1.2 Thermodynamic functions

The Helmholtz free energy, F, is a function of the temperature T and of the density $n = N/V$, or of the volume: $F = F(V, T)$. One can also introduce other so-called thermodynamic potentials, expressed as functions of different variables. These are:

At fixed pressure and temperature – the Gibbs free energy

$$\Phi(P, T) = E - TS + PV = F + PV \ . \tag{1.10}$$

If instead of the temperature T we chose as free variable its conjugate, the entropy, then we obtain the enthalpy

$$W(P, S) = E + PV \ . \tag{1.11}$$

Enthalpy is often used in discussions of chemical reactions, thermodynamics of formation of different phases, etc.

The energy itself is also one of the thermodynamic potentials; it is a function of volume and entropy, $E(V, S)$.

Similar to mechanics, where the system at equilibrium tends to a state with mimimum energy, many-particle systems at finite temperature tend to minimize the free energy, i.e. the corresponding thermodynamic potential F or Φ.

From these definitions it is clear that, e.g.

$$dF = -S\,dT - P\,dV \ , \tag{1.12}$$

from which we obtain

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \ , \tag{1.13}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \ . \tag{1.14}$$

Similarly

$$d\Phi = -S\,dT + V\,dP \ , \tag{1.15}$$

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_P \ , \tag{1.16}$$

$$V = \left(\frac{\partial \Phi}{\partial P}\right)_T \ . \tag{1.17}$$

Other useful thermodynamic quantities are, e.g. the specific heat at constant volume, c_V, and at constant pressure, c_P:

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \ , \tag{1.18}$$

$$c_P = \left(\frac{\partial W}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \ . \tag{1.19}$$

One can express c_P, c_V through F, Φ, using (1.12), (1.15).

Using the expressions given above, one can obtain useful relations between different thermodynamic quantities, e.g. between the specific heat, the thermal expansion coefficient (the volume coefficient of the thermal expansion $\beta = 3\alpha$, where α is the linear thermal expansion)

$$\beta = +\frac{1}{V}\frac{\partial V}{\partial T} , \tag{1.20}$$

and the compressibility

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial P} . \tag{1.21}$$

The resulting connection has the form (see, e.g. Landau and Lifshits 1980, Section 16):

$$c_P - c_V = -T\,\frac{(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T} = VT\,\frac{\beta^2}{\kappa} . \tag{1.22}$$