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# Johannes Diderik van der Waals: A Pioneer in the Molecular Sciences and Nobel Prize Winner in 1910**

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history of chemistry · molecular physics ·
van der Waals, Johannes Diderik

## 1. "An Exceedingly Ingenious Thesis"

On Saturday the 14th of June 1873 the secondary school teacher Johannes Diderik van der Waals at the age of 35 defended his academic thesis before a commission of professors at the University of Leiden.[1] Certainly no one in the audience could at the time imagine that the thesis with the title "*The Continuity of the Gaseous and Liquid States*" (Figure 1) would trigger a revolution in the understanding of the molecular physics of liquids, gases, and their mixtures, lay the foundations of modern thermodynamics and statistical mechanics, and lead 37 years later to a Nobel Prize in Physics for the candidate. In Section § 36 of his dissertation,[2,3] after reviewing and analyzing the contributions of Laplace to the theory of capillarity and the work of Clausius on the virial theorem, he presented his now famous equation of state [Eq. (1)],

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad (1)$$

where $P$, $V$, and $T$ are the pressure, molar volume, and temperature of a substance in either the gas or the liquid state, and $a$ and $b$ are empirical constants. With this seemingly simple formula van der Waals provided the basis for understanding both the gas and liquid phases in terms of the same intermolecular forces between individual pairs of molecules, concisely expressed in terms of $a$ and $b$. With this unifying theory van der Waals could explain and predict the critical point and the behavior of gases above the critical point, and how below the critical point a liquid is transformed into a gas and visa versa.

Recognition of the importance of the new equation of state came slowly partly because, written in Dutch, it was not readily accessible outside the Netherlands. The first review with a short, somewhat laudatory yet critical appraisal appeared in 1874 by the nestor of the kinetic theory of gases in England at the time, James Clerk Maxwell.[4] A year later, however, in an address to the Chemical Society in London Maxwell advised his audience to master what he called the "*low-Dutch language*" in which this "*exceedingly ingenious thesis*" is written.[5] But the breakthrough came only in 1877 when, as van der Waals graciously related in his Nobel Prize lecture of 1910, his formula "*became universally known only as a result of Eilhard Wiedemann's efforts*". Wiedemann was a 25-year-old Privat Dozent who had written a long clear abstract in German in the *Beiblätter* to the *Annalen der Physik*[6] describing van der Waals' theory. Then followed an outburst of research activity largely by Dutch colleagues in which the full significance of van der Waals' formula became widely appreciated. For example, using the law of corresponding states, which van der Waals first proposed in 1880,[7] his colleague and scientific friend Kamerlingh Onnes was able to correctly estimate the critical point of helium, making it possible for his group to liquefy helium for the first time in 1908. With liquid helium as a refrigerant the same group discovered superconductivity in solid mercury in 1911, for which Kamerlingh Onnes received the Nobel Prize in Physics in 1913.

Both the unusual early career of the schoolteacher van der Waals and the intense flurry of research among his Dutch colleagues, triggered by his thesis, were fostered by a favorable scientific environment. Today many Dutch science historians attribute this development to several stages of educational reform in the Netherlands starting in 1863.[8] In that year a new type of secondary school was introduced for children from the middle class called the "Hogere Burger School" (HBS), which included three-year and five-year daytime schools as well as evening schools. These schools, which concentrated on mathematics, physics, and chemistry as well as English, German, and French, were designed to prepare the graduates for positions in trade and manufacture in the newly emerging industries. The period from 1863 to about 1914 is today referred to as the "Second Golden Age" of Dutch science. The biologist de Vries, the paleontologist Dubois, the pathologist Eijkman, the mathematician Brouwer, the chemist van't Hoff, and the physicists Lorentz, van

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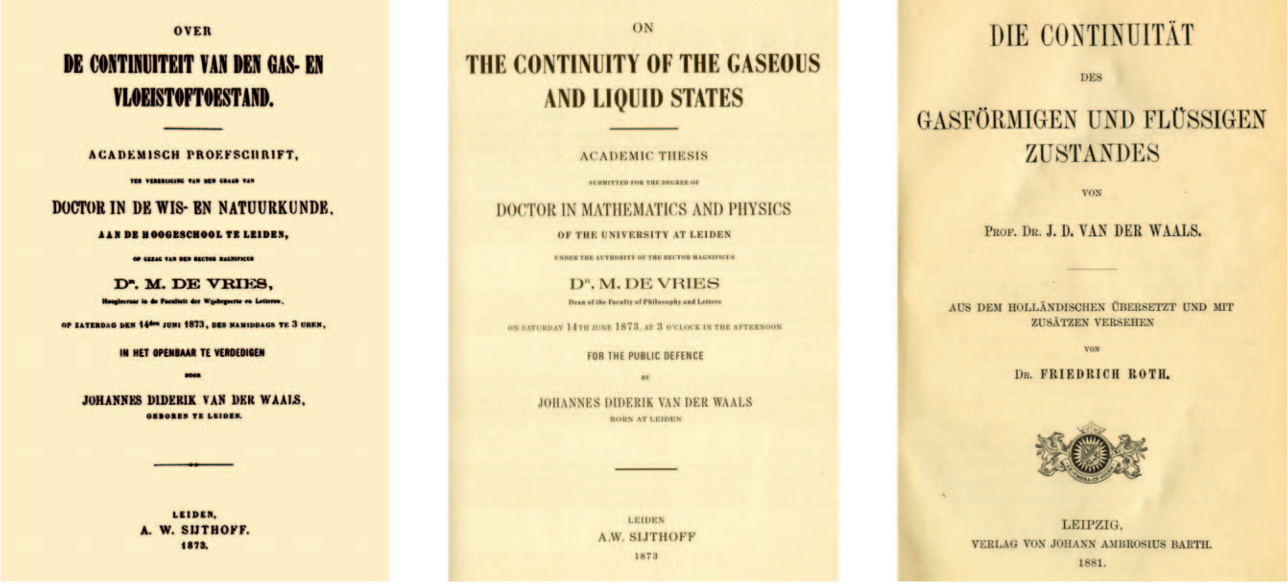

OVER
DE CONTINUITEIT VAN DEN GAS- EN
VLOEISTOFTOESTAND.

ACADEMISCH PROEFSCHRIFT,
TER VERKRIJGING VAN DEN GRAAD VAN
DOCTOR IN DE WIS- EN NATUURKUNDE,
AAN DE HOOGESCHOOL TE LEIDEN,
OP GEZAG VAN DEN RECTOR MAGNIFICUS
Dr. M. DE VRIES,
Hoogleeraar in de Faculteit der Wijsbegeerte en Letteren,
OP ZATERDAG DEN 14den JUNI 1873, DES NAMIDDAGS TE 3 UREN,
IN HET OPENBAAR TE VERDEDIGEN
DOOR
JOHANNES DIDERIK VAN DER WAALS,
GEBOREN TE LEIDEN.

LEIDEN,
A. W. SIJTHOFF.
1873.

ON
THE CONTINUITY OF THE GASEOUS
AND LIQUID STATES

ACADEMIC THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR IN MATHEMATICS AND PHYSICS
OF THE UNIVERSITY AT LEIDEN
UNDER THE AUTHORITY OF THE RECTOR MAGNIFICUS
Dr. M. DE VRIES
Dean of the Faculty of Philosophy and Letters
ON SATURDAY 14TH JUNE 1873, AT 3 O'CLOCK IN THE AFTERNOON
FOR THE PUBLIC DEFENCE
BY
JOHANNES DIDERIK VAN DER WAALS
BORN AT LEIDEN

LEIDEN
A.W. SIJTHOFF
1873

DIE CONTINUITÄT
DES
GASFÖRMIGEN UND FLÜSSIGEN
ZUSTANDES
VON
PROF. DR. J. D. VAN DER WAALS.

AUS DEM HOLLÄNDISCHEN ÜBERSETZT UND MIT
ZUSÄTZEN VERSEHEN
VON
DR. FRIEDRICH ROTH.

LEIPZIG,
VERLAG VON JOHANN AMBROSIUS BARTH.
1881.

**Figure 1.** Title pages of the original dissertation by J. D. van der Waals (left) and the English and German translations (middle and right, respectively). The first German translation by F. Roth appeared in 1881;[2] the first English translation by Threlfall and Adair appeared in 1890 and is reprinted in Ref. [3].

der Waals, Kamerlingh Onnes, and Zeeman all became world leaders in their fields. Four of the 26 Nobel Prizes in chemistry and physics in the short period between 1901 and 1913 were awarded to the latter five Dutch scientists, a far greater number in relation to the small population of the Netherlands than the number generated by the other leading countries.[9] In 1913 the well-known Göttingen physicist Waldemar Voigt (1859–1919) wrote that the appearance of van der Waals' dissertation marked the emergence of the Netherlands as "*a world power in physics*".[10] At the time of his dissertation in 1873 van der Waals (Figure 2) earned his livelihood as a teacher at one of the newly founded HBS schools.

In the following we will describe briefly the state of understanding of liquids and gases up to the time of van der Waals' formula. Then we will relate van der Waals' development as a research scientist and his career up to the Nobel Prize in 1910. In the final section we will review present areas of research which have their roots in van der Waals' many scientific contributions.

## 2. Understanding of Gases and Liquids in the 19th Century

Early in the 1800s great progress had been made in understanding the physics of gases. The work of Boyle (1627–1691), Charles (1746–1823), Avogadro (1776–1856), and Gay-Lussac (1778-1850) had lead to the equation of state of an ideal gas $PV = RT$ by 1802.[11] In 1857 Clausius[12] called attention to the "heat" in the internal degrees of freedom (rotations), and the following year he introduced the concept of a mean free path thereby explaining why the speed of sound and related diffusive processes are much slower than the velocity of the molecules.[13] Inspired by Clausius' article James Clerk Maxwell in 1860 formulated the so-called Maxwell distribution of molecular velocities,[14] which was generalized by Ludwig Boltzmann in 1868 and 1871.[15] In 1867 Maxwell[16] introduced his famous force law according to which molecules repel each other with a central force proportional to the fifth power of the distance. This force law was not generally appreciated at the time. For example in 1877 Oskar Emil Meyer (1824–1907) in his authoritative book on the "*kinetic theory of gases*"[11] rejected Maxwell's repulsive forces and supported the idea of hard sphere particles. Starting in 1862 Clausius published a series of articles in both German and English "*On a Mechanical Theorem Applicable to Heat*" ("*Abhandlung über die mechanische Wärme-Theorie*") in which he introduced what is now called the virial theorem.[17]

**Figure 2.** J. D. van der Waals at about 35 years of age. (source: Wikipedia).

As a result of the mathematically elegant theories of Clausius, Maxwell, and others and their successes in explaining viscosity, diffusion, and heat conductivity, the kinetic theory of gases was fully developed at the time of van der Waals' dissertation. At the same time a number of influential scientists doubted the existence of atoms. Prominent among them were the physical chemist and 1909 Nobel laureate Wilhelm Ostwald (1853–1932)[18] in Germany and Marcelin Berthelot (1827–1907) in France. The physicist and philosopher Ernst Mach (1838–1916) was also an ardent anti-atomist. Even among the gas kineticists there were varying views about the nature of particles in gases. In 1867 Sir William Thomson (later called Lord Kelvin) suggested that atoms were in actuality little vortices,[19] an idea inspired by Hermann von Helmholtz's (1821–1894) mathematical analysis of vortices in liquids.[20] This idea was taken up by O. E. Meyer, who in the final paragraph at the end of his book concluded that vortices would indeed provide a simple explanation for the long, stretched out "molecules" invoked by many of the theories of the time. These varying views explain why van der Waals concluded his Nobel lecture with the observation "*It will be perfectly clear that in all my studies I was quite convinced of the real existence of molecules, that I never regarded them as figments of my imagination…*". Further on he related "*when I began my studies I had the feeling that I was almost alone in holding that view*".

As he writes in the first chapter of his thesis, van der Waals was especially inspired by the work of Clausius and Maxwell and their theories of molecular motion. Even earlier on in his dissertation at the beginning of the preface he starts by stating that the subject of his treatise was to understand a special aspect in the theory of capillarity, which had been formulated by the Marquis de La Place (1749–1827),[21] which van der Waals refers to as a "measure of cohesion". Here he is referring to the attractive forces between the particles. Except for the theory of capillarity there had been few attempts at a theory of liquids, and a coherent kinetic theory was not available.[22] Experiments by Cagniard de la Tour (1777–1859)[23] already in 1822 led to the discovery of the phenomenon of criticality. But van der Waals was especially influenced by Regnault's measurements of the compressibility of various gases published in 1847.[24] The careful measurements of the isotherms of carbon dioxide reported later by Thomas Andrews[25] above and below the critical point, which appeared in 1869 in an article with nearly the same title as van der Waal's dissertation, had a great influence on his work. Not only did it provide reassuring experimental confirmation that his formula was successful in describing the experimental isotherms of both gases and liquids but also the necessary data with which to determine the constants $a$ and $b$.

## 3. van der Waals, The Person[1]

Johannes Diderik van der Waals was born on November 23, 1837 in Leiden as the first of ten children into a carpenter's family of modest means. Little is known of his early childhood except that the family circumstances allowed him to receive a only primary school education, and subsequently visit a more advanced three-year primary school. He left school at about the age of fourteen to take on a job as a teacher in a primary school. Apparently not satisfied with his status he soon enrolled for the first of a series of examinations which enabled him to later become the director of a primary school at the age of 24. Following the introduction of the new HBS secondary schools in 1863 he applied for an HBS teaching position to which he was appointed in 1865. This was also the same year of his marriage to the 18-year-old Anna Magdalena Smit. In the following years his family grew with three daughters. The fourth child was a son, J. D. van der Waals Jr., who became his scientific heir as Professor of Physics at the University of Amsterdam starting in 1908. In 1881 tragedy struck the family when Anna Magdalena died at the age of 34 of tuberculosis.

Starting about 1862 while continuing to earn a living for his family as an HBS teacher, van der Waals enrolled at Leiden University. van der Waals could not take the regular university course since he had not learned Latin at school and could not meet the Latin requirements for the regular university course. Fortunately new legislation was passed upon which he requested and was granted an exemption which enabled him to present his thesis in June 1873. In 1874 a year after receiving his doctorate he became the deputy director of his HBS, and in 1877 he was appointed Director of Secondary Education in the Hague. It was only six months later in 1877 that the importance of his PhD research was finally fully recognized, as evidenced by his appointment as Professor of Physics at the recently newly founded University of Amsterdam, the fourth in the Netherlands of the time. He is known to have had a large teaching load while he was setting up the new Department of Physics. Kipnis et al.[1] report that his "*lectures on general physics were clear, exact and lucid and that they were illustrated by convincing demonstrations*". It is perhaps interesting that "*The lectures on mathematical physics were not so clear*". In 1875 he was elected to the Dutch Royal Academy of Sciences, of which he was general secretary from 1896 to 1912.

Kipnis et al. characterize him as a "*dull and dry-as-dust pedant. A punctual and reticent man of small stature, monotonous in his way of life, he was precise in all matters, his lectures and classes fell on the same hours 9 to 10 and 10 to 11, for many years he kept to his established routine; each day he awoke, ate, and went to bed at the appropriate time. He was too artless, too independent of common conventions, and this aspect of his character led often to difficulties*".[1] One of his students remarked that "*Fame changed neither his behavior nor his habits. He lived as if on an island, in solitude and silence, with his daughters*". He is also more euphemistically characterized "*as a man of sound common sense, with unique self-discipline, an enormous capacity for work, and with a remarkable gift for organization*". van der Waals' modesty can be gleaned from the beginning paragraph of his Nobel lecture "*Now that I am privileged to appear before this distinguished gathering to speak of my theoretical studies on the nature of gases and liquids, I must overcome my diffidence to talk about myself and my own work….*" van der Waals' shyness also explains why today only very few photos of him exist. In one of the few photos (Figure 3) he is seen together with his close scientific friend Kamerlingh Onnes in the latter's laboratory. His favorite maxim in later years nicely characterizes his

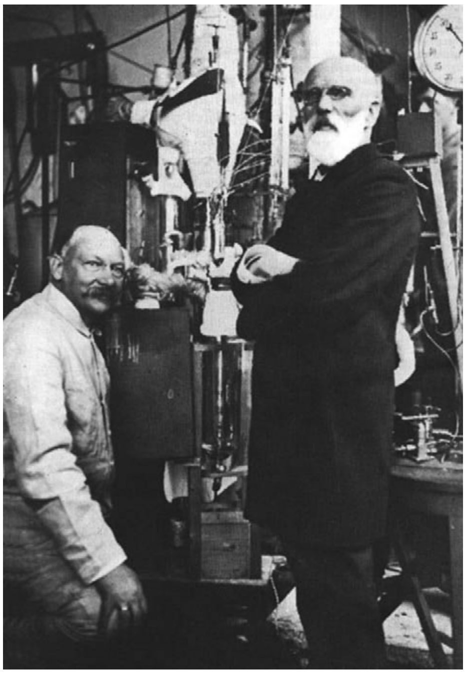

***Figure 3.*** J. D. van der Waals (standing) and Heike Kamerlingh Onnes with the helium liquifier in Kammerlingh Onnes' laboratory at Leiden in 1911 (source: Wikipedia).

research "*Matter will always display attraction*". van der Waals passed away on March 8, 1923.

## 4. van der Waals' Scientific Contributions

The citation of van der Waals' Nobel Prize "*for his work on the equation of state for gases and liquids*" recognizes in large measure his dissertation research. In the first part of his thesis he reviews the virial theorem of Clausius. On the basis of this theory he felt justified in treating "*the elementary parts of a liquid as 'particles'*" as in the case of gases.

In contrast to the earlier theories of Maxwell and Clausius who, in van der Waals terms, accounted for the "breadth" of the particles, he felt that it was important to also account for their "thickness" and thereby treats them as spherical objects. The size of the molecules leads to a reduction in their mean free path by a factor $(V-b)/V$, where $b$ is four times the sum of the volumes of the molecules. Since the pressure is inversely proportional to the mean free path, van der Waals argues that the correct pressure $P'$ is $P' = [V/(V-b)]P$; thereby $PV$ in the ideal gas law is replaced by $P'(V-b)$. This explains his correction to the molar volume.

As mentioned earlier he uses Marquis de La Place's theory of capillarity[21] and the Joule–Thomson effect to justify his assumption that attractive forces are important, while he negates any effect from the repulsive forces. Moreover he concludes that the forces between the particles cancel inside the medium and make themselves felt only at the surface. Then towards the end of the first part of his dissertation in § 36 he presents a simple estimate of the effect of the attractive forces on the pressure by assuming that the molecules at the surface are pulled towards the interior. This effect is proportional to the density of particles being "pulled" times the density of the pulling molecules. Since the density is inversely proportional to the volume, the pressure at the surface is less than the pressure in the interior by an amount $a/V^2$. This simple argument explains the first term $(P+a/V^2)$ in the van der Waals equation. In hindsight this term can be looked upon as an ingenious invention since it means that as $V \rightarrow \infty$ the surface effect vanishes and the van der Waals equation becomes the ideal gas law, while at high temperatures it can be shown that the effect of the attractive forces vanishes. Also with this term his equation becomes a cubic equation in $V$. This makes the isotherms change their shape from monotonic decreasing curves above the critical point to curves with a minimum and a maximum below the critical point as shown in Figure 4. Thus the properties of both gases and liquids and their coexistence are described by a unified theory.

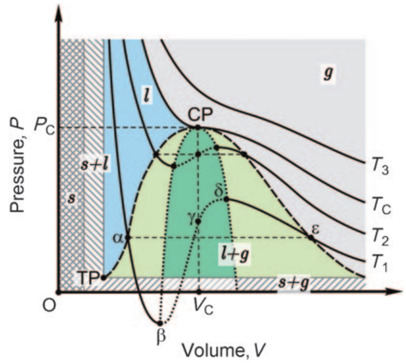

***Figure 4.*** A typical phase diagram showing four typical isotherms predicted by the van der Waals equation of state. *g*, *l*, and *s* denote the gas, liquid, and solid states, $s+l$, $l+g$, and $s+g$ denote regions of coexistence. CP and TP mark the critical and triple points. In the central dark-green region coexistence is always established, wheras in the light-green region the system may be metastable.

The second part of the dissertation is devoted to estimating the constants $a$ and $b$ from gas-compressibility data by Regnault[24] and the isotherms reported by Andrews[25] just a few years earlier. In the final sections he discusses the implications of his equation of state. In 1898 Boltzmann in his famous book "*Vorlesungen der Gastheorie*" points out a number of inconsistences in van der Waals' assumptions and after a more rigorous derivation concludes that van der Waals' formula was completely justified.[26] After the van der Waals equation became generally known, it was realized that it was only approximate. To improve its accuracy, over 91 different modifications were suggested up to 1919.[27] Yet today because of its simplicity and accuracy the original formula is still widely in use.

Figure 4 displays a typical set of isotherms obtained with the van der Waals equation. At temperatures above the critical point (CP) the isotherms reduce to those for an ideal gas. Below the critical point the equal-pressure points on the isotherms, as illustrated by the horizontal line α–ε in Figure 4, mark the transition from a liquid at smaller volumes, for example, at α, to a region of coexistence which ends at a higher volume, for example, at ε, in the pure vapor. In the coexistence region between these extremes the isotherms exhibit a maximum and a minimum reflecting the cubic nature of the van der Waals equation. van der Waals correctly realized that these two extrema determine what today are called spinodals, lines marking the transition of the over-expanded metastable liquid (e.g. point β in Figure 4) or of the supersaturated metastable vapor (point δ). Also van der Waals seems to have realized that under certain conditions the pressure could become negative as indicated by the point β, a condition which can be achieved nowadays using powerful sound pulses. The s-shape of the isotherms is an important difference to the equilibrium measurements of Andrews and an earlier theory by Maxwell which led to only the horizontal lines.

With his formula, van der Waals was also able to predict the critical temperatures, pressures, and volumes as a function of the parameters $a$ and $b$. His results were in surprisingly good agreement with the data available at the time.

Towards the end of his dissertation he estimates roughly the distance between molecules at the instant of encounter from his empirical values of $b$. For ether and alcohol he reports values of 4.0 Å and 2.7 Å, respectively. These distances agree quite well with the distances of closest approach of modern interaction potentials. A simple calculation using present-day potential parameters reveals that the value of $a$ predicted by the van der Waals equation provides a remarkably accurate description of the strength of the long-range dispersion forces. It was only in 1927 that S. C. Wang explained the long-range attraction with the new quantum mechanics.[28]

van der Waals' second important contribution came in 1880 when he pronounced the Law of Corresponding States (LCS), which was published in the journal of the Dutch Academy of Sciences.[7] By dividing the values of volume, temperature, and pressure by their critical values he obtained a universal equation of state which proved to be remarkably accurate. van der Waals felt that the "essential importance" of the law of corresponding states is that it shows that all substances belong to a single genus, "*just as all human beings belong to the genus* Homo" as he put it. Kamerlingh Onnes, who starting in the 1880s collaborated closely with van der Waals, exploited LCS first in his efforts to liquefy air, and later for liquefying $H_2$. It was crucial for Kamerlingh Onnes in his attempt to liquefy helium to be able to correctly predict the critical point of helium, $T = 5.2$ K, from the known isotherms of hydrogen around the critical point. Even today the law of corresponding states and the quantum-modified theory called the "*Quantum theorem of corresponding states*"[29] are of great practical and theoretical importance.

Another major contribution was his theory of binary mixtures entitled "*Molecular theory of a substance composed of two different species*".[30] Here he showed that his equation of state could also be applied to liquid mixtures where the coefficients $a$ and $b$ depend on the mole fraction $x$ to assure that they change continuously as the concentration increases. This problem continued to occupy him up to his final years and triggered extensive theoretical activity among the Dutch colleagues D. J. Korteweg (1848–1941), J. J. van Laar (1869–1938), and J. P. Kuenen (1866–1922). The outcome of these investigations has had an important impact on chemical engineering and even in geochemistry. Another major contribution was concerned with capillary phenomena.[31]

Kamerlingh Onnes in his 1923 obituary[32] also mentions that van der Waals was occupied with the very interesting problem of the conglomeration of a greater number of molecules. Thus it appears that van der Waals very early anticipated the importance of cluster chemistry and physics which has become a broad field of research only within the last 20 years.

## 5. van der Waals' Legacy

The significance of van der Waals' work can be concisely summarized by noting that he was the first to demonstrate that intermolecular forces had an important effect on measurable macroscopic quantities such as the pressure, volume (density), and the state of a given substance. There were many ideas about intermolecular forces in the 19th century which can be traced back to early Greek and Roman philosophers. But van der Waals demonstrated convincingly for the first time that these forces were crucial for an understanding of matter. His work had almost immediately a profound impact on the development of Dutch physics and chemistry. As Kamerlingh Onnes stated,[32] "*He opened up the period (Second Golden Age) of Dutch sciences*". As the leading Dutch authority of this period he taught and inspired many of the chemists and physicists of the Second Golden Age. Even today Dutch scientists stand out as being very strong in molecular and chemical physics. For many years up to the Second World War Amsterdam and Leiden were leading world centers for experimental research in the molecular sciences. Since van der Waals' time many important theoretical, computational, and experimental developments have greatly improved our understanding of the properties of gases and liquids. Statistical mechanics and quantum chemistry have made tremendous advances in these areas largely stimulated by the precision measurements of the equations of state and transport processes by the Dutch scientists. After about the middle of the last century new more accurate data on intermolecular potentials became available from molecular-beam scattering experiments. Subsequent close comparisons between precise scattering experiments and quantum calculations of potentials have helped to refine the methods in both areas. But today, despite tremendous advances, our knowledge of intermolecular forces is still limited to small molecules. Especially the understanding of intermolecular interactions in large biological systems still represents an imposing challenge.

van der Waals' name today is associated with many modern physical concepts, such as vdW bonds, vdW clusters, vdW constants, vdW forces, vdW gases, and vdW radii. The impact on modern science is vividly illustrated in Figure 5 where the number of articles in which the name "van der Waals" appears in the title, abstract, or keywords is plotted as a function of the year of publication. The sharp rise in recent

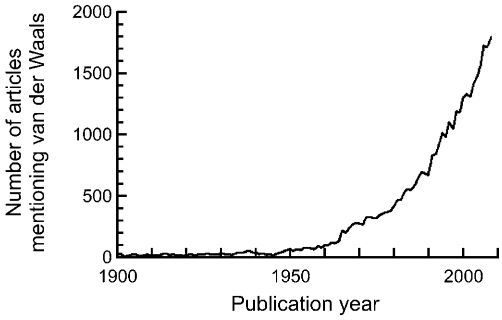

***Figure 5.*** Plot of the number of scientific articles mentioning van der Waals in the title, abstract, or keywords based on the Chemical Abstracts literature files versus the publication year.

years suggests that his influence is still enormous and will continue to grow well into the future.

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