Theo. 4. Statistical Physics.

Lecture 16.

Felix Yu

December 11, 2023.

Last time: Thermodynamic potentials, external constraints
Enthalpy, Helmholtz free energy, Gibbs free energy.

Today: Maxwell's relations.

From last time:

Enthalpy: $H \equiv E - \vec{J}\cdot\vec{x}$

$$dH = TdS - x\cdot d\vec{J} \Rightarrow H(S,J)$$

for fixed mechanical work, no heat

Helmholtz F.E. $F \equiv E - TS$

$$dF = -SdT + \vec{J}\cdot d\vec{x} \Rightarrow F(T,\vec{x})$$

for heat transfer at const. temp.

Gibbs F.E. $G \equiv E - TS - \vec{J}\cdot\vec{x}$

$$dG = -SdT - \vec{x}\cdot d\vec{J} \Rightarrow G(T,\vec{J}).$$

for both mechanical work & heat transfer.

Grand: Heat and chemical work

$$\mathcal{G} \equiv E - TS - \vec{\mu}\cdot\vec{N}.$$

$$d\mathcal{G} = -SdT + \vec{J}\cdot d\vec{x} - \vec{N}\cdot d\vec{\mu} \Rightarrow \mathcal{G}(T,\vec{x},\vec{\mu})$$

For comparison,

$$dE = TdS + \vec{J}\cdot d\vec{x} + \vec{\mu}\cdot d\vec{N}$$

$$\Rightarrow E(S,\vec{x},\vec{N}).$$

As a reminder, $dE = \left(\frac{\partial E}{\partial S}\right)\Big|_{\vec{x},\vec{N}} dS + \left(\frac{\partial E}{\partial x_i}\right)\Big|_{S,x_{j\neq i},\vec{N}} dx_i + \left(\frac{\partial E}{\partial N_i}\right)\Big|_{S,\vec{x},N_{i\neq j}} dN_i$

Also as a reminder:

Partial derivatives can be inverted.

$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1$$

Cyclic change of ~~vars~~ partial vars:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Proof: Consider $x(y,z)$. and $z(x,y)$.

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Plug in to first equation:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x dy$$

Comparing LHS + RHS, we must require

$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1$$

$$\left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = 0 \Rightarrow -\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

Last reminder: double differentials commute.

For $f(x,y) \Rightarrow \quad \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$.

We now can generate nontrivial identities for systems in equilibrium as a result of the thermodynamic potentials constructed before.

$H(S, J)$ from $dH = TdS - \vec{x} \cdot d\vec{J}$.

$$\frac{\partial^2 H}{\partial S \partial J_i} = \frac{\partial^2 H}{\partial J_i \partial S}$$

$$\left(\frac{\partial T}{\partial J_i}\right)_S = -\left(\frac{\partial x_i}{\partial S}\right)_{J_i}$$

Explicit example: $W = -pV$, $dH = TdS + pdV$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$dE = \cancel{dQ} + \cancel{dW} = TdS - pdV$$

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

Can also generate other Maxwell relations from F+G.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

These are not important to memorize. Instead, should know the procedure.

It is also easy to understand the Maxwell relations from a cyclic process & studying the Jacobian of the double integral. (See Blundell & Blundell, p. 181).

Example of usefulness

Entropy of 1 mole of ideal gas.

$$pV = RT$$

$$S(T,V) \Rightarrow \quad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

We can use $$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

as heat capacities at const. volume & pressure, respectively.

Then $$dS = \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T}\right)_V dV$$

Then $$p = \frac{RT}{V} \Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$$

$$dS = \frac{C_V}{T} dT + \frac{R}{V} dV$$

Now it is integrable:

$$S = C_V \int \frac{dT}{T} + R \int \frac{dV}{V}$$

$$= C_V \ln T + R \ln V + \text{const.}$$

Next time: Thermodynamic stability.