

2.C. Some Mechanical Equations of State

Every system is characterized by an **equation of state** which relates its thermal variable, temperature T or entropy S , to its mechanical or chemical ones.

2.C.1. Ideal Gas Law

For an ideal gas, the equation of state is also known as the **ideal gas law**

$$PV = nRT = Nk_B T \quad (2.9)$$

where

$$P = \text{Pressure} \quad [P] = \text{Pascal} = \text{Pa}$$

$$V = \text{Volume} \quad [V] = \text{m}^3$$

$$T = \text{Temperature} \quad [T] = \text{Kelvin} = \text{K}$$

$$n = \text{Number of moles}$$

$$R = \text{Universal gas constant} \approx 8.314 \text{ J} / \text{mol} \cdot \text{K}.$$

$$N = \text{Number of molecules}$$

$$k_B = \text{Boltzmann constant} \approx 1.3806 \times 10^{-23} \text{ J/K}$$

and

$$[X] = \text{units of } X$$

For an ideal gas composed of m different types of molecules (or neutral particles), (2.9) is generalized to

$$PV = \sum_{j=1}^m n_j RT = \sum_{j=1}^m N_j k_B T \quad (2.10)$$

where

$$n_j = \text{Number of moles of the type } j \text{ molecules}$$

$$N_j = \text{Number of type } j \text{ molecules}$$

2.C.2. Virial Expansion

The ideal gas law was found to agree well with experimental observations for all gases at sufficiently low densities and high temperatures.

For moderate concentrations and temperatures, one can improve the accuracy of the ideal gas law using the **virial expansion**

$$P = \frac{nRT}{V} \left[1 + \frac{n}{V} B_2(T) + \left(\frac{n}{V} \right)^2 B_3(T) + \dots \right] \quad (2.11)$$

$$= \frac{nRT}{V} \sum_{j=1}^{\infty} \left(\frac{n}{V} \right)^{j-1} B_j(T) \quad [B_1(T) = 1] \quad (2.11a)$$

where $B_j(T)$ is the j^{th} **virial coefficient**. The ideal gas law thus corresponds to

$$B_j(T) = 0 \quad \forall j \geq 2$$

Since $B_j(T)$ can be calculated for a given inter-molecular interaction potential in statistical mechanics, comparison between the measured and calculated values of $B_j(T)$ is an important means to determine the parameters of such potentials.

As shown in Fig.2.1 in Reichl's text, $B_2(T)$ is usually negative for low T , rises to a maximum as T increases, and then levels off at some positive values at high T .

Note: Although the data in Fig.2.1 are measurements for the quantum gases He & Ar, their behavior is typical of most gases.

2.C.3. Van der Waals Equation of State

In contrast to the brute-force approach of the virial expansion, the van der Waals equation is obtained with specific improvements of the ideal gas model in mind.

In particular, the ideal gas model assumes all molecules in the gas to be non-interacting point particles. Since real molecules have finite sizes, the volume in which they move is reduced from the container volume V by an amount nb , where b is the **effective molar volume**. The ideal gas law should thus be modified to

$$P = \frac{nRT}{V - nb}$$

Since the long range part of the interactions between (neutral) molecules is attractive, it reduces the pressure of the gas. As inter-molecular interactions must be proportional to the square of the molar density $\frac{n}{V}$, we arrive at the **van der Waals equation**

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \quad (2.12a)$$

or

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad (2.12)$$

where a & b are often called **van der Waal constants**.

(2.12a) can be written as

$$\begin{aligned} P &= \frac{nRT}{V} \left[\left(1 - \frac{nb}{V}\right)^{-1} - \frac{an}{RTV} \right] \\ &= \frac{nRT}{V} \left[\sum_{j=1}^{\infty} \left(\frac{nb}{V}\right)^{j-1} - \frac{an}{RTV} \right] \\ &= \frac{nRT}{V} \left[1 + \left(b - \frac{a}{RT}\right) \left(\frac{n}{V}\right) + \sum_{j=3}^{\infty} \left(\frac{nb}{V}\right)^{j-1} \right] \end{aligned}$$

Comparing with (2.11a) then gives

$$B_2^{\text{vdW}}(T) = b - \frac{a}{RT} \quad (2.13)$$

which agrees with Fig.2.1 except for the lack of a maximum.

Thus, the van der Waals gas is a simple but moderately accurate model for dilute gases composed of interacting particles. More interestingly, if we use it to describe a fluid of arbitrary density, it exhibits a 1st order phase transition between the gas and liquid phases [see §3.D.4].

Measured values of the van der Waals constants a & b for various gases can be found in Table 2.1 in Reichl's text.

2.C.4. Solids

For solids at low temperatures, its molar volume $v = \frac{V}{n}$ is given by the equation of state

$$v = v_0(1 + \alpha_P T - \kappa_T P) \quad (2.14)$$

where

$$\begin{aligned} v_0 &= v \Big|_{T=0, P=0} \\ \alpha_P &= \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_{P,n} = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = \text{coefficient of thermal expansion.} \\ &\approx 10^{-4} / K \\ \kappa_T &= -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_{T,n} = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T = \text{isothermal compressibility.} \\ &\approx 10^{-10} / \text{Pa} \approx 10^{-5} / \text{atm} \end{aligned}$$

2.C.5. Elastic Wire or Rod

According to the Hook's law,

$$J = A(T)(L - L_0) \quad (2.15)$$

where

$$\begin{aligned} L &= \text{length of wire.} & L_0 &= L \Big|_{J=0} \\ J &= \text{tension of the wire.} & [J] &= N/m \\ A(T) &\approx A_0 + A_1 T = \text{elastic coefficient.} \end{aligned}$$

A_1 is usually negative but can be positive for nonlinear materials such as rubber.

2.C.6. Surface Tension

The work per unit area needed to extend the free surface area of a liquid is called the **surface tension**, σ , of the liquid. The equation of state takes the form

$$\sigma = \sigma_0 \left(1 - \frac{t}{t'} \right)^n \quad (2.16)$$

where

$$\begin{aligned} t &= \text{temperature in degree Celsius.} \\ t' &\& n \text{ are parameters determined by experiment, with } 1 \lesssim n \lesssim 2. \\ \sigma_0 &= \sigma \Big|_{t=0^\circ\text{C}} \end{aligned}$$

2.C.7. Electric Polarization

For dielectric materials,

$$\mathbf{D} = \mathbf{E} + 4 \pi \mathbf{P} \quad [\text{Gaussian units used.}] \quad (2.17)$$

where

D = displacement.

E = (total) electric field.

P = polarization = induced dipole moment per unit volume.

A typical equation of state for linear homogeneous dielectric materials at moderate temperatures is

$$P = \chi E = \left(a + \frac{b}{T} \right) E \quad (2.18)$$

where χ is the **susceptibility** and a & b are experimental constants.

2.C.8. Curie's Law

For paramagnetic materials,

$$B = H + 4 \pi M \quad [\text{Gaussian units used.}] \quad (2.19)$$

where

B = magnetic induction.

H = magnetic field.

M = magnetization = induced magnetic dipole moment per unit volume.

The equation of state is **Curie's law**

$$M = \chi_M H = \frac{nD}{T} H \quad (2.20)$$

where χ_M is the **magnetic susceptibility** and D is an experimental constant.