Chains Anchored onto Convex Spherical Surfaces. Modification of the Daoud and Cotton Model[1]

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Introduction

The subject of tethered chains has received a great deal of attention in the past decade.[2] In particular, the problem of chains anchored onto solid surfaces is very important for the better understanding of a wide range of phenomena, such as wetting, adhesion, and colloidal stability, to name just a few. The theoretical work in this field was first approached by Alexander,[3] who put forth a scaling description of polar head chains anchored onto a flat surface. Later on, de Gennes[4] and Cantor[5] further developed these theories. The scaling analysis of this problem for curved surfaces was pioneered by Daoud and Cotton,[6] who studied convex spherical surfaces, and by Zhulina *et al.*[7-9] and Wang *et al.*,[10] who studied cylindrical surfaces.

This paper is solely concerned with spherical symmetry layers of anchored chains, and therefore attention shall be paid only to the work of Daoud and Cotton, hereafter referred to as the DC model. The expressions developed herein may be considered as an alternative to the approach of those authors, and they come as the result of an attempt to theoretically predict the findings of previous studies on the adsorption of polystyrene–poly(ethylene oxide) block copolymers onto polystyrene microspheres.[11-14]

Daoud and Cotton Model (DC Model)[6]

Consider then a hard sphere of radius R_P, on whose surface are anchored f polymer chains (see Figure 1a). In the DC model it is considered that the anchored chains do not interact with the surface. Furthermore, it is assumed that the polymer within the tethered layer is in a semidilute regime, and this layer is thus composed of several sublayers of blobs. In each of those sublayers, located at a distance r from the hard-sphere surface, the blob size is constant, $\xi(r)$, and is an increasing function of r (see Figure 1a).

In order to calculate the $\xi(r)$ value, those authors performed a surface balance relating the total area of the sphere of radius $R_P + r$ to the external area of each blob, from which it is possible to obtain the following expression:

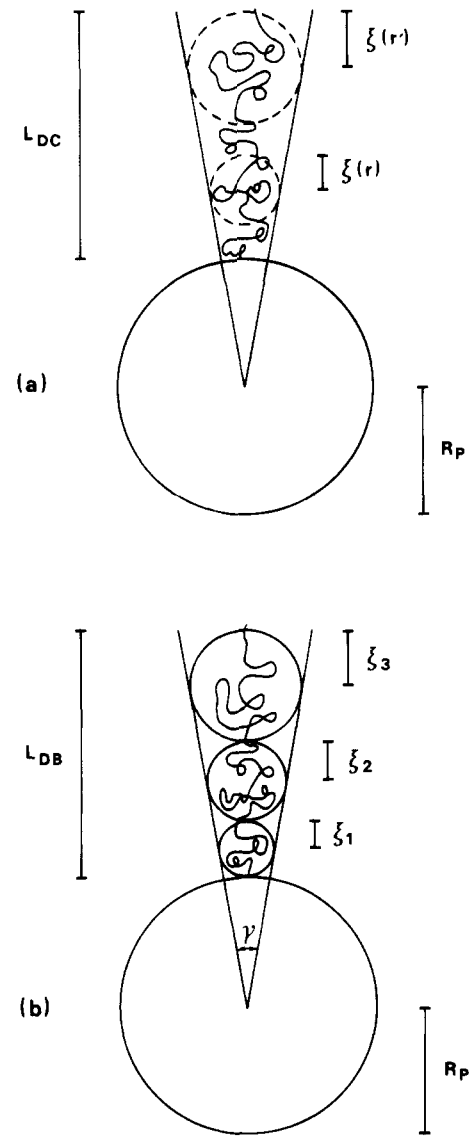

Figure 1. Illustration of the Daoud and Cotton (DC) model (a) and the discrete blob (DB) model (b). L_{DB} and L_{DC} are the anchored layer thicknesses in the DB and DC models, respectively. ξ represents the blob radius, and R_P is the central sphere radius. γ is the angle that defines the cone comprising one set of blobs.

$$\xi(r) \propto f^{-1/2}(R_P + r) \tag{1}$$

The total number of repeating units of one polymer chain, N, is given by the product of the number of repeating units, $N(r)$, comprised within the blob of radius $\xi(r)$, and the number of blobs $dr/2\xi(r)$ (in the original paper $dr/\xi(r)$ is used instead; the factor 2 is the missing proportionality factor in this equation), integrated over the thickness of the tethered layer, L_{DC}:

$$N = \int_0^{L_{DC}} N(r)\, dr/2\xi(r) \tag{2}$$

For a given polymer segment and solvent, $N(r)$ is a function of $\xi(r)$. In particular, if the polymer segment is long enough and the solvent is either a Θ solvent or a good solvent, this function is a power law of the type

$$N(r) = a[\xi(r)]^b \tag{3}$$

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The thickness of the anchored layer of polymers can then be easily calculated by inserting eqs 1 and 3 into eq 2 and solving for L_{DC}

$$L_{DC} = \left[R_P{}^b + \frac{2b}{ac_1} N f^{(b-1)/2}\right]^{1/b} - R_P \qquad (4)$$

where c_1 is an unknown constant resulting from the scaling law in eq 1.

Discrete Blob Model (DB Model)

In order to obtain absolute values, instead of trends, for the thickness of the anchored layer, L, eq 1 should be modified. For that purpose we assumed that the first sublayer of blobs is densely packed around the sphere surface and that each of the other sublayers is densely packed around the previous sublayer.

On a previous paper,[13] a mathematical algorithm was developed to estimate the number of smaller spheres that can be densely packed around a central larger sphere, given the radii of both types of spheres. It was shown then that this procedure yields precise results (the error is smaller than 5%) as long as the radius of the central sphere is equal or larger than the radius of the smaller spheres. Even though the purpose in mind on that paper was different, the same procedure can be applied here, since the problem is exactly the reverse; i.e., the number of blobs in each sublayer is known to be equal to the number of anchored chains, f, and the quantities to be determined are the radii of the blobs in a given sublayer. Using simple geometric arguments (see Figure 1b), it is clear that for the ith sublayer one has

$$\sin\left(\frac{\gamma}{2}\right) = \frac{\xi_i}{R_P + \xi_i + 2\sum_{j=1}^{i-1}\xi_j} \qquad (5)$$

This expression can be solved for ξ_i, and it can be shown by mathematical induction that

$$\xi_i = R_P \Xi (1 + 2\Xi)^{i-1} \qquad (6)$$

where Ξ is given by

$$\Xi = \frac{\sin(\gamma/2)}{1 - \sin(\gamma/2)} \qquad (7)$$

In order to get the value for angle γ, one must make use of the angle α, shown on Figure 2. Thus, based on trigonometric results,[15] these two angles are related by the following expression:

$$\gamma = \cos^{-1}\left(\frac{\cos\alpha}{1 - \cos\alpha}\right) \qquad (8)$$

and the angle α is a function of the number of blobs in each sublayer, f, given by

$$\alpha = \pi(f + 2)/3f \qquad (9)$$

Notice that eq 6 is the equivalent of eq 1 in the DC model, but unlike that expression, no numerical factors were omitted here.

The integral of eq 2 can no longer stand, and it must be transformed into a sum:

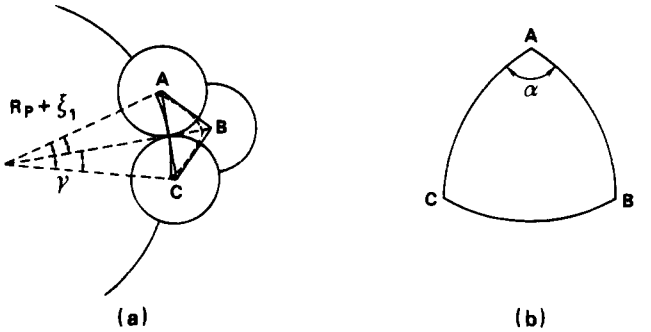

Figure 2. Dense packing of the first sublayer of blobs around the central sphere: (a) Three-dimensional view of three blobs packed on the surface of a larger sphere. R_P is the central sphere radius, and ξ_1 is the radius of the blobs within the first sublayer; the angle γ is subtended by the centers of two adjacent blobs, being this angle equivalent to the angle of the cone tangent to one of the blobs and whose vertice is located at the center of the larger sphere. (b) Top view of the curvilinear triangle obtained by projection of the ABC triangle onto a spherical surface equidistant from the larger sphere surface.

$$N = \sum_{i=1}^{N_{bl}} N_i \qquad (10)$$

where N has the same physical meaning as in eq 2, N_i is the number of monomers within the blob of radius ξ_i, and N_{bl} is the total number of sublayers of blobs that constitute the tethered layer.

In a fashion similar to eq 3, one has

$$N_i = a\xi_i{}^b \qquad (11)$$

Replacing eqs 6 and 11 in eq 10, one obtains

$$N = a(R_P\Xi)^b \frac{(1 + 2\Xi)^{bN_{bl}} - 1}{(1 + 2\Xi)^b - 1} \qquad (12)$$

On the other hand, the tethered layer thickness in this model, L_{DB}, is simply given by

$$L_{DB} = \sum_{i=1}^{N_{bl}} (2\xi_i) \qquad (13)$$

Finally, if one replaces eqs 6 and 12 in eq 13, one obtains

$$L_{DB} = \left[R_P{}^b + \frac{N}{a}\frac{(1 + 2\Xi)^b - 1}{\Xi^b}\right]^{1/b} - R_P \qquad (14)$$

Notice that this last equation's format is analogous to that of the final expression obtained in the Daoud and Cotton model (eq 4).

Comparison of the Two Models

In order to compare the two models, it is necessary to estimate the parameter c_1 in eq 4. In the limit of a very large central sphere ($R_P \gg \xi$) it can be proved[13] that the following surface balance is valid:

$$4\pi(R_P + r)^2 = 2\sqrt{3}f[\xi(r)]^2 \qquad (15)$$

where the first term of the equation represents the total area of a spherical surface of radius $R_P + r$ and the second term is the area occupied by f blobs (and the corresponding interstices) on that surface.

Furthermore, to compare the model predictions, parameters a and b must be known. The experimental work behind this paper deals with a layer of poly(ethylene oxide) chains anchored onto polystyrene surfaces, water being the surrounding medium. Therefore, a and b were replaced by the values obtained by Devanand and Selser[16] for long chains of poly(ethylene oxide) in water; i.e., $a = 16.48$ and $b = 1.715$. Taking this into account, eqs 4 and 14 can be rewritten respectively as

$$L_{DC} = [R_P^{1.715} + 0.131Nf^{0.358}]^{0.583} - R_P \quad (16)$$

$$L_{DB} = \left[R_P^{1.715} + 0.061N\frac{(1+2\Xi)^{1.715}-1}{\Xi^{1.715}}\right]^{0.583} - R_P \quad (17)$$

These two expressions were used in the calculation of L for a wide range of values of N, R_P, and f, and it was verified that, whenever the chosen (N,R_P,f) set corresponds to a number of blobs larger than unity, both models yield results that are equal within an error of less than 1%. This means that, in spite of the differences between the two models and the way parameter c_1 was determined, both models lead to the same final results, even under conditions other than the ones used to estimate the value of c_1. In other words, the error associated with any of these methods is less than 5% as long as $R_P \geq \xi$, covering all the reasonable experimental conditions.

Both models have similar limitations with regards to the assumed chain density profile. For instance, in the limit of a flat surface, i.e., when the radii of gyration of the polymers are much smaller than R_P, both DB and DC models consider a step-function density profile. Even though Milner *et al.*[17] have shown by self-consistent-field calculations that the density profile in this case should be parabolic, the error thus introduced in determining the adsorbed layer thickness is relatively small.

Conclusions

DB and DC models lead to the same results, even though in the first model a multistep blob size function is considered whereas in the latter the blob size is described by a continuous distribution. However, since the DB model pays close attention to the absolute values of all the significant geometrical and physical parameters of the system, it can be used as a tool to predict numerical values of the anchored layer thickness. Furthermore, this model provides important insight into the nature of the missing numerical constants in the DC model, therefore allowing the theoretical calculation of absolute layer thickness values instead of being used merely as a way to predict trends for those values, as previously.

References and Notes

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