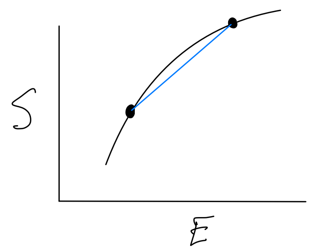
Unit 1-9: Stability and Response Functions

In this section we will regard the number of particles N to always be held constant, so for simplicity of notation I will not write N as a variable.

Entropy

We saw in Notes 1-2 that, in order that the equilibrium state to be stable against spatial fluctuations, it was necessary that the entropy $S(E)$ be a *concave* function of energy E, i.e. $(\partial^2 S/\partial E^2) < 0$.



Concave means that the cord drawn between any two points on the curve always lies *below* the curve.

In a similar way one can show that S must be a concave function of volume V, $(\partial^2 S/\partial V^2) < 0$.

More generally, S must be concave surface in the three dimensional S, E, V space. This requires,

$$S(E + \Delta E, V + \Delta V, N) + S(E - \Delta E, V - \Delta V) < 2S(E, V) \qquad \text{for any } \Delta E \text{ and } \Delta V. \tag{1.9.1}$$

Expanding the left hand side of the above in a Taylor series in ΔE and ΔV, the linear terms cancel, and to quadratic order we get,

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_V (\Delta E)^2 + 2\left(\frac{\partial^2 S}{\partial E \partial V}\right)\Delta E \Delta V + \left(\frac{\partial^2 S}{\partial V^2}\right)_E (\Delta V)^2 < 0 \tag{1.9.2}$$

For $\Delta V = 0$ this gives $(\partial^2 S/\partial E^2)_V < 0$. For $\Delta E = 0$ this gives $(\partial^2 S/\partial V^2)_E < 0$.

More generally, for ΔE and ΔV both non zero, we can rewrite Eq. (1.9.2) as the matrix equation,

$$(\Delta E, \Delta V)\begin{pmatrix} \left(\frac{\partial^2 S}{\partial E^2}\right)_V & \left(\frac{\partial^2 S}{\partial E \partial V}\right) \\ \left(\frac{\partial^2 S}{\partial E \partial V}\right) & \left(\frac{\partial^2 S}{\partial V^2}\right)_E \end{pmatrix}\begin{pmatrix} \Delta E \\ \Delta V \end{pmatrix} < 0 \tag{1.9.3}$$

That this quadratic form is always negative for any choice of ΔE and ΔV implies that both eigenvalues of the matrix of second derivatives of S must be negative, and so the determinant of the matrix must be positive (since the determinant is the product of the eigenvalues). We therefore get,

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_V \left(\frac{\partial^2 S}{\partial V^2}\right)_E - \left(\frac{\partial^2 S}{\partial E \partial V}\right)^2 > 0 \tag{1.9.4}$$

Now note that, since $(\partial S/\partial E)_V = 1/T$, then,

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_V = \frac{\partial}{\partial E}\left(\frac{1}{T}\right)_V = -\frac{1}{T^2}\left(\frac{\partial T}{\partial E}\right)_V = -\frac{1}{T^2 C_V} \tag{1.9.5}$$

where we used partial derivative rule (2) and Eq. (1.8.31) to write, $(\partial T/\partial E)_V = 1/(\partial E/\partial T)_V = 1/C_V$.

Now since we know that $\left(\frac{\partial^2 S}{\partial E^2}\right)_V < 0$, it then follows from Eq. (1.9.5) that we must have $\boxed{C_V > 0}$.

The stability condition for S requires that C_V be positive.

Energy

One can use the minimization principles of the other thermodynamic potentials, E, A, G, etc., to derive other similar stability criteria.

For example, S is maximized $\Rightarrow$ E is minimized. S is concave $\Rightarrow$ E is convex. This requires,

$$E(S+\Delta S, V+\Delta V, N) + E(S-\Delta S, V-\Delta V, N) > 2E(S,V) \tag{1.9.6}$$

Expand the left hand side to second order in a Taylor series in ΔS and ΔV to get

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_V (\Delta S)^2 + 2\left(\frac{\partial^2 E}{\partial S \partial V}\right)\Delta S \Delta V + \left(\frac{\partial^2 E}{\partial V^2}\right)_E (\Delta V)^2 \;>\; 0 \tag{1.9.7}$$

For $\Delta V = 0$ we then have,

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V > 0 \tag{1.9.8}$$

and for $\Delta S = 0$,

$$\left(\frac{\partial^2 E}{\partial V^2}\right)_S = -\left(\frac{\partial p}{\partial V}\right)_S > 0 \tag{1.9.9}$$

More generally, the eigenvalues of the matrix of second derivatives of E must all be positive, so the determinant of this matrix must be positive, and so,

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_V \left(\frac{\partial^2 E}{\partial V^2}\right)_E - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 > 0 \qquad \text{or} \qquad -\left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial p}{\partial V}\right)_S - \left(\frac{\partial T}{\partial V}\right)_S^2 > 0 \tag{1.9.10}$$

Using $\left(\frac{\partial T}{\partial S}\right)_V = \frac{1}{(\partial S/\partial T)_V} = \frac{T}{C_V}$, and $\left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{(\partial V/\partial p)_S} = -\frac{1}{V\kappa_S}$, we then get the following.

For $\Delta V = 0$ we have $\left(\frac{\partial^2 E}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0 \quad \Rightarrow \quad \boxed{C_V > 0}$.

For $\Delta S = 0$ we have $\left(\frac{\partial^2 E}{\partial V^2}\right)_S = -\left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{V\kappa_s} > 0 \quad \Rightarrow \quad \boxed{\kappa_S > 0}$.

And in general from Eq. (1.9.10) we have,

$$\frac{T}{VC_V\kappa_S} > \left(\frac{\partial T}{\partial V}\right)_S^2 \tag{1.9.11}$$

Thus the stability condition on $E(S,V)$ results in conditions on the response functions C_V and κ_S.

Stability Conditions for Other Potentials

What about the potentials A, G, H, and Φ? Are they convex or concave in their variables?

convex $\Rightarrow$ 2nd derivative is positive

concave $\Rightarrow$ 2nd derivative is negative

Second derivatives of potentials are related to the response functions, i.e. C_V, C_p, κ_S, κ_T, α.

So knowing the sign of the 2nd derivatives of the thermodynamic potentials will give a constraint on the corresponding response function.

Helmholtz Free Energy

We now wish to ask, is the Helmholtz Free Energy $A(T, V)$ convex or concave in T and in V? We will determine this by relating the second derivatives of A to the second derivatives of $E(S, V)$, whose behavior is known since E is convex in its variables.

The Helmholtz free energy is $A(T, V) = E - TS$. Consider the second derivative of A with respect to T.

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \Rightarrow \qquad \left(\frac{\partial^2 A}{\partial T^2}\right)_V = -\left(\frac{\partial S}{\partial T}\right)_V \tag{1.9.12}$$

Now we relate this second derivative of A to the corresponding second derivative of E,

$$\left(\frac{\partial E}{\partial S}\right)_V = T \qquad \Rightarrow \qquad \left(\frac{\partial^2 E}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V \tag{1.9.13}$$

Since by result (2) for partial derivatives, $(\partial S/\partial T)_V = 1/(\partial T/\partial S)_V$ we then have,

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_V = \frac{-1}{\left(\frac{\partial T}{\partial S}\right)_V} = \frac{-1}{\left(\frac{\partial^2 E}{\partial S^2}\right)_V} \tag{1.9.14}$$

Since E is convex, we have $\left(\frac{\partial^2 E}{\partial S^2}\right)_V > 0 \quad \Rightarrow \quad \left(\frac{\partial^2 A}{\partial T^2}\right)_V < 0.$

E is convex in $S \quad \Rightarrow \quad A$ is concave in T.

From this we can conclude,

$$0 > \left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} = -\left(\frac{\partial S}{\partial T}\right)_{V,N} = -\frac{C_V}{T} \quad \Rightarrow \quad \boxed{C_V > 0} \tag{1.9.15}$$

Next consider the second derivative of A with respect to V. We have,

$$\left(\frac{\partial A}{\partial V}\right)_T = -p \qquad \Rightarrow \qquad \left(\frac{\partial^2 A}{\partial V^2}\right)_T = -\left(\frac{\partial p}{\partial V}\right)_T \tag{1.9.16}$$

Our goal will be to rewrite derivatives at constant T in terms of derivatives at constant S and V so that we can relate them to $E(S, V)$.

Since $p = -(\partial A/\partial V)_T$, and A depends on T and V, this gives $p(T, V)$ as a function of T and V. However, from $p = -(\partial E/\partial V)_S$ we can also regard $p(S, V)$ as a function of S and V. And from $S = -(\partial A/\partial T)_V$ we can regard $S(T, V)$ as a function of T and V. We can therefore write,

$$p(T, V) = p(S(T, V), V) \tag{1.9.17}$$

and then take the derivative with respect to V at constant T to get,

$$\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial p}{\partial V}\right)_S + \left(\frac{\partial p}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T \tag{1.9.18}$$

Now use the Maxwell relation and result (3) for partial derivatives to rewrite the last factor as,

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial^2 A}{\partial V \partial T}\right) = \left(\frac{\partial p}{\partial T}\right)_V = \frac{(\partial p/\partial S)_V}{(\partial T/\partial S)_V} \tag{1.9.19}$$

So

$$\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial p}{\partial V}\right)_S + \frac{(\partial p/\partial S)_V^2}{(\partial T/\partial S)_V} = -\left(\frac{\partial^2 E}{\partial V^2}\right)_S + \frac{\left(\frac{\partial^2 E}{\partial S \partial V}\right)^2}{\left(\frac{\partial^2 E}{\partial S^2}\right)_V} \tag{1.9.20}$$

So finally we can write,

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} = -\left(\frac{\partial p}{\partial V}\right)_{T,N} = \frac{\left(\frac{\partial^2 E}{\partial V^2}\right)_S \left(\frac{\partial^2 E}{\partial S^2}\right)_V - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2}{\left(\frac{\partial^2 E}{\partial S^2}\right)_V} > 0 \qquad \text{since } E \text{ is convex} \tag{1.9.21}$$

The last inequality follows since the denominator is positive since E is convex, and the numerator is also positive since it is the determinant of the matrix of second derivatives of E and that is also positive since E is convex.

So A is convex in V.

This then gives,

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_T = -\left(\frac{\partial p}{\partial V}\right)_T = \frac{-1}{\left(\frac{\partial V}{\partial p}\right)_T} = \frac{1}{V\kappa_T} > 0 \quad \Rightarrow \quad \boxed{\kappa_T > 0} \tag{1.9.22}$$

The isothermal compressibility must be positive.

To summarize: A is concave in T but convex in V.

Gibbs Free Energy

The Gibbs free energy is $G(T, p, N) = E - TS + pV$.

G is the Legendre transform of E in both S and V. Since E is convex in both S and V we can show that,

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p < 0 \qquad G \text{ is concave in } T \tag{1.9.23}$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_T < 0 \qquad G \text{ is concave in } p \tag{1.9.24}$$

In general, the thermodynamic free energies for constant N (i.e. E and its Legendre transforms) are convex in their extensive variables (S, V) and concave in their intensive variables (T, p).

Le Chatelier's Principle

Le Chatelier stated the above stability results in terms of a general principle:

"Any inhomogeneity that develops in the system should induce a process that tends to eradicate the inhomogeneity."

The is the criterion required for the stability of equilibrium states. It determines the concavity or convexity of the thermodynamic potentials, and the corresponding results for their response functions.