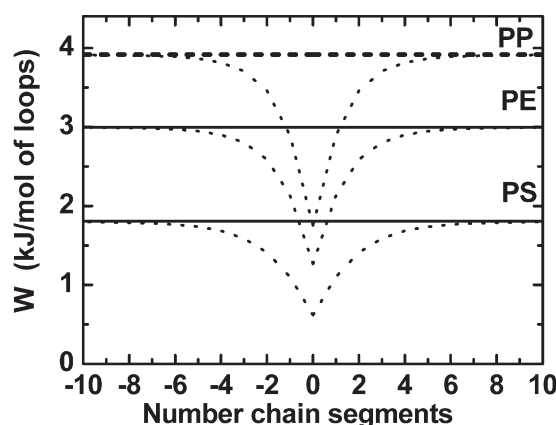


Analysis of the Adequacy of the Representation of Entanglement Effects by Chain Loops^a

José A. Martins*

It is generally considered that polymer chains are intertwined or “entangled” – because they cannot penetrate each other – and that these entanglements are responsible for melt elastic properties. There is no physical definition of entanglement. They are considered to be binary interactions between polymer chains and represented with the looping picture or by slip-links. The interaction energy of chain loops and of two Kuhn monomers is evaluated for several polymers. It is lower than the melt thermal energy, implying that chain loops or any other binary interactions between chain segments cannot account for the properties assigned to entanglements.



Introduction

Entanglements play a central role in the behaviour of all macromolecules, providing that their molecular weight is above a critical value. Most research work published so far aiming to clarify the nature of entanglements has been focused mainly on their effects. Their nature remains still unclear.

For example, crystallisation kinetics and rheological experiments were performed with unentangled polymers (nascent powders) and the results obtained were compared with those of commercial polymer grades.^[1,2] As expected, it was found that the unentangled polymer crystallises faster (because of its lower viscosity), and that if annealed at

a high temperature for a time long enough it becomes progressively more entangled (because of the melt relaxation to a state of higher entropy). The shear modulus increases with time until it reaches a plateau value. Molecular dynamics simulations of the development of entanglements in a fully disentangled polymer melt were performed recently.^[3] The study concluded that, for chains with up to around 20 entanglements, the development of entanglements occurs faster than the time need for the chains to get their unperturbed dimensions, suggesting that topological constraints do not play an important role in the development of the “entanglement network”. Results of other works do not differ too much from those mentioned above, that is, they do not provide any insight into the physical nature of entanglements.

Different groups of authors have tried to clarify the physical nature of entanglement by chain dynamics and atomistic molecular dynamics simulations. Many different approaches have been used, including coarse-grained models,^[4,5] without any fingerprint of the polymer structure at a molecular level, united atom and explicit atom models.^[6,7] In coarse-grained models, information about the effects of entanglement is extracted mainly from chains’ dynamics in the melt. In the atomistic models, that

J. A. Martins

Departamento de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém 4800-058 Guimarães, Portugal, and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal
E-mail: jamartins@dep.uminho.pt

^a Supporting information for this article is available at the bottom of the article’s abstract page, which can be accessed from the journal’s homepage at <http://www.mts-journal.de>, or from the author.

information is obtained mainly from the evaluation of different distribution functions.

Some authors have considered that entanglement constraints must lead to attractive forces between chains, which must be long-lived. Also, its confinement to a certain number of chain segments must imply contacts within, and between, the participating chain segments.^[4] “Incidental” and “persistent” contacts between chain segments were obtained from molecular dynamics simulations of individual entanglements in polymer melts. In these simulations, the contacts were defined as binary interactions: two monomers are in contact when their separation distance is lower than 1.5σ , where σ is the distance at which the interparticle Lennard-Jones potential is zero.

However, entanglements are also represented in other ways, and the way how they are represented is used to build models to explain their behaviour – more specifically, the properties related to entanglements, such as the plateau modulus, the increase in the zero shear rate viscosity with an exponent of 3.4 in the molecular weight for chains with \bar{M}_w above the critical molecular weight, and the viscoelastic properties of all macromolecules (polymers, DNA and proteins). They are represented as a hook in a rope,^[8,9] by a slip-link through which chains can pass freely,^[10,11] considered as purely entropic topological restrictions,^[9] the result of short-range attractions represented by a Lennard-Jones 6–12 potential, but they may also be represented by polymers on a lattice with either zero or infinite potentials. Modelling an entanglement as a weaker constraint, namely as a slip-link, was used to investigate how these constraints change the deformation behaviour in rubbers.^[11]

Several different models have been proposed to explain chain entanglements and relate the polymer molecular weight with chain dimensions and melt viscoelastic properties. A review of some of these models may be found in ref. [12,13]. Among them is the number of chains within the confinement volume of a tube section between entanglements, $P_e \approx a^3/v_k n_{k,e}$, where a is the tube diameter, v_k the volume of a Kuhn monomer and $n_{k,e}$ the number of Kuhn monomers between entanglements. This concept was proposed by Lin,^[14] and it was found that, for all flexible polymers $P_e \approx 20$, that is, around 20 chain segments overlap in a tube section between entanglements. However, no information for the physical nature of entanglements can be obtained from this concept.

Another model is based on the packing length concept due to Witten, Milner and Wang and further developed by Fetters et al.^[15,16] The packing length is defined as the ratio between the volume of the chain and the unperturbed average square end-to-end distance, $p = V/\langle r^2 \rangle_0$. A physical meaning can be extracted for the packing length if the volume of the chain is expressed as the product of the volume of one chain segment by the number of segments in the chain, $V = nV_{\text{seg}}$, and if $\langle r^2 \rangle_0$ is defined in terms of the

parameters of the real chain as $\langle r^2 \rangle_0 = C_\infty nl^2$, where C_∞ is the characteristic ratio and l the length of a chain segment (bond length). Since a chain segment may be viewed as a cylinder with length l and diameter h , the packing length may be expressed as $p \sim h^2/C_\infty l = h^2/l_k$, where l_k is the length of a Kuhn monomer. A chain may then be viewed as made up of freely joined rods of length l_k and diameter h , and the packing length is proportional to the ratio of the cross-sectional area to the length of each rod. This parameter, the packing length, is related to the molecular weight between entanglements, plateau modulus and tube diameter by $M_e \sim \rho p^3$, $G_N^0 \sim T p^{-3}$ and $a = Cp$, respectively, where C is a constant of around 20. Besides the correlations indicated above, no information can be obtained with this model regarding the physical nature of entanglements.

Implicit to all these approaches is that it is forbidden for the chains to overlap and cross, which implies that there is always a physical interaction between neighbouring chain segments separated by the interatomic spacing, and the absence of this interaction when chain segments are farther apart.

It was considered in a recent work of Dealy and Larson that the *strong topological interaction* due to entanglements does not result necessarily from the looping of one molecule around another, “*but more simply from the fact that the displacement of one molecule due to Brownian motion is highly constrained laterally by the other molecules*”, and that this constraint results from the uncrossability of polymer chains.^[17] Emphasizing that entanglement effects don't result necessarily from chain loops do not clarify the role of chain loops in entanglement effects. A surprising and contradictory statement is the assignment of entanglement effects to the constraining effect of neighbouring chains in the motion of one chain segment – the chain uncrossability. Physically, chain uncrossability results from hard-core repulsive interactions, and repulsive potentials cannot explain elastic effects such as those responsible for plateau modulus in entangled polymer melts or the increase in the zero shear rate viscosity with an exponent of 3.4 in the weight-average molecular weight.

It is the purpose of this work to critically analyse the “haze” definition of entanglement expressed in the above sentences. Particularly, this work aims to verify whether it is physically acceptable to represent entanglements by chain loops or by binary interactions between two chain segments of different chains, or of the same chain, such as is used in the slip-link representation of entanglements. It is accepted by most researchers that the looping picture is an inadequate representation of entanglement; however, there is no physical proof of this inadequacy.

It was found that stiff polymer chains, having a good example in DNA, show the same entanglement effects as flexible chains. Mainly because of this experimental result,

it was recognised that the looping picture is a secondary aspect of the entanglement interaction.^[18] A model was then proposed to understand entanglements in terms of local orientational correlations between chains. It was considered that entanglement effects result from the formation of dynamic clusters, with relative order, which are effective when their “aspect ratio” reaches a critical value similar in magnitude to the value needed to have long range order in liquid crystalline polymers.^[18] However, the effective attractive interactions responsible for the clustering were considered to be entropic and topological in nature! It must be stressed again that this recognition of the inadequacy in the representation of entanglements by chain loops did not result from any quantitative evaluation of the interaction energy between the loop and chain.

In addition, it is known from electrodynamics that fluctuations in electric and magnetic fields occur not only because of thermal agitation due to Brownian motion, but also because of the quantum-mechanical uncertainties in the position and momenta of particles and in the strengths of electromagnetic fields. Quoting Parsegian,^[19] “the momentary positions and electric currents of moving charges act on, and react to, other charges and their fields”. “Charge-fluctuation” or van der Waals force arises as the result of the collective coordinated interactions between electric charges, currents and fields averaged over time. In other words, neutral charges in random motion interact with van der Waals interactions. This means that the constraining by other molecules of the displacement of one molecule due to Brownian motion implies the existence of van der Waals interactions between the interacting chain segments. The magnitude of this interaction depends on the geometry of the interacting segments. So far, there are no values in the literature, even thought approximate, for the van der Waals interaction energy between polymer chain segments at the molten state.

Below, the van der Waals interaction energy between two aligned chain segments, not necessarily strictly parallel, and the interaction energy between a loop and a chain at its centre are evaluated. It is expected that these evaluations will contribute to the clarification of the physical nature of entanglement interactions, since they exclude any sort of binary interaction between chain segments (of the same or of different chains) as a possible source of entanglement effects.

Interaction Potential Energy between Two Parallel Chain Segments

Expressions for evaluating the total dispersion energy between two parallel and aligned chain segments were derived in 1962 by Salem.^[20] They consider only dipole/dipole interactions and agree with a previous evaluation for

the interaction potential energy between two parallel rods with infinite length made by de Rocco and Hoover in 1960.^[21] Assumptions made by Salem were criticised by Zwanzig^[22] and the extension of Salem's Equation to periodic linear arrays was carried out by McCullough and Hermans.^[23] A review of some of these works was written by Margenau and Kostner.^[24]

The problem for evaluating the interaction potential energy between two parallel rods was well stated by de Rocco and Hoover.^[21] It is assumed that the atoms are distributed according to a function of position, which for two parallel chains is given by Equation (1). The interaction of pairs of atoms is represented by a pair potential $W(r_{ij})$, where r_{ij} is the distance separating atom n_i in chain 1 from atom n_j in chain 2 (Figure 1). The attractive contribution of $W(r_{ij})$ is expressed by a London law $W = -C/r^6$, where C is the London constant for the interaction between the two rods. In modern theory, this is related to the Hamaker constant A by $A = \pi^2 \rho_1 \rho_2 C$, where ρ_1 and ρ_2 are the number of atoms per unit of volume in rods 1 and 2, respectively. Information about the evaluation of Hamaker constant is given below. The detailed evaluation of $W(r_{ij})$ is described next.

If the separation distance between two parallel chains, taken from the axis of each chain, is D , and the separation distance between consecutive molecules in the chain is λ (Figure 1), then the distance between any n_i^{th} atom of chain 1 and any n_j^{th} atom of chain 2 is given by

$$r = [D^2 + \lambda^2(n_i - n_j)^2]^{1/2} \quad (1)$$

Considering now the additivity of interactions, the attractive interaction potential energy is expressed as a double sum of the pair potential interactions running from $n_i = 1$ to N , for all n_i atoms of chain 1 with all n_j atoms of chain 2, from $n_j = 1$ to N , and vice versa (see Figure 1),

$$W_c = -\frac{C}{r^6} = -C \sum_{n_i=1}^N \sum_{n_j=1}^N \frac{1}{[D^2 + \lambda^2(n_i - n_j)^2]^3} \quad (2)$$

Counting separately the interactions between the n_i^{th} and n_j^{th} atoms with $n_i = n_j$ and $n_i \neq n_j$, the last counting

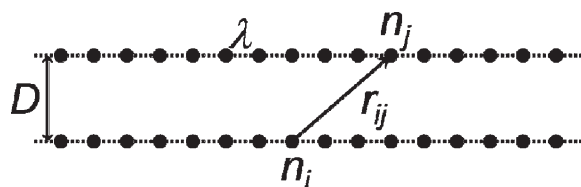


Figure 1. Model for evaluating the interaction potential energy between two parallel chains with length $L = N\lambda$.^[10] The distance between the chains' axes is D , the separation between consecutive molecules in the chain λ , and the distance between two molecules in each chain $|r_{ij}|$, given by Equation (1).

twice because one has to consider interactions of atoms in chain 1 with those of chain 2 and vice versa, then:

$$W_c = -C \left[\frac{N}{D^6} + 2 \sum_{x=1}^{N-1} \frac{(N-x)}{(D^2 + \lambda^2 x^2)^3} \right] \quad (3)$$

In this equation, λx is the distance along the axis of one chain between atoms in chains 1 and 2, $x = |n_i - n_j|$. Equation (3) is the discrete version of the interaction potential energy between two parallel chains with three assumptions only: the pairwise additivity of interactions, the chain isotropy and the absence of intrachain van der Waals interactions.

The corresponding continuous version is obtained under the additional assumptions of very long chains and chain separation D much lower than the chain's length $L = N\lambda$. The result is

$$W_c = -3\pi CL/8\lambda^2 D^5 \quad (4)$$

It is a fact that pairwise additivity, intrinsic to Equation (3) and (4), ignores the influence of neighbouring atoms on the interaction between any pair of atoms. This problem is avoided in the Lifshitz theory of van der Waals interactions because the atomic structure is ignored and the interacting bodies are treated as continuous media.^[19,25]

The forces between them are now derived in terms of their dielectric constants and refractive indexes. In this new formulation, the geometric dependence of the interaction potential energy, expressed in Equation (3) and (4), remains the same, the only difference being that, in the framework of Lifshitz theory, the Hamaker constant is expressed by:

$$A_{\text{total}} = A_{\nu=0} + A_{\nu>0} = \frac{3}{4} k_B T \left(\frac{\varepsilon - \varepsilon_0}{\varepsilon + \varepsilon_0} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \cdot \frac{(n^2 - n_0^2)^2}{(n^2 + n_0^2)^{3/2}} \quad (5)$$

where ε and ε_0 are the static dielectric constants for the polymer and vacuum, respectively, n and n_0 are the corresponding refractive indexes, h and k_B are the Planck and Boltzmann constants, respectively, T is the absolute temperature and ν_e is the main electronic absorption frequency in the UV ($\approx 2.4 \times 10^{15}$ Hz). The total Hamaker constant for two identical chains interacting across vacuum (which is usual in these conditions), contains an entropic zero-frequency contribution ($A_{\nu=0}$), which includes the Keesom and Debye dipolar contributions to the van der Waals interactions, and a dispersion energy contribution ($A_{\nu>0}$), which includes the London energy contribution.^[25] The different frequency sampling contribution may be explicitly included in the Hamaker

constant as,^[19,25]

$$A_{\text{total}} = \frac{3}{2} k_B T \sum_{n=0}^{\infty} \bar{\Delta}_{1n}^2 \quad (5a)$$

with $\bar{\Delta}_{1n} = [\varepsilon(i\nu_n) - \varepsilon_0]/[\varepsilon(i\nu_n) + \varepsilon_0]$, where $\varepsilon(i\nu)$ is the dielectric constant at the imaginary frequencies. For $n \geq 1$, $\nu_n = (2\pi k_B T/h)n$. The prime in \sum' indicates that the $n=0$ term is multiplied by $1/2$, yielding the zero-frequency contribution in Equation (5). Use of Equation (5a) requires knowledge of how the dielectric permittivity of polymer changes with frequency.

Israelachvili^[25] considered that the dielectric permittivity $\varepsilon(i\nu)$ of a medium varies with frequency ν in the same way as its atomic polarisability and expressed this frequency variation for $n \geq 1$ as

$$\varepsilon(i\nu) = 1 + \frac{(\varepsilon - n^2)}{(1 + \nu/\nu_{\text{rot}})} + \frac{(n^2 - 1)}{(1 + \nu^2/\nu_e^2)} \quad (6)$$

where ν_{rot} is the molecular rotational relaxation frequency (lower than 10^{12} s^{-1}) and, as mentioned above, ν_e is the main electronic absorption frequency in UV ($\approx 2.4 \times 10^{15}$ Hz). In Equation (6), as well as in Equation (5), n is the material refractive index. Israelachvili considered also that the dispersion energy is determined solely by this electronic absorption frequency, that is, $\nu_e = \nu_1$, and arrived at Equation (5) for the “symmetric case” of two phases interacting across vacuum. Equation (5) and (5a) neglect retardation effects due to the finite velocity of light. These effects are important for large separation distances between chain segments and/or long interacting chain lengths and imply a dependence of Hamaker constant on D . For the present case, where the interacting chain lengths are small, around 1 Kuhn monomer, and the separation distance between the interacting chains is equal to the intermolecular spacing, retardation effects can be ignored.

In the formalism used by Parsegian,^[19] Equation (3) and (4) are written as

$$W_c = -\frac{3}{2} k_B T \sum_{n=0}^{\infty} \bar{\Delta}_{1n}^2 \frac{1}{\pi^2 \rho^2} \left[\frac{N}{D^6} + 2 \sum_{x=1}^{N-1} \frac{(N-x)}{(D^2 + \lambda^2 x^2)^3} \right] \quad (3a)$$

and

$$W_c \approx -\frac{3}{8} \frac{\pi r_{\text{vw}}^4}{\nu^2} A_{\nu=0} \frac{L}{D^5} = \frac{9\pi}{16} \frac{k_B T r_{\text{vw}}^4}{\nu^2} \sum_{n=0}^{\infty} \bar{\Delta}_{1n}^2 \frac{L}{D^5} \quad (4a)$$

where ρ is the number of atoms per unit of van der Waals volume of chain segment, r_{vw} the chain van der Waals radius and ν the number of atoms per chain segment.

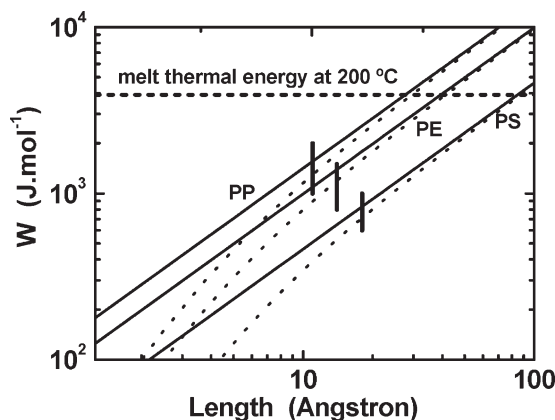


Figure 2. Absolute values of the interaction potential energy between parallel chain segments of different polymers evaluated with Equation (3) – dotted line – and Equation (4) – solid line – for segments starting with length λ up to 239λ , or 300 Å . Data used in this evaluation are in Table 1. The horizontal dashed line indicates the melt thermal energy. Vertical segments indicate the interaction energy between two Kuhn monomers for the different polymers (11 Å for iPP, 14 Å for polyethylene and 18 Å for polystyrene).

Considering one atom per chain segment ($\nu=1$), Equation (4a) is the same as that derived by de Rocco and Hoover and presented with the new formalism by Parsegian (see ref. [19], p. 177, Table C.6).

Results obtained with Equation (3) and (4) for the absolute value of the interaction potential energy of several polymers are indicated by dotted and solid lines, respectively, in Figure 2. For both cases, Equation (5) was used to evaluate the Hamaker constant. The data used to evaluate the interaction potential energy are in Table 1 and the Supporting Information. Only linear polymer chains are considered here. Because we are interested in evaluating the interaction potential energy at the molten state, the

temperature dependent parameters, namely the Hamaker constant and the number density of atoms per unit volume in each chain, were evaluated at 200 °C .

The interaction potential energy of two parallel Kuhn monomers of poly(propylene) (PP) and polyethylene, lengths of 11 and 14 Å , respectively, is around $1\text{ kJ} \cdot \text{mol}^{-1}$. That of a two Kuhn monomers of polystyrene, length 18 Å , is around $0.7\text{ kJ} \cdot \text{mol}^{-1}$. All these values are below the melt thermal energy, represented in the figure by the horizontal dashed line. For interactions between two Kuhn monomers, the deviation between the discrete and continuous equations, Equation (3) and (4), respectively, is around 15%. As expected, larger differences between the values evaluated with the two Equations occur for interacting chain segments with low length, and they almost vanish when this length increases to 60 Å (differences below 2%).

A note must be added here concerning the model shown in Figure 1 and the meaning of parallelism between chain segments. It can be shown that Equation (4) – and Equation (3) – is also valid when chains run in parallel, but are not necessarily straight. A helical arrangements of chain segments yields an Equation similar to Equation (4).^[26] In fact, the most probable situation in polymer melts is not that of strictly aligned and straight chain segments, but instead that of chain segments running in parallel, not necessarily straight. This is what is reported to occur in molecular dynamics simulation of polymer melts, yielding the “persistent” contacts between polymer chains mentioned in the Introduction.^[4]

Other Equations were derived for the interaction potential energy between parallel chains. Among these derivations are those obtained using the density functional theory^[27] and those considering the effects of multipole interactions (dipole/quadrupole and quadrupole/quadrupole interactions).^[28] It was shown that deviations between these Equations and the Equation *originally* derived by

Table 1. Data used to evaluate the interaction potential energy at $T=200\text{ °C}$. The absolute values of the interaction potential energy for a loop and a chain (W_l) – Equation (8) – and two parallel chains segments with a length equal to a Kuhn monomer (W_k) are indicated. The last row contains two values for W_k : the first was evaluated with Equation (4) and the second with Equation (3).

Parameter	Polyethylene	Poly(propylene)	Polystyrene
$A \times 10^{20}/\text{J}$	5.51	5.69	7.54
$C \times 10^{79}/\text{J} \cdot \text{m}^6$	5.64	5.82	1.03
$D/\text{Å}$	4.80	4.50	6.22
$\lambda/\text{Å}$	1.26	1.26	1.30
N_l	24	23	30
$L_l/\text{Å}$	30.2	28.3	39.1
$W_l/\text{kJ} \cdot \text{mol}^{-1}$	3.00	3.91	1.81
$l_k/\text{Å}$	14	11	18
$W_k/\text{kJ} \cdot \text{mol}^{-1}$	1.37/1.18	1.60/1.34	0.84/0.72

Salem do not exceed 4%.^[29] The reason for this difference is discussed below.

Interaction Potential Energy between a Loop and a Chain at its Centre

Since it is considered that, because of the chain intertwining, polymer chains cannot penetrate each other, below is evaluated the interaction potential energy between a loop and a chain at its centre. Furthermore, this is considered an adequate geometrical representation of chain intertwining (in many textbooks and manuscripts, entanglements are represented in this way).^[8,9,11] Figure 3 shows the geometrical construction used for this evaluation. We consider a closed loop of N_l atoms, but an open loop (or a helix turn) could have also been considered yielding a final result similar to the simpler geometrical representation of Figure 3. The separation between two consecutive n_j units is λ and the loop radius is R . A linear chain with N_c atoms, also with a separation between two consecutive n_i units of λ , crosses the centre of the loop. The distance between any n_j atom at the loop and any n_i atom at the chain is

$$r = \left\{ \left[(n_i - 1)\lambda + \frac{\lambda}{2} \right]^2 + R^2 \right\}^{\frac{1}{2}} = \left[\lambda^2 \left(n_i - \frac{1}{2} \right)^2 + R^2 \right]^{\frac{1}{2}} \quad (7)$$

Considering the additivity of interactions, and isotropy of the loop and chain with respect to their radius and axis, respectively, the interaction potential energy between the loop and chain is

$$W_l = -2 \sum_{n_i=1}^{N_c/2} \sum_{n_j=1}^{N_l} \frac{C n_j}{\left[\lambda^2 \left(n_i - \frac{1}{2} \right)^2 + R^2 \right]^3} \quad (8)$$

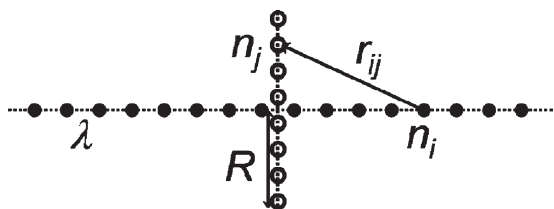


Figure 3. Model used to evaluate the interaction potential energy between a chain (filled circles) and a loop (open circles). The separation between consecutive molecules in the chain and at the loop is λ , the loop radius R and the distance between a molecule at the chain and another at the loop $|r_{ij}|$. The origin of the coordinate system is set at the crossing point between the loop plane and the chain axis.

The factor 2 results from the interactions at the right- and left-hand sides of the loop. Equation (8) may be written as

$$W_l = -\frac{2CN_l}{\lambda^6 N_c^5} \sum_{n_i=1}^{N_c/2} \frac{1}{\left[\left(\frac{2n_i-1}{2N_c} \right)^2 + \frac{1}{\alpha^2} \right]^3} \left(\frac{1}{N_c} \right) \quad (9)$$

with $\alpha = 2\pi N_c/N_l$. The length of the loop is $L_l = 2\pi R = N_l \lambda$. Defining $y = (2n_i - 1)/2N_c$, for a long chain the above summation may be replaced by an integration with adequate changes in the integration limits,

$$W_l = -\frac{2CN_l}{\lambda^6 N_c^5} \int_{1/2N_c}^{(N_c-1)/2N_c} \frac{dy}{[y^2 + \alpha^{-2}]^3} \quad (10)$$

The solution of which, also in the limit of a very long chain, is

$$W_l \cong -\frac{3\pi C \alpha^5 N_l}{8\lambda^6 N_c^5} = -\frac{3\pi C N_l}{8\lambda R^5} = -\frac{3\pi C L_l}{8\lambda^2 R^5} \quad (11)$$

The above Equation is similar to Equation (4), the difference being in the length of the chain, which is replaced by that of the loop. It is also independent of chain length, as expected, because of the approximation made in the limit of very long chains. Equation (8) and (11) can also be written with the formalism used in Equation (3a) and (4a).

In the formalism of Parsegian, Equation (8) is written as

$$W_l = -3k_B T \sum_{n=0}^{\infty} \Delta_{1n}^2 \frac{1}{\pi^2 \rho^2} \sum_{n_i=1}^{N_c/2} \sum_{n_j=1}^{N_l} \frac{n_j}{\left[\lambda^2 \left(n_i - \frac{1}{2} \right)^2 + R^2 \right]^3} \quad (8a)$$

where, as in Equation (3a) and (4a), the sum \sum' is over all sampling frequencies. Also in this formalism, Equation (11) is the same as Equation (4a), with the length of the chain replaced by that of the loop.

Figure 4 shows the results obtained with Equation (8) and (11) for the same polymers as in Figure 2. The interaction potential energy between the loop and the chain is plotted as a function of the number of chain segments to right and left of the loop. The value at the ordinates is the interaction potential energy per mole of loops. Because we are discussing only attractive interactions, all results in Figure 2 and 4, and in the discussion below will be presented in terms of absolute values of the interaction potential energy. Values for the separation distance between the loop and the chain were obtained from experimental data for the intermolecular separation distance between polymer chains at the molten state –

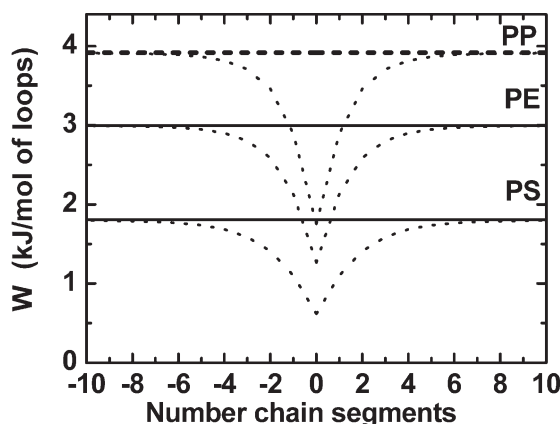


Figure 4. Interaction potential energy between a chain and a loop evaluated with Equation (8) – dotted line – and Equation (11) – solid line. Additional data used in this evaluation is in Table 1 and in the Supporting Information. The thermal energy of the melt is indicated by the horizontal dashed line.

see Table 1 and the Supporting Information. It can be seen that the interaction potential energy increases with increasing number of chain segments and that it stabilises after five chain segments to the left and another five segments to right of the loop, all at around one Kuhn monomer.

The interaction potential energy between a loop of isotactic PP (iPP) and a chain at its centre has approximately the same value as the melt thermal energy. Lower values are obtained for the other two polymers. Since the interaction potential energy was evaluated per chain loop, we could consider that the interaction potential energy per number of loops in a chain, which in principle has several entanglements (loops), would have a much higher value. This argument does not find experimental support. It is known that flow activation energy in melts of linear chains increases with the polymer molecular weight up to a limiting value for chains with critical molecular weight, being constant for chains with higher molecular weight, regardless of its value.^[30]

Discussion on the Validity and Implications of Results Obtained for the Interaction Potential Energy

Because of the implication of results shown in Figure 2 and 4 in the physical definition of entanglement, the obvious question to ask is how accurate are the results for the interaction energy evaluated with Equation (3), (4), (8) and (11)? To answer this question, a brief review of the criticisms raised concerning the derivation of Salem's Equation is presented next. Before proceeding with this discussion, it must be stressed that the only similarity of Equation (3) and (4) with the Equations originally derived

by Salem is in the dependence of the interaction energy on λ and D . As it will be seen, all these criticisms disappear when the new formalism is used and the Hamaker constant is evaluated with Lifshitz theory.

Three main criticisms were raised concerning the derivation of Equation (4) that may be applied also to the derivation of Equation (8) and (11). Two of them were raised by Zwanzig.^[22] These are the pairwise additivity, which says that the total attractive force between large molecules can be obtained by adding together dispersion forces between elementary units taking them two at a time, and the isotropy of the polarisable groups in the chain. Another remark is related to the omission of intrachain interactions.^[31] Evaluation of this additional effect leads to the Equation already derived by Zwanzig, with similar numeric coefficients. Despite these criticisms, it was concluded that results of these two corrections were not very different from those of Salem.^[24,29]

The effect of other interactions, besides the dipole/dipole interaction, was discussed by Langbein.^[28] He started with the argument that an electric field of a dipole fluctuation of atom 1 at the position of atom 2 (T_{12}) induces a reaction field $T_{12}\alpha_2(\omega)T_{21}$ of atom 2 that lowers the energy of the original fluctuation at atom 1, where $\alpha_2(\omega)$ is the atomic polarisability. He then applied the fluctuation/dissipation theorem to obtain the van der Waals energy between atoms 1 and 2 (W_{12}) that was expressed as an integral over all frequency range of the imaginary part of the Fourier transformed polarisability, Equation (2) in ref. [28],

$$W_{12} = -\frac{\hbar}{8\pi^2} \int_{-\infty}^{+\infty} d\omega \operatorname{tr} [\alpha_1(i\omega)T_{12}\alpha_2(i\omega)T_{21}] \quad (12)$$

For dipole/dipole interactions, and assuming isotropic polarisabilities, application of this Equation to two parallel cylinders, cylinder 1 and cylinder 2, with length L , and density of atoms ρ_1 and ρ_2 , respectively, leads to

$$W = -\frac{\hbar}{8\pi^2} \int_{-\infty}^{+\infty} d\omega \rho_1 \alpha_1 \rho_2 \alpha_2 \int_1 ds_1 \int_2 ds_2 \frac{9\pi L}{8|s_1 - s_2|^5} \quad (13)$$

where the last two integrals are performed over the cylinder axis. Their solution was also obtained by Langbein. He found for dipole/dipole interactions a similar dependence of the interaction potential energy as in Equation (4), that is, $W \propto L/\lambda^2 D^5$, and that the terms resulting from contributions of higher-order interactions are in $1/D^7$ for dipole/quadrupole interactions and in $1/D^9$ for quadrupole/quadrupole interactions. In the new formalism, the integral over frequency is related to the Hamaker constant evaluated with Equation (5).

As mentioned above, use of this more accurate Equation leads to an increase of the interaction potential energy compared to Salem's original Equation of only 4%.^[29] Since the Hamaker constant was evaluated with the new formalism, it may be considered that the above deviation is already accounted for in this formalism, and it remains only to correct the effects of dipole/quadrupole and quadrupole/quadrupole interactions, which may be neglected due to their dependencies in D^{-7} and D^{-9} . Because of this dependence, we may consider, as described above, that the relevant contribution to the interaction potential energy results mainly from dipole/dipole interactions.

The evaluation of the van der Waals interaction energy between helical chain molecules^[26] is also important to this work. The result obtained in this case for infinitely long helical molecules contains a zero-order term, $g^{(0)}$, which is independent of the helix oscillatory behaviour, and higher order terms, $g_1^{(2)}, g_1^{(4)}$, exhibiting oscillatory behaviour with respect to the length of the helix, Equation (25) in ref.^[26],

$$W_1 \sim -\frac{CL}{\lambda^2 D^5} \left[g(0) + \left(\frac{\zeta}{D}\right)^2 g_1^{(2)} + \left(\frac{\zeta}{D}\right)^4 g_1^{(4)} \right] \quad (14)$$

where ζ is the helix radius. When the helix radius becomes small, of the order of magnitude of the spacing between two adjacent molecules in the chain, the above Equation reduces also to Equation (4) – see the discussion for limiting cases in ref. [26] pp. 1393–1394. The contribution of terms $g_1^{(2)}$ and $g_1^{(4)}$ is in D^{-7} and D^{-9} , respectively, and for the same reason as above it may be neglected.

This issue is important because we have evaluated in Figure 2 the interaction potential energy between iPP polymer chains. Although these evaluations were made at 200 °C, in the molten state, it is clear that parallel and aligned chain segments of this polymer can only adopt helical conformations. The helix radius is much lower than the a spacing of the iPP monoclinic unit cell, which is 6.65 Å. It is comparable, in order of magnitude, to the projected bond length along the chain axis, which guarantees also the applicability of Equation (3) and (4) to this polymer.

Besides these, other arguments more that contributed to demonstrate the validity of Equation (3), (4), (8) and (11) for evaluating the van der Waals interaction energy are discussed below. It is a fact that pairwise additivity, intrinsic to the above equations, ignores the influence of neighbouring atoms on the interaction between any pair of atoms. As stated by Israelachvili,^[25] among others,^[19] this problem is avoided in the Lifshitz theory because the atomic structure is ignored and the interacting bodies are treated as continuous media (see discussion above). In this new formulation, all above Equations remain the same, the only difference being that, in the framework of Lifshitz theory, the Hamaker constant is expressed by Equation (5). It is

impossible to provide in a manuscript a full discussion of this issue. A discussion of the validity of this approach may be found in ref. [25] p. 179, and also in ref. [19]. For a discussion of the connection between the Hamaker pairwise-summation picture and the Lifshitz formulation of van der Waals interactions, see ref. [19] pp. 208–212.

It is expected that this discussion will have convinced the reader of the validity of the procedure used to evaluate the interaction potential energy between parallel chain segments and a loop with a chain at its centre, and also for the reasonability of the values obtained. Small differences between the values of the Hamaker constant used in this work and others, shown in ref. [19] p. 64 and ref. [25] p. 178, result from the temperature effect on the van der Waals volume. The discussion above shows also the reasonability of values indicated in Figure 2 and 4. Because the interaction potential energy value between a loop and a chain at its centre and between two parallel Kuhn monomers is similar (or below) the melt thermal energy, we can definitely conclude that chain intertwining, described physically by the looping picture, or binary interactions between chain segments cannot account for the elastic properties and solid-like behaviour of entangled and unentangled polymer melts.^[32,33]

Experimental results also confirm the validity of the above predictions. It is considered that chain uncrossability is better demonstrated by experiments with ring polymers since only they are capable of forming mathematically rigorous topological “knots” with neighbouring chains that permanently prevent chain crossing.^[34] However, direct measurement of confining forces in concentrated solutions of linear and circular polymers demonstrate that the confining force imposed by circular polymers was substantially lower and of shorter range than that measured with linear polymers.^[34] Based on these results, it was concluded that circular chains are less effective than linear chains at producing restrictive entanglements.

Still another demonstration that the looping picture and binary contacts between polymer chains cannot explain the elastic properties of polymer melts was obtained with experiments performed with entangled, non-concatenated, ring polystyrenes. It was considered that each polystyrene ring adopts double-folded conformations, and that double folds of neighbouring rings in melts can penetrate each other, open up the folded structure and temporarily block simple sliding motion of loops – see Figure 1f in ref. [35]. It was found, however, that the relaxation modulus of purified entangled ring polymers does not show any plateau, and that a plateau modulus is only observed when small fractions of linear polymer chains are added to the entangled ring polymers.^[35] This behaviour was already reported in 1989 by McKenna et al. in experiments aimed at analysing the effect of small amounts of linear chain contaminants in the viscoelastic behaviour of cyclic

polystyrenes.^[36] The results of these experiments are in agreement with those obtained above for the interaction potential energy between a loop and a chain (Figure 4), indicating that binary contacts between polymer chains, due to their low values of interaction potential energy, cannot explain elastic properties of polymer melts.

Conclusion

Although the key question – how strong an entanglement is – was not answered in this work, we can draw important conclusions concerning the representation of an entanglement. These conclusions are important for macromolecular science in general, because the common geometrical representation of entanglements as binary interactions of chain segments, by chain loops or slip-links, is used to construct models for explaining polymer properties assigned to entanglements.

A common result of Figure 2 and 4 is that the interaction potential energy between two Kuhn monomers, or between a chain and a loop is below the melt thermal energy. This means that interactions between polymer chains with the geometry of a chain loop, a slip-link, or any other binary interaction cannot explain the elasticity of polymer melts.

This fact was recognised in part by Qian in 1997.^[37] He followed a completely different approach than the one used in this work, and he was not as incisive and clear in his conclusions as the results of Figure 2 and 4 demonstrate. He evaluated the amount of coil interpenetration as a function of the polymer molar mass from the coil and polymer melt densities. He concluded: “Perhaps it is worthy to revisit the question of chain entanglement to determine whether it is of a topological nature or of a cohesive nature that works through local nematic interactions. At the flowing temperature of a polymer melt, the cohesive entanglements along the chain are in a state of dynamic equilibrium of entanglement and disentanglement with the neighbouring chain segments of interpenetrated chains. This kind of dynamic bonding and debonding of entanglement points is a necessary condition for a van der Waals network of the polymer melt to be able to flow ... Topological entanglements may naturally exist to a small extent, but they probably do not play a significant role in the physical properties under consideration.”^[38]

It is not physically conceivable that interactions having an interaction energy lower than the melt thermal energy, such as those involving binary interactions (chain loops, slip-links and interactions between two Kuhn monomers), could play any significant role in the elastic properties of polymer melts. Therefore, these geometrical representations cannot be used to illustrate the effects assigned to entanglements. It also means that we probably have to

find a different word to express more properly the molecular interactions between polymer chains responsible for the effects assigned to entanglements. Further research work, especially in atomistic molecular dynamics simulations of local interactions between polymer chains in dense polymer melts, is clearly needed to suggest other possible arrangements between polymer chain segments that might explain the properties assigned to entanglement interactions.

Interactions having energy higher than the melt thermal energy, involving two chain segments in parallel only, which could belong to the same, or different, chains, would require segments with lengths of around 70 Å for polystyrene. Interacting chain lengths with this value, involving segments of two chains only, violates the Maxwell-Boltzmann distribution of the relative population of different conformational states.

The immediate conclusion is that, to explain those properties, we need to foresee other types of geometrical arrangements between polymer chains with interaction energy higher than the thermal energy of the melt, which could be, as suggested by Qian, “of cohesive nature that works through local nematic interactions”, creating a van der Waals network of interactions.^[38] To define the required geometrical arrangement, we need to know, at least approximately, the energy associated with an entanglement interaction. In future works, approximate values for this interaction energy will be presented.

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