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Translation of J. D. van der Waals' "The Thermodynamic Theory of Capillarity Under the Hypothesis of a Continuous Variation of Density"[1]

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Van der Waals justifies the choice of minimization of the (Helmholtz) free energy as the criterion of equilibrium in a liquid–gas system (Sections 1–4). If density ρ is a function of height h then the local free energy density differs from that of a homogeneous fluid by a term proportional to $(d^2\rho/dh^2)$; the extra term arises from the energy not from the entropy (Section 5). He uses this result to show how ρ varies with h (Section 6), how this variation leads to a stable minimum free energy (Section 7), and to calculate the capillary energy or surface tension σ (Section 9). Near the critical point σ varies as $(\tau_k - \tau)^{3/2}$, where τ_k is the critical temperature (Section 11). The paper closes with short discussions of the thickness of the surface layer (Section 12), of the difficulty of assuming that ρ varies discontinuously with height (Section 14), and of the possible effect of derivatives of higher order than $(d^2\rho/dh^2)$ on the free energy and surface tension (Section 15).

KEY WORDS: Capillarity; critical point; free energy density; surface tension.

TRANSLATOR'S INTRODUCTION

The rise of a liquid in a capillary tube is one of the more striking manifestations of the existence of attractive forces between the ultimate particles of matter, and attempts to explain it in these terms go back to the work of Young, Laplace, and Gauss in the early years of the last century. The problem was taken up again by Maxwell$^{(1)}$ in 1876 in his essay on "Capillary Action." Their work shows great theoretical ingenuity and led to essentially correct estimates of the intermolecular energy of liquids, but it suffers from

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two defects. First, the gas–liquid surface was supposed to be a step function in the density, thus restricting the treatment to liquids near their triple points, and second, it was based on an essentially static or mechanical view of matter. The ultimate particles or molecules were mutually interacting entities at rest in an equilibrium state of minimum energy. The first defect was criticized by Poisson as early as 1831, but was not fully eliminated from the Laplace–Maxwell treatment until 1892, when Lord Rayleigh(2) turned his attention to the problem. (Maxwell's brief discussion(1) of continuous density profiles does not lead to any useful results.(2))

Van der Waals' paper of 1893 was the first to attempt to remedy both defects; he allowed density to be a continuous function of height and he used thermodynamic rather than purely mechanical arguments. In this seminal paper we can see not only the origin of much of the work of the last twenty years on the theory of the gas–liquid surface, but also the first attempt, however crude, at developing a thermodynamic treatment of nonuniform systems in general. The essential postulate is a free-energy density which (at a fixed temperature) is determined not only by the local density ρ but also by the density at neighboring points. Hence the local free-energy density can be expressed in terms of ρ and its spatial derivatives at the same point. Like most of his work, it was well-received at the time, but grievously neglected(3) in the forty years after 1914.

In 1958 Cahn and Hilliard(4) rederived the same results in a more modern guise. In the last twenty years this approach has been the foundation for much of the work on the statistical thermodynamics of nonuniform systems,(5–8) including not only surface tension,(7–13) and its behavior near the critical point,(14) but also such related topics as wetting,(15) nucleation,(16,17) spinodal decomposition,(18) and liquid–liquid interfaces.(19) (The references cited are representative, not exhaustive.) This wealth of modern work justifies a translation of the now classic paper of 1893.

The paper itself presents little difficulty for the modern reader, but a few explanations may help. It was first published in Dutch in 1893 by the Royal Academy of Sciences in Amsterdam,(20) but I have not used this version, since I know no Dutch. A translation into German(21) by Ostwald appeared in 1894 and an anonymous translation(22) into French (possibly by van der Waals himself) in 1895. The two translations differ in detail and both contain material not in the original Dutch. The German version generally includes more of the algebra than the French, particularly in Sections 7 and 10. This translation is based on both, but is closer to the French, since this is the shorter. In view of the considerable algebraic differences of these two versions, I have not scrupled to make further rearrangements of some of the equations, particularly by referring back to previous equations by number instead of rewriting them in full.

In Sections 5 and 14 the author discusses the paradox that the sharp surface of Laplace leads to an energy, and so to a surface tension, with a term proportional to the first moment of the intermolecular potential, while the assumption of a continuously variable density leads to the second moment. Lord Rayleigh(2) had previously resolved this paradox within the static treatment of the problem. Modern work(6–9) replaces the moments of the potential by those of the direct correlation function.

In Section 7 van der Waals notes that local densities that exist within the surface layer would be unstable as a homogeneous phase. This point was made first in 1871 by J. Thomson(23) in his discussion of Andrews' work on critical phenomena.

The relation of van der Waals' work to Gibbs' purely macroscopic treatment of 1875–7 is fully discussed in the text. I have supplemented the page references to Gibbs' original paper(24) by adding, in square brackets, the page references in Volume 1 of the more accessible *Collected Works*.(25)

The Appendix describes what we should now call corrections to the mean-field theory. The author uses the term *kinetic* to denote a distribution in which configurations are weighted with the appropriate Boltzmann factor. The original translations have four further Appendices, which are here omitted. (There are no Appendices in the Dutch version.) The second and third contain further discussion of the principle of corresponding states for surface tension near the critical point, extensive tables of the experimental results of others, and an inconclusive discussion of the critical-point exponent of the surface tension. His mean-field theory gives this as 3/2, but the experimental results obstinately lie between 1.2 and 1.3. The fourth Appendix contains further discussion of the "complete differential equation" of Section 15, and the fifth a detailed study of some special cases implied by the potential function $\psi(u) = \exp(-u/\lambda)$ of Sections 12 and 15.

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THE THERMODYNAMIC THEORY OF CAPILLARITY UNDER THE HYPOTHESIS OF A CONTINUOUS VARIATION OF DENSITY

J. D. van der Waals

1. INTRODUCTION

Laplace considered capillary phenomena to be in the domain of statics. Gauss shared this idea; it was by applying the principle of virtual velocities, which allows us to find the conditions of equilibrium in statics, that he was able to formulate the laws of these phenomena. Neither author supposed that the molecules were in thermal motion either in the body of the fluid or in the boundary layer; and if we recall the era in which their theories were developed, this should not surprise us. The molecules for them are therefore at rest; and if this is really the case then the phenomenon is purely static.