

### 3. The law of corresponding states – Van der Waals and Kamerlingh Onnes

#### 3.1 *The principle of corresponding states from the Van der Waals equation*

Van der Waals (1880a,b) formulated the principle of corresponding states on the basis of his equation of state. It has proven to be of immense importance for practical applications and, in various guises, has been in use until the present day.

The simple form of Van der Waals's equation, the prototype of the many cubic equations to follow in the century to come, made it possible for him to calculate explicitly the coordinates of the critical point. The conditions of criticality, Eq. (2.3), applied to the Van der Waals equation yield for these coordinates:

$$P_c = a/(27b^2), \quad V_c = 3b, \quad RT_c = 8a/(27b) \quad (3.1)$$

The *critical ratio*, defined as  $P_c V_c / RT_c$ , equals 3/8 for the Van der Waals equation.

Van der Waals then proposes to use the critical parameters themselves as units of measurement, thus replacing the constants  $a$ ,  $b$  and  $R$ . The resulting equation of state, in what is called a *reduced form*, now reads:

$$(P^* + 3/V^{*2})(3V^* - 1) = 8T^*, \\ \text{with } P^* = P/P_c, \quad V^* = V/V_c, \quad \text{and } T^* = T/T_c \quad (3.2)$$

This is a truly remarkable result. Equation (3.2) is *universal*: all characteristics of individual fluids have disappeared from it or, rather, have been hidden in the reduction factors. The reduced pressures of two fluids are the same if the fluids are in *corresponding states*, that is, at the same reduced volume and temperature.

In his presentations to the Academy, Van der Waals (1880a,b) deduces straightforwardly that in reduced coordinates, the vapor pressure curve and the coexistence curve must be the same ('fall on top of each other') for all fluids. He also points out that this principle can be used to predict the vapor pressure of a substance in a temperature range in which it is not known, by

comparing the vapor pressure curve in a known range with that of a well-characterized reference substance. As an example, Van der Waals obtains crude estimates for then unknown critical pressure and temperature of water by scaling the water vapor pressure curve in the range of 128 to 201°C to that of ether. For ether the vapor pressure curve is known all the way up to the critical point. For water he predicts  $T_c = 390^\circ\text{C}$ , while the presently accepted value is  $373.9^\circ\text{C}$  – not a bad estimate for an extrapolation of over  $150^\circ\text{C}$ .

### 3.2 *Van der Waals tests the principle of corresponding states*

With his characteristic thoroughness, Van der Waals then tries to find out whether saturated vapor volumes of different fluids as functions of temperature indeed fall on top of each other. He consults data from six European laboratories for a dozen fluids with known covolumes  $b$ . For ether, ethanol, acetone, and chloroform he expresses the volumes in units of  $b$  and compares them at two different pressures, which are fixed fractions of the respective critical pressures. He finds that these reduced volumes agree within 2%. Carbon tetrachloride and carbon disulfide, however, are found not to comply.

This particular presentation by Van der Waals (1880a,b) is of interest for two other reasons. First of all, it contains the first indications of his interest in applications to fluid mixtures (see Ch. 3.6), a topic that would take another ten years to ripen (Ch. 4). Secondly, it contains several experiments Van der Waals himself carried out on phase separation of a mixture of carbon dioxide and air at pressures up to 100 bar. These experiments are discussed in Ch. 4

Like Van der Waals himself, scientists were quick to realize the power of the principle of corresponding states. As early as the 1880s the limited accuracy of the Van der Waals equation was well known. For example, the critical ratio of common fluids ranges from 0.23 (water) to 0.29 (noble gases), while the prediction of  $3/8 = 0.375$  grossly overestimates this value. The principle of corresponding states, however, frees the scientist from the particular constraints of the Van der Waals equation. The properties of a fluid can now be predicted if only its critical parameters are known, simply from correspondence with the properties of a well characterized reference fluid. Alternatively, unknown critical properties of a fluid can be predicted if its properties are known in a region not necessarily close to criticality, based on the behavior of the reference fluid.

Van der Waals's tests of the principle of corresponding states for properties such as the coefficient of expansion gave less than convincing results,

but, as Van der Waals (1880a,b) points out, the reliability of the existing experimental results left much to be desired. In his 1913 Nobel lecture, in hindsight, he recalled his disappointment when he found out that the principle of corresponding states had only approximate validity and was thus not a law of nature.

### 3.3 *Importance of the principle of corresponding states for gas liquefaction*

S. Wroblewski made use of the principle in estimating the correct critical temperature of hydrogen ten years before this gas was liquefied by James Dewar in 1898. In the early 1900s Kamerlingh Onnes did not know a priori whether helium could be liquefied at all, so it was essential for him to have an estimate of its critical temperature. But not until a year before the actual liquefaction of helium was Kamerlingh Onnes (1907e) in a position to obtain an accurate estimate. Measuring and comparing  $P$ - $V$  isotherms of hydrogen and helium in regions around the critical point of hydrogen permitted him, on the basis of corresponding states, to estimate the helium critical temperature as 5.3 K. This is only just over 0.1 K above the presently known value of 5.189 K. He then calculated the dimensions for his liquefier and estimated how much liquid air and liquid hydrogen he would need in order to produce liquid helium. He barely made it. Only towards the end of a long, arduous and nerve-wracking day, July 9, 1908, was a liquid-vapor interface finally spotted inside the liquefier. This is how Kamerlingh Onnes (1908) described the achievement in a letter to Van der Waals, at the occasion of the latter's retirement on July 11, 1908:

At the time that the last bottle of liquid hydrogen was coupled [to the liquefier], no [liquid] helium was visible. [Apparently, however], the apparatus had filled up with liquid helium during one of the expansions. A little bit later, the interface appeared. [Translated from the Dutch]

And this is how Kamerlingh Onnes credited Van der Waals:

In what I described to you, your theory has been my guide. To calculate the critical temperature of a permanent gas from the [ $P$ - $V$ ] isotherms brings your dissertation to memory in a new way. The calculations were performed entirely on the basis of the law of corresponding states. Guided by that law, I estimated – even though I did not put that on paper – to need 20 liters [of hydrogen]. Had I estimated a few liters fewer, the experiment would not have succeeded – had I estimated much more, then I would have judged it unwise to proceed, in view of the available resources. [Translated from the Dutch]

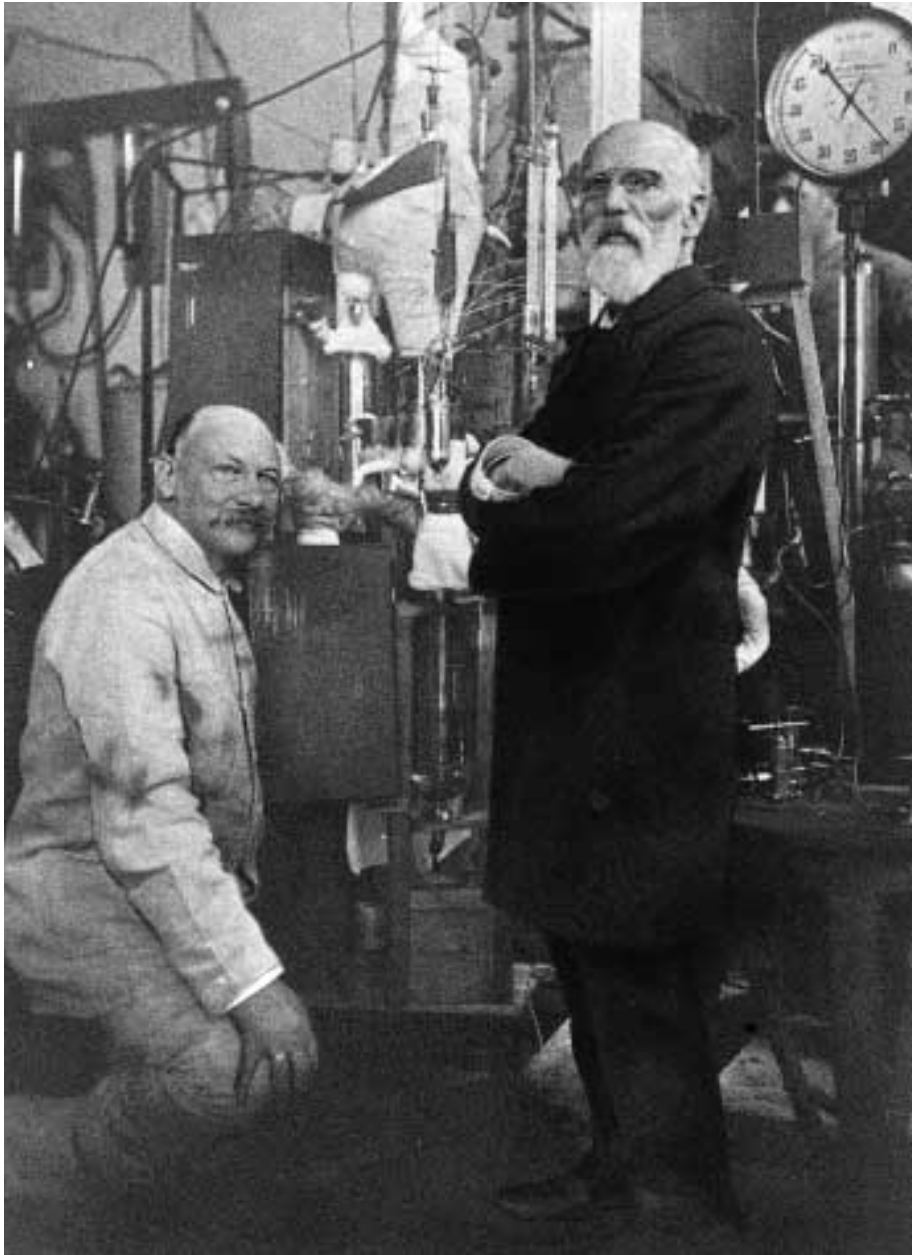


Figure 3.1 Kamerlingh Onnes (l) and Van der Waals posing by the helium liquefaction apparatus. Copied with permission of the Boerhaave Museum, Leiden.

### 3.4 *Kamerlingh Onnes and the principle of mechanical similarity*

3.4.1 *Biographical notes.* Heike Kamerlingh Onnes (1853-1926), was the son of a well-to-do industrialist from whom he inherited his mechanical propensity. He completed his undergraduate studies in physics and mathematics in his hometown, at the University of Groningen. Before he started his graduate work in that city in 1873, he spent three semesters with Bunsen and Kirchhoff in Heidelberg, Germany. By that time he had already won several competitive prizes. In 1879, he obtained his doctorate in physics *magna cum laude* with Prof. R.A. Mees in Groningen. In 1878, he was appointed an assistant to Johannes Bosscha, Professor of Physics at the Delft Polytechnic School. Kamerlingh Onnes was appointed to a professorship at the University of Leiden in 1882.

His 42-year tenure at the University would be filled with remarkable discoveries. He established a world-class laboratory, uniquely equipped for cryogenic work related to the liquefaction of gases. Details on his work in the period of 1880 to 1908 will be encountered in many of the chapters to follow. His crowning achievement was the liquefaction of helium in 1908, which opened the new field of low-temperature physics.

Kamerlingh Onnes was elected to the Royal Netherlands Academy of Arts and Sciences as early as 1883, before his 30<sup>th</sup> birthday. He was elected to the Dutch Society of Sciences in 1886. He received the Nobel prize in physics in 1913.

3.4.2 *Mechanical similarity.* Even before Van der Waals's (1880) presentation on corresponding states appeared in print, Kamerlingh Onnes had grasped the idea, and sought a molecular justification (see Kipnis et al. 1996, p. 105). While still an assistant to Bosscha, he wrote a paper on the foundation of the principle of corresponding states. In December 1880, Van der Waals presented Kamerlingh Onnes's (1881) paper to the Academy. This was the beginning of one of the most fruitful and long-lasting relationships ever between two scientists.

Kamerlingh Onnes's (1881) purpose is to demonstrate that the principle of corresponding states can be derived on the basis of what he calls the principle of similarity of motion, which he ascribes to Newton. He assumes, with Van der Waals, that the molecules are elastic bodies of constant size, which are subjected to attractive forces only when in the boundary layer near a wall, since the attractive forces in the interior of the volume are assumed to balance each other (Ch. 2.4). He realizes that this can be valid only if there is a large number of molecules within the range of attraction (see the second part of the 1881 paper), an issue that would come up time and again, as mentioned in

Ch.2.4. Kamerlingh Onnes ascribes the following characteristic parameters to the molecules of a fluid: the molar mass  $M$ , the molecular volume  $m$ , and the 'absolute molecular attraction'  $A$ . He considered a state in which  $N$  molecules occupy a volume  $v$ , and all have the same speed  $u$  (no Maxwellian distribution!). The problem is to express the external pressure  $p$ , required to keep the system of moving particles in balance, as a function of the five parameters. He solves this problem by deriving a set of scaling relations for  $M$ ,  $A$ ,  $v$ ,  $u$  and  $p$ , which pertain if the units of length, mass, and time are changed. Two fluids are in corresponding states if, by proper scaling of length, time and mass for each fluid, they can be brought into the same 'state of motion.' It is not clearly stated what he means by this, but he must have had in mind an exact mapping of the molecular motion in one system onto that of another system if the systems are in corresponding states. A much later interpretation of Kamerlingh Onnes's intention, in a book by his former student Kuenen (1907, pp. 144-147) supports this. In modern terms: suppose a movie is made of the molecular motions in one fluid. Then, after setting the initial positions and speed of the molecules, choosing the temperature and volume of a second fluid appropriately, and adjusting the film speed, a movie of the molecular motion in a second fluid can be made to be an exact replica of that in the first fluid.

Certainly this argument, which uses none of the insights of statistical mechanics, imposes far more stringent conditions on molecular motion than are necessary for the validity of a law of corresponding states. Moreover, although Kamerlingh Onnes claims that this derivation follows from mechanics with no input from the Van der Waals equation, this does not appear to be quite true. First of all, the assumption of a molecular volume ascribed to molecules considered as elastic hard spheres is one also made in the derivation of the Van der Waals equation. Kamerlingh Onnes's argument, however, does allow for density dependence of the excluded volume. The trickiest part, however, is the scaling of the 'absolute molecular attraction'  $A$ . From the way Kamerlingh Onnes does this, it is clear that he assumes that  $A/V^2$  has the dimension of a pressure. Thus, implicitly, he adopts the attractive term used by Van der Waals.

None of this criticism diminishes the merit of Kamerlingh Onnes's attempt at founding the law of corresponding states on attributes of the molecular interaction and on molecular mass and motion, instead of on a particular form of an equation of state. In the last part of his paper, moreover, Kamerlingh Onnes makes an extremely useful extension of the principle of mechanical similarity to include viscosity. Kamerlingh Onnes's quest would be resumed in the middle of the 20<sup>th</sup> century, after a deeper understanding of intermolecular forces was obtained.

### 3.5 Empirical scale factors

Originally, the principle of corresponding states was tested by making fluid properties dimensionless through the use of either the critical parameters, or the molar gas constant  $R$  and the parameters  $a$  and  $b$ . The first method requires commitment to an unavoidably inaccurate equation of state based on two molecular parameters. Either method suffers from a loss of accuracy due to the fact that the reduction parameters are generally far less well known than the fluid properties to be compared. Kamerlingh Onnes circumvents this problem by making graphs of measured fluid properties coincide through the use of two empirical scale factors, a method to be extensively used by him in subsequent years for pure fluids as well as for fluid mixtures. A set of  $P$ - $V$  isotherms is plotted on a double logarithmic scale for each of two fluids. By superimposing and shifting the plots so as to make them interlace, empirical scale factors are obtained for pressure and volume. Around 1900, Kamerlingh Onnes and his collaborators used different variants of this method, generalizing it to fluid mixtures, see Chapter II. As narrated by Kipnis *et al.* (1996, p. 236), in 1896 the French high-pressure expert Émile Amagat, whom we will encounter in several chapters of this book, devised an ingenious optical projection method for superimposing grids of  $P$ - $V$  isotherms for pairs of fluids. Amagat noted that the principle did not apply universally, but was valid in classes of related substances.

An interesting application, again by Kamerlingh Onnes, was the wedding of the principle of corresponding states to polynomial representations of  $P$ - $V$  isotherms. In the 1880s the deficiencies of the Van der Waals equation were quite well known. Kamerlingh Onnes was beginning to produce accurate  $P$ - $V$  data for several fluids in his laboratory, and he did not like the idea of representing those good data by an inadequate equation of state. Instead, he experimented with describing the data along isotherms by series expansion of the  $PV$  product in terms of the density. He called the coefficients in the expansion *virial coefficients*. The word virial (from the Latin *vis*, genitive *viris*, which means force) is taken from Clausius's exact virial theorem, which relates the average kinetic energy of a system of moving molecules to the average of the inner product of intermolecular force and intermolecular distance.

The *virial expansion*, as it is presently used, is given by

$$PV = RT [1 + B(T)/V + C(T)/V^2 + \dots] \quad (3.3)$$

with the virial coefficients  $B$ ,  $C$ ...still functions of temperature. Kamerlingh Onnes (1901b) used an expression akin to Eq. (3.3). He expanded the product  $PV$ , retaining only as many terms as he needed for practical purposes,

and omitting some of the intermediate powers. Thus, in the 1901 paper, he used the powers 1, 2, 4, 6 and 8. Allowing five adjustable parameters per isotherm, instead of two molecular parameters for the entire data set, obviously must lead to a much more accurate representation of the data. This accuracy, however, comes at a high price: the loss of an underlying molecular model and its predictive power, and the need for additional numerical interpolation between the representations of the individual experimental isotherms.

Kamerlingh Onnes (1901b) dealt with these difficulties in the following way. He used the accurate  $P$ - $V$ - $T$  data published by Amagat for the gases carbon dioxide, nitrogen, oxygen and hydrogen in a range up to a maximum of 3000 atmospheres. The data were brought into reduced form by using the known critical pressure and temperature for each of the fluids. Kamerlingh Onnes represented each of the reduced virial coefficients as a function of reduced temperature, using four adjustable parameters for each of the five virials. The result is a 20-term function of reduced and temperature that represents the entire experimental data set for the four fluids and can be used for interpolation. For these reference fluids, the representation was shown to be accurate to a few tenths of a percent at low pressures, increasing to several percent at the highest pressures. There was a problem with representing states of carbon dioxide close to saturation. The systematic deviations are chiefly due to departures from the law of corresponding states, and partly to uncertainties of the critical parameters.

As reliable data for more diverse fluids became available, however, it became evident that the validity of the law of corresponding states was limited to fluids that were similar in molecular structure. A big divide, for instance, occurred between polar and non-polar fluids. Simple non-polar fluids, such as the noble gases and air constituents, followed the principle of corresponding states to the extent that departures did not greatly exceed the then-available experimental accuracy. Polar fluids such as water and the alcohols displayed what was known, in Van der Waals's time, as *association*. They have an anomalously dense vapor phase, which was ascribed to formation of double molecules. Such substances showed large departures from the law of corresponding states, if compared with non-polar fluids. The critical ratio  $P_c V_c / RT_c$ , for instance, is more than 20% lower for water than it is for argon. Van der Waals and his contemporaries labeled those fluids 'anomalous,' and accepted that the Van der Waals equation would not apply to such fluids.

### 3.6 *The principle of corresponding states as the foundation for a molecular theory of phase separation of fluid mixtures*

In the later part of his first Academy presentation on the law of corresponding states, Van der Waals (1880a) not only speculates about phase separation of fluid mixtures but also presents some experimental results of compression of carbon dioxide mixed with air (see Ch. 4.2). Although his theory of mixtures would still be a decade in the making, he makes some profound statements in 1880. Thus, he rejects the picture underlying Dalton's law that the components of a mixture behave as if the other components are not there. On the contrary, says Van der Waals, in the homogeneous phase the mixture behaves as if it is one fluid. He mentions the possibility of describing a mixture of constant composition by means of two constants  $a$  and  $b$  which are dependent on the composition. This correspondence between a mixture of constant composition and a pure fluid is the key idea that will lead him to his 1890 theory of mixtures. Ch. 4 describes Van der Waals's theory of mixtures and the role the law of corresponding states played in its formulation.

### 3.7 *The principle of corresponding states in the 20th century*

3.7.1 *Two-parameter corresponding states.* The principle of corresponding states, though of limited validity, has been of lasting importance throughout the 120 years since it was first invented. It makes it possible to estimate the thermodynamic properties and the viscosity of a fluid over the entire range of density and temperature on the basis of a few data points (plus the ideal-gas heat capacity, usually very well known from spectroscopy). Knowledge of the properties of a well characterized reference substance is a prerequisite.

Fundamentally, the principle is based on the assumption that, in addition to the universal gas constant, only two properly chosen parameters are needed to make fluid properties dimensionless. Obvious choices for these two parameters were two of the critical parameters, or two molecular constants  $a$  and  $b$ , an energy and a size parameter not necessarily tied to a particular equation of state. The Dutch School was well aware that the choice of parameters is arbitrary, and consequently introduced the idea of experimental scale factors around 1900. All these two-parameter applications are essentially equivalent, and conversions from empirical to critical or to molecular scale factors are straightforward. Which choice to make is a matter of expediency, depending on which scale factors are the best characterized, and on the particular application at hand.

An important new application of the principle of corresponding states originated from a deepening understanding of intermolecular forces, which

began in the 1920s. First proposed by Jones (1924) (who later changed his name to Lennard-Jones), the intermolecular potential  $\varphi(r)$ , with  $r$  the distance between the centers of two molecules, is assumed to be spherically symmetric. It is composed of a steep repulsion at short distance, and an attraction over a somewhat larger range. The empirical repulsive term varies as the inverse of a high power of the distance  $r$  between the centers of a pair of molecules, a repulsion somewhat softer than that between hard spheres. Values between 9 and 15 have been experimented with, but the value 12 is used most often for the sake of mathematical simplicity. The attraction varies as the inverse sixth power of  $r$ , as follows from theoretical considerations:

$$\varphi(r) = \varepsilon [(r/\sigma)^{12} - (r/\sigma)^6]. \quad (3.4)$$

This equation contains two parameters characteristic of individual substances, namely the distance  $\sigma$  at which the interaction potential changes sign, and the energy  $\varepsilon$  which represents the depth of the potential well.

As pointed out by De Boer and Michels (1938), Pitzer (1939), and Guggenheim (1945), such a description of molecular interaction in terms of a universal semi-empirical two-parameter intermolecular potential leads, under certain restrictions, to a principle of corresponding states in terms of the molecular force field. One such restriction is the additivity assumption: interactions between more than two molecules can be written as the sum of pair potentials. Another is that the interactions can be described in terms of classical mechanics, an assumption that is violated for light molecules and at low temperatures.

In the middle of the 20<sup>th</sup> century, thermodynamic and viscosity data were used extensively to determine two-parameter molecular force fields, very much in the spirit of Van der Waals and Kamerlingh Onnes. Alternatively, the Lennard-Jones potential was used to predict these properties. An example is the paper by Rowlinson and Townley (1952) representing to within a few percent the second virial, viscosity and diffusion coefficients of six pure gases and thirteen of their binary mixtures on the basis of the Lennard-Jones 6-12 potential.

This method was used until, predictably, it was found that intermolecular potentials require more than two parameters to be accurately described. Towards the end of the 20<sup>th</sup> century, for small molecules, intermolecular potentials are beginning to be developed from quantum mechanics. These *ab initio* potentials are not universal, and the principle of corresponding states played no role in their development.

3.7.2 *Empirical scale factors.* This book's author used the method of two empirical scale factors, introduced by Kamerlingh Onnes, when testing the

(limited) validity of the law of corresponding states for argon and xenon. See Levelt (1960). Beenakker and Van Eynsbergen (1968) modified the method by plotting iso- $Z$  lines in the  $\log P$ ,  $\log T$  plane, where  $Z$  is the dimensionless quantity  $PVRT$ . The graphs for two different substances can be brought into coincidence by linear shifts of the plots. They found that this could be done to within about 1% for the fluids argon, xenon, nitrogen and methane and suggested that the method could be used for viscosity as well.

In the spirit of Kamerlingh Onnes (1881), Kestin and collaborators (1972, 1977) showed that two-parameter scaling can be simultaneously applied to the second virial coefficient as well as to the viscosity and diffusion coefficients of dilute gases, in which interactions between more than two particles can be neglected. The gases they studied include the noble gases, non-polar diatomic gases and many of their mixtures. In the dilute gas, use of the two-scale-factor principle of corresponding states results in an accuracy approaching that of the best data (0.1%). It was found, however, that the scale factors calculated from critical parameters differ from those found for the dilute gas phase, indicating departures from the principle of corresponding states on the level of 1% in the  $Z$ -factor, consistent with conclusions by Levelt (1960) and by Beenakker and Van Eynsbergen (1968).

3.7.3 *Generalized corresponding states – acentric factor.* A fruitful idea with useful and sometimes profound ramifications has been the generalization of the law of corresponding states to more than two parameters. The basic idea is the following: if additional features are present in the molecular interactions, such as departures from sphericity, or a dipole moment, then systematic departures must be expected from corresponding states as defined by the noble gases. In certain cases, these departures can be represented in terms of a third parameter. One example has been the so-called *acentric factor*  $\omega$ , introduced originally as an empirical parameter by Pitzer *et al.* (1955) to describe the departures from ‘noble-gas’ corresponding states that arise when the principle is applied to larger globular molecules. The Lennard-Jones potential is not centered on the molecular center, but is shifted outwards. Interactions between polar molecules involve more complicated non-central potentials.

The acentric factor of a fluid of multi-atomic molecules is seldom known *a priori*; in practice, it is estimated from easily accessible properties, such as the slope of the vapor pressure curve at a given distance from the critical point. Its value is now known for multitudes of industrial fluids, and correlations based upon this parameter abound in the chemical processing industry and in commercial data bases. *De facto*, it functions as a third parameter in cubic equations applied to fluids composed of multi-atomic, non-spherical or even polar molecules.

3.7.4 *Quantum-mechanical corresponding states.* At the other end of the spectrum from empirical to fundamental is the idea that *quantum effects* must cause departures from corresponding states. Kamerlingh Onnes and Keesom had detected appreciable departures from corresponding states in the gas phase for helium and hydrogen. In footnote 517 of their encyclopedia chapter on the equation of state, Kamerlingh Onnes and Keesom (1912) suggest that the Planck hypothesis, the quantization of phase space in volumes of size  $h$ , should have implications for the equation of state. Byk (1921) introduced the dimensionless Planck constant,  $\Lambda = h / [(kT_c)^{1/2} M^{1/2} (V_c/N)^{1/3}]$ , as a third parameter in the dimensionless free energy. Departures from corresponding states must be expected if the reduced Planck constant is not negligibly small. Molecules of low molar mass  $M$  and low critical temperature, such as the helium isotopes, hydrogen, deuterium and even neon, do have sizable Planck constants.

Jan de Boer and Antonius (Teun) Michels (1938), at the physics department of the University of Amsterdam, proposed making the Planck constant dimensionless by means of the molecular parameters  $\varepsilon$ ,  $\sigma$  and the molecular mass  $m$ . The dimensionless quantum parameter  $\Lambda^*$ , known in the English literature as the De Boer parameter, is defined as  $\Lambda^* = h / \sigma (m\varepsilon)^{1/2}$ . The De Boer parameter is small for most gases, but it is greater than unity for helium-3, helium-4, hydrogen, deuterium and tritium, leading to considerable departures from corresponding states. De Boer (1948a), and De Boer and Lunbeck (1948c) ordered many reduced properties of the light gases as functions of  $\Lambda^*$ . In the tradition of Kamerlingh Onnes, De Boer and Lunbeck (1948b) predicted the critical parameters and the vapor pressure of helium-3 before these properties were measured. In the absence of quantum effects, the helium isotopes should have the same critical properties; in reality, the critical temperature of helium-4 equals 5.19 K, whereas that of helium-3 equals 3.32 K. Lunbeck (1951) also estimated the triple point and critical point values of the hydrogen isotopes HD, HT, DT, and T<sub>2</sub>.

3.7.5 *Chain molecules.* A measure of the validity of the principle of corresponding states is the value of the critical compressibility factor  $Z_c = P_c V_c / RT_c$ . For the heavy noble gases, this factor is close to 0.29. For the helium isotopes, it is slightly over 0.30. For a series of normal alkanes,  $Z_c$  decreases from 0.288 (methane) to 0.262 (pentane). The chain length is an obvious candidate for a generalized principle of corresponding states. Engineering applications abound – see, for instance, Beret and Prausnitz (1975).

### 3.8 *Outlook*

The principle of corresponding states and its generalizations have provided a practical foundation for thermodynamic and transport property predictions in the chemical process industry throughout the 20<sup>th</sup> century. Over large ranges in temperature and density, it is accurate to about 1%, but only within a group of related substances, such as the heavy noble gases, or lower-weight diatomic molecules such as air constituents.

The principle plays a role in several of the following chapters. Foremost, in the next chapter, is Van der Waals's generalization of the principle in order to obtain a theory of fluid mixtures. The Leiden physicists preferred the principle to the use of the Van der Waals equation. Thus Verschaffelt neatly invoked corresponding states to estimate the effects of impurities on critical behavior, see Ch. 10.16.2 and 11.4.6.

