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Deformation of globular polysoaps: extension, confinement and extensional flow

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Abstract. A theoretical model of the extension and confinement of globular polysoaps predicts novel force laws. Polysoaps are polymers comprising of a flexible hydrophilic backbone incorporating, at intervals, amphiphilic monomers. The equilibrium configuration of long polysoaps, that form numerous spherical intrachain micelles, is a spherical globule of close packed micelles. The coupling of the deformation to the hierarchical self organization of the chain gives rise to a distinctive force law involving, for extension, two plateau regimes. When the chain is stretched by extensional flow the two regimes merge and the polysoap exhibits a single globule-stretch transition.

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1 Introduction

Intrachain self assembly can have a strong effect on the elasticity of polymer chains. This is due to the coupling of the chain deformation and the "internal degrees of freedom" of the self assembled structures. The expected behavior can be especially rich when the intrachain self assembly leads to a hierarchical self organization. In the following we present a theoretical discussion of the behavior of a particularly simple model system of this type: globular polysoaps. Polysoaps are hydrophilic, flexible polymers that incorporate, at intervals, m covalently bound amphiphilic monomers [1–3]. The amphiphilic monomers can self assemble into intrachain micelles [4,5]. The equilibrium configuration of a long polysoap, capable of forming numerous, spherical, intrachain micelles, is globular *i.e.,* a sphere comprising of close packed micelles [5]. The self organization of the polysoap involves a three levels hierarchy. One can refer to the sequence of amphiphilic and non amphiphilic monomers as primary structure and to the intrachain micelles as secondary structure (Fig. 1). Similarly, we may refer to the configuration of a string of micelles as tertiary structure. As we shall see, the deformation of globular polysoaps reflects coupling to both secondary and tertiary structures. The effect is especially striking when the chain is extended. Relatively weak deformations couple to the tertiary structure. The situation is similar to that obtained upon deformation of collapsed homopolymers [6,7]. Strong extensions couple to the secondary structure. The resulting scenario is identical to that encountered in the analysis of linear strings of micelles [8–10]. In both regimes, the coupling result is an intramolecular coexistence leading to a plateau in the extension force law (Fig. 2). The combined scenario, involving two plateaus, is distinctive to globular polysoaps. This picture is however modified when the extension is

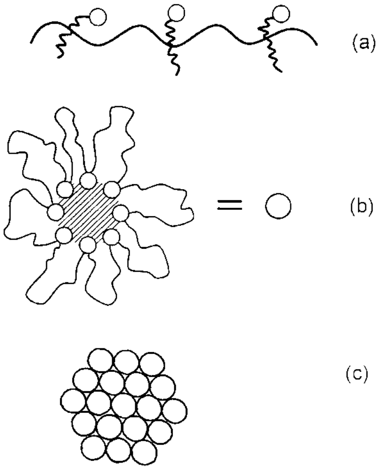

Fig. 1. The hierarchy of self organization of globular polysoaps. The chemical sequence of amphiphilic monomers joined by hydrophilic spacer chains is depicted in (a). The polymerized amphiphiles self assemble into spherical intrachain micelles (b). Finally, the intrachain micelle form a spherical globule of close packed micelles (c). This last configuration is stable because of the exchange attraction.

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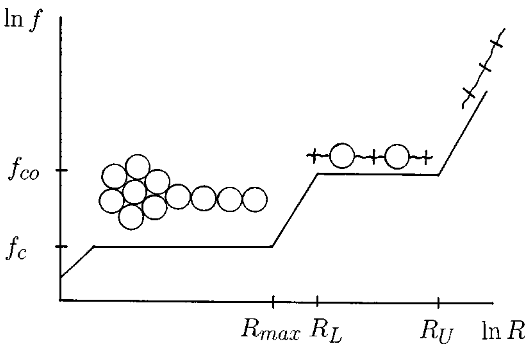

Fig. 2. The force profile characterizing the extension of globular polysoaps when the end to end distance is externally imposed. Intially the globule unfolds into a string of micelles. Stronger deformation favor miceller dissociation. Both regimes involve a plateau associated with a coexistence of two states.

accomplished by an extensional flow. In this situation the two stages merge and the chain undergoes a single globule-stretch transition.

The elasticity of globular polysoaps is of interest from two perspectives. Polysoaps belong to a wider class of hydrophobically modified polymers [11,12]. These are widely used as viscosity modifiers and colloidal stabilizers of fine, water born dispersions. A theoretical understanding of the elasticity of polysoaps can help to elucidate their rheology. To this end we will briefly consider the behavior of globular polysoaps in extensional flow. The problem is also of interest in view of recent developments in the biophysics of biological macromolecules. The hierarchical self assembly of polysoaps is a simple example of the much richer phenomena found in biopolymers such as nucleic acids and proteins. Recent experimental developments enable the measurement of the force laws characterizing the extension of certain biopolymers. Theoretical analysis of the observed traits is however difficult, especially in the case of proteins. From this perspective, the deformation behavior of polysoaps may help in the interpretation of these experimental results. In fact, the force laws predicted for a linear string of micelles [9,10] are qualitatively similar to the force laws measured for DNA [13,14] and Titin [15,16]. While the force laws predicted for globular polysoaps have not been, to our knowledge, observed we speculate that the extension of globular multidomain proteins may exhibit similar features.

The article is organized as follows: the intrachain self assembly of polysoaps is summarized in Section 2. In particular: the structure of intrachain micelles, their interactions, and the configurations of long polysoaps. In Section 3 we analyze the extension elasticity of the stable configuration of long polysoaps *i.e.*, spherical, globular arrays of closely packed intrachain micelles. The behavior of globular polysoaps in extensional flows is discussed in Section 4.

2 Intramolecular self assembly in polysoaps

Our discussion concerns polysoaps in which the amphiphilic monomers are joined by monodispersed, flexible, hydrophilic spacer chains comprising $n \gg 1$ monomers of size b. It is limited to the case of polysoaps that form spherical intrachain micelles. The overall polymerization degree is $N \approx mn \gg 1$. We assume that m is large enough so that a single polysoap forms numerous intrachain micelles. The amphiphilic monomers are characterized by the volume, v, and the length, l, of their hydrophobic tails. It is assumed that the amphiphilic monomers do not adsorb onto the backbone. For simplicity we limit the discussion to solutions of high ionic strength where long range electrostatic interactions are screened out.

2.1 The intrachain micelle

The structure of the intrachain micelles is reminiscent of that of micelles formed by monomeric, non-polymerized amphiphiles. The hydrophobic tails form an inner, dense core. The ionic head groups are localized at the core-water interface. The intrachain micelles are however surrounded by a swollen corona formed by the flexible, hydrophilic spacers joining the amphiphiles (Fig. 1). The corona of spherical micelles is similar to the corona of star polymers. It is thus convenient to describe the intrachain micelles by combining two models [5]: one is the phenomenological model of Israelachvili *et al.* for "simple" micelles [17]. The second is the Daoud-Cotton model for the corona of star polymers [18]. Within this approach the micelle is characterized by the area per head group, a. Because of the constant melt density of the core, a is related to the aggregation number, p, as $p \approx v^2/a^3$. The free energy per micellized amphiphile consists of four terms:

(i) the transfer free energy of the hydrophobic tail from water into the core, $-kT\delta$, where k is the Boltzman constant, T is the temperature and $\delta > 0$. This term does not affect the equilibrium structure of the micelles;
(ii) the surface free energy of the core water interface, γkTa where γ is the surface tension of the core boundary in units of inverse area. This term promotes micellar growth;
(iii) the screened electrostatic repulsion between the head-groups is introduced as K/a where K is a phenomenological constant that depends on T, the ionic strength and the nature of the head group. This term favors smaller micelles;
(iv) the last term, reflecting the repulsion between the coronal loops, is $kTp^{1/2} \ln R_{\text{corona}}$ where $R_{\text{corona}} \approx n^{3/5}p^{1/5}b$ is the span of the corona in a good solvent [19]. This term also favors smaller micelles.

The first three terms, on their own, describe a free micelle formed by unpolymerized amphiphiles. In the equilibrium state γkTa is comparable to K/a. This condition specifies the equilibrium area per head-group in free micelles, $a_o \approx \sqrt{K/\gamma}$. It is convenient to use the equilibrated free micelles as a reference state. It specifies a size scale, a_o or $p_o \approx v^2/a_o^3$ and an energy scale, γa_o. In turn, this suggests a dimensionless variable $u = p/p_o \approx (a_o/a)^3$. Utilizing the packing condition $p \approx v^2/a^3$ it is possible to express the free energy per amphiphile in an intrachain micelle as

$$\epsilon/kT \approx -\delta + \gamma a_o(u^{-1/3} + u^{1/3} + \kappa u^{1/2}). \qquad (1)$$

The $u^{-1/3}$ term reflects the surface contribution, $u^{1/3}$ allows for the head-group repulsion while the last term, $\kappa u^{1/2}$, is due to the coronal contribution. Here $\kappa \approx kTp_o^{1/2}\ln n/\gamma a_o$ is a dimensionless parameter, the ratio of the coronal and the head-group penalties when $a = a_o$. κ measures the relative importance of the coronal term in comparison to γa_o. Because the corona is large compared to the core, the intrachain micelles are typically larger than the corresponding free micelles. However, the equilibrium aggregation number of intrachain micelles, p_{eq}, is always smaller because of the coronal penalty. The importance of this last effect is determined by κ. When $\kappa \ll 1$ the coronal penalty is negligible and $u_{\mathrm{eq}} \approx 1$. In this case the equilibrium area per head group in the intrachain micelle, a_{eq}, is essentially that of a free micelle, that is $a_{\mathrm{eq}} \approx a_o$. The aggregation numbers are also comparable $p_{\mathrm{eq}} \approx p_o$. In the opposite limit, when $\kappa \gg 1$, the equilibrium aggregation number is much smaller. The coronal term, $\kappa u^{1/2}$, is comparable to the surface term, $u^{-1/3}$leading to $u_{\mathrm{eq}} \approx \kappa^{-6/5}$. Most of the following discussion is constructed so as to apply to arbitrary values of κ, provided that intrachain micellization is not repressed altogether. Accordingly it is helpful to simplify the notation. Unless stated otherwise, p and R_{micelle} will refer to the equilibrium values of the unperturbed micelles.

2.2 Micelle-micelle interactions

The corona of an intrachain micelle is structurally similar to the corona of a star. The interactions between the two types of coronas are however qualitatively different. The interaction between two star polymers in a good solvent is purely repulsive. The onset of the repulsion occurs when the coronas are at grazing contact. Closer approach increases the number of repulsive monomer-monomer interactions giving rise to a free energy penalty

$$\Delta F_r/kT \approx p^{3/2}\ln R_{\mathrm{corona}}/D \qquad (2)$$

where $2D$ is the distance between the two centers [20]. In marked distinction, the interaction between the coronas of intrachain micelles result from the superposition of two contributions. First, the "osmotic" repulsion discussed above. Second, an entropic attraction due to the exchange of amphiphiles between the two micelles. Exchange of amphiphiles between simple micelles can take place at any range, even when the distance between the micelles is very large. On the other hand, exchange of polymerized amphiphiles between intrachain micelles can only take place at a finite range because the amphiphiles are joined by spacer chains. The length of the spacers, nb, sets an effective maximal range. The optimal range is $D \approx R_{\mathrm{corona}}$, at grazing contact, so as to avoid stretching the spacer chains and the associated elastic penalty. Such an exchange results in a gain of mixing free energy of roughly $kT\ln 2$ per amphiphile [21]. If all p amphiphiles can exchange, the micelles gain roughly pkT by being at grazing contact while losing only kT of translational entropy. The number of amphiphiles that can undergo exchange when the micelles are at grazing contact is actually smaller. Only the amphiphiles with spacer chains whose midpoints are in the overlap region can exchange without incurring an elastic penalty. A simple estimate of the associated exchange attraction proceeds as follows [5]. The two micellar coronas can interpenetrate up to a depth comparable to the size of the outmost coronal blob $\xi_o \approx R_{\mathrm{corona}}/p^{1/2}$. The free energy penalty associated with such overlap is roughly kT. Such overlap gives rise to a contact area of $A \approx R_{\mathrm{corona}}\,\xi_o$ between the coronas. The end points of the arms of stars tend to be localized at the periphery of the corona. Similar effect is expected for the midpoints of the loops. Accordingly, each ξ_o blob contains a single midpoint. Thus, the number of midpoints in the overlap region is $A/\xi_o^2 \approx p^{1/2}$ and the corresponding exchange free energy is

$$\Delta F_{\mathrm{ex}}/kT \approx -p^{1/2}. \qquad (3)$$

In turn, ΔF_{ex} gives rise to a negative second virial coefficient for micelle-micelle interactions, $B < 0$, whenever $p > 1$. Thus polysoaps experience poor solvent conditions even though the backbone is hydrophilic. Accordingly, polysoaps with $m \gtrsim p$ are expected to precipitate. Long polysoaps, with $m/p \gg 1$ are also expected to exhibit collapsed configurations. It is however important to note an important difference between the situation described above and that of "simple" flexible homopolymers in poor solvents. The attraction between monomers in a poor solvent is instantaneous. The exchange attraction between micelles is not. The exchange is an activation process involving the expulsion of a hydrophobic tail out of the micellar core and into the aqueous medium. The associated characteristic time scales as $\tau \approx \exp(-\delta)$ and is thus tunable by varying the length of the tail. The exchange interaction is only relevant when the observation time is much longer than τ.

2.3 Large scale, tertiary, structure

There is a clear hierarchy in the intrachain self assembly of polysoaps. A short polysoap forms a single intrachain micelle. Long polysoap can form numerous intrachain micelles. In such a case it is useful to distinguish between three levels of the hierarchy of self assembly [4,5]. As in protein science it is convenient to refer to the chemical sequence as primary structure. The next level, the secondary structure, consists of the intrachain micelles. The configuration of the string of micelles defines the tertiary, large scale, structure. Three extreme scenarios may be envisioned for the tertiary structure: a linear string, a branched one and a spherical globule of close packed micelles. The globular, collapsed, state is thermodynamically favored when the exchange attraction is important. The discussion of the deformation behavior, in Section 3, concerns this last state. To introduce the necessary background we focus primarily on the linear string and the globular state.

A linear string of micelles is expected to behave as a self avoiding chain where micelles play the role of monomers. The span of the linear string is

$$R_{\rm string} \approx (m/p)^{3/5} R_{\rm micelle}. \tag{4}$$

Typically the span of the corona is much larger than the radius of the core and the size of the micelle is $R_{\rm micelle} \approx R_{\rm corona}$. The globular state is analogous to the collapsed configuration of a flexible homopolymer. Because the second virial coefficient for micelle-micelle interactions is strongly negative the polysoap forms a spherical globule of close packed micelles with a radius

$$R_{\rm globule} \approx (m/p)^{1/3} R_{\rm micelle}. \tag{5}$$

In this context the intrachain micelles are analogous to collapse blobs. It is possible to assign an effective surface tension, $kT\gamma_{\rm g}$, to the boundary of the globule. It is traceable to the inability of the outermost micelles to undergo exchange interactions at the exterior boundary of the globule. The resulting excess free energy is roughly $p^{1/2}kT$ per micelle leading to

$$\gamma_{\rm g}/kT \approx p^{1/2}/R^2_{\rm micelle}. \tag{6}$$

Before we proceed, it is important to note three features that distinguish the globular form of polysoaps from the collapsed state of flexible homopolymers. First, while the polysoap chain is globally collapsed, $R_{\rm globule} \sim m^{1/3}$, the coronas of constituting micelles are swollen *i.e.*, on length scales smaller than $R_{\rm micelle}$ the density is not uniform. Second, as noted previously, the exchange attraction is an activation process and metastable, non-globular configurations are possible. Finally, $\gamma_{\rm g} \sim p^{1/10}/n^{6/5}$ depends not only on T but also on n. It thus possible to tune $\gamma_{\rm g}$ by changing the length of the spacer chains.

As was noted earlier, other metastable configurations can be adopted by the string of micelles. Of these, the randomly branched configuration is entropically favored. The globular, collapsed state of the branched configuration is identical to that reached by a linear string. Both are characterized by $R_{\rm globule}$ and $\gamma_{\rm g}$ given earlier. However, the underlying topology is different, an issue that will be addressed later.

3 Extension of globular polysoaps

The distinctive features of the elasticity of polysoaps arise because of the coupling of the strain to the "internal" degrees of freedom associated with the secondary and tertiary structure. Both the tertiary and the secondary structure can re-equilibrate thus affecting the corresponding force law according to the Le Chatelier principle. For weak deformations only the tertiary, large scale, structure is affected. In particular, the globule unfolds into a string of micelles. Stronger deformations couple with the secondary structure, the intrachain micelles, by favoring micellar dissociation. In the case considered, when the number of intrachain micelles, m/p, is large and $R_{\rm globule} \gg R_{\rm micelle}$, the two process involved well separated length and force scales.

The extension of the globular configuration is similar to the stretching of a collapsed flexible chain [6,7]. The spherical form of the globule is initially deformed into an ellipsoid while maintaining constant volume corresponding to close packing of the intrachain micelles. Within this linear response regime the free energy penalty incurred is due to the increase of the surface free energy

$$F/kT \approx \gamma_{\rm g} \Delta A \approx \gamma_{\rm g}(R - R_{\rm globule})^2 \tag{7}$$

where $\Delta A \approx (R - R_{\rm globule})^2$ is the surface area increment associated with the deformation. The corresponding restoring force, $f = -\partial F/\partial R$, is proportional to the strain, $(R - R_{\rm globule})$

$$f/kT \approx -\gamma_{\rm g}(R - R_{\rm globule}). \tag{8}$$

This type of process can not proceed indefinitely. If pursued, the distorted globule will assume a cylindrical shape and, eventually, form a string of micelles. This scenario gives rise to a van der Waals loop in the fR diagram. This is indicative of instability with respect to a coexistence of a weakly elongated globule and a stretched string of micelles. The effect is reminiscent of the Rayleigh-Plateau instability [22] involving the break up of a fluid jet into a succession of droplets. The occurrence of a van der Waals loop suggests the onset of a globule-string coexistence. Within the coexistence regime the chain comprises of a string of m'/p micelles and a roughly spherical globule of $(m - m')/p$ micelles. The free energy of this configuration is roughly

$$F/kT \approx \gamma_{\rm g} R^2_{\rm micelle} \left[\left(\frac{m - m'}{p} \right)^{2/3} + \frac{m'}{p} \right] \tag{9}$$

where the first term reflects the surface free energy of the globule and the second the stretching energy of the micellar string. The end to end distance is

$$R \approx R_{\rm micelle} \left[\left(\frac{m - m'}{p} \right)^{1/3} + \frac{m'}{p} \right]. \tag{10}$$

Here the first term is the radius of the globule and the second is the span of the stretched string of micelles. When m' is sufficiently large we may approximate dR as $R_{\rm micelle}{\rm d}m'/p$ and the corresponding force law, $f = -\partial F/\partial R$, is

$$f/kT \approx -\gamma_{\rm g} R^2_{\rm micelle} \left(R^{-1}_{\rm micelle} - r^{-1}_{\rm globule} \right) \tag{11}$$

where $r_{\text{globule}} \approx R_{\text{micelle}}\left(\frac{m-m'}{p}\right)^{1/3}$ denotes the radius of the partialy depleted globule. It is important to note that f decreases as r_{globule} approaches R_{micelle}. As a result different scenarios are expected for the $f = const'$ and the $R = const'$ ensembles. In the first case the globule unravels completely once a critical force, $f_c/kT \approx \gamma_g R_{\text{micelle}} \approx p^{1/2}/R_{\text{micelle}}$, is applied. No globule-coil coexistence is expected. Such a coexistence is however expected when the end to end distance is imposed (Fig. 2). In this case the tension in the string is f_c. The onset of the coexistence occurs when $R \approx R_{\text{globule}} + R_{\text{micelle}}$ as seen by equating f_c/kT to (8). The upper boundary of this regime corresponds to a fully extended string of micelles, $R_{\max} \approx (m/p)R_{\text{micelle}}$.

Some insight regarding f_c may be gained by noting that the corresponding tensile energy per micelle, $f_c R_{\text{micelle}}$, is comparable to the exchange free energy of a micelle at the surface of the globule, $p^{1/2}kT$. It is useful to note that f_c may also be expressed as $f_c/kT \approx 1/\xi_o$ where ξ_o is the size of the outermost coronal blob, $\xi_o \approx R_{\text{micelle}}/p^{1/2}$. Thus f_c is comparable to the tension at the periphery of the unperturbed corona due to the crowding induced stretching of the loops. Hence, subjecting the string of micelles to a tension f_c does not perturb the micellar structure.

Further extension of the unraveled string of micelles is accommodate first by stretching the bridges between the intrachain micelles. Eventually it enforces the dissociation of some of the micelles. This coexistence regime ends when all the micelles are dissociated and the chain deformation proceeds as in a "simple" flexible chain. The free energy of the chain in the stretched bridges regime is

$$F_B/kT \approx m\epsilon_o + (R/R_B)^{5/2}. \tag{12}$$

The first term allows for the lowered free energy of amphiphiles incorporated into unperturbed micelles while the second accounts for the Pincus elastic penalty [23,24] due to the strong stretching of the micellar string. This regime involves strong stretching of m/p bridges comprising each of n monomers. Consequently, the "elastic constant" is specified by $R_B \approx (mn/p)^{3/5}b$. The corresponding force law is

$$f/kT \approx (R/R_B)^{3/2}R_B^{-1}. \tag{13}$$

This regime lasts while the elastic penalty, $(R/R_B)^{5/2}$, is small compared to $m\epsilon_o$, *i.e.,* when $\tau_b \approx (m\gamma a_o)^{-1}(R/R_B)^{5/2} \ll 1$. The micellar structure within this regime is only weakly perturbed. Upon further extension of the chain the elastic penalty couples strongly with the micellar structure and $\tau_b \approx 1$. In this situation it is no longer possible to view the chain as a uniform string of intrachain micelles. Rather, the extension is associated with a coexistence of intrachain micelles and dissociated amphiphiles. The detailed analysis of this scenario is somewhat tedious. The essential features of this regime may be recovered using a simple argument [10]. Two free energies are involved. One is the free energy (12), of a string of micelles in the stretched bridges regime, F_B. The second is the free energy of a fully dissociated, strongly stretched chain $F_{\text{dis}}/kT \approx (R/R_F)^{5/2}$, where $R_F \approx (mn)^{3/5}b \approx p^{3/5}R_B$ is the Flory radius of the flexible, swollen backbone. The bottom of the free energy curve F_B is located at $R_B < R_F$ and is $m|\epsilon_o|$ below the minimum of F_{dis}. For small R, F_B is lower than F_{dis}. However, $R_B < R_F$ and thus the "spring constant" of the fully dissociated chain is weaker. Consequently, the two curves cross at $R_{\text{co}} \approx R_F[m|\epsilon_o|/(p^{3/2}-1)]^{2/5}$. For $R > R_{\text{co}}$ the fully dissociated chain is of lower free energy. The cross over of the free energy curves is a rough indicator for a first order phase transition involving a coexistence between micellized and dissociated amphiphiles. This simple view suggests that the coexistence regime is associated with a plateau in the force law with $f_{\text{co}} \sim R^o$. Strictly speaking, this simple view is wrong. Since the interactions in this system are short ranged, the mixing entropy of the one dimensional mixture of micelles and dissociated amphiphiles disallows a first order phase transition [25]. As a result the tension in the plateau regime is not independent of R. It exhibits instead a weak logarithmic dependence. The cross over regimes at the boundaries of the coexistence regime are also smoothed out. Nevertheless, the force diagram obtained by ignoring the mixing entropy, the $S_{\text{mix}} = 0$ approximation, yields the correct tension and length scales. These can be obtained by the following simple argument. The onset of micellar dissociation is expected to occur when the elastic energy of the stretched bridges is comparable to the micellization free energy of an amphiphile incorporated into an unperturbed micelle. Denoting the span of a stretched bridge by r_{co} we have

$$f_{\text{co}}r_{\text{co}} \approx kT\epsilon_o \approx kT(\gamma a_o - \delta). \tag{14}$$

Since the bridge is strongly stretched the Pincus force law applies [23,24]. Consequently,

$$r_{\text{co}} \approx nb(f_{\text{co}}b/kT)^{2/3}. \tag{15}$$

The combination of (14) and (15) yields

$$f_{\text{co}}b/kT \approx (\mid \epsilon_o \mid /n)^{3/5}. \tag{16}$$

The coexistence regime, within the $S_{\text{mix}} = 0$ approximation, when $f_{\text{co}} \sim R^o$, occurs in a sharply defined range, $R_L < R < R_U$. These boundaries are smeared out when mixing entropy is allowed for. Nevertheless, R_L and R_U provide a good approximation for the boundaries of this regime. To obtain R_L we utilize (13) in the form $f_{\text{co}}/kT \approx (R_L/R_B)^{3/2}R_B^{-1}$ leading to

$$R_L \approx R_B\left(\frac{f_{\text{co}}R_B}{kT}\right)^{2/3}. \tag{17}$$

Similarly we obtain R_U from the force law of the fully dissociated chain, $f_{\text{co}}/kT \approx (R_U/R_F)^{3/2}R_F^{-1}$ leading to

$$R_U \approx R_F\left(\frac{f_{\text{co}}R_F}{kT}\right)^{2/3} \approx pR_L. \tag{18}$$

For $R > R_\mathrm{U}$ all amphiphiles are fully dissociated, there is no trace of the intrachain self assembly and the corresponding force law is

$$f/kT \approx (R/R_\mathrm{F})^{3/2} R_\mathrm{F}^{-1}. \tag{19}$$

Our initial considerations, concerning the globule and its unraveling, followed the discussion of the deformation behavior of a collapsed homopolymer. The collapsed globule is implicitly assumed to be a closely packed linear string of micelles. Such view is meaningless in view of the exchange interactions favoring the globular state. With these in mind it is impossible to assign an amphiphile to a specific micelle and the "topology" of the micellar string is not defined. However, the validity of our analysis does not depend on the topology of the micellar string within the globule. It only requires that the extension is slow enough to allow for the repartioning of the amphiphiles into the "tadpole" configuration obtained in the coexistence regime. This is certainly the case for the equilibrium force laws considered.

Altogether, the extension of a globular polysoaps involves the following regimes. Initially, the extension behavior is similar to that of a collapsed homopolymer. In this range the micelles may be considered as effective monomers. Their structure is unaffected. The globule is first deformed into ellipsoid. Stronger extension results in globule-string coexistence. Eventually, the globule disappears. For stronger extension the micelles can not be considered as monomers of fixed structure. The strain affects their structure. This results in coexistence of dissociated amphiphiles and weakly perturbed micelles. When all the micelles are dissociated the extension behavior reflects the elasticity of the backbone.

4 Compression of a globular polysoap

The confinement behavior of a globular polysoap is not as rich as in the extension case. No coexistence is expected and the force laws do not exhibit plateaus. We can distinguish a number of regimes, characterized by different force laws. These reflect, as in the extension case, coupling to the different levels of the intrachain self organization *i.e.,* globule and micelles. With this in mind we can distinguish between two main regimes. When the distance between the confining plates, D, is in the range $R_\mathrm{globule} \gg D \gg R_\mathrm{micelle}$, the confinement does not affect the micellar structure. In this range only the globular organization is modified. In the range $R_\mathrm{micelle} \gg D \gg b$ the micellar structure is strongly affected.

In the weak confinement regime, $R_\mathrm{globule} > D \gg R_\mathrm{micelle}$, the globule changes its shape while retaining a constant volume $V_\mathrm{globule} \approx (m/p)R^3_\mathrm{micelle}$. For simplicity we focus on the case of inert confining surfaces *i.e.,* non penetrable surfaces that are neither attractive nor repulsive so that the globule surface tension at the wall remains γ_g. Initially, in the linear response regime, it is transformed into an oblate ellipsoid. The resulting change in the surface area of the globule is $\Delta A \approx (R_\mathrm{globule} - D)^2$. The corresponding free energy penalty is

$$F/kT \approx \gamma_\mathrm{g}(R_\mathrm{globule} - D)^2 \tag{20}$$

and the associated restoring force, $f = -\partial F/\partial D$, is

$$f/kT \approx \gamma_\mathrm{g}(R_\mathrm{globule} - D). \tag{21}$$

This force law applies when $R_\mathrm{globule} - D \ll R_\mathrm{globule}$. When $D \ll R_\mathrm{globule}$ the strongly confined globule assumes a disk like shape, with an in-plane radius d specified by $d^2 D \approx V_\mathrm{globule}$. In this regime the dominant contribution to the surface area of the globule is $\Delta A \approx d^2$. The associated free energy penalty, $\gamma_\mathrm{g}\Delta A$, is

$$F/kT \approx \frac{\gamma_\mathrm{g} V_\mathrm{globule}}{D} \approx \frac{m}{p^{1/2}} \frac{R_\mathrm{micelle}}{D} \tag{22}$$

and the resulting restoring force is

$$f/kT \approx \gamma_\mathrm{g} V_\mathrm{globule}/D^2. \tag{23}$$

The claim that the micellar structure is unperturbed in this regime is justified by considering the ratio of the free energy (22) and the free energy of the amphiphiles in an unperturbed micelle, $m\epsilon_o$. This perturbation parameter, $t \approx R_\mathrm{micelle}/D\epsilon_o p^{1/2}$, is indeed small while $D \gg R_\mathrm{micelle}$. Strong confinement, $D \ll R_\mathrm{micelle}$, does affect the micellar structure. In this range the restoring force is dominated by the additive elastic response of the individual micelles. The relevant regimes appear also in the confinement of a linear string of micelles [9]. For brevity we quote the results with a few explanatory notes. Initially, while $D > (n/p)^{3/5} b$, the micellar confinement does not affect the aggregation number. Such weak coronal confinement is associated with a penalty of

$$F/kT \approx p^{3/2} \left(\frac{R_\mathrm{micelle}}{D}\right)^{5/8} \tag{24}$$

per micelle [26]. Accordingly, the force law per polysoap is

$$f/kT \approx \frac{m p^{1/2}}{R_\mathrm{micelle}} \left(\frac{R_\mathrm{micelle}}{D}\right)^{13/8}. \tag{25}$$

Upon further confinement the perturbation parameter grows. When $t \geqslant 1$ the deformation couples strongly to the micellar structure. In this regime the dominant penalty term, due to the micellar confinement, favors smaller micelles. Accordingly, the aggregation number is no longer the equilibrium value characterizing unperturbed micelles. The regimes summarized in the following correspond to the case of $\kappa \ll 1$. In this limit $p \sim (D/R_\mathrm{micelle})^{15/23}$ and the confinement penalty of the polysoap is

$$F/kT \approx m\gamma a_o \left(\frac{\ln n}{\kappa}\right)^{8/23} \left(\frac{R_\mathrm{micelle}}{D}\right)^{5/23} \tag{26}$$

leading to

$$f/kT \approx \frac{m\gamma a_o}{R_{\rm micelle}} \left(\frac{\ln n}{\kappa}\right)^{8/23} \left(\frac{R_{\rm micelle}}{D}\right)^{28/23}. \qquad (27)$$

Finally, in the range $(n/p)^{3/5}b > D > r_{\rm core}$ the aggregation number decreases logarithmically with D and the leading confinement penalty is [27]

$$F/kT \approx p^{2/3}(R_{\rm F}/D)^{5/3} \qquad (28)$$

while the restoring force is

$$f/kT \approx \frac{p^{2/3}}{R_{\rm F}} \left(\frac{R_{\rm F}}{D}\right)^{8/3}. \qquad (29)$$

Qualitatively similar scenario is obtained in the $\kappa \gg 1$ limit.

The weak compression of a globular polysoap is opposed by the surface free energy. It is reminiscent of the confinement of a fluid droplet. In this regime the micelles may be viewed as effective monomers of fixed structure. Stronger deformation, when $D < R_{\rm micelle}$, affect the micellar structure. At first the micellar corona is weakly compressed with no effect on the aggregation number. Stronger compression favors decrease in p.

5 Extensional flow: a globule-stretch transition

In the situations considered thus far the "static" extension behavior was studied *i.e.,* the end to end distance or the tension were externally imposed. Such is the case in optical tweezers experiments, for example. Extension can also be induced by appropriate flow fields. In these experiments one controls the characteristics of the flow, shear rate, velocity, etc. The tension in the chain is due to a hydrodynamic drag force coupling the flow field and the configurations of the chain. The coupling changes with the configuration and abrupt configurational transitions can occur. In the following we will consider the stretching of a globular polysoap by an extensional flow field corresponding to stationary longitudinal shear. In this case the two plateau regimes merge and the polysoap undergoes a single globule-stretch transition. For comparison purposes we first recall, following de Gennes [24], the behavior of "simple" flexible chains subjected such flow field in a good solvent.

The extensional flow field is specified by the Cartesian components

$$\begin{aligned} v_x &= sx, \\ v_y &= -sy/2, \\ v_z &= -sz/2. \end{aligned} \qquad (30)$$

The polymer is placed at the origin, at the stagnation point, and resides there for a time t. It is assumed that t is long compared to characteristic relaxation time of the polymer $t > \tau_{\rm F} \approx \eta R_{\rm F}^3/kT$. The chain is stretched along the x axis by the Stokes friction force. It is possible to distinguish between two limiting regimes. For strong shear, $s\tau_{\rm F} > 1$, the chain is deformed into a prolate ellipsoid. When the ellipsoid is highly extended it can be approximated as a cylinder of length r and diameter d. The frictional force acting on the cylinder is

$$k\eta v_x(x){\rm d}x = k\eta sx{\rm d}x \qquad (31)$$

per element of length dx placed at x. Here η is the viscosity of the solvent and $k = 2\pi/\ln(r/d)$ [28,29]. In the framework of a scaling analysis k may be treated as a constant. The frictional force experienced by the chain is thus

$$f = \int_{-r}^{r} k\eta sx{\rm d}x \approx k\eta sr^2. \qquad (32)$$

As we shall see, an abrupt coil-stretch configurational transition is expected as the shear rate, s, increases. Force balance consideration are insufficient in order to analyze this transition. Towards this end it is necessary to construct the corresponding free energy. This is possible since the flow field is stationary and the resulting drag force can be obtained from the Kramers potential, $F_{\rm Kramers}$. The drag force is given by $f = -\partial F_{\rm Kramers}/\partial r$ where $F_{\rm Kramers} \approx -k\eta sr^3$. It is convenient to express $F_{\rm Kramers}$ in terms of the Zimm relaxation time of the swollen coil $\tau_{\rm F} \approx \eta R_{\rm F}^3/kT$

$$F_{\rm Kramers}/kT \approx -s\tau_{\rm F}\lambda^3 \qquad (33)$$

where $\lambda = r/R_{\rm F} > 1$. The extension of the coil is opposed by the elasticity of the chain. In the strong extension regime the Pincus elastic penalty is applicable

$$F_{\rm el}/kT \approx \lambda^{5/2}. \qquad (34)$$

The total free energy for strong shear, high s, is thus

$$F/kT \approx \lambda^{5/2} - s\tau_{\rm F}\lambda^3. \qquad (35)$$

Eventually, for strong extensions, the finite extensibility of the chain gives rise to a steeper λ dependence. Our discussion will be based on equation (35). It is however important to note the behavior of F for the full shear range. In the weak shear regime, while the chain is weakly stretched, the frictional force is well approximated by the Stokes law for the non-draining coil $f \approx -\eta sR_{\rm F}^2$. The corresponding Kramers potential is $F_{\rm Kramers}/kT \approx -s\tau_{\rm F}\lambda$ while the elastic penalty, in the linear response regime, is $F_{\rm el}/kT \approx \lambda^2$. Note that for $\lambda < 1$ this term is supplemented by a penalty opposing over-proximity of the end points of the coil. Altogether, for small s, $F/kT \approx \lambda^2 - s\tau_{\rm F}\lambda$. Altogether, F can exhibit two distinct minima. For weak shear, low s, the minimum occurs at $\lambda \approx 1$, corresponding to the unperturbed coil, $R_{\rm F} \approx N^{3/5}b$. As s increases, a second minima corresponding to extended configuration develops. Initially the two minima are separated by a high potential barrier preventing the coil-stretch transition. As s increases the barrier shrinks and its position shifts towards

$\lambda \approx 1$. The onset of the coil stretch transition, s_c, may be identified with the disappearance of the barrier. For $s > s_c$ only the second minima, corresponding to $R \sim N$ survives. It is possible to obtain a rough estimate of s_c by analyzing (35). It exhibits a barrier of height $F_{\text{barrier}}/kT \approx (s\tau_F)^{-5}$ at $\lambda_{\text{barrier}} \approx (s\tau_F)^{-3}$. The critical s_c may be identified as

$$s_c \approx 1/\tau_F \tag{36}$$

when $F_{\text{barrier}}/kT \approx 1$ and $\lambda_{\text{barrier}} \approx 1$.

The "static" extension of a "simple" coil, in the absence of the extensional flow field, proceeds smoothly. The initial chain extension follows $F_{\text{el}}/kT \approx \lambda^2$ while stronger extension is described by the Pincus free energy $F_{\text{el}}/kT \approx \lambda^{5/2}$. The corresponding free energy curve exhibits a single minima at $\lambda \approx 1$. No abrupt transition occurs. The coil-stretch transition in a flow field occurs because the hydrodynamic drag force, as described by F_{Kramers}, modifies the free energy curve giving rise to a second minima at $\lambda \gg 1$. This is due to the sharp increase in the frictional force, $\sim \lambda^2$, as the chain is extended. The topography of the free energy curve as s varies determines s_c. The situation is qualitatively different for globular chains. In this case an abrupt configurational transition is expected under "static" conditions, in the absence of a flow field. Consequently it is possible to obtain s_c from force balance considerations. For collapsed homopolymers there is single s_c corresponding to the unraveling of the globule into a stretched coil [30]. In the case of globular polysoaps one may initially expect two critical s, corresponding respectively to: (i) the unraveling of the globule into a stretched string of micelles and (ii) the extension induced dissociation of the of the intrachain micelles. As we shall see this is not the case. The critical shear associated with the unraveling of the globule produces a fully dissociated stretched coil.

The s_c corresponding to the unraveling of the globular polysoap is obtained by balancing the associated tension, $f_c/kT \approx \gamma_g R_{\text{micelle}}$, with the frictional Stokes force acting on the globule whose radius is $R_{\text{globule}} \approx (m/p)^{1/3} R_{\text{micelle}}$. The frictional coefficient of the globule is ηR_{globule} and thus

$$f_c/kT \approx s\eta R^2_{\text{globule}}/kT \tag{37}$$

leading to

$$s_c \eta R^3_{\text{micelle}}/kT \approx p^{7/6}/m^{2/3}. \tag{38}$$

The critical tension in the chain induces full dissociation. This can be seen by comparing f_{co}, as given by (16), to the tension experienced by a fully extended chain of micelles at s_c given by (38). The length of the extended string is $R_{\max} \approx (m/p)R_{\text{micelle}}$, and the corresponding tension is $\eta s_c R^2_{\max}$. The condition $(|\epsilon_o|/n)^{3/5} \approx \eta s_c R^2_{\max}/kT$ specifies $m_{\max}$

$$m_{\max} \approx (\mid \epsilon_o \mid /n)^{4/5} R^{3/2}_{\text{micelle}} p^{5/8} \approx (\mid \epsilon_o \mid)^{4/5} n^{1/10} p^{74/80} \tag{39}$$

such that the polysoap is fully dissociated at s_c if $m > m_{\max}$. Essentially, $m_{\max} \approx p$ and thus a string of $m/p \gg 1$ micelles will undergo a globule-stretch transition leading to complete dissociation when $s > s_c$. The essential physics is as follows. At s_c the drag force on the globule is f_c. This causes unraveling of the globule into a stretched string of micelles of length $R_{\max} \approx (m/p)R_{\text{micelle}}$. As the string unravels the drag force grows as λ^2 while the elastic restoring force grows less rapidly, as $\lambda^{3/2}$. Consequently, the chain extension proceeds further. At the plateau region, $R_L < R < R_U$, the situation is even more extreme because the elastic force grows as $\ln \lambda$. The equilibrium state is eventually reached, for a strongly extended dissociated chain, when finite extensibility effects give rise to a steeper growth of the elastic force.

6 Discussion

Long polysoaps exhibit a hierarchy of self assembly. A secondary structure, the intrachain micelle, is characterized by a short length scale and a relatively high energy scale. The tertiary structure, the configuration of the micellar string, exhibits a larger length scale and a lower energy scale. Both the energy and length scales are well separated in the case of long polysoaps. As a result the deformation behavior of long polysoaps exhibit two distinct regimes. Weak deformations couple to the tertiary structure while stronger strains couple to the secondary structure. In the case considered, of globular polysoaps, the weak deformation behavior is similar to the one predicted for collapsed, flexible homopolymers. The strong deformation scenario is identical to that predicted for linear strings of micelles. The two regimes merge for stretching induced by an extensional flow. In this case the chain undergoes a globule-stretch transition yielding a strongly extended, fully dissociated chain.

A similar separation of length and energy scales may occur in multidomain proteins. The force law characterizing the extension of the muscle protein Titin [15,16] is reminiscent of the force law predicted for polysoaps forming a linear string of micelles [10]. These considerations suggest that the extension behavior of globular multidomain proteins may prove similar to the scenario expected for globular polysoaps.

The discussion presented focused on the equilibrium deformation behavior of an isolated globule. This is appropriate as a first step in the exploration of this problem. A number of important effects were not considered. First, globular polysoaps tend to undergo phase separation involving a gel-like phase and a dilute solution of free globules. Second, finite rate of deformation may lead to hysteresis effects when the internal relaxation times are long. These may play an important role in experimental situations.

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19. We view the micellar corona as identical to the corona of a star with $2p$ arms comprising each of n monomers. The arms crowed each other. In order to lower the number of repulsive monomer-monomer contacts, the arms stretch in the radial direction. Within the Daoud-Cotton model such a corona is envisioned as an array of closed packed blobs arranged in concentric spherical shells. Each coronal chain contributes a single blob to each shell. The size of the blobs in a shell of radius r, $\xi(r)$, is specified by $r^2 \approx p\xi^2$ leading to $\xi \approx r/p^{1/2}$. The span of the corona is determined by the conservation of monomers condition $\int_{R_\text{core}}^{R_\text{corona}} g(r) r \xi^{-1} \mathrm{d}r \approx pn$ where $g(r) \approx (\xi/b)^{5/3}$ is the number of monomers per blob. In the limit of $R_\text{corona} \gg R_\text{core}$ this leads to $R_\text{corona} \approx n^{3/5} p^{1/5} b$. The free energy per arm as obtained by assigning kT to each blob is $\int_{R_\text{core}}^{R_\text{corona}} \xi^{-1} \mathrm{d}r \approx p^{1/2} \ln(R_\text{core} + R_\text{corona}/R_\text{core}) \approx p^{1/2} \ln n$.
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26. A highly simplified derivation of this term involves two steps. First, one obtains the inplane radius of the confined corona by minimizing the corresponding Flory free energy $F/kT \approx (pn)^2/R^2D + pR^2/nb^2$ thus obtaining $R/b \approx (pb/D)^{1/4} n^{3/4}$. This procedure is known to yield the correct coronal dimensions. However, the Flory free energy produces an overestimate of F. Accordingly, in the second step, we estimate F using the kT per blob prescription by viewing the corona as a closed packed array of impenetrable blobs of size $\xi \approx \phi^{-3/4} b$ where ϕ is the average monomer volume fraction in the corona $\phi \approx npb^3/DR^2$ thus leading to (24).
27. The confinement penalty reflects two contributions. One is due to the crowding of the coronal loops. As in the Daoud-Cotton model, this effect is quantified by allocating kT to each "concentration" blob allowing however for the confinement induced change of dimensionality. The second term is due to the confinement of the individual coronal loops and the resulting loss of configurational entropy. The loops are envisioned a sequence of "confinement" blobs of size D comprising each of $g \approx (D/b)^{5/3}$ monomers. The kT per blob prescription, $F/kT \approx np/g$ leads to (28).
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29. The frictional force experienced by a cylinder due to flow of velocity u parallel to its axis is ςu where ς is the frictional coefficient. ς of a cylinder oriented with the flow is well approximated by the frictional coefficient of a prolate ellipsoid of the same length and volume. Denoting the semi-axes of the ellipsoid by a and $b > a$ we have $a/b \approx r/d$. The frictional coefficient of the prolate ellipsoid is $\varsigma = 6\pi\eta R_o (1 - \frac{b^2}{a^2})^{1/2} (b/a)^{-2/3} [\ln(\frac{1+(1-b^2/a^2)^{1/2}}{b/a})]^{-1}$ where R_o is the radius of a sphere of identical volume. In the limit of $b \gg a$ this reduces to $\varsigma \approx \eta a/\ln(2a/b)$. The leading term, ηa, may be obtained by viewing the cylinder as string of spheres of radius d, each experiencing a frictional force of $\varsigma_\text{s} u$ where $\varsigma_\text{s} \approx \eta d$.
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