

Free Energy

In modeling a system in thermal contact with the rest of the world, we have invoked three variables: entropy, energy, and temperature. We place a constraint internal to the system, and associate this constraint to an internal variable.

In this lecture, we will consider an important special case: a system in thermal contact with a thermostat. The thermostat holds the system at a fixed temperature. When the constraint internal to the system is lifted, the associated internal variable changes, and the system exchanges energy with the thermostat. The system is no longer isolated, and the internal variable evolves by an *isothermal process*. For a system held at a fixed temperature, of all values of the internal variable, the most probable value minimizes the Helmholtz free energy. This statement is a useful paraphrase of the fundamental postulate.

To illustrate the process of thermodynamic modeling, we study two types of phase transition. We use experimental observations to motivate the construction of the models.

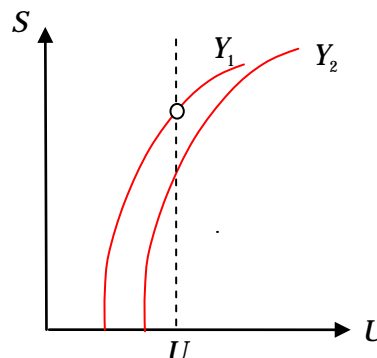
Algorithm to analyze an isolated system with an internal variable. In the first lecture, we have described a basic algorithm of thermodynamics (<http://imechanica.org/node/290>). For a given phenomenon, we construct an isolated system with a set of quantum states. Imagine a constraint internal to the isolated system, and associate the constraint to an internal variable. When the constraint is in effect, the internal variable is at a fixed value, and the isolated system flips among a subset of the quantum states. When the constraint is lifted, the internal variable can take other values, and the isolated system can flip in other subsets of the quantum states. The fundamental postulate implies that, of all values of the internal variable, the most probable value corresponds to the subset having the largest number of the quantum states. In brief, the algorithm is as follows.

- Construct an isolated system.
- Identify an internal variable Y .
- Count the number of quantum states in each subset, $\Omega(Y)$.
- Maximize $\Omega(Y)$ by varying Y .

Entropy $S(U, Y)$. Most systems are not isolated. For example, consider a half bottle of water in thermal contact with the rest of the world. Inside the bottle, water molecules are in two phases: liquid in bottom and vapor on top. We are interested in two variables: the energy in the bottle, and the number of

water molecules in the top half of the bottle. The bottle is sealed to prevent molecules from escaping.

In general terms, consider a system in thermal contact with the rest of the world. We are interested in two variables: the energy of the system U , and an internal variable of the system Y . When the energy U of the system is fixed, and the internal variable Y is allowed to vary, the system becomes an isolated system with an internal variable, and flips among a set of quantum states.



When both U and Y are fixed at specific values, the system flips among a subset of the quantum states that have value Y . Denote the number of the quantum states in this subset by $\Omega(U, Y)$. We write

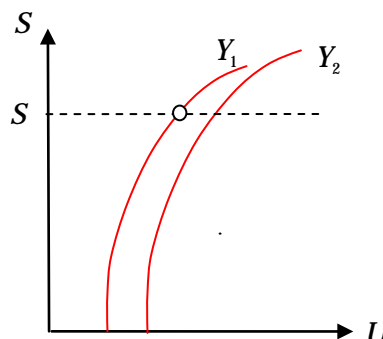
$$S(U, Y) = \log \Omega(U, Y).$$

The fundamental postulate implies the following statement:

At a constant U , of all possible value of Y , the most probable value of Y maximizes the function $S(U, Y)$.

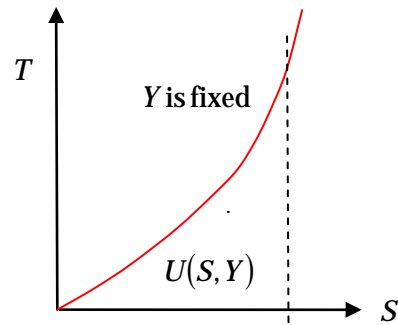
This statement is graphed for the case that the internal variable can take only two values, Y_1 and Y_2 .

Energy $U(S, Y)$. When Y is fixed, S is an increasing function of U . That is, for an isolated system with an internal constraint, the more energy the system has, the more quantum states the system has. Consequently, the function $S(U, Y)$ can be inverted to obtain the function $U(S, Y)$. The two functions characterize the same system. The previous statement of maximal number of quantum states is equivalent to the following statement:



At a constant S , of all possible value of Y , the most probable value of Y minimizes the function $U(S, Y)$.

This statement is graphed for the case that the internal variable can take only two values, Y_1 and Y_2 . The two functions $S(U, Y)$ and $U(S, Y)$ have identical graphs. For the curves graphed, value Y_1 is more probable than value Y_2 .



Entropy-temperature plane. Recall the relation

$$T = \frac{\partial U(S, Y)}{\partial S}.$$

The temperature is a function of the entropy and the internal variable, $T(S, Y)$. Consider a plane with S as the horizontal axis, and T as the vertical axis. In this plane, the function $T(S, Y)$ is a curve for any fixed value of the internal variable Y . The area under the curve is the energy $U(S, Y)$.

Examine coexistent phases using the function $u(s)$. A pure substance is an aggregate of a large number of molecules of the same species. Let s be the entropy per molecule, and u be the energy per molecule. As discussed before (<http://imechanica.org/node/291>), the thermodynamics of the substance is characterized by the function $s(u)$.

For a substance with a nonconvex function $s(u)$, part of the function will not be realized, and will be replaced by a common tangent line. The two tangent points represent coexistent phases. We now use the function $u(s)$ to examine this situation

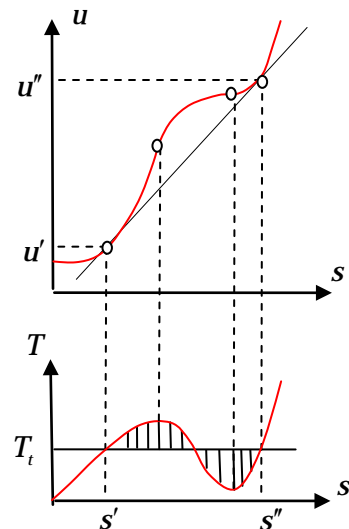
Recall

$$T = \frac{du(s)}{ds}.$$

When the function $u(s)$ is nonconvex, the function $T(s)$ is not a monotonically increasing function. The temperature for the phase transition, T_t , is the slope of the common tangent, so that

$$u' - u'' = T_t(s' - s'').$$

On the (s, T) plane, the area under the curve



$T(s)$ represents the energy $u(s)$. Inspecting the graph, we can readily see that the above condition means that T_i , is at the level such that the two shaded areas are equal. This graphic interpretation is known as *Maxwell's rule*.

Also marked on the $u(s)$ curve are the two inflection points, where

$$\frac{\partial^2 u(s)}{\partial s^2} = 0.$$

The part of the $u(s)$ curve between the inflection points is concave, where a single phase is unstable. Parts of the $u(s)$ curve are convex, but are between the interval (s', s'') . These parts correspond to metastable phases.

Isothermal process. Now consider a system with an internal variable. For example, a bottle of wine can be such a system, where the internal variable can be the extent of fermentation. The wine is in thermal contact with the rest of the world. As the wine ferments, we keep the temperature of the wine fixed, by adding energy to, or extracting energy from, the wine. The change of an internal variable of a system under the condition of a fixed temperature is known as an *isothermal process*.

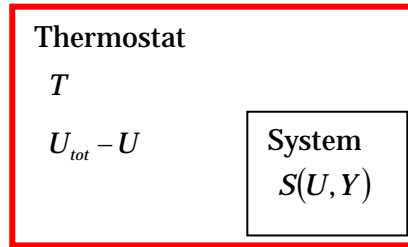
Thermostat. A device that holds temperature constant is called a thermostat, or heat reservoir, or heat bath. An example of a thermostat is the ice-water mixture. The mixture holds the temperature at 0C. When a system is in thermal contact with the ice-water, the amount of ice increases if the system draws energy from the mixture, and the amount of ice decreases if the system gives heat to the mixture. In thermal equilibrium, the temperature of the system is held at 0C, regardless of the value of the internal variable of the system. Of course, thermostats can be constructed by other means.

We characterize a thermostat by a particularly simple thermodynamic model. The thermostat is capable one independent variation: it can exchange energy with the rest of the world by thermal contact. Let T be the temperature of the thermostat. When the energy of the thermostat changes by Q , the entropy of the thermostat changes by

$$\Delta S_{\text{thermostat}} = \frac{Q}{T}.$$

Free energy $F(T, Y)$. A bottle of wine is held at a fixed temperature by a thermostat. We make the composite of the bottle of wine and the thermostat together as an isolated system. The isolated system has two internal variables:

the energy U in the wine, and the internal variable Y . The entropy of wine relates to the two internal variables by the function $S(U, Y)$. Let T be the temperature held by the thermostat. When the system draws energy U from the thermostat, the entropy of the thermostat reduces by U/T . The entropy of the composite is the sum of the entropy of the system and the entropy of the thermostat:



$$S_{\text{composite}}(U, Y) = S(U, Y) - \frac{U}{T}.$$

According to the fundamental postulate, the two internal variables U and Y evolve to increase $S_{\text{composite}}$. Consider an important condition. The bottle of wine exchanges energy rapidly with the thermostat, so that they are in thermal equilibrium, while the wine ferments. That is, the temperature of the wine is the same as that of the thermostat:

$$\frac{\partial S(U, Y)}{\partial U} = \frac{1}{T}.$$

The partial derivative is interpreted as follows. The exchange of energy is so rapid that thermal equilibrium is established while the degree of fermentation remains unchanged.

The above equation defines the function $T(U, Y)$. Further assuming that the temperature and the energy is 1-to-1, we can invert the function $T(U, Y)$, and obtain the function $U(T, Y)$. Consequently, we can rewrite the above function as

$$S_{\text{composite}}(T, Y) = -\frac{U - TS}{T}.$$

At a fixed temperature, the value of Y evolves to increase $S_{\text{composite}}(T, Y)$. Equivalently, the value of Y evolves to decrease the function

$$F = U - TS,$$

The function $F(T, Y)$ now contains quantities of the system alone, and is known as the *Helmholtz free energy* of the system.

We can state the fundamental postulate in terms of the free energy.

When the system is held at a fixed temperature T (i.e., in thermal equilibrium with a thermostat), of all values of the internal variable Y , the most probable value minimizes the function $F(T, Y) = U - TS$.

In this minimization, the temperature is not a variable, but is fixed by the thermostat.

When Y is held constant, taking differential of the free energy $F = U - TS$, we obtain that

$$dF = dU - TdS - SdT.$$

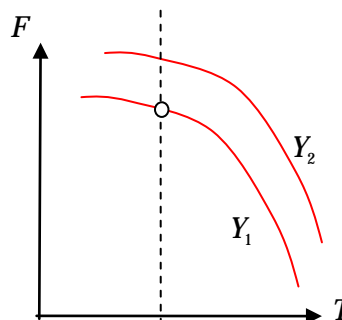
Recall that $dU = TdS$ when Y is held constant. The above equation becomes that

$$dF = -SdT.$$

Consequently, the entropy is

$$S = -\frac{\partial F(T, Y)}{\partial T}.$$

For a constant value of Y , the function $F(T, Y)$ is a monotonically decreasing function of the temperature.



Algorithm to analyze an isothermal process by using the free energy. The above considerations suggest an algorithm to analyze an isothermal process:

- Construct a system in thermal contact with a thermostat of a fixed temperature T .
- Identify an internal variable Y .
- Construct the free energy function $F(T, Y)$.
- Minimize $F(T, Y)$ by holding T fixed and varying Y .

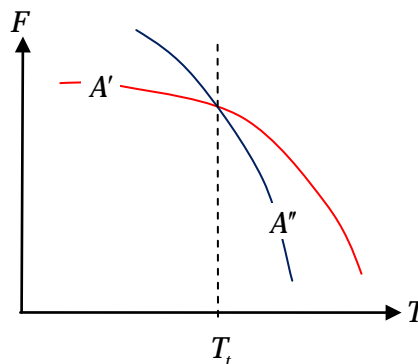
Examine coexistent phases using the free energy. Consider a mixture of two phases held at a temperature T . Let the free energy per molecule in one phase be $f'(T)$, and the free energy per molecule in the other phase be $f''(T)$. The free energy of the mixture is.

$$F = Nf'(T) + N''f''(T).$$

The number of molecules in one phase is the internal variable, to be selected to minimize the total free energy. The equation

$$f'(T) = f''(T)$$

determines the phase-transition temperature T_t . When $T < T_t$, all molecules are in one phase. When $T > T_t$ all molecules are in the other phase.



Recall the definition of the free energy, $f = u - Ts$. The above condition of equilibrium gives becomes

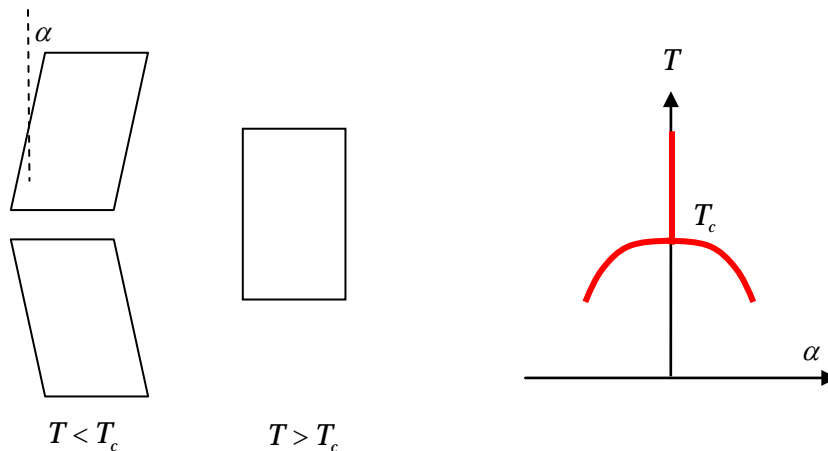
$$u' - T_t s' = u'' - T_t s''.$$

This condition recovers what we have derived before; see the notes on Temperature (<http://imechanica.org/node/291>).

Phase transition of the second kind. As another illustration of thermodynamic modeling, consider the following experimental observation. A crystal has a rectangular symmetry at a high temperature. When the temperature drops below a critical value, T_c , the crystal spontaneously distorts by an angle α . Because of the symmetry, the distortion can go in both directions. Below the critical temperature, the angle of distortion is observed to vary with the temperature. We regard the angle of distortion α as an internal variable, also known as an order parameter. The thermodynamics of the crystal is characterized by the free-energy function $F(T, \alpha)$. To model the experimental observation, we assume that the free-energy function has the following form:

$$F(T, \alpha) = C(T) + \frac{1}{2} A(T - T_c) \alpha^2 + \frac{1}{4} B \alpha^4,$$

where A and B are positive constants. This form is a Taylor expansion in the powers of α . Due to symmetry, the crystal is equally likely to distort in two directions, so that we keep the even powers of α . Let us check if this function does reproduce the observed phase transition.



When $T > T_c$, the coefficient of the α^2 term is positive, so that the equilibrium state is $\alpha = 0$. In this case, the α^4 term is unnecessary to describe the behavior of the crystal.

When $T < T_c$, the coefficient of the α^2 term is negative, and the energy is no longer minimal at $\alpha = 0$. Instead, the energy is minimal at two nonzero angles, denoted as the spontaneous angles, $\pm\alpha_s$. In this case, the α^4 term will ensure that energy goes up again when α is large. Note that

$$\frac{\partial F(T, \alpha)}{\partial \alpha} = A(T - T_c)\alpha + B\alpha^3.$$

Setting $\partial F(T, \alpha)/\partial \alpha = 0$, we find the spontaneous values of the angle:

$$\alpha_s = \pm\sqrt{A(T_c - T)/B}.$$

A significant prediction of this model is

$$\alpha_s \sim (T_c - T)^{1/2}.$$

This prediction should be compared with the angle of distortion observed in the experiment.

