1.5 Response Functions

A great deal can be learned about a macroscopic system through its response to various changes in externally controlled parameters. Important response functions for a PVT system are the specific heats at constant volume and pressure,

$$C_V = \left(\frac{đQ}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{1.51}$$

$$C_P = \left(\frac{đQ}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \tag{1.52}$$

the isothermal and adiabatic compressibilities,

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{1.53}$$

$$K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \tag{1.54}$$

and the coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} . \tag{1.55}$$

Intuitively, we expect the specific heats and compressibilities to be positive and $C_P > C_V, K_T > K_S$. In this section we derive relations between these response functions. The intuition that the response functions are positive will be justified in the following section in which we discuss thermodynamic stability. We begin with the assumption that the entropy has been expressed in terms of T and V and that the number of particles is kept fixed. Then

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \tag{1.56}$$

and

$$T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \tag{1.57}$$

or

$$C_P - C_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P . \tag{1.58}$$

We now use the Maxwell relation (1.48) and the chain rule

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial x}{\partial y}\right)_z = -1 \tag{1.59}$$

which is valid for any three variables obeying an equation of state of the form $f(x,y,z)=0$ to obtain

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \tag{1.60}$$

and

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 = \frac{TV}{K_T}\alpha^2 . \tag{1.61}$$

In a similar way we obtain a relation between the compressibilities K_T and K_S. Assume that the volume V has been obtained as function of S and P. Then

$$dV = \left(\frac{\partial V}{\partial P}\right)_S dP + \left(\frac{\partial V}{\partial S}\right)_P dS \tag{1.62}$$

and

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S - \frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T \tag{1.63}$$

or

$$K_T - K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T . \tag{1.64}$$

The Maxwell relations (1.50) and the equation

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial S}{\partial T}\right)_P^{-1} \tag{1.65}$$

yield

$$K_T - K_S = \frac{TV}{C_P}\alpha^2 . \tag{1.66}$$

Thus (1.61) and (1.66) together produce the interesting and useful exact results

$$C_P(K_T - K_S) = K_T(C_P - C_V) = TV\alpha^2 \tag{1.67}$$

and

$$\frac{C_P}{C_V} = \frac{K_T}{K_S} . \tag{1.68}$$

An analogous derivation, in the case of magnetic systems (see Problem 1.4) produces the equations

$$C_H(\chi_T - \chi_S) = \chi_T(C_H - C_M) = T\left(\frac{\partial M}{\partial T}\right)_H^2 \tag{1.69}$$

where χ_T and χ_S are the isothermal and adiabatic susceptibilities, $\chi_T = (\partial M/\partial H)_T$, $\chi_S = (\partial M/\partial H)_S$, and C_H and C_M are the specific heats at constant applied field and constant magnetization, respectively.