Extending polysoaps in the presence of free amphiphiles

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Intramolecular self-assembly affects the elastic behavior of polymers. ''Denaturing'' agents that weaken the resulting secondary structure strongly modify the force laws characterizing the deformation of such polymers. This behavior is analyzed for the particular case of polysoaps: linear hydrophilic polymers incorporating, at intervals, amphiphilic monomers. In aqueous solution the amphiphiles form intrachain micelles. The deformation behavior of a linear string of spherical intrachain micelles in θ conditions and high ionic strength is analyzed as a function of the concentration of free amphiphiles X. At intermediate extensions intrachain micelles coexist with fully dissociated chain segments leading to a regime where the tension f is weakly dependent on the end to end distance R. The width of the coexistence regime shrinks as X increases. At the same time, the tension at coexistence increases. The fR diagram exhibits thus features reminiscent of a critical point approached via control of X. [S1063-651X(98)03901-4]

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I. INTRODUCTION

Intramolecular self-assembly drastically modifies the configurations of polymers. Denatured proteins, random coil-like objects, can fold into unique three-dimensional structures [1]. Major, though less dramatic, effects also take place in synthetic associating polymers, i.e., flexible copolymers incorporating associating monomers [2]. The intrachain self-assembly of the associating monomers endows the chain with a hierarchical self-organization associated with a rugged free-energy surface [3,4]. In turn, this strongly affects the configurations, dimension, and elasticity of the chains [5,6]. When the self-assembly involves hydrophobic interactions one may modify, and eventually ''denature,'' the self-organization by adding free amphiphiles. This technique was first pioneered and extensively used in the study of proteins [7]. In the following we present a theoretical model for the effect of *free amphiphiles* on the *elasticity* of a certain family of associating polymers: polysoaps [2,8]. These are flexible, hydrophilic chains that incorporate, at intervals, m covalently bound, amphiphilic monomers. We focus on the case of $m \gg 1$ amphiphiles joined by long, hydrophilic, spacer chains consisting of $n \gg 1$ monomers. The total polymerization degree $N \approx nm$ obeys $N \gg n \gg 1$. In water, the polymerized amphiphiles self-assemble into a variety of aggregates, depending on the nature of the amphiphiles, n, etc. For brevity, we confine our analysis to an especially simple case that nevertheless retains the essential features of the system. In particular, we consider a *linear* string of *spherical* intrachain micelles [9] in an aqueous solution of *high* ionic strength. It is assumed that all the polymerized amphiphiles are micellized (Fig. 1). The elasticity of isolated polysoaps assuming this configurations exhibits a distinctive feature [5]. At intermediate extensions, intrachain micelles *coexist* with fully dissociated chain segments (Fig. 2). In this regime, the tension along the chain f is weakly dependent on the end to end distance R. To be precise, $f \sim \ln g(R)$, where $g(r)$ is weakly increasing function of R. The near plateau in the fR diagram is reminiscent of the PV diagram of a fluid coexisting with its vapor. As we shall see, in the presence of free amphiphiles the plateau shrinks while the tension at coexistence f_{co} increases. Eventually, when the surfactant concentration X is large enough the plateau disappears altogether. This is somewhat suggestive of a *critical point* approached via control of X. The physical origin of this behavior is clear. The coexistence regime reflects the equilibration of the secondary structure introduced by the intrachain micelles. The addition of free surfactants gives rise to the formation of mixed micelles incorporating both free and polymerized am-

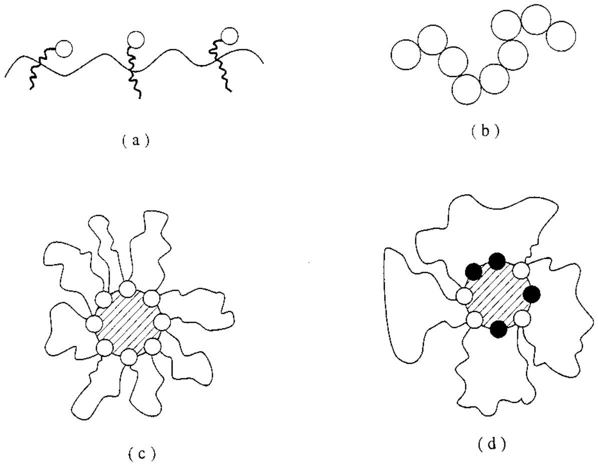

FIG. 1. Our discussion concerns (a) a polysoap that self-assembles into a linear string of spherical intrachain micelles. (b) The unperturbed polysoap behaves as a self-avoiding chain of intrachain micelles depicted as circles. (c) In the absence of free surfactants the intrachain micelles consist only of polymerized amphiphiles. (d) Mixed micelles, incorporating both polymerized and unpolymerized amphiphiles, are formed once the concentration of free surfactants exceeds X_{CAC}.

phiphiles [3,4]. The plateau disappears when the secondary structure is fully ''denatured,'' that is, when every intrachain micelle contains only a single polymerized amphiphile. This fR diagram is of interest from two points of view. First, it is a distinctive aspect of the elasticity of polymers exhibiting secondary structure. Second, it is of practical interest since polysoaps and related polymers are used as viscosity modifiers of dispersions containing free surfactants.

The discussion is limited to spherical intrachain micelles incorporating, in the unperturbed state, $p \approx p_0$ amphiphiles. Here p_0 is the aggregation number of the micelles formed by the free, unpolymerized surfactants. Such intrachain micelles can be obtained by a proper choice of the amphiphilic monomers and n. Linear strings are not the most stable configuration of polysoaps [4]. They are, however, expected as intermediates upon the stretching of more stale configurations: branched strings or globules of close-packed intrachain micelles. Linear strings may also occur as long-lived metastable states. The requirement of high ionic strength ensures the screening of long-ranged electrostatic interactions. In addition, it is assumed that water is a θ solvent for the hydrophilic backbone, which may then be viewed as a Gaussian coil. This simplifies the analysis with no change in the essential physics [6]. Finally, the discussion is limited to amphiphiles that do not adsorb onto the hydrophilic backbone and to the case of free amphiphiles that are chemically identical to the polymerized ones. A brief review of the configurations of unperturbed polysoaps is presented in Sec. II. The extension behavior of isolated polysoaps in the absence of free amphiphiles is summarized in Sec. III. Section IV is devoted to the effect of free surfactants on the fR diagram.

II. THE UNPERTURBED POLYSOAP

Before analyzing the extension behavior of polysoaps, it is helpful to describe the configurations of a single, unperturbed chain. The necessary foundation comprises three topics: (i) the configurations of an isolated polysoap chain, (ii) the interactions of such a chain with free surfactants, and (iii) the regime of validity of the assumption that all polymerized amphiphiles are micellized.

As was stated earlier, an isolated polysoap is assumed to form a linear string of spherical micelles. Within our model the intrachain micelles consist of two regions. The inner region is similar to micelles of free, unpolymerized amphiphiles. It comprises a dense core formed by the hydrophobic tails of the amphiphiles. The polar or ionic head groups straddle the core-water boundary. This region is surrounded by a corona of swollen loops formed by the spacer chains joining the aggregated amphiphiles. Our discussion focuses on starlike 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 the simple phenomenological model [11] yields the free energy per amphiphile in a micelle of aggregation number p, $\epsilon_p kT$ [3]:

$$\epsilon_p \approx \gamma a_0 (u^{-1/3} + u^{1/3} + \kappa u^{1/2}) - \delta. \tag{1}$$

Here γkT is the surface tension of the water-core interface, a_0 is the optimal area per head group in a micelle formed by the free 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 $p_0 \approx v^2/a_0^3$. u is a dimensionless variable $u = p/p_0 = (a_0/a)^3$. The $u^{-1/3}$ term allows for the interfacial free energy per head group. This driving term favors micellar growth. The repulsion between the head groups gives rise to the $u^{1/3}$ term. The third term $u^{1/2}$ arises because of the repulsive interactions between the coronal loops. It corresponds to the free energy per loop in a θ solvent $F_{\text{corona}}/kT \approx p^{1/2}$ [10]. These last two terms reflect free-energy penalties that oppose micellar growth. The relative importance of the penalty terms is determined by $\kappa \approx p_0^{1/2}/\gamma a_0$, the ratio of the coronal penalty to the head group repulsion at $a \approx a_0$. As stated before, for brevity we focus on the limit of $\kappa \ll 1$ when $p \approx p_0$ and $u \approx 1$. In this regime $\epsilon_p \approx \tilde{\epsilon}_p$, where $\tilde{\epsilon}_p kT$, as given by $\tilde{\epsilon}_p \approx \gamma a_0 (u^{-1/3} + u^{1/3}) - \delta$, is the free energy per amphiphile in a micelle formed by free, monomeric surfactants. For $p \approx p_0$, $\tilde{\epsilon}_{p_0} \approx 2\gamma a_0 - \delta$ and the critical micelle concentration X_{CMC} is $\tilde{\epsilon}_{p_0} \approx \ln X_{\text{CMC}}$. It is important to note that a θ solvent for the backbone is in effect a good solvent for the string of micelles [12]. 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 $R_F(p) \approx (m/p)^{3/5} r_{\text{micelle}}(p) \approx R_F u^{-7/20}$. Here $R_F \approx (m/p_0)^{3/5} r_{\text{micelle}}(p_0) \approx m^{3/5} n^{1/2} p_0^{-7/20} b$ is the Flory radius of a string of spherical intrachain micelles when $p \approx p_0$.

The presence of free amphiphiles modifies the picture presented above. The different feature is the formation of mixed micelles consisting of both polymerized and unpolymerized amphiphiles (Fig. 1). It is possible to distinguish between three regimes. Below X_{CAC}, the critical association concentration, no mixed micelles are formed. At X_{CAC}, unpolymerized amphiphiles are incorporated into the micelles. The fraction of polymerized amphiphiles in the mixed micelles α decreases as X increase up to a saturation concentration X_{sat}. At X_{sat}, each mixed micelle incorporates a single polymerized amphiphile, i.e., $\alpha \approx 1/p_0$. Increasing X beyond X_{sat} does not affect the configurations of the chain. The formation of mixed micelles is associated with loss of translational entropy of the unpolymerized amphiphiles. It is thus appropriate to describe the system in terms of $\Omega_0 kT$, the grand canonical potential for the unperturbed string of mixed micelles in contact with a reservoir of free amphiphiles of concentration X. The polysoaps self-assembles into a string of m/q mixed micelles. Each micelle consists of q polymerized amphiphiles and f_a free amphiphiles such that the total aggregation number is $p = q + f_a$. The free energy per amphiphile in a mixed micelle is $\epsilon_p(q) \approx \tilde{\epsilon}_p + (q/p) F_{\text{corona}}/kT$, where $F_{\text{corona}}/kT \approx q^{1/2}$ is the free energy per coronal chain. Defining the reduced variables $u = p/p_0$ and $\alpha = q/p$, we have $\Omega_0(p,q) = (m/q)[p\epsilon_p(q) - f_a \mu/kT]$, where $\mu \approx kT \ln X$ is the chemical potential of the free amphiphiles in the solution. Explicitly,

$$\Omega_0 \approx m[\alpha^{-1} \tilde{\epsilon}_p(u) + \alpha^{1/2} u^{1/2} \kappa \gamma a_0 + (1 - \alpha^{-1}) \ln X]. \tag{2}$$

X_{CAC}, α, and X_{sat}, characterizing the interactions between the unperturbed polysoap and the free amphiphiles, are determined by Ω_0. In the $\kappa \ll 1$ limit, the features of interest are specified by the conditions $\partial\Omega_0/\partial\alpha = \partial\Omega_0/\partial u = 0$ [4]. It is possible, however, to obtain the relevant results using a simpler argument, which will prove useful later on. In the limit of $\kappa \ll 1$ the aggregation number is hardly affected by the coronal penalty and $u \approx 1$. It is thus possible to rewrite Ω_0 as

$$\Omega_0/m \approx \alpha^{-1} \ln \frac{X_{\mathrm{CMC}}}{X} + \gamma a_0 \kappa \alpha^{1/2} + \ln X. \tag{3}$$

The first term favors an increase in α since this lowers the loss of translational entropy. The second term opposes growth of α because of the associated coronal penalty. At equilibrium the two terms are comparable, thus leading to

$$\alpha \approx p_0^{-1/3} \left(\ln \frac{X_{\mathrm{CMC}}}{X} \right)^{2/3}. \tag{4}$$

The critical association concentration X_{CAC} for the onset of the formation of mixed micelles is defined by Eq. (4) together with $\alpha \approx 1$,

$$\ln(X_{\mathrm{CMC}}/X_{\mathrm{CAC}}) \approx p_0^{1/2}. \tag{5}$$

Note that Ω_0/m reduces to ϵ_{p_0} for $\alpha \approx 1$. The saturation concentration X_{sat}, when each intrachain micelle contains a single polymerized amphiphile, is specified by Eq. (4) together with $\alpha \approx 1/p_0$ [14],

$$\ln(X_{\mathrm{CMC}}/X_{\mathrm{sat}}) \approx p_0^{-1} \ll 1. \tag{6}$$

For $X < X_{\mathrm{CAC}}$ there is no effect on r_{micelle} and R. In the range $X_{\mathrm{CAC}} < X < X_{\mathrm{sat}}$, the number of micelles increases from m/p_0 to $m/\alpha p_0$. At the same time, the coronal span shrinks and the micellar radius thus decreases from $r_{\mathrm{micelle}} \approx p_0^{1/4} n^{1/2} b$ to $(\alpha p_0)^{1/4} n^{1/2} b$. The overall result is a gradual swelling of the chain $R_F(\alpha) \approx (m/\alpha p_0)^{3/5} r_{\mathrm{micelle}}(\alpha) \approx R_F \alpha^{-7/20}$. As α approaches $1/p_0$ this picture of the polysoap as a string of starlike micelles deteriorates. At saturation the chain behaves as a structureless random coil. If we assume that the hydrophilic backbone dominates its behavior, we expect Gaussian statistics and a chain span of $R_0 \approx (mn)^{1/2} b$. The equilibrium form for Ω_0 in the $X_{\mathrm{CAC}} < X < X_{\mathrm{sat}}$ range is

$$\Omega_0 \approx m \left[\left(p_0 \ln \frac{X_{\mathrm{CMC}}}{X} \right)^{1/3} + \ln X \right]. \tag{7}$$

The preceding discussion was based on the assumption that all polymerized amphiphiles in the unperturbed chain are micellized. We will also make this assumption later on. It is thus important to define its regime of validity. As we shall see, it becomes untenable once m becomes larger than a certain m_u to be specified later. For $m = m_u$, an average of one micelle per chain is fully dissociated. The underlying physics is as follows. The dissociation is favored 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 α and the fraction of undissociated amphiphiles ψ. This involves inscription of the micelles and the dissociated amphiphiles on a one-dimensional lattice comprising of M_ψ sites. For simplicity, we limit the discussion to micelles comprising of p_0 amphiphiles, i.e., we do not allow for polydispersity in p. The distinctive feature of this system is that M_ψ varies with ψ and α. Since the number of micelles is $\psi m/\alpha p_0$ and the number of dissociated amphiphiles is $m(1-\psi)$,

$$M_\psi \approx m(1-\psi) + \psi m/\alpha p_0. \tag{8}$$

The associated $S_{\mathrm{mix}}(\alpha,\psi)$ is the ideal mixing entropy $S_{\mathrm{mix}}/k = -M_\psi[Y \ln Y + (1-Y)\ln(1-Y)]$, where Y is the fraction of sites occupied by micelles $Y \approx \psi m/\alpha p_0 M_\psi$. This leads to

$$\begin{aligned} S_{\mathrm{mix}}(\alpha,\psi)/k \approx{}& \frac{\psi m}{\alpha p_0} \ln\left[1 + \frac{\alpha p_0(1-\psi)}{\psi}\right] \\ &+ m(1-\psi)\ln\left[1 + \frac{\psi}{\alpha p_0(1-\psi)}\right]. \end{aligned} \tag{9}$$

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

$$\begin{aligned} S'_{\mathrm{mix}}(\alpha,\psi)/k \approx{}& \frac{m}{\alpha p_0} \ln\left[1 + \frac{\alpha p_0(1-\psi)}{\psi}\right] \\ &- m \ln\left[1 + \frac{\psi}{\alpha p_0(1-\psi)}\right]. \end{aligned} \tag{10}$$

$S'_{\mathrm{mix}} = 0$ at $\psi_0 \approx 1/[1 + (\alpha p_0)^{-1/2}]$. For $\alpha = 1$ these expressions reduce to those corresponding to pure intrachain micelles consisting solely of polymerized amphiphiles.

The grand canonical potential for a partially dissociated chain of mixed micelles $\Omega_{\mathrm{chain}} kT$ is

$$\Omega_{\mathrm{chain}} = \psi\Omega_0 - S_{\mathrm{mix}}(\alpha,\psi)/k. \tag{11}$$

For $\alpha = 1$, Ω_{chain} reduces to $F_{\mathrm{chain}}/kT = m\psi\epsilon_{p_0} - S_{\mathrm{mix}}(\psi)/k$, describing an ideal one-dimensional mixture of dissociated amphiphiles and pure intrachain micelles. To study the onset of micelle dissociation it is helpful to consider Ω_{chain} for $\psi \approx 1$ when $S_{\mathrm{mix}}/k \approx -m(1-\psi)\ln \alpha p_0(1-\psi)$. It is convenient to write it as

$$\Omega_{\mathrm{chain}} \approx \Omega_0 + m|A|(1-\psi) + m(1-\psi)\ln \alpha p_0(1-\psi), \tag{12}$$

where $A = \Omega_0/m$ is the free-energy cost per polymerized amphiphiles for the dissociation of a single micelle. The form of Ω_{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 [15]. 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 $\partial\Omega_{\mathrm{chain}}/\partial\psi = 0$ leads to $|A| + \ln \alpha p_0(1-\psi) \approx 0$ or $p_0\alpha(1-\psi) \approx \exp(-|A|)$. 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 $\psi \approx 1 - n_d \alpha p_0/m$, leading to

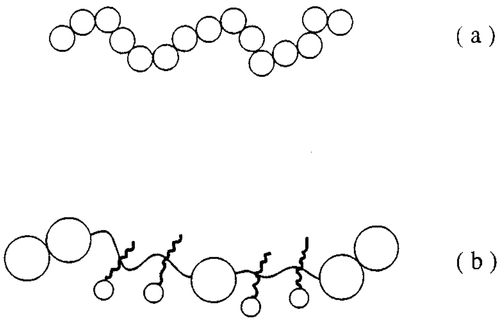

FIG. 2. Two possible scenarios for the extension of a linear string of intrachain micelles in the absence of free surfactants: (a) the uniform extension giving rise to a string of smaller micelles and (b) the coexistence of weakly perturbed micelles and fully dissociated amphiphiles.

$$n_d \approx (\alpha p_0)^{-2} m \exp(-|A|). \tag{13}$$

The condition $n_d = 1$ defines m_u, an average ''chemical distance'' between dissociated micelles

$$m_u \approx (\alpha p_0)^2 \exp(|A|). \tag{14}$$

In turn, it is now possible to express n_d as

$$n_d \approx m/m_u. \tag{15}$$

This also determines the average ψ,

$$\psi \approx 1 - \alpha p_0/m_u \approx 1 - (\alpha p_0)^{-1} \exp(-|A|). \tag{16}$$

These results yield the appropriate expression for $\alpha = 1$ upon noting that in this case $A = \epsilon_{p_0}$. The ''single-phase approximation'' is thus justified while $m \ll m_u$ or, equivalently, $n_d \ll 1$. This condition is easily fulfilled when $X < X_{\rm CAC}$ and $\alpha = 1$. In this range $m_u \approx p_0^2 \exp(|\epsilon_{p_0}| \gg p_0$. However, m_u decreases with α and for $\alpha \approx 1/p_0$ or $X \approx X_{\rm sat}$ we find $m_u \approx \exp[-(\ln X_{\rm CMC} + 1)] \approx \exp(|\epsilon_{p_0}| - 1)$. This m_u is still large. However, the corresponding n_d is closer to unity and the single-phase approximation is poorer. Finally, note that Eq. (14) is actually an upper bound on m_u. This is because the assumed monodisperity $p = p_0$ of the micelles enforces complete micellar dissociation as the only source of dissociated amphiphiles. Allowing for $p < p_0$ would provide dissociated amphiphiles at a lower free-energy cost.

III. EXTENSION OF POLYSOAPS

Before we discuss the effect of free amphiphiles on the extension elasticity of polysoaps, it is necessary to outline the extension behavior of an isolated chain. Our discussion involves three steps. Initially, we consider uniform stretching assuming that all amphiphiles are micellized (Fig. 2). The only effect allowed is a decrease in the aggregation number of the micelles p. This leads to an fR diagram exhibiting a van der Waals loop. In turn, this suggests that the extension involves coexistence of dissociated amphiphiles and weakly perturbed micelles. We then proceed to analyze the coexistence regime within the $S_{\rm mix} = 0$ approximation, i.e., neglecting the mixing entropy of the one-dimensional solution of micelles and dissociated amphiphiles. As a result, the coexistence behavior exhibits features reminiscent of a first-order phase transition: a plateau with $f \sim R^0$ and sharp boundaries. This convenient approximation yields useful length and force scales and a qualitatively correct picture. Finally, we analyze the modifications of the plateau introduced by $S_{\rm mix}$ [6], in particular, smooth crossovers and a logarithmic R dependence.

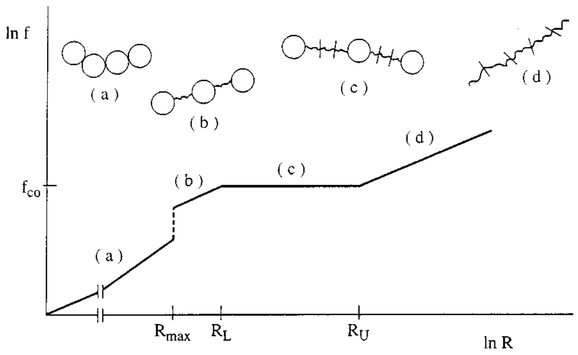

FIG. 3. Schematic plot of $\ln f$ vs $\ln R$ for a polysoap in the absence of free surfactants and within the $S_{\rm mix} = 0$ approximation. (a) for $R_F < R < R_{\max}$ the string of micelles is extended with a minor decrease in the aggregation number. A Gaussian behavior is expected for the weak extension, while for $R_F \ll R < R_{\max}$ the Pincus elasticity is followed. (b) At $R > R_{\max}$ the micelles are still weakly perturbed, but the Gaussian bridges between them are stretched. (c) Between R_L and R_U weakly perturbed micelles coexist with dissociated chain segments giving rise to $f \sim R^0$. (d) Beyond R_U the chain is fully dissociated giving rise to the Gaussian extension of the backbone.

As stated, we first assume that the only effect of the stretching is to decrease the aggregation number from p_0 to p with a concomitant increase in the number of intrachain micelles from m/p_0 to m/p. In this case the free energy of the chain $F_{\rm chain}$ consists of two terms. One, $m\epsilon_p$, allows for the contribution of the aggregated amphiphiles. The second term, $F_{\rm el}$, reflects the stretching free energy of the string. $F_{\rm el}$ may assume three forms. For weak deformations, when linear response is expected, $F_{\rm el} \approx [R/R_F(p)]^2 \approx (R/R_F)^2 u^{7/10}$. This initial Gaussian $F_{\rm el}$ is replaced by the Pincus free energy [16] $F_{\rm el} \approx [R/R_F(p)]^{5/2} \approx (R/R_F)^{5/2} u^{7/8}$ when $R \gg R_F(p)$. Eventually, when R exceeds the length of the fully extended string $R_{\max} \approx (m/p) r_{\rm micelle}(p)$, 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 $F_{\rm el} \approx [R/R_B(p)]^2 \approx (r/R_B)^2 u$, where $R_B \approx (m/p_0)^{1/2} n^{1/2} b$. Finally, the chain is fully unraveled (Fig. 3) and the Gaussian elasticity of the backbone comes into play. This scenario leads to an fR diagram exhibiting a van der Waals loop (Appendix A). In turn, this suggests a coexistence between weakly perturbed micelles and fully dissociated chain segments at intermediate extensions [17].

We now consider the coexistence regime within the $S_{\rm mix} = 0$ approximation. In this regime we expect that 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 $f_{\rm co} \ll f_*$ (Appendix A), we neglect the weak perturbation of the micellar structure and assume $u \approx 1$ or $p \approx p_0$. In a θ solvent, for a given R and T, the free energy of the polysoap is

$$F_{\rm chain}/kT \approx -\psi m|\epsilon_{p_0}| + R^2/R_B^2[\psi + (1-\psi)p_0]. \quad (17)$$

The first term allows for the free energy of the aggregated amphiphiles, while the second reflects the Gaussian elasticity of a polysoap with $\psi m/p_0$ intrachain micelles. To characterize the coexistence regime we may utilize $\partial F_{\rm chain}/\partial\psi = 0$ for a given T and R and for $p \approx p_0$. This condition specifies $\psi = \psi(R)$ at equilibrium and thus yields $F_{\rm chain}(R)$ and the corresponding tension $f = \partial F_{\rm chain}/\partial R$. A simpler analysis is possible. Within the $S_{\rm mix} = 0$ approximation the coexistence is reminiscent of a first-order phase transition. In particular, we expect a plateau $f \sim R^0$ in the fR diagram [5,6]. It is thus appropriate to analyze the equilibrium behavior for constant T and f. The corresponding equilibrium condition, as stated in terms of $G_{\rm chain}(\psi,R) = -\psi m|\epsilon_{p_0}| + F_{\rm el} - fR$, is $dG_{\rm chain} = (\partial G_{\rm chain}/\partial\psi)d\psi + (\partial G_{\rm chain}/\partial R)dR = 0$. The requirement $\partial G_{\rm chain}/\partial\psi = 0$ is equivalent to $\partial F_{\rm chain}/\partial\psi = 0$, while $\partial G_{\rm chain}/\partial R = 0$ sets the R corresponding equal to the imposed f. At coexistence f does not specify a unique R. Rather, $f = f_{\rm co}$ for any $R_L < R < R_U$. For this range we may accordingly substitute f as given by $\partial G_{\rm chain}/\partial R = 0$ into $G_{\rm chain}$, thus obtaining $dG_{\rm chain}/kT = -m|\epsilon_{p_0}|d\psi - (f_{\rm co}/kT)dR = 0$ and

$$d\psi/dR \approx -f_{\rm co}/kTm|\epsilon_{p_0}|. \quad (18)$$

Integration of Eq. (18), together with the condition $\psi(R_U) = 0$, yields $\psi \approx (f_{\rm co}/kTm|\epsilon_{p_0}|)(R_U - R)$. By invoking $\psi(R_L) = 1$ we obtain

$$f_{\rm co}/kT = m|\epsilon_{p_0}|/(R_U - R_L) \quad (19)$$

and

$$\psi \approx (R_U - R)/(R_U - R_L). \quad (20)$$

To obtain the explicit expressions for $f_{\rm co}$, R_L, and R_U we utilize the following three conditions $f_{\rm co}/kT \approx R_U/R_0^2 \approx R_L/R_B^2$. These lead to

$$R_U \approx p_0 R_L; \quad (21)$$

$$R_L \approx [m|\epsilon_{p_0}|/p_0(p_0-1)]^{1/2} R_0,$$
$$R_U \approx [m|\epsilon_{p_0}|p_0/(p_0-1)]^{1/2} R_0; \quad (22)$$

and finally

$$f_{\rm co}/kT \approx [m|\epsilon_{p_0}|p_0/(p_0-1)]^{1/2} R_0^{-1}$$
$$\approx |\epsilon_{p_0}|^{1/2}[p_0/(p_0-1)]^{1/2}(nb^2)^{-1/2}. \quad (23)$$

Upon further extension $R > R_U$, the polysoap is fully unraveled, its free energy is $F_{\rm dis}/kT \approx R^2/R_0^2$, and the corresponding force law is $f/kT \approx R/R_0^2$. Eventually, when the polysoap approaches its fully extended state, its elasticity will be described by the inverse Langevin $\mathcal{L}^*$ form [18].

Physical insight concerning the coexistence regime 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_B. In the stretched bridges regime the leading contributions are $F_B/kT \approx m\epsilon_{p_0} + (R/R_B)^2$. The fully dissociated chain is described by $F_{\rm dis}/kT \approx (R/R_0)^2$. The bottom of the free-energy curve described by F_B is located at $R_B < R_0$ and is $m|\epsilon_{p_0}|$ below the minimum of $F_{\rm dis}$. For weak extensions F_B is lower than $F_{\rm dis}$. However, $R_B < R_0$ and thus the spring constant of the fully dissociated chain is weaker. Consequently, the two curves cross at $R_{\rm co}$ specified by $F_B \approx F_{\rm dis}$ or $R_{\rm co} \approx R_0[m|\epsilon_{p_0}|/(p_0-1)]^{1/2}$. 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 rough argument locates the crossover at $R_{\rm co} \approx (R_U R_L)^{1/2}$. The peak of the ''spinodal curve'' $R_0 < R_* < R_{\rm co}$ corresponds to $(R/R_B)^2 \approx m|\epsilon_{p_0}|$, that is, when the free energy of the micellar string is equal to the minimal free energy of the dissociated chain.

Setting $S_{\rm mix} = 0$ amounts to assuming that the micelles and the dissociated amphiphiles coexist as two ''pure phases.'' In a one-dimensional system this is impossible [15]. The two components must mix thus giving rise to $S_{\rm mix} > 0$. This in turn introduces modifications of the fR diagram at coexistence. The modified fR diagram is specified by

$$F_{\rm chain}/kT \approx m\psi\epsilon_{p_0} + (R/R_B)^2[\psi(1-p_0) + p_0]^{-1} - S_{\rm mix}/k. \quad (24)$$

The elastic term may be viewed as an external field favoring the dissociated ''phase.'' An increase in f, or in the imposed R, always favors a decrease in ψ. On the other hand, $S_{\rm mix}$ consistently favors intermediate values of ψ. It thus lowers $\tilde{f}_{\rm co}/f_{\rm co}$ in the vicinity of $\psi = 1$ while increasing it in the neighborhood of $\psi = 0$. In this case $f_{\rm co} \neq {\rm const}'$ and we can no longer use the simplified analysis described earlier. Furthermore, when we allow for $S_{\rm mix}$ it is impossible to solve for $\tilde{f}_{\rm co} = \tilde{f}_{\rm co}(R)$ explicitly. Instead, we can obtain a parametric solution. In particular, we solve for the equilibrium values of $\tilde{R} = \tilde{R}(\psi)$ and of $\tilde{f}_{\rm co} = \tilde{f}_{\rm co}(\psi)$. Here the tilde is used to distinguish the equilibrium values obtained when allowing for $S_{\rm mix}$ from those obtained previously. The corresponding fR diagram is found numerically (Fig. 4). The condition $\partial F_{\rm chain}/\partial\psi = 0$ yields

$$\tilde{R} = R_B[m|\epsilon_{p_0}| + S'_{\rm mix}/k]^{1/2}[\psi(1-p_0) + p_0]/(p_0-1)^{1/2}. \quad (25)$$

Upon substituting this $\tilde{R}$ into Eq. (24) we obtain $F_{\rm chain}(\psi)$ in equilibrium. The tension at coexistence, as a function of ψ, is $\tilde{f}_{\rm co} = dF_{\rm chain}(\psi)/dR = (dF_{\rm chain}/d\psi)(dR/d\psi)^{-1}$ or

$$\tilde{f}_{\rm co} = f_{\rm co}(1 + S'_{\rm mix}/km|\epsilon_{p_0}|)^{1/2}. \quad (26)$$

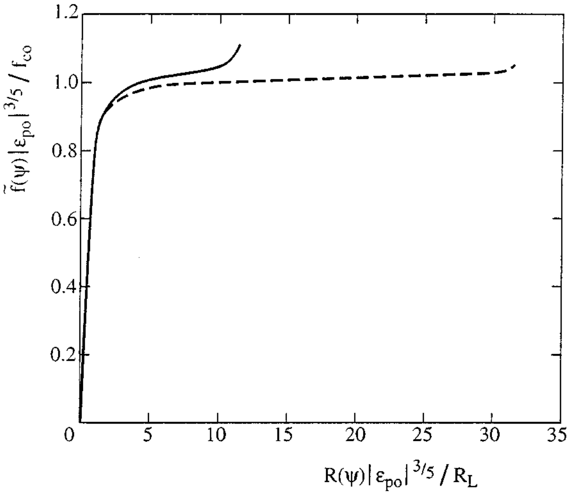

FIG. 4. Effect of $S_{\rm mix}$ on the coexistence regime of the fR diagram in the absence of free surfactants. The sharp plateau is replaced by a sigmoid curve.

Here $f_{\rm co}$ is the tension at coexistence as given by Eq. (23), when $S_{\rm mix}$ is neglected. For $0 \ll \psi \ll 1$ the fR diagram now exhibits a logarithmic correction to $f_{\rm co} \sim R^0$. $\tilde{f}_{\rm co}$ increases weakly with R. $S'_{\rm mix}$ is negligible in the vicinity of $\psi_0 \approx 1 - p_0^{-1/2}$ and the corresponding $\tilde{R}(\psi_0) \approx p_0^{1/2} R_L$. Consequently, in this region it is possible to replace Eq. (25) by Eq. (20). In turn, Eq. (20) yields the lever rule $\psi/(1-\psi) \approx (R_U - R)/(R - R_L)$. By substituting it into $S'_{\rm mix}$ it is possible to approximate $\tilde{f}_{\rm co}$ in this region by

$$\tilde{f}_{\rm co} = f_{\rm co}[1 + \ln g(R)/|\epsilon_{p_0}|]^{1/2}, \tag{27}$$

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

$$g(R) \approx \left[1 + \frac{1}{p_0}\left(\frac{R_U - R}{R - R_L}\right)\right]\left[1 + p_0\left(\frac{R - R_L}{R_U - R}\right)\right]^{1/p_0}. \tag{28}$$

These logarithmic corrections become important in the immediate neighborhood of $\psi = 1$ and 0 where the above approximation is no longer valid. To identify the upper and lower boundaries of the coexistence regime $\tilde{R}_U$ and $\tilde{R}_L$, 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 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 $\psi_{\rm max} \approx 1 - p_0/m$ and $\psi_{\rm min} \approx p_0/m$. The $S_{\rm mix} = 0$ approximation allows us to consider arbitrarily large m and thus to set $\psi_{\rm max} \approx 1$ and $\psi_{\rm min} \approx 0$. In our case, however, we are limited to $m \ll m_u$ and this is no longer possible. To obtain $\tilde{R}_L$ and $\tilde{R}_U$ we use $\tilde{f}(\psi_{\rm max})/kT \approx \tilde{R}_L/R_B^2$ and $\tilde{f}(\psi_{\rm min})/kT \approx \tilde{R}_U/p_0 R_B^2$. These lead to $\tilde{R}_L \approx R_L[1 + S'_{\rm mix}(\psi_{\rm max})/km|\epsilon_{p_0}|]^{1/2}$ and to $\tilde{R}_U \approx R_U[1 + S'_{\rm mix}(\psi_{\rm min})/km|\epsilon_{p_0}|]^{1/2}$, where $R_L \approx R_B^2 f_{\rm co}/kT$ and $R_U \approx p_0 R_B^2 f_{\rm co}/kT$ are the lower and upper boundaries as specified by Eq. (22). Altogether

$$\tilde{R}_L \approx R_L\left[1 + \frac{\ln(p_0^2/m)}{|\epsilon_{p_0}|}\right]^{1/2}, \tag{29}$$

$$\tilde{R}_U \approx R_U\left[1 + \frac{\ln m}{p_0|\epsilon_{p_0}|}\right]^{1/2}. \tag{30}$$

Note that both $\tilde{f}_{\rm co}(\psi_{\rm max})$ and $\tilde{R}_L$ decrease as m increases and vanish when $\ln(p_0^2/m) + |\epsilon_{p_0}| = 0$. In particular, both $\tilde{f}_{\rm co}(\psi_{\rm max})$ and $\tilde{R}_L$ vanish as $|\epsilon_{p_0}|^{-1}\ln(m/m_u)$ when $m \to m_u$. This is due to the growing importance of $S_{\rm mix}$ in destabilizing the micelles in the unperturbed chain. However, as noted before, our analysis as presented above is strictly applicable to the limit of $m \ll m_u$. The study of the extension behavior for $m \approx m_u$ is beyond the scope of this paper. Finally, it is useful to note that for the realistic case of $m \ll m_u$ the $S_{\rm mix} = 0$ approximation yields the essential features of the fR diagram. $\tilde{f}_{\rm co}$, $\tilde{R}_L$, and $\tilde{R}_U$ are well approximated by $f_{\rm co}$, R_L, and R_U.

IV. EFFECT OF FREE AMPHIPHILES ON THE EXTENSION BEHAVIOR

The extension of polysoaps in the presence of free amphiphiles involves mixed micelles comprising of both free and polymerized surfactants. The coupling to a reservoir of free amphiphiles introduces a second ''degree of freedom'' α in addition to u. The formation of mixed micelles is associated with a loss of translational entropy of the free amphiphiles. To account for this feature we cast the argument in terms of an appropriate grand canonical potential. Again, we need to consider the two scenarios discussed above. (i) The extended chain forms a string of uniform mixed micelles. As we shall see, this scenario is qualitatively modified because of the coupling to the amphiphiles reservoir (Appendix B). (ii) The extended polysoap exhibits coexistence between mixed intrachain micelles and fully dissociated polymerized amphiphiles. As before, we will first consider the coexistence scenario within the $S_{\rm mix} = 0$ approximation and introduce the modifications due to $S_{\rm mix}$ later on. In the presence of free amphiphiles, the fR diagram of a uniformly extended chain exhibits a plateau instead of a van der Waals loop. It is thus necessary to compare the plateau regimes associated with the two scenarios in order to decide the actual course of the system. Within our rough model, the coexistence scenario is favored (Appendix B). As a result, the fR diagram is expected to exhibit an ''upper critical point.'' The tension at coexistence increases with X, while the width of the plateau decreases. Eventually the plateau disappears altogether. Initially we focus on the extension behavior when $X > X_{\rm CAC}$. It is assumed that $X_{\rm CAC}$, the critical association concentration for the formation of mixed micelles, is not affected by the deformation. In reality, $X_{\rm CAC}$ is weakly reduced by the stretching, as will be discussed towards the end of this section.

The realized scenario, within our model, involves coexistence of mixed intrachain micelles with fully dissociated polymerized amphiphiles. Again, we initially consider the problem within the $S_{\rm mix}=0$ approximation. As before, we denote the fraction of polymerized amphiphiles that are incorporated into micelles by ψ. The appropriate grand canonical potential is of the form $\Omega_{\rm chain}=\Omega_0+F_{\rm el}$. Ω_0 is obtained from Eq. (2) by substituting ψm for m. The elastic penalty is an appropriately modified form of $F_{\rm el}$ used within the $S_{\rm mix}=0$ treatment of the isolated chain [Eq. (17)]: $F_{\rm el}\approx(R/R_B)^2[(1-\psi)p_0+\psi/\alpha u]^{-1}$. Altogether

$$\Omega_{\rm chain}\approx-m\psi|A(\alpha)|+m\gamma a_0\tau_B[(1-\psi)p_0+\psi/\alpha u]^{-1}, \tag{31}$$

where $A(\alpha)\approx\Omega_0/m$. In the limit of $\kappa\ll1$, when $u\approx1$ and $\tilde{\epsilon}_p\approx\tilde{\epsilon}_{p_0}\approx\ln X_{\rm CMC}$ we have $A\approx p_0{}^{1/3}(\ln X_{\rm CMC}/X)^{1/3}+\ln X$. The equilibrium condition, for a given T and R, is $d\Omega_{\rm chain}=0$. The equilibrium condition for a fixed $f=f_{\rm co}$ involves the grand canonical potential $\Xi_{\rm chain}kT=-m|A|\psi+F_{\rm el}-fR$. Following the procedure described in Sec. III, it leads to the equilibrium condition

$$d\Xi_{\rm chain}=-m|A|d\psi-f_{\rm co}dR=0. \tag{32}$$

Since $|A|$ and $f_{\rm co}$ are independent of ψ and R it is possible to proceed as in the case of extension in the absence of free amphiphiles. The results obtained in the amphiphile free case apply in the present situation upon introduction of the following modifications: (i) replacement of ϵ_{p_0} by $A(\alpha)$ and (ii) replacement of p_0 by $p_0\alpha$ in the expressions for R_B, R_U, and R_L. In particular substituting $R_B(\alpha)\approx(mn/p_0\alpha)^{1/2}$ for R_B thus leads to

$$R_U(\alpha)\approx p_0\alpha R_L(\alpha)\approx[m|A(\alpha)|p_0\alpha/(p_0\alpha-1)]^{1/2}R_0, \tag{33}$$

$$R_L(\alpha)\approx[m|A(\alpha)|/p_0\alpha(p_0\alpha-1)]^{1/2}R_0. \tag{34}$$

As a result,

$$R_U(\alpha)-R_L(\alpha)\approx[m|A(\alpha)|(p_0\alpha-1)/p_0\alpha]^{1/2}R_0. \tag{35}$$

This, together with Eq. (19), leads to

$$f_{\rm co}\approx[|A(\alpha)|p_0\alpha/(p_0\alpha-1)]^{1/2}(nb^2)^{-1/2}. \tag{36}$$

At $X=X_{\rm CAC}$, when $\alpha=1$ we have $A\approx\ln X_{\rm CMC}$. As X increases α decreases, approaching $1/p_0$. This induces shrinkage of the coexistence regime. At the same time, $f_{\rm co}$ increases (Fig. 5). Within this simple approach $f_{\rm co}$ diverges when $\alpha=1/p_0$ and $R_L=R_U$. However, the analysis presented above is only valid up to $\alpha=2/p_0$ when $p_0\alpha\approx2$ and $p_0\alpha-1\approx1$. At this point $R_L\approx R_U\approx R_{\rm crit}$ and

$$R_{\rm crit}\approx(m|A_{\rm crit}|)^{1/2}R_0, \tag{37}$$

while the corresponding tension is

$$f_{\rm crit}\approx(|A_{\rm crit}|/nb^2)^{1/2}. \tag{38}$$

Within our approximations $\alpha\approx2/p_0$ occurs at $X\approx X_{\rm sat}<X_{\rm CP}<X_{\rm CMC}$ and thus $A_{\rm crit}\approx\ln X_{\rm CMC}+1$. This roughly identifies an ''upper critical point'' in the fR diagram.

To further justify this identification note that at $X\approx X_{\rm sat}$ there is no trace left of the secondary structure and the chain is expected to deform as a random coil. The X dependence of the fR diagram can be rationalized, as before, in terms of the free energies $F_{\rm dis}$ and F_B. In the range $X_{\rm CAC}<X<X_{\rm sat}$, $F_{\rm dis}$ is independent of X while F_B is strongly modified by changes in X. This is because R_B is replaced by $R_B(\alpha)$. As X increases, α decreases and $R_B(\alpha)$ approaches R_0. This has two effects: (i) The position of the minimum of F_B is shifted from R_B towards R_0 and (ii) the curvature of F_B approaches the curvature of $F_{\rm dis}$. As a result, at $X\approx X_{\rm sat}$ the two curves no longer intersect. The cross over condition in this case is $-m|A|+[R_{\rm co}/R_B(\alpha)]^2\approx(R_{\rm co}/R_0)^2$, where $R_B(\alpha)\approx R_B\alpha^{-1/2}$. Consequently, $R_{\rm co}\approx R_0[m|A|/(\alpha p_0-1)]^{1/2}$ and $f_{\rm co}/kT\approx R_{\rm co}/R_0^2\approx[m|A|/(\alpha p_0-1)]^{1/2}R_0^{-1}$. Both $R_{\rm co}$ and $f_{\rm co}$ increase as α decreases.

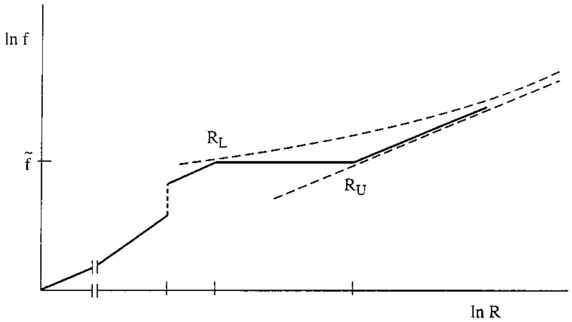

FIG. 5. Effect of free amphiphiles on the fR diagram within the $S_{\rm mix}=0$ approximation. The broken line indicates the position of the boundaries of the coexistence regime as X increases.

To allow for the effects of $S_{\rm mix}$ we need to consider

$$\Omega_{\rm chain}/kT\approx-m\psi|A(\alpha)|+\frac{R^2}{R_B^2[(\psi/\alpha)+(1-\psi)p_0]}-S_{\rm mix}(\alpha,\psi). \tag{39}$$

Following the procedure used in Sec. III, we first obtain $\tilde{R}(\psi)$ from the equilibrium condition $\partial\Omega_{\rm chain}/\partial\psi=0$

$$\tilde{R}\approx\frac{[(\psi/\alpha)+(1-\psi)p_0]}{(p_0-1/\alpha)^{1/2}}[m|A|+S'_{\rm mix}(\alpha,\psi)]^{1/2}. \tag{40}$$

We then obtain the equilibrium $\Omega_{\rm chain}$ by substituting $\tilde{R}$ into Eq. (39). The tension at coexistence, as a function of ψ, is $\tilde{f}_{\rm co}=d\Omega_{\rm chain}(\alpha,\psi)/dR\approx(\partial(\Omega_{\rm chain}/\partial\psi)(\partial\tilde{R}/\partial\psi))^{-1}$ leading to

$$\tilde{f}_{\rm co}\approx f_{\rm co}[1+S'_{\rm mix}(\alpha,\psi)/m|A|k]^{1/2}, \tag{41}$$

where $f_{\rm co}$ is the tension at coexistence within the $S_{\rm mix}=0$ approximation, as given by Eq. (36). In the vicinity of $\psi_0\approx1/[1+(\alpha p_0)^{-1/2}]$, $S_{\rm mix}$ is negligible. To approximate $f_{\rm co}$ in this region we substitute the lever rule $\psi/(1-\psi)\approx[R_U(\alpha)-R]/[R-R_L(\alpha)]$ into $S'_{\rm min}(\alpha,\psi)$, thus obtaining

$$\tilde{f}_{\rm co}\approx f_{\rm co}[1+\ln g(R)]^{1/2}, \tag{42}$$

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

$$g(R)\approx\left[1+\frac{1}{\alpha p_0}\left(\frac{R_U(\alpha)-R}{R-R_L(\alpha)}\right)\right]\left[1+\alpha p_0\left(\frac{R-R_L(\alpha)}{R_U(\alpha)-R}\right)\right]^{1/\alpha p_0}. \tag{43}$$

Assuming that $m\ll m_u$, we identify the boundary of the coexistence regime with $\psi_{\max}\approx 1-\alpha p_0/m$ and $\psi_{\min}\approx\alpha p_0/m$. To obtain $\widetilde{R}_U$ and $\widetilde{R}_L$ we use $\widetilde{f}_{\rm co}(\psi_{\max})\approx\widetilde{R}_L/R_B^2$ and $\widetilde{f}_{\rm co}(\psi_{\min})\approx\widetilde{R}_U/R_0^2$. Because $S'_{\rm mix}(\psi_{\max})/k\approx m\ln[(\alpha p_0)^2/m]$ and $S'_{\rm mix}(\psi_{\min})/k\approx(m/\alpha p_0)\ln m$, we have $\widetilde{f}_{\rm co}(\psi_{\max})\approx f_{\rm co}[1+|A|^{-1}\ln(\alpha p_0)^2/m]^{1/2}$ and $\widetilde{f}_{\rm co}(\psi_{\min})\approx f_{\rm co}[1+(\alpha p_0|A|)^{-1}\ln m]^{1/2}$. Altogether

$$\widetilde{R}_L\approx R_L[1+|A|^{-1}\ln(\alpha p_0)^2/m]^{1/2} \tag{44}$$

and

$$\widetilde{R}_U\approx R_U[1+(\alpha p_0|A|)^{-1}\ln m]^{1/2}. \tag{45}$$

Altogether, our model suggests that the fR diagram of polysoaps exhibits a critical point. As X increases, the width of the plateau shrinks while the tension at coexistence increases. The rough feature of the fR diagram are specified by Eqs. (35)–(38), as obtained via the $S_{\rm mix}=0$ approximation. When the mixing entropy is allowed for the plateau exhibits a logarithmic R dependence and the force at the boundaries changes smoothly into the form expected in the adjacent regimes.

In the preceding discussion $X_{\rm CAC}$ was assumed to be independent of the extension of the chain. In the limits considered in this paper $X_{\rm CAC}$ is actually weakly reduced with the extension. This can be seen by a detailed analysis of (B1). The equilibrium conditions $\partial\Omega_{\rm chain}/\partial u=\partial\Omega_{\rm chain}/\partial\alpha=0$ lead to

$$u^{2/3}+\frac{3}{2}\kappa u^{5/6}+3\tau u^{4/3}=1 \tag{46}$$

and

$$\frac{1}{2\gamma a_0}\ln\frac{X_{\rm CMC}}{X_{\rm CAC}}=1-\frac{1}{3}u^{-1/3}-\frac{2}{3}u^{1/3}. \tag{47}$$

For $\kappa\ll 1$, $\tau\ll 1$, and $u\approx 1$, this leads to $u^{1/3}\approx(1-3\tau-\frac{3}{2}\kappa)^{1/2}$. Substitution in Eq. (47) followed by expansion to first order yields

$$\ln\frac{X_{\rm CMC}}{X_{\rm CAC}}\approx\gamma a_0\left(\tau+\frac{1}{2}\kappa\right),$$

thus indicating that $X_{\rm CAC}$ decreases with τ. This result may be rationalized in terms of the LeChatelier principle [15]. The elastic free energy of the chain is of the form $[R/R_F(\alpha)]^2$ or $[R/R_F(\alpha)]^{5/2}$. Incorporation of free amphiphiles into the chain increases R_F from $m^{3/5}n^{1/2}p_0^{-7/20}b$ to $m^{3/5}n^{1/2}(\alpha p_0)^{-7/20}b$. This makes for a lower elastic penalty and is thus favored.

V. CONCLUDING REMARKS

The distinctive extension behavior of polysoaps is due to their secondary structure. The equilibration of the internal degrees of freedom, associated with the intrachain micelles, gives rise to plateau in the fR diagram. This reflects coexistence of weakly perturbed micelles with fully dissociated chain segments. The secondary structure is denatured by free amphiphiles that form mixed micelles. The secondary structure gradually disappears as X is increased from $X_{\rm CAC}$ to $X_{\rm sat}$. The plateau in the fR diagram, which arises because of this secondary structure, changes accordingly. In particular, the tension at coexistence increases while the width of the coexistence regime decreases. Eventually, at $X\approx X_{\rm sat}$ the plateau disappears, thus giving rise to an ''upper critical point.''

While the preceding discussion is strictly applicable only to polysoaps, it suggests that similar trends may occur in other polymers possessing secondary structure. A force law, similar to that predicted for polysoaps, has been reported for certain biopolymers exhibiting intrachain self-assembly. The experimental results of Cluzel *et al.* [19] and of Smith, Cui, and Bustamante [20] concerning the extension of DNA indeed show a plateau of the type considered above. For this system the plateau was interpreted in terms of a coexistence between two states of the DNA chains [19,21]. The extension behavior of the muscle protein titin, as reported by Kellermayer *et al.* [22], Rief *et al.* [23], and Tskhovrebova *et al.* [24], also reveals a weak plateau at intermediate extensions. The plateau was attributed to the coexistence of folded and unfolded domains. The plateau in the fR diagrams in the three cases is thus traceable to the coexistence of two states in a one-dimensional system subject to a field. This similarity suggests that the fR diagram of biopolymers in the presence of denaturing agents may be similar to that of polysoaps in the presence of free amphiphiles. In the case of DNA intercalation agents act as denaturants. Cluzel *et al.* [19] indeed report that the plateau in the fR diagram of DNA disappears following addition of an intercalation agent, ethidium bromide. In the case of proteins, amphiphiles are among the possible denaturing agents. However, their effect on the fR diagram, to our knowledge, has not been explored. This suggests that it is of interest to study the extension behavior of DNA and of titin in the presence of suitable denaturing agents, in particular, to systematically vary the concentration of the denaturants in order to explore the possibility of an ''upper critical point'' in the force diagram.

APPENDIX A: UNIFORM EXTENSION OF AN ISOLATED POLYSOAP

The free energy of the chain in the uniform extension scenario is

$$F_{\rm chain}/kT\sim m\gamma a_0[u^{-1/3}+u^{1/3}+\tau(R)u^{\eta}]-m\delta, \tag{A1}$$

where $\tau(R)\approx F_{\rm el}(p_0)/kT\gamma a_0 m$ is the ratio of the chain elastic energy to $m\epsilon_p$ for $p\approx p_0$ and a given R. For the initial, Gaussian, regime $\tau=\tau_G(R)\approx(m\gamma a_0)^{-1}(R/R_F)^2$ and $\eta=\frac{7}{10}$, while in the Pincus regime $\tau=\tau_P(R)\approx(m\gamma a_0)^{-1}(R/R_F)^{5/2}$ and $\eta=\frac{7}{8}$. In the stretched bridges regime $\tau=\tau_B(R)\approx(m\gamma a_0)^{-1}(R/R_B)^2$ and $\eta=1$. When $\tau(R)\ll 1$ the head group penalty is dominant. In equilibrium, the leading penalty in $F_{\rm chain}$ is comparable to the driving term. Accordingly, $u\approx 1$ and the micelles are only weakly perturbed. The condition $\tau(R)\ll 1$ is fulfilled in both the

Gaussian and the Pincus regimes. Accordingly, in these regimes $F_{\rm chain}$ is respectively $F_G \approx m\epsilon_{p_0} + kT(R/R_F)^2$ and $F_P \approx m\epsilon_{p_0} + kT(R/R_F)^{5/2}$ and the aggregation number is only weakly reduced. Upon further extension $R > R_{\rm max}$, the stretching proceeds via Gaussian stretching of the bridges. Initially $\tau_B(R) \ll 1$ is fulfilled, the micelles are weakly perturbed, and $F_B \approx m\epsilon_{p_0} + kT(R/R_B)^2$. This regime ends at $R \approx R_*$, defined by $\tau_B(R_*) \approx 1$ or by $R_* \approx R_B)(m\gamma a_0)^{1/2}$ and $f_* \approx (m\gamma a_0)^{1/2}/R_B$. For $R \gg R_*$, $\tau_B \gg 1$ and the elastic penalty in $F_{\rm chain}$ is dominant. Consequently, $\tau_B u$ is comparable to $u^{-1/3}$, thus leading to $\tau_B u^{4/3} \approx 1$. The aggregation number in this regime decrease strongly as $u \approx \tau_B^{-3/4} \approx (m\gamma a_0)^{3/4}(R_B/R)^{3/2}$. Accordingly, $F_B/kT \approx \tau_B^{1/4} \approx (m\gamma a_0)^{-1/4}(R/R_B)^{1/2}$ and the tension in the chain decreases as $f/kT \approx (m\gamma a_0)^{-1/4}(RR_B)^{-1/2}$. Finally, when the chain is fully unraveled (Fig. 3), $u = 1/p_0$, the ideal chain behavior of the backbone in a θ solvent is expected: $F_{\rm chain}$ is $F_{\rm dis}/kT \approx R^2/R_0^2$ and $f/kT \approx R/R_0^2$. Here $R_0 \approx p_0^{1/2}R_B \approx (mn)^{1/2}b$ is the unperturbed span of the unraveled chain. Altogether, the fR diagram exhibits a van der Waals loop.

APPENDIX B: UNIFORM EXTENSION IN THE PRESENCE OF FREE AMPHIPHILES

In the uniform extension scenario, the stretched polysoap self-assembles into a string of m/q mixed micelles consisting each of q polymerized amphiphiles and $p-q$ free amphiphiles such that the total aggregation number is p. The corresponding grand canonical potential, for a given R and T, is $\Omega_{\rm chain} = \Omega_0 + F_{\rm el}$. Here Ω_0 is the grand canonical potential for the unperturbed string of mixed micelles in contact with a reservoir of free amphiphiles of concentration X. $F_{\rm el}$ is the elastic free energy of the string. We focus on the regime where $F_{\rm el}$ is large enough so as to significantly affect the micellar structure. The onset of such coupling occurs when $\kappa \approx \tau(R)$. It is straightforward to check that this condition is only fulfilled in the stretched bridges regime. In this regime $F_{\rm el}/kT \approx [R/R_B(p)]^2 \approx (R/R_B)^2 \alpha u$,where $R_B(p) \approx (m/\alpha u p_0)^{1/2} n^{1/2} b$. Accordingly,

$$\Omega_{\rm chain} \approx m\gamma a_0[\alpha^{-1}(u^{-1/3} + u^{1/3}) + \kappa\alpha^{1/2}u^{1/2} + \tau_B \alpha u] - m\alpha^{-1}\delta + m(1-\alpha^{-1})\ln X. \tag{B1}$$

In the $\kappa \ll 1$ limit $u \approx 1$ and $\Omega_{\rm chain}$ may be written as

$$\Omega_{\rm chain} \approx \alpha^{-1} m \ln(X_{\rm CMC}/X) + m\gamma a_0(\kappa\alpha^{1/2} + \tau_B\alpha) + m \ln X. \tag{B2}$$

Two penalty terms, favoring smaller α, are present. $\kappa\alpha^{1/2}$ reflects the contribution of the coronal penalty. $\tau_B\alpha$ favors smaller α because this weakens the ‘‘spring constant’’ of the chain $1/R_B^2(\alpha) \approx \alpha/R_B^2$, thus lowering the elastic free-energy penalty. We may now distinguish between two regimes. When $\kappa \ll \tau_B$, for weak extensions, the coronal penalty is dominant. In equilibrium, the driving term $\alpha^{-1} m \ln(X_{\rm CMC}/X)$ is comparable to the coronal penalty $m\gamma a_0 \kappa\alpha^{1/2}$, leading to Eq. (4) for α. In this case α depends only on X. The equilibrium $\Omega_{\rm chain}$ in this regime is

$$\Omega_{\rm chain} \approx m p_0^{1/3}\left(\frac{\ln X_{\rm CMC}}{X}\right)^{1/3} + p_0^{-1/3}\left(\frac{\ln X_{\rm CMC}}{X}\right)^{2/3}\left(\frac{R}{R_B}\right)^2 \tag{B3}$$

and the tension in the extended chain $f/kt = \partial\Omega_{\rm chain}/\partial R$ is

$$f/kT \approx p_0^{-1/3}\left(\frac{\ln X_{\rm CMC}}{X}\right)^{2/3}\frac{R}{R_B^2} \approx \frac{\alpha R}{R_B^2}. \tag{B4}$$

In the range of applicability $X_{\rm CAC} < X < X_{\rm sat}$, f decreases as X increases. In particular, $f(X_{\rm CAC})/kT \approx R/R_B^2$ while $f(X_{\rm sat})/kT \approx R/p_0 R_B^2$. This reflects the weakening of the spring constant of the chain α/R_B^2 as X increases. For strong extensions $\tau_B \gg \kappa$, the driving term is comparable to $m\gamma a_0 \tau_B$, thus leading to

$$\alpha \approx \left(m \ln\frac{X_{\rm CMC}}{X}\right)^{1/2}\frac{R_B}{R} \approx \frac{mn^{1/2}}{p_0^{1/2}}\frac{b}{R}\left(\ln\frac{X_{\rm CMC}}{X}\right)^{1/2}. \tag{B5}$$

Note that in this regime α is a function of both R and X. For a given X, an increase in R causes a decrease in α because free amphiphiles are incorporated into the chain so as to maintain $p \approx p_0$. The equilibrium $\Omega_{\rm chain}$ in this range is

$$\Omega_{\rm chain} \approx \left(m \ln\frac{X_{\rm CMC}}{X}\right)^{1/2}\frac{R}{R_B} \tag{B6}$$

and the tension in the chain is independent of R,

$$f_{\rm plateau}/kT \approx \left(m \ln\frac{X_{\rm CMC}}{X}\right)^{1/2}\frac{1}{R_B} \approx \left(\frac{p_0}{nb^2}\ln\frac{X_{\rm CMC}}{X}\right)^{1/2}. \tag{B7}$$

The lower boundary of the plateau regime R_L is roughly defined by the crossover condition $\kappa \approx \tau_B$,

$$R_L/b \approx mn^{1/2}/p_0^{1/4}. \tag{B8}$$

The upper boundary R_U/b corresponds to $\alpha \approx 1/p_0$,

$$R_U/b \approx mn^{1/2}p_0^{1/2}\left(\ln\frac{X_{\rm CMC}}{X}\right)^{1/2}. \tag{B9}$$

For $R > R_U$ the polysoap is fully denatured. There are no remnants of its secondary structure and its elastic behavior is determined by

$$F_{\rm dis}/kT \approx (R/R_0)^2, \tag{B10}$$

leading to

$$f/kT \approx R/R_0^2. \tag{B11}$$

Both $f_{\rm plateau}$ and the width of the plateau regime decrease as X increases. The width of the plateau regime $R_U - R_L$ shrinks as

$$R_U - R_L \approx R_L\left[p_0^{3/4}\left(\ln\frac{X_{\rm CMC}}{X}\right)^{1/2} - 1\right]. \tag{B12}$$

The condition $R_L \approx R_U$ defines a ''lower critical point'' $X_{\rm CP}$, where $p_0^{3/4}(\ln X_{\rm CMC}/X)^{1/2} \approx 1$ or

$$\ln \frac{X_{\rm CMC}}{X_{\rm CP}} \approx \frac{1}{p_0^{3/4}}\,. \tag{B13}$$

Note that $X_{\rm sat} < X_{\rm CP} < X_{\rm CMC}$.

We have described two possible scenarios for the extension of polysoaps in the presence of free amphiphiles: uniform extension and extension with coexistence. Which of the two is the system expected to follow? The scenario associated with the lowest tension is preferred. For $X_{\rm CAC} < X \ll X_{\rm sat}$ the coexistence scheme is clearly favored, $f_{\rm co}(X_{\rm CAC})b/kT \approx n^{-1/2}(|\ln X_{\rm CMC}|)^{1/2} \ll p_0^{3/4} n^{-1/2} \approx f_{\rm plateau}(X_{\rm CAC})b/kT$. However, $f_{\rm co}$ increases with X while $f_{\rm plateau}$ decreases. The two are equal for $X_{\rm co} \approx X_{\rm CMC}^{p_0/(p_0-1)}$. In the following we shall nevertheless argue that the coexistence scenario is expected for the full range of concentrations $X_{\rm CAC} < X < X_{\rm sat}$. However, the situation in the $X_{\rm co} < X < X_{\rm CP}$ regime is less clear-cut. Two factors combine to impede the analysis of this domain. First, the two scenarios differ by numerical factors of order unity. In turn, the rough model we use does not allow to reliably determine such factors. Second, m_u decreases as X increases. In the range of interest $n_d < 1$ is no longer negligible and the validity of the single-phase approximation is questionable. Having said that, we will first examine the situation within our model and later present a physical argument favoring the coexistence picture. For $X > X_{\rm co}$ we have $f_{\rm co} > f_{\rm plateau}$. In particular, $f_{\rm co}(X_{\rm sat})/f_{\rm plateau}(X_{\rm sat}) \approx (|\ln X_{\rm CMC} + 1|)^{1/2} > 1$. However, while the condition $f_{\rm co} < f_{\rm plateau}$ clearly selects the coexistence scenario, $f_{\rm co} > f_{\rm plateau}$ is not sufficient to select the uniform extension. This is because the onset of coexistence takes place at $\tilde{f}_{\rm co}(\psi_{\rm max})$ and $\tilde{f}_{\rm co}(\psi_{\rm max}) \ll f_{\rm co}$ because $S_{\rm mix}$ favors micellar dissociation. At $X_{\rm sat}$ the ratio $f_{\rm co}/f_{\rm plateau} \approx (|\ln X_{\rm CMC} + 1| - \ln m)^{1/2} \approx (-\ln m/m_u)^{1/2}$. Defining Δ via $m = m_u - \Delta$, we have $\tilde{f}_{\rm co}(\psi_{\rm max})/f_{\rm plateau} \approx [-\ln(1-\Delta/m)]^{1/2}$. $\tilde{f}_{\rm co}(\psi_{\rm max})/f_{\rm plateau} \approx \Delta/m \ll 1$ if $\Delta \ll 1$ or $n_d \approx 1$, when the validity of the single-phase approximation is questionable. For $\Delta \approx m_u$, $\tilde{f}_{\rm co}(\psi_{\rm max})/f_{\rm plateau} \approx O(1)$. Altogether, $S_{\rm mix}$ favors the coexistence scenario. However, our rough model does allow for a clear-cut demonstration that $\tilde{f}_{\rm co}(\psi_{\rm max})/f_{\rm plateau} < 1$ at $X_{\rm sat}$. A physical argument favoring the coexistence scenario proceeds as follows. Assume that a crossover indeed occurs at $X \approx X_{\rm co}$. In such a case f for a given R increases with X for $X_{\rm CAC} < X < X_{\rm co}$, but decreases for $X_{\rm co} < X < X_{\rm CP}$. This in turn identifies an unstable region in the corresponding free-energy curve, thus suggesting that the crossover scenario is unphysical. Altogether we expect thus the coexistence scenario to be favored and the fR diagram to exhibit an upper critical point.

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