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Influence of topological constraints on polymer dynamics in dilute and semidilute θ-solutions

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Résumé. — Nous considérons la dynamique de longues chaînes de polymères (comprenant N ≈ 1 maillons) avec contraintes topologiques. Nous proposons un modèle heuristique prenant en compte les effets d'enchevêtrement dans la dynamique. Nous montrons que, dans des conditions θ, 1) le processus le plus lent de relaxation structurelle d’une chaîne isolée est dû à un mouvement diffusif d’enchevêtrements locaux le long du contour de la chaîne ; 2) le temps de relaxation structurel le plus long \( \tau_{\text{max}} \) est beaucoup plus grand que le temps \( \tau_{\text{zimm}} \) du mode de Zimm : \( \tau_{\text{max}} \sim N^{3/2} \) du mode de Zimm, avec \( z = 3 \) ; 3) les propriétés viscoélastiques d’un polymère en solution varient considérablement à une concentration bien définie \( c^* \) de l’ordre de la concentration de recouvrement des polymères : au voisinage de \( c^* \), la viscosité augmente d’un facteur \( N^{3/2} \), la concentration \( c^* \) correspond à l’apparition d’un amas infini de chaînes enchevêtrées dans la solution.

Abstract. — The dynamics of a long polymer chain (consisting of \( N \approx 1 \) « links ») with topological constraints is considered. A heuristic model taking into account an effect of « entanglements » on the dynamics is proposed. It is shown that in theta-conditions : (i) the slowest process of the conformational relaxation of an isolated chain is due to a diffusive motion of local « entanglements » along the chain contour ; (ii) the longest conformational relaxation time \( \tau_{\text{max}} \) essentially exceeds the time \( \tau_{\text{zimm}} \) of the first Zimm mode : \( \tau_{\text{max}} \sim N^{3/2} \), where \( z = 3 \) ; (iii) visco-elastic properties of a polymer solution change considerably at some definite concentration \( c^* \) of the concentration of overlapping of polymer coils : in the vicinity of \( c^* \) the viscosity increases by a large factor of the order of \( N^{3/2} \) ; the concentration \( c^* \) corresponds to the appearance of an infinite cluster of entangled chains in the solution.

1. Introduction.

A considerable attention has been paid during the last decades to the dynamics of linear polymers in solutions (see reviews [1-3] and references therein). The majority of theoretical works dealing with the dynamics of dilute solutions are based on theoretical approaches due to Kirkwood and Riseman [4], Rouse [5] or Zimm [6]. In the following section some of these approaches are briefly considered. All these theories do not take into account the effect of topological constraints (entanglements), i.e. the fact that polymer chains cannot pass « through » each other. It is well known [2, 3] that this effect is important for the dynamics of concentrated polymer solutions. On the other hand the effect of entangle-
ments seems to be unessential for the dynamics of a single chain in a good solvent [7]. In the present work it is shown that in the case of a theta-solution topological constraints are important even in the dilute regime (see also [8]).

From the author’s point of view the main difficulty of a theoretical description of topological effects (a rigorous theory accounting for these effects has not been proposed during the last four decades) is due to the failure to propose a useful perturbation approach. To illustrate the difficulty let us try to construct such an approach. Let us divide (mentally) a polymer chain in segments of two alternating types, the length of the first type segment being \( \ell_1 = p \ell \) and of the second \( \ell_2 = (1 - p) \ell \) (Fig. 1).
Let us postulate an « uncrossing » restriction only for the segments of the first type. Obviously, the case \( p = 0 \) corresponds to a phantom chain and \( p = 1 \) — to a real chain with topological constraints. Therefore the parameter \( p \) can be considered as a perturbation one. Nevertheless a corresponding perturbation scheme would be useless since, in the case \( p < 1 \), all essential (long-lived) topological effects are fully absent: these effects suddenly appear at \( p = 1 \). All other possible (known to the author) perturbation approaches are also useless for the same reason.

As an alternative to a perturbation a heuristic model is proposed in the present work. This model is formulated in section 3 on the basis of the preliminary analysis of essential topological « variables » for the polymer dynamics. The model is studied in section 4 by the renormalization group method. As a result, it is shown that the longest relaxation time, \( \tau_{\text{max}} \), of a polymer chain scales according to the law

\[
\tau_{\text{max}} \propto N^z ,
\]

where \( N \) is the number of links in the chain and \( z \) is greater than 2 (\( z = 3 \)). An effect of this remarkable slowing of relaxation processes (due to topological constraints) on the viscosity of the theta-solution in an intermediate region (between dilute and semidilute conditions) is considered in section 5. The results of this section are compared with experimental data [9]. A qualitative (at least) agreement is found.

It is already worth mentioning in the introduction that the new heuristic model proposed in this work exhibit all the specific topological properties (known to the author). For example, the model provides a reptational behaviour [10, 11] of polymer chains in a concentrated solution.

2. Current models for polymer dynamics in a theta-solution.

According to the classical Rouse model [5] a polymer chain can be considered as a sequence of \( (N + 1) \) beads \( r_0, r_1, \ldots, r_N \) connected by immaterial strings. The number of links is assumed to be large: \( N \gg 1 \). Each link of the Rouse chain corresponds to the segment (subchain) of the macromolecule, long enough to obey the Gaussian statistics.

The longest time for the relaxation of internal modes of the chain is equal to (see, for example [7])

\[
\tau_R = 2 a^2 N^2 / (\pi^2 D_0) ,
\]

where \( D_0 \) is the diffusion constant of a bead and \( a \) is the characteristic size of a link.

Comparing equation (2.1) and (1.1) we get the exponent \( z \) of the Rouse model:

\[
z_R = 2 .
\]

The diffusion constant of a polymer chain as a whole is

\[
D = D_0 / N .
\]

Therefore \( \tau_R \) is of order of the time needed for a chain to diffuse on the distance compared with its size,

\[
R = N^{1/2} a ,
\]

i.e.

\[
\tau_R \approx R^2 / D .
\]

The Rouse model describes a phantom polymer chain without hydrodynamic interaction and in theta-conditions. Zimm [6] had extended the Rouse model in order to account for this interaction. It appears that a long enough polymer chain behaves in a flow field as an impenetrable coil. Therefore the diffusion constant of a chain must be of the same order as for the impenetrable sphere of radius \( R \) [7] :

\[
D = \text{Const.} \ T / (6 \pi \eta_s R) ,
\]

where \( \eta_s \) is the viscosity of the solvent. The longest relaxation time for internal modes can be estimated as before using equation (2.5):

\[
\tau_Z \approx R^2 / D \approx \eta_s R^3 / T \propto N^{3/2} .
\]

Thus the dynamical exponent \( z \) of the Zimm model is equal to

\[
z_0 = 3/2 .
\]

In order to consider not only theta but also good solvents, a generalized version of the theory [12] must be applied. In the present work only theta-solutions are considered.

All the theories mentioned above do not take into
account an effect of entanglements. This effect cannot influence strongly the process of the diffusion of a polymer chain as a whole since this motion does not assume any change of the chain « topology ». Therefore equation (2.6) represents the correct estimate of the diffusion constant of a chain. On the other hand, the effect of topological constraints must undoubtedly slow down the process of the relaxation of internal modes of a chain (this statement can be rigorously proved), i.e., the dynamical exponent \( z \) must be greater than \( z_0 = 3/2 \).

3. A heuristic model for dynamics of a polymer chain with topological constraints.

A mathematical description of the chain topology is rigorously applicable to closed chains only [13]. A linear polymer chain can be closed mentally by the straight segment connecting the ends of the chain. The length \( \lambda \) of this segment is of order of \( R = N^{1/2} a \), i.e. \( \lambda \) is much smaller than the total length of the chain, \( L \ll Na : \lambda \ll L \). Consequently this segment seems to be unessential for the description of the topological state (see [14]).

A topological state (the type of the knot) of a closed chain can be mathematically characterized rather simply. Any knot can be represented as a composition of a number of so-called simple knots \( P_k \) [13]:

\[
Q = n_1 P_1 + n_2 P_2 + \cdots ,
\]

(3.1)

where \( P_1, P_2 \) etc. are simple knots of different types, and \( n_1, n_2 \) etc. are multiplicities of these simple knots.

Let us consider a fragment of a macromolecule consisting of \( g \) « links » (1), short enough compared with the whole chain : \( g \ll N \). Let us use a microscope with the minimal soluble length, \( b \), somewhat smaller than the size of the segment under consideration: \( b \ll g^{1/2} a \). Knots which can be viewed through this microscope on this fragment will be called knots of scale \( b \) (Fig. 2a). The probability that the fragment forms one (or more) simple knot of a given type and of the scale \( b \) is of order of unity. Therefore the total number on the whole chain of simple knots of type \( k \) and of the scale \( b \), \( n_k(b) \), is

\[
n_k(b) \sim N/g \sim (a^2/b^2) N .
\]

(3.2)

Thus the mean number of local knots (of scale \( b \sim a \)),

\[
n_k(b \gg a) \sim N ,
\]

(3.3)

Fig. 2. — A knot of scale \( b \) (a) ; a local entanglement (b).

In the following estimates (within an order of magnitude) large-scale knots are neglected.

Local knots can be treated as a one-dimensional gas on the polymer chain since they interact only weakly and, in particular, can pass through each other. The diffusion constant of a local knot (for the motion along the chain), \( D_k \), is of order of \( D_0 \) (it does not matter whether the hydrodynamic interaction is taken into account or not). The distribution function (concentration) of knots along the chain, \( c_k(s) \), where the coordinate \( s \) is the number of « links » between the knot and an end of the chain \( (0 < s < N) \), satisfies the following diffusion equation:

\[
\frac{\partial c_k}{\partial t} = D_k \frac{\partial^2 c_k}{\partial (sa)^2} ,
\]

\[
c_k(0) = c_k(N) = n_k/N .
\]

(3.4)

Thus topological constraints cause a significant change of \( \tau_{\text{max}} \) (compare Eqs. (3.4) and (2.11) for a polymer chain with the hydrodynamic interaction). The dynamical exponent \( z \) must be not less than two, i.e.

\[
z - z_0 \approx 1/2 .
\]

On the other hand the result (3.4) is rather formal since a relaxation of local knots along the chain cannot appreciably affect any macroscopic conformational property of the macromolecule. More essential processes of the « topological relaxation » are described below.

Let us consider a situation where two (rather short) fragments of the macromolecule (which may

be very distant along the chain) are brought together in the space (Fig. 2b). These two fragments in the equilibrium state can be entangled with rather high probability.

Let us clarify what does entangled state of two fragments mean. To do this let us connect (mentally) the ends of the first fragment and of the second fragment by the straight segment. An entanglement (in the rigorous topological sense) of the two rings obtained will be called an intrinsic entanglement of the initial fragments. We can assume that the two fragments are in an entangled state if their intrinsic entanglement is topologically nontrivial. This definition however is unsatisfactory since it can lead to an ambiguous situation where two fragments of two chains are entangled whereas the two chains as a whole are not entangled (see Fig. 3). In order to eliminate this shortcoming let us consider two longer fragments of the chains containing initial ones. If the intrinsic entanglement of any of such longer fragments contains the intrinsic entanglement of the initial fragments as a topological component then the initial fragments are assumed to be in a true entangled state.

It is possible to attribute some scale (and type) to an entanglement by an analogy with the case of knots. Let us concentrate our attention on the local entanglement (of scale $b - a$). A position of a local entanglement can be characterized by two coordinates along the chain, $s_1$ and $s_2$ (corresponding to each of the entangled « links »). Short-range local entanglements (with $|s_1 - s_2| \sim 1$) are inessential for the conformational relaxation since they can be considered as local knots. Therefore it is only long-range local entanglements (with $|s_2 - s_1| \sim N$) that can be important for conformational dynamics.

The mean number of these entanglements, $M$, is of order of the number of long-range contacts since each contact of two « links » is supplemented by a local entanglement with rather high probability (as was mentioned above). Thus for a polymer chain in theta-conditions [7]

$$M \sim N^{1/2}.$$  

Therefore we can expect that long-range entanglements are indeed very essential for the conformational relaxation of a polymer chain in a theta-solution. Note that, on the other hand, the mean number of long-range contacts in a good solvent is small, $M \ll 1$ [15], and therefore the topological constraints are expected to be unimportant in this case.

It is possible to propose now an abstract model taking topological constraints into account (in theta-conditions). Let us first of all consider an equilibrium « conformational-topological » statistics of a polymer chain.

Let us attribute a topological variable, $\sigma$, to each pair of « links » $s_1, s_2 : \sigma(s_1, s_2) = 0$ if the « links » are not entangled and $\sigma(s_1, s_2) = 1$ in the opposite case. The equilibrium probability, $\varphi$, that the « links » are in an entangled state depends on the distance $r = r(s_2) - r(s_1)$ between them : $\varphi = \varphi(r)$. The function $\varphi(r)$ is determined by the detailed structure of the « links ». Obviously this function must tend to zero in the region $r > a$. Statistical weights $f(r | \sigma)$ corresponding to « entangled » ($\sigma = 1$) and « nonentangled » ($\sigma = 0$) topological states can be written using the function $\varphi(r)$ as follows ;

$$f(r | \sigma) = (1 - \sigma) + (2 \sigma - 1) \varphi(r).$$  \hspace{1cm} (3.6)

The condition

$$f(r | 0) + f(r | 1) = 1$$  \hspace{1cm} (3.7)

(which was taken into account in Eq. (3.6)) implies that there are no volume interactions between the « links », i.e. that the chain is ideal.

A conformational-topological state (« microstate ») of a polymer chain is thus completely determined by the space positions of all « links » $\{r(s), 0 \leq s \leq N\}$ and by the set of topological variables $\{\sigma(s_1, s_2), 0 \leq s_1 < s_2 \leq N\}$. The partition function (the statistical weight of a « microstate »),

$$Z[r, \sigma]$$

is equal to

$$Z[r, \sigma] = Z_0[r] \prod_{s_2 > s_1} f(r(s_2) - r(s_1) | \sigma(s_1, s_2)),$$  \hspace{1cm} (3.8)

where

$$Z_0[r] = \exp \left\{ - \frac{1}{4} a^2 \int (\frac{\partial r}{\partial s})^2 ds \right\}$$  \hspace{1cm} (3.9)

is the well-known statistical factor for an ideal (Gaussian) chain.

If one is interested only in equilibrium conformational (not topological) properties of the chain, the reduced partition function $\bar{Z}[r]$ can be used :

$$\bar{Z}[r] = \sum_{\{\sigma(s_1, s_2)\}} Z[r, \sigma].$$  \hspace{1cm} (3.10)

Fig. 3. — The polymer chains A and A’ are not entangled as a whole whereas their fragments (ab) and (a’ b’), (cd) and (c’ d’) are « entangled » accordingly.
Substituting equation (3.8) into equation (3.10) and taking condition (3.7) into account we get
\[ Z[r] = Z_0[r] , \]
i.e. the conformations of the chain obey the Gaussian statistics (as expected).

Let us consider another situation: a macromolecule without entanglements (strictly speaking, this condition is fulfilled for a closed chain in an unknotted state). Substituting equation (3.6) into equation (3.8) and taking into account that all topological variables are zeroes, we get the conformational partition function for this case:
\[ Z[r] = Z_0[r] \prod_{s_i > s_j} \{1 - \varphi(r(s_2) - r(s_1))\} . \tag{3.11} \]

The conformational weight (3.11) coincides with that for a polymer chain with effective repulsion between the « links » (and without any topological constraints). Thus a closed ideal chain without knots is formally governed by the excluded volume statistics \(^{(2)}\).

The (formal !) excluded volume for two « links » is equal to
\[ v = \int \varphi(r) \, d^3r . \tag{3.12} \]

Let us now consider the dynamics of the model. A change of the « microstate » of the chain is due to two processes: to a conformational motion at a given fixed topological state and to a topological change (i.e. to the motion of local entanglements). The first process corresponds to the motion of a chain with a number of junctions but without any additional topological constraints (since fixed local entanglements are obviously equivalent to junctions). It is natural to suppose that the presence of junctions can only decrease the characteristic time of the conformational relaxation of the polymer chain. Therefore the longest relaxation time due to the first process is rather short: it is shorter than the relaxation time of a linear chain without topological constraints (and without junctions), i.e. than the Rouse time (2.1) or the Zimm time (2.7).

On the other hand the second (topological) process of the relaxation is essentially slower (see below). In the following, only this slow second process will be considered. (Note that considering this process the conformational equilibrium at a given topological state can be assumed, so that any conformational change can be considered as a result of a topological change).

The topological relaxation is due to the motion of local entanglements. It can be shown that an energy dissipation caused by the motion of a local entanglement is mainly due to the local friction in the vicinity of entangled « links » \((s_1, s_2)\) \(^{(2)}\).

The rate of energy dissipation, \(W\), corresponding to the local friction processes is equal to
\[ W = \xi_1 [(\dot{s}_1/\dot{t})^2 + (\dot{s}_2/\dot{t})^2] , \tag{3.13} \]
where \(\xi_1\) is a priming friction constant of an entanglement.

\[ \xi_1 \sim a^2 T/D_0 . \tag{3.14} \]

Note that the presence (or the absence) of the hydrodynamic interaction does not affect the validity of equation (3.13). Therefore the dynamics of the model is basically independent of the intensity of this interaction.

The friction constant \(\xi_1\) generally depends on the type of the entanglement. Moreover, in the general case, the dissipation rate \(W\) must be written in the form
\[ W = \xi_1 (\dot{s}_1/\dot{t})^2 + \xi_2 (\dot{s}_2/\dot{t})^2 + \xi_1 (\dot{s}_1/\dot{t})(\dot{s}_2/\dot{t}) . \]

Nevertheless in order to formulate a minimal model the simplest form (3.6) for \(W\) can be used. All complications mentioned above will appear (if they are essential) during a renormalization of the minimal model.

Local entanglements cannot disappear in a collision since the number of entanglements of any simple type is a topological invariant. There are only two ways to disappear for them: by a tightening of the loop \((\text{of the part of the chain between points } s_1 \text{ and } s_2)\) (Fig. 4a) and by the creeping of one end of the chain « through » the entanglement (Fig. 4b). Note that the first process is possible only if there are no other entanglements between the segment \((s_1, s_2)\) and the outer part of the chain since local entanglements cannot pass « through » each other (i.e. the process shown in figure 5a is impossible).

The model under consideration can be easily generalized in order to include other chains. In a concentrated enough solution, entanglements of a given chain with others must be distributed along the chain with high density. The only possible large-scale motion of the chain in this situation is a reptation « through » these entanglements. Thus the reptative dynamics can be regarded as a particular consequence of the new model.

\(\xi_1\) In the absence of hydrodynamic interaction the large-scale dissipative processes due to the motion of large parts of the chain between entanglements produce some logarithmic correction to the local friction constant which appears to be inessential.
Fig. 4. Processes of disappearance of a local entanglement: the tightening of the loop (a); creeping of an end of the chain (b).

Fig. 5. A topologically impossible motion of local entanglement (a); two local entanglements that cannot be separated due to topological constraints (b); entanglements $s_1 s_2$ and $s'_1 s'_2$ are «connected» by long-range attractive forces (c). Solid lines represent polymer chains, and wave lines, local entanglements.

4. The renormalization group analysis of the new model.

One of the advantages of the new model is that it can be easily generalized for the case of space arbitrary dimensionality, $d$ \(^{(4)}\). It will be shown that $d = 4$ is the critical dimensionality for dynamical properties of the model. The case $d < 4$ can be studied by a standard $\epsilon$-expansion method \cite{18} based on a renormalization group approach.

Let us consider the probability $P(\mathbf{r})$ that two Gaussian chains are in a mutually entangled state ($\mathbf{r}$ is the distance between the centres of mass of the chains). An «integrated probability»

$$B = \int P(\mathbf{r}) \, d^d r$$ \hspace{1cm} (4.1)

can be expressed in terms of partition functions in the following way (compare with Eq. (3.8)):

$$B = V^{-1} \sum_{(s_1, s_2)} \left[ Z_0[\mathbf{r}_1] Z_0[\mathbf{r}_2] \prod_{n=1}^{N} f(\mathbf{r}(s_n) - \mathbf{r}(s_n)) \right] D[\mathbf{r}_1] D[\mathbf{r}_2],$$ \hspace{1cm} (4.2)

where $s_1$ enumerates the «links» of the first chain, $s_2$, of the second, and at least one variable from every set $\{\sigma(s_1, s_2)\}$ must be nonzero (this condition provides that the two chains are entangled). The prefactor $V^{-1}$ ($V \to \infty$ is the total volume of the system) compensates the integration over all translations of the two chains as a whole in the space.

Let us expand equation (4.2) into powers of the function $\varphi$. A diagram representation of the resulting expansion up to the second order is \(^{(5)}:\)

$$B = \begin{array}{c}
\begin{array}{c}
\text{Diagram 1}
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{c}
\text{Diagram 2}
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{c}
\text{Diagram 3}
\end{array}
\end{array}$$ \hspace{1cm} (4.3)

where the Green function

$$G_N(\mathbf{k}) = \exp(-Na^2k^2)$$ \hspace{1cm} (4.4)

is associated with each part of a solid line ($\mathbf{k}$ is a vector of inverse space); and a factor

$$v(\mathbf{k}) = \int \varphi(\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r}) \, d^d r$$ \hspace{1cm} (4.5)

is associated with each wave line.

Usual rules for calculation of the diagrams are assumed (i.e. each diagram assumes an integration over all independent $k$-vectors of all lines and all independent $N$-numbers corresponding to solid lines).

Let us consider $d$-dimensional space,

$$d = 4 - \epsilon, \quad \epsilon \ll 1.$$ \hspace{1cm}

After a simple calculation of the diagrams of equation (4.3) we get

$$B = N^2 v \left\{ 1 - (K_d v/a^d) \ln N + \mathcal{O}((\epsilon + v/a^d)^2) \right\},$$ \hspace{1cm} (4.6)

where $v = v(0)$, $N$ is the number of «links» in each chain, and

$$K_d = S_d/(2\pi)^d = 2^{1-d} \pi^{-d/2}/\Gamma(d/2),$$

($S_d$ is the surface area of unit sphere in $d$ dimensions). Taking into account that the parameter

\(^{(5)}\) Here and afterwards the terms of the relative order $N^{-1}$ are omitted.
\( u = K_d v/a^d \) is small proportionally to \( e \) (see below); we can rewrite equation (4.6) in the form

\[
B = N^2 v \left\{ 1 - u \ln N + O(e^2) \right\}. \tag{4.7}
\]

Let us define a renormalization group transformation using the decimation process \[19\]. Consolidation of \( g = \exp(\tau) \) « links » into one renormalized « link » corresponds to the transformation:

\[
N \to N \exp(-\tau), \quad a \to a \exp(\tau/2). \tag{4.8}
\]

The second transformation (4.7) is due to the Gaussian statistics of each chain. Substituting equation (4.7) into equation (4.6) and taking into account that \( B \) is a macroscopic characteristic independent of \( \tau \), \( B = \text{inv} \), we get the renormalization equation for the parameter \( u \)

\[
\frac{\partial u}{\partial \tau} = eu/2 - u^2 + O(e^2). \tag{4.9}
\]

Equation (4.8) has a stable fixed point

\[
u^* = \frac{e}{2} + O(e^2). \tag{4.10}
\]

Substituting equation (4.9) into equation (4.6) we obtain

\[
B = 4 \pi^2 e R d [1 + O(e)] , \tag{4.11}
\]

where \( R = N^{1/2} a \) is the size of the Gaussian coil. Thus the « probability » of an entanglement, \( B \), decreases to zero as \( d \to 4 \). For \( d > 4 \) the possibility of an entangled state can be neglected, i.e. \( d = 4 \) is an upper critical dimension for the problem. The dynamics of a polymer chain for \( d > 4 \) is adequately described by the Rouse model (the hydrodynamic interaction is of no importance for this case \[20\]):

\[
z = 2 \quad \text{for} \quad d > 4 . \tag{4.12}
\]

Let us now consider the longest topological relaxation time, \( \tau_{\text{max}} \), i.e. the time needed for the process of unlinking of two originally entangled chains \({}^6\). It is natural to suppose the following scaling law for this time:

\[
\tau_{\text{max}} \sim \xi_1 N^{1/2}/T . \tag{4.13}
\]

If there was only one (local) entanglement between the chains, then the relaxation time would be simply the time, \( \tau_1 \), needed for this entanglement to diffuse « through » roughly \( N \) « links » along the chain(s),

\[
\tau_1 \sim \xi_1 N^{2}/T . \tag{4.14}
\]

However, in \( d < 4 \) dimensions, there are in fact a lot of local entanglements between the entangled chains. These entanglements interact strongly (see below) and as a consequence \( \tau_{\text{max}} \) is greater than \( \tau_1 \) (i.e. \( z > 2 \)).

Let us consider a renormalized « link » (a subchain) consisting of \( g \) original « links ». The renormalization implies the following transformations:

\[
N \to N/g , \quad \xi_1 \to \xi_g , \quad \tau_1 \to \tau_g . \tag{4.15}
\]

Taking into account that the time \( \tau_{\text{max}} \), being a macroscopic quantity, must be invariable under the transformation (4.15) we get

\[
\xi_g = \xi_1 g^z . \tag{4.16}
\]

An entanglement of two subchains will be called a complex entanglement since it generally consists of a lot of original local entanglements. Moreover a complex entanglement can contain as a constituent an entanglement between the « links » of the same chain (for example, an upper wave arc in Fig. 5b). The constituents of a complex entanglement are « connected » by a strong interaction either of topological (see Fig. 5b) or of entropic nature. The latter interaction « bounds » for example two entanglements shown in figure 5c. An « energy » of the interaction, \( u_{\text{int}} \), coincides with the conformational free energy of the loop \( s_1 s_2^l s_2^r s_2^l \):

\[
u_{\text{int}} = (Td/2) \ln \left( |s_2^l - s_1| + |s_2^r - s_2| \right) .
\]

Thus there is a long-range attraction between entanglements.

Let \( n \) be the mean number of constituent local entanglements in a complex one. Obviously the mean rate of the energy dissipation due to the motion of a complex entanglement, \( W_g \), is equal to

\[
W_g = n W_1 ,
\]

where \( W_1 \) is determined by equation (3.13). Therefore the diffusion of a single complex entanglement along the chain(s) is \( n \) times slower than that of original local entanglement, i.e.

\[
\tau_g = \xi_g (N/g)^{1/2}/T = \tau_1 n . \tag{4.17}
\]

Using equations (4.14), (4.16) and (4.17) we get

\[
n = g^{z-2} . \tag{4.18}
\]

The mean total number, \( m \), of local (original) entanglements on two subchains (including the short-range entanglements between the « links » of the same chain) is

\[
m \sim g . \tag{4.19}
\]

Taking into account that \( n \ll m \) and using equations (4.17)-(4.19), we get an important inequality:

\[
z \ll 3 . \tag{4.20}
\]

\( ^{6} \) Note that the role of the two chains can play for example the end parts (each consisting of \( N/3 \) « links ») of a single chain.
In order to obtain the dynamical exponent $z$, it is necessary to calculate the mean number $n$ of « connected » local entanglements as a function of the parameter $g$. This mean number can be written as

$$n = \frac{(B_1 + 2B_2 + 3B_3 + \cdots)}{B}, \quad (4.21)$$

where $B_s$ is the statistical weight for (exactly) $s$ « connected » entanglements and

$$B = B_1 + B_2 + B_3 + \cdots \quad (4.22)$$

is the total statistical weight of an entangled state of two subchains (this quantity is defined by Eq. (4.7) provided $N$ is substituted by $g$).

Let us use the $\epsilon$-expansion method. The diagram representation for $B_1$ up to the second order of $\epsilon$ is the following:

$$B_1 = \quad \frac{-2}{-4} \quad (4.23)$$

where number factors before diagrams result in particular from the simplest symmetry operations (transpositions of the chains and of the ends of each chain). Wave lines and the segments of solid lines in the diagrams have the same meaning as previously; upper and lower solid lines as a whole represent the two subchains, each consisting of $g$ « links ».

The first diagram in equation (4.23) corresponds not only to the state with one local entanglement but also to the states with $s > 1$ of « connected » entanglements since additional local entanglements are not forbidden by the rules of calculation of diagrams. The second and the third terms in equation (4.23) exactly compensate that part of the first diagram which is due to the state with $s = 2$.

Similarly we have

$$B_2 = \frac{2}{2} + \frac{2}{2} \quad (4.24)$$

As a result of a calculation of diagrams in equations (4.23) and (4.24) we get:

$$B_1 = g^2 v \left[ 1 - 3 u \ln g + O(\epsilon^3) \right];$$

$$B_2 = g^2 v \left[ 2 u \ln g + O(\epsilon^3) \right]. \quad (4.25)$$

Substituting equations (4.25) into equation (4.21) and taking into account that $B_1 = O(\epsilon^4)$ we get

$$n = 1 + 2 u \ln g + O(\epsilon^3). \quad (4.26)$$

Comparing equations (4.18) and (4.26) we obtain

$$z - 2 = 2 u^* + O(\epsilon^3). \quad (4.27)$$

Substituting equation (4.10) into equation (4.27) we get the exponent $z$ in the first $\epsilon$-approximation:

$$z = 2 + \epsilon + O(\epsilon^2). \quad (4.28)$$

The second order of $\epsilon$-expansion can be obtained analogously (see Appendix). The result is:

$$z = 2 + \epsilon + \epsilon^2/4 + O(\epsilon^3). \quad (4.29)$$

Thus, for $d = 3$, we have $z = 3$ in the first $\epsilon$-approximation and $z = 3.25$ in the second approximation.

The latter result is rather striking: the relaxation time for an isolated Gaussian chain appears to be $\tau_{\text{max}} \sim N^{3.25}$, i.e. longer (for $N > 1$) than the longest time for reptation model, $\tau_{\text{rep}} \sim N^3$. It seems seductive to use this result in order to account for the discrepancy between the prediction of the reptation theory ($\tau_{\text{rep}} \sim N^3$) and the experimental dependence deduced from viscosity measurements in concentrated solutions and melts: $\tau_{\exp} \sim N^{3.4}$, since a relaxation time for a concentrated system obviously must be longer than for one (or two) isolated chain(s). However this is obviously an incorrect way since inequality (4.20) must be remembered. Taking into account equation (4.29) and inequality (4.20) we come to the following most plausible conclusion: the exponent $z$ increases with $\epsilon$ and reaches the value $z = 3$ at $\epsilon = \epsilon_c \sim 0.83$ ($d_c = 4 - \epsilon_c \approx 3.17$); for $d = d_c$ the exponent $z$ remains constant. In particular for $d = 3$ the dynamical exponent is 3 exactly:

$$z = 3 \quad \text{for} \quad d = 3. \quad (4.30)$$

Therefore topological constraints (in 3-dimensional space) produce a remarkable slowing of relaxation processes even for one isolated chain (in 3-solution). This slowing affects not only a conformational dynamics of the chain but also its translational motion. In fact, let us consider the process of the translational diffusion. The diffusion constant of the chain scales as (see Eq. (2.6)):

$$D = \text{Const.} \ N^{-1/2}. \quad (4.31)$$

The prefactor Const. in the latter relation does not depend on $N$ but it does depend on the conformation of the chain. Therefore the prefactor must vary appreciably (the relative change being of order of 1) during the characteristic time of order of

$$\tau_{\text{max}} = \tau_0^* N^3. \quad (4.31)$$

Consequently the translational Brownian motion of the chain at time intervals $t \leq \tau_{\text{max}}$ and on space scales $r \leq r_{\text{max}} = (D\tau_{\text{max}})^{1/2} = a_0^* N^{3/4}$ is not governed by the single-constant diffusion law. Note that
$r_{\text{max}}$ essentially exceeds the size $R$ of the polymer coil: $r_{\text{max}} \gg R$.

Moreover topological constraints produce a number of even stronger (and more interesting) effects. One of these is considered in the next section. Others will be studied in the following publications.

5. Viscosity of a polymer theta-solution in the region of overlapping.

Let us consider a solution of long polymer chains at theta-temperature. The dilute regime is determined by the condition

$$cR^3 \ll 1,$$  \hspace{1cm} (5.1)

where $c$ is the mean number of chains per unit volume. The viscosity $\eta$ of the dilute solution depends on the concentration $c$ in the following way [2]:

$$\eta = \eta_\text{s} f(cR^3),$$

$$f(x) = 1 + \alpha_1 x + \alpha_2 x^2 + \cdots,$$ \hspace{1cm} (5.2)

where $\eta_\text{s}$ is the viscosity of the solvent and $\alpha_1$, $\alpha_2$ are numerical factors. Equation (5.2) in the first approximation can be rewritten in the form:

$$\eta = \eta_\text{s} + \Delta \eta, \hspace{0.5cm} \Delta \eta = \alpha_1 \eta_\text{s} cR^3.$$ \hspace{1cm} (5.3)

The viscosity increment $\Delta \eta$ can be obtained (within the order of magnitude) using the scaling relation [7]:

$$\Delta \eta \sim G \tau$$ \hspace{1cm} (5.4)

where $G$ is the plateau shear elastic modulus for the polymer component and $\tau$ is the characteristic relaxation time for the shear stress. For the dilute solution [7]

$$G \sim cT,$$ \hspace{1cm} (5.5)

and the process of the stress relaxation is not restricted by topological constraints since a shear affine deformation produces no change in a topological state of an isolated polymer coil. Consequently the relaxation time $\tau$ must be of order of the « Zimm time » $\tau_Z$. Substituting equations (2.11) and (5.5) into equation (5.4) we get

$$\Delta \eta \sim \eta_\text{s} cR^3$$

in accordance with equation (5.3).

So far the fact that two (or more) macromolecules may be in a mutually entangled state was not taken into account. For a dilute solution this possibility can be neglected since the mean distance between macromolecules in this regime, $r$, is large compared with their size $R$, $r \gg R$. In more concentrated solutions ($cR^3 \ll 1$) the mean number and spatial dimensions of clusters consisting of entangled chains increase. As a result, it appears some correction to equation (5.3). Nonetheless the general equation (5.2) remains valid until an infinite cluster of entangled chains appears in the solution. The corresponding concentration $c = c^*$ is determined by condition $r \sim R$, i.e.

$$c^* = \kappa / R^3,$$ \hspace{1cm} (5.6)

where $\kappa$ is a numerical factor. For $c > c^*$ the dependence of the viscosity on the concentration must be changed appreciably. In fact, a stress in an infinite cluster cannot relax by the reverse deformation (as it can do for an isolated chain or for a finite cluster). The stress relaxation of an infinite cluster must be accompanied by an essential change of its « topology » : some of the macromolecules must be unlinked and then entangled in another way. Therefore the stress relaxation time of an infinite cluster, $\tau_{\text{inf}}$, is of order of the « topological » time $\tau_{\text{max}}$: $\tau_{\text{inf}} \sim \tau_{\text{max}}$. The plateau modulus of an infinite cluster, $G_{\text{inf}}$, is (within an order of magnitude)

$$G_{\text{inf}} \sim c^* T$$ \hspace{1cm} (5.7)

for $c > c^*$ (a narrow region near the critical point $c = c^*$ is not considered).

Substituting equations (4.27) and (5.7) into equation (5.4) we get

$$\eta \sim \eta_\text{s} N^{z-3/2}, \hspace{0.5cm} c \gg c^*.$$ \hspace{1cm} (5.8)

Comparing equations (5.8) and (5.2) we conclude that, in the vicinity of the concentration $c = c^*$, the viscosity of the solution increases appreciably : in the region between $c = c^*/2$ and $c = 2c^*$ the viscosity increment is determined by the factor of order

$$N^{z-3/2} \gg 1.$$

The conclusions of this section correspond to the following experimental data for the viscosity of theta-solutions. The dependence of the viscosity on the concentration in the region

$$cR^3 = 0.2 \div 2 \left(1\right)$$

is indeed extremely sharp [2]. For concentrations exceeding the concentration of overlapping ($cR^3 \equiv 1$) the dependence of $\eta$ on $cR^3$ appears to be essentially not universal [9] : an additional dependence on the molecular mass of the polymer arises in

\hspace{1cm} \left(1\right) \text{In experimental works a reduced concentration} \\
\text{\hspace{0.5cm} } c[\eta], \text{ where } [\eta] \text{ is the intrinsic viscosity, is generally used. } \\
\text{The reduced concentration is proportional to } cR^3: \\
\text{\hspace{0.5cm} } c[\eta] = 6^{2/3} \Phi_\infty cR^3, \text{ where } \Phi_\infty = 0.47 \left[21\right].
this regime. The data obtained in [9] satisfy the
general equation (5.8) with the empirical value of
the exponent \( z \), being equal to

\[ z = 2.4 \pm 0.2, \quad (5.9) \]

i.e. \( z - z_0 = 0.9 \pm 0.2 \). Therefore the fact that strong
dynamical effects exist in the region of overlapping is
supported as itself by experimental data. Neverthe-
less there is only qualitative agreement between
theoretical predictions and experimental results.

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Appendix.

Calculation of the exponent \( z \) in the second
\( \varepsilon \)-order. — Let us consider equation (4.21) in the
form

\[ n = S/B, \]

where

\[ S = B_1 + 2 B_2 + 3 B_3 + \ldots \quad (A.1) \]

Using equations (4.11), (4.18) we get

\[ S \propto g^{z - d/2}. \quad (A.2) \]

Equation (A.2) can be easily generalized for the case
of entangled chains consisting of different numbers
of « links », \( g_1 \) and \( g_2 \):

\[ S(g_1, g_2) \propto h(g_1/g_2)(g_1 + g_2)^{z - d/2}, \quad (A.3) \]

where \( h(x) \) is a numerical function of order of unity.

Let us define

\[ S(p) = \int S(g_1, g_2) \exp \{-p(g_1 + g_2)\} \, dg_1 \, dg_2. \quad (A.4) \]

Substituting equation (A.3) into equation (A.4) we
get

\[ S(p) \propto p^{-z + d/2}. \quad (A.5) \]

A diagram representation of the function \( S(p) \) up to
the third order of \( \varepsilon \)-expansion is following:

\[ \begin{align*}
S(p) = & \quad + 2 \quad + 4 \\
& \quad - 4 \\
\end{align*} \quad (A.6) \]

Substituting equation (A.9) into (A.8) and compar-
ing the result with equation (A.5) we obtain

\[ -z + d/2 = -4 - \frac{\varepsilon}{2} \Gamma \left( \frac{\varepsilon}{2} \right) \Gamma \left( \frac{d}{2} \right) u^*/

/ \left\{ 1 + u^* \left[ \Gamma \left( \frac{\varepsilon}{2} \right) \Gamma \left( \frac{d}{2} \right) - \frac{2}{\varepsilon} \right] \right\} + \mathcal{O}(\varepsilon^3). \quad (A.10) \]

In order to calculate the fixed point \( u^* \) up to the
second \( \varepsilon \)-order let us define

\[ B(p) = \int B(N_1, N_2) \exp \{-p(N_1 + N_2)\} \times

\times dN_1 \, dN_2, \quad (A.11) \]

where \( B(N_1, N_2) \) is a generalization of the function
\( B(N) \) for the case of chains of different lengths. The
function \( B(p) \) has the following diagram representa-
tion up to the third order of \( \varepsilon \)-expansion:

\[ \begin{align*}
B(p) = & \quad - 2 \quad + 2 \quad + 4 \\
\end{align*} \quad (A.12) \]
After the calculation of the diagrams we get
\[ B(p) = p^{-d} \{ 1 - 2vI_1(p) + 2v^2I_2(p) + 4v^2I_2^2(p) \} \]  
(A.13)

where
\[ I_2(p) = \int G(p, k) G(p, k') G(p, k - k') \times \]
\[ \times d^d k d^d k'/(2\pi)^d \]  
(A.14)

For \( d = 4 \) from equation (A.14) we get
\[ I_2(p) = a^{-8} \{ \text{Const.} + K_4^2 (\ln p)^2/8 \} \]  
(A.15)

The renormalization properties of the quantities \( B \) and \( p \) are the following (compare with Eq. (4.7))
\[ p \rightarrow p \exp(\tau), \quad B \rightarrow B \exp(-2\tau) \]  
(A.16)

Using equations (A.13)-(A.16) we obtain a renormalization equation for the parameter \( u = K_4 v/a^4 \):
\[ \partial u/\partial \tau = eu/2 - u^2 + u^3 + O(\varepsilon) \]  
(A.17)

with the fixed point
\[ u^* = e/2 + e^2/4 + O(\varepsilon^3) \]  
(A.18)

Substituting equation (A.18) into equation (A.10) we finally get
\[ \varepsilon = 2 + e + e^2/4 + O(\varepsilon^3) \]  
(A.19)

References


