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Part II: The effective chemical potential

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Self-consistent field theory for a polymer brush Part II: The effective chemical potential

Andreas Münch, Barbara Wagner

Abstract

The most successful mean-field model to describe the collective behaviour of the large class of macromolecular polymers is the self-consistent field theory (SCFT). Still, even for the simple system of a grafted dry polymer brush, the mean-field equations have to be solved numerically. As one of very few alternatives that offer some analytical tractability the strong-stretching theory (SST) has led to explicit expressions for the effective chemical potential and consequently the free energy to promote an understanding of the underlying physics. Yet, a direct derivation of these analytical results from the SCFT model is still outstanding. In this study we present a systematic asymptotic theory based on matched asymtptotic expansions to obtain the effective chemical potential from the SCFT model for a dry polymer brush for large but finite stretching.

1 Introduction

SCFT has established itself as the mean-field model for polymers of high molecular weight [3, 11]. Since the pioneering works of Edwards [2] and Helfand [4] it has been applied to polymer systems for a range of macromolecular architectures, such as block copolymers, or polyelectrolytes and for different geometrical conditions [3]. It has been experimentally validated for a number of phenomena such as the phenomenon of authophobic dewetting of a polymer film from a chemically identical polymer brush, and various phase transitions of block copolymers [5, 18]. Its success has inspired investigations on the theoretical side to derive approximations that allow analytical understanding and therefore also more physical insight into the problem of interest instead of relying completely on numerical solutions as is the case even for the simple case of a polymer brush. However, for the case of densely grafted chains leading to a stretching of the chain such that their length L is large compared to their radius of gyration R_g, the so-called strong-stretching theory (SST) was developed [7, 8, 14, 15, 19, 20]. However, as discussed in [13] significant discrepancies have been noted and in particular in [10] (and references therein), for the case of autophobic dewetting (relating to the prediction of interfacial tension) SST has been shown to disagree with the experimentally established results, which had been correctly predicted by SCFT.

Initially, the nature of the discrepancies was not clear. Efforts of subsequent investigations sought to improve the SST by including further physical regimes in the approximation, giving rise to a whole family of strong-stretching theories and corrections, and on the other hand improve the numerical resolution of SCFT to allow for computations for higher degrees of stretching. While this has led to a much better agreement between the SST and the numerical SCFT results, a direct comparison with an asymptotic approximation derived directly from the SCFT model equations is still outstanding due to the lack of such a theory [12, 16].

The basic approximation of the SST for the effective potential field μ is the parabolic potential, which has been shown by Milner and coauthors [14, 15]. The average segment concentration is a constant

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and in our (scaled) notation that constant is $\phi(x) = 1$. Assuming the validity of the parabolic potential at least to leading order in $\varepsilon = R_g/L$, a systematic asymptotic treatment given in [17] shows that for the parabolic potential to leading order in ε, the average segment concentration ϕ for SCFT is *not* a constant. In the asymptotic analysis presented here we show that for SCFT, incompressibility $\phi(x) = 1$ can be enforced, too, as required, but with a chemcial potential μ that is different from a parabolic potential. While it may be reasonable to expect that the parabolic approximation for μ needs to be corrected, the fact that it does not give the correct (constant) density even to leading order is somewhat surprising. A correction was given by [16, 20].

The main result of this study is to derive for the first time an expression for the effective chemical μ for SCFT by a systematic analytical approach based on matched asymptotic expansions, for the problem of a dry polymer brush as a fundamental example.

In the following sections we first summarize the formulation of the problem, followed by the expansion in the outer coordinates of the asymptotic problem, the formulation and matching of the boundary layer problems and finally by imposing incrompressibility obtain the chemical potential for SCFT for a strongly stretched polymer brush.

2 Formulation

Here we summarize the the formulation of SCFT [17] for an incompressible polymer brush, consisting of polymer chains densely grafted polymer chains on a planar substrate at $x = 0$. As an effect of the dense grafting, the polymer chain is extended to a length $x = L$ and consists of N segments which each have statistical length a. The model describes the average segment density $\phi(x)$ of the polymer segments in terms of an unknown effective chemical potential $\mu(x)$ that describes the interaction between the chain segments that has to be determined by the global constraint that for an incompressible polymer brush, the density must be a constant.

The density $\phi(x)$ is constructed for μ via two partition functions $q(x,s)$ and $q^*(x,s)$ that are used for obtaining the statistics of the chain part with the free end of the brush and the other at the substrate. Specifically, the partition function $q(x,s)$ describes the density of end of a length sN, where $0 < s < 1$, if $s = 0$ end is free. Similarly, the complementary partition function $q^*(x,s)$ describes the density of end of a length sN, where the $s = 0$ end is attached to the substrate

They are given by the modified diffusion equations for the partition function q:

$$\frac{\partial q}{\partial s} = \varepsilon^2 \frac{\partial^2 q}{\partial x^2} - \frac{\mu}{\varepsilon^2} q, \tag{2.1a}$$

$$q(x,0) = 1, \tag{2.1b}$$

$$\frac{\partial q}{\partial x}(0,0) = 0, \tag{2.1c}$$

$$\frac{\partial q}{\partial x}(1,0) = 0, \tag{2.1d}$$

and for the complementary partition function q^*,

$$\frac{\partial q^*}{\partial s} = \varepsilon^2 \frac{\partial^2 q^*}{\partial x^2} - \frac{\mu}{\varepsilon^2} q^*, \tag{2.1e}$$

$$q^*(x,0) = 2\sqrt{6}\,\varepsilon\delta(x), \tag{2.1f}$$

$$\frac{\partial q^*}{\partial x}(0,0) = 0, \tag{2.1g}$$

$$\frac{\partial q^*}{\partial x}(1,0) = 0. \tag{2.1h}$$

The distribution of the segment s for the full chain is obtained by forming the product $q(x,s)q^*(x,1-s)$, noticing that the argument in q has been replaced by $1-s$ as it is assume that the $s=1$ end is the grafted end of the polymer, while $s=0$ is free. The distribution needs to be normalised, which is done with the help of the full partition function

$$Q = \int_0^1 q(x,s)q^*(x,1-s)\mathrm{d}x. \tag{2.1i}$$

Since Q is constant in s we can obtain the average segment density as

$$\phi = \frac{1}{Q}\int_0^1 q(x,s)q^*(x,1-s)\mathrm{d}s, \tag{2.1j}$$

together with the scaled incompressibility condition

$$\phi = 1, \tag{2.1k}$$

where we have nondimensionalaized the above problem via $x = L\tilde{x}$, $\mu = \tilde{\mu}/\varepsilon^2$, $\varepsilon = R_g/L$, where for ideal Gaussian chains, $R_g = a(N/6)^{1/2}$.

We note that the position of a free end is arbitrary, hence $q(x,0)$ is constant. The situation at $x=0$ and $x=L$ is more delicate, as incompressibility breaks down close to the boundaries, i.e., $\phi(x)$ deviates from one close to $x=0,\,L$ since this would require ϕ to be 1 up to the boundary, but outside of the $[0,L]$, it is zero, contradicting incompressibility since a smooth density profile is required. Therefore, the effective chemical potential μ is not defined within the SCFT theory but has to be determined taking into account the details of the molecular interactions. Taken together, (2.1) constitute and inverse problem for μ.

3 Outer correction for the parabolic potential

In this section, instead of setting μ to be the parabolic potential, we allow for next order corrections by expanding

$$\mu(x) = \mu_0(x) + \varepsilon^2\mu_1(x) + \ldots, \tag{3.1a}$$

with

$$\mu_0(x) = -\frac{\pi^2}{16}x^2, \tag{3.1b}$$

and seek to determine μ_1. For this purpose, we first derive expressions for the corrections to u_0, σ_0, q_0 for general μ_1, for the starred variables, and then the corrections they induce for ϕ. Enforcing $\phi(x)=1$ for fixed $0<x<1$ which then yields an integral equation for μ_1 that we can solve explicitly.

3.1 Solutions for u, σ, q

We expand u as before,

$$u = u_0 + \varepsilon^2 u_1 + \dots. \tag{3.2}$$

The leading order solution u_0 is unchanged from section (I-3.1) in [17]. The problem for u_1 consists of two parts which split the domain at $x = \cos(\pi s/2)$,

$$\partial_s u_1 - \frac{\pi}{2} x \tan(\pi s/2) \partial_x u_1 = \frac{\pi}{2} \tan(\pi s/2) u_1 - \mu_1'(x), \qquad \text{for } x \leq \cos(\pi s/2), \tag{3.3a}$$

$$\partial_s u_1 - \frac{\pi}{2}\sqrt{1-x^2}\partial_x u_1 = -\frac{\pi x u_1}{2\sqrt{1-x^2}} - \frac{\pi}{4(1-x^2)^{\frac{3}{2}}} - \mu_1'(x), \qquad \text{for } x > \cos(\pi s/2), \tag{3.3b}$$

with initial condition

$$u_1(x,0) = 0. \tag{3.3c}$$

In the following, we will focus on the case (3.3a), as we expect it will give the dominant contributions to ϕ. We introduce characteristic variables giving

$$\partial_s u_1 = \frac{\pi}{2} \tan(\pi s/2) u_1 - \mu_1'(\xi \cos(\pi s/2)). \tag{3.4}$$

Together with the initial condition this gives the solution

$$u_1 = -\int_0^s \mu_1'(\xi \cos(\pi t/2)) \frac{\cos(\pi t/2)}{\cos(\pi s/2)} \,\mathrm{d}t, \tag{3.5}$$

hence, in (x,s) variables,

$$u_1(x,s) = -\int_0^s \mu_1' \left(x \frac{\cos(\pi t/2)}{\cos(\pi s/2)} \right) \frac{\cos(\pi t/2)}{\cos(\pi s/2)} \,\mathrm{d}t, \quad \text{for } x < \cos(\pi s/2) \tag{3.6}$$

Now, σ_1 can be obtained from (I-2.13) in [17], yielding

$$\sigma(x,s) = \int_0^x u_0(r,s) + \varepsilon^2 u_1(r,s) \mathrm{d}r - \ln g(s) \tag{3.7}$$

$$= \frac{\pi}{8} x^2 \tan(\pi s/2) - \varepsilon^2 \left[\int_0^s \mu_1 \left(x \frac{\cos(\pi t/2)}{\cos(\pi s/2)} \right) \mathrm{d}t + \ln g(s) \right], \tag{3.8}$$

where the last term emerges from a double integral that is reduced to the above result by swapping the order of integration. The function g combines the contributions from any boundary layer at $x = 0$ that may have been neglected upon approximating u by the outer approximation and the contributions from the last two terms in (I-2.13). Thus

$$q(x,s) = \frac{\exp\left[-\int_0^s \mu_1 \left(x \frac{\cos(\pi t/2)}{\cos(\pi s/2)} \right) \mathrm{d}t \right]}{g(s)} \exp\left(\frac{\pi}{8} \frac{x^2}{\varepsilon^2} \tan(\pi s/2) \right) \quad \text{for } x \leq \cos(\pi s/2). \tag{3.9}$$

3.2 Solutions for u^*, σ^*, q^*

We first look at the initial layer occurring for $s = \mathcal{O}(\varepsilon^2)$ if the exact δ function for q^* is replaced by a Gaussian approximation (I-3.75) so that the initial condition for u^* is as in (I-3.76). Using the scaling

$$s = \varepsilon^2 S, \qquad u^* = \varepsilon^{-2} W^*. \tag{3.10}$$

This gives to leading order

$$\partial_S W_0^* = 2W_0^* \partial_x W_0^* \tag{3.11}$$

with initial condition

$$W_0^* = -2x/\omega^2. \tag{3.12}$$

The solution is

$$W_0^* = -2x/(4S + \omega^2). \tag{3.13}$$

For $S \to \infty$, this behaves like

$$W_0^* \sim -\frac{x}{2S} + \frac{\omega^2 x}{8S}\varepsilon^2. \tag{3.14}$$

The next order correction satisfies

$$\partial_s u_1^* + \frac{\pi}{2} x \cot(\pi s/2)\partial_x u_1^* = -\frac{\pi}{2}\cot(\pi s/2) u_1^* - \mu_1'(x). \tag{3.15}$$

with initial condition obtained from (3.14) as

$$u_1^* \sim \frac{\omega^2}{8s^2} x \quad \text{as } s \to 0. \tag{3.16}$$

We introduce characteristic variables $x = \xi \sin(\pi s/2)$, giving

$$\partial_s u_1^* = -\frac{\pi}{2}\cot(\pi s/2) u_1^* - \mu_1'(\xi \sin(\pi s/2)). \tag{3.17}$$

The solution is

$$u_1^* = -\int_0^s \mu_1'\left(\xi \sin(\pi t/2)\right) \frac{\sin(\pi t/2)}{\sin(\pi s/2)} \mathrm{d}t + \frac{c(\xi)}{\sin(\pi s/2)}. \tag{3.18}$$

Converting back to the (x, s) coordinates and using the initial condition fixes c and gives

$$u_1^*(x,s) = -\int_0^s \mu_1'\left(x\frac{\sin(\pi t/2)}{\sin(\pi s/2)}\right) \frac{\sin(\pi t/2)}{\sin(\pi s/2)} \mathrm{d}t + \frac{\pi^2\omega^2 x}{32\sin^2(\pi s/2)}. \tag{3.19}$$

Now we obtain via (I-2.15) and the initial condition (I-3.75)

$$\begin{aligned}\sigma^* = &-\frac{\pi}{8}x^2\cot(\pi s/2) \\ &+ \varepsilon^2\left[\int_0^s \mu_1\left(x\frac{\sin(\pi t/2)}{\sin(\pi s/2)}\right)\mathrm{d}t + \frac{\pi^2\omega^2 x^2}{64\sin^2(\pi s/2)} - \ln g^*(s)\right] + \mathcal{O}(\varepsilon^4),\end{aligned} \tag{3.20}$$

where $g^*(s)$ incorporates any boundary layer contributions to u at $x = 0$ that may have been dropped upon introducing the outer expansion for u in (I-2.16), and any contributions from the last three terms in the same equation. Hence

$$\begin{aligned}\sigma^*(x, 1-s) = &-\frac{\pi}{8}x^2\tan(\pi s/2) \\ &- \varepsilon^2\left[\int_s^1 \mu_1\left(x\frac{\cos(\pi t/2)}{\cos(\pi s/2)}\right)\mathrm{d}t + \frac{\pi^2\omega^2 x^2}{64\cos^2(\pi s/2)} - \ln g^*(1-s)\right] \\ &+ \mathcal{O}(\varepsilon^4),\end{aligned} \tag{3.21}$$

From this (dropping the error term)

$$q^*(x,1-s) = \frac{\exp\left[-\int_s^1 \mu_1\left(x\frac{\cos(\pi t/2)}{\cos(\pi s/2)}\right)\mathrm{d}t + \frac{\pi^2\omega^2x^2}{64\cos^2(\pi s/2)}\right]}{g^*(1-s)}\exp\left(-\frac{\pi}{8\varepsilon^2}x^2\tan(\pi s/2)\right). \quad (3.22)$$

3.3 Density ϕ and solution for μ_1

From (3.9) and (3.22), we get

$$q(x,s)q^*(x,1-s) = \frac{\exp\left[-\int_0^1 \mu_1\left(\frac{x\cos(\pi t/2)}{\cos(\pi s/2)}\right)\mathrm{d}t + \frac{\pi^2\omega^2x^2}{64\cos^2(\pi s/2)}\right]}{g(s)g^*(1-s)} \quad (3.23)$$

provided $x \leq \cos(\pi s/2)$. We assume that the contributions from $x > \cos(\pi s/2)$ are of lower order (the calculation of which requires knowledge of σ_1 also for $x > \cos(\pi s/2)$, which we have not carried out yet).

Hence, integration with respect to $x = 0 \ldots 1$ reduces to the interval $0 \leq x \leq \cos(\pi s/2)$ so that we get for Q, after a variable transform $x = z\cos(\pi s/2)$,

$$Q = \frac{\cos(\pi s/2)}{g(s)g^*(1-s)}\int_0^1 h(z)\mathrm{d}z, \quad (3.24)$$

with

$$\begin{aligned} h(z) &\equiv \exp\left[-\int_0^1 \mu_1(z\cos(\pi t/2))\mathrm{d}t + \frac{\pi^2\omega^2z^2}{64}\right] \\ &= \exp\left[-\frac{2}{\pi}\int_0^z \frac{\mu_1(\eta)}{\sqrt{z^2-\eta^2}}\mathrm{d}\eta + \frac{\pi^2\omega^2z^2}{64}\right]. \end{aligned} \quad (3.25)$$

Since, to each order, Q has to be independent of s, we need to to assume that the prefactor must cancel, so that

$$\frac{\cos(\pi s/2)}{g(s)g^*(1-s)} = c_Q, \quad (3.26)$$

and therefore

$$Q = c_Q\int_0^1 h(z)\mathrm{d}z. \quad (3.27)$$

Furthermore,

$$\begin{aligned} \phi(x) &= \frac{c_Q}{Q}\int_0^{(2/\pi)\arccos x} \frac{h(x/\cos(\pi s/2))}{\cos(\pi s/2)}\mathrm{d}s \\ &= \frac{2}{\pi}\int_x^1 \frac{1}{r\sqrt{1-r^2}}\frac{h(x/r)}{\int_0^1 h(z)\mathrm{d}z}\mathrm{d}r \\ &= \frac{2}{\pi}\int_x^1 \frac{1}{\sqrt{y^2-x^2}}\frac{h(y)}{\int_0^1 h(z)\mathrm{d}z}\mathrm{d}y. \end{aligned} \quad (3.28)$$

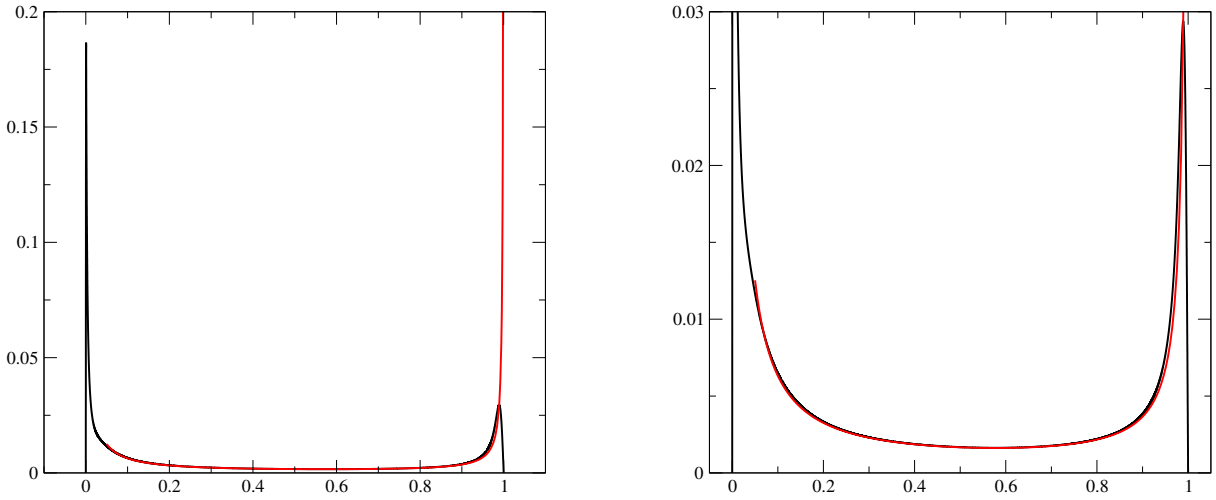

Figure 1: Comparison of the analytical approximation for $u^*(x,1)$, that is $= u_1^*(x,1)$, with the numerical results, via the red and black line, respectively. The right panel is a zoom of the left.

Now we enforce the condition $\phi(x) = 1$. This turns the last expression into an integral equation for h, which has the solution (to be derived via Laplace transform – is solution unique up to the constant factor?)

$$h(y) = \frac{\mathrm{e}^K y}{\sqrt{1-y^2}}, \tag{3.29}$$

where e^K is an arbitrary, positive constant. It has to be positive, as we need to solve (3.25) for μ_1 with the resulting h. Taking the log on both sides gives

$$-\frac{2}{\pi}\int_0^z \frac{\mu_1(\eta)}{\sqrt{z^2-\eta^2}}\mathrm{d}\eta + \frac{\pi^2\omega^2 z^2}{64} = \ln h(z) = \ln(z) - \frac{1}{2}\ln(1-z^2) + K. \tag{3.30}$$

Solving this for μ_1 gives

$$\begin{aligned}\mu_1(x) &= -\frac{x}{\sqrt{1-x^2}}\arctan\left(\frac{x}{\sqrt{1-x^2}}\right) - \ln c - \ln 2 - \ln x - \frac{\pi^2\omega^2 x^2}{32} \\ &= -\frac{x}{\sqrt{1-x^2}}\arcsin(x) - \ln(2cx) - \frac{\pi^2\omega^2 x^2}{32}.\end{aligned} \tag{3.31}$$

From μ_1, we can compute u_1^* via (3.19), and for $s = 1$, this is in fact the approximation for $u^*(x,1)$. We compare this analytical approximation with the numerical solution in fig. 1. The agreement is excellent away from $x = 0$ and $x = 1$, where we expect boundary layers.

4 Boundary layer for the potential at $x = 1$

We adopt the scalings that we found in (I-3.13) and the following equations for the boundary layer at $x = 1$ for the solution to u with the parabolic potential, that is, we introduce

$$x = 1 - \varepsilon^{4/3} z, \quad u = \varepsilon^{2/3} w. \tag{4.1}$$

The x-scaling is consistent with an end layer width for the chains suggested by Likhtman and Semenov [8]. We need to determine the appropriate rescaling for μ. If we expand $\mu_0 + \varepsilon^2 \mu_1$ at $x = 0$ and introduce the rescaling into (4.1) for x, we obtain

$$\mu_0 + \varepsilon^2 \mu_1 \sim -\frac{\pi^2}{16} + \frac{\pi^2}{8} \varepsilon^{4/3} z - \frac{\pi}{2\sqrt{2z}} \varepsilon^{4/3} + \dots, \tag{4.2}$$

thus suggesting that we let

$$\mu(x) = -\frac{\pi^2}{16} + \varepsilon^{4/3} m(z), \tag{4.3}$$

where the leading order of $m(z)$ has to satisfy

$$m_0(z) \sim \frac{\pi^2}{8} z - \frac{\pi}{2\sqrt{2z}} \qquad \text{for } z \to \infty. \tag{4.4}$$

4.1 Determining the boundary layer solution for u

Using these rescalings for u gives to leading order

$$\partial_{\hat{s}} w_0 = \partial_z^2 w_0 - 2 w_0 \partial_z w_0 + \frac{\mathrm{d} m_0}{\mathrm{d} z} \tag{4.5a}$$

We have kept the time derivative to leading order by rescaling $s = \varepsilon^{2/3} \hat{s}$. Initial and boundary conditions are

$$w_0(z, 0) = 0, \tag{4.5b}$$

$$w_0(0, \hat{s}) = 0. \tag{4.5c}$$

Using the scalings for u and x as stated in (4.1) and for s as given in the text in the outer solution (I-3.6) for u yields

$$u_0 = \frac{\pi}{4}(1 - \varepsilon^{4/3} z) \tan(\pi \varepsilon^{2/3} \hat{s}/2) = \frac{\pi}{4}(\pi \varepsilon^{2/3} \hat{s}/2) + \mathcal{O}(\varepsilon^2)$$

Hence, the far-field condition for the leading order solution comes from matching to the outer, giving

$$w_0(z, \hat{s}) \sim \frac{\pi^2}{8} \hat{s} \quad \text{for } z \to \infty. \tag{4.5d}$$

4.2 Determining boundary layer solution for u^*

Using the rescalings for u^* gives to leading order

$$\partial_{s^*} w_0^* = \partial_z^2 w_0^* - 2 w_0^* \partial_z w_0^* + \frac{\mathrm{d} m_0}{\mathrm{d} z} \tag{4.6a}$$

where $dm_0/dz = \pi^2/8$. We have kept the time derivative to leading order by rescaling $s = \varepsilon^{2/3}s^* + 1$. The boundary condition is

$$w_0^*(0, s^*) = 0. \tag{4.6b}$$

Using the scaling for x, i.e. $x = 1 - \varepsilon^{4/3}z$ yields

$$\partial_{s^*} w_0^* = \varepsilon^{8/3}\partial_x^2 w_0^* - 2\varepsilon^{4/3} w_0^* \partial_x w_0^* + \frac{\pi^2}{8}$$

Hence, the far-field condition for the leading order solution comes from matching to the outer, giving

$$w_0^*(z, s^*) \sim \frac{\pi^2}{8} s^* \quad \text{for } z \to \infty. \tag{4.6c}$$

We also need to match the $s \to -\infty$ limit with the solution in region 1B. Following the the derivation given in part I in section I-3.2.2 of [17], we obtain

$$w_0^* \sim -\frac{\pi^2}{8} s \tanh\left(\frac{\pi^2}{8} sz\right) \quad \text{as } s \to -\infty. \tag{4.7}$$

4.3 Density ϕ and boundary layer solution for m_0.

For completeness, we first state some identities that hold for both σ and σ^*, starting with

$$\sigma(x, s) = \int_a^x \partial_x \sigma(r, s)\mathrm{d}r + \int_b^s \partial_s \sigma(a, t)\mathrm{d}t + \sigma(a, b) \tag{4.8}$$

for any $0 \le a \le 1$, $0 \le b \le 1$ (for σ^*: if $\sigma^*(a, b)$ is finite). Since

$$\partial_x \sigma = u, \tag{4.9}$$
$$\partial_s \sigma = \varepsilon^2 \partial_x u + u^2 - \mu, \tag{4.10}$$

we get

$$\sigma(x, s) = \int_a^x u(r, s)\mathrm{d}r + \int_b^s \varepsilon^2 \partial_x u(a, t) + u^2(a, t)\mathrm{d}t - \mu(a)(s - b) + \sigma(a, b), \tag{4.11}$$
$$\sigma^*(x, s) = \int_a^x u^*(r, s)\mathrm{d}r + \int_b^s \varepsilon^2 \partial_x u^*(a, t) + (u^*(a, t))^2\mathrm{d}t - \mu(a)(s - b) + \sigma^*(a, b). \tag{4.12}$$

For the following derivation, we note some special cases:

$$\sigma(x, s) = \int_1^x u(r, s)\mathrm{d}r + \int_0^s \varepsilon^2 \partial_x u(1, t)\mathrm{d}t - \mu(1)s, \tag{4.13}$$

where we have set $a = 1$, $b = 0$ and used that $\sigma(1, 0) = 0$ (initial condition) and $u(1, t) = 0$ (boundary condition).

$$\sigma^*(x, s) = \int_1^x u^*(r, s)\mathrm{d}r + \int_1^s \varepsilon^2 \partial_x u^*(1, t)\mathrm{d}t - \mu(1)(s - 1) + \sigma^*(1, 1), \tag{4.14}$$

where we have set $a = 1$, $b = 1$ and used that $u^*(1, t) = 0$ (boundary condition).

Now we have from (2.1i) that

$$Q = \int_0^1 q^*(x,1)\mathrm{d}x \tag{4.15}$$

hence

$$Q = \int_0^1 \exp\left(\varepsilon^{-2}\left[\int_1^x u^*(r,1)\mathrm{d}r + \sigma^*(1,1)\right]\right)\mathrm{d}x. \tag{4.16}$$

For ϕ, we have from (2.1j)

$$\phi = \frac{1}{Q}\int_0^1 \exp\left(\varepsilon^{-2}\left[\sigma(x,s) + \sigma^*(x,1-s)\right]\right)\mathrm{d}s, \tag{4.17}$$

hence

$$\begin{aligned}\phi = \frac{1}{Q}\int_0^1 \exp\Bigg(\varepsilon^{-2}\Bigg[&\int_1^x u(r,s)\mathrm{d}r + \int_0^s \varepsilon^2\partial_x u(1,t)\mathrm{d}t \\ &+ \int_1^x u^*(r,1-s)\mathrm{d}r + \int_1^{1-s}\varepsilon^2\partial_x u^*(1,t)\mathrm{d}t + \sigma^*(1,1)\Bigg]\Bigg)\mathrm{d}s,\end{aligned} \tag{4.18}$$

which, after using the most recent expression for Q, can be simplified to

$$\phi = \frac{\tilde{I}}{\tilde{Q}}, \tag{4.19a}$$

with

$$\begin{aligned}\tilde{I} = \int_0^1 \exp\Bigg(\varepsilon^{-2}&\left[\int_1^x u(r,s) + u^*(r,1-s)\mathrm{d}r\right] \\ &+ \int_0^s \partial_x u(1,t) - \partial_x u^*(1,1-t)\mathrm{d}t\Bigg)\mathrm{d}s,\end{aligned} \tag{4.19b}$$

$$\tilde{Q} = \int_0^1 \exp\left(\varepsilon^{-2}\left[\int_1^x u^*(r,1)\mathrm{d}r\right]\right)\mathrm{d}x. \tag{4.19c}$$

The problem is closed by enforcing the incompressibility condition, i.e.

$$\phi = 1. \tag{4.20}$$

We now need to insert the expansions to evaluate $\tilde{Q}$ and ϕ. We are at this point mainly interested in the behaviour in the boundary layer at $x = 1$, and so we will evaluate $\tilde{I}$ in this region. For $\tilde{Q}$, we need, however, the fully matched solution for u^* across the entire interval $0 < x < 1$, which we do not have yet. Numerical evaluation for $\varepsilon = 0.025$ gives a value of $Q = 0.083$, which is very close to $\varepsilon^{2/3} = 0.085$, so we will operate on the assumption that

$$\tilde{Q} \sim \varepsilon^{2/3}. \tag{4.21}$$

For $\tilde{I}$, we introduce the boundary layer variables, so that we have

$$u(x,s) + u^*(x,1-s) = \varepsilon^{2/3}\left(w\left(z, s/\varepsilon^{2/3}\right) + w^*\left(z, -s/\varepsilon^{2/3}\right)\right), \tag{4.22}$$

$$= \left(w\left(z,\hat{s}\right) + w^*\left(z,-\hat{s}\right)\right), \tag{4.23}$$

$$\int_1^x u(r,s) + u^*(r,1-s)\mathrm{d}x = \varepsilon^2\int_0^z \left(w(\rho,\hat{s}) + w^*(\rho,-\hat{s})\right)\mathrm{d}\rho, \tag{4.24}$$

so that to leading order we have

$$\varepsilon^{-2}\int_1^x u(x,s)+u^*(x,1-s)\mathrm{d}x=\int_0^z\left(w_0(\rho,\hat{s})+w_0^*(\rho,-\hat{s})\right)\mathrm{d}\rho. \tag{4.25}$$

Next, we have

$$\int_0^s \partial_x u(1,t)\mathrm{d}t=\int_0^{\hat{s}}\partial_z w(0,\tau)\mathrm{d}\tau, \tag{4.26}$$

$$\int_0^s \partial_x u^*(1,1-t)\mathrm{d}t=\int_0^{\hat{s}}\partial_z w^*(0,-\tau)\mathrm{d}\tau, \tag{4.27}$$

so that, to leading order

$$\int_0^s \partial_x u(1,t)-\partial_x u^*(1,1-t)\mathrm{d}t=\int_0^{\hat{s}}\partial_z w_0(0,\tau)-\partial_z w_0^*(0,-\tau)\mathrm{d}\tau. \tag{4.28}$$

Therefore, to leading order

$$\begin{aligned}\tilde{I}=\varepsilon^{2/3}\int_0^{\varepsilon^{-2/3}}\exp\Bigg(&\int_0^z\left(w_0(\rho,\hat{s})+w_0^*(\rho,-\hat{s})\right)\mathrm{d}\rho\\&+\int_0^{\hat{s}}\partial_z w_0(0,\tau)-\partial_z w_0^*(0,-\tau)\mathrm{d}\tau\Bigg)\mathrm{d}\hat{s}\end{aligned} \tag{4.29}$$

Noting (4.21) gives, after taking the limit $\varepsilon\to 0$ in the limit of the outermost integration

$$\begin{aligned}\phi(z)=\int_0^{\infty}\exp\Bigg(&\int_0^z\left(w_0(\rho,\hat{s})+w_0^*(\rho,-\hat{s})\right)\mathrm{d}\rho\\&+\int_0^{\hat{s}}\partial_z w_0(0,\tau)-\partial_z w_0^*(0,-\tau)\mathrm{d}\tau\Bigg)\mathrm{d}\hat{s}\end{aligned} \tag{4.30}$$

With (5.29), that is,

$$\phi(z)=1\quad\text{for } 0\le z<\infty, \tag{4.31}$$

and the initial boundary value problems for w_0 and w_0^* we have a closed problem to solve for determining $\mathrm{d}m_0/\mathrm{d}z$ and hence, up to an integration constant, the boundary layer solution m_0 for the potential.

5 Boundary layer at $x=0$

Near $x=0$, μ_0 and $\varepsilon^2\mu_1$ behave like

$$\mu_0\sim-\frac{\pi^2}{16}x^2,\qquad \varepsilon^2\mu_1\sim(c-\ln 2)\varepsilon^2-\varepsilon^2\ln x.$$

Hence, for sufficiently small x, $\varepsilon^2\mu_1$ actually dominates μ_1. Ignoring the logarithmic contribution, the two terms balance for $x=\mathcal{O}(\varepsilon)$, hence we scale

$$x=\varepsilon y,\qquad \mu=\varepsilon^2 M. \tag{5.1}$$

However, we need a second scaling, for even thinner layers in x. One way to motivate is to consider using a Gaussian of width $\omega\varepsilon^2$ instead of an exact δ-function for the initial data for q^*, that is

$$q^*(x,0) = \frac{2\sqrt{6}}{\sqrt{\pi}\omega\varepsilon}\exp\left(-\frac{x^2}{\omega^2\varepsilon^4}\right), \tag{5.2}$$

hence

$$u^*(x,0) = -\frac{2x}{\omega^2\varepsilon^2}. \tag{5.3}$$

Numerical evidence suggests that for ω fixed and $\varepsilon \to 0$, the potential μ develops a narrow peak at $x = 0$ of width $\mathcal{O}(\varepsilon^2)$ but the height tends to a constant. Hence we use the scaling

$$x = \varepsilon^2 Y, \qquad n = \mu = \varepsilon^2 M. \tag{5.4}$$

5.1 Solutions for u

5.1.1 Region $s = \mathcal{O}(1)$

Innermost boundary layer. Using the scalings (5.4) and also

$$u(x,s) = V(Y,s) \tag{5.5}$$

in (I-2.11a) (for smaller u, all u terms would be subdominant) gives

$$\varepsilon^2\partial_s V = \partial_Y^2 V + 2V\partial_Y V + n_Y, \tag{5.6}$$

with the leading order being

$$\partial_Y^2 V_0 + 2V_0\partial_Y V_0 + n_{0,Y} = 0, \tag{5.7}$$

The boundary condition at $y = 0$ is

$$V_0(0,s) = 0. \tag{5.8}$$

Integrating once with respect to y gives

$$\partial_Y V_0 + V_0^2 + n_0 = a_1(s), \tag{5.9}$$

with a constant of integration $a_1(s)$.

For matching, we need the expansion of V_0 at $y \to \infty$, which is

$$V_0 \sim (a_1(s) - n_{0,\infty})^{1/2} \quad \text{as } Y \to \infty, \tag{5.10}$$

where we have assumed that $n_0 \to n_{0,\infty}$ in this limit.

Next boundary layer. We now use the scalings (5.1). To balance μ_x with the second of the spatial derivatives, we need to assume $u = \mathcal{O}(\varepsilon)$. Hence we also rescale

$$u = \varepsilon U. \tag{5.11}$$

Introducing these new scalings gives

$$\partial_s U = \partial_y^2 U - 2U\partial_y U + \frac{\mathrm{d}M_0}{\mathrm{d}y}, \tag{5.12a}$$

$$U(y,0) = 0. \tag{5.12b}$$

Hence, the leading order problem for U_0 is trivially found to be

$$\partial_s U_0 = \partial_y^2 U_0 - 2U_0\partial_y U_0 + \frac{\mathrm{d}M_0}{\mathrm{d}y}, \tag{5.13a}$$

$$U_0(y,0) = 0, \tag{5.13b}$$

By matching to the expansion of $u_0 + \varepsilon^2 u_1$ at $x = 0$, we obtain the far-field condition

$$U_0 \sim \frac{\pi}{4} y \tan(\pi s/2) - \frac{s}{y} \quad \text{as } y \to \infty. \tag{5.13c}$$

On the other hand, matching U at $y = 0$ with the far-field expansion (5.21) of the innermost solution gives

$$U_0(0,s) = \left(a_1(s) - n_{0,\infty}\right)^{1/2}. \tag{5.13d}$$

5.1.2 Region $s = 1 - \mathcal{O}(\varepsilon)$

The boundary layer structure that we identified for $s = \mathcal{O}(1)$ breaks down when the outer solution in the region $x < \cos(\pi s/2)$ shrinks so that the boundary layer and the corner layer merge, both of which have $\mathcal{O}(\varepsilon)$ width. Hence the breakdown happens when $s = 1 - \mathcal{O}(\varepsilon)$.

5.2 Solutions for u^*

5.2.1 Region $s = \mathcal{O}(\varepsilon^2)$

Here, we use the scalings (5.4). Then the initial condition (5.3) becomes an $\mathcal{O}(1)$ expression for u^*, while to keep the s-derivative, we need to scale it by ε^2, hence

$$s = \varepsilon^2 S, \qquad W^* = u^*. \tag{5.14}$$

Introducing the new variables gives

$$\partial_S W_0^* = \partial_Y^2 W_0^* - 2W_0^*\partial_Y W_0^* + \frac{\mathrm{d}n_0}{\mathrm{d}Y}, \tag{5.15a}$$

$$W_0^*(Y,0) = -\frac{2Y}{\omega^2}, \tag{5.15b}$$

$$W_0^*(0,S) = 0, \tag{5.15c}$$

$$W_0^* \sim -\frac{Y}{2S} \quad \text{as } Y \to \infty. \tag{5.15d}$$

5.2.2 Region $s = \mathcal{O}(1)$

Innermost boundary layer. Using the scalings as for u, that is (5.4) and also

$$V^*(Y,s) = u^*(x,s) \tag{5.16}$$

in (I-2.14a) gives

$$\varepsilon^2 \partial_s V^* = \partial_Y^2 V^* + 2V^* \partial_Y V^* + n_Y, \tag{5.17}$$

with the leading order being

$$\partial_Y^2 V_0^* + 2V_0^* \partial_Y V_0^* + n_{0,Y} = 0, \tag{5.18}$$

The boundary condition at $y = 0$ is

$$V_0^*(0,s) = 0. \tag{5.19}$$

Integrating once with respect to y gives

$$\partial_Y V_0^* + (V_0^*)^2 + n_0 = a_1^*(s), \tag{5.20}$$

with a constant of integration $a_2^*(s)$.

For matching, we need the expansion of V_0^* at $y \to \infty$, which is

$$V_0^* \sim (a_2^*(s) - n_{0,\infty})^{1/2} \quad \text{as } Y \to \infty, \tag{5.21}$$

where we have assumed that $n_0 \to n_{0,\infty}$ in this limit.

Next boundary layer. We now use the scalings (5.1) and proceed as for u. Hence we rescale

$$u^* = \varepsilon U^*. \tag{5.22}$$

Introducing these new scalings and taking the leading order gives

$$\partial_s U_0^* = \partial_y^2 U_0^* - 2U_0^* \partial_y U_0^* + \frac{\mathrm{d}M_0}{\mathrm{d}y}, \tag{5.23a}$$

$$U_0^*(0,s) = 0, \tag{5.23b}$$

$$U_0^* \sim -\frac{\pi}{4} y \cot(\pi s/2) - \frac{s}{y} \quad \text{as } y \to \infty. \tag{5.23c}$$

On the other hand, matching U at $y = 0$ with the far-field expansion (5.21) of the innermost solution gives

$$U_0^*(0,s) = (a_2^*(s) - n_{0,\infty})^{1/2}. \tag{5.23d}$$

5.3 Density ϕ and boundary layer solution for n_0

We first express σ and σ^* in terms of u and u^* (and also μ) via the expressions (4.11) and (4.12) derived in an earlier section, this time integrating from the left interval end. We obtain

$$\sigma(x,s) = \int_0^x u(r,s)\mathrm{d}r + \int_0^s \varepsilon^2 \partial_x u(0,t)\mathrm{d}t - \mu(0)s, \tag{5.24}$$

where we have set $a = 0$, $b = 0$ and used that $\sigma(0,0) = 0$ (initial condition) and $u(0,t) = 0$ (boundary condition). Moreover, we have

$$\sigma^*(x,s) = \int_0^x u^*(r,s)\mathrm{d}r + \int_1^s \varepsilon^2 \partial_x u^*(0,t)\mathrm{d}t - \mu(0)(s-1) + \sigma^*(0,1), \tag{5.25}$$

where we have set $a = 0$, $b = 1$ and used that $u^*(0,t) = 0$ (boundary condition).

Therefore

$$\sigma(x,s) + \sigma^*(x,1-s) = \int_0^x u(r,s) + u^*(r,1-s)\mathrm{d}r \tag{5.26}$$

$$+ \int_0^s \varepsilon^2 \left(\partial_x u(0,t) - \partial_x u(0,1-t)\right)\mathrm{d}t + \sigma^*(0,1). \tag{5.27}$$

Proceeding further, we get

$$\phi = \frac{\tilde{I}}{\tilde{Q}}, \tag{5.28a}$$

with

$$\tilde{I} = \int_0^1 \exp\left(\varepsilon^{-2}\left[\int_0^x u(r,s) + u^*(r,1-s)\mathrm{d}r\right] + \int_0^s \partial_x u(0,t) - \partial_x u^*(0,1-t)\mathrm{d}t\right)\mathrm{d}s, \tag{5.28b}$$

$$\tilde{Q} = \int_0^1 \exp\left(\varepsilon^{-2}\left[\int_0^x u^*(r,1)\mathrm{d}r\right]\right)\mathrm{d}x. \tag{5.28c}$$

For the last expression, we have used the initial condition for u to set $u(0,0) = 0$. The problem is closed by enforcing the incompressibility condition, i.e.

$$\phi = 1. \tag{5.29}$$

We continue with $\tilde{I}$. Rescaling into innermost variables, that is, using the first equation in (5.4), while keeping $s = \mathcal{O}(1)$, we obtain

$$\tilde{I} = \int_0^1 \exp\left(\left[\int_0^Y V(\rho,s) + V^*(\rho,1-s)\mathrm{d}\rho\right] + \varepsilon^{-2}\int_0^s \partial_Y V(0,t) - \partial_Y V^*(0,1-t)\mathrm{d}t\right)\mathrm{d}s, \tag{5.30}$$

To leading order, the integrand in the last expression has to vanish for a all s to give a finite limit, since, due to the dependence on s, the $\mathcal{O}(\varepsilon^{-1})$ contribution cannot be cancelled by $\tilde{Q}$. Hence we need to have

$$\partial_Y V_0(0,s) = \partial_Y V_0^*(0,1-s) \equiv b(s). \tag{5.31}$$

Using this in the problems for V_0 and V_0^*, we obtain

$$\partial_Y V_0 + V_0^2 + n_0 = b(s), \tag{5.32a}$$

$$V_0(0,s) = 0 \tag{5.32b}$$

$$V_0 \sim (b(s) - n_{0,\infty})^{1/2} \quad \text{as } Y \to \infty, \tag{5.32c}$$

and

$$\partial_Y V_0^* + (V_0^*)^2 + n_0 = b(1-s), \tag{5.33a}$$

$$V_0^*(0,s) = 0 \tag{5.33b}$$

$$V_0^* \sim (b(1-s) - n_{0,\infty})^{1/2} \quad \text{as } Y \to \infty. \tag{5.33c}$$

But this implies that $V_0^*(Y, 1-s) = V_0(Y,s)$, hence we only need to solve (5.32), and then obtain to leading order for $\tilde{I}$

$$\tilde{I}_0 = \int_0^1 \exp\left(\int_0^Y V(\rho,s)\mathrm{d}\rho\right)^2 k\left((1-s)/\varepsilon^2\right)\mathrm{d}s. \tag{5.34}$$

The factor last factor in the integrand deserves some explanation. The argument that leads to (5.31) breaks down in the $\mathcal{O}(\varepsilon^2)$ thin s-layer near $s=1$, thus we have to evaluate

$$\ln k(S) = \varepsilon^{-2}\int_0^{1+\varepsilon^2 S} \partial_Y V(0,t) - \partial_Y V^*(0,1-t)\mathrm{d}t \tag{5.35}$$

there explicitly. In terms of the Variables W^* (and correspondingly introduce W we obtain

$$k(S) = \exp\left[\int_{-\infty}^S \partial_Y W_0(0,T) - \partial_Y W_0^*(0,-T)\mathrm{d}T\right]. \tag{5.36}$$

6 Conclusions

The asymptotic analysis given in this article reveals and justifies the different physical regimes of the solution, of the effective chemical potential of a grafted stretched polymer brush, via a systematic mathematical approach that does not rely on physical intuition. As we have shown, this mathematical approach has the ability to uncover subtle features of the solution that are easily missed otherwise and guarantees that all contributions to a correction at a certain level are included. Our analysis also provides a toolbox establishing a mathematical method to treat other and more complex problems, for which no SST theory has been developed. Moreover, our results yield an important limit, against which other models, such as phase-field type models, can be calibrated. These methods, while they offer other analytical approaches, have gained attention again recently as an approach for larger scale simulations required in real-world applications [1, 6, 9], where they offer a significant speed advantage compared to numerical solutions of SCFT and its dynamic variants.

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