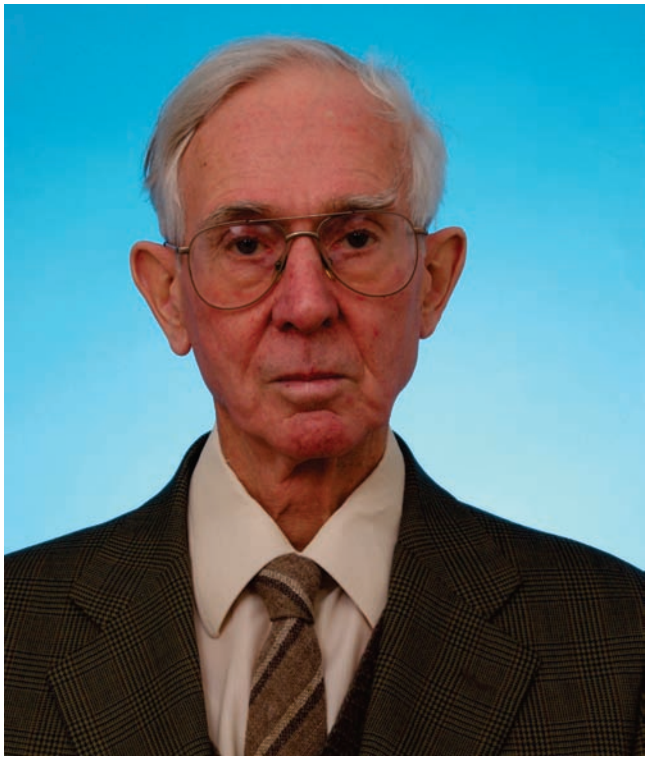

Preface to the Sir John S. Rowlinson Festschrift

This special issue of the *Journal of Chemical and Engineering Data* is in honor of Sir John S. Rowlinson, in recognition of his profound and widely influential contributions to the chemical sciences and technology. Among these are his defining studies of liquids and liquid mixtures by the methods of thermodynamics and statistical mechanics, including the phase transitions and critical points of multicomponent fluids and the structure and tension of the interfaces between phases, and his classic expositions of the content and history of these subjects. He is at present the Dr. Lee's Professor of Chemistry Emeritus at Oxford.

John Rowlinson was born May 12, 1926, in Handforth, Cheshire, U.K. His university education was at Trinity College, Oxford, where he earned a first-class honors B.A. in Chemistry in 1947 and a B.Sc. in 1948 and where he remained for his M.A. and D.Phil., the latter granted in 1950. He went soon after to the United States as a postdoctoral research associate at the Naval Research Laboratory of the University of Wisconsin, in the research group of J. O. Hirschfelder, where he collaborated with C. F. Curtiss on lattice theories of liquids. He returned to the U.K. in 1951, first as an ICI Fellow at the University of Manchester and then as Lecturer and Senior Lecturer there. He moved to Imperial College London (IC) as Professor of Chemical Technology from 1961−1973. It was there, in 1969, that the present writer first collaborated with him, on a project to be described presently. In 1974, Rowlinson was called back to Oxford as the Dr. Lee's Professor of Chemistry, where he followed in the succession from Hinshelwood to Richards to Dainton and from which he retired in 1993. He became Sir John Rowlinson, Knight Bachelor, in 2000.

It should be noted that Rowlinson's contributions to the physical and chemical sciences have not been limited to the papers and books he has written, important and influential as they have been. He has also contributed valuably and tirelessly to science administration in the U.K. As department head in Oxford, he greatly expanded the reach of physical chemistry from its historical strengths in gas-phase spectroscopy and kinetics to include major efforts and advances in the study of condensed phases. He has been President of the Faraday Division of the Royal Society of Chemistry, a Founding Fellow of the (now) Royal Academy of Engineering, Physical Secretary and Vice President of the Royal Society, Vice President of the Royal Institution, and a Member of Council of the British Society for the History of Science. He has been editor of the journal *Molecular Physics* and was the first editor of the Oxford University Press International Series of Monographs in Chemistry. He is called on to serve wherever the requirement is for boundless energy and rare wisdom.

His first research works were mostly experimental, although with keen knowledge of and appreciation for the associated theory. With his Ph.D. supervisor J. D. Lambert, he measured ultrasonic dispersion in gases, which Lambert had himself learned from the then great expert A. Eucken in Göttingen. (Lambert had been sent there by his own Ph.D. supervisor, Hinshelwood, and later succeeded Hinshelwood as chemistry fellow at Trinity, so Rowlinson's ultimately inheriting Hinshelwood's chair was genetically predetermined.) During his work with Lambert, Rowlinson was required, as were all of Lambert's students, to learn glassblowing. He denies having ever become an accomplished glassblower, but that is probably out of

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modesty, for anything he undertakes he learns to do with superb technical facility.

Late in his Manchester days, with his student P. I. Freeman, he determined lower critical solution temperatures (LCSTs) in solutions of hydrocarbons with large discrepancies in molecular weight. The mutual solubility of the two components thus increases with decreasing temperature, and the two are completely miscible at lower temperatures. In the earliest of these studies (1960), they found that almost every solution of a hydrocarbon polymer in a hydrocarbon solvent has such an LCST. This included the remarkable case of polyisobutene + benzene, where they found an LCST at 160 °C, while an upper critical solution temperature (UCST) in that system at 23 °C was already known at the time; thus, an upper critical solution point lying lower in temperature than a lower critical solution point. These studies of LCSTs continued after his move to IC, with his student A. J. Davenport and joined later by then research fellow Graham Saville. They studied solutions of hydrocarbons in which methane was the low-molecular-weight component. A particularly striking example proved to be methane + hex-1-ene, with an LCST at 180 K and a UCST at 134 K. Phase equilibria and critical solution points are prominent subjects in Rowlinson's now classic *Liquids and Liquid Mixtures*, the first, second, and third editions of which (the last with F. L. Swinton as coauthor) originated from his time in Manchester, Imperial College, and Oxford, respectively. At a famous meeting on critical phenomena in 1965 organized by M. S. Green and J. V. Sengers at the National Bureau of Standards (as it was then called) in Washington, D.C., Rowlinson was invited to review the status of experimental measurements of critical phenomena in fluids and their mixtures.

Phase transitions and critical phenomena were also the subject of the joint paper we wrote while the present writer was a visitor with John at IC in 1969. We studied a model we later came to call the "penetrable-sphere" model. In its "primitive" version, it starts as a two-component mixture in which like molecules do not interact at all while unlike molecules repel as hard spheres. At high total densities, the mixture then separates into two phases, each rich in one of the two components and poor in the other. At low total densities, there is only a single phase, so at some intermediate density there is a critical solution point. Then on integrating out the degrees of freedom of one of the two components, we have an equivalent one-component model of liquid−vapor equilibrium with intermolecular interactions wholly different from those in the original model, now including many-body forces and, unlike in the primitive version, with temperature as a significant variable. The model has attracted much attention, including that of mathematicians and mathematical physicists. In a collaboration with the mathematicians J. M. Hammersley and J. W. E. Lewis (1975), Rowlinson used the model as an example to illustrate an important problem of the statistics of functions of randomly distributed particles. He exploited the model for many further illuminating applications, such as to the structure of the interface between its coexisting phases. With his students in Oxford he wrote a series of papers on this (1976−1979), determining the status of local values of the chemical potential and of the energy and free-energy densities in the interface; the connection of the direct correlation function in the interface to the interfacial tension; and a searching test of the van der Waals theory of surface tension. In an important extension of the primitive version of the model from two to three components (1976, 1977), he determined and studied the model's triple points, critical points, tricritical points (where three previously distinct phases become one), and quadruple point (four-phase equilibrium). He wrote a most useful and scholarly review, "Penetrable Sphere Models of Liquid-Vapor Equilibrium", for volume 41 (1980) of the Advances in Chemical Physics series.

He has contributed in many other ways as well to our present understanding of interfaces, including the current theories and their relation to experiment. Again with Graham Saville, and with their students Gustavo Chapela and Stephen Thompson (1975, 1977), he was among the pioneers of computer simulations of interfaces, which is now a major research activity. With senior research assistant Dominic Tildesley and student Jeremy Walton, he confirmed by simulations that the normal component of the pressure tensor is constant through an interface, while demonstrating that the tangential component is not uniquely defined. The alternative definitions all yield the same value for the surface tension but locate the surface of tension at differing heights. This greatly clarified what until then had been a confused and contentious issue.

He made searching analyses of the Tolman curvature correction to the surface tension of small spherical drops, again including the penetrable sphere model for illustration. With Jim Henderson, he showed that in cylindrical symmetry, unlike in spherical symmetry, there is no well-defined Tolman length for the leading curvature correction to the surface tension. Rowlinson, and independently M. P. A. Fisher and M. Wortis, derived the critical-point exponents for the (weak) asymptotic divergence in the Tolman length of a spherical interface as the critical point of the phase equilibrium is approached. Rowlinson and Fisher had exchanged correspondence about this problem, and each of their papers, which appeared almost simultaneously, made reference to the other. This remains an area of intense interest.

Computer simulations of interfacial structure and tension and the applicability of the penetrable-sphere model for illustration of general principles were beautifully reviewed by Rowlinson in his Liversidge Lectures (*Chemical Society Reviews*, 1978). That year I was myself on leave in Oxford, officially attached to the Theoretical Chemistry Department, although my main scientific contact was with John in the Physical Chemistry Laboratory. At the end of my stay, he proposed that we write what ultimately became our monograph *Molecular Theory of Capillarity*. He was the driving force in our collaboration. The work is now a standard reference. Also, toward the end of my stay in Oxford, he showed me a translation he had made from the French and German versions of van der Waals's historic 1893 paper on surface structure and tension. With his permission, on my return to Cornell I called Joel Lebowitz, the editor of the *Journal of Statistical Physics*, and said, "John Rowlinson has translated van der Waals's great paper on surface tension", which is as far as I got when Lebowitz interrupted with, "We'll publish it!" Lebowitz knew Rowlinson from their earlier collaboration on the theory of hard-sphere mixtures and knew that anything John did would be of great interest and value.

It was already widely appreciated in the 1960s (and, indeed, anticipated by van der Waals almost a century earlier) that the structure of simple liquids is determined primarily by the strong repulsive forces between molecules at short distances and that molecules interacting with these forces alone provide a useful reference system in which the effects of the longer-ranged attractions may then be treated as perturbations. In early work, while he was still at IC, Rowlinson had the unique idea that the repulsions themselves, parametrized by a steepness parameter n (as in the repulsive term in a Lennard-Jones n−6 potential), could be treated as perturbations of a hard-sphere reference system ($n = \infty$) by an expansion in inverse powers of n. This proved to be eminently successful, with the first-order term alone yielding a remarkably accurate equation of state for gases at high temperatures and densities.

His broad interests have led him to range widely over the physical sciences. He has written on the theory of glaciers (1971). (He has had first-hand experience of these as a mountain climber; he has even climbed in the Himalayas as well as routinely in the Swiss Alps.) He has written on information theory and on the mathematical bases of rational decisions. In an important paper in *Nature* (1970) and an essay review in *Chemistry and Industry* (1971), he illuminated those subjects while noting some of their myths and irrationalities.

Although this account of John Rowlinson's scientific accomplishments has concentrated on some of his relatively early work, it should be noted that he has remained phenomenally productive of work of the greatest interest to and beyond the year of his formal retirement in 1993. As a few examples among many, on some of which he is the sole author and some in collaboration with students and colleagues, one may note: his study with Alberto Robledo of the distribution functions in the model of hard rods on a finite line (1986); the study of phase equilibria in mixtures of spherical molecules differing in size (1986); a charming paper on the various manifestations of the Yukawa potential in physical science and the relations among them (1989); computer simulations of adsorption of fluids in zeolites (1989, 1993); the mathematics of many-particle systems with repulsive interactions (1990); studies of systems with Gaussian Mayer f functions ("Gaussian" models; 1991−1993); the pressure tensor in nonuniform fluids (1991); the density of the grand-canonical potential in nonuniform systems (1993) and the thermodynamics of inhomogeneous systems (1993); a model of the "drying" transition (where an equilibrium vapor layer intrudes between a liquid and a solid substrate, 1994); the thermodynamics and statistical mechanics of curved liquid surfaces (1994); and a model of adsorption at the interface between fluid phases (1995).

It will be of interest to many readers of this journal that much of Rowlinson's work has contributed importantly to chemical technology, including (from his IC years as Professor of Chemical Technology) on the pedagogical side. He is the coauthor with his then IC colleagues Kenneth Bett and Graham Saville of the much used text *Thermodynamics for Chemical Engineers* (1975), which was published both in the U.K. and the U.S. His contributions to chemical engineering through his development of applicable theory and research on systems of technological interest were recognized by his having been chosen as the first Leland Lecturer at Rice University (1990), on which occasion he spoke on "The Prediction of Physical Properties—A Challenge to Chemical Engineers." He was also the Rossini Lecturer of the International Union of Pure and Applied Chemistry (1992) in recognition of his extensive contributions to chemical thermodynamics.

He has had a deep and longstanding interest in the history of science and has written on it extensively. His writings are notably scholarly and often entail translation from the French or German, as we saw in connection with his translation of van der Waals's 1893 paper. Together with Anne Garrett, he translated, with the title "The Metric System, a Critical Study of its Principles and Practice" (1969), the original French work by M. Danloux-Dumesnils.

He has written often about or in connection with van der Waals. In his "van der Waals revisited" (*Chemistry in Britain*, 1980) he explained for a wide scientific audience the content and significance of that 1893 paper on interfaces. No lesser word than masterwork would do to describe his edition (1988) of van der Waals's 1873 thesis, for which he also wrote a brilliant introductory essay—brilliant both as science and as history. He also appended to the edited version of the thesis his own translation of the German version of van der Waals's important 1890 paper on binary mixtures. He and coauthors Kipnis and Yavelov produced a full-scale scientific biography, *Van der Waals and Molecular Science* (1996).

Rowlinson's "Thomas Andrews and the Critical Point" (*Nature*, 1969), written on the centenary of Andrews's 1869 Bakerian Lecture, is a history of the subject that follows its progress through the almost 150 years from the first observation of a critical point by Cagniard de la Tour in 1822. He has written (2005) on the history of the Maxwell−Boltzmann distribution and very recently (2010) on Joule, Thomson, and the idea of the perfect gas. In his book *Cohesion* (2002), he describes with great scientific rigor and full technical detail the historical development of our present understanding of intermolecular forces and of how they are manifested in the macroscopic properties of matter. At a meeting of the American Chemical Society in Philadelphia in August 2008, Rowlinson received the Edelstein Award, the highest honor of the Society's Division of the History of Chemistry. His award address was entitled "Patrolling the Border between Physics and Chemistry."

He is author or coauthor of several books, five of which have been mentioned already: *Liquids and Liquid Mixtures* and *Molecular Theory of Capillarity*, both of which have been cited in the chemistry, physics, and engineering literatures more than 2000 times; the textbook *Thermodynamics for Chemical Engineers*; the van der Waals biography *Van der Waals and Molecular Science*; and *Cohesion*. In addition, there are *The Perfect Gas* (1963), of which his 2010 paper is a recent echo, and (as coeditor and the author of two of its seven chapters) *Chemistry at Oxford: A History from 1600 to 2005* (2009).

He has received many awards in addition to the ACS History of Chemistry Award already mentioned, including the Meldola Medal of the Royal Institute of Chemistry (1954); the Faraday Society's Marlow Medal and Prize, of which he was the first recipient (1956); the von Hofmann Prize for Chemistry of the Gesellschaft Deutscher Chemiker (1980); the Royal Society's Leverhulme Medal (1993); and an Honorary Medal of the Institute of Physical Chemistry of the Polish Academy of Sciences (1995). He was elected a Foreign Honorary Member of the American Academy of Arts and Sciences in 1994. He has given many named lectures and held visiting professorships, including, I am proud to say, at Cornell University, where he has been Mary Upson Professor of Engineering (1988) and A. D. White Professor at Large, the latter entailing several extended visits in the period 1990−1996.

I now close this account by commending the editors of the *Journal of Chemical and Engineering Data* for their wisdom in having chosen to honor John Rowlinson with this special issue.

B. Widom

Cornell University

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