Heike Kamerlingh—The Virial Equation of State

Jaime Wisniak*
Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

The main scientific contributions of Heike Kamerlingh Onnes (1853-1926) were on thermodynamics, the equation of state, and optical, magnetic, and electrical phenomena. Kamerlingh Onnes proposed the virial equation of state (a significant improvement over the one of van der Waals), extended the concept of corresponding states, performed brilliant work on the achievement of very low temperatures, studied the behaviour of materials at these low temperatures, and discovered the phenomenon of superconductivity. He was awarded the 1913 Nobel Prize for Physics for his investigations on the properties of matter at low temperature, which eventually led him to liquify helium in 1908.

Life and career
Heike Kamerlingh Onnes (Fig. 1) was born on September 21, 1853, in the University town of Groningen, The Netherlands; the eldest of the three sons of Heim Kamerlingh Onnes, owner of a roofing-tile factory near Groningen, and Anna Gerolina Coers of Arnhem, the daughter of an architect. He and his brothers were raised in a home where “all was made subservient to one central purpose, to become men”.

Heike took his secondary education at the “Hoogere Burgerschool” (a secondary school without classical languages), in Groningen and then received supplementary teaching in Greek and Latin, in order to gain admission to a Dutch University. In 1870 he entered the University of Groningen to study physics and mathematics and already at the end of his first year of studies he was awarded a gold medal for a prize essay “A Critical Study of Methods for Vapour Density Determination and of Results Obtained by these Methods in the Light of the Connection Between the Nature of Chemical Compounds and their Vapour Densities”, in a contest sponsored by the Natural Sciences Faculty of the University of Utrecht. The next year he won a Silver Medal for a similar event at the University of Groningen.

He obtained his “candidaats” degree (equivalent to a B.Sc. degree) in 1871 and then transferred to Heidelberg from October 1871 until April 1873, as a student of Robert Wilhelm Bunsen (1811-1899) and Gustav Robert Kirchhoff (1824-1887). While working with Kirchhoff he won the “Seminarpreis”, which entitled him to occupy one of the two existing assistantships in Kirchhoff’s private laboratory. Thereafter he returned to Groningen, where five years later (1878) he passed his “doctoraal” examination (equivalent to a M.Sc. degree) and a year after he obtained the doctor’s degree magna cum laude. In his thesis Nieuwe Bewijzen voor de Aaswenteling der Aarde (New Proofs of the Rotation of the Earth) Kamerlingh Onnes gave theoretical as well as experimental proof that Foucault’s pendulum experiment should be considered as a special case of a large group of phenomena which in a much simpler fashion could be used to prove the rotational movement of the earth.

*E-mail: wisniak@bgumail.bgu.ac.il
In 1878 he joined the Polytechnic School of Delft (which later became the University of Delft), working as assistant under Jan Boscha (1831-1911), and in 1881 he published a paper Algemeene Theorie der Vloeistoffen (General theory of liquids), which dealt with the kinetic theory of the liquid state looking at van der Waals’ law of corresponding states from a mechanistic point of view. This work can be considered as the beginning of his life-long investigations into the properties of matter at low temperatures.

In 1882, he was appointed to the first chair of experimental physics to be founded in The Netherlands at Leiden University, succeeding Peter Leonard Rijke (1812-1901). In his inaugural address in 1882 entitled: “De Beteekenis van het Quantitatief Onderzoek in de Natuurkunde” (The importance of quantitative research in physics) he put forward what was to become the motto of his research: “Door meten tot weten” (Knowledge through measurement), an appreciation of the value of measurements, against pure theoretical work. After this appointment, Kamerlingh Onnes reorganized the Physical Laboratory (now known as the Kamerlingh Onnes Laboratory) to suit his own research program. His researches were mainly based on the theories of Johannes Diderik van der Waals (1837-1923) and Henrik Antoon Lorentz (1853-1928). In particular he had in mind the establishment of a cryogenic laboratory, which would enable him to verify van der Waals’ law of corresponding states over a large range of temperatures. His efforts to reach extremely low temperatures culminated in the liquefaction of helium in 1908. Additional research areas which became well-known included thermodynamics, radioactivity, and observations on optical, magnetic and electrical phenomena, such as the study of fluorescence and phosphorescence, the magnetic rotation of the polarization plane, absorption spectra of crystals in the magnetic field, the Hall effect, dielectric constants, and particularly, the resistance of metals. An epoch-making discovery (1911) was that of the superconductivity of pure metals such as mercury, tin, and lead, at very low temperatures, and following from this the observation of persisting currents.

Kamerlingh Onnes and van der Waals had a strong mutual and positive influence, the opposite of the one that van der Waals had with Johannes Jacobus van de Sande Bakhuyzen (1845-1928) as the Professor of Experimental Physics at the University of Leiden undoubtedly owed much to the support of van der Waals who had been also offered the chair. Lorentz described Kamerlingh Onnes’s work using the words of Hermann Ludwig von Helmholtz (1821-1894) “When a science is in an advanced state the only one who can make fruitful experiments is one who is deeply versed in the theory and knows therefore how to frame the questions, and, conversely, the only one who can theorize successfully is the one who has great practical experience of experimental research.”

In 1887 Kamerlingh Onnes married Maria Adriana Wilhelmina Elisabeth Bijleveld, who would be a strong support for all his academic activities. They had only one child, Albert, who became a high-ranking civil servant at The Hague.

Kamerlingh Onnes’ health was always somewhat delicate and suffered constantly from bronchial problems. After a short illness, he died at Leiden on February 21, 1926.

Honours

Kamerlingh Onnes received many honours for his contributions to science and industry. Already at the age of 30 he was appointed a member of the Royal Academy of Sciences of Amsterdam and two years later he was appointed Rector Magnificus of the University of Leiden. He was one of the founders of the Association (now Instituut) International du Froid. He was a Commander in the Order of the Netherlands Lion, the Order of Orange-Nassau of the Netherlands, the Order of St. Olaf of Norway, and the Order of Polonia Restituta of Poland. He held an honorary doctorate of the University of Berlin and was awarded the Matteucci Medal, the Rumford Medal, the Baumgarten Preis and the Franklin Medal. He was Member of the Society of Friends of Science in Moscow and of the Academies of Sciences in Copenhagen, Uppsala, Turin, Vienna, Göttingen and Halle; Foreign Associate of the Académie des Sciences of Paris; Foreign Member of the Accademia dei Lincei of Rome and the Royal Society of London; Honorary Member of the Physical Society of Stockholm, the Société Helvétique des Sciences Naturelles, the Royal Institution of London, the Sociedad Española de Fisica y Quimica of Madrid, and The Franklin Institute of Philadelphia.

In 1913, Kamerlingh Onnes was awarded the Nobel Prize for Physics for his investigations into the...
properties of matter at low temperature, which led, among other things, to the production of liquid helium\(^2\) (Fig. 2).

** Scientific contributions**

The main scientific contributions of Kamerlingh Onnes were in the areas of thermodynamics, the equation of state, in electricity and in magnetism. He developed the virial equation of state, a significant improvement about that of van der Waals, extended the concept of corresponding states, performed brilliant work on the achievement of very low temperatures (which led to the liquefaction of helium), studied the behaviour of materials at these low temperatures, and discovered the phenomenon of superconductivity.

Here, only one of his main contributions has been described in detail, namely, that of the virial equation of state. Prior to this, the necessary background, namely, the virial theorem, the van der Waals equation of state, and the law of corresponding states, is being provided.

**The virial theorem**

The virial theorem of Clausius was developed by Clausius in 1870\(^7\) and the ratio of the average kinetic energy to the average potential energy of a mechanical system was established. Although the original derivation was based on classical mechanics its conclusions are also valid in quantum mechanics. The interested reader is referred to the book of Hirschefelder et al.\(^8\) for details.

The virial theorem is a powerful tool in the determination of intermolecular forces, and is used directly in the development of an equation of state. Its derivation starts from Newton’s equation of the movement direction of a particle of mass \(m_i\), acted upon by a force \(F_i\) in the \(x\) direction:

\[
(F_i)_x = m_i \frac{d^2 x_i}{dt^2} \tag{1}
\]

Eq. (1) may be written as:

\[
\frac{1}{2} (x(F_i)_x)_i = \frac{1}{2} m_i \frac{d^2 x_i}{dt^2} + \frac{1}{2} \frac{d}{dt} \left( m_i \frac{dx_i}{dt} \right) \tag{2}
\]

Clausius eliminated the last term of Eq. (2) by the smart step of taking its average over a sufficiently long time interval \(\tau\) and observing that according to the theory of heat transfer neither position nor velocity could ever increase indefinitely (since the particle is confined to a region of space). In other words, as \(\tau \to \infty\),

\[
\frac{1}{2} \frac{d}{dt} \left( m_i \frac{dx_i}{dt} \right)_x = \frac{1}{2} \tau \frac{d}{dt} \left( \frac{1}{2} m_i \frac{dx_i}{dt} \right)_x \to 0 \tag{3}
\]

Hence, the time average of Eq. (2) becomes:

\[
-\frac{1}{2} \left[ x(F_i)_x \right] = \frac{1}{2} m_i \frac{d^2 x_i}{dt^2} = \frac{1}{2} m_i \bar{v}_i^2 \tag{4}
\]

Similar equations can be written to describe the motion in the \(y\) and \(z\) directions. Adding the three equations of the form of Eq. (4), one gets,

\[
\Xi_i = -\frac{1}{2} \overline{(r_i \cdot F_i)} = \bar{K}_i \tag{5}
\]

where \(\bar{K}_i\) is the mean value of the kinetic energy of the particle. Clausius named the quantity on the left hand side of Eq. (5) the **virial of the force**.

Since Eq. (5) holds for any particle, it can also be applied to any system of particles to yield:

\[
\Xi = -\frac{1}{2} \sum_i \overline{r_i \cdot F_i} = \bar{K} \tag{6}
\]

where \(\bar{K} = \sum_i \bar{K}_i\) is the total average kinetic energy, \(\Xi = \sum \Xi_i\) is the **total virial** of the system, and \(r_i\) is...
the vector position of the particle acted by the force vector \( F_i \).

According to Eq. (6) the virial theorem states that in a material system in a state of stationary motion the time-average of the kinetic energy is equal to the time-average of the virial. The validity of this remarkable theorem, which relates microscopic quantities with macroscopic quantities, is independent of the particular form of the intermolecular forces.

The proof of the virial theorem by Clausius was a crucial step for everyone trying to construct a realistic equation of state for gases; the task of constructing an equation of state meant, the ability to calculate the virial term and express it in terms of macroscopic variables.

The van der Waals equation of state

Already by the end of seventeenth century Robert Boyle (1627-1691) had shown that at constant temperature, the pressure of a gas varied inversely proportional to its volume. Several attempts were made to correct Boyle’s law, starting with Daniel Bernouilli’s (1700-1782) proposal to replace the volume with \( (V-b) \) where \( b \) was taken to be the volume of the molecules. Similar modifications were proposed by Gustave Adolphe Hirn (1815-1890) in 1863 and Anathase Louis Victoire Dupré (1808-1869) in 1869.

Clausius’s work in 1857, which established that heat transfer was the result of molecular motion, together with the 1853 experiments of James Prescott Joule (1818-1889) and William Thomson, Lord Kelvin (1824-1907) (the Joule-Thomson effect), led to the rejection of the theory supported particularly by Pierre-Simon Laplace (1749-1827) and Siméon-Denis Poisson (1781-1840), that the long-range repulsive and short-range attractive forces between molecules resulted in their being at rest (motionless) when in equilibrium.

In 1873, van der Waals defended his thesis\(^9\) at the University of Leiden where he presented an improved solution to the capillary problem and a new equation of state, based on very general assumptions, Clausius’s virial theorem, and the kinetic theory of gases:

\[
\left( P + \frac{a}{V^2} \right)(v-b) = RT
\]

where \( b \) represented the repulsive forces (found to be four times the volume occupied by the molecules) and \( a \) was a constant included in an expression for the attractive forces that were found to be proportional to the square of the density of the fluid. Eq. (7) was derived using the virial theorem assuming that for one mole of a fluid at pressure \( P \) enclosed in a vessel of volume \( V \), the average kinetic energy was \((3/2)RT\) and the virial of the external forces was \(-3Pv\), so that the virial theorem took the form:

\[
\frac{1}{2} \sum m_i v_i^2 = \frac{3}{2} RT = \frac{3}{2} P v + \frac{1}{2} \sum (R_i)
\]

where the left hand side denotes the kinetic energy and the second term on the right represents the attractive forces between all pairs of molecules with mutual distance \( r_j \) and attractive force \( R_i \) (the components of the force acting on that particular particle). This expression represents the virial of the cohesive pressure, nowadays called internal pressure. Van der Waals showed that the internal pressure was proportional to the square of the density.

Van der Waals interpreted qualitatively the experimentally observed deviations from ideal gas behaviour by assuming that the molecules were attracted to one another at large distances and repelled at very small distances. No assumption was made regarding the particular form of the intermolecular forces, but instead the molecules were treated as entities with shape and size, and the cohesive forces were no longer neglected.

As shown by van der Waals, his equation of state permitted to derive quite accurately Thomas Andrews’s (1813-1885) experimental results\(^{10,11}\) that pointed to the continuity of the transition from the gaseous state to the liquid state.

The principle of corresponding states

Comparison of Eq. (7) with the equation of state for an ideal gas points out that writing an equation for a real gas has exacted a heavy price: The universality of the equation has been lost because the new equation requires identifying the gas with the two constants \( a \) and \( b \). Van der Waals realized that the reason for this drawback was that a real gas could be liquefied, that the liquefaction phenomenon occurred at \( P-T-V \) conditions that were different for each gas, and that the critical constants could be expressed in terms of critical parameters, \( P_c = 1/27b^2 \), \( V_c = 3b \), and \( RT_c = 8a/27b \). To recover the original advantage, van der Waals came out with the idea of expressing the
behaviour of a gas on the basis of reduced properties, $X$, obtained by the linear scaling $X = X/X_c$. The reduced property is then the ratio between the value of the actual property and the value of the property at the critical state. Van der Waals replaced $X$ by $X/X_c$ obtaining
\[
P_i P_v + \frac{a}{v_i^2 v_c} (v_i - b) = RT v_c
\]
Now, replacing the values of the critical properties by their expressions in terms of $a$ and $b$ he obtained the equation:
\[
P_i = \frac{3 v_i}{v_c^2} (3 v_i - 1) = 8 T v_i
\]
Eq. (10), when represented in the $(P, T, V)$ space is a universal relation that carries no identification of the gas and expresses the law of corresponding states (van der Waals called it the equation of the reduced isotherms): Gases at the same reduced conditions display the same behaviour. In other words, the law implies a peculiar similarity among all gases and liquids.

As stated by van der Waals, the reduced equation of state held for all the substances (gaseous and liquid) independent of the nature of the substance: “If we express the pressure in terms of the critical pressure, the volume in terms of the critical volume, and the absolute temperature in terms of the critical temperature, the isotherms for all bodies become the same...This result no longer contains any reference to the specific properties of various bodies, the specific has disappeared.” The differences in behaviour among the different substances were expressed by the parameters $a$ and $b$, which became cancelled in Eq. (10). Thus, if the reduced values of two of the properties were the same for any two substances, then the value of the third reduced property must also be the same and the substances were considered to be in corresponding states. If, for example, the behaviour of a gas and its corresponding liquid was known at all temperatures and pressures, then the state of any gas or liquid at any temperature and pressure could be calculated, if the state at the critical temperature was known.

It should be recognized that the law of corresponding states is only a translation of the equation of state from the $P(T, V)$ surface to the $P(T_c, v_c)$ one. It does not improve the fitting quality of the equation of state, but does make it universal. The reduced equation of state is subject to the condition that at low pressures the gas behaves ideally, so that the number of its adjustable parameters is two. From the microscopic viewpoint it can be shown that the law of corresponding states applies to substances in which the molecules are spherically symmetrical and for which the potential energy curve for interaction between molecules is of universal shape. Inasmuch as no sharp distinction can be made between substances that do, and those that do not conform to the law of corresponding states, such a differentiation must be made about the properties to which it applies: It applies to properties that depend only on the intermolecular energy. The law therefore applies to the second virial coefficient and does not apply to the heat capacity.

Consider now the general equation of state written in the form $z = P v/R T$ where $z$ is the compressibility. Changing the variables to the reduced ones yields:
\[
z = \frac{P_i P_v v_x v_c}{R T_i T_c v_c} = \frac{P_i v_x}{R T_c} v_c v_x = \frac{P T}{v_c} v_x = \frac{P T}{v_c}
\]
According to Eq. (11), the law of corresponding states would be correct if all gases had the same critical compressibility (0.375), as predicted by the van der Waals equation. Unfortunately, this is not the case, the experimental values of the critical compressibility vary between 0.20 and 0.35. In other words, two parameters are not enough to generalize the behaviour of real gases. Modern equations of state are based on a modified expression of the law: Gases that have the same values of the reduced properties and the same value of a third parameter (such as the acentric factor, the critical compressibility, the radius of gyration, etc.) behave in the same manner.

The law of corresponding states was generalized in 1891 by Kamerlingh Onnes and used by Emile Mathias (1861-1942) and Louis Paul Cailletet (1831-1913) to propose their law of rectilinear diameter in 1886. In 1879, Kamerlingh Onnes in his memoir “General Theory of the Fluid State” reformulated the law of corresponding states and showed that the
motion of molecules of all substances when in the corresponding states was dynamically similar: "All mechanical quantities, the derived absolute units of which can be given as powers of the fundamental units of length, mass, and time, will be expressed in these systems of molecules by the same numbers, when measured in the system of absolute units, deduced from the fundamental units of length, mass, and time belonging to each substance. And all such mechanical quantities of a substance in an arbitrary state, can be calculated from those observed with the other substance in the corresponding state by the ratio of the derived absolute units, in which these quantities are measured." 

If one assumed, as was the case with van der Waals' equation of state, that the molecular interactions were characterized only by size and strength, then the molecular motions in two different systems could be made "dynamically similar": the motion of each molecule in the two substances could be made to differ only by factors of length, time, and force scales. When molecular motions could be made dynamically similar, then the two substances were in corresponding states. This was a mechanical rather than a statistical argument and, hence, Kamerlingh Onnes formulated the law of corresponding states as \( l = F(m, n) \). This is a form, which was independent of the particular equation of van der Waals and was valid for any equation of state expressed in terms of two adjustable parameters.

Kamerlingh Onnes proposed to use the law of corresponding states to examine the possibility of cooling hydrogen further by its own expansion. He then used this law to predict from the known experience with oxygen what was to be expected from the apparatus for the cooling of hydrogen; "But let us return to the thermodynamically corresponding substances. If two such substances are brought in corresponding engines and if these engines are set in motion with corresponding velocities, then they will run correspondingly as long as there is given off a corresponding quantity of heat in the corresponding times by the walls of the machine." He then introduced the notion of thermodynamically corresponding operations to argue that "if then in a model, working with oxygen, after a given time a given volume of liquid oxygen is found, there will be obtained in the corresponding hydrogen apparatus after the corresponding time a corresponding volume of liquid hydrogen".

The virial equation of state

Immediately after his appointment to the Chair of Experimental Physics at the University of Leiden in 1882, Kamerlingh Onnes embarked on a program to establish an equation of state of relatively simple substances for as wide a temperature range as possible. As stated by him, the study of the equation of state had to be restricted to low temperatures because of possible chemical changes taking place at a higher temperature. Liquefaction of helium in 1881 was a direct consequence of the law of corresponding states, and more particularly of its reformulation by Kamerlingh Onnes in 1881.

In the opening statements of his paper about the expression of the equation of state of gases by means of a series Kamerlingh Onnes wrote that various methods had been tried to empirically derive functions of the constants \( a \) and \( b \) of van der Waals by means of kinetic or thermodynamic considerations, without much success. Hence, it appeared to him that the best approach was to combine systematically the whole set of experimental data available for the isotherms of several gases and liquids, independently as possible from theoretical considerations and to express them by a series. In his own words: "Although I had in mind the development of the equation of state \( P = f(v, T) \) in a convergent double series in terms of the molecular density \( 1/v \) and the absolute temperature, it follows from the nature of the subject that we can only obtain a representation by a polynomial of a limited number of terms and we need not wonder that this polynomial does not even converge for all densities. Each coefficient of such a polynomial can be determined for an individual isotherm only when the polynomial consists of a moderate number of terms...Therefore the polynomial must be derived from the infinite series not only by approximate combination of the remainder of some terms, but also through suitable omission of intermediate terms...It is obvious that we must try in the first place to bring about an agreement with a number of terms as small as possible but equal for all temperatures."  

He went on to indicate that this goal could not be achieved by looking at the experimental data for one substance only because precise data were available for single substances in very limited ranges. Hence, to a certain extent it, was possible to substitute the data for a single substance with the data of several substances within different limits, and then combine all the...
information by means of the law of corresponding states. Thus, this approach would allow determining the temperature of what he called virial coefficients, and build the general representation of the equation of state.

Kamerlingh Onnes developed the original equation of van der Waals in series, using the following arguments. Defining as \( L \) the dimensionless factor \( \frac{R}{Pcv_c} \) and calling \( v_L = \frac{v}{L} \), transforms the van der Waals equation to:

\[
\left( P + \frac{27}{64v_L^2}\left(v_L - \frac{1}{8}\right) \right) = T \left(1 - \frac{1}{8v_L}\right) \tag{12}
\]

which can also be written as:

\[
Pv_L = \frac{T}{1 - \frac{1}{8v_L}} - \frac{27}{64v_L^2} \tag{13}
\]

Since the value of \( 1/8v_L \) is very small compared to unity then the first term on the right hand side of Eq. (13) can be developed in series to obtain:

\[
Pv_L = T \left[1 + \frac{1}{v_L} \left(\frac{1}{8} - \frac{27}{64T} \right) + \frac{1}{64v_L^2} + \frac{1}{512v_L^3} + ...\right] \tag{14}
\]

Fitting of the experimental data at different temperatures and for different substances indicated that the above series was far from being able to represent the data. For this reason Kamerlingh Onnes changed the above series to another one having the following structure:

\[
Pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \frac{E}{v^4} + \frac{F}{v^5} + ... \tag{15}
\]

making the comment that in the beginning he thought he would use a convergent infinite series in terms of the molar density and the absolute temperature, but in practice he could only obtain a limited number of terms. In addition, it was necessary to omit certain of the intermediate terms. In particular Kamerlingh Onnes found that no improvement was obtained by considering the term involving \( 1/v^3 \) or extending Eq. (15) by adding a term with \( 1/v^4 \).

Kamerlingh Onnes reported that several other forms of the polynomial expansion were tested, but none proved better than the one given by Eq. (15) (the interested reader may look at the other alternatives in the memoir).

The experimental data were then used to determine the coefficients in Eq. (15) (which Kamerlingh Onnes named virial coefficients) as a function of the temperature, with the following structure:

\[
B = b_1 + \frac{b_2}{T} + \frac{b_3}{T^2} + \frac{b_4}{T^3} + \frac{b_5}{T^4} \tag{16}
\]

Kamerlingh Onnes and Crommelin\textsuperscript{17} synthesized Eqs (15) and (16) by combining the measurements on hydrogen, oxygen, nitrogen and ether by Emile Hilaire Amagat (1841-1915)\textsuperscript{18}\textsuperscript{20}, with those of ether and isopentane by William Ramsay (1852-1916) and Thomas Young (1773-1829)\textsuperscript{21}\textsuperscript{22}. The resulting equation had 25 parameters, with which the measured values could be described in a better approximation.

As mentioned before, Kamerlingh Onnes noted that a major problem was that on reduced scales, the results for each substance often did not overlap with those of another. If the law was obeyed strictly this difficulty would disappear but, in practice, it remained a problem. Nevertheless, in the end "an equation of state has been obtained for an imaginary substance, which... is suitable for all calculations for which the validity of the law of corresponding states is assumed. And this equation is of particular use in tracing deviations form the law..."\textsuperscript{16}.

It is important to add that mechanical statistics can be used to derive the different virial coefficients in terms of the intermolecular potential functions and express the deviations from ideal gas behaviour in terms of forces between molecules. The pertinent mathematical expressions indicate that the different virial coefficients represent the interaction in clusters composed of an increasing number of molecules. That is, the second, third, fourth... virial coefficients represent the deviations from ideal behaviour when collisions involving two, three, four... molecules become important in the gas. Since, the effect of pressure is to decrease the distance between molecules, the number of virial terms to be taken into account increases as the pressure is increased. For example, at low pressures, up to about 5 atmospheres, it is enough to consider the second virial coefficient only. The range of validity of the virial expansion is limited by the convergence of the series. The series diverges at about the density of the liquid. Hence the...
primary application of the virial equation of state is in the study of gases at low and moderate pressures.

An additional problem in the development of the virial equation of state appeared when considering the behaviour of mixtures, since a system of this nature may split in various phases of different composition; the question was to determine if these phases could be predicted by the virial equation. In 1891, van der Waals had already published his theory of mixtures and the extension of his equation of state to their description\textsuperscript{23}. For this case, van der Waals proposed that the constants $a$ and $b$ be assumed to depend quadratically on the molar fraction of the mixture:

$$a = a_1(1-x)^2 + 2a_2x(1-x) + a_{22}x^2 \quad \ldots \ (17)$$

$$b = b_1(1-x)^2 + 2b_2x(1-x) + b_{22}x^2 \quad \ldots \ (18)$$

where $a_{11}$, $b_{11}$, $a_{22}$, and $b_{22}$ were the van der Waal’s constants of the pure substances 1 and 2, and $a_{12}$ and $b_{12}$ characterized the mixture. The problem was now to find which values of $V$ and $x$ corresponded to a stable equilibrium of a homogeneous phase at a given temperature, and which values led to a separation into two or more phases. Gibbs had developed the concept of thermodynamic surfaces and found that the representation of the dependence of a thermodynamic surface on its arguments allowed one to visualize the conditions of equilibrium between different states of aggregation, or between different phases in general, more easily than from an analytical treatment. If one constructed a plane that was tangent to the thermodynamic surface at two points, then these points represented coexistent phases.

To solve the stability problem van der Waals used Gibbs’s expression for the energy of a surface, $\psi (T, V, x)$ (which he named the equilibrium surface $\psi$-surface, today the Gibbs energy, $G$), and found that:

$$\psi(T, V, x) = -RT\ln(v-b) - \frac{a}{v}$$

$$+RT[x\ln x + (1-x)\ln(1-x)] \quad \ldots \ (19)$$

Thus for a given temperature it was possible to find the $\psi$-surface as a function of $v$ and $x$, and determine the conditions for the system to separate into two phases.

It is clear that the construction of the $\psi$-surface is always possible since, from the equation of state $\psi$ is known explicitly as a function of $V$ and $x$. Its shape describes the system in a simple way: those parts that are convex to the horizontal $V-x$ plane represent stable homogeneous states, and those parts that are concave are unstable and breakup into two coexisting phases. The unstable and stable regions are separated by the spinodal curve defined by:

$$\left(\frac{\partial^2 \psi}{\partial x^2}\right)_v + \left(\frac{\partial^2 \psi}{\partial v^2}\right)_x - \left(\frac{\partial^2 \psi}{\partial v \partial x}\right)_x = 0 \quad \ldots \ (20)$$

The $\psi$-surface can assume a great variety of shapes, depending on the temperature and on the parameters of the equation of state.

From 1890 onwards, Kamerlingh Onnes embarked on a long series of investigations on the modelling of mixtures carrying the general title “\textit{Contributions to the Knowledge of van der Waals $\psi$-Surface}”\textsuperscript{24-27}. Since van der Waals’s first model of the $\psi$-surface for a binary mixture, was only schematic, Kamerlingh Onnes proposed visualizing it with plaster models. This difficult manual and artistic job was carried out in collaboration with M. Reinganum, a German physicist who studied at Leiden and Amsterdam from 1899 to 1900, and who was later killed in the First World War. The final fruit of their efforts was an impressive object measuring $40\times60\times80$ cm. Even when hollowed out, this weighed 80 kg but “it proved to be satisfactory for several constructions”\textsuperscript{27}.

These plaster models were very useful in the study of the system H$_2$ + He, which Kamerlingh Onnes found to have some very curious properties and which he reported in November 1896 to the Section of Sciences of the Academy of Amsterdam\textsuperscript{28}. In explaining his findings he stated: “If we have an ideal gas and an incompressible liquid without vapour tension, in which the gas does not dissolve, the gas will gather above the liquid under the action of gravity, if the pressure is sufficiently low, whereas the compressed gas will sink in the liquid if the pressure made high enough”.

Van der Waals responded immediately to this publication and at the next meeting of the Section of Sciences he put forward a general criterion for the occurrence of the effect discovered by Kamerlingh Onnes\textsuperscript{29}. In the same meeting, Keesom and Kamerlingh Onnes added more information and also discussed the theory of this phenomenon, which they called the barotropic effect\textsuperscript{25,26}.
Epilogue

Ironically, the virial expansion developed by Kamerlingh Onnes can be used to show the weaknesses of van der Waals's equation of state. This equation may be written as:

\[ I = \frac{RT}{v-b} - \frac{a}{v^2} \]  \hspace{1cm} (21)

Multiplying each side by \( P_v/RT \) we get:

\[ \frac{P_v}{RT} = \frac{v}{v-b} - \frac{a}{RT v} = \frac{1}{1-\frac{b}{v}} \]  \hspace{1cm} (22)

In general, the term \( b/v \) will be very small compared to unity, a fact that can be used to expand the first term in Eq. (22) as a convergent geometric series:

\[ \frac{1}{1-\frac{b}{v}} = 1 + \left( \frac{b}{v} \right) + \left( \frac{b}{v} \right)^2 + \ldots \]  \hspace{1cm} (23)

Replacing in Eq. (23) and rearranging in terms of powers of \( 1/v \):

\[ z = \frac{P_v}{RT} = 1 + \frac{1}{v} \left[ b - \frac{a}{RT} \right] + \left( \frac{b}{v} \right)^2 + \left( \frac{b}{v} \right)^3 + \ldots \]  \hspace{1cm} (24)

Eq. (24) is the virial form of the van der Waals equation. From it we get:

\[ B_{vw} = b - \frac{a}{RT} \]  \hspace{1cm} (25)

\[ C_{vw} = b^2 \]  \hspace{1cm} (26)

\[ D_{vw} = b^3 \]  \hspace{1cm} (27)

where \( B_{vw}, C_{vw}, \) and \( D_{vw} \) are the second, third, and fourth virial coefficients for van der Waals's equation.

Eqs (25) to (27) explain why the van der Waals equation of state is not very accurate: (a) The virial coefficients, from the third on, are not a function of the temperature and (b) the second virial coefficient varies linearly with the reciprocal of \( T \), which is contrary to theory and experience. Hence, we can expect that van der Waals’s equation will not describe the behaviour of the gas at pressures above 5 atm and below this value, it will do it only qualitatively.

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