

Thermodynamics

V. The Van der Waals Equation

5.1 Formulation of the Problem

In this session we will see how can the computer be of help to gain a deeper understanding of a simple equation of physics and to test the agreement between theory and experiment. We consider the van der Waals gas equation. It is obtained from the ideal gas equation by including corrections for real gases.

It is well known that the equation of state for ideal gases describes a gas of point-like particles in the limit of vanishing mutual interaction. The gas particles interact with the container walls only by the transfer of momentum during reflection. The ideal gas equation for one mole of gas is:

$$PV = RT \quad (5.1)$$

Where P is the pressure exerted by the, V the volume of one mole, R the gas constant and T the absolute temperature. The ideal gas equation is a good approximation for inert gases at room temperature and atmospheric pressure, and under these conditions it also applies quite well to air. On the other hand it is no longer valid for butane or carbon dioxide compressed in steel flasks.

Van der Waals adapted the ideal gas equation to real gases by the following changes:

1. Real gas particles have a finite size. When packed as densely as possible they occupy the so-called eigen-volume. The steep rise in pressure shown by the ideal gas equation as $V \rightarrow 0$ must occur in reality when the gas is compressed to its eigen-volume. This is achieved by replacing the volume V in the ideal gas equation by $(V - b)$, where b is the total volume of the particles in one mole.
2. Beyond the short-range region of repulsion there is an attractive force between the gas particles, which is today known as the van der Waals force. It can be calculated in quantum mechanical models as an interaction of induced electric dipoles, which decreases with a high power of the distance between the particles. In the gas equation this attractive force has the effect that the pressure exerted by the container walls on the gas is augmented by an internal pressure, which helps the external pressure to compress the gas. Van der Waals takes account of this internal pressure by the term a/V^2 .

If one inserts the two corrections in the ideal gas equation one obtains the van der Waals equation:

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \quad (5.2)$$

In this equation of state b represents the finite volume of a gas molecule and represents forces of attraction between gas molecules. The van der Waals equation of state predicts a phase transition between liquid, vapor, and critical point above, which there is no phase transition. These aspects are very realistic. However, the above equation of state is not well suited for most molecular liquids.

The isotherms of this equation represent curves of equal temperature in the P-V diagram. For temperatures below a critical temperature T_c ; one has three Values of V for each value of the pressure. This at first appears physically unrealistic. Real gases behave differently. If one decreases the volume at a constant temperature the Pressure increases until the vapour Pressure of the liquid phase is reached. Then condensation follows, and the, pressure no longer increases, until all the gas is liquefied. For further decrease in the volume, the pressure then climbs very steeply.

The van der Waals equation does not contain the Phenomenon of condensation. However it is not physically unrealistic. At least in the immediate neighbourhood of the values of P, V and T where condensation would occur, it still describes rather well the formation of the super-saturated vapour. The incipient condensation in the presence of condensation nuclei must be incorporated into the van der Waals equation by means of an additional prescription. Maxwell has done this by introducing the lines named after him. For each isotherm below the critical temperature Maxwell defines a horizontal line in the P-V diagram, such that the two shaded areas in Fig. 5.1 are of equal size. This can also be formulated as follows: The area of the rectangle below the

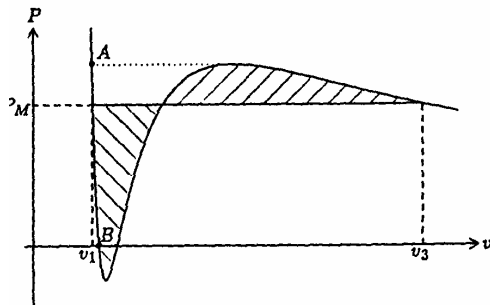


Fig. 5.1. Isotherm curves of the van der Waals equation and the Maxwell line.

Maxwell line must be as large as the integral under the isotherm in the same interval. Then, whenever the gas phase and the liquid phase co-exist, the state of the real gas lies on the Maxwell line and not on the van der Waals isotherm.

As already mentioned, van der Waals adjusted the ideal gas equation to real gases using only two parameters a and b . It was not to be expected that this simple correction would lead to complete agreement between theory and experiment for all real gases. Especially in the overlapping region between repulsion and attraction of the gas particles, the two parameters cannot describe the details of the interaction. With the computer and the repertoire of programs already constructed for numerical and graphical output we can display the isotherms of the van der Waals equation without much effort. The inclusion of the Maxwell lines requires only little computation time. Once one has determined the Maxwell lines for a number of temperatures one obtains a theoretical vapour pressure curve and can compare it with a vapour pressure curve obtained experimentally.

5.2 Numerical Method

The van der Waals equation determines a point in the P-V diagram where the two zeros of the derivative $\partial P / \partial V$ on an isotherm coincide, and as a result the second derivative $\partial^2 P / \partial^2 V$ is also zero; see Fig. 5.1. This point is called the critical point. The associated physical quantities are the critical pressure P_c , the critical temperature T_c and the critical volume V_c . We obtain the critical values such that:

$$\begin{aligned} V_c &= 3b \\ T_c &= \frac{8a}{27Rb} \\ P_c &= \frac{a}{27b^2} \\ P_c V_c &= \frac{3}{8} RT_c \end{aligned} \quad (5.3)$$

(Derive Eq.5.3)

from which we see that the gas pressure at the critical point is 3 times as great as that of the ideal gas at the same density and temperature.

An abbreviated way of writing the van der Waals equation is obtained by introducing the reduced (dimensionless) quantities $p = P/P_c$, $v = V/V_c$ and $t = T/T_c$:

$$\begin{aligned} \left(\frac{pa}{27b^2} + \frac{a}{9b^2 v^2} \right) (3bv - b) &= \frac{8at}{27b} \\ \left(P + \frac{3}{v^2} \right) (3v - 1) &= 8t \end{aligned} \quad (5.4)$$

This makes it clear that the P-V diagrams for all van der Waals gases are similar and differ from each other only by scale factors. It follows from (5.4) that the reduced eigen-volume (volume of the particles) is just 1/3.

The condition for the Maxwell lines is the same in the p-v diagram as in the P-V diagram: the integral under the isotherm must be equal to the area under the Maxwell line. Denoting the end points of the Maxwell line by v_1 and v_3 , and the vapour pressure by p_m , the condition is

$$PM(v_3 - v_1) = \int_{v_1}^{v_3} p(v) dv \quad (5.5)$$

Using (5.4), evaluate the LHS and RHS of (5.5); then equate to obtain:

$$8t \left(\frac{v_3 - v_1}{3v_1 - 1} - \frac{1}{3} \frac{3v_3 - 1}{3v_1 - 1} \right) - 3 \frac{(v_3 - v_1)^2}{v_1^2 v_3} = 0. \quad (5.4)$$

With the relation between v_1 and v_3 (Eq.(5.4)), obtain;

$$\left(\frac{8t}{3v_1 - 1} - \frac{3}{v_1^2} \right) = \frac{8t}{3v_3 - 1} - \frac{3}{v_3^2}$$

$$\frac{24t(v_3 - v_1)}{(3v_1 - 1)(3v_3 - 1)} = \frac{3(v_3^2 - v_1^2)}{v_1^2 v_3^2}, \quad (5.5)$$

$$\frac{8t}{(3v_1 - 1)(3v_3 - 1)} = \frac{v_3 + v_1}{v_1^2 v_3^2}$$

$$v_3 = \frac{(3v_1 - 1)^2 + \sqrt{(3v_1 - 1)^4 - 4v_1(3v_1 - 1)(8tv_1^2 - 3(3v_1 - 1))}}{2(8tv_1^2 - 3(3v_1 - 1))} \quad (5.6)$$

Derive Eq.(5.6)

Using this equation we can replace v_3 in (5.4) by an expression in v_1 and t . The desired solution for v_1 is then obtained as the vanishing point of the function on the left-hand side of (5.4), at the specified temperature t . We cannot calculate this zero analytically, but we can find it on the computer using nested intervals.

For this method we need a lower and an upper limit for v_1 . As the lower limit we take the reduced volume v_A corresponding to the point A in Fig. 5.1. We obtain v_A as the lowest zero of the discriminator occurring in (5.6), because the discriminant states whether there are any volumes other than v_1 giving the same pressure on the isotherm. The upper limit v_{lim} is taken as the reduced volume v_B corresponding to the zero point B in Fig. 5.1, whenever this zero point exists. It is easy to show that the zero point exists if the reduced temperature is lower than 27/32. From the van der Waals equation (5.4) one obtains for $p = 0$

$$\frac{3}{v^2}(3v - 1) = 8t, \quad 8tv^2 - 9v + 3 = 0, \quad v = \frac{9 \pm \sqrt{81 - 96t}}{16t} \quad (5.7)$$

Derive Eq.(5.7)

When $t \leq 27/32$ there are two real solutions. The smaller one is the desired limit v_B . For reduced temperatures $t > 27/32$ the isotherms have no zeros. In this case it can be shown analytically (or demonstrated numerically) that $v_{lim}=1$ fulfils all the conditions which we place on an upper limit, namely: a) $v_{lim}=1$ lies between the minimum and the maximum of the van der Waals isotherm, i.e. it is certainly greater than the left-hand end of the Maxwell line, b) equation (5.6) is valid in the entire interval $[v_A, 1]$ and fulfils the condition $v_3 > v_1$. As the upper limit v_{lim} , we accordingly have $v_{lim}=v_B$ if $t \leq 27/32$ and $v_{lim}=1$, if $t > 27/32$.

5.3 Programming

The method of nested intervals, which we shall use to determine the zero point of (5.4) taking account of (5.6), is also known by the name of the bisection method. It is applicable in the following problem formulation: given a continuous function $f(x)$ on an interval $[a, b]$, it is required to find a zero point x_0 of the function $f(x)$ with $a < x_0 < b$. The bisection method assumes that either $f(a) > 0, f(b) < 0$ or $f(a) < 0, f(b) > 0$, i.e. that at least one zero point of odd order exists. This assumption can be expressed in compact form by

$$f(a) \cdot f(b) < 0 \quad (5.8)$$

With $x_1 = a$ and $x_2 = b$ we come to the first step of the method: bisecting the interval $[x_1, x_2]$, one obtains

$$x_0 = 1/2(x_1 + x_2) \quad (5.9)$$

and calculates $f(x_0)$.

The second step is to test whether, for a pre-specified accuracy limit E

$$|x_1 - x_2| \leq E \quad (5.10)$$

If this is the case, then x_0 is the desired approximation to the zero point. If this is not so, one tests whether the condition

$$f(x_0) \cdot f(x_2) < 0 \quad (5.11)$$

is fulfilled. If so, then a zero point lies between x_0 and x_2 . We take $[x_0, x_2]$ as the new interval $[x_1, x_2]$ and return to the first step. If not, then either

$$f(x_0) = 0, \quad (5.12a)$$

in which case we have found the required zero point, or else

$$f(x_1) - f(x_0) < 0 \quad (5.12b)$$

In the latter case we take $[x_i, x_0]$ as the new interval $[x_1, x_2]$ and return to the first step.

In order to be independent of our particular example, we do not incorporate the zero point determination into the main program THERM, but write a subroutine with the name BISEKT.

The subroutine BISEKT needs 4 input parameters, namely the function f , the interval limits a and b , and also the accuracy limit ϵ . As output one obtains (at most) one zero point x_0 (see list of parameters in line 100). The function f must be available as a FUNCTION subprogram $F(x)$. One can follow the execution of the bisection method line by line. The progress of the calculation is guided by the four questions: (5.8) in line 106 (in the case of non-fulfilment the program stops), (5.10) in line 111, (5.11) in line 112 and (5.12) in line 116.

The function $f(v_1)$, whose zero point we wish to determine, stands on the left-hand side of (5.4),

$$f(v_1) = 8t \left(\frac{v_3 - v_1}{3v_1 - 1} - \frac{1}{3} \ln \frac{3v_3 - 1}{3v_1 - 1} \right) - 3 \frac{(v_3 - v_1)^2}{v_1^2 v_3} \quad (5.13)$$

where v_3 is to be substituted using (5.8). The function $f(v_1)$ is defined in the interval $[v_A, v_{lim}]$. In the bisection method one may extend the region of definition of the function f by appending functions, as long as no new zero points are created thereby. We make use of this possibility and extend the region of definition of $f(v_1)$ over the interval $[1/3, 1]$, by setting

$$f(v_1) = +1 \quad \text{in the interval} \quad [1/3, v_A] \quad (5.14)$$

$$f(v_1) = -1 \quad \text{in the interval} \quad [v_{lim}, 1] \quad (5.15)$$

The limit v_{limit} can easily be determined. From (5.15) one then has at once the function values in the (possibly null) interval $[v_{limit}, 1]$.

The limit v_A , which would be more difficult to determine, need not be explicitly calculated. If, for an argument v_1 in the interval $[1/3, v_{lim}]$, the discriminant of equation (5.6)

$$v_3 = (3v_1 - 1)^4 - 4v_1(3v_1 - 1)(8tv_1^2 - 3(3v_1 - 1)) \quad (5.16)$$

has a negative value, then (5.14) is valid. If the value of the discriminant is greater than or equal to zero, then one calculates v_3 from (5.6) and $f(v_1)$ from (5.13). We generate the function $f(v_1)$ by the FUNCTION subprogram FKT(v_1). We transfer the temperature value needed for the computation by means of the COMMON block /TEMPER/ (line 203), as the calling program BISEKT does not know this variable. In order to economise in writing and computing we work with the following abbreviations: the variable TERM contains the value of the expression $3v_1 - 1$ (line 214), the variables DENOM and DISKRI relate to the denominator and the discriminant in equation (5.6) (lines 215 and 216).

One recognises in FKT the following equations: (5.6) in line 218, (5.7) in line 207, (5.15) in line 212 and (5.14) in line 222. The lines (209-212) ensure that FKT is defined for all values of the argument. One therefore avoids the question whether the argument lies in the region where the function is defined.

So far the discussion has been almost entirely about how the volumes v_1 and v_3 for the Maxwell line could be calculated. We shall now also consider the van der Waals isotherm in a definite volume interval $[v_{min}, v_{max}]$. For this purpose we shall divide this interval into $i_v=200$ sub-intervals and obtain $i_v + 1$ grid points.

$$v^{(i)} = ih + v_{min}; i = 0, 1, 2, \dots, i_v \quad (5.17)$$

with the mesh width

$$h = \frac{v_{max} - v_{min}}{i_v} \quad (5.18)$$

We notice, meanwhile, that v_{min} must be greater than The values of the pressures at the grid points follow from (5.4) and are

$$p^{(i)} = \frac{8t}{3v^{(i)} - 1} - \frac{3}{(v^{(i)})^2} \quad (5.19)$$

The pressure p_m at the Maxwell line is obtained in the same way:

$$PM = \frac{8t}{3v_1 - 1} - \frac{3}{v_1^2} \quad (5.20)$$

(Derive Eq.5.20)

Consider now the main program. The values for i_v and ϵ , together with the eigen-volume are specified in a PARAMETER instruction (line 302); the values for v_{min} , v_{max} and t are input.

After the grid points have been calculated from (5.17) in the DO-loop of lines 307 to 309, the pressure values on the van der Waals isotherm are calculated from (5.19) in the DO-loop of lines 310 to 312. If the temperature is smaller than the critical temperature, i.e. $t < 1$, the subroutine BISEXT is called (line 314), which transfers the value of v_1 to THERM. With the abbreviations TERM, DENON and DISKRI already known, V_3 is calculated from (5.6) in line 318, and in the following line we obtain P_m from (5.20).

5.4 Exercises

5.4.1 Plot P versus V to show the isotherms of the van der Waals equation Eq(5.1), i.e. the curves of equal temperature in the P - V diagram.

5.4.2 Consider the p - v diagram for a number of different temperatures. Find the vapour pressure p_m for various reduced temperatures t . Draw the function $PM(t)$ between $t = 0.25$ and $t = 1$ on a logarithmic scale.

5.4.3 Carbon dioxide has a critical temperature of 31.1°C and a critical pressure of 72.95atm . Calculate the critical volume according to van der Waals. Compare the volume of one mole of CO_2 according to the ideal gas equation and according to van der Waals, at 40°C and for 1, 10, 100 and 1000 atmospheres.

Note: One mole of ideal gas at one atmosphere and 0°C has a volume of 22420 cm^3 , and consequently at one atmosphere and 40°C it has a volume of 25700 cm^3 .

5.4.4 Table 1 shows the measured boiling temperatures for the gases CH_4 , NH_3 , H_2O , HF and Ne at various pressures. Find the boiling temperatures according to van der Waals, using the curve obtained in Exercise 5.4.1. For which gases do you find good agreement, and for which poor?

Table 1: Measured boiling temperatures of CH_4 , NH_3 , H_2O , HF , Ne .

| Gas | CH_4 | NH_3 | H_2O | HF | Ne |
|---|---------------|---------------|----------------------|-------------|-------------|
| Molecular Weight | 16.04 | 17.03 | 18.02 | 20.01 | 20.18 |
| Critical press. (atm) | 47.2 | 115.2 | 218.0 | 66.2 | 27.1 |
| Critical Temp. (K) | 190.6 | 405.5 | 647.4 | 461 | 44.4 |
| Boiling temperature (K) measured | | | | | |
| At 1atm | 111.7 | 239.7 | 373.2 | 292.7 | 27.07 |
| At 2atm | | 254.5 | 393.3 | 313.3 | 29.63 |
| At 5atm | 134.9 | 277.9 | 425.6 | 343.1 | 33.81 |
| At 10atm | 148.4 | 298.9 | 453.7 | 371.5 | 37.65 |
| At 20atm | 164.7 | 323.3 | 486.3 | | 42.35 |
| At 40atm | 186.9 | 352.1 | 524.3 | | |

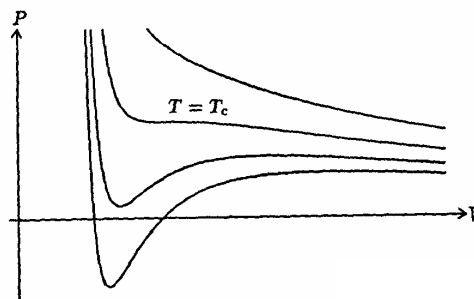
5.4.5 Propane (C_3H_8), butane (C_4H_{10}) and mixtures of the two are handled as liquid gas in canisters for heating of camp-cookers, soldering irons, etc. Notices on the canisters warn the user not to subject the containers to any high temperatures. Using the vapour pressure curve from Exercise 5.4.2, estimate to what extent these warnings are justified. How high in the pressure according to van der Waals at 20°C , and how much does it increase if the container is heated to 50, 70 or 100°C ?

Table 2: Critical data for liquid gases in household use.

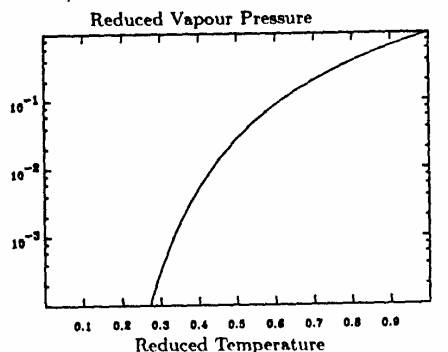
| Gas | C_3H_8 | C_4H_{10} |
|---|------------------------|---------------------------|
| Molecular Weight | 44.10 | 58.12 |
| Critical Pressure (atm) | 42.1 | 37.4 |
| Critical Temperature ($^\circ\text{C}$) | 96.8 | 152.01 |

5.5 Solutions to the Exercises

5.5.1 Isotherms of the van der Waals equation.



5.5.2 Figure 5.12 shows the curve of the vapour pressure $PM(t)$ versus t . Since $PM(t)$ varies by about three orders of magnitude between $t = 0.25$ and $t = 1$, a logarithmic scale is required. As one can see, in the neighbourhood of the critical point a fall of about 15% in t leads to a halving of the vapour pressure. Further below the critical point a fall of a few per cent in t is enough to halve the vapour pressure.



5.5.3 The exercise can be carried out by the program most simply if the desired pressure is chosen as the lower or upper limit of the pressure region displayed in the graphics window. After some calculation one obtains the following values for the volume of a mole at 40°C:

| Volume of a mole in cm ³ | | | |
|-------------------------------------|--------------------|------------------------|-------|
| | ideal gas equation | VAN DER WAALS equation | |
| At 1 atm | 25700 | 25590 | 25574 |
| At 10 atm | 2570 | 2470 | 2448 |
| At 100 atm | 257 | 89 | 69.3 |
| At 1000 atm | 25.7 | 54 | 40 |

We see that especially at higher pressures the volumes of a mole determined from the van der Waals equation lie nearer to the experimental values than those determined from the ideal gas equation. That the agreement cannot be perfect is clear from the fact that the values $P_c=72.95$ atm and $T_c=31.1^\circ\text{C}$ lead to a critical volume for the mole $V_c=128$ cm³, whereas the experimentally determined value for V_c is about 100cm³.

5.5.4 The calculated boiling temperatures (Table 3) do not agree particularly well with the experimental values for any of the gases. The agreement is particularly poor for H₂O, nearly as bad are those of NH₃ and HF, and hence for the molecules with a permanent electric dipole moment. Accurate agreement is indeed not to be expected, however, since the van der Waals equation was developed as an improvement for the ideal gas equation, seeking to describe better the behaviour of real gases by the introduction of only two new parameters.

| Gas | CH ₄ | NH ₃ | H ₂ O | HF | Ne |
|---|-----------------|-----------------|------------------|-----|----|
| Boiling temperature (K) calculated | | | | | |
| At 1 atm | 92 | 173 | 240 | 212 | 23 |
| At 2 atm | 102 | 190 | 261 | 233 | 26 |
| At 5 atm | 118 | 217 | 295 | 270 | 31 |
| At 10 atm | 135 | 243 | 328 | 306 | 35 |
| At 20 atm | 156 | 276 | 368 | 351 | 41 |
| At 40 atm | 183 | 318 | 418 | 408 | |

5.5.5 Obtain the following vapour pressures:

| Temperature (°C) | 0 | 20 | 50 | 70 | 100 |
|--|------|------|------|------|-----|
| Vapour pressure (atm) | | | | | |
| for propane (C ₃ H ₈) | 11.0 | 15.4 | 23.9 | 30.9 | |

| | | | | | |
|---|-----|-----|------|------|------|
| for butane (C₄H₁₀) | 4.8 | 6.9 | 11.3 | 14.9 | 21.7 |
|---|-----|-----|------|------|------|

A rise from 20°C to 70°C more than doubles the pressure in the container for both gases. The actual increase is even greater than that calculated from the van der Waals equation. Since even 70°C can be exceeded if one leaves the containers in the boot of a car in the sunshine, the warnings are thoroughly justified.