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Stretching globular polymers. II. Macroscopic cross-linked networks

A. Craig and E. M. Terentjev[a]
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom

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We expand upon the results for the force-extension behavior of single-collapsed polymer chains to consider the mechanical response of networks of cross-linked globular polymers in poor solvent. Force-strain curves are obtained under the affine deformation approximation for networked globules with both disordered and ordered globule conformations. Due to their large stored lengths, these networks would be capable of reaching extremely large strains. They also show anomalous nonmonotonic force-strain response, as a consequence of the nonmonotonic force-extension curves of their constituent globules. Finally, we consider the stability of ordered and disordered globules in these networks and propose means taken from biological and colloid science to stabilize networked globules. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1898214]

I. INTRODUCTION

Despite the advances described in the preceding paper[1] in understanding single chains, there has been a paucity of work that considers polymer globules in the bulk or as networks. Existing literature on networks of polymers in poor solvent seems limited to studies of grafted polymers,[2–4] which form nematic melts rather than distinct globules. However, the ability to crystallize globular proteins, and the stable conformations of proteins in the tight confines of the cytosol attest to the existence and stability of individual polymer globules in poor solvent, even when densely packed. As such, the study of dense, globular polymer systems appears worthwhile.

Here we develop theoretical models of the force-extension behavior for various semiflexible polymer globules and covalently cross-linked networks of these globules. Sec. II reviews the affine assumption and "ghost network" model used to treat networks in this paper. These models are then applied to the free energies obtained for ordered and disordered globules in related work[1] and the results presented in Sec. III. Section IV discusses the notable features of these networks' mechanical response. We note the capacity for both high maximum strains and anomalous nonmonotonic force-strain behavior in these networks, which arise from the properties of the individual globules considered in Ref. 1 and constitute the central results of this paper.

II. NETWORK FORMALISM

Having discussed the force-extension behavior of single globules, we now examine cross-linked networks of such globular chains, using the basic aspects of rubber elasticity.[5] While networks of real polymers are subject to entanglement effects and other constraints that complicate their response to stretching, we will neglect such complexities and consider a basic network of "phantom" chains. In this model, chains interact only at their endpoints, which are permanently cross-linked together. For a network of polymer globules, we can imagine this model would hold even better than in classical rubber elasticity theory if a small section of free chain exists to separate the globules and attach to cross-linkers. As noted in Sec. III below, we will neglect the influence of such linkers on the network's stretching behavior, but they are necessary to ensure that the phantom network conditions hold in our hypothetical globular networks.

Following the phantom chain model, we can now calculate the total free energy under stretching. For a chain having some end-to-end vector $\mathbf{R}$ in its initial ("reference") state, a deformation described by the tensor $\underline{\underline{\lambda}}$ takes us to a final ("target") end-to-end vector $\mathbf{R}'=\underline{\underline{\lambda}}\cdot\mathbf{R}$. If we have an individual chain free-energy function $F_s(\mathbf{R})$ (where s denotes the single chain) and the end-to-end probability distribution $P(\mathbf{R})$, the quenched network average

$$F=\int d\mathbf{R}P(\mathbf{R})F_s(\mathbf{R}) \tag{1}$$

yields the average free energy in the reference state per chain, while the free energy in the target state follows as:

$$F(\underline{\underline{\lambda}})=\int d\mathbf{R}P_{\underline{\underline{\lambda}}}(\mathbf{R})F_s(\underline{\underline{\lambda}}\cdot\mathbf{R}), \tag{2}$$

where $P_{\underline{\underline{\lambda}}}(\mathbf{R})$ is the distribution of end-to-end vectors in the target state.

We now call upon the affine deformation assumption, which holds that the network deforms on the microscopic scale (here, between connected cross-links) exactly as it does macroscopically. We consider this approximation to be valid in the regime where individual chains are not stretched completely taut, i.e.,

$$\lambda R_0 \leqslant L \tag{3}$$

with $R_0=|\mathbf{R}|$ for the reference state (we use this quantity on the assumption that $F(r,\theta,\phi)=F(r)$ in spherical coordinates). Note that in the coming sections, we will terminate all force-strain curves at the strain λ where the equality holds. The affine approximation appears formally as

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[a] Electronic mail: emt1000@cam.ac.uk

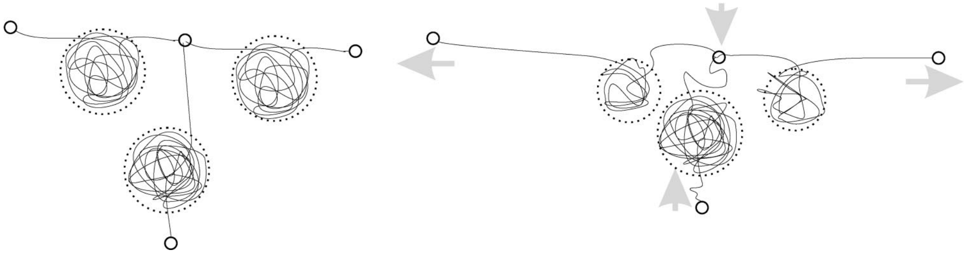

FIG. 1. Cross-linked networks of globules in native and partially stretched conformations.

$$P_{\underline{\underline{\lambda}}}(R_0) = P_{\underline{\underline{1}}}(R_0), \tag{4}$$

where $P_{\underline{\underline{1}}}(R_0)$ is the end-to-end distribution in the reference state and is given at equilibrium by the formula

$$P_{\underline{\underline{1}}}(R_0) = \frac{e^{-\beta F_s(R)}}{\int d\mathbf{R}e^{-\beta F_s(R)}}. \tag{5}$$

Thus, the distribution of chains at network formation remains fixed upon deformation: the topological quenching of a network described in here. If we now assume that the deformation is generated by a uniaxial stretch along the (arbitrary) z axis of the system, transverse symmetry and incompressibility gives us

$$\underline{\underline{\lambda}} = \begin{pmatrix} \lambda^{-1/2} & 0 & 0 \\ 0 & \lambda^{-1/2} & 0 \\ 0 & 0 & \lambda \end{pmatrix}. \tag{6}$$

Transforming into spherical coordinates with the polar axis along z, the reference-state vectors $\mathbf{R}$ are scaled by a factor η given by

$$\eta(\theta,\lambda) = \sqrt{\lambda^{-1}\sin^2\theta + \lambda^2\cos^2\theta}. \tag{7}$$

Assuming that the angular distribution of the polymer endpoints is isotropic in the reference state, i.e.,

$$\begin{aligned} dN(\theta,\phi) &= \frac{1}{2\pi}\sin\theta d\theta d\phi, \\ dN(\theta) &= \sin\theta d\theta, \end{aligned} \tag{8}$$

we can use the relation $dN/d\eta = (dN/d\theta)(d\theta/d\eta)$ and Eq. (7) to arrive at the stretching distribution

$$\begin{aligned} dN(\eta) &= \sin\theta \frac{\lambda\sqrt{\lambda^{-1}\sin^2\theta + \lambda^2\cos^2\theta}}{\sin\theta\cos\theta(\lambda^3-1)}d\eta \\ &= \lambda\eta[(\lambda^3-1)(\lambda\eta^2-1)]^{-1/2}d\eta, \end{aligned} \tag{9}$$

which can be approximated in the large extension limit $\lambda, \eta \gg 1$ as

$$dN(\eta) \approx \frac{1}{\lambda}d\eta. \tag{10}$$

The limit (10) is of use in understanding the qualitative features of the network force-strain curves, particularly the persistence of the nonmonotonic and discontinuous features found in the force-extension curves of individual globules.

III. STRETCHING NETWORKS OF GLOBULAR CHAINS

We now can combine the free-energy functions of single-ordered and disordered globules from[1] with the full stretching distribution given by Eq. (9) to obtain the free energy of a network of collapsed globules. As mentioned in Sec. II, we will assume that the globules are covalently cross-linked together, and spaced away from the cross-links by linker groups that neither extend appreciably as the cross-links pull apart, nor compress the globule when the cross-links are pushed together. Ideally these linkers should be long enough to prevent unbound chains from sticking to each other or intact globules, and so allow individual globules to reform when the network relaxes. For linker length $\mathcal{L}_{\text{linker}}$ and persistence length ϕ_{linker}, this situation may obtain when $\phi_{\text{linker}} \sim O(\mathcal{L}_{\text{linker}})$, or if the linkers are in their "good solvent" regime and assume an extended conformation. We schematically illustrate this situation in Fig. 1. Even under these conditions we expect the globules will adhere to each other, particularly disordered globules with their generic surface-contact term. Borisov and Halperin treat this effect in the context of polysoaps in,[6–9] and obtain a force-extension relation for separating globules. We expect globule separation to dominate the network mechanical response for small deformations, but as we focus our attention on the response at high strains, we will neglect it in this paper. Interglobular adhesion will also be discussed in Sec. IV.

We now place Eqs. (4) and (9) into Eq. (2) to obtain the final form of the average free energy of deformation per strand, given as

$$F(\lambda) = \int_0^{R_{\max}} dR_0 \int_1^{\lambda} d\eta \frac{\lambda\eta F_s(\eta R_0)P(R_0)}{\sqrt{(\lambda^3-1)(\lambda\eta^2-1)}}, \tag{11}$$

where $F_s(x)$ is the single-chain free energy for end-to-end distance x, R_0 an initial end-to-end distance in the reference state, $P(R_0)$ the probability of finding a globule with R_0 in the network, and $R_{\max}$ the largest end-to-end distance in the reference state (i.e., the size of the globule). The total macroscopic energy of a network with N strands and deformation λ is clearly $NF(\lambda)$.

Several other points must be established before evaluating the free energy of deformation, particularly the reference end-to-end distribution $P(R_0)$. We can identify two plausible forms of $P(R_0)$ for globules: the "on-shell" case where the endpoint distribution is identical for all globules, and a "floppy" case where not all of the chain is tightly bound to the globule and the endpoint distribution is broader. In both cases, we assume that the cross-linking between globules is isotropic. In the on-shell case, we claim that the free ends of the polymer start on the surface of the globule, which amounts to the condition

$$P(R_0) = \delta(R_0 - R_{\text{glob}}), \tag{12}$$

where $R_{\text{glob}}=(3Lb^2/4\pi)^{1/3}$.

By comparison, the floppy case assumes that we begin with some unbound length $\mathcal{L}_0$ with the same persistence length as the polymer in the globule (note that this length is not that of the linker). Provided that the presence of the globule does not unduly affect the endpoint distribution of this unbound length, we use the free-end semiflexible propagator for $\phi \approx \mathcal{L}_0$ given in Ref. 10 as our $P(R_0)$. We so arrive at

$$P(R_0) = \left(\frac{3}{2\pi\langle R^2\rangle}\right)^{3/2} \exp\left[-\frac{3}{2\langle R^2\rangle}(R_0 - \sqrt{\langle R^2\rangle})^2\right], \tag{13}$$

where

$$\langle R^2\rangle = \frac{3}{2\xi}\left\{\mathcal{L}_0 - \frac{3}{2\xi}\left[1 + \frac{3}{2\sqrt{3\phi\xi}}\coth\left(\mathcal{L}_0\sqrt{\frac{\xi}{3\phi\xi}}\right)\right]^{-1}\right\}, \tag{14}$$

$$\xi = \frac{3}{4\phi}\left[1 - \left(\frac{\chi}{\mathcal{L}_0}\right)^2\right]^{-2}. \tag{15}$$

While one cannot necessarily speak of a R_{glob} for this case, we will use $R_{\max}=L_0$ in calculating the free energy in Eq. (11) and the maximum strain on the network in Eq. (3).

We will use the terms on-shell to refer to the networks with the initial end-to-end distribution of Eq. (12) and floppy to refer to networks with the initial distribution of Eq. (13) through the rest of the paper.

A final assumption is that those globules with $\eta < 1$ in Eq. (7) are not actually compressed by contact forces and do not contribute to changes in the free energy. This is the situation one might expect if the molecules linking globules are fairly flexible, and long enough to space the incompressible globules well apart from each other.

While all of these conditions do simplify computation of the free energy, it is still necessary to use numerical techniques to fully calculate the free energy and its derivatives. We obtain the actual force-strain curves by an approximation to the actual derivative; we fit a linear function to a sample of five free-energy points separated by $\Delta\lambda = 10^{-5}$ and take the resulting least-squares slope as the value of the derivative.

In general, we will refer to force-strain rather than stress-strain behavior in this paper, since the extremely high strains that were attained in deforming individual globules are a property of networked globules as well. As stress is defined as $\sigma = \text{force}/\text{area} = f\lambda/A_0$ for initial sample area A_0, salient features of the curves can become difficult to see at large λ, hence our choice to present force-strain curves over stress-strain curves for these materials. Note that the force-strain curves are given in the dimensionless force unit $\tilde{f}$ as an average per chain; the actual mechanical response should simply be proportional to the average number of chains in the network.

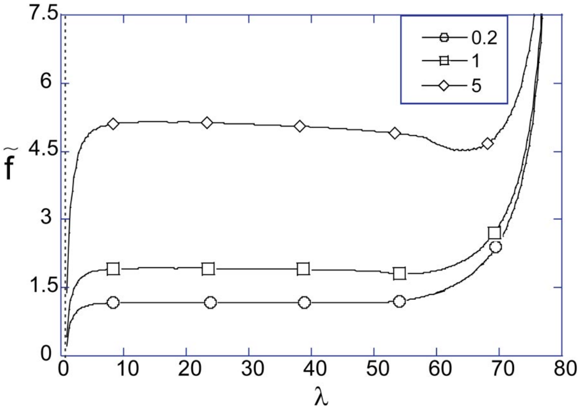

FIG. 2. Force-strain curves for networked random globules with varying surface tension Γ (values indicated on plot), for chain stiffness $\phi=1$, and length $\mathcal{L}=1000$. The dashed line indicates the reference strain $\lambda=1$.

A. Networks of random globules

Using the formalism of Eq. (11) and the free energy found in Ref. 1 for random globules, we now examine the stretching behavior of networks of random globules. For an on-shell treatment, we obtain force-strain curves dominated by force plateaus that extend over long strains. For conditions with $\Gamma \sim O(\phi)$, we obtain nonmonotonic behavior in the force-strain curves much as we did in the force-extension curves of individual chains. This can be seen in Figs. 2 and 3. One will notice that the average force per chain is inevitably lower than that of a single chain at the same "strain" x/R_{glob}, as globules with initial end-to-end vectors nearly perpendicular to the direction of the stretch will remain unextended at all strains.

In light of the results[1] for single toroidal globules, we expect networks of toroidal globules to exhibit force-strain behavior akin to that of networked random globules, since both types of globules possess essentially similar force plateaus and discontinuous unbinding transitions. The on-shell curve of a network of toroidal globules is plotted in Fig. 4, and clearly displays nonmonotonic behavior as well.

B. Networks of ordered globules

We now turn our attention to networks of ordered globules, both in series and taken singly as in.[1] Since we have

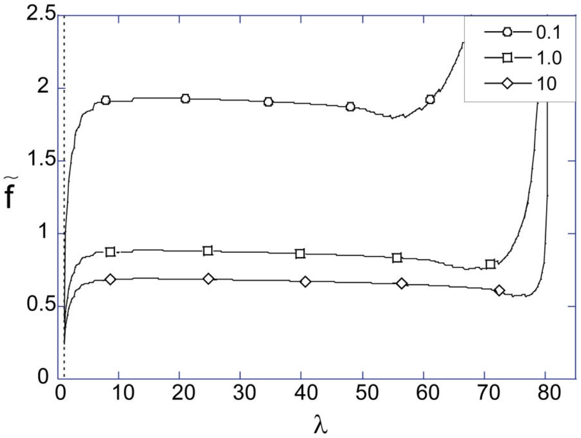

FIG. 3. Force-strain curves for networked random globules with varying chain stiffness ϕ (values indicated on plot), for surface tension $\Gamma=10$, and length $\mathcal{L}=1000$. The dashed line indicates the reference strain $\lambda=1$.

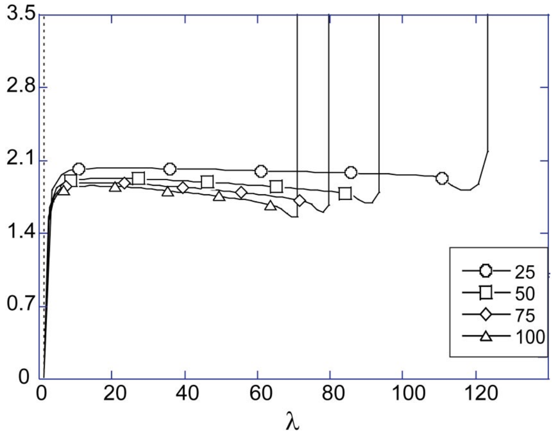

FIG. 4. Force-strain curves for networked toroidal globules with varying chain stiffness ϕ (values indicated on plot), for surface tension $\Gamma=1$, and length $\mathcal{L}=1000$. The dashed line indicates the reference strain $\lambda=1$.

explicitly given these globules some initial unbound length, it seems natural to use the floppy approximation for the case $\mathcal{L}-\mathcal{L}_{\text{bound}}\geqslant\phi$. The floppy approximation is also suited to a series of ordered globules that is already in a partially extended conformation, like the "necklaces" conjectured for partially stretched random copolymers.[11,12] However, we can also justify the use of the on-shell approximation under some circumstances. In particular, the on-shell approximation would be suitable for single-ordered globules with free length $\mathcal{L}-\mathcal{L}_{\text{bound}}\leqslant\phi$ or for a series of globules with a weak interglobular adhesion causes the globules to form a cluster with a well-defined radius. Note, however, that we neglect any presumed interglobular adhesive force in the actual calculation of the force-strain curve. We present results for both approximations below, with Fig. 5 being the on-shell case and Fig. 6 the floppy cross-linking case.

As one would expect, the average force per chain is generally below the force one would obtain at a similar strain for a single series of linked ordered globules. Unlike the on-shell case, all of the curves for the floppy case appear to have their maxima at roughly the same force, despite covering two decades of the rigidity ϕ. This is likely the result of the way in which the radial distribution function of Eq. (13) changes as a function of ϕ. For large ϕ, the distribution (13) is so narrow as to resemble the on-shell case, while at smaller ϕ, it resembles a Gaussian centered near $R_0=0$. Though decreasing ϕ raises the maximum force on the network, as Fig. 5 demonstrates, a low chain rigidity ϕ also means that many of the globules will not be significantly deformed due to their low initial R_0. We also do not observe a significant rise in the force near the full extension $\lambda=\mathcal{L}/R_{\text{glob}}$ for the floppy case, as even globules with $\mathbf{R}_0$ parallel to the direction of stretching may not be fully extended if they have $R_0<R_{\max}$.

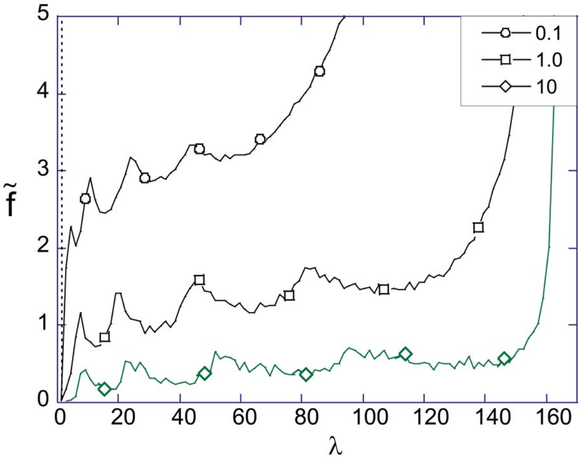

FIG. 5. On-shell approximation of force-strain curves for networked series of ordered globules with varying chain stiffness ϕ (values indicated on plot), for surface tension $\Gamma=1$, total length $\mathcal{L}=1000$, cutoff forces $\tilde{f}_i/kT=\{10,10,10,10\}$, and bound lengths $L_i/kT=\{145,145,145,145\}$. The dashed line indicates the reference strain $\lambda=1$.

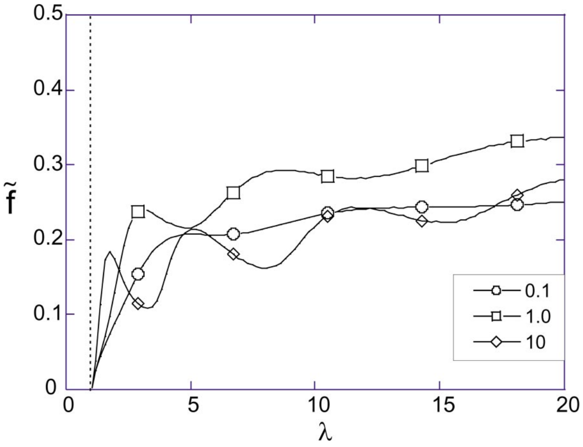

FIG. 6. Floppy approximation of force-strain curves for networked series of ordered globules with varying chain stiffness ϕ (values indicated on plot), for surface tension $\Gamma=1$, total length $\mathcal{L}=1000$, cutoff forces $\tilde{f}_i/kT=\{10,10,10,10\}$, and bound lengths $L_i/kT=\{145,145,145,145\}$. The dashed line indicates the reference strain $\lambda=1$.

IV. DISCUSSION

While a full evaluation of the network free energy is necessarily numerical, especially for the floppy case with a nontrivial endpoint distribution, we can still analytically approximate the force-strain behavior of networks of globules. Perhaps the easiest case to treat is that of ordered globules and series of ordered globules in the on-shell case. If we assume that the free energy remains relatively constant with strain except when the chain is nearly taut (i.e., we are about to break open a globule), we can model the free energy as a series of step functions

$$\mathcal{F}(\eta)\approx\sum_i \Delta\mathcal{F}_i\theta(\eta-\eta_i), \tag{16}$$

where $\theta(x)$ is a step function, and $\Delta\mathcal{F}_i$ and η_i are the free-energy cost and microscopic chain extension associated with the ith globule unbinding, respectively. This approximation should apply to the first paper's model of chained ordered globules for $\phi\sim\mathcal{L}$. Let us now invoke the further assumption that all the globules are identical, that is, $\Delta\mathcal{F}_i=\Delta\mathcal{F}$ and $\eta_{i+1}-\eta_i=\Delta\eta$ for all i, which appears to be a suitable approximation to experiment (Refs. 1,13). We then take the constant distribution $dN/d\eta = \lambda^{-1}$ of Eq. (10) to arrive at the averaged free energy

$$\mathcal{F}(\lambda) = \lambda^{-1}\int_1^{\lambda} \sum_j \Delta\mathcal{F}\theta(\eta - j\Delta\eta),$$
$$= \Delta\mathcal{F}/\lambda\left\{n_u(\lambda - \Delta\eta n_u) + \tfrac{1}{2}\Delta\eta[(n_u - 1)n_u]\right\}, \qquad (17)$$

where $n_u = \eta \operatorname{div} \Delta\eta$, $a \operatorname{div} b$ being defined as the integer part of a/b. Taking $\tilde{\mathrm{f}} = -d\mathcal{F}/d\lambda$, we get

$$\tilde{\mathrm{f}}(\lambda) = \Delta\mathcal{F}\left[\frac{\Delta\eta}{2\lambda^2}(n_u^2 + n_u) + \delta_{\zeta,0}\right], \qquad (18)$$

where ζ is defined as $\eta \bmod \Delta\eta$. The force is positive but decreasing at all strains save when $\zeta = 0$, where the force jumps before decaying away again. Thus, networks of ordered globules in series or single random globules should display nonmonotonic force-strain curves, assuming that their initial distributions $P(R_0)$ are on-shell and the step-function approximation to the free energy is accurate [i.e., $\mathcal{L}/\phi \sim O(1)$].

However, if we assume that $P(R_0)$ is nonzero for a range of R_0 rather than a single value, as in the floppy cross-linking case, then monotonic force-strain curves may reinerge. If $P(R_0)$ is, in fact, Gaussian distributed about some R_0' with standard deviation ρ, we obtain a $dN(\eta)$ approximated by the convolution

$$dN(\eta) = \int_0^{\infty} d\eta' \frac{\eta'}{\rho\sqrt{2\pi}}\theta(\eta - \eta')e^{-(\eta' R_0' - R_0')^2/2\rho^2}. \qquad (19)$$

For $\rho \ll R_0$, the results of Eq. (19) can be approximated as

$$dN(\eta) \approx \tanh\left(\frac{\eta R_0' - R_0'}{\rho}\right). \qquad (20)$$

When applied to the free energy of Eq. (16), we expect this $dN(\eta)$ to yield a nonmonotonic force-strain curve only so long as $\rho/R_0' < \Delta\eta$; for larger ratio of ρ/R_0', we will gain free energy at a nearly constant rate as we cross the "steps" in Eq. (16), and so should obtain a flat or monotonically increasing force-strain curve. Similarly, we would expect that a free-energy $\mathcal{F}(\eta)$ which has a force plateau followed by a drop across the interval $\{\eta_c, \eta_c + \Delta\}$ would display a nonmonotonic force-strain curve for $\rho/R_0' < \Delta$ and a flat or increasing curve otherwise.

Unfortunately, we anticipate significant practical difficulties in creating the networks of distinct globules we discuss here. While we claim interglobular adhesion can be ignored, it is an open question whether densely packed polymers will form individual, separate globules (as our model requires) instead of a dense interpenetrating melt. A naive means of guaranteeing stability would be to form the network in good solvent and reduce solvent quality while keeping it under tension, thus keeping the globules separated.

More sophisticated are strategies for preventing a melt even if we cross-link the globules after they are already in the collapsed state. One expects particular difficulties with disordered globules, which may gradually merge into one another as a result of thermal excitations. However, we expect that the energetic cost of unwinding an entire loop of chain will make the toroidal globules relatively stable against merging, and even spherical globules may prove stable if cross-linked beneath their glass transition temperature. One might improve the disordered globules' stability by decorating the main chain with solvophilic side groups, which would separate the globules much like emulsifiers space droplets in a colloid.

By comparison, the existence of a preferred set of contacts within each ordered globule should help stabilize them against the tendency to form an interpenetrating melt. Globular proteins (such as lactoglobulin and albumin) can remain stable as dense solutions and even solids, though it is expected that high concentrations may result in aggregation of amyloidogenic proteins. Regardless, proteinaceous or small-molecule chaperones could be incorporated into the network to stabilize the globules,[14] provides a review of the crowded macromolecular environments' influence in biology and natural stabilization mechanisms.

The tendency to form a melt or an aggregate phase also becomes a concern in the regime where the globules have been extended and released their length as free chains. Recalling our poor solvent environment, these free chains will stick together if allowed to touch. Contacts between extended chains could well prevent them from reforming separate globules upon relaxation, introducing a significant hysteresis effect potentially destroying the nonmonotonic force-strain curves we expect for globular networks. One might hope to avoid such difficulties by separating strands by large distances, though is is questionable if the maximum load on such a disperse network would be adequate for real applications. Again, the addition of solvophilic side chains to physically separate free chains or chaperones to assist in reforming ordered globules may be viable means of preventing a melt.

Less dramatic, but still significant, are the potential theoretical concerns about the networks described in this paper. One might imagine that nonaffine deformation would be pronounced in a network in which chains can release length quickly, as would occur when a globule unbinds. Indeed, nonaffine models have long been part of the theory of more conventional polymer networks,[15,16] though their results are generally akin to those of affine deformation theory in the regime where few of the chains are pulled completely taut in the affine approximation. One might also object to the neglect of linkers in our paper's treatment, given their likely nonnegligible contribution to the free energy. However, the floppy case can be regarded as an analog to a network having linkers with $\phi_{\mathrm{linker}} = \phi_{\mathrm{chain}}$, but as noted previously, nonmonotonic force-strain behavior persists for sufficiently high ϕ and narrow initial distribution $P(R_0)$. As such, we do not believe the neglect of linkers critically undermines our conclusions.

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