Remarks on van der Waals's equation, the cohesion pressure of a gas, and the role of intermolecular forces

W.F.X. Frank[1*] and D. Großmann[2]†

[1] Universität Ulm, Oberer Eselsberg, 89069 Ulm, Germany
[2] Institut für klinische Biochemie, Tannenstraße 4 A, 97294 Unterpleichfeld, Germany

(†) *D. Großmann died in 2006. It is up to me (W.F.) to proof the rudimentary calculations and results of past years with modern facilities, to expand them and to write down the results.*

Key words: van der Waals's equation, cohesion pressure, molecular collisions, collision duration time, H. Hertz's collision theory

The cohesion pressure of a real gas is considered to be caused by the collision interaction of the gas molecules. The collision duration time of two molecules is taken not to be zero but being of finite value τ. This time of collision duration is calculated according to the collision theory of Heinrich Hertz. This leads to a new calculation of the cohesion pressure of the gas which is compared with the van der Waals a-constant. The comparison shows an equivalence of both descriptions of the cohesion pressure for gases consisting of molecules with spherical symmetry. Deviations from spherical symmetry are discussed. The new description doesn't need the assumption of intermolecular attractive forces for particles with spherical symmetry.

Symbols and units

Name	Symbol	Definition	SI unit
pressure	p		Pa
volume	V		m^3
Avogadro's constant	L		$6{,}02 \times 10^{23}\ mol^{-1}$
Boltzmann's constant	k		$1{,}38 \times 10^{-23}\ JK^{-1}$
gas constant	R	$R=Lk$	$8{,}31\ J\ K^{-1} mol^{-1}$
temperature	T		K
total number of particles	N		
number concentration	n	$n = N/V$	m^{-3}
amount of substance	=		
number of moles	n_m	$n_m = N/L$	mol^{-1}
molar mass	M		$kg\ mol^{-1}$

Corresponding author: Prof. Dr. Werner Frank,
Ferdinand-Arauner-Str. 4
91807 Solnhofen
E-Mail: wfxfrank@t-online.de

1. Introduction

When we today (2010) are concerned with the question of how to interpret the behavior of a real gas, its deviation from the ideal gas equation and the condensation phenomena, a justification of this endeavor is needed. Since van der Waals's paper of 1881 [1] the deviation of a real gas from the ideal behavior is described by two correctional changes of pressure p and volume V of the ideal gas equation:

$$(p + a/V^2)(V - b) = RT \qquad (1)$$

a/V^2 describes the cohesion pressure of the gas and b the co-volume, that is the 4-fold volume of the gas particles. The constants a and b can be calculated from the measured values p_c,T_c and V_c, the so called critical values of the gas. These values define the critical point. The respective relations are

$$a = \frac{27}{8} bRT_c; \quad b = \frac{V_c}{3} \qquad (2)$$

The values for a and b given in relevant tables (see e.g. Landolt-Börnstein [2], Handbook of Chemistry and Physics [3], and recently internet Tables [4]) are calculated using equations (2).

Whereas the volume correction b is identified as the 4-fold volume of the particles, even in the first paper of van der Waals [1], the interpretation of the pressure correction constant a, considered to cause the additional pressure, called cohesion pressure of a gas, has lead to a tremendous number of publications during the more than hundred years. The common idea of interpreting the cohesion pressure of a real gas is the assumption of repulsive and attractive forces between the particles. These forces are derived from potential functions of different types. Very common are the functions of Lennard-Jones [5] and those of Buckingham [6] and Corner [7]. For nonpolar molecules, including closed-shell atoms like in noble gases, normally the dispersion interaction forces (Heitler and London [8]) are used.

In this paper we shall present an alternative concept for the cohesion pressure of a gas. It is based on considering the molecules as solid elastic spheres, according to Boltzmann [9]. The spheres undergo elastic collisions, the collision duration time is taken as a real non-zero value. The collision theory of Heinrich Hertz [10], applied here to molecular collisions of molecules with spherical symmetry, provides a method to calculate the collision duration time of colliding molecules. This leads to a description of cohesion pressure of gases from those molecules without the assumption of intermolecular attractive forces. The results from the new expression for the cohesion pressure are compared with common van der Waals a-constants and found to be equivalent.

2. An alternative concept for the interaction of neutral atoms – Introduction of the collision model

2.1 The basic ideas

The collision model presented here was initialized by the authors already when they were young students. They treated this idea more or less intensive over several decades.

Our early considerations were initialized by our doubt about the dispersion interaction forces between noble gas atoms (Heitler and London [8]). Noble gas atoms appeared to us like solid elastic

spheres comparable to billiard-balls. But as even noble gases exhibit the normal behavior of real gases showing cohesion pressure (internal pressure, in German: *Binnendruck*) we looked for another starting point to describe the phenomena. We left aside the concept of potential functions and started with the statement, that the number of collisions in a perfect (or ideal) gas must be zero, because the particles consist of point masses with dimension zero. Such point masses can only transfer a momentum to the walls generating the gas pressure, but have no mutual interaction between each other and collisions don't happen.

However, even Boltzmann [9] stated “no known gas has exactly the properties which we attribute to an ideal gas" (translated from German: “kein bekanntes Gas, (besitzt) exakt die Eigenschaften, die wir einem idealen Gas zuschreiben”). So we assumed tentatively, according to Boltzmann [9], that the atoms of a noble gas may be considered as solid elastic spheres whose only interaction are elastic collisions without any attractive or repulsive forces. We considered, however, that the duration of the collision, the time two atoms are in surface contact, is greater than zero and has to be taken into account.

We develop our concept in following steps:

2.2 The ideal gas

The equation of state of an ideal gas is

$$pV = n_m RT \tag{3}$$

If we put $n_m = N/L$, and $R = Lk$ we can write eq. (3) in the following form:

$p = \frac{N}{V} kT$ or with $N/V = n$, n number of particles per volume unit we have

$$p=nkT \tag{4}$$

This means – as starting point for the following considerations – that at a given temperature the gas pressure is solely determined by the number of point masses per unit volume. Mutual collisions of the gas atoms don't take place because point masses cannot collide with each other; they only transfer momentum to the walls generating the gas pressure.

2.3 The van der Waals equation describing the behavior of real gases

When the temperature is lowered the deviations from the ideal behavior of a real gas (e.g. a noble gas) can be described by modifying the ideal gas equation. The first and most famous of these modifications is that of van der Waals [1]:

$$\left(p + \frac{n_m^2 a}{V^2} \right)\left(V - n_m b\right) = n_m RT \tag{5}$$

The term $n^2_m a/V^2$ describes the change of the gas pressure compared to that of an ideal gas; $n_m b$ takes into account that the volume of gas atoms is not zero. The two “van der Waals constants” a and b of the equation exhibit themselves as functions of temperature and volume, as found by van Laar [11] and Seiler [12].

This equation describes the gas behavior down to condensation into the liquid phase rather well. However, total quantitative agreement of the equation with measured values is normally not given. Therefore a big variety of equations of state were formulated in order to describe actual results, but all of them are valid only in a limited range (see for instance the equations of state referred by Atkins [13], by Berthelot, Dieterici, Beattie-Bridgman). A better description of the experimental values is principally possible by the viral expansion originated by Kammerling Onnes (cf. Atkins [13]). Such equations try to fit exactly the experimental pV diagrams but all have the disadvantage of being only mathematical fits without real physical meaning.

The basis for a molecular interpretation of these phenomena, leading to the concept of intermolecular forces, is treated in numerous publications. We refer to Hirschfelder, Curtis and Bird [14], Stuart [15], Briegleb [16] and a more recent one, Israelachvili [17].

2.4 The collision model

In none of the functions mentioned above, to define the repulsive and attractive forces between the atoms, is taken into account that the duration of collision (collision time) between two gas atoms is greater than zero.

We assume that the collision duration of two particles in a gas has the value τ (seconds). Let us consider the gas, e.g. a noble gas as consisting of single atoms being solid elastic spheres comparable to billiard balls. If we would take a photo shot of the gas with an exposure time τ , we would find a certain fraction of atoms being involved in the collision process. This means that these particles stick together and, therefore, they have to be considered as only one particle, from the point of view of the kinetic gas theory.

As a consequence the number of those atoms contributing to the gas pressure – i.e. bouncing against the wall – has to be reduced by half the number of atoms attached to one another during collision process (bouncing of pairs with the wall at the moment of collisions are assumed to be very seldom and therefor their contribution to the pressure is neglected).

The number density of such pairs in collision process is

$$n_{col} = \frac{1}{2}\tau z \qquad (6)$$

where z is the collision rate density, i.e. the number of collisions of all particles per volume and second.

On the other hand, z is equal to the number of collisions of a single particle z_s times $n/2$, where $n = N/V$

$$z = z_s \frac{n}{2}$$

The collision frequency z_s of a single atom can be found by simple considerations (see any textbook of physical chemistry, e.g. Brdicka [13a]):

$$z_s = \sqrt{2}\,\pi d^2 n\bar{v} \quad \text{and} \quad z = \frac{\sqrt{2}}{4}\pi d^2 n^2 \bar{v} \tag{7}$$

where d = effective diameter of a particle and v = root mean square speed of a particle.

The number density of single atoms contributing to the pressure of the gas is therefore n_{eff}

$$n_{eff} = n - n_{col}$$

$$n_{eff} = n - \frac{1}{2}\tau z = n - \frac{1}{2}\tau z_s \frac{n}{2} \tag{8}$$

$$n_{eff} = n - \tau\frac{\sqrt{2}}{4}\pi d^2 n^2 \bar{v}$$

If we replace n by n_{eff} in eq. (4) we obtain

$$p = \left(n - \frac{1}{2}\tau z\right)kT \tag{9}$$

and by replacing z

$$p = \left(n - \frac{\sqrt{2}}{4}\pi d^2 n^2 \bar{v}\tau\right)kT \tag{10}$$

We rewrite this expression in order to compare it with the cohesion coefficient of van der Waals equation using the identities :

$$n = N/V,\ kL = R,\ N/L = n_{\text{m}}$$

and obtain

$$p = n_m RT - \frac{n_m^2}{V^2} RT \cdot \tau\frac{\sqrt{2}}{4}\pi d^2 \bar{v} L \tag{11}$$

We write the van der Waals equation in the following form:

$$p = \frac{n_m RT}{V - bn_m} - \frac{n_m^2 a}{V^2} \tag{1a}$$

Comparison of the coefficients (disregarding b) gives:

$$a = \frac{\sqrt{2}}{4}\pi d^2 L\bar{v}RT\tau \tag{12}$$

with $\bar{v} = \sqrt{\frac{3RT}{M}}$ (13)

M = molar mass in [kg mol $^{-1}$]

To sum up: The number of gas kinetic effective particles is equal to the total number of particles per volume reduced by half the number of pairs in a temporary collision process with collision duration time τ. We have obtained an expression for the cohesion pressure which now contains the duration time for the collision of an atomic or molecular gas, respectively. The SI unit of the expression of eq. (12) is Nm^4 / mol^2, the same as for the van der Waals a-constant.

We shall now check this expression and compare it with tabulated a-values for different substances, beginning with the noble gases.

3. Deductions from the collision model

3.1 Calculation of duration time of atomic collisions from van der Waals constant *a*

Eq. (12) enables the possibility to calculate the duration time of atomic collisions:

$$\tau = \frac{4a}{\sqrt{2}\pi d^2 \bar{v} RLT} \quad (14)$$

As an example we calculate the τ value for argon. As a is derived from T_c we have to use the critical temperature also here. The van der Waals constant a of argon is (see Tab. 1):

$$a_{Argon} = 0.1355 \frac{Jm^3}{mol^2}$$

The other values of argon needed for the calculation with eq. (14) are:

$$\frac{\sqrt{2}}{4}\pi = 1.11; \quad d^2 = 8.6 \cdot 10^{-20} m^2; \quad \bar{v} = 3.2 \cdot 10^2 \frac{m}{s}; \quad R = 8.31 \frac{J}{molK};$$

$$L = 6.02 \cdot 10^{23} \frac{1}{mol}; \quad T_c = 151K$$

$$a = 1.11 \cdot 8.6 \cdot 10^{-20} \cdot 3.2 \cdot 10^2 \cdot 8.31 \cdot 1{,}51 \cdot 10^2 \cdot 6{,}02 \cdot 10^{23} \cdot \tau$$

So we have:

$$0.1355 = 2.3 \cdot 10^{10} \tau$$

$$\tau = 5.9 \cdot 10^{-12} s$$

For the collision duration time of two Ar atoms at the critical temperature we obtain

$$\tau \approx 6 \text{ ps} \quad (15)$$

In order to check the reliability of this value we looked for references. Kittel [18] gives in "Thermal Physics" a collision rate for Ar atoms of 10^{10}/s. After Oldenberg [19] real collision duration times of gas molecules are much longer as with "head on" collisions, due to the torque moments at non-central collisions. Therefore the order of magnitude calculated above seems to be reasonable.

3.2 Comparison of the van der Waals *a*-values with the new expression for the cohesion pressure

Eq. (12) can be written :

$$a = \frac{\sqrt{2}}{4}\pi d^2 \sqrt{\frac{3RT}{M}} L\sqrt{R^2T^2}\,\tau \qquad \text{or}$$

$$a = \frac{\sqrt{2}}{4}\pi L\sqrt{3\mathrm{R}^3}\left(d^2\sqrt{T^3}\,\frac{1}{\sqrt{M}}\right)\tau \qquad (16)$$

We combine all constants in a pre-factor:

$$C_1 = \frac{\sqrt{2}}{4}\pi L\sqrt{3\mathrm{R}^3} \qquad \text{and obtain}$$

$$a = C_1\left(d^2\sqrt{T^3}\,\frac{1}{\sqrt{M}}\right)\tau \qquad (17)$$

Now we are able to compare the tabulated *a*-values from literature with the calculated ones, using *M*, suitable values for T and d (see below 3.2.1) , and, first of all, the collision duration time τ.

3.2.1 The parameters *M, T* and *d*

For *M* we took the molar mass of the gas under consideration. Since *a* and *d* are calculated from critical data we take for the temperature the critical temperature T_c, and for *d* the value calculated from the van der Waals *b* constant. The *a* and *b* values are found in standard table works, Landolt-Börnstein [2], Handbook of Chemistry and Physics [3] and from the Internet [4].

The following Tables (1– 6) are taken from [4] which are based on [3].

3.2.2 The collision duration time in the theory of Hertz

Looking for a possibility to estimate the collision duration time, we found the paper of H. Hertz "On the touching of solid elastic bodies" (German: *Über die Berührung fester elastischer Körper*) [10]. Hertz defined the collision duration as twice the time between the first contact of the two bodies until the complete formation of the plane deformation surface (which is a circle in case of two colliding spheres). A complete summary of the collision theory of Hertz is given by Szabó [20]. Hertz's theory is confirmed very well by macroscopic experiments (Ramsauer [21], Schreuer [22]).

First we discuss the relation given by Szabò [20] (p. 475, eq (32)): The collision duration of two identical solid elastic spheres is given by

$$\tau \;=\; 2.9432 \;\sqrt[5]{\frac{25}{16}\;\frac{\alpha^3}{\bar{v}_R}\;\left(\frac{m_1 m_2}{m_1+m_2}\right)^2} \qquad (18)$$

with v_R = root mean square speed of the spheres and m their masses. α is a parameter characterizing the deformation of the spheres during the collision process:

$$\alpha = \sqrt[3]{\frac{9}{64}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\left(\frac{1-\nu_1}{G_1}+\frac{1-\nu_2}{G_2}\right)^2} \qquad (19)$$

with r_1 and r_2 radii of the spheres, ν_1 and ν_2 Poison's constants, G_1 and G_2 shear moduli, respectively.

3.2.3 Simplified application of Hertz's formula to the collision of noble gas atoms

As a first attempt we took into account only the 5th root of the squared colliding masses. All other quantities were taken as constant and were combined into a constant pre-factor.

We have

$$a \;=\; C_2 d^2 \sqrt{T_c^3}\,\frac{1}{\sqrt{M}}\sqrt[5]{M^2}\,; \quad M^{-\frac{1}{2}}\cdot M^{\frac{2}{5}} \;=\; M^{-\frac{1}{10}}$$

$$a \;=\; C_2 d^2 \sqrt{T_c^3}\,\frac{1}{\sqrt[10]{M}} \qquad (20)$$

This expression has now to be calculated for different substances and to be compared with the corresponding *a*-values from the literature. In order to demonstrate the relevance of this concept it is sufficient to plot only the variable part of eq. (20) (in arbitrary units) versus the van der Waals *a*-value in a log-log-diagram.

4. Proof of the new expression of the cohesion pressure in comparison with tabulated *a*-values

4.1 Noble gases

The group of noble gases (with closed electronic shell structure) appeared to us suitable for checking the validity of the new collision duration concept. In Tab.1 the *a*-values are listed versus the values calculated according to eq. (20). The values of *a*, T_c and *d* are taken from the internet [4]. This leads to Fig.1, a log-log-plot of conventional *a*-values against the right-hand side of eq. (20). The graph exhibits a 45° straight line beginning with Neon up to Radon. Unexpectedly, there is an equivalence of our calculated values for the cohesion pressure with the classical van der Waals *a*-constants. Helium and Neon are clearly outside of this straight line which needs a special discussion.

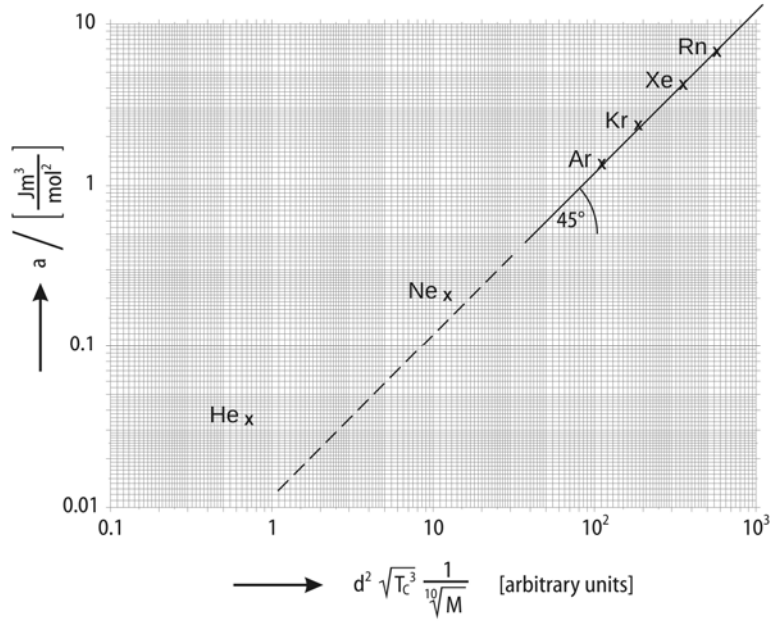


Fig. 1: Noble gases

4.1.2 The Behavior of Helium and Neon

The data of He and Neon are clearly outside of this straight line. We interpret this by comparing the atomic diameter with the thermal deBroglie wavelength

$$\lambda_0 = \frac{h}{\sqrt{2\pi MkT}} \tag{21}$$

h Planck's constant; if we take the atomic mass for M and T_c for the temperature we get the following table:

	$d/0.1nm$	$\lambda_0/0.1nm$
He	2.7	3.8
Ne	2.4	0.6
Ar	2.95	0.2
Kr	3.16	0.13
Xe	3.45	0.08

λ_0 defines the border between classical physical calculations and the domain of quantum mechanics. We may conclude from this table that our considerations applying the collision theory of Hertz to atomic collisions of noble gases are justified for Ar and larger atoms. He and Ne have to be treated with quantum mechanics which is outside the scope of this paper (the same is the case for hydrogen and all of its isotopes which are not considered here).

4.2 n-Alkanes

After this step we looked for further data in order to check our collision duration concept in comparison with van der Waals *a*-constants of other substances. The internet-table [4] exhibits *a*-values of 228 different molecules. From this table we calculated (using Excel) the values for

$$d^2, \sqrt{T_c^3} \quad \text{and} \quad \frac{1}{\sqrt[10]{M}}$$

resulting in an amount of data to continue comparing given van der Waals *a*-values with our new calculations. The *a*-values of the homologue series of n-Alkanes starting with CH_4 up to $C_{15}H_{32}$ are listed in Tab.2 and plotted in Fig.2. For comparison with the behavior of noble gases the straight line from Fig.1 is also drawn. Only methane and ethane lay on the line of the noble gas plot. The values for chain molecules with increased length deviate continuously from the noble gas line. This is easily understood because only parts of the chain molecules are involved in the collision processes.

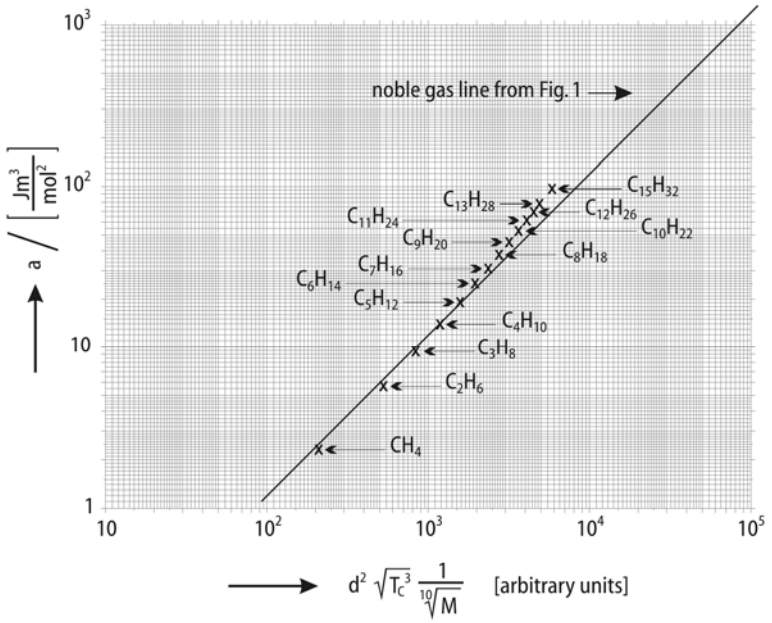


Fig. 2: n-Alkanes C_nH_{2n+2} from CH_4 up to $C_{15}H_{32}$ (missing $C_{14}H_{30}$)

4.3 Molecules with permanent dipole moment containing Hydrogen

Tab.3 lists the respective a-values from literature versus our calculated values according to eq. (20). They are plotted in Fig. 3 together with the 45° noble gas line. All calculated values are on the right-hand side of the noble gas line. The reason for this is the dipole character of these substances. Dipole molecules exhibit always a mutual attraction compared to non-polar ones. This was calculated in 1929 by Debye [23]. Nevertheless, the deviation from the noble gas behavior is not very dramatic. After Israelachvili [17] the mutual attraction due to permanent dipole moments below *1 D (1 D = 1 Debye)* is only weak. Stronger attractions appear only if the dipole moments are stronger than *1 D* so for water *(1.8 D)* and for ammonium chloride *(ca. 1.5 D)*. These two substances show a bigger distance from the noble gas line.

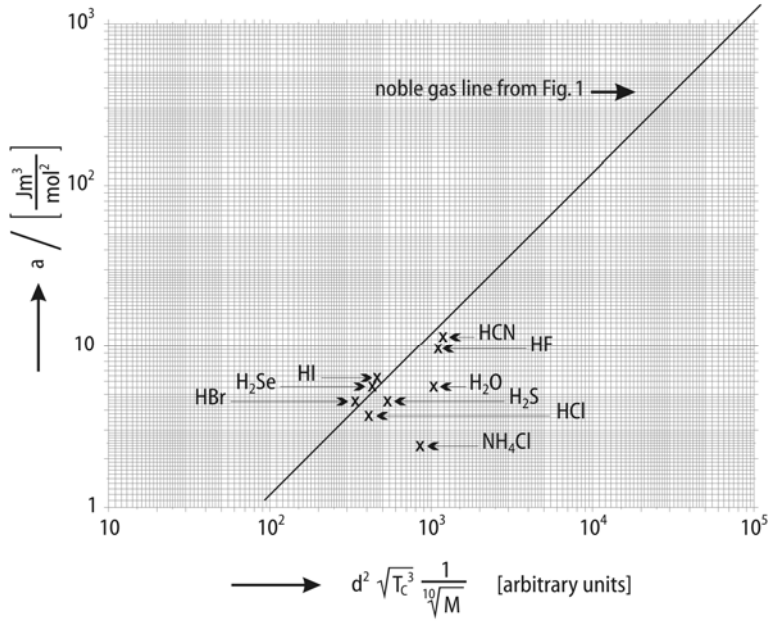


Fig. 3: Molecules with permanent dipole moment

4.4 Molecules of type XY_4

An interesting result is shown in Fig.4 with data from Tab.4. These substances have a large symmetry so that always the total molecule is involved in the collision process. Consequently their behavior is like that of noble gases.

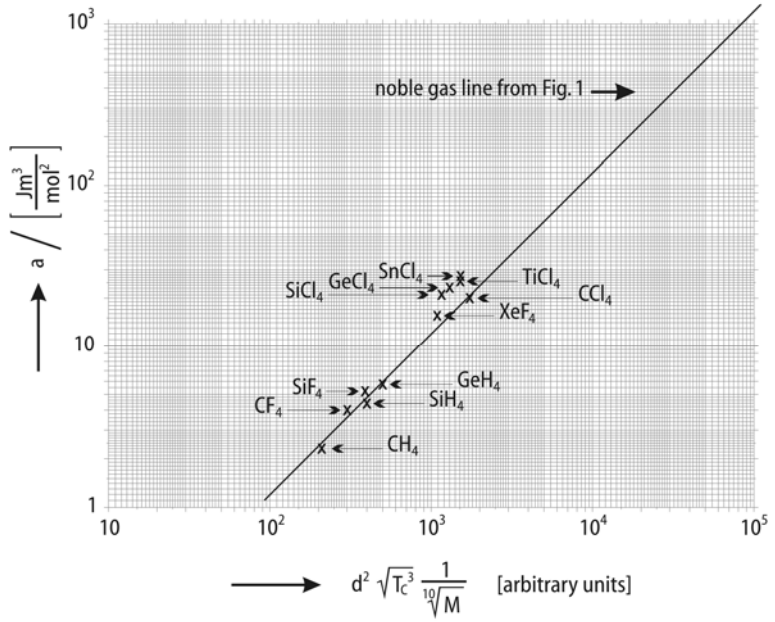


Fig. 4: XY_4 compounds

4.5 Molecules of type XY_6 and some heavy atoms

Fig.5 (with the values from Tab.5) shows the results from three heavy molecules. SF_6, WF_6 and UF_6 laying on the noble gas line, whereas the gases of single atoms Hg, S, Se and P are "relatively far away" from the noble gas behavior. We have no explanation for this result. We suppose that probably a high polarizability of these substances is the reason why they behave like dipole gases.

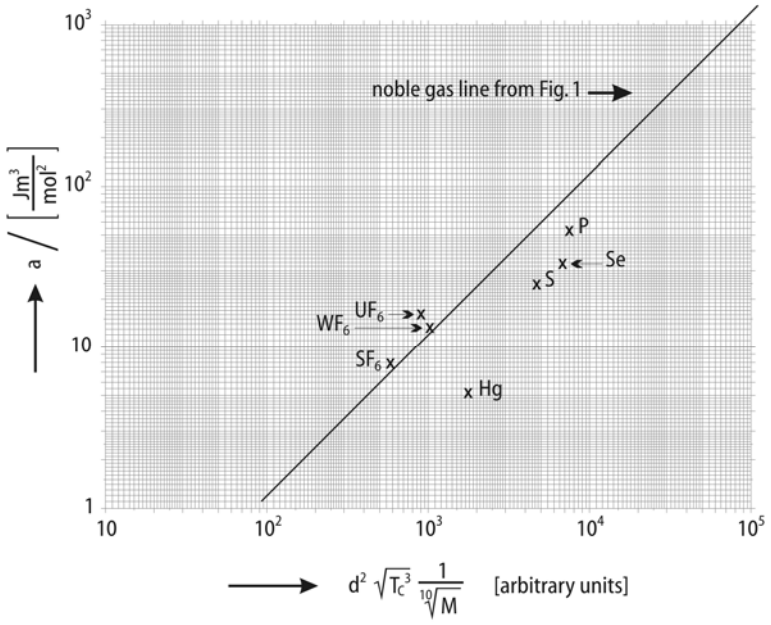


Fig. 5: XY_6 compounds and single atoms

5. A more crucial discussion of Hertz's formula

If we additionally take into account the values $r_1 = r_2 = d/2$ and v the Hertz's formula, as given by Szabó [20], we have to consider eq. (18) in the following form

$$\tau = C \sqrt[5]{\frac{2}{d}\,\frac{1}{\bar{v}}\,M^2} \tag{22}$$

Then we can proceed as in eq. (20). v is again the root mean square speed of the gas particles

$$\bar{v} = \sqrt{\frac{3RT}{M}}$$

We obtain

$$a = Cd^2\sqrt{T_c^3}\;\;\frac{1}{\sqrt{M}}\;\;\sqrt[5]{\frac{1}{d}M^2\left(\frac{3RT_c}{M}\right)^{-\frac{1}{2}}}$$

$$a \;=\; Cd^2\sqrt{T_c^3}\,M^{-\frac{1}{2}} \quad \frac{M^{\frac{1}{10}}M^{\frac{2}{5}}}{d^{\frac{1}{5}}\,(3R)^{\frac{1}{10}}T_c^{\frac{1}{10}}}$$

$(3\mathrm{R})^{\frac{1}{10}}$ is lumped into the constant: $C' \;=\; C\cdot(3\mathrm{R})^{-\frac{1}{10}}$

$$a = C' d^2\; d^{-\frac{1}{5}} T_c^{\frac{3}{2}} T_c^{-\frac{1}{10}} M^{-\frac{1}{2}} M^{\frac{1}{10}} M^{\frac{2}{5}}$$

Considering that $M^{-\frac{1}{2}}M^{\frac{1}{10}}M^{\frac{2}{5}}$ is = 1
we have now

$$a = C' d^{\frac{9}{5}} T_c^{\frac{7}{5}} \qquad (23)$$

The mass of the colliding spheres is now eliminated.

Proceeding as above – comparing van der Waals *a*-values versus the results from eq. (23) - like in the Figs.1 – 5, we get no significant difference compared to the simplified evaluation regarding only 5^{th} root out of M^2 as in Eq. (20). In Fig.6 this is illustratively shown for the noble gases. The *45°* angle of the line remains the same as in Fig.1.

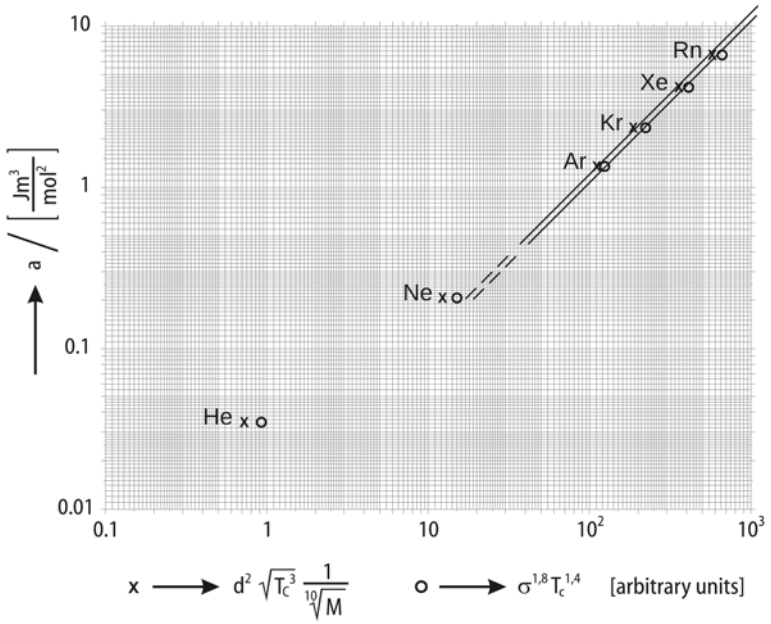


Fig. 6: Comparison of the simplified application of Hertz's theory and a more crucial one, demonstrated at noble gases. The simplified method is obviously sufficient.

The temperature plays the important role whereas the diameter of the particles is only of small importance (but not to be neglected).

6. Conclusions

The deviation from the behavior of an ideal gas, described by van der Waals in his famous formula by modification of the equation of an ideal gas, is discussed using an alternative concept: We consider (i) the particles (atoms or molecules) of the real gas as solid elastic spheres like billiard balls (following Boltzmann) and (ii) take into account that the collision duration time of two such particles is small but not zero. Assuming the time of duration of a collision process τ, an equation is derived which describes the cohesion behavior similar to the constant "*a*" of van der Waals. This new equation contains beside the collision duration time also the measured values of the critical data. Calculating the collision duration after the theory of Hertz, a similar equation for the cohesion pressure is derived which can be compared with the van der Waals "*a*" values tabulated in different publications. The comparison is done for the group of noble gases, using log- log- graphs neglecting constant factors. A *45*°-correlation of the *a*-values tabulated with those calculated using the collision theory of Hertz is found. For noble gases the limit of this treatment of gas atoms as solid elastic spheres is discussed. The homologous series of n-Alkanes deviates continuously from the noble gas line because only parts of the chain molecule are involved in the collision processes. Molecules with permanent dipole moments exhibit the expected behavior – deviation from the noble gas line - because the dipoles cause a general mutual attraction of the molecules leading to an enhanced cohesion pressure. More complex molecules are treated the same way, any deviations from the simple collision model can properly be explained by the polarity of the molecules.

Interpretation of the behavior of real gases by introducing a finite collision duration time of the particles and applying the collision theory of Hertz does not need the assumption of attractive forces between molecules of spherical symmetry.

In this concept, condensation of a gas takes place when the time of collision duration is comparable to the time of flight, the time between two collisions of the particles.

Acknowledgment: We are indebted and thankful to G.W.H. Höhne for fruitful discussions and critical reading of the manuscript. Thanks also to J. Frank for valuable contributions in numerous discussions and for computer assistance.

References

[1] J.D. van der Waals, Die Kontinuität des gasförmigen und flüssigen Zustandes, Leipzig, Johann Ambrosius Barth (1881)

[2] Landolt-Börnstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik.
I. Band, I. Teil: Atome und Ionen. 6.Auflage, Berlin-Göttingen-Heidelberg, Springer-Verlag 1950
II.Band, I. Teil: Mechanisch-Thermische Zustandsgrößen. 6. Auflage, Berlin-Göttingen-Heidelberg, Springer-Verlag 1971

[3] Handbook of Chemistry and Physics, Ed. R.C. Weast, 53rd Edition, The Chemical Rubber Co., Cleveland-Ohio 1972/73

[4] Internet Table: van der Waals Constants for Real Gases
http://www2.ucdsb.on.ca/tiss/stretton/Database/van_der_Waals_constants.ht

[5] J.E. Lennard-Jones, Cohesion, Proc. Phys. Soc. **43**, 461- 482 (1931)

[6] R.A. Buckingham, The Classical Equation of State of Gaseous Helium, Neon and Argon, Proc. Roy. Soc. **A 168**, 264 - 283 (1938)

[7] J. Corner, Intermolecular Potentials in Neon and Argon, Trans. Faraday Soc. **44**, 914 (1948)

[8] W. Heitler und F. London, Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik, Z. f. Physik, **44**, 455 - 472 (1927)

[9] L. Boltzmann, Vorlesungen über Gastheorie, I. und II. Teil, Nachdruck Akademische Druck und Verlagsanstalt, Graz 1981

[10] H. Hertz, Über die Berührung fester elastischer Körper, Gesammelte Werke, Band I. Hrsg. Ph. Lenard, Leipzig, Johann Ambrosius Barth 1895, p. 155 – 175.

[11] J.J. van Laar, Die Zustandsgleichung von Gasen und Flüssigkeiten, Leipzig 1924

[12] R. Seiler, Messung der Isothermen realer Gase (Kohlensäure und Frigen 13), Staatsexamensarbeit, Universität Mainz 1964

[13] P.W. Atkins, Physical Chemistry, 6. Edition, Oxford University Press 2001

[13a] R.Brdicka, Grundlagen der Physikalischen Chemie, VEB Deutscher Verlag der Wissenschaften, Berlin 1958

[14] J.O. Hirschfelder, Ch.F. Curtis and R.B. Bird, Molecular Theory of Gases and Liquids, New York – London – Sydney, John Wiley & Sons 1954

[15] H.A. Stuart, Molekülstruktur, 3. Auflage, Berlin-Heidelberg-New York, Springer-Verlag 1967

[16] G. Briegleb, Zwischenmolekulare Kräfte und Molekülstruktur, Stuttgart, Verlag von Ferdinand Enke 1937

[17] J. Israelachvili, Intermolecular & Surface Forces, 2. Edition, Academic Press, an imprint of Elsevier, 1991

[18] Ch. Kittel, Physik der Wärme, R.Oldenbourg Verlag, München Wien und John Wiley & Sons GmbH Frankfurt/Main 1973

[19] O.Oldenberg, Duration of Atomic Collisions, Am. J. Phys. **25**, 94 – 97 (1957)

[20] I. Szabó, Geschichte der mechanischen Prinzipien, 2. Auflage, Basel, Boston, Stuttgart, Birkhäuser-Verlag 1979

[21] C. Ramsauer, Experimentelle und theoretische Grundlagen des elastischen und mechanischen Stoßes, Annalen der Physik, Vierte Folge, Band **30,** 417 – 494 (1909)

[22] E. Schreuer, Weichheit, Stoßdauer und innere Dämpfung technischer Gummimischungen, Kolloid-Z., **129**, 123-127 (1952)

[23] P. Debye, Polar Molecules, The Chemical Catalog Company 1929, Reprint by Dover Publications

Tables

In tables 1 – 6 the van der Waals constants *a* and *b* from literature are compared with the variable part of the new expression for the cohesion pressure of gases using Hertz' collision theory.

a in [bar Liters²/mol²], *b* in [Liters/mol.], *d* is the diameter of a particle in [nm], *Tc* the critical temperatur T_c, *M* the molar mass of the gas particles. The last column gives the variable part of the new expression using Hertz's theory of elastic collision.

Table 1: Noble Gases

Formula	Name	a	b	d/nm 0.925*b^(1/3)	Tc/K 3,563*(a/b)	M	d^2*Tc^(3/2)*1/M^0.1
He	**Helium**	**0,0346**	**0,0238**	0,266	5,17982353	4,0026	0,7270
Ne	**Neon**	**0,2080**	**0,0167**	0,237	44,3244019	20,0000	12,2438
Ar	**Argon**	**1,3550**	**0,0320**	0,294	150,823649	39,9480	110,5716
Kr	**Krypton**	**2,3250**	**0,0396**	0,315	209,191288	121,7881	186,1873
Xe	**Xenon**	**4,1920**	**0,0516**	0,344	289,683786	131,0000	359,1420
Rn	**Radon**	**6,6010**	**0,0624**	0,367	376,973281	222,0000	574,3002

Table 2: n-Alkanes

Formula	Name	**a**	**b**	d/nm 0.925*b^(1/3)	Tc/K 3,563*(a/b)	M	**d^2*Tc^(3/2)*1/M^0.1**
CH_4	**Methane**	**2,3000**	**0,0430**	0,324	190,534759	16,0000	**209,4888**
C_2H_6	**Ethane**	**5,5700**	**0,0650**	0,372	305,368672	30,0000	**525,5985**
C_3H_8	**Propane**	**9,3850**	**0,0904**	0,415	369,734133	44,0000	**840,0295**
C_4H_{10}	**Butane**	**13,9300**	**0,1168**	0,452	424,936558	58,1000	**1193,7926**
C_5H_{12}	**Pentane**	**19,1300**	**0,1451**	0,486	469,746313	72,1500	**1569,0911**
C_6H_{14}	**Hexane**	**24,9700**	**0,1753**	0,518	507,519167	86,2000	**1963,5758**
C_7H_{16}	**Heptane**	**30,8900**	**0,2038**	0,544	540,044504	100,2000	**2342,9086**
C_8H_{18}	**Octane**	**37,8600**	**0,2372**	0,572	568,698061	114,0000	**2763,2755**
C_9H_{20}	**Nonane**	**45,1100**	**0,2702**	0,598	594,844301	128,2600	**3192,9947**
$C_{10}H_{22}$	**Decane**	**52,8800**	**0,3051**	0,622	617,539954	142,3000	**3616,2452**
$C_{11}H_{24}$	**Undecane**	**60,8800**	**0,3396**	0,645	638,738045	156,0000	**4053,1357**
$C_{12}H_{26}$	**Dodecane**	**69,1400**	**0,3741**	0,667	658,502593	170,0000	**4498,2440**
$C_{13}H_{28}$	**Tridecane**	**77,9400**	**0,4109**	0,687	675,834072	184,0000	**4922,5690**
$C_{15}H_{32}$	**Pentadecane**	**96,5000**	**0,4857**	0,727	707,905085	212,0000	**5826,3663**

Table 3: Molecules with permanent dipole moments containing Hydrogen

Formula	Name	**a**	**b**	d/nm	Tc/K	M	**d^2*Tc^(3/2)*1/M^0.1**
				0.925*b^(1/3)	3,563*(a/b)		
H_2O	**Water**	**5,5370**	**0,0305**	0,289	647,04267	18,0000	**1030,0909**
HF	**Hydrogen fluoride**	**9,5650**	**0,0739**	0,388	461,16502	20,0000	**1106,6483**
HCN	**Hydrogen cyanide**	**11,2900**	**0,0881**	0,412	456,805246	27,0000	**1189,9932**
H_2S	**Hydrogen sulphide**	**4,5440**	**0,0434**	0,325	373,133717	34,0000	**535,5587**
HCl	**Hydrogen chloride**	**3,7000**	**0,0406**	0,318	324,626939	36,5000	**412,8903**
NH_4Cl	**Ammonium chloride**	**2,3800**	**0,0073**	0,180	1155,30518	53,5000	**852,9146**
H_2Se	**Hydrogen selenide**	**5,5230**	**0,0479**	0,284	410,82357	81,0000	**431,6784**
HBr	**Hydrogen bromide**	**4,5000**	**0,0442**	0,276	363,159683	80,9000	**339,8397**
HI	**Hydrogen iodide**	**6,3090**	**0,0530**	0,293	423,891514	128,0000	**462,5346**

Table 4: Molecules of type XY4

Formula	Name	**a**	**b**	d/nm	Tc/K	M	**d^2*Tc^(3/2)*1/M^0.1**
				0.925*b^(1/3)	3,563*(a/b)		
CH_4	**Methane**	**2,3000**	**0,0430**	0,324	190,534759	16,0000	**209,4888**
SiH_4	**Silane**	**4,3800**	**0,0579**	0,358	269,532642	32,1000	**400,8212**
GeH_4	**Germane**	**5,7430**	**0,0656**	0,373	312,163371	76,6000	**497,4663**
CF_4	**Tetrafluoromethane**	**4,0400**	**0,0633**	0,369	227,581344	87,9800	**298,2214**
SiF_4	**Silicon tetrafluoride**	**5,2590**	**0,0724**	0,386	258,952695	104,0000	**389,3661**
CCl_4	**Tetrachloromethane**	**20,0100**	**0,1281**	0,466	556,562295	153,0000	**1727,4258**
$SiCl_4$	**Silicon tetrachloride**	**20,9600**	**0,1470**	0,412	508,030476	169,9000	**1164,1142**
$TiCl_4$	**Titanium(IV) chloride**	**25,4700**	**0,1423**	0,408	637,734434	346,2000	**1492,1040**
XeF_4	**Xenon tetrafluoride**	**15,5200**	**0,0904**	0,350	612,039402	207,0000	**1091,0037**
$GeCl_4$	**Germanium tetrachloride**	**23,1200**	**0,1489**	0,414	553,234117	214,2000	**1303,7071**
$SnCl_4$	**Stannic chloride**	**27,2500**	**0,1641**	0,428	591,662096	260,5000	**1508,5891**

Table 5: Molecules of type XY6 and some heavy atoms

Formula	Name	a	b	d/nm	Tc/K	M	d^2*Tc^(3/2)*1/M^0.1
				0.925*b^(1/3)	3,563*(a/b)		
P	**Phosphorus**	**53,6000**	**0,1570**	0,499	1216,41274	30,9700	**7499,3832**
S	**Sulphur**	**24,3000**	**0,0660**	0,374	1311,83182	32,0700	**4696,7967**
Se	**Selenium**	**33,4000**	**0,0675**	0,377	1763,02519	78,9600	**6788,0969**
SF_6	**Sulphur hexafluoride**	**7,8570**	**0,0879**	0,411	318,626121	146,0300	**584,6605**
Hg	**Mercury**	**5,1930**	**0,0106**	0,203	1750,48808	200,0000	**1777,9417**
WF_6	**Tungsten(VI) fluoride**	**13,2500**	**0,1063**	0,438	444,118062	297,0000	**1017,5583**
UF_6	**Uranium(VI) fluoride**	**16,0100**	**0,1128**	0,377	505,70594	352,0000	**900,9505**

Table 6: Comparison of simplified application of Hertz's theory and a more crucial one, demonstrated for noble gases

Formula	Name	a	b	d/nm	Tc/K	d^2*Tc^(3/2)*1/M^0.1	d^(9/5)*Tc^(7/5)
				0.925*b^(1/3)	3,563*(a/b)		
He	**Helium**	**0,0346**	**0,0238**	0,266	5,17982353	**0,7270**	**0,9232**
Ne	**Neon**	**0,2080**	**0,0167**	0,237	44,3244019	**12,2438**	**15,0852**
Ar	**Argon**	**1,3550**	**0,0320**	0,294	150,823649	**110,5716**	**123,6908**
Kr	**Krypton**	**2,3250**	**0,0396**	0,315	209,191288	**186,1873**	**222,1707**
Xe	**Xenon**	**4,1920**	**0,0516**	0,344	289,683786	**359,1420**	**410,5728**
Rn	**Radon**	**6,6010**	**0,0624**	0,367	376,973281	**574,3002**	**665,5986**