

Specific heat 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:

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

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

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

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

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

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

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

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,

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

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

where the thermal expansion coefficient $\beta \equiv \left(\frac{\partial V}{\partial T}\right)_P / V$.

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

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

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

$$C_P = C_V + TV\beta^2 B \quad (9)$$

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:

$$C_P/C_V = \kappa_T/\kappa_S \quad (10)$$

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

Specific heat at constant pressure and volume for a special useful case

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

$$E_i = \sum \epsilon_j$$

$\epsilon_j \propto V^{-\gamma}$ (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)

$$P = -\frac{\partial E_B}{\partial V} + k_B T \frac{\partial \ln Z}{\partial V} = \frac{k_B T}{Z} \sum \exp(-\beta E_i) (-\beta) \frac{\partial E_i}{\partial V} = -\frac{\partial E_B}{\partial V} + \gamma \frac{E_D}{V} \quad (D \text{ means “dynamic”})$$

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

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

$$\frac{C_P}{C_V} = 1 + \delta, \quad \delta = \frac{T \gamma^2 C_V}{V B} = T \gamma \beta$$

Generally, $\gamma \sim 1 - 2$ and $\beta \lesssim 1 \times 10^{-4} / K$, and thus the correction is on the order of a few percent at the most.

For the electronic term, $E_B = 0$.

$$E_D = E_G + E_T$$

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

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

$$P = P_G + P_T$$

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

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

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

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

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 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:

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

$$C_V \propto N_l k_B$$

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

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

$$\delta = \frac{T\gamma^2 C_V}{VB} \approx \frac{T\gamma^2}{VB} N_l k_B \sim 1$$