

Chapter 2

The equation of state

The equation of state (EOS) is a nontrivial relation linking the thermodynamic variables specifying the state of a macroscopic physical system. The most popular example is Boyle's *ideal gas law*, stating that the pressure of a collection of N noninteracting, pointlike classical particles, enclosed in a volume V , grows linearly with the temperature T and the average particle density $n = N/V$.

The ideal gas law provides a good description of very dilute systems, in which interaction effects can be neglected. In general, the EOS can be written expanding the pressure, P , in powers of the density (from now on, we will use units such that $K_B = 1$) according to

$$P = nT [1 + nB(T) + n^2C(T) + \dots] . \quad (2.1)$$

The coefficients appearing in the above series, called *virial expansion*, depend on temperature only and describe the departure from the ideal gas law arising from interactions.

The EOS carries a great deal of dynamical information and provides a link between measurable *macroscopic* quantities, such as pressure and temperature, and the forces acting between the constituents of the system at *microscopic* level.

2.1 The van der Waals fluid

This dynamical content of the EOS can be best illustrated using the van der Waals fluid as an example. This system consists of a collection of particles interacting through a potential featuring a strong repulsive core followed by a weaker attractive tail, as schematically illustrated in Fig.2.1.

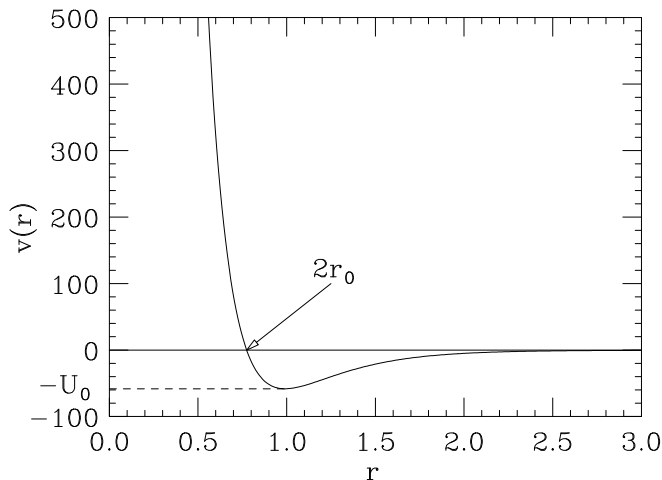


Figure 2.1: Behavior of the potential describing the interactions between constituents of a van der Waals fluid (both the interparticle distance r and $v(r)$ are given in arbitrary units).

The EOS of a van der Waals fluid is usually written in the form

$$P = \frac{nT}{1 - nb} - an^2, \quad (2.2)$$

where the two quantities a and b account for interaction effects. We will now show that a and b can be simply related to the potential $v(r)$.

The total energy of a system consisting of N nonrelativistic particles of mass m , enclosed in the volume V and interacting through the potential v , is

$$E = K + U \quad (2.3)$$

with

$$K = \sum_{i=1}^N \frac{p_i^2}{2m}, \quad (2.4)$$

and

$$U = \sum_{j>i=1}^N v(|\mathbf{r}_i - \mathbf{r}_j|). \quad (2.5)$$

where \mathbf{r}_i and \mathbf{p}_i denote position and momentum of the i -th particle, respectively.

The free energy at temperature T can be obtained from

$$F = -T \log \int e^{-\frac{E}{T}} d\Gamma \quad (2.6)$$

where $d\Gamma$ is the phase space volume element

$$d\Gamma = \prod_{i=1}^N d^3r_i \prod_{i=1}^N \frac{d^3p_i}{(2\pi)^3}. \quad (2.7)$$

Substitution of Eq. (2.3) in the right hand side of Eq. (2.6) leads to the factorization of the integral. For an ideal gas (IG), i.e. when $U = 0$, integration over the particle coordinates simply yields the result V^N and one finds

$$F_{IG} = -T \log V^N \int \prod_{i=1}^N \frac{d^3p_i}{(2\pi)^3} e^{-\frac{K}{T}}, \quad (2.8)$$

implying in turn

$$\begin{aligned} F &= F_{IG} - T \log \frac{1}{V^N} \int \prod_{i=1}^N d^3r_i e^{-\frac{U}{T}} \\ &= F_{IG} - T \log \left[\frac{1}{V^N} \int \prod_{i=1}^N d^3r_i \left(e^{-\frac{U}{T}} - 1 \right) + 1 \right]. \end{aligned} \quad (2.9)$$

We will now make the assumption that the system be so dilute that the probability of simultaneous collisions involving more than two particles be negligible. As the particles are identical, we can then rewrite the integral appearing in the second line of Eq. (2.9) as

$$\frac{N(N-1)}{2V^N} \int \prod_{i=1}^N d^3r_i \left(e^{-\frac{v_{12}^2}{T}} - 1 \right), \quad (2.10)$$

where $v_{ij} = v(|\mathbf{r}_i - \mathbf{r}_j|)$. The integrand only depends on the positions of particles 1 and 2, so that the remaining integrations, yielding a factor V^{N-2} , can be carried out right away. Moreover, as N is a large number $N(N-1) \approx N^2$, and Eq. (2.9) becomes

$$F = F_{IG} - T \log \left[\frac{1}{2} \left(\frac{N}{V} \right)^2 \int d^3r_1 d^3r_2 \left(e^{-\frac{v_{12}^2}{T}} - 1 \right) + 1 \right]. \quad (2.11)$$

In the low density limit, which is appropriate as we are dealing with a dilute system, the integral in the above equation, being proportional to $(N/V)^2$ is small. We can therefore use the result $\log(x+1) \approx x$ at $x \ll 1$ to obtain

$$F = F_{IG} - \frac{T}{2} \left(\frac{N}{V} \right)^2 \int d^3r_1 d^3r_2 \left(e^{-\frac{v_{12}^2}{T}} - 1 \right). \quad (2.12)$$

The interaction potential depends on the relative coordinate only. Hence, defining

$$\mathbf{R}_{12} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \quad , \quad \mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2 \quad (2.13)$$

we can replace

$$\int d^3r_1 d^3r_2 \left(e^{-\frac{v_{12}}{T}} - 1 \right) \rightarrow V \int d^3r_{12} \left(e^{-\frac{v_{12}}{T}} - 1 \right) \quad (2.14)$$

to obtain

$$F = F_{IG} + \frac{N^2 T B(T)}{V} \quad , \quad (2.15)$$

with

$$B(T) = \frac{1}{2} \int d^3r_{12} \left(1 - e^{-\frac{v_{12}}{T}} \right) \quad . \quad (2.16)$$

Finally, from

$$P = - \left(\frac{\partial F}{\partial V} \right)_{N,T} \quad (2.17)$$

and

$$P_{IG} = \frac{N}{V} T \quad (2.18)$$

it follows that the EOS of a dilute gas can be written as a virial expansion, including terms of first and second order in the particle density N/V (compare to Eq. (2.1))

$$P = \frac{N}{V} T \left[1 + \frac{N}{V} B(T) \right] \quad . \quad (2.19)$$

Let us now go back to the van der Waals fluid, and consider the expansion of the quantity $B(T)$ of Eq. (2.16) in powers of the ratio U_0/T , $U_0 > 0$ being the depth of the attractive part of the interparticle potential (see Fig. 2.1).

First, we split the integral in two parts according to (see Fig. 2.1)

$$B(T) = 2\pi \int_0^{2r_0} \left(1 - e^{-\frac{v_{12}}{T}} \right) r_{12}^2 dr_{12} + 2\pi \int_{2r_0}^{\infty} \left(1 - e^{-\frac{v_{12}}{T}} \right) r_{12}^2 dr_{12} \quad . \quad (2.20)$$

At $0 \leq r_{12} \leq 2r_0$ the potential energy is positive and very large, implying that the exponential $\exp -v_{12}/T$ is small and can be neglected. As a consequence, we can define the quantity b as

$$b = 2\pi \int_0^{2r_0} \left(1 - e^{-\frac{v_{12}}{T}} \right) r_{12}^2 dr_{12} \approx \frac{16\pi}{3} r_0^3 \quad . \quad (2.21)$$

Note that, if we interpret r_0 as the particle radius, b equals four times its volume.

Consider now the second integral in the right hand side of Eq. (2.20). For $U_0/T \ll 1$ the inequality $|v_{12}|/T \leq U_0/T$ implies

$$|v_{12}|/T \ll 1, \quad (2.22)$$

and the integrand can be expanded in series of powers of v_{12}/T . Keeping the first nonvanishing term we obtain the result (recall that for $2r_0 \leq r_{12} \leq \infty$ v_{12} is always negative)

$$-\frac{2\pi}{T} \int_{2r_0}^{\infty} |v_{12}| r_{12}^2 dr_{12} = -\frac{a}{T}, \quad (2.23)$$

that defines the positive constant a . Collecting the two pieces together we can write

$$B(T) = b - \frac{a}{T}, \quad (2.24)$$

yielding (see Eq. (2.15))

$$F = F_{IG} + \frac{N^2}{V} (bT - a). \quad (2.25)$$

To write the EOS in the form $P = P(N/V)$ we make use of the general expression of the free energy of the ideal gas

$$F_{IG} = -NT \log \frac{eV}{N} + Nf(T), \quad (2.26)$$

where $f(T)$ is a function of temperature only. Substitution into Eq. (2.25) leads to

$$F = Nf(T) - NT \log \frac{e}{N} - NT \left(\log V - \frac{Nb}{V} \right) - \frac{N^2 a}{V}. \quad (2.27)$$

According with the hypothesis that the system be diluted, we now make the assumption that

$$Nb \ll V, \quad (2.28)$$

implying

$$\log(V - Nb) = \log V + \log \left(1 - \frac{Nb}{V} \right) \approx \log V - \frac{Nb}{V} \quad (2.29)$$

and

$$\begin{aligned} F &= Nf(T) - NT \log \frac{e}{N} (V - Nb) - \frac{N^2 a}{V} \\ &= F_{IG} - NT \log \left(1 - \frac{Nb}{V} \right) - \frac{N^2 a}{V}. \end{aligned} \quad (2.30)$$

Note that the above equation yields the correct result, $F = F_{IG}$, in the limit of infinite dilution, corresponding to $V \rightarrow \infty$. On the other hand, it also implies that the system cannot be compressed indefinitely, as for $Nb/V > 1$ the argument of the logarithm becomes negative.

Knowing the free energy, we can finally obtain the pressure from Eq. (2.17), leading to

$$P = \frac{N}{V}T + NT \frac{Nb}{V(V - Nb)} - \left(\frac{N}{V}\right)^2 a = \frac{NT}{V - Nb} - \left(\frac{N}{V}\right)^2 a, \quad (2.31)$$

i.e. to Eq. (2.2) with $n = N/V$.

Equation (2.31) can also be rewritten in the form

$$\left[P + \left(\frac{N}{V}\right)^2 a \right] (V - Nb) = NT \quad (2.32)$$

showing that (compare to the ideal gas EOS, $PV = NT$) the occurrence of interactions between the particles results in an increase of the pressure, driven by the constant a , and a decrease of the available volume, driven by the constant b (recall that $b \propto r_0^3$ can be related to the particle volume).

In spite of its simplicity, the van der Waals EOS provides a fairly accurate description of systems exhibiting a liquid-gas phase transition, like water (in this case the values of the parameters entering Eq. (2.31) are $a = 2 \times 10^{-48} \text{ J m}^3$ and $b = 6 \times 10^{-29} \text{ m}^3$).

Defining the quantities

$$P_c = \frac{a}{27b^2}, \quad V_c = 3Nb, \quad T_c = \frac{8a}{27b}, \quad (2.33)$$

and introducing the new adimensional variables

$$\tilde{P} = \frac{P}{P_c}, \quad \tilde{V} = \frac{V}{V_c}, \quad \tilde{T} = \frac{T}{T_c}, \quad (2.34)$$

the van der Waals EOS can be rewritten in the form

$$\left(\tilde{P} + \frac{3}{\tilde{V}^2}\right) \left(\tilde{V} - \frac{1}{3}\right) = \frac{8}{3}\tilde{T}. \quad (2.35)$$

Note that the above relation is universal, as it does not explicitly depend on the constants a and b .

Figure 2.2 shows the relation between pressure in units of the critical pressure, \tilde{P} , and density in units of the critical density, $\tilde{n} = V_c/V$, for different values of \tilde{T} . It appears that at $T < T_c$, i.e. $\tilde{T} < 1$, the curves exhibit both

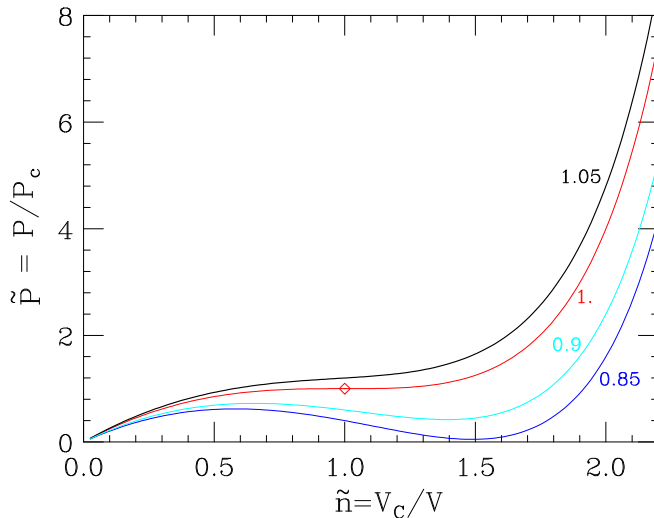


Figure 2.2: Behavior of the pressure (in units of the critical pressure) as a function of density (in units of the critical density) for a van der Waals fluid. The different curves are labelled according to the value of the ratio $\tilde{T} = T/T_c$, T_c being the critical temperature. The diamond corresponds to the critical point $\tilde{P} = \tilde{V} = 1$.

a maximum and a minimum, whereas at $T > T_c$, i.e. $\tilde{T} > 1$, \tilde{P} becomes a monotonically increasing function of \tilde{n} . The curve corresponding to the critical temperature $T = T_c$ features a point of abscissa \tilde{n}_c such that

$$\left(\frac{\partial \tilde{P}}{\partial \tilde{n}} \right)_{\tilde{n}=\tilde{n}_c} = \left(\frac{\partial^2 \tilde{P}}{\partial \tilde{n}^2} \right)_{\tilde{n}=\tilde{n}_c} = 0. \quad (2.36)$$

This point is called *critical point*. From Eqs. (2.35) and (2.36) it follows that $\tilde{n}_c = 1$ and $\tilde{P}(\tilde{n}_c) = 1$.

As already pointed out, the van der Waals EOS describes a system exhibiting a liquid-gas phase transition. For $T > T_c$ the system is in the liquid phase at density $n > n_c$ ($n_c = N/V_c$) and in the gas phase at $n < n_c$. For $T < T_c$ there is a density region $n_1 < n < n_2$, with $n_1 < n_c$ and $n_2 > n_c$, in which the two phases coexist. The values of n_1 and n_2 are determined by the requirements

$$P(n_1) = P(n_2) \quad (2.37)$$

and

$$P(n_1) \left(\frac{1}{n_2} - \frac{1}{n_1} \right) = - \int_{n_1}^{n_2} P(n) \frac{dn}{n^2}. \quad (2.38)$$

These features are best illustrated by the *phase diagram* of Fig. 2.3, showing the boundary of the regions corresponding to the different phases in the (\tilde{n}, \tilde{T}) plane.

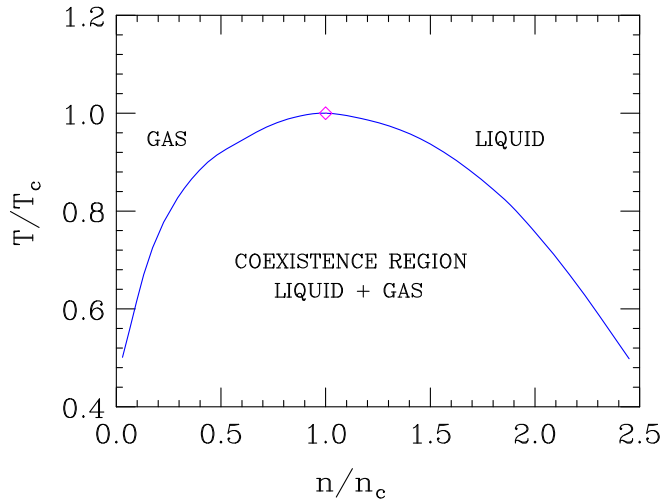


Figure 2.3: Phase diagram of a van der Waals fluid.

The example of the van der Waals fluid shows that the EOS contains information on the dynamics driving the interactions between the constituents of the system at microscopic level. The rather simple structure of the phase diagram of Fig. 2.3 reflects the simplicity of the potential represented in Fig. 2.1.

In the case of strongly interacting matter, the complexity of the underlying dynamics leads to a much richer structure, schematically illustrated in Fig. 2.4.

Under standard terrestrial conditions the elementary degrees of freedom of the fundamental theory of strong interactions (Quantum Chromo-Dynamics, or QCD) are confined within hadrons, and protons and neutrons cluster to form nuclei. At much larger density and/or temperature, however, the situation dramatically changes, and many different forms of matter are expected to become energetically favoured. In the following sections we will discuss the structure of matter at large density and low temperature, relevant to the understanding of neutron star properties.