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Validity of the scaling functional approach for polymer interfaces as a variational theory

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We discuss the soundness of the scaling functional (SF) approach proposed by Aubouy Guiselin and Raphaël [Macromolecules **29**, 7261 (1996)] to describe polymeric interfaces. In particular, we demonstrate that this approach is a variational theory. We emphasize the role of SF theory as an important link between ground-state theories suitable to describe adsorbed layers, and "classical" theories for polymer brushes.

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I. INTRODUCTION

Polymer interfaces are layers made of polymeric chains in direct contact with a boundary which may be a solid/liquid, liquid/liquid interface or a more complex surface such as a membrane. Because they have applications in such diverse fields as colloid stabilization, coating, tribology, galenic, they have been the subject of active research since the 1980s both from a fundamental and applied point of view. At present, there are two well established self-consistent-field (SCF) theories to describe polymer layers. They both start from the partition function of an ensemble of chains in contact with the interface treated in mean field, but they soon proceed in a marked different way. Eventually, they become very different type of theories, depending on whether the chains are reversibly adsorbed, and there is an adsorbed state which dominates the solution of the associated Schrödinger equation (ground-state dominance (GSD) theories [1,2]), or they are end tethered to a repulsive surface (so-called "brushes"), and the path integral is dominated by the classical solution (classical theories [3–5]).

Because the two types of theories are very different in spirit, there is a conceptual gap for intermediate cases. In other words, there is no mean-field theory available to describe both adsorption and grafting of polymers within the same formalism. Such case arises, e.g., when chains are grafted onto an attractive surface. In principle, at least, one should be able to go in a continuous way from adsordedlike to brushlike layers by tuning the amount of chains per unit surface.

A tentative to bridge such gap was proposed in a series of papers where the so-called scaling functionnal (SF) approach is developed [6,7]. This is an approach where the layer of monodisperse adsorbed chains (N monomers of size a) is considered as a thermodynamic ensemble of interacting loops and tails. These loops are polydisperse in size, and the main tool is the "loop size profile" S such that

$$S(n)=S_0\int_n^N P(u)du, \tag{1}$$

where P is the statistical distribution of loop sizes in monomer units, and S_0 is the total number (per cm^2) of loops. The free energy (per cm^2) of the layer of chains is written as

$$\mathcal{F}\{S\}\cong\frac{k_BT}{a^2}\int_0^N\left\{k[a^2S(n)]^{\beta}+[-a^2S'(n)]\times\ln\left[-\frac{S'(n)}{S_0}\right]\right\}dn, \tag{2}$$

where $k\cong 1$ is a constant, k_BT is the thermal energy, and $S'(n)=dS/dn$. The first term on the right hand side (rhs) of Eq. (2) accounts for loop interactions (which depend on solvent conditions through the value of the exponent β, see Table I). The second term on the rhs of Eq. (2) is the usual entropy associated with a set of polydisperse objects. Similarly, the extension of the layer is computed as

$$L\{S\}\cong a\int_0^N[a^2S(n)]^{\alpha}dn, \tag{3}$$

where the exponent α is given in Table I. In the SF approach, the layer of chains is actually described as a polydisperse polymer brush (the role of the chains being played here by the "pseudoloops," i.e., half loops) *plus* an entropic term which stems from the fact that the size distribution is not fixed by any external operator, but the system of loops is in thermodynamic equilibrium.

If we impose monodisperse pseudoloops $[P(u)=\delta(u-N)]$ and $S_0=\sigma$, the grafting density, we immediately recover the standard results for polymer brushes. In good solvent conditions, these are the extension $L\cong aN(a^2\sigma)^{1/3}$, the free energy $\mathcal{F}\cong k_BTN(a^2\sigma)^{11/6}$, and the volume fraction of monomers $\Phi\cong(a^2\sigma)^{2/3}$. On the other hand, if we let the polydispersity free to minimize the thermodynamical potential (with $S_0=a^{-2}$ to account for attraction), we recover the

TABLE I. Values of the scaling exponents for the layer thickness and the free energy.

Type of solvent	Good	Θ	Melt	"Mean field"
α	1/3	1/2	1	1/3
β	11/6	2	3	5/3

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results found for reversibly adsorbed chains. In good solvent conditions, we find that the volume fraction of monomer scales as $\Phi(z)\cong(a/z)^{4/3}$, and the extension as $L\cong aN^{3/5}$.

Such an idea proved to be successful in describing many different kinds of polymer layers (grafted, reversibly adsorbed [6], irreversibly adsorbed [8]), whatever the solvent quality (good solvent, Θ solvent, and melt, i.e., no solvent). The approach was further expanded to the cases of convex interfaces [9].

The success of this phenomenological approach leads us to address the status of Eq. (2). The SF approach is so far an elegant model but not a theory because Eq. (2) is not deduced from first principles, and the set of approximations involved is not explicit. Recently, the SF approach was applied to the issue of surface tension of polymeric liquids [10–12]. Here again, the SF approach proved to be successful in reproducing the experimental features in great detail. However, because the results presented in Ref. [10] are different from the results of the self-consistent-field theory on the same issue, it seems important to clarify the soundness of the SF approach. This question is addressed here in some detail.

The SF approach raises two questions essentially: (a) is it sound? (b) is it valid? The first question addresses the status of the SF approach, the second has to do with the validity of the results that we will find by using it. Obviously, these two issues are linked. Because "sound" is sometimes used for "crude" or "inaccurate," it is useful to carefully explain what we mean by "sound" and "valid" before we start arguing.

As it stands, the SF approach is a phenomenological description. This is useful in issues where we do not have any theory available. On the other hand, suppose we are in a position to compare a phenomenological approach to a theory on the same issue. The theory will always prevail. If the two results are in agreement, this is fine, but then the phenomenology is a trick to qualitatively understand the issue, and essentially does not bring new features. If, on the contrary, the two results are different, there is always the suspicion that the phenomenological approach is a good idea extrapolated to an issue where this idea is too simple, and therefore, the result is wrong. We simply say "the approach is not sound." Accuracy then is less relevant.

The debate is quite different when we have to compare two theories on the same issue. If somehow we were able to deduce the SF approach from first principles, and therefore prove that this is a theory, then the question of soundness would be resolved. Of course this would be done within approximations, and the theory may be crude or inaccurate to treat the issue, but it is sound. Then the debate over accuracy is essential to evaluate the results.

We see that the status of the SF approach is the first question to be addressed, and depending on the answer, the debate over validity will be different. In Sec. II, we deduce the effective free energy, Eq. (2), from first principles. In doing so, we demonstrate that the SF approach is indeed a variational theory for polymer layers. Then we are led to ask the second question: is it valid? Such task involves comparing the results found with SF theory to SCF theories both at a formal level, and at the level of the results. In Sec. III, we address this question.

II. STATUS

A. Variational free energy

We consider a set of N_C monodisperse, linear, neutral chains in contact with a solid plane (area Σ). We assume that the layer is uniform in the directions parallel to the surface. Our starting point is the partition function $\mathcal{Z}$ of the chains, each characterized by the path $z_i(n)$, where z_i is the position normal to the surface and n is the curvilinear index ($1\leqslant i \leqslant N_C$):

$$\mathcal{Z}=\prod_{i=1}^{N_C}\int_0^\infty dz_i(0)\int_0^\infty dz_i(N)\int\mathcal{D}\{z_i\}\exp\left[-\frac{\mathcal{H}}{k_BT}\right], \quad (4)$$

where the effective Hamiltonian $\mathcal{H}$ is the sum of an elastic (entropic) contribution,

$$\mathcal{H}_{\text{el}}=\frac{3}{2}\frac{k_BT}{a^2}\sum_{i=1}^{N_C}\int_0^N\left(\frac{dz_i}{dn}\right)^2 dn \quad (5)$$

and an excluded-volume (two-body) interaction with parameter v,

$$\mathcal{H}_{\text{ex}}=\frac{vk_BT}{2\Sigma}\sum_{i,j=1}^{N_C}\int_0^N\int_0^N\delta(z_i(n)-z_j(n'))dndn', \quad (6)$$

where δ is the Dirac distribution. We limit ourselves to two-body interactions and thus neglect interactions of further order. This is not valid for a Θ solvent (where $v=0$), but as we shall see in Sec. II B, the correct free energy for this type of solvent is easily introduced afterwards. The volume fraction at distance z is written as

$$\phi(z)=\frac{1}{\Sigma}\sum_{i=1}^{N_C}\int_0^N\delta(z-z_i(n))dn. \quad (7)$$

Regardless of the particular microscopic situation that is realized, we can always decompose the chain into loops and tails, and rewrite $\mathcal{H}$ accordingly. This amounts to cutting the integrals into smaller pieces, by identifying the monomers either in contact with the surface or at the top of the loops and that we note $n_{i,\alpha}$. Each piece corresponds to the complete path of a loop or a tail. The "cutting" scheme is described in Fig. 1. We implicitly assume that the loops are symmetric, which comes from the translation invariance parallel to the solid surface. Hence mathematically, these identified monomers have a "null velocity": $dz_i/dn|_{n_{i,\alpha}}=0$ for each i and α. The chain i is then cut into N_i pieces of size $m_{i,\alpha}=n_{i,\alpha}-n_{i,\alpha-1}$, where $1\leqslant\alpha\leqslant N_i$ with $\Sigma_\alpha m_{i,\alpha}=N$. For tails, we consider the full path from the extreme monomer to the first monomer in direct contact with the surface, as expected. The loops are cut into two pieces of equal length, which we shall call pseudoloops. Clearly, as far as mathematics is concerned, tails and pseudoloops are similar objects: these are chain segments starting at the surface and

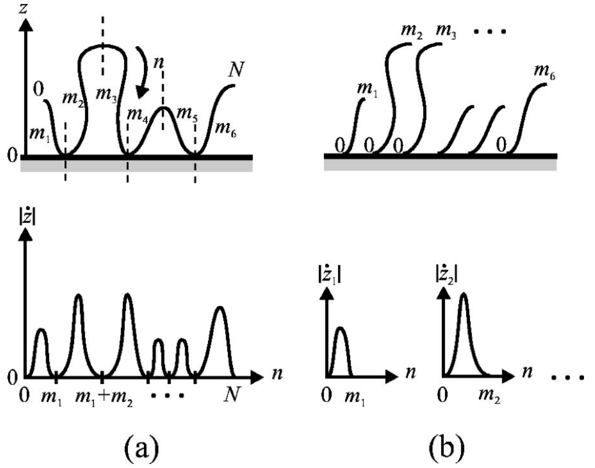

FIG. 1. As far as the Hamiltonian is concerned, each chain in contact with the boundary (a) with associated path $z(n)$ $(1<n<N)$ is formally equivalent to the set of pseudoloops (b) obtained by cutting the loops into two equal pieces with associated paths $\{z_\alpha(n), 1<n<m_\alpha\}$.

ending somewhere in the solution with no velocity at these extreme monomers (cf. Fig. 1). For that reason, we shall not distinguish between tails and pseudoloops in the rest of the paper, and refer to both of them as "pseudoloops." As is obvious, such decomposition (a) is always possible, (b) is unambiguous, (c) lets the partition function $\mathcal{Z}$ be identical without any approximation, provided that we supplement the cutting procedure by the constraint (later referred to as $\mathcal{C}$) that the free extremities of the chain *segments* originating from the same loop should be at the same height *z*. Then $(m_{i,\alpha},\{z_{i,\alpha}\})_{\alpha=1,N_i}$ designates the set of sizes and paths of pseudoloops for chain *i*, and we rewrite the Hamiltonian:

$$\mathcal{H}=\frac{3}{2}\frac{k_BT}{a^2}\sum_{i=1}^{N_C}\sum_{\alpha=1}^{N_i}\int_0^{m_{i,\alpha}}\left(\frac{dz_{i,\alpha}}{dn}\right)^2 dn + \frac{vk_BT}{2\Sigma}\sum_{i,j=1}^{N_C}\sum_{\alpha,\beta=1}^{N_i}\int_0^{m_{i,\alpha}}\int_0^{m_{j,\beta}}\delta(z_{i,\alpha}(n) - z_{j,\beta}(n'))dn\,dn'. \tag{8}$$

Computing exactly the partition function of the system with the Hamiltonian, Eq. (8), is clearly out of reach. Rather, we implement the variational principle which necessitates two steps [13]. First, we need to choose a trial probability such that $\mathcal{P}_T$ is a good approximation of the actual probability, $\mathcal{P}=\mathcal{Z}^{-1}\exp[-\mathcal{H}/k_BT]$, but nevertheless allows for analytical calculations. Second, we approximate the exact free energy $\mathcal{F}$ of the system by the extremum of the functional $\mathcal{F}_{\text{var}}\{\mathcal{P}_T\}=\langle\mathcal{H}\rangle_{\mathcal{P}_T}+k_BT\langle\ln\mathcal{P}_T\rangle_{\mathcal{P}_T}$. Of these two steps, the second one is the simplest because it is purely a matter of calculation. Only the first one is significant as regards the physics, since the success of the variational theory lies in finding an appropriate trial function. The guess $\mathcal{P}_T$ is a functional form with free unspecified parameters. By minimizing $\mathcal{F}_{\text{var}}\{\mathcal{P}_T\}$ with respect to these parameters, we will obtain $\mathcal{P}_T$ with the chosen functional form that best approximates $\mathcal{P}$. This is what ultimately controls the difference between $\mathcal{F}$ and the approximation $\mathcal{F}_{\text{var}}$. Note that the choice of the ensemble of functions over which we shall perform the minimization is arbitrary. It is a guess, not an approximation which could be somehow quantified *a priori*.

Our guess for $\mathcal{P}_T$ is

$$\mathcal{P}_T(\{(m_{i,\alpha},\{z_{i,\alpha}\})_{\alpha=1,N_i}\}_{i=1,N_C})=\prod_{i=1}^{N_C}\prod_{\alpha=1}^{N_i}P(m_{i,\alpha},\{z_{i,\alpha}\}), \tag{9}$$

where $\int_0^N P(m_{i,\alpha},\{z_{i,\alpha}\})dm=1$. Equation (9) is a mean-field-type approximation for the pseudoloops since their probability distributions are decorrelated (hypothesis *A*). Furthermore, we assume that *the path* $\{z_{i,\alpha}\}$ *is the same for all the pseudoloops* and is noted $\{z\}$ (hypothesis *B*). Because $P(m_{i,\alpha},\{z_{i,\alpha}\})$ does not depend on the particular pseudoloop that is considered, we can drop the indices and write $P(m,\{z\})$. Hence the probability distribution reads $\mathcal{P}_T=P(m,\{z\})^B$, where $B=\Sigma_{i=1}^{N_C}N_i$ is the number of pseudoloops at the interface. The crucial point is that $\mathcal{P}_T$ no more depends on the complete set of sizes and path, $\{m_{i,\alpha},\{z_{i,\alpha}\}\}$, but only on (a) the size of the pseudoloop, *m*, and on (b) the path *z*, chosen to be the same for all pseudoloops. Importantly, the constraint $\mathcal{C}$ is automatically fulfilled with our approximation since two pseudoloops originating from the same loop have the same size *m* and thus terminate at the same height $z(m)$. Then, the system is described by two functions: $P(m)$, the probability that we have a pseudoloop of size *m*, and $z(n)$, the path of the chain segments. Hence, the trial free energy is obtained by minimizing $\mathcal{F}_{\text{var}}$ with respect to changes in *z* and *P* (later, we will find it more convenient to work with *S*, rather than *P*).

With Eq. (9), we find

$$\langle\mathcal{H}_{\text{ex}}\rangle_{\mathcal{P}_T}=\frac{1}{2}\frac{v\Sigma}{a^6}k_BT\int dz\Phi^2(z), \tag{10}$$

where

$$\Phi(z)\equiv\langle\phi(z)\rangle_{\mathcal{P}_T}=a^3S_0\int_0^N dmP(m)\int_0^m\delta(z-z(n))dn \tag{11}$$

and

$$\langle\mathcal{H}_{\text{el}}\rangle_{\mathcal{P}_T}=\frac{3}{2}\frac{k_BT}{a^2}\Sigma S_0\int_0^N dmP(m)\int_0^m\dot{z}^2(n)dn, \tag{12}$$

where $B=\Sigma S_0$ (hence S_0 is the "grafting density" of pseudoloops), and $\dot{z}=dz/dn$. Similarly, the entropic part of $\mathcal{F}_{\text{var}}$ is found to be

$$k_BT\langle\ln\mathcal{P}_T\rangle_{\mathcal{P}_T}=k_BT\Sigma S_0\int_0^N dmP(m)\ln P(m). \tag{13}$$

Combining all these results and integrating by parts and using Eq. (1), we find

$$\frac{\mathcal{F}_{\mathrm{var}}(\{S\},\{\dot{z}\})}{k_B T\Sigma}=\int_0^N\left\{\frac{3}{2a^2}\dot{z}^2(n)S(n)+\frac{v}{2}\frac{S^2(n)}{\dot{z}(n)}-S'(n)\ln\left(-\frac{S'(n)}{S_0}\right)\right\}dn. \tag{14}$$

Note that $\Phi(z)=S(n(z))/\dot{z}$. Equation (14) is the central result of this paper which we now discuss. To get the best approximation, we minimize Eq. (14) with respect to $\dot{z}$ which yields $\dot{z}=(va^2/6)^{1/3}S^{1/3}$, and when this result is introduced back into Eq. (14), we find Eq. (2) with $\beta=5/3$ and $k=(3.6^{1/3}/4)(v/a^3)^{2/3}$. We thus find the mean-field version of our effective free energy, Eq. (2), with a numerical coefficient k of order 1.

The formal derivation presented here brings an interesting remark. In the early developments of the SF theory, the entropic part in Eq. (2) was introduced (and interpreted) as a contribution arising from combinatorial arrangements of pseudoloops at the surface: the presence of the interface breaks down the symmetry of the solution and these monomers in contact with the surface become *distinguishable*. We see that the entropic term in Eq. (14) is formally that contribution arising from the entropy of the trial probability.

B. Generalization to other solvent conditions

The generalization to other solvent conditions, i.e., good solvent, Θ solvent, and melt, has been done in Refs. [6,7] and deserves some comments.

In the case of a melt, the excluded-volume interactions are screened at all scales, and our mean-field approximation for pseudoloops is automatically verified. The probability distribution is then related to the Green function of a chain by $P(m)\propto G(0,z(m);m)$, where $z(m)$ is self-consistently determined via the constraint $\dot{z}(n)=S_0\int_n^N P(m)dm$ [$\phi(z)=1$ everywhere in an incompressible melt].

For a good solvent, the osmotic [Eq. (12)] and elastic terms [Eq. (10)] are easily renormalized, following the des Cloiseaux law [14], and using semidilute blobs [15]. However, the approximation which consists in neglecting correlations between pseudoloops is *a priori* not verified. Thus, the transformation of $k_BT\langle\ln\mathcal{P}_T\rangle_{\mathcal{P}_T}$ in $k_BT\Sigma S_0\int_0^N dm P(m)\ln P(m)$ is not justified. However, correlations between monomers inside the same pseudoloop are taken into account through the blob renormalization.

Hence we have demonstrated that the SF approach is a variational theory, and Eq. (2) is sound.

III. VALIDITY

Of course, that the SF theory is sound (in the sense that it is deduced from first principles) does not guarantee at all that it is accurate, or even simply valid to describe polymeric layers. This is because we have made approximations whose range of validity remains to be examined.

A priori, we could distinguish three different points of view to discuss the issue of accuracy: (a) internal, (b) external, and (c) experimental.

A. Internal estimate of accuracy

Internal means that we are able to estimate the error that we have made in approximating the initial Hamiltonian, and thus propose an internal criterion of validity, very much like the Lifshitz criterion of validity for mean-field theories. This requires that we define a relevant parameter which would quantify the difference between the initial and the approximated Hamiltonian, i.e., the two assumptions that we made.

Concerning hypothesis *A*, we know that the mean-field approximation for the loops is not valid in good solvent conditions. This implies that the last term of Eq. (14) is wrong. However, the renormalization with semidilute blobs of the first two terms takes into account the swelling of the pseudoloops (hence correlations between monomers) on scales smaller than the pseudoloop sizes. Thus for loops at least larger than one blob size, the excluded-volume interactions are screened and these loops are decorrelated. Hence, the entropic term of Eq. (14) is justified for a large number of the pseudoloops and even if it is not fully satisfying, this is the best way we can take into account these correlations unless we are led to use renormalization group theory, which has been done for one chain but not for many chains [16].

The hypothesis *B* is the crudest assumption in our theory. We assume that all pseudoloops have the same *mean* path $z(n)$. It is easy to show that for a melt, we find by minimization $z_{\mathrm{eq}}(n)\simeq n^{1/2}$, which is the best variational approximation with our probability distribution, Eq. (9). This result is quite similar to the Flory theorem $R\simeq aN^{1/2}$ for the extension of a polymer chain in a melt. Of course this result is valid for large n, since for a random walk, fluctuations around this value are proportional to $n^{-1/2}$. This result may not be valid for small loops. However, with variational theories, the estimate of this error is impossible.

B. External estimate of accuracy

External means that we compare the SF theory with another theory. For polymeric layers, the obvious candidate is SCF theories. *A priori*, there are two ways to do that: (a) a formal comparison, (b) a comparison of the results that we obtain on a given issue. A formal comparison is simple when the two theories have a common language. Unfortunately, this is not the case for SCF theories and the SF theory. The former is deduced from the initial Hamiltonian through a mean-field-type approximation for monomer-monomer correlations, which is then applied to the problem of polymer at interfaces, whereas the latter proceeds in *first* rewriting the Hamiltonian for chains at interfaces and *then* using a mean-field approximation for pseudoloops. Because of this different order for these two steps, we do not know the way to formally compare SCF and SF theories. Then we are left with comparing the results.

There are two issues where such comparison is possible: (a) brushes in the infinite stretching limit, ‘‘mean-field’’ solvent conditions, and (b) reversibly adsorbed layers, mean-field solvent conditions. These issues are conceptually important because we know exactly the solution of the SCF theory in the asymptotic limit $N \to \infty$.

1. Brushes

As shown by Netz and Schick [17] and Li and Witten [18], the theory of polymer brushes proposed simultaneously by Milner, Witten, and Cates (MWC) and Skvortsov *et al.* in Refs. [4,5], which consists in keeping the classic path in the partition function, can also be considered as a variational approach. However, the trial probability is different, and the layer is described by two functions: g, such that $g(z_0)dz_0$ is the probability that the chain free extremity belongs to the interval $[z_0, z_0+dz_0]$, and e, such that $e(z,z_0)=|dz/dn|$ is the extension at position z for a chain whose free extremity is situated at z_0. Paths (described by e) are chosen such that polymers are grafted at one end (with grafting density σ), i.e., $\int_0^\infty dz_0/e(z,z_0)=N$ (which leads to the so-called equal time argument). The variational free energy (per cm^2) is [17]

$$\frac{\mathcal{F}_{\mathrm{MWC}}}{k_BT}=\frac{v}{2}\int_0^\infty \Phi^2(z)dz+\sigma\int_0^\infty dz_0 g(z_0)\int_0^{z_0}\frac{3}{2a^2}e(z,z_0)dz +\sigma\int_0^\infty g(z_0)\ln[g(z_0)]dz_0, \qquad (15)$$

with $\Phi(z)=\sigma\int_z^\infty dz_0[g(z_0)/e(z,z_0)]$. Note that in the context of brushes, the entropic contribution in Eq. (15), which is similar to that in Eq. (14), is the entropy of the chain-end distribution [17,19,20]. Simple arguments show that the first two terms on the rhs of Eq. (15) scale as $N(a^2\sigma)^{5/3}$, whereas $\int g(z_0)\ln[g(z_0)]dz_0 \sim 1$. Hence, in the strong stretching limit, $N(a^2\sigma)^{2/3} \gg 1$, the entropic contribution to $\mathcal{F}_{\mathrm{MWC}}$ is negligible [17]. However, this term is conceptually important and has a physical significance since $e(z_0,z_0)$ is the tension sustained by the free chain ends. Hence, we see that Eqs. (14) and (15) are formally very close, but the choices for, respectively, $z(n)$ and $e(z,z_0)$ are different.

To compare the SF theory with the MWC theory, we concentrate on monodisperse brushes [hence the entropic contribution in Eq. (14) disappears] in the strong stretching limit [hence, we neglect the entropic contribution in Eq. (15)]. We find that in equilibrium $\mathcal{F}^*_{\mathrm{MWC}}=0.892\mathcal{F}^*$. We see that the extremum of $\mathcal{F}^*_{\mathrm{MWC}}$ is lower and according to the variational criterion, the MWC theory is a better approximation of the exact free energy. See Refs. [18,21] for a thorough discussion of this difference. It is related to the different choices for the paths where the MWC choice (i.e., the equal time argument) is less restrictive. The reason is that in the SF theory for brushes, we impose an additional constraint: all chain free extremities are situated in the outer edge of the layer, in a fashion similar to the Flory approach (or the Alexander–de Gennes, which is similar in spirit but introduces the correct scaling exponents). Formally, this amounts to imposing a δ-type function for g, a restriction motivated by our desire to keep the SF theory tractable in a wider range of situations. Eventually, we find the same results for L and $\mathcal{F}^*$ at the scaling level, although the description of the volume fraction profile is more accurate in the MWC theory.

2. Adsorbed layers

Presumably, the case of reversibly adsorbed polymers is more significant for our purpose since our variational approach is based on a ‘‘loop description,’’ which is justified for the homogeneous adsorption.

If we go to reversible adsorption, we have to turn our attention to GSD theory. Although desirable, it is not so simple to compare the SF theory with GSD theories. There are two reasons for this: (a) the GSD theory uses the analogy between the partition function $\mathcal{Z}$ and the Green propagator in quantum mechanics, which does not allow a description in ‘‘polymer trajectories’’; (b) in this theory, the free energy is expressed in terms of the mean monomer concentration $\Phi(z)$, a quantity not simply related to our probability density $P(m)$. Indeed, the partition function of a chain having one end at z and the other free, $\mathcal{Z}(N,z)$, in the SCF theory, is the solution of the Schrödinger equation: $\partial\mathcal{Z}/\partial N =(a^2/6)\partial^2\mathcal{Z}/\partial z^2 - U\mathcal{Z}$, where the external potential U is the sum of the attractive potential due to the surface U_{surf} and the self-consistent potential U_{SCF}. For the adsorbed chains, there is a ground state of negative energy $-\varepsilon N k_BT$ which dominates the solution, and (in the limiting case where $\varepsilon N \gg 1$) the free energy approximates to

$$\mathcal{F}_{\mathrm{GSD}}=k_BT\int_0^\infty dz\left[\kappa(\Phi)\left(\frac{d\Phi}{dz}\right)^2+U(z)\Phi(z)\right], \qquad (16)$$

where $\kappa(\Phi)=a^2/(24\Phi)$. As shown by Lifshitz and des Cloiseaux [22,23], the square gradient term in Eq. (16) has essentially an entropic origin [24], whereas the polymeric nature of the liquid can be neglected in the molecular field $U_{\mathrm{SCF}}(z)$ (which is estimated for a monomeric liquid). Then we are led to think that the elastic and entropic parts in Eq. (14) are related to the square gradient term, but we are not able to rewrite the former as the latter at the moment.

In the absence of any clue to formally compare Eqs. (14) and (16), we shall compare their results for infinite chains and mean-field potential, a limit where the GSD theory happens to be exact. If we minimize the free energy, Eq. (14), with the boundary conditions $S(0)=a^{-2}$, $S(N\to\infty)=0$, we find $a^2S_{\mathrm{eq}}(n)=k'^{3/2}/(n+k')^{3/2}$ where $k'=[3/(2k)]^{4/9}$, which yields $\Phi(z)\sim z^{-2}$, essentially the solution found by minimizing Eq. (16). Similarly, we find that $\mathcal{F}^*\cong k_BT/a^2$ as with the GSD theory. Hence, we find a very good agreement for infinite chains.

That the agreement should be better (in the sense that both the scaling and the concentration profile are identical) for adsorption than for brushes reflects the validity of our initial assumption that all pseudoloops have the same path. As explained in Ref. [25], for very polydisperse layers, we expect a stratification of the locations of the free chain ends above the surface. This is because the free ends of a long chain locate further away from the surface than that of a short chain to take advantage of a lower osmotic pressure (the concentration decreases away from the interface). In the continuum limit, this argument suggests that every pseudoloop is similarly extended, and therefore validates our guess.

C. Experimental estimate of accuracy

To evaluate the accuracy of a variational theory, the ultimate and major argument is to compare the value of the free energy at its minimum to experiments. The good candidate is thus the surface tension of polymeric liquids, γ. We have shown in Refs. [10–12] that the SF approach allows the calculation of the variations of $\gamma(N)$ in very good agreement with experimental data found in the literature. This is a good test for the theory which has been done both for melts and semidilute solutions (in good solvent).

It is important to note that the SCF theory in the GSD approximation leads to a different result for the melt surface tension. The finite chain correction in that case is proportional to N^{-1}. We found a larger correction in $\ln N/N^{1/2}$. An explanation of this discrepancy is that the SCF description relates the surface tension to the gradients in volume fraction which are localized in a very thin layer of thickness a (indeed this approach is not valid for large gradients). We argue that this dependence comes from the chain reorganization on a larger layer, whose thickness is the radius of gyration of a chain. In this layer, the volume fraction is constant. Thus it cannot be described by the SCF approach whereas the SF approach uses different tools, namely $z(n)$ and $S(n)$, which allows such a description. Hence, for adsorbed layers from a melt and a semidilute solution, we see that these two approaches are quite different.

IV. CONCLUDING REMARKS

This paper aims at clarifying the debate concerning the soundness of the scaling functional approach. In view of this, the demonstration that the SF approach is a variational theory is certainly the essential and most significant result of this paper (Sec. II). But we think we have made clear a certain number of points (Sec. III). These are as follows.

(1) The SF approach is a variational theory and therefore has the same epistemological status as SCF theories for brushes (‘‘classical’’ solution) and adsorbed chains (GSD). Of course, the approximations made are different and each of these theories has a different range of validity.

(2) Because the SF theory is a variational theory, we are not able to properly quantify the approximations that are involved, and therefore we are unable to define the range of validity of this theory.

(3) There is no way that we know to formally compare the two theories because the first step in approximating the initial Hamiltonian is different.

(4) Each time a direct comparison with SCF theory is possible, we find (a) always the same scaling results, and (b) sometimes the same analytical result. Thus we conclude that the SCF theory does not provide any argument against the SF theory.

That the GSD approximation to the SCF theory is formally justified and quantifiable in mean-field solvent conditions does not guarantee that the result that we find is accurate for real solvent conditions and notably for the melt case. A description only in terms of volume fraction [see Eq. (16)] comes also from a variational argument [23] and has not been quantitatively justified in real systems. In other words, the GSD in the limit $N\rightarrow\infty$ is the exact solution of the SCF theory, but still an approximate solution of the initial Hamiltonian.

The crucial point regarding our approximations (cutting loops into two tails and describing all the pseudoloops with the same path) is whether the distinction between loops and tails is important enough to modify the conclusions of a simple theory in which it is neglected. When we are in a position to directly evaluate the consequences of these approximations, we find that this distinction does not affect the scaling results. It is interesting to note that the distinction between loops and tails has been done self-consistently for the SCF theory but is put *ad hoc* for other types of solvents [2]. Therefore we conclude that there is no valid argument to support that these approximations are not sound, provided that we remain at a scaling level of description.

Finally, we assume in this approach that a large number of loops are formed at the interface. This imposes both a sharp interface and the presence of many adsorbed chains. Therefore, this theory does not apply to single-chain adsorption and to systems such as interfaces between incompatible polymers or diblock copolymers, for which other approaches based on the SCF theory have been developed [26,27].

As a conclusion, the SF theory proposes a compromise between a precise description of the polymeric layer and a wide ranging scaling-type theory valid for arbitrary polymer layers, various solvent conditions, and various geometries. Since it does not require a comparable amount of mathematics and has a wider range of applicability than both theories, it is very likely that the SF theory will become an important piece of our understanding of polymeric interfaces.

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