# Swelling and collapse of polymer networks

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The swelling of a polymer network in a good solvent and of the collapse of this sample in a poor solvent is discussed theoretically for networks prepared in the presence of a large amount of diluent. The notation used is convenient for comparison with the theory of the swelling and collapse of a single macromolecule. The reference state for the networks under consideration must be chosen near the $\theta$ temperature for the corresponding linear macromolecule. For a free network and a network with fixed dimensions along one or two axes we obtain asymptotic results for the swelling of the network in a good solvent; these do not coincide with the classical Flory results. Results for the collapse of the network, which takes place upon cooling below the $\theta$-point are also obtained. The collapse can occur either as a discrete first order phase transition (if the network chains are stiff or if it is stretched along one or two axes), or as a continuous non-phase transition (located in a narrow temperature range).

## INTRODUCTION

Considerable attention has been paid recently to the experimental investigation of the influence of volume interactions on polymer network properties[1–9] (for a theoretical introduction to this field see ref 10). In particular, the study of the conformational behaviour of the network sample surrounded by an excess of solvent, i.e. swelling in the good solvent and collapse in the poor solvent has attracted investigation[1,2,7,10].

The theory of the swelling and collapse of a single polymer macromolecule surrounded by the solvent has now been fundamentally constructed (see review, ref 11). The aim of this article is to apply the methods and the terminology of this theory to the problem of the swelling and collapse of the polymer networks. We shall consider only networks prepared in the presence of a large amount of diluent; thus crosslinked networks prepared in the dry state are beyond the scope of this paper.

In order to ensure direct analogies with the case of a single macromolecule, we shall use a system of network parameters which is somewhat different from that commonly used[10]. The author believes that this system of parameters is the most natural one for a polymer network.

Let the network polymer chains be the persistent chains of width $d$ and of persistent length $l$. We denote a portion of the chain of length $\sim d$, as the 'monomer'. Let $m \gg 1$ be the average number of monomers in the chain between two nearest neighbour branch points, and let $N$ be the total number of monomers in the network. We shall assume that the monomers interact with a second virial coefficient $B$ and a third virial coefficient $C$ (more exactly, we should use the effective virial coefficients $B^*$ and $C^*$ renormalized due to the connectivity of monomers in the chain[12]; we shall imply that such a renormalization is already performed). For a network with a small average monomer concentration $n$ within a network, the free energy $F_{\text{int}}$ of the volume interaction of the monomers is:

$$F_{\text{int}} = NTBn + NTCn^2 \qquad (1)$$

where $T$ is the temperature (the Boltzmann constant is taken to be unity here and below). In the case of network swelling, it will be enough to take into account only the first term in expression (1); the term incorporating the third virial coefficient $C$ will be important in the theory for the collapse of the network. Accounting for the next terms in the virial expansion is not necessary, since, as will be seen from the final results, at $m \gg 1$ the average monomer concentration within the network is small in all the situations under study in this paper – compare with ref 11.

We also assume that the functionality of the branch points is not high ($f = 3 \sim 4$). In this case, as shown in refs 3 and 4 for a swelling network in good or $\theta$ solvents, the degree of interpenetration of the coils formed by different network chains is small (in other words, the so-called Ziabicki factor[13] is close to unity). Therefore the average monomer concentration within the network is of the same order of magnitude as the average monomer concentration within a polymeric coil of $m$ monomers.

Finally, we shall use the traditional assumption that the network chains deform affinely together with the macroscopic sample. The existence of enormous numbers of topological restrictions on the possible deformations of the network chains makes impossible any essential deviation from affinity.

## FREE ENERGY OF THE NETWORK

The problem of accounting for volume interactions in a polymer network prepared in the presence of diluent is *in one respect* more simple than the corresponding problem for a single linear macromolecule. This results from the possibility of neglecting the surface free energy terms for a macroscopic sample. Consequently, the free energy of a polymer network can be represented as the sum of $F_{\text{int}}$ (see expression 1) and $F_{\text{el}}$, the free energy of elastic deformation for the network. (It must be recalled that in the case of a single macromolecule the surface free energy $F_s$ must be taken into account as well, and that the swelling of the macromolecule can be described by the interplay of $F_{\text{int}}$ and $F_{\text{el}}$, whereas its collapse is described by the interplay of $F_{\text{int}}$ and $F_s$[11].)

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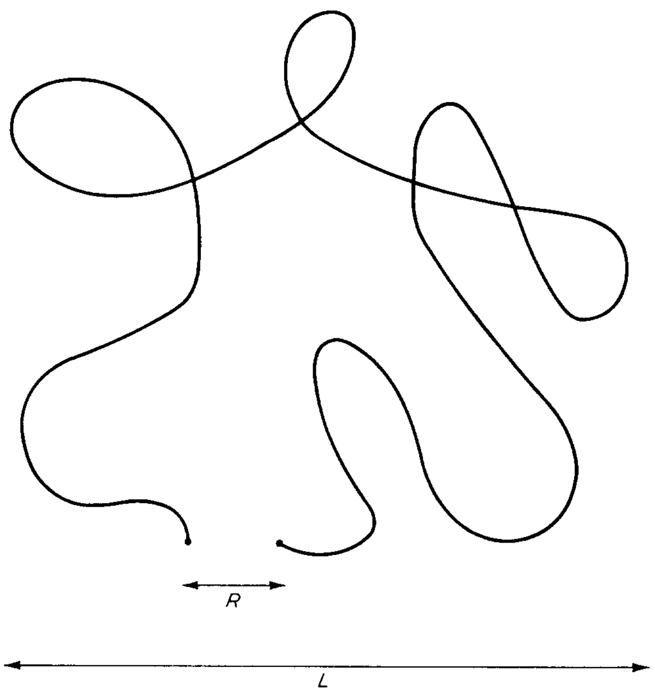

*Figure 1* Typical conformation of the chain between two nearest neighbour branch points in the collapsed state. Due to the affinity principle the average distance between the ends of this chain is $R \sim m^{1/3}$. The chain itself, being situated in the concentrated solution of other chains, obeys Gaussian statistics; its average spatial dimensions $L \sim m^{1/2}$. Thus in the typical conformation $R \ll L$.

Volume interactions in the polymer network prepared in the presence of diluent can also lead to a problem which is more complex compared with a single macromolecule. This becomes apparent when considering $F_{el}$, which may be expressed by the familiar[1,10] Flory form:

$$F_{el} = \nu T\left[\frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3}{2} - \frac{2}{f}\ln(\alpha_x\alpha_y\alpha_z)\right] \qquad (2)$$

where: $\nu$ is the number of elastically effective network chains; and $\alpha_x$, $\alpha_y$ and $\alpha_z$ are the deformation ratios of the network along $Ox$, $Oy$ and $Oz$ with respect to a hypothetical reference state, in which all the network chains are Gaussian coils unperturbed by volume interactions. In the case of a single macromolecule such a reference state is realized at the $\theta$ temperature; for a polymer network prepared by cross-linking in the absence of diluent the dry state acts as a reference state, since polymer chains exhibit Gaussian statistics in the bulk. This was used by Flory[14] in his classical theory of elastic deformation and swelling.

However, when a large amount of diluent is present, the state which corresponds to the complete absence of volume interactions cannot be realized. Indeed, it is easy to show[15,16], that in the absence of volume interactions the monomer concentration within the network tends to infinity when $N \to \infty$. Naturally this is never the case under real conditions. Thus it is *never* possible to neglect completely the role of the volume interactions in the polymer network; the chains are *never* strictly Gaussian, and thus the reference state can be chosen only approximately. In this state the conformation of the network chains must be most close to the conformation of unperturbed Gaussian coils. It should be emphasized that equation (2) is therefore approximate for this case and thus, strictly speaking, the results obtained based on this formula should be valid only in orders of magnitude.

It is clear from the discussion above that the reference state for the polymer network under consideration must be chosen somewhere near the $\theta$ temperature for the corresponding linear macromolecule. In this case the conformation of the network chains is closest to the unperturbed conformation: in the good solvent the network chains swell with respect to their unperturbed dimensions; below the $\theta$-temperature (see below) the collapse of the network occurs, and due to the affinity principle the network chains take-up the 'contracted' conformation of the type shown in *Figure 1* (see the caption to *Figure 1*)*.

The average monomer concentration $n_0$ within the network in the reference state is of the same order of magnitude as the average monomer concentration within the polymeric coil of $m$ monomers at the $\theta$ temperature (see Introduction), i.e.[17]:

$$n_0 = k\frac{1}{m^{1/2}p^{3/2}d^3} \qquad (2)$$

where $p = l/d$, and $k$ is the parameter of order unity. Formulae (1)–(3) determine completely the free energy of a polymer network. The more exact assignment of the reference state (i.e. the calculation of the parameter $k$) is not justified owing to inaccuracy of the theory. The parameter $k$ must be regarded as the phenomenological adjustable parameter of order unity, which depends on the details of the network structure.

The definition of the reference state (the $\theta$ state of a polymer network†) differs considerably from that used in the Flory theory[14] (the dry network in the absence of diluent). Our definition is valid for the networks prepared in the presence of a large amount of diluent. Indeed, in this latter case the dry network is to a large extent collapsed; thus the network chains adopt the supercoiled conformation (in the terminology of ref 10) shown in *Figure 1* and the choice of this state as the reference state is not correct.

It must be noted that in some papers (see the review, ref 10), the reference state was identified with the state of the network under the formation conditions. However, it is physically clear that the conditions of formation affect the network properties only indirectly through the network parameters ($\nu$, $k$ and $m$), but not directly (this was confirmed experimentally in ref 4), and thus bear no relation to the reference state.

The free energy of a polymer network $F = F_{int} + F_{el}$ in our notation may now be written as follows for the three cases below.

(a) Free swelling or collapse of the network: $\alpha_x = \alpha_y = \alpha_z \equiv \alpha$; $n = n_0/\alpha^3$, thus

$$F = 3\nu T\left(\frac{\alpha^2 - 1}{2} - \frac{2}{f}\ln\alpha\right) + NT\left(\frac{Bn_0}{\alpha^3} + \frac{Cn_0^2}{\alpha^6}\right) \qquad (4)$$

(b) free swelling or collapse along the axes $Ox$ and $Oy$

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* It must be noted that this definition of the reference state seems to coincide with one implicitly adopted in ref 7.

† Although we have shown that the reference state must be chosen somewhere near the $\theta$ temperature for the corresponding linear macromolecule (this 'inaccurate' statement is sufficient to write $n_0$ in the form shown in equation (3)), it does not mean that the reference state corresponds exactly to the $\theta$ state.

and fixed dimensions along the axis O$z$: $\alpha_x = \alpha_y \equiv \alpha$; $\alpha_z \equiv \sigma$ = constant; $n = n_0/\alpha^2\sigma$, thus

$$F = \nu T\left(\frac{2\alpha^2 + \sigma^2 - 3}{2} - \frac{2}{f}\ln \alpha^2\sigma\right) + NT\left(\frac{Bn_0}{\alpha^2\sigma} + \frac{Cn_0^2}{\alpha^4\sigma^2}\right) \quad (5)$$

(c) free swelling or collapse along the axis O$x$ and fixed dimensions along the axes O$y$ and O$z$: $\alpha_x \equiv \alpha$; $\alpha_y \equiv \sigma_1$ = constant; $\alpha_z \equiv \sigma_2$ = constant; $n = n_0/\alpha\sigma_1\sigma_2$, thus:

$$F = \nu T\left(\frac{\alpha^2 + \sigma_1^2 + \sigma_2^2 - 3}{2} - \frac{2}{f}\ln \alpha\sigma_1\sigma_2\right) + NT\left(\frac{Bn_0}{\alpha\sigma_1\sigma_2} + \frac{Cn_0^2}{\alpha^2\sigma_1^2\sigma_2^2}\right) \quad (6)$$

The equilibrium values of $\alpha$ can be obtained by minimization of expressions (4)–(6). The concentration $n_0$ is given by (3). We shall consider only the networks with a small number of structural defects such as pendant chains, loops, etc., in this case the number of elastically effective network chains, $\nu$, is equal to $N/m$.

The system of parameters used in the expressions (3)–(6) is not the traditional one[10], which, in the author's opinion, is overburden by the parameters of the order of unity. The form (4)–(6) of the free energy is convenient for the comparison with the theory of a single macromolecule[11], as well as for the complete analysis of network swelling and collapse (see below).

## SWELLING OF THE NETWORK

The equilibrium values of the swelling coefficients $\alpha$ can be determined by minimization of expressions (4)–(6) with respect to $\alpha$. Thus, using $\partial F/\partial\alpha = 0$ we obtain the following equations:

$$\text{(a)} \quad \alpha^5 - \frac{2}{f}\alpha^3 - \frac{y}{\alpha^3} = x \quad (7)$$

$$\text{(b)} \quad \alpha^4 - \frac{2}{f}\alpha^2 - \frac{y}{\alpha^2\sigma^2} = \frac{x}{\sigma} \quad (8)$$

$$\text{(c)} \quad \alpha^3 - \frac{2}{f}\alpha - \frac{y}{\alpha\sigma_1^2\sigma_2^2} = \frac{x}{\sigma_1\sigma_2} \quad (9)$$

where

$$x \equiv Bn_0m = k\frac{Bm^{1/2}}{p^{3/2}d^3}$$

$$y \equiv 2Cn_0^2m = 2k^2\frac{C}{p^3d^6} \quad ‡$$

We now consider the swelling of the network in the good solvent. In this case the average monomer concentration within the network is so small that it is possible to discount the terms with the third virial coefficient $C$ in (7)–(9) (compare with ref 11). Furthermore, at $m \gg 1$ we have $\alpha^2 \gg 1$, and thus in order to obtain an asymptotic swelling law it is possible to neglect the second terms on the left-hand side of equations (7)–(9) with respect to the first terms. As a result we obtain:

For (a) the network swells so that $\alpha^2 \sim x^{2/5} \sim m^{1/5}$. Comparing this result with Flory's theory[14], the ratio of the monomer concentration in the dry network to the monomer concentration in the swollen network, given the symbol $q$ in the Flory theory, in our notation is proportional to $\alpha^3/n_0$ ($q \sim \alpha^3/n_0$). In our theory, therefore, $q \sim m^{4/5}$ while in the Flory theory $q \sim m^{3/5}$. So the asymptotic swelling law for the networks prepared in the presence of diluent is different from the corresponding law for the networks cross-linked in the dry state where the Flory theory is valid.

For (b): the swelling coefficient $\alpha^2$ is proportional to $m^{1/4}$, i.e. $q \sim \alpha^2\sigma/n_0 \sim m^{3/4}$. When the network is stretched along the O$z$ axis (i.e. when $\sigma > 1$) the coefficient $\alpha^2$ decreases, $\alpha^2 \sim \sigma^{-1/2}$. When the network is compressed along the O$z$ axis (i.e. when $\sigma < 1$) the value of $\alpha^2$ increases. At the maximum possible stretching $\sigma \sim m^{1/2}$ there is no swelling along the axes O$x$ and O$y$.

For (c): the value of $\alpha^2$ is proportional to $m^{1/3}$, i.e. $q \sim \alpha\sigma_1\sigma_2/n_0 \sim m^{2/3}$. The stretching of the network again leads to a decrease in swelling, and *vice versa*: $\alpha^2 \sim (\sigma_1\sigma_2)^{-2/3}$

It should be pointed out that the power dependences $\alpha^2 \sim m^s$ are valid only in the asymptotic limit $m \gg 1$. If $m$ is not large, these dependences must be modified.

## COLLAPSE OF THE NETWORK

We shall now consider network conformation below the $\theta$ point. When the temperature is lowered below the $\theta$-temperature a single linear polymer macromolecule undergoes a collapse[11], i.e. a phase transition from the coil to the globular state occurs; this transition is first order in the case of a stiff-chain macromolecule and second order in the case of a flexible-chain macromolecule.

In order to study the behaviour of a polymer network below the $\theta$ temperature we consider the function $\alpha^2(x)$ given by equations (7)–(9)* with negative values of $x$ (since at $T < \theta$ $B < 0$). In all the three cases at $y$ larger than some critical value $y_{cr}$ ($y > y_{cr}$) the plot $\alpha^2(x)$ has the form of the curve A in *Figure 2*, and at $y < y_{cr}$ the function $\alpha^2(x)$ is non-monotone at $x < 0$ (curve B in *Figure 2*). Thus, when the temperature is lowered below the $\theta$-point in the case $y < y_{cr}$ the discrete first order phase transition occurs and in the case $y > y_{cr}$ the increase in the average monomer concentration within the network is continuous. From comparison with the case of a single macromolecule[11] it is clear that the first order phase transition at $y < y_{cr}$ must be identified with the transition of the network from the coil to the globular state (or collapse): above the transition temperature the fluctuations of the monomer concentration within the network are of order of the concentration itself,

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‡ The fact that $\alpha^2 \neq 1$, when $B = C = 0$, is not surprising and is connected with the uncertainty in the determination of the reference state in this theory. It is important that at $B = C = 0$, $\alpha$ is of order unity (since $f$ is of order unity).

* Analogous equations for swelling coefficient can be obtained in the case of a single macromolecule, if both swelling and collapse are described in terms of the interplay of $F_{int}$ and $F_{el}$ (see refs 8, 9: the results given are not exact, since for a single macromolecule the surface free energy $F_s$ is much more important than $F_{el}$ in the collapse region[11]). So the consideration of the collapse in our case is almost completely analogous to the corresponding consideration in the refs 18, 19.

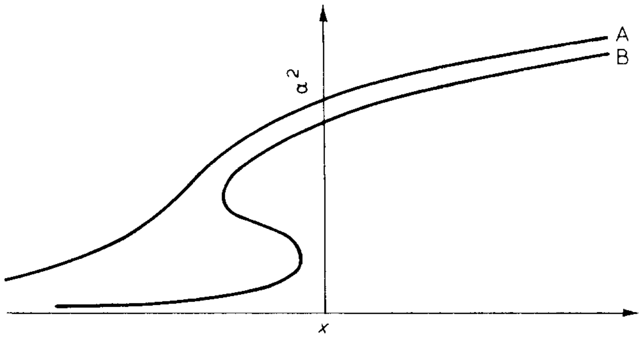

*Figure 2* Function $\alpha^2(x)$ at $y > y_{cr}$ (the curve A) and at $y < y_{cr}$ (curve B)

below the transition temperature the fluctuations are small. For $y > y_{cr}$ the transition from the coil to the globular state (collapse) also takes place, but this transition is not discrete and occurs in the finite, although narrow temperature interval (detailed analysis shows that $\Delta T/T \sim m^{-1/2} \ll 1$). Since $\Delta T$ does not tend to zero at $N \to \infty$, according to the terminology introduced in ref 11 the collapse of the network at $y > y_{cr}$ is not a phase transition.

From equations (7)–(9) we obtain values of $y_{cr}$ as follows: for (a) $y_{cr} = 0.36/f^4$; for (b) $y_{cr} = 0.30\sigma^2/f^3$; for (c) $y_{cr} = \sigma_1^2\sigma_2^2/3f^2$. Taking into account $y = 2k^2C/p^3d^6$ and the estimation $C \sim d^6$, which follows from our definition of a monomer (see ref 17‡), it is possible to make the following conclusions.

For (a) the type of the collapse depends basically on the degree of network chain stiffness: for stiff enough chains ($p \gg 1$) $y < y_{cr}$ and the collapse is a first order phase transition; for flexible chains ($p \sim 1$) $y > y_{cr}$ and the collapse is the continuous non-phase transition. The critical value $p_{cr} \sim 1$, at which the transition becomes discrete, depends on the parameter $k \sim 1$, which describes the details of the network structure, and also on the functionality of the branch points $f \sim 1$ (the greater $f$ becomes, the smaller is the region of discrete collapse).

In cases (b) and (c) one more parameter appears – the degree of the deformation of the network sample, $\sigma$. If $\sigma > 1$ (stretching), the value of $y_{cr}$ essentially increases (the region of discrete collapse becomes much larger) and *vice versa*. At significant stretching the collapse of the network is a first order phase transition independent of chain stiffness.

Substituting the solutions of equations (7)–(9) in expressions (4)–(6) for the free energy and taking into account the estimation

$$B \sim d^3\frac{T-\theta}{T} \equiv d^3\tau$$

which is true near the $\theta$-point, it is easy to obtain the temperature, $T_c$, at which the network undergoes the collapse in the case $y < y_{cr}$. In all the three cases

$$\tau_c \equiv \frac{T_c - \theta}{\theta} \sim -m^{-1/2}$$

neglecting logarithmic factors, i.e. $\tau_c$ depends only on $m$, but is independent of the degree of the stiffness of the network chains $p$ and of the degree of deformation of the network, $\sigma$. If $y < y_{cr}$ the average monomer concentration within the network changes abruptly at the collapse point from its coil value $n_c \cong n_0$ (case a); $n_c \cong n_0/\sigma$ (case b) or $n_c \cong n_0/\sigma_1\sigma_2$ (case c)) to its globular value $n_g$ ($n_g \sim m^{-1/2}$ ignoring logarithmic factors in all the three cases). The relative change in concentration at the collapse point is (ignoring again logarithmic factors):

For (a):

$$\frac{n_g - n_c}{n_c} \sim p^{3/2}$$

For (b):

$$\frac{n_g - n_c}{n_c} \sim p^{3/2}\sigma$$

For (c):

$$\frac{n_g - n_c}{n_c} \sim \sigma_1\sigma_2 p^{3/2}$$

When the temperature is lowered below the collapse point, the average monomer concentration within the network changes in accordance with the laws of a globular phase – $n_g \sim |\tau|$ in all three cases[17].

The calculations in this section are very similar to those performed in ref 20, where the related problem of the phase separation of the network into two phases with different polymer concentrations are considered.

The collapse of a polymer network surrounded by the excess of the solvent (polyacrylamide in the acetone–water mixture) was studied experimentally in the recent article[7]‡). It was shown that under some conditions the collapse of the gel is a first order phase transition and under other conditions the collapse transition is continuous, although it occurs in a narrow temperature interval. It was found that the character of the collapse depends on the conditions of gel preparation and on the composition of the acetone–water mixture. These facts are in agreement with our theory, since the conditions of gel preparation affect the parameter $k$ (and not the degree of the chain stiffness $p = l/d$, as supposed in ref 7), and the composition of the acetone–water mixture affects the parameter $C$. Further experimental study of this system – in particular the study of the swelling of the gel and the change in its collapse characteristics depending on the deformation of the network, would permit verification of the other conclusions of this paper§).

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‡ The temperature dependence of $C$ is negligible in the narrow transition region

‡ Ref 7 also contains the theoretical consideration of the collapse for cases (a) (the free network). Although it differs in some respects from our consideration, the final results in ref 7 and in this paper are in the qualitative agreement.

§ When the conclusions of this paper are compared with experiment we should have in mind that the above results are strictly valid if: (i) the networks are prepared in the presence of a large amount of diluent; (ii) the networks have a small number of structural defects. In practice these requirements can be somewhat contradictory[4]. The results for the networks with the defects of known type can be simply obtained along the lines of this paper.

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