CHM 421/621
Statistical Mechanics

Lecture 17 Alternative Formulations

Introduction and Review

Lecture Plan

Review of Thermodynamics

Basic Formalism

Conditions of Equilibrium

Equilibrium Relations

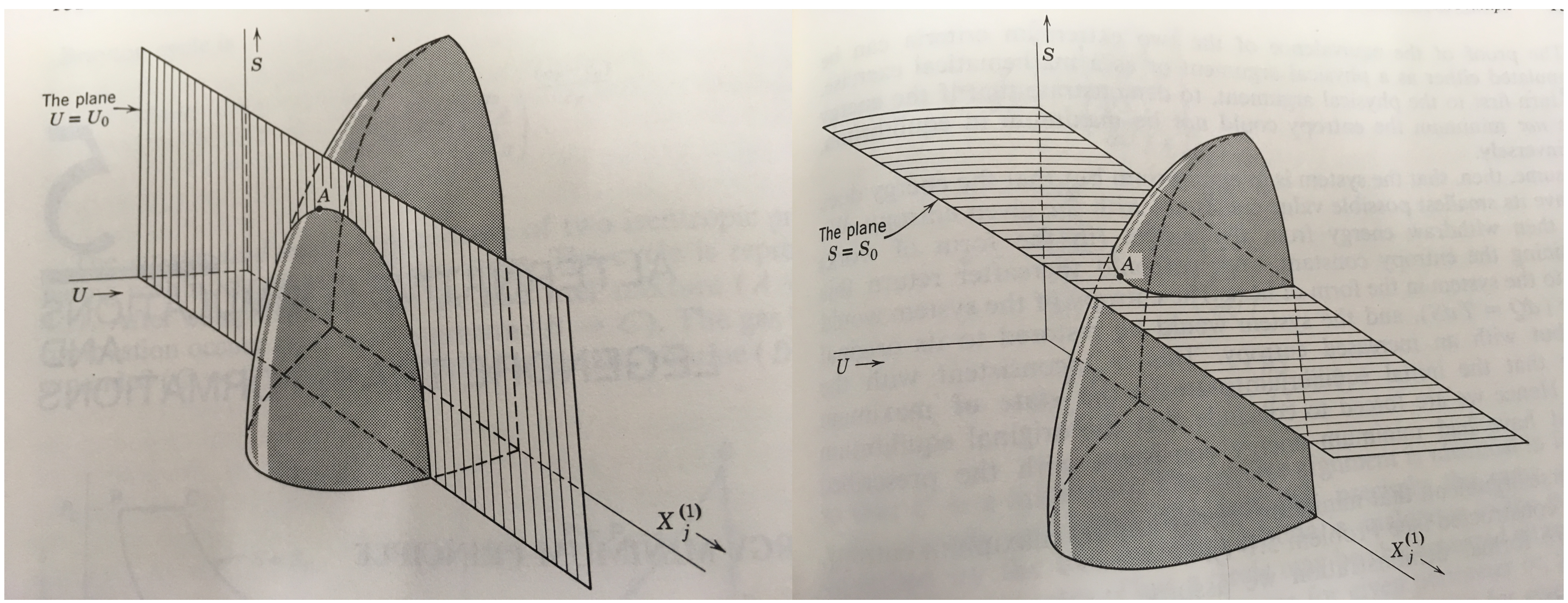
Legendre Transformed Representations

Stability of Thermodynamic Systems

Alternative formulations

Minimum energy principle

The equilibrium value of any unconstrained internal parameter is such as to minimise the energy for the given value of the total entropy.



Taken from Callen, Sec. 5-1

The properties of thee fundamental equation, i.e., t*he single-valuedness of U w.r.t. S and* $\left(\frac{\partial S}{\partial U}\right)_X > 0$ ensure that this can happen.

Alternative formulations

Minimum energy principle

Proof :

Consider a composite system. At a given energy *U* we have that

Entropy maximisation => $\left(\frac{\partial S}{\partial X}\right)_U = 0$ and $\left(\frac{\partial^2 S}{\partial X^2}\right)_U < 0$

where we have denoted a generic extensive parameter for one of the sub-systems as *X* for simplicity of notation. We also take it to be implicit that all other parameters are held fixed in the derivative.

We further assume the following notation for the corresponding (energetic) conjugate variables

$$P \equiv \left(\frac{\partial U}{\partial X}\right)_S$$

Alternative formulations

Minimum energy principle

Proof :

Now,

$$P = \left(\frac{\partial U}{\partial X}\right)_S = -T\left(\frac{\partial S}{\partial X}\right)_U$$

How?

$$= 0$$

=> *U* has an extremum at the same point *X*.

Now to classify the extremum as a maximum or a minimum …

Alternative formulations

Minimum energy principle

Proof :

Let's calculate $\left(\frac{\partial^2 U}{\partial X^2}\right)_S$

$$= \left(\frac{\partial P}{\partial X}\right)_S$$

$$= \left(\frac{\partial P}{\partial U}\right)_X \left(\frac{\partial U}{\partial X}\right)_S + \left(\frac{\partial P}{\partial X}\right)_U$$

How?

$$= \left(\frac{\partial P}{\partial U}\right)_X P + \left(\frac{\partial P}{\partial X}\right)_U \quad = \left(\frac{\partial P}{\partial X}\right)_U$$

At *P* = *0*

Thus, *U* is minimum!

$$= -T\frac{\partial^2 S}{\partial X^2} > 0$$

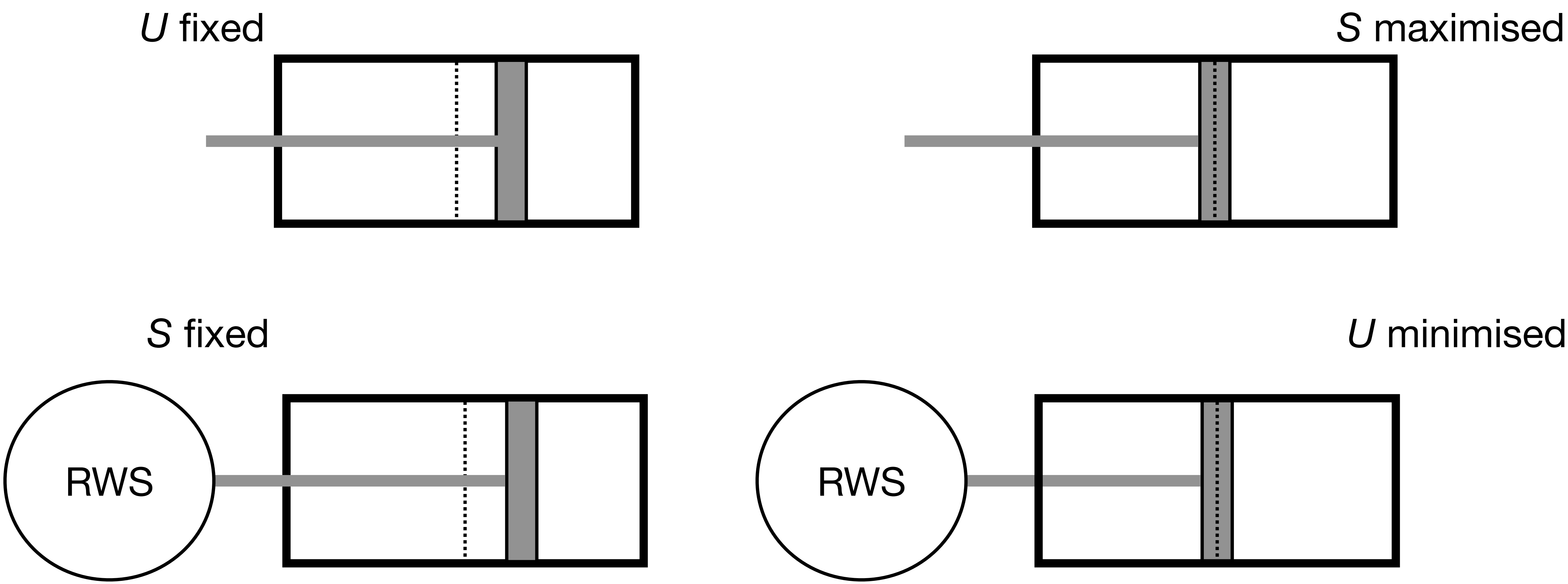
at $\frac{\partial S}{\partial X} = 0$

How?

Alternative formulations

Minimum energy principle

Illustration :



Can use this principle instead of entropy maximisation for solving problems.