

Physics 127a: Class Notes

Lecture 10: Other Ensembles/Thermodynamic Potentials

Thermodynamic potentials

We can define various other ensembles, by considering systems in equilibrium with reservoirs under various combinations of E, V, N transfer. This leads using similar methods to *thermodynamic potentials* (cf. A, Ω, \dots) that are functions of the *natural variables* that are fixed in the particular equilibrium (e.g. T, N, V for A). These are useful in describing physical systems in these equilibrium situations. The handout [Thermodynamic Potentials](#) brings together the various equilibria and corresponding thermodynamic potentials.

The thermodynamic potentials are useful in various ways, as will be listed below. We have derived the results in specific cases, and I will not repeat the derivations here.

- The thermodynamic potential increases (S) or decreases (all others) in the relaxation of a prepared macroscopic fluctuation to equilibrium when the appropriate natural variables are held fixed.
- The thermodynamic potential is a maximum (S) or minimum (all others) in equilibrium, again when the appropriate natural variables are held fixed.
- The probability of a macroscopic fluctuation at fixed natural variables is given by $e^{-\beta\Delta(\text{potential})}$ (or $e^{\beta(T\Delta S)} = e^{\Delta S/k}$ for the entropy).
- Different potentials are related by a *Legendre transformation*, e.g.

$$E(S) \rightarrow A(T) = E(S) - TS \quad \text{with} \quad T = \frac{\partial E}{\partial S} \rightarrow S(T) \quad (1)$$

(more on this later)

- The thermodynamic identity $d(\text{potential}) = \dots$, e.g.

$$dE = TdS - PdV + \mu dN \quad (2)$$

$$dA = -SdT - PdV + \mu dN \quad (3)$$

gives the differential form of the dependence on the natural variables. This is useful in relating the fields T, μ, P and conserved variables E, V, N or entropy to derivatives of the potentials. Furthermore, equating the cross derivatives

$$\frac{\partial(\text{potential})}{\partial V_1 \partial V_2} = \frac{\partial(\text{potential})}{\partial V_2 \partial V_1} \quad (4)$$

gives us *Maxwell Relations*. These are useful in relating different thermodynamic measurements (see an elementary thermodynamics book). For example, for A , equating the expressions

$$\frac{\partial}{\partial T} \left(\left(\frac{\partial A}{\partial V} \right)_T \right)_V = - \left(\frac{\partial P}{\partial T} \right)_V \quad (5)$$

$$\frac{\partial}{\partial V} \left(\left(\frac{\partial A}{\partial T} \right)_V \right)_T = - \left(\frac{\partial S}{\partial V} \right)_T \quad (6)$$

gives us the Maxwell relation

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \quad (7)$$

- There are a couple of other identities between partial derivatives that are purely mathematical relationships, with no physical content, but are useful in manipulating thermodynamic quantities.

The first thing to note is that

$$\left(\frac{\partial x}{\partial y}\right)_{z\dots} = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_{z\dots}} \quad (8)$$

where in the partial derivatives we hold everything else constant. This relation follows in the same way as for full derivatives.

Now suppose we have a functional relationship

$$z = z(x, y). \quad (9)$$

Then we can write the differential expression

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy. \quad (10)$$

Now forming the derivative with respect to y at constant z ($dz = 0$)

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x = 0, \quad (11)$$

which gives

$$\left(\frac{\partial z}{\partial y}\right)_x = -\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \quad (12)$$

or

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y}. \quad (13)$$

Using Eq. (8) we can write this in a symmetric form that is convenient to remember (known as the *reciprocity theorem*)

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \quad (14)$$

- Extensivity can be used to “build” a system out of elementary sub-units with the increments given by the thermodynamic identity. This gives *Euler Relations* for the potentials, e.g.

$$E = TS - PV + \mu N, \quad (15)$$

$$A = -PV + \mu N. \quad (16)$$

Differentiating one of these and comparing with the thermodynamic identity gives the *Gibbs-Duhem* relation

$$d\mu = -sdT + vdP \quad (17)$$

showing that *two* intensive variables are enough to define the thermodynamic state of a single component system.

- The thermodynamic potentials have various physical uses, e.g.
 - the free energy A is the mechanical work available at fixed temperature
 - the change in enthalpy $H = E + PV$ gives the heat released in a chemical reaction at fixed pressure

Note

- The entropy appears with different signs and an extra T factor in various of these. This reflects the different convention in defining $S = k \ln \left(\sum_{j, \text{accessible}} \right)$ compared with $A = -kT \ln \left(\sum_j e^{-\beta E_j} \right)$ for example, rather than any fundamental difference.
- Many of these results can be derived by considering system+reservoir as an isolated super-system.

Stability and Convexity

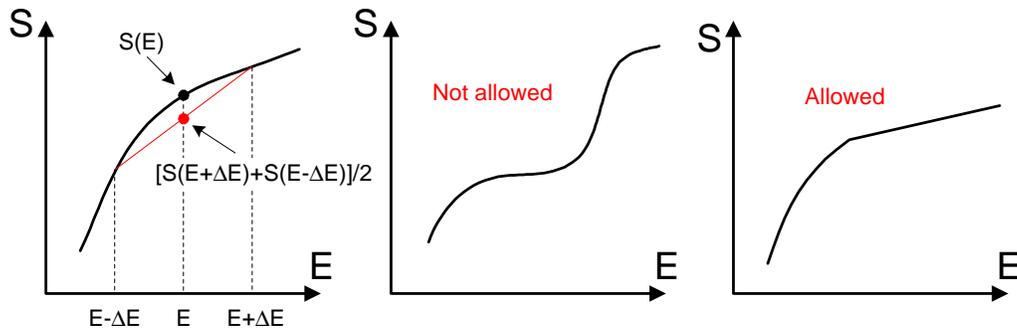
The stability of macroscopic thermodynamic systems imposes *convexity* constraints on the thermodynamic potentials.

For example consider the entropy $S(E, N, V)$ of a particular system.

Make two identical copies of the system, and place them in weak thermal contact. For the combined system of energy $2E$, number $2N$, volume $2V$ to be stable against a macroscopic fluctuation of the energy partition to $E + \Delta E, E - \Delta E$ we must have

$$S(E + \Delta E, N, V) + S(E - \Delta E, N, V) \leq 2S(E, V, N), \tag{18}$$

for *any* ΔE . Geometrically, any chord joining two points on the $S(E)$ curve must lie *below* the curve (see figure). We call such a curve *concave*.



For *small* ΔE we get the differential condition

$$\left(\frac{\partial^2 S}{\partial E^2} \right)_{N, V} \leq 0. \tag{19}$$

The chord condition Eq. (18) is a stricter constraint.

Interchanging the E and S axes, we see that the $E(S)$ curve must be *convex* i.e. any chord must lie *above* the curve.

The condition is readily extended to the other thermodynamic potentials. They, like the energy, are *minimum* in equilibrium, and so are *convex* functions of any dependence on the extensive variables E, N, V by the same sort of stability argument, now in contact with the appropriate reservoirs. On the other hand we will see that a Legendre transformation to an intensive conjugate variable T, μ, P reverses the convexity. Thus the thermodynamic potentials $A, G \dots$ are *concave* functions of the dependence on their intensive natural variables T, μ, P .

Example 1: $A(T, N, V)$ is a *concave* function of T , and a *convex* function of N and V .

Example 2: $G(T, P, N)$ (the Gibbs potential) is a *concave* function of T and P , and a *convex* function of N .

Legendre Transforms

We have derived various thermodynamics potentials that naturally depend on different variables, e.g. the energy $E(S, V, N)$ that appears in the microcanonical ensemble describing an isolated system and $A(T, V, N)$ that appears in the canonical ensemble describing a system in contact with a heat bath at temperature T . These are related by

$$A = E - TS, \quad (20)$$

an example of a Legendre transformation. It is informative to understand such Legendre transformations in a more general context.

Since we can consider each pair of variables separately (i.e. S, T or P, V etc.), lets look at a thermodynamic potential $Y(X)$ with thermodynamic identity $dY = x dX$ introducing the variable x conjugate to (paired with) X . Let's suppose that X is extensive, and then x is intensive.

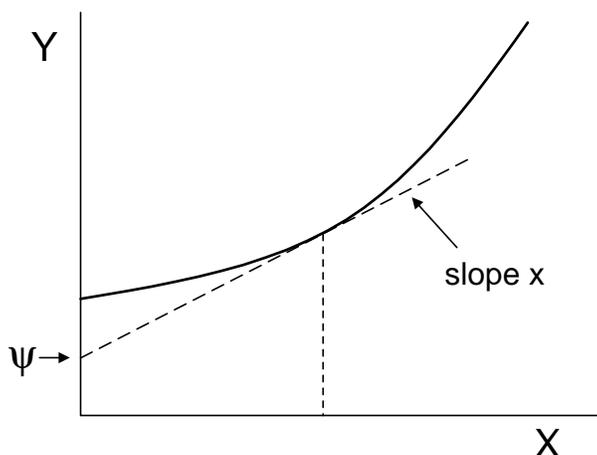


Figure 1: Geometrical Picture of a Legendre transformation $Y(X) \rightarrow \psi(x)$.

Suppose we want to go from a representation in terms of X to one in terms of the intensive variable x defined by

$$x = \frac{\partial Y}{\partial X} \quad (\text{all other variables held constant}). \quad (21)$$

We could imagine simply using Eq. (21) to find $X(x)$ which when substituted into $Y(X)$ gives $Y(x)$. However information is lost if we just know $Y(x)$ —it is easy to see that knowing Y as a function of the slope does not uniquely specify $Y(X)$.

Instead we use the idea of “Pluecker line geometry” that tells us that the curve $Y(X)$ may alternatively be specified in terms of the tangents to the curve at each point: the curve is the envelope of the tangents. The tangent at the point X can be specified by the slope $x(X)$ and the intercept ψ on the Y axis which by simple geometry is $\psi = Y(X) - x(X)X$, see figure (1). Therefore we define the Legendre transformed function as

$$\psi(x) = Y(X) - xX \quad (22)$$

where $X(x)$ is given by inverting Eq. (21), which for a smooth concave or convex curve is unique (as we will see, thermodynamic potentials have this “convexity property”). Furthermore we have

$$d\psi = -XdX \quad (23)$$

and then

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{\partial X}{\partial x} = -1 / \left(\frac{\partial x}{\partial X} \right) = -1 / \left(\frac{\partial^2 Y}{\partial X^2} \right) \quad (24)$$

so that if $Y(X)$ is smooth and convex ($\partial^2 Y / \partial X^2 > 0$) then $\psi(x)$ will be smooth and concave.

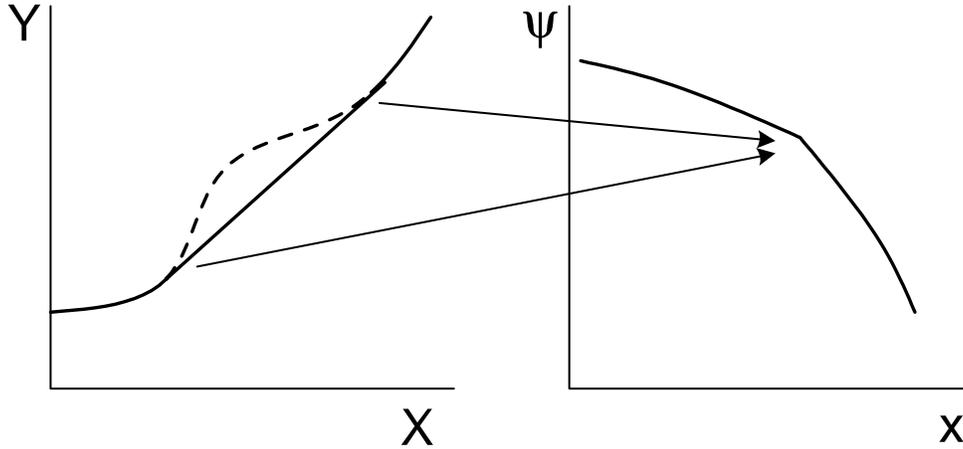


Figure 2: Legendre transformation of a $Y(X)$ formed by the “common tangent” construction. (Note: the dashed portion corresponds to unphysical results). The straight portion of $Y(X)$ translates into a single point of $\psi(x)$ where the slope changes discontinuously.

Points (or lines) where the second derivative is zero or infinity are *critical points* and correspond to phase transitions. An example is shown in figure 2.