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Adsorption and collapse transitions in a linear polymer chain near an attractive wall

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We deduce the qualitative phase diagram of a long flexible neutral polymer chain immersed in a poor solvent near an attracting surface using phenomenological arguments. The actual positions of the phase boundaries are estimated numerically from series expansion up to 19 sites of a self-attracting self-avoiding walk in three dimensions. In two dimensions, we calculate phase boundaries analytically in some cases for a partially directed model. Both the numerical and analytical results corroborate the proposed qualitative phase diagram.

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I. INTRODUCTION

The behavior of flexible polymers in solution at large length scales is independent of the chemical nature of the polymer and the solvent, and these universal scaling properties are well understood in terms of the renormalization group approach [1,2]. The polymer chain is known to undergo a transition from a random-coil phase to a globular phase as the temperature or the pH of the solution is varied. The model of a self-avoiding walk on a lattice with on-site repulsion and nearest-neighbor attraction provides a simple model for understanding the collapse transition in polymers [3].

When the chain interacts with an impenetrable surface its conformational properties are strongly modified [4,5]. Competition between the lower internal energy near an attractive wall and the higher entropy away from it results in a transition, where for a strongly attractive surface the polymer sticks to the surface, and for weak attraction it stays away from the surface. This behavior finds applications in lubrication, adhesion, surface protection, etc. [6].

If there is also self-attraction in the polymer, there is the possibility of a collapse transition in both the desorbed and adsorbed states. In addition, there is a surface-attached globular (SAG) phase, in which the polymeric globule gets attached to the attractive surface [7]. In the thermodynamic limit, the SAG phase has the same free energy per monomer as the bulk globular phase, and the transition between them is a surface transition. In earlier papers [7,8], we discussed the phase diagram in this case, and investigated the phase diagram in a lattice model using extrapolation of exact series expansions. This scheme has been found to give satisfactory results as it can take into account the corrections to scaling. To achieve the same accuracy by the Monte Carlo method, a chain of about two orders of magnitude longer than in the exact enumeration method has to be considered [9].

In this paper, we show that the qualitative features of the phase diagram in three dimensions can be determined by simple phenomenological arguments. In the case of a partially directed polymer in two dimensions, we determine the exact phase diagram of the SAG phase analytically. In this case, the polymer has different behavior depending on whether it is near the wall perpendicular to the preferred direction (SAG1) or the wall parallel to the preferred direction (SAG2). We determine the phase boundaries of SAG1 and SAG2 phases by calculating their orientation dependent surface energy. We also determine the transition between SAG1 and SAG2 phases when both walls are present. We also summarize our results of analysis of exact series expansion in three dimensions which we have extended by two more terms.

The paper is organized as follows. Section II contains the definition of the model and of the various phases. In Sec. III, we briefly review earlier work before providing arguments for the qualitative nature of the phase diagram in two and three dimensions. The phase diagram obtained is compared with numerical results from series expansion in Sec. IV. Section V contains the analytical results obtained for the partially directed model.

II. MODEL AND DEFINITIONS

A simple lattice model for a linear polymer in a poor solvent is a self-avoiding walk (SAW) on a regular lattice with an attractive interaction energy ϵ_u between pairs of sites of the walk which are unit distance apart but not consecutive along the walk. The adsorbing surface is modeled by restricting the walk to lie in a upper half plane and by associating an attractive energy ϵ_s with each monomer (site of the walk) lying on the surface. In the partially directed self-avoiding walk (PDSAW) in two dimensions, there is an additional restriction that the walk cannot take steps in the negative x direction.

We will work with the reduced variables $\omega = e^{\beta\epsilon_s}$ and $u = e^{\beta\epsilon_u}$, where β is the inverse temperature. For clarity of argument, we start by defining the different phases. Consider a polymer chain consisting of N monomers, attached to the attractive surface at one end. If ϵ_s and ϵ_u are small in magnitude, the polymer exists in the swollen random-coil phase, away from the surface. In this phase, the mean radius of gyration varies as N^{ν} where ν takes the self-avoiding walk value [$\nu \approx 0.588$ in (3D) and $\nu = 3/4$ in 2D]. The number of monomers in contact with the surface is of order 1 in this case. We shall call this phase the desorbed extended (DE)

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phase. If ϵ_u is large and ϵ_s is small, the polymer exists away from the wall as a compact ball of finite density. In this case, the radius of gyration of the polymer varies as $N^{1/d}$ in d dimensions. We shall call this phase the desorbed collapsed (DC) phase. If the surface attraction ϵ_s is sufficiently large, the polymer sticks close to the surface. In this case, a finite fraction of monomers are on the surface, and the extent of the polymer perpendicular to the surface is finite. Along the surface the polymer roughly acts as a polymer chain in $d-1$ dimensions. Depending on whether the attractive self-interaction is large or small, the polymer is in a collapsed phase with its transverse size varying as $N^{1/(d-1)}$, or in the extended phase with the transverse size varying as $N^{\nu'}$, where ν' is the self-avoiding walk exponent in $d-1$ dimensions. We shall call these phases the adsorbed collapsed (AC) and the adsorbed extended (AE) phases, respectively. In addition to these phases, the polymer may exist as a collapsed globule of finite density which sticks to the surface. In this case, the size of the polymer in the directions transverse and perpendicular to the surface varies as $N^{1/d}$ and the number of monomers in contact with the surface varies as $N^{(d-1)/d}$. We shall call this phase the surface-adsorbed globular phase. Note that in two dimensions there is no distinction between the AC and the AE phases.

The polymer undergoes a transition between the extended and collapsed phases as the temperature is varied. At the transition temperature between the DC and the DE phases, called the θ point, the critical behavior is described by a tricritical point of the $O(n)$ $(n\rightarrow 0)$ spin system. At the θ point, $R_b \sim N^{\nu_\theta}$ with $\nu_\theta = 4/7$ for 2D [10] and 1/2 for 3D [1]. The transition from AE to AC is described by ν_θ corresponding to one lower dimension. In two dimensions, at the multicritical point where the DE, DC, and AE phases meet, the geometrical properties of the chain can be related to the perimeter of percolation clusters near a wall, and hence can be determined exactly [11].

III. QUALITATIVE PHASE DIAGRAM

First, we briefly review earlier work on this problem. In one of the earliest papers on the subject, Bouchaud and Vannimenus derived the exact phase diagram on a Sierpinski gasket [12]. The phase diagram consisted of the AE, DE, and DC phases. In [13], the phase diagram in two dimensions was obtained approximately by series expansions and it was found to be qualitatively similar to that for the gasket. In [7], the possibility of the existence of the SAG phase in two dimensions was discussed based on analysis of series expansions. Evidence for the existence of a surface transition from the SAG to DC phase was also presented. A variant of the model, the PDSAW model in two dimensions, has been more amenable to analytical calculations. For a PDSAW in two dimensions, the exact calculation of the phase boundary between the collapsed and the extended phases [14–16] was numerically confirmed in [17]. The phase diagram thus obtained is qualitatively similar to that of the undirected two-dimensional model. In [18], the existence of the SAG phase in the PDSAW was suggested based on series expansion analysis.

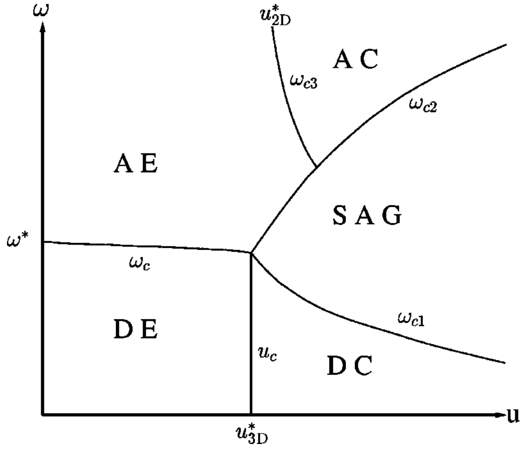

FIG. 1. The qualitative phase diagram in three dimensions.

The model is less studied in three dimensions. Monte Carlo simulations [19] and series expansion analysis [8] on the cubic lattice showed the existence of four phases: AE, AC, DE, and DC. While [19] claimed the existence of two multicritical points, the earlier preliminary results [8] obtained from series expansion seemed to support one multicritical point. More careful analysis of the series, reported later in this paper, shows that there are indeed two multicritical points. The question of whether or not a SAG phase exists in three-dimensions has not been addressed so far. Also, the possibility of surface transitions among the collapsed phases has not been explicitly dealt with. Thus, in spite of many earlier studies, the qualitative behavior of the system is not fully established.

We now determine the qualitative nature of the phase diagram from phenomenological considerations. If the wall is repulsive, i.e., $\omega \leqslant 1$, the polymer will be in the desorbed state. As u is increased from 1 to ∞, the polymer undergoes a collapse transition from the DE to the DC phase at a critical value u^*_{3D} (see Fig. 1). This transition value u^*_{3D} is clearly independent of ω, and the boundary between the DE and DC phases is vertical. If u and w are both near 1, clearly, the polymer is in the DE phase. As ω is increased from 1 to ∞ the polymer undergoes a transition from the DE to the AE phase. Let this transition occur at a critical curve $\omega_c(u)$ that intersects the ω axis at ω^*.

Now, consider the case when both u and ω are large. At $T=0$, the polymer has the density 1, and can be described as a Hamiltonian walk. The bulk attractive energy per site is $-(d-1)\epsilon_u$, and there is a surface energy which is easily seen to be $d\epsilon_u N^{(d-1)/d}$. Then the free energy of the DC phase at $T=0$ is

$$E_{DC} = -(d-1)\epsilon_u N + d\epsilon_u N^{(d-1)/d}. \tag{1}$$

In the SAG phase, at $T=0$, the polymer exists as a rectangular parallelepiped of size $L_\parallel$ and $L_\perp$ in directions parallel and perpendicular to the surface. Its bulk energy is the same as in the DC phase and the surface energy is $(\epsilon_u - \epsilon_s)L_\parallel^{d-1} + (d-1)\epsilon_u N/L_\parallel$. Minimizing the surface energy with respect to $L_\parallel$, we obtain

$$\mathrm{E}_{\mathrm{SAG}}=-(d-1)\epsilon_u N+d\epsilon_u^{(d-1)/d}(\epsilon_u-\epsilon_s)^{1/d}N^{(d-1)/d}. \tag{2}$$

In the AC phase, we have $L_\perp=1$, $L_\parallel=N^{1/(d-1)}$, and the free energy at $T=0$ is

$$\mathrm{E}_{\mathrm{AC}}=-(d-2)\epsilon_u N-\epsilon_s N+(d-1)\epsilon_u N^{(d-2)/(d-1)}. \tag{3}$$

Comparing the energies of these phases, we see that the SAG phase has lower free energy than the DC or the AC phases for $0\leqslant\epsilon_s\leqslant\epsilon_u$. Thus the lower and upper boundaries of the SAG phase (lines ω_{c1} and ω_{c2} in Fig. 1) tend to $\omega_{c1}=1$ and $w_{c2}=u$ for large u.

If $\omega=\infty$, the polymer is adsorbed onto the $(d-1)$-dimensional surface. In $d>2$, there is a transition from the AE to the AC phase at the critical value of $u=u_{d-1}^*$, corresponding to a $(d-1)$-dimensional collapse. Clearly, $u_{d-1}^*>u_d^*$. The partition function, when written as a perturbation series in ω^{-1}, is

$$Z(u,\omega)=Z_0(u)\omega^N \times\left[1+\frac{N}{\omega^2}\left(n_0+\frac{n_1}{u}+\frac{n_2}{u^2}\right)+\cdots\right], \tag{4}$$

where n_j is the fraction of bonds whose end points have exactly j nearest-neighbor monomers. We expect that n_0 is larger in the AE phase as compared to the AC phase, while n_1 and n_2 are smaller. Using $n_0=1-n_1-n_2$ in Eq. (4), it follows that for large but finite ω, the free energy is lower for the AE phase. Hence, the phase boundary ω_{c3} between the AE and AC phases should curve to the right.

The phase diagram for the two-dimensional problem is qualitatively the same as that of the three-dimensional problem except that there is no AC phase, and hence no ω_{c3} phase boundary. We now argue that the phase boundaries u_c, ω_c, ω_{c1}, and ω_{c2} meet at one point. For the sake of clarity, we will illustrate the arguments for the two-dimensional problem. In the DC and the SAG phases, the polymer is a compact two-dimensional object with finite density. We define $\sigma(\theta)$ as the surface tension between the surface of this object and the liquid, where θ is the angle the surface makes with the horizontal. For a shape $r(\theta)$, the free energy is a sum of two terms: the bulk term, which depends on u alone, and a surface term, which can be written as an integral over the angle dependent $\sigma(\theta)$.

Near the phase boundary ω_{c2} separating the AE and the SAG phases, the shape is highly anisotropic and $R_s\gg R_b$, where R_s and R_b are the extent of the polymer along and perpendicular to the surface. R_s diverges as we approach the phase boundary from within the SAG phase. The additional cost of creating two surfaces of orientation $\theta=0$ should be zero. Hence, along the phase boundary ω_{c2}, we have

$$\sigma(0)+\sigma_w=0, \tag{5}$$

where σ_w is the free energy cost per unit length when the polymer is along the wall. Near the phase boundary ω_{c1} separating the DC and the SAG phases, the shape of the SAG is such that the part in contact with the wall has orientation $\theta=0$. Clearly, this configuration becomes unfavorable in comparison to the DC phase when

$$\sigma(0)=\sigma_w. \tag{6}$$

For the DE-DC transition, clearly the surface tension must vanish at the collapse point. Thus, along u_c we have

$$\sigma(0)=0. \tag{7}$$

It is clear that the point corresponding to $\sigma(0)=\sigma_w=0$ lies on all the three lines Eqs. (5)–(7). It still remains to argue that ω_c will also pass through the same point as the other phase boundaries. Let u and ω be transformed to u' and ω' under a scale transformation as

$$u'=f(u), \tag{8}$$

$$\omega'=g(u,\omega). \tag{9}$$

The function $f(u)$ is independent of the surface parameter ω because u is a bulk parameter. There will be three fixed points for Eq. (8), namely, $u=0$, $u=u^*$, and $u=\infty$ where u^* is the only repulsive fixed point. Consider Eq. (9) when u is fixed at each of its three fixed points. In the simplest scenario, for each value of u, there will be three fixed points of Eq. (9). The schematic diagram showing the renormalization group flows between these nine fixed points is shown in Fig. 2. The attractive fixed points A_1, A_2, C_1, and C_2 correspond to the four phases. The fixed points A, B_1, C, and B_2 correspond to the four critical phases corresponding to the phase boundaries and the point B corresponds to the repulsive multicritical point.

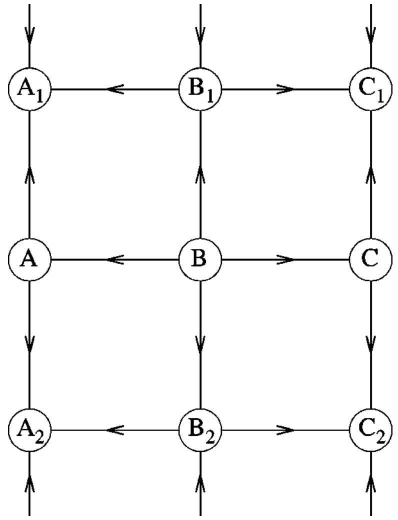

FIG. 2. The schematic flow diagram in two dimensions.

IV. SERIES EXPANSION RESULTS

We enumerated all SAWs up to a certain length on the cubic lattice in which the first site of the walk lies at the origin and all sites are confined to the half plane $y\geqslant0$. Let $C_N(N_s,N_u)$ be the number of SAWs of N sites having N_s

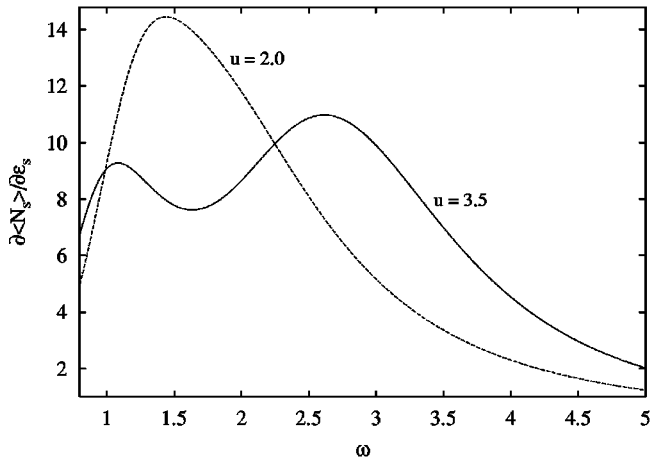

FIG. 3. The dependence of $\partial\langle N_s\rangle/\partial\epsilon_s$ on ω. For $u=2.0$, there is only one peak corresponding to the DE to AE transition. For $u=3.5$, there are two peaks corresponding to the DC to SAG to AC transitions.

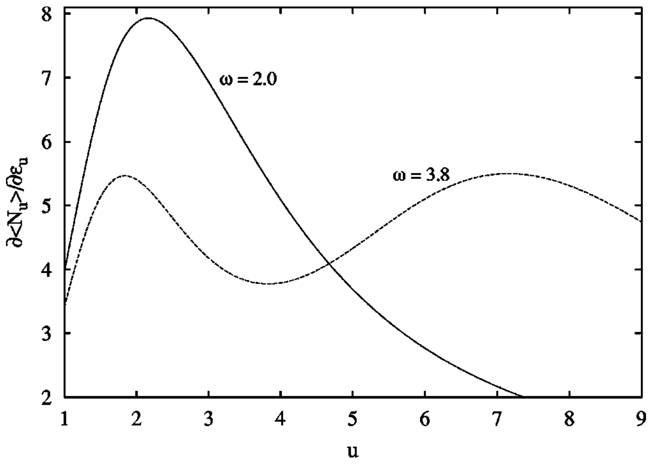

FIG. 4. The dependence of $\partial\langle N_u\rangle/\partial\epsilon_u$ on u. For $\omega=2.0$ there is only one peak corresponding to the DE to DC transition. For $\omega=3.8$, there are two peaks corresponding to the AE to AC to SAG transitions.

monomers on $y=0$ and N_u nearest-neighbor monomer pairs. In [8], we reported the enumeration and analysis of the series $C_N(N_s,N_u)$ up to $N=17$ for the cubic lattice. We have now extended the series for three-dimensions by two terms and reanalyzed the data to obtain a better estimate of the phase boundaries.

For fixed u, we identify the position of the phase boundary separating the desorbed phase from the adsorbed or attached phases as that value of ω at which $\partial\langle N_s\rangle/\partial\epsilon_s$ is a maximum. Figure 3 shows the variation of $\partial\langle N_s\rangle/\partial\epsilon_s$ for two values of u for $N=19$.

For fixed ω, we identify the position of the phase boundary separating the extended phase from the collapsed phase as that value of u at which $\partial\langle N_u\rangle/\partial\epsilon_u$ is a maximum. Figure 4 shows the variation of $\partial\langle N_u\rangle/\partial\epsilon_u$ for two values of ω for $N=19$.

The values of $u^*_{3\,\mathrm{D}}$ and ω^* obtained by this method are 2.00 and 1.49, respectively. The previous results were $u^*_{3\,\mathrm{D}}=1.76$ by the series expansion method [8] and $\omega^*=1.45$ by the Monte Carlo method [20] and $\omega^*=1.5$ by the series expansion method [21]. It is possible to obtain better estimates of $u^*_{3\mathrm{D}}$ as well as the phase boundaries by extrapolating for large N. Let

$$Z_N(\omega,u)=\sum_{N_s,N_u} C_N(N_s,N_u)\,\omega^{N_s}u^{N_u} \tag{10}$$

be the partition function. Then, the reduced free energy per monomer can be written as

$$G(\omega,u)=\lim_{N\to\infty}\frac{1}{N}\ln Z_N(\omega,u). \tag{11}$$

We refer to [7,8] for details of the methods used for extrapolating to large N in Eq. (11). The phase boundaries are then found from the maxima of $\partial^2G(\omega,u)/\partial\epsilon_s^2$ $(=\partial\langle N_s\rangle/\partial\epsilon_s)$ and $\partial^2G(\omega,u)/\partial\epsilon_u^2$ $(=\partial\langle N_u\rangle/\partial\epsilon_u)$.

Using the above method, we obtain $u^*_{3\mathrm{D}}=1.76$ and $\omega^*=1.48$, which accord fairly well with the previously obtained results. The phase diagram obtained from series analysis agrees qualitatively with the phase diagram proposed in Sec. III (see Fig. 1).

V. ANALYTIC CALCULATION FOR THE TWO-DIMENSIONAL DIRECTED POLYMER

In this section, we analytically determine the phase boundary separating the SAG phase from the DC and AE phases in the PDSAW model. We do so by calculating the macroscopic shape of the collapsed phases at low temperatures. At zero temperature, it is easy to see that the configurational energy of the polymer is minimized if it assumes a square shape of size $\sqrt{N}\times\sqrt{N}$. For small nonzero temperatures, the polymer assumes a shape that is slightly perturbed from this zero temperature square shape. We will derive an effective surface energy for these fluctuations in Sec. V A. Using these results, we determine the shapes of SAG1 and SAG2 phases in Sec. V B. In Sec. V C, we calculate the phase boundary between the various phases.

A. Effective surface energy

For the directed polymer in the collapsed or SAG phase, the density in the bulk is exactly 1 and the configuration is "frozen." Only the position of the boundary can change, as there is some fluctuation of height allowed at the boundary. Thus $f_{\mathrm{bulk}}(\mathrm{SAG})=f_{\mathrm{bulk}}(\mathrm{DC})=-\epsilon_u$, independent of ω. Consider a polymer shape as shown in Fig. 5. The energy of the configuration is

$$E=-\epsilon_uN+\frac{\epsilon_u}{2}(a_1+a_2+2b)+\frac{\epsilon_u}{2}\sum_{j=0}^{b-2}|y_{j+2}-y_j|. \tag{12}$$

By a redefinition of E, we drop the bulk term proportional to N. The shape of the polymer is determined by the rest of the

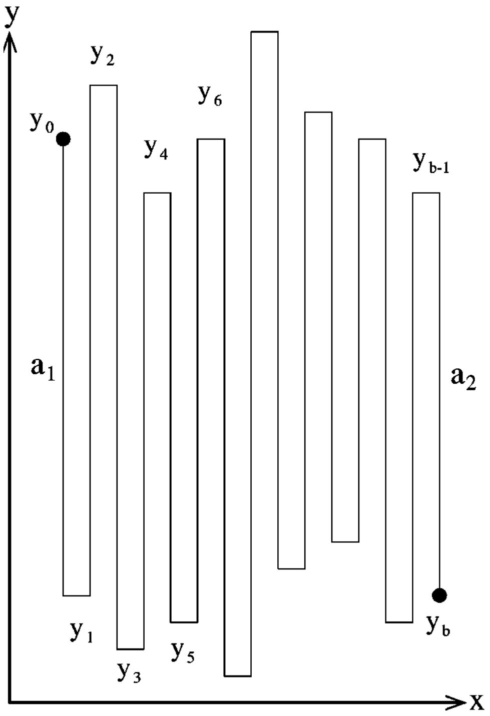

FIG. 5. Schematic diagram of a partially directed polymer for $T \gtrsim 0$.

terms which are all proportional to $\sqrt{N}$. We replace the terms under the summation by an integral over an effective orientation dependent surface energy $f(\theta)$, where θ is the angle the surface makes with the horizontal. In this case, it is straightforward to calculate $f(\theta)$. Consider all possible walks with an average slope $\tan(\theta) = y/x$. Then, the sum over all weighted paths is

$$e^{-\beta x \sec(\theta) f(\theta)} = \sum_{y_1, \ldots, y_x} \delta\left(\sum_{i=1}^{x} y_i - y \right) \prod_{i=1}^{x} p^{|y_i|}, \tag{13}$$

where $p = e^{-\beta \epsilon_u/2}$ and δ is the usual Kronecker delta function. Taking the Laplace transform with respect to *y*, we obtain independent summations over y_i. These are easily done, giving

$$f(\theta) = \frac{1}{\beta}\left[\sin\theta \ln(z_0) + \frac{\cos\theta}{2} \ln \frac{(z_0 - p)(1 - p z_0)}{z_0(1 - p^2)} \right], \tag{14}$$

where

$$z_0 = \frac{(1+p^2)\tan\theta + \sqrt{(1-p^2)^2 \tan^2\theta + p^2}}{p(1 + 2\tan\theta)}. \tag{15}$$

We also need to calculate the energy cost σ_w of adsorbing onto the wall unit length of the polymer. For SAG1, it is trivially equal to $\sigma_{w1} = -\epsilon_s$. We calculate σ_{w2} for SAG2 by the transfer matrix method. If ψ_i denotes the *y* coordinate of the lowest portion of the polymer at site *i*, then the weight of obtaining ψ_{i+2} from ψ_i is $\langle \psi_i | T | \psi_{i+2} \rangle = [1 + (\omega^2 - 1)\delta_{\psi_{i+2},0}] u^{-|\psi_i - \psi_{i+2}|/2}$. By trying out an ansatz $\psi_l = \alpha^l + \delta_{l,0}\psi_0$ for the eigenfunction, it is not difficult to verify that the largest eigenvalue of the transfer matrix *T* is

$$\Lambda = \frac{\omega^2(\omega^2 - 1)(u - 1)}{\omega^2(u - 1) - u}. \tag{16}$$

Then, $\sigma_{w2} = -\ln(\Lambda)/(2\beta)$. Clearly, as $u \to \infty$, σ_{w2} has the correct limit $-\epsilon_s$.

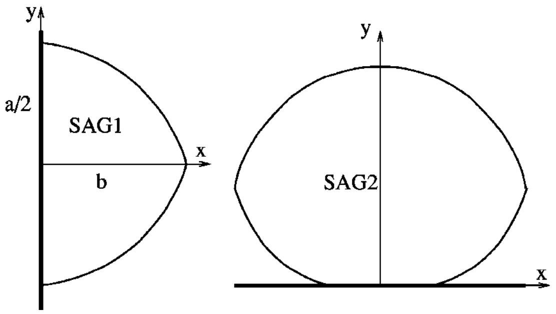

FIG. 6. Schematic diagram of the macroscopic shapes of SAG1 and SAG2.

B. Calculation of the macroscopic shape

In this subsection we describe the shape determined by minimizing the surface energy of the collapsed phases. Given the expression for the temperature and orientation dependent $f(\theta)$, and also the value of surface energy of the polymer attached to the wall, it is straightforward to determine the globular shape that minimizes the surface energy given a fixed volume. This is the classical Wulff construction. The result is that the macroscopic shape of the polymer is given by

$$e^{2\beta\lambda y} = c_2 e^{\beta\lambda x}(1 - p c_1 e^{-\beta\lambda x})(c_1 e^{-\beta\lambda x} - p), \tag{17}$$

where the two constants c_1 and c_2 are fixed by the two boundary conditions. The Lagrange multiplier λ is determined by the constraint that the total area under the curves is *N*. The constants c_1 and c_2 are now varied to obtain the shape with the lowest surface energy.

We briefly describe the calculation of c_1 and c_2 for SAG1. The corresponding calculation for SAG2 is a straightforward generalization and we omit the details. Let the macroscopic shape of SAG1 have linear extent *a* and *b* in the two directions (see Fig. 6). The two constants c_1 and c_2 in Eq. (17) are fixed by the two boundary conditions $y(0) = a/2$ and $y(b) = 0$. Let $g = \exp(\beta\lambda a)$ and $h = \exp(-\beta\lambda b)$. Then,

$$g = \frac{(1 - p c_1)(c_1 - p)}{c_2}, \tag{18}$$

$$h = \frac{(1 - p c_1 h)(c_1 h - p)}{c_2}, \tag{19}$$

where *h* and *g* are functions of only c_1 and c_2. We fix the Lagrange multiplier λ by the constraint that $\int_0^b y\,dx = N/2$. We obtain λ as a function of c_1 and c_2 as

$$\beta^2\lambda^2 N=\int_0^{-\ln(h)} dz\, \ln\frac{(1-pc_1e^{-z})(c_1e^{-z}-p)e^z}{c_2}. \tag{20}$$

We also require the integral of the surface free energy along the curve $y(x)$. Using Eqs. (17), (14), and (15), we obtain

$$F=\frac{\ln(h)}{2\beta^2\lambda}\ln\frac{(u-1)c_1}{c_2 u}-\frac{\ln(g)}{2\beta^2\lambda}\ln c_1+\lambda N, \tag{21}$$

where F is the total surface energy along the curve.

The total surface energy for SAG1 may be obtained from Eq. (12) to which the energy gain of attaching to the wall has been added. Then from Eqs. (12) and (21) we obtain

$$E=\frac{\ln(h)}{2\beta^2\lambda}\ln\frac{(u-1)c_1}{c_2 u^2}+\frac{\ln(g)}{2\beta^2\lambda}\frac{\sqrt{u}}{c_1\omega}+\lambda N. \tag{22}$$

We now minimize E with respect to the variables c_1 and c_2. Differentiating with respect to c_1 and c_2 and simplifying, we obtain

$$0=\ln\frac{\sqrt{u}}{c_1\omega}\left[\frac{1}{g}\frac{dg}{dc_1}-\frac{\ln(g)}{\lambda}\frac{d\lambda}{dc_1}\right] +\ln\frac{(u-1)c_1}{c_2u^2}\left[\frac{1}{h}\frac{dh}{dc_1}-\frac{\ln(h)}{\lambda}\frac{d\lambda}{dc_1}\right], \tag{23}$$

and

$$0=\ln\frac{\sqrt{u}}{c_1\omega}\left[\frac{1}{g}\frac{dg}{dc_2}-\frac{\ln(g)}{\lambda}\frac{d\lambda}{dc_2}\right] +\ln\frac{(u-1)c_1}{c_2u^2}\left[\frac{1}{h}\frac{dh}{dc_2}-\frac{\ln(h)}{\lambda}\frac{d\lambda}{dc_2}\right]. \tag{24}$$

The solution of Eqs. (23) and (24) is $\ln[\sqrt{u}/(c_1\omega)]=0$ and $\ln[(u-1)c_1/(c_2u^2)]=0$, implying

$$c_1=\frac{\sqrt{u}}{\omega}, \tag{25}$$

$$c_2=\frac{u-1}{\omega u^{3/2}}. \tag{26}$$

The calculation for SAG2 proceeds on similar lines except for the fact that the shape consists of one extra segment. Figure 7 shows the shape of the SAG polymer for different values of ω. All the shapes lie on top of each other if we scale the coordinates as $X=\beta\lambda x$ and $Y=\beta\lambda y$.

C. Phase diagram

We calculate the phase diagram for the directed polymer from Eqs. (5)–(7). These equations give most of the phase boundaries except the transitions involving SAG1. This is because the shape in contact with the surface does not have orientation $\theta=0$. This anomaly arises due to the constraint of directedness. The surface transition from SAG1 to SAG2 is one in which the globule would have lower free energy if attached to the x wall rather than the y wall.

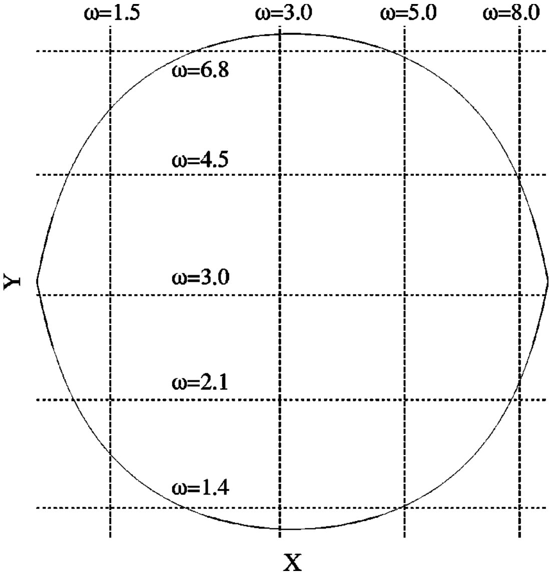

FIG. 7. The shape of SAG polymer is shown for different values of ω when u is kept fixed at 10.0. The position of the wall is denoted by a dotted line (vertical for SAG1 and horizontal for SAG2). The shape of SAG1 corresponds to the part of the curve from the wall to the right, while the shape of SAG2 corresponds to part of the curve above the wall.

Transition from DC to DE (u_c). The critical value u_c is obtained from Eq. (7), i.e, $\sigma(0)=0$. This is equivalent to the $2f(0)+\epsilon_u=0$. Substituting for $f(0)$, we obtain

$$\frac{\sqrt{u}-1}{\sqrt{u}+1}=\frac{1}{u}, \tag{27}$$

which has the solution

$$u_c=3.382\,98\ldots. \tag{28}$$

Note that this result matches exactly with the result for the DC-DE transition obtained by the transfer matrix method [14–16].

Transition from SAG1 to AE (ω_{c2}). This phase boundary is determined by equating the coefficient of $N^{1/d}$ in the perpendicular extent of the polymer in the SAG1 phase to zero. Using Eqs. (19), (25), and (26) and setting $h=1$, we obtain the phase boundary

$$\omega_{c2}=\frac{1+u^2+\sqrt{(1+u^2)^2-4u^3}}{2u}. \tag{29}$$

This solution has a natural boundary at $u=u_c$ at which value the expression under the square root sign becomes equal to zero.

Transition from SAG1 to DC (ω_{c1}). The transition from SAG1 to DC occurs when the energy cost of creating a globule sticking to the wall becomes equal to the energy of a DC polymer. This can be determined by setting the linear extent of SAG1 along the wall to zero. Using Eqs. (18), (25), and (26) and setting $g=1$, we obtain the phase boundary

$$\omega_{c1}(u)=\frac{1+u^2-\sqrt{(1+u^2)^2-4u^3}}{2u}. \tag{30}$$

Previous analytical studies on the PDSAW [14–16] considered the case when the wall was only along the x direction. The results obtained above for SAG1 are for a wall along the y direction. While the numerical values for the phase boundary differ, the phase diagrams are qualitatively similar.

Transition from SAG2 to AE (ω_{c2}). From Eq. (5), the phase boundary ω_{c2} is given by $\sigma(0)+\sigma_w=0$. Substituting the values of the surface energies and solving for ω, we obtain

$$\omega_{c2}^2=\frac{\alpha+\sqrt{\alpha^2-4u^3}}{2(1+\sqrt{u})}, \tag{31}$$

where $\alpha=1+\sqrt{u}-u^2+u^{5/2}$. The phase boundary ω_{c2} has a natural boundary at $u=u_c$, at which value the expression under the square root sign becomes equal to zero. The result differs from the transfer matrix result [14–16], $\omega_{c2}=(u+1)/2+\sqrt{(u^2+1)^2-4u^3}/2(u-1)$. However, this discrepancy is solely due to the fact that we consider only one wall, while the transfer matrix approach required two parallel walls. This corresponds to changing Eq. (5) to $2\sigma_{w2}+\epsilon_u=0$.

Transition from SAG2 to DC (ω_{c1}). From Eq. (6), this transition occurs when $\sigma(0)=\sigma_w$. The resulting equation can be solved to obtain

$$\omega_{c1}^2=\frac{\sqrt{u}}{\sqrt{u}-1}. \tag{32}$$

This covers all the transitions when we consider SAG1 and SAG2 separately. But if we consider the scenario where the possibility of both SAG's are allowed, then there is a surface transition from one to the other when u and ω are varied.

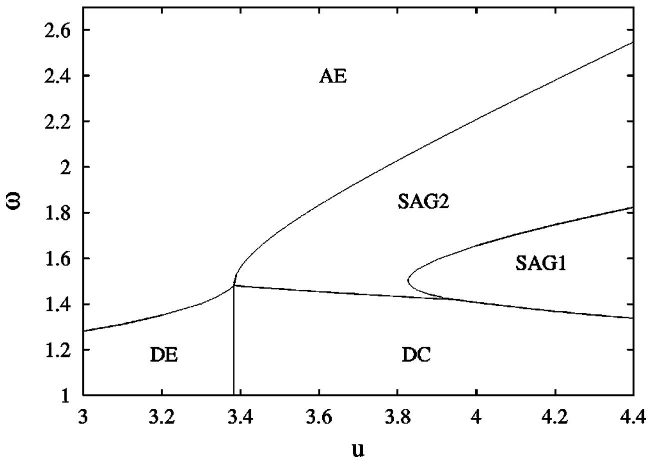

FIG. 8. The phase diagram for the two-dimensional PDSAW model. The DE-AE phase boundary is schematic.

Transition from SAG1 to SAG2. This transition is determined by equating the surface energies of SAG1 and SAG2. However, it turns out that we cannot obtain a closed form expression for the phase boundary. Instead, we solved for it numerically using MATHEMATICA.

In Fig. 8, we plot the phase diagram when both SAG1 and SAG2 are allowed to exist. Note that the phase diagram obtained is qualitatively similar to the phase diagram proposed in Sec. III. The additional transition between the SAG's is a consequence of the directed nature of the PDSAW model.

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