Stability of thermal equilibrium [tln20]

Consider a fluid system with $N = \text{const}$ in thermal equilibrium at temperature T_0 and pressure p_0. Any deviation from that state must cause an increase in Gibbs free energy:

$$G(T_0, p_0) = U(S, V) - T_0 S + p_0 V.$$

Effects of fluctuations in entropy and volume:

$$\begin{aligned}\delta G &= \left[\left(\frac{\partial U}{\partial S}\right)_V - T_0\right]\delta S + \left[\left(\frac{\partial U}{\partial V}\right)_S + p_0\right]\delta V \\ &+ \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial S^2}\right)(\delta S)^2 + 2\left(\frac{\partial^2 U}{\partial S \delta V}\right)\delta S \delta V + \left(\frac{\partial^2 U}{\partial V^2}\right)(\delta V)^2\right]\end{aligned}$$

Equilibrium condition: $\left(\frac{\partial U}{\partial S}\right)_V - T_0 = 0, \quad \left(\frac{\partial U}{\partial V}\right)_S + p_0 = 0$

Stability condition: $\left(\frac{\partial^2 U}{\partial S^2}\right)(\delta S)^2 + 2\left(\frac{\partial^2 U}{\partial S \delta V}\right)\delta S \delta V + \left(\frac{\partial^2 U}{\partial V^2}\right)(\delta V)^2 > 0.$

Condition for positive definite quadratic form:

$$\frac{\partial^2 U}{\partial S^2} > 0, \quad \frac{\partial^2 U}{\partial V^2} > 0, \quad \frac{\partial^2 U}{\partial S^2}\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \delta V}\right)^2 > 0.$$

Implications:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0 \;\Rightarrow\; C_V > 0.$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S = -\left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{V\kappa_S} > 0 \;\Rightarrow\; \kappa_S > 0.$$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V \left(\frac{\partial^2 U}{\partial V^2}\right)_S > \left(\frac{\partial^2 U}{\partial S \delta V}\right)^2 \;\Rightarrow\; \frac{T}{V\kappa_S C_V} > \left(\frac{\partial T}{\partial V}\right)_S^2$$