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AD-A215 501

International Symposium
on
SURFACE INTERACTIONS

Neve Ilan, (Jerusalem Hills), and Rehovot
Israel, March 13-18, 1988

PROGRAMME AND ABSTRACTS

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Sponsors

The Israeli Academy of Sciences and Humanities

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Chairman: J. Klein (Weizmann Institute of Science)

S. Alexander (Hebrew University, Jerusalem)

A. Ben-Shaul (Hebrew University, Jerusalem)

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A. Marmur (Technion, Haifa)

Z. Priel (Ben-Gurion University, Beer-Sheba)

J. Sagiv (Weizmann Institute, Rehovot)

A. Silberberg (Weizmann Institute, Rehovot)

Conference Secretary : Mrs. H. Sharan (Weizmann Institute)

Coordinator : Y. Berman (Weizmann Institute)

GENERAL INFORMATION

Conference Secretariat and Information Desk The desk will be open as follows:

Sunday, March 13 - from 14:00

Monday - Thursday, March 14-17: 08:00 - 16:00 hrs.

Friday, March 18, 08:00 - 13:00.

A representative of ORTRA, the conference travel agent, will be at the Information Desk daily to assist in reconfirming return flights, to arrange post-meeting tours and accommodation, car-rental, etc.

Slides: A technician will be available in all sessions. Lecturers who have slides are requested to contact him before the start of their session.

Posters: These will be displayed in Hall C. The size of each display area is 1.2 m wide by 1.1 m high. The poster-boards are numbered consecutively (28-65) and participants presenting posters should use the board number corresponding to their abstract number. Poster sessions will be held on Tuesday Morning and on Thursday late-afternoon, as detailed in the programme.

Posters should be put up on Monday late afternoon or evening, and will be displayed all week. They should be taken down by Friday 12.00.

Meals:

Breakfast will be served from 07:00

Lunch is served from 13:00

Dinner: on Sunday, 13 March - from 19:30-20:30

Other days, as in programme. (at 17:45 or 18:00).

Bar: A cash bar (and snack-bar) in the Hotel Lobby will be open at most hours during the day. Following the evening sessions the bar will be open until midnight, or later if required.

Mixer: On Sunday 13th March, from 20:30 (following dinner), complementary drinks will be available for the participants in the Hotel Lobby.

Identification badges: Name tags should be worn at all times.

Complementary tour: A tour of the Old City of Jerusalem is planned for Tuesday afternoon, including the Via Dolorosa, the Cardo and a panoramic view of Jerusalem. Leaving Neve ilan at 14:00 on Tuesday 15 March, returning for dinner.

Accompanying persons: A programme for accompanying persons has been organized. Details have been circulated and will be announced at the meeting. Additional tours may be arranged.

Foreign currency and postal services: Foreign currency can be exchanged at the reception desk of the Guesthouse. Postal services are also available at the reception desk of the Guesthouse.

Facilities available at the Guesthouse include tennis courts and a heated covered swimming pool. Details at the Reception.

Public Transport:

(a) Jerusalem to Neve Ilan:

Bus no. 85 or 86, Leaving platform 8 (central bus station), Ticket - 2 IS.
Travel time ca. 30 minutes.

Departure times - 06:30-21:30 (hourly on the ½ hour) and a final bus at 23:00.

(b) Neve Ilan to Jerusalem

Departures times: 06:00, 07:00, 08:00, then 10:20 - 21:20 hourly at 20 minutes past the hour.

(c) Neve Ilan to Tel-Aviv

One bus daily, leaving 08:45. Travel time ca. 1½ hours.

Neve Ilan Guesthouse

Telephone: 02-341241
Telex : 26265 NVILN
Address : Neve Ilan Hilltop Resort
D.N. Harei Yehuda 90850
Israel.

PROGRAMME

SUNDAY 13 March

- 14:00- Registration Desk open
19:30-20:30 Dinner
20:30 Drinks and mixer in hotel lobby.

MONDAY 14 March

- 08:30-09:30 Registration
09:30-09:40 Symposium Opening

Morning Session

- Chairs: **P. Stenius** (Institute for Surface Chemistry, Stockholm)
A. Marmur (Technion, Haifa)
- 09:40-10:40 **H.K. Christenson** (ANU, Canberra)
"Cavitation and the interaction of hydrophobic surfaces" (40+20)
- 10:40-11:10 Coffee
- 11:10-11:30 **R. Kjellander** (ANU, Canberra)
"Interdependence of van der Waals and double-layer forces" (15+5)
- 11:30-11:50 **T. Odijk** (Delft University)
"Instability of nematic semi-flexible surfaces" (15+5)
- 11:50-12:50 **J.C. Eriksson** (Royal Institute of Technology, Stockholm)
"Forces between hydrophobically adsorbed surfactant monolayers" (40+20)
- 13:00 Lunch

Afternoon Session

- Chairs: **J.A. Mann** (Case Western University, Cleveland)
M. Lahav (Weizmann Institute, Rehovot)
- 14:30-15:30 **J. Sagiv** (Weizmann Institute, Rehovot)
"Self-assembling monolayers for modifying surface interactions" (40+20)
- 15:30-16:00 Coffee
- 16:00-17:00 **V.A. Parsegian** (N.I.H., Bethesda)
"Interplay of steric and surface forces between biopolymers" (40+20)
- 17:45 Dinner

Evening Session

Chairs: **R.P. Rand** (Brock University, St. Catharines, Canada)
A. Ben-Shaul (Hebrew University, Jerusalem)

19:15-20:15 **P.F. Luckham** (Imperial College, London)
"Measurement of the interactions between simulated cell surfaces"
(40+20)

20:15-21:15 **E. Evans** (University of British Columbia)
"Long-range polymer depletion forces between lipid bilayer
membranes" (40+20)

TUESDAY 15 March

Morning Session

Chairs: **G. Jannink** (LLB, Saclay)
S. Alexander (Hebrew University, Jerusalem)

08:45-09:45 **S.F. Edwards** (Cambridge University)
"The size of a polymer on a rough surface" (40+20)

09:45-10:45 **D. Avnir** (Hebrew University, Jerusalem)
"Interaction of molecules with rough (fractal) surfaces" (40+20)

10:45-11:15 Coffee

11:15-13:00 **POSTER SESSION I.**

13:00 Lunch, followed by guided tour of Jerusalem

17:45 Dinner

Evening Session

Chairs: **G. Fleer** (Wageningen University)
Y. Kantor (Tel-Aviv University)

19:15-20:15 **R. Ball** (Cambridge University)
"Can surface bound states be induced by surface roughness?" (40+20)

20:15-21:15 **T. Cosgrove** (University of Bristol)
"The adsorption and depletion of polymers at the solid/solution
interface" (40+20)

WEDNESDAY 16 March

08:30 Buses to Weizmann Institute

Morning Session

Chairs: **J.D. Hoffman** (Midland Molecular Institute)
A. Silberberg (Weizmann Institute, Rehovot)

09:30-10:30 **P.G. de Gennes** (College de France, Paris)
"Flexible polymers at interfaces" (40+20)

10:30-11:00 Coffee

11:00-12:00 **J.N. Israelachvili** (Univ. of California at Santa Barbara)
"Liquid structuring at solid surfaces probed by force measurements"
(40+20)

12:00-13:00 **L.J. Fetters** (Exxon Research, Clinton)
"Model polymers for surfaces and other studies" (40+20)

13:10 Lunch (at Weizmann Institute)

Afternoon Session

Chairs: **G. Hadziioannou** (IBM, San Jose)
J.M. Georges (ECL, Lyon)

14:15-15:15 **C.F. Quate** (Stanford University)
"Molecular imaging with the scanning tunneling microscope and the
atomic force microscope" (40+20)

15:30 Organized Tour of Weizmann Institute and Weizmann's House
(optional).

17:00 Buses to Neve Ilan (Departing from the Weizmann House)

18:00 Dinner

Evening Session

Chairs: **M. Cates** (Cambridge University)
Y. Rabin (Weizmann Institute, Rehovot)

19:30-20:30 **P. Pincus** (University of California at Santa Barbara)
"Interactions between polymers and small colloidal particles" (40+20)

THURSDAY 17 March

Morning Session

Chairs: **D.T. Wu** (Du Pont, Philadelphia)
M. Hair (Xerox Research, Ontario)

08:45-09:45 **J.M.H.M. Scheutjens** and G. Fleer (Wageningen Agricultural
University)
"Structure and interactions between adsorbed layers of block
copolymers" (40+20)

09:45-10:05 **S.T. Milner** and T.A. Witten (Exxon Research, Clinton), and M. Cates (I.T.P. Santa Barbara)
"Theory of the grafted polymer brush" (15+5)

10:05-10:25 C.M. Marques, **J.F. Joanny**, (ENS, Lyon) and L. Leibler (ESPCI, Paris)
"Adsorption of di-block copolymers" (15+5)

10:25-10:55 Coffee

10:55-11:55 **J. Klein** (Weizmann Institute, Rehovot)
"Forces between surfaces with end-grafted chains" (40+20)

11:55-12:55 **M. Tirrell** (University of Minnesota)
"Block copolymer adsorption on solids" (40+20)

13:00 Lunch. Afternoon free.

17:00-18:00 **POSTER SESSION II.**

18:00 Conference Dinner

Evening Session

Chair: **J.N. Israelachvili** (University of California at Santa Barbara)

20:00-21:00 **D. Tabor** (University of Cambridge)
"From friction to surface forces and reptation"

FRIDAY 18 March

Morning Session

Chairs: **F. Brochard-Wyart** (College de France, Paris)
A. Gast (Stanford University)

08:30-09:30 **A. Halperin** (Hebrew University, Jerusalem)
"Phase behaviour and dynamics of grafted polymer layers"(40+20)

09:30-09:50 **E. Eisenriegler** (KFA, Julich) and H.W. Diehl (University of Essen)
"Adsorption of a θ -polymer at a surface" (15+5)

09:50-10:10 **G. Jannink** (LLB, Saclay)
"Reflectivity profile of polymer solution interfaces observed by neutrons"(15+5)

10:10-10:40 Coffee

10:40-11:40 **K. Kremer** (University of Mainz)
"Computer simulations of polymers near surfaces" (40+20)

11:40 **Closing of Symposium**

12:00-13:00 Lunch.

* * * * *

ABSTRACTS

- 1 - 27 - Lectures in order of programme**
- 28 - 65 - Posters, grouped loosely according to topic.**

CAVITATION AND THE INTERACTION OF MACROSCOPIC HYDROPHOBIC SURFACES

H.K. Christenson
Department of Applied Mathematics
Research School of Physical Sciences
Australian National University
Canberra ACT 2601
AUSTRALIA

Accurate measurements of the interaction between uncharged hydrocarbon and fluorocarbon monolayer-coated surfaces in conductivity water show that the range of the attraction extends to a separation of at least 80 nm. This hydrophobic interaction between macroscopic surfaces can be approximated by an exponential function with two decay lengths of 2-3 and 13-16 nm respectively. The much shorter-range attractive forces measured between monolayers adsorbed from solution may be due to the formation of partial bilayers. Spontaneous cavitation occurs between the hydrophobic surfaces, either as soon as they come into contact (fluorocarbon) or as the surfaces are separated from contact (hydrocarbon). This suggests that the extreme range of the attraction may have its origin in the metastability of water films between very hydrophobic surfaces.

**Van der Waals and double layer forces are interdependent;
some practical consequences.**

Roland Kjellander
Dept. of Applied Mathematics
Research School of Physical Sciences
Australian National University
Canberra, ACT 2601
AUSTRALIA

In classical theories of the interaction between colloid particles in electrolyte solutions, like the DLVO theory, it is implicitly assumed that the Van der Waals (VdW) interaction and the double layer interaction are independent of each other. The net interaction is then simply given by the sum of the VdW force from the Lifshitz theory and double layer force from the Poisson-Boltzmann theory. However, in more accurate theories where ion-ion correlations and image charge effects are included, the VdW and the double layer interactions are no longer independent. The theoretical treatment now predicts an additional attractive force of Van der Waals type (electrostatic fluctuation force) due to the ion-ion correlations, *i.e.* the double layer force contains a VdW force component. Furthermore, the image charge contribution to the double layer force cancels the static (zero-frequency) part of the VdW force. Physically, this implies that the VdW interaction between the dielectric media is partly shielded by the electrolyte; its static part being replaced by a force due to the charge density fluctuations in the electrolyte.

These additional forces - not predicted by the DLVO theory - have important consequences in practice. For example, in aqueous solutions of 1:2 or 2:2 electrolytes (the divalent ion being the counterion to the surface charge), the double layer force may become strongly attractive at short surface separations. This has been confirmed by direct measurements of the forces between two mica surfaces in CaCl_2 solution. Both the strength and the range of the attractive force agree with the theoretical prediction. Furthermore, the attractive double layer force explains in a semi-quantitative manner the restricted swelling of various Ca-clays in water.

Instability of Nematic Semiflexible Surfaces

Theo Odijk
Laboratory of Polymer Technology,
Faculty of Chemistry and Chemical Engineering and
Material Science,
Delft University of Technology,
Julianalaan 136,
2628 BL Delft,
The Netherlands.

Experiments show that at high enough concentrations nematic solutions of disclike micelles may coalesce to form a smectic¹. Nematic sheets of semiflexible micelles have, however, not been observed. We address the instability of this phase by appealing to the excluded-volume effect^{2,3} and the theory of constrained surfaces⁴. Our arguments are similar in spirit to those developed for nematic polymers⁵.

For an unconfined surface thermally induced orientational fluctuations depend logarithmically on the distance along the surface. This results in the well-known exponential dependence of the persistence length on the elastic modulus⁶. However, for a nematically constrained surface a smaller length scale comes into play viz. the deflection length.

The deflection length λ can be used to derive the total free energy consisting of the excluded-volume effect between platelets of size λ and the orientational entropy of nematic confinement. It turns out that it is impossible to minimize the total free energy. Thus, nematically rippled surfaces are not stable.

- 1) M.J. Sammon, J.A.N. Zasadzinski and M.R. Kuzma, Phys. Rev. Lett. 57, 2834 (1986).
- 2) L. Onsager, Ann. N.Y. Acad. Sci. 51, 627 (1949).
- 3) R. Eppenga and D. Frenkel, Mol. Phys. 34, 667 (1984).
- 4) W. Helfrich, Naturforsch. 33a, 305 (1978).
- 5) T. Odijk, Macromolecules 19, 2313 (1986).
- 6) P.G. de Gennes and C. Tanpin, J. Phys. Chem. 86, 2294 (1982).

FORCES BETWEEN HYDROPHOBICALLY ADSORBED SURFACTANT MONOLAYERS

Jan Christer Eriksson

Department of Physical Chemistry

The Royal Institute of Technology

S-100 44 STOCKHOLM Sweden

A review is presented of the recent experimental and theoretical endeavours of the Surface Force Research Group in Stockholm including the following topics.

- i) Hydrophobic attraction and repulsive hydration forces. Outline of a simple, semi-quantitative theory based on previous notions about parallel and antiparallel orientation polarizations of the water molecules at hydrophobic and hydrophilic surfaces, respectively.
- ii) The formation of, and interaction between, adsorbed surfactant monolayers ($C_{12}NH_3^+Cl^-$ and $C_{12}(CH_3)_2N-O$). A molecular calculation scheme has been developed for mixed $C_{12}NH_3^+/C_{12}OH$ monolayers that enables theoretical predictions of the surface tension of surfactant solutions as well as of the surface forces operating between monolayers interacting at *constant chemical potentials* (rather than at constant charge density or constant surface potential).
- iii) Interaction forces between adsorbed insulin layers.

SELF-ASSEMBLING MONOLAYERS FOR MODIFYING SURFACE INTERACTIONS

Jacob Sagiv

Department of Isotope Research, The Weizmann Institute, Rehovot.

The study of surface interactions has reached the stage where solid organic surfaces with precisely defined composition and structure, at the molecular level, are demanded.

A general approach to the engineering of such organic surfaces, as well as to that of more complex molecular superstructures at solid-fluid interfaces, will be presented. It is based on the spontaneous self-assembly of highly ordered monolayers and their subsequent in situ chemical modification. The key roles of film stability and structural perfection in the chemical manipulation of such preassembled films will be discussed.

Preliminary data on some highly perfect self-assembled monolayers on mica will be presented.

THE INTERPLAY OF STERIC AND SURFACE FORCES BETWEEN BIOPOLYMERS
V.A.Parsegian, R. Podgornik, D.C. Rau, National Institutes of Health,
Bethesda, MD USA

Using the Osmotic Stress method, we have simultaneously measured the mean intermolecular repulsive force and the lateral fluctuations in polymer-condensed arrays of parallel DNA double helices. The observed forces in no way resemble the salt-screened electrostatic double layer forces traditionally expected in this polyelectrolyte system. At molecular surface separations < 10 Angstroms, repulsion varies exponentially with characteristic decay constants, 3 to 3.4 Angstroms, insensitive to ionic species and to ionic strength. (We have previously associated this interaction with the "hydration force" seen much earlier between lipid bilayers.) At larger distances, the force is again exponential, though sensitive to salt species and concentration; its decay length is about twice the theoretical Debye length, except at very high ionic strengths where it is about twice the hydration decay length. The continuous increase in lateral fluctuations that we see at these larger separations suggests that extended molecular repulsion is due to a progressive increase in configurational entropy due in turn to the onset of positional disorder in the DNA double helices.

At least in this one system where molecular forces and motion have been systematically measured,

(a) it is probably inappropriate to use the idea of a discrete "chi" parameter to describe surface solvation;

(b) double layer repulsions between polymers may be expected to decay far more slowly than predicted from theories or measurements entailing rigid surfaces;

(c) steric interactions should be seen as intimately coupled to the long-range electrostatic double layer or hydration forces that effectively prevent the mutual approach of polymers far from actual contact.

INTERACTIONS BETWEEN SIMULATED CELL SURFACES

Paul F. Luckham

Dept. Chem. Eng. and Chem. Tech.

Imperial College, London, U.K.

In recent years we have been utilising the "mica technique" to simulate the approach of two biological cells. The mica surfaces are coated with a lipid, or lipid plus protein bilayer, by deposition from a Langmuir trough in order to simulate cell surfaces. The forces between the surfaces as a function of the distance of separation are measured. Initially the interactions between model cell surfaces were measured, eg phosphatidylcholine, more recently however our experiments have been oriented to the study of systems with more biological relevance.

Myelin is a membrane which wraps around axons in order to provide insulation. In contrast to most membranes which are unilamella, the myelin sheath is multilamella, i.e. consisting of 5-20 lamellae which surround nerve axons. When the myelin sheath is damaged serious breakdown of the nervous system occurs and demyelinating disorders such as multiple sclerosis occur. A protein, myelin basic protein, occurs between the myelin lamella, its role is unclear but it has been proposed that it "holds" the lamella of the myelin sheath together. We have mimicked this system. A mixed bilayer of cerebroside sulphate and cholesterol 60/40 wt% (two of the commonest constituents of the myelin sheath) was deposited onto mica from a Langmuir trough. The forces between this bilayer were found to be repulsive at all surface separations. At large separations a long range repulsive force was measured which increased exponentially with decreasing surface separation. Experimentation with electrolytes and theoretical analysis shows that the force is due to electrical double layer overlap. At short distances of separation a much stronger repulsive force is measured due to the two bilayers themselves coming into contact. In a second series of experiments the forces between the same lipid bilayers into which myelin basic protein was incorporated, have been measured. At large separations double layer interactions are again observed, however when the lipid surfaces are brought to within some 15nm a strong attractive force is measured. Forces upto 15mN.m^{-1} are measured. These results are repeatable for the same contact positions and reproducible from experiment to experiment although the absolute magnitude of the attractive force may vary by a factor of two. Thus our experiments have shown that strong attractive forces exist between lipid surfaces bearing myelin basic protein and they support the hypothesis that the protein is responsible for "holding" the myelin sheath together.

Recently we have extended our studies to measure the interactions between the more biologically specific lipids, the gangliosides. The hydrophilic headgroup of these lipids contain several carbohydrate residues and are thought to play a role in cell recognition processes. To date we have studied the forces between bilayers of the ganglioside GM_1 , diluted in a phosphatidylcholine or ethanolamine matrix. Preliminary results for this system will also be presented.

ABSTRACT

LONG-RANGE POLYMER DEPLETION FORCES BETWEEN LIPID BILAYER MEMBRANES

by

Evan A. Evans

Departments of Pathology and Physics
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Surfactant bilayers in aqueous media interact non-specifically via long range electrostatic, electrodynamic, and solvation forces. Even though the magnitude of each interaction can be very large, the free energy minimum at stable contact is usually small with a progressive increase in depth as bilayer separation decreases. Addition of large, non-adsorbing polymers (e.g. dextran or polyethylene oxide) can greatly augment the weak natural attraction between bilayers to force them into closer proximity. With micromechanical experiments on giant bilayer vesicles, direct measurements have been made of free energy potentials for assembly of two bilayers to adhesive contact in salt solutions and in concentrated polymer solutions. Results for neutral and charged lipid bilayers in salt buffer correlate reasonably well with classical prescriptions for van der Waals attraction and electric double-layer repulsion based on structural data derived from published X-ray diffraction studies. Attraction in concentrated solutions of non-adsorbing polymers is greatly enhanced by interaction of depletion layers due to polymer exclusion from the bilayer surfaces. For equilibrium exchange of polymer between the gap and bulk regions, the added attraction is simply the osmotic pressure difference between the bulk polymer concentration and the depreciated value at the mid-point of bilayer separation. With only the virial coefficients derived from osmotic pressure measurements of the polymer solutions, a self-consistent mean field (SCMF) theory predicts the concentration-dependence of the attraction energies very well for all molecular weights tested and also predicts the observed attenuation of attraction for electric double-layer repulsion between charged bilayers in polymer solutions. For neutral lipids, the SCMF theory predicts that no polymer remains in the gap at equilibrium separation.

THE SIZE OF POLYMERS ON A ROUGH SURFACE

S.F. Edwards

Cavendish Laboratory, Madingley Road, Cambridge, ENGLAND

ABSTRACT

The simplest study of polymer size only discusses the swelling or contraction of the molecule when it experiences self repulsion or self attraction, and these problems can be considered to have been solved. However when the molecule experiences a fixed environment which is random remarkable new phenomena appear. Examples could be a polymer lying on a rough surface. There is an essential difference between the size of the molecule when the interacting system is fixed, and when it can move e.g. a fixed rough surface as against a surface with moveable impurities lying on it.

For the rough surface the polymer contracts and without self repulsion takes up a size inversely proportional to the strength of the scattering of an element of roughness and the concentration of rough elements.

The Interactions of Molecules with Irregular Fractal Surfaces

Dina Farin and David Avnir

Department of Organic Chemistry and
The Fritz Haber Research Center for Molecular Dynamics
The Hebrew University of Jerusalem, Jerusalem 91904, Israel.

Multiple resolution analysis of molecule/surface interactions and reactions proved to be a useful tool in quantifying the effects that the geometric details of a surface have on heterogeneous chemical processes, and in quantifying the degree of the effective geometric irregularity, as "seen" by these processes. Resolution changes are made by using either particles or molecules of various sizes. The scaling relations thus obtained have the general form:

$$\text{molecule-surface interaction parameter} \propto (\text{resolution parameter})^{\beta}$$

in which β is a simple function of the effective fractal dimension of the surface towards the specific interaction. Weak physical adsorptions, strong chemical adsorptions and virtually all types of surface reactions are describable by this approach. Over one hundred experimental cases are analysed in the references below and in earlier references cited therein. Of the various molecule/surface processes two families will be described in some detail: as an example for the use of molecules for resolution analysis, polymer adsorptions will be discussed with special emphasis on the information provided by this analysis on the adsorption conformation of the polymer-molecule under plateau conditions. As an example for the use of particles as yardsticks we shall discuss catalytic reactions on dispersed metals. We found that the activity of most types of catalytic processes scales with the metal particle size so that the effective dimension (the reaction dimension) of these processes indicates the specific population of active sites and their distribution.

Some 1987 references: For a short review, see Proc. IUPAC Symp. "Characterization of Porous Solids", 1987, to appear in: Stud. Surf. Sci. Catal., Elsevier, Amsterdam, 1988; *J. Am. Chem. Soc.*, in press, **110** (1988); *J. Phys. Chem.*, **91**, 5517 (1987); *J. Chromatogr.*, **406**, 317 (1987); *Chem. Phys. Lett.*, **139**, 109, 115 (1987); *J. Am. Chem. Soc.*, **109**, 2931 (1987).

CAN SURFACE BOUND STATES BE INDUCED BY INTERFACIAL ROUGHNESS?

R C Ball, M Blunt,

Cavendish Laboratory, Madingley Rd, Cambridge CB3 0HE, UK,

and W Barford,

Rutherford Appleton Laboratory, Oxfordshire OX11 0QX, UK.

Within mean field theory there is direct analogy between the 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.

This talk will discuss cases where the balance can be tipped in favour of bound states by corrugation of the interface. It is not sufficient to use a single parameter of surface affinity, and the effect of asymmetry and spatial extent of the binding potential will be explored.

The adsorption and depletion of polymers at the solid/solution interface

T.Cosgrove, T.G. Heath, J.R.P. Webster, A.R. Jones and K. Ryan

University of Bristol, Cantock's Close Bristol BS8 1TS, United Kingdom.

Polymers will adsorb at solid surfaces if the net loss in translational and configurational entropy is compensated by an enthalpic gain on adsorption. χ_s , the net exchange adsorption energy, must be greater than χ_{sc} , the critical value. The non adsorption of polymers has been widely discussed but little information exists on this phenomenon at the molecular level. The most interesting approach has been that of the group in Paris who have used the evanescent wave technique to obtain the thickness of the depletion zone. Many of the techniques available to study adsorption cannot be used to study depletion directly. The main reason for this is the difficulty in differentiating between a small zone of dilute polymer solution at the interface and a concentrated polymer solution in the bulk. In this paper we shall discuss new approaches to this problem using Nuclear Magnetic Resonance and Small Angle Neutron Scattering.

FLEXIBLE POLYMERS AT INTERFACES

P.G. De Gennes

Physique de la Matiere Condensee

College de France

Paris, France.

ABSTRACT

Three idealized dynamical problems will be considered:

1. Growth of an adsorbed layer;
2. Exchanges between adsorbed and solute chains;
3. Reptation of a chain along the adsorbing wall.

LIQUID STRUCTURING AT SOLID INTERFACES PROBED BY STATIC AND DYNAMIC FORCE MEASUREMENTS

Jacob Israelachvili

Department of Chemical and Nuclear Engineering
and Materials Department
University of California, Santa Barbara
California 93106, USA

The Surface Forces Apparatus which was originally designed for measuring the equilibrium (i.e. static) force laws between two surfaces in liquids has been recently modified to enable time-dependent (i.e. dynamic) interactions to be measured with similar precision. In particular, it is now possible to directly measure the "viscosity profile" across a liquid film between two surfaces (i.e. the viscosity as a function of the distance between the two surfaces). The aims of these studies on pure one-component liquids and polymer melts were (i) to investigate the nature of the transition from simple liquid-like behaviour to that characteristic of polymers, (ii) to establish whether there are any correlations between the equilibrium forces and the dynamic interactions, and (iii) to see what insights can be obtained from these studies into the structuring of chain molecules near surfaces or confined between two surfaces.

Results are presented of the equilibrium forces between two molecularly smooth surfaces immersed in simple liquids, liquid alkanes up to hexadecane (n=16), as well as various polymer liquids or "melts" with the number of segments varying from n=20 to n=65. The results show that for the simple liquids, including alkanes up to hexadecane, the short-range force is generally a decaying oscillatory function of the surface separation, superimposed on a longer-ranged van der Waals attractive tail. This is as expected from theoretical modelling of simple liquids. In addition, the dynamic studies on these simple (Newtonian) liquids show that for films as thin as 10 molecular diameters the viscosity of the films is the same as the bulk value already from the first (or at most second) layer of liquid molecules adjacent to the molecularly smooth mica surfaces.

In contrast to these results with simple liquids, similar measurements with chain molecules (polymer melts) having more than 20 segments (e.g. liquid polybutadienes with n=20, or polydimethylsiloxanes) show that these already exhibit "polymer-like" interactions which are very similar to those between polymer-coated surfaces interacting in a good solvent. Thus it was found that there is a monotonic long-range repulsion extending a few R_g , but

that closer to the surfaces these linear molecules preferentially orient parallel to the molecularly smooth mica surfaces (as do liquid alkanes), and that the segments in contact with the surfaces appear to be quite strongly "bound" to them. It is concluded that the transition from simple short-chained molecules (like alkanes) at surfaces to that characteristic of longer-chained polymers is essentially a transition from a quasi-ordered discrete layering of segments parallel to surfaces, extending a few segment diameters, to a more random disordered state farther out describable by mean-field and scaling theories.

Likewise, measurements of the viscosity profiles across polymer melts show that the effective hydrodynamic layer thickness were all close to $2R_g$, beyond which the liquids appear to be perfectly Newtonian so long as the shear rate remains low.

All the above findings are in good qualitative agreement with recent theoretical predictions. Some preliminary results will also be presented using a new device for measuring the viscosity profiles in thin films at very high shear rates where interesting deviations from Newtonian behavior are observed.

Model Polymers For Surfaces and Other Studies
L. J. Fetters
Exxon Research and Engineering Company

The preparation of homopolymers and block copolymers with near-monodisperse molecular weight distribution is of both academic and commercial value. The absence, in certain cases, of a spontaneous termination step during propagation allows the preparation of macromolecules of various architecture: linear, graft, H-shaped, rings, and stars. Furthermore, the retention of chain-end reactivity following polymerization offers a pathway to the preparation of polymers bearing a specific end group. This combination of features has led to the preparation of model polymers which have facilitated studies of polymer adsorption, block copolymer morphology, chain dynamics, diffusion (both tracer and self-diffusion), unperturbed chain dimensions and their respective temperature coefficients, and rheology. These investigations have benefited from the narrow distribution of chain-lengths present in the samples. The materials evaluated have been prepared via the anionic polymerization of styrene and dienes and by the subsequent hydrogenation (or deuteration) of the polydienes. This latter procedure--or the use of the appropriate deuterated monomer--has been used for the preparation of samples used in neutron scattering experiments.

The preparation of near-monodisperse polymers tipped with polar groups yields materials of potential interest in adsorption studies. Groups of interest are zwitterionic, and carboxylic or sulfonic acid units. The latter species can be converted, by the appropriate neutralization step, into various ionic structures. The preparation and application of these materials will be discussed as will other model polymers of interest to polymer physicists.

MOLECULAR IMAGING WITH THE STM AND THE AFM

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ABSTRACT

The scanning tunneling microscope (STM) which uses a sharp tungsten tip to scan a smooth surface, gives us the means of imaging atomic structure on flat conducting surfaces. The atomic force microscope (AFM) provides us with similar information on insulating surfaces. Together, these new tools permit us to directly image structures on the atomic scale. These instruments operate in multiple environments and at various temperatures.

We will begin our talk with a review of the principles that underlie this instrumentation and describe the latest versions of the new microscopes.

It is now possible to use both the STM and the AFM to record high contrast images of organic molecules and monomolecular films. Molecules of Copper Phthalocyanine, Sorbic Acid and Dimethyl Phthalate have been successfully imaged in various laboratories. We will include evidence of long range order in molecular films of cd arachidate, liquid crystals (K-24), and poly(octadecyl-acrylate) (PODA). We will further demonstrate the utility of the AFM in this field by displaying AFM images of PODA that correlate with the images from the STM.

Tunneling electrons have been used for multiple purposes - (1) the direct imaging of molecular complexes, (2) the excitation of their vibrational spectra, and (3) the modification of their structure. In our talk we will describe these three modes of operation so as to illustrate the capabilities and limitations of the overall system.

INTERACTIONS BETWEEN POLYMERS AND SMALL COLLOIDAL PARTICLES

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The interactions between colloidal particles, micelles, emulsion droplets, etc. and polymers are important in many areas of processing science and technology. In particular, polymers are agents which are often involved in dispersion control and the rheological properties of the resulting suspensions. In this presentation, we shall discuss the interactions between both homopolymers and end-grafted chains with small (where the polymer radius of gyration exceeds the particle diameter) colloidal particles. We shall emphasize the case of adsorbing interactions. In this context, we shall consider: i) the nature of the attachments of the polymer to the particles; ii) the role of stoichiometry; iii) the forces between the coupled polymer-particle moieties. We shall make contact with some existing experimental data mainly originating with neutron scattering measurements.

Structure of and Interactions between Adsorbed Layers of Block Copolymers

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Diblock copolymers are excellent stabilisers for colloidal systems. One of the blocks (A) should adsorb on the particle surfaces, whereas the other block (B) provides for the steric repulsion when another particle approaches. It seems obvious that for an optimal effect the solvent should be very poor for the A-blocks and good for the B-blocks. However, a problem occurs for insoluble A-blocks, as formation of micelles interferes with the adsorption of the polymer. In this contribution we will report on some preliminary theoretical predictions, obtained from a Self-consistent Field lattice model.

It appears that insolubility of the A-blocks is not essential. Preferential adsorption of A-blocks occurs whenever the affinity of A-segments for the surface is stronger than that of the B-segments. Even if a homopolymer of only B-segments adsorbs readily, the B-segments are completely removed from the surface by a homopolymer of slightly stronger adsorbing A-segments. The segment density profiles of adsorbing block copolymers reveal that the surface is saturated with A-segments, that there is some overlap of A- and B-segments close to the surface, and that the density profile of B-blocks is similar to that of end-grafted non-adsorbing polymer. The overlap of A- and B-segments is determined mainly by the interaction parameter χ_{AB} . The hydrodynamic layer thickness depends only on the extension of the B-blocks and would be a good characteristic of the adsorbed polymer, as it is experimentally accessible.

The adsorbed amount of diblock copolymer with A- and B-blocks of equal length is higher than that of A or B homopolymer chains of the same total length. Upon variation of the relative block length of A and B at constant total chain length, maximum adsorption occurs when the adsorbing block is much shorter than half of the chain length. With increasing adsorption energy of A-segments, the optimum shifts to shorter A-blocks.

The interaction between two adsorbed layers of diblock copolymer is mainly repulsive. Bridging attraction occurs only if the A-blocks are relatively long and the adsorbed amount is very low, or if the polymer may escape from the gap between the surfaces (full equilibrium during particle approach). However, there is always a repulsive barrier. An adsorbed polymer layer in restricted equilibrium (no escape of polymer from the gap) is less soft than one in full equilibrium.

Theory of the Grafted Polymer Brush

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We calculate the free energy of surfaces coated with grafted polymers in a solvent. We use a self-consistent field (SCF) method appropriate for weak excluded-volume interaction and at moderately high surface coverage. We give the exact solution for the "classical limit" of our SCF equations which shows that, at high molecular weight, the concentration profile approaches a parabolic form rather than the step-function suggested by Alexander and de Gennes. We compute the force required to compress the brush, and discuss current and future experiments. Effects of polydispersity are considered. The bending moduli of brushes are computed for both moderate and melt densities, and for mixtures of short and long chains. An extension of the method to the good-solvent, semi-dilute regime is described.

ADSORPTION OF DIBLOCK COPOLYMERS

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Adsorption of diblock copolymers is now sometimes used to make grafted polymer layers around colloidal particles in order to increase the colloidal stability. One end of the copolymer molecule, the anchor A, strongly adsorbs onto the solid surface and the other end, the buoy B, repelled by the surface forms a polymer brush around the particles.

We present a theory of the adsorption of such copolymers when both blocks are strongly incompatible in two different types of solvents: in a highly selective solvent which is a poor solvent for the anchor and a good solvent for the buoy, and in a non selective solvent which is a good solvent for both blocks.

In a highly selective solvent, the anchor precipitates on the solid surface where it makes a molten layer. The thickness of this layer or equivalently the chain surface density then strongly depends on the long range character of the molecular interactions between solid and monomers A which we choose to be Van-der-Waals like. Four adsorption regimes are found according to the value of the bulk chemical potential of the copolymer molecules in the external solution. This chemical potential is governed by the phase behavior of the copolymer solution. Two examples are considered, micellar and lamellar organisation.

In a non selective good solvent, the anchor forms a self-similar layer on the solid surface. Both the surface density and the polymer concentration profile are determined within the framework of a mean field theory. Scaling laws are then proposed to take into account properly the good solvent behavior.

FORCES BETWEEN SURFACES WITH END-GRAFTED CHAINS

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ABSTRACT

We* have measured the forces acting between smooth solid (mica) surfaces in organic solvents both in the absence and in the presence of polymers (in good solvent conditions) anchored onto the surfaces at one end only. The measured interactions differ significantly from those between surfaces with **adsorbed** polymers of the same size and in the same solvency conditions, especially as regards the range of the interactions and the absence of the characteristic hysteretic behaviour observed with adsorbed chains.

Simultaneously we determined the mean inter-anchor spacing of the grafted chains on the mica substrates, and could thus make a direct absolute comparison between our results and theoretical predictions of such interactions. The variation of the thickness of the grafted layers with polymer **molecular weight** will be discussed. Finally, we compare these interactions to recent measurements using polystyrene/polyethylene-oxide block copolymers.

* Together with Hillary Taunton, Chris Toprackioglu and Lew Fetters, *Nature*, in press.

BLOCK COPOLYMER ADSORPTION ON SOLIDS

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ABSTRACT

Block copolymers are amphiphilic macromolecules that can be manipulated so that different parts of the molecule have selective affinities for solvent and surface. Recent data on adsorbed amounts and configurations of adsorbed block copolymers will be presented. These data have been obtained with a combination of force measurements, x-ray photoelectron spectroscopy and ellipsometry. The most extensively studied system is polystyrene-polyvinyl pyridene but more recently, data on polyethylene oxide-polystyrene and on poly-n-butyl methacrylic with a strongly adsorbing end group have been obtained. The ensemble of data show that this type of molecule adopts an extended configuration on the surface, the extent of which depends on the adsorbed amount. The pattern observed is similar to that predicted by recent models of grafted layers.

From Friction to Surface Forces and Reptation: Some Lucky Breaks

David Tabor, Cavendish Laboratory, Cambridge U.K.

Friction lies at the dirty end of surface science - not only because engineering surfaces are usually contaminated - but also because the sliding process between contacting asperities is complex and poorly defined. However, research starting from such an unfavourable base sometimes has its felicitous surprises. This paper recounts three such events during studies of friction.

1. Windscreen wiper blades: adhesion and surface energy, double layer repulsive forces.

To study the behaviour of wiper blades a model system was set up in which a smooth rubber hemisphere was loaded against a glass flat and the contact studied by optical interferometry. The surfaces were found to adhere and later analysis was able to explain this in terms of surface energy and viscoelasticity. In the presence of certain liquids the surfaces floated apart the thickness of the liquid film depending on the applied load and on the pH. This provided the first (?) direct measurement of the electrical double layer repulsive forces. Some practical ideas about wiper blades also emerged.

2. Area of contact: surface forces.

Philip Bowden had suggested the use of mica as a model material for friction studies since it is molecularly smooth and optical interference could be used to study the contact and sliding behaviour. Early experiments were most promising but a serious drawback was the limited stiffness i.e. the floppiness of mica sheets. A major breakthrough occurred when it proved possible to glue the mica sheets onto cylindrical glass supports. Two such specimens with their axes mounted orthogonally gave a favourable arrangement for studying contact areas, friction and lubrication. The arrangements also provided a unique means of measuring van der Waals forces directly as a function of the distance between the specimens and showed the transition from normal to retarded forces. By luck rather than foresight many factors that could have ruined these pioneering experiments proved to be unimportant.

3. Friction of polyethylene, diffusion and reptation.

Many forms of low density polythene contain small quantities of oleamide. This diffuses to the surface so, preventing adhesion between polythene sheets. The lubricating properties of these films was studied and it was found ^{that} if the film was worn away it could be renewed by further diffusion from the bulk to the surface. This led to a study, quite unrelated to friction, of the diffusion of diffusants of increasing molecular weight through molten polythene. The results provided direct support for the theory of reptation. Hydrostatic pressure reduced the diffusion rate and the activation volume deduced was found to be independent of the size of the diffusant molecule suggesting that a crank shaft motion constituted the micromolecular mechanism of reptation. Some lucky features marked this work.

The paper concludes with some general remarks on luck in research and on the problem of research in unfashionable fields.

PHASE BEHAVIOR AND DYNAMICS OF GRAFTED POLYMER LAYERS.

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ABSTRACT

Polymers attached to an otherwise repulsive surface by a headgroup only are known as grafted chains. For high grafting densities such coils are strongly stretched along the normal to the surface. This effect is especially pronounced for flat surfaces. While the most direct probe of the system is afforded by its force [vs.] distance profiles, the stretched configurations lead to other, more macroscopic, effects. In particular we consider: (1) The collapse behavior of densely grafted chains-the coils retain their stretched configurations even in a poor solvents. (2) Phase separation of a mixture of chemically distinct and laterally mobile grafted chains-the phase behavior reflects the coupling of the grafting density and the chain's configuration. (3) The desorption dynamics of a single "degrafted" chain out of a flat densely grafted layer-the expulsion kinetics are non diffusive even in equilibrium.

ADSORPTION OF A θ -POLYMER AT A SURFACE

E. Eisenriegler (KFA Jülich, FRG) and
H.W. Diehl (Univ. Essen, FRG)

Polymer adsorption may be investigated by field theory methods. For a θ -polymer near the adsorption point (which separates nonadsorbed from adsorbed behavior) we use a field theory in d -dimensional semi-infinite space with interactions $t\rho$, $u\rho^2$, $v\rho^3$ in the bulk and $t_1\rho$, $u_1\rho^2$ on the surface. Here $\rho = \phi^2$, with ϕ the Landau Ginzburg field, corresponds to the monomer density of the polymer chain and $t, \dots, u_1$ are recognized as one, two, ... - body monomer interaction strengths. In the physically interesting dimension $d = 3$ the nonlinear interactions v and u_1 become marginal in a renormalization group (RG) sense and perturbative RG calculations may lead to asymptotically exact predictions. For a chain with $N \gg 1$ monomers, fixed with one end at the surface we consider the average number $M(0)$ of monomers at the surface, right at the θ and adsorption point. If $v > 0$ and u_1 not too negative, we find

$$M(0) \sim N^{\frac{1}{2}} \cdot (\ln N)^{\frac{12+\ln 2}{88}} \cdot \exp\left[-\left(\frac{1}{22}\ln N\right)^{\frac{1}{2}}\right]$$

For the variation of the average monomer number $M(z)$ in a layer between z and $z+dz$ with distance z from the surface we get

$$M(z) \sim M(0) \cdot [\ln \mu z]^{-\frac{12+\ln 2}{88}} \cdot \exp\left[\left(\frac{1}{11}\ln \mu z\right)^{\frac{1}{2}}\right]$$

provided z is much larger than a microscopic length scale μ^{-1} but much smaller than the mean end to end distance of a θ chain in infinite space. Due to the logarithms occurring in exponents the deviations from corresponding ideal chain results are stronger than one usually finds in the upper critical dimension (when only powers of logs occur).

(oral presentation preferred)

REFLECTIVITY PROFILE OF POLYMER SOLUTION INTERFACES NEAR TOTAL
REFLECTION. AN ISOTOPIC COMPOSITION EFFECT OBSERVED BY NEUTRONS

by

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Near total reflection, the reflectivity function is very sensitive to structural correlations between interface and bulk, in a manner which is not yet fully understood : multiple collision effects are here dominant.

In the case of a neutron radiation, there exists an interesting isotopic effect related to the sign of the neutron interaction with the scattering centers. A repulsive perturbation may forbid the transmission of the shorter wave, whereas an attractive perturbation has effects which are less drastic. These effects are thus not symmetric with respect to the change in the sign of the perturbation potential.

This fact is used to determine as accurately as possible the polymer concentration profile, in a solution near the surface, from the reflectivity function.

We make use of two predictions. The first is the distorted wave (or 1st Born) approximation, which allows to calculate a reflectivity function for a given concentration profile and vice versa, as shown by E. Bouchaud, X. Sun, B. Farnoux, M. Daoud and G. Jannink. The second is the essential singularity near total reflection, predicted by S. Dietrich and R. Schack for a radiation having a repulsive perturbation potential with respect to bulk interaction. These predictions are however restricted to limiting cases, and are not sufficient to interpret the reflectivity data of X. Sun, E. Bouchaud, B. Farnoux, A. Lapp and G. Jannink. We discuss these results in terms of the propagation equation and interpret the observed enhanced reflectivity associated to the repulsive case, as a result of the polymer concentration at the interface.

Simulations of Polymers near Surfaces

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The numerical investigation of the critical adsorption of polymers is discussed for various cases. Penetrable and impenetrable surfaces are considered. Especially the behavior for various solvent conditions is discussed. Polymers in a θ -solution display a qualitatively different behavior than chains in good solvent. Thus the adsorption of a θ -chain can be viewed as a transition from a 3-d θ -solvent chain to a 2-d good solvent chain. This causes a qualitatively different behavior of the density profile for good and θ -solvents. Other upcoming investigations are briefly reviewed.

THE STRUCTURE OF HARD SPHERE FLUID IN NARROW PORES.
INTEGRAL EQUATIONS AND MONTE CARLO SIMULATIONS.

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The distribution of hard spheres between hard walls and in cylindrical pores in equilibrium with the bulk fluid of given chemical potential is studied by different integral equation approaches and by means of the Grand Canonical Ensemble Monte Carlo simulations. The adsorption of the fluid in the pores is considered and the solvation force between the hard plates immersed in the fluid is determined as a function of the separation between the plates. The applicability of the Percus-Yevick approximation and of the Percus shielding approach is confirmed for the situations when the pore diameters exceeded sufficiently the size of the fluid particles. In extremely narrow pores, the truncated cluster expansion of the fluid density profile proved more suitable. The above considerations were extended to more realistic models involving a waterlike fluid to be reported separately.

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ABSTRACT

This poster deals with radial distributions functions: $g(r)$ in highly diluted colloidal solutions (SDS-water-oil).

The first part is concerned with a theoretical study exhibiting the influence on the behavior of dispersed oil couplets, of an excess of SDS, aggregated as micelles. This study has been developed consistently i) with hard spheres hypothesis and ii) with DLVO like potentials.

The second part consists in the description of an experimental technique and in preliminary results, the aim of which is determination of $g(r)$ via Optical Nomarsky microscopy and imaging process.

ORDERING OF MONODISPERSED POLYMER LATICES
INDUCED BY TEMPERATURE GRADIENT

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The behaviour of ordering of latex particles induced by a temperature gradient through the latex suspension has been investigated. A latex suspension including monodispersed particles with $2a=160 - 410$ nm, was filled in a flat glass-cell with thickness of 1 mm and a temperature gradient of $20 - 60$ °C/mm was supplied between the two flat windows by circulating a cooling(T_c) and a warming water(T_w) around the each window. Detecting that under a suitable condition, the latex sample shows a brilliant iridescence on the cooling window and the condition is much dependent on the value of $\Delta T (= T_w - T_c)$, on the solid contents in the suspension, the ionic strength in the medium, and the particle size and the charge density of latex sample.

In order to measure the interparticle distances in the ordered layers induced by a temperature gradient, the reflection spectra of visible light incidented from the cooling window were recorded. The spectrum pattern is geneally weak at beginning, gradually strengthens with shifting the peak to shorter wavelength by the elapsed time and finally becomes to a saturated one. Following to the treatments of Krieger, the interparticle distance($2D$) in the ordered layers was calculated from the peak wavelength and plotted against the elapsed time. It is found that the $2D$ shifts to the shorter distance as the time goes on and asymptotically reaches to an equilibrium distance($2D_{eq}$) afte 50-60 min has passed. Under a constant ionic strength, the $2D_{eq}$ decreases with increasing the value of ΔT and under a fixed temperature condition, the $2D_{eq}$ increases with decreasing the salt concentration. Furthermore, the spectroscopic data have enable us the calculation of the enhanced ratio of latex particles deposited on the cooling window. It is realized that the enhanced ratios are ranged from 1.5 to 2.5 and increase steeply with the value of ΔT and the salt concentration, especially in the systems including the small size particles.

INFLUENCE OF STERIC STABILIZATION LAYER ON THE CRYSTALLIZATION OF
COLLOIDAL SILICA PARTICLES

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Abstract of poster presentation:

Colloidal silica spheres were coated with stearylalcohol and polyisobutylene, thus forming uncharged sterically stabilized particles. By increasing the thickness of the stabilization layer (accomplished by changing the molecular weight of the polymer), the short-range interaction between the particles was varied from a nearly hard sphere potential to a somewhat softer potential.

Study of the crystallization phenomena of these systems revealed that the rate of crystallization increased dramatically as the thickness of the organic stabilization layer was increased. Light scattering experiments of the ordering phenomena that lead to the formation of colloidal crystals will be presented.

NOVEL SILVER METAL "LIQUID-LIKE" FILMS (MELLF)-INTRODUCTION

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We report on novel silver films which are confined within the interface of two immiscible liquids. On the one hand, these films exhibit macroscopic "Liquid-Like" behaviour, they flow and heal immediately upon rupture, indicating a discontinuous structure. On the other hand, the films have a high specular reflectivity much as continuous smooth silver films have.

The films are produced by a chemical reduction of silver ions, and stabilized with specific surfactants (anionic surfactants).

We present here some experimental evidence showing that these films are colloidal dispersions restricted to the interfacial region. The particles are enveloped by the surfactants and other anions admitted into the MELLF. This spatial restriction and their stabilization are a result of a delicate balance of forces operating in the interfacial region and between the individual particles. Their exact nature is not yet fully clear. We discuss the experimental findings pertaining to surface and interfacial tensions, polarity of the phases, the charges within the layer and its structure and composition.

MORE ABOUT SILVER METAL "LIQUID-LIKE" FILMS

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Beer-Sheva, 84120, ISRAEL

We present further and more complete experimental evidence pertaining to the composition and structure of the silver MELLFs, introduced in a parallel presentation.

Electron microscopy of dried films shows a highly dispersed structure and clusters that have an internal structure. The basic internal units are several nanometers in size. Electron diffraction of those dried films shows, in addition to diffraction rings of silver FCC structure, rings which, by comparison, we found them to belong mostly to the surfactants or their silver salts. Dynamic photon correlation light scattering from disrupted MELLF revealed particles with an average diameter of 1290nm, the actual sizes ranging from 900nm to 3000nm. In reflectance spectra from the silver MELLF in its natural state, the main feature is the 320nm silver interband transition. In addition, a long tail extending into the visible range may indicate surface plasmons or other localized plasmons. The spectra strongly resemble those of rough silver films and are significantly different from those of a silver colloidal suspension. Raman scattering measurements on the films in their natural state show the presence of surfactants (or their salts) in the interfacial films. Evidence exists that the Raman spectra are surface enhanced. The interfacial silver MELLF show no detectable conductivity in their natural state or even as dried films. Moire deflectometry of the films in their natural state indicates a total thickness of a few microns, consistent with the dynamic light scattering. Transmission studies, on the other hand, give a thickness of several tens of nanometers, in terms of equivalent continuous silver films.

A colloidal model for the film is consistent with these results, with silver metal nuclei, several nanometer large. Each particle adsorbs to its face anions which charge the particles and is the main factor in the stabilization of the colloid. This layer also serves as the "lubricant" which imparts the "Liquid-Like" properties to the film.

VAN DER WAALS FORCES MEASUREMENT

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Poster presentation

A home built apparatus able to measure Van der Waals forces will be described. The main difference with previous such devices is the piezoelectric control of the distance between the two surfaces in interaction.

I think that preliminary results concerning with the interaction between mica surfaces in electrolyte will be available for the symposium and comparison with previous results could be done.

**DIELECTRIC CHANGES OF PHOSPHOLIPID BILAYERS
IN THE PRESENCE OF A FOREIGN MOLECULE : 17 β OESTRADIOL**

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N.S.W., Kensington 2033, AUSTRALIA.

Adding the hormone 17 β Oestradiol to a phospholipid bilayer changes the dielectric properties of a bilayer membrane. It decreases severalfold the electrical impedance of the polar regions and consequently shunts the hydrocarbon region with the aqueous phase.

Surface Phase Transitions and Electrical Double Layer near Critical Point

V.M. Nabutovsky, Shabazi 19/7, Rehovot, Israel

Any system close to its critical point, such as a phase-separation or liquid-vapor critical point, is instable. Near the surface such a system forms easily the surface phases different from the bulk ones. Equilibrium between these phases depends strongly upon boundary conditions. One can induce a transition between these phases by changing the boundary conditions at the surface.

If in the system under consideration mobile charges (ions, electrons, charged vacancies) exist, then they form electric double layer near the surface. The structure of the surface phases depends upon the electrical potential on the surface, owing to the interaction of the double layer with the solvent. Changing an external electric field one can induce the phase transition near the surface.

On the other hand, the structure of the surface phase influences on the structure of the electric double layer. Therefore, the surface potential and capacitance bear an information about the surface structure.

We predicted these phenomena and calculated the surface layer structure, the surface phase transitions, the surface potential and capacitance on the basis of the generalized Poisson-Boltzman and Landau-Ginsburg set of non-linear equations. These equations connect the order-parameter and charge densities.

Other systems with the similar phenomena are solid state materials: magnetics, superionics, ferroelectrics. Charges in these materials can be both ions and electrons (in semi-conductors).

Surface capacitance or optical experiments are relevant to investigate these phenomena.

VARIATIONS IN THE HYDRATION FORCE BETWEEN BIMOLECULAR LAYERS.

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It is now generally recognized that hydration forces dominate close interactions of lipid hydrophilic surfaces. The commonality of their characteristics have been reasonably established. However differences in measured net repulsion suggest there exists a variety of behavior wider than expected from earlier models of hydration and fluctuation repulsion balanced by van der Waals attraction. To find a basis for this diverse behavior we have looked more closely at measured structural parameters, maximum degrees of hydration and interbilayer repulsive forces measured using the osmotic stress method which allows one to go to far greater forces than any other method. We describe here results from lamellar phases of the following lipids; 1-palmitoyl-2-oleoyl-PE (POPE), egg PE, transphosphatidylated egg PE (egg PE-T), mono- and di- methylated egg PE-T, (MMPE and DMPE), 1-stearoyl-2-oleoyl-PC (SOPC), POPE / SOPC mixtures, digalactosyldiacylglycerol (DGDG), dioleoylphosphatidylserine (DOPS) and dihexadecyldimethylammonium (DHDA). POPE and SOPC bilayers differ not only in their maximum degrees of hydration but also in the empirical hydration force coefficients and decay lengths that characterize their interaction. When mixed with POPE, SOPC effects sudden and disproportionate increases in hydration. POPE, egg PE and eggPE-T differ in their degrees of maximum hydration. A single methylation of eggPE-T almost completely converts its hydration and bilayer repulsive properties to that of the fully methylated egg PC; little progression of hydration is seen with successive methylations. DOPS in .8M NaCl more closely resembles the PE's than the PC's. DGDG hydrates even less than some PE's. DHDA with its very small polar group nevertheless hydrates in high salt, to about the same extent as POPE.

A number of interesting theoretical questions must now be recognized. In order to reconcile these observations with the conventional scheme of balancing interbilayer hydration and fluctuation-enhanced repulsion vs van der Waals attraction, it appears necessary to relinquish the fundamental idea that hydration forces decay with an exponential constant determined by the properties of the aqueous medium. Alternatively one might retain that idea if one recognizes the possibility that polar group hydration can have an attractive component to it, an attraction via water bridges between correlated zwitterionic or other complementary polar groups on apposing bilayer surfaces. The same Marcelja and Radic formalism that accounts so well for the repulsive component can be used to estimate the attractive. It is possible that the variable maximum hydration of different bilayers results in part from variable contributions of attractive and repulsive hydration components, factors related to polar group solubility.

HYDRATION FORCE BY COMPUTER SIMULATION

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The Grand Canonical Ensemble Monte Carlo method is applied to study the hydration force between uncharged surfaces. The model system consists of two parallel smooth plates and about 100 water molecules confined in the Monte Carlo cell with periodic boundary conditions applied in the directions parallel to the walls. Water molecules are modelled as dipolar spheres with anisotropic sticky pair potential that mimics hydrogen bonding. Using the hard core potential for water-wall interactions the pressure between the two interfaces is studied as a function of the wall-wall separation. The comparison with experimental data for hydrocarbon hydration is made.

THE INTERACTION BETWEEN AN AIR BUBBLE AND A HYDROPHILIC OR HYDROPHOBIC MICA SURFACE.

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ABSTRACT

A microscopic method of observing the liquid film formed between an air bubble and a solid surface, developed by Scheludko, Platikanov and Tchaliowska, has been used to study the wetting properties of (i) initially clean, freshly cleaved muscovite mica, (ii) hydrophobed mica, (iii) these surfaces submerged in dilute pentaethyleneoxide dodecyl ether (C12E5) solution. The results obtained on thin film life times, contact angle hysteresis and rate of expansion of the meniscus perimeter reflect the importance of hydrophobic attraction forces, attractive and repulsive electrostatic forces as well as repulsive solvation forces. Clean mica submerged in very dilute DAC solution is extensively hydrophobed only from the three-phase contact line where a condensed surfactant monolayer apparently forms as a result of electrostatic and hydrophobic attraction.

For hydrophobed mica there is a transition from wetting behaviour with marked contact angle hysteresis to hysteresis-free wetting at $C(\text{DAC}) = 1$ micromole/l. This is attributed to the formation of a surfactant-rich precursor film. At higher surfactant concentrations, $C(\text{DAC})$ greater than 1 mmol/l, the wetting properties of initially clean mica and hydrophobed mica are quite similar. Hydrophobed mica when submerged in c:a 1 mmol/l C12E5, shows hydrophilic behaviour, but the mean life-time of the film decreases with increasing temperature. This appears to be related to a decreased repulsion or transition to weak attraction between the ethylene oxide chains, as is also indicated by previously conducted direct measurements of the interaction forces.

SILICA-SILOXANE MECHANICAL MIXTURES. SATURATED ADSORPTION. NMR APPROACH.

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Silica-Siloxane systems resulting from a mechanical mixing can form clusters or microgels or infinite clusters swollen by free polymer chains. The nature of the mixture depends upon the chain molecular weight and the concentration of silica particles. The adsorption process upon the silica surface occurs through H-bonds.

1) Saturated adsorption : screening effect

The adsorbed polymer phase is characterized from the residual amount of polymer Q_r left bound to silica when all free chains are removed from the mixture. The variable Q_r is found to vary as a linear function of the chain molecular weight : $Q_r \propto \overline{Mn}$. This striking result reveals that the number of fixed chains n_c per unit mass of silica is constant whatever the chain length :

$n_c = 2.6 \times 10^{18} g^{-1}$, ($2 \times 10^3 \leq \overline{Mn} \leq 3 \times 10^5$). The number of h-bonds involved in the binding process is $n_H = 60$.

2) Treated silica : collective binding process

Evidence for the collective character of the binding process of a given chain is obtained from a chemical treatment of the silica surfaces. The extent of the treatment is varied from 0 to 75 % of the surface. Using a Bernouilli statistics, it is shown that about half of a chain-site must be treated to prevent the binding process.

3) Reversible swelling

Infinite clusters behave like gel systems. When all free chains are eliminated, they can be reversibly swollen using a good solvent. The maximum swelling value Q_m is interpreted from a mean field approximation :

$$Q_m^{5/3} - Q_m/2 \propto Q_r$$

4) Statistical structure : NMR investigations

Statistical structures of the adsorbed phase between particles are investigated applying NMR. It is shown that chain entanglements play a crucial role. The dependence of a suitable NMR parameter upon the progressive swelling ratio Q leads to a semi-local (50 Å) characterization of the mixtures.

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ADSORPTION ON CHEMICALLY MODIFIED SILICA SURFACES

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ABSTRACT

An experimental investigation of the adsorption of polyvinylpyrrolidone (PVP) from aqueous solutions onto virgin and chemically modified silica surfaces is reported. The chemically modified silica surfaces consisted of vinyl, isobutyl and PVP functionality. Vinyl and isobutyl surface groups were obtained by surface silylation while a chemically bonded PVP phase was obtained by a graft polymerization technique. Adsorption isotherms for PVP are reported for the above modified surfaces. The effective thickness of the adsorbed layer was determined by the hydrodynamic technique. These measurements are compared with recent data for polystyrene which establishes that shear-thickening of adsorbed polymer layers can occur in shear flows. The sensitivity of the hydrodynamic method to the degree of surface coverage is evaluated with the aim of establishing the utility of this method to quantify the degree of surface-polymer interaction.

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The Viscoelasticity
of Associated
Red Cell Cytoskeleton Proteins

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ABSTRACT:

We wish to report on the determination of the complex shear modulus of the associated protein components of the human red cell cytoskeleton.

The cytoskeletons were extracted from red cell ghosts with TRITON X-100, using the method of Shen *et al.* [1]. The skeletons were washed to remove the detergent then dissociated and solubilized according to the method of Ohanian and Gratzer [2]. The protein concentration of the final solution (spectrin, actin, and Band 4.1) was 1.7 mg./ml. This solution was stored at 4 C until used.

The shear apparatus described by Abraham *et al.* [3] was modified by replacing the conical cup with a cup of 10 ml volume. This cup was equipped with a TEFLON coated magnetic stirrer and an injection port, which made it possible to introduce or extract material below the subphase surface. The subphase for all measurements was a buffer which supports reassociation of the cytoskeleton components [4]; the composition was: 0.1 M NaCl; 30 mM Tris; 0.1 mM $MgCl_2$; 0.1 mM ATP; 0.5 mM DTT; pH 8.0. Initialization measurements were made on the buffer, then 500 microliters were withdrawn through the port. These were replaced with 500 microliters of cytoskeleton solution. The solution was stirred for 2 minutes, at a rate which did not twist the torsion pendulum, before commencing measurements of the damping. Measurements were repeated at intervals for a period of 108 minutes. The apparatus was then cleaned and the procedure repeated with the modification of spreading a monolayer of bovine brain phosphatidyl serine (BBPS) on the buffer before injecting the cytoskeleton. BBPS is the major component of the inner surface of the red cell membrane and has been shown to have a complex modulus at this frequency of ca. 22 millidynes/cm. [5].

After 108 minutes the real component of the complex shear modulus of the uncovered cytoskeleton had leveled out at 1.71 dynes/cm. and the surface viscosity (the complex component divided by the frequency) was 87 millidynes-sec/cm. By contrast, with the BBPS covered buffer, the shear modulus had leveled out at only 0.14 dynes/cm and the surface viscosity was 1.2 millidyne-sec/cm. Some inferences will be drawn and comments on the limitations of the measurements will be made.

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Elastic Properties of Amphiphilic Films: A Molecular Theory

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The elastic properties of amphiphilic monolayers and bilayers are studied by means of a mean-field statistical thermodynamic theory. This theory has previously been used to study chain organization and thermodynamics of amphiphile molecules in micelles and bilayers, revealing very good agreement with experimental data and (the few available) large scale computer simulations. The central quantity of the theory is the probability distribution function (*pdf*) of chain conformations, which is derived by minimization of the conformational free energy of the chains, subject to the packing constraints imposed on any chain by its neighbors. The packing constraints are specified by the curvature of the oil/water interface and by the average density of the chain heads at the interface. These constraints determine the lateral pressure profile which appears in the *pdf* and which accounts for the free energy changes associated with inter-chain repulsion.

The bending (splay) constant k and the saddle splay constant $\bar{k}$ can be calculated by evaluating the chain's free energy at different curvatures (and for different types of deformations). An alternative way of calculating the elastic constants consists of evaluating different moments of the lateral pressure profile and its derivatives for the *planar* film. We have used both ways to study systematically (and for the first time from a molecular approach) the behavior of k and $\bar{k}$ as a function of: (i) average area per head-group (two dimensional density); (ii) chain length; (iii) composition in mixed aggregates. Both monolayers and bilayers have been investigated.

The main findings are as follows. Qualitatively, the dependence of the elastic constants on the three parameters above is the same for monolayers and bilayers. The elastic constants decrease rapidly with the average area per molecule, e.g., for a bilayer of C_{12} molecules k decreases from ~ 100 kT to kT and $\bar{k}$ from 50 kT to 0.1 kT when the area increases from $\sim 25 \text{ \AA}^2$ to $45 \text{ \AA}^2$. Both k and $\bar{k}$ increase strongly with chain length n , roughly proportional to $n^{2.5}$. An important and interesting effect is the ability of short chain molecules to lower the bending constants when added to a film composed by long molecules. For example, the bending constant of an equimolar C_{16}/C_6 film is lower than the corresponding constant of a pure C_{16} film at the same area per molecule. For lamellar amphiphilic systems a very similar effect has been found experimentally.

Nearfield Optical Interactions between Surfaces

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Electromagnetic fields can get dramatically enhanced at strongly curved parts of a surface because of shape or Mie resonances, excitation of particle plasmons and the lightning rod effect.¹ Among others, the enhancement gives rise to roughness-induced electrical breakdown and surface-enhanced Raman scattering. In combination with the surface curvature, the enhanced fields are also responsible for the relatively strong elastic light scattering from microscopic protrusions on a surface; a process closely related to the Mie scattering from small spheres.

We found that the scattering efficiency from a surface protrusion reacts with extreme sensitivity upon variations of the dielectric properties in its immediate environment.^{2,3} To study this phenomenon a near-field optical scanning (NFOS) microscope was conceived which employs a geometry similar to that of an STM with an illuminated tiny aperture or asperity replacing the tunnel tip.³⁻⁶ Images with up to 20 nm resolution and excellent contrast were obtained.

Besides unprecedented optical resolution the NFOS microscope is a convenient tool to study the electromagnetic interaction between two nearby bodies as a function of distance and shape. We found, for instance, that a plasmon, localized in a protrusion, came in resonance with the exciting HeNe laser radiation at separations of 20 to 50 nm from a test surface within a very narrow distance range.⁷

In summary, NFOS microscopy opens a new way to study microscopic electromagnetic surface interactions as well as optical structures far beyond the diffraction limit.

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SELF-ASSEMBLING FUNCTIONALIZED MONOLAYERS

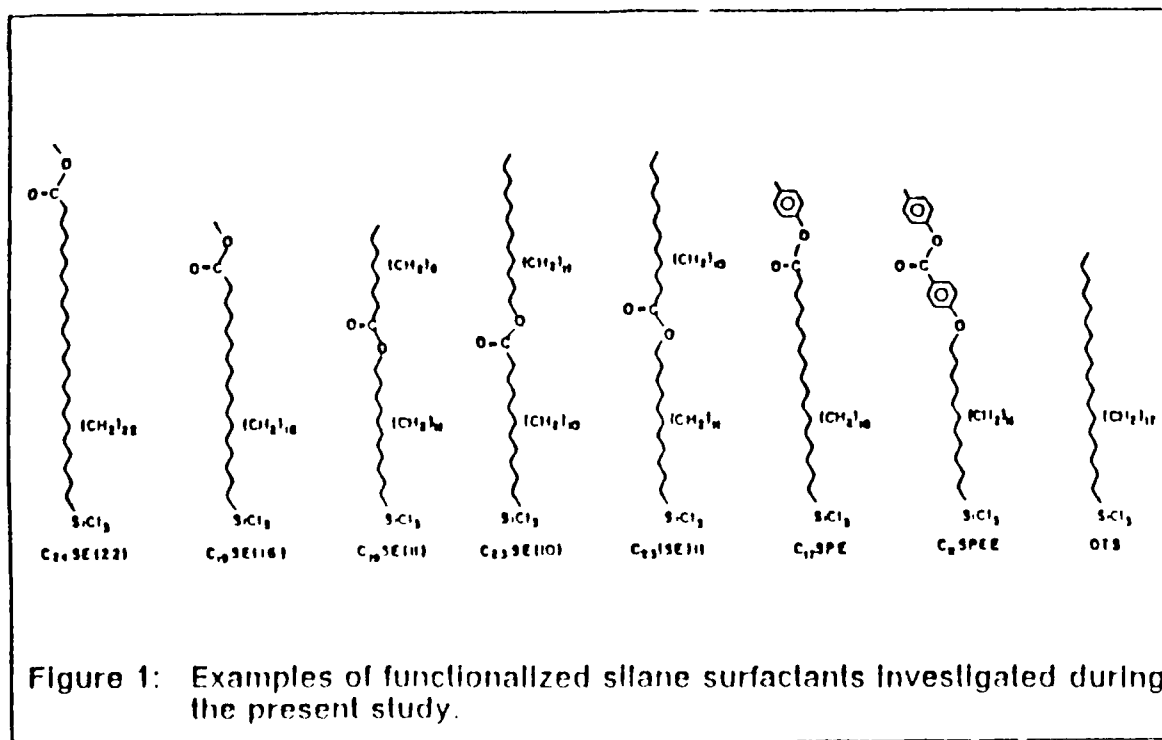
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Molecular self-assembly from organic solutions provides an attractive approach to the preparation of organized supramolecular structures on solid supports. The method has been successfully applied to the construction of highly ordered monolayers and, more recently, also to the preparation of organized multilayer films using bifunctional components provided with potentially reactive outer functions.

So far, only relatively simple compounds, usually aliphatic long chain amphiphiles, have been used as building units of films prepared by self-assembly. In order to produce a larger variety of functionalized monolayers, with interesting new properties, more complex film forming materials should become available.

We wish to report results of a study of the self-assembly and surface chemical modification of a series of bifunctional surfactants containing a trichlorosilyl binding head group and a second ester or ether function in the non-polar part of the aliphatic chain. The complexity of the surfactants was increased by coupling (through the ester/ether function) aromatic moieties to the end of the chain (Fig.1).



A NEW CLASS OF SELF-ASSEMBLING MULTILAYER ORGANIZATES: STRUCTURES WITH IONIC OR
SUCCESSIVE IONIC - COVALENT INTERLAYER COUPLING

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We report on the extension of the monolayer self-assembly approach to the construction of solid-supported multilayer structures with IONIC as well as any combination of sequential IONIC and COVALENT interlayer coupling. The method, based on a two-step process consisting of monolayer formation by spontaneous adsorption from solution and in-situ chemical activation of the exposed film surface, provides precise control of the deposition of discrete monolayers and the selection of the desired mode of interlayer coupling.

No systematic tendency for deterioration of the film quality with increasing number of superimposed layers could be detected in the present studied films. This opens the way to the construction of high-quality layered structures via molecular self-assembly.

The double-polar nature of the monolayers in such multilayer films results in strong layer-to-layer binding at each interlayer boundary, thus affording remarkable overall structural robustness. While ionic binding allows enhanced intralayer mobility, covalent binding may be utilized to add extra chemical and mechanical stability to such mixed-type molecular structures. The rich ion-exchange chemistry displayed by the ionic layers in both AQUEOUS and ORGANIC environments, in conjunction with the options provided by covalent linking, offer unprecedented synthetic possibilities for the construction of a variety of novel monolayer organizates.

THIN FILM ADHESION AS A FUNCTION OF SUBSTRATE STRUCTURE

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We have studied interactions taking place across the interface between thin films, both polymer films on the order of 2-5 microns, as well as Langmuir-Blodgett monolayers, and inorganic substrates.

In an attempt to correlate the structure of the substrate surface with film behavior (structural as well as mechanical), we have chosen crystalline substrates like single crystal quartz of different crystallographic orientation, and silicon wafers (with (100) and (111) orientation).

We have found significant differences in the adhesion quality (as measured by peel tests) of polyimide films on substrates varying only in crystallographic orientation.

We have analyzed these differences in terms of the changes in the chemistry of the interfaces and will present results from angle resolved ESCA, Auger and FTIR measurements.

STOCHASTIC DYNAMICS OF MONOMOLECULAR FILMS

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The equilibrium properties of long-chain monomolecular films can be computed from position-velocity trajectories generated by stochastic differential equations of the Langevin type that are subject to constraints such as constant bond lengths. Several interactions must be modeled including the obvious inter and intra molecular forces of the long-chain species spread at a liquid/gas interface to form a monolayer. Of special interest is the force that constrains the molecules of the monolayer to move in the interfacial region. We report results of simulations based on a monolayer composed of chains of six spheres-of-influence with polar and hydrocarbon interactions allowed. In addition, each sphere-of-influence moves in a potential that represents contributions from the anisotropic nature of the interface. The details of this potential will be discussed. Clustering effects will be shown. Various correlation functions will be shown.

Molecular Beam Scattering from Organized Amphiphilic Monolayers

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The interfaces between gases or liquids and a solid surface can be examined by many techniques. Such studies often provide macroscopic and/or time-averaged results. Molecular beam scattering, by providing state-specific information, is the key to understanding many monolayer properties on the molecular level. In these experiments, an isolated molecule in a well defined initial state (internal and translational energies), interacts by single or multiple collisions with a surface and the resulting energy redistribution in the scattered molecule is probed. Because of the collision-free conditions, the only interaction has been that with the surface.

In this study, molecular beam scattering is used to probe the interaction between various gases and an ordered, organic, monolayer surface. The three different amphiphilic monolayer films chosen are composed of either octadecyltrichlorosilane (OTS), arachidic acid (C_{20}), or 11,11,211,211 perfluorodecyl-10- carboxy-1-decanoate (PFAD). Whereas the first two amphiphiles expose a long aliphatic chain, the latter exposes a perfluorinated species. None of these species are chemically reactive to the gases being scattered (noble gases, and diatomic oxygen, nitrogen, and nitric oxide). The scattering results should therefore be dominated by kinematic effects.

Separate studies have been made of translational, rotational, and vibrational energy transfer during the interaction. In addition, modelling and simulations of the results have given insight on the factors dominating energy transfer in general. These results have implications on scattering from such varied surfaces as metallic, semiconductor, and ionic crystal faces.

*International Symposium on Surface Interactions
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NONLINEAR OPTICAL STUDIES OF ADSORBATE MONOLAYERS ON SURFACES

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Optical second harmonic generation (SHG) is a highly surface sensitive technique ideally suited for the study of adsorbate molecules at the surface of isotropic or centrosymmetric substrates. We will show how SHG may be used to study the orientation of adsorbates at surfaces, the stabilization and equilibration of Langmuir monolayers, chemical reactions in monolayers, etc.

However, SHG is generally not applicable to centrosymmetric molecular adsorbate layers. For such cases we have also examined the feasibility of using third harmonic generation (THG) as a probe for surface adsorbates. Results will be presented for monolayers of several polydiacetylenes.

THE STATISTICAL MECHANICS OF NON-EQUILIBRIUM POLYMER ADSORPTION

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Experiments on adsorbed polymers and computer simulations of the dynamics of adsorbing polymers strongly suggest that for polymer adsorption in the regime where the difference of free energy between an adsorbed and desorbed segment is of the order $k_B T$ (the strong coupling regime) the adsorbed polymers assume non-equilibrium profiles. They may be considered to be in a glassy state.

In this paper we develop non-equilibrium mean field theories to predict the statistical properties of polymers adsorbed onto flat surfaces in such a regime.

The first theory is a relatively simple sequential model in which it is assumed that the polymer adsorbs in increments such that at each stage of the adsorption process the polymer increments which have already adsorbed are completely unable to equilibrate as more increments adsorb.

It is shown that the polymer density profiles closely resemble equilibrium profiles (the density falls off as $1/\text{distance}^2$ which is the same as the mean field equilibrium result) but that the adsorbate concentration is greatly reduced.

The second is a more sophisticated theory in which only the surface segments of the adsorbed polymer increments cannot equilibrate whereas the loops may as more polymer adsorbs.

In spite of the increased complexity of this model the predictions are essentially identical to those of the previous model in the strong coupling limit.

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POLYMER ADSORPTION AND ELECTRON BINDING ON ROUGH AND FRACTAL SURFACES

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ABSTRACT

A mean-field theory is used to study the adsorption of polymer chains, both with and without excluded volume interactions, on a rough surface. In particular, the adsorption on a fractal surface generated from a hierarchy of sinusoidal perturbations is investigated. It is found that there is a simple scaling relation between the free energy of a polymer adsorbed on a fractal and on a plane surface. Furthermore, deviations from scaling are found.

It is found that roughness enhances the adsorption of polymer. The problem is mathematically equivalent to the binding of quantum mechanical particles by rough surfaces.

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Abstract for Neve Ilan Meeting, March 13-18, 1988

THEORY OF THE GRAFTED POLYMER BRUSH

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ABSTRACT: We study the statistics of a grafted polymer brush, consisting of a set of monodisperse chains in solution, each attached irreversibly by one end to a flat surface. We use a self-consistent field (SCF) method, valid in the limit of weak excluded volume and at moderately high surface coverage. Exploiting the fact that the chains are highly stretched, we map the problem (in the long chain limit) onto one involving the motion of classical particles in an equal-time potential, which we solve exactly. The resulting density profile for the brush takes a parabolic form: $\phi(x) = A - Bx^2$, with $0 < x < (A/B)^{1/2}$. This result contrasts with an earlier ansatz of a step function profile, but is in very good agreement with recent numerical SCF computations. The force between brushes that are compressed together is also calculated; while for strong compression the behavior is similar to that predicted from the step-function ansatz, the force exerted under conditions of weak compression is qualitatively softer. An extension of the theory to describe the scaling regime (strong excluded volume, lower coverage) yields a density profile for the brush that is qualitatively similar to the parabola found in SCF. The opposite limit of very high coverage and strong excluded volume (so that the density near the grafting surface approaches that of a melt) is treated by adopting a Flory-Huggins expression for the osmotic repulsion between chains; in the athermal case, we find $\phi(x) = 1 - \exp(Bx^2 - A)$. This profile approaches a parabola in the outer parts of the brush, but saturates to a plateau in the region near the wall. Various experiments are suggested that would test directly our new theoretical predictions.

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**HYDRODYNAMIC LAYER THICKNESSES OF
TERMINALLY ANCHORED POLYMERS AT THE SOLID-LIQUID INTERFACES**

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Hydrodynamic layer thicknesses of acrylic polymers terminally anchored onto the surfaces of silica particles have been measured using photon correlation spectroscopy. Variables studied were molecular weight, surface coverage, monomer size and solution properties. Results will be discussed in the light of current theories. Study was carried out using a versatile, experimental model system scheme we have developed, using mono-disperse silica particles prepared by the method of Stober (1968), and low dispersity methacrylate polymers with different monomer sizes prepared by the group transfer polymerization process (Sogah, 1987). Polymers are anchored by a trimethoxy silane end group and grafting is carried out without going through the "dry" stage by using a "common" solvent chosen to provide both electrostatic stabilization for the particles and solubilization for the polymers.

INTERACTION BETWEEN GRAFTED SOLID SURFACE IN NEMALIC LIQUID.

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abstract

We discuss the nematic order parameter and the polymer concentration profiles for a solid surface carrying a set of grafted chains (N monomers per chain, fraction of grafted sites (σ) immersed in a nematic solvent. It is assumed 1) that the polymer does not adsorb on the wall surface 2) that no nematic order is induced directly by the wall 3) that the nematic order is suppressed inside a solute polymer coil. The zone occupied by the chains may be nematic (N) or isotropic (I). The chains may be stretched (S) or unstretched (US). The unstretched chains are collapsed (US, C) or ideal (US, Id) depending upon the size of the ideal chain $N^{1/2}$ as compared to ξ , the nematic coherence length. The combination of these criteria gives five regimes. We also discuss the interaction between two grafted surfaces in a nematic solvent.

Computer Simulation of Polymers Adsorbed to a Surface

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Polymer adsorption has been studied with the help of the "scanning simulation method" [Meirovitch, *Macromolecules* **18**, 563 (1985)]. Two models are investigated, a single random walk (RW) and a single self-avoiding walk (SAW), attached to an attracting wall on a simple cubic lattice. For the RW model (without excluded volume), which has been solved analytically, walks of up to $N=10^5$ steps can be simulated reliably. Also for the SAW model which does not have an analytical solution, we simulate relatively long chains, c. up to 1000 steps (as compared to $N\sim 100$ studied before). This ability to construct long chains, leads to very precise estimates of critical exponents and of transition temperatures T_a (from an adsorbed to unadsorbed state), and critical exponents. Close to T_a we test the validity of various crossover scaling forms predicted by Eisenrigler, Kremer and Binder [*J. Chem. Phys.* **77**, 6296 (1982)] for a continuum model. For both RW and SAW models we demonstrate that correction to scaling terms become important above T_a , for quantities dependent on the distance from the surface. These corrections can be neglected only for very large chain length, much larger than can realized experimentally.

ADSORPTION OF POLYSTYRENE FROM CYCLOHEXANE ONTO MICA

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Mica is indispensable for the study of surface interactions because the surface of mica is molecularly smooth. For the purpose of studying the steric interaction between polymer layers, the polymers are adsorbed at first onto two sheets of mica and the force acting between the two surfaces is measured. While the force measurement has been extensively carried out by several research groups, no systematic study has been reported of the polymer adsorption onto mica. The present study concerns with the adsorption of polystyrene (mol wt $1 \times 10^5 \sim 3 \times 10^6$) from cyclohexane solution onto mica at the θ -temperature (307.5 K). The experimental method consists of the following two approaches: (1) the measurement of adsorbed amount as a function of time using a microbalance technique¹ and (2) the observation of the polystyrene films removed from mica sheets².

The process of polymer adsorption has been investigated in the range of solution concentration from 0.005 to 0.5 mg ml⁻¹. The experimental results show that, in the very dilute region of around 0.005 mg ml⁻¹, (1) the adsorbance begins to rise and reaches $1.5 \sim 2.0$ mg m⁻² after a certain period of induction time, (2) the initial rise in adsorbance corresponds to the formation of continuous films and (3) the rate of increase in adsorbance subsequent to the initial rise is slow; in the moderately concentrated region of about 0.1 to 0.5 mg ml⁻¹, the surface of mica is covered with polystyrene films of more than 2 mg m⁻² within a few seconds from the beginning of the adsorption and then polystyrene molecules are adsorbed onto the adsorbed polystyrene film up to the equilibrium adsorbance for prolonged adsorption.

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**Poster Abstract: Symposium on Surface Interactions
Polymer Adsorption via Internal Reflection Interferometry**

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In this poster we present a new approach to studying dynamic processes at solid-liquid interfaces. The technique utilizes the evanescent waves created by total internal reflection to probe an interfacial solution. The light undergoing internal reflection undergoes a phase change monitored with a simple interferometer. Computerized data acquisition allows us to track the adsorption process over a period of hours with tenth second resolution if desired. We study the adsorption kinetics of simple homopolymers and block copolymers. We compare results from these two different adsorption processes and describe models for the adsorption kinetics.

EVANESCENT WAVE INDUCED FLUORESCENCE STUDIES

OF POLYMER LAYERS ADSORBED ON SAPPHIRE SURFACES

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It is well known that in polymer solutions the local concentration of polymer near a solid wall differs strongly from the bulk solution. In the case of attractive forces, there is an excess of polymer at the solid-solution interface. Theoretical monomer concentration profiles have been proposed using either mean-field or scaling theories. Until recently(1) no decisive experimental determination of this profile has been done.

We shall present data of the concentration profile of an adsorbed layer, obtained by the Evanescent Wave Induced Fluorescence Technique(2). The experiments have been performed with PMMA ($1.2 \times 10^5 < M_w < 1.2 \times 10^6$) labelled with anthracene (2×10^{-4} molar) dissolved in toluene. The solid surface is a well-polished, clean surface of sapphire, attractive for PMMA. The kinetics of adsorption of various molecular weight polymer have been recorded. The technique enables us to follow the evolution of the excess surface and the determination of the first and second moment of the monomer distribution at the interface. The results of the "plateau" will be compared to theoretical predictions.

Kinetics of exchange between the adsorbed layer and the bulk solution, for various couple of molecular weight (bulk/adsorbed) will also be presented and discussed.

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**POLYMER ADSORBED-LAYER THICKNESS
AND ADSORPTION ENERGY**

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MEASUREMENTS OF SURFACES FORCES IN A COLLOIDAL SOLUTION OF CALCIUM
CARBONATE DISPERSED IN DODECANE

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ABSTRACT

The principles of a new surface force instrument are presented. Its features allow the intermolecular forces and rheology between a sphere and a plane to be measured continuously and simultaneously. A "transfer function" gives both the viscous and elastic behavior of the interface. The study of the alumina-n.dodecane-alumina interface shows that, if the layer thickness is greater than 5 nm, the dodecane behaves like a newtonian liquid with its bulk viscosity. For distances of less than 5 nm, deviations are attributed to steric effects, and the surface roughness of the solids. At the same time, during the inward and outward approach a hysteresis in the interaction force occurs. A comparison between experimental curves and the theoretical attractive Van der Waals force shows best agreement in the unloading period, and when the roughness is very slight.

We also measure the forces and the mechanical impedance between two alumina surfaces separated by a colloidal solution of calcium carbonate very dispersed in dodecane.

We show the adsorption of the colloid and an increase of solids adhesion.

DYNAMICS OF SURFACE BOUND POLYMERS

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The microscopic structure and dynamics of polymers bound to solid materials determine many of the properties of polymer-solid interfaces and consequently the properties of the materials made from them. The microscopic structure of the adsorbed polymer has been the subject of experimental and theoretical work, but so far very little work has been done on the microscopic dynamics of polymers on surfaces. We will report the results of nuclear magnetic resonance (NMR) studies of polymers adsorbed on surfaces. The motivation of this work is to determine how the surface influences the rate and mechanism of polymer backbone motion. In this way we will develop an understanding of the dynamics of the polymer on the surface.

Two types of different studies have been performed using solids-NMR techniques. The first is the study of poly(isopropyl acrylate) on Cab-O-Sil surfaces. Since this material is near its glass transition temperature it has a good deal of backbone motion. It happens, for this polymer at room temperature that the molecular motion is of the right frequency that the backbone carbons do not cross-polarize efficiently resulting in a spectrum which has no backbone resonances. In contrast, the backbone motion of the polymer adsorbed on the solid is slowed down considerably. The spectra of the polymer adsorbed on the surface shows all of the resonances. We have studied this phenomena as a function of the surface coverage. The results correlate with molecular motion experienced by the polymer as a function of the distance from the surface. We have also studied other chemically similar polymers which are glassy and noted the effect of chemical additives on their spectra.

We have also used deuterium NMR to probe the dynamics of styrene segments as a function of the distance from the surface. This has been done through the synthesis of tri-block polymers of vinylpyridene-styrene-deuterostyrene. The synthesis was performed by Dr. Ferdrich Schwab of Mobil Chemical Co. These polymers have the deuterostyrene either next to the vinylpyridene or at the ends of the chain. The deuterium NMR quadrupole powder patterns may be interpreted in terms of the molecular motion as a function of distance of the segment from the attached group.

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Dynamic behaviour of flexible polymers
at a solid/liquid interface

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Summary

The mean time spent by a macromolecule adsorbed at a solid/liquid interface was measured at adsorption equilibrium by carrying out adsorption with radioactive labelled polymers and subsequently exposing the surface to a solution of unlabelled polymers. Two different systems were investigated :

- polyacrylamide adsorbed in aqueous media on modified silica (ref. 1)
- polystyrene adsorbed in tetracarbon chloride on silica beads.

In both cases, the exchange between labelled and unlabelled polymers takes place at the interface at a very slow rate. The exchange of polyacrylamide follows an apparent second order reaction rate. For polystyrene the situation is more complex. The two domains in the adsorption isotherms corresponding to two different conformational states of the polymer surface layer are reflected in the dynamical behaviour. At low concentration, the behaviour of polystyrene and polyacrylamide is remarkably similar. However at large surface coverage, the exchange of labelled/unlabelled polystyrene does not follow a simple law.

Questions such as thermodynamic equilibrium or metastable surface state are discussed in the context of recent theoretical developments (ref. 2).

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**KINETICS OF ADSORPTION OF BLOCK COPOLYMERS
AS REVEALED BY
SURFACE PLASMA OSCILLATIONS**

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The kinetics of adsorption of diblock copolymers of poly(vinyl-2-pyridine) and polystyrene from toluene solutions on silver surfaces has been studied by Surface Plasmon Spectroscopy. This technique affords a measure of the quantity of adsorbed polymer and an estimate of the thickness of the adsorbed layer. The kinetics of adsorption appear highly dependent on the concentration of the solution and on the composition of the copolymer. The presence of micelles at higher concentrations leads to a high initial rate of adsorption. Adsorption of unimers proceeds more slowly. The structure of the interface can be described as a thin layer of molten PVP and a brush of extended PS chains, but the surface is much less covered than expected, suggesting a non-uniform distribution of the adsorbed molecules.

"EQUILIBRIUM" AND DYNAMIC BEHAVIOR OF THIN FILM POLYMER MELTS

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We have measured the "equilibrium" forces between two mica surfaces separated by a thin liquid film of a perfluorinated polyether. The observed force law was monotonically repulsive and had a range which was on the order of ten times the radius of gyration of the polymer molecules. The results can be explained by hypothesizing that some of the polymer chains are effectively "pinned" to the surfaces and thus are not free to exchange with chains in the bulk reservoir on the timescale of the experiments. An attempt was made to investigate via Monte Carlo simulations the confining effect of a polymer melt between two parallel plates. We found that when the separation between the plates is comparable to the radius of gyration of the polymer molecules in the bulk, the shape of the polymer coils becomes highly anisotropic. As the separation between the plates is decreased, we find that the free energy of an incompressible system is affected in at least two opposing ways. The actual number of deformed molecules decreases, yet the molecules that remain between the plates become progressively more deformed. At this stage it is very difficult to infer which of these two effects will determine the shape range and sign of the resulting forces.

We have also investigated the response of the same polymer melt to both sinusoidal and step perturbations in the distance between the two surfaces as a function of the film thickness. We have developed a simple rheological model for a linear, viscoelastic fluid which relates the experimental data to the effective viscosity of the confined fluid. For surface separations greater than approximately 1500Å, the effective viscosity of the fluid film was found to be the same as the macroscopically measured value reported for the bulk polymer. For a surface separation of 840Å, the effective viscosity was found to be greater than the bulk value. The results obtained from the dynamic experiments agreed with those obtained from the transient experiments.

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