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A. Halperin[a]
[a] Max-Planck-Institut für Polymerforschung Postfach 31 48, Maim, FRG

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THE PHASE BEHAVIOR OF TETHERED CHAINS – AN OVERVIEW

A. Halperin
Max–Planck–Institut für Polymerforschung
Postfach 31 48, W – 6500 Mainz, FRG

ABSTRACT

Theoretical arguments suggest a rich variety of phase transitions involving grafted chains: (1) The "pancake—cigar" transition occurs in tethered layers consisting of weakly adsorbing grafted chains. This first order transition involves coexistence of uniformly adsorbed and grafted chains. (2) The tilting transition occurs in lamellae formed by rod—coil block copolymers. The orientation of the rods with respect to the lamellar normal evolves via a first order phase transition reminiscent of the S_A—S_C transition in liquid crystals. (3) The stretching of a dense brush immersed in a poor solvent involves a first order phase transition. This gives rise to a distinctive $f \sim L^0$ force law associated with the coexistence of a dense, collapsed brush and a dilute brush of stretched chains. (4) Finally a whole family of demixing transitions are predicted. The precise behavior is determined by the operative constraints on the mobility of the chains.

I – INTRODUCTION

Experimentally little is known of the phase behavior of tethered chains. Yet, theoretical considerations suggest a rich repertoire of phase transitions involving such moieties [1]. These are of interest for practical as well as fundamental reasons. As we shall discuss, phase transitions involving tethered chains enable novel strategies for materials design. One may, for example, use demixing in a binary layer to align electrical dipoles in order to produce ferroelectric or paraelectric materials [2,3]. These phase transitions are also of interest because they reflect the distinctive attributes of tethered chains that is, constrained mobility and stretched configurations. As a result familiar transitions take new forms while in other cases the phase behavior is unique to tethered layers. Thus, the demixing of binary, dense layers of irreversibly grafted chains involves configurational changes [4–6]. In marked distinction to the behavior of free chains there is no translational contribution. Finally, some phase transitions in tethered layers are related to transitions occurring in systems of short chain amphiphiles and mesogenes. Such is the case for the liquid expanded – liquid condensed transition in monolayers of low molecular weight amphiphiles [7] and the smectic A – smectic C transition in short chain liquid crystals [3,8,9]. The study of the tethered chains analogs affords two advantages characteristic of polymeric model systems. First, it is possible to base the theoretical discussion on the asymptotic properties of the chains thus simplifying the analysis. Also, the polymerization degree of the macromolecular analogs may be varied over a much wider range while studying the ensuing trends.

The phase behavior of tethered chains and of block copolymers are closely related since the experimental realization of tethered layers often involves block copolymers. However, it is important to note that the overlap is only partial. In some cases only one of the blocks is actively involved in the transition while the other block(s) provide the grafting mechanism. In such cases one may argue that the transition is not inherently copolymeric since other grafting modes may be used with no change in the phenomenology. In other situations all blocks are involved and the transition is indeed copolymeric. The second scenario may only take place in the strong segregation limit where the junctions of the blocks are constrained to a narrow interface thus providing effective tethering.

The overview we present in the following focuses on the phase behavior of flat grafted layers formed by neutral flexible chains ("brushes"). Because of the paucity of experimental work in this area it is mostly concerned with theory. Four phase transitions will be considered in some detail: (1) The "pancake–cigar" transition in brushes comprising chains capable of uniform adsorption [7]. (2) The tilting transition in lamellae formed by rod–coil diblock copolymers [3,8,9]. (3) The phase transition associated with the stretching of a brush immersed in a poor solvent [10,11]. (4) Demixing in a binary brush. A number of scenarios are possible depending on the constraints on the mobility of the chains [3–6,12,13]. We will mostly focus on the case of laterally mobile chains [12]. We conclude with some remarks on the collapse of brushes immersed in poor solvents [14–18].

II – THE "PANCAKE–CIGAR" TRANSITION

This phase transition was considered by Alexander in 1977 in his pioneering paper on tethered chains [7]. It is expected to occur in brushes comprising of chains capable of uniform adsorption i.e., where all monomers experience a weak attractive energy, of $-\delta kT$, to the surface. The control parameter is the area per chain, σ. As σ is varied a first order phase transition is expected to occur around $\sigma \sim R_F^{-2}$. It involves the coexistence of uniformly adsorbed chains and stretched tethered chains.

For concreteness consider an experimental scheme based on an insoluble monolayer of A–B diblock copolymer at a liquid–air interface. The B block is insoluble and acts as a bouy while the A block is soluble and weakly adsorbing at the interface. A Langmuir trough is used to control σ. The quantity of interest is the surface pressure, Π, as a function of σ. We obtain $\Pi(\sigma)$ on the basis of two assumptions: (1) The compression of the monolayer takes place as a continuous process. (2) The distribution of monomers throughout the monolayer is uniform i.e., for a layer of thickness L the probability of finding a monomer of size a at the surface is $\sim a/L$.

In the <u>dilute</u> layer, when the chains do not interact, each A block forms a flat "pancake" of thickness $L \approx \delta^{-3/2}a$ at the surface. L is set by the balance of the confinement free energy, $N(a/L)^{5/3}kT$, and the surface attraction $-kT\delta\, N(a/L)$. In this regime the adsorbed A blocks forms a two dimensional self–avoiding string of L blobs at the surface. Their in–plane radius $R_\parallel/a \approx N^{3/4}(a/L)^{1/4}$ sets the overlap threshold $\Gamma^* \approx Na^2/R_\parallel^2 \approx N^{-1/2}\delta^{-3}$. As $\Gamma = Na^2/\sigma$ decreases past Γ^* the chains begin to overlap and a semidilute solution is formed. However, at this stage the correlation length, $\xi_\parallel/a \approx \Gamma^{-3/2}(L/a)^{1/2}$, is larger than L and the solution is thus two dimensional. The layer may be envisioned as close packed array of two dimensional $\xi_\parallel$ blobs comprising each of a self–avoiding string of L blobs. In this regime the free energy per chain is supplemented by chain–chain interaction term, $kT\,N\Gamma^2(a/L)$, obtained by assigning kT to each $\xi_\parallel$ blob. The layer thickness, $L/a \approx (\delta - \Gamma^2)^{-3/2}$ is essentially that of the isolated "pancakes". The equilibrium free energy per chain is $F/kT \approx -N(\delta - \Gamma^2)^{5/2}$. Upon compression $\xi_\parallel$ decreases and below $\xi_\parallel \approx L$ the layer behaves as a normal three dimensional semidilute solution characterized by a correlation length $\xi \approx \phi^{-3/4}a$. At this stage the layer is pictured as a multilayered array of close packed ξ blobs formed by overlapping but unstretched chains. The free energy per chain consists of the confinement and surface interaction terms supplemented by chain–chain interaction term of the form $kT\,N\phi^{5/4}$ where $\phi \approx Na^2/\sigma L$. For this regime we find $L \approx (\Gamma^5/\delta^4)a$ and an equilibrium free energy per chain of $F/kT \approx -N(\delta/\Gamma)^5$. Further compression leads to the dense brush regime. A stretching penalty $(L^2/Na^2)\,\phi^{1/4}$ replaces the confinement term. Furthermore, this term is dominant with respect to the surface interactions. Accordingly, one recovers the familiar $L/a \approx N(a^2/\sigma)^{1/3}$ and $F/kT \approx N(a^2/\sigma)^{5/6}$.

By applying $\Pi = -\partial F/\partial\sigma$ in the various regimes we find the qualitative features of the Π–σ diagram. In particular

2D semidilute:	$\Pi a^2/kT \approx (Na^2/\sigma)^3[\delta - (Na^2/\sigma)^2]^{3/2}$	$\Gamma < \delta^{1/2}$
3D semidilute unstretched:	$\Pi a^2/kT \approx (\sigma/Na^2)^4\delta^5$	$(N\delta^6)^{1/7} > \Gamma > \delta^{1/2}$
3D semidilute stretched brush:	$\Pi a^2/kT \approx N(a^2/\sigma)^{11/6}$	$\Gamma \gg (N\delta^6)^{1/7}$

In the dilute and the two dimensional semidilute regimes the surface interactions are dominant. In essence the chains are uniformly adsorbed and the presence of strong grafting sites is irrelevant. The opposite case is found in the brush regime where the surface interactions are negligible and the grafting constraint is all important. In these regimes Π grows as σ decreases. The opposite trend is found in the intermediate, three dimensional semidilute, unstretched regime: Π decreases with σ. Thus, the Π–σ diagram exhibits a van der Waals loop and the intermediate regime is unstable. A first order phase transition, associated with the coexistence of brushes and two dimensional semidilute regions, is expected. This should give rise to a plateau in the Π–σ diagram. To understand the instability note that the layer thickness in the intermediate regime grows steeply as σ decreases, $L \sim \sigma^{-5}$. This is accompanied by a decrease in the number of surface interactions, $\sim a/L$, and in Π, $\Pi a^2/kT \approx \delta\Gamma(a/L)$.

The discussion presented above is certainly oversimplified. A complete description of the problem must account for the fine structure of the adsorbed layer. An appropriate description of the dilute and two dimensional semidilute regimes was given by Bouchaud and Daoud [19]. The three dimensional unstretched regime may be studied using detailed self consistent field methods [20].

The "pancake–cigar" transition is of special interest because it is reminiscent of the liquid expanded–liquid condensed transition in monolayers of short chain surfactants. Also, this transition is distinctive to tethered layers because only one block is actively involved.

A similar experiment was carried out by Granick and Herz [21]. However, in their system the A blocks were non–adsorbing. Some evidence for this transition was reported recently [22].

III – THE TILTING TRANSITION

In the "pancake–cigar" transition only one of the blocks is actively involved. In the next example both blocks play an active role. The diblock copolymer in this case consists of a flexible A coil comprising of N_A monomers and a rigid, rod like block of diameter d and length $L \gg d$. The phase transition is expected to occur in lamellae formed by such rod–coil copolymers in a selective solvent i.e., good solvent for the coils but a percipitant for the rods [3,8]. The lamellae consist of a core of close packed rods decorated by a brush–like corona of soluble A coils swollen by the solvent. For highly selective solvents and highly incompatible blocks we may assume that the core attains optimal packing i.e., the rods are aligned and their tips toe a single plane. The transition involves tilting of the rods with respect to the lamellar normal. It is a first order phase transition and it may occur as a result of change in N_A, the core–corona surface tension, γ, or temperature, T.

The transition is due to interplay of the core's surface energy and the deformation penalty of the tethered chains in the corona. Tilting the rods increases the separation between grafting sites in the tilt plane from d to $d/\cos\Theta$ where Θ denotes the tilt angle. Consequently, the area per A block, σ, increases from d^2 to $d^2/\cos\Theta$ while the free energy of the A block, F_{brush}, decreases from $N_A(a/d)^{5/3}kT$ to $N_A(a/d)^{5/3}\cos^{5/6}\Theta kT$. At the same time the exposed surface area of the rods grows from d^2 to $d^2(1 + |\tan\Theta|)$ with a corresponding growth in the surface energy. Altogether, the free energy per chain, F_{chain}, may be written as

$$F_{chain}/kT \approx \gamma d^2/kT + N_A(a/d)^{5/3}[\delta\ |\tan\Theta| + \cos^{5/6}\Theta]$$

where $\delta = (\gamma\ d^2/kT)\ N_A^{-1}\ (a/d)^{5/3}$ is the ratio of the surface energy and F_{brush} in the untilted, $\Theta = 0$, lamella. The term in square brackets, which contains all Θ dependent contributions, determines the phase behavior. A single dimensionless control parameter, δ, is involved. Clearly, when δ is large the surface energy is dominant and tilt is unlikely. When δ is small the deformation penalty, F_{brush}, is important and tilt is favored. The evidence for a phase transition in the development of tilt is contained in the behavior of F_{chain} as function of Θ for variety of δ. For high δ F is monotonously increasing. An inflection point develops for $\delta = 0.33$ and for lower δ two minima are present, corresponding to tilted and untilted states. The two minima attain equal depth for $\delta = 0.26$ and for lower δ values the tilted state is more stable [8]. The complement of the tilt angle scales as $N_A{}^{-6/11}$ [23].

The origin of the first order phase transition, within this picture, is in the small Θ behavior of F_{brush} and the surface energy. The surface term grows as Θ^2 while F_{brush} decreases as Θ. Consequently the $\Theta = 0$ state is always a local minimum separated by a barrier from the minimum of the tilted state.

The tilting transition is reminiscent of the smectic A– smectic C transition in low molecular weight mesogenes. The comparison is meaningful in view of the structural similarity between rod–coil block copolymers and low molecular weight mesogenes.

Finally a remark on experiments. The development of tilt in rod–coil lamellae was observed by Douy and Gallot in 1987 [24]. However, their study did not establish the nature of the process.

The tilting S_A–S_C, transition in melt of rod–coil block copolymers was recently analyzed by Semenov [9]. Another related problem involves rod–coil diblock copolymers at a liquid interface between selective solvents. In this case one expects a system of laterally mobile, grafted rods [25–27]. The development of orientational order in this system is of interest as a simple model for monolayers of short chain surfactants.

IV – THE STRETCHING TRANSITION

The next transition involves the stretching behavior of a brush immersed in a poor solvent ΔT below the Θ temperature [10,11]. Initially we can think of a system comprising two plates which are bridged by twice grafted chains. The question is: How does the restoring force vary as a function of the distance between the plates, L? The discussion requires a brief reminder of the collapsed state as described in terms of blobs. The relevant blobs, "collapse blobs", of size ξ_c are chain segments exhibiting Gaussian statistics and incorporating $g_c \approx (\Theta/\Delta T)^2$ monomers. Up to this length scale the monomer–momoner attraction is too weak to perturb the Gaussian behavior. Collapse blobs are attracted to each other and a collapsed globule may be viewed as a spherical droplet consisting of close packed ξ_c blobs. The radius of the globule is $r_c \approx (N/g_c)^{1/3}$ ξ_c and it is endowed with surface tension of kT/ξ_c^2.

It is helpful to begin with the deformation behavior of a single collapsed globule [10]. This corresponds to the case of two plates bridged by non overlapping chains. Consider the deformation of a single globule assuming that the process is continuous. Initially the spherical globule is deformed into an "egg". For weak deformations the change in the surface area and the associated surface energy is quadratic, $\sim(L-r_c)^2$. This gives rise to a linear response, $f \sim L$. For stronger deformations the "egg" is transformed into a "cigar" of length L. For $L \gg r_c$ the lateral surface area is dominant. Since the cigar consists of close packed ξ_c blobs, volume is conserved. A a result the surface area and the associated surface energy scale as $L^{1/2}$ while the restoring force scales $L^{-1/2}$. Finally, when the diameter of the cigar is comparable to ξ_c, further deformation requires rearrangement of the blob structure. The chain is pictured as a stretched string of Gaussian Pincus blobs of size ξ_p set by $\xi_p f \approx kT$. The associated restoring force is again linear, $f \sim L$. The sequence $f \sim L$, $f \sim L^{-1/2}$, $f \sim L$ describes a van der Waals loop in the fL diagram, indicative of the instability of the cigar structure. This is suggestive of a first order phase transition involving a coexistence of a globule and a stretched coil. For a single, finite coil a proper phase transition is, of course, impossible. Furthermore, the analysis should also allow for finite size effects due to the change in the surface area of the globule when monomers are redistributed among the two "phases". A detailed discussion of these issues is beyond the scope of this review. However, the single chain case does alert us to the possibility of a phase transition associated with the stretching of a collapsed brush.

The collapsed brush is pictured as a layer of close packed ξ_c blobs [11]. As in the good solvent case each tethered chain is, in effect, confined to a virtual cylinder of diameter $d = \sigma^{1/2}$. The thickness of the layer is thus $L_0 \approx N(a/d)^2\ \xi_c$. Note that the thickness of a dense brush is linear in N irrespective of the solvent quality. The stretching of a collapsed brush involves three stages: (1) For small deformations, $\Delta L \approx h$, one expects linear response $f \sim h$. The restoring force is due to increase in surface energy because of the deformation of the brush boundary: The layer develops "goose pimples", hemispherical deformations of height h. (2) The next stage is a first order phase transition involving the coexistence of a weakly deformed, collapsed brush and a dilute brush of stretched chain segments. To characterize this stage it is necessary to equate the monomeric chemical potentials in the two phases. Denote the number of monomers per chain in the collapsed and in the stretched brush by N_c and N_s respectively. The free energy per chain due to the segment embedded in the collapsed brush, F_c, is given by the $-$ kT per ξ_c blob ansatz supplemented by a surface term, $F_c/kT \approx -N_c/g_c + (d^2 + h^2)/\xi_c$. The corresponding chemical potential is $\mu_c/kT \approx -g_c^{-1}$. The treatment of the dilute brush is less straightforward. As in the single chain case the stretched segments are pictured as stretched strings of Pincus blobs of size ξ_s. However, the lateral fluctuations of these strings, $\langle \Delta r_{\parallel}^2 \rangle \approx Na^2$ are larger than σ and chain–chain interactions must be allowed for. The standard prescription for the density of the interaction free energy of a semidilute solution, kT/ξ^3, fails in this case because the blobs are not close packed. A similar situation was considered by Rabin and Alexander for the good solvent case [28] and their approach is easily implemented for our system. Each blob is said to experience an interaction energy of order $kT\phi_b$ where $\phi_b \approx \xi^2/d^2$ is the blob volume fraction. However, in the poor solvent case the interactions are attractive rather than repulsive and the blobs exhibit Gaussian statistics rather than self–avoidance. The free energy per chain due to the N_s monomers in the stretched brush, F_s, consists of an elastic contribution, given by the kT per Pincus blob, supplemented by a blob–blob interaction term. Altogether $F_s/kT \approx L^2/N_s - (N_s/g_s)\ (\xi_s/d)^2$ where g_s is the number of monomers in a Pincus blob. The corresponding chemical potential at constant L is $\mu_s/kT \approx - g_s^{-1} - (a/d)^2$. The equality of μ_s and μ_c determines g_s and thus all equilibrium characteristics of the stretched brush. In particular it yields the force law

$$f \approx (kT/\xi_c)\ (1 - \xi_c^2/d^2)^{1/2} \qquad \xi_c(1 - \xi_c^2/d^2)^{-1/2} \leq L \leq (Na^2/\xi_c)(1 - \xi_c^2/d^2)^{1/2}$$

As expected f in the coexistence regime is constant, independent of L, $f \sim L^{\circ}$. (3) Finally, when all monomers are incorporated into the stretched brush, we enter the third regime. In it the restoring force is dominated by the elastic restoring force with minor corrections due to blob–blob interactions, $f/kT \approx L/R_0^2 + (R_0/d)^2 L^{-1}$. Altogether the fL diagram exhibits three regions: A narrow linear response regime for weak deformation. This is followed by a plateau, $f \sim L^{\circ}$, corresponding to the coexistence regime. For larger deformations a Gaussian force law with minor interaction corrections is expected.

How observable is this behavior? Some aspects may manifest themselves in the frictional behavior of brushes immersed in poor solvents. This may be probed by using force measurement apparatus capable of lateral motion [29]. A more direct observation is possible with lamellar gels [11,30]. These may be formed from a lamellar melt of ABA triblock copolymers. The network arises because B blocks may bridge different A domains. This structure is then frozen by selective crosslinking, use of glassy A blocks etc. An aligned lamellar gel immersed in a poor solvent for the B blocks should exhibit the fL diagram considered above.

V – THE DEMIXING TRANSITIONS

The demixing of binary brushes, comprising chemically distinct chains, involves a large family of phase transitions. The different scenarios are associated with different constraints on the mobility of the chains. Two mobilities are of primary importance: (1) lateral mobility within the layer and (2) exchange with the bulk. Other possible constraints involve the relative mobilities of the tethered chains. The simplest case involves unhindered lateral mobility but no exchange i.e., the terminal anchor group is free to move along the grafting surface but it cannot break away [2]. Lateral segregation may take place but the overall composition of the layer remains constant. A possible realization of this scenario is based on mixture of AB and AC diblock copolymers at a liquid interface between selective solvents. The second scenario is both richer and more realistic: Both lateral mobility and exchange are allowed. The exchange involves free chains in the reservoir as well as other aggregates. Clearly, the composition of layer may vary in this case. A possible realization, in this case as well, involves a mixture of AB and AC diblock copolymers at the interface between selective solvents. While certain, limited aspects of this problem were analyzed [13,31], the full analysis of this problem is yet to appear. The strongest constraint is placed on fully immobile, irreversibly grafted chains. This third scenario was recently analyzed by Witten and Milner [4] and by Marko and Witten [5,6]. In a sense this is the most interesting case since the frozen mobility forces the chains to segregate via configurational changes. Two types of transitions were proposed. "Layering" involves vertical segregation. The system separates into a lower A rich layer and an upper B rich layer. The second mode, "rippling", involves the formation of a composition wave in the layer i.e., the layer exhibits periodic stripes of A rich and B rich domains. Both transitions are predicted to be of second order. In both cases the segregation is penalized by loss of configurational rather than translational entropy.

In the following we focus on the simplest scenario, of lateral segregation [12], because it affords interesting options for materials design. In particular we consider the demixing of a mixed binary layer comprising of laterally mobile chains. The mole fraction of A chains is x. We focus on the symmetrical case i.e., A and B chains are of equal length and the solvent is equally good for both. For simplicity the AB interactions are sufficiently weak so that the binary layer is identical in structure to a single component system. The free energy per chain, F_{chain}, consists of three terms: (1) Free energy of a single component layer, F_0. (2) Mixing energy written as χ' x (1–x) where χ' is the interaction parameter between A and B chains. (3) The mixing entropy of an ideal, two dimensional gas of mobile head groups. Altogether F_{chain} is given by

$$F_{chain}/kT = F_0/kT + \chi' x(1-x) + x\ln x + (1-x)\ln(1-x)$$

The same form is found for random mixing of monomeric moieties as well as for the ternary system of two polymers, A and B, and a solvent. The distinctive features of the grafted layer are expressed in the dependence of χ' on N and d. For simplicity the layer is viewed as a slab of semidilute solution i.e., close packed blobs of constant size $\xi \sim \phi^{-3/4}$ incorporating $g \sim \phi^{-5/4}$ monomers. If we approximate the blob–blob interaction parameter by the monomeric interaction parameter we obtain the familiar [32] $\chi' \approx (N/g)\chi \approx N\phi^{5/4}\chi$. This χ' reflects the stretched configurations adopted by densely grafted tethered chains because of the d dependence due to $\phi \approx (a/d)^{4/3}$. In particular

$$\chi' \approx N(a^2/\sigma)^{5/6}\chi$$

The stretched configurations affect χ' via the dilution of the layer, and the resulting decrease in number of binary contacts. The layer is thus less prone to phase separation than a reference system comprising of unstretched chains. Such is the case for a brush confined by a non adsorbing wall at a distance R_F from the grafting surface. In this system $\phi \approx N^{2/5}(a/d)^2$ and $\chi' \approx N^{3/2}(a^2/\sigma)^{5/4}\chi$.

The lateral demixing is of interest because it provides novel means for materials design. Two schemes illustrate this point: The Petschek–Wiefling design for ferroelectric and paraelectric materials and a design for two dimensional surfactants. The Petschek–Wiefling scheme [2,3] is based on the use of ABC coil–rod–coil triblock copolymers. The rod block carries an electrical dipole oriented consistently from A to C. To illustrate the basic idea consider lamellae formed by these copolymers in a selective solvent i.e., a percipitant for the rods but good solvent for the flexible A and C blocks. In this case one may consider a dilute lamellar phase and focus on a single lamella. The lamella consists of a core of insoluble rods with their axes aligned and two brushes of A and C blocks swollen by the solvent. In the high temperature limit the brushes are mixed and the electrical dipoles randomly aligned. When the temperature is lowered the demixing of the incompatible A and C blocks forces the alignment of the electrical dipoles carried by the rods. The second scheme is also based on the use of ABC triblock copolymers. These are either linear chains or ABC stars. For brevity we consider the ABC stars at a liquid interface, say air–liquid, such that the B arm is insoluble in the liquid which is a good solvent for A and C. In this case the B arm acts as an anchor to the interface. A mixed brush of A and C chains is produced. These are laterally mobile however, the A and C blocks are connected. In effect, the system behaves as a solution of two dimensional diblock copolymers in a non selective solvent [1]. One expects this system to form two dimensional mesophases reminiscent of those formed by three dimensional solutions and melts of diblock copolymers. By adding AB diblock copolymers we expect to obtain the two dimensional analog of AC diblock copolymers in a melt of A homopolymers.

VI – A LITTLE ON COLLAPSE

The collapse behavior of tethered chains and free polymers is markedly different [14–18]. The involvement of a phase transition is clearly established for polyelectrolyte brushes [17–18]. The collapse of neutral brushes is a continuous process for densely grafted, strongly stretched chains [14–16]. The possibility of a phase transition in the collapse of weakly stretched brushes is yet to be analyzed in detail.

It is important to note two qualitative features which distinguish the collapse behavior of tethered chains [14]: (1) While the collapse of free chains is accompanied by phase separation, the collapse of tethered chains anchored to a surface does not involve percipitation. In particular, it is possible to study collapsed tethered chains at constant coverage. (2) The thickness of a dense brush remains linear in N irrespective of the solvent quality. This "weak collapse" is markedly different from the "strong collapse" of free chains where the characteristic dimensions of the chain vary from $\sim N^{3/5}$ to $\sim N^{1/3}$. The weak collapse behavior of densely grafted chains was observed by Auroy et al. [33].

VII – CONCLUDING REMARKS

Theoretical studies concerning the phase behavior of tethered chains reveal a rich repertoire of phase transitions. It is rich in number and in type due to the interplay of stretched configurations and a variety of possible constraints on the mobility of the chains.

Experimental observations confirming some of the predictions summarized above do exist. However many questions remain unanswered because the experiments were not concerned with the study of phase behavior. Experimentally, this is clearly one of the least explored facets of tethered chains. The phase behavior of tethered chains affords many interesting opportunities for future study.

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