Macromolecular Conformations in Solutions. I. Model for Chains with Partial Flexibility

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Less-than fully flexible polymer chains in solution are considered. Each chain is represented by relatively rigid and with relatively low pervaded volume groupings of monomeric units called compact bundles, intercalated with extended bundles. A partition function for the system is constructed in terms of numbers of possible kinds of pairs of neighboring bundles, and of configurational energies. Results of the extremization of the partition function show an interplay of the interaction forces as decisive for the behavior of the system. The parameters characterizing the system are related to those in the Flory free-volume theory of liquids and solutions. The resulting equations enable evaluation of the relative concentration of compact bundles and of the numbers of pairs of neighboring bundles of different kinds. The model is related to some experimental evidence. Possible connections to structures of polymer-containing phases other than solutions are pointed out.

1. FORMULATION OF THE PROBLEM

Polymeric molecules in liquid phases are often grossly divided into rigid and flexible ones. There is, of course, growing interest in rigid polymers, including liquid crystals. On the other hand, we have the evident success of the assumption of complete flexibility. Quite a few properties of polymers in solutions can be explained in terms of the freely-jointed-chain model, which leads to a Gaussian distribution of segment densities.

It is only natural to expect that the existing virtually unlimited variety of polymer solutions should provide us with a full range of possible

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flexibility behavior of chains: from flexible via *partially rigid* to completely rigid ones. As with so many other aspects of polymer science, the first serious attack on the problem of partial flexibility is due to Flory.[1] He has noted that values of configurational dimensions of polymer molecules in dilute solutions are often about twice those calculated assuming free rotation about all single bonds.

The present interest in the problem of semiflexibility stems from work on drag reduction (DR) and mechanical degradation in polymer solutions in flow (MDF). Given the practical importance of both these phenomena, a large body of experimental information about them has been accumulated. Attempts to rationalize this information in general have not been successful. Various approaches provide explanations for some aspects of DR and MDF, and then lead to conclusions in opposition to experimental facts for some other aspects. Important experimental findings have been called contrary to expectations or puzzling. This author has developed an approach to DR and MDF, predictions from which are in agreement with the totality of experimental facts.[2] The model involves the assumption that a polymeric chain in solution contains groupings of monomeric units called *compact bundles* intercalated with other groupings called *extended bundles*. A compact bundle has relatively higher rigidity and, as its name suggests, pervades a relatively lower volume of the solvent than an extended bundle containing the same number of monomeric units.

A word on terminology is immediately in order. The word "bundle" has already been used by Pechhold and collaborators[3] with an entirely different meaning. We are forced to appropriate this word, however, since the otherwise very rich English language does not seem to have enough words to describe a set of connected monomeric units within a chain. Quite a few meanings have been ascribed to the word "segment"; and words like "submolecule," "supersegment," or even "blob" have been used too. Moreover, Schelten and Stamm[4] have proven experimentally by diffuse neutron scattering in polyethylene melts that "bundles" as envisaged by Pechhold do not exist.

The idea of concomitant existence of compact and extended bundles, developed within the framework of the study of drag reduction and mechanical degradation, has in fact already been implied by Flory. He assumes[1] the existence of a favorable arrangement of consecutive segments, the configurational free energy of which differs by an amount ϵ from other possible arrangements. These other configurations, possibly different among themselves (ϵ is apparently an average value) correspond to what we call the extended bundles. Flory points out that the stiffness of the chain is involved. He leaves open the question of the number of

monomeric units in an arrangement; the number clearly depends on the specific polymer and specific solvent, and similarly we do not ascribe any specific value to the average number of monomeric units in our bundle.

Relevant for the applications mentioned above is the number N_{ce} of pairs of nearest neighbor bundles such that one of them is compact and the other one extended; N_{cc} and N_{ee} are defined similarly. Our partition function as defined below takes this explicitly into account. Also in distinction to Flory,[1] we do not place our chains and solvent molecules on a lattice. The liquid coordination number z, as determinable by diffractometry, is introduced, along with an internal coordination number ζ. The latter for polymeric molecules is related to local branching at a given segment.

Extensive literature exists on the so-called helix-coil transitions in polypeptide chains. Basic work on this problem has been done by Rice and his colleagues,[5] and also by Zimm and Bragg;[6,7] current research represents essentially variations on their work. The transformation from a completely helical chain to a chain without helicity is a very sharp one. As noted by Zimm and Bragg,[7] a change of a few degrees in temperature or a few percent in solvent composition is sufficient to complete it. We know that many properties of polymeric chains are successively treated with the chain environment regarded as a continuum.[8] The stability of the helical structure in polypeptides in solution results from intramolecular hydrogen bonding; the solvent plays a subordinate role. Thus, the polypeptide chains represent a rather degenerate case of the behavior in which we are interested. We are concerned with chains for which the transition from the completely compact state to the state without compact regions is a slow one, and passes through the entire gamut of possible intermediate states. For each such state, there exists a set of external conditions under which the state is a stable one. A slight perturbation of the conditions should result in a state close to the original one, rather than in a drastically different state. For our problem the polymer–solvent interactions are important. But, to assure a reasonable degree of generality, we have to take also into account the intramolecular interactions in the polymeric chain, and also the solvent–solvent interactions.

The scope of the present paper is determined by the foregoing considerations. First, in Section 2, we construct a model of the polymeric chain, consisting of compact and extended bundles, and define quantities pertaining to it. In Section 3 we write the partition function for our system, and apply the usual methods of statistical mechanics. This necessarily brings us into the realm of thermodynamics; the importance of intermolecular interactions has been stressed already. Therefore, in Section 4 we make a

connection between the parameters characterizing our system and a very successful theory of the liquid state, developed by Flory.[9,10] Since the aspects of chain conformations studied here are related to various properties of polymeric materials, some such connections are discussed in Section 5.

Consequences of our model are pursued in the following paper[11] on the basis of numerical calculations; the results provide a number of checks of physical reality of our assumptions.

It should be stressed that the present study does not constitute a negation of the homogeneous chain model. Many properties of polymer solutions are insensitive to the homogeneity—or otherwise—of the chains; we are studying here relatively subtle effects. At the same time, and as already noted, there exist polymer solution properties which cannot be explained if complete homogeneity is assumed.

2. DEFINITIONS

Consider a system of N_1 monomer plus N_2 polymer molecules. Each polymeric molecule contains r segments, and also consists of b bundles. Since the bundles are either compact or extended, we have, in obvious notation,

$$b_c + b_e = b \tag{1}$$

The terminology we have adopted shows that both kinds of bundles are on equal footing. As Rice and his colleagues[5] did in a similar situation, we assume that the number of segments r_b in a compact bundle (akin to their "helical section") is the same as in an extended bundle. Therefore

$$br_b = r \tag{2}$$

If bundles are not of the same length, and a distribution of bundle sizes exists, then r_b is an average parameter.

As noted in Section 1, we also characterize the polymeric chain from the point of view of kinds of pairs of neighboring bundles N_{ce}, N_{cc}, and N_{ee}. For instance, denoting each compact bundle by c and each extended one by e, in the sequence

$$cccceeeecc \tag{3}$$

we have $b = 10$, $b_c = 6$, $N_{ce} = 2$, $N_{cc} = 4$, and $N_{ee} = 3$.

Since the maximum number of partitions in a row of m objects is $m - 1$, we have

$$N_{cc} + N_{ee} + N_{ce} = b - 1 \simeq b \tag{4}$$

Neglecting again unity for sufficiently long chains, we have also

$$2N_{cc} + N_{ce} = 2b_c \tag{5a}$$

$$2N_{ee} + N_{ce} = 2b_e \tag{5b}$$

It will be convenient at some stages to use fractions x_{ce} defined by

$$x_{ce} = \frac{N_{ce}}{N_{cc} + N_{ce}} = \frac{N_{ce}}{b_c + (N_{ce}/2)} \tag{6}$$

The system is characterized by a coordination number z; among other things, this takes care of the excluded volume problem. In general, z depends on temperature and density;[12,13] it is obtainable from diffractometric measurements via an integration of the pair radial distribution function $g(R)$. Thus, each polymer segment has z nearest neighbors, and so has each monomer molecule. We denote by ζ the number of nearest neighbor sites which are occupied by segments directly connected to a given segment. Thus, in a chain without branches and without cycles, disregarding the end-of-chain effects, the average value of ζ for the chain is 2. At a segment at which branching occurs, where we have, say, $\zeta = 4$, there are also two values of $\zeta = 1$ at the end of the two branches, and the average of $\zeta = 2$ is preserved. On the other hand, in molecules containing cycles, an average value for the chain of $\zeta > 2$ will be obtained.

According to our definitions, each polymer segment has $z - \zeta$ external nearest neighbors with which it interacts. Consider a segment in a compact bundle surrounded by compact bundles. Denote by $(z - \zeta)\nu_m$ the average number of interactions with other polymer segments (nonnearest neighbors in the same chain or in other chains). The remainder, that is $(z - \zeta)(1 - \nu_m)$, is the number of interacting pairs of our segment with its nearest neighbor solvent molecules. Take now a segment in a compact bundle surrounded by extended bundles. Such a segment is also an average representative, since in a compact bundle we might have half of the segments adjacent to an extended bundle and another half adjacent to a compact bundle. (The procedure we use is equivalent to breaking all compact bundles into halves, and then reassembling the halves adjacent to other compact bundles separately from the halves adjacent to extended bundles.) Now we denote by $(z - \zeta)\nu_t$ the average numbers of interactions of such a segment with other polymer segments (indexes m and t denote "middle" and "terminal," since we are dealing with location in a string of compact bundles). Analogously, for a segment in an extended bundle we denote by $(z - \zeta)\nu_e$ the average number of interactions with other polymer segments.

The parameters ν_m, ν_t, and ν_e are of importance for solutions other than highly dilute. Another polymeric chain might then touch a bundle

under consideration. Also, in view of entanglements, another bundle from the same macromolecule might touch a given bundle.

If the polymer concentration in solution is not very high, all $z - \zeta$ external interactions of a segment in an extended bundle are directed towards solvent molecules, and characterization of such segments in terms of a ν_e parameter is not necessary. Since our treatment is not significantly affected by specific values of ν-type parameters, for the time being we shall confine ourselves to the simpler version with $\nu_e = 0$. Thus, the definitions of ζ, ν_m and ν_t given about complete the specification of the polymer chain structure.

We now pass to interactions of monomer molecules and of polymeric segments. There are three types of them: 1-1, 1-2, and 2-2. In agreement with Flory[9,10] we define the average interaction energy $u_{yy'}$, per pair $y-y'$ by

$$u_{yy'} = - \eta_{yy'}/v \tag{7}$$

where v is the segment volume. Except for a very improbable case of a pressure so high that the repulsion is dominant, $\eta_{yy'}$ represents an attractive interaction. Therefore, $u_{yy'}$ is a positive quantity.

3. CONSTRUCTION OF THE MODEL

For the partition function of our liquid system we being with the function constructed by Flory.[9,10] For simplicity, instead of the entire system, we shall now study a subsystem containing one polymer molecule plus its share of N_1/N_2 monomer molecules. The partition function of the subsystem has the same form as that for the entire system,[9,10] that is,

$$Q = Q^{\mathrm{comb}} Q^{fv} Q^c \tag{8}$$

The combinatorial factor Q^{comb} is related to the fraction of the three-dimensional space taken by polymeric chains and the other part taken by the solvent and is independent of the compactness (or otherwise) of the chain. The free volume factor Q^{fv} depends on the experimental values of molar volume V (or segmental volume v), of isobaric expansivity α, and of isothermal compressibility κ_T. We shall now concentrate on the configurational (or interactional, or potential energy) factor Q^c. We make summation of all possible kinds of interactions in the subsystem, and express the respective energies in terms of the parameters defined in the preceding section. We also note that there is a certain number of ways, call it Ω, of realizing a configuration with a prescribed number b_c of compact bundles

and with b_e extended bundles. The result is

$$
Q^c = \sum_{b_c, b_e, N_{ce}} \Omega \exp\left\{ \frac{-\beta}{v} - \left[\frac{N_1 z \eta_{11}}{2N_2} + r_b(z - \zeta) \right. \right.
$$

$$
\times \left\{ b_c \left[(1 - x_{ce})(1 - \nu_m) + x_{ce}(1 - \nu_t) \right] + b_e \right\} \left(\eta_{12} - \frac{\eta_{11}}{2} \right)
$$

$$
\left. \left. + \frac{1}{2} r_b(z - \zeta) b_c \left[(1 - x_{ce})\nu_m + x_{ce}\nu_t \right] \eta_{22} \right] \right\} \tag{9}
$$

The first term in the exponential expression represents solvent–solvent interactions, the second interactions of middle compact bundles (surrounded by other compact bundles) with solvent molecules, and so on. The parameter $\beta = (kT)^{-1}$, where k is the Boltzmann constant and T the thermodynamic temperature. For a given relative mass (molecular weight) M of the polymer, the value of b is fixed. Equation (9) contains then two variables, such as b_c and N_{ce}. The latter is related to x_{ce} via Equation (6); we have written (9) in terms of x_{ce} for brevity.

Consider now the factor Ω. A bundle is either compact or extended. Clearly, the problem treated first by Ernst Ising at Hamburg University in his Ph.D. thesis on ferromagnetism[14] resurfaces here once more: we have a set such that its elements can occur in one of two possible states. Our chain is a quasi-one-dimensional entity. Rothstein[15] has analyzed on the quadratic lattice configurations of model chains (beads and rigid links, with links meeting at a bead at 90° and 180°). He has found that the set of chain configurations splits up into mutually inaccessible families. No such splitting has been found in one dimension, so the fact that our problem can be treated in one dimension is an advantage. From combinatorics we have

$$
\Omega = \frac{b_c! \, b_e!}{(b_c - N_{ce}/2)! \, (b_e - N_{ce}/2)! \left[(N_{ce}/2)! \right]^2} \tag{10}
$$

We can now apply the usual procedures of statistical mechanics (or of information theory): the maximum term $Q^{c\max}$ of Q^c is taken; the Stirling approximation is introduced into (10); then two extremizations are performed, one by differentiation with respect to b_c, treating N_{ce} and the remaining parameters constant, the other vice versa:

$$
\left(\frac{\partial \ln Q^{c\max}}{\partial b_c} \right)_{N_{ce}} = 0 \tag{11a}
$$

$$
\left(\frac{\partial \ln Q^{c\max}}{\partial N_{ce}} \right)_{b_c} = 0 \tag{11b}
$$

The results are

$$\ln \frac{b_c(b - b_c - N_{ce}/2)}{(b - b_c)(b_c - N_{ce}/2)} + \frac{\beta(z - \zeta)r_b}{2v}$$

$$\times \left[\nu_m - 2(\nu_m - \nu_t)\left(\frac{N_{ce}/2}{b_c + (N_{ce}/2)} \right)^2 \right](\eta_{11} + \eta_{22} - 2\eta_{12}) = 0 \quad (12)$$

$$\ln \frac{(b_c - N_{ce}/2)(b - b_c - N_{ce}/2)}{(N_{ce}/2)^2}$$

$$+ \frac{\beta r_b}{v}(z - \zeta)(\nu_m - \nu_t)\left(\frac{b_c}{b_c + N_{ce}/2} \right)^2 (\eta_{11} + \eta_{22} - 2\eta_{12}) = 0 \quad (13)$$

We note that $2\eta_{12}$, η_{11}, and η_{22}, which had different factors in (9), now have identical factors. Equations (12) and (13) contain the same two unknowns, b_c and N_{ce}. The equations are not explicit in the unknowns, and numerical solutions of this pair of equations are reported in Part 2[11] for various energy terms $\eta_{11} + \eta_{22} - 2\eta_{12}$.

The factors featuring in the logarithmic terms in Equations (12) and (13) can be related to N_{ce} and N_{ee} via Equations (5). The substitution leads to a certain improvement in perspicuity, for Equation (13) in particular. The results are

$$\ln \frac{b_c N_{ee}}{b_e N_{cc}} = - \frac{\beta(z - \zeta)r_b}{2v} \left[\nu_m - 2(\nu_m - \nu_t)\left(\frac{N_{ce}/2}{b_c + N_{ce}/2} \right)^2 \right]$$

$$\times (\eta_{11} + \eta_{22} - 2\eta_{12}) \quad (14)$$

$$\ln \frac{4N_{cc}N_{ee}}{N_{ce}^2} = \frac{\beta(z - \zeta)(\nu_m - \nu_t)r_b}{v} \left(\frac{b_c}{b_c + N_{ce}/2} \right)^2 (\eta_{11} + \eta_{22} - 2\eta_{12})$$

$$\quad (15)$$

Before we discuss various consequences of (14) and (15), let us make a simple comparison. The classical and widely used quasichemical formula of Guggenheim[16,17] can be written in our notation as

$$\ln \frac{4N_{cc}N_{ee}}{N_{ce}^2} = \frac{\beta}{v}(\eta_{11} + \eta_{22} - 2\eta_{12}) \quad (16)$$

Thus, (16) is a simplified version of (15); certain factors absent from (16) have been introduced in the derivation of (15).

Interesting simulation of simple chains (n-alkanes, that is snakes from the point of view of graph theorists) was made by Khalatur.[18] He has generated the chains according to the procedure of Yoon and Flory[19] by the Monte Carlo method. The polymer–polymer interaction parameter, corresponding to our η_{22}, was varied. An increase of η_{22} has produced a distinct decrease in volume pervaded by each chain. As noted by Khalatur, similar results have been reported earlier by Dashevskii.[20] Now, Eq. (15) implies that an increase in η_{22} should produce higher values of N_{cc}. It follows from the definition that an increase in N_{cc} has to be accompanied by a decrease in pervaded volume. If $b_c > b/2$, simultaneously N_{ce} becomes smaller; thus the sharp effect observed by Khalatur. We find that various approaches lead to the same mutually coherent picture. We shall consider more in detail the effect of interaction energies (and of temperature) upon macromolecular sizes in Part II.[11] Before, however, discussing various other consequences of the present model we shall provide the necessary connection to the Flory theory of liquids and solutions in the following section.

4. THERMODYNAMICS OF SOLUTIONS

The theory of equilibrium properties of liquids and solutions developed by Flory[9] gives by far the best agreement with the experimental results. There exists considerable literature on the theory. Among other things, the theory has been satisfactorily extended to liquid metals and to binary liquid alloys.[21] Further, it has been extended to ternary mixtures,[22] and very good results obtained for a system of organic liquids, a system of condensed gases, and also for liquid metal alloys. Given the virtual universality of the theory, we had on purpose used the Flory partition function, Eq. (8), to represent our system. Subsequently, the configurational factor Q^C was represented in terms of special parameters characterizing compact and extended bundles of the polymeric chain. We shall now provide the connection between these parameters, and the standard parameters used to represent the Q^C term.

First, we write the configurational energy U^c for the system [cf. Eq. (7)] as

$$- U^c v = N_{11}\eta_{11} + N_{22}\eta_{22} + N_{12}\eta_{12} \tag{17}$$

where N_{yy} represents the number of interacting pairs y–y'. The configurational energy of the subsystem considered in the preceding section is U^c/N_2. Flory[9] has introduced a parameter s which is a measure of the interacting surface area, namely, s_y is the number of interaction contact

sites per y-type segment. Parameters s_1 and s_2 are related to N_{yy}, s by[9]

$$N_1 s_1 = 2N_{11} + N_{22} \tag{18a}$$

$$N_2 r s_2 = 2N_{22} + N_{12} \tag{18b}$$

Since $r_1 = 1$ in our system, the r_1 factor has been omitted in the left-hand side of Eq. (18a), and the subscript has been dropped from r_2. Equations (18) have the same form as Eqs. (5). From the substitution of (18) into (17) we have

$$-U^c = (N_1 s_1 - N_{12})\frac{\eta_{11}}{2v} + (N_2 r s_2 - N_{12})\frac{\eta_{22}}{2v} + N_{12}\frac{\eta_{12}}{v} \tag{19}$$

On the other hand, in terms of the treatment of compact and extended bundles in the preceding section [cf. the exponential term in Eq. (9)], we have

$$-U^c = (N_1 z - N_{12})\frac{\eta_{11}}{2v}$$

$$+ N_2 r_b (z - \zeta) b_c \big[(1 - x_{ce}) \nu_m + x_{ce} \nu_t \big] \frac{\eta_{22}}{2v}$$

$$+ N_2 r_b (z - \zeta) \big[b_c \big[(1 - x_{ce})(1 - \nu_m) + x_{ce}(1 - \nu_t) \big] + b_e \big] \frac{\eta_{12}}{v}$$

$$\tag{20}$$

By comparison of the respective right-hand side term of (19) and (20) we have first

$$s_1 = z \tag{21}$$

Further, on the basis of the random mixing approximation,[9] N_{12} in (19) is given by

$$N_{12} = \frac{N_1 N_2 r s_1 s_2}{N_1 s_1 + N_2 r s_2} \tag{22}$$

Therefore, introducing the symbol f for

$$f = r_b(z - \zeta) - \big[b_c \big[(1 - x_{ce})(1 - \nu_m) + x_{ce}(1 - \nu_t) + b_e \big] \tag{23}$$

we have

$$s_2 = \frac{f N_1 z}{r(N_1 z - f N_2)} \tag{24}$$

Since the partition function of our system has been cast in the Flory form of Eq. (8), Eqs. (21) and (24) assure the complete compatibility of our treatment with the Flory theory of the liquid state.

In calculations based on the Flory theory, several approaches to the s parameters have been used. One consists[23] in putting $s_1 = s_2 = 1$, obviously a crude assumption. Another consists in treating the ratio s_2/s_1 as an adjustable parameter, together with an energetic parameter such as $\eta_{11} + \eta_{22} - 2\eta_{12}$. A third possibility consists in the use of group surface area schemes, such as the Bondi scheme.[24] As noted by Eichinger and Flory[25] the group schemes tend to overestimate the s_2/s_1 ratio. Considerable overestimates have been found in calculations for a series of systems of natural rubber with organic solvents.[26]

Return now to one of the two extreme cases with which we have started this paper: the "ideal" fully extended quasilinear chain. For such a chain the parameters ν_m and ν_t are zeros by definition, in Eq. (23) we have $b_e = b$, and f acquires its "ideal" or maximum value, namely, $(z - \zeta)r$ [see Eq. (2)]. In a real system, the more compact it is, the smaller the corresponding value of f. For a given z, a decrease in f produces a decrease in s_2; this at a rate faster than linear, since simultaneously the numerator is decreasing and the denominator is increasing. Thus, any scheme which does not take into account the compactness of parts of the polymeric chain has necessarily to *overestimate* the s_2/s_1 ratio—as indeed is observed.

5. DISCUSSION

For simplicity we have considered a monodispersive system. Generalization of the present theory to polydispersive systems is possible. Alternatively, the present equations are applicable to polydispersive systems as they stand, only some of the quantities become averages over distributions of molecular masses.

The model discussed does not take special cognizance of chain entanglements, except for the fact that values of the parameters ν_m, ν_t, and ν_e are affected by them. A detailed treatment of entanglements can be developed in terms of knots and linkages, as proposed by Frank-Kamenetskii and his colleagues,[27,28] and discussed in Chapter 9 of Ref. 29.

There is no reason why a relationship between chain conformation, rigidity, and thermodynamic properties should be limited to very long chains. Interesting properties of oligomeric molecules of alkynes have been pointed out by Kehiaian,[30] and enthalpies of mixing H^E of 1 − hexyne and 3-hexyne with some hydrocarbons have been measured by Wilhelm, Inglese, Grolier, and Kehiaian.[31] As noted in Ref. 31, 3-hexyne is a more rigid molecule that 1-hexyne; multiple bonds result in larger rigidity, and in 1-hexyne the remainder of the molecule constitutes a relatively flexible tail. At 298.15 K 1-hexyne has the volume $V = 115.44$ cm^3 mol^{-1}, enthalpy of

vaporization $H^{vap} = 32.10$ kJ mol^{-1}. The respective values for 3-hexyne are $V = 114.16$ cm^3 mol^{-1} and $H^{vap} = 34.99$ kJ mol^{-1}. The normal boiling points of these hydrocarbons are, in the same order, $T_b = 344.5$ K and $T_b = 354.6$ K. Wilhelm *et al.*[31] point out the importance of geometrical packing in determining the thermodynamic properties. Let us assume that the intersegmental interactions in both hydrocarbons are comparable. More efficient packing in 3-hexyne should produce shorter average intersegmental distances, and thus [see an interaction potential $u(R)$ curve, such as in Fig. 4.2.1 in Ref. 29) larger absolute values of the configurational energy U^c. Consequently, 3-hexyne should have smaller molar volume, higher vaporization enthalpy, and higher normal boiling point than 1-hexyne—as indeed is observed.

Wilhelm, Inglese, Grolier, and Kehiaian[31] have analyzed their experimental enthalpies of mixing H^E by calculating the contribution of orientational forces to the Helmholtz excess function of mixing A^E from the equation of Pople[32] in terms of dipole moments. The resulting values are quite small, so the main contribution to H^E has to be of a different origin. We note that in all cases H^E values obtained by Wilhlem *et. al.*[31] for a given hydrocarbon with 1-hexyne are higher than for the same hydrocarbon with 3-hexyne. An explanation of the same kind as given above for pure alkynes is applicable. Addition of 1-hexyne to a given hydrocarbon produces a structure which is *less* compact than if more rigid 3-hexyne is added. Consequently, in binary mixtures containing 1-hexyne we have larger average intersegmental distances $\bar{R}$ and less negative (smaller absolute values) pair interaction energies $u(R)$. The total configurational energy U^c is also less negative, and we have H^E (1-hexyne mixtures) > H^E (3-hexyne mixtures). Again, our approach predicts correctly the observed behavior.

Consider now briefly connections of the present structural model, if any, to structures of polymer-containing phases other than solutions: melts, amorphous solids, and crystals. As for melts, Schelten and Stamm[4] have found small but distinct differences between the pair radial distribution functions of polyethylene and *n*-hexatriacontane. They note deviations of the experimental scattering functions from the respective Debye functions. These differences have been already explained by Yoon and Flory[33] in terms of configurational geometry. Of course, our model of chains in solution represents an attempt to seize the geometry in a relatively simple way. Interesting also in the present context is that in 1945 Charlesby[34] had pointed out the existence of what he called the memory effect in polyethylene films: conservation of orientation even after prolonged heating above the melting point. Much later, Kamel and Charlesby[35-37] reported pulsed NMR spin–spin relaxation (T_2) spectra for solid and

molten polymers, including copolymers.[36] Their results became available when the work described in this paper was already in progress. Kamel and Charlesby have found three components in the spectra of the melts: one (relatively small) called T_{2L} represents relatively short and highly mobile chains, which are sometimes present; a second called T_{2S} corresponds to what had been the amorphous component before melting; the third component called T_{2X} represents relatively dense well-packed regions resulting from melting of crystalline domains. Concentrations of the components were determined. It is tempting to transfer our model of chains in solution to melts, and identify the main components of the spectra: T_{2X} with compact bundles and T_{2S} with extended bundles. One would then say that Kamel and Charlesby have determined the average b_c/b values for their polymers.

As for solid amorphous polymers, quite a variety of conformational models have been proposed, as reviewed for instance by Przygocki.[38] Most of these models, including the meander model of Pechhold,[3] involve strongly exaggerated notions of the extent of order reigning in amorphous polymers. Fischer and Dettenmaier[39] have reviewed the experimental data and found no support for long-range-order models such as the meander model. Further, a careful analysis of all the pertinent experimental evidence has led Flory[40] to the conclusion that only very short-range correlations of the axes of neighboring chain sequences exist.

In semicrystalline polymers we have again the parentage relationship to our model already discussed for melts, with crystalline stems related to compact bundles. A considerable literature has been devoted to the discussion of adjacent vs. nonadjacent reentry of a macromolecule chain into the same crystalline lamella during solidification. Of course, the supposedly turning around crystalline stem does not correspond to any structure in any phase discussed (or mentioned) in this paper. In his Concluding Observations at a Farady Discussion, Flory[41] has expressed the hope that rationality may eventually prevail in this area. There are, however, still attempts to justify adjacent reentry with various more or less specious arguments. It has to be said that adjacent reentry occurring repeatedly cannot be reconciled with the physics of polymeric chains, in particular because of the existence of excluded volume of each stem emerging from the crystalline part. At the same time, such reentry would violate everything the theory of information has taught us.[42–46] As discussed elsewhere (Refs. 43, 44, 46 and Chapter 3 of Ref. 29), statistical mechanics is a consequence of the theory of information. Thus, an important part of polymer science would lose its firm basis at the same time; only a tenuous connection to semiergodicity would remain.

Macromolecules in general have branches, and branching of polyethylene has been studied by Rueda, Balta Calleja, and Hidalgo[47] with x-ray

diffractometry and IR spectroscopy. The Madrid group has concluded[47] that structures of low-density polyethylene can only be explained by *interruptions* of crystalline lamellae by amorphous regions. But let us for simplicity confine ourselves to chains without branches. For every polymer crystallization process, fully adjacent reentry would require the existence of a large number of Adjacent Reentry Demons, somewhat similar in their operation to the Maxwell Demon. Each of the Demons would have to scrutinize incoming candidates (that is: polymeric chains) and send back into the amorphous oblivion all chains but the "right" one. An appeal to rationality is worth making when deciding whether such demons exist.

Finally, let us return to polymer solutions. The existence of bundles of the two kinds is compatible with the presence of twists and entanglements. It is also compatible with the usual Gaussian statistics. Electron microscopy studies of Aharoni[48–51] show that a polymeric chain consists of regions of high density separated by regions of lower segmental density. This has been found in amorphous materials produced by forced and very fast drying of solutions, such that the polymer structure characteristic for solutions has been preserved. The instantaneous shape and segmental density of individual chain molecules are neither symmetrical nor Gaussian. However, both the shape and segmental density become spherical and Gaussian when an average is taken over all angles and/or a large population of molecules. The usefulness of direct studies of individual polymeric chains has already been stressed elsewhere (Chap. 9 of Ref. 29). The high- and low-density regions observed by Aharoni provide a direct experimental confirmation of our model of compact and extended bundles in a polymeric chain.

ACKNOWLEDGMENTS

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