melting for the alkanes that have rotator phases at atmospheric pressure. For alkanes from 44 carbons to poly(methylene), which have no stable rotator phases at 1 atm, the theory predicts rotator-phase melting temperatures that are nearly identical with the experimentally observed crystalline melting temperatures.

Many liquid paraffins freeze to stable "rotator" phases a few degrees above the temperatures at which they undergo phase transitions to form fully ordered crystals. First observed by Müller,[1] these are partially disordered states in which the chains form layered arrays; however, unlike the chains in fully ordered crystal phases, the chains in rotator phases exhibit some degree of rotational freedom. For *n*-alkane chains having odd numbers of carbons (n_c),

stable rotator phases are observed for $9 \leq n_c \leq 43$; for n_c even, they are found for $22 \leq n_c \leq 42$. For other values of n_c, the chains freeze directly to an ordered, crystalline phase. Although the rotator phases exhibit considerable polymorphism[2-6] (determined by the degree of tilt of the chain axis with respect to the layer normal and by the symmetry of the chain centers of mass within a layer), the melting of rotator phases does not exhibit even/odd variation of temperature and enthalpy of melting with chain length, which characterizes the rotator phase to ordered crystal transition. Interest in these rotator phases derives, in part, from their presumed close resemblance to the state of organization of the alkyl chains in frozen surfactant monolayers and bilayers.

Here we develop a statistical thermodynamic treatment to account for the chain-length dependence of the molecular interactions responsible for the melting of n-alkanes from their "rotator" phases to the liquid state. This work is in the spirit of previous "equation of state" theories of the liquid state of alkanes.[7] There are three principal premises of our approach: (i) We assume that the differences in the thermal properties of the various polymorphs within the rotator phase are negligible. This is supported, for example, by the observation that the enthalpy of transition from the orthorhombic to hexagonal polymorphs of the rotator phase of C23 alkanes is only 80 cal/mol;[6] this is less than 1% of its enthalpy of melting.[8] For longer chains, the transitions within the rotator phase may be more complicated; however, the enthalpy changes are still expected to be negligible.[5] (ii) The chains are assumed to be completely conformationally disordered in the liquid state and fully conformationally ordered and all trans in the rotator state. Recent experiments show that there is some conformational disorder in the rotator state, but it is relatively small.[9] (iii) The partition function for the system is assumed to be factorable into an intramolecular configurational or combinatorial term, independent of the volume, and a volume-dependent intermolecular term. We discuss these contributions in turn.

Volume-Independent Interactions

Upon fusion, chain molecules are subject to configurational and translational free energy changes. The configurational free energies may be comprehended through rotational isomeric state theory,[10,11] provided that the configurations of a molecule in the liquid state are the same as those of a single isolated chain unperturbed by neighboring chains. The validity of this premise has been confirmed through neutron scattering experiments on liquid n-alkanes.[12] Enumeration of the configurational isomers requires specification of the values of two constants: the trans–gauche energy difference, E_{tg}, and the gauche(+)–gauche(−) "pentane interference" energy difference E_{gg}. We adopt the value $E_{gg} = 2000$ cal/mol;[10-12] the results are relatively insensitive to this quantity. The value of $E_{tg} = 500 \pm 100$ cal/mol is widely adopted for alkane liquids,[10-12] although recent measurements at higher pressures in liquid n-hexane give better agreement with 900 cal/mol.[13] Therefore, inasmuch as this value may differ in the solid state, we consider several possible values below. Statistical weights may be defined in terms of these energies; in the notation of Jernigan and Flory[11]

$$\sigma = \exp[-E_{tg}/RT] \qquad (1a)$$

$$\omega = \exp[-E_{gg}/RT] \qquad (1b)$$

where RT is the gas constant multiplied by absolute temperature. These weights may be combined in a statistical weight matrix

$$U = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \qquad (2)$$

from which the configurational partition function of the liquid can be computed as

$$Z_c(n_c,T) = J^*U^{n_c-3}J \qquad (3)$$

where

$$J^* = \text{row } (1, 0, 0) \qquad J = \text{col } (1, 1, 1)$$

The corresponding Helmholtz free energy is

$$F_c = -RT \ln Z_c \qquad (4)$$

which is linearly proportional to $n_c - 3$ to good approximation and is strongly dependent on temperature. It follows from the assumption of complete configurational order in the rotator phase that $F_c(\text{rot}) = 0$; thus the configurational contribution to the free energy of fusion is

$$\Delta F_c = F_c(\text{liq}) - F_c(\text{rot}) = -RT \ln Z_c \qquad (5)$$

where Z_c is given by eq 3. The entropic and enthalpic contributions to the free energy are calculated by differentiating with respect to temperature

$$\Delta S_c = -\frac{\partial \Delta F_c}{\partial T} = R \ln Z_c + RT\frac{\partial \ln Z_c}{\partial T} \qquad (6)$$

$$\Delta H_c \cong \Delta E_c = \Delta F_c + T\Delta S_c = RT^2\frac{\partial \ln Z_c}{\partial T} \qquad (7)$$

For melting at atmospheric pressure, $p\Delta V \ll \Delta E$, so the enthalpy and energy changes of melting are nearly equal.

Flory and Vrij[14] have pointed out that there is an additional entropic contribution to the free energy of fusion due to translational order of the solid state that is lost upon melting to the liquid. The parallel chains in the rotator phases are arrayed in two-dimensional planar layers. The terminal methyl ends of the chains in one layer abut those of another in localized planar regions of space. Thus the decrease in chain free energy upon fusion can be written in the form

$$\Delta F_{trans} = -T\Delta S_{trans} = -RT \ln (\zeta n_c) \qquad (8)$$

where the constant ζ can be construed as reflecting the degree of localization (in the solid) of the termini, or equivalently centers of mass of the chains, along an axis parallel to the chains. In the absence of suitable molecular theory, the constant is determined through an a posteriori fit to the experimental data (see below); we find that $\zeta \cong 5$. Since the length of a methylene group along the chain axis is 1.27 Å, this value of ζ corresponds to a localization of approximately 0.25 Å, or 10% of the segmental repeat length (two methylene units).

Volume-Dependent Interactions

Approximate equations of state of small-molecule liquids have been formulated by Eyring and Hirschfelder,[15] Prigogine,[16] and others, in which it is assumed that the intermolecular partition function can be factored into two parts: an energetic term accounting for van der Waals attractions and an entropic term that describes the "free volume" of the system. The shortcomings of this approach are well-known, but our present purpose is served by its simplicity and tractability; with fair success, it has been adapted for alkane liquids by Flory, Orwoll, and Vrij (FOV).[7] The attractive energy is taken to be inversely proportional to volume. The free volume contribution is computed on the assumption that the chain segments act as hard spheres; the restrictions imposed by their inter-

connecting covalent bonds are taken into account through a parameter, c, in the notation of FOV[7]. The chain-length dependence of the intermolecular free energy is accounted for by considering chain segments to be of two types, middle or end, approximately corresponding to methylene and terminal methyl groups, respectively. By assuming different interaction energies, numbers of contacts, and hard-core volumes for the middle and end segments, FOV express the intermolecular energy and free volume contributions as functions of chain length. The resulting FOV molar energy, entropy, and free energy for the liquid state of *n*-alkanes are given by

$$E_V = -(n_c + n_e)E_0/\tilde{V} \tag{9}$$

$$S_V = 3(n_c + n_e)cR \ln [\tilde{V}^{1/3} - 1] \tag{10}$$

$$F_V = E_V - TS_V \tag{11}$$

where $\tilde{V} = V/V^*$, V^* is the effective hard-core minimum volume of the amorphous liquid, E_0 is the energy at $T = 0$ K, and n_e is a small constant, which they have determined to be approximately 1.1. The FOV reduced equation of state is obtained by differentiation of the intermolecular free energy with respect to volume, inasmuch as the intramolecular contribution is presumed to be independent of volume

$$\tilde{p} = -\frac{1}{\tilde{V}^2} + \tilde{T}\left(\frac{\tilde{V}^{-2/3}}{\tilde{V}^{1/3} - 1}\right) \tag{12}$$

where $\tilde{p} = p/p^*$ and $\tilde{T} = T/T^*$. T^*, p^*, V^*, and E_0 are given as explicit functions of $(n_c + n_e)$ and are interrelated by

$$p^*V^* = cRT^* = E_0 \tag{13}$$

By fitting eq 12 and thermal expansion and thermal pressure coefficients derived therefrom with the few adjustable parameters of the theory, Flory et al.[7,19] obtained good agreement with experimental data for a wide range of chain lengths and temperatures, principally at low pressures ($p = 1$ atm). The best fit values of the adjustable parameters were found to vary only slightly with temperature. Using these values, one may readily calculate contributions to the free energies of liquid alkanes, as functions of temperature and chain length.

In order to account for volume-dependent effects of melting, we generalize the FOV equation of state to describe both the liquid and rotator phases. To do so, we derive the potential energy function from a chain pair interaction potential which reflects the difference in molecular organization between the two states. The attractions among chains will not be as in a liquid of methylene groups because the covalent bonds interconnecting them along the chain are virtually incompressible by the weak dispersion forces; the London forces largely affect only intermolecular interactions. Taking the chain connectivity into account, Salem showed that the attractive potential between two infinite parallel chains should depend inversely on the fifth power of the intermolecular separation.[17] Moreover, he showed that this form of the potential should hold for relatively small intermolecular separations for chains of the finite lengths that are of interest here. Inasmuch as the dispersion forces are largely isotropic and thus are not very dependent on relative orientation,[17,18] this form of the potential should not seriously err in representing nonparallel chains of the same average separation. Thus we adopt this inverse fifth power dependence on intermolecular separation as a suitable model for the dispersion forces among alkyl chains in both rotator and amorphous liquid phases.

We assume that the repulsive potential between two alkane chains can be characterized by a power law with exponent p, the value of which is the same for liquid and rotator phases. Unlike the attractive interaction, however, the repulsive term is not isotropic, so it is to be expected that the repulsion depends on the relative orientations of methylene groups on neighboring chains, the intermolecular separation of the repulsive interaction decreasing with increasing chain alignment. The pair potential for both states is thus taken to be

$$u(r) = u_0\left[\left(\frac{r}{\alpha r_0}\right)^{-p} - \left(\frac{p}{5}\right)\left(\frac{r}{r_0}\right)^{-5}\right] \tag{14}$$

The factor α in eq 14 accounts for this difference in the range of the repulsion. In the amorphous liquid state, $\alpha = 1$, and the minimum of the potential occurs at $r = r_0$; for the rotator phase, $\alpha < 1$. This potential can be expressed as

$$u(r) = u_0\alpha^{-5p/(p-5)}\left[\left(\frac{r}{r_0'}\right)^{-p} - \left(\frac{p}{5}\right)\left(\frac{r}{r_0'}\right)^{-5}\right] \tag{15}$$

where we define

$$r_0' = r_0\alpha^{p/(p-5)} \tag{16}$$

In this form, it is evident that the minimum in the potential function occurs at $r = r_0' \le r_0$, which thus depends on the physical state of the system through α, the value of which is computed below.

The total interaction potential ϕ, is computed as the integral over the pair correlation function, $g(r)$

$$\phi = \int_0^\infty u(r)g(\mathbf{r}) \, d\mathbf{r} \tag{17}$$

We adopt a mean-field approach; the correlation function is approximated as having cylindrical symmetry and depending only on bulk density for both liquid and rotator states

$$g(\mathbf{r}) \, d\mathbf{r} \sim (1/V)r \, dr \qquad r \ge r_m \tag{18a}$$

$$g(\mathbf{r}) \, d\mathbf{r} = 0 \qquad r < r_m \tag{18b}$$

where r_m specifies the effective hard-core minimum distance of approach of two chains; it will differ for the rotator and liquid states. Here, we leave out multiplicative constants, for they will subsequently be replaced by parameters that have been fit to the liquid-state measurements by Orwoll and Flory.[19] Substitution of eq 15 and 18 into eq 17 and evaluation of the integral lead to

$$\phi \sim u_0\left(\frac{r_0^2}{V}\right)\alpha^{-3p/(p-5)}\gamma \tag{19}$$

where

$$\gamma \sim \left(\frac{1}{p-2}\right)\left(\frac{r_m}{r_0'}\right)^{-(p-2)} - \left(\frac{p}{15}\right)\left(\frac{r_m}{r_0'}\right)^{-3} \tag{20}$$

The values of α and γ will depend on whether the system is in the rotator or the liquid state. We are at liberty to choose a multiplicative constant to normalize γ such that $\alpha = 1$ and $\gamma = 1$ in the liquid state; then $\alpha = \alpha_r$, and $\gamma = \gamma_r$ in the rotator phase. If r_m were directly proportional to r_0' as a function of chain alignment, then γ would be completely independent of the state of the system. To the extent that this proportionality does not hold and to the extent that the mean-field approximation errs in representing differences in the true correlation function between

the two states, γ_r is taken to be a parameter that is adjusted within a narrow range around $\gamma_r \gtrsim 1$ to provide agreement largely with density measurements. The interaction energy for either state can therefore be expressed in terms of a single potential function

$$\phi \sim \frac{\gamma}{V}\alpha^{-3p/(p-5)} \tag{21}$$

Written in terms of the FOV liquid-state constants (see eq 9)

$$E_V = \frac{-(n_c + n_e)E_0\gamma}{\tilde{V}}\alpha^{-3p/(p-5)} \tag{22}$$

The free volume entropy is also a function of state, since the "hard-core" minimum volume, V_m, is lower in the rotator than in the liquid phase; $V_m(\alpha) \leq V^*$, the equality holding by definition for the liquid ($\alpha = 1$). This entropy may be computed by replacing V^* by V_m in eq 10. Since the chains are incompressible along their backbones, $V_m \sim r_m{}^2$. If we suppose, as noted above, that $\gamma_r \simeq 1$, then

$$\frac{r_m(\text{rot})}{r_m(\text{liq})} = \frac{r_0'(\text{rot})}{r_0'(\text{liq})} \tag{23}$$

and we have

$$\frac{V_m(\text{rot})}{V_m(\text{liq})} = \left[\frac{r_0'(\text{rot})}{r_0'(\text{liq})}\right]^2 = \alpha_r{}^{2p/(p-5)} \tag{24}$$

where

$$V_m(\alpha) = V^*\alpha^{2p/(p-5)} \qquad V^* = V_m(\alpha = 1) \tag{25}$$

Defining $x(\alpha) = \alpha^{2p/3(p-5)}$, eq 10 can be generalized to give the volume and state dependence of the free volume entropy

$$S_V = 3(n_c + n_e)nR \ln [\tilde{V}^{1/3}x^{-1} - 1] \tag{26}$$

Combining eq 22 and 26, the volume-dependent contribution to the free energy (per mole of molecules) is

$$F_V = -(n_c + n_e)\left\{\frac{E_0\gamma x^{-9/2}}{\tilde{V}} + 3cRT \ln [\tilde{V}^{1/3}x^{-1} - 1]\right\} \tag{27}$$

where the state dependence is incorporated in the factors x and γ. Salem suggested[17] that p might be arbitrarily chosen to be approximately 25; for our purposes, it need not be specified. This is shown as follows. Setting the volume derivative of the free energy, eq 27, equal to zero, we obtain the equation of state at approximately atmospheric pressure

$$\left(\frac{\tilde{V}^{1/3} - x}{\tilde{V}^{4/3}}\right)\gamma x^{-9/2} = \tilde{T} \tag{28}$$

For the liquid ($x = 1$, $\gamma = 1$), eq 28 reduces to the $p = 0$ isobar of FOV as it must

$$(\tilde{V}_l{}^{1/3} - 1)/\tilde{V}_l{}^{4/3} = \tilde{T} \tag{29}$$

where $\tilde{V}_l$ is the reduced volume of the liquid state.

The reduced volume in the rotator phase, $\tilde{V}_r$, may be expressed for a given temperature (and in particular, at the melting temperature) as a function of $\tilde{V}_l$. Defining the volume, relative to that of the liquid, as $\delta = V/V_l$, then for the rotator phase

$$\delta_r = V_r/V_l = \tilde{V}_r/\tilde{V}_l \tag{30}$$

When the two states are in equilibrium, T is fixed. Thus,

combining eq 28 and 29 evaluated at $\delta = \delta_r$, $x = x_r$, and $\tilde{V} = \tilde{V}_r$, we obtain

$$\delta_r{}^{1/3}\tilde{V}_l{}^{1/3} - x_r = \delta_r{}^{4/3}x_r{}^{9/2}\gamma_r{}^{-1}(\tilde{V}_l{}^{4/3} - 1) \tag{31}$$

Provided x_r and γ_r are known, eq 31 may be solved for δ_r since $\tilde{V}_l$ can be obtained from the zero-pressure isobar of the liquid (see eq 29). Since the factor x_r depends on α_r, it reflects the reduction in range of the repulsion due to ordering of the chains upon freezing. The quantity x_r should depend on the relative numbers of methylene and terminal methyl groups. We assume the dependence is linear

$$x_r = \left(\frac{n_c - 2}{n_c}\right)x_2 + \left(\frac{2}{n_c}\right)x_3 \tag{32}$$

where x_2 and x_3 are parameters determined as indicated below. For infinitely long chains, $x_r = x_2$.

Thus, the free energy, F_V, of the volume-dependent interactions is

$$F_V = -(n_c + n_e)E_0\left\{\frac{\delta^{-1}\gamma x^{-9/2}}{\tilde{V}_l} + 3\tilde{T} \ln (\delta^{1/3}\tilde{V}_l{}^{1/3}x^{-1} - 1)\right\} \tag{33}$$

where $\delta = 1$ for the liquid and $\delta = \delta_r$ for the rotator phase. The volume-dependent contribution to the free energy of fusion is given through the combination of eq 31 and 33

$$\Delta F_V = F_V(\text{liq}) - F_V(\text{rot}) =$$
$$(n_c + n_e)E_0\left\{\frac{\delta_r{}^{-1}\gamma_r x_r{}^{-9/2} - 1}{\tilde{V}_l} - 3\tilde{T} \ln [\delta_r{}^{-4/3}x_r{}^{-7/2}\gamma_r]\right\} \tag{34}$$

The net result of these contributions is to strongly favor the rotator phase; i.e., F_V is always positive. Using eq 34 and the definition of T^*, eq 13, we obtain the enthalpic and entropic contributions respectively as

$$\Delta H_V \simeq \Delta E_V = (n_c + n_e)E_0\left(\frac{\delta_r{}^{-1}\gamma_r x_r{}^{-9/2} - 1}{\tilde{V}_l}\right) \tag{35}$$

$$\Delta S_V = 3(n_c + n_e)cR \ln [\delta_r{}^{-4/3}x_r{}^{-7/2}\gamma_r] \tag{36}$$

The total Helmholtz free energy of fusion is the sum of the volume-dependent, configurational, and translational components given by eq 5, 8, and 34. For equilibrium fusion at constant pressure and temperature, the Gibbs free energy does not change; i.e., $\Delta G = 0$. To very good approximation, $\Delta F \simeq \Delta G$ (since $\Delta E \simeq \Delta H$; see above); thus

$$\Delta F(n_c,T) = \Delta F_V + \Delta F_c + \Delta F_{\text{trans}} = 0 \tag{37}$$

from which we may compute enthalpies, entropies, temperatures, and volume changes of fusion as functions of chain length.

The quantities n_e, E_0, and $\tilde{V}_l$ ($\tilde{T}$), which appear in eq 34, are obtained from experiments on chains in the liquid state. In the treatment of FOV, the parameters E_0, V^*, and T^* (or, equivalently, p^*, V^*, and T^*; see eq 13) depend only on chain length and on three constants, $p_\infty{}^*$, $V_\infty{}^*$, and $T_\infty{}^*$, which represent the limit of infinite chain length. Orwoll and Flory[19] found that the best fit values of these parameters vary somewhat with temperature. Surprisingly, however, when evaluated at the known melting temperatures, E_0 and $\tilde{T}$ are virtually the same for all chain

Table I
Experimental Volume Changes of Melting from the Rotator Phase[a]

|	ΔV, cm³/g			ΔV, cm³/g	
n_c	dilatometry	X-ray diffraction	n_c	dilatometry	X-ray diffraction
11	≤0.10 (24)		24	0.1215 (20)	0.130 (4)
13	0.1283 (22)			0.130 (21)	
15	0.1292 (22)			0.122 (19)	
17		0.118 (2)	25	0.123 (19)	0.131 (3)
19	0.127 (23)	0.123 (2)	26	0.1254 (20)	0.132 (4)
	0.135 (19)			0.125 (19)	
21	0.127 (21)	0.124 (2)	27	0.128 (19)	0.133 (5)
	0.128 (19)		28	0.1329 (20)	
22	0.131 (21)	0.127 (4)		0.128 (19)	
	0.128 (19)		32	0.1346 (20)	
23	0.129 (21)	0.128 (3)	36	0.1377 (20)	
	0.120 (19)				

[a] Literature references are given in parentheses.

lengths. Since $\tilde{V}_1$ is a function only of $\tilde{T}$ (see eq 29), the expression for ΔF_V, eq 34, can be simplified considerably by taking $\tilde{V}_1$ to be independent of n_c at the melt temperature, $T_{\text{melt}}(n_c)$. From the data of Orwoll and Flory[19], we conclude that $E_0 = 1.57$ kcal/(mol CH₂) and $\tilde{V}_1 = 1.23$ ($\tilde{T}_{\text{melt}} = 0.0542$); errors incurred in adoption of these values are less than ±2% over the range $9 \leq n_c \leq 43$. The parameters x_2, x_3, γ_r, and ζ are established through agreement of experimental temperatures, enthalpies, and volume changes of melting, discussed below, with the values calculated through use of eq 30, 31, and 37.

Comparison with Experiments

Predictions of volume changes upon melting may be compared with experiments; these comparisons are required to establish the values of x_2, x_3, and γ_r. Volume changes are measured most directly through dilatometry,[20-25] the principal advantage of which is that liquid- and rotator-phase volumes can be measured in the same experiment. Alternatively, the volume of the rotator phase may be determined through X-ray diffraction studies,[2-6] but this requires the extrapolation of the volume to the melting temperature, often when the thermal expansion coefficient is large, and it requires independent measurement of V_1. In a third approach, considerably more indirect than these, the volume change is calculated from the Clausius–Clapeyron equation, which requires measured enthalpies of fusion, which are themselves subject to considerable imprecision, and it requires the pressure dependences of the melting temperatures,[23,26] which are linearly extrapolated over many kilobars to 1-atm pressure. Possible errors incurred from such long extrapolations may be large and the often assumed linearity of these extrapolations is questionable. This method is sufficiently imprecise that it obscures the small chain-length dependence of ΔV observed by dilatometry and X-ray diffraction. Thus we consider below, as being most reliable, only volume change measurements from dilatometry and X-ray diffraction experiments.

We comment here on the dilatometry results that are included in Table I. In the experiments of Templin,[21] the volume is given over a range of temperatures that include the rotator/liquid-state transition for C24, C26, C28, C32, and C36 alkanes, along with tabulated extrapolations to the melt temperatures. The transitions are quite sharp for C28, C32, and C36 and are somewhat less so for C24 and C26; thus the former may be more reliable. Templin's measured amorphous volumes at the melting temperatures are somewhat different from generally accepted values,
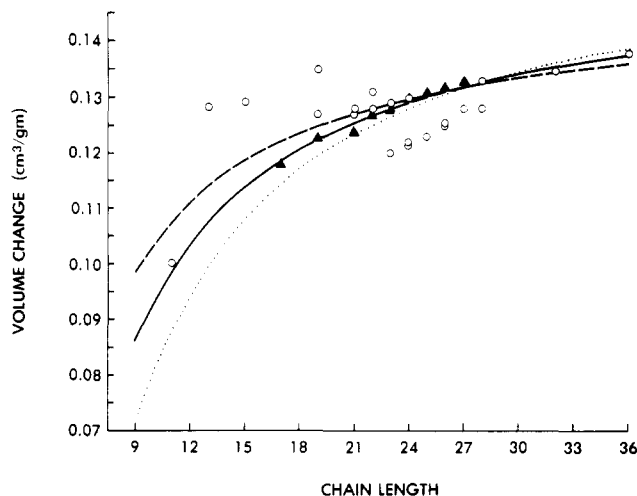
Figure 1. Volume changes of fusion to the rotator phase. Experimental values (see Table I); dilatometry (O), X-ray diffraction (▲). Theoretical predictions for different values of model parameters (see Table II): $E_{\text{tg}} = 600$ cal/mol (—–—); $E_{\text{tg}} = 900$ cal/mol (—); $E_{\text{tg}} = 1200$ cal/mol (···).

given for example by Wurflinger and Schneider[26] through use of the polynomial expansions of Orwoll and Flory;[19] e.g., they do not decrease monotonically with increasing chain length. The widely quoted note of Schaerer et al.[20] reports data for C19 and C21 through C28, but only changes in volume are reported; the absolute values of V and V_r are not reported and thus cannot be compared with those from other sources. Nelson et al.[23] reported ΔV for C13 and C15 at 1 atm, but not for other chain lengths for which comparison could be made with other investigations. More recently, Dollhopf et al.[24] presented the full temperature dependence of volume for C19 at 3 atm (which shows considerable hysteresis at the transition) from which both V_1 and V_r can be obtained at the melt temperature. A recent study of the pressure–volume isotherms of C11 just above the melting point permits an upper estimate of the corresponding volume change.[25] Volume changes and V_1 are reported for C20–C24 by Sackmann and Venker,[22] but the data for C20 are suspect inasmuch as its rotator phase is probably not stable.[20,21] However, the values for V_1 from that study are in agreement with the generally accepted values; for example, see ref 26.

Also included in Table I are results of X-ray crystallography measurements of volume changes of the transition. Recent X-ray studies demonstrate the polymorphism of C17, C19, C21–C28, C30, C32, and C34 rotator phases.[2-5] The temperature dependence of V_r has been reported directly for C17, C19, and C21,[2] and the temperature dependence of the X-ray spacings for C23 and C25[3] and C22, C24 and C26.[4] From the latter, we have determined volumes from the product of the unit cell dimensions. For the longer chains, spacings are reported only for C27 at the melting temperature.[5] Although extensive temperature measurements have recently been performed on the alkanes of odd chain lengths from C11 to C25,[6] only lateral unit cell dimensions are reported and not the long spacings. From the results of these various X-ray studies, we have estimated the rotator-phase volumes at the melting temperatures. They have been combined with estimates of V_1 given by the averaged values of Wurflinger and Schneider[26] and through the polynomial expansions of Orwoll and Flory[19] and are presented in Table I and plotted along with the dilatometry results in Figure 1. Also plotted in Figure 1 are the volume changes predicted according to the theory. It is evident that there is considerable variability in the data. Nevertheless, the data,

Table II

Best Fit Values of the Model Parameters $(x_2, x_3, \gamma_r, \zeta)$ for Three Values of E_{tg}: Predictions for Polyethylene $(n_c \rightarrow \infty)$ of the Temperature, Enthalpy, and Volume Changes of Fusion (All from the Rotator Phase at 1 atm)

E_{tg}, cal/mol	x_2	x_3	γ_r	ζ	T_∞, °C	ΔH_∞, cal/mol	ΔV_∞, cm³/g
600	0.9781	1.0536	1.1564	5.41	145.2	836	0.1596
900	0.97647	1.0342	1.078	4.76	146.1	766	0.1539
1200	0.97505	1.0166	1.014	3.63	147.6	688	0.1481
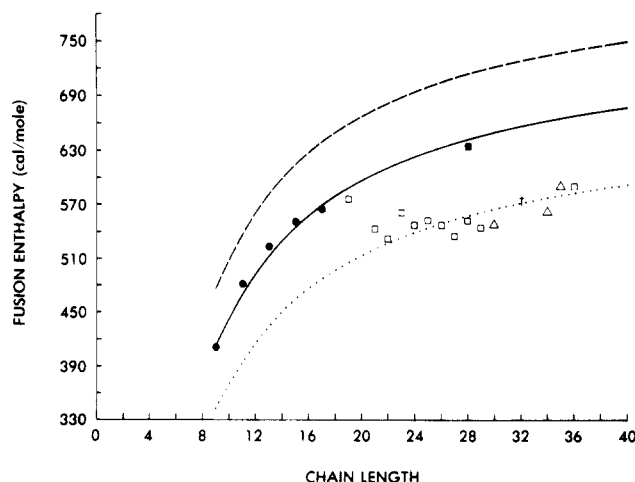
Figure 2. Enthalpies of fusion to the rotator phase, $\Delta H_{mol}/n_c$. Experimental values: (●) ref 27 and 29; (□) ref 20; (△) ref 30; (†) ref 8; (■) ref 21. Theoretical predictions: E_{tg} = 600 cal/mol (---), E_{tg} = 900 cal/mol (—), E_{tg} = 1200 cal/mol (···).
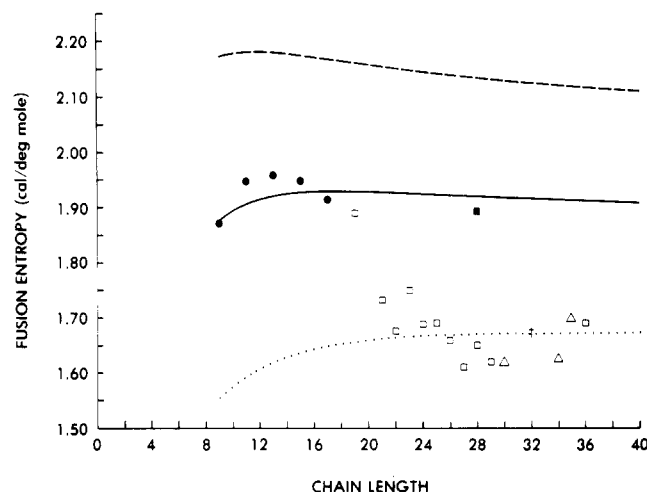

Figure 3. Entropies of fusion to the rotator phase, $\Delta S_{mol}/n_c$. Experimental values and theoretical predictions as in Figure 2.

particularly from the X-ray experiments, indicate a trend of increasing ΔV with increasing chain length as predicted by the theory.

Experimental measurements of molar enthalpies and entropies of fusion are also subject to considerable variability. These data are shown in Figure 2 and 3. The most widely accepted experimental values for the enthalpies of fusion are from the compilation of Broadhurst,[8] which derives principally from two sources. For odd chain lengths C9–C15, they are taken from the extensive tabulations of Finke et al.[27] (Note that the C17 value, erroneously attributed by Broadhurst to ref 27, was taken from Rossini et al.[28]) Data for C17 has been taken more recently.[29] For the longer chains C19, C21–C29, and C36, the data of Schaerer et al.[20] show substantial variability. Broadhurst[8] also cites earlier work[30] on C30, C34, and C35 and a private communication for C32. For C28, Templin[21] extrapolated dT_m/dp_m, which he found to be a relatively linear function of pressure to atmospheric pressure and combined this with his observed volume change, through the Clausius–Clapeyron equation, to obtain $\Delta \bar{H}/n_c = 630 \pm 10\%$ cal/mol.

The melting temperatures of the n-alkanes are much more accurately known than the experimental volumes or enthalpies of fusion. Therefore, the parameters x_2, x_3, γ_r, and ζ are chosen to establish (i) best fit agreement between eq 37 and observed rotator-phase melting temperatures,[8,27–29] and (ii) approximate agreement of eq 31 and the volume changes of fusion, in both cases over the entire range of chain lengths $(9 \leq n_c \leq 43)$. Best values of the parameters are given in Table II for each of three different values of E_{tg}. In all three cases, the root mean square error in the predicted melt temperatures for $9 \leq n_c \leq 40$ was less than 0.15 °C. The value of E_{tg} strongly affects the predictions of volumes, enthalpies, and entropies of fusion (see Figures 1–3). The best value of E_{tg} is found to be approximately 900 cal/(mol CH₂), considerably higher than the widely adopted value of 500 ± 100 cal/(mol CH₂).[10]
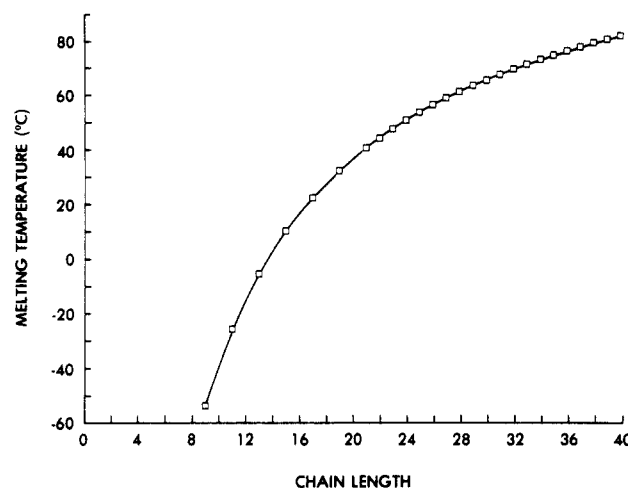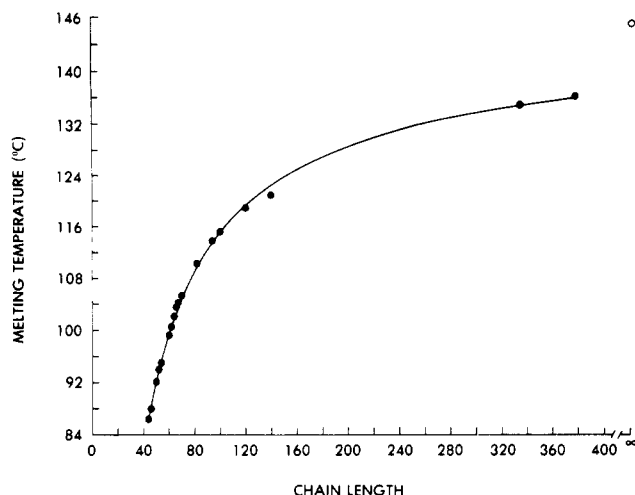

Figure 4. Rotator-phase melting temperatures. Experimental values (□) from ref 8 and 27–29; theoretical predictions for E_{tg} = 900 cal/mol (—).

but in agreement with the recent results of Wong et al.[13] Neutron scattering functions and radii of gyration of C16 and C36 measured in solution and in the melt are best predicted by E_{tg} = 600–800 cal/mol.[12] However, inasmuch as the radii of gyration change by less than 10% over that range and the scattering functions are even less sensitive, a value of E_{tg} = 900 cal/mol predicts these quantities to nearly within the limit of the experimental errors.[12] The predicted melting temperatures for this value of E_{tg} are shown in Figure 4.

The theory and experiments described here pertain only to the melting of the rotator phase, which is observed for $9 \leq n_c \leq 43$. For $n_c > 43$, liquid paraffins freeze directly to the orthorhombic crystalline phase.[8] However, it is interesting that the observed crystal melting temperatures for chains ranging in length from $n_c = 44$ to poly(methylene) coincide remarkably closely with the corresponding predicted rotator-phase melting temperatures for those molecules. These predictions are plotted and compared

Figure 5. Melting temperatures for $n_c \geq 44$. Experimental values (●) for melting from the crystal;[8,31-33] predictions of rotator-phase melting for E_{tg} = 900 cal/mol given by continuous curve and (○) for $n_c = \infty$.

with the experimental compilations of Broadhurst[8] for 44 $\leq n_c \leq$ 400 in Figure 5. Data for chains longer than n_c = 100[31-33] must be interpreted with some caution, however, for those systems may exhibit chain folding and may be sufficiently polydisperse that the formation of true molecular crystals is prohibited.[33,34] If so, the observed melting temperatures should be lower than those expected of monodisperse crystals of fully extended chains. This is consistent with the following prediction of the theory. Because rotator phases are not observed for these systems, the melt temperature of the putative rotator phase must be less than or equal to that of the crystal. Inasmuch as the observed melting temperatures for very long chains (see Table I of ref 33) are below those predicted for the rotator phase, then they must also be below the true crystal melting temperature.

The theory also predicts the melting properties of the rotator phase of poly(methylene) (see Table II). Extrapolating the theoretical predictions to $n_c = \infty$ leads to a predicted rotator-phase melting temperature of 146.1 °C, which is remarkably close to the value predicted for melting from the crystal by Flory and Vrij,[14] Mandelkern and Stack,[34] and Broadhurst,[35] but is about 5 °C higher than that obtained by Wunderlich and Czornyj.[33] The theory predicts ΔH_∞ = 765 cal/(mol CH$_2$) and ΔV_∞ = 0.1539 cm^3/g for the fusion of liquid poly(methylene) to the putative rotator phase for E_{tg} = 900 cal/mol. These values are approximately 75% and 65% of the measured enthalpy and extrapolated volume changes of fusion to the crystal, respectively, as reported by Wunderlich and Czornyj.[33] These percentages are approximately the same as those for shorter chains for which the thermodynamic properties of the rotator and orthorhombic crystal phases can be measured independently.[8,21-29]. It is tempting to speculate that the additional decrease in enthalpy required to reach the crystal from the liquid, beyond that required to reach the rotator phase, can be accounted for by the additional van der Waals attractions that should accompany the decreased volume of the crystal compared to the rotator phase. The additional entropy change to the crystal cannot be accounted for on the simple basis of the free volume changes, however.

For short chains, $n_c < 9$, the molecules freeze to a crystalline phase. Thus, as for the case discussed above, the predicted melt temperatures of the putative rotator phase should lie below those of the experimentally observed crystal melting temperatures. In agreement with
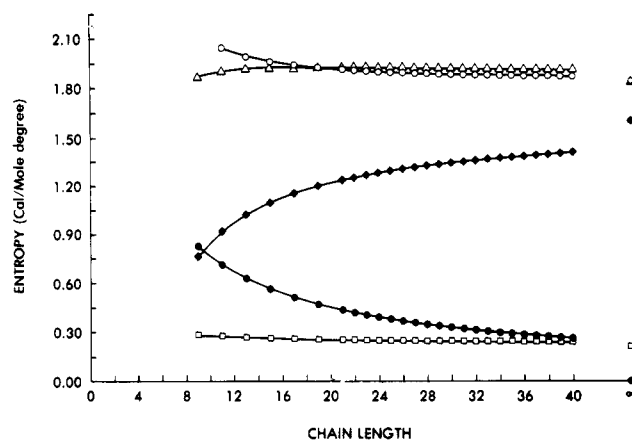
Figure 6. Predicted contributions to total entropy (△) of melting ($\Delta S_{mol}/n_c$): (□) volume-dependent interactions ($\Delta S_V/n_c$): (◆) configurational ($\Delta S_c/n_c$); (●) translational ($\Delta S_{trans}/n_c$). Total (○) molar entropy increment per CH$_2$ ($\partial \Delta S_{mol}/\partial n_c$).
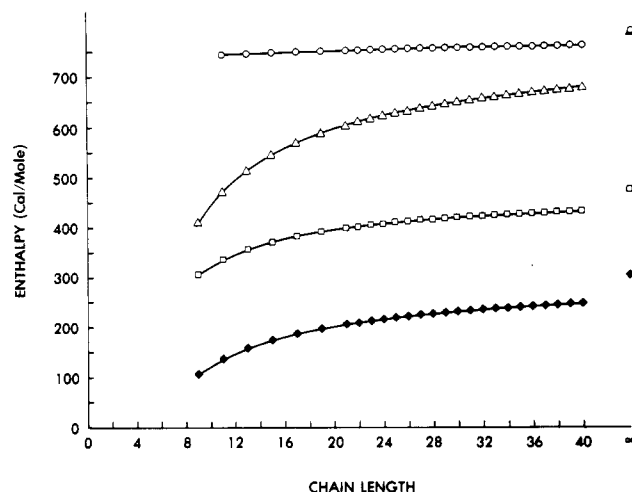
Figure 7. Predicted contributions to total enthalpy (△) of melting ($\Delta H_{mol}/n_c$): (□) volume-dependent interactions ($\Delta H_V/n_c$); (◆) configurational ($\Delta H_c/n_c$). Total (○) molar enthalpy increment per CH$_2$ ($\partial \Delta H_{mol}/\partial n_c$).

this, theory predicts the melt temperatures to be −96.7 °C for C7 and −173 °C for C5, which are 6 and 42 °C, respectively, below their observed transition temperatures.[28]

Predictions of the various contributions to the molar entropies and enthalpies of fusion are shown in Figures 6 and 7. It is evident that the principal contribution to the entropy of fusion of long chains is due to the increase in configurational freedom, whereas for short chains the translational contribution is nearly equally important. The total molar entropy of fusion is predicted to be somewhat nonlinear with chain length, manifested by a decrease in slope from 2.05 to 1.87 (eu/mol)/n_c, as n_c increases from 9 to 40. The enthalpy of fusion is due largely to dispersion forces and to a lesser extent to the trans/gauche intramolecular energies. The slope of the molar enthalpy of fusion is nearly independent of chain length, varying by only 2% for $9 \leq n_c \leq 40$.

An important caution is suggested by this work. The constant-volume entropy of melting of crystalline alkanes is often ascribed entirely to chain conformational contributions. Our analysis, although only a treatment of freezing to the rotator, rather than crystalline phases, shows that that is likely to be a relatively severe oversimplification, for two reasons. First, this neglects the translational contribution, eq 8, which is significant for short chains (see figure 6). Secondly, at constant volume,

the efficiency of packing decreases upon melting; the effective hard-core volume increases, decreasing the free volume. Thus, the constant-volume contribution to the entropy should be less than that due to chain conformations alone. This is consistent with the conclusion drawn by Robertson from heat capacity and equation of state measurements on poly(methylene) glasses, from which conformational and constant-volume entropies can be independently estimated.[36] In constant-pressure melting, on the other hand, the increase in volume is predicted to be greater than the increase in hard-core volume; thus the free volume will increase and the conformational entropy is an underestimate of the constant-pressure entropy of fusion.

Registry No. Polyethylene (homopolymer), 9002-88-4.

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Interaction between Two Adsorbed Polymer Layers

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ABSTRACT: The effect of adsorbing homopolymer on the interaction between two parallel surfaces is examined in some detail. The results are relevant for the stabilization and flocculation of colloids by adsorbed polymer. The free energy of interaction is derived directly from the partition function using a previously developed lattice model for adsorption of polymers from solution. Comparison with other theories shows partial agreement as well as remarkable discrepancies. Results are presented for a system in full equilibrium with a polymer solution of constant concentration and for a system with a constant amount of polymer between the surfaces. At full equilibrium the force between the surfaces is always attractive due to bridging polymer. With decreasing surface separation a part of the polymer molecules leaves the gap, an increasing fraction of the remaining polymer adsorbs on both surfaces simultaneously, and eventually a monolayer of polymer segments sticks the surfaces together. When the polymer is unable to leave the gap, a strong repulsion between the surfaces appears at small separations and the interaction free energy is mainly determined by the adsorbed amount of polymer, irrespective of chain length. With a large amount of polymer between the surfaces the force is always repulsive, except in a very poor solvent. At smaller surface coverages a minimum in the free energy of interaction develops as a function of surface separation. Recent experimental data confirm our prediction that bridging attraction can also occur in good solvents. As the adsorption of polymer increases with increasing chain length, high molecular weight polymer is a better stabilizer than low molecular weight polymer.

I. Introduction

Polymer adsorption is a very effective tool for controlling the stability of colloidal suspensions.[1-3] For instance, high molecular weight flocculants rapidly remove the last submicroscopic particles in one of the last stages of water treatment. In this case uncovered particles are caught by tails and loops extending from covered ones, so that polymer bridges are formed. The same mechanism is operating in particle separation by flotation.[4,5] Bridging can occur only when the adsorbed amount of polymer is below saturation. At high polymer concentrations all particles are fully covered and the dangling tails and loops form a steric barrier against flocculation. Steric stabilization has important applications in paint industry and food technology. In all these phenomena, steric and/or bridging interactions constitute an important contribution,