

Mathematical Analysis of the van der Waals Equation

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Abstract

The parametric cubic van der Waals polynomial $pV^3 - (RT + bp)V^2 + aV - ab$ is analysed mathematically and some new generic features (theoretically, for any substance) are revealed: the temperature range for applicability of the van der Waals equation, $T > a/(4Rb)$, and the isolation intervals, at any given temperature between $a/(4Rb)$ and the critical temperature $8a/(27Rb)$, of the three volumes on the isobar–isotherm: $3b/2 < V_A \leq 3b$, $2b < V_B < (3 + \sqrt{5})b$, and $3b < V_C < b + RT/p$. The unstable states of the van der Waals model have also been generically localized: they lie in an interval within the isolation interval of V_B . In the case of a unique intersection point of an isotherm with an isobar, the isolation interval of this unique volume is also determined. A discussion on finding the volumes $V_{A,B,C}$, on the premise of Maxwell’s hypothesis, is also presented.

Keywords: van der Waals equation; Maxwell’s hypothesis; Cubic equation; Root isolation intervals.

1 Introduction

Johannes Diderik van der Waals was awarded Nobel Prize in 1910 “for his work on the equation of state for gases and liquids”. This work originated in his doctoral thesis from 1873 [1], where he put forward an “equation of state” accommodating both the gaseous and liquid states of a substance and also demonstrated that these two states are of the same nature and merge continuously into each other: the van der Waals equation predicts critical behaviour and the experimentally observed transition between gas and liquid. There are two factors due to which a non-dilute aggregate of moving particles fails to comply with the ideal gas law: the proper volume of the particles (one has to account for the volume b of the molecules, leading to less available volume, $V - b$, for their motion) and the so-called internal pressure a/V^2 (with $a > 0$), due to the mutual attraction of the gas molecules. Each of these two factors is associated with a correcting term, hence generalizing the ideal gas law $pV = RT$ of Clapeyron to

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT. \quad (1)$$

Van der Waals never expected that in his equation, a and b would be constants [2], so that the equation would agree numerically with the experiments. As far back as 1873, he emphasized the possibility that a might vary with the temperature (as $a \sim 1/T$) and also recognized the variability of b with V and not with T [2]. Later, he suggested that, even with constant b , the van der Waals equation is valid for a single substance and that many phenomena would be explained qualitatively provided that a suitable value for a and b were introduced for mixtures [2]. For the purposes of the mathematical analysis of the van der Waals equation in this paper and for the determination of some of its generic features (applying, theoretically, to all substances), the parameters a and b will be taken as two positive constants.

It is the richer mathematical structure of a cubic equation that allows, when used as equation of state, to accommodate critical behaviour and phase transitions and the van der Waals equation is the first proposed such equation (it is cubic in the volume V). It has been followed by over 200 different cubic equations of state aimed at studying various phase phenomena in multi-component mixtures (many of these equations of state are modifications of the original van der Waals equation) — see [3] for the study of equation-of-state methods for the modelling of phase equilibria, [4] for a review on cubic equations of state, and the references therein. The van der Waals equation has been extensively studied and applied to various models for almost 150 years — see the review [5] and the significant reference list in it. However, as cubic equation, it is mathematically fairly complex and its mathematical aspects, including how to solve the equation, are rarely, if ever, discussed.

Without loss of generality, the coefficients of the van der Waals equation can be considered to be integer numbers. This can be seen in the following way. Any measurement has finite precision and hence, irrational or transcendental numbers cannot be recorded in result of measurement. Measured quantities, as the pressure p and the temperature T , which enter the van der Waals equation as parameters, are represented by numbers

with finite number of digits after their decimal points. The parameters a and b , as well as the universal gas constant R , are also such numbers (obtained in their own right via measurements with finite precision). Hence, the coefficients of the van der Waals equation, which are functions of all these, are also such numbers (within, of course, the chosen level of accuracy). Representing them as rational numbers and multiplying across by the highest denominator (some power of 10), renders all coefficients of the van der Waals equation integer.

It is not possible to obtain a solution of the van der Waals equation when it is in symbolic form, i.e. without having the equation parameters fixed at certain values. The reason for this is the so called *casus irreducibilis*. The van der Waals polynomial, cubic in V , is an irreducible one, namely, it cannot be factored into nontrivial polynomials over the same field (of the rational numbers). And, when an irreducible cubic polynomial is present and when all of whose roots are real and distinct, getting the roots by radicals involves taking cube roots of complex numbers, the latter appearing due to the necessity to involve imaginary numbers in the Cardano formulæ by taking the square root of a negative number. The cube root of a general complex number cannot be expressed in the form $a + bi$, where a and b involve only real radicals. This is the *casus irreducibilis* — termed so in the 16th century, as it was not possible back then to take roots of negative numbers (the thinking, at the time, was “geometrical” and numbers had to be positive — as they represented lengths, areas, etc. — negative numbers were avoided). For temperatures below the critical temperature and for pressures below the critical pressure, the van der Waals equation falls, by construction, manifestly into the realm of *casus irreducibilis* — it has three distinct positive real roots.

The van der Waals equation can be solved only point-wise in the parameter space, that is, for fixed values of p , T , a , and b , with the very significant complication arising from the fact that p and T are not independent due to Maxwell’s hypothesis (which is also referred to as Maxwell’s construction). The roots can be found only in this case — either numerically or by using the explicit Cardano formulæ for the roots of the cubic (after depressing the equation — eliminating the quadratic term — by a suitable coordinate transformation).

The aim of this work is to address certain mathematical aspects of the *symbolic* van der Waals equation (when the parameters are not fixed) and to reveal features which are common for all substances, for all pressures and temperatures. As the roots of the *symbolic* equation cannot be determined, this paper finds finite intervals such that one, and only one, root of the van der Waals equation is contained in each of them. These are the so called *root isolation intervals* and this is the first remedy in the study of the location of the roots. Following ideas developed in [8]–[10] for the mathematical analysis of polynomials of different degrees, it is found that, when the van der Waals equation has three real roots $V_A < V_B < V_C$, they satisfy $3b/2 < V_A \leq 3b$, $2b < V_B < (3 + \sqrt{5})b$, and $3b < V_C < b + RT/p$. This result is generic and it stems from the structure of the van der Waals equation and not from physical considerations (except imposing positivity on pressure and lower bound of the volume). The unstable states of the van der Waals model are also generically localized: they lie within the isolation interval of V_B .

2 The van der Waals Equation and Maxwell's Hypothesis

The van der Waals equation is often written as

$$p(V) = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{RTV^2 - aV + ab}{V^2(V-b)} \quad (2)$$

or as

$$pV^3 - (RT + bp)V^2 + aV - ab = 0. \quad (3)$$

Only physically meaningful values of p , V , and T will be considered: p and T will be strictly positive [it will be shown that, in fact, T must be greater than $T_0 = a/(4Rb)$], while V will be strictly greater than b (the volume cannot be smaller than the volume of the molecules). The graph of $p(V)$ for different T is shown on Figure 1.

Equation (3) is a cubic polynomial in the volume V . In addition to the model parameters a and b (R is the universal gas constant), one can consider p and T as just two further parameters with their variation leading to different roots V for this equation. However, p and T are not independent from each other. That is, in order to solve the van der Waals equation, one has to uncover the relationship between p and T in it.

Maxwell assumes that the second law of thermodynamics must be valid even when unstable states intervene between the initial and final states [6]. For the van der Waals equation, the unstable states are those for which the pressure decreases with the decrease of the volume, namely, those between the local minimum (point M) and the local maximum (point N) of $p(V)$ — see Figure (1). Applying $TdS = dU + pdV$ to the cycle, involving such unstable states, from point A , via points M , B , and N to point C along the isotherm (with the segment from M via B to N consisting entirely of unstable points) and then returning from point C , via point B , to point A along the isobar (see Figure 1), yields $T\oint dS = \oint dU + \oint p dV$. Given that, over any cycle, $\oint dS = 0 = \oint dU$, one gets $\oint p dV = 0$ and, hence, the two areas bounded by the isotherm and the isobar are equal — see [7], problem 48, and [6]. This means that the isobar, on which points A , B , and C lie, connects the two phases A and C , which are in contact at equilibrium. If this is not satisfied, then the two phases A and C cannot be in equilibrium, even though they lie on the same isotherm and the same isobar [6]. Maxwell's hypothesis therefore dictates that there should be a constraint between p and T in the van der Waals equation. That is, if T is fixed, p is immediately fixed too. Only then the van der Waals equation would yield three volumes that satisfy the Maxwell hypothesis.

As the temperature increases, the pressure also increases. The points A and C on the isotherm–isobar get closer to each other in such manner that, at all times, the two areas bounded by the isobar and the isotherm remain equal. At temperature equal to the critical temperature T_{cr} , the pressure takes the critical value p_{cr} and A , B , and C coalesce at D . The volume at that point, V_D , is called critical volume V_{cr} . Thus, as there is a triple root $V_{cr} = V_A = V_B = V_C$ when $T = T_{cr}$ and $p = p_{cr}$, the intersection of the isobar with the isotherm is at the inflection point V_{cr} of the isotherm and the tangent of the isotherm at the inflection point is the isobar — parallel to the abscissa.

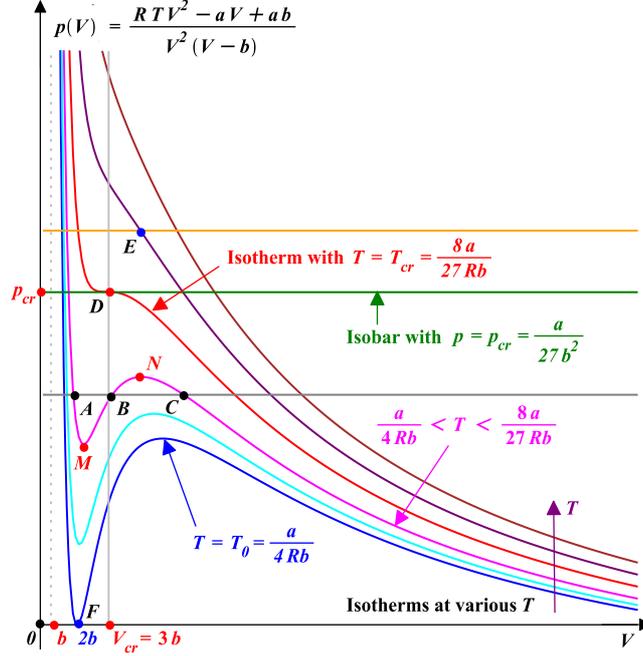


Figure 1

The Van der Waals equation of state $p(V) = \frac{RTV^2 - aV + ab}{V^2(V-b)}$ for various temperatures

Macroscopically, the system represents a single phase at this state [7]. For $T < T_{cr}$, point A corresponds to liquid and is stable, while point C corresponds to gaseous state of the given substance and is meta-stable [7]. Point B is unstable and cannot be realized in nature. Upon the isothermal compression of a gas, once volume V_C is reached, the evolution on the $p-V$ diagram no longer follows the isotherm. Some of the gas becomes liquefied and the two phases, gas (point C) and liquid (point A), exist simultaneously in equilibrium at the same temperature and pressure [7]. Further compression (beyond volume V_A) liquefies all of the gas.

A very essential part in the realization of this construct is the fact that the three distinct roots $V_{A,B,C}$, existing for $T < T_{cr}$, coalesce simultaneously into one triple root V_{cr} at $T = T_{cr}$.

3 Isolation Intervals of the Roots of the van der Waals Equation

If the discriminant of the general cubic $Ax^3 + Bx^2 + Cx + D$ polynomial is negative, then there will be one real root and a pair of complex-conjugate roots; if it is positive, there will be three distinct real roots. If the discriminant is zero, the cubic will have a multiple root: a double root and a single root, when $B^2 \neq 3AC$, or a triple root $-B/3A$ when $B^2 = 3AC$. Under variation of the parameters of the equation, the discriminant can,

eventually, change its sign. In the most general situation, when the discriminant is zero, one does not necessarily have $B^2 = 3AC$. This means the following. As, under variation of the parameters of the cubic, the discriminant approaches zero from below, there is one real root and a pair of complex-conjugate roots whose imaginary parts get smaller and smaller. The two complex-conjugate roots coalesce into a double real root when the discriminant becomes zero. When the discriminant becomes positive, this double real root bifurcates into two distinct real roots, the distance between which increases with the increase of the discriminant. For the van der Waals equation, there is a very distinctive feature: it has a triple root at the critical temperature T_{cr} and critical pressure p_{cr} . This is “built into” the van der Waals equation by Maxwell’s hypothesis: should there be a double root and a single root, rather than a triple root, Maxwell’s hypothesis would fail as one of the two areas would be zero. Hence, when the discriminant (which depends on p and T , as well as a and b) approaches zero, $B^2 - 3AC$ also approaches zero. The van der Waals discriminant is

$$\Delta = -4a \left[b^4 p^3 + (3RTb^3 + 2ab^2)p^2 + (3R^2T^2b^2 - 5RTab + a^2)p + R^2T^2 \left(RTb - \frac{a}{4} \right) \right]. \quad (4)$$

It is not simple to analyze as it is cubic in p and cubic in T . The term $B^2 = 3AC$ is

$$b^2 p^2 + (2RTb - 3a)p + R^2 T^2. \quad (5)$$

Both polynomials (4) and (5) are simultaneously zero if one takes $T = (8a)/(27Rb)$ and $p = a/(27b^2)$. These critical values of the temperature and the pressure are well known, but will be confirmed further, following a different analysis.

Note that Maxwell’s hypothesis prevents the van der Waals equation from having a double root (as one of the two areas will be zero in such case). If a multiple root is present, this could only be the triple root $V_{cr} = 3b$ when $T = T_{cr}$ and $p = p_{cr}$.

Consider the van der Waals equation in the form (2). One can immediately determine the temperature range for applicability of the equation. The graph of $p(V)$ exhibits a local minimum and a local maximum for temperature below the critical. With the decrease of the temperature, the “dip” gets closer to the abscissa. Setting $p(V) = 0$, yields the quadratic equation $RTV^2 - aV + ab = 0$. The roots of this equation are real when the discriminant $-4abRT + a^2$ is positive, that is, when $T < T_0 = a/(4Rb)$. In such case, the curve $p(V)$ will cross the abscissa at $V_{1,2} = (a \pm \sqrt{-4abRT + a^2})/(2RT)$. If the discriminant is zero [i.e. $T = T_0 = a/(4Rb)$], the curve $p(V)$ will have a double zero root at $V = a/(2RT_0) = 2b$. The pressure cannot become zero for a finite volume or be negative — at any volume. Hence, this discriminant must be negative and, thus, $T > T_0 = a/(4Rb)$ — the minimum allowed temperature (otherwise the van der Waals equation will be “pushed” too far).

There is another characteristic temperature associated with the van der Waals equation. Note that, as the temperature increases, the curve on the $p-V$ diagram resembles the curve of an ideal gas with equation of state $pV = RT$. The question is, at what temperature the two could be identified? Equating $pV = RTV/(V - b) - a/V$ from the van

der Waals equation to RT from the Clapeyron law, one gets $T = a(V - b)/(VRb) = [a/(Rb)](1 - b/V)$. If the real gas is to resemble an ideal gas, then the molecular volume b must be much smaller than V . Hence, one can take $b/V \rightarrow 0$ when seeking to emulate ideal gas behaviour. In this limit, one gets $T = T_b = a/(Rb) = 4T_0 = (27/8)T_{cr}$. This temperature is called the Boyle temperature.

To confirm that the critical temperature is indeed $8a/(27Rb)$ and that the critical pressure and volume are $a/(27b^2)$ and $3b$, respectively, consider the van der Waals polynomial $w(V) \equiv pV^3 - (RT + bp)V^2 + aV - ab$ from (3) and re-write it as $V^3w^*(V^*)$ where

$$w^*(V^*) = -abV^{*3} + aV^{*2} - (RT + bp)V^* + p \quad (6)$$

and $V^* = 1/V$ [this can be done as the free term ab in the van der Waals polynomial $w(V)$ is not zero and thus 0 is not its root]. Hence, the roots of the van der Waals equation are the reciprocals of the roots of $w^*(V^*)$. The reason for the passage to the reciprocal polynomial $w^*(V^*)$ becomes apparent when one writes the equation $w^*(V^*) = 0$ as $-abV^{*3} + aV^{*2} = (RT + bp)V^* - p$. Then the roots of $w^*(V^*)$ are the intersection points of $-abV^{*3} + aV^{*2}$ and $(RT + bp)V^* - p$. With this trick, the parameters T and p were “transferred” from the cubic to the straight line. The cubic $-abV^{*3} + aV^{*2}$ is now “fixed” by the parameters a and b only. By varying p , the y -intercept of the straight line $(RT + bp)V^* - p$ varies, as well as its slope. While variation of the temperature only affects its slope. This makes the analysis much simpler (as opposed to having to analyse a cubic with curvature depending on both p and T , as would have been the case, had one split the original van der Waals equation in a similar manner).

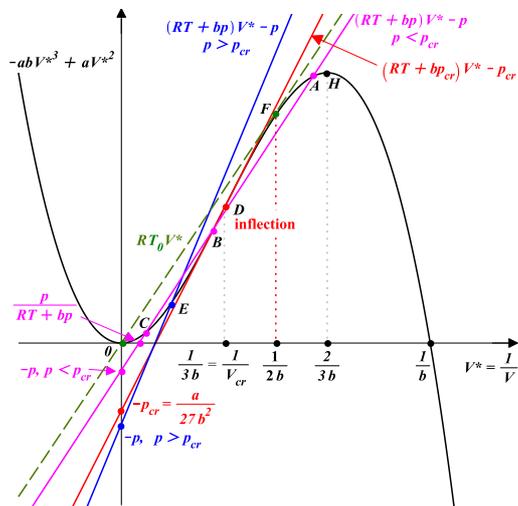


Figure 2a

The equation reciprocal to the Van der Waals equation: $-abV^{*3} + aV^{*2} = (RT + bp)V^* - p$

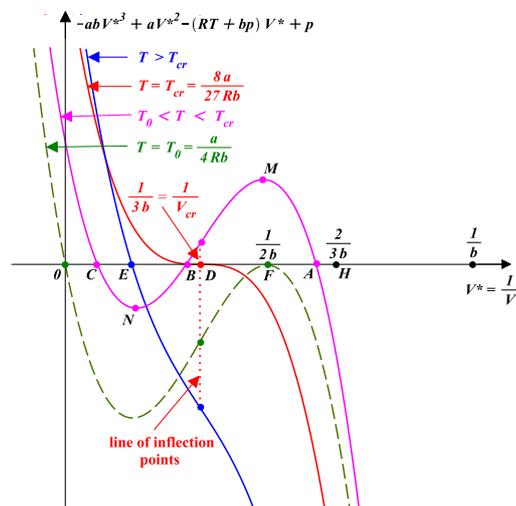


Figure 2b

The polynomial reciprocal to the van der Waals polynomial: $-abV^{*3} + aV^{*2} - (RT + bp)V^* + p$

Introduce

$$w_L^*(V^*) = -abV^{*3} + aV^{*2}, \quad (7)$$

$$w_R^*(V^*) = (RT + bp)V^* - p. \quad (8)$$

Hence, $w^*(V^*) = w_L^*(V^*) - w_R^*(V^*)$. The graphs of $w_{L,R}^*(V^*)$ are shown on Figure 2a and that of $w^*(V^*)$ — on Figure 2b. The inflection point $w_L^*(V^*)$ (point D on the graphs) depends only on the equation parameters a and b and occurs at $V^* = 1/(3b)$. This coincides with the inflection of the whole $w^*(V^*)$, as $w_R^*(V^*)$ is linear in V . Thus, the critical volume for the van der Waals equation is $V_{cr} = 3b$. One also has $w_L^*[1/(3b)] = 2a/(27b^2)$. The van der Waals equation must have a triple root at $V_{cr} = 3b$. Hence, at $V^* = 1/(3b)$, the straight line $w_R^*(V^*)$ must have the same slope as the cubic $w_L^*(V^*)$ and it must also pass through point $(1/(3b), 2a/(27b^2))$. The slope of $w_L^*(V^*)$ at $1/(3b)$ is its derivative at that point, namely, $a/(3b)$ and the equation of the tangent line through the inflection point of $w_L^*(V^*)$ is $w_t^*(V^*) = aV/(3b) - a/(27b^2)$. To determine to what temperature and pressure the tangent line $w_t^*(V^*)$ corresponds, compare the respective coefficients of $w_t^*(V^*)$ and $w_R^*(V^*)$. One immediately determines that $p_{cr} = a/(27b^2)$ and, hence, upon inserting this into $RT + bp = aV/(3b)$, one gets $T_{cr} = 8a/(27Rb)$.

As p decreases, the intersection point of $w_R^*(V^*) = (RT + bp)V^* - p$ with the ordinate moves towards zero from below. As already seen, in the limit $p = 0$, the corresponding temperature is $T_0 = a/(4Rb)$ and $V = 2b$ is a double root (this in an unphysical situation). Then the straight line $w_R^*(V^*)$ will tend to RT_0V^* — the dashed line through the origin on Figure 2a, or the dashed curve through the origin, $w_L^*(V^*) - RT_0V^*$, on Figure 2b. This unphysical curve is a limit curve. The physically possible curves correspond to higher T and higher p . With the increase of p and T , the straight line $w_R^*(V^*)$ exhibits both counter-clockwise rotation and downward translation (see Figure 2a). This straight line cannot intersect the cubic $w_L^*(V^*)$ three times on one side of the inflection point D which has abscissa $V^* = 1/(3b)$. One of the intersection points (C) is necessarily to the left of D . As the cubic $w_L^*(V^*)$ is never negative for $V^* < 1/b$, intersection with the straight line $w_R^*(V^*)$ is possible only when the graph of the straight line is above the abscissa. Hence, the isolation interval of the smallest root V_C^* is $p/(RT + bp) < V_C^* < 1/(3b)$. Thus, the biggest root of the van der Waals equation satisfies: $3b < V_C < b + RT/p$. Note that here T must be greater than T_0 and the pressure — smaller than p_{cr} . Note also that p cannot tend to zero, as in such case, one of the two areas bounded by the isobar and the isotherm will have negligible area, while the area of the other will tend to infinity and this is not allowed by Maxwell's hypothesis.

One of the other two intersection points of $w_L^*(V^*)$ with $w_R^*(V^*)$, that is, point A , is necessarily to the right of the inflection point D , i.e. $V_A^* > 1/(3b)$ — see Figure 2a. Point A could be on either side of point F . However, point A cannot be to the right of point H , that is $V_A^* < 2/(3b)$ for the following reason. For any $p > 0$, the root V_A is smallest for the isotherm $T = T_0 = a/(4Rb)$. If one bounds it from below, then the smallest root of each isotherm with $T_0 < T < T_{cr}$ will also be bound from below. The polynomial reciprocal to the van der Waals polynomial with $T = T_0$ is $w_0^*(V^*) = abV^{*3} + aV^{*2} - [a/(4b) + bp]V^* + p$. Its discriminant in V^* is $(ap/4)(-16b^4p^2 - 44ab^2p + a^2)$ and it is positive for $p <$

$a(5\sqrt{5} - 11)/(8b^2)$. The polynomial reciprocal to the van der Waals polynomial will have 3 real roots in this case. When $p = a(5\sqrt{5} - 11)/(8b^2)$, the roots are $(\sqrt{5} - 1)/(2b)$ and the double root $(3 - \sqrt{5})/(4b)$. Therefore, the local maximum of the isotherm $T = T_0 = a/(4Rb)$ will occur at the double root $V = 4b/(3 - \sqrt{5})$ and the corresponding pressure will be $a(5\sqrt{5} - 11)/(8b^2)$. The other root will be $4b/(\sqrt{5} - 1)$. Next, ask the following question: which straight line, parallel to $w_R^*(V^*) = RT_0V^*$, passes through the local maximum of $w_L^*(V^*)$, that is through point $(2/(3b), 4a/(27b^2))$? The answer is $[a/(4b)]V^* - a/(54b^2)$. This auxiliary straight line is tangent to $w_L^*(V^*) = 4a/(27b^2)$ at point $1/(6b)$. Any parallel straight line below this one will intersect $w_L^*(V^*)$ only once — beyond the local maximum of $w_L^*(V^*)$. In other words, if there are three intersection points, they necessarily are for $V^* < 2/(3b)$. As p increases from zero, the straight line $w_R^*(V^*) = (RT + bp)V^* - p$ “departs” from the dashed line $-RT_0V^*$ on Figure 2a — not only by “sliding” down, but also by rotating counter-clockwise. Hence, if the polynomial $w^*(V^*)$ has three real roots, they are all to the left of point H on Figures 2a and 2b. The isolation interval of the biggest root V_A^* is therefore $1/(3b) < V_A^* < 2/(3b)$ and the smallest root of the van der Waals equation satisfies $3b/2 < V_A < 3b$.

The middle root V_B of the van der Waals equation could be on either side of the inflection point D with abscissa $3b$ (see Figures 2a and 2b), but it is never smaller than $2b$ — point F on Figure 1. From above, V_B is bounded by V_C , which, in turn and as already seen, is bounded by $b + RT/p$. Thus the isolation interval of V_B is $2b < V_B < b + RT/p$.

4 Isolation Intervals of the Local Extrema of $p(V)$

The isolation interval of the middle root of the van der Waals equation can be narrowed down by the determination of the isolation intervals of the local extrema of the curve $p(V)$, the knowledge of which is important in its own right in order to localize the unstable states of the van der Waals model. This can be done in a similar way and as follows.

The numerator of the derivative of $p(V)$ from (2) with respect to V (at any constant T) is

$$\pi(V) = -RTV^3 + 2aV^2 - 4abV + 2ab^2. \quad (9)$$

Using the same trick as before, one can determine the roots of equation $\pi(V) = 0$ as the reciprocals of the roots of

$$\pi^*(V^*) = \pi_R^*(V^*) - \pi_L^*(V^*), \quad (10)$$

where:

$$\pi_L^*(V^*) = 2ab^2V^{*3} - 4abV^{*2}, \quad (11)$$

$$\pi_R^*(V^*) = -2aV^* + RT. \quad (12)$$

This time, it is the parameter T that has been “transferred” from the cubic to the straight line. The cubic $2ab^2V^{*3} - 4abV^{*2}$ is also “fixed” by the parameters a and b

only. By varying T , only the y -intercept of the negative-slope straight line $-2aV^* + RT$ varies. The graphs of $\pi_L^*(V^*)$ and $\pi_R^*(V^*)$ are shown on Figure 3a and the graph of $\pi^*(V^*) = \pi_L^*(V^*) - \pi_R^*(V^*)$ is shown on Figure 3b.

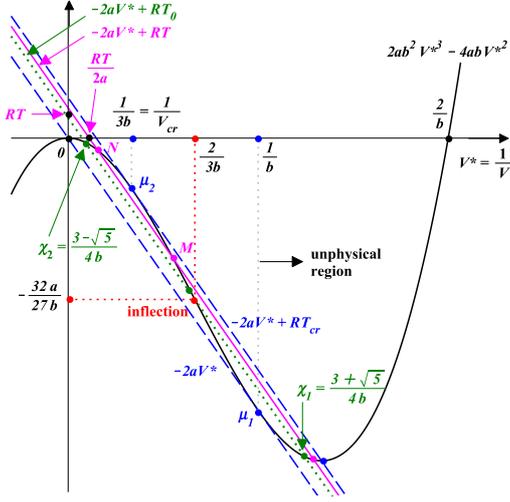


Figure 3a

The equation

$$ab^2 V^{*3} - 4abV^{*2} = -2aV^* + RT$$

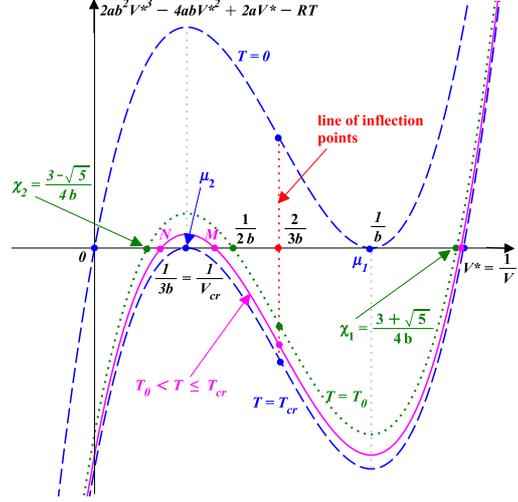


Figure 3b

The polynomial

$$\pi^*(V^*) = ab^2 V^{*3} - 4abV^{*2} + 2aV^* - RT$$

One can pose the question: at what values of V^* are the graphs of $\pi_L^*(V^*)$ and $\pi_R^*(V^*)$ tangent to each other, that is, when does the full $\pi^*(V^*)$ have a double root μ ? One can “slide” the full $\pi^*(V^*)$ up and down by varying its free term RT (Figure 3a) and, at two certain values of T , this will be realized. In terms of the two “parts” $\pi_L^*(V^*)$ and $\pi_R^*(V^*)$ on Figure 3a, only the latter is sensitive to the temperature. When the full $\pi^*(V^*)$ has a double root μ , $\pi_R^*(V^*)$ is tangent to $\pi_L^*(V^*)$ at point μ . This implies equality of the two functions and equality of their derivatives at that point. Hence, from the latter, μ are the roots of $(d/dV)\pi_L^*(V^*) = -(d/dV)\pi_R^*(V^*)$. This is the quadratic equation $3ab^2V^{*2} - 4abV^* + a = 0$ and its roots are $\mu_1 = 1/b$ and $\mu_2 = 1/(3b)$. From the former, one also has $\pi_L^*(\mu_{1,2}) = \pi_R^*(\mu_{1,2})$ and therefore $RT_{1,2} = 2ab^2\mu_{1,2}^3 - 4ab\mu_{1,2}^2 + 2a\mu_{1,2}$. One immediately gets that $T_2 = T_{cr} = 8a/(27Rb^2)$ and $T_1 = 0$. Hence, two limiting straight lines appear: $-2aV^* + RT_{cr}$ and $-2aV^*$. These are represented by the dashed lines on Figure 3a. The corresponding “full” limiting curves on Figure 3b are the dashed $2ab^2V^{*3} - 4abV^{*2} + 2aV^* - RT_{cr}$ and $2ab^2V^{*3} - 4abV^{*2} + 2aV^*$, which passes through the origin. Noting next that T must be greater than T_0 , the physical straight lines on Figure 3a are those between the dotted line $-2aV^* + RT_0$ and the upper dashed line $-2aV^* + RT_{cr}$. On Figure 3b, the physical curves are those between the lower dashed curve $2ab^2V^{*3} - 4abV^{*2} + 2aV^* - RT_{cr}$ and the dotted curve $2ab^2V^{*3} - 4abV^{*2} + 2aV^* - RT_0$. Note next that the inflection point of $\pi_L^*(V^*)$ is at $V^* = 2/(3b)$. The dotted line

(corresponding to $T = T_0$) intersects $\pi_L^*(V^*)$ at $V^* = 1/(2b)$ as seen earlier when T_0 was determined — to the left of inflection point $V^* = 2/(3b)$ — see Figure 3a.

When $T_0 < T < T_{cr}$, the discriminant $-4a^2RTb^3(27RTb-8a)$ of $\pi(V)$ is positive. Hence, $p(V)$ has three extrema. One of them is in the unphysical region $0 < V < b$, while the isolation intervals of the other two extrema — the local minimum at V_M and the local maximum at V_N — can be immediately read from Figures 3a and 3b as follows. The local minimum of $\pi^*(V^*)$ is at point M whose abscissa is between $\mu_2 = 1/(3b)$ and the intersection point $1/(2b)$ of $2ab^2V^{*3} - 4abV^{*2}$ with the dotted line $-2aV^* + RT_0$ (Figure 3a). The local maximum of $\pi^*(V^*)$ is at point N whose abscissa is between $RT/2a$ (the intersection point of the straight line $-2aV^* + RT$ with the abscissa and $\mu_2 = 1/(3b)$) (Figure 3a). The dotted curve $2ab^2V^{*3} - 4abV^{*2} + 2aV^* - RT_0$ on Figure 3b intersects the abscissa at $1/(2b)$. One can immediately determine the other two points $\chi_{1,2}$ at which the dotted curve intersects the abscissa again. These are $\chi_{1,2} = (3 \pm \sqrt{5})/(4b)$ and are roots of $V^{*2} - (3/2b)V^* + 1/(4b^2) = 0$. On Figure 3a, $\chi_{1,2}$ are the points of intersection of the dotted line $2aV^* + RT_0$ with $2ab^2V^{*3} - 4abV^{*2}$. Note that the smaller root χ_2 has already been encountered: It is the point at which the bottom isotherm $T = T_0 = a/(4Rb)$ has its local maximum.

When $T > T_{cr} = 8a/(27Rb)$, the discriminant $-4a^2RTb^3(27RTb-8a)$ of $\pi(V)$ is negative and $p'(V)$ has only one real root. The root is beyond μ_1 , that is, it is in the unphysical region $0 < V < b$ (Figures 3a and 3b).

Therefore, the isolation intervals of the two extrema of $p(V)$ (which exist for $T_0 < T < T_{cr}$) are as follows. The local minimum M is at volume V_M such that $2b < V_M < 3b$. The local maximum N is at volume V_N such that $3b < V_N < (3 + \sqrt{5})b \approx 5.236b$.

The unstable states of the van der Waals model are therefore between the lower bound of the local minimum and the upper bound of the local maximum, that is, they are lie in an interval within the interval $(2b, (3 + \sqrt{5})b)$. The root V_B of the van der Waals equation has a narrower isolation interval: $2b < V_B < (3 + \sqrt{5})b$.

Isobars and isotherms do not, necessarily, intersect at three points. For temperatures above the critical value $T_{cr} = 8a/(27Rb)$, there is a unique positive value of V for each positive value of p , i.e. each isotherm with $T > T_{cr}$ is intersected only once by any isobar (i.e. for any pressure). While, for temperatures in the range $a/(4Rb) < T < 8a/(27Rb)$, Maxwell's hypothesis dictates there must be three real roots with appropriate spacing, so that the two areas are equal, and this fixes the value of p . Any other value of p when $a/(4Rb) < T < 8a/(27Rb)$ is thus unphysical in the context of Maxwell's hypothesis, including those isobars which intersect an isotherm below the critical at one point only.

For temperatures $T > T_{cr}$ and for pressures $p \geq p_{cr}$, the volume V_E is bound by b from below — happening, clearly, at any temperature when p is infinitely large (see Figure 1). The volume V_E is bound from above by $b + RT/p$ — the intersection of $(RT + bp)V^* - p$ and the abscissa V^* — see Figure 2a. The maximum of the upper bound $b + RT/p$, for any finite $T > T_{cr}$ and for $p \geq p_{cr}$, is $b + RT/\min(p) = b + RT/p_{cr} = b + (27Rb^2/a)T$, thus $b < V_E < b + (27Rb^2/a)T$ in this case. On the other hand, for any fixed temperature above T_{cr} , with the increase of the pressure, the volume V_E tends to b from above.

For temperatures $T > T_{cr}$ and for pressures $p < p_{cr}$, the unique intersection point E of

the isobar and the isotherm will be bound from below by the critical volume. Then the isolation interval of V_E will be $3b < V_E < b + RT/p$. With $p \rightarrow 0$, clearly $V_E \rightarrow \infty$ (see Figure 1).

5 On Finding the Roots of the van der Waals Equation

Consider next how the three real roots V_A, V_B , and V_C of the cubic van der Waals equation can be found for temperatures between $T_0 = a/(4Rb)$ and the critical $T_{cr} = 8a/(27Rb)$ and for positive pressures below the critical $p_{cr} = a/(27b^2)$. The three real roots V_A, V_B , and V_C of

$$pV^3 - (RT + bp)V^2 + aV - ab = 0 \quad (13)$$

are related through the Viète formulæ:

$$V_A + V_B + V_C = b + \frac{RT}{p}, \quad (14)$$

$$V_A V_B + V_A V_C + V_B V_C = \frac{a}{p}, \quad (15)$$

$$V_A V_B V_C = \frac{ab}{p}. \quad (16)$$

It was determined earlier that V_C is bound from above by $b + RT/p$. From the first Viète formula, one can immediately see that, in fact, $V_C = b + RT/p - (V_A + V_B)$.

The equality of the two areas bounded by the isotherm and the isobar is [6]

$$\int_{V_A}^{V_B} \left(p - \frac{RT}{V-b} + \frac{a}{V^2} \right) dV = \int_{V_B}^{V_C} \left(\frac{RT}{V-b} - \frac{a}{V^2} - p \right) dV. \quad (17)$$

Performing the integration and solving for p yields [6]

$$p = \frac{RT}{V_C - V_A} \ln \frac{V_C - b}{V_A - b} - \frac{a}{V_A V_C}. \quad (18)$$

To determine the three unknowns p , V_A , and V_C in (18), assuming that T is given, Boltzmann suggests [6] to use (18), together with the two conditions: that V_A is the smallest and V_C the largest root of the van der Waals equation [6]. This can be done as follows. The van der Waals equation can be re-written as

$$\begin{aligned} pV^3 - (RT + bp)V^2 + aV - ab &= p(V - V_A)(V - V_B)(V - V_C) \\ &= p(V - V_A) \left[V^2 - \left(b + \frac{RT}{p} - V_A \right) V + \frac{ab}{pV_A} \right] = 0 \end{aligned} \quad (19)$$

with the help of the first and third Viète formulae.

As already seen, the stable volume (the smallest root) V_A varies continuously and

monotonously between just above $\sqrt{3}b$ (when $T \rightarrow T_0^+$) and just below $3b$ (when $T \rightarrow T_{cr}^-$). If T is fixed to \tilde{T} (by choosing an isotherm between T_0 and T_{cr}), then, due to Maxwell's hypothesis, p gets immediately fixed as well — to a value \tilde{p} below $p_{cr} = a/(27b^2)$. Hence, V_A , the left-most intersection point of the chosen isotherm with the fixed isobar p , is also uniquely fixed as some real number in the interval $(\sqrt{3}b, 3b)$. The other two roots of the van der Waals equation are the zeros of the quadratic polynomial in the square brackets of (19), namely, $V^2 - (b + RT/p - V_A)V + ab/(pV_A)$, with $T = \tilde{T}$ and $p = \tilde{p}$. These are:

$$V_{C,B} = \frac{-(V_A - b)\tilde{p} + R\tilde{T} \pm \sqrt{(V_A - b)^2\tilde{p}^2 + (-2R\tilde{T}V_A + 2Rb\tilde{T} - \frac{4ab}{V_A})\tilde{p} + R^2\tilde{T}^2}}{2\tilde{p}} \quad (20)$$

Next, take $T = \tilde{T}$ in (18) and replace p with $\tilde{p} = (R\tilde{T}V_A^2 - aV_A + ab)/[V_A^2(V_A - b)]$ on the left-hand side of (18). Replace \tilde{p} in (20) also with $(R\tilde{T}V_A^2 - aV_A + ab)/[V_A^2(V_A - b)]$ and substitute V_C in (18). This yields an equation for the smallest root of the van der Waals equation, the stable V_A , for the selected temperature \tilde{T} . Once V_A is determined from (18), one immediately finds $\tilde{p} = (R\tilde{T}V_A^2 - aV_A + ab)/[V_A^2(V_A - b)]$ explicitly for \tilde{T} . Finally, the remaining two positive and greater roots V_B and V_C of the van der Waals equation are then easily obtained from (20) when one substitutes into it the already determined V_A and \tilde{p} for the chosen \tilde{T} .

6 Discussion and Conclusions

The results reported allow one to trace the isothermal compression of *any substance* subjected to the van der Waals model at any temperature below the critical, starting at the gaseous phase at high volumes, in the following manner. The isolation interval of the biggest van der Waals root V_C is $3b < V_C < V_0 + b$, where $V_0 = RT/p$ is the ideal gas volume. Hence, when the volume reaches a value somewhere below $V_0 + b$, the phase of supercooled vapour commences (point C on Figure 1). This phase continues until the local maximum (point N on Figure 1) is reached, which cannot happen for volumes above $(3 + \sqrt{5})b$ — the upper end of the isolation interval of the local maximum N . The states between points N and M (the local maximum and the local minimum, respectively, see Figure 1) are unstable and cannot be realized as the pressure drops with the drop of the volume. This is the phase in which both gas and liquid co-exist. With the further compression of the substance beyond the local minimum M , only superheated liquid exists. As the lower end of the isolation interval of the local minimum M is determined as $2b$, one can be certain that there is no gas at volume $V < 2b$ — one only has superheated liquid. Once the volume gets below $3b/2$ — the lower end of the isolation interval of the smallest root V_A — the phase is entirely that of liquid (compression below b is impossible in the van der Waals model).

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