Size and Scaling in Ideal Polymer Networks

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(December 31, 2021)

Abstract

The scattering function and radius of gyration of an ideal polymer network are calculated depending on the strength of the bonds that form the crosslinks. Our calculations are based on an exact theorem for the characteristic function of a polydisperse phantom network that allows for treating the crosslinks between pairs of randomly selected monomers as quenched variables without resorting to replica methods. From this new approach it is found that the scattering function of an ideal network obeys a master curve which depends on one single parameter $x = (ak)^2 N/M$, where $ak$ is the product of the persistence length times the scattering wavevector, $N$ the total number of monomers and $M$ the crosslinks in the system. By varying the crosslinking potential from infinity (hard $\delta$-constraints) to zero (free chain), we have also studied the crossover of the radius of gyration from the collapsed regime where $R_g \approx O(1)$ to the extended regime $R_g \approx O(\sqrt{N})$. In the crossover regime the network size $R_g$ is found to be proportional to $(N/M)^{1/4}$. The latter result can be understood in terms of a simple Flory argument.

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I. INTRODUCTION

Sufficiently crosslinked macromolecules form solid-like rubber networks whose spectacular elastic properties are commonly believed to be of entropic origin. As a consequence polymeric networks are often successfully modeled as a set of independent random walks with the only restriction that the end points deform affinely under external stress. In a real network, however, permanent junctions between the macromolecules are randomly formed upon fabrication leading to a high degree of polydispersity. To meet with this complicated physical situation more sophisticated theoretical models are required.

Recently various analytical studies [1–7] have aimed at a statistical description of polymer networks taking randomness of the crosslinking positions into account. The mathematical challenge that arises in any of these approaches is that the permanent junction-points between macromolecules are frozen and cannot be treated within the framework of Gibbsian statistical mechanics. This has first been realized by Edwards [1] and his replica formalism has by now become the standard approach in the field of polymer networks. Unfortunately the replica method forces strong approximations to remain analytically tractable. A recent work by Panyukov and Rabin [4] seems to overcome several difficulties and derives promising results for the elasticity.

In this study we use a different route of thought. It has recently been shown [8] that for randomly crosslinked Gaussian structures substantial progress can be made by invoking quite different mathematical tools than replica field theory. The purpose of the paper is to report on further progress in this direction. Our working model is an ideal polymer chain of $N$ monomers with $M$ randomly selected pairs of monomers constrained to be in close neighborhood. The distance constraints are modelled by harmonic potentials. By varying the strength of the crosslinking potential we can continuously switch from a network situation with hard $\delta$-constraints to the case of a free chain.

Although the above model is highly idealized, the system is most interesting in its own right, since it is considered a first step towards a systematic theory of polymer networks.
and gels. Moreover, the statistics of a huge macromolecule crosslinked to itself (randomly or not) has attracted a lot of attention recently because of its possible implications to protein structure reconstruction from NMR data [9–11]. Despite of the recent interest to the best of our knowledge these are the first exact results for ideal networks that have been reported.

II. THE IDEAL NETWORK

We adopt the minimal model of a huge Gaussian chain that is \( M \) times crosslinked to itself. In the Hamiltonian only terms that model chain connectedness and contributions due to crosslinking are retained. Complicating factors such as entanglements, excluded volume are deliberately neglected from the start. An appropriate Hamiltonian to begin with is

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

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

\[
z = \left( \frac{\epsilon}{a} \right)^2 \tag{2}
\]

as the mean squared distance between monomers that form the crosslinks measured in units of the persistence length \( a \) 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 [8] that the model in (1) is equivalent to the Deam-Edwards model [1] without excluded-volume interaction if averages are understood in the following sense

\[
\langle ... \rangle_0 = \lim_{z \to 0} \frac{\int \Pi_{i=0}^{N} d\mathbf{R}_i e^{-\beta H_0} \cdots}{\int \Pi_{i=0}^{N} d\mathbf{R}_i e^{-\beta H_0}}. \tag{3}
\]

It is interesting to note that the entire range \( 0 \geq z < \infty \) can be treated with the same formalism. In [8] we have explicitly shown that all limits are mathematically well defined.
Thus the here presented method is indeed able to cover the range of all crosslink strengths, i.e., from very soft to the quenched case.

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

$$
\prod_{e=1}^{M} \left\{ \frac{2}{N^2} \sum_{0 \leq i < j \leq N} \right\}
$$

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. CHARACTERISTIC FUNCTION

In this section a brief review of the central mathematical theorem for the characteristic function of a Gaussian structure with internal $\delta$-constraints is given, together with its extension to arbitrary crosslinking potential $z$. The characteristic function for the problem is introduced as

$$
Z_0(E; C) = \langle e^{iE \cdot r} \rangle_0
$$

from which all expectation values can be obtained via differentiation. Simplifying notation has been adopted, where $r_j \equiv R_j - R_{j-1}$ ($j = 1, ..., N$) denote bond vectors along the backbone of the chain, and $E = (E_1, ..., E_N)$, $r = (r_1, ..., r_N)$ are $N$-dimensional super-vectors with $d$-dimensional vector components. Thus $Z_0(E; C)$ is also the partition function.
of an ideal network in the presence of external fields $\mathbf{E}_j$. Note that $Z_0(\mathbf{E}; C)$ depends explicitly on all external fields contained in the vector $\mathbf{E}$, as well as on all crosslink positions $C$.

Without going into mathematical details, it is now possible to proof the following analytically exact projection theorem [8]

$$Z_0(\mathbf{E}; C) = \exp \left(-\frac{a^2}{2d} \mathbf{E}^2_\perp \right),$$  

(6)

where $\mathbf{E}_\perp$ is the length of the external field vector $\mathbf{E}$ projected perpendicular to the vector space spanned by "crosslink vectors"

$$\mathbf{p}_e = (0, \ldots, 0, 1, 1, \ldots, 1, 0, \ldots, 0).$$  

(7)

The above statement can be pictured in the following intuitive manner (figure 2). For each crosslink specified by the pair of integers $1 \leq i_e < j_e \leq N$, form the corresponding $N$-dimensional vector $\mathbf{p}_e$, Eq. (7), where the 1’s are assumed to run from the $(i_e + 1)$th to the $j_e$th position. The rest of the $N$ components are filled with 0’s. The whole set of $M$ vectors $\mathbf{p}_1, ..., \mathbf{p}_M$ defines a characteristic vector space for the problem, say $U$. There is an unique decomposition of any field vector $\mathbf{E}$ parallel and perpendicular to $U$ (figure 2), viz., $\mathbf{E} = \mathbf{E}_\parallel + \mathbf{E}_\perp$. The operator that projects $\mathbf{E}$ on $U$ can be constructed from $\mathbf{p}_e$ for any realization of crosslinks $C$. It is given by $\mathcal{P}\mathcal{P}^+$, where $\mathcal{P}$ is the $N \times M$ rectangular matrix associated with the crosslink vectors $\mathbf{p}_e$ ($e = 1, ..., M$),

$$\mathcal{P} \equiv (\mathbf{p}_1, ..., \mathbf{p}_M),$$  

(8)

while $\mathcal{P}^+$ is a generalized inverse of $\mathcal{P}$ [12].

The projection theorem (6) is only valid for hard crosslinking constraints $z = 0$. A generalization to arbitrary crosslinking potential $z$ is, however, possible using the methods of Ref. [8]. Only the final result for the characteristic function is quoted which reads

$$Z_0(z, \mathbf{E}; C) = \exp \left[-\frac{a^2}{2d} \left(\mathbf{E}^2 - \sum_{e=1}^{M} \frac{(x_e \mathbf{E})^2}{1 + (z/w_e^2)}\right)\right],$$  

(9)
Here \( \mathbf{x}_e \) denotes any orthonormal basis associated with \( \mathbf{p}_e \) \((e = 1, \ldots, M)\), and \( w_e \) are corresponding singular values \[^{12}\]. For tetrafunctional crosslinks it was shown that \( w_e \) is always positive. \(^{3}\) From (9) it is straightforward to obtain expressions for the radius of gyration and structure factor.

By the scattering function (form factor) we mean density fluctuations \[^{13}\] normalized to one

\[
S_0(k, z; C) = \langle |\rho_k|^2 \rangle_0
\]

\[
\equiv \frac{1}{N^2} \sum_{i,j=0}^{N} \langle \exp \left( i k (\mathbf{R}_i - \mathbf{R}_j) \right) \rangle_0 ,
\]

where \( k \) is the scattering wavevector, and the average is over the measure in (3) without having taken the \( z \to 0 \) limit. In the following no distinction between \( N \) and \( N + 1 \) will be made since \( N \) is assumed to be large. From Eq. (9) an exact expression for \( S_0 \) can be obtained by introducing the external field vector \( \mathbf{E} = k \mathbf{c}_{ij} \), where

\[
\mathbf{c}_{ij} = (0, \ldots, 0, 1, 1, \ldots, 1, 0, \ldots, 0) ,
\]

\( i + 1 \) to \( j \)

and \( k = |k| \). From (8) and (10) it is found

\[
S_0(k, z; C) = \frac{1}{N}
\]

\[
+ \frac{2}{N^2} \sum_{i<j}^N \exp \left[ -\frac{a^2 k^2}{2d} \left( j - i - \sum_{e=1}^{M} \frac{(\mathbf{x}_e \cdot \mathbf{c}_{ij})^2}{1 + (z/w_e^2)} \right) \right] .
\]

Similarly for the radius of gyration \[^{13}\]

\[
\left( \frac{R_g(\,z; C)}{a} \right)^2 = \frac{N}{6} - \frac{1}{N^2} \sum_{i<j}^N \sum_{e=1}^{M} \frac{(\mathbf{x}_e \cdot \mathbf{c}_{ij})^2}{1 + (z/w_e^2)} .
\]

It is worthwhile to note that the applicability of these results is not limited to random networks since all crosslinking coordinates are still implicit in the formulas through \( \mathbf{x}_e \) and \( w_e \). By selecting different ensembles for \( C=\{i_e, j_e\}_{e=1}^M \) (random or not) any generalized Gaussian structure with internal crosslinking constrained can be treated by the same method. Further generalizations of the working model \(^{14}\) to structures built from more than one chain
are feasible as long as the objects under investigation are simply connected. Otherwise the
phantom character of the chains and the neglect of entanglements leads to delocalization of
those clusters of the network which are not connected via crosslinks. A similar percolation
problem arises at the vulcanization transition [14] which, however, is not an objective of this
study.

IV. DISCUSSION OF RESULTS

In applying Eqs. (12) and (13) to random networks, one has to deal with a sufficient
number of monomers $N$ and crosslinks $M$. Moreover, the positions of crosslinks $C = \{i_e, j_e\}_{e=1}^M$
have to be chosen at random. The simplest scenario is to pick $2M$ integers $i_e, j_e$ ($e = 1, ..., M$) from the uniform distribution, Eq. (4), defined on the interval $[0, N]$. For a
given realization $C$ we compute an orthonormal basis $x_e$ and singular values $w_e$ of $p_e$ ($e = 1, ..., M$). Any standard technique like singular value decomposition [15] will suffice, for the
orthonormalization process presents only a minor numerical task. We find that for number of
monomers $N > 10000$ and crosslinks $M > 200$ fluctuations between different realizations of
$C$ differ by less than 1 percent. This also presents an estimate for the numerical uncertainty
of the calculation.

A. Scaling behavior of scattering function

Within the framework of the Dean-Edwards model $(z = 0)$ it was demonstrated [8] that the scattering function $S_0$ of an ideal network is an universal function of wavevector $k$
and mean crosslink density $M/N$ as long as $N$ and $M$ are sufficiently large to ensure self-
averaging. A scaling form for $S_0$ is motivated by the following argument. For a linear polymer
without crosslinks the scattering intensity $S_0(x)$ depends only on the product $x = k^2 R_g^2$, where $R_g^2 = a^2 N/6$ is the radius of gyration of the chain and $S_0(x) = 2(e^{-x} - 1 + x)/x^2$
the Debye function [13]. In close analogy it was shown that for hard constraints $(z = 0)$
the radius of gyration of an ideal network is given by $R_g^2 \approx 0.26 a^2 N/M$ which suggests a
scaling behavior, similar to that of linear chains without crosslinks. This scaling hypothesis for ideal networks was confirmed by our calculation based on the expressions in Eqs. (12) and (13).

The numerically exact result for the scattering function is presented in figure 3. In the Kratky plot of figure 3, $xS_0(x)$ has been evaluated as a function of $\sqrt{x} \equiv kR_g$ for $z = 0$. Independent of details of crosslinking topology C, all networks investigated fall on the same master curve (solid line). Statistical fluctuations between different networks were too small in the self-averaging regime to be seen on the scales used in figure 3. No indication of a power-law decay for intermediate wavevectors $k$ or other simplifying feature was detected, besides the pronounced maximum in the Kratky plot at $\sqrt{x} \simeq 2$ which reflects the strong correlations of the monomers due to crosslinking. For comparison, the case of a linear polymer with $z \to \infty$ (Debye function, dashed line) was also computed from (12).

The results of $S_0$ for different values of crosslinking potential $z$ are illustrated in figure 4 for a network with $N = 10000$ and $M = 200$. By increasing the strength of the constraint from left to right, large deviations of $S_0$ from ideal chain behavior (Debye function, left curve) arise on smaller and smaller length scales. For $z = 0$ the network character persists down to even the shortest length scale $k \approx 1$ as a consequence of the high degree of crosslinking in the system ($M/N = 0.02$). For sufficiently large wavevectors all curves decay as $k^{-2}$ as expected when the scanning wavelength becomes small compared to the mesh size of the network. Again, the master curve for $S_0$ can be obtained by plotting the $x$-axis in units of $R_g$.

### B. The collapse transition

In figure 5 we have calculated the radius of gyration of a network of $N$ monomers and $M$ crosslinks as a function of $\sqrt{z} = \varepsilon/a$ by use of Eq. (13). From this investigation we can clearly distinguish three different scaling regimes.
\[
\left( \frac{R_g}{a} \right)^2 \simeq \begin{cases} 
0.26 \frac{N}{M} , & \text{if } \varepsilon \ll \varepsilon_1 \\
0.34 \left( \varepsilon/a \right) \left( \frac{N}{M} \right)^{1/2} , & \text{if } \varepsilon_1 \ll \varepsilon \ll \varepsilon_2 \\
\frac{N}{6} , & \text{if } \varepsilon \gg \varepsilon_2 ,
\end{cases}
\] (14)

with crossovers at \( \varepsilon_1 \simeq a \sqrt{N/M} \) and \( \varepsilon_2 \simeq a \sqrt{MN} \). The plateau values in figure 5 correspond to the two extremes \( R_g^2/a^2 = 0.26 N/M \) \((z \to 0)\) to the left and \( R_g^2/a^2 = N/6 \) \((z \to \infty)\) to the right.

In particular our investigation showed that the cases \( z = 0 \) (hard constraints) and \( z = 1 \) (constraints of the order of the persistence length \( a \)) only differ by a numerical prefactor which varies from 0.26 for \( z = 0 \) to about 0.27 for \( z = 1 \). From this we conclude that an ideal network subject to \textit{uncorrelated} crosslinking constraints is collapsed in a sense that its size is proportional to the square root of \( N/M \). Therefore \( R_g/a \simeq \mathcal{O}(1) \) since \( M/N \) is the mean crosslink density in the network and of order unity in the thermodynamic limit \( N, M \to \infty \). This finding seems to be at variance with current speculations regarding the collapse transition of macromolecules \([10]\), where it was argued that a critical number of crosslinks \( M \geq M_c \simeq N/\log N \) will force the system to collapse. Our result for \( z = 0 \) is in agreement with recent Monte Carlo simulations by Kantor and Kardar \([11]\) who found for the mean squared end-to-end distance \( R_g^2/a^2 \simeq 1.5 N/M \). This suggests the same one to six ratio for \((R_g/R)^2\) in ideal networks as for linear polymers without crosslinking constraints and excluded-volume interaction \([13]\). We believe that the discrepancy between our exact results and these suggested in \([10]\) are due to the approximations used there.

Conversely, a free chain \((z \to \infty)\) is an extended object with \( R_g/a \simeq \mathcal{O}(\sqrt{N}) \). Between the collapsed and the extended regime we find a smooth crossover with \((R_g/a)^2\) being proportional to \((\varepsilon/a)\sqrt{N/M} \). Remarkably this is the same scaling as for randomly branched polymers without excluded volume interaction. In the following we discuss the different conformational states of the system in terms of simple scaling arguments.
C. Flory estimates

For completeness we first note that the free chain regime is trivial since \( R^2_s/a^2 = N/6 \) is an exact solution of (13) for \( z \rightarrow \infty \). To understand the scaling behavior of \( R_s \) in the other two regimes the free energy of the Hamiltonian in Eq. (1) is discussed within Flory theory. The connectivity term in (1) 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 \[16\].

An estimate of the crosslink term in (1) requires more attention. First we consider soft crosslinks when \( \varepsilon \gg a \). In this regime the second term of the Hamiltonian is estimated by \( M(R/\varepsilon)^2 \), because the mean squared distance between a pair of constrained monomers is of order \( \varepsilon^2 \). The relevant part of the total Flory free energy then is

\[
\mathcal{F}_0 \sim \frac{Na^2}{R^2} + \frac{MR^2}{\varepsilon^2}.
\]

(15)

Minimization of the free energy with respect to \( R \) yields the scaling relation \( R/a \sim (\varepsilon/a)^{1/2}(N/M)^{1/4} \) in agreement with (14). The appearance of the branched polymer exponent 1/4 can be assigned to the change of connectivity of the chain when \( \varepsilon \simeq O(\sqrt{NM}) \).

The case of hard crosslinks \( \varepsilon \simeq O(a) \) is more difficult to obtain. 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. From this mean-field argument the crosslink term is estimated to be of the order \( M[R^2/(a^2N/M)] \). 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

\[
\mathcal{F}_0 \sim \frac{Na^2}{R^2} + \frac{M^2R^2}{Na^2}.
\]

(16)

From there \( (R/a) \sim (N/M)^{1/2} \) as was shown exactly for the network regime.
ACKNOWLEDGMENTS

M.P.S. gratefully acknowledges financial support by the DFG, Sonderforschungsbereich 262.
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FIGURES

FIG. 1. Modelling of a soft crosslink between two monomers $i_e$ and $j_e$. A spring constant $\varepsilon \to 0$ leads to hard $\delta$-constraints, $\varepsilon \to \infty$ to free chain behavior.

FIG. 2. External field vector $\mathbf{E}$ projected parallel and perpendicular to $U$. The vector space $U$ is spanned by the vectors $\mathbf{p}_e$ defined in Eq. (7). The sketch is for two crosslinks $e = 1, 2$.

FIG. 3. Kratky plot of $xS_0(x)$ for the ideal network ($z = 0$, solid line) and linear chain ($z \to \infty$, Debye function, dashed line) as a function of $\sqrt{x} = kR_g$ in $d = 3$. The open circles show a second realization of $C$ to demonstrate self-averaging. Note that we measure length scales in terms of $R_g$ and use a normalization $S_0(0) = 1$ different to that in the experimental literature.

FIG. 4. Structure function $S_0$ for different crosslinking potentials $z$. From right to left $z = 0, 10, 10^2, 10^3, 10^4, 10^5, \infty$ for a network size of $N = 10000$ and $M = 200$ plotted in dimensionless units $q = ka/\sqrt{2d}$. The left curve ($z \to \infty$) is the Debye function of a linear chain.

FIG. 5. Radius of gyration of a polymer chain as a function of $\sqrt{z} = \varepsilon/a$. For the three solid curves the number of monomers was varied from top to bottom $N = 5000, 10000, 20000$; $M$ was kept constant at 200. The short dashed line shows a network with $N = 20000$ and $M = 400$. 