8 Pressure

Historically there has been comparatively little work on how phase transitions in materials depend on pressure, as opposed to temperature. For experimental work on materials, it is difficult to achieve pressures of thermodynamic importance, whereas high temperatures are obtained easily. The situation is reversed for computational work. The thermodynamic variable complementary to pressure is volume, whereas temperature is complemented by entropy. It is comparatively easier to calculate the free energy of materials with different volumes, as opposed to calculating all different sources of entropy.

Recently there have been rapid advances in high pressure experimental techniques, often driven by interest in the geophysics of the Earth. Nevertheless, new materials are formed under extreme conditions of pressure and temperature, and some such as diamond can be recovered at ambient pressures. The use of pressure to tune the electronic structure of materials can be a useful research tool for furthering our understanding of materials properties. Sometimes the changes in interatomic distances caused by pressure can be induced by chemical modifications of materials, so experiments at high pressures can point directions for materials discovery.

This Chapter 8 begins with basic considerations of the thermodynamics of materials under pressure, and how phase diagrams are altered by temperature and pressure together. Volume changes can also be induced by temperature, and the concept of "thermal pressure" from non-harmonic phonons is explained. The electronic energy accounts for most of the PV contribution to the free energy, and there is a brief description of how electron energies are altered by pressure. The chapter ends with a discussion about using pressure to investigate kinetic processes, and the meaning of an activation volume.

8.1 Materials under Pressure at Low Temperatures

The behavior of solids under pressure, at least high pressures that induce substantial changes in volume, is more complicated than the behavior of gases. Nevertheless, it is useful to compare gases to solids to see how the thermodynamic extensive variable, V, depends on the thermodynamic intensive variables T and P.

8.1.1 Gases (for comparison)

Recall the equation of state for an ideal gas comprised of non-interacting atoms

$$PV = Nk_{\mathrm{B}}T \,. \tag{8.1}$$

Non-ideal gases are often treated with two Van der Waals corrections:

- The volume for the gas is a bit less than the physical volume it occupies because the molecules themselves take up space. The quantity V in Eq. 8.1 is replaced by $V - Nb$, where b is an atomic parameter with units of volume.
- An attractive interaction between the gas molecules tends to increase the pressure a bit. This can be considered as a surface tension that pulls inwards on a group of gas molecules. The quantity P in Eq. 8.1 is replaced by $P + a(N/V)^2$. The quadratic dependence of $1/V^2$ is expected because the number of atoms affected goes as $1/V$, and the force between them may also go as $1/V$. (Also, if the correction went simply as $1/V$, it would prove uninteresting in Eq. 8.1.)

The Van der Waals equation of state (EOS) is

$$\left[P + a\frac{N^2}{V^2}\right]\left[V - Nb\right] = Nk_{\mathrm{B}}T \,. \tag{8.2}$$

Equation 8.2 works surprisingly well for the gas phase when the parameters a and b are small and the gas is “gas-like.” Equation 8.2 can be converted to this dimensionless form

$$\mathcal{P} = \frac{\mathcal{T}}{\mathcal{V} - 1} - \frac{1}{\mathcal{V}^2} \,, \tag{8.3}$$

with the definitions

$$\mathcal{P} \equiv P\frac{b^2}{a} \,, \tag{8.4}$$

$$\mathcal{V} \equiv \frac{V}{Nb} \,, \tag{8.5}$$

$$\mathcal{T} \equiv k_{\mathrm{B}}T\frac{b}{a} \,. \tag{8.6}$$

Figure 8.1 shows the Van der Waals EOS of Eq. 8.2 for a fixed a and b, but with varying temperature. At high temperatures the behavior approaches that of an ideal gas, with $P \propto T/V$ (Eq. 8.1). More interesting behavior occurs at low temperatures. It can be shown that below the critical pressure and critical temperature

$$P_{\mathrm{crit}} = \frac{1}{27}\frac{a}{b^2} \,, \tag{8.7}$$

$$k_{\mathrm{B}}T_{\mathrm{crit}} = \frac{8}{27}\frac{a}{b} \,, \tag{8.8}$$

a two-phase coexistence between a high-density and a low-density phase appears. This is point “C” in Fig. 8.1a, for which the volume is

$$V_{\mathrm{crit}} = 3\,b\,N \,. \tag{8.9}$$

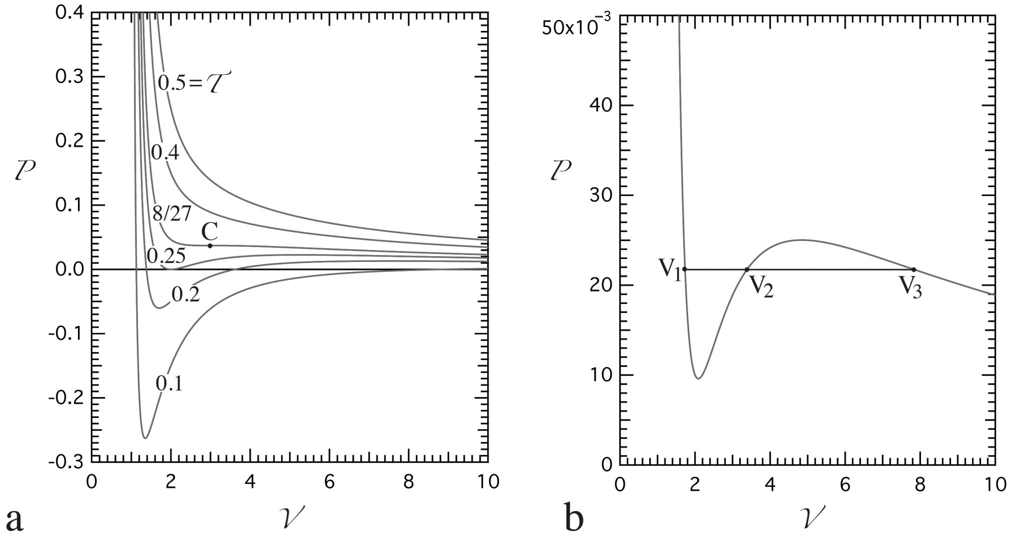

Fig. 8.1 (**a**) Isothermals of the Van der Waal's equation of state Eq. 8.2, plotted with rescaled variables of Eqs. 8.4 - 8.6. (**b**) Maxwell construction for $T = 0.26a/(bk_\mathrm{B})$.

At lower temperatures, such as $k_\mathrm{B}T = 0.26a/b$ shown in Fig. 8.1b, the same pressure corresponds to three different volumes V_1, V_2, and V_3. We can ignore V_2 because it is unphysical – at V_2 an increase in pressure causes an expansion (and likewise, the material shrinks if pressure is reduced). Nevertheless, the volumes V_1 and V_3 can be interpreted as the specific volumes of a liquid and as a gas, respectively. We find the pressure that defines V_1 and V_3 from the condition that the chemical potentials of the gas and liquid are equal in equilibrium, i.e., $\mu_3 = \mu_1$. Along a $P(V)$ curve, the change in chemical potential is $1/N \int P\,\mathrm{d}V$. Starting at a chemical potential of μ_1 at the point V_1 in Fig. 8.1b

$$\mu_3 = \mu_1 + \frac{1}{N}\int_{V_1}^{V_3} P(V)\,\mathrm{d}V\,. \tag{8.10}$$

The integral must be zero if $\mu_3 = \mu_1$. The areas above and below the horizontal line in Fig. 8.1b must therefore be equal, and this "Maxwell construction" defines the pressure of the horizontal line.

A dimensionless ratio can be formed from Eqs. 8.7, 8.8, 8.9

$$\frac{P_\mathrm{crit}\,V_\mathrm{crit}}{Nk_\mathrm{B}\,T_\mathrm{crit}} = \frac{3}{8}\,. \tag{8.11}$$

Rescaled appropriately, the Van der Waals equations of state for all gases are the same. This is approximately true in practice, although the dimensionless ratio is lower than 3/8, often around 0.25 to 0.3, and varies for different gases. Some characteristics of a generic gas are presented in Table 8.1, for comparison with the characteristics of a solid.

Table 8.1 Pressures and Temperatures of Gases and Solids

	Gas	Solid
Pressure	$P > 0$	$P > -P_{\text{coh}}$
Temperature	$T > 0$	$T \geq 0$
Stresses	isotropic	anisotropic
Typical Pressure	1 Atm = 0.1 MPa	10 GPa = 10^5 Atm

This instability of the Van der Waals EOS below a critical temperature can be used to model a pressure-induced liquifaction, for example, or the liquid-gas phase boundary at constant pressure. The approach has problems with quantitative details, but it gives the essential behavior, and is worthy of more study than given here.

8.1.2 Solids (for comparison)

The ideal gas behavior shown at the top of Fig. 8.1a, i.e., $P \propto T/V$ for large T, V, is never appropriate for a solid. At $P = 0$, for example, the solid has a finite volume. Table 8.1 shows that on the scale of familiar pressures in gases, a solid is essentially incompressible. More familiar are small compressions of solids and elastic behavior, where typical materials deform as springs. The bulk modulus of a solid, B,

$$B \equiv -V \frac{\mathrm{d}P}{\mathrm{d}V} , \tag{8.12}$$

is typically a few times 100 GPa, and the elastic energy per unit volume under uniform dilation is

$$E_{\text{el}} = \frac{1}{2} B \, \delta^2 , \tag{8.13}$$

where δ is the fractional change in volume.

Equation 8.12 can be handy as a definition of B if the elastic energy is needed, and not individual strains or stresses of Section 6.4. The elastic constants originate from second derivatives of the interatomic potentials, which give tensorial "springs" between atoms as explained in Sect. 6.3. These springs are loaded in different directions when different stresses are applied to a material, but all strains are linear with stresses, and the macroscopic response of the material is still that of a spring. It is possible to relate the interatomic force constants to the macroscopic elastic