

Elastic Properties of Polymer Networks

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Received: 15 May 1996 / Accepted: 6 August 1996 / Published: 27 September 1996

Abstract

Many fundamental questions for the understanding of polymer melts and networks are more suitably addressed by current computer simulations than by experiments. The reason is that simulations have simultaneous access to the microscopic structure and the macroscopic behavior of well-defined model systems. The coarse-grained models used often bear little relation to actual chemical species. This is justified by the experimentally established universality of polymer dynamics and no limitation for the test and development of theories which are directed at these universal aspects. The difficulties already encountered on this level will be illustrated for entanglements between polymers which dominate the dynamic in dense systems.

For practical purposes it would, of course, be desirable to predict the characteristic length and time scales of experimental systems from the chemical structure of the polymer chains. Due to the extremely long relaxation times it is impossible to achieve this in brute-force simulations of truly microscopic models. Systematic coarse-graining combined with a better theoretical understanding seem to offer a practical alternative.

Keywords: polymers networks, dynamics, polymer properties, microscopic models

Introduction

Polymer networks are the basic structural element of systems as different as tire rubber and gels. They are not only technically important but also commonly found in biological systems such as the cytoskeleton. Networks of flexible macromolecules display an elastic and thermoelastic behaviour quite different from ordinary solids. [1] Crystals, metals, ceramics, or glasses can be stretched only minimally. Small deformations of the sample extend down to atomic scales and lead to an increase of the internal energy. Rubber-like materials reversibly sustain elongations of up to 1000% with small strain elastic moduli that are four or five orders of

magnitude smaller than for other solids. Most importantly, the tension induced by a deformation is almost exclusively due to a decrease in entropy. As a consequence, the underlying mechanism has to be different from the case of conventional solids.

The key problem in the theory of rubber elasticity is the correct identification of the microscopic sources of this entropy change. An at least qualitative explanation was found in the 1930, when it was realized that rubber is the result of cross linking a melt of long flexible chain molecules. Such polymers adopt random coil conformations and behave as entropic springs. The classical theories of rubber elasticity [1] estimate the elastic properties of a polymer network from the elongation of the network strands. This explanation ne-

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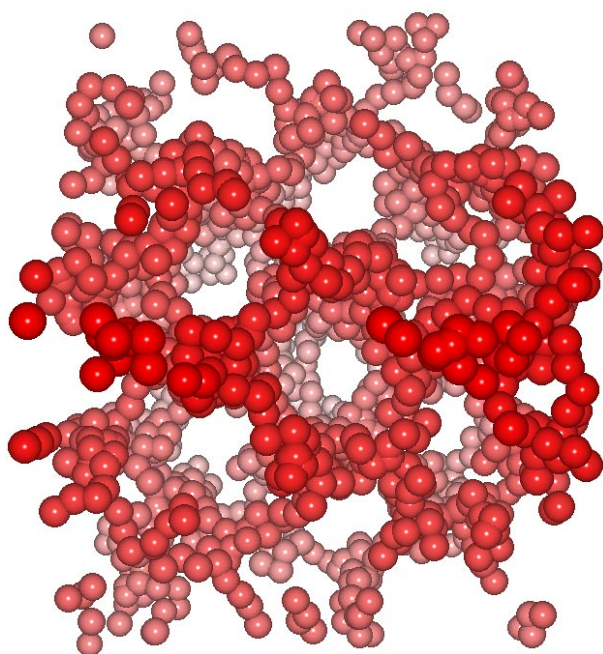


Figure 1. Network of bead-spring polymer chains with the connectivity of a diamond lattice. The typical extension of the network strands corresponds to that of free chains in a melt. The “loose” monomers are due to the representation using periodic boundary conditions.

glects the mutual impenetrability of the chains, although it is the reason for the viscoelastic properties of un-cross-linked polymer melts. [2] The well-known “magic putty” jumps, when formed accordingly, like an ordinary elastic ball. Left to rest on a table, it flows like thick honey. The difference between the two situations lies in the typical time scale over which the force acts on the material. This behavior is universal in the sense that beyond a chemistry-dependent minimal chain length all polymers follow the same laws.

A simple microscopic explanation of these laws is provided by the tube model [2]. Entanglements with other molecules restrict each polymer to a one-dimensional diffusion along its own coarse-grained contour (reptation). The tube is permanently reformed at its ends. To relax the tension in a sheared melt the chains have to reptate out of their original tubes. On shorter time scales the melt displays rubber elasticity with a time and chain length independent modulus; on larger time scales the melt flows like a viscous fluid with a viscosity that increases by a factor of ten when the chain length is doubled. On the whole the tube model is in good agreement with experiments. What is lacking, however, is an understanding of the relation between the parameters of the tube model and the chemical structure of the polymers. Considering how much energy is required in order to pump and to stir intermediate and final products in synthetic production the need for a microscopic understanding of entan-

glement effects becomes obvious. Here the investigation of polymer networks offers a couple of advantages. Cross-linked chains are subject to the same, in their nature topological constraints as chains in a melt without having the possibility to free themselves by reptation. Furthermore, from a mathematical point of view entanglements are only rigorously defined between closed curves like the meshes of a network. Remarkably enough, there is no definite experimental answer to the question, if and how much entanglement effects contribute to the elasticity of polymer networks.

One reason are the great difficulties in the chemical preparation and characterisation of model networks. A randomly cross-linked melt of linear polymers has a highly irregular connectivity. Typical defects are polydispersity, dangling ends and clusters, and self loops. These imperfections are present to some degree in all experimental system and a serious complication in a study of the consequences of topology conservation. The second reason is that although it is comparatively simple to measure the macroscopic properties such as the shear modulus, experiments provide little microscopic information.

Computer simulations offer a couple of important advantages over experiments [3]. We mention the greater freedom in and control over the formation of the networks, the access to the microscopic structure and dynamics, or the possible realization of Gedankenexperiments such as the comparison of otherwise identical systems with and without topology conservation. The key, however, to the optimal use of the information available in a computer simulation is the simultaneous determination of macroscopic quantities. Unfortunately, it is particularly complicated to determine in a simulation what is easily accessible in experiments: the macroscopic elastic properties. The long relaxation times require corresponding computer resources, so that the present simulations were the first in which shear moduli could be measured reliably by investigating strained samples. Since we also have complete access to the microscopic structure and dynamics in both, the strained and the unstrained state, we are in a unique position to test statistical mechanical theories of rubber elasticity without invoking adjustable parameters.

Simulations of model networks

In this paper we summarize results of molecular dynamics simulations of model polymer networks with diamond lattice connectivity, where we have exploited all of the advantages mentioned above. Such systems, which cannot be prepared experimentally, are free of “chemical” defects in the network structure. Thus, the effect of physical knots and entanglements is isolated from other sources of quenched disorder.

The individual diamond networks are spanned across the simulation volume via periodic boundary conditions. We have chosen an average distance between connected

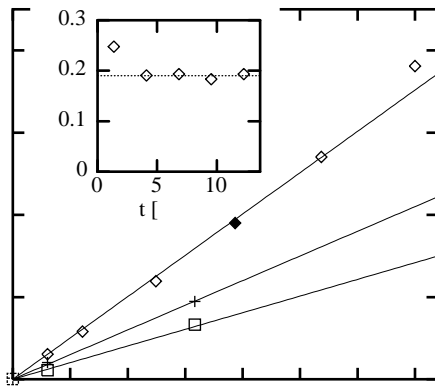


Figure 2. Stress relaxation (inset) and stress-strain curves for diamond networks in the common representation $\sigma(\lambda)$ versus $\lambda^2 - \lambda^{-1}$: $N=44$ (\square), $N=26$ (+), ($N=12$) (\diamond). The shear modulus is given by the slope.

crosslinks equal to the root mean square end-to-end distance of the corresponding chains in a melt. The density of a single diamond net decreases with the strand length. To reach melt density we place several of these structures in the simulation box and work with interpenetrating diamond networks (IPDN). On the length scale of the network strands the structure is similar to experimental systems, which are also locally interpenetrating with nearest neighbor crosslinks that are not connected by a network strand.

We follow two distinct strategies to isolate the entanglement effects. One is to calculate quenched averages for otherwise identical systems with different topology. In our simulations of randomly and of regularly IPDN we employ interaction potentials which ensure the mutual impenetrability of the chains, thereby preserving the topological state from the end of the preparation process. The second strategy is to calculate annealed averages over different topologies. This can either be achieved trivially by simulating non-interacting phantom chains or by using interaction potentials that allow chains to cut through each other but nevertheless preserve the monomer packing of the melt. The structure of the chains is almost identical for all systems and by comparing their behaviour we can directly access the effects of the topological constraints.

As already explained chemical details are not important for the understanding of the *universal* aspects of rubber elasticity, even though they are, of course, crucial when it comes to preparing experimental systems with as few defects as possible. For our simulations we used the same coarse-grained model as in earlier investigations of polymer melts and networks [4, 5, 6]. The network strands were modeled as freely

jointed bead spring chains of uniform length N . They were crosslinked by four-functional monomers into networks with the connectivity of a diamond lattice. There were two types of interactions, an excluded volume interaction, U_{LV} , between all monomers and a bond potential, U_{FENE} , between chemical nearest neighbors. With ϵ , σ and τ as the Lennard-Jones units of energy, length and time we worked at a temperature $k_B T = 1\epsilon$ and at a density $\rho = 0.85 \sigma^{-3}$. The average bond length was $l = 0.97 \sigma$ and topology was conserved. The relevant length and time scales for chains in a melt are the mean-square end-to-end distance $\langle R^2 \rangle (N) \approx 1.7 l^2 N$, the melt entanglement length $N_e \approx 35$ monomers and the Rouse time $\tau_{Rouse} \approx 1.5 N^2 \tau$ [4]. We carried out molecular dynamics simulations, where the system was weakly coupled to a heat bath. The same samples were simulated first in the unstrained state and subsequently elongated by typically 50%. Deformations were implemented as a short sequence of small step changes at the beginning of the runs. We measured the pressure tensor, \hat{P} , and watched the relaxation of the normal tension $\sigma = P_{xx} - \frac{1}{2} (P_{yy} + P_{zz})$ to a plateau value (inset in Figure 2). The stress relaxation was completed after a period of about $2\tau_{Rouse}$ compared to our overall simulation times of the order of $10\tau_{Rouse}$. For our largest systems this is equivalent to $8 \cdot 10^{10}$ particle updates. Data from the initial relaxation period was discarded for the analysis of conformational properties.

By varying the interaction potentials we can investigate systems which differ only in the mutual penetrability of the chains. The simplest example are “phantom” networks, in which the excluded volume interaction is switched off ex-

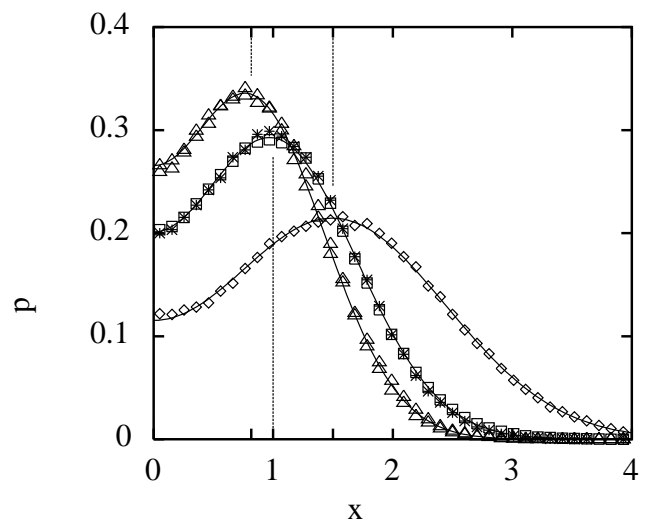


Figure 3. End-to-end distance distribution of the network strands for $N=44$ in the un-strained (\square) and strained state ($\parallel \diamond$ and $\perp \Delta$, $\lambda = 1.5$). For comparison: data for phantom networks (*). Distances are measured in units of the lattice constant x_l of the diamond lattice.

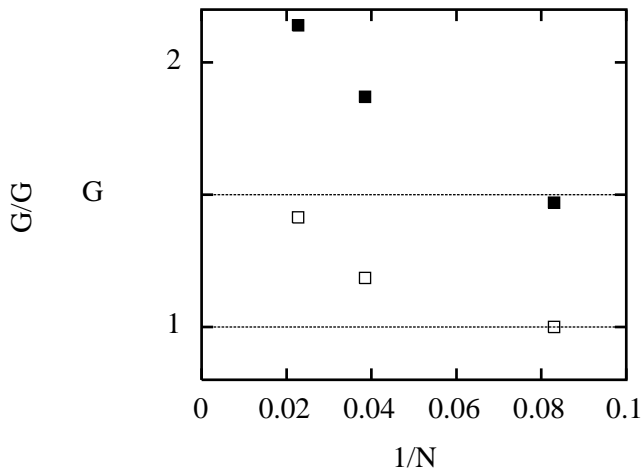


Figure 4. Strand length dependence of the shear modulus normalized to the phantom model prediction G_{ph} . The filled symbols represent the measured values G/G_{ph} and the open symbols indicate the classical prediction G_{class}/G_{ph} . $G_{aff}/G_{ph} = 3/2$ is the upper limit for any classical theory.

cept for nearest and next-nearest neighbors along the chains. Different strands of the network can now freely penetrate each other. What is important to note, is that the structure of the chains (and in particular $\langle R^2 \rangle$) is almost identical to the original case. This is, on the one hand, useful for the preparation of relaxed initial conformations. More importantly and in contrast to experiments, the comparison allows to quantify the effect of topology conservation on the elastic properties of polymer networks.

Simulations of regularly IPDN start from intercalating conformations of strongly swollen networks with completely stretched strands. In MD runs the conformations are slowly compressed to melt density. The important point is that the topology conserving LJ interaction between all monomers is used right from the beginning.

The preparation of the initial conformations for the randomly IPDN is illustrated in the first video sequence. The networks are set up at melt density. Between the crosslinks on the diamond lattice sites we place phantom chains generated in Monte Carlo simulations with the proper end-to-end distance. After the relaxation of the lattice structure in MD runs for phantom chains, we introduce the repulsive excluded volume interaction between the monomers. This is done by slowly building up a cosine potential up to a point where the monomer distances are large enough for the LJ potential. From that point onwards the random topology is quenched and the random entanglements between meshes of the different networks become permanent.

We have investigated systems with strand lengths $N = 12, 26, 44$ corresponding to $n = 5, 7, 9$ independent, but mutually interpenetrating diamond networks. The total number of particles ranged from 8000 and to 51264 monomers. The density of elastically active strands is given by $\rho_{strand} = \rho /$

$(N+1/2)$. Macroscopically our systems behave as ideal rubber with a purely entropic elasticity and exhibit the classical stress-strain relation (Figure 2). The measured shear moduli G for systems with conserved random topology are between 50% ($N=12$) to 100% ($N=44$) larger than in the other cases [7].

The classical theories of rubber elasticity

The most important step to an understanding of rubber elasticity is the examination of the typical conformations of a polymer chain in a melt [1]. Independent of their chemical structure all chain molecules adopt random coil conformations on large length scales. Important with regard to the elastic properties is that for a random coil those conformations are the most probable in which the chain ends are close together. An external force pulling the chain ends apart therefore forces the polymer to adopt a less probable conformation. The internal energies, on the other hand, remain practically unchanged as long as the polymer is not stretched completely. It is the loss of entropy which is responsible for the restoring forces. The force-elongation relation corresponds to that of a linear spring.

The classical theories calculate the elastic properties by treating the network strands as independent entropic springs and estimating their elongation under deformations of the sample. The predicted shear moduli are of the order of $k_B T$ times ρ_{strand} the density of elastically active network strands. Remarkably enough, the result (including the prefactors) is completely independent of the chemical structure of the polymers. It is, however, far from obvious that the chains may be treated as independent. The reason is the mutual impenetrability of the polymers which severely restricts the conformations accessible to individual network strands. In spite of weighty theoretical arguments [9, 10] the importance of entanglements for the elasticity of polymer networks has been disputed for decades, not least because the stress-strain relations of most experimental systems fit the predictions of the classical theories.

Test of the classical theories

The state of a network of (entropic) springs is most conveniently characterized by distribution functions $p(x)$, $p(y)$ and $p(z)$ for the Cartesian components of the spring end-to-end vectors (Figure 3). For the original unstrained state the distribution functions are identical for phantom networks and randomly IPDN and can be calculated analytically. The mean elongation is given by the bond lengths of the diamond lattice r_1 . The actual end-to-end distances fluctuate around corresponding values, so that $p(x)$ etc. are given by a superposition of two Gaussian centered at $\pm x_1$.

Figure 3 illustrates the changes in the spring elongations after a deformation of the sample. While they increase par-

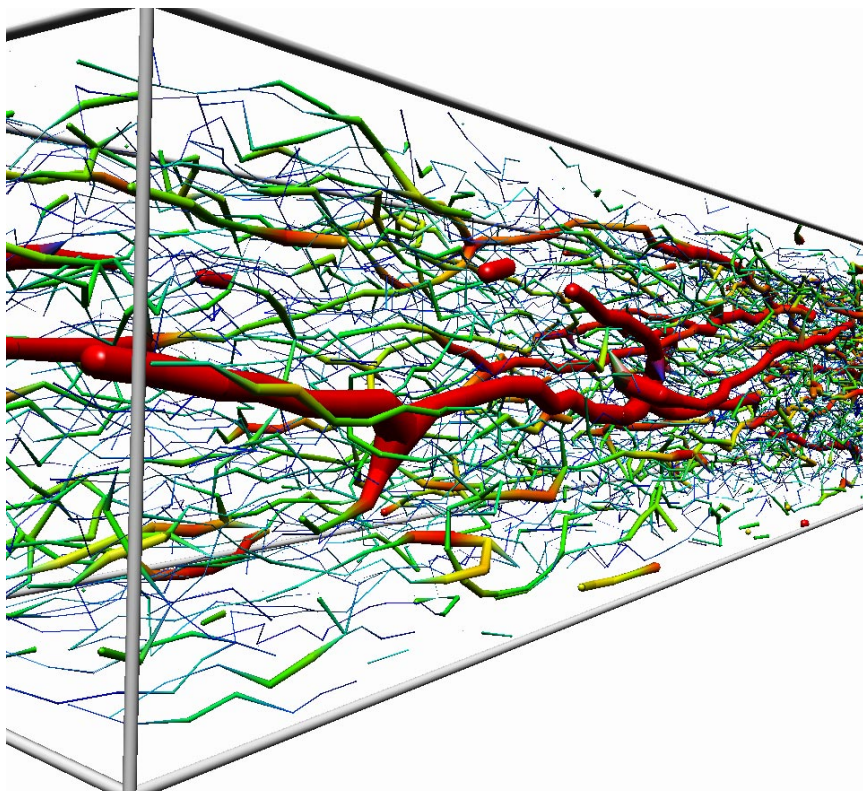


Figure 5. Conformation of strained randomly interpenetrating diamond networks ($\lambda=3.2$). In the non-linear regime there are a few highly stretched paths (marked by thick radii and in red) where a large fraction of the induced tension is localized. The apparent interruption of the chains is due to the representation in periodic boundary conditions.

allel to the elongation, they actually decrease in the perpendicular directions. The maxima change “affinely” with the outer dimensions of the sample: If the simulation box is stretched by a factor of two in x -direction, the same holds for the x -component of the mean elongation of the network strands. At the same time the size of the simulation box as well as the mean elongations in y - and z -direction are reduced by a factor of $\sqrt{2}$, so that the volume remains unchanged.[a] This behavior is fulfilled almost exactly by experimental systems. In our simulations the volume conservation was enforced. Regarding the width of the distributions our results confirm the crossover from phantom to affine behavior with increasing chain length which has been discussed in the framework of the most sophisticated classical theories [8]. Decisive, however, is the quantitative comparison of the classical moduli calculated from the change in the elongation of the network strands with the measured moduli. Figure 4 demonstrates that *the true change in entropy and accordingly the true modulus are by far higher than the values one obtains within the classical picture* [7]. This result shows that a theory that aims to calculate the effects of topology conservation from limitations in the cross-link fluctuations is bound to overlook relevant contributions to the total entropy change even if no further approximations are being made. The discrepancy grows with increasing chain length.

Entangled meshes

Explaining the discrepancy by including the topological constraints in a first principles statistical mechanical treatment has proven extremely complicated [9, 10, 11, 12]. Progress is often due to the study of comparatively simple models of the effects of the topological constraints. It is therefore of great importance to clarify, if a model captures the relevant physics. Simulations can play an important role in answering this question. As an example we refer the reader to the classical theories discussed above. As we have shown, it makes little sense to pursue this approach with ever more sophisticated refinements.

The reason for the increase of the modulus due to topology conservation can be illustrated by an analysis of the stress distribution in strongly stretched networks (see Figure 5 and the second video sequence). Our simulations show that in randomly IPDN with topology conservation a large part of the tension is localized on *topologically* shortest paths through the system. These paths are composed of strands as well as meshes with physical entanglements propagating the tension in the same manner as chemical cross-links. The way the chains fail to release a link is an artefact of our model. At too large stresses the connected beads at the contact point are driven so far apart that the chains can slip through each other. Thus, in contrast to a real system, the chains do not break in the process. Since the energy threshold is of the order of $70 k_B T$ such events do not occur at small elongations.

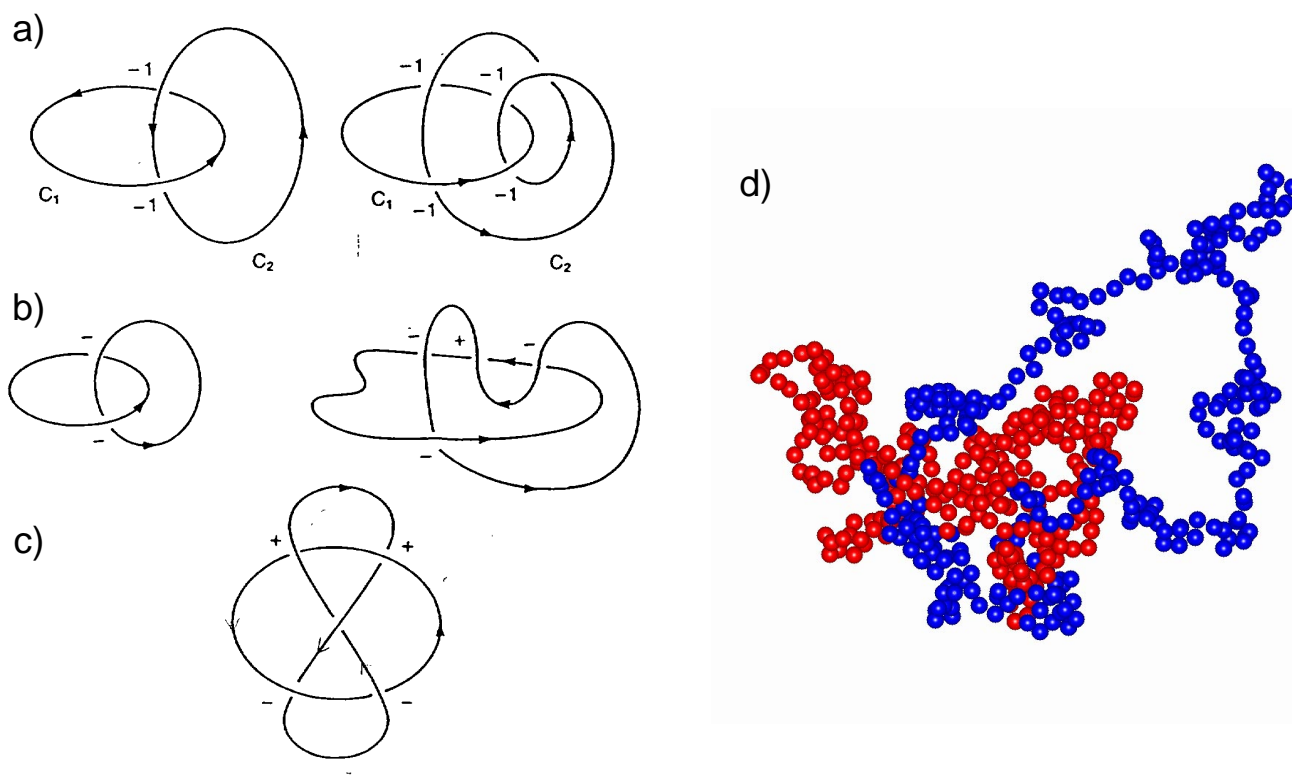


Figure 6. a) Illustration of the index method for characterizing links. b) Invariance of the linking number under deformations. c) Trapped figure eight: a linked pair of curves with $I=0$. d) Example from the simulation for two linked meshes.

The stress localization in diamond networks is completely unexpected from the point of view of the classical theory, since all network strands are equivalent. The highly artificial regularly IPDN mimic a situation where this equivalence is preserved for a conserved topology. When these networks are stretched, all strands contribute equally to the elastic response. The high tensions we observed along a few paths and at much lower elongations in the first case, occur now homogeneously throughout the whole system when all strands are stretched to their full contour length.

A similar analysis can be performed for swollen networks (see the third video sequence).

For a single diamond network swelling reveals the regular connectivity, i.e. it leads to a state similarly to what is shown in figure 1 but with stretched network strands. For regularly IPDN the individual diamond "lattices" can move against each other. In the case of randomly IPDN, however, the entanglements lead to an alignment of the network strands and the formation of pores.

Modeling the effects of topology conservation requires two steps [9, 10]: the characterization of the entanglements and an estimate of their contribution to the restoring forces resisting a deformation of the sample. The first part is a math-

ematical problem and the subject of knot theory, which deals with classifying single ("knots") and several ("links") closed curves embedded in three dimensional space. Usually the classification starts from a projection of the curves onto a plane. The most important tool are topological invariants, i.e. numbers or polynomials which retain their values for different projections as well as under continuous deformations of the curves which do not require opening and closing the rings in between. A topological invariant is the more suitable for the purpose of classification, the less frequent identical values are assigned to different knots or links, as they are tubulated in extensive lists.

A simple example for the approximate characterization of links is the Gauss linking number. It can be calculated by a method where all crossing points of the two curves in a projection are indexed by $\pm 1/2$ (Figure 6). The sign depends on the direction into which the tangent vector of the upper curve has to be rotated in order to coincide with the one of the bridged curve. The linking number I is defined as the sum of the indices and is a topological invariant. There are, however, a few examples (Figure 6c) for linked curves with linking number zero, so that the classification is not completely reliable.

For estimating the interaction between meshes of a network the mathematical link tables are only of limited use. On the one hand the classification is too detailed (it makes little sense to distinguish between more complex entanglements of two rings and to neglect interactions between three or more rings). On the other hand the link tables provide no

information on the likelihood of the occurrence of particular links for random walk-like ring polymers.

The simplest way to motivate an effective topological interaction between ring polymers is based on a center of mass distance-dependent linking probability [13]. The argument is analogous to the treatment of a polymer chain as entropic spring. Since there are less conformations of two linked rings with a large center of mass distance, the rings behave as if connected by an entropic spring. By the same rationale there is a repulsive entropic interaction between non-linked rings. In the framework of a network theory Graessley and Pearson [14] treated entanglements between meshes as additional entropic springs and predicted a contribution proportional to the entanglement density ρ_{ent} to the modulus. The prefactor depends on the interaction law and can be estimated from linking probabilities, which, in general, are accessible only through computer simulations.

It is very difficult, if not impossible, to decide in experiments, whether or not such an approach makes sense. In the framework of our simulations we determined the degree of linking for all mesh pairs in the system and estimated a topology contribution to the modulus on the basis of the model of Graessley and Pearson without invoking any adjustable parameters. The comparison with the measured values was surprisingly positive. We observed the predicted proportionality $G - G_{ph} = 0.85 k_B T \rho_{ent}$, with a prefactor of the same order of magnitude as the estimate of $1.3 k_B T$ [15]. In view of the substantial simplifications the agreement is quite remarkable.

Summary

We presented the first simulations of model polymer networks in which shear moduli could be measured reliably by investigating strained samples. This enabled us to prove quantitatively that the classical treatment of the network strands as independent entropic springs omits important contributions to the total entropy change in deformed networks. The reason is the quenching of the topology (e.g. the state of linking of mesh pairs) during the formation network. We have estimated a topology contribution to the modulus in the framework of a simple theory based on entropic interactions between loops. The agreement with the measured values constitutes a small, but nevertheless *quantitatively* controlled step towards a topological theory of rubber elasticity. A great

challenge for future work is the derivation of the empirically very successful tube model from considerations based on the topological character of the constraints. It is difficult to imagine that the necessary information for a test of such a theory could be obtained in experiments. In our view, this makes simulations an indispensable intermediate step in the understanding of the viscoelasticity of polymeric materials.

References and Footnotes

- [a]. This behavior is fulfilled almost exactly by experimental systems. In our simulations the volume conservation was enforced
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