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Stability Conditions

No one welcomes chaos, but why crave stability and predictability?

Hugh Mackay, Australian psychologist

So far, we have implicitly assumed that the systems we have studied are stable. For example, we have been assuming that the density of a gas will remain uniform, rather than having most of the particles clump together in one part of the container, leaving the rest of the volume nearly empty. Gases are usually well behaved in this respect, but we all know from experience that molecules of H_2O can clump together, form drops, and rain on us.

The question of stability therefore leads naturally to a consideration of phase transitions, in which the properties of a material change drastically in response to small changes in temperature or pressure.

In this chapter we will discuss the stability of thermodynamic systems. We will find that certain inequalities must be satisfied for a system to be stable. The violation of these inequalities signals a phase transition and a number of interesting and important phenomena—including rain.

The methods used in this chapter are based on the extremum principles derived in Chapter 15. Those extremum principles were valid for composite systems, in which the energy, volume, or particle number of the subsystems was varied.

In this chapter we look inside a composite system to see what conditions a subsystem must satisfy as a consequence of the extremum principles in Chapter 15. These are called the ‘intrinsic’ stability conditions. Since any thermodynamic system could become a subsystem of some composite system, the stability conditions we derive will be valid for all thermodynamic systems.

16.1 Intrinsic Stability

Several approaches have been developed during the history of thermodynamics to derive the intrinsic stability conditions. The one used here has the advantage of being mathematically simple. Its only drawback is that it might seem to be a special case, but it really does produce the most general intrinsic stability conditions.

Although all stability conditions can be obtained from any of the extremum principles derived in Chapter 15, there are advantages to using different thermodynamic potentials for different stability conditions to simplify the derivations, as we will see in the following sections.

16.2 Stability Criteria based on the Energy Minimum Principle

Consider two arbitrary thermodynamic systems. Denote the properties of the first as S , U , V , N , and so on, and distinguish the properties of the second with a hat, \hat{S} , \hat{U} , \hat{V} , \hat{N} , and so forth. Combine the two systems to form a composite system, which is thermally isolated from the rest of the universe.

Allow the subsystems to interact with each other through a partition, which can be fixed or moveable, diathermal or adiabatic, impervious to particles or not, as you choose. Denote the quantity being exchanged as X . As in Chapter 15, X can denote any variable that describes how much of something is contained in the system. For example, the wall might be diathermal and X the energy of a subsystem, or the wall might be moveable and X the volume of a subsystem. However, X must be an extensive variable; it cannot be the temperature or pressure.

16.2.1 Stability with Respect to Volume Changes

As we saw in Section 15.1, the total energy is a minimum at equilibrium for constant total volume. Suppose we have a moveable wall (piston) separating the subsystems, as in the lower diagram in Fig. 15.1, and we use it to increase V to $V + \Delta V$, while decreasing \hat{V} to $\hat{V} - \Delta V$. The energy minimum principle would then demand that the change in total energy must be non-negative,

$$\begin{aligned}\Delta U_{total} &= U(S, V + \Delta V, N) - U(S, V, N) \\ &\quad + \hat{U}(\hat{S}, \hat{V} - \Delta V, \hat{N}) - \hat{U}(\hat{S}, \hat{V}, \hat{N}) \\ &\geq 0.\end{aligned}\tag{16.1}$$

The equality will hold only when $\Delta V = 0$. The volume transferred need not be small; the inequality is completely general.

Now take the special case that the properties of the two systems are identical. Eq. (16.1) can then be simplified to give an equation that must be true for a single system,

$$U(S, V + \Delta V, N) + U(S, V - \Delta V, N) - 2U(S, V, N) \geq 0.\tag{16.2}$$

This equation must also hold for arbitrary values of ΔV ; it is not limited to small changes.

Now divide both sides of eq. (16.2) by $(\Delta V)^2$ and take the limit of $\Delta V \rightarrow 0$,

$$\lim_{\Delta V \rightarrow 0} \left[\frac{U(S, V + \Delta V, N) + U(S, V - \Delta V, N) - 2U(S, V, N)}{(\Delta V)^2} \right] = \left(\frac{\partial^2 U}{\partial V^2} \right)_{S,N} \geq 0. \quad (16.3)$$

This gives us a stability condition on a second derivative.

Since we know that

$$\left(\frac{\partial U}{\partial V} \right)_{S,N} = -P, \quad (16.4)$$

eq. (16.3) can also be expressed as a stability condition on a first derivative,

$$- \left(\frac{\partial P}{\partial V} \right)_{S,N} \geq 0. \quad (16.5)$$

If we define an isentropic (constant entropy) compressibility in analogy to the isothermal compressibility in eq. (14.14),

$$\kappa_S = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{S,N} \quad (16.6)$$

we find that κ_S must also be positive for stability,

$$- \left(\frac{\partial P}{\partial V} \right)_{S,N} = \frac{-1}{\left(\frac{\partial V}{\partial P} \right)_S} = \frac{V}{\kappa_S} \geq 0 \quad (16.7)$$

or, since $V > 0$

$$\kappa_S \geq 0. \quad (16.8)$$

This means that if you increase the pressure on a system, its volume will decrease. Eq. (16.8) is true for all thermodynamic systems.

The stability conditions in this chapter are expressed as inequalities for second partial derivatives of the thermodynamic potentials. This makes them look very much like the extremum principles in Chapter 15. However, these inequalities do not represent extremum principles, because the corresponding first derivatives are not necessarily zero, as they must be at an extremum.

16.2.2 Stability with Respect to Heat Transfer

We can use the same method as in Subsection 16.2.1 to consider the consequences of transferring some amount of entropy between the subsystems. The energy minimum principle again demands that the change in total energy be non-negative,

$$\begin{aligned}\Delta U_{total} &= U(S + \Delta S, V, N) - U(S, V, N) \\ &\quad + \hat{U}(\hat{S} - \Delta S, \hat{V}, \hat{N}) - \hat{U}(\hat{S}, \hat{V}, \hat{N}) \\ &\geq 0.\end{aligned}\tag{16.9}$$

The equality will hold only when $\Delta S = 0$. The entropy transferred need not be small; this inequality is also completely general.

Now again take the special case that the properties of the two systems are identical. Eq. (16.9) can then be simplified to give an equation that must be true for a single system,

$$U(S + \Delta S, V, N) + U(S - \Delta S, V, N) - 2U(S, V, N) \geq 0.\tag{16.10}$$

This equation must also hold for arbitrary values of ΔS ; it is not limited to small changes in entropy.

Divide both sides of eq. (16.10) by $(\Delta S)^2$ and take the limit of $\Delta S \rightarrow 0$,

$$\lim_{\Delta S \rightarrow 0} \left[\frac{U(S + \Delta S, V, N) + U(S - \Delta S, V, N) - 2U(S, V, N)}{(\Delta S)^2} \right] = \left(\frac{\partial^2 U}{\partial S^2} \right)_{V, N} \geq 0.\tag{16.11}$$

Since we know that

$$\left(\frac{\partial U}{\partial S} \right)_{V, N} = T,\tag{16.12}$$

eq. (16.11) can be expressed as a stability condition on a first derivative,

$$\left(\frac{\partial T}{\partial S} \right)_{V, N} \geq 0.\tag{16.13}$$

This inequality can be rewritten in terms of the specific heat at constant volume,

$$\left(\frac{\partial T}{\partial S} \right)_{V, N} = 1 / \left(\frac{\partial S}{\partial T} \right)_{V, N} = \frac{T}{Nc_V} \geq 0.\tag{16.14}$$

If the temperature is assumed to be positive, a condition for the system to be stable is

$$c_V \geq 0.\tag{16.15}$$

This means that if heat is added to a system, its temperature will increase, which certainly agrees with experience. Eq. (16.15) is valid for all thermodynamic systems.

16.3 Stability Criteria based on the Helmholtz Free Energy Minimum Principle

Now we extend the stability criteria to cases in which the temperature of the composite system is held constant. This makes it natural to use the Helmholtz free energy minimization principle.

Recall that we do not (yet) have a stability condition involving derivatives with respect to temperature, so we will only look at the case of moving a piston to vary the volume.

The experiment we consider is the same as that illustrated in the lower picture in Fig. 15.1, except that instead of being thermally isolated, the entire cylinder is in contact with a heat bath at temperature T .

The Helmholtz free energy minimization principle now leads to the condition:

$$F(T, V + \Delta V, N) + F(T, V - \Delta V, N) - 2F(T, V, N) \geq 0. \quad (16.16)$$

This equation must also hold for arbitrary values of ΔV ; it is not limited to small changes in the volumes of the subsystems.

Dividing eq. (16.16) by $(\Delta V)^2$ and taking the limit of $\Delta V \rightarrow 0$, we find a new stability condition,

$$\lim_{\Delta V \rightarrow 0} \left[\frac{F(T, V + \Delta V, N) + F(T, V - \Delta V, N) - 2F(T, V, N)}{(\Delta V)^2} \right] = \left(\frac{\partial^2 F}{\partial V^2} \right)_{T,N} \geq 0. \quad (16.17)$$

Since we know that

$$\left(\frac{\partial F}{\partial V} \right)_{T,N} = -P, \quad (16.18)$$

we can rewrite eq. (16.17) as

$$-\left(\frac{\partial P}{\partial V} \right)_{T,N} \geq 0. \quad (16.19)$$

Recalling the definition of the isothermal compressibility in eq. (14.14),

$$\kappa_T = \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N}, \quad (16.20)$$

eq. (16.19) becomes

$$-\left(\frac{\partial P}{\partial V}\right)_{T,N} = \frac{-1}{\left(\frac{\partial V}{\partial P}\right)_{T,N}} = \frac{1}{V\kappa_T} \geq 0. \quad (16.21)$$

This tells us that the isothermal compressibility is also non-negative for all systems,

$$\kappa_T \geq 0. \quad (16.22)$$

16.4 Stability Criteria based on the Enthalpy Minimization Principle

Next we consider a consequence of the enthalpy minimization principle. Here, we are looking at a situation in which the total pressure on the system and on each of its subsystems is constant. We will consider an experiment in which heat is transferred between the identical subsystems. The derivation should look familiar, since it follows the same pattern used in previous derivations.

The enthalpy minimization principle gives us the condition:

$$H(S + \Delta S, P, N) + H(S - \Delta S, P, N) - 2H(S, P, N) \geq 0. \quad (16.23)$$

This equation must also hold for arbitrary values of ΔS ; it is not limited to small changes.

Dividing eq. (16.23) by $(\Delta S)^2$ and taking the limit of $\Delta S \rightarrow 0$, we find yet another stability condition,

$$\lim_{\Delta S \rightarrow 0} \left[\frac{H(S + \Delta S, P, N) + H(S - \Delta S, P, N) - 2H(S, P, N)}{(\Delta S)^2} \right] = \left(\frac{\partial^2 H}{\partial S^2} \right)_{P,N} \geq 0. \quad (16.24)$$

Since we know that

$$\left(\frac{\partial H}{\partial S} \right)_{P,N} = T, \quad (16.25)$$

we can rewrite eq. (16.24) as

$$\left(\frac{\partial T}{\partial S} \right)_{P,N} \geq 0. \quad (16.26)$$

Recalling the definition of the specific heat at constant pressure in eq. (14.15),

$$c_P = \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_{P,N}, \quad (16.27)$$

eq. (16.26) becomes

$$\left(\frac{\partial T}{\partial S}\right)_{P,N} = \frac{1}{\left(\frac{\partial S}{\partial T}\right)_{P,N}} = \frac{T}{Nc_P} \geq 0. \quad (16.28)$$

This tells us that the specific heat at constant pressure is non-negative,

$$c_P \geq 0. \quad (16.29)$$

16.5 Inequalities for Compressibilities and Specific Heats

In Chapter 14 we derived a relationship between the specific heats at constant pressure and constant volume. According to eq. (14.73),

$$c_P = c_V + \frac{\alpha^2 TV}{N\kappa_T}. \quad (16.30)$$

Since all quantities in the second term on the right are non-negative, we immediately have another inequality,

$$c_P \geq c_V. \quad (16.31)$$

The equality would only occur when $\alpha = 0$, which can actually happen! Liquid water has $\alpha = 0$, and its maximum density at a temperature of 3.98°C and atmospheric pressure. Note that we have no stability condition on the coefficient of thermal expansion, α , even though we expect most things to expand when heated. This is as it should be, since there are several examples of materials that contract when heated, including water just above the freezing point. This does not affect the inequality in eq. (16.31), since only the square of α occurs in eq. (16.30).

There is an equation and an inequality linking κ_S and κ_T that are similar to those linking c_P and c_V . However, they are more fun to derive yourself, so they will be left as an exercise.

16.6 Other Stability Criteria

When we derived stability conditions for various second derivatives, we explicitly excluded derivatives with respect to T , P , or μ . Addressing this omission turns out to be quite easy, but requires a method that is different from that used in Chapters 15 and 16. One example will reveal the nature of the derivation.

We will derive a stability condition for the second derivative of the Helmholtz free energy with respect to temperature. We know that the first derivative gives the negative of the entropy,

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S. \quad (16.32)$$

Take the partial derivative of eq. (16.32) with respect to temperature to find an expression for the quantity in which we are interested,

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} = -\left(\frac{\partial S}{\partial T}\right)_{V,N}. \quad (16.33)$$

The right-hand side of eq. (16.33) is, of course, equal to $-Nc_V/T$, which must be negative. However, we are more concerned with relating it to the second derivative of the energy with respect to entropy, because that reveals a general property of thermodynamic potentials.

The first derivative of the energy with respect to entropy gives the temperature,

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T. \quad (16.34)$$

Now take the second derivative of U with respect to S ,

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} = \left(\frac{\partial T}{\partial S}\right)_{V,N} \geq 0. \quad (16.35)$$

The last inequality in eq. (16.35) is just the stability condition in eq. (16.11) that we derived earlier in this chapter.

Since we have the identity

$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = 1 / \left(\frac{\partial T}{\partial S}\right)_{V,N}, \quad (16.36)$$

we find that the second partial derivative of F with respect to T must be negative:

$$\begin{aligned} \left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} &= -\left(\frac{\partial S}{\partial T}\right)_{V,N} \\ &= -1 / \left(\frac{\partial T}{\partial S}\right)_{V,N} \\ &= -1 / \left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} \\ &\leq 0. \end{aligned} \quad (16.37)$$

Eq. (16.37) shows that the second partial derivative of F with respect to T must have the opposite sign from the second partial derivative of U with respect to S . It can be seen from the derivation that quite generally the second partial derivative of the Legendre transform (F in this case) with respect to the new variable (T) has the opposite sign from the second partial derivative of the original function (U) with respect to the old variable (S). It is also a general rule that the two second derivatives are negative reciprocals of each other.

Because of the simple relationship between the second derivatives of Legendre transforms, we can skip the explicit derivations of the remaining inequalities and simply summarize them in Table 16.1.

Table 16.1 Summary of inequalities for second partial derivatives of thermodynamic potentials that are required for stability.

$U(S, V, N)$	$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} \geq 0$	$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N} \leq 0$
$F(T, V, N)$	$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} \leq 0$	$\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} \geq 0$
$H(S, P, N)$	$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} \geq 0$	$\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} \leq 0$
$G(T, P, N)$	$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \leq 0$	$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \geq 0$

I highly recommend memorizing the results shown in Table 16.1. Remembering them is easy because of the simplicity of their derivation, and they can save you from avoidable errors. It is astonishing how often these inequalities are violated in published data. Some prominent scientists have even made a hobby of collecting examples from the literature. Do not let them find any exhibits for their collections in your work!

16.7 Problems

PROBLEM 16.1

Thermodynamic stability

- Starting with the stability conditions on the second derivatives of the Helmholtz free energy, prove that for the Gibbs free energy we have the general inequality:

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \leq 0.$$

- Use this inequality to prove that the isothermal compressibility is positive.

PROBLEM 16.2**A rubber band**

The essential issues in the following questions concern whether the sign of some quantity is positive or negative. *Getting the signs right is essential!*

Consider an ordinary rubber band. If the length of the rubber band is L , and we apply a tension τ , a small change in length will change the energy of the rubber band by τdL . Assuming the number of molecules in the rubber band is fixed, the differential form of the fundamental relation in the energy representation is

$$dU = TdS + \tau dL.$$

Note that the sign of the τdL term is positive, in contrast to the more common $-PdV$ term.

1. Experimental question!

Determine the sign of the quantity $\left(\frac{\partial T}{\partial L}\right)_S$ experimentally.

Obtain a rubber band—preferably a clean rubber band.

Stretch the rubber band quickly and, using your forehead as a thermometer, determine whether it becomes hotter or colder. If the rubber band is very clean, you might try using your lips, which are more sensitive.

Since you are only interested in the sign of the derivative, you do not really have to carry out the experiment under true adiabatic (constant entropy) conditions. It will be sufficient if you simply do it quickly.

2. Now imagine that one end of the rubber band is attached to a hook in the ceiling, while the other end is attached to a weight. After the system is allowed to come to equilibrium with the weight hanging down, the rubber band is heated with a hair dryer.

Using the result of your experiment with a rubber band and your knowledge of thermodynamic identities and stability conditions, predict whether the weight will rise or fall.
