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Decomposition of Entropy and Enthalpy for the Melting Transition of Polyethylene

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ABSTRACT: In order to estimate the relative importance of various features to the melting transition of polyethylene it is useful to make estimates, based on as much data as possible, of how much each feature contributes to the entropy change and to the enthalpy change. Most of the enthalpy change (980 cal/mol CH_2) is accounted for by a cohesive, van der Waals energy term ($\Delta U_{vdW} \sim 720$ cal/mol) and a rotameric term ($\Delta U_R \sim 200$ cal/mol). The entropy change (2.36 eu) is adequately accounted for by a conformational term ($\Delta S_C \sim 1.7$ eu), an excluded volume term ($\Delta S_X \sim -0.7$ eu), and a volume expansion term ($\Delta S_V \sim 1.3$ eu). In view of the differences between these results and previous results, the statistical mechanical fundamentals of such decompositions are discussed in detail and reasons for rejecting some previous conventions are given. The magnitudes of the volume term ΔS_V and the cohesive term ΔU_{vdW} indicate that such interactions and the concomitant volume expansion are major factors in the melting of polyethylene.

I. Introduction

To being to understand a phase transition it is useful and appropriate to do some simple approximate, phenomenological calculations to evaluate those features that one thinks might play major roles in the transition. One procedure is to identify the different distinct features that might be important and then to study them quantitatively one at a time. In the case of polymer melting such calculations have usually focused on the entropy, which has been decomposed[1-10] as follows:

$$\Delta S_M = \Delta S_C + \Delta S_V \tag{1}$$

In eq 1 ΔS_M is the measured entropy of melting obtained from the measured enthalpy, ΔH_M, divided by the melting temperature, T_M. The first term of the decomposition, ΔS_C, is the increase in conformational entropy of single chains. The second term in the decomposition, ΔS_V, is defined to be the entropy increase that would have occurred if the measured volume increase had occurred without any other kinds of disordering, such as conformational disordering. A more refined decomposition[11-13] that has in fact led to the previous one is

$$\Delta S_M = \Delta S_R + \Delta S_V + \Delta S_D \tag{2}$$

The term, ΔS_R, where the R stands for rotational isomerism, accounts for chain conformational entropy, but it also includes excluded volume effects. The final term, ΔS_D, has been called the disordering entropy. It includes all other effects. It has been associated with the communal entropy[7-10] and it has been called the disordering entropy common to all liquids;[11-13] other possible sources will be mentioned later.

Another decomposition, one that has not received so much attention, focuses on the enthalpy as follows:[14-17]

$$\Delta H_M = \Delta U_R + \Delta U_{vdW} + \Delta U_0 + P\Delta V \tag{3}$$

where each U_i is the internal energy for the ith feature in the system, ΔU_R is the change in trans-gauche rotameric energy, ΔU_{vdW} is the change in cohesive van der Waals energy due to the volume change, and ΔU_0 is a small error term that includes all other effects. The $P\Delta V$ term is numerically negligible for polymer melting at atmospheric pressure, amounting to less than 0.01% of the total enthalpy[5] of melting in polyethylene ($\Delta H_M = 980$ cal/mol CH_2), but this term will be included formally for completeness.

The first reason that decompositions such as the ones in eq 1-3 could be useful is that, if the sum of the decomposed terms adds up to the measured total, then one has some confidence that one knows all the most important features of the transition. The second reason concerns the relative magnitudes of the substituent contributions to ΔH_M or ΔS_M. These relative magnitudes give some measure of the relative importance of the various features that give rise to them. Of course, in a complete statistical mechanical treatment of a model with several different features, the ensuing transition is really due to all the features. For example, it is possible that two model features may be essential for the transition in the sense that it would not occur at all if either were absent. Another example is that the change in excluded volume interaction, ΔU_X, is by definition zero, so excluded volume interactions play no role in the enthalpy decomposition; nevertheless, no sharp transition would ever occur without them. Therefore, such decompositions, even if performed accurately, should be interpreted cautiously. Nevertheless, if one of the terms in both the entropy and the enthalpy decompositions is small compared with the others, then the corresponding physical feature can often be said to be minor. Then, when one attempts to construct complete statistical mechanical theories, one has some justification in ignoring such minor features so that the model can be

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simplified; such simplification often allows the statistical mechanical calculations to be carried out more reliably.

The conclusions that have been obtained from eq 1 and 3 regarding the relative size of the contributions from various physical features are quite different. For polyethylene published calculations[1-5] conclude that the term ΔS_C amounts to about 75% of ΔS_M, making it the dominant term, with ΔS_V accounting for the remainder. This is consistent with the idea that the volume expansion plays a relatively minor role in the melting transition compared with the configurational disordering. However, the enthalpy decomposition[14-17] indicates that ΔU_{vdW}, which is an energy change brought about primarily by the volume change, amounts to about 75% of ΔH_M. Understanding this disagreement is one purpose of this paper. As we shall see, neither of the previous approaches has revealed the full picture.

Section II will focus on the enthalpy decomposition, beginning with a brief exposition of the statistical mechanical fundamentals and proceeding to describe the detailed calculations used to obtain numerical estimates. Although a detailed calculation of this type has been reported before,[14] it has been in a paper focusing on lipid bilayers. Also, additional data for polyethylene has been found that makes the calculations more firmly based and that changes previous numerical estimates slightly. In section III the statistical mechanical fundamentals of entropy decompositions are discussed. This is not as straightforward as are the fundamentals of the enthalpy decomposition; as will be shown, the entropy decomposition is not well defined in the general case. Nevertheless, one may still make rough approximations, recognizing that one must be careful about the meaning of various contributions. In section IV previous entropy decompositions are critically reviewed. In section V we attempt to combine the best of the previous entropy decompositions with the enthalpy decomposition and some simple theory to come up with rough estimates to be used in a new entropy decomposition. The consequences for theories of polymer melting are discussed in section VI.

II. Enthalpy Decomposition

Even though full and complete statistical mechanical calculations for phase transitions are notoriously difficult, the fundamental idea of the decomposition of transition entropy or enthalpy is properly discussed with the formalism of statistical mechanics. Consider the enthalpy decomposition, which is written

$$\Delta H_M = \sum \langle \Delta U_i \rangle + P\langle \Delta V \rangle \tag{4}$$

where each ΔU_i is the change in internal energy due to feature i in the molecular model and the angular brackets denote averages over all permissible states in an isobaric ensemble[18] at pressure P and temperature T. Each state, denoted by the subscript s in the subsequent equations, is weighted by its appropriate probability

$$p_s = \exp\{-\beta[\sum (U_i)_s + PV_s]\}/Z \tag{5}$$

where Z is the partition function and $\beta = 1/kT$. For example

$$\langle U_R \rangle = \sum (U_R)_s p_s = \sum N f_s \epsilon p_s = N\epsilon f \tag{6}$$

where ϵ is the energy difference between a gauche bond and a trans bond, f_s is the fraction of the total of the N bonds in the system that are gauche in the state s and f is the ensemble average of f_s. (For convenience the higher energy of g^+g^- sequences is not explicitly written as part of ΔU_R in eq 6. Its numerical contribution to $\langle U_R \rangle$ is negligible.) The rotameric/configurational contribution to the enthalpy of melting is then computed from

$$\Delta U_R = \lim_{T \to T_M^+} \langle U_R \rangle - \lim_{T \to T_M^-} \langle U_R \rangle \tag{7}$$

(For convenience, we will not write the angular brackets for changes such as ΔU_R.) Similarly, intermolecular van der Waals energies, U_{vdW}, are also well-defined sums over states

$$\langle U_{vdW} \rangle = \sum (U_{vdW})_s p_s \tag{8}$$

where U_{vdW} is calculated for each state s in the usual way. Even though we do not attempt, in this paper, to perform the sums over states from first principles, it is clear that the quantities ΔU_i have a precise and well-defined meaning in statistical mechanics. What we will attempt to do is to make estimates for the two terms, ΔU_{vdW} and ΔU_R, making use of as much experimental information as possible.

Let us begin by estimating the internal energy changes due to rotational isomerism, which we will call ΔU_R, but which could equally well be called ΔU_C. It is usually assumed that the perfect crystal is composed essentially of all-trans chains right up to the melting point. Of course, most real crystals are formed by quenching and so the morphology is more complicated with lamellar regions interspersed with more amorphous regions which require a nonzero fraction f of gauche rotamers. However, if these kinetic effects are discounted or if one considers the extended-chain crystals,[5] then it appears that f is rather close to zero, although one does not necessarily expect it to remain precisely zero right up to T_M. More refined values in the range $0 < f < 0.05$ for the crystal will not change any conclusions in this paper.

The fraction f in the liquid state is usually assumed to be the same as it is in a vapor at the same temperature. In other words, intermolecular interactions are assumed not to affect the equilibrium distribution of gauche rotamers. Flory's classical theory[19] of polymer-chain models has been thought of as supporting this assumption. In fact, this assumption is built into the statistical mechanical approximations employed in that theory. We have stated that such an assumption is most unlikely to hold precisely because intermolecular interactions will always induce short-range order in any condensed liquid.[20,21] Except for very exceptional circumstances (essentially a set of measure zero) short-range order will always alter the conformational statistics away from the noninteracting limit. However, it is not clear at this time even in which direction f will be altered for realistic models of polyethylene. Flory[22] has argued strongly that there is no empirical evidence for such deviations in real polymers, so it seems reasonable, as a first approximation, to take f to be the same as for the noninteracting chain limit. Some feeling for the likely error might come from Monte carlo calculations; the result of some current calculations in two-dimensional models is that f at T_M is about 25% lower than the classical Flory estimate and about 10% lower in three-dimensional models,[23] but Petschek[24] has recently shown that these Monte Carlo results do not satisfy a rigorous bound, so these errors may be in the Monte Carlo calculations rather than in the classical calculations.

The noninteracting value of f depends upon the trans–gauche energy difference ϵ, which is usually taken to be in the range $500 \leq \epsilon \leq 600$ cal/mol for polyethylene.[25,26] If one ignores the "pentane effect" exclusion[27] of g^+g^- pairs, then

$$f = 2x/(1 + 2x) \tag{9}$$

where $x = \exp(-\epsilon/kT)$. This yields $f = 0.52$ at $T_M = 416$

K. If the pentane exclusion is included, then f is reduced to about 0.39. This latter value gives the best estimate

$$\Delta U_R = Nf\epsilon = 0.20 \text{ kcal/mol CH}_2 \qquad (10)$$

It might be emphasized that an absolute upper bound is $f = 1$, which would give $\Delta U_R = 0.50$ kcal/mol CH_2; this is only half of ΔH_M, so it is clear that the rotational isomeric energy is not able to account for all the enthalpy of transition. The best estimate is about 20% from eq 10, and it is most unlikely that it is greater than 25%, which is the value obtained by ignoring the pentane exclusion in eq 9. It may also be noted that ΔU_R is rather insensitive to changes in ϵ in the range 0.4–0.6 kcal/mol because the increase in the ϵ factor in eq 10 is nearly balanced by the decrease in the f factor.

Realizing that the *intra*molecular internal energy change, ΔU_R, is far too small to account for the observed enthalpy of melting, let us now turn to a second source of enthalpy change. Polyethylene undergoes a large volume change upon melting, from about 1.04 to about 1.27 cm^3/g.[5] In the melted state each hydrocarbon chain is on average further from its neighbors than in the crystalline state. To accomplish such a change requires an energy or enthalpy input to do work against the cohesive *inter*molecular interactions that keep the system in a condensed state. These cohesive forces, which are basically attractive van der Waals interactions, are rather large. Although theoretical calculations have been made for them,[28] the overall size has been most firmly established by analysis of calorimetric data by Billmeyer,[29] using a basic procedure that has been very successful in various systems, such as in estimating the residual entropy of ice.[30,31] By adding the experimental enthalpies from very low temperatures to the dilute vapor at high temperatures, subtracting the ideal gas enthalpy of the vapor as determined from spectroscopy, and extrapolating to infinite chain length, Billmeyer found that the heat of sublimation of polyethylene chains at 0 K is

$$\Delta U_{\text{sub}} = 1.84 \pm 0.03 \text{ kcal/mol CH}_2 \qquad (11)$$

An independent assessment of one of the errors in the extrapolation can be obtained by comparing Billmeyer's $\Delta H_M = 922 \pm 15$ cal/mol CH_2 with the more recent value, 980 ± 50 cal/mol CH_2 obtained with extended-chain crystals.[5] This suggests that one might consider increasing ΔU_{sub} to 1.90 kcal/mol CH_2. However, as transitions become sharper with better crystals, C_P near but outside the transition tends to become smaller; this subtracts enthalpy from the single-phase regions, thereby compensating for the increase in ΔH_M. Therefore, we will continue to use Billmeyer's original value, emphasizing that this is not inconsistent with using the more modern value for ΔH_M.

Clearly, ΔU_{sub} is the energy input required to achieve an infinite separation of polyethylene chains at 0 K. Our task is to decompose ΔU_{sub} into separate pieces corresponding to various identifiable steps starting from the perfect crystal at 0 K to the dilute vapor. The first step, which results in an energy that we call ΔU_{solid}, is due to thermal expansion from 0 K to just below T_M. The second step, which is the one of direct interest for this paper, is the change in cohesive energy during melting, which we are calling ΔU_{vdW}. Additional steps are the thermal expansion of the liquid followed by vaporization. Volume and X-ray measurements and some simple theory will be employed to perform the calculations of ΔU_{solid} and ΔU_{vdW}.

The theory begins by considering that the form of intermolecular interactions between two long parallel hydrocarbon chains separated by a distance r is given roughly[28] by

$$U = (2U_0/24)[(r_0/r)^{25} - 5(r_0/r)^5] \qquad (12)$$

which has a minimum at r_0. The most important part of eq 12 is the longer range attractive r^{-5} van der Waals term; the reason it goes as r^{-5} instead of the usual r^{-6} is simply that an integration over all monomers along each chain has been performed. The 25th power in the repulsive term is not at all certain. It may be thought of as a compromise between 6–12 Leonard-Jones type potentials and interactions with even more rapidly exponentially decaying repulsive interactions.[32,33] Salem's rationale[28] for proposing this simple form was that his more detailed calculation of specific hydrogen–hydrogen repulsions yields a term 20% as large as (and of opposite sign to) the attractive r^{-5} term. To model that result with a simple power law dependence fixes the repusive exponential as −25. As we shall see, this repulsive term is not crucially important for our numerical estimate.

The coefficient $U_0/24$ is most reliably obtained from Billmeyer's experimental result, eq 11. If one ignores interactions between chains further away than nearest neighbors and assumes a simple hexagonal packing of chains with six nearest neighbors, then

$$U_{\text{sub}} = (6/2)[U(\infty) - U(r_0)] \qquad (13)$$

Equation 12 yields $U_{\text{sub}} = U_0 = 1.84$ kcal/mol CH_2. We now describe a refined calculation that does not ignore further neighbors and does not assume hexagonal packing of chains. Summing over all pairs of neighbors i yields the following approximation for the cohesive energy:

$$U(\mathbf{r}) = (U_0/24)\sum n_i[(r_0/r_i)^{25} - 5(r_0/r_i)^5] \qquad (14)$$

where n_i is the number of neighbors at distance r_i and $\mathbf{r}$ is a shorthand notation for all values r_i. First, we evaluate r_0. To do this, we first note that at 0 K $U(\mathbf{r})$ must be a minimum as a function of the r_i. Of course, the r_i are not all independent variables. We simplify to one independent variable, $y = r_0/r_1$, where r_1 is the nearest-neighbor distance, by noting that the ratio of unit cell parameters, a/b, of the orthorhombic unit cell is nearly a constant for low temperatures.[34] Therefore, we have

$$0 = dU/dr_1 = -(25U_0/24)\sum(n_i/r_i)[y^{25}(r_1/r_i)^{25} - y^5(r_1/r_i)^5] \qquad (15)$$

where all quantities are to be evaluated at 0 K and the quantities (r_1/r_i) are taken to be constant. Summing over i gives a simple equation for y from which one obtains $r_0 = 4.36$ Å. This result may be compared with the nearest-neighbor distance, $r_1 = 4.302$ Å, for the four nearest neighbors at 0 K, obtained from the fitting formula of Davis et al.[35] The result that r_0 is larger than r_1 indicates that there is a net repulsive force between nearest-neighbor chains at 0 K, but this is balanced by the net attractive force between further neighbor chains, including the two at 4.854 Å.[35] Once r_0 is determined, it is a simple numerical calculation to obtain the heat of sublimation from eq 14 in terms of U_0 and to set this equal to the experimental value. This yields $U_0 = 1.77$ kcal/mol CH_2. That this result for U_0 is slightly lower than the value obtained after eq 13 using only nearest neighbors is expected because of the contribution of the additional interactions.

The way in which eq 14 will be used to calculate ΔU_{solid} is indicated in Figure 1 for each pair of chains. When T is increased from 0 K to T_M, the mean interchain spacing increases, resulting in a change in internal cohesive energy that can be read off Figure 1. In order to verify that this a sensible procedure, it may also be useful to examine Figure 2, which shows the potential felt by a chain surrounded by two other fixed chains whose separation cor-

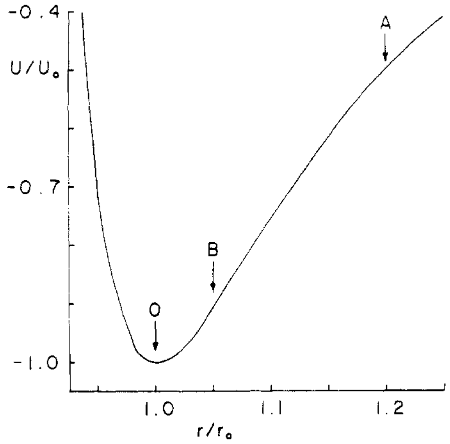

Figure 1. Intermolecular interaction energy, $U(r)/U_0$, for two parallel chains with separation r according to the empirical formula, eq 12. The three arrows labeled 0, B, and A correspond respectively to the mean spacings at 0 K, just below T_M, and just above T_M. Calculations reported in the text using eq 14 also include further neighbors and the orthorhombic symmetry of the polyethylene crystal.

responds to the mean density. This potential well is rather flat in the middle with a value in the middle given by the sum of the potentials read off Figure 1. (We ignore the weaker further neighbor interactions in these figures but not in the calculations.) To obtain the r_i distances just below the melting transition we use Swan's X-ray results,[34] namely four nearest neighbors at 4.576 Å and two at 4.936 Å. Together with the usual 1.27-Å half-repeat along the c axis, these results yield a volume V = 1.041 mL/g. Dilatometry measurements[36] also yield V = 1.040 mL/g. This is only slightly larger than the 1.0338 mL/g that would be obtained by using the fitting formula of Davis et al.[35] to 414.6 °C, well beyond their recommended upper limit of 333 K. From eq 14 one then obtains ΔU_{solid} = 0.18 kcal/mol CH_2, only about 10% of the total cohesive energy at 0 K. It is worth noting that various intramolecular vibrations are hindered at low temperatures by the excluded volume interactions in the sense that their classical intramolecular amplitudes are larger than the well width shown in Figure 2. As the crystal expands with temperature, the near-neighbor chains move further apart and this well broadens, as shown in Figure 2a, thereby unhindering the vibrations. Such vibrational unhindering will also result in contributions to the specific heat and the enthalpy;[37] these contributions are independent of the cohesive energy being calculated here.

We now propose to calculate ΔU_{vdW} due to melting of the crystal in the same way as we calculated ΔU_{solid} above. At first sight this seems unwarranted because the liquid is a tangled array of chains, not a parallel array of straight chains with spacing, when compared to the crystal, increased by a factor proportional to the square root of the volume change ΔV_M. However, the longer range attractive van der Waals interactions are mostly isotropic, in contrast to the excluded volume repulsive interactions. Estimates made for liquid crystal studies[38,39] indicate that the anisotropic part of the long-range van der Waals interactions is at least an order or magnitude smaller than the isotropic part even for molecules having more local molecular anisotropy than polyethylene. Salem also uses the isotropic approximation in dealing with hydrocarbon chains. This has been criticized by Zwanzig,[40] who, however, admits that various averages performed by Salem will tend to lead to cancellation of errors. For our purposes it is likely that the anisotropic nature of the bond polarizabilities are already fairly well averaged even in the well-ordered crys-

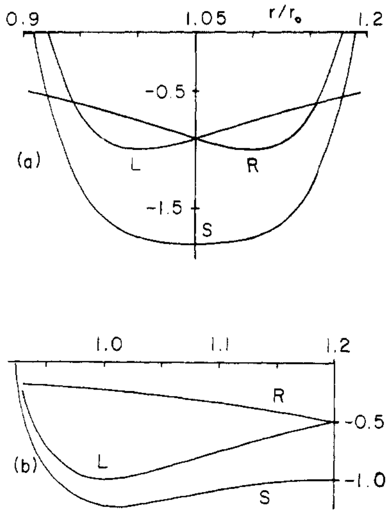

Figure 2. (a) The curve labeled S is the intermolecular potential between a chain molecule located at position r and two other parallel chain molecules located at $r = 0$ and $r = 2.1r_0$, so the mean spacing between molecules is $r = 1.05r_0$, which corresponds to just below the melting transition for polyethylene. The curves labeled L and R are the individual contributions to S from each of the two fixed molecules. (b) Same as (a) except that the two fixed molecules are located at $r = 0$ and $2.4r_0$ so the mean spacing is $1.2r_0$, which corresponds to the density of liquid polyethylene just above the melting temperature. The total potential S is symmetric about $1.2r_0$. The difference in the potentials at $r = 1.05r_0$ in (a) and at $r = 1.2r_0$ in (b) corresponds to the potential differences at A and B in Figure 1. Further neighbor interactions and the orthorhombic symmetry of the polyethylene crystal are not accounted for in the figure.

talline state because of the two differently oriented chains in each unit cell and two different C–C and C–H bond directions for each chain. Therefore, we believe it is an adequate approximation to ignore any anisotropic part of the interaction altogether. Then the van der Waals interaction does not depend upon the conformational state of the chains at all, provided that the spacings between molecules, now not all parallel, are roughly uniform, i.e., so that each molecule is roughly in the flat portion of the well in Figure 2. We have argued in the past[14] that this assumption is likely to be violated to a degree because tangled configurations may require tight contacts in order to accommodate all the chains, even with the increased available volume, and we have suggested that this could be compensated by ignoring the uncertain repulsive part of the interaction in eq 14. This is a rather fine point that only increases our estimates of ΔU_{vdW} by about 14%, and we will present both results. The main point is that one can obtain a reliable estimate of ΔU_{vdW} by doing the liquid-state calculation for any configurational state with the liquid density. The simplest state for which to do the calculation is the expanded all-trans parallel chain state in which the chains are arranged in a hexagonal array. The fact that this state is atypical of the liquid, although highly relevant to calculating many other properties such as ΔU_R, is in first approximation irrelevant to calculating ΔU_{vdW} because these interactions are nearly isotropic and not dependent upon conformation. We should also emphasize that this argument does not suggest that melting is to be thought of as a sequence of two steps, the first consisting of uniform expansion of the solid state followed by a second step involving conformational disordering. It is a firmly based equilibrium statistical calculation, although it necessarily involves approximations as do the calculations of all ΔU_i or ΔS_i in this and previous papers. It may also be noted that this discussion indicates that ΔU_{vdW} is

Table I
Summary of Values Used in U_{vdW} Calculation in Eq 14 (r_0 = 4.36 Å and U_0 = 1.77 kcal/mol CH_2)[a]

T, K	r_1	r_2	ref
0	4.302	4.854	35
414	4.576	4.936	34
415	5.198	5.198	eq 16

[a] r_1 is the distance between a molecule and its four nearest neighbors, and r_2 is the distance between a molecule and its two next nearest neighbors in an orthorhombic array of parallel rods. Above the transition at 414.6 K a hexagonal array is used with six nearest neighbors.

closely associated with the volume change of the system.

Table I shows the relevant quantities that are used to obtain ΔU_{vdW} from eq 14. The only quantity not already commented upon that is needed to complete the calculation is the value of the interchain spacing, r_a, to be used just above T_M. This is obtained from the measured volume,[41] V = 1.2765 mL/g, just above T_M and the formula

$$V = (3^{1/2}/2)(1.27\ \text{Å})r_a^2(6.023 \times 10^{23})/(14.02\ \text{g}) \qquad (16)$$

appropriate for a hexagonal array of chains. Using eq 14 with no modification yields ΔU_{vdW} = 630 cal/mol CH_2. As mentioned above, there are reasonable grounds for ignoring the repulsive part of the interaction in this calculation. Doing this increases ΔU_{vdW} to 720 cal/mol CH_2. The difference between these two values is an indication of the size of the error in these estimates.

A number of years ago, before the work of Billmeyer and before other experimental results necessary to make the preceding estimates, Bunn[42] estimated the cohesive energy to be 680 cal/mol CH_2. His estimate was based on $L - RT$, where L is the latent heat of vaporization at the *boiling* point. It is remarkable that that estimate is in such good agreement with ours.

We may now compare the results for the enthalpy decomposition with the experimental value of the total enthalpy change, ΔH_M = 980 ± 50 cal/mol CH_2. If we use the best values, ΔU_R = 200 cal/mol CH_2 and ΔU_{vdW} = 720 cal/mol CH_2, then only 60 cal/mol of enthalpy is unaccounted for, which we place in the other, catchall term, ΔU_0. Use of the value ΔU_{vdW} = 630 cal/mol leaves 150 cal/mol unaccounted for. Some of the possible sources for ΔU_0 might be an additional unhindering of the vibrations upon melting or an additional energy that might be required in straining the hydrocarbon chains away from their energy minima in the trans or gauche wells in the liquid phase. We will not attempt here to calculate ΔU_0 from any other source; it suffices for our purposes that ΔU_0 is a relatively small correction term in the enthalpy decomposition.

It may be mentioned that Volkenstein has proposed a theory in which the unhindering of the vibrations is one of the primary mechanisms driving melting.[43] In that model the vibrations are completely hindered in the solid phase and completely unhindered in the melt. Such a complete unhindering is certainly exaggerated. There is evidence from the anomalous specific heat increase over a temperature range of 100 degrees or so below the transition that the vibrations are becoming gradually unhindered as the crystal expands.[37] Also, the chains need not have greatly increased vibrational freedom in the melt, despite its greater volume, because the entanglement of the disordered chains may require even tighter interchain contacts than in the conformationally ordered crystal. However, Gujrati and Goldstein[44] have shown that about one-third of the entropy difference between crystal and supercooled liquid phases of molecular crystals at the glass temperature may be vibrational in origin, but it is not clear to what extent this may apply to polymers at the melting temperature. Therefore, while it is recognized that such effects will play a role, it seems that their role should be smaller than in the Volkenstein theory.

III. Fundamentals of Entropy Decompositions

Let us now turn to the entropy decomposition. There is a basic difference between the entropy decomposition and the enthalpy/energy decomposition. The energy, and also each different contribution to the energy, can be calculated for each individual microstate of the system without knowledge of the other states or of the temperature or of which ensemble is appropriate. This is impossible for the entropy, which does not exist in isolation for a single state. For example, if one attempts to express the entropy as a sum over states, the best one can do is

$$\langle S \rangle = \sum S_s p_s = -k\sum(\ln p_s)p_s \qquad (17)$$

From eq 5

$$\ln p_s = -\sum(U_i)_s/kT - PV_s/kT - \ln Z \qquad (18)$$

This shows that S_s is not calculable for a single isolated state because calculation of the partition function Z requires knowledge of all states. Combining eq 17 and 18 yields the standard thermodynamic relation

$$S = (U + PV - G)/T \qquad (19)$$

where G is the Gibbs free energy, $G = -kT \ln Z$. Next we note that $\Delta(\ln Z) = 0 = \Delta G$ for an isothermal, isobaric phase transition in single-component systems. Then eq 17 and 18 may be combined and the differences taken between the crystal and melted phases to obtain

$$\langle \Delta S \rangle = \sum\sum(\Delta U_i)_s/T_M + P\langle \Delta V \rangle/T_M \qquad (20)$$

At this point it might seem natural to identify

$$\langle \Delta S_i \rangle = \langle \Delta U_i \rangle / T_M \qquad (21)$$

but this is essentially just the enthalpy decomposition.

Another approach to the entropy decomposition starts with the thermodynamic relation, eq 19, and writes

$$\langle \Delta S_i \rangle = (\langle \Delta U_i \rangle - \langle \Delta A_i \rangle)/T_M \qquad (22)$$

where $A = G - PV$ is the Helmholtz free energy. In this approach the problem of defining the entropy decomposition becomes the same as the problem of defining a free energy decomposition

$$\langle \Delta A \rangle = \sum \langle \Delta A_i \rangle \qquad (23)$$

Such a free energy decomposition exists if and only if the partition function can be written as a product of independent partition functions for each term in the decomposition

$$Z = \prod Z_i \qquad (24)$$

where

$$Z_i = \sum \exp(-\beta(U_i)_s) \qquad (25)$$

and the sum in eq 25 involves only the degrees of freedom associated with the ith energy, U_i. This condition is a very strong one. It does not allow the possibility that certain values of U_i may be allowed for some states with one value of U_j and not for other states with a different value of U_j, where j is a different term in the decomposition. A very simple example is a three-state system with two types of energy, U_1 and U_2; in this example the energy U_1 may be 0 or δ and the energy U_2 may be 0 or ϵ, but U_2 may be ϵ only if $U_1 = \delta$. Something quite similar has been found to occur for grid-locked polymer models[20,45] for which one cannot realize the higher energy disordered states (ϵ) unless there is an increase in volume with a corresponding increase in cohesive energy (δ). Clearly, then, the entropy decomposition is not well defined in the general case. Only if the system obeys eq 24 or if approximations are made to allow use of eq 24 can one obtain an entropy decomposition. This fundamental limitation, which is not present in the enthalpy decomposition, should be clearly realized.

Even though the entropy decomposition is fundamentally poorly defined for the general case, there may still be some value in considering it in the context of the approximation in eq 24. The preceding development also emphasizes that the entropy decomposition is inextricably connected to the free energy decomposision, which is in many ways a more significant quantity to consider. In particular, if a new disordering feature i is added to a system and if the new system melts at a lower temperature, then ΔA_i should be negative, thereby driving the transition forward against those other features that would prevent it from melting until a higher temperature.

IV. Critical Review of Previous Entropy Decompositions

The pivotal paper for previous entropy decompositions for polymers was written by Starkweather and Boyd,[11] abbreviated SB. While the simplified eq 1 ultimately employed by SB, was applied previously[1] and many times thereafter,[2-10,12,13] the SB paper examined the method most completely and it established some conventions followed, often tacitly, by many later authors.

Let us begin our analysis of the SB paper with their discussion of ΔS_R. As noted in our introduction, their ΔS_R also includes the effects of the excluded volume interactions, so it is not the same as the ΔS_C used by many workers. SB based their calculation of ΔS_R on the classical Flory–Huggins theory of a lattice model.[19] While we have been and continue to be highly critical of this theory of melting,[20,21,46-48] the Huggins calculation, suitably modified, provides a reasonable first approximation for calculating this one component of the transition entropy. (It is certainly a far superior approximation to the use of single-chain calculations, which ignore completely the excluded volume constraint between chains.) This theory separates the change in free energy ΔA_R into two terms that can be written as

$$\Delta A_R = \Delta A_X + \Delta A_C \tag{26}$$

where

$$\Delta A_X = -RT\gamma$$

and

$$\Delta A_C = -RT \ln \lambda$$

The λ term in eq 26 pertains exclusively to the rotational isomerism of a single chain. In the original Flory theory[19] it is just

$$\lambda = 1 + (q - 2) \exp(-\epsilon/kT) \tag{27}$$

where $q - 1$ is the number of ways to continue a chain. For the usual rotational isomerism of polyethylene chains, $q = 4$. SB modified this term by excluding any g^+g^- pairs; this yields

$$2\lambda = 1 + x + [1 + 6x + x^2]^{1/2} \tag{28}$$

where $x = \exp(-\epsilon/kT)$. The γ term in eq 26 pertains to the excluded volume effect between chains, correcting for the unrestricted probability implicit in eq 27. For this term SB modified the Flory theory by using the more accurate Huggins combinatorial factor,[49,50] which yields

$$\gamma = [(z/2) - 1] \ln [1 - (2/z)] \tag{29}$$

where z is an effective coordination number of the lattice that need not be equal to q.[50] SB used $z = 8$ in their calculations, which yields $\gamma = -0.863$.

From eq 26–29 one obtains the configurational transition entropy

$$\Delta S_R = -\partial \Delta A_R/\partial T = \Delta S_X + \Delta S_C \tag{30}$$

where

$$\Delta S_X = R\gamma$$

and

$$\Delta S_C = R[\ln \lambda + f\epsilon/kT]$$

where the terms on the right-hand side of eq 30 are to be evaluated in the liquid state and f is determined by

$$Nf\epsilon = \Delta U_R = \partial(\Delta A_R/T)/\partial(1/T) = N\epsilon[\mathrm{d} \ln \lambda/\mathrm{d} \ln x] \tag{31}$$

The combination of using $z = 8$ and using the improved "pentane effect"[27] form of λ in eq 28 leads to an undesirable result that apparently was not fully appreciated by SB. This result is that the transition entropy, ΔS_R in eq 30 is actually negative with values in the range -0.13 to -0.02 eu for the temperature (410 K) and the values of ϵ (about 500 cal/mol) used by SB. (This result also occurs in Mandelkern's discussion,[51] but there the problem is further exacerbated by an even more negative ΔS_R because of the use of the original Flory combinatorial factor,[19] which overestimates the effect of the excluded volume interactions much more than the more accurate[20,21,50] Huggins factor.[49]) The transition free energy, ΔA_R, is also positive in SB's calculation. This means that the transition, if it were to occur for the values of the parameters T and ϵ chosen by SB, must be driven by some other physical effects and that the rotational isomerism is actually hindering, not driving, the transition. Indeed, as we shall see later in this section, SB require the disordering term ΔA_D and the volume term ΔA_V to make up for the positive ΔA_R computed above. Since it has been conclusively shown by Bunn[42] that the rotational isomerism does actually promote the transition at temperatures lower than if it were not present, it is unreasonable to follow SB literally at this point.

The second contribution in previous entropy decompositions of polymer melting is ΔS_V, which was proposed in a general discussion of melting for all substances by Slater,[52] whom we quote as follows (italics added): "Let us, then, *tentatively* assume that the relation of change of entropy to change of volume in going from one phase to another is about the same as when we change the volume of a single phase." "In this case, using the thermodynamic relation $(\partial S/\partial V)_T = (\partial P/\partial T)_V = \alpha/\beta$, we have

$$\Delta S_V = (\alpha/\beta)\Delta V \tag{32}$$

This is certainly a very crude assumption, ... in most cases the calculated entropies of melting are of the right order of magnitude, but in most cases they are decidedly smaller than the observed ones." "Of course, ... there is great variation from one material to another, and occasional materials, ..., actually have a decrease of volume on melting, ..., so that in such cases relation (32) *is obviously incorrect*."

Since ΔS_V as computed from eq 32, with experimental values for α/β, is usually a good deal smaller than ΔS_M, another entropy term called the disordering entropy, ΔS_D, has been defined[53] to balance the entropy equation for monatomic metals, so that

$$\Delta S_M = \Delta S_V + \Delta S_D \tag{33}$$

Oriani[53] identified ΔS_D with disordering of the lattice structure, and he provided an interesting interstitial type theory to correlate the values of ΔS_D obtained from eq 32 and 33. We must emphasize here, however, that these empirical values of ΔS_D are scattered from 0.97 to 1.8 eu (even when 3 exceptional cases out of 14 are ignored). While the concept of ΔS_D may be valid for the (nonexceptional) metals Oriani considers, no clear value of ΔS_D emerges for use in polymer calculations. Nevertheless, for reasons that will become clearer later, SB chose $\Delta S_D = 1.72$ eu to use in the polymer decomposition. SB also declare that ΔS_D is "common to all liquids arising from the over-restrictiveness of a lattice treatment which we call the long-range disorder contribution". While a lattice constraint would indeed distort the entropy decomposition in the direction suggested by SB, the use of the upper range of the values of ΔS_D obtained for mostly *monatomic* metals would appear to be unwarranted, as has been noted by Tsujita et al.[12] and by Smith.[13] Indeed, removing the lattice constraint on long-chain polymers in a melt surely results in a smaller increase in entropy when measured per monomeric unit than removing the lattice restraint on monatomic metals because, once a small segment of a chain is fixed in space, the remaining monomeric units on the same chain are fixed within the constraints of the rotational isomeric model. No such restriction exists for monatomic metals. The most obvious lattice constraint that is removed is only the three translational and three rotational degrees of freedom for each whole chain. Like the communal entropy,[54] this would have a negligible effect on the transition entropy when measured per CH_2 group for long-chain polyethylene. In addition, the ϵ parameters in the rotational isomeric model are really free energies,[43] which implicitly include a variation in rotameric angles and which automatically take the chain off the lattice. Since the variation in angles will likely be more constrained in the crystalline state than in the liquid state (although free angular rotation also does not exist in the liquid state due to the excluded volume interaction and tight contacts between conformationally disordered molecules), an additional source of disordering entropy is inherent in the rotational isomeric model. But regarding its size, Tsujita et al.[12] use a more reasonable value $\Delta S_D = 0.11$ eu for polyethylene, far smaller than that used by SB.

SB then separated ΔS_R into two terms (see their eq 10). The first term is the term that we call ΔS_C in eq 30 and that SB call ΔS_g. (Most authors since SB have called this ΔS_C, where the C stands for conformational, and we will do likewise.) ΔS_C is the contribution to the entropy that is obtained by considering only single isolated chains in a Θ solvent. The large negative excluded volume contribution to the transition entropy, $R\gamma$ in eq 30, amounting to $-0.86R = -1.72$ eu, was not given a name by SB. In eq 30 this is the excluded volume entropy, ΔS_X. SB decided that ΔS_D should "be largely compensatory" with ΔS_X. This assumes that ΔS_D is in the *upper* range of values found for monatomic metals. This rather weak argument (also repeated by Tonelli[55]) has apparently been the theoretical basis for the neglect of both ΔS_X and of the more nebulous ΔS_D. Instead, we believe that ΔS_D is rather small, along with Tsujita et al.,[12] and that ΔS_X is a substantial negative term, so that no such "compensation" should be claimed.

Following SB most papers on the entropy decomposition have assumed that $\Delta S_X + \Delta S_D = 0$ and have concerned themselves only with the simplified equation

$$\Delta S_M = \Delta S_C + \Delta S_V \tag{34}$$

where ΔS_C is the single-chain entropy that is also the entropy difference between the crystal at $T = 0$ K and the dilute vapor at T_M. The best numerical agreement for eq 34 was obtained by Tonelli,[4] who calculated ΔS_V using liquid-phase measurements in eq 32. However, such good agreement is spoiled by more accurate calculations of ΔS_V. (See Table II for literature values for polyethylene.) It has been pointed out a number of times[56,57] that an integration over volume change in eq 32 is required to take into account the pressure dependence of α/β. A most thorough discussion of this point is given by Turturro and Bianchi,[7] who performed careful measurements on alkanes of 11–19 carbons, but unfortunately, did not do polyethylene. Their refined values of ΔS_V for the alkanes were higher than those obtained by the simple method used by Tonelli[4] for polyethylene. Tsujita et al.[12] performed measurements for polyethylene and obtained a value for ΔS_V almost twice as high as Tonelli's value, and this increase in ΔS_V is also supported by a more recent analysis of Miller.[6] (Miller obtained agreement with eq 34) but only by increasing ϵ to the unacceptably high value of 1.2 kcal/mol.)

Table II
Some Literature Values for the Entropy Decomposition of Polyethylene

ref	ΔS_V, eu	ΔS_C, eu	ΔS_M, eu
1	0.46	1.84	2.30
2	0.34	1.8	2.27
3	0.58	1.79	2.37
4	0.52	1.76	2.29
6	1.06	1.30	2.36
11[a]	0.52	1.70	2.30
12[b]	0.91	1.51	2.53
58	0.64–1.2		

[a] $\Delta S_D = 1.72 = -\Delta S_X$. [b] $\Delta S_D = 0.11$.

A very strong criticism of the entire concept of the separation in eq 34 was made by Karasz, Couchman, and Klempner[58] in a paper to be abbreviated KCK. The first concern that they emphasized regarding the ΔS_V term is the fact that its value depends upon the thermodynamic path taken. Usually, it has been calculated by considering the configurational ΔS_C melting to take place hypothetically at constant volume and then for a second step to involve volume expansion in the liquid with liquid values of α/β used to compute ΔS_V in eq 32. One can equally well consider the reverse hypothetical order for which ΔS_V is computed from the solid-phase values of α/β. While the two paths seemed to give the same results for the very few (two) metals for which Oriani tested it, KCK find that for polyethylene $\Delta S_V = 0.64$ eu for the first way and 1.2 eu the second way. Following Kubachewski's paper[59] on metals KCK also considered hypothetical constant volume processes accomplished by changing temperature rather than pressure. Without a fundamental statistical theory to determine which is the appropriate process to use in eq 34, these two options must be considered on an equal footing. However, KCK show that this second option leads to values of ΔS_V of 3.8 or 5.7 eu, depending upon whether liquid or solid values are used. This numerical chaos emphasized by KCK can perhaps be alleviated by application of the refined methods of computing ΔS_V with extrapolated values of α/β into the unstable transition region.[7,12,56,57] In particular, the estimate of 0.91 eu given by Tsujita et al.[12] is nearly midway between the values of 0.64 and 1.2 eu given by KCK for the liquid and solid sides, respectively. However, there is no path that is obviously the uniquely correct one, nor can there be as long as the question is only addressed at the level of phenomenological thermodynamics. The meaning of a purely phenomenological ΔS_V, calculated by eq 32 or some variant, is not well related to fundamental statistical quantities. Another concern mentioned by KCK is that ΔS_V, as measured thermodynamically, may contain contributions from conformational entropy changes. Such contributions do not occur in the classical theory.[19] However, as we shall see in the text section, one other term, namely, ΔS_X, *is* strongly volume-dependent, even in the classical theory. It is not at all clear how these are mixed into the purely thermodynamic calculation using eq 32 or some variant.[7,12,56,57]

We therefore concur with KCK[58] that the validity of the simple entropy decomposition in eq 34 is basically suspect, but our primary argument for this conclusion is the inconsistency of mixing the ΔS_V term, which is so far undefined at the microscopic, statistical level, with the purely statistical ΔS_C term. Of course, thermodynamically one can calculate ΔS_V and then compute the difference with ΔS_M and call it ΔS_C. Conversely, one may calculate ΔS_C from statistical mechanics, subtract it from ΔS_M, and call the result ΔS_V. However, it is unlikely that the two methods have defined the same quantities. The fact that the numerical values of ΔS_C and ΔS_V have sometimes seemed to agree with ΔS_M in eq 34 can be discounted as due to inaccurate methods of calculating ΔS_V and disregard of the major term, ΔS_X, as discussed above.

V. New Entropy and Free Energy Decomposition

In this section we use the best parts of preceding entropy decompositions along with the enthalpy decomposition. The basic assumption that the free energy is decomposable will be made and the highly approximate classical theory will be used.

The difference between our use of the classical theory in this section and the usage of SB is that we will include the volume expansion in our calculations. This does not affect ΔA_C in eq 26–28 but it does change the excluded volume contribution. This change may be easily calculated by following the derivation in section 7 of ref 20; only the result will be quoted here

$$\Delta A_X = (RT_M/a)\{(2-a)\ln[2/(2-a)] + (1-a)\ln(1-a)\} \qquad (35)$$

where we have taken the coordination number of the lattice to be $q = z = 4$ and a is defined to be the density of the melt divided by the density of the crystal just below T_M. We now use the experimental values $a = 0.8$, $\epsilon = 500$ cal/mol CH$_2$, and $T_M = 414.6$ K to obtain

$$\Delta A_X = 300 \text{ cal/mol CH}_2$$

$$\Delta A_C = -502 \text{ cal/mol CH}_2$$

$$\Delta A_R = -202 \text{ cal/mol CH}_2 \qquad (36)$$

where eq 28 is used for ΔA_C and eq 26 for ΔA_R. Using eq 30 one has

$$\Delta S_X = -0.72 \text{ eu}$$

$$\Delta S_C = 1.69 \text{ eu} \qquad (37)$$

and ΔS_C would be adjusted to Tonelli's value[4] of 1.77 eu if the pentane exclusion of g^+g^- pairs were not made complete.

The negative value of ΔA_R in eq 36 is significant. Since the total ΔA is essentially zero because $P\Delta V$ is so small, the free energy change due to all remaining terms in the decomposition, defined to be ΔA_{-R}, must satisfy

$$-\Delta A_R = \Delta A_{-R} \sim 202 \text{ cal/mol CH}_2 \qquad (38)$$

This conforms nicely to Bunn's discussion[42] that rotational isomerism does indeed decrease T_M because without the negative ΔA_R contribution the transition free energy would be positive at T_M and the system would only melt at some higher temperature.

The positive ΔA_X term is a purely entropic contribution that reflects the difficulty of packing disordered chains. The numerical value of ΔA_X that is obtained with the SB analysis, eq 26 and 29 with $q = z = 4$, is 571 cal/mol CH$_2$. The difference between their estimate and ours reflects the fact that it is more difficult to pack disordered chains at a higher density than at a lower one. We might also note that the classical approximation, which is well-known to be inaccurate for high densities,[20,21,46–48] is more likely to be better for the lower densities of the melt considered here. This reduction in ΔA_X, from 571 cal/mol in the SB calculation to our 300 cal/mol, is clearly due to the volume expansion of polyethylene, so one might choose to retain $\Delta A_X = 571$ cal/mol and add a term -271 cal/mol to the volume expansion term, ΔA_V. We do not prefer this because this ΔA_X term would not even exist if it were not for the rotational isomerism. However, the need to choose between such conventions illustrates the artibrariness of entropy decompositions involving features that are fundamentally interacting.

The second part of our new decomposition deals with all other contributions whose free energy has been designated ΔA_{-R}. In the enthalpy decomposition we identified all other energy terms, which we here call ΔU_{-R}, primarily with the van der Waals cohesive energy, $\Delta U_{vdW} \sim 720$ cal/mol CH$_2$, although there was a small amount of enthalpy unaccounted for and which will also be included in

$$\Delta U_{-R} = \Delta H_M - \Delta U_R \sim 780 \text{ cal/mol CH}_2 \qquad (39)$$

From the defining relation

$$\Delta S_{-R} = (\Delta U_{-R} - \Delta A_{-R})/T_M \qquad (40)$$

and from eq 36, 38–40 we have

$$\Delta S_{-R} = 1.39 \text{ eu} \qquad (41)$$

Notice that ΔS_{-R} has been *defined* so that ΔS_R and ΔS_{-R} add up to the experimental ΔS. The final goal is to obtain some insight into the sources of ΔS_{-R}.

We first note that numerically the enthalpic ΔU_{-R} contribution to ΔS_{-R} in eq 40 is much larger than the ΔA_{-R} contribution. In turn, the major contribution to ΔU_{-R} is the van der Waals interaction that accompanies the volume expansion. Therefore, the volume expansion term ΔS_V is identified as a major source for ΔS_{-R}. This may be formalized by writing

$$\Delta S_{-R} = \Delta S_V + \Delta S_0 \qquad (42)$$

where the new term, ΔS_0, may be thought of as the error term in this new decomposition. Because the task of enumerating degrees of nonconformational freedom that become allowed upon undergoing a volume change is too difficult, we will instead make three estimates of ΔS_V and ΔS_0 based on thermodynamics.

Our first estimate is $\Delta S_V \sim \Delta U_{vdW}/T_M$. This approximation is based entirely upon the relatively reliable ΔU_{vdW} calculation, but it clearly neglects any contributions from ΔA_V. This leads to $\Delta S_V = 1.74$ eu and $\Delta S_0 = -0.35$ eu.

The second estimate is a variant of the preceding one. We attempt to assign a fraction of ΔA_{-R} to ΔA_V. A rough way to do this is by simple proportion

$$\Delta A_V/\Delta A_{-R} = \Delta U_{vdW}/\Delta U_{-R} \qquad (43)$$

This yields $\Delta S_V = 1.29$ eu and $\Delta S_0 = 0.10$ eu.

The third way to estimate ΔS_V is to follow the Slater method, eq 32, but with the necessary variant to account for the volume dependence of α/β.[7,12,56,57] Using an average of the best values of ΔS_V obtained this way[6,12] yields $\Delta S_V = 0.99$ eu and $\Delta S_0 = 0.40$ eu.

VI. Conclusions and Consequences for Theories of Polymer Melting

We advocate the following entropy and enthalpy decompositions:

$$\Delta S_M = \Delta S_C + \Delta S_X + \Delta S_V + \Delta S_0$$
$$\Delta H_M = \Delta U_R + \Delta U_{vdW} + \Delta U_0 + P\Delta V \qquad (44)$$

In contrast to many previous entropy decompositions, we believe that neglect of the excluded volume term, ΔS_X, as being largely compensatory with a rather nebulous liquid disordering, ΔS_D, term is conceptually misleading as well as being numerically incorrect. We consider ΔS_X explicitly and include whatever ΔS_D stands for in ΔS_0. The terms ΔS_0 and ΔU_0 are error terms that include all other sources of entropy and enthalpy not explicitly considered in the identifiable terms. For polyethylene we have made the following rough estimates:

$$\Delta S_C \sim 1.69 \text{ eu}$$
$$\Delta S_R = \Delta S_C + \Delta S_X \sim 0.97 \text{ eu}$$
$$\Delta S_X \sim -0.72 \text{ eu}$$
$$\Delta S_V \sim 0.99\text{–}1.74 \text{ eu}$$
$$\Delta S_0 \sim +0.40 \text{ to } -0.35 \text{ eu}$$
$$\Delta U_R \sim 200 \text{ cal/mol CH}$$
$$\Delta U_{vdW} \sim 720 \text{ cal/mol CH}_2$$
$$\Delta U_0 \sim 60 \text{ cal/mol CH}_2 \qquad (45)$$

The preceding numerical values are based on a number of theoretical assumptions that are unlikely to be completely correct. The most fundamental is the assumption, discussed in some detail in section III, that an entropy decomposition is meaningful. To make it meaningful, one must assume that the free energy is separable. Even if such a separation can be performed approximately, it may not be unique, and we identified one contribution that could be classified as either a volume contribution or a rotational isomeric contribution. Aside from these fundamental considerations, we have also used parts of the classical theory of polymer melting to estimate ΔU_R, ΔS_R, ΔS_0 and ΔS_X. This theory has been shown to be numerically incorrect in important instances.[20,21,46–48] However, it is likely to be more accurate at the lower densities at which we have used it. In particular, a volume expansion was allowed for in the ΔS_X calculation which gives a considerably different result than that obtained in previous calculations that did not include it. In our opinion our most reliable values are for ΔU_{vdW} and ΔU_R. The fact that ΔU_{vdW} is large and that this term is tied to the volume change suggests that ΔS_V should be an important term in the entropy decomposition. However, our estimate of ΔS_V is less accurate than for the other quantities because of the difficulty of estimating it from microscopic first principles. Nevertheless, there is agreement from three thermodynamic approximations that ΔS_V is a major term in the decomposition. Furthermore, the value of the error term, ΔS_0, is clustered around zero for these three thermodynamic approximations of ΔS_V.

We emphasize that the preceding estimates could not have been made without the use of structural data and thermodynamic data, such as the volume change at the transition. Such phenomenological estimates are not meant to take the place of fundamental statistical mechanical calculations that should be based solely on a description of the microstates of the system. Rather, these estimates are made to determine those features that are important to the system and that should be included in detailed statistical mechanical calculations.

The estimates in eq 44 indicate that there are three features that play major roles in polymer melting. It has long been recognized that conformational disordering of the chains is one such major feature. It is sometimes forgotten, though it is obvious, that the excluded volume interaction is also essential; otherwise, the chains would begin disordering gradually as soon as the temperature is raised above 0 K and there would be no abrupt cooperative phase transition at T_M. The importance of the excluded volume interactions is nicely illustrated by the large negative value of ΔS_X in eq 44. The result that ΔS_X is negative is appropriate because the excluded volume interaction does not decrease the number of allowed configurations for the crystal state of all parallel chains ($S_X = 0$), but it severely reduces the number of configurations of single-chain conformations in the melt ($S_X < 0$) below the number calculated from eq 26, 27 and 30. The importance of cohesive energies, i.e., the longer range attractive van der Waals interactions, might also have seemed obvious. However, a theory of Flory[19] relegated these interactions and the concomitant volume changes to a position of "minor" importance. The conclusion in this paper that ΔS_V has a comparable magnitude with ΔS_X and ΔS_C is in clear disagreement with Flory's theory. The volume change and the large change in cohesive energy is a major, necessary term in the entropy/enthalpy decomposition. It should also play a major role in better theories of the melting transition, a conclusion that we have also come to using a somewhat different line of reasoning.[20,45]

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Phenomenological Relationship between Dielectric Relaxation and Thermodynamic Recovery Processes near the Glass Transition

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ABSTRACT: Applying the experimental dielectric relaxation spectrum of amorphous poly(vinyl acetate) in the form of Dirac δ's over 6 decades of time to the basic nonlinear differential equation for the thermodynamic recovery process accurately reproduced volume relaxation data. Experimental dielectric relaxation time follows the Vogel–Fulcher (or WLF) equation, as is well-known. The thermodynamic recovery time from volume data[5] was found to be precisely equal to the dielectric relaxation time near T_g but at lower temperatures to diverge from the extrapolation of the dielectric data. The recovery time will depend on the fictive temperature following the *same* Vogel formula rather than Narayanaswamy's formula, but its temperature dependence follows the Arrhenius formula. The shift of the relaxation time with aging was calculated from the equations thus evaluated and was shown to agree with viscoelastic and dielectric data, clearly showing that this relaxation time should not be confused with the "effective" τ obtained from the overall rate of thermodynamic recovery. These phenomena are common to polymers and nonpolymers, since both poly(vinyl acetate) and glucose were found to exhibit all of the physical properties that are essential to the behavior studied.

The physics of slow relaxation processes in glass-forming liquids continue to interest many workers. Substantial progress has been made on the phenomenological understanding of the thermodynamic recovery process due notably to the work of Moynihan and co-workers,[1-3] and Kovacs and co-workers,[4,5] through the introduction of the distribution of relaxation times superimposed on the nonlinear dependence of relaxation time on the change of the structure. Their fundamental differential equations are essentially the same nonlinear equation with distributed order parameters. Moynihan (M model) invoked the Kohlrausch–Williams–Watts relaxation function,[6] while Kovacs, Aklonis, Hutchinson, and Ramos[4] (KAHR model) used a double box-shaped distribution of relaxation times. The variations in density fluctuations at various stages of recovery were implied in the solution of the differential equation, but the relaxation spectrum was assumed to remain unchanged throughout the recovery process. Both, as well as others who have studied similar problems extensively,[7-9] utilized the formula of Tool[10] or Narayanaswamy[11] for the temperature and structure dependence of the relaxation spectrum, which is reduced to an Arrhenius type dependence with an extremely large activation energy along the equilibrium liquidus line.

A bothersome question remains still unresolved with respect to the relationship between the dielectric or viscoelastic relaxation time and the volume or enthalpy relaxation (recovery) time extrapolated to equilibrium. Kovacs, Stratton, and Ferry[12] have shown that the viscoelastic and volumetric data near T_g do not coincide with the curve calculated from data obtained at higher temperatures. Sasabe and Moynihan[2] have also shown that the extrapolation of dielectric data from high temperature does not coincide with the enthalpic data near T_g. Yet the work presented here will show that the basic distribution of the recovery times can be assumed to be essentially the same as the relaxation spectrum and, moreover, that the relaxation and the recovery times do coincide near the glass temperature. Indeed, if there were no relationship at all between the two relaxation processes, it would be even more difficult to explain some of the empirical links that seem to exist between the two processes.

In this work we have applied the experimental dielectric spectrum as the order parameters to the essentially same basic differential equation used by all these workers. Our model has an advantage to allow for adding a number of possible variations. In the process we have learned that the Arrhenius type structure term in Narayanaswamy's equation should be replaced by the Vogel type formula.[13] Since in our study each order parameter can be traced during the aging (recovery) process, we were also able to

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