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Polysoaps and Biopolymers: The Effect of Secondary Structure on the Extension Elasticity

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Abstract: Extension of DNA and the protein titin reveals a plateau in the force *vs.* end-to-end distance diagram. A similar feature is predicted for the stretching elasticity of long polysoaps. These are linear hydrophilic chains that incorporate, at intervals, covalently bound amphiphilic monomers. In water, the amphiphilic monomers self-assemble into intrachain micelles thus endowing the chain with a secondary structure. The similarity in the force laws is traceable to the equilibration of the secondary structure. For polysoaps forming a linear string of micelles, the plateau is associated with a coexistence of weakly perturbed micelles and fully dissociated amphiphiles. Similar scenarios can be invoked to explain the behaviour of DNA and titin. The resulting functional form seems to depend only weakly on the precise nature of the system.

Introduction

Recent experimental developments, involving micropipets, laser twizzers and antibodies, enable the measurement of the force laws characterising the extension of certain biopolymers. So far, these studies have been conducted on DNA [1] and the muscle protein titin [2]. The plots of the force, f, versus end-to-end distance, R, reveal a novel feature. An initial regime, consistent with the behaviour of a worm-like chain, is followed by a weak plateau. In the weak plateau, the increase in f with R is much weaker than the $f \sim R$ typical of Gaussian elasticity. A similar force was recently predicted [3, 4, 5] for a family of synthetic polymer, polysoaps [6]. Polysoaps consist of a flexible hydrophilic backbone incorporating, at intervals, covalently bound amphiphilic monomers. As we will discuss, the similarity in the force laws is not spurious. It arises because polysoaps [7, 8], like DNA and proteins, undergo an intramolecular self-assembly leading to a hierarchy of self-organisation. In the following, we will briefly discuss the similarities between the configurations of polysoaps and of biopolymers. We then present a brief discussion of the plateau regime [3, 4].

Borrowing from the protein terminology, we may refer to the monomer sequence as *primary* structure. In water, the amphiphilic monomers self-assemble into intrachain micelles. These comprise of a dense core formed by the hydrophobic tails of the amphiphiles. The polar head groups straddle the core-water boundary. The structure of this inner

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part of the intrachain micelle is similar to the structure of micelles formed by monomeric amphiphiles [9]. The dense inner core is surrounded by a semidilute corona of swollen loops formed by the spacer chains upon aggregation. In the following, we limit the discussion to spherical intrachain micelles. In this case the structure of the corona is reminiscent of star-like polymers [10]. The intrachain micelles may be considered a *secondary* structure. When the number of amphiphiles in the chain, m, exceeds the equilibrium aggregation number of the intrachain micelles, p_{eq}, the polysoaps self-assemble into a string of micelles. In the case of long polysoaps, $m \gg p_{\text{eq}}$, the string may adopt numerous configurations. We refer to the configurations adopted by the string of micelles as *ternary* structure. The simplest configurations to envision are: a linear string, a randomly branched string and a spherical globule of closely packed micelles. This last configuration arises as a consequence of bridging attraction between different micelles due to the exchange of amphiphiles. In polysoaps, this gives rise to spacer chains that bridge different micelles. The globular state is predicted to be the most stable [8]. However, different configurations may occur as long-lived metastable states. This feature arises because configurational rearrangement is an activation process. It involves repartitioning of amphiphiles between different micelles. In turn, this involves, as an intermediate step, the expulsion of amphiphiles from existing micelles into the surrounding aqueous medium. As a result, the free energy surface characterising the configurational phase space of polysoaps is rugged. This feature has been occasionally used to define "complex systems" as opposed to simple systems whose free energy surface exhibits a single minimum [11]. A ruggedness of the free energy surface is also a characteristic of proteins. However, in this case, the ruggedness is due to frustration, a feature which is absent in simple polysoaps comprising a single type of amphiphilic monomers.

Proteins, like polysoaps, exhibit a hierarchy of intrachain self-organisation characterized by a rugged free energy surface. Before we discuss some more similarities, it is important to stress the limitations of this correspondence. Biopolymers, proteins and DNA incorporate a larger number of monomer units and a much richer repertoire of interactions. In this context, directed interactions, such as hydrogen bonds are of special importance. As a result, biopolymers can assume unique structures. In folded proteins, the positions of most atoms are uniquely specified. This detailed structure, and the associated functions, have no counterpart in polysoaps. However, other similarities do exist on a more "coarse-grained", large-scale level. Both proteins and polysoaps [7, 8] unfold, denature when treated with free surfactants. Polysoaps are predicted to undergo both cold and hot denaturation [12] as is the case for proteins, i.e. the self-organisation disappears both at high and low temperatures. The detailed features of the process for polysoaps and for proteins are different. The similarities are traceable to the key role of hydrophobic interactions in driving the self-assembly of the two types of macromolecules. Another common feature concerns the gelation behaviour. Polysoaps, like proteins, form physical gels. These involve secondary structures incorporating monomer units belonging to different polymers. This brings us to the similarity, noted earlier, in the extension elasticities. In the following, we will discuss the plateau regime expected when a *linear* string of spherical micelles is stretched.

The unperturbed polysoap

Our discussion focuses on polysoaps forming spherical, star-like micelles whose size is dominated by the corona. In a θ solvent, the size of such micelles, as given by a Flory-type theory [10], is $r_{\text{micelle}} \approx p^{1/4} n^{1/2} b$ where b is a characteristic monomer size. Modification of simple phenomenological model [9] yields the free energy per amphiphile in a micelle of aggregation number p, $\epsilon_p kT$ [7]

$$\epsilon_p \approx \gamma a_o (u^{-1/3} + u^{1/3} + \kappa u^{1/2}) - \delta \tag{1}$$

Here γkT is the surface tension of the water-core interface, a_o is the optimum area per head group in a micelle formed by non-polymerized amphiphiles and $-\delta kT$ is the transfer free energy of a hydrophobic tail from water into the micellar core. For spherical micelles, p is related to the volume of the hydrophobic tail, v, and to the area per head group, a, as $p \approx v^2/a^3$ and thus $p_o \approx v^2/a_o^3$. u is a dimensionless variable $u = p/p_o = (a_o/a)^3$. The $u^{-1/3}$ term allows for the interfacial free energy per head group and thus favours micellar growth. The repulsion between the head groups gives rise to the $u^{1/3}$ term. The third, $u^{1/2}$, term arises because of the repulsive interactions between the coronal loops. In a θ solvent, the free energy per loop is $F_{\text{corona}}/kT \approx p^{1/2}$ [10]. These last two terms reflect free energy penalties that oppose micellar growth. The relative importance of the penalty terms is determined by $\kappa \approx p_o^{1/2}/\gamma a_o$, the ratio of the coronal penalty and the head group repulsion at $a \approx a_o$. For brevity, we focus on the limit of $\kappa \ll 1$ when $p \approx p_o$ and $u \approx 1$. For $p \approx p_o$, $\epsilon_{p_o} \approx 2\gamma a_o - \delta$ and the critical micelle concentration X_{cmc}, is $\epsilon_{p_o} \approx \ln X_{\text{cmc}}$. It is important to note that a θ solvent for the backbone is, in effect, a good solvent for the string of micelles. The θ temperature for star polymers is lower than the θ temperature of the corresponding linear chain [13]. Accordingly, the micellar coronas do not interpenetrate significantly. A string of intrachain micelles is thus self-avoiding and its span is the Flory radius $R_{\text{F}}(p) \approx (m/p)^{3/5} r_{\text{micelle}}(p) \approx R_{\text{F}} u^{-7/20}$. Here $R_{\text{F}} \approx (m/p_o)^{3/5} r_{\text{micelle}}(p_o) \approx m^{3/5} n^{1/2} p_o^{-7/20} b$ is the Flory radius of a string of spherical intrachain micelles when $p \approx p_o$.

Our discussion is based on the assumption that all polymerized amphiphiles in the unperturbed chain are micellized. The validity of this assumption depends on m. It is untenable once m becomes larger than a certain m_u to be specified. For $m \approx m_u$, an average of one micelle per chain is fully dissociated. The underlying physics is as follows. The dissociation is favoured by the mixing entropy of the one-dimensional mixture of micelles and dissociated amphiphiles, S_{mix}. In turn, the importance of this mixing entropy grows with m. To specify m_u, it is first necessary to obtain an explicit expression for S_{mix} as a function of the fraction of associated amphiphiles, ψ. This involves inscription of the micelles and the dissociated amphiphiles on a one-dimensional lattice comprising M_ψ sites. The distinctive feature of this system is that M_ψ varies with ψ. Since the number of micelles is $\psi m/p_o$ and the number of dissociated amphiphiles is $m(1-\psi)$, $M_\psi \approx m(1-\psi)+\psi m/p_o$. The associated $S_{\text{mix}}(\psi)$ is the ideal mixing entropy $S_{\text{mix}}/k = -M_\psi[Y \ln Y + (1-Y)\ln(1-Y)]$ where Y is the fraction of sites occupied by micelles, $Y \approx \psi m/p_o M_\psi$. This leads to

$$S_{\text{mix}}(\psi)/k \approx \frac{\psi m}{p_o}\ln[1+\frac{p_o(1-\psi)}{\psi}] + m(1-\psi)\ln[1+\frac{\psi}{p_o(1-\psi)}] \tag{2}$$

For future reference, it is useful to provide the expression for $S'_{\text{mix}} \equiv \mathrm{d}S_{\text{mix}}/\mathrm{d}\psi$

$$S'_{\text{mix}}(\psi)/k \approx \frac{m}{p_o}\ln[1+\frac{p_o(1-\psi)}{\psi}] - m\ln[1+\frac{\psi}{p_o(1-\psi)}] \tag{3}$$

The free energy of a partially dissociated chain of micelles is $F_{\text{chain}}/kT = m\psi\epsilon_{p_o} - S_{\text{mix}}(\psi)/k$ describing an ideal one-dimensional mixture of dissociated amphiphiles and intrachain micelles. To consider the onset of micelle dissociation, it is helpful to consider F_{chain} for $\psi \approx 1$ when $S_{\text{mix}}/k \approx -m(1-\psi)\ln p_o(1-\psi)$. It is convenient to write it as

$$F_{\text{chain}} \approx F_o + m|\epsilon_{p_o}|(1-\psi) + m(1-\psi)\ln p_o(1-\psi) \tag{4}$$

where $|\epsilon_{p_o}|$ is the free energy cost per polymerized amphiphiles for the dissociation of a single micelle. The form of F_{chain} is similar to that of the free energy used to demonstrate the impossibility of the coexistence of two semi-infinite phases in a one-dimensional system experiencing short-range interactions [14]. In the present case, we can identify the micellized and dissociated states with the two phases. The assumption of a fully micellized chain amounts to assuming a single, defect-free, one-dimensional phase of finite size. The equilibrium condition $\partial F_{\text{chain}}/\partial\psi = 0$ leads to $p_o\alpha(1-\psi) \approx \exp(-|\epsilon_{p_o}|)$. It is helpful to recast this result in terms of the average number of dissociated micelles per chain, n_{d}. This is related to ψ as $\psi \approx 1 - n_{\text{d}}p_o/m$ leading to $n_{\text{d}} \approx p_o^{-2}m\exp(-|\epsilon_{p_o}|)$. The condition $n_{\text{d}} = 1$ defines m_u

$$m_u \approx p_o^2 \exp(|\epsilon_{p_o}|) \tag{5}$$

and thus

$$n_{\text{d}} \approx m/m_u \tag{6}$$

The "single-phase approximation" is thus justified while $m \ll m_u$ or, equivalently, $n_{\rm d} \ll 1$. This condition is easily fulfilled since $m_u \gg 1$ because $p_o \gg 1$ and $X_{\rm cmc} \ll 1$.

Extension of linear string of micelles

The elasticity of a linear string of micelles is expected to reflect a coupling to its "internal degrees of freedom", i.e., the micellar structure. According to the Le Chatelier principle [14], the equilibration of the micellar structure should lower the tension in the chain [3, 4, 5]. To obtain an explicit force law, it is necessary to consider the statistical mechanics of the model. The simplest possible scenario involves uniform extension. It is assumed that the extension results only in repartitioning of the amphiphiles among a greater number of smaller micelles. The analysis of this scenario leads to an fR diagram exhibiting, for intermediate extensions, a van der Waals loop. This suggests that, for this range, weakly perturbed micelles coexist with fully dissociated amphiphiles. The weak and strong deformation behaviour is unmodified. The stretching free energy of the string, $F_{\rm el}$ may assume three forms. For weak deformations, when linear response is expected, $F_{\rm el} \approx [R/R_{\rm F}(p)]^2 \approx (R/R_{\rm F})^2 u^{7/10}$. This initial Gaussian $F_{\rm el}$ is replaced by the Pincus free energy [15], $F_{\rm el} \approx [R/R_{\rm F}(p)]^{5/2} \approx (R/R_{\rm F})^{5/2} u^{7/8}$ when $R \gg R_{\rm F}(p)$. Eventually, when R exceeds the length of the fully extended string of micelles, $R_{\rm max} \approx (m/p) r_{\rm micelle}(p)$, a third regime comes into play. In it, the bridges between the micelles are stretched. Since the backbone experiences a θ solvent, the stretching involves a linear string of m/p Gaussian bridges consisting each of n monomers. Consequently, $F_{\rm el}$ is Gaussian with $F_{\rm el} \approx [R/R_{\rm B}(p)]^2 \approx (R/R_{\rm B})^2 u$ where $R_{\rm B} \approx (m/p_o)^{1/2} n^{1/2} b$. The relative importance of the elastic penalty is measured by the dimensionless parameter $\tau(R)$. $\tau(R) \approx F_{\rm el}(p_o)/kT\gamma a_o m$ is the ratio of the chain elastic energy and $m\epsilon_p$ for $p \approx p_o$ and a given R. The boundary of the instable region is identified by $\tau(R_*) \approx 1$. It occurs in the stretched bridges regime, for $R_* \approx R_{\rm B}(m\gamma a_o)^{1/2}$ and $f_* \approx (m\gamma a_o)^{1/2}/R_{\rm B}$.

When the role of $S_{\rm mix}$ is ignored, the coexistence regime exhibits features reminiscent of a first-order phase transition. In particular $f \sim R^o$. Physical insight concerning this behaviour may be gained by considering two free energies: the free energy of a stretched, fully dissociated chain, $F_{\rm dis}$, and the free energy of an extended string of unperturbed micelles in the stretched bridges regime, $F_{\rm B}$. In the stretched bridges regime, the leading contributions are $F_{\rm B}/kT \approx m\epsilon_{p_o} + (R/R_{\rm B})^2$. The fully dissociated chain is described by $F_{\rm dis}/kT \approx (R/R_o)^2$. The bottom of the free energy curve described by $F_{\rm B}$ is located at $R_{\rm B} < R_o$ and is $m|\epsilon_{p_o}|$ below the minimum of $F_{\rm dis}$. For weak extensions, $F_{\rm B}$ is lower than $F_{\rm dis}$. However, $R_{\rm B} < R_o$ and thus the spring constant of the fully dissociated chain is weaker. Consequently, the two curves cross at $R_{\rm co}$ specified by $F_{\rm B} \approx F_{\rm dis}$ or $R_{\rm co} \approx$

$R_o[m|\epsilon_{p_o}|/(p_o-1)]^{1/2}$. For $R < R_{\rm co}$ the string of micelles is of lower free energy while for $R > R_{\rm co}$, the lower free energy corresponds to the fully dissociated chain. This cross-over is a rough diagnostic for a first-order phase transition. This rough argument locates the cross-over at $R_{\rm co} \approx (R_{\rm U}R_{\rm L})^{1/2}$. The peak of the "spinodal curve" $R_o < R_* < R_{\rm co}$ corresponds to $(R/R_{\rm B})^2 \approx m|\epsilon_{p_o}|$, i.e., when the free energy of the micellar string is equal to the minimal free energy of the dissociated chain. A more detailed analysis proceeds as follows. At coexistence, only a fraction, $0 < \psi < 1$, of the amphiphiles will be incorporated into micelles. Thus, ψm amphiphiles will form weakly perturbed intrachain micelles while the remaining $(1-\psi)m$ surfactants will be dissociated. Since the onset of coexistence is expected to occur at $f_{\rm co} \ll f_*$, we neglect the weak perturbation of the micellar structure and assume $u \approx 1$ or $p \approx p_o$. In a θ solvent, for a given R and T, the free energy of the polysoap is

$$F_{\rm chain}/kT \approx -\psi m|\epsilon_{p_o}| + R^2/R_{\rm B}^2[\psi + (1-\psi)p_o] \tag{7}$$

The first term allows for the free energy of the aggregated amphiphiles while the second reflects the Gaussian elasticity of a polysoap with $\psi m/p_o$ intrachain micelles. Within the $S_{\rm mix} = 0$ approximation, the coexistence is reminiscent of a first-order phase transition and $f \sim R^o$ is expected [3, 4]. It is thus appropriate to analyze the equilibrium behaviour for constant T and f. The corresponding equilibrium condition, as stated in terms of $G_{\rm chain}(\psi, R) = -\psi m|\epsilon_{p_o}| + F_{\rm el} - fR$, is $\mathrm{d}G_{\rm chain} = (\partial G_{\rm chain}/\partial\psi)\mathrm{d}\psi + (\partial G_{\rm chain}/\partial R)\mathrm{d}R = 0$. At coexistence, f does not specify a unique R. Rather, $f = f_{\rm co}$ for any $R_{\rm L} < R < R_{\rm U}$. The equilibrium condition in this range is thus $\mathrm{d}G_{\rm chain}/kT = -m|\epsilon_{p_o}|\mathrm{d}\psi - (f_{\rm co}/kT)\mathrm{d}R = 0$ and

$$\mathrm{d}\psi/\mathrm{d}R \approx -f_{\rm co}/kTm|\epsilon_{p_o}| \tag{8}$$

Integration of Eq. 8, together with the condition $\psi(R_{\rm U}) = 0$ yields

$$\psi \approx (f_{\rm co}/kTm|\epsilon_{p_o}|)(R_{\rm U} - R).$$

By invoking $\psi(R_{\rm L}) = 1$, we obtain

$$f_{\rm co}/kT = m|\epsilon_{p_o}|/(R_{\rm U} - R_{\rm L}) \tag{9}$$

and

$$\psi \approx (R_{\rm U} - R)/(R_{\rm U} - R_{\rm L}) \tag{10}$$

To obtain the explicit expressions for $f_{\rm co}$, $R_{\rm L}$ and $R_{\rm U}$, we utilize the following three conditions: $f_{\rm co}/kT \approx R_{\rm U}/R_o^2 \approx R_{\rm L}/R_{\rm B}^2$. These lead to $R_{\rm U} \approx p_oR_{\rm L}$, and to

$$R_{\rm L} \approx [m|\epsilon_{p_o}|/p_o(p_o-1)]^{1/2}R_o;\, R_{\rm U} \approx [m|\epsilon_{p_o}|p_o/(p_o-1)]^{1/2}R_o \tag{11}$$

and, finally, to

$$f_{\rm co}/kT \approx [m|\epsilon_{p_o}|p_o/(p_o-1)]^{1/2}R_o^{-1} \approx |\epsilon_{p_o}|^{1/2}[p_o/(p_o-1)]^{1/2}(nb^2)^{-1/2} \tag{12}$$

Upon further extension, $R > R_{\mathrm{U}}$, the polysoap is fully unravelled, its free energy is $F_{\mathrm{dis}}/kT \approx R^2/R_o^2$ and the corresponding force law is $f/kT \approx R/R_o^2$. Eventually, when the polysoap approaches its fully extended state, its elasticity will be described by the inverse Langevin $\mathcal{L}^*$ form.

In reality, $S_{\mathrm{mix}} \neq 0$. This, in turn, introduces modifications of the fR diagram at coexistence. The modified fR diagram is specified by

$$F_{\mathrm{chain}}/kT \approx m\psi\epsilon_{p_o} + (R/R_{\mathrm{B}})^2[\psi(1-p_o)+p_o]^{-1} - S_{\mathrm{mix}}/k \tag{13}$$

The elastic term may be viewed as an external field favouring the dissociated "phase". An increase in f, or in the imposed R, always favours a decrease in ψ. On the other hand, S_{mix} always favours intermediate values of ψ. It thus lowers $\tilde{f}_{\mathrm{co}}/f_{\mathrm{co}}$ in the vicinity of $\psi = 1$ while increasing it in the neighbourhood of $\psi = 0$. Here the tilde is used to distinguish the equilibrium values obtained when allowing for S_{mix} from those obtained previously. When $S_{\mathrm{mix}} \neq 0$, $f_{\mathrm{co}} \neq \mathrm{const}'$ and we can no longer use the simplified analysis described earlier. Furthermore, when we allow for S_{mix}, it is impossible to solve for $\tilde{f}_{\mathrm{co}} = \tilde{f}_{\mathrm{co}}(R)$ explicitly. Instead, we can obtain a parametric solution. In particular, we solve for the equilibrium values of $\tilde{R} = \tilde{R}(\psi)$ and of $\tilde{f}_{\mathrm{co}} = \tilde{f}_{\mathrm{co}}(\psi)$. The condition $\partial F_{\mathrm{chain}}/\partial\psi = 0$ yields

$$\tilde{R} = R_{\mathrm{B}}[m|\epsilon_{p_o}| + S'_{\mathrm{mix}}/k]^{1/2}[\psi(1-p_o)+p_o]/(p_o-1)^{1/2} \tag{14}$$

Upon substituting this $\tilde{R}$ into Eq. 13, we obtain $F_{\mathrm{chain}}(\psi)$ in equilibrium. The tension at coexistence, as a function of ψ, is

$$\tilde{f}_{\mathrm{co}} = \mathrm{d}F_{\mathrm{chain}}(\psi)/\mathrm{d}R = (\mathrm{d}F_{\mathrm{chain}}/\mathrm{d}\psi)(\mathrm{d}R/\mathrm{d}\psi)^{-1}$$

or

$$\tilde{f}_{\mathrm{co}} = f_{\mathrm{co}}(1 + S'_{\mathrm{mix}}/km|\epsilon_{p_o}|)^{1/2} \tag{15}$$

where f_{co} is the tension at coexistence as given by Eq. 12, when S_{mix} is neglected. For $0 \ll \psi \ll 1$, the fR diagram now exhibits a logarithmic correction to $f_{\mathrm{co}} \sim R^o$. $\tilde{f}_{\mathrm{co}}$ increases weakly with R. S'_{mix} is negligible in the vicinity of $\psi_o \approx 1 - p_o^{-1/2}$ and the corresponding $\tilde{R}(\psi_o) \approx p_o^{1/2}R_{\mathrm{L}}$. Consequently, in this region, it is possible to replace Eq. 14 by Eq. 10. In turn, Eq. 10 yields the lever rule, $\psi/(1-\psi) \approx (R_{\mathrm{U}} - R)/(R - R_{\mathrm{L}})$. By substituting it into S'_{mix}, it is possible to approximate $\tilde{f}_{\mathrm{co}}$ in this region by

$$\tilde{f}_{\mathrm{co}} = f_{\mathrm{co}}(1 + \ln g(R)/|\epsilon_{p_o}|)^{1/2} \tag{16}$$

where $g(R)$ is a slowly increasing function of R

$$g(R) \approx [1 + \frac{1}{p_o}(\frac{R_{\mathrm{U}} - R}{R - R_{\mathrm{L}}})][1 + p_o(\frac{R - R_{\mathrm{L}}}{R_{\mathrm{U}} - R})]^{1/p_o} \tag{17}$$

These logarithmic corrections become important in the immediate neighbourhood of $\psi = 1$ and $\psi = 0$ where the above approximation is no longer valid. To identify the upper and lower boundaries of the coexistence regime, $\tilde{R}_{\mathrm{U}}$ and $\tilde{R}_{\mathrm{L}}$, it is necessary to carefully specify the corresponding values of ψ. As was stated earlier, it is assumed that prior to the onset of coexistence, all amphiphiles are assembled into micelles. In the coexistence regime, we further assume that fully dissociated amphiphiles coexist with weakly perturbed micelles. Within this approximation, the lower and the upper boundaries of the coexistence regime correspond, respectively, to chains supporting one dissociated micelle and to chains supporting a single undissociated micelle. In other words, the maximal and minimal values of ψ at coexistence are respectively $\psi_{\mathrm{max}} \approx 1 - p_o/m$ and $\psi_{\mathrm{min}} \approx p_o/m$. The $S_{\mathrm{mix}} = 0$ approximation allows us to consider arbitrarily large m and thus to set $\psi_{\mathrm{max}} \approx 1$ and $\psi_{\mathrm{min}} \approx 0$. In our case, however, we are limited to $m \ll m_u$ and this is no longer possible. To obtain $\tilde{R}_{\mathrm{L}}$ and $\tilde{R}_{\mathrm{U}}$, we use $\tilde{f}(\psi_{\mathrm{max}})/kT \approx \tilde{R}_{\mathrm{L}}/R_{\mathrm{B}}^2$ and $\tilde{f}(\psi_{\mathrm{min}})/kT \approx \tilde{R}_{\mathrm{U}}/p_o R_{\mathrm{B}}^2$. Altogether

$$\tilde{R}_{\mathrm{L}} \approx R_{\mathrm{L}}[1 + \frac{\ln(p_o^2/m)}{|\epsilon_{p_o}|}]^{1/2} \qquad (18)$$

$$\tilde{R}_{\mathrm{U}} \approx R_{\mathrm{U}}[1 + \frac{\ln m}{p_o|\epsilon_{p_o}|}]^{1/2} \qquad (19)$$

Note that both $\tilde{f}_{\mathrm{co}}(\psi_{\mathrm{max}})$ and $\tilde{R}_{\mathrm{L}}$ decrease as m increases and vanish when $\ln(p_o^2/m)+|\epsilon_{p_o}| = 0$. In particular, both $\tilde{f}_{\mathrm{co}}(\psi_{\mathrm{max}})$ and $\tilde{R}_{\mathrm{L}}$ vanish as $|\epsilon_{p_o}|^{-1}\ln(m/m_u)$ when $m \to m_u$. This is due to the growing importance of S_{mix} in destabilizing the micelles in the unperturbed chain.

Concluding remarks

Our understanding of the statistical mechanics of polysoaps is at an early stage. The problem is of practical interest because of the numerous applications of polysoaps as viscosity modifiers. A better understanding of their molecular design parameters and their effect on their performance is clearly desirable. In addition, the behaviour of synthetic polymers with secondary structure is of fundamental interest. The study of polysoaps may prove interesting also because of their similarities to biopolymers. The fR diagram discussed above, and its modifications by denaturing agents [5], is an example of possible benefits to the biopolymer community.

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