The Energy Minimum Principle

We have learned that in equilibrium entropy of a thermodynamic system and its environment is maximized

In classical physics, we know that static equilibrium of mechanical objects is achieved by minimizing their energy

We will show that there is a connection between the entropy maximum and the energy minimum principles

The entropy maximum principle was introduced first because it has clear microscopic explanation – a macrostate with maximum entropy is realized by the maximum number of microstates. Now we will ***derive*** the energy minimum principle from the entropy maximum principle.

Notes

The energy minimum principle

We have introduced energy and entropy representations of the fundamental relation:

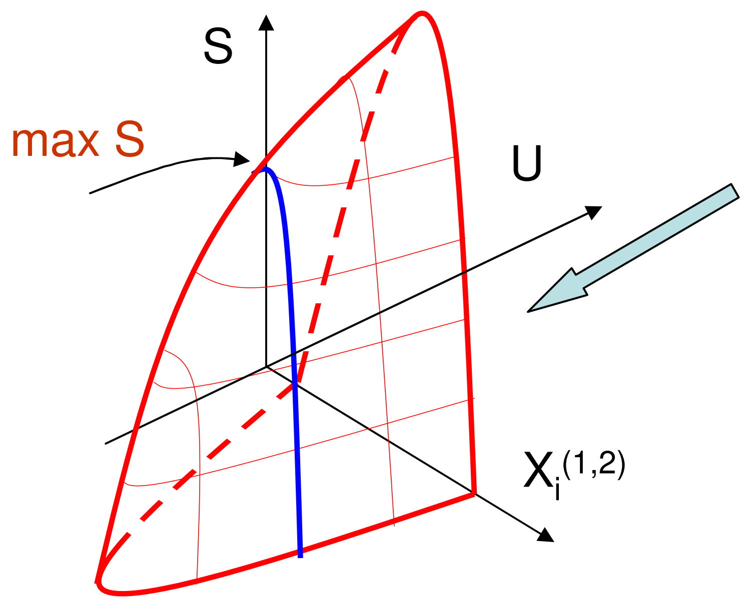
$$U = U(S, V, N, \ldots) \qquad\qquad S = S(U, V, N, \ldots)$$

One of these two representations is more convenient than the other for each particular problem (e. g. when equations of state are known as functions of U and V, the entropy representation is more convenient).

However, we have only formulated the extremum (maximum) principle in the entropy representation. In many cases, it is convenient to work in the energy representation and thus to have an extremum principle for energy.

Notes

The energy minimum principle: geometric argument

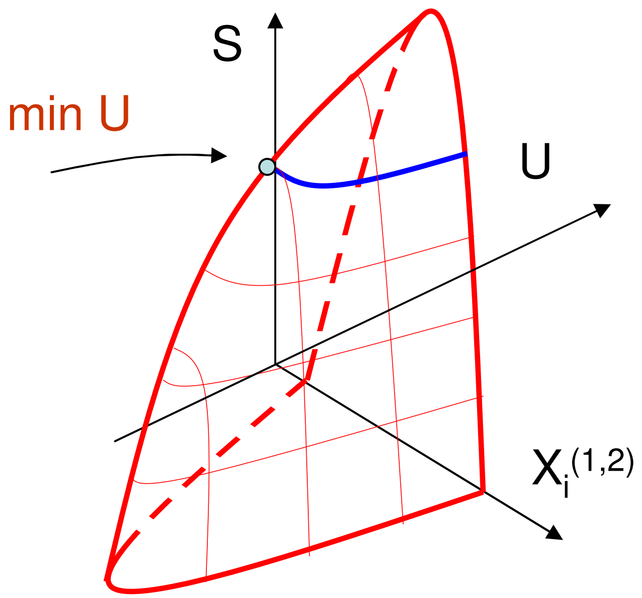


Plot of the entropy, S, of a *composite* system as a function of the energy, U, of the *composite* system and any other *unconstrained* extensive parameter.

For a *fixed* total energy U, the unconstrained extensive parameters take values that *maximize* the total entropy S.

Notes

The energy minimum principle: geometric argument



Now we note that the same state has minimum energy for this particular value of entropy! This is the consequence of the properties of S vs U, namely that

$$\frac{\partial S}{\partial U} > 0$$ and U is a single-valued function of S

Therefore, for a *fixed* total entropy S, the unconstrained extensive parameters take values that *minimize* the total energy U.

Notes

Legendre Transformations

- In both energy and entropy representations, the extensive coordinates (V, N ...) are independent variables while the conjugate intensive coordinates (P, μ …) are derivatives.

- It is often more convenient to have intensive coordinates such as P and T as independent variables because they are simpler to control in experiments.

- Therefore, we need a formulation of thermodynamics in which **intensive** coordinates play roles of independent variables.

- This formulation of thermodynamics can be obtained from the one we developed in the energy representation by a mathematical trick called the **Legendre transformation**.

- The Legendre transformations are very common in physics, for example they are used to derive the Hamilton formalism from the Lagrange formalism in mechanics.

Notes

Legendre Transformations

Let us consider a function of variables X: $$Y = Y(X_0, ... X_r)$$

Let us assume that this function contains all information about the system of interest (it is a fundamental relation)

Let us also call the derivatives of this function P: $$P_k = \frac{\partial Y}{\partial X_k}$$

Our goal is to derive a function of *variables* P that also **contains all information about the system of interest**.

Notes

1D Example

Let us consider a fundamental relation $Y = Y(X)$

then $P(X) = \dfrac{dY(X)}{dX}$

We would like to get a form of the fundamental relation where P is the independent variable.

Naïve approach, solve $P(X) = \dfrac{dY(X)}{dX}$ to get $X(P)$

Substitute the result into the fundamental relation: $Y = Y(X(P)) = f(P)$

This approach does not work because $f(P)$ has less information than $Y(X)$!

Notes

1D Example

Let us use an example to illustrate why this approach does not work

$$Y = X^2 + 1 \quad \Rightarrow \quad P(X) = \frac{dY(X)}{dX} = 2X \quad \Rightarrow \quad X = \frac{P}{2} \quad \Rightarrow$$

$$Y = Y(X(P)) = \frac{P^2}{4} + 1 \quad \Rightarrow \quad Y(P) = \frac{P^2}{4} + 1$$

What is wrong with this new fundamental relation? We lost some information that was present in the original fundamental relation $Y = X^2 - 1$

How cane we prove that we lost information? If we have not lost information, then we should be able to reconstruct $Y(X)$ given our $Y(P)$.

Notes

1D Example

$$\boxed{Y(P)=\frac{P^2}{4}+1 \quad \xrightarrow{?} \quad Y = X^2+1}$$

$$P(X)=\frac{dY(X)}{dX} \Rightarrow Y(P(X))=\frac{1}{4}\left(\frac{dY}{dX}\right)^2+1=Y(X) \Rightarrow$$

$$\Rightarrow \frac{dY}{\sqrt{Y-1}}=2dX \Rightarrow 2d\sqrt{Y-1}=2dX \Rightarrow \sqrt{Y-1}=X+C \Rightarrow$$

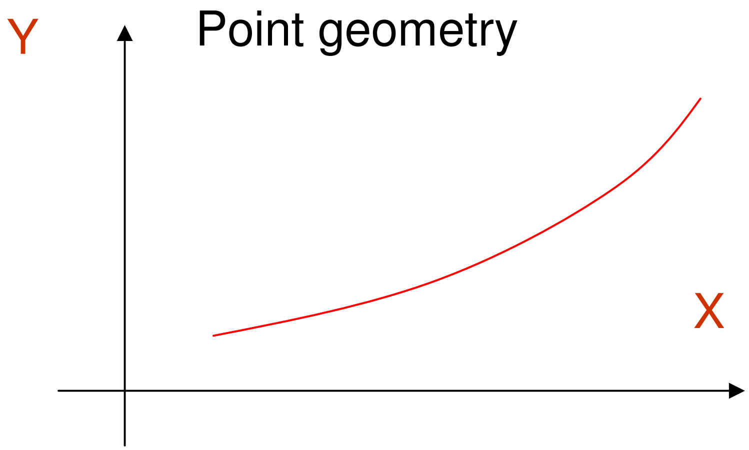
$$\boxed{Y(X)=(X+C)^2+1}$$

We failed to unambiguously reconstruct the original fundamental relation because now we have an arbitrary constant which cannot be determined. We need another way of generating a fundamental relation as a function of P !

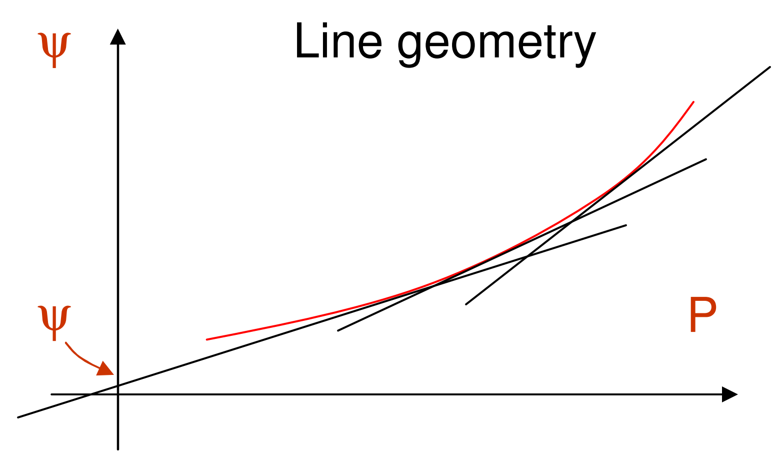
Notes

Legendre Transformations: 1D case

The correct solution of the problem has its roots in the so-called line geometry. The main idea is that a curve can be *equally* represented as either a set of points or a set of tangential lines.



For each value of X, we specify a value of Y.
Point is described by two numbers: X and Y



For each point of the curve, we specify a tangential line: $P*X+\psi$
Point is described by two numbers: P and ψ

Notes

Legendre Transformations: 1D case

The relation $Y(X)$ singles out a subset of points in the (X,Y) plane that represents our function.

The relation $\psi(P)$ singles out a subset of tangential lines among all possible lines (ψ,P) that represents our function.

The function $\psi(P)$ relates slope P to the ordinate intercept ψ of the tangential lines. This function unambiguously reconstructs $Y(X)$ and thus carries all the information contained in $Y(X)$. Thus $\psi(P)$ can serve as a fundamental relation with intensive independent parameter (because P is the slope of $Y(X)$ and this is the derivative $\partial Y/\partial X$).

Notes

Legendre Transformations: 1D case

How to calculate $\psi(P)$ given the relation $Y(X)$?

We have a function $\psi(P)$ that goes through a point with coordinates (X,Y) and has a slope P and y-axis intercept ψ:

$$P = \frac{Y - \psi}{X - 0} \quad \Longrightarrow \quad \boxed{\psi = Y - PX}$$

To eliminate X and Y from the above equation, we need two more equations which are:

$$Y = Y(X) \qquad \text{and} \qquad P = Y'(X) = P(X)$$

ψ(P) is called a *Legendre transform* of Y(X)

Notes

Legendre Transformation: 1D Example

Let us consider how Legendre transformation applies to our 1D example:

$$Y = X^2 + 1$$

$$\boxed{\psi = Y - PX}$$

$$Y = Y(X) \Rightarrow \psi = X^2 + 1 - PX$$

$$P = Y'(X) = P(X) \Rightarrow P = 2X \Rightarrow X = \frac{P}{2} \Rightarrow$$

$$\psi = \left(\frac{P}{2}\right)^2 + 1 - P\frac{P}{2} = 1 - \frac{P^2}{4} \Rightarrow \boxed{\psi = 1 - \frac{P^2}{4}}$$

Notes

Inverse Legendre Transformations: 1D case

Differentiating $\boxed{\psi = Y - PX}$ $\Rightarrow$ $d\psi = dY - PdX - XdP = -XdP$

because $P = \dfrac{dY}{dX}$ $\Rightarrow$ $dY - PdX = 0$ (true by definition of P)

Therefore: $X = -\dfrac{d\psi}{dP}$

Using this relation along with $\psi = \psi(P)$ and $\boxed{Y = \psi + XP}$

We can recover $Y = Y(X)$

This is the inverse Legendre transform

Notes

Inverse Legendre Transformation: 1D Example

Let us consider how inverse Legendre transformation applies to our 1D example:

$$\psi = 1 - \frac{P^2}{4} \qquad \boxed{Y = \psi + XP}$$

$$\psi = \psi(P) \Rightarrow Y = 1 - \frac{P^2}{4} + XP$$

$$X = -\frac{d\psi}{dP} \Rightarrow X = \frac{P}{2} \Rightarrow P = 2X \Rightarrow Y = 1 - \frac{(2X)^2}{4} + X\,2X$$

$$\Rightarrow \boxed{Y = X^2 + 1}$$

The inverse Legendre transformation has recovered the original fundamental relation!

Notes

Legendre Transformations: arbitrary dimensionality

$$Y = Y(X_0, X_1, \ldots) \qquad P_k = \frac{\partial Y}{\partial X_k}$$

Legendre transformation: $$\boxed{\psi = Y - \sum_k P_k X_k}$$

Inverse Legendre transformation: $$\boxed{Y = \psi + \sum_k X_k P_k}$$

One may also have partial Legendre transformations, when the function Y is transformed only with respect to some of its coordinates.

Notes

Thermodynamic potentials

By applying Legendre transformations to the fundamental relation in the energy representation, we can obtain various **thermodynamic potentials**

$$U = U(S, V, N\ldots) \quad \Rightarrow \quad \tilde{U} = \tilde{U}(T, P, \mu\ldots)$$

Transformation with respect to S only: *Helmholtz free energy **F***

$$U = U(S, V, N\ldots) \qquad T = \frac{\partial U}{\partial S}$$

Solve these two equations to eliminate S and U (express S and U as functions of the rest of the variables). Then substitute these S and U into the Legendre transform:

$$F(T, V, N, \ldots) = U - TS = U(S(T, V, N), V, N\ldots) - TS(T, V, N\ldots)$$

Notes

Thermodynamic potentials

Transformation with respect to V only: *Enthalpy H*

$$U = U(S, V, N...) \qquad P = -\frac{\partial U}{\partial V}$$

Solve these two equations to eliminate V and U (express V and U as function of the rest of the variables). Then substitute these V and U into the Legendre transform:

$$H(S, P, N, ...) = U + PV =$$
$$U(S, V(P, S, N...), N...) + PV(P, S, N...)$$

Notes

Thermodynamic potentials

Transformation with respect to both S and V: *Gibbs free energy G*

$$U = U(S, V, N...) \qquad P = -\frac{\partial U}{\partial V} \qquad T = \frac{\partial U}{\partial S}$$

Solve these two equations to eliminate S, V and U (express S, V and U as function of the rest of the variables). Then substitute these S, V and U into the Legendre transform:

$$G(P,T,N,...) = U - TS + PV =$$
$$U(S(P,T,N,...), V(P,T,N,...), N...) - TS(P,T,N,...) + PV(P,T,N,...)$$

Notes