Two Types of Topological Constraints in Polymer Networks

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ABSTRACT: It is proposed to distinguish two types of topological constraints in the nonphantom network: one corresponds to entanglements between different subchains in the network, and the other can be described as self-entanglement of a subchain with itself. The number of effective entanglements of the intersubchain type is found to be an increasing function of the network swelling ratio α. This explains the experimentally observed nonmonotonic dependence of the elastic modulus of the network on α. A new "preparation parameter", $\mathcal{P}$, is introduced which characterizes the degree of entanglement between subchains of the network and which depends on network preparation. The relative importance of constraints of intra- and intersubchain types depends on the value of $\mathcal{P}$. Intrasubchain constraints prevail in a network with small $\mathcal{P}$ in the collapsed regime and, in the strongly collapsed regime, lead to a crumpled-globule structure of the network.

1. Introduction

The problem of topological constraints is one of the most interesting in the theory of polymer networks. By topological constraints we mean the restriction of the available part of the phase space caused by uncrossability of real (i.e., nonphantom) polymer chains. (This terminology follows the classical work of Edwards.[1]) It is widely believed that these constraints, or, in other words, entanglements, play a major role in the observed deviations of real network behavior from the predictions of the classical theory, as, for instance, manifested by the so-called Mooney–Rivlin corrections in the theory of network elasticity.[2]

In spite of considerable theoretical efforts, an exhaustive theory of nonphantom networks with topological constraints has not been obtained up to now. With the exception of some phenomenological and semiempirical approaches, most known microscopic theories are versions of the "tube" model[3-5] or the so-called "chain in an array of obstacles".[6,7] Many of these models are based on sound physical ideas and in some cases appeared to be quite successful. Nevertheless, all of them are of quite limited applicability and have some essential shortcomings from a fundamental point of view. (See, for example, refs 8 and 9 for further details.) An attempt to formulate a new, more rigorous, approach was proposed recently by Goldbart and Goldenfeld[10] and independently by Paniukov.[11] It is very beautiful and is based on general ideas of the theory of disordered systems, such as the concept of self-averaging,[12] and, technically, on the use of the replica trick. (By the way, the replica trick itself was first proposed by Edwards just in the context of network theory.[13]) However, the assumption of self-averaging of the free energy seems to be problematic for networks, because of the nonlocal character of entanglements, and it is not so easy to justify it. The formulation of a constructive and physically sound approximation remains a great problem in the framework of this theory.

In this situation it seems useful to continue the qualitative discussion of the problem. In the present paper the following ideas are discussed:

a. Two classes of topological constraints can be distinguished for any network, namely, intersubchain entanglements between different subchains and intrasubchain entanglements between different parts of one subchain (Figure 1).

b. Intersubchain entanglements become more effective with network swelling, while intrasubchain constraints behave in the opposite way.

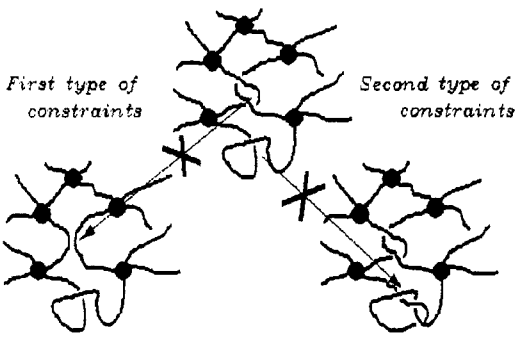

Figure 1. Schematic representation of two types of topological constraints in the network.

c. Change of the effectiveness of intersubchain entanglements causes the swelling dependence (in some cases a nonmonotonic one) of the equilibrium elastic modulus of the network.

d. The network can be characterized by a special "preparation parameter", $\mathcal{P}$, which depends only on the method of network preparation and controls the relative role of the two different types of constraints.

e. For some networks (with small $\mathcal{P}$ value) the regime of strong collapse corresponds to dominance of the constraints of the intra-type, and in this case the network microstate has to be of the so-called crumpled-globule type.[14,15]

2. Effectiveness of Entanglements and Its Change with Network Swelling or Collapse

The system of topological constraints in any real network is formed in the course of network preparation, and the topological state of the network as a whole, as well as mutual and individual topology of subchains, cannot be changed by any continuous deformation of some subchains. This is why at first glance the idea of change of something connected with topological constraints seems to be nonsense.

Different entanglements, however, in reality are not all of the same importance. In any real system, some constraints exist which do not play any appreciable role, i.e., do not restrict appreciably the available part of the phase space, and, therefore, do not contribute essentially to the thermodynamic properties of the system. Moreover, it is possible to imagine restrictions which play an important role in one macroscopic state and which exert a considerably reduced influence in some other mac-

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Figure 2. Simple model illustrating the possible change of effectiveness of entanglement. The obstacle restricts a large phase volume in case A and a smaller one in case B.

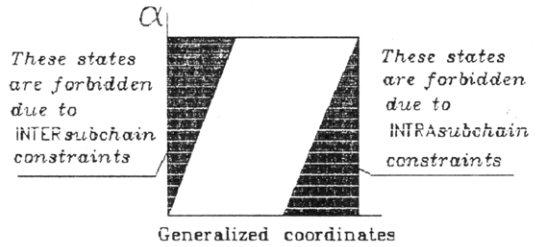

Figure 3. Schematic representation of the conformational space of the network. Here α is the swelling or collapse ratio, and it is proportional to the size of the sample. The second axis corresponds to the other generalized coordinates.

rostates. This idea is illustrated roughly and qualitatively in Figure 2.

The system of constraints is, of course, a strong topological invariant, but the *effectiveness* of some entanglements is typically changeable in the course of the continuous deformation of the polymer chains. The author believes the situation in a real nonphantom network to be just of this type (see also Figure 3).

Let us denote by M_{tot} the total number of effective topological entanglements per subchain in the network. Since there are two types of entanglements, one can write

$$M_{tot} = M_{extra} + M_{intra} \tag{1}$$

where M_{extra} and M_{intra} are the numbers of effective entanglements of the given chain with other chains and with itself, respectively. Thus, the main problem of the present paper is the estimation of the values M_{tot}, M_{extra}, and M_{intra} and their dependencies on the network volume.

3. Estimation of the Number of Effective Entanglements

Let us start with an estimation of the total number of effective entanglements per subchain in the network, M_{tot}. It is determined completely by the network density. Indeed, let us consider a sample network. First of all, it is a system of polymer chains with a definite polymer concentration or volume fraction ϕ (<1). Of course, there are some contacts between different monomer units, and the distance along the chain between two neighboring contacts, h_0, is a well-known function[4,16] of ϕ.

A mean-field-type theory is usually adequate for the network under consideration. In particular, this type of description is applicable at the Θ-point, i.e., in the range of network collapse. This is why mean-field theory is used in the main part of the present paper. The opposite case of strong fluctuations will be considered in the Appendix.

For the above-defined value of h_0 the mean-field theory gives the obvious estimate $h_0 \sim 1/\phi$. It is noteworthy that this value does not depend on temperature: although the pair virial coefficient vanishes at the Θ-point, pairwise contacts still exist. Entanglements are formed by some small fraction of the contacts, as has been investigated in

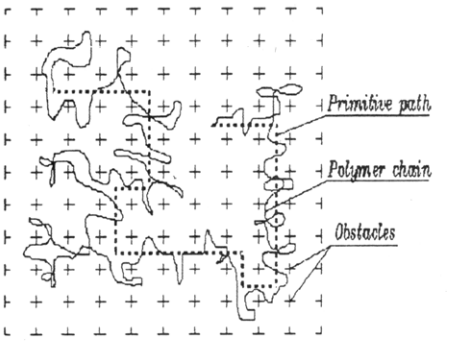

Figure 4. Phantom chain in an array of nonphantom obstacles. The dashed line represents the primitive path.

detail in the context of reptation theory.[3-5] The fraction of entanglements among all contacts is usually written as $1/N_e$. Thus, the distance along the chain between two neighboring effective entanglements scales as $h \sim h_0 N_e \sim N_e/\phi$. Therefore, the number of effective entanglements of a given subchain, both with other subchains and with itself, obeys an estimate of the type

$$M_{tot} \sim N/h \sim \phi N/N_e \tag{2}$$

where N is the number of monomers per subchain.

Now let us remember that our system is the network, so that there are some cross-links which fix the network topology. To avoid misunderstandings, we would like to emphasize once again our definition of what we call network topology. Sometimes this terminology is used for the structure of the network as a so-called "chemical graph".[17] On the contrary, we imply the topology to be connected with this graph embedded in real $3D$ space, i.e., with mutual space positions of the network elements.

Fixing the network topology provides each subchain with a fixed topological invariant. The rigorous and effective construction of the topological invariant for such a complicated system is not yet known (at least, to the author). For qualitative estimation we will characterize the topological state of each subchain by the value of the so-called primitive path;[6,7,9] let us denote it as μd where d is the chain thickness.

The primitive path is an analog of the tube axis line in reptation theory; it is defined rigorously in the framework of the model "polymer chain in an array of obstacles", as shown on Figure 4: μd is the length of the shortest line which is topologically equivalent to the line of the chain backbone. This definition implies the chain itself to be phantom, but of course with the prohibition to intersect the obstacles. It means, in particular, that only one class of topological constraints, namely, the *inter*subchain ones, are taken into account in this model. Of course, a primitive path cannot be defined rigorously for the case of a complex real network. Nevertheless, there is some coarse mean trajectory for each subchain in the network, and the scale of its length is refered to as μd.

Fixing of some primitive path, or the existence of some mean trajectory, implies breakdown of the subchain Gaussian statistics. Indeed, let us return to the very beginning and start with a solution of disconnected long linear chains dissolved at a certain volume fraction ϕ. In accordance with the classical Flory theorem, the chains are Gaussian in this system on all scales because of the mean-field assumption (see also the Appendix). Without cross-links, the system remains ergodic in the sense that Gaussian statistics govern the ensemble of simultaneous states of different chains as well as the ensemble of sequential states of one chain. On the contrary, when

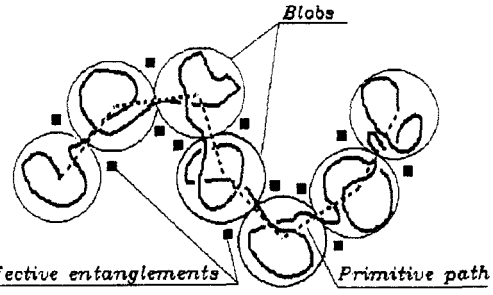

Figure 5. Subchain with a fixed primitive path represented as a chain of Pincus blobs. The number of effective obstacles (shown by squares), which forms the primitive path, is on the order of the number of blobs.

cross-links are "switched on", ergodicity breaks down because the ensemble of single-chain states becomes much more restricted, although the ensemble of states of different chains in a macroscopic sample remains practically unaffected.

The simplest example here is fixing the end points of a single linear polymer chain at a distance r from each other: although the entropy can be written as ln $p(r)$, where $p(r)$ is Gaussian, the ensemble of chain states is only a *sub*set of the whole Gaussian ensemble and obviously does not coincide with the ensemble of states of different chains with different values of r. It leads, of course, to the necessity of invoking some force to fix the end-to-end distance r.[18] The situation in the network is exactly the same: the ensemble of states of each subchain consists of states from the Gaussian ensemble, but this ensemble itself is only a part of the whole Gaussian ensemble.

From the analogy of fixing of the primitive path with that of fixing the end-to-end distance it follows immediately that fixation of network topology causes the existence of an entropic force which compresses the network; because of this force and without volume interactions, or without the excluded-volume effects, the network should collapse dramatically to a nonphysical zero volume, in accordance with the prediction of Ronca and Allegra.[19]

Thus, the existence of the definite primitive path scale μd means that the subchain should be considered as a chain of Pincus-type blobs,[18] each of f monomers and size r_f. The chain of blobs is completely stressed along the tube of the primitive path, so that

$$(N/f)r_f \sim \mu d \tag{3}$$

On the other hand, subchain statistics remain Gaussian inside the blob, so that $r_f \sim dp^{1/2}f^{1/2}$ where the chain stiffness parameter is $p = l/d$, and l is the effective Kuhn segment length of the given polymer; $p \leq 1$. Thus, $f \sim p(N/\mu)^2$. Since the primitive path is formed with some effective obstacles, the number of these obstacles has to be on the order 1 per blob or per f monomers, as illustrated in Figure 5. These effective obstacles correspond to the entanglements of the given subchain with the other ones; they form the external constraints for the given subchain. Therefore, the number of these effective obstacles per subchain is just the above-defined M_{extra}:

$$M_{extra} \sim N/f \sim \mu^2/pN \tag{4}$$

4. "Preparation Parameter" of the Network

The length of the primitive path changes in the course of network swelling or collapse; i.e., the value of μ depends on ϕ. Supposing these deformations to be affine, we can write $\mu \sim \phi^{-1/3}$. The coefficient in this relation is, however, also of importance, since it depends on the method of network preparation. Let us define the parameter

$$\mathcal{P} = \mu^3\phi/N^3 \tag{5}$$

and let us call it conventionally the preparation parameter of the network. In terms of this preparation parameter we can write $\mu = \phi^{-1/3}\mathcal{P}^{1/3}N$, so that

$$M_{extra} \sim \phi^{-2/3}\mathcal{P}^{2/3}N/p \tag{6}$$

We now discuss briefly the main properties of the preparation parameter. Its value depends on the method of network preparation but does not depend on the prepared network volume or on the swelling ratio. In general, it is a characteristic of the given network which does not change with network deformation. It is easy to see that $0 \leq \mathcal{P} \leq 1$. Small values of $\mathcal{P}$ correspond to a network with a weak degree of entanglement of different subchains with each other. A network with an extremely small value of the preparation parameter can be synthesized by rapid concentration of a solution of globules and fast cross-linking of these chains before interpenetration. On the other hand, large values of $\mathcal{P}$ correspond to a high degree of entanglement; the principal way of synthesizing such a network is to cross-link long linear chains in the equilibrium melt with a relatively small amount of cross-linkers.

It is noteworthy that for a network with a given value of preparation parameter $\mathcal{P}$ only states with $\phi \geq \mathcal{P}$ are possible: further swelling to states with $\phi < \mathcal{P}$, i.e., with $\mu > N$, is strongly forbidden by the topological constraints. (The length of the primitive path cannot exceed the contour length of the chain!)

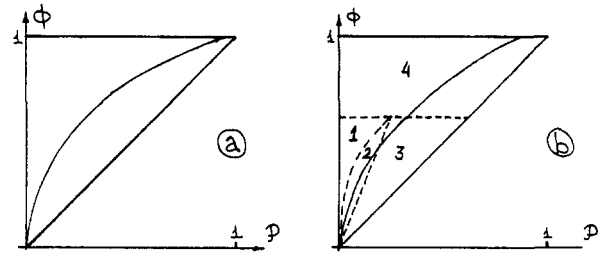

Figure 6. Diagram of topological states of the network, where ϕ characterizes the degree of network compression and $\mathcal{P}$ characterizes the way of network preparation (eq 5). Part a is the result of mean-field theory for the network in a Θ or poor solvent; part b is the result of scaling theory for the network in a good solvent. The regions 1–4 in part b correspond to the regimes i–iii and the mean field listed in the Appendix, respectively. The crossover dashed lines between these regions obey equations of the type $\phi \sim \mathcal{P}^{2/5}(r/p)^{-3/5}$ (1–2), $\phi \sim \mathcal{P}(p/r)^3$ (2–3), and $\phi \sim r/p^3$ (1–4 and 3–4).

5. Diagram of Topological States of the Network

Let us discuss now the results in eqs 2 and 6. It is clear that constraints of the intrasubchain type are of importance if $M_{extra} < M_{tot}$. Comparing estimates in 2 and 6, we find the following condition for *intra*constraints dominance:

$$\phi > \mathcal{P}^{2/5}(N_e/p)^{3/5} \tag{7}$$

This result is illustrated in Figure 6a where the diagram of different topological regimes of the network is plotted in terms of ϕ versus $\mathcal{P}$; an analogous diagram is shown in Figure 6b for the case of a strongly fluctuating polymer system and is discussed in the Appendix. Only the region above the diagonal $\phi = \mathcal{P}$ corresponds to allowed physical states. (The nonphysical situation with $\mu > N$ corresponds to the region below the diagonal.) Most of the topological constraints are of the *intra*subchain type in the states

above the solid crossover line in Figure 6, and *inter*subchain entanglements prevail in the states below this line.

An interesting conclusion concerns the situation in the strong collapse regime, when $\phi \to 1$. For a weakly entangled network with a small value of the preparation parameter $\mathcal{P}$ this regime corresponds to the dominance of *intra*subchain constraints and it means that the so-called crumpled-globule state should be formed in the collapsed state of the network with small $\mathcal{P}$. The concept of this state was introduced in ref 14 for the linear chain, and it was applied in ref 15 for the nonphantom network. The main feature of the strongly compressed network in this state is the dense packing of crumpled unlike links. Simply speaking, some fraction of empty holes remains in the compressed network of this type due to the *intra*subchain constraints. In accordance with eq 7, a regime of this type occurs at $\phi \to 1$ for the network with $\mathcal{P} < (p/N_e)^{2/3}$. In particular, it takes place for any value of $\mathcal{P}$, i.e., for any network, if the chemical nature of the subchains obeys the condition $p > N_e$.

6. On the Volume Behavior of a Polymer Network Elastic Modulus

The estimated number of effective entanglements of the *inter*subchain type, M_{extra}, can also be considered from another point of view. It seems natural to suppose that only entanglements of the extra-type contribute strongly to the network elasticity. From this point of view, M_{extra} is the number of effective physical cross-links per subchain.

Let us consider, for example, the following type of experiment. Take the sample network, fix the conditions (temperature, solvent, etc.), wait for a sufficiently long time, and then measure the equilibrium Young's modulus of the sample under a very small deformation. Then we repeat the experiment under other conditions, etc. After all, we can investigate the dependence of the equilibrium elastic modulus, E, on the network volume or on the swelling ratio α. Such experiments have been described in refs 20–22.

We can easily estimate the elastic modulus E from our previous results. Indeed, in accordance with classical Flory theory $E \sim \alpha^2 \nu_{eff}$, where ν_{eff} is the total number of effective cross-links per unit volume and the factor α^2 originates from the fact that the modulus has to be refered to unit cross section. Since $\nu_{eff} \sim \nu(1 + M_{extra})\alpha^{-3}$ and $\phi \sim \alpha^{-3}$, we obtain the estimate

$$E \sim \alpha^2 \nu_{eff} \sim \nu[1/\alpha + \text{const}\ \alpha \mathcal{P}^{2/3} N/p] \qquad (8)$$

The most interesting feature of this result is the possibility of a nonmonotonic dependence of the elastic modulus on the swelling or collapse ratio α. Dependencies of this type have been observed experimentally.[19-21]

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Appendix. Scaling Considerations for the Case of a Strongly Fluctuating Polymer System

In this appendix we discuss briefly the generalization of our estimate for the case when the mean-field approach is invalid and scaling arguments should be used. The regions of applicability of these two approaches on the temperature–concentration diagram of a polymer solution are well-known for flexible chains with $p = 1$ as well as for semiflexible ones with $p > 1$ (see, for example, Chapter 4 of ref 16 or Chapter 13 of the ref 23).

As to the distance between pair contacts along the chain, it obeys an estimate of the type

$$h_0 \sim \phi^{-5/4}\tau^{1/4}p^{-3/4} \qquad \text{in the scaling regime}$$

$$h_0 \sim \phi^{-1} \qquad \text{in the mean-field regime} \qquad (9)$$

Here τ is, as usual, the deviation from the Θ-temperature, $\tau = (T - \Theta)/T$.

The most delicate problem is estimation of the value of f, the number of monomers per Pincus-type blob for the given length of primitive path μd in a system with density ϕ. We recall that the existence of this type of blobs, or the existence of an effective stress on each subchain, in our system is caused by fixing the topology or the length of the primitive path. Thus, it is characteristic for strongly fluctuating polymers in the same way as for weakly fluctuating ones. In particular, the value of f can be estimated via the relation (3), but with another size of blob, r_f. To estimate the value of r_f, let us denote by g the number of monomers per "concentrational" blob in the semidilute solution of concentration ϕ (see, for example, ref 16, Chapter 4)

$$g \sim \phi^{-5/4}(\tau p)^{-3/4} \qquad (10)$$

and let i be the scale of ideal behavior of an individual chain (see also ref 6)

$$i \sim \tau^{-2}p^3 \qquad (11)$$

As in eq 10, we use Flory's value for the critical exponent $\nu \sim 3/5$. As is well-known, chain statistics in the solution is Gaussian on scales below i and above g, and this corresponds to the swollen coil regime at intermediate scales between i and g. Therefore, there are three possible regimes:

(i) If $f > g$, each f blob is a Gaussian chain of concentrational g blobs, $r_f \sim \zeta(f/g)^{1/2}$ and

$$f \sim (\tau p/\phi)^{1/4}(N/\mu) \sim (\tau p)^{1/4}\phi^{5/12}\mathcal{P}^{-2/3} \qquad (12)$$

where ζ is correlation length in semidilute solution, $\zeta \sim d\phi^{-3/4}(\tau p)^{-1/4}$, and $\mathcal{P}$ is defined according to eq 5.

(ii) If $g > f > i$, then each f blob is a swollen coil of monomers, $r_f \sim df^{3/5}\tau^{1/5}p^{1/5}$, and

$$f \sim (\tau p/\phi)^{1/2}(N/\mu)^{5/2} \sim (\tau p)^{1/2}(\phi/\mathcal{P})^{5/6} \qquad (13)$$

(iii) If $i > f$, then each f blob is a Gaussian coil of monomers, $r_f \sim dp^{1/2}f^{1/2}$, and

$$f \sim p(N/\mu)^2 \sim p(\phi/\mathcal{P})^{2/3} \qquad (14)$$

Finally, for the region $\phi > \tau/p^3$ a mean-field approach, and therefore the results mentioned in the text, is valid even for the polymer in a good solvent.

The condition of *intra*chain constraint dominance $M_{extra} < M_{tot}$ can be written in the form $f > h = h_0/N_e$. Thus, all the situations can be easily analyzed with the relations (9–14). The results are summarized in Figure 6b.

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