The Swelling of Olympic Gels

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The swelling equilibrium of Olympic gels, which are composed of entangled cyclic polymers, is studied by Monte Carlo Simulations. In contrast to chemically crosslinked polymer networks, we observe that Olympic gels made of chains with a larger degree of polymerization, \( N \), exhibit a smaller equilibrium swelling degree, \( Q \propto N^{-0.38} \phi_0^{-0.72} \), at the same polymer volume fraction \( \phi_0 \) at network preparation. This observation is explained by a desinterspersion process of overlapping non-concatenated rings upon swelling.

Olympic gels \[1, 2\] are networks made of cyclic polymers ("rings") connected by the mutual topological inclusion of polymer strands, see Fig. 1 with their elastic properties depending exclusively on the degree of entanglements caused by the linking of the rings. This particular difference to conventional polymer networks and gels makes these materials an interesting model system, since the pristine effect of entanglements on thermodynamic properties of polymers is accessible. In particular, such gels could reveal the role of entanglements for equilibrium swelling of polymer networks, which is an outstanding problem in polymer physics. Since the term Olympic gels has been coined by de Gennes \[2\], however, the challenge to synthesize such materials has not been mastered yet, although possible pathways for their synthesis have been proposed \[1\].

In the present simulation study we construct Olympic gels, characterize their topological state, and simulate isotropic swelling in athermal solvent. We find that the equilibrium degree of swelling of Olympic gels is described by a negative power as function of the degree of polymerization, \( N \), of the rings, see Fig. 2 in marked contrast to standard models of network swelling \[3\]. We will show that this result is a direct consequence of a desinterspersion process originally proposed by Bastide \[4\], which allows polymer rings to swell in part at no elastic deformation.

Let us first recall the essential predictions of the Flory-Rehner (FR) \[5\] model for equilibrium swelling of polymer networks. The latter can be characterized by the equilibrium degree of swelling, \( Q \), which is defined by the ratio of the polymer volume at swelling equilibrium with respect to the pure polymer volume in the dry state. In the FR-model, it is assumed that the net change of free energy upon swelling is solely given by the sum of the change of free energy of mixing of the solvent with the polymer and the free energy change of an affine elastic deformation of the network strands. One can express this condition by equating the elastic osmotic pressure resulting from an isotropic deformation of Gaussian chains and the osmotic pressure of mixing, \( \Pi_{el} = \Pi_{mix} \). The gel is prepared at a polymer volume fraction \( \phi_0 \), where the elastically active network chains (or rings) have an average extension of \( R_0 \). The equilibrium degree of swelling of a polymer gel with an average elastic strand length, \( N \), is reached at a polymer volume fraction \( \phi < \phi_0 \), for which network strands in solution exhibit an extension \( R_{ref} \) solely due to excluded volume interactions. With these parameters, the elastic “pressure” can be written as

\[
\Pi_{el}(\phi) \approx \frac{kT}{b^3} \frac{\phi^2}{N} \left(\frac{\lambda R_0}{R_{ref}}\right)^2 \approx \frac{kT}{b^3} \frac{\phi^2}{N} \left(\frac{\phi_0}{\phi_0}\right)^{2/3} \left(\frac{\phi}{\phi_0}\right)^{28/3 - 1}.
\]

Here, \( \lambda \) denotes the linear deformation ratio of the strands, \( \lambda^3 = \phi_0/\phi \), \( k \) is the Boltzmann constant, \( T \) the absolute temperature, and \( b \) denotes the root mean square length of a Kuhn segment. The osmotic pressure due to mixing is given by Des Cloizeaux’s law \[2\]

\[
\Pi_{mix}(\phi) \approx \frac{kT}{b^3} \phi^{3\nu/(3\nu - 1)}.
\]

Both equations take into account the excluded volume effect for swelling in good solvent with the exponent \( \nu \approx 0.588 \) which is most appropriate for the present simulation study. Equating both expressions one obtains the equilibrium degree of swelling

\[
Q = \frac{1}{\phi} \approx N^{3(3\nu - 1)/4} \phi_0^{-1/4} \approx N^{0.57} \phi_0^{-0.25}.
\]

The hallmark of this text book result \[\ref{3}\] is that the equilibrium degree of swelling grows with increasing strand length \( N \) and decreases weakly with increasing polymer volume fraction \( \phi_0 \) at preparation state. Eq. \[\ref{1}\] is derived by assuming an affine deformation of the chain ends and thus, it is assumed that no swelling is possible without the free energy penalty of elastic deformation.

In Fig. 2 we display our simulation results for the equilibrium swelling of Olympic gels. In contrast to the FR prediction we observe a reduction of the degree of swelling with increasing chain length, see inset of Fig. 2. The best overlap of all simulation data is consistent with an ad hoc scaling law given by

\[
Q \approx N^{-0.28} \phi_0^{-0.72}
\]
Figure 2: The scaling of the equilibrium degree of swelling. Inset: unscaled data. The line indicates the proposed scaling $Q \propto N^{-0.28} \phi_0^{-0.72}$.

Table I: $N$ is the degree of polymerization of the rings, $M$ the number of rings per sample, $\phi_0$ the polymer volume fraction at preparation conditions, $f_n$ the average number of concatenated pairs of rings per ring, $Q$ the equilibrium degree of swelling, $D^2$ and $D_0^2$ are the square average distances of two opposite monomers of a ring in the swollen and the preparation state, $P$ and $P_0$ are the overlap numbers in the swollen state and the preparation state.

| Sample | #1 | #2 | #3 | #4 | #5 | #6 | #7 | #8 | #9 |
|--------|----|----|----|----|----|----|----|----|----|
| $N$    | 128| 256| 256| 512| 512| 1024|1024|1024|1024|
| $M$    | 1024| 512| 2048| 2048| 1024| 1024| 1024| 1024| 1024|
| $\phi_0$ | 0.5 | 0.5 | 0.25 | 0.5 | 0.25 | 0.125 | 0.5 | 0.25 | 0.0625 |
| $f_n$  | 2.7 | 5.64 | 2.89 | 10.9 | 6.04 | 2.98 | 17.7 | 10.08 | 2.76 |
| $Q$    | 14.9 | 10.5 | 25.7 | 9.54 | 17.0 | 38.3 | 8.6 | 14.5 | 39.8 |
| $D^2$  | 169.7 | 316 | 429 | 670 | 855 | 1056 | 1252 | 1581 | 2442 |
| $D_0^2$ | 513 | 1191 | 1140 | 2618 | 2726 | 2608 | 5354 | 5790 | 5310 |
| $P_0$  | 2.70 | 4.50 | 2.83 | 6.28 | 4.08 | 2.44 | 10.3 | 7.10 | 2.89 |
| $P$    | 1.15 | 2.80 | 1.10 | 5.81 | 3.12 | 1.21 | 9.8 | 5.96 | 1.32 |

To simulate Olympic gels we used a GPU-version of the bond fluctuation method, which is an efficient simulation method for polymers in the semi-dilute and concentrated regime. The preparation of the samples is identical to our previous work for the concatenated series of melts except of using a non-periodic box as simulation container. By including diagonal moves in the preparation step of Olympic gels we allow the crossing of bonds without a change in the excluded volume constraints. By returning to the original set of moves the thus created topology is conserved. The key parameters of the samples are summarized in Table I. In the present work, we focus on samples with an average number of concatenations per ring $f_n \geq 2$, for which we can identify a well developed dominant largest cluster (gel). $f_n$ is as shown in the main plot of Figure 2. We will explain this unexpected behavior in this letter after a more detailed analysis of the simulation data.

After preparation, the networks are placed into the middle of a large simulation container and swollen to equilibrium, which was monitored by the drop in the polymer volume fraction near the middle of the gel. Empty lattice sites model a perfect athermal solvent. The equilibrium degree of swelling $Q$ is determined by analyzing $\phi^{-1}$ for the innermost 50% of the monomers. We consider $\phi = 0.5$ as melt concentration with the reference value $Q = 1$. The polymer volume fraction at swelling equilibrium for any sample is below 1/16, which justifies a semi-dilute approximation of chain conformations. The overlap number of a given ring, $P$, is determined by counting the centers of mass of other rings in a sphere with radius $D$ around the center of mass of each ring, whereby $D$ is the average distance of two opposite monomers of a ring. For convenience, we also use $D$ to measure the deformation of the rings. Note that the chains are only weakly deformed with a maximum $D/D_0 \approx 2.07$ for all samples.

In Figure 3 we display the apparent affine deformation part $\overline{Q}_a/Q$ of swelling given by

$$\overline{Q}_a = (D/D_0)^3,$$

where $D_0$ is the ring extension at preparation conditions. According to the FR-modell we have $Q \equiv \overline{Q}_a$ per definition. Figure 3 displays $\overline{Q}_a$ as a function of the degree of equilibrium swelling. Large values for $Q$ are obtained by a non-affine swelling while the limit of small $Q$ is well described by an apparently fully affine deformation of the chains. The data of Figure 3 indicate a relation in the vicinity of $\overline{Q}_a/Q \propto Q^{-1.95}$ for all samples of our study with a small additional correction as function of $\phi_0$. After preparation, the networks are placed into the middle of a large simulation container and swollen to equilibrium, which was monitored by the drop in the polymer volume fraction near the middle of the gel. Empty lattice sites model a perfect athermal solvent. The equilibrium degree of swelling $Q$ is determined by analyzing $\phi^{-1}$ for the innermost 50% of the monomers. We consider $\phi = 0.5$ as melt concentration with the reference value $Q = 1$. The polymer volume fraction at swelling equilibrium for any sample is below 1/16, which justifies a semi-dilute approximation of chain conformations. The overlap number of a given ring, $P$, is determined by counting the centers of mass of other rings in a sphere with radius $D$ around the center of mass of each ring, whereby $D$ is the average distance of two opposite monomers of a ring. For convenience, we also use $D$ to measure the deformation of the rings. Note that the chains are only weakly deformed with a maximum $D/D_0 \approx 2.07$ for all samples.

Figure 3: The fraction of the apparent affine contribution $\overline{Q}_a$ to the equilibrium degree of swelling $Q$. The lines indicate best fits with power laws $\propto Q^{-1.9 \pm 0.2}$ and $\propto Q^{-1.95 \pm 0.08}$ for $\phi_0 = 1/4$ and $\phi_0 = 1/2$ respectively.

$$f_n \propto \phi_0^{\nu/(3\nu-1)} N \propto \phi_0^{0.77} N. \quad (5)$$
One possible mechanism for the observed non-affine swelling is the rearrangement of cyclic polymers upon swelling without elastic deformation. To identify such rearrangements, we distinguish between concatenated and non-concatenated rings which are overlapping at preparation conditions. The distance distributions of centers of mass of these ring populations is then analyzed at swelling equilibrium. The data of the two overlapping populations of sample #6, see Table I, with small \( f_n \) is shown in Figure 4 as an example. The data show that non-concatenated rings essentially are squeezed out of the volume \( 4\pi D^3/3 \) while the concatenated rings remain within a distance of order \( D \).

As consequence, the overlap number, \( P \), at swelling equilibrium is roughly proportional to \( f_n \) for all samples of our study as shown in Figure 5. Note that \( f_n \) grows linearly with \( N \) and thus, more rapidly than the Flory number \( P \) of overlapping molecules. As mentioned in Ref. 9, \( f_n \) must converge towards \( P_0 \) for large \( N \). Convergence is nearly reached for the samples with the largest values of \( f_n \). To show this convergence, we added the data for \( P_0 \propto f_n^{0.27} \propto \phi_0^{0.65}N^{1/2} \) in Fig. 5 ignoring the weak extra \( \phi_0 \) - dependence of \( P_0 \).

Based upon the above observations, we argue that the dominating contribution to the non-affine swelling stems from the desinterspersion of non-concatenated rings upon swelling in the partially concatenated regime with \( f_n \propto N \). To derive the equilibrium swelling condition in this regime, we assume full desinterspersion of overlapping non-concatenated rings and an affine deformation of the concatenated rings. For the sake of the argument let us introduce an intermediate state of swelling that we call the “desinterspersed state” and denote this state by subscript ’des’. In the desinterspersed state, the total number of correlation volumes per volume of a ring, \( R_{des}^3/\xi_{des}^3 \), can be approximated by the number of blobs per chain, \( N/g_{des} \) times the number \( f_n \propto \phi_0^{\nu/(3\nu-1)}N \) of overlapping concatenated chains

\[
\frac{R_{des}^3}{\xi_{des}^3} \approx \frac{N}{g_{des}} f_n.
\]

We consider the polymer volume fraction at the desinterspersed state

\[
\phi_{des} \approx \frac{b^3 g_{des}}{\xi_{des}^3} f_n \propto \frac{b^3 N^2}{R_{des}^3} \phi_0^{\nu/(3\nu-1)}
\]

as reference state for the onset of the affine deformation. The size of a non-deformed ring

\[
R_{des} \approx bN^{1/2} \phi_{des}^{-(\nu-1)/(3\nu-1)}
\]

at polymer volume fraction \( \phi_{des} \) leads to a degree of swelling in the desinterspersed state

\[
Q_{des} = 1/\phi_{des} \sim N^{-(3\nu-1)/2} \phi_0^{-2\nu} \sim N^{-0.76} \phi_0^{-1.18}.
\]

This result is the key to understand the negative power for \( N \) at the equilibrium degree of swelling.

For \( f_n > 1 \), desinterspersion must stop at a polymer volume fraction larger than the overlap concentration \( \phi^* \propto N^{-(3\nu-1)} \) proposed by De Gennes 2. In fact, we find \( \phi_{des} \propto 1/\phi^* \), which shows that desinterspersion becomes increasingly difficult with increasing overlap of the rings. Since \( \phi_{des} \gg \phi^* \), swelling equilibrium is reached by an additional elastic deformation of the rings. We consider only the permanent entanglements as approximated by the number of concatenations to be relevant at swelling equilibrium and assume that higher topological invariants are not important for the partially concatenated regime with \( f_n \propto N \). To apply the affine model for deformation, we subdivide the \( N \) segments of the ring into \( f_n \) elastic chains by assuming that for small \( f_n \lesssim 10 \) all concatenated chains are deforming the concatenating ring at swelling equilibrium. Swelling equilibrium is
found by using $\phi_{des}$ as new “preparation condition” instead of $\phi_0$ in Eq. (1). This leads to

$$Q \approx \left( \frac{N}{f_n(\phi_0)} \right)^{3(3\nu - 1)/4} \phi_{des}^{-1/4} \approx N^{-(3\nu - 1)/4} \phi_0^{-5\nu/4}$$

and thus, $Q \approx N^{-0.19} \phi_0^{-0.74}$, which is in good agreement with our ad hoc scaling prediction in Eq.(1) for the simulation data.

As direct consequence of this model we find that the apparent affine fraction of swelling depends on the desinterspersed state

$$\overline{Q}_a = \left( \frac{R_a}{R_{g,0}} \right)^3 = \left( \frac{R_{des}}{R_{g,0}} \right)^3 \left( \frac{R_a}{R_{des}} \right)^3 = \left( \frac{R_{des}}{R_{g,0}} \right)^3 Q_a.$$ (12)

Since the true affine fraction $Q_a/Q = 1/Q_{des}$ is related to the equilibrium degree of swelling by $Q_a(Q)/Q \propto Q_{des}^{-1}(Q) \propto Q^{-4}$, see Eq.(11), the apparent affine fraction of swelling is also universal, i.e. is independent of the length of the rings:

$$\overline{Q}_a/Q = \left( \frac{R_{des}}{R_{g,0}} \right)^3 \frac{Q_a}{Q} \propto \phi_0^{3(\nu - 1/2)/(3\nu - 1)} Q_{-2}(3\nu - 1)$$

with a strong dependence, $\overline{Q}_a/Q \propto Q^{-2.62}$, on $Q$. A similar universality is observed in Fig.3 which is a striking evidence for the existence of the desinterspersed process.

To conclude, Olympic gels display a highly non-affine swelling behavior due to desinterspersion processes, if the linking number $f_n$ is smaller than the Flory number $P$. This latter condition characterizes the partially concatenated regime, for which a pairwise analysis of linked states seems to be sufficient [9]. The good qualitative agreement between simulation data and model further indicates that each concatenation may contribute a pair of elastic strands to the network, which might be a reasonable approximation for the partially concatenated regime.

It is important to point out here, that the structure of any network can be decomposed into a set of connected cycles [11], whereby the average cycle size is of order 8 chains for typical strand lengths around 50-100 Kuhn segments between 4-functional junctions [12]. Therefore, most elastomers are located in the regime $f_n \propto N$ where desinterspersion of non-concatenated cyclic structures upon swelling occurs. Based upon our results, therefore, we expect a clear impact of desinterspersion onto the equilibrium swelling degree of polymer gels. This view is supported by simulations that detect a non-affine swelling of crosslinked networks on length scales much larger than the size of individual network strands [13] and by experiments that measure a vanishing non-affine contribution to elasticity at large degrees of swelling [14]. Scattering and NMR data indicate that the initial swelling may be dominated by a desinterspersion process that is followed by a deformation of the chains [3], which is in full accord with our model but in opposite order as the assumption used by Painter and Shenoy [13]. In particular, the length scale at which the deformation becomes affine is an essential parameter that needs to be understood in the framework of elasticity models that predict a non-affine deformation behavior [10]. Our analysis of Olympic gels gives a fresh view on the problem of swelling of polymer gels in general and reveals that connectivity caused by topological concatenation can lead to a qualitatively different swelling behavior.

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| Sample | #1 | #2 | #3 | #4 | #5 | #6 | #7 | #8 | #9 |
|--------|----|----|----|----|----|----|----|----|----|
| N      | 128 | 256 | 256 | 512 | 512 | 512 | 1024 | 1024 | 1024 |
| M      | 1024 | 512 | 2048 | 2048 | 1024 | 512 | 1024 | 512 | 1024 |
| $\phi_0$ | 0.5 | 0.5 | 0.25 | 0.25 | 0.25 | 0.125 | 0.5 | 0.25 | 0.0625 |
| $f_n$  | 2.7 | 5.64 | 2.89 | 10.9 | 6.04 | 2.98 | 17.7 | 10.08 | 2.76 |
| $Q$    | 14.9 | 10.5 | 25.7 | 9.54 | 17.0 | 38.3 | 8.6 | 14.5 | 39.8 |
| $D_0^2$ | 339 | 632 | 857 | 1340 | 1710 | 2113 | 2505 | 3163 | 4884 |
| $D^2$  | 1027 | 2382 | 2281 | 5236 | 5452 | 5216 | 10708 | 11579 | 10621 |
| $P_0$  | 9.03 | 13.1 | 9.59 | 18.8 | 12.9 | 8.19 | 27.5 | 19.1 | 9.37 |
| $P$    | 3.64 | 8.37 | 3.61 | 17.0 | 9.49 | 3.85 | 26.3 | 16.5 | 4.62 |