Crosslinked polymer chains with excluded volume: A new class of branched polymers?

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In this note microgels with and without excluded volume interactions are considered. Based on earlier exact computations on Gaussian microgels, which are formed by self-crosslinking (with M crosslinks) of polymer chains with chain length \( N \) Flory type approximations are used to get first insight to their behavior in solution. It is shown that two different types of microgels exist: A special type of branched polymer whose size scales as \( R \propto N^{2/5}M^{-1/5} \), instead of \( R \propto N^{1/2} \). The second type are \( c^- \)-microgels whose average mesh sizes \( r \) are swollen and form self avoiding walks with a scaling law of the form \( r = a(N/M)^{3/5} \).

I. INTRODUCTION

In recent publications we have shown that the problem of non-interacting self crosslinked chains can be solved exactly for a given crosslink configuration \( [1,2] \). In these papers the size of the crosslinked chain has been calculated in different regimes of the crosslink coupling strength. The results presented there agree perfectly with simulations carried out independently by Kantor and Kardar \( [3,4] \). Moreover the method which was employed could be transformed to dynamical problems. There exact results can be produced also \( [5,6] \).

Bryngelson and Thirumalai \( [6] \) had investigated a similar model of an isolated polymer chain consisting of \( N \) monomers subject to \( M \) crosslinking constraints by a variational technique. It was claimed that a sufficient number of crosslinks forces the polymer to undergo a transition from an extended \( (R^2 \propto N) \) to a collapsed state with mean squared end-to-end distance \( R^2 \) of order unity. These authors had drawn their conclusion from a variational computation, but their results to not fully agree with our exact evaluations \( [6,7] \).

On the other hand, whenever excluded volume effects come into play, the problem becomes extremely difficult and the size of the microgel cannot be computed exactly. Although the exact "bare" propagator for these networks is known exactly from the previous work, renormalization group calculations cannot be carried out easily, because the mathematics becomes very involved and to carry out systematic perturbation expansion seems to be impossible. Apart from the results on the size of microgels with excluded volume, it is suggested that a gel linked with weak crosslinks \( [6,7] \) defines a new class of branched polymers. These weak (or soft) crosslinks can be visualized by polymer chains of different chain flexibility themselves. Although these gels scale in the Gaussian limit with the same exponent as branched polymers the molecules behave completely different when excluded volume is present: They do not swell the same way as classical branched polymers \( [6,7] \).

The paper is organized as follows. In the next section we briefly recall the results on the ideal network, which are then reproduced by simple scaling estimates. In the following we discuss excluded volume effects on the basis of Flory arguments \( [3,7,9] \). It is shown there that the cases of weak and strong crosslinks yield very different results, in agreement with the physical pictures on branched polymers and gels.

II. THE IDEAL NETWORK

We adopt the minimal model of Deam and Edwards \( [9,10] \), i.e., a Gaussian polymer chain that is \( M \) times crosslinked to itself (see figure (1)). In the Hamiltonian only terms that model chain connectivity and contributions due to crosslinking are retained. Complicating factors such as entanglements, excluded volume are deliberately neglected from the start. An appropriate discrete Hamiltonian to begin with is

\[
\beta H_0 = \frac{d}{2a^2} \sum_{i=1}^{N} (\mathbf{R}_i - \mathbf{R}_{i-1})^2 + \frac{d}{2\varepsilon^2} \sum_{e=1}^{M} (\mathbf{R}_{i_e} - \mathbf{R}_{j_e})^2.
\]

(1)

We have assumed \( N + 1 \) monomers whose locations in space are given by \( d \)-dimensional vectors \( \mathbf{R}_i \) ( \( i = 0, 1, ..., N \) ). Distance constraints exist between pairs of monomers labeled by \( i_e \) and \( j_e \). For further use we introduce the inverse strength of the crosslinking potential

\[
z = \left( \frac{\varepsilon}{\alpha} \right)^2
\]

(2)
as the mean squared distance between monomers that form the crosslinks measured in units of the persistence length \( \alpha \) of the chain (figure (1)). Limiting cases are given by \( z = 0 \) (hard \( \delta \)-constraints) and \( z \rightarrow \infty \) (free chain). The whole crosslinking topology is specified by a set of \( 2M \) integers \( C = \{i_e, j_e\}_{e=1}^{M} \). It has been shown \( [11,12] \) that the model in \( \beta = 0 \) is equivalent to the Deam-Edwards model \( \beta = 0 \) without excluded-volume interaction if averages are understood in the following sense...
\[ \langle ... \rangle_0 = \lim_{\varepsilon \to 0} \frac{\prod_{i=0}^{N} d\mathbf{R}_i e^{-\beta \mathcal{H}_0} ...}{\prod_{i=0}^{N} d\mathbf{R}_i e^{-\beta \mathcal{H}_0}} . \tag{3} \]

Fig.(1) A simple representation of a microgel

To model \( M \) uncorrelated crosslinks the distribution of frozen variables \( C \) is assumed to be uniform

\[ \mathcal{P}(C) = \prod_{e=1}^{M} \left\{ \frac{2}{N^2} \sum_{0 \leq i < j \leq N} \right\} \tag{4} \]

Other distributions are in principle possible but not considered in this investigation. As usual for systems with permanent constraints care must be taken in evaluating averages of physical quantities. The strategy here is not to start with the quenched average over the frozen variables by employing for instance the replica trick, but to keep explicitly all crosslink coordinates \( C \) during the calculation. Only at the very end the physical observable of interest is evaluated for a particular realization of \( C \) which is generated by the distribution in (4). Clearly both approaches will give the same results if only self-averaging quantities are considered.

The Hamiltonian in Eq. (1) together with the uniform distribution of crosslinks (4) defines our working model for the ideal network.

**III. SCALING ESTIMATES OF THE BARE NETWORK HAMILTONIAN**

In this section we recall briefly the exact results for the size of the crosslinked chain. In fact, these can be estimated (apart from uninteresting constant) from the Hamiltonian (1) by simple Flory type arguments. We are here in the lucky position that the scaling results can be checked directly with the corresponding exact computations and will provide additional confidence, when we turn to the excluded volume case shortly below.

These results will provide a scaling basis for considerations for gels with excluded volume. Here we claim that the Hamiltonian given by Eq. (1) contains three different regimes. These regimes appear naturally: The first will be the trivial free chain limit, that appears naturally if the crosslink constraint disappears for \( \varepsilon \to \infty \). A second regime can be expected, when the crosslinks are soft, i.e., corresponding to a finite and relatively large value of \( \varepsilon \). The microgel regime itself will correspond to the case of hard crosslinks \( \varepsilon \to 0 \). Let us now going to discuss these three cases in more detail.

1. free polymer regime: \( \varepsilon \to \infty \)

   This regime is the trivial solution of the problem and corresponds to vanishing or alternatively to very weak crosslink constraints. Thus the free chain result

   \[ R_{g}^2 = \frac{a^2}{6} N \]

   must be recovered.

2. branched polymer regime: \( \varepsilon \sim O(N^{1/2}) \)

   The connectivity term models the standard entropic elasticity of a Gaussian chain, i.e., \( R^2/(Na^2) + Na^2/R^2 \), where \( R \) is a measure of the size of the system. The first term accounts for stretching, whereas the second term describes the response due to compression [8]. For relatively soft crosslinks, i.e. \( \varepsilon >> a \), the crosslink term requires appropriate attention. In the regime of relatively large \( \varepsilon \) the second term of the Hamiltonian is estimated by simple dimensional analysis to \( M(R/\varepsilon)^2 \), because the mean squared distance between a pair of constrained monomers is of order \( \varepsilon^2 \). Thus, the physically relevant parts of the total Flory free energy are then

   \[ \mathcal{F} \approx \frac{a^2 N}{R^2} + M \frac{R^2}{\varepsilon^2} . \]
The first term corresponds to the entropy penalty due to the chain shrinking of the effectively "attractive" crosslinks. That means we consider the only values for $\varepsilon$ in the limits

$$\sqrt{N} < \frac{\varepsilon}{a} < \sqrt{NM} \quad (5)$$

The second term of the free energy describes the harmonic potential for the crosslink constraint. Minimization yields the at first sight surprising result

$$R_g \approx a \sqrt{\frac{F}{N M}} \quad (6)$$

This result is in a way surprising in the sense that the same scaling exponent appears like in the ideal branched polymer. This is indeed physically sensible, since the soft crosslink potential connects loosely $M$ monomers and changes the connectivity of the originally linear chain to a randomly branched polymer object.

On the other hand the branched polymer result suggested the mapping on the classical branched polymer limit introduced by Stockmayer and Zimm [12], although in the computation of these authors no loops are present. In contrast to the microgels build up of self crosslinked chains, where many loops form the network. Nevertheless it is tempting to assume that the branching index $\Lambda$ defined by Stockmayer size of the ideal branched molecule via $R \equiv a(N/\Lambda)^{1/4}$. Comparison with eq.(6) suggests $\Lambda \approx M(a/\varepsilon)^2$. It is interesting to note that the two natural limits on $\Lambda$, i.e., those from the classical theory of branched polymers

$$\Lambda = \begin{cases} 1/N & \text{linear chain} \\ M/N & \text{branched limit} \end{cases}$$

reproduce exactly the limits on $\varepsilon$ in eq.(5). This surprising fact shows that for the configurational scaling properties on the overall size of the gel loops do not seem to play a significant role. For the latter statements we had of course we have ignored the detailed internal structure of the microgel. Instead we had considered only the overall size of the crosslinked chain.

3. network regime: $\varepsilon \to 0$

The case of hard crosslinks $\varepsilon \approx O(a)$ is more difficult to obtain. To find a reasonable estimate we picture the system as a coarse-grained random walk over the $M$ crosslinks with an effective step length proportional to $N/M$, i.e., the mean number of monomers between crosslinks. Then the crosslink term is estimated to be of the order

$$M[R^2/(a^2 N/M)]$$. The latter expression has the effect that it tries to shrink the chain upon cost of confinement entropy. A suitable Flory free energy is given by

$$F \approx \frac{a^2 N}{R^2} + M \frac{R^2}{a^2(N/M)}$$

and the size of the network is given by

$$R_g \approx a \left( \frac{N}{M} \right)^{1/2} \quad (7)$$

We have performed a more extensive and exact study on the same working model [13]. These scaling estimates agree with the exact computation and are summarized for completeness:

Based on an exact theorem derived in Ref. [13] we have calculated the radius of gyration $R_g$ of a chain of $N$ monomers with $M$ uncorrelated crosslinks. Our derivation also allowed for variation of the strength of the constraint $z = (\varepsilon/a)^2$, where $a$ denotes the persistence length of the chain and $\varepsilon$ the mean distance between two monomers that form a crosslink. Thus, in our model $z = 0$ corresponds to delta constraints (the case usually considered in the literature), $z = 1$ yields soft constraints, and $z \to \infty$ leads to the ideal chain. From this study we could clearly distinguish between three different scaling regimes and these are nicely in agreement with the naive scaling estimates.

$$R_g^2/a^2 \propto \begin{cases} \frac{N}{M} & \text{(hard gel)} \\ z \sqrt{\frac{N}{M}} & \text{(branched)} \\ N & \text{(free chain)} \end{cases}, \quad \text{if } z \gtrsim 1 \quad (8)$$

In particular, our investigation showed that the cases $z = 0$ (hard constraint) and $z = 1$ only differ by a numerical prefactor which varies from 0.26 ($z = 0$) to 0.27 ($z = 1$). Thus $R_g^2/a^2 \propto N/M$ for the network situation which seems to be at variance with the conclusions by Bryngelson et al. [6] who argued that a critical number of crosslinks $M \geq M_c \sim N/\log N$ will cause the polymer chain to collapse [3]. Our result is in agreement with recent MC simulations by Kantor and Kardar [7] who found for the end-to-end distance $R^2 = 1.5N/M$. This indicates the same one to six ratio $R_g^2/R^2$ as for ideal polymers without crosslinks and excluded-volume interaction. For completeness, for $z \to \infty$ we recover the case of a free chain with $R_g^2/a^2 = N/6$.

The polymer subject to internal crosslinking constraints is collapsed in a sense that $R_g$ is always proportional to the square root of $N/M$. This corresponds somehow also to the random crosslinking process, especially by the random choice of the two monomer pairs, which form a crosslink. In the following we are going to discuss the effect of excluded volume. If the ideal
limit is left and self avoidance are taken into account, firstly, the appearance of the ratio \( N/M \) is no longer obvious and secondly the space dimension and the number of crosslinks will play a crucial role.

IV. EXCLUDED VOLUME EFFECTS

The Hamiltonian of the network is must extended by the total repulsive excluded volume of all monomers and in given by

\[
\mathcal{H} = \frac{d}{2\alpha^2} \sum_i^N (\mathbf{R}_i - \mathbf{R}_{i+1})^2 + \frac{d}{2\varepsilon} \sum_{\epsilon=1}^M (\mathbf{R}_{\epsilon} - \mathbf{R}_{\epsilon+1})^2 + \frac{\nu}{2} \sum_{i \neq j} \delta (\mathbf{R}_i - \mathbf{R}_j) \tag{9}
\]

The first two terms correspond to the non interacting network as above and the last term in the Hamiltonian is the total excluded volume energy. Although the exact propagator of the bare problem is known, there is no realistic hope that excluded volume effects can be treated in a sophisticated way. In fact, the bare propagator of the problem can only be represented in a matrix form, and is not easy to handle for analytical purposes. Thus we only employ Flory estimates in the following section to get a first insight about the effects of the excluded volume interactions.

A. Soft crosslinks \( \varepsilon \gg a \)

To do this we estimate the terms from the above equation by the free energy

\[
\mathcal{F} \simeq M \frac{R^2}{\varepsilon^2} + \nu \frac{N^2}{R^d} \tag{10}
\]

where \( d \) is the space dimension. The latter term in the free energy is the well known excluded volume term for a chain with \( N \) segments. Minimization of the free energy yields the size of the microgel

\[
R \simeq a \left( \frac{\varepsilon}{a} \right)^{1/(d+2)} \left( \frac{N^2}{M} \right)^{1/(d+2)} \tag{11}
\]

or in three dimensions

\[
R(\varepsilon) \simeq a \left( \frac{\varepsilon}{a} \right)^{2/5} M^{-1/5} N^{2/5} \]

This result provides two important observations. The first is that the scaling \( (N/M) \) is destroyed trivially by excluded volume. The second is that the distance constrained polymer chain does not scale as a branched chain, when excluded volume has been taken into account. This would mean \( R \propto N^{5/(2(d+2))} \) (or in three dimensions \( R \propto N^{1/2} \)), which is the Isaacson Lubensky value and well confirmed by experimental studies. Physically this means that the distance constraint is much more restrictive and excluded volume forces are not able to overcome this constraint. Mathematically this is also clear, since a constraint in the partition function is much stronger than the excluded volume (pseudo) potential. Of course, a special regime for the constraint variable \( \varepsilon \) exists such that the crosslinked polymer appears as swollen branched chain. In this case \( \varepsilon^2 \sim a^2 M \sqrt{N} \) and independent of the space dimension.

The natural question, how such types of polymers can be realized, can be answered in such a way, that \( \varepsilon \) can be viewed as the mean distance of a ”soft” crosslink, made out of a linear polymer itself. These soft crosslinks for then themselves a random walk of \( M \) steps with a step length \( a \sqrt{\varepsilon} \). This agrees with the imagination that these soft crosslink potential change the connectivity of an original linear polymer. Note that the upper limit for the value of \( \varepsilon^2 \sim a^2 N M \) recovers formally the free chain. The constraint is then physically so small that it has no effect on the conformation.

It is clear that given size of \( \varepsilon \) the number of crosslinks cannot be arbitrary large. The largest number of crosslinks is of the order of

\[
M \lesssim \left( \frac{\varepsilon}{a} \right)^2 N^{(d-2)/d} \tag{12}
\]

i.e., when the crosslinked polymer is given by its extremal minimal size \( R \approx a N^{1/d} \).

B. Hard crosslinks \( \varepsilon = 0 \)

The case of hard crosslinks requires a more careful treatment of the crosslink term. Here we use the same picture as above where the Gaussian network has been treated. Thus the scaling of the crosslink term is given by a random walk through the crosslinks \( R \propto M \sqrt{a^2 (N/M)} \). This term is then relevant to the dominant elastic contribution in the free energy which balances excluded volume.

For a large number of crosslinks \( N >> M >> 1 \) the corresponding Flory free energy is then given by

\[
\mathcal{F} = M^2 \frac{R^2}{a^2 N} + \nu \frac{N^2}{R^d} \tag{13}
\]

The size of the microgel is

\[
R \simeq a \left( \frac{N^3}{M^2} \right)^{1/(d+2)} \tag{14}
\]

This result can be written in the more instructive form in three dimensions as
This intuitive equation describes a swollen microgel, where the mean strand length \( \frac{N}{M} \) is fully swollen and forms a self avoiding walk. In other words the microgel can be visualized as a \( c^* \) - gel, where the blob size defined by the strands form self avoiding walks.

In the hard crosslinked microgel the number of crosslinks cannot be arbitrary. As in the previous case a similar limit exists, which would correspond to the maximum density of the gel. The limiting density corresponds to a densely packed network in space, i.e., to a size \( R \approx aN^{1/d} \). Therefore this limit requires an upper bound for the number of crosslinks

\[
M \leq N^{(d-1)/d} = N^{2/3}.
\]

Clearly the latter condition holds only for dimensions less than four, since \( d = 4 \) is the upper critical dimension for the excluded volume term which is independent of the crosslink state.

\[ R \approx aM^{1/5} \left( \frac{N}{M} \right)^{3/5} \] (15)

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\[ M \leq N^{(d-1)/d} = N^{2/3} \] (16)

V. SUMMARY

In this note we have presented reasonable scaling estimates for the size of self crosslinked chains and microgels. Although the estimates are simple they yield physically understandable results. The main conclusion is that the two types of gels may exist, i.e., soft gels, where the crosslinks are extended objects themselves, and hard gels which consists of point like crosslinks. Their swelling behavior is completely different and fall in two separate classes of physical systems.

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