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 $B \gg P_T$.

So, in conclusion, we have calculated what the difference in C_V and C_P is in solids, and how it is small in general, especially at low temperatures. The calculation also shows that at high temperatures where the solid starts to break the difference can become larger and even substantial. This is easy to understand conceptually, if we go to the high temperature – the gas phase. In the gas phase C_P and C_V will be *very* different. The general formalism in the top portion of page 2 applies in this phase as well, and you should be able to derive the following well-known result for an ideal gas: $C_P - C_V = Nk_B$.