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HAL Id: jpa-00212402
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Submitted on 1 Jan 1990

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Short Communication

Forces between asymmetric polymer brushes

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(Reçu le 25 janvier 1990, accepté le 6 février 1990)

Abstract. — We study the equilibrium compression of asymmetric polymer brushes grafted on flat plates, under athermal and theta solvent conditions, using a lattice self-consistent field (SCF) approach. We find that the separation \( d \) between two plates coated asymmetrically with brushes of type 1 and 2, as a function of the force \( F \), obeys the “bisection rule”, \( d(F) = (d_1(F) + d_2(F))/2 \) where \( d_1(F) \) and \( d_2(F) \) are the corresponding separations for the symmetric brushes of type 1 and 2 respectively. The bisection rule is easily explained if one assumes no interpenetration of the two brushes. However, a study of the polymer volume fraction profiles suggests that the bisection rule is well obeyed even when there is strong interpenetration. The relevance of this work to recent experiments on asymmetric brushes is discussed.

1. Introduction.

The physics of end-absorbed polymer layers (grafted polymers) finds application in fields such as tribology, adhesion, pharmaceuticals, waste-water treatments etc.. Grafted polymers on colloidal particles provide an efficient way of controlling the stability and other physical properties of colloidal suspensions [1]. Knowledge of the interaction between such particles coated with polymer chains is of interest in the context of coagulation and structure formation in disperse systems [2 - 3]. In this short communication we give the first detailed theoretical analysis of the force between asymmetric grafted polymer layers. We study both the force profiles and the degree of interpenetration of the two brushes.

In the so-called “classical” limit [4] of infinitely long chains, polymers in a brush are strongly stretched and even when forced together do not interpenetrate [4 – 5]. This gives rise to the “bisection rule”:

\[ d(F) = (d_1(F) + d_2(F))/2 \]

which states that the separation \( d \) of plates coated with asymmetric brushes corresponding to some force \( F \) is the average of separations of symmetric brushes of type 1 and 2 with the same force. The results presented below of our lattice self-consistent field (SCF) calculation show that this rule is well obeyed, not only for long chains, but also for relatively short chains and when there is interpenetration between the brushes; however in this case the physical interpretation of
the rule is different. Preliminary experimental data of Watanabe and Tirrell [8] appear to indicate departures from the bisection rule for certain combinations of surface coverage and chain lengths in the two opposing brushes. This contrasts with the calculations presented here and the origin of any experimental departure therefore remains unexplained by the present theory.

2. Self-consistent field theory.

Numerical methods based on the lattice self-consistent field equations developed by Scheutjens and Fleer (SF) have previously been applied to grafted polymer brushes [6 - 7]. We refer to these papers and references therein for details of the method.

Essentially the object is to determine the Boltzmann segment weighting factors in a self-consistent potential field. These weights are then combined to form the statistical weights of chains in their various conformations subject to the boundary condition that each chain is attached to a wall. The Flory-Huggins approximation is applied, which averages out chain concentration fluctuations in each layer. The result is a cheminsal potential field perpendicular to the grafting surface. The volume fractions of the various segment types are determined by this potential field which depends self-consistently on local concentrations according to the Flory-Huggins equation of state [1, 6-7].

In order to obtain force/separation profiles we require an expression for the free energy of a system of two opposed plates coated with polymers. We used the expression obtained by Van Lent et al. [7] for the excess free energy per site in units of $k_BT$ for a system of grafted and free components in equilibrium, where $k_B$ is the Boltzmann constant and $T$ the absolute temperature.

3. Results.

All the results below are for non-adsorbing polymers of the same species grafted to flat surfaces in two opposed layers. Figures 1a and b are log-log plots of force/separation profiles for the compression of grafted symmetric and asymmetric brushes in an athermal solvent. The notation $N(\sigma)$ indicates chains having $N$ segments and coverage $\sigma$. From figure 1a we observe that the bisection rule is well obeyed for the asymmetric brushes having $N_{\text{long}}/N_{\text{short}} = 2$ and $\sigma_{\text{long}}/\sigma_{\text{short}} = 1$ (case A). The force/separation profile lies midway between the short/short and long/long profiles. The dots are bisection rule values, i.e. $d(F) = (d_1(F) + d_2(F))/2$, with $d_1(F)$ and $d_2(F)$ those found for the short/short and long/long cases.

Figure 1b has $N_{\text{long}}/N_{\text{short}} = 2$ and $\sigma_{\text{long}}/\sigma_{\text{short}} = 1/2$ for the asymmetric brushes and hence the same grafted amount on each plate (case B). The force/separation profile for the asymmetric brushes again follow the bisected values (dots). At small enough separations, roughly speaking less than $R_s$, where $R_s$ is the sum of the radii of gyration of a free chain from each side of the plate, the three curves for case B converge. This is expected since the force is then purely osmotic in origin and depends only on the total grafted amount. Figures 1c,d are for the same sets of brushes (case A and case B) respectively but in a theta solvent. The brushes are now less extended from the surface, but the bisection rule is still obeyed for both cases. The above calculations were repeated for a range of different values of $N$ and $\sigma$ and we observed no significant deviation from the predictions based on the bisection rule.

Figures 2a,c show the polymer volume fraction profiles for symmetric brushes 20(0.05)/20(0.05) (this denotes a symmetric brush composed of chains having 20 segments at surface coverage of 0.05) at separations $d = 8, 12$ and 16 of the plates in an athermal solvent (solid curves) and a theta solvent (dashed curves). Figures 2d and e are for brushes 20(0.05)/40 (0.025) and
We make the following observations. As \( d \) decreases, the degree of interpenetration increases. All of these brushes are quite far from the classical limit and interpenetration effects are obviously strong. When the separation is less than \( R_s \), the total volume fraction of the polymer become almost homogeneous; from figures 2a,d and e there is for \( d = 8 \) a near-uniform total density \( \phi_{total} \sim 0.275 \) in each case. In this region we expect that the force becomes insensitive to chain length and coverage, and even to the fact the chains are grafted, depending instead only on the total amount of polymers between the plates.

For larger separations (\( d > R_s \)), the dependence of the profile on the separate parameters becomes apparent, as does that on the solvent quality: brushes in theta solvent are less extended and of course the interactions between them start at smaller separation compared to athermal case.
Fig. 2. — (a,b,c) Volume fraction profiles for symmetric brushes 20(0.05)/20(0.05) in athermal (solid curves) solvent and theta (dashed curves) solvent conditions for separations \( d = 8, 12 \) and 16 respectively. (d,e) Volume fraction profiles for brushes 20(0.05)/40(0.025) and 40(0.025)/40(0.025) respectively for separation \( d = 8 \).
To quantify the interpenetration between opposing brushes, we introduce the parameter $\beta$ at separation $d$, defined as

$$\beta(d) = \frac{d}{\theta_1 \theta_2} \sum_{z=1}^{d} \phi_1(z) \phi_2(z)$$

where $\phi_1(z)$ is the volume fraction in layer $z$ of brush 1 and $\theta_1 = \sum_{z=1}^{d} \phi_1(z)$ its total grafted amount; similarly for brush 2. We motivate this definition of $\beta$ by imagining a situation with the two components 1 and 2 uniformly distributed throughout the volume (irrespective of whether this corresponds to the minimum of free energy). This gives an average volume fractions $\theta_1/d$ and $\theta_2/d$ in each layer and $\beta$ is defined to be unity for this limit of total interpenetration.

Figures 3a,b show plots of $\beta(d)$ vs. $d$ for cases A and B respectively under athermal (solid curves) and theta solvent (dashed curves) conditions. We note that the $\beta$ parameter increases monotonically with decreasing separation $d$ indicating a greater degree of interpenetration. For good solvents the behaviour of $\beta$ at onset (large $d$) is roughly cubic, as would be predicted from the classical limit picture [4] were one to simply overlay the profiles from each brush (since in that limit the density of the brush rises linearly from zero at the tip). Of course this is not consistent with the fact that brushes in this limit should hardly interpenetrate at all [4], but the observation may be useful for estimating qualitatively the behaviour of relatively short-chain brushes such as the ones considered here. For small enough separations ($d < R_a$) the $\beta$ curves for the athermal and theta brushes converge, i.e. the athermal and theta volume fraction profiles collapse onto each other as the effect of solvent quality become less significant. (This is already evident from figures 2a,d and e for example at separation $d = 8$.)

Fig. 3. — (a) Plot of interpenetration parameter $\beta(d)$ vs. separation $d$ of plates for brushes 20(0.05)/20 (0.05), 20(0.05)/40(0.05) and 40(0.05)/40(0.05) in athermal (solid curves) solvent and theta (dashed curves) solvent conditions. (b) Plot of interpenetration parameter $\beta(d)$ vs. separation $d$ of plates for brushes 20(0.05)/20(0.05), 20(0.05)/40(0.025) and 40(0.025)/40(0.025) in athermal (solid curves) solvent and theta (dashed curves) solvent conditions.
The effects of interpenetration are elucidated further in figure 4, which is a log-log plot of the force/separation profile for the compression of symmetric brushes 20(0.05)/20(0.05). The solid curve is the profile obtained when there is interpenetration between the brushes while the dashed curve show the profile if interpenetration were not allowed to occur. (This is the same as the force required to compress a single brush against a hard wall.) We see that for moderate separations the force of compression is considerably smaller when interpenetration is allowed, confirming that in the non-classical regime of short chains and low coverages we cannot ignore the effects of interpenetration.

![Log-log plot of force/separation profile](image)

**Fig. 4.** Log($F(d)$) vs. log($d$) for symmetric brushes 20(0.05)/20(0.05) with (solid curves) and without (dashed curves) interpenetration.

### 4. Discussion.

As mentioned earlier the bisection-rule is easily explained for the "classical limit" case of $N \to \infty$, since in the asymmetric brush the force $F$ of compression is determined by matching the discontinuity in osmotic pressure at the front of each brush [4]; the brush heights $d/2$ for each side of the system may be added to give the total. In the other extreme of strong compression, the force between the plates may be thought of as that due to a near-homogeneous concentration of polymers, whether or not interpenetration occurs. The fact that the force depends only on the mean density $\bar{\phi}$ between the plates leads directly the bisection-rule for small enough separations $d > R_s$, as may be seen from the fact that $d(\bar{\phi}) = (d_1(\bar{\phi}) + d_2(\bar{\phi}))/2$. Our numerical results indicate that, between these two limits, there is little scope for significant departures from the rule. Because of the relatively small number of segments and low coverages used in our numerical iterations, the size of the brush is only a few times the radius of gyration of free polymer in the same solvent but still a significant fraction of the fully extended length. This of course implies that we are well within the non-classical regime and so we should expect the interpenetration zone (overlap regime) to be a significant fraction of the separation of the plates whenever $d < R_s$. This is indeed observed. One would expect these conditions to be optimal for observing departures from the bisection rule but all our results suggest that even under these fairly extreme conditions the departures are not significant.

Part of the motivation for this work comes from force-balance experiments on polymers grafted onto two cylindrical mica surfaces carried out recently by Watanabe and Tirrell [8]. They observed...
deviations in the $G/R$ profile for the asymmetric brushes of case B towards the short/short symmetric brush profile. Here $G$ is the force between the curved plates and $R$ is the radius of curvature of the cylindrical surface. Under the Derjaguin approximation \cite{1} the measured force $G(d)$ at separation $d$ is related to the energy of compression $V(d)$ in a flat plate geometry according to:

$$G(d)/R = 2\pi V(d).$$

To check for the bisection rule experimentally one would in principle have to do a numerical differentiation of $G(d)/2\pi R$ to obtain the corresponding flat plate geometry force $F(d)$, and then apply the bisection rule. Alternatively for theoretical predictions (such as those found analytically using the classical limit equations) \cite{4} one must first apply the rule and then integrate the resulting $F(d)$ curve to get $G(d)$. In terms of fitting experimental data, either method is very cumbersome and it would be helpful to find a simpler approach.

One suggestion \cite{8} is to construct $G(d) = (G_1(2d_1) + G_2(2d_2))/2$, and minimize over $d_1$ and $d_2$ subject to constraint $d_1 + d_2 = d$. For non-interpenetrating (classical) brushes on curved surfaces, this corresponds to a variational procedure in which the boundary of the opposing layers is presumed flat, i.e. parallel to the horizontal axis between the curved surfaces, and at a position chosen so as to minimize the total energy. Consideration of the same minimization applied directly to the potential $V(d)$ in the corresponding flat geometry suggests that this is exact in the classical limit. For the numerical curves we have generated, we have found that this procedure gives results for $V(d)$ very close to those actually computed, even in cases of relatively strong interpenetration (for which the physical interpretation is much less clear). Thus the above construction for $G(d)$ does appear to provide a reliable basis for the analysis of experimental data.

Acknowledgements.

Most of this work was carried out at Wageningen University, The Netherlands, under the support of E.S.F. (A.A. in Chemistry and Physics of Polymer Surfaces and Interfaces) and Trinity College, Cambridge. We are grateful to R. Israels, B. van Lent, P. Barneveld and C. Wijmans for use of their original computer program and assistance in its modifications. We also thank Jan Scheutjens, Tom Witten, Matt Tirrell and Pete Barker for helpful discussions. We thank Matt Tirrell for showing to us the experimental results of reference \cite{8} prior to publication. DFKS gratefully acknowledges financial support from Trinity College, Cambridge. Part of this work was funded by N.S.F. (USA) under grant number PHY82-17853 at the University of California in Santa Barbara.

References

\begin{enumerate}
\item MILNER S.T, Europhys. Lett. 7 (1988) 695, and to be published.
\item VAN LENT B., ISRAELS R., SCHEUTJENS J., FLEER G., to be published.
\item WATANABE H., TIRRELL M., to be published.
\end{enumerate}