CHM 421/621
Statistical Mechanics

Lecture 19 Alternative Extermination Principles

Introduction and Review

Lecture Plan

Review of Thermodynamics

Basic Formalism

Conditions of Equilibrium

Equilibrium Relations

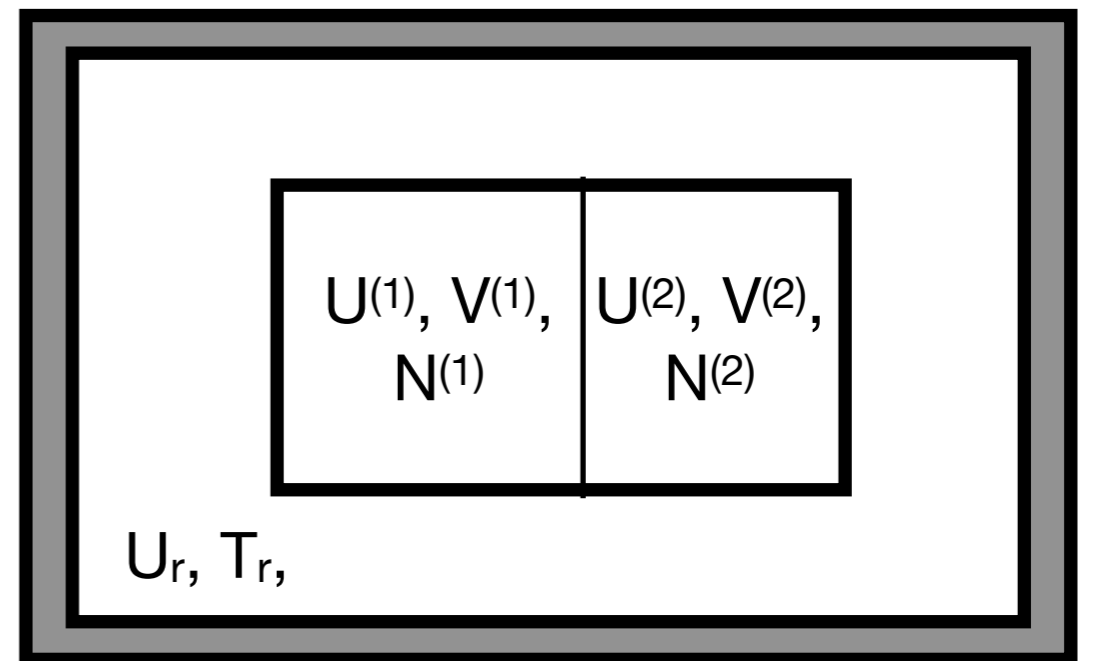Legendre Transformed Representations

Stability of Thermodynamic Systems

Legendre Transformations

Extremisation principle in the transformed representations :

It is desirable to have an extermination principle in the L.T. representations to check for thermodynamic equilibrium.

Consider a composite system in thermal contact with a heat reservoir at temperature T_r.

Suppose some internal constraint in the composite system is removed. We need a mathematical condition to predict the resulting equilibrium state.

$U^{(1)}, V^{(1)}, N^{(1)}$ $\quad$ $U^{(2)}, V^{(2)}, N^{(2)}$

$U_r, T_r,$

Thermal/Heat reservoir: A reversible heat source that is so large that any heat transfer interest does not alter its temperature.
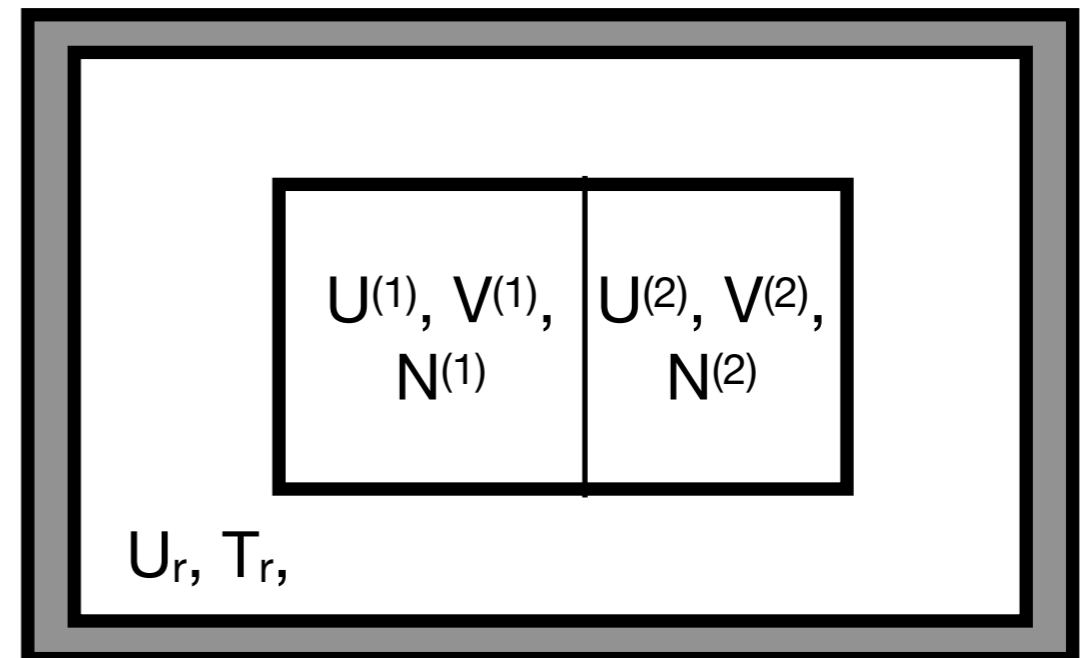
$$N_r \to \infty$$

Legendre Transformations

Extremisation principle in the transformed representations :

At equilibrium the total energy of the system + reservoir is a minimum at constant entropy.

$$\implies \quad \begin{aligned} d(U + U_r) &= 0 \\ d(S + S_r) &= 0 \\ d^2(U + U_r) &= d^2 U > 0 \end{aligned}$$

Why?

$$d^2 U_r \sim \frac{\partial^2 U_r}{\partial X_j^r \partial X_k^r} dX_j^r dX_k^r$$

$$\frac{\partial^2 U_r}{\partial X_j^r \partial X_k^r} \sim \frac{1}{N_r}$$

U(1), V(1), N(1)

U(2), V(2), N(2)

Ur, Tr,

Legendre Transformations

Extremisation principle in the transformed representations :

Consider a diathermal, impermeable rigid wall separating sub-systems.

$$dU|_{V,N} = T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)}$$

$$
\begin{aligned}
d(U + U_r)|_{V,N} &= T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)} + T^r dS^r \\
&= T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)} - T^r(dS^{(1)} + dS^{(2)}) \\
&= (T^{(1)} - T_r)dS^{(1)} + (T^{(2)} - T_r)dS^{(2)} = 0
\end{aligned}
$$

$$\boxed{\implies T^{(1)} = T^{(2)} = T_r}$$ 0th Law

Legendre Transformations

Extremisation principle in the transformed representations :

Since for the reservoir $\quad dU_r = T_r dS_r$

$$d(U + U_r) = dU + T_r dS_r = 0$$

Or, since total entropy is constant,

$$dU - T_r dS = 0$$
$$d(U - T_r S) = 0$$

Since T_r is constant and S is an independent variable, we get

$$d^2 U = d^2(U - T_r S) > 0$$

Legendre Transformations

Extremisation principle in the transformed representations :

Given that the temperature of the system (T) is the same as that of the reservoir at thermal equilibrium we can just look for the minimum of

$$F = U - TS$$

Subject to the condition that $T = T_r$.

Helmholtz potential minimum principle

Thus, the equilibrium value of any unconstrained internal parameter in a system in diathermal contact with a heat reservoir minimises the Helmholtz free energy over a manifold of states for which $T = T_r$.

Legendre Transformations

**Extremisation principle in the transformed representations :**

Similar principles can be derived for the other potentials as well

Intensive variables controlled	Relevant Potential	Condition for equilibrium	
T	F	Minimized	
P	H	Minimized	**w.r.t unconstrained variables**
T, P	G	Minimized	
$P_1, P_2, \ldots$	$U[P_1, P_2, \ldots]$	Minimized	

Legendre Transformations

Physical meaning of Thermodynamic Potentials:

Helmholtz free energy

diathermal   adiabatic

Thermal
Reservoir   System   Reversible
Work
Source
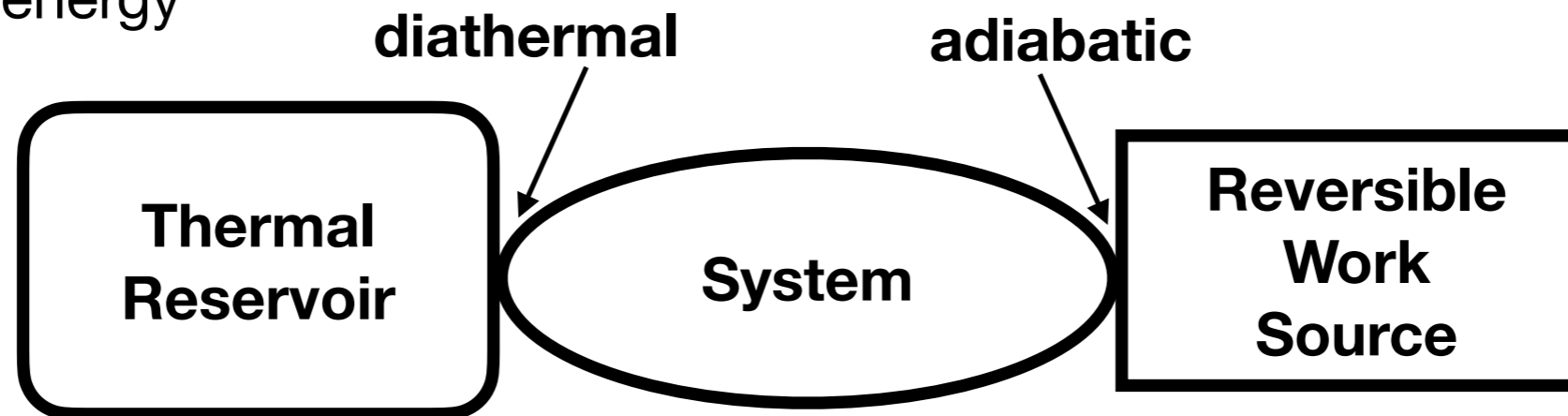
In any reversible process in the system,

$$dU = \delta W + \delta Q \implies dU_r = -\delta Q$$

since heat given out by system is taken up by thermal reservoir.
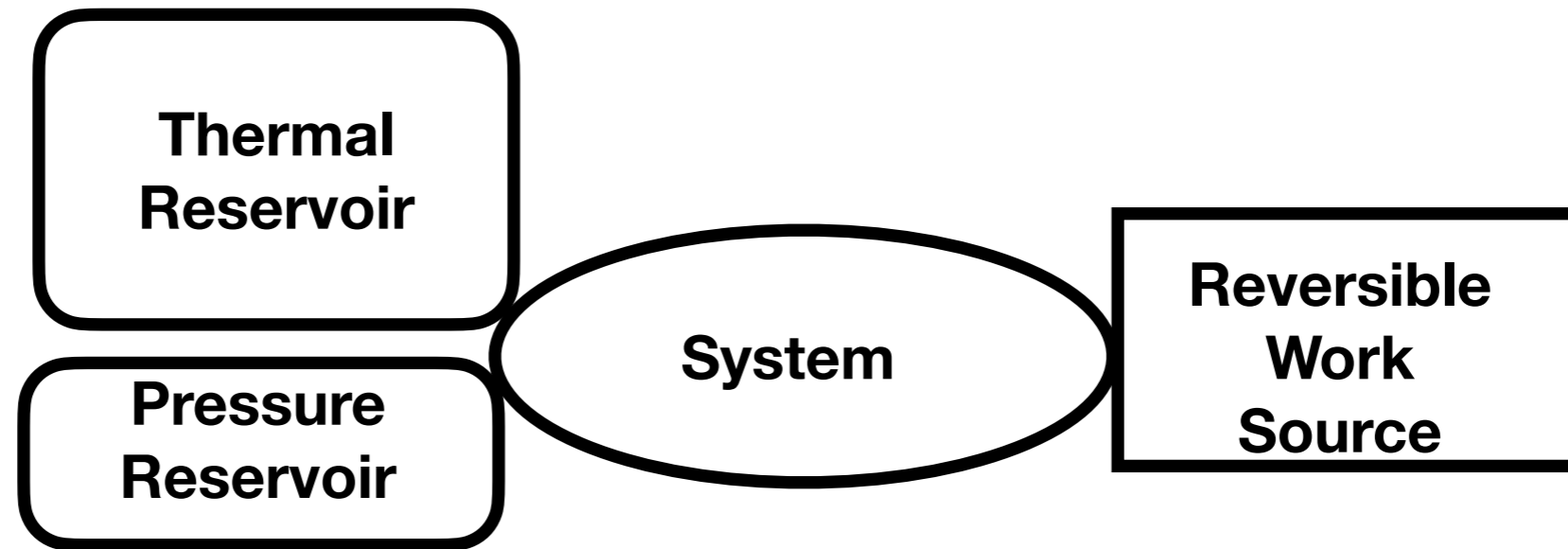
Work done by system is used up by work source

$$\implies \delta W_{RWS} = -\delta W = -dU + \delta Q$$
$$= -dU - dU_r = -dU - T_r dS_r$$
$$= -d(U - T_r S) = -dF$$

The decrease in Helmholtz free energy is equal to the reversible work delivered by the system when in contact with a thermal reservoir.

Legendre Transformations

Physical meaning of Thermodynamic Potentials:

Gibbs free energy

In any reversible process in the system,

$$dU = -dU_r + P_r dV_r + \delta W_{non-mech}$$

$$= T_r dS - P_r dV + \delta W_{non-mech}$$

$$\implies \delta W_{non-mech} = d(U - T_r S + P_r V)$$

$$= d(U - TS + PV) = dG$$

Or $\quad \delta W_{RWS} = -\delta W_{non-mech} = -dG$

The decrease in Gibbs free energy is equal to the reversible non-mechanical work delivered by the system when in contact with thermal and a pressure reservoirs.