Legendre Transformations: arbitrary dimensionality

$$Y = Y(X_0, X_1, \ldots)$$

$$P_k = \frac{\partial Y}{\partial X_k}$$

Legendre transformation:

$$\psi = Y - \sum_k P_k X_k$$

Inverse Legendre transformation:

$$Y = \psi + \sum_k X_k P_k$$

One may also have partial Legendre transformations, when the function Y is transformed only with respect to some of its coordinates.
Legendre transform contain all information in the original fundamental relation.

Thermodynamic potentials

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

$$U = U(S,V,N...) \implies \tilde{U} = \tilde{U}(T,P,\mu...)$$

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

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

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:

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

Thermodynamic potentials

Transformation with respect to V only: *Enthalpy H*

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

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:
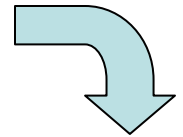
$$\Rightarrow \quad \begin{aligned} H(S, P, N,...) &= U + PV = \\ U(S, V(P, S, N...), N...) &+ PV(P, S, N...) \end{aligned}$$

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:

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

How to calculate the Helmholtz free energy

A recipe of calculating the free energy from the fundamental relation in the energy representation $U=U(S,V,N,..)$ (Legendre transformation):

1. Calculate T as a function of S, V, N:
$$T(S,V,N) = \frac{\partial U}{\partial S}$$

2. Solve the two equations: $U = U(S,V,N...)$ and $T = T(S,V,N)$

   in order to express U and S as functions of T, V and N:

$$U = U(T,V,N...) \qquad S = S(T,V,N...)$$

3. Substitute these functions into the Legendre transform for the Helmholtz free energy:
$$F(T,V,N,...) = U(T,V,N,...) - TS(T,V,N,...)$$

Example: Helmholtz free energy for van der Waals fluid

The fundamental relation in the entropy representation:

$$s = R\ln(v-b) + cR\ln(u+a/v) + s_0$$

We can rewrite it in the energy representation:

$$u = \exp\left(\frac{s-s_0}{cR}\right)(v-b)^{-\frac{1}{c}} - \frac{a}{v}$$

Eliminating molar quantities:
$$U = N\exp\left(\frac{S-S_0}{cRN}\right)\left(\frac{V}{N}-b\right)^{-\frac{1}{c}} - \frac{a}{V}N^2$$

Example: Helmholtz free energy for van der Waals fluid

1. $T(S,V,N) = \dfrac{\partial U}{\partial S}$ $\implies$ $T = \dfrac{1}{cR}\exp\left(\dfrac{S-S_0}{cRN}\right)\left(\dfrac{V}{N}-b\right)^{-\frac{1}{c}}$

2. $\left.\begin{array}{l} U = N\exp\left(\dfrac{S-S_0}{cRN}\right)\left(\dfrac{V}{N}-b\right)^{-\frac{1}{c}} - \dfrac{a}{V}N^2 \\[4em] T = \dfrac{1}{cR}\exp\left(\dfrac{S-S_0}{cRN}\right)\left(\dfrac{V}{N}-b\right)^{-\frac{1}{c}} \end{array}\right\}$ Solve for U and S

$U = cNRT - \dfrac{a}{V}N^2$

$S = NR\ln\left(\dfrac{V}{N}-b\right) + cNR\ln(cRT) + S_0$

Example: Helmholtz free energy for van der Waals fluid

3.

$$F = U - TS$$

$$F = cNRT - \frac{a}{V}N^2 - T\left(NR\ln\left(\frac{V}{N} - b\right) + cNR\ln(cRT) + S_0\right)$$

$$\boxed{F(T,V,N) = cNRT\left(1 - \ln(cRT)\right) - NRT\ln\left(\frac{V}{N} - b\right) - \frac{a}{V}N^2 + TS_0}$$

The minimum principle for Helmholtz free energy

We know that U(S,V,N,…) of a *composite system* is at minimum with respect to unconstrained extensive parameters in equilibrium. What about F(T,V,N,..) ?

We will now show that F(T,V,N,…) of the *system of interest* is also at minimum with respect to it unconstrained extensive parameters *if the system is in thermal equilibrium with a thermal reservoir at a temperature T.*

Therefore, F(T,V,N,…) is ideal for finding equilibrium states of *systems of interest* that are in contact with thermal reservoirs. It is simpler than finding the minimum of U(S,V,N,…) since T = const and thus we have effectively reduced the number of thermodynamic coordinates by one, also we do not have to worry about the thermal reservoir. We have traded generality (consider only systems in contact with a thermal reservoir) for simplicity (reduced the number of coordinates and eliminated explicit consideration of thermal reservoir).

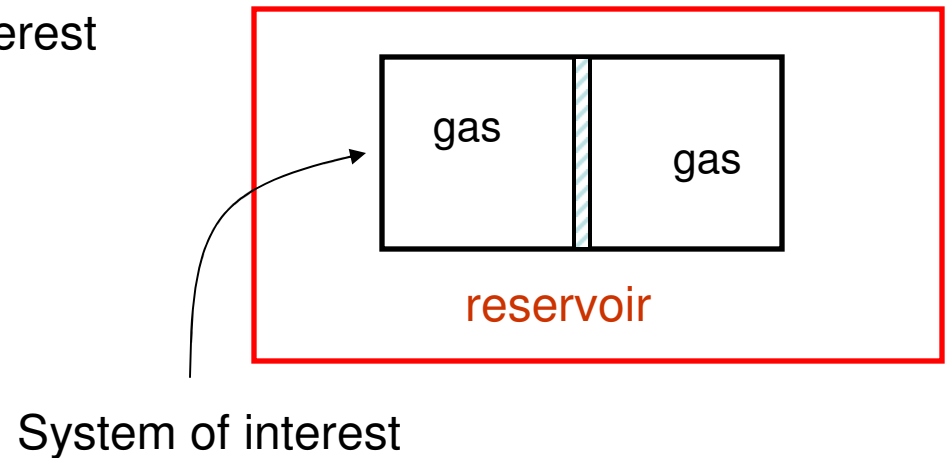# *Proof of the minimum principle for Helmholtz free energy*

Consider a composite system in thermal contact with a thermal reservoir.

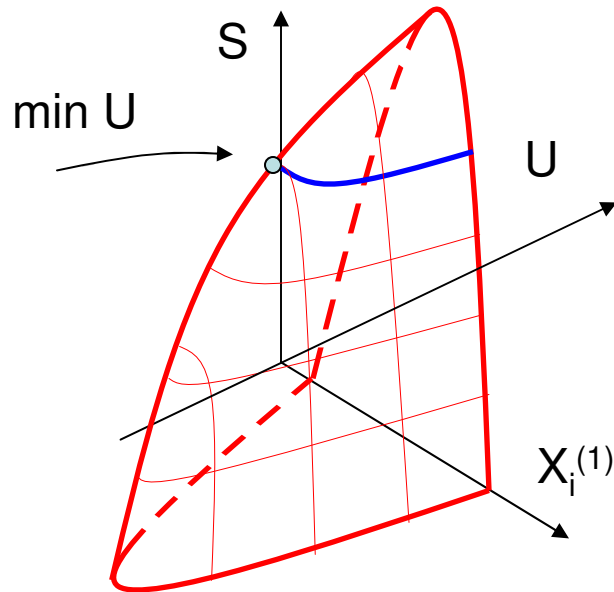U – internal energy of the system of interest

U_r – internal energy of the reservoir

S – entropy of the system of interest

S_r – entropy of the reservoir

gas

gas

reservoir

System of interest

The internal energy minimum principle

If we know the entropy S of the system + reservoir, then there is only one point on the line S = const that describes an equilibrium state of the composite system.

This point corresponds to the maximum of entropy with respect to the unconstrained variable.

From geometrical considerations and the fact that $dS/dU > 0$, the same point is the minimum of internal energy at S = const
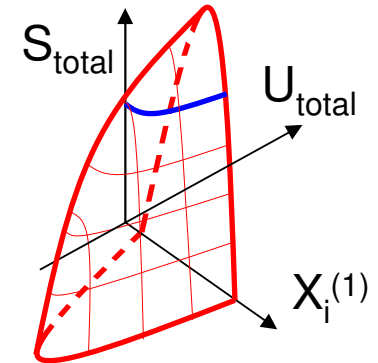
Therefore, the state of equilibrium of system + reservoir for a given total entropy is achieved at the minimum of internal energy U of the system + reservoir.

Proof of the minimum principle for Helmholtz free energy

We know that the internal energy of the composite system + reservoir is at minimum in equilibrium:

$$d(U + U_r) = 0 \qquad d^2(U + U_r) > 0$$

On the surface of constant entropy: $\qquad d(S + S_r) = 0$

We can also show that the internal energy of the system of interest itself is at minimum:

$$d^2(U + U_r) > 0 \implies d^2 U > 0 \qquad \text{because} \qquad d^2 U \gg d^2 U_r$$

Proof of the minimum principle for Helmholtz free energy

To prove: $d^2 U \gg d^2 U_r$

$$d^2 U_r = \sum_{j,k} \frac{\partial^2 U^r}{\partial X_j^r \partial X_k^r} dX_j^r dX_k^r \qquad \text{and} \qquad \frac{\partial^2 U^r}{\partial X_j^r \partial X_k^r} \sim \frac{N^r}{N^r N^r} \sim \frac{1}{N^r}$$

Thus $$\frac{\partial^2 U^r}{\partial X_j^r \partial X_k^r} \ll \frac{\partial^2 U}{\partial X_j \partial X_k}$$

This condition is true because the reservoir is much larger than the composite system of interest.

Proof of the minimum principle for Helmholtz free energy

$$d\left(S + S_r\right) = 0 \implies dS_r = -dS$$

$$d\left(U + U_r\right) = \ldots + TdS + T^r dS^r = \ldots + TdS - T^r dS = 0$$

For arbitrary small dS:

$$d\left(U + U_r\right) = \ldots + (T - T^r)dS = 0 \implies T = T^r$$

Proof of the minimum principle for Helmholtz free energy

Since no work is done on the reservoir (walls with thermal reservoir are rigid):

$$d(U + U_r) = dU + T^r dS^r = 0$$

since $\quad d(S + S_r) = 0 \quad \Longrightarrow \quad dU - T^r dS = 0$

Because T^r is constant: $\quad d(U - T^r S) = 0$

Therefore, the quantity $\quad U - T^r S \quad$ has an extremum in equilibrium.

# *Proof of the minimum principle for Helmholtz free energy*

$$d\left(U - T^r S\right) = 0$$

One can also show that $\quad d^2\left(U - T^r S\right) > 0 \quad$ so the extremum is a minimum

We know that $\quad T = T^r \quad$ in our case of the system in contact with

the thermal reservoir. Therefore we can replace T^r with T.

$$\boxed{d\left(U - TS\right) = dF = 0}$$

Utility of the Helmholtz free energy: Example

For example, let us consider a system that consists of two chambers filled with N_1 and N_2 moles of ideal gas and separated by a movable impermeable piston. We need to find the equilibrium state of the system.

gas

gas

reservoir T^r
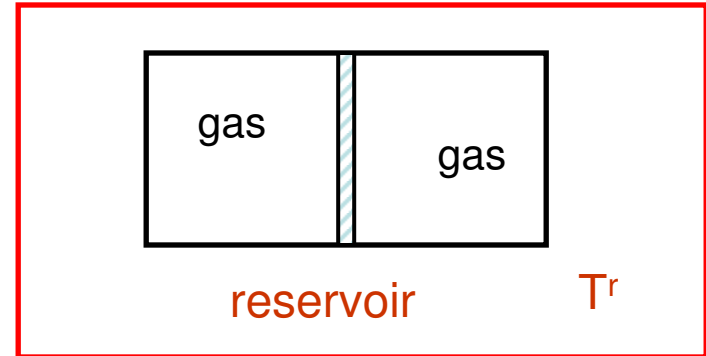
The only unconstrained extensive variable of the free energy $F(T,V,N)$ is volume

$$dF = 0 = d(F_1 + F_2) \implies \left(\frac{\partial F_1}{\partial V_1}\right)_T - \left(\frac{\partial F_2}{\partial V_2}\right)_T = 0 = -(P_1 - P_2)$$

$$P = \frac{RT}{v} \implies \frac{RT^r}{v_1} = \frac{RT^r}{v_2} \implies v_1 = v_2 \implies \frac{V_1}{N_1} = \frac{V_2}{N_2}$$

Utility of the Helmholtz free energy: Example

$$\frac{V_1}{N_1} = \frac{V_2}{N_2}$$

In addition $V_1 + V_2 = V_t$ where V_t is the total volume of the composite system.

Therefore: $\qquad V_1 = \frac{N_1}{N_1 + N_2} V_t \qquad\qquad V_2 = \frac{N_2}{N_1 + N_2} V_t$

Here we solved two equations with two unknowns (V_1 and V_2). If we were to minimize the internal energy, we would have to solve five equations with five unknowns (V_1, V_2, S_1, S_2 and S^r).

Why is the Helmholtz potential called "free energy"?

The Helmholtz potential **F(T,V,N,...)** characterizes the maximum work one can extract from a system at constant temperature (in contact with a thermal reservoir). It is the energy that is "free" to be converted into work at constant T.

To find maximum work, we need to consider a reversible process: $dS = -dS^r$
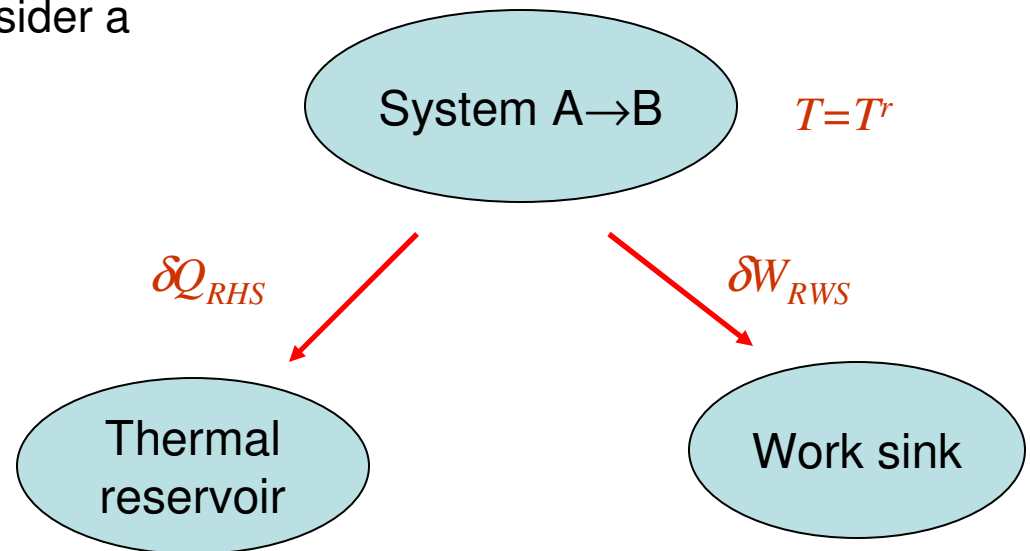
$dU = U_B - U_A = -\delta W_{RWS} - \delta Q_{RHS}$

$\delta W_{RWS} = -dU - \delta Q_{RHS}$

$\delta W_{RWS} = -dU - T^r dS^r$

$\delta W_{RWS} = -dU + T^r dS$

$\delta W_{RWS} = -(dU - T dS)$

$\delta W_{RWS} = -dF$

System A→B $T=T^r$

δQ_{RHS} δW_{RWS}

Thermal reservoir   Work sink

Work is equal to the decrease of free energy of the system!