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Functionality dependence for molecular nonaffine deformation of polymer networks

Gerhard Glatting*
Abteilung Nuklearmedizin, Universität Ulm, Robert-Koch-Straße 8, 89081 Ulm, Germany

and Roland G. Winkler and Peter Reineker
Abteilung Theoretische Physik, Universität Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany
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The dependence of the stress–strain behaviour of polymer networks on functionality is investigated. The network is described in terms of a gas of simple units of arbitrary functionality f. The macroscopic deformation is taken into account by constraints, which allow molecular nonaffine deformations. For Gaussian network strands the model leads to the same stress–strain dependence as in the well known model, but shows a modified dependence of the modulus on functionality. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Polymeric networks are widely used in technological applications. Although the main reason for their large reversible elasticity is understood to originate from their molecular structure (long linear polymer chains crosslinked to form a network[1]), no simple, i.e. straightforward, theory exists, which describes the properties of these elastomers adequately. There exist a large variety of phenomenological[2–4] and theoretical models, for example the tube model[5–7], slip-link model[8,9], junction-fluctuation model[10] and special single-chain models[11–15], which explicitly assume a specific mechanism for the interaction of the network strands in order to fit experimental data of (stress–strain) experiments correctly. The assumed mechanisms, their mathematical implementation or the neglect of other mechanisms need further discussion, because these models fail to describe all modes of stress–strain experiments with the same set of parameters[7]. Therefore, we present as an alternative approach an analytical description for the molecular nonaffine deformation of polymer networks. Recently[16,17] we introduced the model without accounting for network functionality. The purpose of that publication was to work out the main ideas of the model for a simple case[16] and for polydisperse polymer networks[17]. As functionality is of *major* importance for the formation of a network, we now extend the model to an arbitrary functionality f.

In the next section we introduce the model, i.e. the expression for the total entropy of a network. Thereafter, the dependence of the entropy on the geometry of the introduced simple unit is calculated. The quasi-affine deformation of the network and a special macroscopic constraint are considered.

* To whom correspondence should be addressed

THEORETICAL MODEL

In order to include the network functionality into the model described in refs 16 and 17 we replace the simplest unit of the description—one network strand—by f strands, which are connected chemically in one crosslink (*Figure 1*). Therefore, the simplest unit (index su), i.e. one crosslink with its network strands, already includes features which depend on functionality. The total entropy of the network $S_{\rm net}(\Lambda)$ is given—analogous to equation (1) in refs 16 and 17—by the sum of the entropies of the simple units [first term of equation (1) following], the contribution to the entropy due to mixing of simple units (second term), the constraint of fixed number of simple units $\tilde{M}$ (Lagrange parameter $\mu - 1$), and the macroscopic constraints ruling the deformation (Lagrange parameters γ_j)

$$\begin{aligned} S_{\rm net}(\Lambda) = k_{\rm B} \int M(\{\vec{r}_i\}) S_{\rm su}(\{\vec{r}_i\}) \prod_{i=1}^{f-1} d^3 r_i + k_{\rm B} \\ \times \left\{ \tilde{M} \ln \tilde{M} - \int M(\{\vec{r}_i\}) \ln M(\{\vec{r}_i\}) \prod_{i=1}^{f-1} d^3 r_i \right\} \\ + k_{\rm B}(\mu - 1) \left\{ \tilde{M} - \int M(\{\vec{r}_i\}) \prod_{i=1}^{f-1} d^3 r_i \right\} \\ + k_{\rm B} \sum_{j=1}^{n} \gamma_j \\ \times \left\{ \int M(\{\vec{r}_i\}) g_j(\{\vec{r}_i\}) \prod_{i=1}^{f-1} d^3 r_i - G_j(\Lambda) \right\} \end{aligned} \quad (1)$$

Λ is the deformation matrix, i.e. $\Lambda_{mn} = \lambda_n \delta_{mn}$, $m, n = x, y, z$ (δ_{mn} = Kronecker delta), where the λ_n are the deformation ratios relative to the undeformed state.

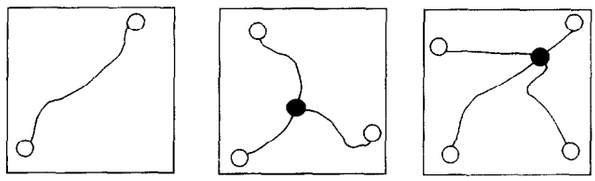

Figure 1 Simple units for various functionalities: filled circles are internal crosslink points

k_B is the Boltzmann constant and $k_B S_{su}(\{\vec{r}_i\})$ the entropy of the simple unit. $\{\vec{r}_i\} = \{\vec{r}_1, \ldots, \vec{r}_{f-1}\}$ stands for the $3(f-1)$ degrees of freedom of one simple unit ($\vec{r}_i$ are the coordinates of the free ends of the strands); the three translational degrees of freedom of the simple unit are integrated according to

$$\int \ldots \delta\left(\sum_{i=1}^{f} \vec{r}_i\right) \prod_{i=1}^{f} \mathrm{d}^3 r_i = \int \ldots \prod_{i=1}^{f-1} \mathrm{d}^3 r_i \qquad (2)$$

Thus, $\vec{r}_f$ is replaced by

$$\vec{r}_f = -\sum_{i=1}^{f-1} \vec{r}_i \qquad (3)$$

The internal degrees of freedom of the central crosslink are already included in $S_{su}(\{\vec{r}_i\})$ (see equation (9)). $M(\{\vec{r}_i\})$ gives the distribution of the simple units depending on the coordinates $\vec{r}_i$ of its strand ends (empty circles in *Figure 1*). The total number of simple units $\tilde{M}$ depends on the number of network strands M according to

$$\tilde{M} = \frac{2M}{f} \qquad (4)$$

and is accounted for in equation (1) by the Lagrangian multiplier $\mu - 1$. The factor two is a consequence of the fact that every network strand belongs to two crosslinks, and network vacancies are not considered in this model, although the inclusion of vacancies is straightforward.

$G_j(\Lambda)$ is a macroscopic parameter, which is defined by experiment[16]. Because macroscopic deformation causes changes in lengths, the macroscopic parameter must be a function of all molecular lengths in the considered sample. In our approximation of a noninteracting gas of indistinguishable simple units the macroscopic sample is simply the sum over the contributions of any simple unit $g_j(\{\vec{r}_i\})$, i.e.

$$\int M(\{\vec{r}_i\}) g_j(\{\vec{r}_i\}) \prod_{i=1}^{f-1} \mathrm{d}^3 r_i \qquad (5)$$

This expression must be equal to the deformed macroscopic parameter relative to the undeformed state, i.e. to

$$G_j(\Lambda) = \int M_0(\{\vec{r}_i\}) g_j(\{\Lambda \vec{r}_i\}) \prod_{i=1}^{f-1} \mathrm{d}^3 r_i \qquad (6)$$

where $M_0(\{\vec{r}_i\})$ is the distribution of simple units without macroscopic constraints (see equation (1)). In our 'gas' model $M_0(\{\vec{r}_i\})$ is calculated from equation (1) with $\gamma_j = 0$. Clearly $G_j(\Lambda)$ corresponds to the case that the contribution $g_j(\{\vec{r}_i\})$ of any simple unit is increased proportionally to the macroscopic deformation.

Note that equation (1) cannot describe affine deformation, because the introduction of $\tilde{M}$ constraints (one for every simple unit) would mean that the units are distinguishable, i.e. the assumed contribution of the entropy of mixing would be inconsistent.

Distribution $\mathrm{M}(\{\vec{r}_i\})$ *without external constraints*

Variation of equation (1) (cf. ref. 17) with respect to the distribution $M(\{\vec{r}_i\})$ with $\gamma_i = 0$ leads to

$$M_0(\{\vec{r}_i\}) = \tilde{M} \frac{\mathrm{e}^{S_{su}(\{\vec{r}_i\})}}{\int \mathrm{e}^{S_{su}(\{\vec{r}_i\})} \prod_{i=1}^{f-1} \mathrm{d}^3 r_i} \qquad (7)$$

where the Lagrangian parameter μ is already eliminated.

Entropy of one simple unit of functionality f

The entropy of the simple unit can be calculated from the partition function. Assuming Gaussian partition functions for single strands with modulus a we obtain the partition function for the simple unit

$$Z(\{\vec{r}_i\}) = \text{const} \int \mathrm{d}^3 r \exp\left\{-a \sum_{i=1}^{f} (\vec{r}_i - \vec{r})^2\right\} \qquad (8)$$

$\vec{r}$ is the coordinate of the central crosslink, which is the integration variable. Since we assumed Gaussian chains we immediately obtain with equation (3)

$$S_{su}(\{\vec{r}_i\}) = \ln Z(\{\vec{r}_i\}) = S_0 - a\left[\sum_{i=1}^{f-1} \vec{r}_i^{\,2} + \left(\sum_{i=1}^{f-1} \vec{r}_i\right)^2\right] \qquad (9)$$

Thus, the dependence on functionality enters into equation (1) through the entropy of the simple unit (S_0 is a constant).

RESULTS

Quasi-affine deformation

As quasi-affine limit we define (see refs 16, 17) the case when *all* functions $g_j(\{\vec{r}_i\})$, e.g. the set of all polynomials, are taken as constraints. A transformation of variables in the constraints [last line of equation (1)] immediately yields

$$M(\{\vec{r}_i\}) = M_0(\Lambda^{-1}\{\vec{r}_i\}) \left(\sqrt{I_3}\right)^{(1-f)} \qquad (10)$$

Inserting equation (10) into equation (1) followed by straightforward calculation results in

$$S_{\text{net}}^{\text{quasi-affine}}(\Lambda) = k_B \left\{ \int S_{su}(\Lambda\{\vec{r}_i\}) M_0(\{\vec{r}_i\}) \prod_{i=1}^{f=1} \mathrm{d}^3 r_i + M\left(1 - \frac{1}{f}\right) \ln I_3 \right\} \qquad (11)$$

$$= S_{\text{net},0} - M k_B \left(1 - \frac{1}{f}\right) \{I_1 - \ln I_3\} \qquad (12)$$

where equations (7) and (9) and the deformation invariants

$$I_1 = \lambda_x^2 + \lambda_y^2 + \lambda_z^2, \quad I_2 = \lambda_x^2\lambda_y^2 + \lambda_x^2\lambda_z^2 + \lambda_y^2\lambda_z^2, \quad I_3 = \lambda_x^2\lambda_y^2\lambda_z^2 \qquad (13)$$

were used. $S_{\text{net},0}$ includes constant terms. Now we

calculate the stress from the free energy $F(\Lambda)$ according to

$$\sigma_m = \frac{dF(\Lambda)}{d\lambda_m} = -T\frac{dS_{net}(\Lambda)}{d\lambda_m}$$
$$= Mk_BT\left(1-\frac{1}{f}\right)\frac{d}{d\lambda_m}\{I_1 - \ln I_3\} \qquad (14)$$

This expression is proportional to the result of the model without consideration of functionality[16]. Both models are obviously equivalent for the case $f = 2$, where the simple unit is just a single strand (*Figure 1*). Graessley[18] obtained qualitatively the same result but a different prefactor $((1 - 2/f)$ instead of $(1 - 1/f))$ for an infinite network with affinely deformed outer crosslinks and freely fluctuating internal ones.

Special macroscopic constraint

We now investigate the case that there are just three macroscopic constraints; we choose (for simplicity and symmetry arguments)

$$g_l(\{\vec{r}_i\}) = \frac{1}{2}\left\{\sum_{i,j=1}^{f}(x_{l,i} - x_{l,j})^2\right\}, \quad x_l = x, y, z \qquad (15)$$

The index l indicates that we take into account only the l-th component of the vectors $\vec{r}_i$. In $g_l(\{\vec{r}_i\})$ we sum over all end-to-end distances of the simple unit ($\vec{r}_i$ are the coordinates of the external points). The case of a single strand as simple unit[16] is obtained for $f = 2$. Use of the constraint that the centre of gravity is fixed at the origin (equation (3)) leads to

$$g_l(\{\vec{r}_i\}) = f\left\{\sum_{i=1}^{f-1}x_{l,i}^2 + \left(\sum_{i=1}^{f-1}x_{l,i}\right)^2\right\}, \quad x_l = x, y, z \qquad (16)$$

With these functions we calculate the maximum of the entropy by variation of the entropy $S_{net}(\Lambda)$ with respect to the distribution $M(\{\vec{r}_i\})$, which gives the following expression for the Lagrange parameter

$$\gamma_j = \frac{a}{f}\left(1 - \frac{1}{\lambda_j^2}\right) \qquad (17)$$

According to equation (14) we then get for the stresses

$$\sigma_m = Mk_BT\left(1-\frac{1}{f}\right)\frac{d}{d\lambda_m}\{I_1 - \ln I_3\} \qquad (18)$$

which is identical with the quasi-affine case (equation (14)). This is a consequence of the use of Gaussian strands.

The modulus at $\lambda = 1$ is different from the proportionality $(1 - 2/f)$ derived theoretically in refs 18 and 19 but in slightly better agreement with the experiments of Mark[20] (*Figure 2*). Especially the ratio of the moduli for $f = \infty$ and $f = 3$ is 1.5 compared to 3 in the theories of refs 18 and 19. The experimental ratio for $f = 37$ is $\simeq 1.4$[20], showing very good agreement with the model. Nevertheless, both models deviate systematically from the data.

DISCUSSION

In this paper we have shown how to include the functionality of crosslinks into a recently introduced model for the behaviour of polymer networks. We showed that the predicted functionality dependence of the modulus agrees with the experiments of Mark[20] slightly better than that from other theories[18,19].

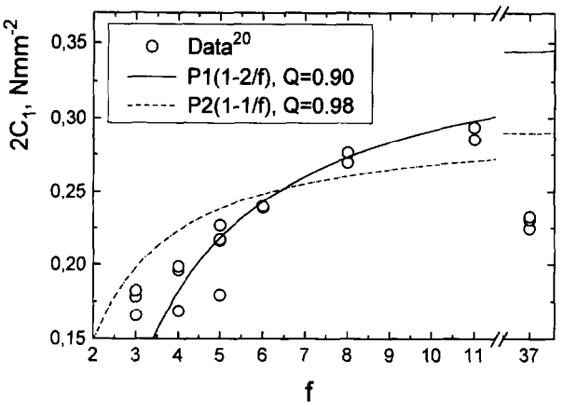

Figure 2 Dependence of the modulus on functionality f. Data for the elasticity constant $2C_1$ from Mark[20] are fitted with the models. Q is the goodness of fit. The fit parameters are $P1 = 0.365$ and $P2 = 0.298$

The main advantage of the model is its straightforward applicability to calculations of the network entropy without requiring a special mechanism for the molecular nonaffine deformation. This simplifies mathematical calculation and therefore allows a straightforward treatment of various features of networks, for example polydispersity[17] and network vacancies.

Naturally, the result for $S_{net}(\Lambda)$ depends on the particular choice for $g_j(\{\vec{r}_i\})$. Unfortunately, the expression for $g_j(\{\vec{r}_i\})$ corresponding to the experimental situation cannot be given simply. However, it must possess the unit of *length*, because macroscopically the *length* of the sample is changed[16]. In the present paper we considered two special cases to show how functionality can be incorporated into the model. In a final analysis the results correspond to other results obtained in literature[18,19,21], except for the functionality dependence. Nevertheless, the crucial point is the use of just macroscopic constraints (which allow nonaffine deformation on a molecular scale) resulting in good agreement with experimental measurements.

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