

The Maxwell relations

A number of second derivatives of the fundamental relation have clear physical significance and can be measured experimentally. For example:

Isothermal compressibility $\kappa_T = -\frac{1}{V} \frac{\partial^2 G}{\partial P^2} = -\frac{1}{V} \frac{\partial V}{\partial P}$

The property of the energy (or entropy) as being a differential function of its variables gives rise to a number of relations between the second derivatives, e. g. :

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

The Maxwell relations

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

is equivalent to:

$$-\left(\frac{\partial P}{\partial S}\right)_{V, N_1, N_2, \dots} = \left(\frac{\partial T}{\partial V}\right)_{S, N_1, N_2, \dots}$$

Since this relation is not intuitively obvious, it may be regarded as a success of thermodynamics.

The Maxwell relations

Given the fact that we can write down the fundamental relation employing various thermodynamic potentials such as F , H , G , ... the number of second derivative is large. However, the Maxwell relations reduce the number of independent second derivatives.

Our goal is to learn how to obtain the relations among the second derivatives without memorizing a lot of information.

For a simple one-component system described by the fundamental relation $U(S, V, N)$, there are nine second derivatives, only six of them are independent from each other.

In general, if a thermodynamic system has n independent coordinates, there are $n(n+1)/2$ independent second derivatives.

$$\left(\begin{array}{ccc} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial S \partial N} \\ \frac{\partial^2 U}{\partial V \partial S} & \frac{\partial^2 U}{\partial V^2} & \frac{\partial^2 U}{\partial V \partial N} \\ \frac{\partial^2 U}{\partial N \partial S} & \frac{\partial^2 U}{\partial N \partial V} & \frac{\partial^2 U}{\partial N^2} \end{array} \right)$$

The Maxwell relations: a single-component system

For a single-component system with conserved mole number, N , there are only three independent second derivatives:

$$\frac{\partial^2 G}{\partial T \partial P} \quad \frac{\partial^2 G}{\partial T^2} \quad \frac{\partial^2 G}{\partial P^2}$$

Other second derivatives, such as e. g.: $\frac{\partial^2 U}{\partial S \partial V}$

$$\begin{pmatrix} \frac{\partial^2 G}{\partial T^2} & \frac{\partial^2 G}{\partial T \partial P} & \frac{\partial^2 G}{\partial T \partial N} \\ \frac{\partial^2 G}{\partial P \partial T} & \frac{\partial^2 G}{\partial P^2} & \frac{\partial^2 G}{\partial P \partial N} \\ \frac{\partial^2 G}{\partial N \partial T} & \frac{\partial^2 G}{\partial N \partial P} & \frac{\partial^2 G}{\partial N^2} \end{pmatrix}$$

can all be expressed via the above three, which are trivially related to three measurable physical parameters ($dg = -sdT + vdP + \mu dN$):

The Maxwell relations: a single-component system

Coefficient of thermal expansion

$$\alpha = \frac{1}{v} \frac{\partial^2 g}{\partial T \partial P} = \frac{1}{v} \frac{\partial v}{\partial T}$$

Molar heat capacity at constant pressure

$$c_p = -T \frac{\partial^2 g}{\partial T^2} = T \frac{\partial s}{\partial T} = \frac{\delta Q}{dT}$$

Isothermal compressibility

$$\kappa_T = -\frac{1}{v} \frac{\partial^2 g}{\partial P^2} = -\frac{1}{v} \frac{\partial v}{\partial P}$$

A general procedure for reducing any derivative to a combination of α , κ_T , and c_p is given on pages 187-189 of *Callen*. It is tedious but straightforward, you should read it and know it exists. You will also have a chance to practice it in a couple of homework exercises.

Stability of thermodynamic systems

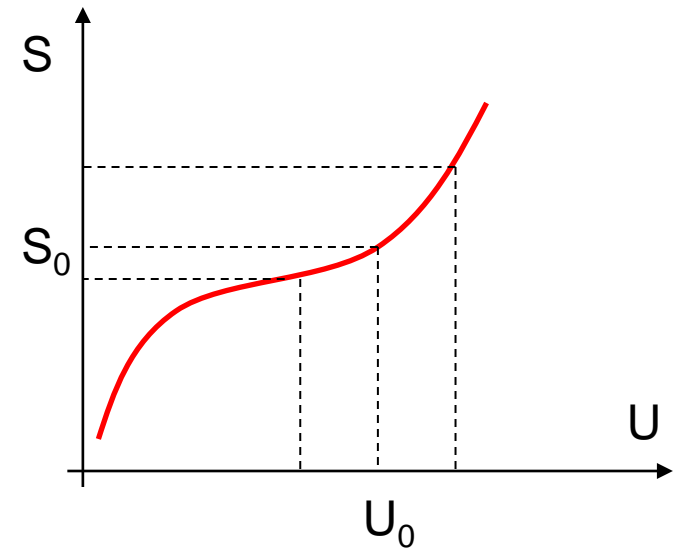
The entropy maximum principle states that in equilibrium:

$$dS = 0$$

$$d^2S < 0$$

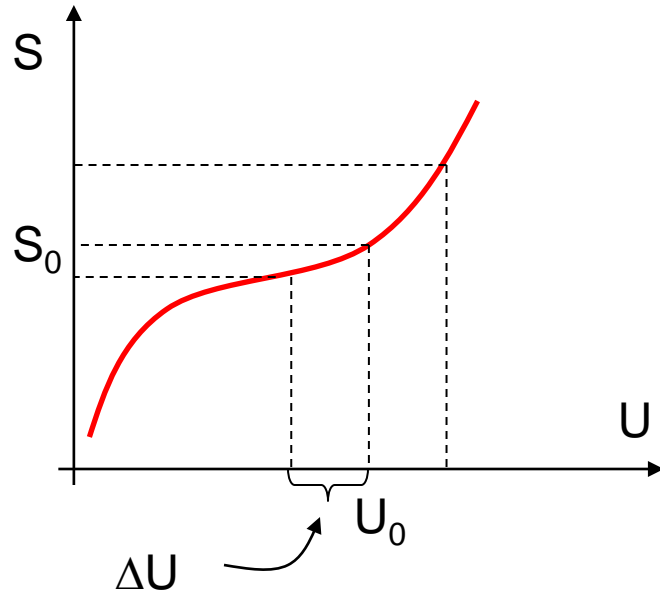
Let us consider what restrictions these two conditions imply for the functional form of the dependence of S on extensive parameters of a thermodynamic system.

Let us consider two identical systems with the following dependence of entropy on energy for each of the systems:



Stability of thermodynamic systems

Consider a homogeneous system with the fundamental relation shown below and divide it on two equal sub-systems



Initially both sub-systems have energy U_0 and entropy S_0 .

Let us consider what happens to the total entropy of the system if some energy ΔU is transferred from one sub-system to another.

In this case, the entropy of the composite system will be $S(U_0 + \Delta U) + S(U_0 - \Delta U) > 2S_0$.

Therefore the entropy of the system increases and the energy will flow from one sub-system to the other, creating a temperature difference.

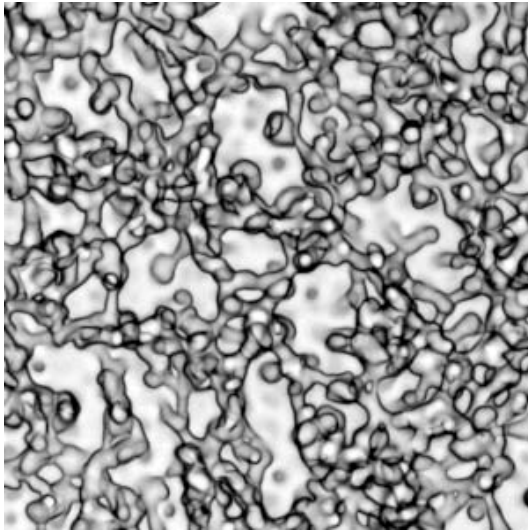
Therefore, the initial homogeneous state of the system is not the equilibrium state.

Phase Separation

If the homogeneous state of the system is not the equilibrium state, the system will spontaneously **become inhomogeneous**, or will **separate into phases**. **Phases** are different states of a system that have different macroscopic parameters (e. g. density).

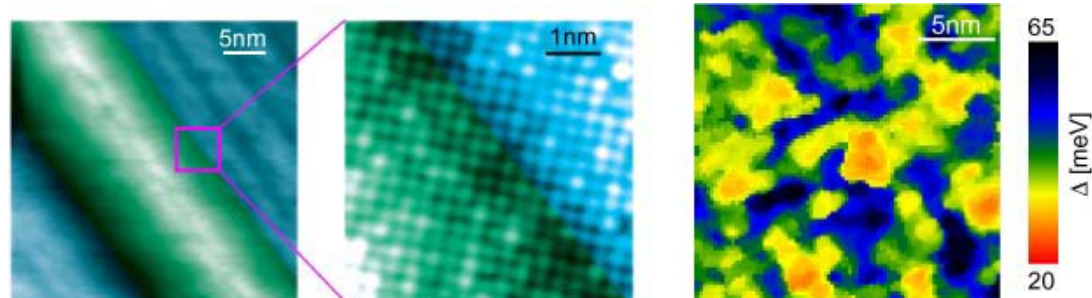
Phase separation takes place in phase transitions. When a system undergoes a transition from one macroscopically different state to another it goes through a region of phase separation (e. g. water-to-vapor phase transition).

Phase Separation Examples



Two liquids. Above a certain temperature they form a homogeneous mixture. Below this temperature they phase separate.

Phase separation is ubiquitous.



Electronic phase separation in perfect crystals of strongly correlated materials. Homogeneous crystal breaks into regions of normal metal and superconductor.

Stability of thermodynamic systems

To have a stable system, the following condition has to be met:

$$S(U + \Delta U, V, N) + S(U - \Delta U, V, N) \leq 2S(U, V, N) \quad \text{for arbitrary } \Delta U$$

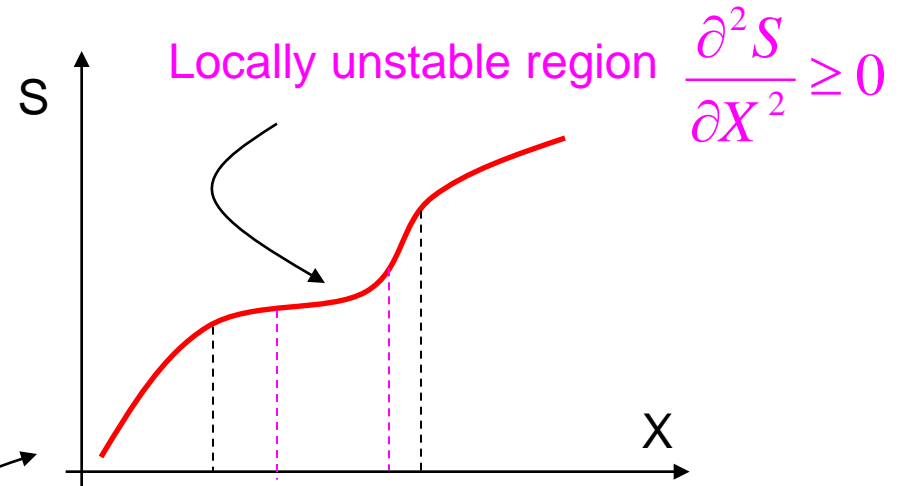
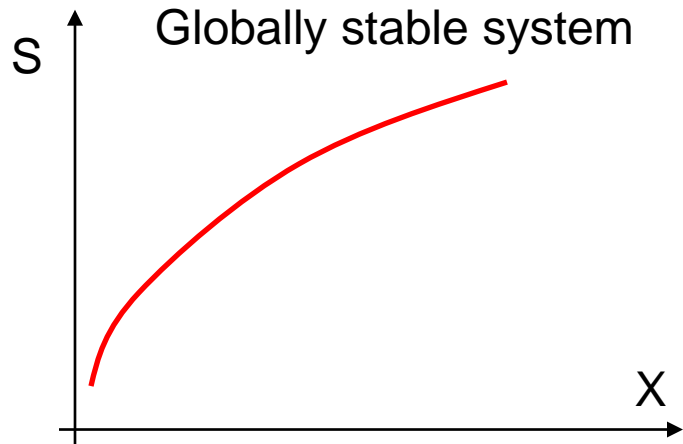
For infinitesimal dU , the above condition reduces to:

$$S(U + dU, V, N) + S(U - dU, V, N) - 2S(U, V, N) \leq 0 \quad \Rightarrow \quad \frac{\partial^2 S}{\partial U^2} \leq 0$$

Similar argument applies to spontaneous variations of any extensive variable, e. g. V :

$$S(U, V + \Delta V, N) + S(U, V - \Delta V, N) \leq 2S(U, V, N) \quad \Rightarrow \quad \frac{\partial^2 S}{\partial V^2} \leq 0$$

Stability of thermodynamic systems



Fundamental relations of this shape are frequently obtained from statistical mechanics or purely thermodynamic models (e. g. van der Waals fluid). These fundamental relations are called the **underlying fundamental relations**. These relations carry information on system stability and possible phase transitions.

Stability: higher dimensions

If we consider simultaneous fluctuations of energy and volume, the stability condition is that:

$$S(U + \Delta U, V + \Delta V, N) + S(U - \Delta U, V - \Delta V, N) \leq 2S(U, V, N)$$

for any values of ΔU and ΔV .

Local stability criteria are now a little more complex:

$$\frac{\partial^2 S}{\partial U^2} \leq 0 \quad \frac{\partial^2 S}{\partial V^2} \leq 0 \quad \frac{\partial^2 S}{\partial V^2} \frac{\partial^2 S}{\partial U^2} - \left(\frac{\partial^2 S}{\partial U \partial V} \right)^2 \geq 0$$

Determinant of Hessian matrix



Physical consequences of stability conditions

Stability conditions result in limitations on the possible values assumed by physically measurable quantities.

$$\frac{\partial^2 S}{\partial U^2} = \frac{\partial}{\partial U} \frac{1}{T} = -\frac{1}{T^2} \left(\frac{\partial T}{\partial U} \right)_{V,N} = -\frac{1}{T^2 N c_v} \leq 0$$

Therefore: $c_v \geq 0$

The molar heat capacity at constant volume must be positive.

Stability conditions in the energy representation

From the fact that the **internal energy** of the system should be **at minimum in equilibrium**, we can derive the condition for stability in the energy representation:

$$U(S + \Delta S, V + \Delta V, N) + U(S - \Delta S, V - \Delta V, N) \geq 2U(S, V, N)$$

The local stability criteria in the energy representation are:

$$\frac{\partial^2 U}{\partial S^2} = \frac{\partial T}{\partial S} \geq 0 \quad \frac{\partial^2 U}{\partial V^2} = -\frac{\partial P}{\partial V} \geq 0 \quad \frac{\partial^2 U}{\partial V^2} \frac{\partial^2 U}{\partial S^2} - \left(\frac{\partial^2 U}{\partial S \partial V} \right)^2 \geq 0$$

Stability conditions for other thermodynamic potentials

Equations used in Legendre transformations:

$$P = \frac{\partial U(X)}{\partial X} \qquad X = -\frac{\partial U(P)}{\partial P}$$

Here P is a generalized intensive parameter conjugate to the extensive parameter X and $U(P)$ is the Legendre transform of $U(X)$.

Stability conditions for other thermodynamic potentials

$$\frac{\partial P}{\partial X} = \frac{\partial U^2(X)}{\partial X^2}$$

$$\frac{\partial X}{\partial P} = -\frac{\partial^2 U(P)}{\partial P^2}$$

$$\frac{\partial P}{\partial X} = \frac{1}{\frac{\partial X}{\partial P}}$$



$$\frac{\partial U^2(X)}{\partial X^2} = -\frac{1}{\frac{\partial^2 U(P)}{\partial P^2}}$$

Therefore, the sign of the second derivative of the Legendre transform of the internal energy is opposite to that of the internal energy.

Stability conditions for other thermodynamic potentials

Internal energy: $\frac{\partial^2 U}{\partial S^2} \geq 0$ $\frac{\partial^2 U}{\partial V^2} \geq 0$

Helmholtz potential: $\frac{\partial^2 F}{\partial T^2} \leq 0$ $\frac{\partial^2 F}{\partial V^2} \geq 0$

Enthalpy: $\frac{\partial^2 H}{\partial S^2} \geq 0$ $\frac{\partial^2 H}{\partial P^2} \leq 0$

Gibbs potential: $\frac{\partial^2 G}{\partial T^2} \leq 0$ $\frac{\partial^2 G}{\partial P^2} \leq 0$

Exercise: derive stability conditions for the determinant of the Hessians matrix for various thermodynamic potentials.

Note the difference of stability criteria with respect to extensive and intensive coordinates

Physical consequences of stability conditions

Any of the just written stability conditions generates a constraint on some physical quantity, e. g.:

$$\frac{\partial^2 F}{\partial V^2} \geq 0 \quad \longrightarrow \quad \frac{\partial^2 F}{\partial V^2} = -\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{V\kappa_T} \geq 0 \quad \longrightarrow \quad \kappa_T \geq 0$$

The isothermal compressibility of a **stable** thermodynamic system is non-negative.

Physical consequences of stability conditions

From the Maxwell relations we can also derive:

$$c_P - c_v = \frac{T\nu\alpha^2}{\kappa_T} \quad \frac{\kappa_S}{\kappa_T} = \frac{c_v}{c_P}$$

$$c_P - c_v = \frac{T\nu\alpha^2}{\kappa_T} \quad \longrightarrow \quad c_P \geq c_v \geq 0$$

$$\frac{\kappa_S}{\kappa_T} = \frac{c_v}{c_P} \quad \longrightarrow \quad \kappa_T \geq \kappa_S \geq 0$$