Appendix A: Heat capacity at constant pressure and volume

Ref: Reif, Fundamentals of Statistical and Thermal Physics, p. 168

A general relation between C_P and C_V can be obtained this way. Taking (T, P) as independent variables (N or μ, if it is a valid thermodynamic variable, is implied, fixed, and of no concern here) we can write:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \tag{1}$$

Multiplying T and noting that $C = \frac{dQ}{dT} = T\frac{\partial S}{\partial T}$ this equation can be re-written as:

$$TdS = C_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \tag{2}$$

Changing independent variables from (T, P) to (T, V), we note:

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \tag{3}$$

In order to relate C_P and C_V, insert (3) to (2), consider the case $dV = 0$, and divide by dT:

$$C_V = C_P + T\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \tag{4}$$

From $dH = -SdT + VdP$, (H: enthalpy) we obtain a Maxwell's relation: $\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$. Thus,

$$C_V = C_P - T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V = C_P - TV\alpha\left(\frac{\partial P}{\partial T}\right)_V \tag{5}$$

$$C_P = C_V + TV\alpha\left(\frac{\partial P}{\partial T}\right)_V \tag{6}$$

where the volume thermal expansion coefficient $\alpha \equiv \left(\frac{\partial V}{\partial T}\right)_P / V$. [Note that the *volume* thermal expansion coefficient is 3 times the *linear* thermal expansion coefficient.]

Using Euler's chain rule $\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P / \left(\frac{\partial V}{\partial P}\right)_T$, and the bulk modulus $B \equiv -V\left(\frac{\partial P}{\partial V}\right)_T$, we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha B \tag{7}$$

$$C_P = C_V + TV\left(\frac{\partial P}{\partial T}\right)_V^2 / B \tag{8}$$

$$C_P = C_V + TV\alpha^2 B \tag{9}$$

Another expression in terms of compressibility (inverse of bulk modulus) is of general interest. In terms of isothermal compressibility κ_T and adiabatic compressibility κ_S, the following holds:

$$C_P/C_V = \kappa_T/\kappa_S \tag{10}$$

since $\kappa_S V \equiv -\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial S}{\partial P}\right)_V / \left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V / \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = \left(\frac{C_V}{C_P}\right)\left(-\frac{\partial V}{\partial P}\right)_T \equiv \frac{C_V}{C_P}\kappa_T V.$

Special, but very useful, case when $\epsilon_j \propto V^{-\gamma}$

$$Z = \sum \exp(-\beta E_i)$$

$E_i = \sum \epsilon_j$ and $E_D \equiv -\partial \ln Z / \partial\beta$ (D means "dynamic")

$\epsilon_j \propto V^{-\gamma}$ (γ: Grüneisen constant for phonons, $\frac{2}{3}$ for electrons in 3D, $\frac{1}{3}$ for photons in 3D)

$F = E_B(V) - k_B T \ln Z$ (E_B is the "background" energy – e.g. lattice potential energy)

$$P = -\frac{\partial E_B}{\partial V} + k_B T \frac{\partial \ln Z}{\partial V} = -\frac{\partial E_B}{\partial V} + \frac{k_B T}{Z} \sum \exp(-\beta E_i)\,(-\beta)\frac{\partial E_i}{\partial V} = -\frac{\partial E_B}{\partial V} + \gamma \frac{E_D}{V}$$

$$P = -\frac{\partial E_B}{\partial V} + \gamma \frac{E_D}{V}$$

$$\alpha B = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\gamma C_V}{V}$$

$$\frac{C_P}{C_V} = 1 + \delta, \quad \delta = \frac{T\gamma^2 C_V}{VB} = T\gamma\alpha$$

Generally, $\gamma \sim 1 - 2$ and $\alpha \lesssim 1 \times 10^{-4}\ /K$, and thus the correction term δ would be generally quite small compared to 1 (perhaps can reach O(0.1) close to the melting temperature?).

For the electronic term, $E_B = 0$.

$$E_D = E_G + E_T$$

$$E_G = \frac{3}{5} N \varepsilon_F \propto V^{-\gamma}$$

$$E_T = \frac{\pi^2}{6}(k_B T)^2 g(\varepsilon_F) \propto V^{\gamma}, \qquad g(\varepsilon_F) = \frac{3N}{2\varepsilon_F}, \qquad C_V = \frac{\pi^2}{2}\frac{k_B^2 T}{\varepsilon_F}$$

$$P = P_G + P_T$$

$$P_G = \gamma \frac{3}{5} N \varepsilon_F \frac{1}{V} \propto V^{-\gamma-1}$$

$$P_T = \gamma \frac{\pi^2}{6}(k_B T)^2 \frac{3N}{2\varepsilon_F}\frac{1}{V} \propto V^{\gamma-1}$$

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T = (1+\gamma)P_G + (1-\gamma)P_T \approx (1+\gamma)P_G$$

$$\delta = \frac{T\gamma^2 C_V}{VB} \approx \frac{T\gamma^2 C_V}{V(1+\gamma)P_G} = \frac{5\gamma\pi^2(k_B T)^2}{6\varepsilon_F^2(1+\gamma)} = \frac{1}{3}\pi^2\left(\frac{T}{T_F}\right)^2$$

For the lattice term, E_B = lattice binding energy.

$$P = -\frac{\partial E_B}{\partial V} + \gamma\frac{E_D}{V} = -\frac{\partial E_B}{\partial V} + \frac{\gamma}{V}(E_G + E_T) \equiv -\frac{\partial E_B}{\partial V} + P_G + P_T$$

$$E_G = \frac{9}{8}N_l\hbar\omega_D \propto V^{-\gamma}$$

$$P_G = \frac{\gamma}{V}\frac{9}{8}N_l\hbar\omega_D \propto V^{-\gamma-1}$$

At low T:

$$E_T \propto T^4\omega_D^{-3} \propto V^{3\gamma}$$

$$P_T \propto V^{3\gamma-1}$$

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T = V\frac{\partial^2 E_B}{\partial V^2} + (1+\gamma)P_G + (1-3\gamma)P_T \approx V\frac{\partial^2 E_B}{\partial V^2} + (1+\gamma)P_G$$

$$C \approx \frac{12\pi^4}{5}N\left(\frac{T}{\theta_D}\right)^3 k_B$$

$$\delta = \frac{T\gamma^2 C_V}{VB} \approx \frac{\gamma^2}{VB}\frac{12\pi^4}{5}N_l\left(\frac{T}{\theta_D}\right)^3 k_B T$$

Replacing the bulk modulus with the term coming from P_G, it can be seen that $\delta \lesssim \left(\frac{T}{\theta_D}\right)^4$. However, note that the dominant contribution for the bulk modulus would be from E_B, and so δ would be even smaller, multiplied by a small numerical factor $\frac{\theta_D}{E_{binding}}$ where $E_{binding}$ is the binding energy of an atom/ion.

At high T:

$$E_T \propto N_l k_B T \propto V^0$$

$$C_V \propto N_l k_B$$

$$P_T \sim N_l\frac{k_B T}{V} \propto V^{-1}$$

$B = -V\left(\frac{\partial P}{\partial V}\right)_T = V\frac{\partial^2 E_B}{\partial V^2} + (1+\gamma)P_G + P_T \approx V\frac{\partial^2 E_B}{\partial V^2} + P_T$ Below the melting temperature one expects that the first term to be more dominant than the second term. [Melting temperature is only a few percent of the cohesive energy.]

$\delta = \frac{T\gamma^2 C_V}{VB} \approx \frac{T\gamma^2}{VB}N_l k_B \approx \gamma^2\frac{P_T}{B}$ would be small below melting since $B \gg P_T$.