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 cross-linked polymer networks, we observe that Olympic gels made of chains with a larger degree of polymerization, N, exhibit a smaller equilibrium swelling degree, $Q \propto N^{-0.28}\phi_0^{-0.72}$, at the same polymer volume fraction ϕ_0 at network preparation. This observation is explained by a desinterspersion (reorganization with release of nontrapped entanglements) process of overlapping nonconcatenated rings upon swelling.

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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 from 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 of synthesizing such materials has not yet been mastered, although possible pathways for their synthesis have been proposed [1].

In the present Letter, 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 a 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 (reorganization with release of nontrapped entanglements) process originally proposed by Bastide [4], which allows polymer rings to swell in part at no elastic deformation.

First, let us 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, $\Pi_{\mathrm{el}} = \Pi_{\mathrm{mix}}$. The gel is prepared at a polymer volume fraction ϕ_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

$$\Pi_{\mathrm{el}}(\phi) \approx \frac{kT}{b^3}\frac{\phi}{N}\left(\frac{\lambda R_0}{R_{\mathrm{ref}}}\right)^2 \approx \frac{kT\phi}{Nb^3}\left(\frac{\phi_0}{\phi}\right)^{2/3}\left(\frac{\phi}{\phi_0}\right)^{(2\nu-1)/(3\nu-1)}. \quad (1)$$

Here, λ 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]

$$\Pi_{\mathrm{mix}}(\phi) \approx \frac{kT}{b^3}\phi^{3\nu/(3\nu-1)}. \quad (2)$$

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 simulations. Equating both expressions one obtains the equilibrium degree of swelling

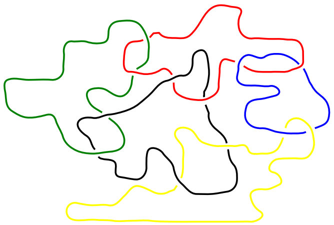

FIG. 1 (color online). Sketch of an Olympic gel.

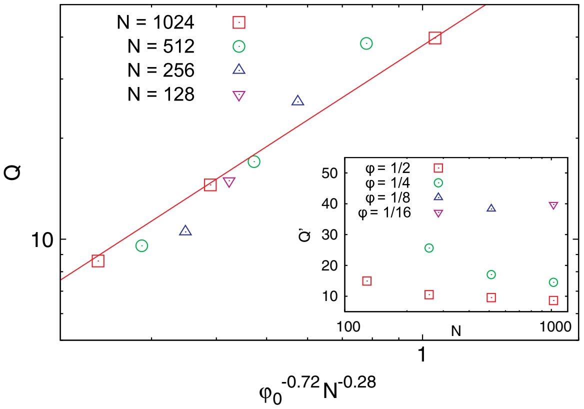

FIG. 2 (color online). The scaling of the equilibrium degree of swelling. Inset: unscaled data. The line indicates the proposed scaling $Q \propto N^{-0.28}\phi_0^{-0.72}$.

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

The hallmark of this textbook result [3] is that the equilibrium degree of swelling grows with increasing strand length N and decreases weakly with increasing polymer volume fraction ϕ_0 at preparation state. Equation (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

$$Q \approx N^{-0.28}\phi_0^{-0.72}, \tag{4}$$

as shown in the main plot of Fig. 2. We will explain this unexpected behavior in this Letter after a more detailed analysis of the simulation data.

To simulate Olympic gels, we used a GPU version [6] of the bond fluctuation method [7], which is an efficient simulation method for polymers in the semidilute and concentrated regime [8]. The preparation of the samples is identical to our previous work [9] for the concatenated series of melts except for using a nonperiodic box as a 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 topology created is conserved. The key parameters of the samples are summarized in Table I. In the present Letter, 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 determined as described in [9] and follows the prediction

TABLE I. N is the degree of polymerization of the rings, M the number of rings per sample, ϕ_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	512	1024	1024	1024
M	1024	512	2048	2048	1024	512	1024	512	1024
ϕ_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_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

$$f_n \propto \phi_0^{\nu/(3\nu-1)}N \propto \phi_0^{0.77}N. \tag{5}$$

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 athermal solvent. The equilibrium degree of swelling Q is determined by analyzing ϕ^{-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 semidilute 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 Fig. 3, we display the apparent affine deformation part $\bar{Q}_a/Q$ of swelling given by

$$\bar{Q}_a = (D/D_0)^3, \tag{6}$$

where D_0 is the ring extension at preparation conditions. According to the FR model, we have $Q \equiv \bar{Q}_a$ per definition [3,10]. Figure 3 displays $\bar{Q}$ as a function of the degree of equilibrium swelling. Large values for Q are obtained by a nonaffine swelling while the limit of small Q is well described by an apparently fully affine deformation of the chains. The data of Fig. 3 indicate a relation in the vicinity of $\bar{Q}_a/Q \propto Q^{-1.95}$ for all samples of our Letter with a small additional correction as a function of ϕ_0.

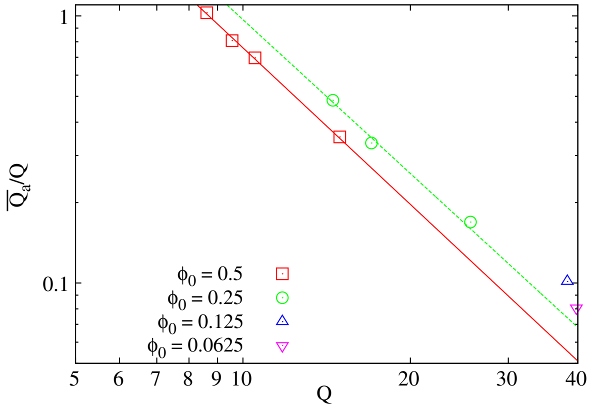

FIG. 3 (color online). The fraction of the apparent affine contribution $\bar{Q}_a$ to the equilibrium degree of swelling Q. The lines indicate best fits with power laws $\propto Q^{-1.9\pm0.2}$ and $\propto Q^{-1.95\pm0.08}$ for $\phi_0 = 1/4$ and $\phi_0 = 1/2$, respectively.

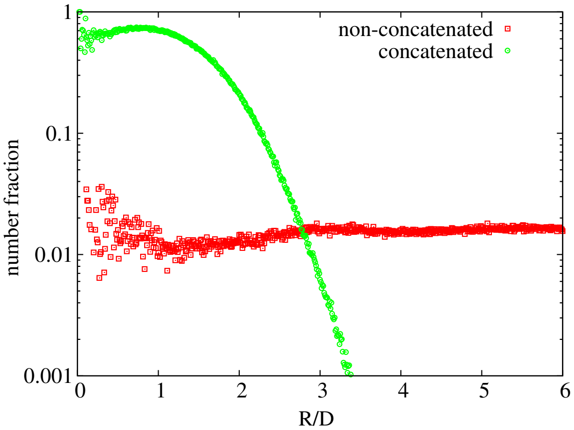

FIG. 4 (color online). Normalized distance distribution between centers of mass of previously overlapping nonconcatenated and concatenated rings at swelling equilibrium (sample 6).

One possible mechanism for the observed nonaffine swelling is the rearrangement of cyclic polymers upon swelling without elastic deformation. To identify such rearrangements, we distinguish between concatenated and nonconcatenated 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 Fig. 4 as an example. The data show that nonconcatenated 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 a consequence, the overlap number, P, at swelling equilibrium is roughly proportional to f_n for all samples of our Letter, as shown in Fig. 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 $P_0 \propto f_n \phi_0^{0.27} \propto \phi_0^{0.65} N^{1/2}$ in Fig. 5 ignoring the weak extra ϕ_0 dependence of P_0.

Based upon the above observations, we argue that the dominating contribution to the nonaffine swelling stems from the desinterspersion of nonconcatenated 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 nonconcatenated rings and an affine deformation of the concatenated rings. For the sake of 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, $R_{\mathrm{des}}^3/\xi_{\mathrm{des}}^3$, 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

$$\frac{R_{\mathrm{des}}^3}{\xi_{\mathrm{des}}^3} \approx \frac{N}{g_{\mathrm{des}}} f_n. \tag{7}$$

We consider the polymer volume fraction at the desinterspersed state

$$\phi_{\mathrm{des}} \approx \frac{b^3 g_{\mathrm{des}}}{\xi_{\mathrm{des}}^3} \propto \frac{b^3 N^2}{R_{\mathrm{des}}^3} \phi_0^{\nu/(3\nu-1)}, \tag{8}$$

as a reference state for the onset of the affine deformation. The size of a nondeformed ring

$$R_{\mathrm{des}} \approx b N^{1/2} \phi_{\mathrm{des}}^{-(\nu-1/2)/(3\nu-1)}, \tag{9}$$

at polymer volume fraction ϕ_{des} leads to a degree of swelling in the desinterspersed state

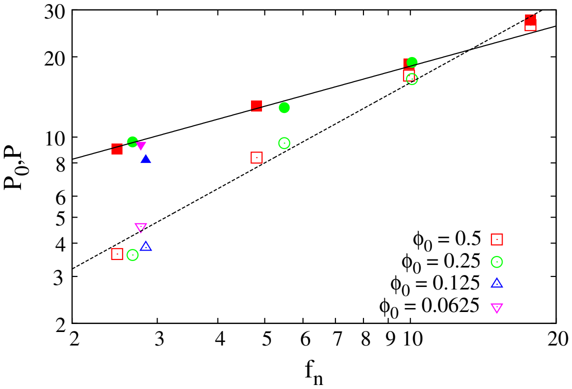

FIG. 5 (color online). The overlap number of cyclic polymers in the preparation state, P_0 (filled symbols), at swelling equilibrium, P (hollow symbols), as a function of the average number of concatenations per ring, f_n. The dashed line indicates $P \propto f_n$ and the solid line indicates $P_0 \propto f_n^{1/2}$.

$$Q_{\mathrm{des}} = 1/\phi_{\mathrm{des}} \sim N^{-(3\nu-1)}\phi_0^{-2\nu} \sim N^{-0.76}\phi_0^{-1.18}. \qquad (10)$$

This result is the key to understanding 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 $\phi_{\mathrm{des}} \propto 1/\phi^*$, which shows that desinterspersion becomes increasingly difficult with increasing overlap of the rings. Since $\phi_{\mathrm{des}} \gg \phi^*$, 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 ϕ_{des} as a new "preparation condition," instead of ϕ_0 in Eq. (1). This leads to

$$Q \approx \left(\frac{N}{f_n(\phi_0)}\right)^{3(3\nu-1)/4}\phi_{\mathrm{des}}^{-1/4} \approx N^{-(3\nu-1)/4}\phi_0^{-5\nu/4}, \qquad (11)$$

and thus, $Q \approx N^{-0.19}\phi_0^{-0.74}$, which is in good agreement with our *ad hoc* scaling prediction in Eq. (4) for the simulation data.

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

$$\bar{Q}_a = \left(\frac{R_g}{R_{g,0}}\right)^3 = \left(\frac{R_{\mathrm{des}}}{R_{g,0}}\right)^3\left(\frac{R_g}{R_{\mathrm{des}}}\right)^3 = \left(\frac{R_{\mathrm{des}}}{R_{g,0}}\right)^3 Q_a. \quad (12)$$

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

$$\frac{\bar{Q}_a}{Q} = \left(\frac{R_{\mathrm{des}}}{R_{g,0}}\right)^3\frac{Q_a}{Q} \propto \phi_0^{3(\nu-1/2)/(3\nu-1)}Q^{-2/(3\nu-1)}, \qquad (13)$$

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

To conclude, Olympic gels display a highly nonaffine swelling behavior due to desinterspersion processes, if the linking number f_n is smaller than the Flory number P. The 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, 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 four functional junctions [12]. Therefore, most elastomers are located in the regime $f_n \propto N$ where desinterspersion of nonconcatenated 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 nonaffine swelling of cross-linked networks on length scales much larger than the size of individual network strands [13] and by experiments that measure a vanishing nonaffine 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 [4], which is in full accord with our model but in opposite order of the assumption used by Painter and Shenoy [15]. 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 nonaffine deformation behavior [10]. Our analysis of Olympic gels gives a fresh view of the problem of the 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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