Possible Role of Force Balance on Entanglements

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SUMMARY: The usual assumption of affine deformation of the strands of a polymeric network appears not to fulfil force balance over the nodes of the network in case such nodes are entanglements. In an effort to improve over the classical theory of Doi and Edwards for entangled polymers, a simple model is here proposed which is so constructed as to obey force balance. Explicit predictions for step strains are here obtained which compare very favourably with data, not only of damping function, but also of normal stress ratio.

Introduction

The role of force balance on the nodes of polymeric networks is not often considered. The usual approach to network theories is *via* kinematic assumptions. It is typically assumed that the end-to-end vectors of the network strands deform 'affinely', *i.e.*, that they behave as if they were imbedded in the continuum.

For the case of permanent networks, in which all nodes are chemical crosslinks, affinity is in fact compatible with the force balance on the nodes of the network. With the usual assumption of a linear elastic force in the strands (Gaussian chains), if the force balance on a node is satisfied at equilibrium, it remains satisfied after the deformation has been applied. Mathematically, if $\mathbf{R}_i$ is the end-to-end vector of the i-th strand at equilibrium, and $\mathbf{F}_i = H_i \mathbf{R}_i$ the corresponding entropic force, the balance on a node is written as

$$\sum_i H_i \mathbf{R}_i = \mathbf{0} \tag{1}$$

where the sum is over all strands emerging from the node. Now, if the deformation is described by the tensor $\mathbf{E}$, affinity changes $\mathbf{R}_i$ into $\mathbf{E}\cdot\mathbf{R}_i$, and the sum of all forces acting on the node becomes $\mathbf{E}\cdot\sum H_i \mathbf{R}_i$. Hence, since the H_i's have not changed, the force balance is automatically satisfied.

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In the case of entanglements, the situation differs significantly, however. Indeed, monomers can slide over entanglements from one strand to the next along the chain, and they are in fact expected to do so as a consequence of deformation. There follows that the elasticity coefficients H_i will no longer be the same after deformation. In other words, although the chains remain Gaussian, the system becomes nonlinear. Under these conditions, affinity does not guarantee fulfilment of the force balance on the node. On the contrary, the affinity assumption leads to *force unbalance* in the general case.

Such an unbalance can be readily verified for the case of the tube model of Doi and Edwards[1]. A central aspect of that theory is the concept that the entangled polymer, *i.e.*, the chain in the tube, experiences (aside from fluctuations, and excluding fast flows) a constant tension given by $3kT/a$, where kT is thermal energy, and a is the mesh size of the entangled network or, equivalently, the tube diameter. Hence, the force balance on a node of the entangled network may be written as

$$\sum_i \mathbf{F}_i = \frac{3kT}{a} \sum_i \mathbf{u}_i = \mathbf{0} \tag{2}$$

where the $\mathbf{u}_i$'s are unit vectors along the strands, and we may assume that Eq. (2) is verified at equilibrium. In view of the affinity assumption, the forces acting on the node after a deformation $\mathbf{E}$ sum up to

$$\frac{3kT}{a} \mathbf{E} \cdot \sum_i \frac{\mathbf{u}_i}{|\mathbf{E} \cdot \mathbf{u}_i|} \neq \mathbf{0} \tag{3}$$

Generally, the sum in Eq. (3) is nonzero in spite of the fact that $\sum \mathbf{u}_i = \mathbf{0}$.

It appears sensible to assume that the force balance should be satisfied in the entangled network as well as in the chemically crosslinked one. The conclusion seems to follow that the usual affinity assumption for the strands of the entangled network, if convenient for calculation purposes, is physically inadequate. Lacking a theoretical description of an entangled network which obeys force balance on the nodes, we propose in the following a very simple 3-chain model which in a way satisfies the balance automatically. Consequences

of the 'constitutive equation' obtained from this elementary model for the case of step strain are then briefly examined.

The 3-chain model

Let us imagine that our network is made up of chains which have all their strands oriented along three mutually orthogonal directions, as if the nodes of the network were confined to a cubic lattice. Moreover, for entanglements involving two chains only, the four strands emerging from the node are assumed to lay on the same plane (see Fig. 1). It is apparent that, since the tension in the chains is a constant, the assumed geometry automatically satisfies the force balance on the nodes. Furthermore, if the lattice is oriented along the principal directions of the deformation, *the force balance remains fulfilled also after deformation.*

For such a simple structure of the network, all calculations can be made on the basis of one representative chain strand for each direction, *i.e.*, the whole network is described by 3 chain strands only. In particular, the stress tensor is given by the following sum of three dyadic products, one for each direction of the lattice

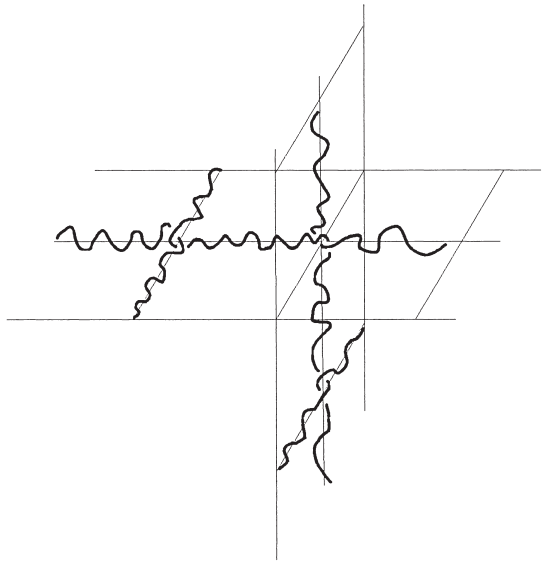

Fig. 1: The network of entangled chains with nodes on a cubic lattice. At each entanglement in this figure all four chain strands lie on the same plane.

$$\mathbf{T} = \frac{\nu}{3}\left(\mathbf{F}_1\mathbf{R}_1 + \mathbf{F}_2\mathbf{R}_2 + \mathbf{F}_3\mathbf{R}_3\right) = \frac{\nu kT}{a}\left(\mathbf{u}_1\mathbf{R}_1 + \mathbf{u}_2\mathbf{R}_2 + \mathbf{u}_3\mathbf{R}_3\right) \tag{4}$$

where ν is the number of network strands per unit volume. Under equilibrium conditions, $\mathbf{R}_i = a\,\mathbf{u}_i$. Hence, we obtain the isotropic stress $\mathbf{T} = \nu kT\,(\mathbf{u}_1\mathbf{u}_1 + \mathbf{u}_2\mathbf{u}_2 + \mathbf{u}_3\mathbf{u}_3) = \nu kT\,\mathbf{1}$. After applying a deformation with principal stretch ratios λ_i's, the strand end-to-end vectors become $\mathbf{R}_i = a\,\lambda_i\,\mathbf{u}_i$, giving for the stress

$$\mathbf{T} = \nu kT\left(\lambda_1\mathbf{u}_1\mathbf{u}_1 + \lambda_2\mathbf{u}_2\mathbf{u}_2 + \lambda_3\mathbf{u}_3\mathbf{u}_3\right) = \nu kT\,\mathbf{C}^{-1/2} \tag{5}$$

where $\mathbf{C}^{-1/2}$ is the square root of the Finger tensor $\mathbf{C}^{-1}$, the eigenvalues of $\mathbf{C}^{-1}$ being λ_i^2.

The equation we just derived, with ν a constant, only applies to small deformations, such that $\lambda_1+\lambda_2+\lambda_3 \cong 3$. For larger deformations, we must account for the fact that the assumption of a constant tension $3kT/a$ also implies that the overall length of the primitive chains remains constant. More specifically, a large deformation initially increases the length of the primitive chain, which then (in a time of the order of the Rouse time of the chain) retracts back to the original length[1]. During retraction, the number of strands per unit volume decreases in inverse proportion to the average increase of strand length, so that the primitive chain recovers the equilibrium length. Since the strand length scales with $\lambda_1+\lambda_2+\lambda_3 = \mathrm{tr}(\mathbf{C}^{-1/2})$, the extension of Eq. (5) to large deformations becomes (ν maintaining the meaning of strand density at equilibrium)

$$\mathbf{T} = 3\,\nu\,kT\,\frac{\mathbf{C}^{-1/2}}{\mathrm{tr}(\mathbf{C}^{-1/2})} \tag{6}$$

Equation (6) gives the stress generated by an arbitrary step deformation of the entangled network according to the simple 3-chain model. As we shall see in the next section, the predictions of this 'constitutive equation' are similar to those obtained from the theory of Doi and Edwards, and in fact somewhat better. The tensor $\mathbf{C}^{-1/2}$ here appearing is a special case of the Seth tensor $\mathbf{C}^{-a}$ sometimes proposed in phenomenological equations for rubber or for viscoelastic liquids[2]. Larson[3] relates the $\mathbf{C}^{-1/2}$ tensor to the disclination lines in liquid crystals, which also carry a constant tension. To the authors' knowledge, however, $\mathbf{C}^{-1/2}$ had

never been related to the network of entangled chains, nor to fulfilment of the force balance on the nodes of the network.

Step Strain

We shall consider the case of a shear deformation γ. With the usual choice of coordinates (1 is shear direction, 2 is gradient, and 3 is neutral) the Finger tensor has the well known components

$$\mathbf{C}^{-1} = \begin{vmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \tag{7}$$

from which we obtain

$$\mathbf{C}^{-1/2} = \begin{vmatrix} (2+\gamma^2)(4+\gamma^2)^{-1/2} & \gamma(4+\gamma^2)^{-1/2} & 0 \\ \gamma(4+\gamma^2)^{-1/2} & 2(4+\gamma^2)^{-1/2} & 0 \\ 0 & 0 & 1 \end{vmatrix} \tag{8}$$

with the trace

$$\mathrm{tr}\left(\mathbf{C}^{-1/2}\right) = 1+\left(4+\gamma^2\right)^{1/2} \tag{9}$$

For the purpose of comparison with data, the relevant quantities are the so-called 'damping function' $h(\gamma)$, and the normal stress ratio $\Psi(\gamma) = -N_2/N_1$, which are readily obtained from Eq. (6) and Eqs. (8, 9) as

$$h(\gamma) = \frac{6}{4+\gamma^2+\left(4+\gamma^2\right)^{1/2}} \tag{10}$$

$$\Psi(\gamma) = \frac{\left(4+\gamma^2\right)^{1/2} - 2}{\gamma^2} \tag{11}$$

Notice that, in the limit of vanishing deformations, one obtains

$$\lim_{\gamma \to 0} \Psi(\gamma) = \frac{1}{4} \tag{12}$$

a result already reported by Larson[2,3].

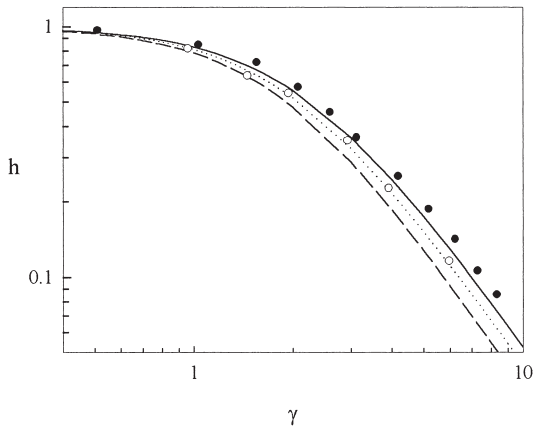

Fig. 2: Different predictions for the damping function are compared with recent data for narrow MWD polymers (open and filled symbols are from refs. 4 and 5, respectively). Solid line is Eq. (10), dotted and dashed lines are Doi-Edwards theory, with and without IAA.

Figures 2 and 3 show the curves corresponding to Eq. (10) and Eq. (11), respectively. In both these figures, data are for essentially monodisperse polymers. In Fig. (2), damping function data[4,5] are, as usual, in good agreement with the theory of Doi and Edwards (both with and without IAA). However, also Eq. (10) behaves very well, and perhaps fits the data even better.

The data in Fig. 3 were obtained recently with accurate optical techniques[6,7]. The agreement with the prediction of Eq. (11) is remarkably good. Notice that for the case of the normal stress ratio Ψ, the prediction of Doi-Edwards theory is considerably worse (lower curve); a

feature that motivated previous attempts at finding a remedy[8]. Predictions by using IAA (uppermost curve in Fig. 3) are better, but not very significant, as IAA is an approximation made for mathematical convenience, and never to improve description of the actual physics. Moreover, it is well known that the IAA limiting Ψ value at small deformations or deformation rates (Ψ=2/7) is incompatible with the Weissenberg effect. Indeed, a positive Weissenberg effect requires $\Psi < 1/4$.

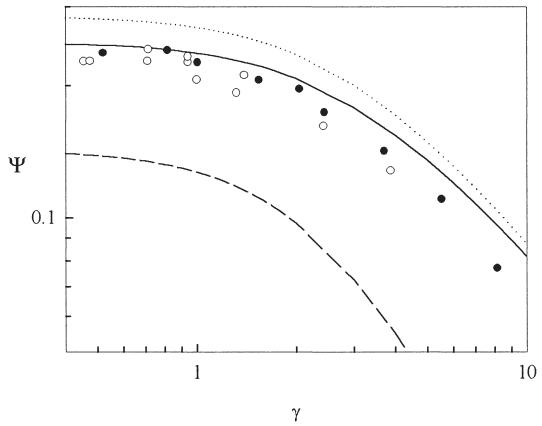

Fig. 3: The analogous comparison for the normal stress ratio Ψ. Filled and open symbols are for a solution[6] and a melt[7], respectively. Solid curve is Eq. (11), dotted and dashed lines are Doi-Edwards theory, with and without IAA.

Conclusions

We have argued that for the case of entangled polymers the assumption of affine deformation of the end-to-end vector of the network strands is in conflict with the requirement of force balance on the nodes of the network. However, for the case of a step deformation, affinity and force balance can be reconciled if the network is represented by a simple 3-chain model. Indeed, such a model is compatible with arbitrary nonlinear behaviour of the strand elasticity.

Using the model in conjunction with Doi-Edwards assumption of a constant chain tension gives a simple result, Eq. (6), which compares with data remarkably well. Notice that the difference between tensor $\mathbf{Q}$ of Doi-Edwards theory and $\mathbf{C}^{-1/2}/\mathrm{tr}(\mathbf{C}^{-1/2})$ of Eq. (6) merely consists in the following. In calculating tensor $\mathbf{Q}$, network strands oriented along *all*

directions in space are considered, and assumed to deform affinely. However, as noted before, this seems incompatible with force balance. Equation (6) on the other hand uses *the same assumptions* of Doi-Edwards theory, but limited to chains oriented *only* along the 3 principal directions of deformation; a trick to somehow fulfil the force balance.

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