CHM 421/621
Statistical Mechanics

Lecture 7 Intensive variables and Equilibrium

Introduction and Review

Lecture Plan

Review of Thermodynamics

Basic Formalism

- Extensive variables and equilibrium states
- Fundamental question in thermodynamics
- Entropy function
- Postulates regarding entropy function

Conditions of Equilibrium

Equilibrium Relations

Legendre Transformed Representations

Stability of Thermodynamic Systems

Basic Formalism

Entropy Function

Postulate 2: There exists a function, called the entropy *S,* of the extensive parameters of any composite system, defined for all equilibrium states and having the following property:

The values assumed by the extensive parameters in the absence (removal) of an internal constraint are those that maximise the entropy over the manifold of constrained equilibrium states.

$$S \equiv S(U, V, N) \xrightarrow{\hspace{2cm}} \text{Fundamental Relation}$$

At equilibrium, $dS = 0$

Also called the entropy maximisation postulate.

Basic Formalism

Entropy Function

For a composite system in the presence of internal constraints

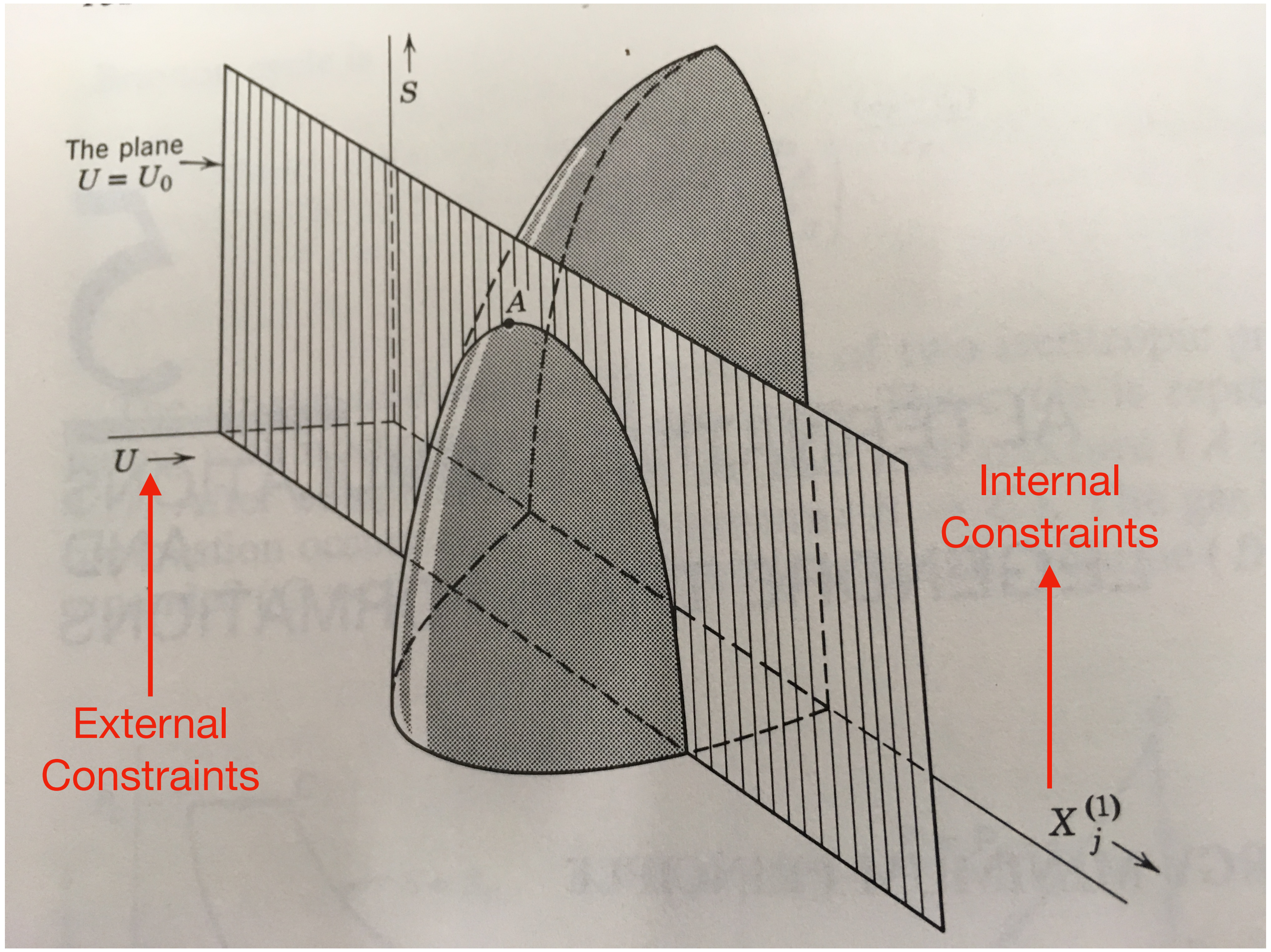
$$S \equiv S(U, V, N; U^{(1)}, V^{(1)}, N^{(1)})$$

Every such (equilibrium) state is presumed to achievable by application of appropriate constraints/walls.

Manifold of constrained states

The set of all equilibrium states corresponding to the same total (*U*,*V*,*N*) but different ($U^{(1)}$,$V^{(1)}$,$N^{(1)}$).

Entropy maximisation postulate



E.g. $\max_{V^{(1)}} \left\{ S(U, V, N; U^{(1)}, V^{(1)}, N^{(1)}) \right\}$

Basic Formalism

Postulates Regarding Entropy Function

Postulate 3: The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous, differentiable and a monotonically increasing function of the energy.

$$S = \sum_{\alpha} S^{(\alpha)}$$

Where $S^{(\alpha)} \equiv S^{(\alpha)}(U^{(\alpha)}, V^{(\alpha)}, N^{(\alpha)})$

Additivity property also implies that for a simple system the entropy is a homogenous function of the extensive parameters.

$$\boxed{S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)}$$

Basic Formalism

Postulates Regarding Entropy Function

Postulate 3: The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous, differentiable and a monotonically increasing function of the energy.

Note that the extensivity of *S, U, V* allow us to scale the properties of a system of *N* moles from this of a system of 1 mole.

i.e. $$S(U,V,N) = N\ S(U/N, V/N, 1) \equiv N\ s(u,v)$$

Molar quantities

Basic Formalism

Postulates Regarding Entropy Function

Postulate 3: The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous, differentiable and a monotonically increasing function of the energy.

Monotonicity implies that

$$\boxed{\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0}$$

This is an important requirement because, as it turns out, the reciprocal of this derivative will be the temperature of the system.

Basic Formalism

Postulates Regarding Entropy Function

Postulate 3: The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous, differentiable and a monotonically increasing function of the energy.

Continuity, differentiability and monotonicity imply that the entropy can be inverted w.r.t. the energy and that the latter is a single-valued, continuous, differentiable function of *S,V,N*.

i.e. $S \equiv S(U,V,N) \Longrightarrow U \equiv U(S,V,N)$

Energy Fundamental Relation

Basic Formalism

Postulates Regarding Entropy Function

Postulate 4: The entropy of any system vanishes in the state for which

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = 0$$

The immediate implication is that unlike *U, S* has a uniquely defined zero.

Connections to third law of thermodynamics.

Basic Formalism

Exercise

Is the following a valid fundamental relation?

(a)

$$S = \left(\frac{R}{\theta}\right)^{\frac{1}{3}} \left(\frac{NU}{V}\right)^{\frac{2}{3}}$$

No. *S* is not extensive.

(b)

$$S = \left(\frac{R^2}{\theta v_0}\right)^{\frac{1}{3}} (NVU)^{\frac{1}{3}}$$

Yes.

(c)

$$S = \left(\frac{R^2\theta}{\theta v_0^3}\right) \frac{V^3}{NU}$$

No. *S* is not a monotonically increasing function of U

Basic Formalism

The program

- Set up fundamental equation
- By differentiation determine extrema (equilibrium)
- From second derivatives determine if each extremum stable or unstable
- Derive *U,V,N* from the stable extremum

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{V,U} dN$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

Basic Formalism

Intensive variables

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

$$T \qquad\qquad -P \qquad\qquad \mu$$

Compare with $dU = TdS - PdV + \mu dN$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{V,U} dN$$

$$\frac{1}{T} \qquad\qquad \frac{P}{T} \qquad\qquad -\frac{\mu}{T}$$

Basic Formalism

Intensive variables

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N,X} dS + \sum_j \left(\frac{\partial U}{\partial X_j}\right)_{S,N,X} dX_j$$

$$T \qquad\qquad\qquad\qquad\qquad P_j$$

$$dU = TdS + \sum_j P_j dX_j$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N,X} dU + \sum_j \left(\frac{\partial S}{\partial X_j}\right)_{U,N,X} dX_j$$

$$\frac{1}{T} \qquad\qquad\qquad\qquad\qquad -\frac{P_j}{T}$$

X_j -> Generalized Displacement

P_j -> Generalized forces

Note: When $X_j = V$

$P_j = -P$

Basic Formalism

Intensive variables (multi-component system)

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \sum_{j=1}^{r} \left(\frac{\partial U}{\partial N_j}\right)_{S,V} dN_j$$

T Temperature

$-P$ Pressure

μ_j Electrochemical potential of j^{th} component

$$dU = TdS - PdV + \mu_1 dN_1 + \cdots + \mu_r dN_r$$

Note that when N_j are kept constant then, since $-PdV$ is just the mechanical work done, we can write

$$TdS = dU - \delta W = \delta Q$$

Quasi-static heat flux into the system

Basic Formalism

Equations of state

The definition of the intensive variables imply that

$$T = T(S, V, N_1, N_2, ..., N_r)$$

$$P = P(S, V, N_1, N_2, ..., N_r)$$

$$\mu_j = \mu_j(S, V, N_1, N_2, ..., N_r)$$

Such relationships, expressing intensive parameters as functions of the independent extensive parameters are called *equations of state*.

In the general notation for extensive variables

$$T = T(S, X_1, X_2, ...)$$

$$P_j = P_j(S, X_1, X_2, ...)$$

Basic Formalism

Equations of state

The fact that *U* is homogenous first order functions of the extensive parameters means that

$$T(\lambda S, \lambda V, \lambda N_1, ..., \lambda N_r) = T(S, V, N_1, ..., N_r)$$

i.e. *T* is homogenous zero order function of extensive parameters.
Similarly for *P* and μ_j.

Thus, temperature (pressure) of a portion of a system is the same as the temperature of the whole system.

Basic Formalism

Exercise

Find the three equations state for a system with the fundamental equation

$$U = \left(\frac{v_0\theta}{R^2}\right)\frac{S^3}{NV}$$

Answer

$$T = \left(\frac{3v_0\theta}{R^2}\right)\frac{S^2}{NV}$$

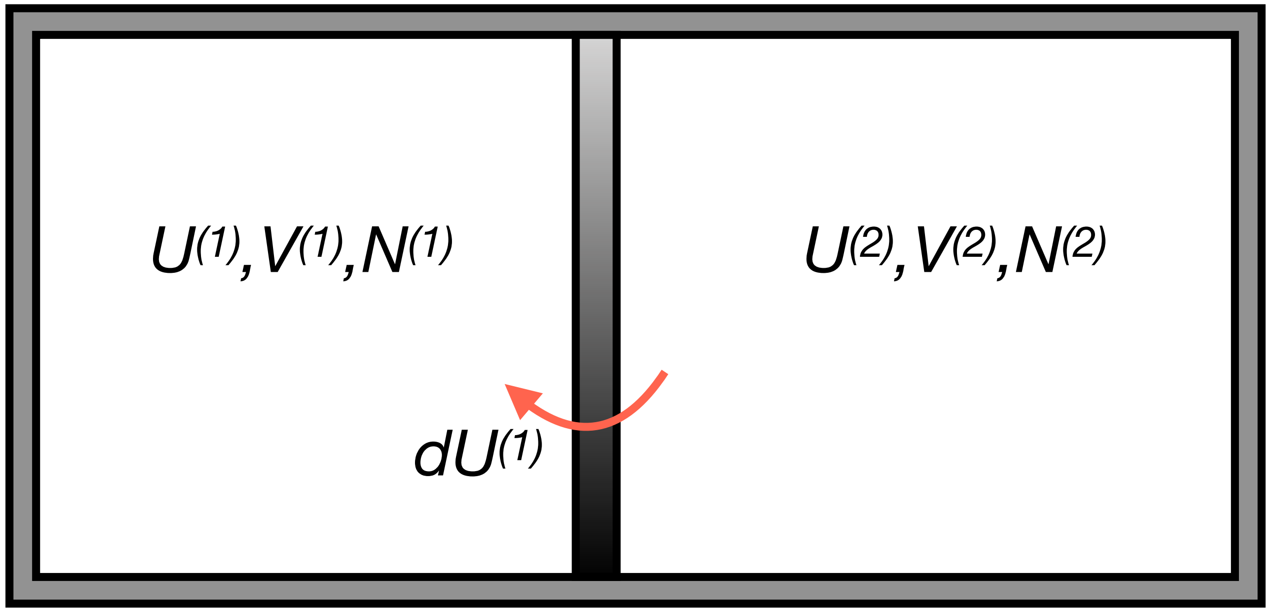
$$P = \left(\frac{v_0\theta}{R^2}\right)\frac{S^3}{NV^2}$$

$$\mu = -\left(\frac{v_0\theta}{R^2}\right)\frac{S^3}{N^2V}$$

Basic Formalism

Conditions of Equilibrium (Thermal)

Consider a closed system with a rigid, adiabatic and impermeable partition separating two subsystems 1 and 2.



Partition is made diathermal. Under what conditions would no heat flow occur?

$$U = U^{(1)} + U^{(2)} = \text{Constant}$$

$N, V, N^{(i)}, V^{(i)}$ are Constant

$$S = S^{(1)} + S^{(2)}$$

At equilibrium, an infinitesimal transfer of internal energy *dU* from system 2 to 1 will not change the entropy of the system

$$dS = dS^{(1)} + dS^{(2)} = 0$$

Basic Formalism

Conditions of Equilibrium (Thermal)

$$dS = dS^{(1)} + dS^{(2)} = 0$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU^{(1)} = 0$$

Since *dN* and *dV* are 0 for both subsystems

$$\Longrightarrow \boxed{T_1 = T_2}$$

Thus, the heat flow would stop when the two temperatures are equal.

Direction of flow

If T_1 and T_2 are initial temperatures (differing only slightly) before the wall is made diathermal then

$$\Delta S \approx \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Delta U > 0$$

Thus, the direction of transfer is from high to low temperature.

$$T_1 > T_2 \implies \Delta U < 0$$