

IV. Applications to simple systems

Recall that a **simple system** is one for which the dynamical variables are a density, the temperature, the pressure and the entropy, all fields over a subset of \mathbb{R}^3 , possibly with movable boundaries. The paradigm of a simple system is an ideal gas; in the first application we shall consider the problem of propagation of sound in an ideal gas.

This process is not within the province of thermodynamics as it is usually understood, but it is an important part of a theory of the dynamics of fluids, and of adiabatic thermodynamics. The theory was developed by Laplace (1825). See also Biot (1802)

IV.1. Propagation of **sound** in an ideal gas

This is the first of several sections devoted to the **propagation of sound**. We are here dealing with the simplest case, the propagation of a plane **pressure wave** in an ideal gas.

The difficult part was to know what theory to apply to this phenomenon. One starts with a gas at equilibrium, density, pressure and temperature uniform and time independent, and considers a first order **perturbation** of this system

$$\rho = \rho_0 + \epsilon\rho_1, \quad T = T_0 + \epsilon T_1,$$

with **harmonic perturbations**, e.g. $\rho_0 \propto \exp i(kx + \omega t)$, k and ω constant.

We may be sure that there will be a fluctuation of density and pressure but it is possible to entertain some doubts concerning the temperature. Newton's isothermal theory of sound propagation (Proposition 49 of Book II of the Principia) postulates that the temperature is fixed and that the equation of continuity as well as the Bernoulli equation apply. He also needs a relation between density and pressure and for this he uses the ideal gas law.

Here is the detailed paradigm for the use of the **Euler-Lagrange equations** in perturbation theory:

Write down the expression for the Lagrangian, with the appropriate formula for f :

$$\mathcal{L} = \rho(\dot{\Phi} - \vec{v}^2/2) - \mathcal{R}T \ln \frac{\rho}{T^n} + \rho ST. \quad (4.1.1)$$

then use the Euler-Lagrange equations:

1. Variation of Φ gives the equation of continuity; to first order in ϵ ,

$$\dot{\rho}_1 = -(\rho_0 v_1) \quad , \quad \ddot{\rho}_1 = -\rho_0 \dot{v}_1.$$

2. Variation with respect to the temperature tells us that ρ/T^n is uniform, see Eq.(4.1.3) below.
3. Variation of the density gives

$$\dot{\Phi} = \mathcal{R}T \left(\ln \frac{\rho}{T^n} + 1 \right) + ST. \quad (4.1.2)$$

Thus

$$\dot{\vec{v}} = -\vec{\nabla} \mathcal{R}T \left(\ln \frac{\rho}{T^n} + 1 \right).$$

It follows that, at equilibrium, when $\vec{v} = 0$, the density and the temperature are both uniform; there is no need to vary the entropy distribution to assure us.

In Newton's theory of sound propagation T is held fixed and the calculation goes as follows, using the last 2 equations. If a prime denotes the spatial derivative in the direction of propagation, then

$$\frac{\ddot{\rho}_1}{\rho_0} = -\dot{v}'_1 = \dot{\Phi}''_1 = \mathcal{R}T \frac{\rho''_1}{\rho_0}$$

and thus

$$c^2 = \omega^2/k^2 = \mathcal{R}T.$$

Using $T = 293$ and $\mathcal{R}_{\text{air}} = .8314 \times 10^8 / 28.96$ gives $c = 290 \text{ m/sec}$. The actual value is 343 m/sec .

A better result is obtained with the assumption, first proposed by Laplace (1806), that sound propagation is “**adiabatic**”. **That is to say that it is governed by the Euler-Lagrange equations of our Lagrangian**, with a fixed value of S . In Laplace's theory ρ and T are related by the **adiabatic condition**; it is the Euler-Lagrange equations, or more precisely the **constraint**, obtained by variation of \mathcal{L} with respect to T ,

$$\mathcal{R}\rho(\ln \frac{\rho}{T^n} - n) + \rho S = 0 \quad (4.1.3)$$

The ratio ρ/T^n is thus fixed and therefore $dT/T_0 = (1/n)d\rho/\rho_0$, so the same calculation gives

$$\frac{\ddot{\rho}_1}{\rho_0} = -\dot{v}'_1 = \dot{\Phi}''_1 = (1 + \frac{1}{n})\mathcal{R}T \frac{\rho''_1}{\rho_0} = \gamma\mathcal{R}T \frac{\rho''_1}{\rho_0}.$$

and

$$c^2 = \gamma\mathcal{R}T.$$

We shall always assume that the **specific entropy** is fixed. For this reason it is useful to repeat the last calculation, that of Laplace, in somewhat greater generality.

In this book all calculations begin by writing down the expression for \mathcal{L} :

$$\int d^3x \mathcal{L} = \int d^3x \left(\rho(\dot{\Phi} - \vec{v}^2/2) - W(\rho, T) \right), \quad W = f + sT,$$

The three Euler-Lagrange equations are

$$\dot{\rho} + \vec{\nabla} \cdot (\rho \vec{v}) = 0, \quad \left. \frac{\partial W}{\partial T} \right|_{\rho} = 0, \quad \dot{\Phi} - \vec{v}^2/2 = \left. \frac{\partial W}{\partial \rho} \right|_T.$$

As we have seen, for this to simplify we need (a) for the entropy density s to be linear in ρ , $s = \rho S$ and (b) that the specific entropy S is uniform. The first condition is satisfied by an ideal gas; it is not always pointed out that the second condition (the isentropic assumption) is used as well, to get the formula (see Section III.1)

$$\begin{aligned} \vec{\nabla} p &= \vec{\nabla} \left(\rho \frac{\partial f}{\partial \rho} - f \right) = \rho \vec{\nabla} \left. \frac{\partial W}{\partial \rho} \right|_S. \\ \frac{\ddot{\rho}_1}{\rho_0} &= -\dot{v}'_1 = \left. \partial_x \frac{p'}{\rho} \right|_S = \left. \frac{\rho''_1}{\rho} \frac{dp}{d\rho} \right|_{\text{adiab.}}. \end{aligned} \quad (4.1.4)$$

The speed of propagation is thus the square root of the **adiabatic derivative** of p with respect to ρ ; that is, the partial derivative of the function $p(\rho, S)$ that is obtained from $p(\rho, T)$ when T is expressed in terms of ρ with the use of the adiabatic relation $\partial W/\partial T|_{\rho} = 0$,

$$\left. \frac{dp}{d\rho} \right|_{\text{adiab.}} = \left. \frac{\partial p}{\partial \rho} \right|_T + \left. \frac{\partial p}{\partial T} \right|_{\rho} \left. \frac{\partial T}{\partial \rho} \right|_S. \quad (4.1.5)$$

For an ideal gas the equations are

$$\dot{\rho} + \text{div}(\rho \vec{v}) = 0, \quad \mathcal{R} \left(\ln \frac{\rho}{T^n} - n \right) + S = 0, \quad \dot{\Phi} - \vec{v}^2/2 = \mu + ST = (n+1)\mathcal{R}T, \quad (4.1.6)$$

where μ is the chemical potential (Section II.7) and

$$\left. \frac{dp}{d\rho} \right|_{\text{adiab.}} = \gamma \mathcal{R}T. \quad (4.1.7)$$

For air $\gamma = 1.4$, which gives a speed of sound in air as 343 m/sec . The result is an excellent prediction for air and other gases at atmospheric temperature and pressure. See the web article “Laplace and the Speed of Sound”.¹ Laplace’s calculation is found in an article by his protegé Biot (1802).

Corrollary. If the adiabatic derivative p is negative the system is **unstable**; the perturbation grows exponentially.

¹

www.nd.edu/ powers/ame.20231/finn1964.pdf

Remark. It deserves to be emphasized that the adiabatic condition was needed, which would be something of a surprise if it were interpreted as no more than a formula that determines the entropy. We do not need the value of the entropy, but we used the fact that it is uniform (the polytropic condition) and that it is constant in time. In other words, the specific entropy density, not only the total entropy, is an adiabatic invariant. At least, the assumption that it is so, is a successful assumption as far as the propagation of pressure waves is concerned. It should also be emphasized, once again, that this work of Laplace, 200 years old, when translated to the modern idiom is an undeniably successful use of entropy for a system that is not in equilibrium.

Radial wave

A radial wave, originating at the center of a Cartesian Coordinate system and propagating in the direction of the radius vector, or else converging on the center, requires a source or an absorber at either end. The propagation of the wave from source to absorber can be discussed without a specification of the emitter or the transmitter; all that is needed is the boundary conditions. We postulate spherical symmetry; the boundaries are spheres of radii r_0, r_1 , with $0 \leq r_0 < r_1 < \infty$.

We consider a first order perturbation of a static configuration in which all the field variables are uniform and the flow velocity is zero. The appropriate generalization of (4.1.4) is, for an ideal gas,

$$\partial_t^2 \delta\rho = \gamma \mathcal{R} T_0 \Delta \delta\rho$$

Setting $\partial_t \delta\rho = i\omega \delta\rho$ we get the radial, 3-dimensional Helmholtz equation

$$(k^2 + r^{-2} \partial_r r^2 \partial_r) \delta\rho = 0, \quad k^2 = \frac{\omega^2}{\gamma \mathcal{R} T_0}.$$

It has 2 independent solutions, both singular at the origin,

$$\delta\rho(t, r) = \frac{1}{r} e^{i\omega t \pm ikr}.$$

With the freedom to choose the sign of k we can construct a wave traveling into or out of the origin. These solutions will be singular at the origin, evidence of a source or a sink. In the case of a converging wave we can speculate about the mechanism by which the energy can be accounted for; **sono-luminescence** is one way.

IV.2. The van der Waals fluid

Van der Waals (1873) proposed a physically motivated modification of the ideal gas law. For 1 gram or one mole of gas it takes the form

$$p = \frac{\mathcal{R}T}{V - b} - \frac{a}{V^2}. \quad (4.2.1)$$

In this section V stands for $1/\rho$. For any amount of gas it is

$$p = \frac{\mathcal{R}\rho T}{1 - b\rho} - a\rho^2. \quad (4.2.2)$$

The main interest of this formula is that it accounts for the condensation of the gas at low temperatures, but at first we shall examine the pure, gaseous phase only.

The parameter $b > 0$ is “the excluded volume”, intended to take into account the fact that the volume available to a particle of the gas is diminished by the fraction of the total that is occupied by the other particles. This arises from the point of view that regards a gas as a collection of classical particles, which is not wholly justified since the particles obey quantum statistics (about which more elsewhere). A dramatic effect of this change in the expression for the free energy density is that, when the gas is strongly compressed, the density increases as before, but now it is limited by the value $\rho = 1/b$. As this limit is approached the pressure grows without bounds.

The second term is meant to take into account a direct interaction between the particles. This is probably the first example of a suggestion to model an interaction by the addition of a polynomial in the density to the free energy density. It was justified by a study of inter particle interactions, but attempts to predict the values of the parameters by particle dynamics have been unsuccessful, to the point of disfavoring, for a time, the work of van der Waals (Uhlenbeck 1937). In modern times the parameters a and b are treated as phenomenological, to be adjusted to a best fit of observed thermodynamical properties, independently for each type of gas. The parameter a is normally positive, which indicates an **attractive force**. To make the pressure positive we may restrict the value of a ,

$$\frac{a}{\mathcal{R}T} < 4b,$$

but negative pressures actually occur, as **metastable** configurations (Ramsey 1956) and van der Waals’ theory is successful in that domain as well.

The van der Waals expression has the great merit that it never leads to unreasonable predictions. There have been many proposals to improve the agreement with experiment but here we shall work with the original proposal, Eq.(4.2.2). Some generalizations will be considered later in this chapter.

Fig.4.2.1 shows the pressure as a function of the volume for several values of the temperature. At very high temperatures or large volumes the pressure is given fairly accurately by the ideal gas law, and there is just one real value (and 2 complex values) of the volume for each value of (p, T) . At lower temperatures, when

$$T < T_c,$$

there are 3 real values of the volume for each value of (p, T) .² This is the domain within which condensation takes place and a liquid phase coexists with the gas. The “critical temperature” T_c is the highest temperature at which the gas and the liquid can coexist. At this temperature

$$\left. \frac{\partial p}{\partial V} \right|_T = 0, \quad \text{and} \quad \left. \frac{\partial^2 p}{\partial V^2} \right|_T = 0. \quad (4.2.3)$$

The critical temperature T_c and the associated critical pressure and density are

$$\mathcal{R}T_c = \frac{8}{27} \frac{a}{b}, \quad p_c = \frac{1}{27} \frac{a}{b^2}, \quad \rho_c = \frac{1}{3b}.$$

For He₄ the experimental values in cgs units are

$$T_{\text{cr}} = 5.19, \quad \rho_{\text{cr}} = .0696, \quad p_{\text{cr}} = .227 \times 10^7, \quad V_{\text{cr}} = 14.35;$$

and in the same units the parameter values are reported to be

$$a = 2162.5 \times 10^6, \quad b = 5.9.$$

This is not quite right, it improves if we change the critical density to .05625, then

$$p_{\text{cr}} = \frac{.8314 \times 10^8 \times 5.19 \times .05625}{4(2/3)} - 2162.5 \times 10^6 \times .05625^2 = 2.2596 \times 10^6.$$

²The values of T_c for real gases range from 5K for helium “... to values well beyond measurement.” (Rowlinson 1959)

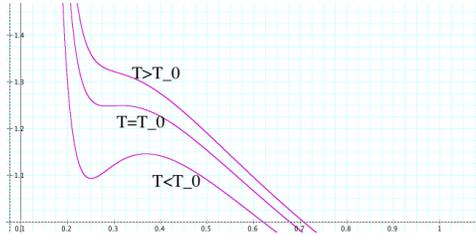


Fig.4.2.1. Loci of constant T in the V, P plane according van der Waals. The abscissa is the specific volume $V = 1/\rho$, the ordinate is the pressure.

In the more popular units,

$$\rho_{\text{cr}} = 56.25/4 = 14.0625 \text{ mol/L}, \quad a = 2162.5 \times 16 = 34600 \text{ PaL}^2/\text{mol}^2,$$

$$b = (3 \times 14.0625)^{-1} = .02370 \text{ L/mol},$$

$$T_{\text{cr}} = 5.19, \quad \rho_{\text{cr}} = 14.0625 \text{ mol/L}, \quad p_{\text{cr}} = .227 \times 10^7.$$

Now

$$p_{\text{cr}} = \frac{.8314 \times 10^5 \times 5.19 \times 14.0625}{(2/3)} - 34600 \times 14.0625^2 = 2.2596 \times 10^6.$$

Finally, in bars, multiply all three terms by 10^{-5} .

$$p_{\text{cr}} \frac{.8314 \times 5.19 \times 14.0625}{(2/3)} - .3460 \times 14.0625^2 = 22.596 \text{ bar}.$$

The principal application of van der Waals' formula is to the study of the **change of phase**. But a relation between pressure, volume and temperature is not sufficient to determine all the thermodynamical properties of the system; in particular, it is not enough information to determine the formula for the free energy, nor the internal energy, and it is not enough to predict the speed of propagation of sound.

Van der Waals' formula does not determine the free energy. The equation $p = -\partial F/\partial V$ has the general solution

$$F(V, T) = -\mathcal{R}T \ln(V - b) - \frac{a}{V} + \psi(T).$$

This can also be expressed as

$$F(V, T) = -\mathcal{R}T \ln\{(V - b)T^n\} - \frac{a}{V} + \tilde{\psi}(T).$$

This form is suggested by the expectation that the gas becomes an ideal gas in the limit when $a = b = \tilde{\psi} = 0$. If $\tilde{\psi}(T) = 0$ then

$$S = -\frac{\partial F}{\partial T} = \mathcal{R} \ln\{(V - b)T^n\} + n\mathcal{R} \quad (4.2.4),$$

where V is the molar volume, and if S is uniform this gives a modification of the polytropic relation obeyed by an ideal gas,

$$k := \frac{1}{(V - b)T^n} = \text{constant}.$$

The internal energy is simply

$$U = n\mathcal{R}T - \frac{a}{V}$$

or, in terms of the natural variables,

$$u(\rho, s) = n\mathcal{R}\rho\left(\frac{\rho}{1 - b\rho}\right)^{1/n}k^{-1/n} - a\rho^2, \quad k = e^{S/\mathcal{R} - n}. \quad (4.2.5)$$

From now on we shall take $\tilde{\psi} = 0$ as our definition of the van der Waals gas, thus

$$F_{\text{vdW}}(V, T) = -\mathcal{R}T \ln(V - b)T^n - \frac{a}{V}. \quad (4.2.6)$$

Let us compare this approach with that of Rowlinson (1959). He does not use an expression for the free energy, or the internal energy, but he says (page 71) that $\partial U/\partial V|_T \propto 1/V^2$ and he reports that this is approximately verified for 5 liquids between the triple point and the critical point. The choice $\hat{\psi}(T) = 0$ is thus indicated for a gas that satisfies van der Waals' relation while preserving some properties of the ideal gas. We shall refer to this fluid as a van der Waals' fluid. Later we shall see how Rowlinson gets some of his results by postulating the mere existence of an analytic expression for F . The above formula for the free energy is used by Lemmon et al (2000).

See Fig.4.2.1. When the temperature is fixed below the critical temperature, and the pressure is fixed in the interval between the two stationary points, then the relation (4.2.2) allows for 3 values of the density,

$$\rho_1 < \rho_0 < \rho_2,$$

as is illustrated in Fig.4.3.1. The middle value is an unstable equilibrium³ and will be ignored from now on. What happens to the gas as the temperature is lowered past the critical point is complicated. But, by action of surface tension and gravity there results, if one waits long enough, a separation of the fluid into two phases, the liquid taking up the lower part of the vessel. We are not prepared to account for this transformation and limit ourselves to describe the result. The separation is observed, not predicted, but once it is admitted to occur the theory has much to say about it.

IV.3. Saturation

Consider a homogeneous body of gas with total mass 1, temperature $T < T_c$. As the gas is compressed the temperature is maintained by contact with a reservoir, the process carried out slowly so that the system goes through a sequence of equilibria. The pressure increases until the point A in the Fig. 3.4.1 is reached. One observes that, as the volume is reduced further the gas gradually converts, at constant pressure, to the liquid phase, until the point B is reached when all the gas has been converted. In the case of water at normal atmospheric pressure the density increases by a factor of 1 700.⁴

In what follows we shall make frequent reference to “the temperature”. We have found that the Euler-Lagrange equations, for a homogeneous system at rest, demand a uniform temperature. During condensation the system separates into two parts. A discontinuity in the temperature would give rise to an entropic force. The experiments are unequivocal: at equilibrium, both phases have the same temperature.

The van der Waals gas at the point A is characterized by a uniform, specific entropy density S_A . The same is true of the van der Waal’s liquid at the point B , though with a different value, S_B , say. The formula (2.2.3) in Section II.2 tells us that $S_A > S_B$.

³It is unstable in a mechanical sense (Rowlinson 1959 page 20) and also in the sense of the preceding section.

⁴We are ignoring the interesting phenomenon of metastable states. Some catalyst is needed for the process of condensation to begin. Apparently, it is possible to reach the maximum on the pressure curve by increasing the pressure, and the minimum by decreasing it. The pressure at the minimum is not necessarily positive. See Rowlinson (1959) page 21 and Ramsey (1956).

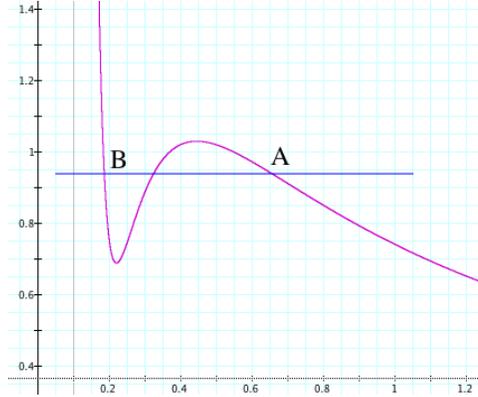


Fig.4.3.1. **Maxwell's rule.** The saturation pressure (= vapor pressure) is the value at the horizontal line that makes the two enclosed areas equal. The coordinates as in Fig. 4.2.1. *B* is the **bubble point**, *A* is the **dew point**

We are considering configurations of adiabatic equilibrium only, so the flow velocity vanishes. The effective Lagrangian is thus

$$\int d^3x \left(\rho_\ell \dot{\Phi}_\ell + \rho_g \dot{\Phi}_g - f - sT \right), \quad (4.3.1)$$

where $\dot{\Phi}_\ell$ and $\dot{\Phi}_g$ are real numbers. The integrals extend over the region occupied by the liquid and over the region occupied by the fluid. We have here a first example of a rule that we expect to apply universally:

**The Lagrangian of a compound system is,
at least in a first approximation,
the algebraic sum of the Lagrangians of the components.**

The field $\dot{\Phi}$ takes different values in the gas and in the liquid. The velocity potential is uniform for equilibrium configurations, except for a possible discontinuity at the meniscus. We consider the equations of motion, restricted to the stationary case, all fields time independent.

Local variation with respect to the density gives, with T and P fixed, in either phase,

$$\dot{\Phi} - ST - \frac{\partial}{\partial \rho} f = 0, \quad (4.3.2)$$

and variation of the temperature gives the adiabatic relation

$$\left. \frac{\partial}{\partial T}(f + sT) \right|_{\rho} = 0. \quad (4.3.3)$$

For a stationary state with $\vec{v} = 0$ this implies that all the fields are uniform within each phase and, except for density and entropy, continuous throughout.

This is a complete description of the stationary system, for given values of temperature and pressure. Global variation of both densities leads to the conclusion that both parts have the same temperature and pressure. A complementary global variation of the density will help to specify the **vapor pressure**; that is, the location of the point A in the figure, the pressure of coexistence. This point is determined by Maxwell's rule, that we shall discuss next, before completing the discussion of the equations of motion.

The above Lagrangian also applies to metastable configurations (Reisman 1971).

Interpretation of the **velocity potential**

In a homogeneous fluid at rest the velocity potential fulfills the role of Lagrange multiplier; in a fluid that is separated into a liquid and a gaseous phase it has a more interesting interpretation. The discontinuity in $\dot{\Phi}$, across a boundary of thickness x ; is

$$\Delta \dot{\Phi} = \dot{\Phi}_g - \dot{\Phi}_\ell = \Delta \vec{x} \cdot \vec{a} = \vec{x} \cdot \vec{F} / \rho;$$

it is the work required to lift one gram of matter out of the liquid. It is equal to $\Delta \vec{v}^2 / 2$ and we thus have

$$\Delta \dot{\Phi} = \frac{1}{2} \vec{v}_{\text{esc}}^2, \quad (4.3.4)$$

where \vec{v}_{esc} is the escape velocity required to overcome the surface tension. The interpretation of $\rho \Delta \dot{\Phi}$ as the energy of evaporation of one cm^3 of the liquid is thus natural. In a famous experiment, designed for education and employing the simplest means, the **surface tension** was measured and related to the **evaporation energy** (also measured). From these data Avogadro's number could be calculated. The value is about 6×10^{23} . Here are some web posts ⁵⁶

⁵Ishita Patel, M. S. surface tension, wsimson.tripod.com/offline/surf-tension.pdf

⁶National Physical... resource.npl.co.uk/mtdata/surfacetension.htm

Van der Waals has developed a more detailed model for the transition region, the “**squared gradient model**”, where the above picture is made more explicit (van der Waals 1893).

With two independent densities and associated velocity potentials we have two independent equations of continuity. This is because, in the bulk, whichever component is present is conserved. Conversion takes place only on the phase boundary. That no surface energy is included in the energy density is an idealization. In the squared gradient model (*op cit*), the single field $\dot{\Phi}$ varies continuously from $\dot{\Phi}_g$ to $\dot{\Phi}_\ell$ in the finite boundary layer.

Because the two spatial divisions of the system each contain only one fluid component, either liquid or gas, the adiabatic condition holds separately in both,

$$S_B = -\mathcal{R}(\ln \frac{\rho_g}{(1 - \rho_g)T^n} - n), \quad S_A = -\mathcal{R}(\ln \frac{\rho_\ell}{(1 - \rho_\ell)T^n} - n). \quad (4.3.3)$$

In the pure gas domain, as in the pure liquid domain, there is only one velocity potential and, in particular, in the stationary case, only one independent parameter $\dot{\Phi}$. As the gas condenses, all properties of each component remain constant, except for the total mass of each. Consequently, $\dot{\Phi}_g$ and $\dot{\Phi}_\ell$ remain constant during isothermal compression. The two parameters are different, because the fixed values of p and T allows for 2 stable values of the density.

IV.4. **Dew point, bubble point, Maxwell’s rule**

We turn to the question of predicting the values of the densities and the pressure at A and at B in Fig.4.3.1, the state of equilibrium or coexistence of gas and liquid.

Variation of the density in either region gives the information that the dynamical variables are constant in each; nothing more, since the term $\dot{\Phi}$ in (4.3.2) contains a Lagrange multiplier. Additional information is obtained by the supplemental, piecewise uniform variation with $\delta\rho_1 + \delta\rho_2 = 0$, namely

$$\text{Disc } \dot{\Phi} = \text{Disc}(\mu + ST). \quad (4.4.1)$$

Here

$$\mu = \left. \frac{\partial f}{\partial \rho} \right|_T$$

is the chemical potential. This relation is standard thermodynamics. We shall assume that the entropy density is $s = \rho_g S_B + \rho_\ell S_A$ - which is also standard since the two phases are separated. This implies that the specific entropy difference is $S_B - S_A$ and Boltzmann's theory then identifies $T(S_B - S_A)$ with ϵ at equilibrium. (De Groot and Mazur).

It remains only to discover the state of lowest 'energy'. An unequivocal result of 200 years of study is that the 'energy' that characterizes the ground state in this isolated system is the free energy $F = \int d^3 f$, with the *caveat* that the traditional Lagrange multiplier must be taken into account. The action principle suggests that 'energy density' is synonymous with Hamiltonian density, in this case $f + sT$. To overcome this conflict we have suggested replacing the entropy, so far treated as a mere constant, by $\dot{\sigma}$, please see Section II.9.

Now Eq. (4.4.1) should better be written

$$\text{Disc}(\dot{\Phi} - \dot{\sigma}T) = \text{Disc } \mu. \quad (4.4.1')$$

The principle of **maximum entropy** at equilibrium implies that for a fixed value of the temperature, the left side vanish, making μ continuous. It is nevertheless instructive to work out the implications of the equivalent minimization of the energy. It too implies the continuity of the **chemical potential**. It remains only to consider the variation of the respective volumes of liquid and gas. The 'energy' is the total Hamiltonian

$$H = V_1 f_1 + V_2 f_2 + \epsilon V_2. \quad (4.4.2)$$

The last term, with ϵ an arbitrary constant, allows for the normalization of the Hamiltonian. It would be needed to make this expression for H minimal with respect to variations of the partial volumes, but actually it is irrelevant since the values of the dynamical variables are already fixed by the Euler-Lagrange equations - the state of equilibrium is uniquely determined in terms of the fixed parameters $S_A, S_B, \dot{\Phi}_g$ and $\dot{\Phi}_\ell$. To alter the relative amounts of liquid and vapor we must change the value of the Lagrange multipliers.

The state of equilibrium is thus characterized by

$$\text{Disc } \mu = \text{Disc}(\dot{\Phi} - ST) = 0. \quad (4.4.3)$$

Both statements are verified experimentally. Because we're not aware of any convincing theoretical argument that the free energy must be minimal, and

because it can only be proved within the framework of an action principle, or by experience, we prefer to regard this result as an experimental fact. It has been supported by numerous other experiments, and for this reason we have tweaked our action principle so as to identify the free energy, rather than the internal energy, with the Hamiltonian (Section III.9).

The conventional point of view is essentially the same. The on shell value of μ is the specific Gibbs potential,

$$\mu = \frac{\partial f}{\partial \rho} = \frac{f + p}{\rho} = F + VP = G(p, T).$$

Because “this function is a function of T and p ” it follows that the slope of the free energy density has the same value in either phase. But this statement is not trivial. The familiar argument is

$$d(F + VP) = \frac{\partial F}{\partial T} dT + \frac{\partial F}{\partial V} dV + VdP + PdV = -SdT + VdP.$$

This shows only that the value of the function $F + VP$ is defined locally by T and P . It does not imply that the value is the same at the points A and B .

Callen, in his highly admired text book (Callen 1960), makes the same point. His strategy throughout the book is to invoke maximal entropy to arrive at an operative statement of the principle of minimum energy, with the interpretation ‘energy’ (of an isolated system) = free energy. In this case the axiom of greatest entropy makes the left side of (4.4.1’) equal to zero and this implies that $\mu_1 = \mu_2$. The principle of maximal entropy is thus confirmed by experience.

From Callen’s point of view the statement $\text{Disc}(\dot{\Phi} - ST) = 0$ reflects the fact that the two phases are in a type of diathermal contact where the heat is exchanged by means of transmutation.

It is an experimental fact that $F + VP$ (F if the volume is fixed) does have the same value for both components of the saturated phase. It implies that the horizontal line in Fig.4.3.1 divides the enclosed area in two equal parts and that the slope $\partial f/\partial \rho$ (the chemical potential) has the same value at the points A, B . This condition fixes a unique relation between p and T . An actual example, with numbers and figures, will be presented later.

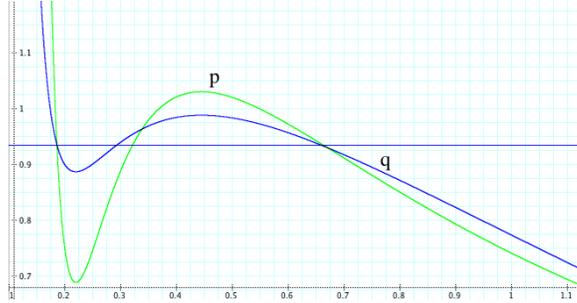


Fig.4.4.1. Coexistence, schematic. The curves are the values of p and μ , plotted against the molar volume.

The difference $\epsilon = \dot{\Phi}_g - \dot{\Phi}_\ell$ is the specific heat of evaporation, or latent heat; for

$$\epsilon = (S_g - S_\ell)T = \Delta Q, \quad (4.4.4)$$

where ΔQ is the amount of heat needed, per gram, to convert the liquid to gas. This last equation is sometimes presented without justification. It means that the energy that is supplied to bring about the evaporation at constant temperature and pressure is entirely entropic. This is in accord with the principle that the entropy tends to assume the highest possible value. In the context of the action principle it implies that the free energy is minimum.

The **adiabatic relation** is local, so it applies separately in both regions,

$$S_i = \mathcal{R} \ln \frac{\rho_i}{(1 - b\rho_i)T^n} - n, \quad i = 1(g), 2(\ell).$$

Consequently,

$$S_1 - S_2 = \mathcal{R} \ln \frac{\rho_1}{\rho_2} \frac{1 - b\rho_2}{1 - b\rho_1},$$

which determines the evaporation energy ϵ . See Saha's formula in Section V.8.

When applied to the evaporation of water at 373 K this gives a value for the heat of evaporation that is compared to the actual value of 2260 J/g. ⁷

Finally, since both $p = \rho \partial f / \partial \rho - f$ and $\partial f / \partial \rho$ are continuous it follows that

$$f(\rho_\ell) - f(\rho_g) = (\rho_\ell - \rho_g) \left. \frac{\partial f}{\partial \rho} \right|_{\rho=\rho_g}, \quad (4.4.5)$$

⁷I used $\mathcal{R}_{\text{air}} = .46 \text{ J/g}$ and $V_{\text{liq}}/V_{\text{gas}} = 1700$.

so that the two points on the curve $f(\rho)$ have a **common tangent**, as illustrated in Fig. 4.4.2.

Conversely, when a straight line is drawn so as to touch the f locus at two points, then the pressure has the same value at both points. This could have been predicted on the basis of the fact that the function $f + p$ has zeros at both points.

The function $f(T, \rho)$ thus plays exactly the role that Rowlinson attributes to the free energy while at the same time giving it a curious twist since he says that there is no analytic expression for the free energy. Indeed, the free energy is the function

$$\int_{\text{liq}} d^3x f(T, \rho_1) + \int_{\text{gas}} d^3x f(T, \rho_g)$$

of the 3 variables T, ρ_1, ρ_2 . It depends on the function f but also on the amount of vapor that is present. The analytic density $f(T, \rho)$ is nevertheless the key.



Fig.4.4.2. The common tangent. This is a graph showing the free energy density against the density. The common tangent identifies the two coexistent densities. They become minima if a suitable, immaterial linear term is added to the definition of f .

The location of the line of condensation, connecting the points A and B in Fig. 4.4.1, cannot be deduced from the expression for the pressure, nor from the variation of the Gibbs function. The principle of maximum entropy or minimum (at least stationary) energy has to be invoked. This conclusion

is not novel. What may be new is the perspective that allows to transfer the lesson to other contexts.

Normalizing the free energy density

We return to the concept of minimum energy. For most purposes the free energy is defined up to a term linear in the density. The action contains only

$$f + \rho ST = f - \rho \delta ST + \rho(S + \delta S)T =: \hat{f} + \hat{s}T.$$

The value of δS is immaterial. But when we discuss the transformation from one phase to the other it is convenient to arrange it so that no change of free energy occurs. For this reason we find it convenient to normalize the free energy density in such a way that the common tangent is horizontal. To accomplish this, given any expression for f we must calculate the equilibrium value of μ and use it in defining the **normalized free energy** density and the normalized specific entropy by

$$\hat{f} = f + \rho(S - \mu)T, \quad \hat{S} = S + \mu. \quad (4.4.6)$$

In the next section we show how this can be helpful.

This has the effect of re-normalizing the entropy as well. As we said, during condensation and during evaporation at constant temperature the normalized free energy remains constant and only the entropy is affected.

Calculating the **dew point** for Argon.

At the point where the liquid is in equilibrium (coexistence) with the gas the pressure depends only on the temperature; this pressure is the vapor pressure. To find the **vapor pressure** of Argon as a function of the temperature we must determine the two densities at which both the pressure,

$$P = \frac{\mathcal{R}T\rho}{1 - b\rho} - a\rho^2,$$

and the chemical potential

$$\mu = \frac{\partial f}{\partial \rho} = \mathcal{R}T \left(\ln \frac{\rho}{(1 - b\rho)T^n} + \frac{1}{1 - b\rho} \right) - 2a\rho$$

have the same values. Data for Argon are:

$$\text{Argon, } m = 40, n = 3/2, T_c = 150K, p_c = 4.9MPa.$$

Setting $a = 1.355 \text{ L}^2\text{bar/mol}^2$, $b = .03201 \text{ L/mol}$ in van der Waals formula gives $T_c = 152.6$, $p_c = 4.96 \text{ MPa} = .003912 \mathcal{R}T_c$ and $\rho_c = .0104$.

The simplest way to determine the dew point; that is, the saturation pressure for a chosen value of T , is to plot, in the x, y plane, the loci $p(x) = p(y)$ and $\mu(x) = \mu(y)$, namely, with the densities x and y in Kg/cm^3 ,

$$\ln \frac{x}{1 - 32x} + \frac{1}{1 - 32x} - \frac{16478}{T}(2x) = \ln \frac{y}{1 - 32y} + \frac{1}{1 - 32y} - \frac{16478}{T}(2y),$$

$$\frac{x}{1 - 32x} - \frac{16478}{T}x^2 = \frac{y}{1 - 32y} - \frac{16478}{T}y^2.$$

The dew point is found by inspection of Fig.4.4.3. This figure shows the loci of points (x, y) where $p(x) = p(y)$, resp. $q(x) = q(y)$ for the case that $T = 140$. They intersect at the points where x, y are the densities of the dew point, in grams per liter,

$$\rho_\ell = .01662 \text{ and } \rho_g = .00492.$$

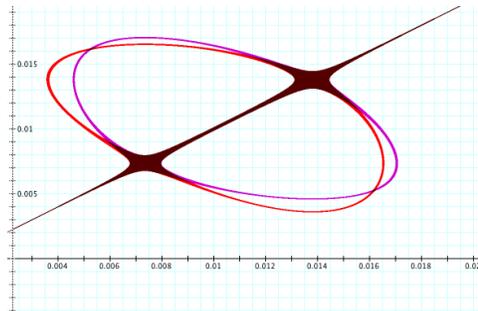
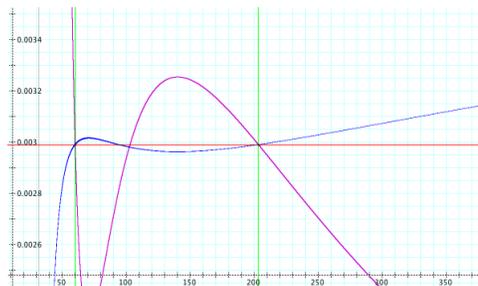


Fig.4.4.3. Argon. The two curves are loci of points (x, y) where $p(x) = p(y)$, resp. $\mu(x) = \mu(y)$. The values of x and y at the intersection of the two curves are the liquid and gas densities at saturation, in grams per liter. Here $T = 140\text{K}$.



In Fig.4.4.4. The same information is shown. The abscissa is the density. The two curves are the pressure (purple) and the chemical potential (blue), the latter scaled to pass through the dew point densities. The horizontal line is determined by Maxwell's rule.

Another way to find the dew point is to plot the free energy and find the two points with a common tangent, see Fig.4.4.5. To read the figure we normalize f and S , then expand the vertical coordinate, to convert Fig 4.4.5 to Fig 4.4.6.

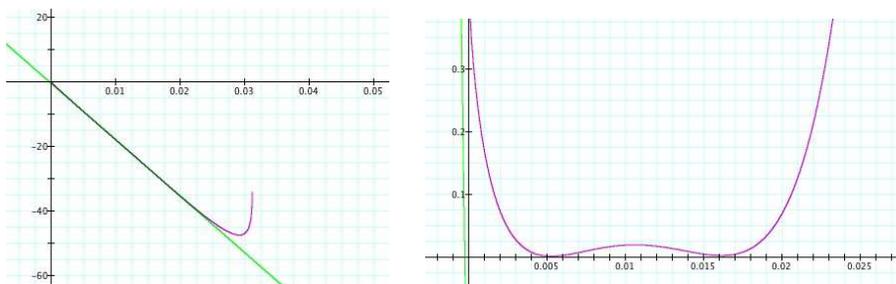


Fig.4.4.5. Argon. The common tangent. A plot of the free energy density of Argon at $T = 140K$ against the density.

Fig. 4.4.6. To get an accurate reading of the points of contact add a linear function to make the tangent horizontal.

Table 1: Dew point for Argon

T	ρ_1	ρ_2	p/RT_c
145	.0152	.0060	.0038
140	.0166	.0049	.0033
135	.0178	.0041	.0030
130	.0188	.0034	.0027
125	.0197	.0028	.0024
120	.0205	.0023	.0020
110	.0231	.0010	.0011

IV.5. The critical point

The nature of the **critical point** is of great interest. It has been the object of very extensive investigations, most notably with the help of the renormalization group.

The critical point, a fixed point where ρ_1, ρ_2, T and p have well defined values, is the state with the highest value of T at which coexistence occurs.

The van der Waals equation fails to give the correct relation between temperature and pressure in the saturation region. Nevertheless, we begin by studying this equation in the neighborhood of the critical point. We introduce “reduced” variables as follows,

$$\mathcal{R}T = \mathcal{R}T_c + t, \quad p = p_c + dp, \quad \rho = \rho_c + d\rho,$$

where the critical values are

$$\mathcal{R}T_c = \frac{8}{27} \frac{a}{b}, \quad p_c = \frac{1}{27} \frac{a}{b^2}, \quad \rho_c = \frac{1}{3b}. \quad (4.5.1)$$

In terms of these variables the van der Waals equation takes the following form (exactly; the reduced variables are not differentials but finite displacements from the critical point)

$$\frac{1}{3b}(t - 2bdp) + (t + bdp)d\rho + ab d\rho^3 = 0. \quad (5.5.2)$$

For fixed temperature and pressure this equation for $d\rho$ has either 1 or 3 real roots. In the region of one real root this root is the density, and the relation is a true equation of state. In the domain of 3 real roots the temperature and pressure are related and the (average) density is undetermined in the interval between the smallest and the largest roots.

Expanding the equation $q_A = q_B$, namely

$$\mathcal{R}T \left(\ln \frac{\rho_1}{1 - b\rho_1} + \frac{1}{1 - b\rho_1} \right) - 2a\rho_1 = \mathcal{R}T \left(\ln \frac{\rho_2}{1 - b\rho_2} + \frac{1}{1 - b\rho_2} \right) - 2a\rho_2$$

in the neighbourhood of the critical point we find, to lowest order in $d\rho$, the simple statement that $d\rho_1^2 = d\rho_2^2$. If the three real solutions of (5.5.2) are $d\rho_1 < d\rho_0 < d\rho_2$, then we have $d\rho_1 + d\rho_2 = 0$. In addition,

$$d\rho_1 + d\rho_2 + d\rho_0 = 0,$$

$$d\rho_1 d\rho_2 d\rho_0 = \frac{-1}{3ab^2}(t - 2bdp), \quad (d\rho_1 + d\rho_2)d\rho_0 + d\rho_1 d\rho_2 = \frac{t + bdp}{ab}.$$

This implies that, to lowest order in $d\rho$, $t - 2bdp = 0$, so that only one direction in the t, dp plane leads from the critical point into the saturation region.

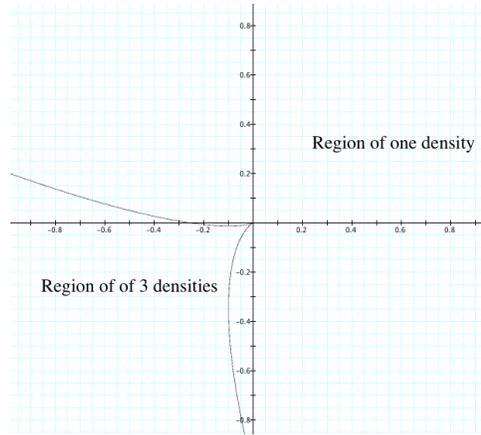


Fig.4.5.1. The two curves mark the border of the region (above and right) of the pure phase in the reduced variables t, dp .

We obtain direct confirmation of this conclusion by writing down the condition for the existence of three real roots of Eq.(3.2),

$$\frac{(t + bdp)^3}{3a} + \frac{(t - 2bdp)^2}{4b} < 0. \quad (4.5.3)$$

This defines a curve with two branches that meet at the origin with a common tangent, the line $t = -2bdp$.

In the saturation region there is a fixed relation between temperature and pressure, so that there is only one path along which the critical point can be approached. On this path the average density is related to the entropy and varies between ρ_1 and ρ_3 . Any path that leaves the critical point in another direction begins in the region of a single real root, in the region of a pure phase. There is no condensation in a (sufficiently small) neighborhood of the critical point. The linearized theory and the description of small perturbations around the critical point are therefore unexpectedly simple and regular, to be regarded as problems of a single phase governed by the Lagrangian (4.3.1).

IV.6. Sound propagation at the critical point

For a first application, let us calculate the speed of propagation of sound in Helium according to van der Waals. Fig.4.6.1 shows the speed of sound as measured.

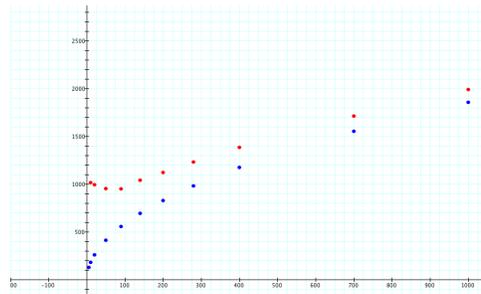


Fig.4.6.1. Helium sound against temperature for fixed pressure, $p = .01 \text{ atm}$. (red) and $p = 50 \text{ atm}$ (blue), against temperature, from $T = 5.19$ to $T = 1000$;

The next figure shows values obtained from van der Waals' formula with critical parameters

$$\text{Helium: } a = 0.0346 \text{ bar Lit}^2/\text{mol}^2, \quad b = 0.174 \text{ Lit/mol}.$$

The calculation is straightforward (see below), using the equation of continuity and the integrated form of the Bernoulli equation, as in the case of an ideal gas; the square of the speed is the adiabatic derivative of the pressure with respect to the density, where “adiabatic” now means that the temperature is evaluated according to

$$\left. \frac{\partial(f + \rho ST)}{\partial T} \right|_{\rho, S} = 0;$$

that is, $(V - b)T^n = \text{constant}$. This use of the word adiabatic is standard and explains why the last equation is referred to as the adiabatic relation.

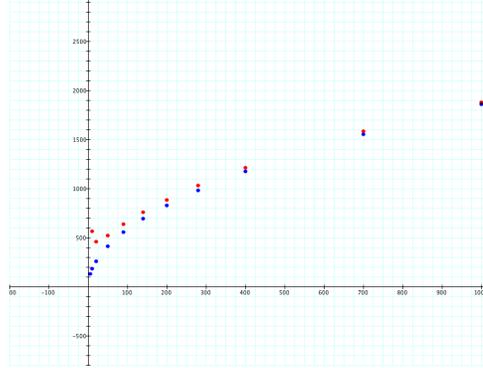


Fig. 4.6.2. Helium sound speed as calculated using Eq. (4.6.1).

The equations that govern a first order, adiabatic perturbation of a pure phase in equilibrium, in which the perturbed fields depend on only one spatial coordinate, are the linearized equations of motion,

$$\frac{d\ddot{\rho}}{\rho} = -\dot{v}' = \frac{\partial^2 \rho}{\partial x^2} \frac{\partial}{\partial \rho} (f + sT) \Big|_S.$$

See Section IV.1. The derivative is one of the definitions of the chemical potential. As always, since the specific entropy is uniform, this leads to

$$c^2 = \frac{\partial p}{\partial \rho} \Big|_S,$$

In the present case

$$T = \left(\frac{\rho}{(1 - b\rho)k} \right)^{1/n}, \quad p = \frac{\mathcal{R}}{k^{1/n}} \left(\frac{\rho}{(1 - b\rho)} \right)^{1+1/n} - a\rho^2$$

and

$$c^2 = \frac{\gamma \mathcal{R} T}{(1 - b\rho)^2} - 2a\rho. \quad (4.6.1)$$

At the critical point this reduces to

$$c^2 = \frac{.8314 \times 10^8 \times 5.19}{4} \frac{5/3}{(1 - 17.4 \times .0697)^2} - 2 \times .0697^2 \times 2162.5 \times 10^6.$$

The result is $c = 134.5$ m/s. The numerical value applies to helium, with $n = 3/2$; it is a small deviation from Laplace's formula $\sqrt{\gamma \mathcal{R} T} = 134.1$ m/s.

Table 4.3, at the end of the chapter, gives a range of values. Comparison with Table 4.4 shows little deviation from experiments, or from measured values, at low pressures, but at the highest pressure the fit to experiment is very bad, showing no improvement with respect to the ideal gas model. A better fit is achieved with the general cubic model discussed at the end of the chapter.

IV.7. Refinements of the expression for the internal energy

The heat capacity

We consider the region of one phase, at or above the critical point. We shall attempt to account for the anomalies in this region by variation of the heat of evaporation, more precisely the parameter ϵ , with temperature. The potential, with this term now included, is

$$V_1(T, \rho) = \mathcal{R}\rho T \ln \frac{\rho}{(1 - b\rho)T^n k_0} - \kappa(\rho) - \rho\epsilon_1(T).$$

The pressure is not affected. We shall assume that the function ϵ takes the form

$$\epsilon(T) = \alpha(T - T_c)^{1-\beta}.$$

We expect that α is positive and that β is small, positive, to make the evaporation energy zero at the critical point. Then

$$C_V = n\mathcal{R} + \alpha\beta(1 - \beta)t^{-\beta}, \quad t := T - T_c$$

is infinite at the critical point. Experiments with helium indicate that $\alpha < 0$ and that $\beta \approx .04$.

The speed of sound

With $\tilde{\psi} = \epsilon$ there is a correction to Eq. (3.3),

$$\frac{d\dot{p}}{\rho} = \frac{T''}{\rho} \frac{\partial p}{\partial T} + \frac{\rho''}{\rho} \frac{\partial p}{\partial \rho} + \epsilon_1''(T).$$

This is supplemented by the on shell condition

$$\ln \frac{\rho}{(1 - b\rho)T^n k_0} - n = \epsilon_1'/\mathcal{R}, \quad (4.7.1)$$

which implies that, to first order,

$$(n + \epsilon_1'' T/\mathcal{R}) \frac{dT}{T} = \frac{1}{1 - b\rho} \frac{d\rho}{\rho}.$$

Hence

$$\frac{d\ddot{\rho}}{\rho} = \mathcal{R} T'' \frac{1}{1 - b\rho} + \frac{\rho''}{\rho} \frac{\partial p}{\partial \rho} + \dots,$$

which gives for the speed c of sound propagation

$$c^2 = \frac{\mathcal{R}T}{n(1 - b\rho)^2} + \frac{\partial p}{\partial \rho} + \dots$$

What follows is the general third order equation of state. Evaluating the second term in (4.7.2) we find

$$c^2 = \frac{\gamma \mathcal{R}T}{(1 - b\rho)^2} - \frac{a}{\rho^2} \frac{2(\mathcal{V} - b) + x}{((\mathcal{V} - b)^2 + x(\mathcal{V} - b) + y)^2}.$$

Experiment shows a pronounced dip in the speed of sound as a function of density or temperature, in a small region above the critical point. To first order in the perturbation it is

$$= \frac{\rho''}{\rho} \left(\frac{\mathcal{R}T}{(1 - b\rho)^2} - 2a \right) + T'' \frac{\mathcal{R}}{1 - b\rho}.$$

The last term was simplified with the help of the modified on shell condition, namely

$$\mathcal{R} \left(\ln \frac{\rho}{(1 - b\rho) T^n k_0} - n \right) + \epsilon' = 0.$$

This also gives us

$$dT = \frac{1}{1 - T\epsilon''/n\mathcal{R}} \frac{T}{n} \frac{1}{1 - b\rho} \frac{d\rho}{\rho}.$$

Thus

$$c^2 = \frac{d\rho''/\rho}{dT''/T} = \mathcal{R} dT'' \left(n + \frac{1}{1 - b\rho} + \frac{\epsilon' - T\epsilon''}{\mathcal{R}} \right) + d\rho'' \left(\frac{b\rho T}{(1 - b\rho)^2} - 2a \right).$$

To first order in ϵ it gives the squared speed

$$c^2 = \frac{\mathcal{R}T}{(1 - b\rho)^2} \left(\gamma + \frac{T/n\mathcal{R}\epsilon''}{1 - T/n\mathcal{R}\epsilon''} \right).$$

IV.8. The cubic equation of state

It is sometimes of interest to reduce the errors inherent in the van der Waals expression for the pressure, and many suggestions have been made. A generalization developed by Patel and Teja takes the form

$$p = \frac{\mathcal{R}T}{1 - b\rho} - \frac{a\rho^2}{(1 - c\rho)(1 - d\rho)}, \quad (4.8.1)$$

with a certain relation between the parameters b, c, d . The associated free energy density is

$$f(\rho, T) = \rho\mathcal{R}T \ln \frac{\rho}{(1 - b\rho)T^n} + \frac{a\rho}{c - d} \ln \frac{1 - c\rho}{1 - d\rho} + \rho\psi(T), \quad k_0 = \text{constant},$$

the function ψ arbitrary so far. There are arguments to show that this function can best be taken to be zero; in that case the internal energy density is

$$U = n\mathcal{R}T + \frac{a}{c - d} \ln \frac{1 - c\rho}{1 - d\rho}.$$

The van der Waals gas is the case in which $c = d = 0$.

Provisionally, we shall set $\psi = 0$, deferring refinements until they are needed, as when we take up the study of the neighborhood of the critical point; then

$$f(T, \rho, S) = \mathcal{R}T\rho \ln \frac{\rho}{(1 - b\rho)T^n} + \kappa(\rho), \quad (4.8.2)$$

where

$$\kappa(\rho) = \frac{a\rho}{c - d} \ln \frac{1 - c\rho}{1 - d\rho}.$$

The adiabatic condition (2.4) (from variation of T) is

$$\ln \frac{\rho}{(1 - b\rho)T^n k_0} = n, \quad (4.8.3)$$

and the on shell internal energy density at equilibrium is

$$u = n\mathcal{R}\rho T + \rho\kappa(\rho) + \text{constant } \rho.$$

We use the expression (4.6.1) for the pressure,

$$p = \frac{\mathcal{R}T}{(\mathcal{V} - b)} - \frac{a}{(\mathcal{V} - c)(\mathcal{V} - d)}, \quad (4.8.4)$$

but specialize to the case considered by Patel and Teja (Patel 2004). The calculations are much simplified when we introduce $\mathcal{V}' = \mathcal{V} - b$, and define x, y by writing

$$p = \frac{\mathcal{R}T}{\mathcal{V}'} - \frac{a}{\mathcal{V}'^2 + x\mathcal{V}' + y}. \quad (4.8.5)$$

The special case considered by Patel and Teja is the case that $y = 2b^2$.

An extremum of this function of \mathcal{V}' occurs at

$$\frac{\mathcal{R}T}{a} = \frac{\mathcal{V}'^2(2\mathcal{V}' + x)}{(\mathcal{V}'^2 + x\mathcal{V}' + y)^2},$$

where

$$\frac{\mathcal{R}T}{p} = \frac{\mathcal{V}'^2(2\mathcal{V}' + x)}{\mathcal{V}'^2 - y}. \quad (4.8.6)$$

At the critical point

$$\mathcal{V}'^3 - 3y\mathcal{V}' - xy = 0, \quad x = y^{-1}\mathcal{V}'(\mathcal{V}'^2 - 3y).$$

Finally, at the critical point the value of b is given by the experimental values of the compressibility $Z_{\text{cr}} = \mathcal{R}T/p$ and the density ρ_{cr} by

$$\left. \frac{\mathcal{R}T}{p\mathcal{V}} \right|_{\text{cr}} = \frac{(\mathcal{V} - b)^3}{y\mathcal{V}}.$$

For He_4 the experimental values are

$$T_{\text{cr}} = 5.19, \quad \rho_{\text{cr}} = .0697, \quad p_{\text{cr}} = .227 \times 10^7, \quad Z_{\text{cr}} = .301, \quad \mathcal{V}_{\text{cr}} = 14.35,$$

and the parameters are

$$a = 2.378 \times 10^9, \quad b = 3.61, \quad x = 15.31, \quad y = 26.06.$$

These parameters were used to calculate the speeds given in lines labelled “cubic” in Table 4.3.

IV.9. Stability

This is a concept that will become very difficult later, as we come to deal with more complicated problems. We have already studied the van der Waals gas; it will provide the first illustration.

Suppose that the velocity is zero, then the Bernoulli equation tells us that

$$\rho \dot{\vec{v}} = -\vec{\nabla} p.$$

In simple systems the temperature can be eliminated with the help of the adiabatic condition; then the pressure is a function of the density and the specific entropy, supposed constant, hence

$$\rho \dot{\vec{v}} + \left. \frac{\partial p}{\partial \rho} \right|_S \vec{\nabla} \rho = 0.$$

If the velocity is to the right, say, and the acceleration is in the same direction, then the space between the particles will increase and the density must decrease; this implies that, for stability, $dp/d\rho$ is positive. In more detail, suppose the acceleration is in the positive x direction and imagine a virtual change that makes the acceleration increase. Then by the equation of continuity the gradient of the density must decrease. So again, the coefficient must be positive.

An equivalent argument is to calculate the speed of propagation of sound. We found that its square is the adiabatic derivative of the pressure with respect to the density and learned that if this is positive we will have wave propagation, while if it is negative there will be decay.

In the case of the van der Waals fluid, this condition is violated in the rising part of the curve that shows pressure against volume. Where $dp/d(1/\rho)$ is positive, the configuration is unstable. If we approach this region along an isotherm, from right to left, then after passing the point of coexistence we enter a metastable region. In the absence of a disturbance, as the pressure is increased slowly, condensation can be avoided, but a small disturbance may initiate a catastrophic condensation. If the top of the curve is reached condensation becomes inevitable. Similarly, the region below the bubble point may be entered without actually creating evaporation, even so far as to make the pressure negative, but upon a catalytic perturbation evaporation will be rapid.

Table 2: Liquid/vapor critical temperature and pressure

Substance	Critical temperature	Critical pressure
Argon	-122.4 C (150.8 K)	48.1 atm (4,870 kPa)
Ammonia	132.4 C (405.6 K)	111.3 atm (11,280 kPa)
Bromine	310.8 C (584.0 K)	23102 atm (10,300 kPa)
Caesium	1,664.85 C	94 atm (9,500 kPa)
Chlorine	143.8 C (417.0 K)	76.0 atm (7,700 kPa)
Ethanol	241 C (514 K)	62.18 atm (6,300 kPa)
Fluorine	-128.85 C (144.30 K)	51.5 atm (5,220 kPa)
Helium	-267.96 C (5.19 K)	2.24 atm (227 kPa)
Hydrogen	-239.95 C (33.20 K)	12.8 atm (1,300 kPa)
Krypton	-63.8 C (209.4 K)	54.3 atm (5,500 kPa)
CH ₄ (Met.)	-82.3 C (190.9 K)	45.79 atm (4,640 kPa)
Neon	-228.75 C (44.40 K)	27.2 atm (2,760 kPa)
Nitrogen	146.9 C (126.3 K)	33.5 atm (3,390 kPa)
Oxygen	-118.6 C (154.6 K)	49.8 atm (5,050 kPa)
CO ₂	31.04 C (304.19 K)	72.8 atm (7,380 kPa)
N ₂ O	36.4 C (309.6 K)	71.5 atm (7,240 kPa)
H ₂ SO ₄	654 C (927 K)	45.4 atm (4,600 kPa)
Xenon	16.6 C (289.8 K)	57.6 atm (5,840 kPa)
Lithium	2,950 C (3,220 K)	652 atm (66,100 kPa)
Mercury	1,476.9 C (1,750.1 K)	1,720 atm (174,000 kPa)
Sulfur	1,040.85 C (1,314.00 K)	207 atm (21,000 kPa)
Iron	8,227 C (8,500 K)	
Gold	6,977 C (7,250 K)	5,000 atm (510,000 kPa)
Aluminium	7,577 C (7,850 K)	
Water	373.946 C (647.096 K)	217.7 atm (22.06 MPa)

Table 3: Some van der Waals parameters

	$a(L^2atm/mol^2)$	$b(L/mol)$
Acetic acid	17.71	0.1065
Anhydride	20.158	0.1263
Acetone	16.02	0.1124
Acetonitrile	17.81	0.1168
Acetylene	4.516	0.0522
Ammonia= NH_3	4.225	0.0371
Argon	1.355	0.0320
Benzene	18.24(.82)	0.1154(.1193)
Bromobenzene	28.94	0.1539
Butane= C_4H_{10}	14.66(13.89)	0.1226(.1164)
Carbon dioxide	3.640(.658)	0.04267(.0429)
Carbon disulfide	11.77(.25)	0.07685(.0726)
Carbon monoxide	1.505(.472)	0.039 85(.0395)
Carbon tetrachloride	19.7483	0.1281
Chlorine = Cl_2)	6.579(.343)	0.05622(.0542)
Chlorobenzene	25.77	0.1453
Chloroethane	11.05(.66)	0.08651(.0903)
Chloromethane	7.570	0.06483
Cyanogen= C_2N_2	7.769	0.06901
Cyclohexane	23.11(21.92)	0.1424(.1411)
Diethyl ether	17.61	0.1344
Diethyl sulfide	19.00	0.1214
Dimethyl ether	8.180(.690)	0.07246(.0774)
Dimethyl sulfide	13.04	0.09213
Ethane= C_2H_6	5.562(.580)	0.0638(.0651)
Ethanethiol	11.39	0.08098
Ethanol= C_2H_5OH	12.18(.56)	0.08407
Ethyl acetate	20.72	0.1412
Ethylamine	10.74	0.08409
Fluorobenzene	20.19	0.1286
Fluoromethane	4.692	0.05264
Freon	10.78	0.0998
Germanium tetrachl.	22.90	0.1485
Helium	0.03457	0.0237
Hexane= C_6H_{14}	24.71	0.1735
Hydrogen= H_2	0.2476(.2452)	0.02661(-.265)
Hydrogen bromide	4.510	0.04431
Hydrogen chloride	3.716	0.04081
Hydrogen selenide	11.638	0.04637
Hydrogen sulfide	4.490	0.04287

Table 4: Continuation, van der Waals parameters

	$a(L^2 atm/mol^2)$	$b(L/mol)$
Iodobenzene	33.52	0.1656
Krypton	2.349(5.193)	0.03978(.0106)
Mercury=Hg	8.200	0.01696
Methane= CH_4	2.283(.303)	0.04278(.0431)
Methanol	9.649(.476)	0.06702(.0659)
Neon	0.2135(.208)	0.01709(.0167)
Nitric oxide	1.358	0.02789(.0289)
Nitrogen= Ni_2	1.408(.370)	0.03913(.0387)
Nitrogen dioxide	5.354	0.04424
Nitrous oxide	3.832	0.04415
Oxygen	1.378	0.03183
Pentane	19.26(.09)	0.146(.1449)
Phosphine= PH_3	4.692	0.05156
Propane= C_3H_8	8.779(9.39)	0.08445(.0905)
Silane= SiH_4	4.377	0.05786
Silicon tetrafluoride	4.251	0.05571
Sulfur dioxide	6.803	0.05636
Tin tetrachloride	27.27	0.1642
Toluene= C_7H_8	7 24.38(.86)	0.1463(.1497)
Water	5.536	0.03049
Xenon	4.250(.192)	0.05105(.0516)

Table 5: Helium sound speed

$p = .01$			$p = 1$			$p = 50$		
T	ρ	v	T	ρ	v	T	ρ	v
5.19	.0001	134.0	5.19	.001	133.3	5.19	.1417	780.0
10	.5 E-4	186.1	10	.5 E-3	186.1	10	.118	569.5
20	.23 E-4	263.2	20	.24 E-3	263.4	20	.08	462.5
50	.1 E-4	416.2	50	.1 E-3	416.5	50	.04	524.7
90	.55 E-5	558.4	90	.55 E-4	558.5	90	.021	642.4
140	.34 E-5	696.4	140	.34 E-4	696.5	140	.016	764.5
200	24 E-5	832.5	200	.24 E-4	832.5	200	.0113	889.1
280	.17 E-5	984.9	280	.17 E-4	985.0	280	.0082	1033
400	.12 E-5	1177	400	.12 E-4	1177	400	.0058	1217
700	.7 E-6	1557	700	.7 E-5	1557	700	.0034	1589
1000	.5 E-6	1861	1000	.5 E-5	1884	1000	.00237	1887

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