melting, crystallization does not reproduce the original single-crystal structure. The crystals obtained from disordered phases are characterized by less planar backbones and more extended side chains compared to the PDA structures found in their as-polymerized single crystals. The unit cell is expanded in the a direction, and the resulting morphology consists of spherulites or lamellar aggregates (the latter preserving the backbone orientation of the original single crystals).

Registry No. Poly(ETCD) [R = $(CH_2)_4O(CO)NHC_2H_5$] (homopolymer), 63809-82-5; poly(ETCD) [R = $(CH_2)_4O(CO)NHC_2H_5$] (SRU), 83441-81-0.

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Some Ideas Concerning the Elasticity of Biopolymer Networks

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ABSTRACT: We consider a network composed of flexible chains which may increase their length by pulling more chain from a compact source. This models the partial unwinding under strain of the helical junction zones which exist in many biopolymer systems. (We draw on the ideas of Nishinari et al. but reach completely different conclusions.) Following the assumptions of the standard affine deformation theory of Gaussian networks, we show that this network will be intrinsically unstable at extension ratios of $\lambda \geq 2.3$, where complete unwinding of the junction zones will occur. We find that low functionality junctions in this network are relatively unstable and that there will be a tendency for certain chains to collapse completely, leading to the formation of a reduced number of junction zones of high effective functionality. We investigate the effects of extended inflexible junction zones on the network elasticity. It is found that the junction zones must be large in comparison to the length of the connecting flexible chains before any substantial difference in the modulus occurs from that of a purely Gaussian network with simple cross-links.

1. Introduction

The properties of natural rubbers and networks of flexible synthetic polymers can be explained to a large degree by the familiar phantom network theory, which considers Gaussian chains interacting only at their end points. There are, however, many types of polymer networks for which the ideas of completely flexible chains and permanent covalent cross-links are clearly inappropriate. In this paper we attempt to explain some of the properties of physical networks formed from polypeptide and polysaccharide biopolymers. Although these two classes of polymers are entirely different in their molecular structure, the mechanisms of aggregation by hydrogen bond formation which occur in these molecules result in network structures which have a marked similarity.

The formation of extended helical junction zones is common in these systems. For example, gelatin is a gel formed when denatured collagen (a structural protein found widely in animal tissue) partially re-forms its triple helical structure. The polysaccharides agarose and carrageenan (both derived from seaweed) are thought to form double helices, whilst the alginates are thought to form extended junction zones through the influence of cations such as Ca^{2+} (the so-called egg-box model). These structures are discussed in the review by Clark and Ross-Murphy.[2]

For our purposes, we will treat all these structures as assemblies of rods (representing the ordered junction zones) with flexible chains connecting them. To produce the simplest theory we will follow the assumptions of the standard phantom network model. In particular, we neglect the enthalpies of bending and stretching of chain segments and only consider the contribution to the free energy of the enthalpy of hydrogen bond formation and the entropy of the chains. A model by Doi and Kuzuu[3] for networks of rigid rods neglects entropy and focuses on the bending enthalpy. This model predicts an extremely low modulus for small deformations, followed by a rapid increase in stress as the strain becomes large enough to cause significant numbers of rods to bend. This behavior is not observed in biopolymer gels. McEvoy et al.[4] have found that both gelatin and agarose gels show almost linear

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stress–strain relationships before fracturing at extension ratios of $\lambda = 1.3$–2.0. It is probable that both entropic and enthalpic contributions are important in these systems; however there remain various problems in dealing with the purely entropic extreme for networks of non-Gaussian chains which must be tackled first.

The other important feature of the junction zones is their semipermanent nature. Unlike covalent bonds, they may associate and dissociate under thermal fluctuations, since the hydrogen bonds holding them together are relatively weak. We investigate here the elastic properties of networks in which the junction zones have the freedom to partially or totally unwind. The section below is based on the work of Nishinari et al.,[1] but we disagree with their conclusions for a number of reasons (see ref 10).

2. The Reel-Chain Network

We will at first neglect the size of the junction zones, considering them to be much smaller than the chains connecting them. We consider a Gaussian chain of contour length L and step length l connected to a source from which chain may be drawn at a cost of ϵ per unit length. The constant ϵ includes the energy required to break hydrogen bonds in the junction zone and the entropy gain per segment released. The source acts like the reel on a fishing line. If the source is in equilibrium with the chain, then the partition function for the reel–chain unit at fixed span r is

$$Z(r) = \int_0^\infty dL \exp\left(-\frac{\epsilon L}{k_B T}\right)\left(\frac{3}{2\pi L l}\right)^{3/2} \exp\left(-\frac{3r^2}{2Ll}\right) \tag{2.1}$$

The infinite upper limit on the integral assumes that there is an infinite source of chain. Whilst a finite cutoff would be more realistic, we will show that the interesting stress–strain behavior of this system is not dependent on this cutoff. We therefore set the upper limit to infinity in order that the partition function may be obtainable analytically, yielding

$$Z(r) \propto \frac{1}{r} e^{-\beta r} \tag{2.2}$$

with

$$\beta = \left(\frac{6\epsilon}{l k_B T}\right)^{1/2} \tag{2.3}$$

This partition function takes full account of both entropic and enthalpic contributions. We show elsewhere[11] that the same partition function arises in a model for entanglement effects in rubber elasticity, but β has a different physical significance in this case.

We now connect the units in a network and make the following assumptions.

1. The end-to-end vector distribution for a chain unit between cross-links is the same as it would be for a free unit of this type.
2. Cross-link points deform affinely.
3. The material is incompressible.

Assumption 1 is a key point in the standard phantom network theory (see Flory[5]). It is likely to be valid for chains linked instantaneously in a melt or concentrated solution, as has been discussed by the present authors,[6] but for biopolymers, where slow formation of junction zones is envisaged, it is not such a good assumption. (The reel part of the unit does not, after all, exist until the network is formed!) However, we will show that the predictions of the present simple theory are relatively insensitive to the initial distribution of spans between cross-links, and the free chain distribution will serve as well as any.

In the case of Gaussian chains, the inclusion of junction fluctuations merely introduces a numerical factor into the stress–strain relationship for the affine deformation theory. This simplification will unfortunately not be true for non-Gaussian networks, since the fluctuations will in general be strain dependent. It is to be expected, however, that the simplification of assumption 2 will not qualitatively change the physics of the problem.

Assumption 3 is essentially true for all the substances considered here. Compression of the gels would require a significant change in the water content, and this has been shown (Hart et al.[7]) to take long times and high pressures to achieve.

Consider a chain unit with initial span r and at an angle θ to the z axis. After application of an extension λ along the z axis, with corresponding compression by a factor $\lambda^{-1/2}$ along the x and y axes, r is transformed to r', where

$$r' = Mr$$

$$M = \left(\frac{1}{\lambda} + \left(\lambda^2 - \frac{1}{\lambda}\right)\cos^2\theta\right)^{1/2} \tag{2.4}$$

The free energy of the network in the deformed state is

$$\frac{F}{N k_B T} = \langle \ln Mr + \beta M r \rangle_{r,\theta} + \text{constant} \tag{2.5}$$

where N is the number of chain units per unit volume and the configurational average is over the initially isotropic distribution of angles and the initial distribution of spans (eq 2.2)

$$\langle \cdots \rangle_{r,\theta} = \int_{-1}^{1} \frac{d(\cos\theta)}{2} \int_0^\infty dr\, r^2 Z(r) \cdots \tag{2.6}$$

Differentiating with respect to λ yields the stress σ:

$$\frac{\sigma}{N k_B T} = \left\langle \left(\frac{1}{M} + \beta r\right)\frac{\partial M}{\partial \lambda}\right\rangle_{r,\theta} \equiv \left\langle \left(\frac{1}{M} + \beta \bar{r}\right)\frac{\partial M}{\partial \lambda}\right\rangle_{\theta} \tag{2.7}$$

The stress is dependent on $\bar{r}$, the mean absolute value of the span under the formation conditions, and is not very sensitive to the details of the radial distribution. It follows from assumption 1 that

$$\frac{\sigma}{N k_B T} = \left\langle \left(\frac{1}{M} + 2\right)\frac{\partial M}{\partial \lambda}\right\rangle_{\theta} \tag{2.8}$$

The stress is proportional to $k_B T$ and independent of the binding energy, ϵ. The Young's modulus, E, characterizing the small deformation behavior is

$$\frac{E}{N k_B T} = \frac{11}{5} \tag{2.9}$$

and the large λ limit of stress from (2.8) is

$$\frac{\sigma}{N k_B T} \approx 1 + \frac{1}{\lambda} \qquad \lambda \gg 1 \tag{2.10}$$

Thus, σ goes through a maximum as the strain is increased: the system has a yield point. Figure 1 shows the full stress–strain curve calculated numerically. The maximum occurs at $\lambda \approx 4.5$, at which point $\sigma/(N k_B T) \approx 1.125$. This is the point of spinodal decomposition beyond which the curvature of the free energy becomes negative. However, $\sigma/(N k_B T) \geq 1$ for $\lambda \geq 2.3$, and the free energy of the network can be minimized by fractionating into regions

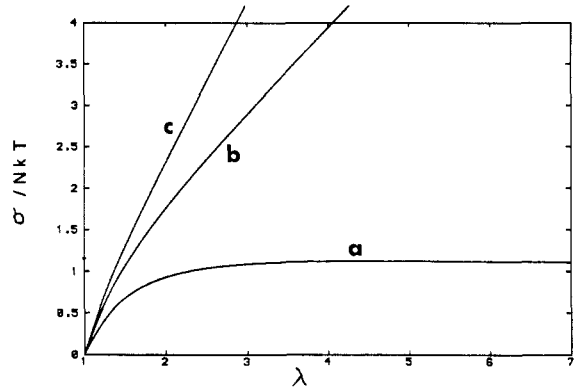

Figure 1. Stress as a function of extension ratio for three networks in uniaxial extension. (a) Reel-chain network, showing instability at $\lambda > 2.3$. (b) Gaussian network. (c) Rod-chain network with $a^2/3S = 1$.

of $\lambda = 2.3$ and regions of $\lambda = \infty$; i.e., the network fails at $\lambda \approx 2.3$.

We thus have a molecular criterion for failure. If the strain is too large, then certain junction zones will completely unwind, causing catastrophic network failure. If a finite upper limit of integration had been introduced in (2.1), then we would also have needed to include a term in the partition function representing the uncross-linked states which would exist with finite probability even at $\lambda = 1$. The result of this would be a failure at slightly lower strains, but for the same reasons.

The predictions of this model are in good qualitative agreement with the experiments of McEvoy et al.[4] both with regard to the order of magnitude of the strain at the break point and the approximately linear stress–strain curve up to this point. It is not possible to attribute the failure of gels to this mechanism with certainty, but this does provide an explanation of the relatively "weak" nature of the gels. Failure occurs at much lower strains than for many covalently cross-linked elastomers and at stresses which are probably too low to cause breakage of permanent bonds. Also evident from the experiments was a marked strain rate dependence of the strain required to break the sample. This is an indication of the importance of nonequilibrium effects. Helix formation, i.e., "setting" of the gels, takes place over a period of hours, and presumably helix unwinding can also only occur at a limited rate. It is not clear whether an equilibrium of bonded and nonbonded chain segments at the ends of the junction zones really exists within the experimental time scale.

A single reel–chain unit does not behave like a Gaussian chain in any limit. Its free energy is

$$\frac{F(r)}{k_B T} = \ln r + \beta r + \text{constant} \tag{2.11}$$

The effective force in the chain is

$$\frac{1}{k_B T}\frac{\partial F}{\partial r} = \frac{1}{r} + \beta \tag{2.12}$$

This force actually decreases with r, so the more a unit is extended, the easier it is to extend it further. This is the reason for the failure of the network. The free energy also diverges at small r due to the logarithmic term. This is clearly unphysical. We emphasize, however, that it is the behavior of $F(r)$ at large r that causes the failure, rather than the unphysical small r behavior. In compression (biaxial extension), when more chains are shortened rather than lengthened, then it is found that no failure point occurs. The stress increases as $\lambda^{-3/2}$ for $\lambda \ll 1$, rather than λ^{-2} as in the Gaussian network, where $\sigma \propto \lambda - \lambda^{-2}$.

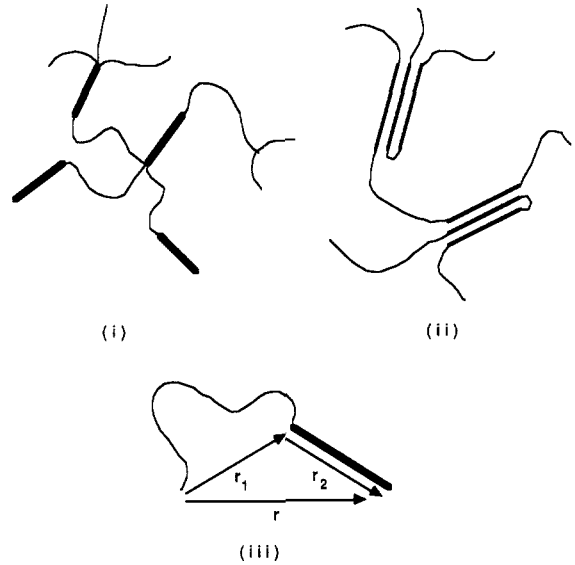

Figure 2. (i) Rod–chain network. (ii) representation of the triple helical junction zones in gelatin. (iii) Single rod–chain unit.

The fortuitous cancellation of β from (2.8) is a result of using the same distribution (eq 2.2) to determine both the probability of a given span r occurring and the value of the free energy at that span. It is thus a somewhat artificial consequence of assumption 1. This point is discussed further in section 5, where it is shown that the effects of removing the restriction of assumption 1 are likely to be small, providing the temperature is not close to the melting temperature, T_m.

3. The Rod-Chain Network

Before proceeding to make the treatment of unwinding junction zones more realistic, we will consider the effects of the size and inflexibility of the junction zones when unwinding is not permitted. The network of Figure 2i consists of many units, each of which is a rod of length a connected to a Gaussian chain with mean square end-to-end distance $\langle r^2 \rangle = 3S$. We note that this arrangement of rods and chains corresponds exactly to a model of helix formation in gelatin (see, e.g., Busnel et al.[8]) in which the helices are nucleated by formation of a kink in one of the chains. Each helix thus contains two strands from one molecule and one from another, as is shown schematically in Figure 2ii. We consider the way the modulus depends on the relative length of rod and chain.

Consider one rod–chain unit as in Figure 2iii. The probability distributions of the end-to-end vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ are known,

$$p_1(\mathbf{r}_1) = \frac{1}{(2\pi S)^{3/2}} \exp\left(-\frac{r_1^2}{2S}\right) \tag{3.1}$$

$$p_2(\mathbf{r}_2) = \frac{1}{4\pi a^2}\delta(r_2 - a) \tag{3.2}$$

and hence the total end-to-end vector $\mathbf{r} = \mathbf{r}_1 + \mathbf{r}_2$ has a distribution $p(\mathbf{r})$, given by

$$p(\mathbf{r}) \propto \frac{1}{arS^{1/2}}\left(\exp\left(-\frac{(r-a)^2}{2S}\right) - \exp\left(-\frac{(r+a)^2}{2S}\right)\right)$$
$$\propto \frac{1}{arS^{1/2}} \exp\left(-\frac{a^2}{2S} - \frac{r^2}{2S}\right) \sinh\left(\frac{ar}{S}\right) \tag{3.3}$$

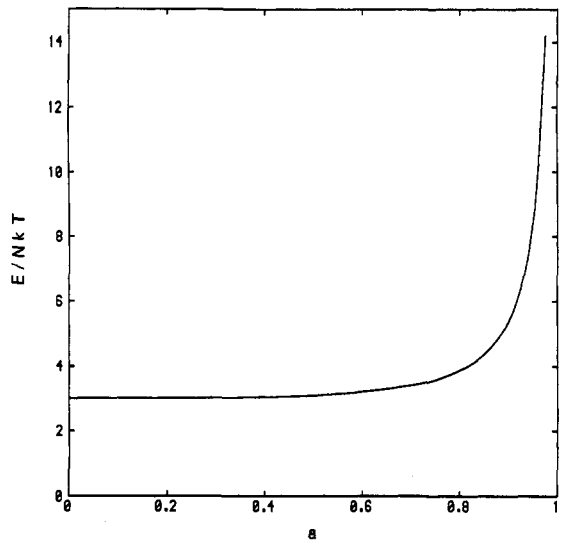

Figure 3. Effect of increasing junction zone size on the Young's modulus of the rod–chain network. The zone length a is measured as a proportion of the total rms length of the unit.

Making the same assumptions as in section 2, we find that the stress is

$$\frac{\sigma}{Nk_BT} = \left\langle \left(\frac{1}{M} + \frac{Mr^2}{S} - \frac{ar/S}{\tanh\left(\frac{aMr}{S}\right)} \right) M' \right\rangle_{r,\theta} \tag{3.4}$$

This is plotted in Figure 1 for the case $a^2/3S = 1$. As for the purely Gaussian network ($a = 0$), the stress–strain relationship is linear at large λ. We find that the Young's modulus is

$$\frac{E}{Nk_BT} = \begin{cases} 3 + O(a^4/S^2) & a^2/S \ll 1 \\ \frac{1}{5}\frac{a^2}{S} + \frac{14}{5} + O\left(\frac{S}{a^2}\right) & a^2/S \gg 1 \end{cases} \tag{3.5}$$

The defect of the theory for large a^2/S is apparent. As $S \to 0$, the unit becomes a rigid rod, and it is not possible to deform a rigid rod network affinely, hence the prediction of an infinite modulus. Many biopolymer gels are thought to contain a high helix content, and the results of this section must therefore be treated with caution. We may, however, draw one important conclusion from the above analysis. For small a^2/S, the Young's modulus is equal to its Gaussian value of $3Nk_BT$ up to order a^4/S^2. The absence of the a^2/S term means that rods have to be relatively long in comparison with the chains before they have any effect on the modulus. This is demonstrated in Figure 3, where the numerically calculated value of the modulus is plotted as a function of a and the total root mean square length of the unit has been maintained constant; i.e., $r_{rms} = (a^2 + 3S)^{1/2} = 1$. The modulus only differs noticeably from 3 for $a \geq 0.75$.

An attempt at the problem of calculating the entropy of a network of freely hinged rods has been made by Boue, et al.,[9] who demonstrate that such a network has a modulus of order Nk_BT, providing the mean functionality is less than 6, when complete locking occurs.

4. The Reel-Chain-Rod Network

A real molecule may evidently not collapse to a point. The simplification of neglecting the junction zone size made in section 2 causes the free energy of the reel–chain unit to diverge as $r \to 0$. We therefore wish to improve the model slightly by allowing collapse of the unit to a rod rather than a point. We consider a source of chain on the end of a rod of length a. We neglect changes in length of the rod (=junction zone) when chain is pulled out. The Fourier transform of the partition function for the reel–chain–rod unit is obtained from the transforms of (2.2) and (3.2):

$$\bar{Z}(k) = \frac{1}{\beta^2 + k^2}\frac{\sin ka}{ka} \tag{4.1}$$

Hence, the partition function

$$Z(r) \propto \begin{cases} \frac{1}{r}e^{-\beta a}\sinh \beta r & r < a \\ \frac{1}{r}e^{-\beta r}\sinh \beta a & r > a \end{cases} \tag{4.2}$$

The free energy of the reel–chain–rod unit has the same form as that of the reel–chain unit for $r > a$ and has a minimum at $r = a$. It no longer diverges as $r \to 0$. This is shown in Figure 4, in comparison with the parabolic free energy of a Gaussian chain.

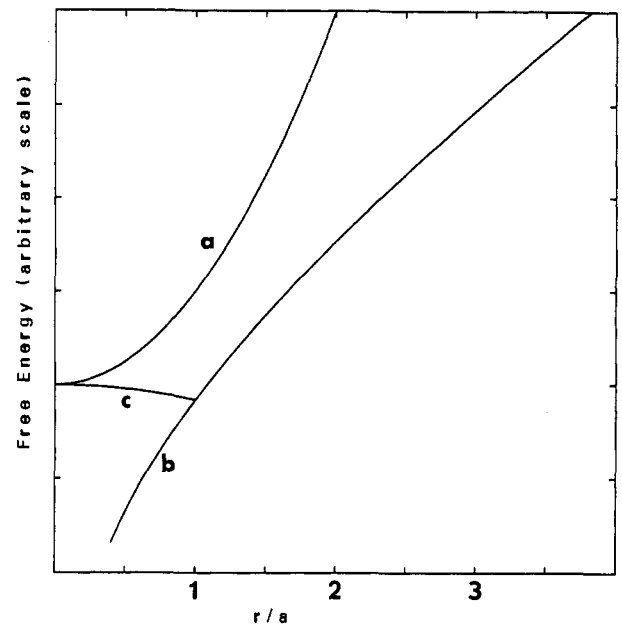

Figure 4. Free energy of various single-chain units as a function of span. (a) Gaussian chain. (b) Reel–chain unit. (c) Reel–chain–rod unit.

The shape of the stress–strain curve for the network is determined by the dimensionless constant $B = a\beta$. When the usual assumptions are made, it is found that the curve differs by no more than a few percent from the reel–chain curve for all λ and for all B. The large λ limit of the stress is

$$\frac{\sigma}{Nk_BT} \approx 1 + h(B) + \frac{1}{\lambda} \tag{4.3}$$

where

$$h(B) = \frac{1}{B}e^{-B} - \left(\frac{B}{2} + 1 + \frac{1}{B}\right)e^{-2B}$$

We note that $h(B)$ is small and positive for all B and has a maximum of $h \approx 0.03$ at $B \approx 1$. Similarly the Young's modulus remains equal to $(11/5)Nk_BT$ almost independently of B. Thus, introducing the rod makes surprisingly little difference.

We now consider the simple arrangement of reel–chain–rod units in Figure 5. Junctions A and B are connected by one unit and are situated a distance r apart ($r \geq a$). The other chains emerging from A and B have their outer ends fixed on spheres of radius r centered at A and B, in positions such that the angular separation is maxi-

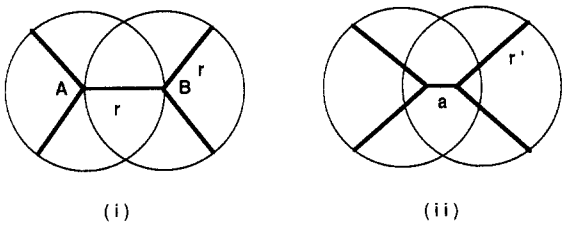

Figure 5. Simple configuration of reel–chain–rod units showing possible collapse of central unit.

mum (e.g., 120° planar arrangement for functionality ϕ = 3, etc.).

All the chains have a span greater than a; therefore, the free energy of each chain is given by the function $F(r)$ in (2.12). The free energy of this configuration is

$$\mathcal{F}_1 = (2\phi - 1)F(r) \tag{4.4}$$

Since $d^2F/dr^2 < 0$, it is favorable under certain circumstances for the central chain to collapse to its rod configuration as in Figure 5ii, causing the other units to be stretched. For simplicity, we assume that the ends of the outer units stay fixed. The new free energy is

$$\mathcal{F}_2 = F(a) + \sum_{i=1}^{2\phi-2} F(r_i') \tag{4.5}$$

where r_i' is the length of the ith outer unit after collapse of the central one. The lengths r_i' may easily be obtained for the simple geometry described here. The noncollapsed arrangement is stable if $\mathcal{F}_2 > \mathcal{F}_1$ and is unstable otherwise. Stability depends on the values of B, r/a, and ϕ in the way shown in Figure 6. We see that low functionality junctions are relatively unstable, since it is possible for a unit to collapse whilst stretching only a small number of other units. If a relatively small compared with r, the collapse of one unit effectively creates one new junction of functionality $2\phi - 2$, which will have a greater stability with respect to further possible collapse. (The reel–chain unit would technically always be unstable to this mode of collapse.)

To draw conclusions from this model applicable to the complete network, we could possibly take r to be the rms length of the unit, which is a function of the conditions of formation and the state of strain. B depends on temperature in some way, and as discussed in section 5, it may be either an increasing or a decreasing function of T. Relaxation of the outer junction points to new mean positions should also be taken into account. Thus, it is very difficult to proceed from Figure 6 to a phase diagram in the variables λ and T. The conclusion that high functionality junctions are more stable will remain true in the complete network. It is to be expected that under certain conditions of T and λ some of the units will collapse to form combined junction zones of high effective functionality.

5. Generalizations

If we wish to consider the temperature dependence of the modulus of the reel–chain system, it is necessary to improve on assumption 1. One possibility is to assume that the initial distribution of spans (i.e., $Z(r)$ from (2.2)) which goes into the radial averaging of (2.5)–(2.7) has the constant β set equal to β_f, its value at the temperature of formation T_f, whilst the free energy of a chain at a temperature $T \neq T_f$ is determined by the value $\beta(T)$ appropriate to that temperature. Equation 2.8 then generalizes to

$$\frac{\sigma}{Nk_BT} = \left\langle \left(\frac{1}{M} + \frac{2\beta(T)}{\beta_f} \right) \frac{\partial M}{\partial \lambda} \right\rangle \tag{5.1}$$

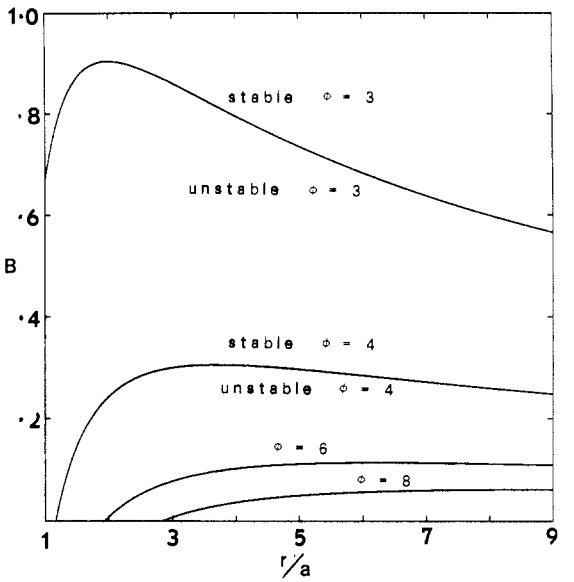

Figure 6. Regions of stability and instability for the configuration in Figure 5 for various functionalities ϕ.

which means that the stress is no longer directly proportional to T. We note, however, that the range of T available is typically very small. For example, in gelatin gels $T > 0$ °C (where the solvent freezes) and $T < 35$ °C (where the gel melts). The absolute temperature can only change by ~10%, and we therefore expect that, provided T does not approach the melting temperature T_m, the effect of removing assumption 1 will be very small.

If $T \rightarrow T_m$, then there will be a substantial reduction in the number of junction zones present. It will be inappropriate to put the infinite upper limit into the integral of (2.1). We do not consider this situation here.

The way in which β varies with temperature is governed by the rate of change of the persistence length. From (2.3) we have

$$\frac{\beta(T)}{\beta_f} = \left(\frac{T_f l_f}{T l(T)} \right)^{1/2} \tag{5.2}$$

If $l(T)$ varies exponentially with temperature according to the relation

$$\frac{l(T)}{l_f} = \exp\left(-\frac{\Delta}{k_BT_f} + \frac{\Delta}{k_BT} \right) \tag{5.3}$$

then it is straightforward to show that if $\Delta/(k_BT_f) > 1$ then $\beta(T)$ is an increasing function of T at temperature close to T_f, and if $\Delta/(k_BT_f) < 1$ then it is a decreasing function. The behavior of $\beta(T)$ thus depends critically on the unknown constant Δ and will be different for each particular type of molecule.

The paper of Nishinari et al.[1] on this subject used Langevin chains rather than Gaussian chains as we do here. The Langevin approximation for the partition function of a chain of n freely hinged rods of length l is

$$Z_n(r) = C_n \left(\frac{\sinh \beta_L}{\beta_L} \right)^n e^{-\beta_L r} \tag{5.4}$$

where

$$\coth \beta_L + \frac{1}{\beta_L} = \frac{r}{nl}$$

If such a chain is connected to a source of chain segments, then we may obtain a partition function equivalent to (2.1)

$$Z(r) = \int_0^\infty dn \exp\left(-\frac{\epsilon n}{k_B T}\right) Z_n(r) \tag{5.5}$$

where ϵ is the energy to release one chain segment from the junction zone. In performing this integral, it is important to consider the dependence of the normalization constant C_n on n. The steepest descents solution of this integral (which which is entirely in keeping with the approximate nature of the Langevin partition function) is

$$Z(r) \propto \frac{1}{r} e^{-\beta^* L r} \tag{5.6}$$

where

$$\frac{\sinh \beta^*_L}{\beta^*_L} = \exp\left(\frac{\epsilon}{k_B T}\right) \tag{5.7}$$

Equation 5.6 is of exactly the same form as (2.3), and although the value of β is different, this will cancel out of the stress formula anyway.

The meaning of this is qualitatively clear. Rather than approach its extension limit and pay a high free-energy "cost" due to the reduction in entropy, the Langevin chain will always prefer to pull out another chain segment from the junction zone. As long as a Langevin chain does not approach its extension limit, it behaves the same way as a Gaussian chain. The effects of limited extensibility are thus entirely outweighed by the unwinding junction zone.

6. Conclusions

We have modeled the hydrogen-bonded junction zones occurring in biopolymer gels by assuming that there is an equilibrium of chain segments binding and being released from the junction zones at their ends. The simplest reel–chain network was found to be unstable in uniaxial extension at $\lambda \geq 2.3$. Altering the size of the junction zones and introducing the limited extensibility of the chains was found to have almost no effect on the elastic properties, since the unwinding process which occurs when such a network is stretched is the dominant factor determining the stress–strain relationship. Due to the negative curvature of the free energy of the reel–chain unit, the network can in some conditions lower its free energy by allowing the complete collapse of some chains and increasing the unwinding of the neighboring chains. The resulting network would then contain combined junctions of high effective functionality.

An exact treatment of the network of non-Gaussian chains still has, of course, to be found. The full complexity of this problem can be understood when it is realized that junction point fluctuations are dependent on the strain and that not only do the junction points not deform affinely but neither do their mean positions. It is the absence of these complications in the Gaussian network which allows an exact solution in this case.

The treatment of the effects of the large size and rodlike nature of the junction zones must be taken as a very rough approximation. It is possible to conclude, however, with some certainty that if such junction zones are unable to unwind then there will only be a noticeable effect on the modulus if the length of the junction zones is large in comparison with the length of the free chains. The stress–strain curve can be expected to remain of a similar shape to the purely Gaussian network, as is shown by the present model.

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References and Notes

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