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Interfacial Properties of Hydrosoluble Polymers

June 15, 1993-June 15, 1996

FINAL REPORT

During this period, we treated a oleo of problems associated with the interfacial properties of macromolecules. Many of them concerned indirect interactions between surfaces engendered by intervening species. The issues ranged from colloidal forces to membrane induced coupling between embedded macromolecules (membrane-bound proteins). During this period, the DOE also provided partial support for several graduate students and post-doctoral fellows including: G. Subramanian (still graduate student in Materials at UCSB), D. R. M. Williams (Australian National University, Canberra), V. Kumaran (Chemical Engineering, Indian Institute of Science, Bangalore), K. Palmer (currently working for a consulting firm in San Francisco).

PUBLISHED PAPERS

Membrane Interactions with Polymers and Colloids

This manuscript [1] provides a brief discussion of three problems associated with decorated fluctuating membranes. These are: (i) structural effects on a lamellar phase of dispersed colloidal particles; (ii) the Casimir-like interaction between inclusions in membranes associated with bilayer undulations; (iii) the structure of repulsive membranes which have a few adhesive sites.

[1] P. Pincus, **Membrane Interactions with Polymers and Colloids**, Physics of Complex Fluids and Biological Systems, edited by W. Sung, Y. H. Jeong, S. I. Choi (Min Eum Sa, Seoul), 1993.

Escape Transitions and Force Laws for Compressed Polymer Mushrooms

We [1] describe the behavior of grafted polymer mushrooms compressed by finite-size particles. Compression of single fixed mushrooms can lead to a first-order escape transition or, in certain circumstances, hysteresis. These transitions or hysteresis can be seen either in the chain radius or in the compressional force law. In the man-mushroom regime the force law is modified by the presence of escaped chains. For surface mobile chains the chains can

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evacuate from under the particle leading to a force law with a maximum at about 3/4 of a mushroom size. This maximum implies that the system undergoes a collapse transition above a critical pressure or yield stress $P_c \approx kT\sigma_0 R_{F3}^{-1}$, where σ_0 is the grafting density and R_{F3} is the unperturbed mushroom size

[1] G. Subramanian, D.R.M. Williams and P.A. Pincus, **Escape Transitions and Force Laws for Compressed Polymer Mushrooms**, Physics Letters, **29** (4), (1995) 285-290.

Interaction between Finite-Sized Particles and End Grafted Polymers

We [1] describe the deformation behavior of polymer brushes and mushrooms compressed by finite-sized particles for the cases where the chains are fixed or mobile on the grafting surface. When the size of the particle is large compared to the grafting distance of the chains, the force on the particle is the same to lowest order in compression for both the fixed and surface mobile chains. Compression of a single mushroom can lead to a first order like escape transition, where part of the chain escapes from under the particle. These transitions can be seen either in the chain radius or in the compressional force law behavior. For surface mobile mushrooms, the force is considerably smaller because of the evacuation of chains from under the particle. The force law in this case also exhibits a maximum at a certain compression indicating that the system undergoes a collapse transition above a critical pressure or yield stress $P_c \approx kT\sigma_0 R_{F3}^{-1}$, where σ_0 is the grafting density (chains/area) and R_{F3} is the unperturbed mushroom size. Finally, we consider the case of bending of stiff chains grafted to a solid surface. In the case of a single chain, the force is a constant for weak compressions. In the multichain case, the force can be substantially lower because of the escape of chains from under the particle.

[1] G. Subramanian, D.R.M. Williams, and P.A. Pincus, **Interaction between Finite-Sized Particles and End Grafted Polymers**, Macromolecules, **29** (1996), 4045-4050.

One long chain among shorter chains: the Flory approach revisited

We [1] consider the mean square end-to-end distance of a long chain immersed in a monodisperse, concentrated solution of shorter, chemically identical chains. In contrast with the earlier work of Flory, no simplifying assumption on the wave vector dependence of the effective potential between segments is made. In order to obtain a closed form expression for the dimension of the long chain, we first derive a general expression for the mean square end-to end distance of

flexible chain with arbitrary two-body interactions using the Edwards-Singh method.

[1] E. Raphaël, G.H. Fredrickson and P. Pincus, **One long chain among shorter chains: the Flory approach revisited**, *J. Phys. II France*, **2** (1992) 1811-1823.

Conformation of Star Polymers in High Molecular Weight Solvents

Ten years ago Daoud and Cotton proposed a very elegant model for the static properties of an isolated star-shaped polymer in a solvent of low molecular weight. Here we [1] investigate the static behavior of a star-shaped polymer (f arms; N monomer per arm) dissolved in a melt of linear chains (with degree fraction varies as $\phi_N(r) \approx 1$ (meltlike region) for $r < af^{1/2} P^{1/4}$ for $r > af^{1/2} P^{1/4}$). We briefly discuss concentration effects. In addition to this analysis, we also review and discuss some of the properties of polymer chains tethered by one end to a flat solid surface. Our whole study is restricted to scaling laws; the exact prefactors in all our formulas remain undetermined.

[1] E. Raphaël, P. Pincus, and G.H. Fredrickson, **Conformation of Star Polymers in High Molecular Weight Solvents**, *Macromolecules* **26**, (1993) 1996-2006.

Membrane-Induced Interactions between Inclusions

The properties of membranes containing inclusions, such as proteins or colloidal particles, are calculated as a function of the bilayer interfacial energy and bending coefficients. We [1] find that the inclusion-imposed perturbation leads to damped oscillations in the membrane profile and, hence, to nonmonotonic short-ranged, membrane-induced interaction between inclusions. The preferred spacing between inclusions is predicted to depend on the spontaneous curvature of the amphiphile and the magnitude of the perturbation at the inclusion boundary.

[1] N. Dan, P. Pincus and S.A. Safran, **Membrane-Induced Interactions between Inclusions**, *Langmuir*, **9** (1993) 2768-2771.

Filled Polymer Brushes: A Hydrodynamic Analogy

We [1] study the problem of an arbitrarily shaped polymer brush confined to an arbitrary geometry. The polymer brush problem in the absence of chain ends is described by Laplace's equation. Hydrodynamics and the polymer brush

problem are thus identical. This analogy allows us to calculate the chain trajectories and the energy needed to deform any brush. In particular, we study the problem of a melt star near a wall. We then study the problem of a polymer brush filled with small particles, and calculate the force on these particles. There is one subtlety – the pressure in the polymer case is the negative of the hydrodynamic pressure.

[1] D.R.M. Williams and P.A. Pincus, **Filled Polymer Brushes: A Hydrodynamic Analogy**, *Europhysics Letters*, **24** (1993) 29-34

Polymer adsorption at liquid/air interfaces under lateral pressure

We [1] present calculations of surface tension of absorbed polymer solutions at the liquid/air interface. Lateral changes in the area per monomer on the surface are induced by changing the surface pressure (lateral compression), while keeping the total surface excess fixed. Lateral compression of the absorbed layer immersed in a good solvent results in an increase in the surface monomer concentration and surface pressure up to a critical area per monomer value where the compressibility of the system vanishes. Our mean-field model is not appropriate to describe more compressed states. Calculations are repeated in theta and solvent conditions, and yield similar behavior of the isotherms.

[1] V. Aharonson, D. Andelman, A. Zilman, P.A. Pincus and E. Raphaël, **Polymer adsorption at liquid/air interfaces under lateral pressure**, *Physica A*, **204** (1994) 1-16.

Flow induced instability of the interface between a fluid and a gel at low Reynolds number

The stability of the interface between a gel of thickness HR and a Newtonian fluid of thickness R subjected to a linear shear flow is studied in the limit where inertial effects are negligible. The shear stress for the gel contains an elastic part that depends on the local displacement field and a viscous component that depends on the velocity field. The shear flow at the surface tends to destabilize the surface fluctuations, and the critical strain rate γ_c , which is the minimum strain rate required for unstable fluctuations, is determined as a function of the dimensionless quantities H , $\eta_r = (\eta_g / \eta_f)$, and $T = (\Gamma / ER)$. Here η_g and η_f are the gel and fluid viscosities, E is the gel elasticity, Γ is the surface tension of the gel – fluid interface and the strain rate γ is scaled by (E / η_f) . In the limit $H \rightarrow \infty$, γ_c decreases proportional to H^{-1} independent of η_r and T . But at finite H , γ_c is strongly dependent on η_r and T . For $\eta_r \geq 1$, the interface is stable for all values of the strain rate for $H < \sqrt{\eta_r}$, while there are unstable traveling waves for $H > \sqrt{\eta_r}$.

For $\eta_r=1$ and $H\rightarrow 1$, we find that $\gamma_c \propto (H-1)^{-1/2}$ for $T=0$ and $\gamma_c \propto (H-1)^{-3/4} T^{1/4}$ for $T \neq 0$. For $\eta_r > 1$, the analysis indicates that $\gamma_c \propto (H - \sqrt{\eta_r})^{-1}$ independent of T for $H \rightarrow \sqrt{\eta_r}$. For $\eta_r > 1$, the onset of instability depends strongly on the parameter T . For $T = 0$, the critical strain rate is finite in the limit $H \rightarrow 0$, while for $T \neq 0$ the critical strain rate diverges at a finite value of H . This minimum H decreases proportional to η_r and η_r are the gel η_r for large T . The instability is caused by the energy transfer from the mean flow to the fluctuations due to the work done by the mean flow at the interface.

V. Kumaran, G.H. Fredrickson and P. Pincus, **Flow induced instability of the interface between a fluid and a gel at low Reynolds number**, J. Phys. II France, 4 (1994) 893-911.

Fluctuation-induced forces in stacked fluid membranes

We [1] present a new entropic interaction between foreign inclusions (e.g. proteins) confined to fluid membranes in a layered phase. This interaction arises from the coupling of thermal shape fluctuations to the variation in rigidity associated with the presence of inclusions. The force between inclusions exhibits interesting nonmonotonic behavior as a function of the separation distance. At large separation, we find a weak power law attraction between inclusions of similar composition.

[1] K.M. Palmer, M. Goulian and P. Pincus, **Fluctuation-induced forces in stacked fluid membranes**, J. Phys. II France, 4 (1994) 805-817.