ChE lecture

MOLECULAR THEORY OF FLUID MICROSTRUCTURES

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MANY OF THE CURRENT courses on the statistical thermodynamics are restricted to bulk phase phenomena. However, interfacial and colloidal phenomena are involved in important ways in engineering processes and products. Associated with and perhaps even determinant of interfacial and colloidal properties are what we call fluid microstructures. A fluid microstructure is a region in a fluid in which densities and/or compositions vary appreciably over distances of the order of magnitude of the range of molecular forces. Examples of fluid microstructure include fluid-fluid interfaces, fluid-solid interfaces, multiphase contact regions, thin films, drops and bubbles, micelles, microemulsions, liquid crystals, lipid bilayers, vesicles, emollients, foams, spinodally developing density variations, and gels.

H. Ted Davis received his B.S. from Furman Univ. (1959) and his Ph.D. from the Univ. of Chicago (1962). He joined the ChE department at the University of Minnesota in 1963 and is the author of over 100 publications in scientific and engineering journals and edited books. His research interests include statistical mechanics of equilibrium and transport processes, experimental and theoretical investigation of the physico-chemical processes in flow in porous media as related to petroleum recovery, interfacial and colloid science, mathematical modelling of transport, reaction and mechanical properties of disordered media, liquid electronics, and heat and water movement in food systems. Professor Davis recently became head of the Department of Chemical Engineering and Materials Science.

Fluid microstructures are ubiquitous in the products and uses of products of the emollient, detergent, coating, and processed foods industries. Foams, bubbles, drops, films (membranes), gels, and microporous solids are frequently involved in separation and reaction processes of the chemical industry as well as pollution control and water treatment industry, and the natural processes of biological systems. Capillarity, wettability, and multiphase flow in porous media are controlled to a great extent by fluid microstructures—multiphase flow phenomena in porous media are involved in natural and induced ground water movement, solution mineral leaching, petroleum recovery, processes, and wood fiber treatment and manufacturing processes. Emulsion polymerization is a well established industrial process now. Micellar or microemulsion reaction processes are under investigation for their ultimate practical utility. And liquid crystals are commonplace as watch dials and thermometers. The importance of bilayers in cellular structure, and the organizational and transport processes of living matter is thoroughly established although incompletely understood. Vesicles are under active investigation as potential vessels for drug delivery to specific sites in living organisms. The foods industry is also researching vesicle behavior for future application.

The list of processes and systems in which fluid microstructures are consequential goes on and on and will not be produced here. What is relevant to this paper is the fact that in spite of the wide involvement of fluid microstructures in technological and natural processes and products and even though interfacial science is an old classical subject, the fundamental basis for understanding the behavior of fluid microstructures still forms an exciting and developing subject. Among the objects of current theoretical interest are the local density and stress (pressure) distributions associated with the fluid microstructures; interfacial tension and other stress moments; contact angle of three phase contact

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lines; film tensions, stability, and disjoining pressure; and contact angle and meniscus shape. The course deals with the modern theory of such objects. In the remainder of this article we shall try to exhibit the spirit of the theory developed in the course introduced in a previous article.*

In an inhomogeneous system, the thermodynamic functions depend on the density distribution $n(\mathbf{r})$. For example, for the pair potential model, the average attractive energy is

$$\langle u_A^N \rangle = \frac{1}{2} \int \int n(\mathbf{r})\, n(\mathbf{r}')\, g(\mathbf{r},\mathbf{r}')\, u_A(|\mathbf{r}-\mathbf{r}'|)\, d^3r\, d^3r' . \quad (1)$$

To simplify the theory, we assume as in the VDW theory that g depends only on $|\mathbf{r}'-\mathbf{r}|$, expand $n(\mathbf{r}')$ about $\mathbf{r}$ in the integrand of Eq. (1), and truncate the series after third order in gradients of n to obtain

$$\langle u_A^N \rangle = \int [-n^2(\mathbf{r})a - \frac{n(\mathbf{r})c}{2} \nabla^2 n(\mathbf{r})]\, d^3r , \quad (2)$$

where ∇ is the gradient operator, a is the Van der Waals energy parameter, and

$$c \equiv -\frac{1}{3} \int s^2\, u_A(s)\, g(s)\, d^3s . \quad (3)$$

The so-called gradient theory represented by Eq. (2) yields quite good results for planar interfaces [2, 3, 4, 5]. In the rigorous developments [2], c depends on density and temperature, but the dependence is weak [4] and will be ignored here. The Helmholtz free energy of inhomogeneous fluid can be expressed in the form $F = \int f(\mathbf{r})\, d^3r$, where $f(\mathbf{r})$ is the Helmholtz free energy density at position $\mathbf{r}$ in the fluid. With arguments similar to those supporting the VDW theory of homogeneous fluid, Equation (3) leads to

$$F = \int [f_o(n) - \frac{n}{2} c \nabla^2 n]\, d^3r , \quad (4)$$

where $f_o(n)$ is the Helmholtz free energy density of homogeneous fluid. The chemical potential, determined from Eq. (4) as the change in F per unit material added by changing the fluid density locally at constant T and V, of inhomogeneous fluid is

$$\mu = \mu_o(n) - c \nabla^2 n . \quad (5)$$

$\mu_o(n)$ is the chemical potential of homogeneous fluid at density n.

At equilibrium μ is constant throughout the system so that Eq. (5) becomes a partial differential equation determining those fluid microstructures allowed at equilibrium. The factors in the equation determining the nature of a microstructure are the chemical potential of homogeneous fluid, $\mu_o(n)$, which dictates the existence of a particular microstructure, and the *influence parameter* c, which determines the length scale of the microstructure. The kind of microstructure predicted will depend on the temperature and chemical potential set and on the nature of any boundary conditions set. This will be illustrated now with some examples.

Consider a planar interface whose normal is in the x-direction and cross-sectional area is A. In one dimension the Laplacian $\nabla^2 n$ becomes simply the second derivative d^2n/dx^2 of density. Equation (5) can be rearranged by multiplication by dn/dx into an integrable form and then integrated to yield

$$\frac{1}{2} c \left[\frac{dn}{dx}\right]^2 = \omega(n) + K;$$

$$dx = -\sqrt{\frac{c}{2}}\, dn / \sqrt{\omega(n) + K} \quad (6)$$

where K is a constant of integration and

$$\omega(n) \equiv f_o(n) - n\mu \quad (7)$$

The boundary conditions of a planar interface are $n(x) \to n_l$ as $x \to -\infty$ and $n(x) \to n_g$ as $x \to \infty$, where n_l and n_g are the bulk phase liquid and vapor density, respectively. The boundary conditions are equivalent to the conditions of thermodynamic equilibrium:

$$\mu = \mu_o(n_g) = \mu_o(n_l) ;$$
$$-K = \omega(n_g) = \omega(n_l) = -P_N , \quad (8)$$

where P_N is the bulk phase pressure (which is also equal to the normal component of pressure, which is constant throughout the planar system).

*CEE, Fall 1979, page 198.

The surface tension γ of the interface, computed from the thermodynamic relation

$$\gamma = (\partial F/\partial A)_{T,V,N},$$

is given by

$$\gamma = \int_{-\infty}^{\infty} c \left[\frac{dn}{dx}\right]^2 dx = \int_{n_g}^{n_l} [c\Delta\omega(n)]^{1/2}\, dn\,, \tag{9}$$

where the second formula is obtained by eliminating dx with the aid of Eq. (6). $\Delta\omega(n) = \omega(n) - \omega(n_l)$.

Equation (9) illustrates the fact that the broader an interface, i.e., the slower the density change across the interface, the smaller the tension. And, by referring to Fig. 1 in which the function $\Delta\omega(n)$ is shown as a function of n, one sees that low tensions occur as the temperature approaches the critical point and the free energy surface of homogeneous fluid flattens out between the minimal characteristic of phase equilibria.

For a planar system, gradient theory yields the following relationship between the transverse pressure P_T (measured with a transducer whose normal lies in the interfacial plane) and the normal pressure P_N (measured with a transducer whose surface lies in the interfacial plane):

$$P_T = \frac{1}{3} P_N + \frac{2}{3} P_o(n)\,. \tag{10}$$

$P_o(n)$ is the pressure of homogeneous fluid at density n. The tension can also be computed from

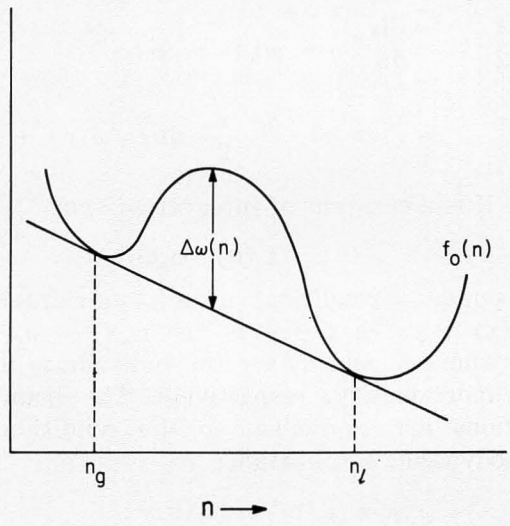

FIGURE 1. Illustration of tension determining function $\Delta\omega(n) = \omega(n) - \omega(n_l)$ of a one-component fluid. $f_o(n)$ is the Helmholtz free energy density of homogeneous fluid.

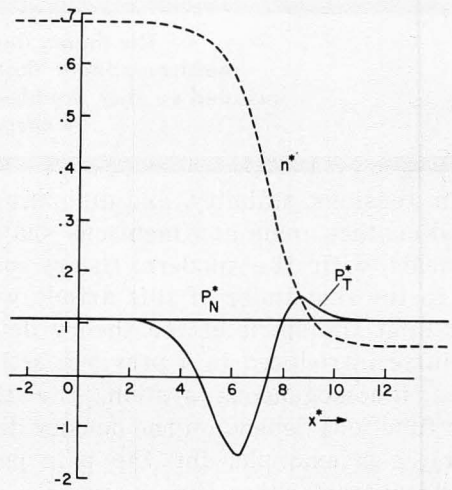

FIGURE 2. Profiles of density, normal pressure, and transverse pressure across a planar interface of a Van der Waals fluid at $T^* = 0.223$. $n^* \equiv nb$, $P^* \equiv Pb^2/a$, and $x^* = x\sqrt{a/c}$.

the formula

$$\gamma = \int_{-\infty}^{\infty} (P_N - P_T)\, dx\,. \tag{11}$$

In Fig. 2, the density profile and the pressure component profiles are shown for a planar interface of a VDW fluid. From the curves we observe that the interfacial zone is under tension (P_T actually negative) on the dense side of the interfacial zone and is under compression ($P_T > P_N$) on the dilute side of the zone. This behavior seems typical of low temperature fluids for which the pressure isotherm $P_o(n)$ goes through negative values in the Van der Waals loop. Experimentally, the magnitude of tension and the fact that it increases with decreasing temperature imply that P_T has to have a region of negative values at sufficiently low temperatures. Formula (10) brings out the fact that the values of $P_o(n)$ in the spinodal region are physically meaningful and contribute importantly to interfacial structure and tension.

Other fluid microstructures can be obtained by using different boundary conditions. For example, planar thin films result with the boundary conditions $dn/dx = 0$ at $x = 0$ and $n \to n_B$ as $x \to \pm\infty$. Liquid crystals result from periodic boundary conditions. Drops and bubbles are obtained by assuming n to depend only on the radial distance r from their centers. For this case

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of six students returned to the United Kingdom. They spent about a week at the University College of Swansea and another week at Imperial College in London. This year's group consisted of four men and two women. As before, two weeks were available for independent travel. At Swansea the group's tutor was again Dean Hopkins and this year's topic was an evaluation of competing zinc smelting processes. At Imperial College the group's tutor was Dr. Stephen Richardson (no relation to Professor Richardson at Swansea) and there they were concerned with a computer controlled set of adsorption-desorption columns.

We plan to continue the program again this year, keeping the group size at about five or six. This seems to be an ideal size. It is large enough so that the tutor can lecture without feeling foolish, and at the same time it is small enough to be invited into someone's home. The students are unchaperoned and no academic credit is given. This format obviously places a high level of responsibility upon the individual student and calls for initiative and good judgment on their parts.

THE DEPARTMENT'S ASSESSMENT

WE FEEL THAT THE PROGRAM allows our students to penetrate the veneer of ordinary tourism and to interact in a meaningful way with teachers and students from a different culture. To be successful, a program such as this requires a group of highly capable students and we currently have these in unprecedented abundance. We are happy to be able to give recognition to these very fine students and we think that our funds are very wisely spent. □

ACKNOWLEDGMENTS

By way of acknowledgment, we wish to thank our industrial sponsors for their generous support. They have been enthusiastic in support of our use of a fraction of their awards for this program. The supporting firms have been: Diamond Shamrock, Du Pont, Mobil, Ethyl, Shell, Celanese, Exxon, Union Camp, and Union Carbide. Dean Paul Torgersen has generously supported the program from his discretionary funds. Dr. Henry McGee, the department head, has been an enthusiastic supporter of the program as has Dr. Peter Rony, a member of our departmental honorifics committee. Dr. Rony received an award of a somewhat similar type as an undergraduate at Caltech, and he has been an enthusiastic and valuable resource in the planning of our programs. Finally, we would recognize the very fine students who have received the awards. We have placed great confidence in them and they have acquitted themselves well.

MOLECULAR THEORY

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$\nabla^2 n = \frac{d^2n}{dr^2} + \frac{2}{r}\frac{dn}{dr}$ and the boundary conditions for Eq. (5.5) are $\frac{dn}{dr} = 0$ at $r = 0$ and $n \to n_B$ as $r \to \infty$. In the limit of large drops and bubbles the pressure difference ΔP between inside and outside obeys the Young-Laplace equation $\Delta P = 2\,\gamma/R$, R being the drop radius. As the drops become smaller the above theory shows that this relationship fails, the pressure difference being greatly overestimated by the Young-Laplace equation.

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In Memorium

Fred N. Peebles

Dean Peebles was born on April 4, 1920, in Paris, TN. His technical education started at Memphis Technical High School and advanced through bachelors, masters and Ph.D. degrees in ChE at the University of Tennessee. He served engineering education extraordinarily well as professor, department chairman and dean at the U. of Tennessee. During his career, he received numerous awards for his contributions to the University, the community and the engineering profession. He was a member of numerous professional and honorary societies and was the author of many scientific articles. His generosity of spirit infused his institutions' commitment to expanding dramatically the opportunities for minorities to enter the engineering profession. Loved by faculty and students alike, Fred gave unstintingly of himself in assuring their proper development and personal well-being.