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## Can surface bound states be induced by interfacial roughness?

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**Abstract.** We show that long polymer chains may bind to surfaces which are curved or rough if the equivalent planar interface is sufficiently close to supporting bound states. Analogous results apply to the binding of point quantum mechanical particles.

Attractive interactions favour binding preferentially on the invaginations of the surface, but we find that entropy/kinetic energy favours binding at the outward extremities. Which effect dominates depends on details of the interaction potential and both cases should be observable in practice.

### 1. Introduction

Within mean-field theory there is a direct analogy between the existence of electronic surface states and the question of whether polymer molecules will bind at a surface. In polymer terms, the molecules will bind if the attractive potential energy associated with being near the surface can outweigh the entropy loss from the restriction of configurations available.

If the surface potential is not quite attractive enough to bind polymer when flat, then corrugation can aid binding as follows. For a sinusoidal corrugation one might anticipate that some parts will become locally more favourable to bind at, others less: the polymer will then preferentially occupy the favourable regions, and net binding can result.

Hone *et al* [1] have considered the related case of a 'transparent' boundary which presents only the surface attraction (polymer being allowed on both sides of the interface) and so always binds material, with the effect enhanced by corrugation of the interface.

Even the cases of binding at spherical and cylindrical surfaces, discussed by Pincus *et al* [2], present some subtlety in the curvature dependence of the polymer entropy balance, and we show below that some of their earlier results were in error.

### 2. Basic problem

Our starting point in the polymer problem is the interaction between the monomer units and the material behind or at the surface. A relevant example is the combination of an attractive van der Waals interaction with the material behind the wall and a hard core repulsion with the molecules at the surface. In this example only the attractive part is additive over the material of the wall, but both parts have the important feature of being additive over the monomer units.

When the interactions are monomer additive one can compute from them a monomer potential  $U(X)$  giving the total interaction of a single monomer as a function of distance  $X$  from the wall. Explicit calculations of van der Waals potentials near surfaces of constant curvature have been published by Nabutovskii *et al* [3] and the effect of more complicated interactions has been studied in Monte Carlo simulation [4].

In the one-electron problem a potential formulation applies even to non-additive interactions, such as image forces. These are, at large distance, Coulombic in form and so there will always be bound surface states. Rahman and Maradrudin [5] showed that surface corrugation enhances the surface attraction of the image potential, and Garcia *et al* [6] computed the effect of corrugation on Ag(100) surface electronic states. Nabutovskii and Romanov calculated the spectrum of electronic states bound to spherical surfaces [7], and showed [8] that the curvature corrections with the image potential are logarithmic rather than simply perturbative.

We focus attention on situations where the existence of surface states is in question. Typically the potential will have a steep repulsive (i.e. positive) part corresponding to the impenetrability of the wall, followed by a shallow attractive (i.e. negative) tail. We shall assume that the attractive tail is, to a good approximation, of finite range: this would appear to exclude unscreened image potentials, but sufficiently rapid power laws, such as from the van der Waals interaction, are included below. We will also mostly assume that this range exceeds the chain persistence length to justify the continuum analysis below in the polymer case, but it is still short compared with the spatial extent (perpendicular to the surface) of any resulting bound states.

The time-independent Schrödinger equation governs both the bound electron states and, within mean-field theory, the binding of long polymer chains at the surface. In terms of the normalised eigenfunctions obeying

$$E\Psi_E = -b^2/6\nabla^2\Psi_E + U(\mathbf{R})\Psi_E \quad (2.1)$$

the statistical weight for a polymer chain of  $N$  monomers to span from point  $\mathbf{R}$  to point  $\mathbf{R}'$  is given by

$$G(\mathbf{R}, \mathbf{R}'; N) = \sum_E \Psi_E(\mathbf{R})\Psi_E(\mathbf{R}') e^{-NE} \quad (2.2)$$

where the coefficient  $b$  is the effective length per monomer in three dimensions [9].

In the limit of bound long chains the propagator  $G$  is dominated by the lowest eigenfunction, so that for both polymer and electron problems we focus on the ground state and whether it is bound to the region of the surface. It is convenient to work with rescaled lengths  $x$  and write the bound-state energy as  $-\alpha^2$ , so that the equation for the lowest state becomes

$$\alpha^2\Psi = \nabla^2\Psi - U\Psi. \quad (2.3)$$

The significance of the excited states in the polymer problem would be that their spacing indicates the scale at which finite molecular weight becomes significant, but this will not be pursued in this paper.

### 3. Solution for flat boundary

The problem with a flat boundary reduces to a one-dimensional calculation in which the solution  $\Psi(x)$  can be integrated forwards from a value of zero inside the wall; see

Jones and Richmond [10]. De Gennes [11] introduced the simplification of following the logarithmic derivative

$$\kappa = -(1/\Psi) d\Psi/dx \tag{3.1}$$

which evolves rapidly in the region of attractive potential but is thereafter constant for a solution matched to the appropriate exponential decay outside:

$$\Psi_{\text{outside}} = \text{constant } e^{-\alpha x}. \tag{3.2}$$

Thus if  $\kappa(\alpha)$  denotes the value integrated from the wall to just outside the range of the potential, then the condition for a bound state is

$$\kappa(\alpha) = \alpha. \tag{3.3}$$

We have assumed that continuum differential equations govern the chain statistics even inside the range of the attractive potential near the wall. However the characterisation in terms of the boundary parameter  $\kappa(\alpha)$  is more general because it represents the appropriate constraint to be applied to the solution  $\Psi$  outside. Thus  $\kappa(\alpha)$  also has a phenomenological status, although from such a point of view little can be said in general about the effect of curvature.

For a potential of finite range  $\kappa$  is analytic and, near the lowest state, decreasing in  $\alpha^2$  with

$$\kappa(\alpha) = \kappa(0) - B\alpha^2 + \text{order } B^2\alpha^4 \tag{3.4}$$

where the coefficient  $B$  is of order the range of the potential (for example, strictly one-half the range in the case of a square well). Thus the condition for any bound states to exist is simply

$$\kappa(0) > 0. \tag{3.5}$$

This condition is exact in neglect of excluded-volume interaction between the monomers, and in the one-electron limit. Within mean-field theory for the polymer it remains exact, because at the threshold of adsorption the mean density can be asymptotically small. However the full excluded-volume effect is, of course, strongly correlated and would shift the threshold.

#### 4. Adaptation to curved and buckled surfaces

We seek to formulate the properties of a surface of arbitrary curvature relative to those it would have if flat, and will work in the approximation that the local radii of curvature are large compared with the range of significant interactions.

The first effect to be considered is that the potential as a function of distance  $x$  from the wall (now defined along the local normal) will itself be altered from its value  $U_0(x)$  for a flat wall. To first order in the curvature we will then have

$$U(x) = U_0(x) + (\sigma/2)U_1(x) \tag{4.1}$$

where  $\sigma$  is the sum of the principal curvatures (reciprocal radii). We take positive curvature to represent protuberances of the surface; in the likely case that these have less attractive total potential,  $U_1(x)$  will then be positive.

Not only is the potential altered by the curvature but also its consequences for binding must be computed on a curved boundary. It is convenient to separate these conditions by computing first how the above correction to the potential would alter the  $\kappa$  value at a flat surface, and second how boundary curvature alters the nature of the matching conditions just outside the range of the potential.

It is not difficult to show that for a flat wall the potential  $U$  in (4.1) gives, to first order in  $\sigma$ , a boundary parameter

$$\kappa = \kappa_0 - (q/2)\sigma \tag{4.2}$$

where  $\kappa_0$  is the value corresponding to the potential  $U_0$  and in terms of the corresponding bound-state solution  $\Psi_0$  (not to be confused with earlier subscripts  $E$  for energy) we have

$$q = \int_0^{x \gg B} U_1 \Psi_0^2 dx' / \Psi_0^2(x). \tag{4.3}$$

Values of  $q$  will be discussed separately below.

Now we turn to the effect of boundary curvature on the integration through the potential to obtain the matching conditions, neglecting in this calculation the variation of  $U$  along the surface. In terms of the normal coordinate  $x$  and perpendicular surface coordinates  $s$  we have

$$\partial^2 \Psi / \partial x^2 + \sigma_1 / (1 + x\sigma_1) \partial \Psi / \partial x + \sigma_2 / (1 + x\sigma_2) \partial \Psi / \partial x + \partial^2 \Psi / \partial s^2 - U \Psi = \alpha^2 \Psi. \tag{4.4}$$

The terms to first order in the principal curvatures  $\sigma_1, \sigma_2$  can be more easily taken into account by making the substitution

$$\phi = J \Psi \quad J = \prod_i (1 + x\sigma_i)^{1/2} \tag{4.5}$$

in terms of which

$$\partial^2 \phi / \partial x^2 - U \phi = \alpha^2 \phi + [\frac{1}{4}(\sigma_1 - \sigma_2)^2 - J \partial^2 / \partial s^2 J^{-1}] \phi \tag{4.6}$$

where we have neglected terms only at order  $\sigma^3$ . If we neglect the dependence on  $x$  of the term in square brackets in (4.6), we can treat it as a correction to  $\alpha^2$ . Expanding  $\kappa$  about the original value of  $\alpha^2$  then gives the matching condition in terms of  $\Psi$  as

$$-\partial \Psi / \partial x = [\kappa(\alpha) + \sigma/2] \Psi + B[\partial^2 / \partial s^2 - \frac{1}{4}(\sigma_1 - \sigma_2)^2] \Psi. \tag{4.7}$$

The term linear in the curvature can be interpreted in terms of the gain in phase space as the solution ‘spreads’ radially from the wall; its presence was not previously suspected and neglecting it led to an error in [2] (see below). Of the terms in  $B$  the first is important because it presents a singular perturbation, whereas the second is of the same order as the difference between evaluating the curvatures in the linear term at the wall and a distance  $B$  away.

It is important to note that, in the above calculation and thus (4.7), the value of  $\kappa$  is that appropriate to  $U$  rather than  $U_0$  at a flat boundary. In terms of  $\kappa_0$ , the value obtaining for the same interactions at a flat boundary, we then have the boundary matching condition:

$$-\partial \Psi / \partial n = [\kappa_0 + (1 - q)\sigma/2] \Psi + B[\partial^2 / \partial s^2 - \frac{1}{4}(\sigma_1 - \sigma_2)^2] \Psi \tag{4.8}$$

where we have restored the conventional  $n$  for normal coordinate and the formal definition of  $B$  is given by

$$B = -\partial \kappa(\alpha) / \partial (\alpha^2). \tag{4.9}$$

**5. Bind at spheres and cylinders**

If we assume that  $B\sigma$  is small (and consider the radially symmetric solutions) the matching conditions reduce to

$$\kappa_0 + (1 - q)\sigma/2 = -\partial \ln \Psi / \partial r. \tag{5.1}$$

For a sphere of radius  $R$ , outside which  $\Psi = \text{constant} \times e^{-\alpha r} / r$ , this reduces to

$$\kappa_0 - q/R = \alpha. \tag{5.2}$$

Thus all effects of spherical curvature cancel for a sphere except for the change in the potential (a result which can readily be checked directly, and is in contrast to the conclusion of [2]—see their equation (2.7)). Whether a sphere is easier or harder to bind to depends simply on the sign of  $q$ .

For a cylinder of radius  $R$  we obtain

$$\kappa_0 + (1 - q)/2R = -\partial \ln K_0(\alpha r) / \partial r|_{r=R}. \tag{5.3}$$

If we use the small argument asymptotic form of the modified Bessel function  $K_0$  (see [12]) this reduces to

$$\alpha R = 2 e^{-\gamma} \exp\{-1/[\kappa_0 R + (1 - q)/2]\} \tag{5.4}$$

in the limit of small  $\alpha R$ . (The value of the coefficient is  $2 e^{-\gamma} = 1.1229 \dots$ ) Thus the threshold for binding to a cylinder lies at

$$\kappa_0 = (q - 1)/2R \tag{5.5}$$

so that, even if  $\kappa_0$  is slightly negative, for  $q < 1$  there will be binding on sufficiently small cylinders. There is an important contrast between this result and that of [2], where neglecting both the curvature corrections to the boundary condition (4.7) and to the potential (4.1)-(4.4) led to the equivalent of (5.4) with the crucial term in  $(q - 1)/2$  missing.

**6. Sinusoidally buckled surface**

We consider the surface

$$x = a \cos ky \tag{6.1}$$

with the wall material on the negative  $x$  side. To make the problem more tractable we also take the simplifying limit of small amplitude relative to the buckle period, i.e.

$$\varepsilon = ka \ll 1. \tag{6.2}$$

In this limit we obtain results to lowest significant order in  $\varepsilon$  from a series solution for the field  $\Psi$ :

$$\Psi = \sum_0^\infty \psi_n \exp(-\alpha_n x) \cos nky \tag{6.3}$$

where

$$\alpha_n^2 = \alpha^2 + (nk)^2. \tag{6.4}$$

In principle one computes  $(1/\Psi)\partial\Psi/\partial n$  from the series and matches it to  $\kappa + \sigma/2$  computed along the boundary from (6.1). This is greatly simplified by the observation that

$$\psi_n = \text{order } \varepsilon^n \psi_0 \quad (6.5)$$

enabling the leading behaviour in  $\varepsilon$  to be extracted from the lowest Fourier coefficients with respect to  $y$ .

We find

$$\Psi_1 = \frac{1}{2}(1-q)\varepsilon k \psi_0 / (\alpha_1 - \alpha) + \text{order } \varepsilon^3 \quad (6.6)$$

and then use this result to compute the matching of the zeroth Fourier components to order  $\varepsilon^2$ . This reduces to the desired condition on  $\alpha$ :

$$\alpha(1 + (1-2q)\varepsilon^2/4) = \kappa_0 + (\varepsilon^2/8)(q-1)^2 k^2 / (\alpha_1 - \alpha) + \text{order } \varepsilon^3. \quad (6.7)$$

The correction on the left-hand side cannot qualitatively change the outcome for  $\alpha$  within our assumption of small  $\varepsilon$ , but the term on the right-hand side introduces the scale of the wavevector  $k$  directly into the equation. In the limit where  $|\kappa_0|$  is small compared to  $k$  we have consistently that  $\alpha_1 \approx k$  and the dominant contributions to  $\alpha$  are given by

$$\alpha = \kappa_0 + (\varepsilon^2/8)(q-1)^2 k + \text{order } \varepsilon^3. \quad (6.8)$$

The above result shows that, as expected, binding is favoured overall by buckling, irrespective of the sign of curvature favoured locally. The length scale of the binding is also interesting, being the scale of the roughness  $k^{-1}$ , provided this dominates over the bare effect. The form obtained for  $\psi_1$  shows that the local binding preference occurs in analogy to our calculation for the cylinder, favouring the bumps for  $q < 1$  and the troughs for  $q > 1$ .

The importance of chain entropy/electron kinetic energy in the problem shows up in the critical value of  $q$  being not zero but unity. For small molecule adsorption it would normally be argued that adsorption occurs preferentially in the dips because, in the present terminology,  $q > 0$ . The additional preference for the bumps in our case can be interpreted in terms of the lower degree of confinement imposed by adsorption there.

It is natural to enquire as to whether a 'less cylindrical' corrugation of the surface would still show the entropic curvature correction (which cancelled for a sphere). A simple example is provided by the 'checkerboard' displacement:

$$x = \sqrt{2} a \cos[k(y+z)/2] \cos[k(y-z)/2] = (a/\sqrt{2})(\cos ky + \cos kz) \quad (6.9)$$

where the parameters have been chosen to match the characteristic wavevector and RMS corrugation amplitude of the previous case. It is not difficult to see that to second order in  $\varepsilon$  this gives the same result for  $\alpha$  as before.

## 7. Curvature correction to the potential

The above results exhibit a competition between the entropy favouring binding at bumps and the potential most likely to favour binding at dips in the surface. To resolve this competition we need to evaluate the coefficient  $q$  given by (4.3). A particular issue which arises is whether there is any general reason why  $q$  might fall on the critical value of unity at which the net effect of cylindrical curvature vanishes.

We present here only very limited results, specifically for the following ‘truncated power law’ interaction between each monomer and unit volume of the wall material:

$$V(r) = \begin{cases} -Ar^{-m} & r > a \\ +\infty & r < a. \end{cases} \tag{7.1}$$

For the case  $m = 6$  this could be regarded as a crude unretarded van der Waals plus steric repulsion model, and existing work [3] will allow us to go beyond additivity. The assumption of additivity over the material behind the interface is only appropriate when the mismatch of dielectric constant across the interface is small, but this is consistent with focusing on marginally binding cases and provides a useful explicit example where everything can readily be calculated.

Integrating over the material behind a flat wall then gives the potential (for  $x > a$ )

$$U_0(x) = -[2\pi A/(m-2)(m-3)]x^{3-m} \tag{7.2}$$

and the corresponding correction for weak curvature is  $(\sigma/2)U_1(x)$  where

$$U_1(x) = [2\pi A/(m-2)(m-4)]x^{4-m}. \tag{7.3}$$

Clearly these results are only meaningful for  $m > 4$ , and we will further restrict attention to  $m > 5$  below. In the case of  $m = 6$  they are equivalent to the results of Nabutovskii *et al* [3] (see their equations (10) and (11) in the appropriate limit of small mismatch of dielectric constant across the interface).

The significance of these successive restrictions on the power law index  $m$  are all essentially that the interaction, and in turn the potential, be sufficiently short ranged, so that it is really the region of the potential near the short-distance cutoff,  $a$ , which dominates. The most severe restriction  $m > 5$  is that this applies even to the integral (4.3) for the curvature correction to the boundary parameter.

To compute  $q$  from formula (4.3), at marginal binding it is convenient to define  $\Psi_0^2$  to be normalised to unity just outside the range of  $U$ . With a change of variable

$$2\pi A/[(m-2)(m-3)]x^{5-m} = y^2(m-5)^2/4 \tag{7.4}$$

the equation for  $\Psi_0$  can be related to a Bessel equation and the integral (4.3) for  $q$  reduces to

$$q = (1+2\nu)/(1+\nu) \frac{1}{2\nu} \int_0^j dy y f_\nu(y)^2 \tag{7.5}$$

where the Bessel parameter is

$$\nu = 1/(m-5) \tag{7.6}$$

and, for  $m > 5$ ,  $f_\nu(y)$  is given directly in terms of a Bessel function:

$$f_\nu(y) = \Gamma(\nu+1)(2/y)^\nu J_\nu(y). \tag{7.7}$$

Notice that, for  $m > 5$ , large  $x$  corresponds to  $y = 0$ , and hence the choice of normalisation  $f_\nu(0) = 1$  in (7.7) above. The upper limit of the integration corresponds to the point where the infinite repulsion sets in and so must be at a zero of  $J_\nu(y)$ , and for marginal adsorption this must be the first zero away from the origin in  $y$ : that is  $j = j_{\nu,1}$  in the notation of [12].

For the physically motivated case of  $m = 6$  we have evaluated numerically the integral in equation (7.5) and obtained a value of 1.6755 (7). This gives  $q = 1.256$  (5) which is just enough for the potential to dominate over entropy effects.



Will the potential always dominate over the entropy (i.e.  $q > 1$ )? Approximate analysis suggests that our expression (7.5) for  $q$  remains larger than unity for all  $m \geq 5$ , but focusing on the full van der Waals result offers a possibility. If we assume that there is a fairly sharp high frequency cutoff to the dielectric modes contributing to the (unretarded) van der Waals interaction, then the work of Nabutovskii *et al* [3] leads (in the present notation) to

$$U_1(x)/U_0(x) = [(\varepsilon + 2)/(\varepsilon + 1)]x \quad (7.8)$$

where here  $\varepsilon$  is the ratio of the dielectric constants behind and ahead of the interface. Our results above for  $m = 6$  correspond to  $\varepsilon = 1$ , but this now generalises for the unretarded van der Waals interaction to

$$q = 0.8377 \dots (\varepsilon + 2)/(\varepsilon + 1). \quad (7.9)$$

Thus it appears that in the limit of large dielectric mismatch, such as one would have if the surface material were a metal, we do (just) attain  $q < 1$  and dominance of the entropy effects.

## 8. Conclusions

The key result of this paper is that, under certain circumstances, a surface which is curved, or corrugated, or rough, will adsorb polymer/trap electrons when its flat equivalent does not. Qualitatively, when the magnitude of the curvature exceeds that of the 'bare' de Gennes boundary parameter  $\kappa_0$ , then the former controls the binding and its scale.

Entropy/kinetic energy effects alone favour binding at the protuberances of the surface, but have to compete against the important countereffect of the attractive potential. For a range of pairwise additive power law interactions we found that the effect of the potential dominates, but in the (non-additive) limit of a surface of much higher dielectric constant than the solution, the entropy effects win. There is no obvious realisation of the latter case for the electron problem, but one should be able to look for preferential binding of polymer to the protuberances of a metallic surface.

In the polymer version of this problem we have resorted to two rather demanding limits. Firstly, we have assumed it appropriate to use continuum analysis of the polymer configurations even inside the range of the potential of attraction to the surface. In cases of binding due to close contact interactions this is not appropriate, and we have little basis for going beyond the approximation of constant  $\kappa$ . Secondly, our binding results are all in the limit of 'high' molecular weight, which in this context means that the dimensions of the unbound coils would have been very large compared with the scale of localisation  $\alpha^{-1}$  which we calculate.

A further complication in real polymers is excluded volume. It is known that in simple models this significantly shifts the criteria for marginal adsorption at a flat surface [13], but we surmise that the spirit of our results should still apply to polymers adsorbing from good solvents, provided that  $\kappa_0$  is taken as the net empirical value for the flat surface.

The best test of our results would be a three-way comparison between binding at spheres, cylinders and flats, all with the same marginally binding system; note that our results do not quantitatively agree with previous authors [2] for the curved cases.

A more practicable (and possibly useful) test might be presented by studying the preferential adsorption of polymer on distorted spheres. If a system could be tuned so that perfect spheres did not adsorb whereas distorted ones did, the resulting increase in effective hydrodynamic radius of the latter could be used to separate them by ultracentrifugation. More dramatically, it might be possible to drive preferential flocculation of the aspherical particles if sufficiently little polymer is used.

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