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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 Δs 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 Δs, the thermodynamic properties of the two coexisting phases as functions of Δs. The van der Waals coexistence curves are compared with pressure–temperature–density data on He^4, Xe, and H_2O.

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 μ_l, μ_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

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

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

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

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

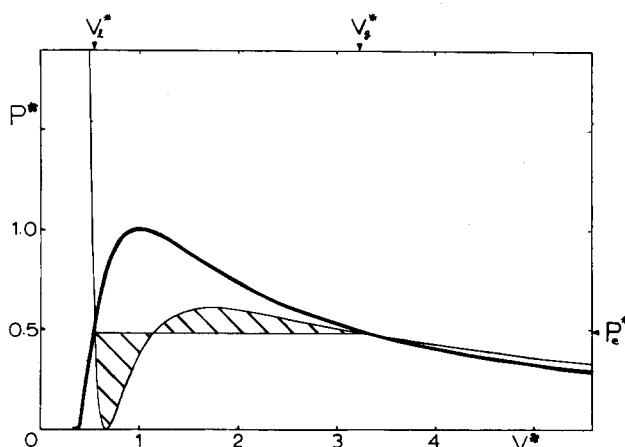$$\Delta s = s_g - s_l = \log \frac{v_g - b}{v_l - b}. \qquad (6)$$

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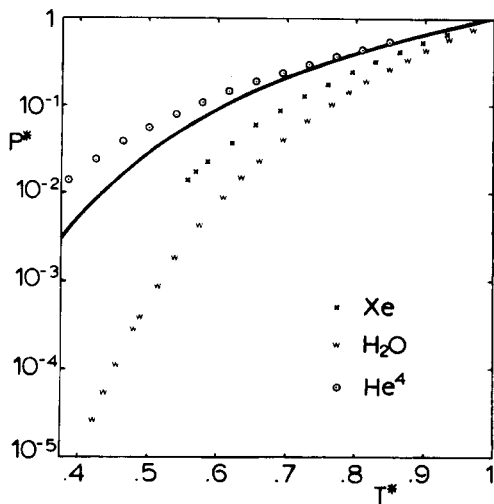
Fig. 2. The van der Waals vapor pressure curve p^* vs T^* (heavy line), compared with experimental data for He^4 (Ref. 7), Xe (Ref. 8), and H_2O (Ref. 9).

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 $\frac{7}{5} - \frac{3}{5}T^*$ 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

$$x_+ = b/(v_l - b), \quad x_- = b/(v_g - b).$$ (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:

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

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

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

we set both sides equal to δ, we find

$$x_\pm = F(\pm \delta),$$ (10)

where $F(\delta) = \delta/(1 - e^{-\delta})$. Returning to (8), we set both sides equal to Δs. 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

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

where

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

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

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

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

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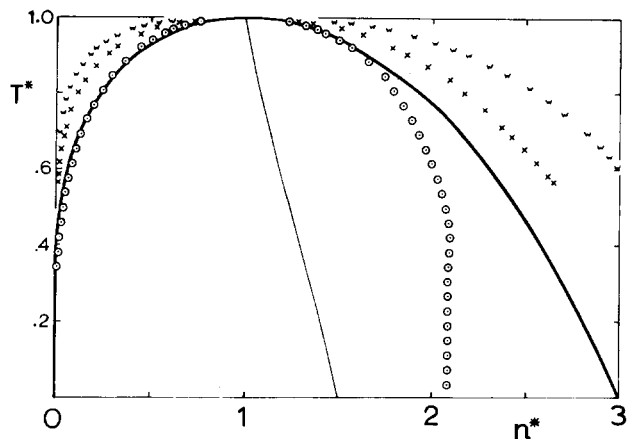
and the density difference.

$$\Delta n^* = n_l^* - n_g^* = (6f/g)\sinh(\Delta s/2).$$ (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 Δs 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, Δs is small. The leading terms in the small Δs expansions are

$$T^* \to 1 - (\Delta s)^2/36, \quad p^* \to 1 - (\Delta s)^2/9,$$

$$\bar{n}^* \to 1 - (\Delta s)^2/90, \quad \Delta n^* \to \frac{2}{3}\Delta s[1 - (\Delta s)^2/45].$$ (17)

Thus p^* and $\bar{n}^*$ are linear in T^* near the critical point, while $\Delta n^* \to 4\sqrt{(1 - T^*)}$, which shows that the β 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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Spatial relations between force and acceleration in relativistic mechanics

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The lack of parallelism between the force and acceleration vectors has several apparently paradoxical consequences that have been examined recently in the Journal. This article uses a different and more general mode of analysis than previous authors to derive quite general, rather than particular, results.

The fact that a force vector and its corresponding acceleration vector are generally not parallel was naturally noticed long ago. Recently, Ficken[1] and González-Díaz[2] have analyzed the relation between these vectors in some detail.

Unfortunately, these authors have used a mode of analysis that is not conducive to the drawing of general conclusions. Rather have they examined many particular situations.

There are three vectors involved in the discussion. The velocity vector $\mathbf{v}$ of the particle experiencing the force $\mathbf{F}$, and its consequent acceleration $\mathbf{a}$.

Ficken and González-Díaz have conducted their analyses in terms of the components of these vectors along mutally perpendicular axes, particularizing their analyses to the case where (i) $\mathbf{v}$ lies in the X–Y plane with equal X and Y components (Ficken) and (ii) $\mathbf{v}$ has equal X, Y, and Z components (González-Díaz). Then Ficken examines the ratio of the components a_y/a_x for particular values of $\mathbf{v}$, as a function of the ratio of the force components F_x/F_y, and González-Díaz extends this analysis to involve F_y/F_z and a_z/a_y.

The purpose of this paper is to present a more transparent analysis of the spatial relations between $\mathbf{v}$, $\mathbf{F}$, and $\mathbf{a}$, from which general conclusions may be drawn, and, of course, the particular conclusions of Ficken and González-Díaz.

The momentum $\mathbf{p}$ of a point particle with rest mass m_0 and velocity $\mathbf{v}$ is

$$\mathbf{p} = m_0 \mathbf{v} \gamma, \tag{1}$$

where

$$1/\gamma = (1 - v^2/c^2)^{1/2},$$

from which we have

$$\mathbf{v} = \mathbf{p}/(m_0^2 + p^2/c^2)^{1/2}. \tag{2}$$

Differentiating with respect to time, and writing $\mathbf{a}$ for $d\mathbf{v}/dt$ and $\mathbf{F}$ for $d\mathbf{p}/dt$,

$$\gamma m_0 \mathbf{a} = \mathbf{F} - \mathbf{v}(\mathbf{v} \cdot \mathbf{F})/c^2, \tag{3}$$

from which we see that $\mathbf{a}$, $\mathbf{F}$, and $\mathbf{v}$ are coplanar.

If we construct an X axis parallel to $\mathbf{v}$ and a Y axis normal to $\mathbf{v}$, in the plane $(\mathbf{F},\mathbf{v})$, and take the components of Eq. (3), we find

$$\gamma m_0 a_x = F_x/\gamma^2$$

or

$$(\gamma^3 m_0)a_x = F_x, \tag{4}$$

and

$$(\gamma m_0)a_y = F_y. \tag{5}$$

Hence (γm_0) and $(\gamma^3 m_0)$ are often described as the "transverse" and "longitudinal" masses.

From Eq. (3) it is clear the force and acceleration are parallel only when (i) $v = 0$ (the Newtonian limit); (ii) $\mathbf{F}$ is parallel to $\mathbf{v}$; or (iii) $\mathbf{F}$ is perpendicular to $\mathbf{v}$.

In all other cases there is an *acute* angle between the force and acceleration.

To show this one examines the scalar product of $\mathbf{a}$ and $\mathbf{F}$, by taking the scalar product of $\mathbf{F}$ and Eq. (3):

$$\gamma m_0 \mathbf{a} \cdot \mathbf{F} = \mathbf{F} \cdot \mathbf{F} - (\mathbf{v} \cdot \mathbf{F})^2/c^2. \tag{6}$$

Since $(\mathbf{v} \cdot \mathbf{F})^2 \leqslant v^2 F^2 \leqslant c^2 F^2$ we have

$$\gamma m_0 \mathbf{a} \cdot \mathbf{F} \geqslant F^2 - F^2 = 0. \tag{7}$$

Hence if ψ is the angle that $\mathbf{F}$ makes with $\mathbf{a}$ then $-\pi/2 \leqslant \psi \leqslant \pi/2$.

Let θ be the angle that $\mathbf{v}$ makes with $\mathbf{F}$. We need not consider negative values of θ but may consider it to range from 0 to π. If $\mathbf{F}$ lies between $\mathbf{v}$ and $\mathbf{a}$, then ψ is to be regarded as positive, but negative if $\mathbf{a}$ lies between $\mathbf{F}$ and $\mathbf{v}$, so that the angle between $\mathbf{v}$ and $\mathbf{a}$ is always $\theta + \psi$ (Fig. 1).

An explicit expression for $\tan \psi$ can be found by writing $\mathbf{a} \cdot \mathbf{F} = aF \cos \psi$, $\mathbf{v} \cdot \mathbf{F} = vF \cos \theta$, and $\mathbf{a} \cdot \mathbf{v} = av \cos(\psi + \theta)$ in Eq. (6) and in the scalar product, of Eq. (3) with $\mathbf{a}$. One then obtains, respectively, the following equations:

$$\gamma m_0 aF \cos \psi = F^2 - v^2 F^2 \cos^2 \theta /c^2 \tag{8}$$

and

$$\gamma m_0 a^2 = aF \cos \psi - aFv^2 \cos \theta \cos(\psi + \theta)/c^2. \tag{9}$$