

Conformational transitions of single polymer adsorption in poor solvent: Wetting transition due to molecular confinement induced line tension

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(Received 26 August 2015; revised manuscript received 4 April 2016; published 18 July 2016)

We report a theory capable of describing conformational transitions for single polymer adsorption in a poor solvent. We show that an additional molecular confinement effect near the contact line can act exactly like line tension, playing a critical role in the behavior of an adsorbed polymer chain. Using this theory, distinct conformational states: desorbed globule (DG), surface attached cap (SAC), and adsorbed lens (AL), can be vividly revealed, resembling the drying-wetting transition of a nanodroplet. But the transitions between these states can behave rather differently from those in the usual wetting transitions. The DG-SAC transition is discrete, occurring at the adsorption threshold when the globule size at the desorbed state is equal to the adsorption blob. The SAC-AL transition is smooth for finite chain lengths, but can change to discontinuous in the infinite chain limit, characterized by the different end-to-end exponent $3/8$ and the unique crossover exponent $1/4$. Distinctive critical exponents near this transition are also determined, indicating that it is an additional universality class of phase transitions. This work also sheds light on nanodrop spreading, wherein the important role played by line tension might simply be a manifestation of the local molecular confinement near the contact line.

DOI: [10.1103/PhysRevE.94.012501](https://doi.org/10.1103/PhysRevE.94.012501)

I. INTRODUCTION

Polymer adsorption is a phenomenon involving association or binding of polymer chains onto a substrate, as occurs in many applications such as coating, surface functionalization, self-assembly deposition, and thin film preparation. How to control the behavior of a polymer chain so as to acquire desired functionalities demands a detailed knowledge of how a chain changes its conformation due to adsorption. Hence, this subject is of both fundamental and technological importance to polymer science and engineering.

The behavior of an adsorbed polymer chain strongly depends on the solvent quality. In good solvents, a chain tends to extend itself over a surface to gain more contacts with the surface [1,2]. In poor solvents, however, chain spreading would be resisted by the chain's natural tendency to minimize its contacts with the solvent. So in this case how a polymer chain behaves would be determined by nontrivial interplays between chain-surface and intersegmental interactions. In fact, this problem is so complicated that it is unlikely that a single theory can be developed to explain the diversity of conformational behaviors [3–7]. Therefore, not only is the nature of polymer adsorption in a poor solvent not well understood, but also most of its aspects are largely unexplored.

In this paper we will focus on how a *single* polymer chain is adsorbed on an attracting surface under the poor solvent condition, and develop a theory to describe how the chain changes its conformation. Such a theory is needed to fill up the gaps in the existing theoretical and simulation studies and its development is motivated by the following incentives.

First, on the theoretical side, a classical theory has been long developed for single polymer adsorption in good or theta solvents [1,2]. This theory is based on the notion of de Gennes's blob, under which chain statistics are not altered by adsorption provided that adsorption is *weak* at the monomer level [1,2].

In poor solvents, however, no theory can satisfactorily account for the behavior of an adsorbed polymer chain. While there are several theoretical attempts, they are either qualitative or lack the ability to describe in detail how a chain changes its conformation [8–12]. There is a need to fill up this gap.

Second, because the interactions between a chain and the underlying surface are generally complex, studying this problem often relies on computer simulations [3–7]. But the limitation of computer simulations is that they can handle only short chains (of the number of polymerizations $N < 10^3$). So resolution of the behavior for long chains, especially approaching the thermodynamic limit, could still be far beyond the current computational capability. In addition, because short chains are more susceptible to Brownian randomization, most simulations are carried out in the regime where adsorption and poor solvent effects are *strong* so that apparent conformational changes can be observed. As a result, the physics in the weak regime, which is expected to differ from that in the strong regime, is completely left out. Moreover, in practice, when both adsorption and poor solvents are in the strong regime, phase separation will be inevitable, so that polymer chains hardly remain at the single molecule level. For the above reasons, long chain adsorption in the weak regime appears to be the only missing piece that has not yet been fully studied.

Third, as a polymer chain in a poor solvent tends to minimize its contact area to the solvent, this surface-tension-like effect suggests that an adsorbed polymer chain will behave like a liquid droplet [8,9,13], similar to the usual wetting-dewetting seen in critical (continuous) wetting. This analogy seems to have the advantage of elucidating some physics [8,9,13]. However, because there is an additional entropic effect associated with conformational changes of a polymer chain but this effect does not exist in a droplet, such an analogy in fact is *not* exact. A complete analogy can be made only if such an entropic effect can be incorporated into the description of how an adsorbed polymer chain changes its conformation. But unlike the good or theta solvent counterpart where the entropic contribution is well known [1,2], how a

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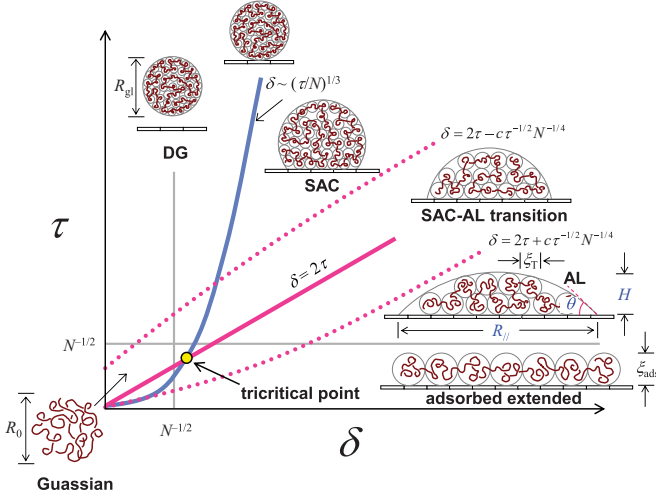


FIG. 1. Distinct conformational states: DG (desorbed globule), SAC (surface absorbed cap), and AL (adsorbed lens), can exist for adsorption of a single polymer chain in a poor solvent, depending on the reduced temperature τ and the adsorption strength δ . The DG-SAC transition (blue line) is discrete. The SAC-AL transition is continuous. However, it can become discontinuous in the thermodynamic limit ($N \rightarrow \infty$) as the crossover region (enclosed by dotted pink lines) shrinks toward the transition boundary (pink line) as the chain size $N \rightarrow \infty$.

chain's conformational entropy changes in a poor solvent is still not clear.

Alternatively, the wetting-dewetting of single chain adsorption in a poor solvent might closely resemble the spreading of a nanodroplet where an additional line tension is often involved [14,15]. Therefore, establishing an exact correspondence between these two seems to hinge on whether an equivalent line tension can exist in the former. If so, could the line tension be derived from the entropic effect? This is also a question we want to answer.

Motivated by the above, in this article we develop a self-consistent theory capable of describing various conformational states for single polymer adsorption in a poor solvent (see Fig. 1). Extending de Gennes' blob idea [1], this theory is built specifically for the scenario where both adsorption and poor solvent effects are *weak*. In contrast to most simulations which are done for the *strong* regime and show a diversity of features for *short* chains [3–7], this theory allows us not only to unveil various conformational states in the weak regime, but also to demonstrate universality on approaching the *long* chain or the thermodynamic limit. And more importantly, we derive an additional line tension term arising from the molecular confinement effect near the contact line, which enables us to establish an exact correspondence with nanodrop spreading. As will be seen shortly, the transition between desorbed and partially absorbed states is discrete, whereas a continuous transition can occur between partially absorbed and completely absorbed states. The latter is identified as an additional class of conformational transition, characterized by the unique crossover exponent 1/4 and the exponent 3/8 for the end-to-end chain distance. The critical exponents near this transition are also determined, indicating that it is not only

distinct from the usual critical wetting transitions, but also a different universality class of phase transition.

II. FREE ENERGY: AN ADDITIONAL LINE TENSION TERM

Here we describe how the theory is developed. Because we focus on the weak regime, the solvent quality is taken slightly below the Θ point, so in the desorbed state the chain takes the form of a compact globule of size $R_{gl} \sim a\tau^{-1/3} - N^{1/3}$, where a is the monomer size, $\tau \equiv (\Theta - T)/\Theta (> 0)$ the reduced temperature measuring the closeness to the Θ point, and N the number of polymerizations. If adsorption is sufficiently strong to deform the chain but not enough to change the chain statistics (i.e., the density $\sim N/R_{gl}^3 \sim \tau/a^3$ remains unchanged), whenever the chain deforms, it can always be thought of as an *incompressible* droplet made of close-packed thermal blobs of size $\xi_T \sim ag^{1/2} \sim a/\tau$ with $g \sim \tau^{-2}$ being the number of monomers inside a blob [1]. The chain self-energy is then $F_0/k_B T = N/g \sim N\tau^2$. Here we assume $N^{-1/2} < \tau < 1$ to ensure that the chain can still remain compact at the *single molecule* level without phase separation. As the chain essentially behaves like a drop, it takes the form of a spherical cap under the constant volume constraint:

$$V = (\pi/6)H(3R_{||}^2/4 + H^2) = (\pi/6)R_{gl}^3, \quad (1)$$

where the base diameter $R_{||}$ and height H can be related to the apparent contact angle θ through $\tan(\theta/2) = 2H/R_{||}$.

The chain free energy F_{chain} consists of three parts: surface tension F_{surf} , adsorption F_{ads} , and confinement F_{confine} . Including the segment-solvent contact areas from both the cap surface area $\pi(R_{||}^2/4 + H^2)$ and the base area $\pi R_{||}^2/4$, F_{surf} is found to be

$$F_{\text{surf}}/k_B T = \pi(R_{||}^2/2 + H^2)/(\pi\xi_T^2/4). \quad (2)$$

In the absence of adsorption, Eq. (2) guarantees a perfectly spherical globule (i.e., $R_{||} = 0$ and $H = R_{gl}$) after minimizing F_{surf} under Eq. (1).

Adsorption tends to lower the chain's free energy. We also assume this effect is weak with small energy gain for a monomer absorbed onto the surface, $-\delta k_B T (N^{-1/2} < \delta < 1)$ [1]. A thermal blob attached to an absorbing surface has about a fraction $f = a/\xi_T \sim \tau$ of monomers absorbed onto the surface. Since the number of blobs on the surface is $m = (R_{||}/\xi_T)^2$, the amount of absorbed monomers is $n_{\text{ads}} = mfg \sim m\tau^{-1}$, giving the adsorption energy $-m(\delta/\tau)k_B T$, namely,

$$F_{\text{ads}}/k_B T = -(\delta/\tau) (R_{||}/\xi_T)^2. \quad (3)$$

However, when the chain spreads due to adsorption, chain compression tends to raise the chain's free energy to prevent chain spreading indefinitely. There are two contributions to this entropic free energy. One comes from the entropic penalty for the chain segments in contact with the bottom surface, as already included in part of F_{surf} given by Eq. (2). The other arises from the effect of confinement by the cap. As shown in the Appendix, it takes the form of

$$F_{\text{confine}}/k_B T = \pi R_{||}^2/2\xi_T H. \quad (4a)$$

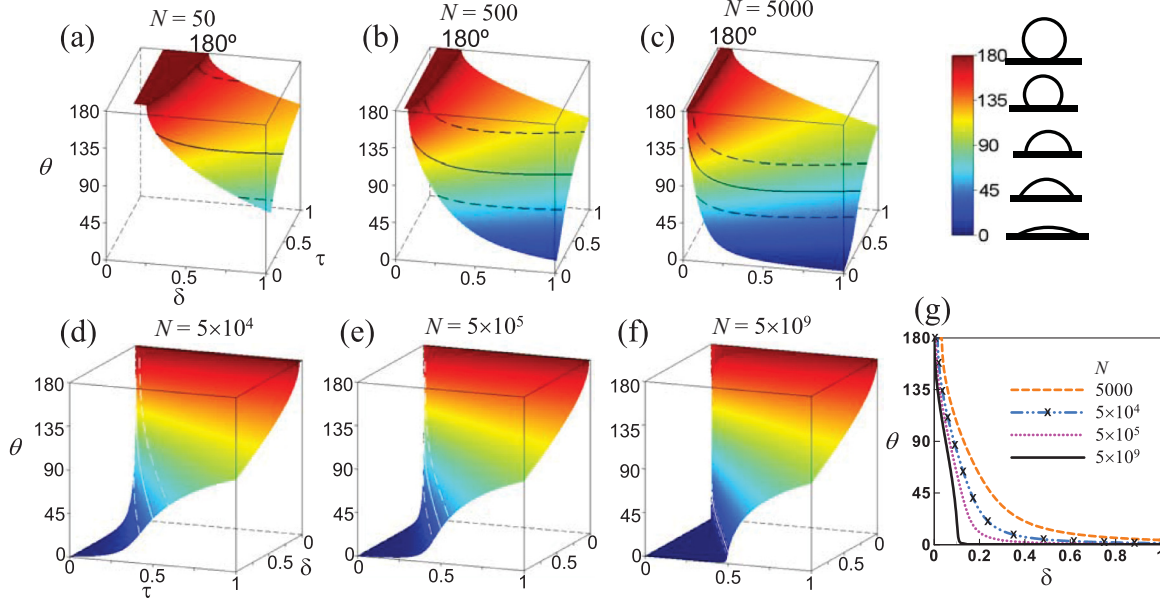


FIG. 2. Apparent contact angle θ as a function of τ and δ for various values of the chain size N (a)–(f). As N is increased, the DG zone shrinks (a)–(c), whereas the SAC-AL transition is getting sharper (d)–(f). Solid line away from the 180° plateau is the SAC-AL transition point $\delta = 2\tau$, with the crossover zone indicated by dashed lines. (g) plots θ vs δ at $\tau = 0.05$, showing that the SAC-AC transition can become discontinuous at $\delta = 2\tau = 0.1$ when N becomes sufficiently large.

In fact, this confinement energy can be recognized as the work done by *line tension* on the periphery πR_{\parallel} :

$$\sigma = k_B T / [\xi_T \tan(\theta/2)]. \quad (4b)$$

For small θ , σ is reduced to $2k_B T / \xi_T \theta$, consistent with the result for a polymer chain confined by a wedge [16]. This line-tension-like energy tends to resist chain spreading via reducing R_{\parallel} as much as possible. So in the situation where adsorption dominates over poor solvent, F_{confine} can compensate the entropic loss due to chain spreading caused by adsorption and thereby keep the chain extended on the surface. On the other hand, if poor solvent dominates, this energy would help the chain to return to the desorbed globule state. This transition from the globule state to the adsorbed state resembles the drying-wetting transition of a droplet on a surface, and is impossible to capture without such a line tension term as given by Eq. (4).

Adding up Eqs. (2)–(4), the chain's free energy (in reference to F_0) reads

$$\frac{F}{k_B T} = \frac{\pi R_{\parallel}^2}{2\xi_T H} + \frac{1}{\xi_T^2} [-\varepsilon R_{\parallel}^2 + 4H^2]. \quad (5)$$

Here $\varepsilon \equiv \delta/\tau - 2$ measures the strength of adsorption relative to a poor solvent and > 0 (< 0) means that adsorption is stronger (weaker). The equilibrium shape of the chain is determined by minimization of Eq. (5) under Eq. (1).

III. RESULTS

First of all, we present the phase diagram by looking at how the contact angle θ varies with δ and τ , as sketched in Fig. 1. There are three distinct conformational states: desorbed globule (DG), surface attached cap (SAC), and adsorbed lens (AL), distinguished by different power laws in N for R_{\parallel} and

H , as will be shown later. The DG occurs for small δ or large τ , while the AL takes place for large δ or small τ . In between these two states, the chain is partially absorbed and takes the form of the SAC. But near the critical point $\varepsilon = 0$ where adsorption and poor solvent effects cancel out exactly, there is an added crossover zone between SAC and AL.

Figure 2 shows how the actual phase boundaries change with the chain size N . First of all, the DG-SAC transition—the sharp boundary of the 180° plateau—is *discrete*. This transition is manifest for short chains with $N \leq 5000$. If the chain is too short, such as $N = 50$, the AL state (roughly for $\theta < 30^\circ$) does not emerge until $N = 500$. Increasing N disfavors the DG (because the DG zone shrinks), but favors the AL (because the AL zone expands). It also favors the SAC (since both the DG and SAC-AL transition zones shrink). But when N is increased to 50 000 or higher, the SAC-AL transition gets sharper. At a sufficiently large N like $N = 5 \times 10^9$, the transition becomes *discontinuous* and is precisely located at $\delta = 2\tau$ (i.e., $\varepsilon = 0$), the critical state where adsorption and poor solvent effects cancel out exactly.

In the large- N limit, Table I(a) lists various scaling results. In addition to R_{\parallel} , H , and F , we also look at the fraction of adsorbed monomers, z , the ratio of the number of monomers adsorbed on the surface to the total: $z \equiv N_{\text{ads}}/N = (R_{\parallel}/a)^2 \tau N^{-1}$ with $N_{\text{ads}} = (R_{\parallel}/\xi_T)^2 g(a/\xi_T)$ being proportional to the number of blobs adsorbed on the surface $(R_{\parallel}/\xi_T)^2$. As shown in Table I(a), the results for the $\varepsilon < 0$, $\varepsilon = 0$, and $\varepsilon > 0$ cases are rather distinct, corresponding to different conformational states. Below we identify how characteristics of these different states vary with δ , τ , and N , and how their transitions take place:

(i) *Desorbed globule* (DG). This state occurs when adsorption is weak ($\delta/\tau \ll 1$), giving $R_{\parallel} = 0$ and $H = R_{\text{gl}} \sim a\tau^{-1/3} N^{1/3}$ just as in the case without adsorption. And yet

TABLE I. (a) Various scaling results in the large- N limit. (b) Results rescaled by the corresponding power laws in N at the SAC-AL transition point $\varepsilon = 0$, showing that they all (except for $\theta > 120^\circ$) can be written as certain powers in $|\varepsilon|N^{1/4}$.

(a)	$\varepsilon < 0$				(b)	$\varepsilon < 0$			
	$\theta > 120^\circ$	$\theta < 120^\circ$	$\varepsilon = 0$	$\varepsilon > 0$		$\theta > 120^\circ$	$\theta < 120^\circ$	$\varepsilon = 0$	$\varepsilon > 0$
$\frac{R_{\parallel}}{a}$	$\tau^{-1/3} \varepsilon ^{-1/2}N^{1/3}$	$\tau^{-1/3} \varepsilon ^{-1/6}N^{1/3}$	$\tau^{-1/4}N^{3/8}$	$\varepsilon^{1/2}N^{1/2}$	$\frac{R_{\parallel}/a}{N^{3/8}}$	$\tau^{-1/3} \varepsilon ^{-1/2}N^{-1/24}$	$\tau^{-1/3}(\varepsilon N^{1/4})^{-1/6}$	$\tau^{-1/4}$	$(\varepsilon N^{1/4})^{1/2}$
$\frac{H}{a}$	$\tau^{-1/3}N^{1/3}$	$\tau^{-1/3} \varepsilon ^{1/3}N^{1/3}$	$\tau^{-1/2}N^{1/4}$	$\tau^{-1}\varepsilon^{-1}$	$\frac{H/a}{N^{1/4}}$	$\tau^{-1/3}N^{1/12}$	$\tau^{-1/3}(\varepsilon N^{1/4})^{1/3}$	$\tau^{-1/2}$	$\tau^{-1}(\varepsilon N^{1/4})^{-1}$
z	$\tau^{1/3} \varepsilon ^{-1}N^{-1/3}$	$\tau^{1/3} \varepsilon ^{-1/3}N^{-1/3}$	$\tau^{1/2}N^{-1/4}$	$\tau\varepsilon$	$\frac{z}{N^{-1/4}}$	$\tau^{1/3} \varepsilon ^{-1}N^{-1/12}$	$\tau^{1/3}(\varepsilon N^{1/4})^{-1/3}$	$\tau^{1/2}$	$\tau(\varepsilon N^{1/4})$
$\frac{F}{k_B T}$	$\tau^{4/3}N^{2/3}$	$\tau^{4/3} \varepsilon ^{2/3}N^{2/3}$	$\tau N^{1/2}$	$-\tau^2\varepsilon^2 N$	$\frac{F/k_B T}{N^{1/2}}$	$\tau^{4/3}N^{1/6}$	$\tau^{4/3}(\varepsilon N^{1/4})^{2/3}$	τ	$-\tau^2(\varepsilon N^{1/4})^2$

a sufficiently long chain could provide more contacts to the surface and hence still be absorbed onto the surface. An onset of adsorption occurs when $H = R_{\text{gl}}$ is about the size of the adsorption blob a/δ [2], giving the adsorption threshold $\delta_{\text{crit}} \sim (\tau/N)^{1/3}$ (blue line in Fig. 1) at which the chain starts to deform from the DG state.

(ii) *Surface attached cap* (SAC). When $\delta > \delta_{\text{crit}}$ but is not sufficient to flatten the chain, i.e., $\delta_{\text{crit}}/\tau - 2 < \varepsilon < 0$, the chain is partially absorbed on the surface and takes a caplike shape. In this case, although both R_{\parallel} and H have the same poor solvent scaling $N^{1/3}$ as does R_{gl} (because adsorption is still weak here), they can vary with τ and δ in two different ways. If δ is slightly greater than δ_{crit} such that $3R_{\parallel}^2/4 < H^2$ in Eq. (1) or $\theta > 120^\circ$ [because $\tan(\theta/2) = 2H/R_{\parallel}$], only a small fraction of chain segments are absorbed on the surface, giving $H \sim R_{\text{gl}} \sim a\tau^{-1/3}N^{1/3}$ from Eq. (1). Together with $|\varepsilon|R_{\parallel}^2 \sim H^2$ from Eq. (5), by balancing F_{ads} and F_{surf} , we get $R_{\parallel} \sim a\tau^{-1/3} - |\varepsilon|^{-1/2} - N^{1/3}$ and hence $z \sim \tau^{1/3} - |\varepsilon|^{-1}N^{1/3}$.

Conversely, if δ is sufficiently large compared to $\delta_{\text{crit}} \sim (\tau/N)^{1/3}$ especially for long chains, the chain can get more expanded, so that $3R_{\parallel}^2/4 > H^2$ in Eq. (1) or $\theta < 120^\circ$. This requires $R_{\parallel}^2 H \sim R_{\text{gl}}^3 \sim a^3\tau^{-1} - N$ from Eq. (1). Using $|\varepsilon|R_{\parallel}^2 \sim H^2$ from Eq. (5) again, we obtain $R_{\parallel} \sim a\tau^{-1/3}|\varepsilon|^{-1/6}N^{1/3}$ and $H \sim a\tau^{-1/3}|\varepsilon|^{-1/3}N^{1/3}$. $z \sim a/H \sim \tau^{1/3}|\varepsilon|^{1/3}N^{-1/3}$ can then be readily found from the latter.

(iii) *Adsorbed lens* (AL). When adsorption is strong ($\delta/\tau \gg 1$), the chain can be compressed into a ‘‘pancake’’ with $R_{\parallel} \gg H$. This state is determined by balancing $R_{\parallel}^2/\xi_T H$ with $\varepsilon R_{\parallel}^2/\xi_T^2$ in Eq. (5). Together with $R_{\parallel}^2 H \sim R_{\text{gl}}^3 \sim a^3\tau^{-1}N$ from Eq. (1), we obtain $R_{\parallel} \sim a\varepsilon^{1/2}N^{1/2}$. This has exactly the same $N^{1/2}$ scaling as the ideal chain’s $R_{\parallel} \sim aN^{1/2}$ under the athermal condition $\tau \ll N^{-1/2}$. The chain’s height $H \sim a\varepsilon^{-1}\tau^{-1} \sim a/\delta$ is therefore the size of the adsorption blob with $z \sim \delta$, exactly as for adsorption of an ideal chain [2].

(iv) *SAC-AL transition*. This transition occurs near the critical point $\delta = 2\tau$ or $\varepsilon = 0$ where adsorption and poor solvent effects cancel out exactly. With $R_{\parallel}^2 H \sim R_{\text{gl}}^3 \sim a^3\tau^{-1}N$ from Eq. (1) (because $\theta < 120^\circ$ here), the chain conformation is determined by balancing $R_{\parallel}^2/\xi_T H$ with the lateral surface energy H^2/ξ_T^2 in Eq. (5). This yields $R_{\parallel} \sim a\tau^{-1/4}N^{3/8}$ and $H \sim a\tau^{-1/2}N^{1/4}$ (and hence $z \sim a/H \sim \tau^{1/2}N^{-1/4}$) completely different from the results for SAC and AL. Note that if ε is not zero but small, the transition can still occur within the so-called *crossover zone* around $\varepsilon = 0$. This happens when the surface energy $|\varepsilon|R_{\parallel}^2/\xi_T^2 \sim |\varepsilon|\tau^{3/2}N^{3/4}$

is comparable to or less than the chain energy $\tau N^{1/2}$ at $\varepsilon = 0$, i.e., $2\tau - c\tau^{-1/2}N^{-1/4} \leq \delta \leq 2\tau + c\tau^{-1/2}N^{-1/4}$ (with $c = 2^{1/4}\pi \approx 3.73$ when the above energies are evaluated more accurately), as indicated by pink dotted lines in Fig. 1.

Figure 3 plots $R_{\parallel}/aN^{3/8}$ against ε , showing that all the curves with various values of N cross at the very same point $\varepsilon = 0$. R_{\parallel} for $\varepsilon < 0$ and $\varepsilon > 0$ are found to scale as $N^{1/3}$ and $N^{1/2}$, respectively (see the insets). These results confirm the various scalings for R_{\parallel} . The corresponding scalings for H and z are also confirmed (not shown). In terms of crossover scaling near $\varepsilon = 0$, having the results in Table I(a) rescaled by the corresponding power laws in N at $\varepsilon = 0$, we find that they all vary as certain powers in $|\varepsilon|N^{1/4}$, as shown in Table I(b) (the $\theta > 120^\circ$ case is an exception because it is away from the critical $\varepsilon = 0$ state). In other words, they can be expressed in a universal finite-size scaling form $N^\lambda f(\varepsilon N^\varphi)$ with the unique crossover exponent $\varphi = 1/4$.

To better understand the nature of the SAC-AL transition around the critical point $\delta = 2\tau$, we make an analogy to magnetism by taking z as the ‘‘surface magnetization’’ and δ as the ordering field. Because we focus on large N with δ being close to the SAC-AL transition point 2τ , this yields $R_{\parallel} \gg H$. This reduces the fraction of absorbed monomers to $z \approx a/H$, which can be shown to be exactly identical to

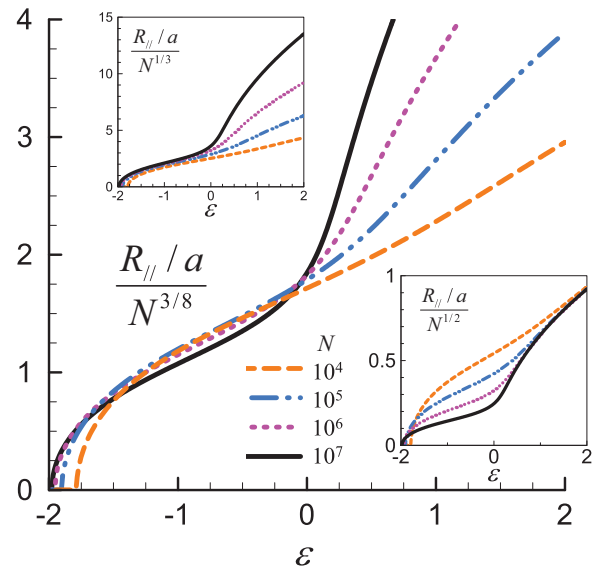


FIG. 3. $R_{\parallel}(\varepsilon = 0) \propto N^{3/8}$, as confirmed by the result that all the curves with different values of N cross at $\varepsilon = 0$. For $\varepsilon < 0$ and $\varepsilon > 0$, R_{\parallel} scales as $N^{1/3}$ and $N^{1/2}$, respectively (see the insets). $\tau = 0.2$.

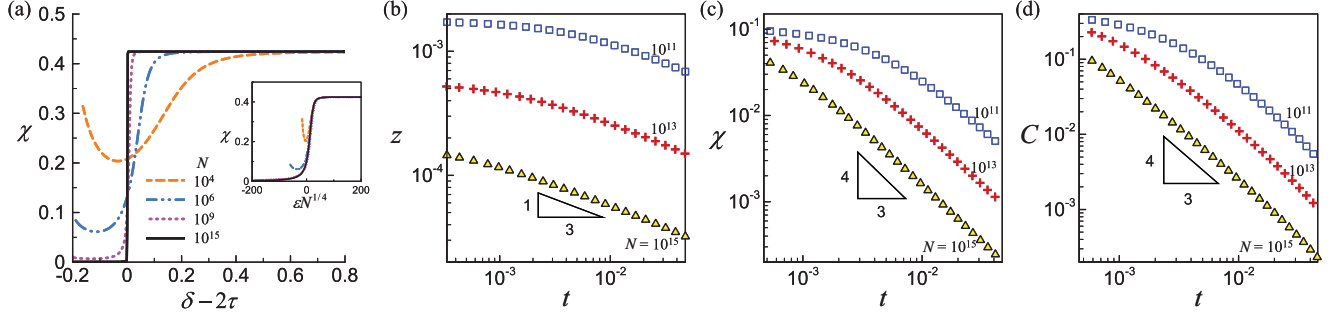


FIG. 4. (a) Surface susceptibility χ against $\delta - 2\tau (\equiv \varepsilon\delta)$ at $\tau = 0.1$, showing an apparent jump for a sufficiently large N . Inset shows collapse of the curves on plotting χ against $\varepsilon N^{1/4}$. Distinctive critical exponents for the fraction of adsorbed monomers z , χ , and the heat capacity C can be obtained by plotting them against $t \equiv (T_w - T)/T_w$ in the small- t regime. In (b) and (c), $\tau = 0.4$. In (d), $\delta = 0.4$.

the surface magnetization $\partial(F/N)/\partial\delta$. We further define the surface susceptibility as $\chi \equiv (\partial z/\partial\delta)_\tau$. Figure 4(a) plots χ against $\delta - 2\tau$. It clearly shows that, while the transition is continuous for a given N , it gets sharper as N is increased. The width of the transition (i.e., the crossover region) scales as $N^{-1/4}$ as all the curves collapse on plotting χ against $\varepsilon N^{1/4}$ (see the inset), in accordance with the crossover scaling seen in Table I(b).

Accordingly, as $N \rightarrow \infty$ the crossover zone vanishes and χ displays an apparent jump at $\delta = 2\tau$, so that the transition becomes *discontinuous*. This jump is identified as associated with the divergence as $\varepsilon \rightarrow 0^-$ but not with $\varepsilon \rightarrow 0^+$ (which gives a finite value for χ). To quantify this divergence, we define the new reduced temperature as

$$t \equiv (T_w - T)/T_w = (-\tau\varepsilon/2)\Theta/T_w. \quad (6)$$

Here $T_w = (1 - \delta/2)\Theta$ is the critical wetting temperature at $\varepsilon = 0$, indicating a shift of the Θ point due to adsorption, as in Ref. [9]. As $t \rightarrow 0^+$, we expect z , χ , the “specific heat” $C \equiv -[\partial^2(F/N)/\partial^2\tau]_\delta$, and the correlation length ξ to diverge as $z \propto t^{-\beta}$, $\chi \propto t^{-\gamma}$, $C \propto t^{-\alpha}$, and $\xi \propto t^{-\nu}$. We use the scalings for $\varepsilon < 0$ and $\theta < 120^\circ$ in Table I(a) to determine β , γ , and α . ν can then be determined by the hyperscaling for critical wetting $2 - \alpha = (d - 1)\nu$ (with dimension $d = 3$) [17]. These critical exponents are found to be

$$\beta = 1/3, \quad \gamma = 4/3, \quad \alpha = 4/3, \quad \nu = 1/3. \quad (7)$$

Figures 4(b)–4(d) show numerical confirmations for the first three. Notice that, to extract these exponents numerically, not only must N be sufficiently large but also ε must be chosen outside the crossover zone: $|\varepsilon| > c\tau^{-1/2}N^{-1/4}$. As these exponents are distinct from those of the usual wetting transitions, the present SAC-AL transition can be classified as an additional type of wetting transition.

IV. DISCUSSION

We have demonstrated that an analytical theory can be developed for single chain adsorption under poor solvent conditions. This theory is made specifically for the weak regime in which the solvent quality is slightly below the Θ point, $N^{-1/2} < \tau < 1$, and the adsorption strength is also small at the monomer level, $N^{-1/2} < \delta < 1$. Under these conditions, the chain can be treated as an incompressible droplet so that an analogy to wetting can be established. But in contrast to

the usual wetting, there is an additional line tension arising from the molecular confinement effect near the contact line. As shown in Sec. III, we find three distinct conformational states: DG, SAC, and AL, corresponding to the scenarios when adsorption is weaker than, comparable to, and stronger than the poor solvent effect, respectively. In fact, the DG, SAC, and AL seem to resemble the “desorbed compact,” “layered,” and “adsorbed extended” states, respectively, seen in simulations [4].

Aside from its ability to describe various conformation states, this theory can provide much more insight into how one state changes to another. The DG-SAC transition, i.e., the onset of chain adsorption, is discrete and occurs when the globule size $R_{gl} \sim a\tau^{-1/3}N^{1/3}$ is about the size of the adsorption blob $D \sim a/\delta$. So the resulting adsorption threshold $\delta_{crit} \sim (\tau/N)^{1/3}$ means that the longer a chain is the more easily it can adsorb onto a surface. The SAC-AL transition occurs when $\delta \sim 2\tau$, corresponding to the situation where D is about the size of the thermal blob $\xi_T \sim a/\tau$, in agreement with the qualitative theory given in Ref. [9]. This transition is continuous for a finite chain size but can become discontinuous as the thermodynamic limit is approached.

The SAC-AL transition has the following features. First, the transition is characterized by the end-to-end exponent $3/8$ which is different from $1/2$ for the coil-globule transition [18]. Second, the corresponding crossover region also becomes much broader, varying with $N^{-1/4}$ in width compared to $N^{-1/2}$ for the coil-globule transition [18]. The resulting crossover scalings are also distinct from those for polymer adsorption in good solvents [19]. Last and more important, we identify that this transition has rather distinctive critical exponents compared to those obtained by the classical Cahn-Landau theory for wetting transitions [20]. Therefore, it is different type of wetting transition. In comparison with existing literature, the present work not only recovers many results shown in previous theoretical reports, but also complements simulations.

On the theoretical side, Grosberg seems to the first to draw a phase diagram and sketch a theory to qualitatively describe the features of globular polymer adsorption [8]. Our theory essentially resolves the low-temperature (i.e., weak poor solvent) and weak adsorption corner in his phase diagram. Other studies employed Flory-Huggins-type theories to describe the “phase-separated” situation where the dilute polymer phase is in equilibrium with the more concentrated phase [9–11]. Johner and Joanny used a self-consistent field theory to describe the behavior of single-chain adsorption in a

poor solvent [9]. They showed that the chain behavior critically depends on the adsorption-to-thermal blob size ratio D/ξ_T . This leads to two regimes: partial wetting ($D/\xi_T > 1$) and complete wetting ($D/\xi_T < 1$), corresponding to the DG and AL states, respectively, shown by the present work. These two regimes cross over at $D/\xi_T \sim 1$, which also corresponds to the SAC-AL transition reported here. Dolinnyi provided a more detailed analysis for the transition between these two regimes [10]. Although his theory was also constructed for the two-phase situation, he showed that on approaching the transition point the spreading coefficient is proportional to $N^{-1/4}$, which is exactly the same factor found by the present theory for the SAC-AL transition. Note that the same $N^{-1/4}$ factor also appears in the critical interfacial tension for polymer demixing [21,22]. As the present theory is built specifically for a single chain, it is somewhat surprising that it still yields the identical dependence on N as obtained by the mean-field approach. But in terms of critical exponents, $\nu = 1/3$ [based on $2 - \alpha = (d - 1)\nu$ or $2/9$ if $2 - \alpha = d\nu$ is used] found here is different from $\nu = 1/4$ obtained from the mean-field theory [21]. This distinction is attributed to the inclusion of the additional confinement energy term [see Eq. (4)] in the present analysis.

As many previously reported aspects can be captured by the present theory, this proves that our theory does enable us to capture the correct physics. As the theory can further describe how a polymer chain changes its conformation, it can fill up the gaps in these previous theoretical studies that lack such a capability.

In addition, the present work also complements simulations. Because we focus on the weak regime which is close to the tricritical point where all the DG, SAC, and AL states emerge, it is not always possible to resolve phase boundaries using simulations for this regime. For the DG-SAC transition, because the phase boundary is located at $\delta_{\text{crit}} \sim (\tau/N)^{1/3}$, a short chain will start to deform at a higher value of δ than a long chain. Also, because this transition marks an onset of chain adsorption, this is why we see the apparent DG “plateau” for short chains in a sizable range of δ [see Figs. 2(a) and 2(b)]. This also explains why this transition can be easily captured by simulations [4] for short chains with $N < 10^3$. In fact, this transition seems to correspond to the transition from the “desorbed compact” to the “layered” state seen in simulations [4].

On the other hand, the SAC-AL transition could be difficult to observe for short chains because the width of the crossover region scales as $N^{-1/4}$ that is much broader than the $N^{-1/2}$ scaling normally seen [18]. It has been shown by simulations [4] that, even in the regime where adsorption is moderately strong, the actual conformational state cannot be clearly identified, which could be reminiscent of this transition. To resolve the chain behavior near this transition, it is necessary to employ long chains. However, running simulations for long chains with $N > 10^3$ or higher could be quite time consuming. So our theory is able to describe this transition by going beyond the computer limitations. Also, given the much broader $N^{-1/4}$ crossover region predicted by the present theory, to see a sharp SAC-AL transition the chain size N must be 10^4 or higher, which provides a useful estimate for future investigations on this transition using computer simulations.

It is worth mentioning that most simulations were carried out for the strong regime where either the solvent quality is very poor or/and the adsorption strength is not small at the

monomer level [3–7]. In this regime, a chain could undergo a structural change at the intersegment level to exhibit a variety of conformational states [3–7]. In particular, because of the strong compaction effect, an absorbed chain could even experience monomer packing and a freezing transition [3,5]. In contrast to these simulation studies, the present study focuses on the weak regime without structural changes at the intersegment level. Hence, such internal molecular effects do not occur. Nevertheless, the present theory provides an important piece of the picture needed for the complete phase diagram, which is difficult to obtain using computer simulations, as discussed earlier. And more importantly, as already demonstrated, a universality can exist in the weak regime, whereas it is unlikely to exist in the strong regime. This universality might also provide renewed insights into critical phenomena in the presence of surfaces [23].

We emphasize that all the results reported here cannot be obtained without the added confinement energy term Eq. (4a). We show that this term actually acts like line tension Eq. (4b). This line tension is in effect a positive one, which tends to increase the contact angle to resist the chain spreading due to adsorption—it is this term that makes an equilibrium state possible when adsorption is stronger than the poor solvent effect.

Such a line tension σ has a magnitude of $\sim k_B T / \xi_T \sim k_B T \tau / a$, consistent with Ref. [9]. While σ is determined by the solvent quality through τ , because we assume $N^{-1/2} < \tau < 1$, its magnitude is limited by the chain size N . A chain having $a \sim 0.2$ nm at $T = 300$ K for $N = 10^2$ has $\sigma \sim 10^{-12}$ J/m. A much longer chain such as $N = 10^4$, under which a much sharper SAC-AL transition can occur, can allow a much higher line tension $\sigma \sim 10^{-10}$ J/m. These values are within the typical line tension range $\sigma = 10^{-12} - 10^{-10}$ J/m reported previously [24–26]. But in contrast to these previous reports, this work demonstrates that the origin of the line tension can stem from the molecular confinement effect near the contact line.

From a broader perspective, the present problem is also closely relevant to nanodrop spreading in that the important role played by line tension might simply be a manifestation of the local molecular confinement near the contact line. It has been shown that line tension can affect the wetting behavior of a small droplet [14,15] and that the wetting transition with line tension differs from that without [17]. If a droplet has a (positive) line tension that behaves like the one reported here [see Eq. (4b)], its wetting behavior will also be distinct from that of the constant line tension case [14]. Since a similar line tension effect might likely occur in spreading of a polymeric liquid; perhaps one can use a polymeric nanodroplet to test if its wetting behavior resembles that of the absorbed polymer chain that we find here.

In terms of experiments, we have not seen any single molecule experiments that can be compared to or used to test our theory. Perhaps the reason is that it is difficult to keep a polymer solution sufficiently dilute without phase separation under the poor solvent condition. This is also the reason why most of the existing theoretical studies consider the “phase-separated” situation [9–11]. Nevertheless, when a phase separation occurs, the polymer concentration in the dilute phase could be so low that chains therein could behave like single molecules. If the dilute phase can exist alone by completely segregating itself from the coexisting concentrated

phase, it will be possible to test our theory experimentally by inserting a suitable substrate into the dilute phase.

As this work has demonstrated an exact correspondence between single chain adsorption and wetting, it provides the advantage of understanding a polymer adsorption problem by studying the analogous wetting problem. Likewise, because this correspondence is established with the line tension term, how a chain changes its conformation due to adsorption might provide a renewed understanding of how line tension works at the molecular scale. This might offer an alternative to resolve the longstanding debate about the origin of line tension. Although the critical exponents and finite size scaling reported here currently cannot be tested by experiments and simulations, they do display interesting features that could be the subject of a more general and thorough investigation in the future.

ACKNOWLEDGMENT

This work is supported by the Ministry of Science and Technology of Taiwan under Grant No. 101-2221-E-006-230-MY3.

APPENDIX: DERIVATION OF THE LINE TENSION TERM

Consider a small ring-shaped control volume of height $h(x)$ and radius x , containing the number of monomers $dn = \rho_T 2\pi x h dx$. With the confinement energy per monomer $k_B T a^2/h^2$, the confinement energy for this control volume is $a^2 dn/h^2 = 2\pi \rho_T a^2 x h^{-1} dx = 2\pi (x/\xi_T) h^{-1} dx$. Integrating the above from $x = 0$ to $x = R_{\parallel}/2$ and making use of $r = R_{\parallel}/2 \sin \phi$, $H = r(1 - \cos \phi)$, $x = r \sin \phi$, and $h = r(\cos \phi - 1) + H$, we get $F_{\text{confine}}/k_B T = (\pi R_{\parallel}/\xi_T) f(\theta)$ with $f(\theta) = (\sin \theta)^{-1} \int_0^{\theta^-} (\sin \phi \cos \phi)(\cos \phi - \cos \theta)^{-1} d\phi \approx (1 + B \cos \theta)/\sin \theta$, where $B = \ln(1/\varepsilon) - 1$ with $\varepsilon = (\cos \theta^- - \cos \theta)/(1 - \cos \theta)$. In the above integral, a singularity (in B) can exist at the “wedge point” $\phi = \theta$ where chain segments are subject to *infinite* entropic penalty, which is physically inadmissible. The singularity can be relieved by a *microscopic cutoff* in the size of the thermal blob, ξ_T . This causes θ^- to be slightly smaller than the apparent angle θ . Here we take $B = 1$ to ensure that F_{confine} vanishes as θ approaches 180° at the desorbed state. $f(\theta)$ is then reduced to $\cot(\theta/2) = R_{\parallel}/2H$, and hence Eq. (4).

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