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Book Review: *On the Continuity of the Gaseous and Liquid States*

On the Continuity of the Gaseous and Liquid States. J. D. van der Waals. Edited with an Introductory Essay by J. S. Rowlinson. Volume XIV of Studies in Statistical Mechanics. North-Holland, Amsterdam, 1988. xiv + 301 pp. $84.25.

The kinetic theory of gases has been part of physical science for a quarter of a millenium—Daniel Bernouilli first published the modern (elementary) version in 1738. The famous dissertation of Johannes Diderik van der Waals (1837–1923), which appeared in 1873, thus belongs to the mature phase of our subject rather than its childhood. By 1873 the basic assumption of the theory—that gas pressure is primarily due to molecular impacts rather than to long-range forces or a "caloric" heat fluid—had been given a firm foundation by Rudolf Clausius and James Clerk Maxwell. The principles of energy conservation and thermodynamics, generally accepted by scientists after the 1850s, suggested that heat is related to molecular motion; Clausius and Maxwell went further by showing that many properties of gases could be explained by assuming that the space occupied by the molecules (or in which they exert forces) is much smaller than the volume filled by the gas. One might suppose, with hindsight, that removing this assumption would be a logical next step in the development of the theory.

From this point of view it is surprising that the important task of extending the kinetic theory to dense gases and liquids was effectively begun not by Clausius, Maxwell, or one of their students, but by a 35-year-old Dutch schoolteacher, largely self-educated in advanced physics. In his introduction to this new edition of van der Waals' thesis, J. S. Rowlinson shows how the thesis and its later development depended heavily on the work of Clausius and Maxwell, but also notes that these two brilliant theorists both failed to understand on first reading the simple argument for the factor of 4 in the co-volume term b/v. Perhaps one should make some allowance for their unfamiliarity with the Dutch language, but the fact remains that they were scooped by a newcomer on a simple result in their own field of expertise and failed to confirm this result when given the opportunity.

But van der Waals' treatment of the effect of finite molecular size —that is, of short-range repulsive forces—was less significant than his incorporation of a term representing longer-term attractive forces into the equation of state. Here he relied more on an intuitive understanding of how these forces would affect the properties of a liquid, inspired by Laplace's theory of capillarity, than on rigorous mathematical derivation of the consequences of a well-defined hypothesis. In fact, the a/v^2 term in the van der Waals equation cannot be derived from any physically plausible attractive force law, but only from an artificial force that decreases very slowly at large distances, as was pointed out by Ludwig Boltzmann and confirmed much later by Kac, Uhlenbeck, and Hemmer. But van der Waals' equation of state belongs in that small, serendipitous set of results that are much better than the premises from which they are deduced. They are sometimes dismissed as "semiempirical" because of their near coincidence with experimental data and apparent lack of theoretical foundation. But at least in this case the theoretical foundation is both respectable and amenable to further development, as Rowlinson shows.

Nevertheless, it was just by stopping at a b/v approximation for molecular size effects and an a/v^2 approximation for the effect of attractive forces that van der Waals was able to arrive at an equation that could be easily solved (as a cubic in v) and thus led directly to such startling consequences. As the title of his thesis indicates, the equation was able to describe the continuity of gases and liquids above the critical point, as well as giving a qualitative indication of the nature of the critical point itself. With the help of Maxwell's construction, one could also see how the system makes a discontinuous transition between gas and liquid below the critical point. Van der Waals thus created the first molecular thery of phase transitions. That his theory was not mathematically rigorous is less significant than its use of the *same model of a molecule* for both gases and liquids. This is now a commonplace, but it was not so in the 19th century [see the article on "liquidons" and "gasons" by J. M. H. Levelt Sengers, *Physica* **98A**:363 (1979)].

By showing that the property of being gaseous or liquid might be mathematically derived from a single model of molecules that are individually neither gaseous nor liquid, van der Waals refuted in advance a philosophical thesis that has become popular in some circles in the 20th century. According to this thesis (sometimes called "holism"), there are different levels of complexity in nature, and one cannot expect to "reduce" phenomena on one level to those on a lower (more fundamental) level because there are certain principles that come into operation only at higher levels. Thus, for example, biology cannot (or should not) be reduced to chemistry, psychology cannot (or should not) be reduced to biology, and so on. Reducing the properties of a macrosystem (gas, liquid, or solid) to those of a microsystem (atoms or molecules) is a prime example of an impossible (or at least improper) enterprise—according to this thesis. It is, of course, just what statistical mechanics is all about. From a philosophical viewpoint, van der Waals was one of the great reductionists.

As a classic of science, *Continuity* deserves to be readily available in an accurate translation of its original edition. Up to now, those of us who do not read Dutch have had to rely on an English translation of Friedrich Roth's substantially modified German translation of the thesis. Rowlinson has eliminated Roth's additions and restored sections of the original that were omitted by Roth, in an attempt to bring the English version closer to the Dutch text of 1873. I am not qualified to judge the accuracy of the translation from Dutch, but I am nevertheless delighted that it is available. In addition, Rowlinson has included a new English translation of an 1890 paper by van der Waals on mixtures, which had been included in the second German edition of the thesis.

This book is a substantial contribution to the documentation of 19th century physical science and should certainly be purchased by the library of every respectable university and scientific institution. But in his 92-page essay on "Van der Waals and the physics of liquids," Rowlinson addresses not so much the historians of science, but instead contemporary physicists, physical chemists, and chemical engineers, who still, he says, can learn something from van der Waals. He traces the development of liquid theory (including mixtures and phase transitions) through the 1970s, arguing that scientists were seduced away from the true path by lattice theories and have only recently returned to the more effective approach of van der Waals. Modern practitioners of statistical mechanics will enjoy this exposition, but will also be provoked into disputing some of its claims. If so, Rowlinson will have succeeded in producing not just an impressive monument but a living memorial to a great scientist.

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