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Elasticity of entangled polymer loops: Olympic gels

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In this Rapid Communication we present a scaling theory for the elasticity of olympic gels, i.e., gels where the elasticity is a consequence of topology only. It is shown that two deformation regimes exist. The first is the nonaffine deformation regime where the free energy scales linear with the deformation. In the large (affine) deformation regime the free energy is shown to scale as $F \propto \lambda^{5/2}$ where λ is the deformation ratio. Thus a highly non-Hookian stress-strain relation is predicted. [S1063-651X(97)50408-9]

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In this Rapid Communication we compute the scaling of the elastic modulus of an olympic gel. This name has been created by de Gennes [1] since the configuration of such gels resembles very much the olympic rings. Olympic gels are very peculiar elastic materials as their elasticity does not come from crosslinks as in conventional rubbers. Actually ideal olympic gels do not contain any crosslinks, but consist of concatenated rings only. In this sense the elasticity of such materials is expected to be very different from classical rubbers and strong deviations from the non-Hookian deformation behavior [2,3] (as observed in the low deformation regime in conventional rubbers) must be expected. Actually, the elasticity of such olympic gels has not been calculated yet and we attempt to present a simple argument in this issue. Apart from the case of synthetic materials these considerations are important for biological systems too. It is well known that highly entangled DNA rings exist and play an important role in biology [4–7]

Unless, as in conventional soft materials, such as rubbers, the precise calculation of the modulus of topological gels is difficult, the exact topological state of the gel must be known. Specifying topological states is a general problem in polymer physics and has been discussed in [8]. The corresponding mathematical problem is the classification of knots and links [9]. Despite its incompleteness already noted in [8], in general the Gauss invariant is used in polymer physics because it is the most simple invariant that explicitly contains the polymer conformation in contrast to algebraic invariants in knot theory. Even using the Gauss invariant, it is, in general, not very simple to describe the linking status of the network. Only for the easy case of a nonconcatenated melt of rings this seems to be possible, but here already many complications appear [10].

The synthesis and preparation of such gels is also a very difficult task. Some of the problems are already discussed in de Gennes' book [1]. The crucial point is that the ring closure of the chains must be carried out at concentrations larger than the overlap concentration c^*. The reaction process is carried out in two steps: First a certain amount of rings is cyclicized by end group reaction. Then further linear chains are added to the given sample. These additional rings are then cyclicized again. With variation of the concentration different entanglement numbers can be expected. The solvent must then be evaporated to get the bulk network. In such an ideal synthesis the topological state of the network depends on the concentration of preparation. One limit is the cyclization in the linear melt state (a *gedanken* experiment). Such prepared topological gels will be important for motivation of the following scaling analysis. Assume therefore a condensed melt of linear chains. It is well known that the excluded volume forces are screened out [1,11]. The screening of the excluded volume can also be asserted to the strong interpenetration of linear (= one-dimensional connectivity) chains [12]. As a result, the chains behave Gaussian in the melt. If then each long chain is closed to a ring (*in gedanken*), the size of the ring polymer would not change. The reason for this is that each ring is (in average) concatenated by $n \simeq \varrho l^3 N^{1/2}$, where ϱ is the density of the melt, l the typical size of a monomer, and N the degree of polymerization. In the limit of scaling, n can be identified by the winding number. Such natural conjectures have also been mentioned by Cates *et al.* [13]. For a more rigorous definition of the winding number in such gel-like systems we refer the reader to our previous publication [10]. In this paper we had already confirmed the scaling conjecture presented first by Cates *et al.* [13] by careful treatment of the Gaussian linking number. The main result there was to show that the conformation of a ring in an unlinked melt of rings is naturally non-Gaussian, i.e., the size $R \propto N^{\nu}$, where $\nu < 1/2$.

In the present work we treat dense *linked* olympic gels without solvent. The discussion of solvent free gels yields the ''bare'' scaling of the elastic modulus without additional contributions from the excluded volume and swelling.

To do this, we have to use nonconventional arguments, because most of the theories for ideal, ordinary rubber networks are ''single chain theories,'' i.e., all the elasticity of the network is computed by the contribution of the elasticity of one single network strand, which is then multiplied by the number of elastically active chains [3]. These well-known results can be summarized by the free energy of the network as a function of deformation $F \propto M k_B T \lambda^2$, where M is the number of active chains and λ is the deformation ratio of the chain. Although this seems to be very simplified, the results are in reasonable agreement with low deformation experiments and recent simulations [14], as long as higher order effects at large deformations are ignored. In this work we put forward a scaling theory in a similar spirit. To do this we estimate the single ring behavior and conclude from this basis the elasticity of the entire gel. For the subsequent analysis we need the following assumptions: the rings are not self-knotted; the topological state of the network can be described by a global winding number n, which on the average is the same for each ring in the network; and the direct influence of excluded volume effects is ignored. Again, these assumptions seem to be crude, but these turn out to be sufficient for the type of analysis presented here. A mathematical formulation of the problem of elasticity of the olympic gel will be presented elsewhere [15].

In the following we start from a Flory-type estimate of the free energy of an entangled ring in an olympic gel, where the average winding number of each ring is assumed to be n. The free energy of an entangled ring in a network can be written as

$$F = k_B T \frac{N}{R^2} + \text{const} \times \frac{R^3}{nN}. \tag{1}$$

Here the first term is the Gaussian elastic part of the ring in the gel and the second term represents the pressure experienced by the ring that comes from all the surrounding rings. If the ring is not entangled with the others the second term would read R^3/N obtained by replacing n by $n+1$ in Eq. (1) and $n=0$. Note that in this case the present ansatz for the free energy agrees with the one proposed by Cates and Deutsch [13] for nonconcatenated ring melts. If, however, other polymers are entangled with the ring under consideration, they exert a repulsive force per winding number from inside and outside the ring, and consequently they do not contribute to the packing pressure. By this, we mean that the dense melt of rings is as closely packed as possible. Thus one ring experiences a pressure induced by the surrounding ones. The packing term is, however, reduced by the average winding number. The factor $1/n$ in front of the second term has its reason in the ‘‘screening’’ of the packing pressure. Each of the other rings that is entangled with the ring polymer under consideration, reduces the packing pressure. In the limit of the cyclization in the melt the free energy contribution must be of the order of $O(1)$, since the rings must be Gaussian. Note that the free energy described by Eq. (1) does not contain an upper critical dimension. The interaction term is therefore important in all spatial dimensions. Instead of an upper critical dimension it contains a limiting winding number such that $R \propto \sqrt{N}$, corresponding to the melt cyclization *gedanken* experiment. Minimization of the free energy with respect to R yields the size for the ring in the network

$$R_N \propto n^{1/5} N^{2/5}, \tag{2}$$

where all (to the purpose of this paper) irrelevant constants have been dropped. The latter equation has interesting consequences. For small n the scaling results agree with those proposed by Cates *et al.* [13]. The rings appear compressed in the melt. Similar findings have been put forward by a more rigorous theory by us recently [10] and by numerical simulations of the problem [16,17]. On the other hand, if the mean winding number is close to that given by the average density of the system, i.e., $n \propto \sqrt{N}$, the ring is Gaussian at melt cyclization conditions. In this case the topological effects are screened and the ring finds itself in a natural melt environment. If the winding number is larger, for example, $n \propto N$, then too many rings are connected with each other and the ring configuration stretches out. So far the requirements have been satisfied by the simple scaling ansatz.

The next task is now to find the asymptotic distribution function for the typical size r of the ring in the gel. A reasonable form of the distribution function is given by $P(r,N,n) = \mathcal{N} r^{\theta} f(r/R_N)$, where $\mathcal{N}$ is a suitable but uninteresting normalization. θ determines the short distance behavior and the function $f(x)$ has to be determined. In fact, for the elasticity the knowledge of the scaling function f is sufficient, because the power in front of the distribution function yields only irrelevant (logarithmic) corrections. To find the appropriate distribution function, we start from the asymptotic behavior of the scattering function defined by the size of the ring. Then, by standard methods, such as steepest descent Fourier inversion [1], it is easily found that the asymptotic form of the distribution is given by

$$P(r,N,n) \propto \exp\left\{ -\left(\frac{r}{R_N} \right)^{5/3} \right\}, \tag{3}$$

This asymptotic form will be sufficient in the scaling limit. This is indeed the key equation of the paper. Together with Eq. (2) it yields the correct asymptotic behavior of the distribution function. For low values of the average winding number n it contains the limits suggested in [13].

The olympic gel is considered to be entropy elastic. Thus we may conclude that the elastic free energy of the typical ring in the olympic gel as a function of its elongation r is given by

$$F_s(r) \propto T \frac{1}{(nN^2)^{1/3}} r^{5/3}. \tag{4}$$

The tension is given by the derivative and thus we find a nonlinear force extension relationship due to the non-Gaussian structure of the rings in the network, i.e.,

$$f = T \frac{1}{(nN^2)^{1/3}} r^{2/3}. \tag{5}$$

The latter result is the force extension law for one ring in the olympic gel, and corresponds to the according single-chain deformation law in conventional rubber theory, i.e., $f = (T/N) r$ [2]. Therefore (non-)Hookian deformation behavior in olympic gels cannot be expected.

At this point we have the possibility to observe two different deformation processes and regimes. At low deformations the entanglements do not act as severe constraints, but have many degrees of freedom, similar to entanglements in conventional rubbers. It has been shown that there the entanglements yield a ‘‘softening’’ of the modulus, if compared to the classical Gaussian theory [3,18,19]. This softening of the modulus corresponds to the slippage and sliding of entanglements. This happens if the deformation of the individual ring in the gel is such that only the mean contour between two entanglements, i.e., N/n take part on the deformation. This defines the deformation ratio $\lambda_0 = (N/n)/(R_N) \cong (N/n^2)^{3/5}$. Note that λ_0 in the melt preparation conditions, when $n \propto \sqrt{N}$, is $O(1)$, which is physically sensible: At high degree of entangling the topological constraints act immediately as crosslinks from the lowest deformation. From the arguments presented in [3,18] the maximum deformation can be estimated to $\lambda_{\max}=O(\sqrt{N/n})$. The latter is always less than λ_0 as long as $n \leqslant N^{1/7}$. For the validity of the scaling arguments this must always be the case here.

Consider first the low deformation regime $\lambda<\lambda_0$. In the low deformation regime of olympic gels the slippage of the topological constraints dominates. The main problem with the low deformation regime is that the relevant chain length is not fixed [3,18,20]. To see this point consider conventional rubbers, where the fixed length scale is given by the mesh size. In such olympic gels a clear length scale (at least in the low deformation regime) cannot be defined, because the system is ruled by a large number of degrees of freedom.

It has been shown that the deformation process can then be described by an effective distribution $\widetilde{P}(r)=\int dNp(N)P(r,N,n)$ function on the level of a single ring. As a consistent model we choose for $p(N)$ the entanglements slack [21], $p(N)\propto \exp(-N/N_0)$, which has been successfully applied to entanglement problems (see [3] and references therein). N_0 is a mean excursion of the ring form the most probable conformation. The effective distribution is then given by the asymptotic form

$$\widetilde{P}(r,N_0,n)\propto \exp\left(-\frac{r}{n^{1/5}N_0^{2/5}}\right), \tag{6}$$

which is consistent with Eq. (2) since the mean size of the ring is not altered. The macroscopic free energy of an ensemble of M_R rings (per unit volume) is then given by multiplying the above equation by the number of constraints present. These are the number of entanglements $M_R n$. To introduce the deformation we replace r by λR_N and average thus over the conformation as in the simplest theories in classical networks. The total free energy is then estimated by

$$F=TM_R n\lambda, \tag{7}$$

The non-Hookian linear increase of the free energy is entirely due to the large degrees of freedom of the constraints, and is in some way similar to the low deformation regime in highly entangled rubbers, with strong entanglement sliding, when the sliplink contribution becomes very weak (see [3] for details). Consequently, the free energy of the olympic gel is linear in the elongation λ, and the interesting result is that the force needed for elongating the gel is constant, i.e., $f=TnM_R$ in the low deformation regime. In terms of macroscopic variables it is given by $f=(T\varrho)/N$, where $\varrho=M_R N$ is the macroscopic density of the gel. Such a deformation regime is not observable in classical (highly entangled) gels, because in olympic gels the degrees of freedom of the noncrosslinked polymers are much larger, leading to a very weak solid. This is, of course, because olympic gels consist only of entanglements.

At larger deformations ($\lambda>\lambda_0$) the individual chains are deformed also, and the topological constraints act as crosslinks. Therefore the free energy must be proportional to the effective number of constraints, i.e., $M_R n$. In this case we obtain

$$F\cong M_R n\lambda^{5/3}=\varrho\frac{n}{N}\lambda^{5/3}. \tag{8}$$

Obviously $M_R n$ is the effective number of crosslinks in the (affine) deformation regime, where the topological constraints act almost as crosslinks. The measured force f is then given by the derivative of the free energy with respect to the deformation λ, i.e., $f\cong\varrho(n/N)\lambda^{2/5}$, and is larger by a factor of n due to the number of constraints but much weaker in the deformation dependence when compared to classical rubbers. In the latter case the force is roughly given by $f=\varrho(1/N)\lambda$ [2]. The factor of $1/(N/n)$ in the force can indeed be interpreted by the effective mesh size of the olympic gel distance.

In summary, we have presented a simple calculation of the elasticity of olympic gels as a classical example of weak solids. We found two relevant deformation regimes which are determined by the topological state of the network. The first is the nonaffine regime where the modulus is very weak indeed and the scaling is determined by the average winding number and the degree of polymerization of the rings. In the second deformation regime the topological constraints act similar as crosslinks. Therefore the (low deformation $\lambda\approx 1$) modulus is given by $G_{\text{affine}}\cong\varrho(n/N)$. When the mean winding number n is of the order of $\sqrt{N}$ then the modulus becomes larger compared to the classical rubber. This case corresponds to ring closure of the polymers in the melt state. This high modulus in the affine regime is naturally determined by the large number of effective crosslinks. We expect that the present results have some applications in biological systems, too.

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