

Polymeric brushes with density dependent excluded volume parameters

P. Anderson, D. Hong, P. Lam, B. Vugmeister

▶ To cite this version:

P. Anderson, D. Hong, P. Lam, B. Vugmeister. Polymeric brushes with density dependent excluded volume parameters. Journal de Physique II, 1994, 4 (7), pp.1157-1164. 10.1051/jp2:1994187 . jpa-00248035

HAL Id: jpa-00248035 https://hal.science/jpa-00248035

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés. Classification *Physics Abstracts* 82.65D — 68.42 — 02.70

Polymeric brushes with density dependent excluded volume parameters

P. Anderson, D. C. Hong (*), P. M. Lam (**) and B. E. Vugmeister

Department of Physics and Center for Polymer Science and Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.

(Received 25 November 1993, revised 17 February 1994, accepted 30 March 1994)

Abstract. — Based on the recognition made by de Gennes that the excluded volume parameter of poly-ethylene-oxide (PEO) might depend on the local monomer density, we study the structure of PEO brushes in the limit where a local minimum is present in the free energy functional. Within the frame work of self-consistent-field theory advocated by Miller. Witten and Cates, the model predicts that a very dense state exists near the wall as the strength of the attractive interaction between the backbone and the wall is tuned. This dense state occurs through the first order phase transition. Even without an attractive interaction, for large surface coverage, we find the collapse of polymer chains near the wall.

1. Introduction.

The study of statics and dynamics of polymeric brushes has received renewed interest recently [1-13]. The brushes, formed by linear polymers with their ends anchored at the solidliquid interface, can provide long range repulsive forces between particles, and hence forbid the formation of larger aggregates via coagulation. For this reason, it is widely accepted as an effective method of colloidal stabilization. In the past few years, there have been several major steps toward our understanding of these polymeric brushes. The first one was the scaling study by de Gennes [1] and Alexander [2]. The next major step was the discovery of the parabolic potential within the framework of self-consistent theory [4-6]. de Gennes was the first who recognized the failure of classical analysis based on simple free energy arguments and made several scaling corrections to the classical results. Alexander further refined his theory by considering the stretching energy and presented several new result. Among them was the step function density profile of the brush and, in particular, the prediction of the first order phase transition : when the attractive energy between the backbones and the wall is strong enough, the brush undergoes a first order phase transition from a pancake to a fully stretched brush formation. Based on his scaling results, Alexander showed analytically that the surface pressure, Π , is not a monotonic function of the surface coverage σ . Instead, there exists an

^(*) To whom correspondence should be addressed.

^(**) Department of Physics, Southern University, Baton rouge, LA 70813, U.S.A.

unstable regime where Π in fact decreases much the same as what is happening in van der Waals liquids. He thus concluded that the transition should be first order.

Recently, Ou-Yang and Gao [12] presented the results of dynamic light scattering experiments on the adsorption of water-soluble PEO onto polystyrene latex particles. The PEO polymers used in their experiments have hydrophobic groups at both ends, which prefer to stay on the polystyrene surface rather than in the bulk (water). In addition there exists an attractive interaction between the monomers along the backbone and the polystyrene surface. Thus, this system appears to be an ideal realization of the polymeric brushes considered by Alexander. Ou-Yang and Gao measured the hydrodynamic radius, R, of the latex particle as a function of bulk polymer concentration, and observed a sharp rise in R over a quite narrow window of concentration. While the experimental set-up of this experiment, apart from the fact that the polymers have two absorbing ends instead of one, is similar to that considered in Alexander's paper and hence the result appears to confirm Alexander's picture of Pancake-Brush transition in the regime of low surface coverage, the experimental result without hydrophobic ends seems to indicate that a different mechanism other than what was considered by Alexander might be in action : the study of the adsorption of homopolymers of PEO without hydrophobic groups at both ends reveals that the hydrodynamic radius appears to increase without bound as a function of bulk concentration, an indication that PEO polymers might pile up on top of each other. This behavior is quite unusual and contrary to most adsorption studies reported to date, where quick saturation occurs. While it is not clear at this moment what is responsible for such an unusual behavior, we recognize that it seems to be a clear indication that a different mechanism other than the one proposed by Alexander could be in action for PEO brushes in the regime of high surface coverage. This is the motivation of this study.

2. Polymeric brushes with density dependent excluded volume parameter.

Our starting point is a recognition first made by de Gennes that the excluded volume parameter, ω , of PEO might depend on polymer density [13]. When a monomer (of PEO) is surrounded by solvent such as water, the interaction between monomers is mediated through the hydrogen bonding between solvent molecules and monomers, and hence could be densitydependent. For example, in a region of higher monomer density, solvent molecules are expelled causing the suppression of the formation of hydrogen bonding. Thus the excluded volume parameter, ω , might reduce its strength in a region of high monomer density. Indeed, this conjecture seems to be consistent with a recent experimental result where PEO polymers appear to have formed aggregates in water [14]. Aggregation could occur if the excluded volume parameter switches its sign in a region of high monomer density and becomes effectively attractive. Such a situation might have a substantial impact on the way polymers segregate or form aggregates [13]. In this work, however, we exclude the situation where ω becomes negative because for PEO brushes the density does not seem to be that high.

Suppose that ω weakly depends on polymer volume fraction, Φ , such that

.

$$w(\boldsymbol{\Phi}(\mathbf{r})) = w_2 \cdot (1 - \xi_1 \cdot \boldsymbol{\Phi}(\mathbf{r}) + \xi_2 \cdot \boldsymbol{\Phi}(\mathbf{r})^2 + \cdot \cdot \cdot).$$
(1)

We include a higher order term in order to ensure that ω remains positive in a good solvent. Without such a term, ω will keep decreasing, changing sign at $\Phi = 1/\xi_1$. The second order term will bend it over to positive values. Now, due to the higher order terms in ω , the total potential energy of the polymer chain (or backbone), $U(\mathbf{r}) \approx w \Phi^2$, will in turn contain higher order terms,

$$U(\mathbf{r}) = \int d\mathbf{r} \left[\frac{1}{2} w_2 \cdot \Phi^2(\mathbf{r}) - \frac{1}{3} w_3 \cdot \Phi^3(\mathbf{r}) + \frac{1}{4} w_4 \cdot \Phi^4(\mathbf{r}) - \Phi(\mathbf{r}) \cdot \varepsilon f(\mathbf{r}) \right]$$
(2a)

where we have included an attractive interaction term, $f(\mathbf{r})$, between the backbone and the surface with $\varepsilon > 0$ being its strength. $f(\mathbf{r})$ is expected to be a rapidly decreasing function of \mathbf{r} . In this work, we assume that

$$f(\mathbf{r}) = \theta\left(\left|\mathbf{r}\right| - \Delta\right) \tag{2b}$$

where θ is the step function and Δ is the range of interaction. The polymer volume fraction $\Phi(\mathbf{r})$ is given by

$$\Phi(\mathbf{r}) = \sum_{i=1}^{N} \int_{0}^{N} \mathrm{d}n \ \delta(\mathbf{r}_{i}(n) - \mathbf{r})$$
(2c)

where N is the total number of monomers in one chain and K is the total number of adsorbed polymer chains on the wall. The surface coverage σ on a wall of linear dimension L is thus given by $\sigma = K/L^2$. We now expand the interaction energy $U(\mathbf{r})$ around the average concentration $\phi(\mathbf{r}) = \langle \Phi(\mathbf{r}) \rangle$. Writing $\Phi(\mathbf{r}) = \phi(\mathbf{r}) + \delta \Phi(\mathbf{r})$, we find

$$U(\mathbf{r}) = \Sigma_{i} \left[w_{2} \int_{0}^{N} dn\phi(\mathbf{r}_{i}(n)) - w_{3} \int_{0}^{N} dn\phi^{2}(\mathbf{r}_{i}(n)) + w_{4} \int_{0}^{N} dn\phi^{3}(\mathbf{r}_{i}(n)) - \varepsilon f(\mathbf{r}_{i}(n)) \right]$$
(3)

where we have utilized the fact that for any spatially dependent function $g(\mathbf{r})$,

$$\int d\mathbf{r} \boldsymbol{\Phi}(\mathbf{r}) g(\mathbf{r}) = \boldsymbol{\Sigma}_{i} \int_{0}^{N} dn g(\mathbf{r}_{i}(n)) .$$
(4)

Also notice that $\Phi^2(\mathbf{r}) = 2 \Phi(\mathbf{r}) \cdot \phi(\mathbf{r}) + (\delta \Phi^2(\mathbf{r})) - \phi^2(\mathbf{r})$ and $\phi(\mathbf{r})$ is a scalar and $\Phi(\mathbf{r})$ is an operator which, upon acting on the function g, produces (4). In the Mean field approximation we drop out all the terms proportional to $\delta \Phi(\mathbf{r})$. Adding the elastic energy to the potential energy, we finally obtain the Mean field Hamiltonian of the system,

$$H = \Sigma_{i} \left[\int_{0}^{N} \mathrm{d}n \left(\partial r_{i}(n) / \partial n \right)^{2} + w_{2} \int_{0}^{N} \mathrm{d}n\phi \left(\mathbf{r}_{i}(n) \right) - w_{3} \int_{0}^{N} \mathrm{d}n\phi^{2}(\mathbf{r}_{i}(n)) + w_{4} \int_{0}^{N} \mathrm{d}n\phi^{3}(\mathbf{r}_{i}(n)) - \varepsilon f\left(\mathbf{r}_{i}(n) \right) \right]$$
(5)

Equilibrium configurations are determined by minimizing the above Hamiltonian w.r.t. the path $\mathbf{r}_i(n)$, i.e., $\delta H/\delta \mathbf{r}_i(n) = 0$. Note that the system has translational symmetry along the x and y axes. Hence, we only consider the equation of motion along the z axis, i.e. the vertical axis to the absorbing wall, which yields the equation of motion for $z_i(n)$:

$$d^{2}z(n)/dn^{2} = -dU(z(n))/dz$$
(6)

with

$$U(z(n)) = w_2 \phi(z(n)) - w_3 \phi^2(z(n)) + w_4 \phi^3(z(n)) - \varepsilon f(z(n))$$
(7)

where we have suppressed the index *i*. Equation (6) is the equation of motion for a particle of unit mass (m = 1) traveling in a potential, *U*, with zero initial velocity (because there exists no stress at the far end of the chain) if one regards the monomer index *n* as time. Miller, Witten, and Cates [6] made a crucial observation that the functional form *U* must be parabolic, namely $U(z) = B(z^2 - h^2)$, because no matter where the particle initiates its motion, it arrives at the origin $(\mathbf{r} = 0)$ at the same time, more precisely at 1/4 of the period. Note that the potential

vanishes at the height of the brush, z = h. Since the period of the harmonic oscillator is given by $T = \omega/2\pi = (1/2\pi) \sqrt{k/m}$ with the spring constant k = 2B ad the period T = 4N, we find $B = \pi^2/8 N^2$. Hence, the exact expression for the potential U(z) is given by :

$$U(z) = (\pi^{2}/8 N^{2}) \cdot (h^{2} - z^{2}).$$
(8)

Note that the right hand side of equation (7) gives the real physical interactions while the equal time constraint determines the left hand side, i.e. equation (8). Next, the density $\phi(z)$ in (7) must satisfy the sum rule :

$$N\sigma = \int_0^h \mathrm{d}z\phi(z) \tag{9}$$

whish is simply a statement of the conservation of mass.

Our task is to solve equations (7), (8) and (9) self-consistently in order to obtain information on the structure and nature of the thermodynamic transition of PEO brushes as the control parameters are tuned.

We now present numerical results.

3. Results.

We first make a few qualitative observations.

First, notice that the function at the right hand side of (7) is cubic in the density ϕ , which can either continue to increase or has a local minimum over a narrow range of parameters. More precisely, consider the derivative of the cubic function with $\varepsilon = 0$, $g(\phi) = 2 w_2 \phi - 3 w_3 \phi^2 + 4 w_4 \phi^3 g(\phi)$ has two solutions, ϕ_- and ϕ_+ , if $9 w_3^2 > 32 w_2 \cdot w_4$, for which case a local minimum exists. If $f(\phi_+) > 0$, the local minimum is above zero. But g has no solutions if $9 w_3^2 < 32 w_2 \cdot w_4$, for which case the function continues to increase without bound. We expect that interesting results might occur in the former case as will be shown shortly. To the best of our knowledge, experimental values for w_3 and w_4 for PEO are not available at this moment but we assume in this work that a local minimum exists for PEO brushes and the control parameters satisfy the inequality in such a way as to insure this.

Second, with $w_3 = w_4 = 0$, exact solutions for (7) and (8) can be readily obtained [15]. In this case, inspection of (7) reveals that the density profile is simply the parabolic profile modified near the wall by the interaction term $\varepsilon f(z)$. An integration of (8) then gives us the analytic form for the height h as a function of external parameters.

Now the question here is whether we expect quantitative changes with the presence of w_3 and w_4 . With $w_3 = w_4 = 0$ the surface coverage $\Gamma = \phi (z = 0)$ is a continuous function of either the strength of the interaction ε or the surface density σ . However, in the presence of w_3 and w_4 with a local minimum present in the free energy functional $f(\phi)$, we expect a jump in Γ as the interaction strength ε increases. This is graphically shown in figure 1. Graphically, Γ is given by the value of ϕ at the intersection of the horizontal line and the curve. Therefore, we find for $\varepsilon > \varepsilon_1$, only one solution exists which is a monotonically increasing function of ε . However, for $\varepsilon < \varepsilon_1$, three solutions exists, which signals the first order transition. Conventional Maxwell construction predicts a jump in the surface coverage Γ over a very narrow range of the interaction parameter, thus making a nontrivial prediction for PEO brushes that the surface coverage undergoes a first order phase transition if plotted as a function of interaction strength, ε , between the backbone and the wall.

In figure 2 is plotted the density profile for $\varepsilon = -0.25$ and $\Delta = 6$ with $w_2 = 1$, $w_3 = -0.6$ and $w_4 = 0.1$. If the strength ε is increased from zero, the density profile



Fig. 1. — Free energy functional $f(\phi) = 2 w_2 \phi - 3 w_3 \phi^2 + 4 w_4 \phi^3$ as a function of local polymer density ϕ . If $9 w_3^2 > 32 w_2 w_4$, then a local minimum exists. The surface density $\Gamma = \phi (z = 0)$ is obtained graphically by the intersection between $f(\phi)$ and the straight line. For the interaction strength $\varepsilon < \varepsilon_1$, only one solution exists, while for $\varepsilon_1 < \varepsilon < \varepsilon_2$ three solutions exist. Conventional Maxwell construction yields a jump in Γ as ε crosses ε_2 .



Fig. 2. — Density profile $\phi(z)$ for $\varepsilon = -0.25$. Note that a very dense state exists near the wall.

 $\phi(z)$ is initially given by $\phi(z) = U(z) + \varepsilon f(z)$, until at around $-|\varepsilon| = -0.25$, where numerical solutions reveal that a dense state appears near the wall: i.e., at $z \approx 0$, $\Gamma = \phi(z = 0)$ rises by nearly a factor 7. This dense state occurs with the presence of the two body term and thus is distinctly different from that occurring in a poor solvent, where the two body interaction term *vanishes* and the third body attractive interaction term drives the brush to collapse near the wall [15]. The prediction of this dense state near the wall is one of the most interesting features of this work.

In figure 3 is shown the surface coverage Γ as a function of ε for the parameters $w_2 = 1$, $w_3 = -0.6$, and $w_4 = 0.1$, for which a local minimum exists. The chain length is N = 100 and the surface density $\sigma = 0.05$. Interesting questions involve the structure of the PEO polymers adsorbed onto the latex particles. First, we notice that the attractive interaction



Fig. 3. — Surface density Γ as a function of interaction strength ϵ . Note the discontinuity in Γ over a narrow range of ϵ .

is short range and is operative only near the wall. Hence it is reasonable to assume that $\Delta \ll h$, in which case we suspect that the density profile of PEO brushes away from the wall might not be affected by the presence of the very dense state mentioned above. In order to confirm this picture, we also plot the brush height h as a function of surface coverage σ when such a dense state exists near the wall. As shown in figure 4, there are regions where height h increases relatively slowly. For N = 150, such a plateau occurs in a range of $\sigma = 0.17 - 0.26$ and $\sigma > 0.55$, which is not shown in the figure. Examination of the density profile reveals that the dense state starts to appear at the beginning of the plateau regime and the marked increase in Γ is observed near the *end* of the plateau regime, beyond which Γ increases slowly. Hence, it appears that the onset of the dense state does not signal the transition to the pancake state. The existence of the dense state does not seem to alter the density profile much, and it exists in the *brush* regime. We thus do not associate the appearance of the dense state to the onset of pancake regime.



Fig. 4. — Brush height, h, as a function of surface coverage σ . There exists a regime where h increases relatively slowly, where polymer chains are fully stretched.

In a real experiment, the polystyrene latex particles onto which brushes form are in equilibrium with the bulk, satisfying the relation, $-\Delta + \ln (\sigma) = \log c$, with Δ being the absorption energy of the hydrophobic group onto the latex particle and, c being the bulk concentration. In a typical experiment, σ is about 0.05-0.1, beyond which micelle formation

occurs in the bulk, making it very difficult to study the adsorption in high concentration. For this reason, even though the increase beyond the plateau regime is mathematically well defined in our model, it is unlikely that such a regime can be realizable by a competitive adsorption as was done in reference [12]. But it might be easily done by controlling the chemistry of the hydropholic group at the end.

Finally, we point out that the model presented in this paper predicts the existence of a dense state even in the absence of an attractive interaction *if the surface coverage*, σ , *is high*. We show in figure 5 the density profile with $\varepsilon = 0$ for (a) $\sigma = 0.05$ and (b) $\sigma = 0.635$. For low surface coverage, tuning w_3 and w_4 do not change the density profile much. However, for high surface coverage, note the appearance of the dense state near the wall. The polymer chains are collapsed near the wall, which is caused by the substantially enhanced attraction due to the w_3 term in (1) for high σ . We show how such dense state exists. take for simplicity the de Gennes-Alexander step function profile [1, 2]. Then equation (9) gives a relation between the height and σ . Substituting it back to (7), we find a self-consistent equation for the surface coverage $\phi(0)$ as a function of σ and ε , the control parameters. For $\varepsilon = 0$, by increasing σ , the point where two graphs meet moves to the right and thus produces a jump beyond the critical σ_c . For a fixed σ , changing ε would produce the same result. Such dense states without the attractive interaction might be useful in understanding the formation of aggregates of PEO chains in an aqueous solvent [13].

In summary, then, we have studied the conformation of PEO brushes in the limit where a local minimum exists in the free energy functional and showed some of the unusual features of PEO polymeric brushes in an aqueous solvent. In particular, we showed that a very dense state exists when the interaction strength between the surface and the backbone reaches a critical value. This dense state occurs through a first order phase transition. We have also observed a plateau regime in the brush height when plotted against the surface coverage, where the height scales linearly with the polymer chain length N. Recently Bekiranov *et al.* showed by the Flory argument that a single chain PEO in an aqueous solvent exhibits unusual pressure dependence because of the hydrogen bonding [16] between the monomer the monomer and solvent, which appears to be in line with the Hamiltonian chosen by us in this paper.



Fig. 5. — Density profile without the attractive interaction $\varepsilon = 0$. (a) PEO brush with $w_3 = -0.6$ and $w_4 = 0.1$ for $\sigma = 0.05$. Also is plotted the density profile with $w_3 = w_4 = 0$. There are very little differences. (b) PEO brush with $w_3 = -0.6$, $w_4 = 0.1$ for $\sigma = 0.635$. In this case, the polymers are smashed near the wall and a very dense states appears.

Acknowledgements.

This work is supported by the NSF-IUCRC program through the Center for Polymer Science and Engineering. We wish to thank J. Marko for helpful suggestions and discussions during the course of this work. We also wish to thank D. Ou-Yang and M. Daoud for discussions and comments on the paper. We also wish to thank M. Daoud for sending us reference [16]. After the submission of this work, we were informed that Wagner *et al.* [17] used the identical approach and studied the collapse of polymer brushes induced by *n*-clusters. We wish to thank the referee for bringing this paper to our attention.

Note added in proof : density cannot be greater than one. So, all the graphical solutions must be confined for $0 < \phi < 1$. Density profile in figures 3 and 5 can be made below one with appropriate parameters such as $w_3 = -0.93$, $w_4 = 1.67$ or $w_3 = -1.4$, $w_4 = 2.1$, which seem to be more realistic. Kim and Cao [18] recently observed a dense state of PEO monolayers at the air-water interface, which seems to be a strong confirmation of the prediction of this paper.

References.

- [1] de Gennes P. G., J. Phys. France 37 (1976) 1443; Macromolecules 13 (1980) 1096.
- [2] Alexander S., J. Phys. France 38 (1977) 983.
- [3] Dolan A. K. and Edwards S. F., Proc. R. Soc. London 337 (1974) 509; 343 (1975) 427.
- [4] Semenov A. N., Sov. Phys. JETP 61 (1985) 7339.
- [5] Zhulina E. B. and Birshtein T. M., Vysokomol. Soedin. A 28 (1986) 2589; Polymer 30 (1989) 170.
- [6] Milner S. T., Witten T. A. and Cates M. E., Macromolecules 22 (1989) 853; Europhys. Lett. 5 (1988) 413.
- [7] Charkrabarti and Toral R., Macromolecules 23 (1990) 2016.
- [8] Ball R. C., Marko J. F., Milner S. and Witten T. W., Macromolecules 24 (1991) 693.
- [9] Murat M. and Grest G., Phys. Rev. lett. 63 (1989) 1074.
- [10] Dickman R. and Hong D. C., J. Chem. Phys. 95 (1991) 4650.
- [11] Marko J. F. and Witten T. W., Macromolecules 25 (1992) 296.
- [12] Ou-Yang H. D. and Gao Z., J. Phys. France 1 (1991) 1375.
- [13] de Gennes P. G., C.R. Acad. Sci. paris, Serie II 313 (1991) 1117; See also, Simple views on condensed matter (World Scientific, 1992) p. 217.
- [14] PEO appears to aggregate in the bulk. (See Ref. [13] for details.)
- [15] Marko J. F., Johner A. and Marques C., J. Chem. Phys. (In press, 1993).
- [16] Bekiranov S., Bruinsma R. and Pincus P., A primitive model for single chain/aqueous solutions behavior of PEO under pressure (Preprint).
- [17] Wagner M., Brochard-Wyart F., Hervet H. and de Gennes P. G., Colloid and Polymer Science 271 (1993) 621. While the method is identical, their potential energy, $U(\phi)$, is different from ours (Eq. (7), namely: $U(\phi) = \rho(T) (\phi - \phi^n) + (1 - \phi) \ln (1 - \phi)$. Note that this does not include the interaction term between the backbone and surface. Thus, while the mathematical form of the free energy function with $\rho(T) = 1$ has a local minimum with the negative energy (Fig. 2 of their paper) such as ours, the underlying mechanism for the collapse to the wall is different. In the case considered here, the local minimum (Fig. 1) moves downward below zero by the attractive interaction between the wall and the backbone.
- [18] Kim M. W. and Cao B. H., Europhys. Lett. 24 (1993) 229.