This paper pointed out that a fluid (such as an adsorbed gas) in contact with a surface can be regarded as the limiting case of a fluid mixture in which one of the species is very large and present in very low concentration. It showed how approximate theories of liquids based on the Ornstein-Zernike equation, such as the Percus-Yevick and hypernetted chain theories, can be applied in this situation, leading to theories of liquid surfaces and interfaces. (The SCI® indicates that this paper has been cited in more than 170 publications.)

A Theoretical Method for Gas-Liquid-Solid Interfaces

J.A. Barker, F.F. Abraham, and D. Henderson
Almaden Research Center
IBM Research Division
650 Harry Road
San Jose, CA 95120

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By 1976 the theory of liquids had been developed to the extent that it was possible to make quantitative predictions of the solid-liquid-gas phase diagram and of the static and dynamic properties of liquids starting from information on the forces between molecules. This understanding was based on a large body of work by us and many others involving advances in statistical mechanics (integral equations and perturbation theories, Monte Carlo and molecular dynamics computer simulations) and knowledge of intermolecular forces.

In view of these developments, it seemed timely to turn our attention to inhomogeneous fluids, that is, fluids with spatially varying density. Examples of this arise in the neighborhood of the gas-liquid interface and for a liquid or gaseous phase in contact with a solid surface. We had already performed computer simulations of the gas-liquid interface and of small clusters of molecules, and it seemed desirable to develop theoretical methods analogous to those found useful in the study of uniform fluids. This would make possible theoretical studies of the liquid surface and of adsorption phenomena, including the important special case of the electrolyte-electrode interface.

There was already a well-developed theoretical formalism for liquid solutions, and it occurred to one of us (FFA) that it was possible and desirable to treat the theory of inhomogeneous fluids as a special case of this existing theory, rather than to develop a completely new approach. To do this we imagined the surface as a very large solute molecule, dissolved in the liquid at very low concentration. At first we attempted to implement this by computer simulation. Then we realized that all that was needed was to take the formal mathematical limit of extreme dilution and infinite size for the "solute" molecules. Then the solute-solute density correlation function gave the density profile at the interface, and the logarithm of the solute-solute correlation function gave the interaction potential (free energy) between two surfaces. The integral equation formalism of liquid state theory could be applied immediately.

This proved to be a powerful idea with far-reaching consequences. Independently, J.W. Perram and E.R. Smith and J.K. Percus developed similar ideas, but they considered rather special systems. Although the application considered in our paper was to the hard sphere fluid, the equations developed were general and could be applied to any system. In particular they have been applied to electrolyte-electrode interfaces leading to new models that include solvent and metal effects and to increased interest in interfacial electrochemistry.

The effect of our paper was to make theoretical methods for the study of fluid surfaces and interfaces immediately available to anyone versed in the then current theory of bulk fluids. Its citation record indicates that that was a useful thing to do.