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★**How fluids unmix.**

Discoveries by the school of van der Waals and Kamerlingh Onnes.

History of Science and Scholarship in the Netherlands, 4.

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It is a bit unusual that an important theory in physics develops essentially in a small-sized country, thanks to several first-rate scientists. This happened in the Netherlands, during the period that was later called a “second golden age” (the first one being that of painters, sailors and traders). As explained in this book, the second golden age was boosted by an ambitious educational reform. This observation would be useful nowadays in developed countries.

The main heroes of this volume are two physicists, Johannes Diderik van der Waals (1837–1923, Nobel prize in 1910) and Heike Kamerlingh Onnes (1853–1926, Nobel prize in 1913), and a mathematician, Diederik Johannes Korteweg (1848–1941). Other prominent figures are Jacobus Henricus van’t Hoff (1852–1911, Nobel prize in 1901), Willem Hendrik Keesom (1876–1956), Johannes Petrus Kuenen (1866–1922) and Johannes Jacobus van Laar (1860–1938). Among non-Dutch players, one should cite J. C. Maxwell, J. W. Gibbs and L. D. Landau.

The story begins in 1873, with van der Waals’ thesis. After experimental observations by T. Andrews, and inspired by Gibbs’ rule of phases, van der Waals realized that an appropriate non-convex energy of a fluid may be used to identify the possible liquid-vapor equilibria: at a given temperature, they are given by bi-tangents. In either P-V or P-T variables, this yields bi-tangent planes to the graph of corresponding energies. In addition, he provided the first theoretical derivation of a non-monotone equation of state, giving rise to a non-convex energy by integration. For this purpose, he made two hypotheses. First, the molecules display an excluded volume, below which no compression is possible. The second is a mean-field assumption, which turned out to be a matter of controversy when more and more accurate experiments were made near criticality.

Van der Waals’ thesis was revolutionary in many respects. At the time it was written, the molecular structure of fluids had not been accepted by most physicists, and liquid and vapor were often considered as chemically distinct. Treating both phases as a unique fluid was not in the XIXth century style. Next, an important by-product of van der Waals’ thesis was universality: Every fluid must have a liquid and a vapor phase below some critical temperature, and all fluids display similar behaviour around their critical points, after appropriate rescaling. This went against the common belief at a time when many gases were believed to be “permanent”, that is, unable to liquefy. The reason for this belief, which seems absurd nowadays, is that these gases have a critical temperature much lower than 0°C. For instance, oxygen ($T_c = 155$ K) was considered permanent, while carbon dioxide ($T_c = 304$ K) was not. A very important consequence of van der Waals’ universality was the possibility to evaluate, with reasonable accuracy, the coordinates of the critical point for every fluid, by extrapolating from a small amount of data. This allowed experimenters to calibrate their

apparatus when trying to liquefy various fluids. The experimental side of this story culminated with the liquefaction of hydrogen ($T_c = 33$ K) by J. Dewar in 1898 and of helium ($T_c = 5.189$ K!) by Kamerlingh Onnes on July 9, 1908.

The role of van der Waals is considerable also from the mathematical perspective. As explained above, he introduced mathematics into the physics of phase equilibrium, and therefore allowed for calculations and prediction. His equation of state extends the perfect gas law $PV = RT$ of Boyle and Gay-Lussac to denser configurations (of course, the perfect gas law could not explain liquids and phase equilibria). The reviewer's opinion is that van der Waals introduced nonlinearity in the physics of fluids, long before mathematicians themselves turned to nonlinearity in most subjects, and even before Einstein considered a nonlinear universe!

To dampen our enthusiasm, one must say that the fluid continuity, from liquid to vapor through super-critical fluid, was not invented by van der Waals and had already been postulated. However, this fundamental property of fluids had contradictors till the middle of the XXth century.

The success of his theory led van der Waals to consider fluid mixtures instead of pure components. It was a somewhat smaller step, as it amounted to introducing one more variable (a molar concentration) in the energy. Here again, the core of the theory was a passage from the "linear" laws of Dalton and Raoult, valid at small densities and concentrations, to a nonlinear context. This generalization turned out to be extremely rich and fruitful; the list of industrial applications of this theory is endless. At least, at a theoretical level, let us mention the prediction by Kuenen of retrograde condensation, when the mixture is composed of two fluids with very different critical pressures, but similar critical temperatures. Another corollary of practical importance is azeotropy, according to which one cannot obtain a pure component by distillation; for instance, the system water-alcohol can provide only a 96% pure alcohol at atmospheric pressure. Raoult's law did not allow azeotropy.

Since this review is written mainly for mathematicians, it is fair to speak of the role played by Korteweg. The reader must first forget about the KdV equation, since it does not matter here. What Korteweg did was carry out a systematic study of the double tangent planes to a surface, say the graph of an energy. Below the critical point, an analytic mathematical surface develops a fold, called a plait, an old Dutch word, by the Dutch school. This could be translated as "fold" in English, or "pli" in French. A double tangent plane defines two tangency points called connodes. The plait is bounded by the locus of the connodes, the connodal, presently called the coexistence curve. Between two associated connodes is a tie line. A plait ends where the tie line shrinks to a point (the plait point, now called the critical point). Korteweg's systematic study, and his Taylor expansion of Helmholtz energy near the critical point, led van der Waals to define critical exponents. In spite of its fundamental importance, this notion was much criticized because of experimental evidence that the theoretical exponents were wrong. However, experiments and measurements near the critical point are extremely difficult, and Kamerlingh Onnes spent several years in disproving wrong explanations. The mean-field assumption, which is too crude to represent faithfully a fluid near its critical point, was the actual cause of this discrepancy. Van der Waals himself, with De Vries and Ramsey, participated in the experimental discovery of irrational critical exponents, which are now explained through statistical mechanics.

Because of his work on parameter-dependent energies (useful in the physics of mixtures), Kor-

teweg should be considered the creator of the theory of deformations of analytic surfaces. He therefore opened the door to the theory of singularities, including catastrophe theory. Much of his work was lost and rediscovered, particularly by Landau in the context of ferromagnetism, where the critical point bears the name “Curie-Weiss point”.

Nowadays, the name of van der Waals remains popular among mathematicians working on conservation laws and compressible fluid dynamics. However, the trend is now to study dynamical effects rather than equilibrium properties. For this purpose, one has to incorporate the energy of capillarity, again a concept due to van der Waals. Then the interfaces become irreversible, and the liquid-vapor parameters across them may differ significantly from “connodes”. The interested reader may consult papers by Slemrod and colleagues, by Truskinovski, by Benzoni-Gavage and others. To mention just one entry point, see [H. T. Fan and M. Slemrod, in *Handbook of mathematical fluid dynamics, Vol. I*, 373–420, North-Holland, Amsterdam, 2002; [MR1942467 \(2003j:76085\)](#)].

Above all, I found the book extremely well written and informative. I learnt a lot, including at a scientific level. All the facets of the development of this body of scientific knowledge are presented, including the personalities of scientists and the controversies that sometimes arose between them. I recommend this book to any mathematician interested in the development of mathematical ideas in physics, and to anyone working on mathematical models of phase transitions. It seems to me that such a book could help in narrowing the gap between physicists and mathematicians.

Reviewed by *Denis Serre*

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