

2.9: Equilibrium and Stability

Equilibrium

Suppose we have two systems, A and B, which are free to exchange energy, volume, and particle number, subject to overall conservation rules

$$E_A + E_B = E \quad , \quad V_A + V_B = V \quad , \quad N_A + N_B = N \quad , \quad (2.9.1)$$

where E , V , and N are fixed. Now let us compute the change in the total entropy of the combined systems when they are allowed to exchange energy, volume, or particle number. We assume that the entropy is additive,

$$dS = \left[\left(\frac{\partial S_A}{\partial E_A} \right)_{V_A, N_A} - \left(\frac{\partial S_B}{\partial E_B} \right)_{V_B, N_B} \right] dE_A + \left[\left(\frac{\partial S_A}{\partial V_A} \right)_{E_A, N_A} - \left(\frac{\partial S_B}{\partial V_B} \right)_{E_B, N_B} \right] dV_A + \left[\left(\frac{\partial S_A}{\partial N_A} \right)_{E_A, V_A} - \left(\frac{\partial S_B}{\partial N_B} \right)_{E_B, V_B} \right] dN_A .$$

Note that we have used $dE_B = -dE_A$, $dV_B = -dV_A$, and $dN_B = -dN_A$. Now we know from the Second Law that spontaneous processes result in $T dS > 0$, which means that S tends to a maximum. If S is a maximum, it must be that the coefficients of dE_A , dV_A , and dN_A all vanish, else we could increase the total entropy of the system by a judicious choice of these three differentials. From $T dS = dE + p dV - \mu, dN$, we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V, N} \quad , \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{E, N} \quad , \quad \frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{E, V} . \quad (2.9.2)$$

Thus, we conclude that in order for the system to be in equilibrium, so that S is maximized and can increase no further under spontaneous processes, we must have

$$\begin{aligned} T_A &= T_B & (\text{thermal equilibrium}) \\ \frac{p_A}{T_A} &= \frac{p_B}{T_B} & (\text{mechanical equilibrium}) \\ \frac{\mu_A}{T_A} &= \frac{\mu_B}{T_B} & (\text{chemical equilibrium}) \end{aligned}$$

Stability

Next, consider a uniform system with energy $E' = 2E$, volume $V' = 2V$, and particle number $N' = 2N$. We wish to check that this system is not unstable with respect to spontaneously becoming inhomogeneous. To that end, we imagine dividing the system in half. Each half would have energy E , volume V , and particle number N . But suppose we divided up these quantities differently, so that the left half had slightly different energy, volume, and particle number than the right, as depicted in Figure 2.9.1. Does the entropy increase or decrease? We have

$$\begin{aligned} \Delta S &= S(E + \Delta E, V + \Delta V, N + \Delta N) + S(E - \Delta E, V - \Delta V, N - \Delta N) - S(2E, 2V, 2N) \\ &= \frac{\partial^2 S}{\partial E^2} (\Delta E)^2 + \frac{\partial^2 S}{\partial V^2} (\Delta V)^2 + \frac{\partial^2 S}{\partial N^2} (\Delta N)^2 \\ &\quad + 2 \frac{\partial^2 S}{\partial E \partial V} \Delta E \Delta V + 2 \frac{\partial^2 S}{\partial E \partial N} \Delta E \Delta N + 2 \frac{\partial^2 S}{\partial V \partial N} \Delta V \Delta N . \end{aligned}$$

Thus, we can write

$$\Delta S = \sum_{i,j} Q_{ij} \Psi_i \Psi_j , \quad (2.9.3)$$

where

$$Q = \begin{pmatrix} \frac{\partial^2 S}{\partial E^2} & \frac{\partial^2 S}{\partial E \partial V} & \frac{\partial^2 S}{\partial E \partial N} \\ \frac{\partial^2 S}{\partial E \partial V} & \frac{\partial^2 S}{\partial V^2} & \frac{\partial^2 S}{\partial V \partial N} \\ \frac{\partial^2 S}{\partial E \partial N} & \frac{\partial^2 S}{\partial V \partial N} & \frac{\partial^2 S}{\partial N^2} \end{pmatrix} \quad (2.9.4)$$

is the matrix of second derivatives, known in mathematical parlance as the *Hessian*, and $\Psi = (\Delta E, \Delta V, \Delta N)$. Note that Q is a symmetric matrix.

$E + \Delta E$	$E - \Delta E$
$V + \Delta V$	$V - \Delta V$
$N + \Delta N$	$N - \Delta N$

Figure 2.9.1 : To check for an instability, we compare the energy of a system to its total energy when we reappportion its energy, volume, and particle number slightly unequally.

Since S must be a maximum in order for the system to be in equilibrium, we are tempted to conclude that the homogeneous system is stable if and only if all three eigenvalues of Q are negative. If one or more of the eigenvalues is positive, then it is possible to choose a set of variations Ψ such that $\Delta S > 0$, which would contradict the assumption that the homogeneous state is one of maximum entropy. A matrix with this restriction is said to be *negative definite*. While it is true that Q can have no positive eigenvalues, it is clear from homogeneity of $S(E, V, N)$ that one of the three eigenvalues must be zero, corresponding to the eigenvector $\Psi = (E, V, N)$. Homogeneity means $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$. Now let us take $\lambda = 1 + \eta$, where η is infinitesimal. Then $\Delta E = \eta E$, $\Delta V = \eta V$, and $\Delta N = \eta N$, and homogeneity says $S(E \pm \Delta E, V \pm \Delta V, N \pm \Delta N) = (1 \pm \eta) S(E, V, N)$ and $\Delta S = (1 + \eta)S + (1 - \eta)S - 2S = 0$. We then have a slightly weaker characterization of Q as *negative semidefinite*.

However, if we fix one of the components of $(\Delta E, \Delta V, \Delta N)$ to be zero, then Ψ must have some component orthogonal to the zero eigenvector, in which case $\Delta S < 0$. Suppose we set $\Delta N = 0$ and we just examine the stability with respect to inhomogeneities in energy and volume. We then restrict our attention to the upper left 2×2 submatrix of Q . A general symmetric 2×2 matrix may be written

$$Q = \begin{pmatrix} a & b \\ b & c \end{pmatrix} \quad (2.9.5)$$

It is easy to solve for the eigenvalues of Q . One finds

$$\lambda_{\pm} = \left(\frac{a+c}{2} \right) \pm \sqrt{\left(\frac{a-c}{2} \right)^2 + b^2}. \quad (2.9.6)$$

In order for Q to be negative definite, we require $\lambda_+ < 0$ and $\lambda_- < 0$. Thus, $\text{Tr } Q = a + c = \lambda_+ + \lambda_- < 0$ and $\det Q = ac - b^2 = \lambda_+ \lambda_- > 0$. Taken together, these conditions require

$$a < 0, \quad c < 0, \quad ac > b^2. \quad (2.9.7)$$

Going back to thermodynamic variables, this requires

$$\frac{\partial^2 S}{\partial E^2} < 0, \quad \frac{\partial^2 S}{\partial V^2} < 0, \quad \frac{\partial^2 S}{\partial E^2} \cdot \frac{\partial^2 S}{\partial V^2} > \left(\frac{\partial^2 S}{\partial E \partial V} \right)^2. \quad (2.9.8)$$

Thus the entropy is a concave function of E and V at fixed N . Had we set $\Delta E = 0$ and considered the lower right 2×2 submatrix of Q , we'd have concluded that $S(V, N)$ is concave at fixed E . Since $\left(\frac{\partial S}{\partial E} \right)_V = T^{-1}$, we have $\frac{\partial^2 S}{\partial E^2} = -\frac{1}{T^2} \left(\frac{\partial T}{\partial E} \right)_V = -\frac{C_V}{T^2} < 0$ and we conclude $C_V > 0$ for stability.

Many thermodynamic systems are held at fixed (T, p, N) , which suggests we examine the stability criteria for $G(T, p, N)$. Suppose our system is in equilibrium with a reservoir at temperature T_0 and pressure p_0 . Then, suppressing N (which is assumed constant), we have

$$G(T_0, p_0) = E - T_0 S + p_0 V. \quad (2.9.9)$$

Now suppose there is a fluctuation in the entropy and the volume of our system, which is held at fixed particle number. Going to second order in ΔS and ΔV , we have

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

Equilibrium requires that the coefficients of ΔS and ΔV both vanish, that $T = \left(\frac{\partial E}{\partial S} \right)_{V,N} = T_0$ and $p = -\left(\frac{\partial E}{\partial V} \right)_{S,N} = p_0$. The condition for stability is that $\Delta G > 0$ for all $(\Delta S, \Delta V)$. Stability therefore requires that the Hessian matrix Q be positive definite, with

$$Q = \begin{pmatrix} \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S \partial V} \\ \frac{\partial^2 E}{\partial S \partial V} & \frac{\partial^2 E}{\partial V^2} \end{pmatrix}. \quad (2.9.10)$$

Thus, we have the following three conditions:

$$\begin{aligned} \frac{\partial^2 E}{\partial S^2} &= \left(\frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V} > 0 \\ \frac{\partial^2 E}{\partial V^2} &= -\left(\frac{\partial p}{\partial V} \right)_S = \frac{1}{V \kappa_S} > 0 \\ \frac{\partial^2 E}{\partial S^2} \cdot \frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S \partial V} \right)^2 &= \frac{T}{V \kappa_S C_V} - \left(\frac{\partial T}{\partial V} \right)_S^2 > 0. \end{aligned}$$

As we shall discuss below, the quantity $\alpha_S \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{S,N}$ is the adiabatic thermal expansivity coefficient. We therefore conclude that stability of any thermodynamic system requires

$$\frac{C_V}{T} > 0, \quad \kappa_S > 0, \quad \alpha_S > \sqrt{\frac{\kappa_S C_V}{VT}}. \quad (2.9.11)$$

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