

This discussion was a portion of the symposium "Interfaces and Thin Films," organized by John Armstrong, Dean E. Eastman, and George M. Whitesides, held March 23 and 24, 1987, at the National Academy of Sciences, Washington, D.C.

Open discussion of papers by McConnell, Rice, and Andelman

DR. EASTMAN: We can entertain questions from the audience, or perhaps you have questions among yourselves.

RALPH NUZZO: (AT&T Bell Laboratories, Murray Hill, NJ): I want to ask Professor McConnell what the protonation state of the phosphate is. Is it the same in the solid and liquid-like regions? Do any of these structures respond to the pH of the subphase?

DR. MCCONNELL: There are effects of pH and ionic strength on the shapes of solid domains. Due to surface buffering and Debye screening, these effects are often quite small. However, in certain cases changes of pH and ionic strength trigger large changes in the shapes of lipid domains, apparently due to phase transitions involving changes in the structure of the solid domains at the molecular level, such as chain tilt (see ref. 1).

An experimental and theoretical study of the effects of pH and ionic strength on pressure-area curves of phospholipid monolayers has been given by Helm *et al.* (2). These investigators treat electrostatic contributions to the surface pressures but do not address the problem considered in our extended abstract, the nonhorizontal pressure-area isotherm in the solid-fluid two-phase region.

ALEX DE LOZANNE (University of Texas, Austin): To the last speaker, superconductors of type I, in a magnetic field, go into the mixed state and show very similar patterns to what you showed in the beginning. Do the same models apply to this case?

DR. ANDELMAN: I am not sure. The model that applies to the thin magnetic films that I showed is the dipolar Ising model.

JACOB ISRAELACHVILI (University of California, Santa Barbara): I have questions for McConnell, Rice, and Andelman, experimental and theoretical. First, I would like to address some questions to McConnell and Andelman concerning these very interesting structures. First of all, there was work by Pallas and Pethica, recently published, addressing itself to the issue of whether these transitions are, indeed, first order or not.

They claim that if you go to great extremes to purify the samples, everything that in the past looked like a curved transition—I do not know how you call it—becomes nice and sharp and first order.

Also, some work by Marcelja, some theoretical work, indicated that you must have a first-order phase transition, regardless of any sort of interactions that you add into the system. You cannot have things that are not perfectly plateaued and horizontal.

Also, are these structures equilibrium structures? My fourth question, still on this matter, is, can you apply dipole interactions to a system where we know that we have water, we have ions, and we have screening of electrostatic interactions, and where, even in pure water at pH 7, the Debye length is such that the electric field will be screened over distances of maybe a couple of thousand angstroms.

That totally changes any comparison with magnetic systems, unless, of course, you assume magnetic monopoles. So, those are my four questions to the first and third speakers.

DR. EASTMAN: Let's stop there, please, and take four at a time.

DR. MCCONNELL: At any interface between any two substances, there is a polarization density or bipole density. Therefore, there is always a long-range repulsion.

The issue about the order of the phase transition is tricky. Andelman has pointed out that there can be phase transitions between these structures. There can be a transition between a stripe phase [and a] hexagonal phase of the solid domains.

In my extended abstract, a proof is given that electrostatic effects can produce a finite slope of the pressure-area curve in the solid-fluid two-phase region.

DR. ANDELMAN: I'll try to answer your four questions. Regarding the works of Pallas and Pethica that you mentioned, I do not see any contradiction between them and our theory. The transition lines that we are getting are always first order. Thus, isotherms have a horizontal plateau in all two-phase regions. However, isotherms are not flat in any of the single-phase regions, and this includes the modulated phases.

Your second point has to do with the dispute over the liquid-expanded, liquid-condensed transition. Our work does not directly relate to this controversy. I think that both theoretically and experimentally this transition is not well understood. Hopefully, new experimental techniques such as synchrotron x-ray diffraction will be of help in the future.

You also raised the question whether the structures seen in the epifluorescence experiments are equilibrium structures. The theory that I presented assumes thermodynamic equilibrium. In addition, we are currently investigating the effect of electrostatic forces on spinodal decomposition and on nucleation and growth in these monolayers. In my opinion, it is still not clear whether these structures are in true equilibrium or whether they are deep metastable states. In many cases, the phenomenon is reversible and is stable on time scales of hours or days. The periodicity of the modulated structures is quite reproducible and can be explained as an equilibrium phenomenon.

Your last point had to do with screening of electrostatic interactions in aqueous solutions. Recent experiments of Möhwald *et al.* (3) suggest that at least part of the dipolar contribution comes from the section of the amphiphile that is above the water/air surface. In these cases, the screening of the water is not important.

PETER PERSHAN (Harvard University, Cambridge, MA): A comment and a question to David. First, in terms of the pH-dependent subphase and ionic concentration, I do not remember the actual reference, but there is a gentleman in England who has done x-ray specular reflectivity from monolayers, not of lecithins but of simple soaps, as a function of pH and salt concentration in the liquid below the surface.

Since he could quite clearly see the changes of the ionic distribution below the surface, this is a technique that can be applied to examine these types of things.

The question to David is, Bob Birgeneau showed these spiral patterns from the work of Bob Meyer and Ron Pindak, which, as I understand, can be attributed to an in-plane electric dipole moment. Have you considered in-plane dipole moments in addition to the normal ones?

DR. ANDELMAN: No, I did not, but it is something that certainly should be done. I know that Deryagin wrote a paper with this idea, and recently I saw a preprint by Gabay, Garel, and Botet where they explain the chirality seen in some of the phospholipids by an inplane dipole component.

In the experiment by R. Meyer and R. Pindak, mentioned yesterday in the talk of Professor Birgeneau, a uniform state of the free-standing liquid-crystal film was a result of a perpendicular magnetic field. It will be interesting to try to do the same for amphiphilic monolayers, though the applied field should probably be much larger.

FREDERICK MUELLER (Los Alamos National Laboratory, Los Alamos, NM): I have a question for Professor Rice. Yesterday we were fascinated to hear about some fascinating new sets of oxides, and my question for you has to do with oxygen in the systems now as an impurity in the following sense.

In doing these beautiful experiments, one knows about the existence of sesquioxides of cesium. I am sure you thought of this; how did you take care, in these experiments, to be careful about the oxygen concentration and did it have any effects?

DR. RICE: The material was prepared in ultrahigh vacuum, and the vacuum was monitored with a field-ion microscope, so that we know that the oxygen partial pressure in the cell at the time was below 10^{-11} torr (it could not be recorded) (1 torr = 133 Pa). The whole experiment was run under ion-pump conditions.

DR. MUELLER: Yes, but would you anticipate that you could still have very thin oxides under the cesium layer, as you were showing?

DR. RICE: The experiment I showed you was on mercury.

DR. MUELLER: No, I am speaking now about the sodium/cesium experiment.

DR. RICE: That was a simulation.

DR. MUELLER: I am sorry. I misunderstood.

DR. RICE: But we have prepared to do that experiment. I guess the best answer I can give you with respect to oxygen impurity is that the cell is prepared to be monitored in the same way as I just described, as was already done for pure cesium in reflectivity measurements (Sheis and Rice); that the alkali metal on the walls will act as a getter; and, finally, that cesium oxide is denser than cesium and should sink.

PAUL K. HANSMAN (University of California, Santa Barbara): I have a question for Harden McConnell and David Andelman. David, you mentioned, toward the end of your talk, about some synchrotron work on the structure, and I noticed you were very careful to call them solids and not crystals.

I just wonder what is known by that technique and others (there may be some others that have not been discussed) about what the ordering is in these solids and what would be the benefits, say, to your long-term application of knowing that order?

DR. MCCONNELL: I can mention some recent work by Möhwald and collaborators. This group observed wide-angle x-ray diffraction corresponding to 4.4 Å and an out-of-plane intensity distribution characteristic of a monomolecular film.

The answer to the other part of your question—to what extent do these results have any impact on biophysics/biochemistry work—is very simple. Anything you can learn is helpful, for sure. That is the name of the game in molecular biology; anything you can learn about the system is very, very helpful.

At the present time, the only information we have had to guide our own work has been this fluorescence machine to measure lateral diffusion and fluorescence anisotropy.

DR. WHITESIDES: Stuart Rice, the structure that you had for stearic acid on mercury suggested hexagonal closest packing of the hydrocarbon chains. The question is, do you know anything about the order of the carboxylic acid head groups and what is going on down there, since those are certainly spherical and, perhaps arguably, not even easily registrable with the hydrocarbons?

DR. RICE: Our original idea was that there would not need to be any registry of the monolayer with the surface because it is a fluid surface. I do not know whether the carboxyl group ionizes or not. It is conceivable that, at the concentrations we are talking about, hydrogen will dissolve in mercury. If it does, the electron density will generate a very short shielding length, anyway, so the fact that you have ionized groups really will not matter. You would have a shielding length something like the inverse Fermi wavelength.

The best answer that I can give you is that we do not know anything about the head-group configuration and order. I think of the monolayer structure at the moment as something like that of the rotator phase in the lamellar paraffin hydrocarbons. We do not even really know for certain that the axes of the molecules are vertical as opposed to all tilted.

All I can say is that the fact that we can see as much intensity as we do with carbon against mercury implies that the projection of the carbon electron density on the plane of mercury has to be almost perfect. That can, of course, be the case either if the chains are tilted or if they are vertical, but it eliminates the possibility of having any significant concentration of bent molecules, and so forth.

THEODORE MADEY (National Bureau of Standards, Gaithersburg, MD): I have a general question for all of the panelists. Most of the discussion has centered upon the equilibrium or static properties of these interfaces. In fact, is there any manifestation of dynamic effects?

For example, in the case of water, free evaporation into vacuum at room temperature is sufficiently high that you can expect to lose millions of monolayers a second. Now, granted, in equilibrium there is not a great loss of matter, but there is going to be a lot of churning around at the interface as a result of molecular exchange.

Is there any manifestation of such phenomena in any of the sorts of things you have been discussing?

DR. MCCONNELL: That is something one works strenuously to avoid. My students put a thin coverslip very close to the surface to avoid evaporation and turbulence. With respect to other kinetic effects, Möhwald has done some beautiful work in studying the kinetics for solid-domain formation on compression.

Under some circumstances, one does get, so to speak, diffusion-limited structures. They may be fractal structures or snowflake-type structures. These show up quite beautifully in the fluorescence technique because, as the solid is formed, these fingers move out, and they move out faster than molecules can diffuse away. So, there is a brilliant fluorescent halo around these growing solid domains. This result has been published by the Möhwald group.

DR. RICE: In our case, after achieving the very low pressure conditions that you mentioned, the cell is sealed. There are some old data in the literature by White, who claims that the temperature dependence of the surface tension of divalent metals such as zinc and mercury depends, in fact, upon whether one observes them at the equilibrium vapor pressure or under pumping conditions. But we work as nearly as possible under equilibrium conditions.

STEPHEN GAROFF (Schlumberger-Doll Research Center, Richville, CT): Professor Rice, we have heard about layering at interfaces of fluids several times now, Professor Pershan's

work, and the older work of Jacob Israelachvili, where, between the mica plates, you see many oscillations. Your calculations seem to remove them for dielectrics. Can you compare the sorts of molecular dynamics results you got for metals with, particularly, the mica-plate experiments?

DR. RICE: The source of the stratification at the liquid/metal/vapor interface is the strong density dependence of the interaction, as calculated with a second-order pseudopotential representation, which is the common one for bulk metals. It is the variation of that part of the interaction which behaves like a one-body potential.

So, in effect, the variation of the electron density builds a wall, and it is the layering of the spheres, spherical particles, against the wall which generates the stratification just as it does with a real wall, as opposed to one which is generated by the transition from delocalized to localized electrons.

The stratification which is seen in the osmotic pressure or the direct mica force experiments has to do with the geometry of packing of the molecules. You get close enough that you can only fit in one layer or two layers or three layers, and you get oscillations in the fourth, which are the consequences of the packing. That is a different situation—namely, it is a

geometry effect as opposed to a density-dependent interaction effect.

In the molecular crystals, you have, in essence, the same thing, except on a different length scale, because what Peter pointed out was that the existence of the surface, in a sense, acted as a wall, and you had a layering of the liquid-crystal molecules along that wall, which then generated a pseudopropagating order down three or four layers.

DR. PERSHAN: Do I understand correctly that the oscillations in the metal are at twice the Fermi momentum?

DR. RICE: No, they are at the atomic diameter, because it is layering the spheres against the potential walls. In fact, I can show you that (Fig. 3 from Rice paper in this symposium). I can show you where the Fermi oscillations are. The dashed line there is the self-consistent electron distribution or a positive distribution which has the shape of a solid line. That is incommensurate with the ionic size. You can also see the spillover here, which is the dipole layer.

1. Heckl, W. M. & Möhwald, H. (1986) *Ber. Bunsenges. Phys. Chem.* **90**, 1159–1171.
2. Helm, A., Loshuber, L., Lösche, M. & Möhwald, H. (1986) *Colloid Polym. Sci.* **264**, 46–55.
3. Miller, A. & Möhwald, H. (1986) *Europhys. Lett.* **2**, 67–74.