Response functions [tln7]

Second partial derivatives of thermodynamic potentials with respect to natural independent variables. Response functions describe how one thermodynamic function responds to a change of another thermodynamic function under controlled conditions. Response functions are important because of their experimental accessibility. Consider a system with $N = \text{const}$.

Thermal response functions (heat capacities): $C \equiv \dfrac{\delta Q}{\delta T}$

$$\delta Q = TdS = \begin{cases} T\left(\dfrac{\partial S}{\partial T}\right)_X dT + T\left(\dfrac{\partial S}{\partial X}\right)_T dX & \text{for } S(T,X) \\[2ex] T\left(\dfrac{\partial S}{\partial T}\right)_Y dT + T\left(\dfrac{\partial S}{\partial Y}\right)_T dY & \text{for } S(T,Y) \end{cases}$$

$$\Rightarrow\; C_X = T\left(\frac{\partial S}{\partial T}\right)_X = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_X, \quad C_Y = T\left(\frac{\partial S}{\partial T}\right)_Y = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_Y$$

where $X \equiv V, M$ and $Y \equiv -p, H$.

Equivalent expressions of C_X, C_Y are derived from $\delta Q = dU - YdX$:

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_X dT + \left[\left(\frac{\partial U}{\partial X}\right)_T - Y\right] dX \quad \text{for } U(T,X)$$

$$\Rightarrow\; C_X \equiv \left.\frac{\delta Q}{\delta T}\right|_X = \left(\frac{\partial U}{\partial T}\right)_X$$

$$\Rightarrow\; C_Y \equiv \left.\frac{\delta Q}{\delta T}\right|_Y = C_X + \left[\left(\frac{\partial U}{\partial X}\right)_T - Y\right]\left(\frac{\partial X}{\partial T}\right)_Y$$

Also, from $\delta Q = dE + XdY$ we infer $C_Y = \left(\dfrac{\partial E}{\partial T}\right)_Y$

Note that $U(T,X)$ and $E(T,Y)$ are not thermodynamic potentials.

Mechanical response functions

Isothermal compressibility: $\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_T$

Adiabatic compressibility: $\kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = -\frac{1}{V}\left(\frac{\partial^2 E}{\partial p^2}\right)_S$

Thermal expansivity: $\alpha_p \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

Relations with thermal response functions C_p, C_V:

$$\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S}, \quad C_p = \frac{TV\alpha_p^2}{\kappa_T - \kappa_S}, \quad C_V = \frac{TV\alpha_p^2\kappa_S}{\kappa_T(\kappa_T - \kappa_S)}$$

$$\Rightarrow \quad C_p - C_V = \frac{TV\alpha_p^2}{\kappa_T} > 0$$

Magnetic response functions

Isothermal susceptibility: $\chi_T \equiv \left(\frac{\partial M}{\partial H}\right)_T = -\left(\frac{\partial^2 G}{\partial H^2}\right)_T = \left(\frac{\partial^2 A}{\partial M^2}\right)_T^{-1}$

Adiabatic susceptibility: $\chi_S \equiv \left(\frac{\partial M}{\partial H}\right)_S = -\left(\frac{\partial^2 E}{\partial H^2}\right)_S$

"You name it": $\alpha_H \equiv -\left(\frac{\partial M}{\partial T}\right)_H$

Relations with thermal response functions C_H, C_M:

$$\frac{C_H}{C_M} = \frac{\chi_T}{\chi_S}, \quad C_H = \frac{T\alpha_H^2}{\chi_T - \chi_S}, \quad C_M = \frac{T\alpha_H^2\chi_S}{\chi_T(\chi_T - \chi_S)}$$

$$\Rightarrow \quad C_H - C_M = \frac{T\alpha_H^2}{\chi_T}$$