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Topological Constraints in Polymer Network Strong Collapse

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ABSTRACT: The quantitative theory of strong collapse of a polymer gel based on the concept of the crumpled globule state of a nonphantom polymer chain is proposed. The theoretical explanation of the experimental results of T. Tanaka et al.[5] on equilibrium gel swelling for the strong collapse regime is given. It is shown that the theory is in a good agreement with experimental data. Some applications of the concept of the crumpled globule state to the general problems concerning the equilibrium properties of nonphantom networks are also discussed briefly.

1. Introduction

The collapse transition in polymer gels under changing of external conditions at first was discovered by T. Tanaka[1] in 1978. There exist now a number of corresponding investigations, both theoretical[2,3] and experimental.[4,5] The phenomenon of gel collapse is very interesting from a scientific point of view, as well as in connection with possibilities of its technological and biological applications.

It is quite natural to imagine a polymer gel collapse as coil–globule phase transition in subchains forming the network. The simple mean-field theory based on this idea gives a qualitatively correct description of many observable properties of the collapse transition, including some delicate features, such as, for example, reversible collapse of the gel in a complex (two-component) solvent.[6,7]

Nevertheless, the simplest theory has a lot of obvious but serious defects. First of all, it neglects the influence of topological constraints on subchain conformations; i.e., it neglects the fact of subchain nonphantomness.

However, unlike the high elasticity of networks where the topological constraints (which can be described by the so-called Mooney–Rivlin corrections[8,9]) become essential only under strong stretches, for the collapsed networks a serious discrepancy between simplest theory and experimental data was observed in ref 5 in the strong compression regime (see Figure 2). (In the work in ref 5 the equilibrium swelling and collapse of *N*-isopropylacrylamide gel in pure water at various temperatures was investigated.)

It is noteworthy that the quantitative comparison of experimental data with the theoretical results of ref 5 is possible due to the fact that authors in ref 5 in addition to the experimental data on temperature dependence of sample gel volume had used also the results of independent measurements of two important parameters: ν, the number of subchains per unit volume in the initial state of network, and ΔH, the enthalpy of polymer–solvent mixing. The value of ΔH determines the temperature dependence of the Flory parameter χ

$$\chi = \frac{\Delta H - T\Delta S}{2k_B T} = \frac{\Delta H}{2k_B T} - \frac{\Delta S}{2k_B} \tag{1}$$

where T is the temperature and k_B is Boltzmann constant.

The authors of ref 5 tried to match the theory with the experimental data by fitting of parameters ν and ΔH. It required reduction of ΔH up to 10^3 times and an increase of ν up to 10^2 times. Such great variations, of course, do not have any physical sense. Moreover, we must note that the real value of ν cannot exceed ν_{max} and could only be smaller than the upper estimation of ν presented in ref 5.

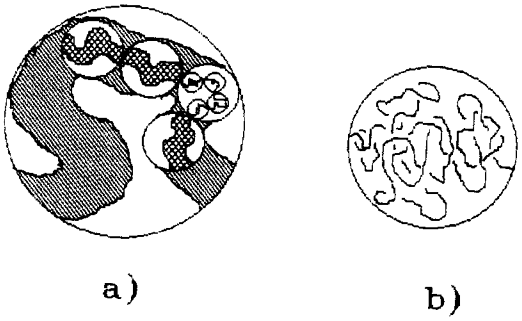

Figure 1. Schematic representation of (a) the crumpled globule state for a single nonphantom chain and (b) the equilibrium globule state for a single linear chain.

Any explanations of this discrepancy are absent in ref 5. That is why in the present work we try to explain it, and in this connection we propose the following hypothesis: due to the topological constraints, the network subchains can form the so-called crumpled globule state;[10,11] just the peculiarities of this state allow us to claim good agreement of our theoretical description and experimental results obtained in ref 5.

The concept of the crumpled globule state was introduced in refs 10 and 11 in the course of investigation of the kinetics of the coil–globule transition (i.e., collapse) of a single nonphantom chain. The main feature of the crumpled state is as follows: in this state every chain part on any arbitrary scale is globulized in itself and is segregated in space from all other parts of the same scale. Such structure is self-similar in the broad interval of scales, because each part of a chain (being globulized in itself) consists of subglobules (or crumples) of smaller scales segregated from each other. The crumpled globule state of a single chain is shown schematically in Figure 1a; for comparison the equilibrium globule state of the linear chain is shown in Figure 1b. (For more details see the Appendix.)

In this paper it will be demonstrated that the theory based on the concept of the crumpled globule state is in better agreement with the experimental data of ref 5 than the usual mean-field theory.

The present paper is organized as follows. In section 2 the ordinary mean-field theory of the phantom network swelling and collapse will be redescribed and presented in a most convenient form. In section 3 an interpolation expression for the additional topological contribution to the free energy of the collapsed network caused by crumpled globule states of the network subchains will be proposed. In section 4 the equation of state of a nonphantom network will be derived and compared quantitatively with the experimental data of ref 5. Section 5

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contains some additional arguments about our main result concerning the interpolation expression for the topological contribution to the free energy of a network. General problems of equilibrium properties of a nonphantom network will be discussed briefly in section 6. Finally, in the Appendix additional information concerning formation of the equilibrium crumpled globule will be given.

2. Mean-Field Theory of Equilibrium Swelling and Collapse of a Phantom Network

Swelling and collapse of the polymer network can be characterized by the linear expansion factor $\alpha = (V/V_0)^{1/3}$ where V and V_0 are the network sample volumes in the current state and in the so-called initial one, respectively. Of course, another equivalent expression for the linear expansion factor reads

$$\alpha = (\phi_0/\phi)^{1/3} \tag{2}$$

where ϕ_0 and ϕ are volume fractions of polymer in the initial and the current states of the network, respectively.

For the initial state it is most convenient to use such a state of network where the subchain statistics is at most similar to the Gaussian one. Of course, such an initial state in general is not equal to the network state under the preparation conditions. However, for the real conditions of the experiment[5] we have some reasons to believe that statistics of subchains in the network under the preparation conditions is practically Gaussian-like. That is why it will be supposed below (as it was also conjectured in ref 5) that the case $\alpha = 1$ corresponds just to the preparation conditions.

In the framework of the usual mean-field theory, the expression for the free energy of the network without any topological constraints can be written in the following form:

$$F_{\text{phant}} = F_{\text{el}} + F_{\text{int}} + F_{\text{i}} \tag{3}$$

Here F_{phant} means that we consider the phantom network only (i.e., the network consisting of phantom subchains). As usual, F_{el} is an elastic energy of subchain deformations, F_{int} is the contribution of volume interactions among links of subchains, and F_{i} is an additional term for the electrically charged network.

For the elastic free energy it is easy to write down the usual expression taking into account the fact that in the initial state (i.e., at $\alpha = 1$) all the subchains are Gaussian-like (for more details see, for example, ref 8)

$$\frac{F_{\text{el}}}{k_{\text{B}}T} = \frac{3\phi}{N}\left\{\frac{1}{2}(\alpha^2 - 1) - \frac{2}{m}\ln \alpha\right\} \tag{4}$$

where N is the total number of links per subchain and m is the network functionality (below we will suppose $m = 4$).

Volume interactions can be described in the framework of the usual Flory–Huggins model (see, for example, ref 8 or 12)

$$F_{\text{int}}/k_{\text{B}}T = (1 - \phi)\ln(1 - \phi) + \phi - \chi\phi^2 \tag{5}$$

where χ is a well-known Flory–Huggins parameter (see eq 1).

The main contribution to the value F_{i} for the charged polyelectrolyte network is due to the translational entropy of the counterion gas (see, for example, ref 8); therefore

$$\frac{F_{\text{i}}}{k_{\text{B}}T} = \frac{\phi f}{N}\ln\left(\frac{\phi f}{N}\right) \tag{6}$$

where f is the number of counterions per subchain.

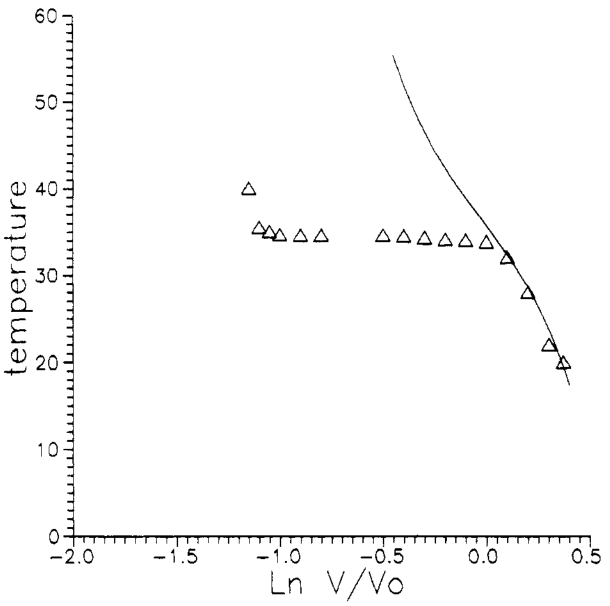


Figure 2. Equilibrium swelling curve for the uncharged gel: points, experimental data of ref 5; line, the result of mean-field theory, which neglects all the topological constraints (eq 8). The main discrepancy is in the strong collapse regime.

An equilibrium dependence $\alpha(T)$ (or $T(\alpha)$) for the real experimental conditions of ref 5 can be obtained from the usual condition $\pi = 0$, where π is the osmotic pressure; i.e.

$$\pi = \phi^2 \frac{\partial}{\partial\phi}\left(\frac{F}{\phi}\right) \tag{7}$$

If we will take into account eqs 2–6 as well as condition 1, then it will be easy to see that the equation of state of the phantom network for the observable variables T and α has the form

$$\frac{1}{T} = \frac{\Delta S}{\Delta H} + \frac{k_{\text{B}}}{\Delta H {\phi_0}^2}\{\nu \text{v}/N_{\text{a}}[(1 + 2f)\alpha^3 - 2\alpha^5] - 2\alpha^6 \ln(1 - \phi_0/\alpha^3) - 2\phi_0\alpha^3\} \tag{8}$$

In eq 8 we have used an obvious fact that $\phi_0/N = \nu\text{v}/N_{\text{A}}$, where v/N_{A} is the volume of one chain link ($\text{v} \simeq 5 \times 10^{-3}$ L is the molar volume, N_{A} is Avogadro's number) and ν is the number of subchains per unit volume in the gel under the preparation conditions.

The resulting eq 7 in ref 5 was compared with the experimental data, and this comparison demonstrates some essential deviations of the mean-field theory predictions from experimental data[5] (see Figure 2).

It is important that all the parameters in eq 8 were supposed in ref 5 to be known from independent measurements:

(a) The value of ν was estimated in ref 5 from the amount of cross-linker used in the gel preparation (of course, it is only upper estimation). There was obtained $\nu < \nu_{\max} \simeq 1.0 \times 10^{22}$ L^{-1}.

(b) The value of ΔH was introduced in ref 5 from ref 13: $\Delta H \simeq -8.7 \times 10^{-14}$ erg.

(c) The value of ΔS was estimated in ref 5 as follows: $\Delta S \simeq \Delta H/T^*$ where T^* is the temperature corresponding to the horizontal part of the experimental swelling curve.

(d) Estimation of the value ϕ_0 is the most delicate problem. In ref 5 it was determined, from the supposition, that the singularity observed on the equilibrium swelling curve in the high-temperature regime is caused by the gel approaching to the state with densely packed links, i.e., with $\phi = 1$. Therefore, this singularity is described by the term $\sim\ln(1 - \phi_0/\alpha^3) = \ln(1 - \phi_0/\alpha^3)$ in eq 8, and it

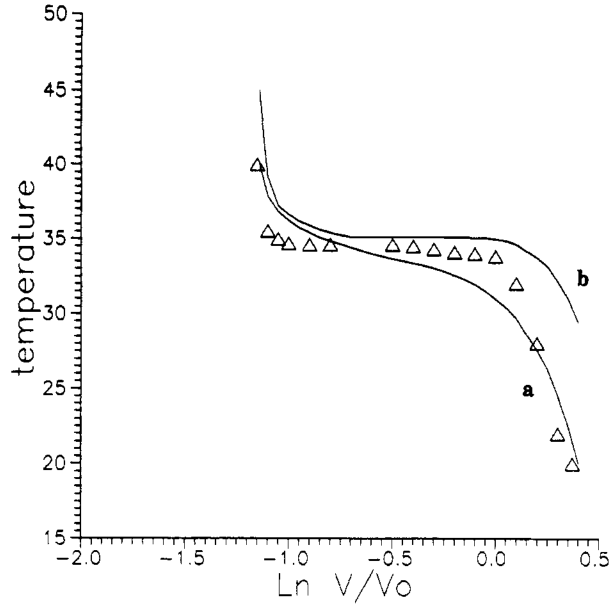


Figure 3. Equilibrium swelling curves for the uncharged (a) and charged (b) gels: points, experimental data of ref 5; lines, result of our theory based on the concept of the crumpled globule state (eq 11).

corresponds to the condition $\phi_0/\alpha^3 \rightarrow 1$. Because the singularity on the experimental curve corresponds to the point $\alpha = (0.07)^{1/3}$, then $\phi_0 \simeq 0.07$ ($\phi_0 \simeq 0.070 \pm 0.005$).

When these real values of parameters are used, it can be seen that the theoretical prediction (eq 8) differs essentially from the experimental data, as is shown in Figure 2.

3. Interpolation Expression for the Topological Contribution to the Free Energy of a Nonphantom Network

As was mentioned in section 1, the main defect of the simplest theory described above concerns the neglecting of all the topological constraints. However, in the strong collapse regime the existence of such constraints may lead to the crumpled state formation in subchains. If we denote $F_{\text{top.}}$ as an additional contribution term to the free energy caused by topological constraints, then we can rewrite the total free energy as follows:

$$F = F_{\text{phant}} + F_{\text{top.}} \tag{9}$$

Being in the framework of mean-field theory, we must put the expression 9 into osmotic pressure definition eq 7, and taking into account the $\pi = 0$ condition, we get the equation of state of a nonphantom network. It will be the natural generalization of eq 8.

Of course, we cannot calculate $F_{\text{top.}}$ exactly. However, we will present in section 5 some phenomenological qualitative conjectures concerning the following hypothesis: the final state of nonphantom network collapse is not the state with densely packed links (Figure 4a) but with densely packed crumples (Figure 4b). Such crumples are impenetrable for each other due to the topological constraints. In this connection for the $F_{\text{top.}}$ we propose an extrapolation expression that has a form

$$F_{\text{top.}} = -\lambda\phi^2 \ln (1 - \beta\phi) \tag{10}$$

where λ and β are numberic parameters. The physical meanings of λ and β we will discuss in section 5; here we give only a resulting estimation of numerical values used in eq 10, $\lambda \approx {}^1/_6$, $\beta \approx 12$ $(1 < \beta < 30)$.

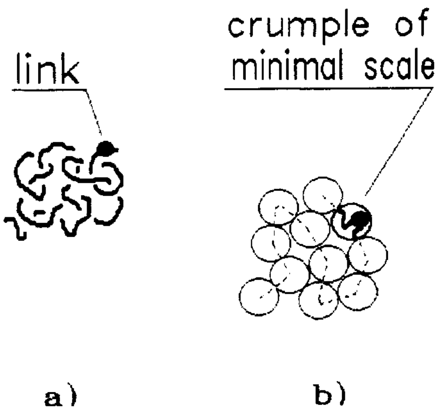


Figure 4. Schematic representation of the state with extremely dense packing of links (a) and minimal crumples (b).

Before some speculations about eq 10, let us derive in the next section the equation of state of the nonphantom network and let us compare the result obtained in such a way with the experiment described in ref 5.

4. Equation of State of the Nonphantom Network: Theory and Comparison with Experiment

Equations 7, 9, and 10 lead to the following form of the equation of state:

$$\frac{1}{T} = \frac{\Delta S}{\Delta H} + \frac{k_{\text{B}}}{\Delta H {\phi_0}^2}\Bigg\{\nu\text{v}/N_{\text{A}}[(1 + 2f)\alpha^3 - 2\alpha^5] - 2\alpha^6 \ln (1 - \phi_0/\alpha^3) - 2\phi_0\alpha^3 - \frac{2\lambda}{\beta}{\phi_0}^2 \ln (1 - \beta\phi_0/\alpha^3) + \frac{2\lambda{\phi_0}^4}{1 - \beta\phi_0/\alpha^3}\alpha^{-6}\Bigg\} \tag{11}$$

For the parameters v, f, ΔH, ν, and ΔS we must use the same numeric values as those in eq 8 because they are known from independent measurements. However, it does not concern the value of ϕ_0, which was determined from the indirect condition $\phi_0/{\alpha_{\text{sing.}}}^3 = 1$ and which now we are going to determine in a new way from the conditions $\beta\phi_0/{\alpha_{\text{sing.}}}^3 = 1$. This new condition means that the observable singularity to the term $\ln (1 - \beta\phi_0/\alpha^3)$ instead of $\ln (1 - \phi_0/\alpha^3)$ written above. For the values

$$\lambda = {}^1/_6 \text{ and } \beta = 12 \tag{12}$$

we have

$${\phi_0}^{\text{new}} = {\alpha_{\text{sing.}}}^3/\beta \cong 0.006$$

(compared to ${\phi_0}^{\text{old}} = 0.07$).

The T-dependence of the swelling ratio $V/V_0 = \alpha^3$ calculated from eq 11 for $\Delta H = -2.3 \times 10^{-13}$ erg is in better agreement with the experimental data than the best fit values of ref 5 for uncharged networks ($f = 0$), as well as for charged ones (see parts a and b of Figure 3, respectively).

To avoid some misunderstandings, let us clarify now the following question: why does the addition of only a *repulsive* term lead to a decrease of the sample volume for the fixed temperature? The answer is simple: the diminishing of the value of parameter ϕ_0 (${\phi_0}^{\text{new}} = {\phi_0}^{\text{old}}/\beta$) means, roughly speaking, an effective reduction of the excluded-volume effect. If we plot T versus α^3 using a new ϕ_0 value, keeping other parameters invariable in classic eq 8, i.e., in eq 11 without the two last terms, then this graphic will lie lower than presented in Figure 2 and will have singularity at the point $\alpha_{\text{sing.}}/\beta^{1/3} < \alpha_{\text{sing}}$. The last two terms in eq 11 are connected with topological repulsion (see eq 10) playing a major role in the strong contraction regime only and shift the singularity to the correct point $\alpha_{\mathrm{sing.}} = 0.07^{1/3}$.

5. Conjectures on the Topological Contribution to the Network Free Energy

Let us discuss now the main point of the present work: the interpolation expression described by eq 10. This form of the expression for the topological contribution to the free energy of the network is proposed in accordance with the following three arguments:

1. The expression for the entropy of the crumpled globule is found in ref 11 (it is shortly reviewed in the Appendix). Therefore, for the total free energy we have

$$\frac{1}{v}(F_{\mathrm{int}} + F_{\mathrm{top.}}) = Bn^2 + Cn^3 + \frac{a^6}{N}n^3 + \dots \qquad (13)$$

Here as in eqs 4–6 F_{int} and $F_{\mathrm{top.}}$ are the contributions to the free energy per volume v of the unit cell of the effective Flory–Huggins lattice; B and C are two- and three-body coupling constants of monomers, $n = \phi/v$ is the number of monomers per unit volume, a is a parameter of the standard beads-on-string model of the polymer chain, and N_{e} is also a well-known parameter of the reptation model (see, for example, ref 8 and 12). Because

$$(1/v)F_{\mathrm{int}} = Bn^2 + Cn^3 \qquad (14)$$

according to eqs 13 and 14 we have

$$F_{\mathrm{top.}} = v\frac{a^6}{N_{\mathrm{e}}} \simeq \frac{1}{6}\left(\frac{a^6}{CN_{\mathrm{e}}}\right)\phi^3, \quad \text{when } \phi \to 0 \qquad (15)$$

where $\phi = nv$ and $C = v^2/6$ (the last definition is clear from comparison of eqs 5 and 14).

Equation 15 has a simple physical meaning: it describes the entropy loss due to the crumples formation and reflects the fact that ϕ-dependence of the smallest crumple scale is of order ϕ^{-2} and the virial expansion of $F_{\mathrm{top.}}$ begins with a term of order ϕ^3. (For more details see ref 11 and the Appendix.)

2. For the single chain the density of the crumpled state is less than that of the usual equilibrium one, which is connected with additional topological repulsive-type volume interactions between crumples and is reflected in the following inequality:

$$\frac{n_{\mathrm{crump}}}{n_{\mathrm{eq}}} = \frac{1}{1 + (\mathrm{constant})(a^6/CN_{\mathrm{e}})} < 1 \qquad (16)$$

3. In connection with eq 16 we propose the conjecture that the final state of the nonphantom network (or closed-chain) collapse corresponds to the most dense packing of crumples of minimal (for the given chemical nature of chain) scale *but not links*. Correspondingly, the maximal volume fraction of polymer is now

$$\phi_{\max} = 1/\beta < 1 \qquad (17)$$

Of course, this conjecture is totally empirical.

In the framework of the hypothesis about dense crumple packing it is obvious that near the most dense packing point (i.e., for $\phi \to \phi_{\max}$) the free energy can be calculated by using trivial lattice gas theory (or Flory–Huggins theory) and therefore has logarithmic singularity.

It is easy to see that expression 10 is the simplest equation satisfying all the above-mentioned conditions 2–4.

Let us now briefly discuss the question about the numerical values of parameters λ and β. Through comparison of eqs 10 and 15–17, it is easy to obtain

$$\beta = 1 + (\mathrm{constant})(a^6/CN_{\mathrm{e}}); \quad \lambda = (1/6)[1 - (1/\beta)] \qquad (18)$$

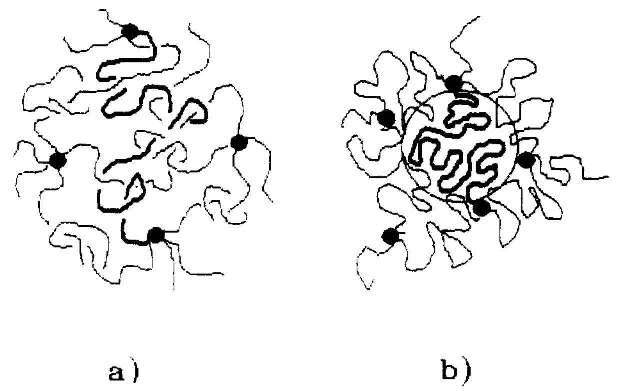


Figure 5. Schematic representation of the networks prepared from the systems of penetrated coils (a) and segregated globules (b).

The dimensionless ratio C/a^6 characterizes the rigidity of the polymer chain; $C/a^6 \approx (d/l)^3$, where l and d are the length and thickness of the effective chain segment. Really parameter C/a^6 changes from one chemical nature of chain to another one in the broad interval between 10^{-5} for the DNA double helix and 0.03 for polystyrene.[8,15]

The parameter N_{e} also depends on the chain flexibility. Therefore, it is difficult to estimate the value of β exactly, and we can suppose only that β lies in the interval $1 < \beta < 30$. This supposition is, of course, in full agreement with eq 12.

6. Conclusion

Here we will discuss briefly the general question concerning the role of topological constraints in the equilibrium properties of the nonphantom network.

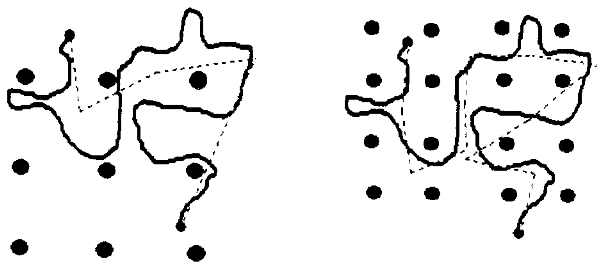
In general two types of topological constraints are meaningful: between different subchains and between different parts of one subchain.

The constraints of the first type play the main role in the swelling (or tension) of a network prepared from a system of *coils* strongly penetrated through each other. This case is shown schematically in Figure 5a, and it is just a typical nature of the Mooney–Rivlin corrections (ref 9). This type of constraint is not discussed in the present paper (but was a subject of our previous investigations[16,17]).

At the same time the constraints of the second type are of the main importance, in particular, for the network prepared from *collapsed chains* (Figure 5b).

We stress in conclusion that the most important fact in the interplay of both types of constraints is as follows:

In the course of compression of the network (or the gel collapse) the role of the constraints of the first type decreases, but that of the second one increases. This fact could be explained with the help of the so-called "chain in an array of obstacles" model (see refs 8, 16, and 17 and Figure 6). The length of the primitive path plays in this model the role of topological invariant (Figure 6). When the network collapses, this length decreases. At the same time the length of the subchain itself is constant of course. Therefore, the network compression or collapse leads to the formation of crumples of gradually increasing scale. Impenetrability of the crumples based on their topological properties (see refs 10 and 11) leads just to the complete crumpled state formation.



a) b)

Figure 6. Compression of an array of obstacles, containing the polymer chain. The length of the primitive path (dashed line) decreases during the compression.

Appendix

The concept of the *crumpled globule* state of the nonphantom polymer chain was proposed in refs 10 and 11 in connection with the investigation of the kinetics of coil–globule phase transition.

The crumpled globule state differs dramatically from the equilibrium one in the following respects. In the equilibrium globule chain parts are similar to chains in the melt and according to Flory theorem are Gaussian-like, having the fractal dimension $d_f = 2$ in a broad interval of scales.

At the same time in the crumpled globule each part is globulized in itself with the nontrivial fractal dimension $d_f = 3$.

The nature of the last fact is as follows. Let us consider, globulized in itself, part (called "blob" for short) of long chain that is in contact with other globulized parts of the same chain. If the chain is nonphantom and has no free ends (closed chain, subchain of a network, long chain in course of fast collapse), then these parts are mutually impenetrable. Really, other chain parts (other blobs) play the role of an effective lattice of obstacles surrounding the test blob, but it was shown in refs 16 and 17 that the M-link ring chain without volume interactions not entangled with any of obstacles has the size

$$R^{(o)}(M) \sim aM^{1/4} \tag{A.1}$$

As $R^{(o)}$ is the size of the equilibrium chain part in the lattice of obstacles, then the entropy loss of ring chain, S, as a function of its size, R, reaches its maximum for $R \simeq R^{(o)}$ and the further chain swelling for values of R exceeding $R^{(o)}(M)$ is entropically unfavorable. At the same time for a material chain with excluded volume, the following inequality must be fulfilled:

$$R(M) \geqslant aM^{1/3} \tag{A.2}$$

In connection with the obvious relation $R(M) > R^{(o)}(M)$, the swelling of chain part connected with their mutual interpenetration by the loops does not occur in the system with the constant density and volume interactions. It means that the blob size of every scale coincides with its own size in the crumpled globule state, and these blobs are mutually segregated in space on every scale.

Just the system of densely packed globulized blobs corresponds to the chain with the fractal dimension $d_f = 3$ ($d_f = 3$ is realized from the smallest scale g^* up to the full globule size). The value g^* is of order

$$g^* = N_e(na^3)^{-2} \tag{A.3}$$

where N_e is the well-known parameter of the reptation model and n is the globule density.

The last estimation was obtained in ref 11 by using the following arguments: $g = (na^3)^{-2}$ is the mean length of the chain part between two neighboring contacts along the chain with other parts; consequently, $N_e g$ is the mean length of the chain part between topological contacts (entanglements). Of course, in the phantom chain Gaussian blobs of size g are strongly overlapped with other ones because pair contacts between monomers are insignificant under Θ-conditions. However, for the nonphantom chain these pair contacts are essential from the topological point of view because chain crossings are prohibited independent of the value and sign of the virial coefficient and arguments mentioned above are valid.

The entropy loss connected with the crumpled state formation can be estimated as follows:

$$S \simeq -N/g^* \tag{A.4}$$

When this estimation was used, the corresponding crumpled globule density n was obtained (see eq 16).

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