The Adsorption and Collapse Transitions in a Linear Polymer Chain near an Attractive Wall

R. Rajesh$^1$, Deepak Dhar$^1$, Debaprasad Giri$^2$, Sanjay Kumar$^3$ and Yashwant Singh$^3$

$^1$ Department of Theoretical Physics, Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai-400005, India
$^2$ Centre for Theoretical Studies, I. I. T., Kharagpur-721302, W. B., India
$^3$ Department of Physics, Banaras Hindu University, Varanasi 221005, U. P., India

(March 22, 2022)

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 analytically phase boundaries in some cases for a partially directed model. Both the numerical as well as analytical results corroborate the proposed qualitative phase diagram.

PACS number(s) : 64.60.-i,68.35.Rh,05.50.+q

I. INTRODUCTION

The behaviour 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 renormalisation 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 nearest-neighbour attractive or repulsive interactions provides a simple model to understand the collapse transition in polymers [3].

When the chain interacts with an impenetrable surface its conformational properties are strongly modified [4,5]. There is a competition between the lowering of internal energy near an attractive wall, and the loss of entropy due to constraints imposed by the impenetrable surface. For a strongly attractive surface, the polymer sticks to the surface, and for weak attraction, the preferred state is away from the surface. Thus, there is a transition from the state when the chain is mostly attached to the surface to a detached state, when the temperature is increased. This behaviour finds applications in lubrication, adhesion, surface protection, etc [6].

If there is self-attraction as well as attraction to the surface, there is the possibility of a collapse transition in the desorbed polymer, or in the polymer adsorbed on the surface. 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 had 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. In this case, the polymer has different behaviour 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 summarise our results of analysis of exact series expansion in three dimensions which we have extended by two more terms.

The paper is organised as follows. Sec. 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. Sec. 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 $\epsilon_u$ between pairs of sites of the walk which are unit distance apart but not joined by an step of the walk. The adsorbing surface is modelled by restricting the walk to lie in a upper half plane and by associating an attractive energy $\epsilon_s$ 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 $\omega = e^{\beta u}$ and $u = e^{\beta \epsilon}$, where $\beta$ is the inverse temperature. For the sake of easy reference, we now define all the phases that we will encounter later on, at one place. Consider a polymer consisting of $N$ monomers whose one end is attached to a fixed site on the surface. If $\epsilon_a$ and $\epsilon_s$ 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 $N^\nu$ where $\nu$ 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 one in this case. We shall call this phase the desorbed extended (DE) phase. If $\epsilon_a$ is large and $\epsilon_s$ 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 $\epsilon_s$ 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 $\nu'$ 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 globule (SAG) phase. Note that in 2-dimensions, the AC and the AE phases cannot be distinguished from one another.

The polymer undergoes a transition from the extended to the collapsed phase when the temperature is varied. At the transition temperature between the DC and the DE phases, called the $\theta$-point, the critical behavior is described by a tricritical point of the $O(n)$ ($n \to 0$) spin system. At the $\theta$-point, $R_b \sim N^{\nu_\theta}$ with $\nu_\theta = 4/7$ for 2D [14] and 1/2 for 3D [1]. The transition from AE to AC is described by $\nu_\theta$ corresponding to one lower dimension.

### III. QUALITATIVE PHASE DIAGRAM

We first briefly review earlier results obtained for the model when both the monomer-monomer interaction as well as the interaction with the wall are attractive. One of the earlier papers on such systems was by Bouchaud and Vannimenus [11], in which the the phase diagram of a polymer living on a Sierpinski gasket was analytically derived. The phase diagram consisted of the AE, DE and the DC phases. In [12], the phase diagram in 2-dimensions was obtained approximately by series expansions and it was found to be qualitatively similar to that for the gasket. In [13], the possibility of the existence of the SAG phase in 2-dimensions was pointed out 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 2-dimensions, has been more amenable to analytical calculations. For PDSAW, in 2-dimensions, the exact calculation of the phase boundary between the collapsed and the extended phases [13] [14] has been numerically confirmed in [15]. The phase diagram thus obtained is qualitatively similar to the un-directed 2-dimensional model. In [17], the existence of the SAG phase in the PDSAW has been argued for, based on series expansion analysis.

The model is less studied in 3-dimensions. Monte Carlo simulations [18] and series expansion analysis [19] on the cubic lattice showed the existence of four phases: AE, AC, DE and DC. While [18] claimed the existence of two multicritical points, the earlier preliminary results [19] obtained from series expansion seemed to support one multicritical point. More careful analysis of the series, reported later in the paper, shows that there are indeed two multicritical points. The question of whether an SAG phase exists in 3-dimensions or not 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 behaviour of the system is not fully established.

We now determine the qualitative nature of the phase diagram from phenomenological considerations. Consider the case when the interaction with the wall is repulsive, i.e., $\omega \leq 1$. The polymer will be in a desorbed state because proximity to the surface results in increase of internal energy as well as loss of entropy. As $u$ is increased from 1 to $\infty$, the polymer undergoes a collapse transition from a desorbed expanded state (DE) to a desorbed collapsed state (DC) at a critical value $u_{3d}^*$ (see Fig. [2]). When the interaction with the wall is attractive, there is a competition between lowering of free energy and loss of entropy as the wall is approached. For $\epsilon_s \gtrsim 0$, the loss of entropy is more dominant and hence the polymer remains desorbed. Now, as $u$ is varied, the polymer undergoes a transition from DE to DC at the same critical value $u_{3d}^*$. Therefore, in the lower part of the phase diagram, there is a vertical phase boundary $u = u_c$ separating the DE and the DC phases.

Consider now the case when the interaction between nearest neighbour monomers is close to zero, i.e., $u \gtrsim 1$. [20]
Clearly, the polymer will be in the DE phase. Now, as $\omega$ is varied from 1 to $\infty$ the polymer undergoes a transition from DE to one in which it is adsorbed onto the wall and extended, i.e., the AE phase. Let this transition occur at a critical curve $\omega_c(u)$ that intersects the $\omega$-axis at $\omega^\ast$.

As $u$ is increased from 1 to $\infty$, the polymer will undergo a collapse transition, while still remaining adsorbed, from AE to AC. This transition occurs at the critical value of $(d - 1)$-dimensional collapse $u^\ast_{d-1}$. Since the critical temperature for collapse transition increases with dimension, $u^\ast_{d-1} > u^\ast_d$. We will now argue that the curve $\omega_{c3}$ originating from $(u^\ast_{d-1}, \infty)$ bends to the right when $\omega$ is decreased to a finite but large value. The partition function, when written as perturbation series in $\omega^{-1}$, is

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

where $n_j$ is the fraction of bonds such that their end points have exactly $j$ nearest neighbour monomers. Clearly, $n_0$ 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 $\omega$, the free energy is lower for the AE phase. Hence, the phase boundary $\omega_{c3}$ curves to the right.

The phase diagram for the 2-dimensional problem is qualitatively the same as that of the 3-dimensional problem except that there is no AC phase, and hence no $\omega_{c3}$ phase boundary. We now argue that the phase boundaries $u_c$, $\omega_c$, $\omega_{c1}$ and $\omega_{c2}$ meet at one point. For the sake of clarity, we will illustrate the arguments for the 2-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 $\theta$ 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 $\omega_{c2}$ 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. Additional cost of creating two surfaces of orientation $\theta = 0$ should be zero. Hence, along the phase boundary $\omega_{c2}$, we have

$$\sigma(0) + \sigma_w = 0,$$

where $\sigma_w$ is the free energy cost per unit length when the polymer is along the wall. Near the phase boundary $\omega_{c2}$ separating the DC and the SAG phases, the shape of SAG is such that the part in contact with the wall has orientation $\theta = 0$. Clearly, this configuration becomes unfavourable in comparison to the DC phase where

$$\sigma(0) = \sigma_w.$$
For the DE — DC transition, clearly the surface tension must vanish at the collapse point. Thus, along $u_c$ we have

$$\sigma(0) = 0. \quad (7)$$

From Eqs. 5-7, it is clear that if any two of the phase boundaries intersect at some point, then the third will also pass through that point.

It still remains to be shown that $\omega_c$ will also pass through the same point as the other phase boundaries. Let $u$ and $\omega$ get transformed to $u'$ and $\omega'$ under a scale transformation as

$$u' = f(u), \quad (8)$$

$$\omega' = g(u, \omega). \quad (9)$$

The function $f(u)$ is independent of the surface parameter $\omega$ 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. 8 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. 8, one corresponding to no attraction, one to very strong attraction and the third a repulsive fixed point. After fixing the flow directions, the final flow diagram looks schematically as shown in Fig. 3. The 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.

$$\text{FIG. 2. The schematic flow diagram.}$$

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 other sites are confined to the half plane $y \geq 0$. Let $C_N(N_s, N_u)$ be the number of SAWs of $N$ sites having $N_s$ monomers on $y = 0$ and $N_u$ nearest neighbour 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 3-dimensions by two terms and reanalysed 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 $\omega$ at which $\partial \langle N_s \rangle / \partial \epsilon_s$ is a maximum. Fig. 3 shows the variation of $\partial \langle N_s \rangle / \partial \epsilon_s$ for two values of $u$ for $N = 19$.

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

For fixed $\omega$, 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. Fig. 4 shows the variation of $\partial \langle N_u \rangle / \partial \epsilon_u$ for two values of $\omega$ for $N = 19$.

$$\text{FIG. 4. The dependence of } \partial \langle N_u \rangle / \partial \epsilon_u \text{ on } u \text{ is shown. For } \omega = 2.0 \text{ there is only one peak corresponding to the DE to DC transition. For } \omega = 3.8 \text{, there are two peaks corresponding to the AE to AC to SAG transition.}$$
The values of \( u^*_{3d} \) and \( \omega^* \) obtained by this method is 2.00 and 1.49 respectively. The previous results were \( u^*_{3d} = 1.76 \) by series expansion method [8] and \( \omega^* = 1.45 \) by Monte Carlo method [19] and \( \omega^* = 1.5 \) by series expansion method [20]. It is possible to obtain better estimates of \( u^*_{3d} \) as well as the phase boundaries by extrapolating for large \( N \). Let

\[
Z_N(\omega, u) = \sum_{N_s, N_u} C_N(N_s, N_u) \omega^{N_s} u^{N_u},
\]

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

\[
G(\omega, u) = \lim_{N \to \infty} \frac{1}{N} \log Z_N(\omega, u).
\]

We refer to [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 \( \frac{\partial^2 G(\omega, u)}{\partial \omega^2} \) and \( \frac{\partial^2 G(\omega, u)}{\partial u^2} \) respectively.

The phase diagram thus obtained is shown in Fig. 5. We obtain \( u^*_{3d} = 1.76 \) and \( \omega^* = 1.48 \) which agrees fairly well with the previously obtained results. The phase diagram obtained from series analysis agrees qualitatively with the phase diagram proposed in Sec. IV.

V. ANALYTIC CALCULATION FOR THE TWO DIMENSIONAL DIRECTED POLYMER

In this section, we determine the phase boundary separating the SAG phase from the DC and the 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 minimised if it assumes a square shape of size \( \sqrt{N} \) by \( \sqrt{N} \). For small nonzero temperatures, the polymer assumes a shape which 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 shape of SAG1 and SAG2 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 the SAG phases, the density in the bulk is exactly one 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 \( f_{\text{bulk}}(\text{SAG}) = f_{\text{bulk}}(\text{DC}) = -\epsilon_u \), independent of \( \omega \). Consider a polymer shape as shown in Fig. 6.

![Schematic diagram of a partially directed polymer for \( T \geq 0 \)](image)

The energy of the configuration is

\[
E = -\epsilon_u N + \frac{\epsilon_u}{2}(a_1 + a_2 + 2b) + \frac{\epsilon_u}{2} \sum_{j=0}^{b-2} |y_{j+2} - y_j|.
\]

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 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 \( \theta \) 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
where \( p = e^{-\beta x\csc(\theta)} f(\theta) \) and \( \delta \) is the usual Kronecker delta function. Taking Laplace transform with respect to \( y \), we obtain independent summations over \( y_i \). These are easily done giving

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

where

\[
z_0 = \frac{(1 + p^2) \tan \theta + \sqrt{(1 - p^2)^2 \tan^2 \theta + p^2}}{p(1 + 2 \tan \theta)}.
\]

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

\[
\Lambda = \frac{\omega^2 (\omega^2 - 1)(u - 1)}{\omega^2 (u - 1) - u}.
\]

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

### B. Calculation of the macroscopic shape

In this subsection we describe the shape determined by minimising 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 polymer attached to the wall, it is straightforward to determine the globular shape which minimises 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

\[
e^{-\beta x \sec(\theta)} f(\theta) = \sum_{y_1, y_2} \delta \left( \sum_{i=1}^x y_i - y \right) \prod_{i=1}^x p^{[y_i]}, \tag{13}
\]

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

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

where

\[
z_0 = \frac{(1 + p^2) \tan \theta + \sqrt{(1 - p^2)^2 \tan^2 \theta + p^2}}{p(1 + 2 \tan \theta)}.
\]

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

\[
\Lambda = \frac{\omega^2 (\omega^2 - 1)(u - 1)}{\omega^2 (u - 1) - u}.
\]

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

### C. Phase Diagram

We calculate the phase diagram for the directed polymer from Eqs. [3][4]. These equations give most of the phase boundaries except the transition between SAG1 and DC and the transition between SAG1 and SAG2. The SAG1-DC transition is not given by Eq. [3] 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 \( \omega \) 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. [3], i.e., \( \sigma(0) = 0 \). This is equivalent to the \( 2f(0) + \epsilon_u = 0 \). Substituting for \( f(0) \), we obtain

\[
\frac{\sqrt{u} - 1}{\sqrt{u} + 1} = \frac{1}{u},
\]

which has the solution

\[
u_c = 3.38298, \ldots \tag{19}
\]

Note that this result matches exactly with the result for DC-DE transition obtained by the transfer matrix method [3][4].

**Transition from SAG1 to AE (\( \omega_2 \)):** This phase boundary is determined by equating the perpendicular extent of the SAG1 phase above the wall, to zero. This condition gives rise to the phase boundary

\[
\text{[Equation]}.
\]
\[ \omega_{c2} = \frac{1 + u^2 + \sqrt{(1 + u^2)^2 - 4u^3}}{2u}. \] (20)

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 (\( \omega_{c1} \))**:

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. We omit the algebra and state the final result

\[ \omega_{c1}(u) = \frac{1 + u^2 - \sqrt{(1 + u^2)^2 - 4u^3}}{2u}. \] (21)

Previous analytical studies on the PDSAW [13–15] had 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 (\( \omega_{c2} \))**:

From Eq. [3], the phase boundary \( \omega_{c2} \) is given by \( \sigma(0) + \sigma_w = 0 \). Substituting the values of the surface energies and solving for \( \omega \), we obtain

\[ \omega_{c2}^2 = \frac{\alpha + \sqrt{\alpha^2 - 4u^3}}{2(1 + \sqrt{u})}, \] (22)

where \( \alpha = 1 + \sqrt{u} - u^2 + u^{5/2} \). The phase boundary \( \omega_{c2} \) 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 [13,15] \( \omega_{c2} = \frac{\alpha + \sqrt{\alpha^2 - 4u^3}}{2(1 + \sqrt{u})} \). However, this discrepancy is solely due to the fact that we consider only wall, while the transfer matrix approach required two parallel walls. This corresponds to changing Eq. [3] to \( 2\sigma_w + \epsilon_u = 0 \).

**Transition from SAG2 to DC (\( \omega_{c1} \))**:

From Eq. [4], this transition occurs when \( \sigma(0) = \sigma_w \). The resulting equation can be solved to obtain

\[ \omega_{c1}^2 = \frac{\sqrt{u}}{\sqrt{u} - 1}. \] (23)

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 \( \omega \) are varied.

**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.

The work at B. H. U. was supported by the Department of Science and Technology (India) through a project grant.

[1] P. G. de Gennes, *Scaling concepts in polymer Physics* (Cornell Univ. Press, Ithaca, 1979).
[2] J. des Cloiseaux and G. Jannink, *Polymers in Solution* (Clarendon, Oxford, 1980).
[3] C. Vanderzande, *Lattice models of polymers* (Cambridge University Press, UK, 1998).
[4] E. Eisenriegler, *Polymers near surfaces* (World Scientific, Singapore, 1993).
[5] K. Dé Bell and T. Lookmann, Rev. Mod. Phys. 65, 87 (1993).
[6] D. Napper, *Polymeric Stabilization of Colloidal Disper- sion* (Academic, New York, 1983).
[7] Y. Singh, D. Giri and S. Kumar, J. Phys. A 34, L67 (2001).
[8] Y. Singh, S. Kumar and D. Giri, J. Phys. A 32, L407 (1999).
[9] P. Grassberger and R. Hegger, Phys. Rev. E 51, 2674 (1995); J. Phys. I (France) 5, 597 (1995).
[10] D. Duplantier and H. Saleur, Phys. Rev. Lett. 59, 539 (1987).
[11] E. Bouchaud and J. Vannimenus, J. Phys. France, 50, 2931 (1989).
[12] D. P. Foster, E. Orlandini and M. C. Tesi, J. Phys. A 25, L1211 (1992).
[13] D. P. Foster, J. Phys. A 23, L1135 (1990).
[14] F. Igloi, Phys. Rev. A 43, 3194 (1991).
[15] D. P. Foster and J. M. Yeomans, Physica A 177, 443 (1991).
[16] A. R. Veal, J. M. Yeomans and G. Jug, J. Phys A 23, L109 (1990).
[17] P. K. Mishra and Y. Singh, cond-mat/0009345.

[18] T. Vrobová and S. G. Whittington, J. Phys. A 31, 3989 (1998).

[19] L. Ma, K. M. Middlemess, S. H. P. Bly and S. G. Whittington, J. Chem. Soc. Faraday Trans. 74, 721 (1978).

[20] T. Ishinabe, J. Chem. Phys 76, 5589 (1982).