

CHM 421/621

Statistical Mechanics

Lecture 15 Maxwell's Relations

Introduction and Review

Lecture Plan

Review of Thermodynamics

Basic Formalism

Conditions of Equilibrium

Equilibrium Relations

Legendre Transformed Representations

Stability of Thermodynamic Systems

Stability of Thermodynamic Systems

Stability criteria for thermodynamic potentials

Similar criteria can be derived for the other potentials

$$U(S + \Delta S, V + \Delta V, N) + U(S - \Delta S, V - \Delta V, N) \geq 2U(S, V, N)$$

i.e. the stable energy surface should lie above its target planes (convex).

Locally this leads to

$$\begin{aligned}\frac{\partial^2 U}{\partial S^2} &= \frac{\partial T}{\partial S} \geq 0 \\ \frac{\partial^2 U}{\partial V^2} &= -\frac{\partial P}{\partial V} \geq 0 \\ \frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \frac{\partial^2 U}{\partial S \partial V} &\leq 0\end{aligned}$$

Stability of Thermodynamic Systems

Stability criteria for thermodynamic potentials

These results can be extended easily to the Legendre transforms of the energy.

$$P_j = \frac{\partial U}{\partial X_j} \quad X_j = -\frac{\partial U[P_j]}{\partial P_j}$$
$$\implies \frac{\partial X_j}{\partial P_j} = -\frac{\partial^2 U[P_j]}{\partial P_j^2} = 1 / \frac{\partial^2 U}{\partial X_j^2}$$

Thus, the sign of $\frac{\partial^2 U[P]}{\partial P^2}$ is opposite to the sign of $\frac{\partial^2 U}{\partial X^2}$

i.e., if U is a convex function of X then $U[P]$ is a concave function of P .

Stability of Thermodynamic Systems

Stability criteria for thermodynamic potentials

Thus, for Helmholtz potential we have, since $F = U[T]$,

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} \leq 0 \quad \left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} \geq 0$$

For Enthalpy we have, since $H = U[P]$,

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} \geq 0 \quad \left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} \leq 0$$

For Gibbs free energy we have, since $G = U[P, T]$,

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \leq 0 \quad \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \leq 0$$

Therefore, for constant N , the thermodynamic potentials are concave functions of their extensive variables and convex functions of their intensive variables.

Stability of Thermodynamic Systems

Physical significance of stability criteria

The isothermal compressibility of a stable thermodynamic system **must** always be positive. i.e. $\kappa_T > 0$

Why?

You can also show that

$$c_P \geq c_v \geq 0$$

$$\kappa_T \geq \kappa_S \geq 0$$

Home-work

Maxwell Relations

Equivalence of mixed derivatives

$$\frac{\partial^2 U}{\partial X_i \partial X_j} = \frac{\partial^2 U}{\partial X_j \partial X_i}$$

$$\frac{\partial P_j}{\partial X_i} = \frac{\partial P_i}{\partial X_j}$$

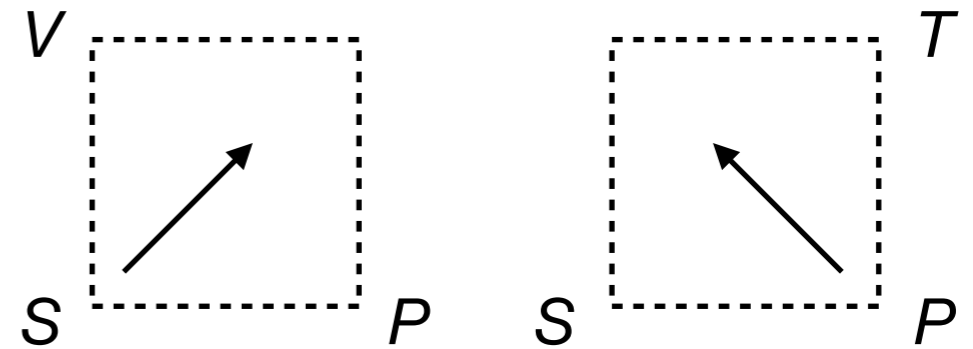
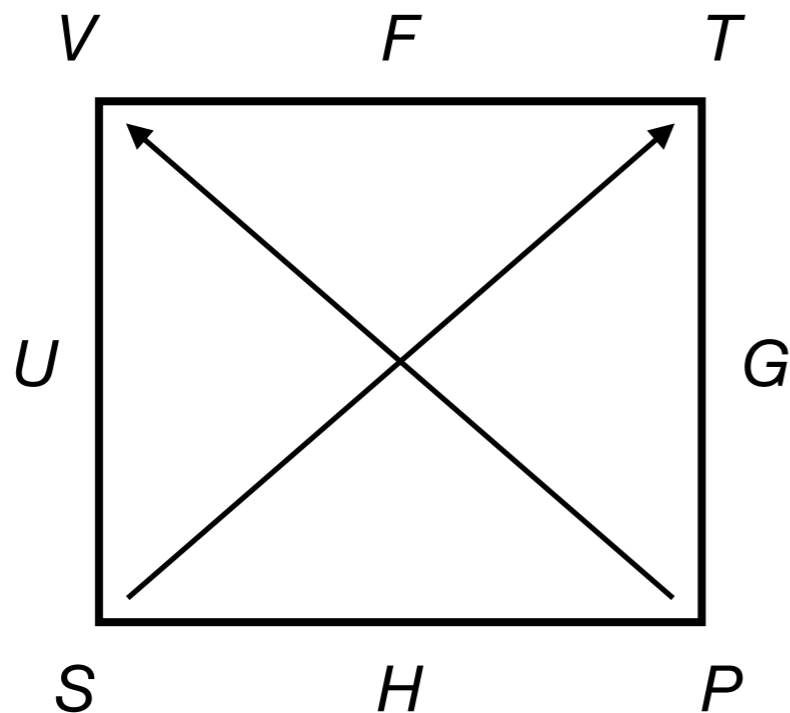
E.g.

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = - \left(\frac{\partial P}{\partial S}\right)_{V,N}$$

Similar relations can also be derived from other thermodynamic potentials as well.

Maxwell Relations

Mnemonic



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

Valid Facts and Theoretical Understanding Generate Solutions to Hard Problems

- For other derivatives rotate the square (with arrows) so that the quantity in the numerator is always at right or left top corners.
- If arrows appear unsymmetrical then add a minus sign to one side of the equation.

Maxwell Relations

Problem 1.

In the immediate vicinity of the state T_0, v_0 the volume of particular system of 1 mole is observed to vary according to the relationship

$$v = v_0 + a(T - T_0) + b(P - P_0)$$

Calculate the heat transfer dQ to the system if the molar volume is changed by a small increment $dv = v - v_0$ at constant temperature T_0 .

Solution: Since heat is transferred *via* volume change, we need to relate the entropy change to the volume change.

Now,

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{\left(\frac{s}{P}\right)_T}{\left(\frac{v}{P}\right)_T}$$
$$= -\left(\frac{\partial v}{\partial T}\right)_P \frac{1}{b} = -a/b$$

Therefore,

$$\partial Q = T_0 dS = T_0 \left(\frac{\partial s}{\partial v}\right)_T dv = -\frac{T_0 a (v - v_0)}{b}$$

Where we have used a Maxwell relation and the given $v(T,P)$.

Maxwell Relations

Problem 2.

Derive the following relations

$$TdS = C_v dT + \frac{T\alpha}{\kappa_T} dV$$

$$TdS = C_P dT - TV\alpha dP$$

$$c_v = c_p - \frac{Tv\alpha^2}{\kappa_T}$$

Maxwell Relations

Reducing derivatives

All first and second derivatives in thermodynamics can be cast in terms of three basic derivatives

$$-\frac{c_P}{T} = \left(\frac{\partial^2 g}{\partial T^2} \right)_P = - \left(\frac{\partial s}{\partial T} \right)_P$$

$$v\alpha = \left(\frac{\partial^2 g}{\partial T \partial P} \right) = \left(\frac{\partial v}{\partial T} \right)_P$$

$$-v\kappa_T = \left(\frac{\partial^2 g}{\partial P^2} \right)_T = \left(\frac{\partial v}{\partial P} \right)_T$$

Here s , v and g are molar entropy, volume and Gibbs free energy. Similarly, c_v and c_P are specific heat capacities (per mole).

Maxwell Relations

Problem 3.

Reduce the following derivative into the basic derivatives.

$$\left(\frac{\partial P}{\partial U}\right)_{G.N}$$

Use the following:

$$\left(\frac{\partial X}{\partial Y}\right)_Z = 1 / \left(\frac{\partial Y}{\partial X}\right)_Z$$

$$\left(\frac{\partial X}{\partial Y}\right)_Z = \left(\frac{\partial X}{\partial W}\right)_Z / \left(\frac{\partial Y}{\partial W}\right)_Z$$

$$\left(\frac{\partial X}{\partial Y}\right)_Z = - \left(\frac{\partial Z}{\partial Y}\right)_X / \left(\frac{\partial Z}{\partial X}\right)_Y$$

Maxwell Relations

Solution

First show

$$\begin{aligned} \left(\frac{\partial P}{\partial U}\right)_{G,N} &= \left[\left(\frac{\partial U}{\partial P}\right)_{G,N}\right]^{-1} \\ &= \left[-T \frac{-S \left(\frac{\partial T}{\partial P}\right)_{S,N} + V}{-S \left(\frac{\partial T}{\partial S}\right)_{P,N}} + P \frac{-S \left(\frac{\partial T}{\partial P}\right)_{V,N} + V}{-S \left(\frac{\partial T}{\partial V}\right)_{P,N}}\right]^{-1} \end{aligned}$$

Rule 1. If the dvt. contains any potentials, bring them one by one to the numerator and eliminate using Maxwell relations.

Maxwell Relations

Solution

Rule 2. If any dvt. contains the entropy, bring it to the numerator. If one of the Maxwell relations now eliminates the entropy, invoke it. If not, use derivative with respect to T in both numerator and denominator of the dvt. The numerator would then be expressible as one of the specific heats (c_p or c_v).

Show that

$$\left(\frac{\partial T}{\partial P}\right)_{S,N} = vT\alpha/c_P$$

Maxwell Relations

Solution

Rule 3. Bring volume to the numerator. The remaining derivative will be expressible in terms of α and κ_T

Show that

$$\left(\frac{\partial T}{\partial P}\right)_{V,N} = \frac{\kappa_T}{\alpha}$$

Rule 4. If c_v appears, use the relation derived earlier to eliminate in favour of the 3 basic derivatives.