# Parametric solution of the van der Waals liquid–vapor coexistence curve

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The van der Waals equation of state together with Maxwell's equal area rule, leads to a transcendental equation linking the densities of the two coexisting phases. Gibbs solved this in parametric form. We show that the parameter can be chosen to be the difference $\Delta s$ between the entropy per molecule in the vapour and the entropy per molecule in the liquid. The parametric solution gives, for an arbitrary positive value of $\Delta s$, the thermodynamic properties of the two coexisting phases as functions of $\Delta s$. The van der Waals coexistence curves are compared with pressure–temperature–density data on He$^4$, Xe, and H$_2$O.

The transition between the liquid and vapor states is a fascinating phenomenon. But even the simplest phenomenological equation of state, the van der Waals equation[1]

$$p = T/(v-b) - a/v^2 \qquad (1)$$

leads, when combined with the Maxwell equal area rule,[2] to a rather forbidding transcendental equation linking the densities of the two coexisting phases. Gibbs obtained a parametric solution of this equation; it can be found in the notes that E. B. Wilson made of Gibbs's lectures.[3] Later versions, obtained independently, exist[4,5] (the first version of this note was yet another).

The advantage of a parametric solution is that it makes the simplest liquid–vapor coexistence curves accessible to students: they can enjoy doing the algebra, and then have fun plotting the curves using a programmable calculator. The fact that the parameter can be chosen so as to have direct physical meaning is an added bonus.

When the two phases are in equilibrium, their pressures and chemical potentials are equal: these are the conditions for mechanical and diffusive equilibrium, respectively. The equality of pressures gives

$$\frac{T}{v_l - b} - \frac{a}{v_l^2} = p_e = \frac{T}{v_g - b} - \frac{a}{v_g^2}, \qquad (2)$$

where $v_l$ and $v_g$ are the volumes per molecule in the liquid and gas, and $p_e$ is the pressure at equilibrium. The equality of the chemical potentials $\mu_l$, $\mu_g$ (Gibbs free energies per molecule) gives the Maxwell rule that the hatched areas in the $p$–$v$ diagram (Fig. 1) be equal. For, $d\mu = v\,dp - s\,dT$ where $s$ is the entropy per molecule; by integrating $d\mu$ along the isotherm from one intersection with the horizontal line $p = p_e$ to the other, we find

$$0 = \mu_g - \mu_l = \int_{\text{liq}}^{\text{gas}} v\,dp = p_e(v_g - v_l) - \int_{\text{liq}}^{\text{gas}} p\,dv. \qquad (3)$$

The geometrical interpretation of the equality of $p_e(v_g - v_l)$ and

$$\int_{\text{liq}}^{\text{gas}} p\,dv$$

is Maxwell's rule. (The weakness of this construction, as is well known, is that the integration is along the unstable as well as along the metastable parts of the isotherm of a hypothetical homogeneous fluid phase.) From (3) and the van der Waals equation we obtain

$$T \log \frac{v_g - b}{v_l - b} + a\left(\frac{1}{v_g} - \frac{1}{v_l}\right) = p_e(v_g - v_l). \qquad (4)$$

Combining (4) with the two equalities (2) we can eliminate $T$ and $p_e$, and are left with a transcendental equation linking the two volumes:

$$\log \frac{v_g - b}{v_l - b} = \frac{v_g - v_l}{v_g + v_l}\left(\frac{v_l}{v_l - b} + \frac{v_g}{v_g - b}\right). \qquad (5)$$

The left-hand side of this equation is the difference between the entropy per molecule in the two phases (energy and temperature here have the same dimensionality; entropy is then dimensionless). For, $\mu = e - Ts + pv$, where $e$ is the energy per molecule; equality of chemical potential and pressure within the two phases gives $T\Delta s = \Delta e + p\Delta v$; $\Delta e = -a\Delta(1/v)$ from integration of the thermodynamic relation $(\partial e/\partial v)_T = T(\partial p/\partial T)_v - p$; and $p\Delta v$ is given by (4); putting these results together gives

$$\Delta s = s_g - s_l = \log \frac{v_g - b}{v_l - b}. \qquad (6)$$

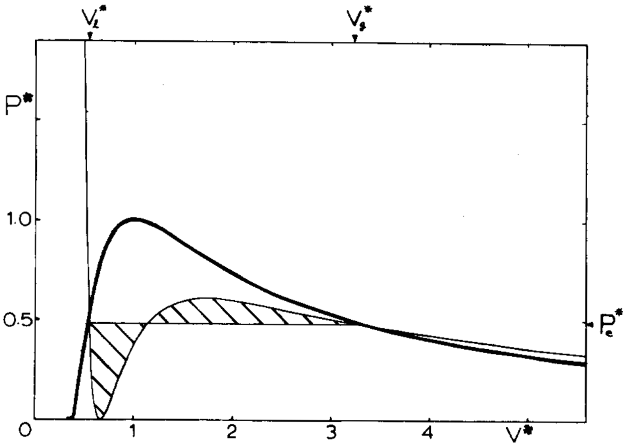

Fig. 1. Heavy line shows the $p^*(= p/p_c)$ and $v^*(= v/v_c)$ values at which the liquid and vapor are in equilibrium, according to the van der Waals equation. It is constructed from the van der Waals isotherms using the Maxwell equal area rule. As an example of this construction we show the isotherm $T/T_c = 27/32 = 0.84375$; the horizontal line $p^* = p_e^*$ is positioned so as to make the two hatched areas equal. The outer intersections of $p^* = p_e^*$ with the $T^* = 27/32$ isotherm give the volumes per molecule $v_l^*$ and $v_g^*$ in the two phases at this temperature; these are indicated on the diagram.

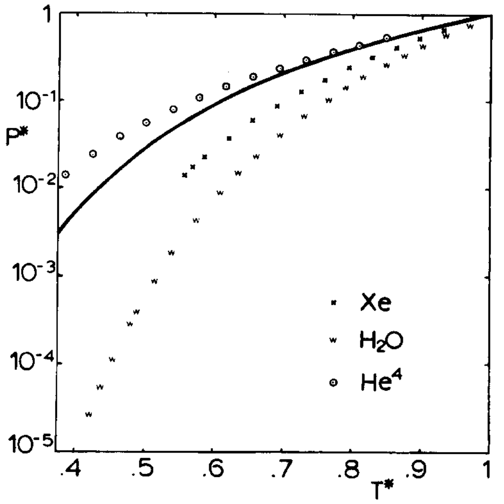

Fig. 2. The van der Waals vapor pressure curve $p^*$ vs $T^*$ (heavy line), compared with experimental data for $He^4$ (Ref. 7), Xe (Ref. 8), and $H_2O$ (Ref. 9).

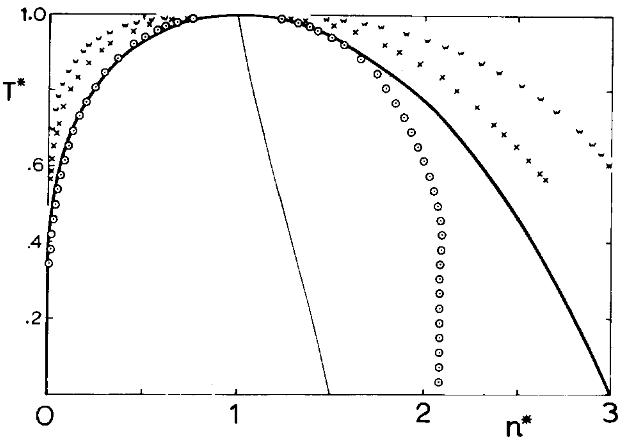

Fig. 3. The van der Waals $T^*$ vs $n^*$ coexistence curve (heavy line) compared with data for $He^4$ (Ref. 10), Xe (Ref. 11), and $H_2O$ (Ref. 9). Also shown is the average of the liquid and vapor densities, or "diameter." This appears to be rectilinear, but is not: $\bar{n}^*$ is asymptotic to $\frac{7}{5} - \frac{2}{5}T^*$ near $T^* = 1$, and to $\frac{3}{2} - \frac{4}{9}T^*$ near $T^* = 0$.

To solve (5) parametrically, it helps to transform to new variables

$$x_+ = b/(v_l - b), \quad x_- = b/(v_g - b). \tag{7}$$

As it stands, the right-hand side of (5) has cubic form in numerator and denominator; in terms of the new variables it has quadratic form:

$$\log \frac{x_+}{x_-} = \frac{(x_+ - x_-)(x_+ + x_- + 2)}{2x_+x_- + x_+ + x_-}. \tag{8}$$

Those unfamiliar with parametric solutions of transcendental equations may wish to try a simpler one first: if in the equation[6]

$$\log (x_+/x_-) = x_+ - x_-, \tag{9}$$

we set both sides equal to $\delta$, we find

$$x_\pm = F(\pm\delta), \tag{10}$$

where $F(\delta) = \delta/(1 - e^{-\delta})$. Returning to (8), we set both sides equal to $\Delta s$. From the left-hand side we get $x_+ = e^{\Delta s}x_-$, and from the right-hand side we get a linear equation for either $x_+$ or $x_-$. Solving this, we find

$$x_\pm(\Delta s) = e^{\pm\Delta s/2}f(\Delta s/2), \tag{11}$$

where

$$f(y) = \frac{y\cosh y - \sinh y}{\sinh y \cosh y - y}. \tag{12}$$

In terms of $x_\pm(\Delta s)$ we can find the coexistent volumes, and then the equilibrium temperature and pressure from (2) and (4). It is convenient to express all these as reduced variables (fractions of the critical values) $v^* = v/v_c$, $T^* = T/T_c$, and $p^* = p/p_c$, where, for the van der Waals fluid, $v_c = 3b$, $T_c = 8a/27b$, $p_c = a/27b^2$. In terms of $f(\Delta s/2)$, $c = \cosh \Delta s/2$, and $g = 1 + 2cf + f^2$, we find

$$T^* = (27/4)f(c+f)/g^2, \tag{13}$$

$$p^* = 27f^2(1 - f^2)/g^2. \tag{14}$$

Also of interest are the average of the liquid and vapor densities

$$\bar{n}^* = \tfrac{1}{2}(n_l^* + n_v^*) = \tfrac{1}{2}\left(\frac{v_c}{v_l} + \frac{v_c}{v_g}\right) = 3f(c+f)/g, \tag{15}$$

and the density difference.

$$\Delta n^* = n_l^* - n_g^* = (6f/g)\sinh(\Delta s/2). \tag{16}$$

The coexistence of the two phases is now completely specified in parametric form (other quantities of interest may be found from the above: for example, the latent heat equals $T\Delta s$, and the difference between the Helmholtz free energies per molecule in the two phases equals $-a\Delta n - T\Delta s$). As $\Delta s$ varies from zero to infinity, the reduced temperature and pressure decrease from unity to zero. Figures 2 and 3 compare the van der Waals $p^* - T^*$ and $T^* - n^*$ coexistence curves with experimental data.

Near the critical point, $\Delta s$ is small. The leading terms in the small $\Delta s$ expansions are

$$\begin{aligned} &T^* \to 1 - (\Delta s)^2/36, \quad p^* \to 1 - (\Delta s)^2/9, \\ &\bar{n}^* \to 1 - (\Delta s)^2/90, \quad \Delta n^* \to \tfrac{2}{3}\Delta s[1 - (\Delta s)^2/45]. \end{aligned} \tag{17}$$

Thus $p^*$ and $\bar{n}^*$ are linear in $T^*$ near the critical point, while $\Delta n^* \to 4\surd(1 - T^*)$, which shows that the $\beta$ exponent, defined by $\Delta n \sim |\Delta T|^\beta$, takes the classical value $\frac{1}{2}$.

Simple limiting forms may also be found in the low-temperature limit. But since only the isotopes of helium have liquid–vapor equilibrium down to absolute zero, these are of lesser interest.

## ACKNOWLEDGMENT

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