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Book Review: *Molecular Theory of Capillarity*

Molecular Theory of Capillarity. By J. R. Rowlinson and B. Widom

The phenomenology of the interface between two fluids or between a fluid and substrate has a venerable history, but the microscopic theory behind the phenomena has advanced erratically. The field is certainly in a state of flux, with no dearth of unanswered questions, both qualitative and quantitative. Perhaps the leading question is to what extent it is a new field at all. Of course, the equilibrium theory is universally accepted as emanating from mean values generated by use of the N-particle Boltzmann factor—as is that of bulk fluids. But to what extent does the knowledge of thermodynamics and low-order distributions in bulk fluids—there is a great deal and it is reliable—imply the characteristics of interfacial states? At the lowest level, can one get reliable energetics—surface tension, curvature effects, three-phase conformations, . . . in this way? In a more detailed fashion, is there an array of possibilities for transition density profiles, including oscillatory, or is this merely a quantitative problem, affected only marginally by thermodynamic parameters and mechanical ones such as curvature? Are there physically discernible aspects—such as capillary waves—which harbor most of the observed effects, and can these be isolated in special circumstances, such as the critical region? Are questions as to the existence of the thermodynamic limit merely pedantic or indicative of basic problems?

All of these questions are touched upon, and intelligently treated in a largely unified fashion, in the book under review. It suits our collective ego to observe that quantitative progress in the last few years has eclipsed that of the preceding century, but it is only fair to recognize that the basic ideas, with few exceptions, were quite explicit in the work of Van der Waals a century ago. The authors, past and present masters of the statistical mechanics of real fluids, present here a relaxed and balanced account of the field from its inception until very recent times, emphasizing the Van der Waals picture, but with good coverage as well of the less than earth-shaking modifications needed to round it out.

The text may be regarded as informally organized into three units:

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phenomenology and empirical theory of the interface, approximations based upon exact statistical mechanics, and extension to three-phase and critical phenomena. The first unit opens of course with a historical review of the concepts involved in capillary effects and the experiments through which an understanding was arrived at. The level of understanding rapidly progresses to the microscopic, albeit at a mean field level, and that in its primitive static form. The second chapter focuses on the more reliable thermodynamic viewpoint, depending as it does on the general structure of statistical mechanics, affirming the existence of, but leaving open the explicit functional form of the basic free energies to be filled in by experiment and ultimately by detailed theory. Questions that naturally arise include the dependence of surface tension on curvature and the nominal location of the interface—both going back to Gibbs—and interpretations that naturally arise including the concept of local energy density to describe a highly nonuniform fluid. In Chapter 3, the emphasis returns again to the microscopic picture of Van der Waals, establishing with care the excess free energy density that is so basic to all of these considerations, and which is used thereafter in the text. The nonuniformity correction in square gradient form is introduced and the two amalgamated in a surface tension computation. The chapter is a bit rambling in a surface tension computation. The chapter is a bit rambling and discursive, but that is responsible for its charm. Included is a nice generalization of local free energy density to a function of particle density and entropy density as well, and the contribution of this picture to phenomenology is sketched.

In the second unit of four chapters, the treatment becomes more quantitative and attuned to a modern statistical mechanical viewpoint. It starts with a standard review of distribution functions in nonuniform fluids, both in canonical and grand canonical format, including, however, the nonstandard item of potential distributions. Density functional methods are presented, without the reader being warned that although a change in free energy is path independent, approximations tend not to be, allowing a clever practitioner to get almost any answer he wants. Alternative definitions of surface tension are set forth and their equivalence demonstrated, with the usual cavalier treatment of boundary conditions. Dynamics is introduced in this derivation for the first and only time (it is not really necessary here), but not in the topic of capillary wave fluctuations. Application to both planar and spherical surfaces is made.

The next chapter is this group descends from the in-principle stratosphere of exact statistical mechanics, via the mean field approximation for which the potential distribution method is a natural vehicle. After analyzing the Van der Waals hard-core-plus-long-tail fluid from this viewpoint, the authors focus on the lattice gas, two-component lattice gas in Bethe–Guggenheim approximation, and Widom–Rowlinson penetrable sphere model, as examples in which the empirical behavior studied previously arises more reliably from approximations to exact microscopic theory. Since experimental evidence for the detailed microscopic structure is so meager, they next turn to evidence from the computer simulation, presenting a brief but quite complete survey of conclusions on surface thickness, profile, and surface tension arrived at in this fashion. It is then reasonable to return to more detailed analytic approximations to the form of the interface. This is first done by a YBG equation closed by inserting locally uniform radial distributions at variously defined bulk densities, then via nonuniform linear response and free energy density functionals with approximate direct correlation inserted, and via PY and modified Van der Waals approximations. The resulting profiles are all too thin, giving evidence for the omission of capillary wave effects in every approximation. Finally, a neat discussion of perturbation methods and resulting surface tension is presented.

The concluding section of the book consists of two chapters in which more complex, and more interesting, phenomenology is introduced. First, there is the matter of three-phase equilibrium, with its associated contact line, and the degenerate limit of Antonow spreading, in which one phase appears not as bulk fluid but just as a separating film. The nature of the profile is now investigated by multiphase Van der Waals models, as is the possibility of interfacial transitions, e.g., the Cahn transition, for two- and three-phase equilibria. Application is made to the computation of line tension. The second and final chapter provides a comfortable entree into the very active field of interfacial behavior in the critical region. This is examined primarily via critical region extension of the mean field Van der Waals approach, and applied as well to critical end points and tricritical points. The barest elements of renormalization group theory are included.

In summary, this text is a rather successful attempt at organizing for the uninitiated—without boring the expert—a field which is in somewhat of a disorganized state. The vehicle employed by the authors is the unsurprising one of Van der Waals theory with both its qualitative and quantitative implications, but the fashion of its use is impressively uncluttered and effective. The authors pay much more than "lip service" to numerous other approaches that have been suggested. Their hearts seem, however, not to be in this, and—I would guess—they rely mainly on second-hand reports on such work. In general, I find the degree of accessibility of the text unusually high, and would recommend it not only to those entering the field, but as supplementary reading for any student interested in the fluid state.

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