

# Statistical Mechanics

Physics 406 at **University of Michigan**

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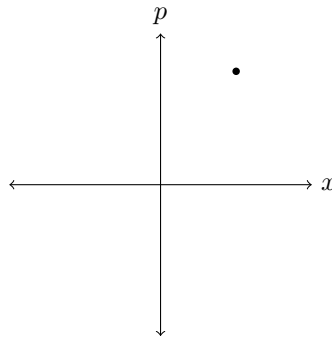
**Lecture 1.** (Jan 05) *States, Probability and Binomial Distribution*

Figure 1: Phase space of 1-D particle

**Lecture 2.** (Jan 10) *Ensembles*

Lagrange multipliers

$$S = -k \sum_r p_r \ln(p_r) \quad (0.1)$$

Microcanonical ensemble: All accessible microstate are equally probable

**Lecture 3.** (Jan 12) *Finding total microstate*

$N$  particles in volume  $V$  with energy between  $E, E + \delta E$ . Counting number of microstate by using phase space

simplifying example : a 1-D particle has only  $x$  and  $p$ . Plot in phase space Example in harmonic oscillator with ellipse and shading in  $\phi(E)$  and  $\Omega(E)$  Include text in caption explaining equations below it.

Moving to 3-D talk about degrees of freedom and volume of  $h_0$ .

Integrating to get  $\Phi(E)$  with multiintegrals and then taylor approx to get  $\Omega$

Quantum Description- specify microstate with quantum numbers

example with simp harmon oscill

**Lecture 4.** (Jan 19) *More on Microcanonical Ensemble*

$\Omega(E) = \#$  of states with energy between  $E + \delta E$

Describing energy levels of each particle, think N-cube

Now particle can interact!! Mechanical interactions and thermal interactions(both macro descriptions).

1 isolated system at equilibrium  $\rightarrow$  same system but with partition, now 2 systems.  $A^0$  is comprised of  $A, A'$ .

Macro parameters of  $A^0$  are for both states ( $N, V, E, T, \dots$ ).

**Thermal Interaction** External parameters of  $A, A'$  are fixed but mean energy transferred from one system to the other as a result of purely thermal interactions called heat. Probabilities of energy states can change when systems interact  $P(r)$

**Mechanical Interaction** External Parameters of  $A, A'$  change, one does *work* on the other! This causes the mean energies of  $A, A'$  to change.

$$\bar{E} = \sum_r p_r E_r$$

Pure thermal and purely mech example in inf sqwell

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## Lecture 5. (Jan 24)

Pure thermal interaction changes  $p_r$

Pure mechanical interaction changes  $E_r$

March 23rd

Stable vs unstable equilibrium

use gibbs and helmholts free energy

isolated system vs in contact with temp or pressure reservoir

equilibrium in contact

system A changes states, exchanging heat or work. How much work can it do?

Isolated system {Reservoir(A,  $T_0, P_0$ ) - work source} A does  $W^*$ , energy, volume, and entropy increase by  $\Delta E, \Delta V, \Delta S$

change of volume and entropy is opposite of change in A bc of first law  $W^* + \Delta E - \underbrace{P_0 \Delta V_0 + T \Delta S_0}_{\text{reservoir}} = 0$

2nd law says  $\Delta(S + S_0) \geq 0$  which means  $\Delta S_0 \geq -\Delta S$

Sub in to first law equation

$W^* \leq -\Delta(E - T_0 S + P_0 V) = -\Delta G_0$  Not Gibbs free energy bc  $T_0, P_0$  refer to reservoir, not to A, mixed with both variables.  $G_0 = G$  when A is in equilibrium with res

Since system is isolated, it starts and ends at  $T, P = T_0, P_0$

meaning  $W^* \leq -\Delta(E - TS + PV) = -\Delta G$  which is Gibb free energy.

System has fixed volume too,  $\Delta V = 0$

$W^* \leq -\Delta(E - T_0 S) = -\Delta G$

if  $T = T_0 \rightarrow W^* \leq -\Delta F$  Helmholtz for A.

$W^* \leq -\Delta G$  in general

$W^* \leq -\Delta F$  for fixed volume

So  $-\Delta G$  and  $-\Delta F$  are maximum work that can be done-! "Free" Energy!

Spontaneous process defined as process with  $W^* = 0$

$0 \leq -\Delta G_0 \rightarrow \Delta G_0 \leq 0 \rightarrow (G_{0f} - G_{0i}) \leq 0 \rightarrow \boxed{G_{0f} \leq G_{0i}}$

For fixed volume:  $\Delta F_0 \leq 0$

In equilibrium, systems in contact with T,P reservoirs, there can be no change in gibbs or helmholtz, meaning that final can't be less than initial, meaning that it must be a minimum!

analogue (?) with of  $S = S_{max}$  for isolated sys in eq

Stability of thermo system. system A in reservoir, res has  $T_0, P_0$ . How do perterbations/fluctuations change  $G_0$ ? Thinking abt stabel vs unstable equilibrium.

Begin by characterizing A by  $T, V$ .

$$\left(\frac{\partial G_0}{\partial T}\right)_V = 0, \left(\frac{\partial G_0}{\partial V}\right)_T = 0$$

Expanding about minimum  $G_{min}$ .

$$G_0 = G_{min} + \frac{1}{2} \left(\frac{\partial^2 G_0}{\partial T^2}\right)_V \Big|_{G=G_{min}} (\Delta T)^2 + \frac{1}{2} \left(\frac{\partial^2 G_0}{\partial V^2}\right)_T \Big|_{G=G_{min}} (\Delta V)^2 + \frac{\partial G_0}{\partial TV} \Big|_{G=G_{min}} \Delta T \Delta V + \dots$$

Now calculate derivs.

$$\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V - T_0 \left(\frac{\partial S}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V - T_0 \left(\frac{\partial S}{\partial T}\right)_V$$

So  $T = T_0$

$$\left(\frac{\partial G_0}{\partial V}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T - T_0 \left(\frac{\partial S}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial T}\right)_V - p - T_0 \left(\frac{\partial S}{\partial T}\right)_V + p_0 = 0$$

so  $P = P_0$

$$\begin{aligned}\left(\frac{\partial^2 G_0}{\partial V^2}\right)_T &= T\left(\frac{\partial^2 S}{\partial V^2}\right)_T - \left(\frac{\partial P}{\partial V}\right)_T - T_0\left(\frac{\partial^2 S}{\partial V^2}\right)_T = -\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{V\kappa} \\ \left(\frac{\partial^2 G_0}{\partial T^2}\right)_V &= T\left(\frac{\partial^2 S}{\partial T^2}\right)_V + \left(\frac{\partial S}{\partial T}\right)_V - T_0 - \left(\frac{\partial^2 S}{\partial T^2}\right)_V \\ &= \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \\ \frac{\partial G_0}{\partial TV} &= T\frac{\partial S}{\partial TV} - T_0\frac{\partial S}{\partial TV} = 0\end{aligned}$$

Combining them all together to get:

$$G_0 = G_{min} + \underbrace{\frac{C_V}{2T_0}(\Delta T)^2 + \frac{1}{2V\kappa}(\Delta V)^2}_{\text{Must be } > 0 \text{ for stable}}$$

So stable if  $C_V$  and  $\kappa > 0$

Monday March 28th

Phase Transitions as applications of thermodynamic instability, aka  $C_V$  or  $\kappa < 0$ . Phase transitions accompany changes of internal energy of system.

Change in crystalline structure.

Change in conductor to superconductor.

Must consider non ideal gasses. Van-der Waals gas.

For 1 mol of VDW gas:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

Consider isotherms on p-v diagram in Desmos, there is a section for low T where  $\frac{\partial P}{\partial V} > 0$

System with 2 possible phases in contact with temp and pressure reservoir. Gibbs free energy.

$$G(T, P) \equiv G(T, P)/\text{mole} \quad \nu_i \equiv \# \text{ moles in phase } i$$

For equilibrium

$$G_T = \nu_1 g_1 + \nu_2 g_2$$

must be a minimum. Constraint is that

$$\nu_1 + \nu_2 = \nu$$

Three possibilities

- $g_1 < g_2$  At equilibrium  $G_T = \nu g_1$
- $g_1 > g_2$  At equilibrium  $G_T = \nu g_2$
- $g_1 = g_2$  At equilibrium  $G_T = \nu_1 g_1 + \nu_2 g_2$

Phase diagram is a P-T diagram with lines that represent  $g_i = g_j$  for two phases  $i, j$

For phase change:

$$\begin{aligned}g_1 &= g_2 \\ E_1 - TS_1 + PV_1 &= E_2 - TS_2 + PV_2 \\ (E_1 - E_2) - \underbrace{T(S_1 - S_2)}_Q + P(V_1 - V_2) &= 0\end{aligned}$$

First order phase transitions.

Characterized by:

- 
- $g(T, P)$  is continuous across boundary between phases.
  - The first partial derivatives are discontinuous.  $\left(\frac{\partial g}{\partial P}\right)_T = v$ ,  $\left(\frac{\partial g}{\partial T}\right)_P = -s$  So in first order latent heat is absorbed or given off. take differentials and group together to get

$$\Delta \frac{\partial g}{\partial P} = v_1 - v_2 = \Delta v \text{ Change in molar volume}$$

$$\Delta \frac{\partial g}{\partial T} = -(s_1 - s_2) = -\Delta s \text{ Change in molar entropy}$$

the amount of molar latent heat that must be absorbed is  $l$  so  $\Delta S = l/T$

$$\frac{\partial P}{\partial T} = \frac{\Delta S}{\Delta V} = \frac{l}{T \Delta V}$$

Clausius-Clapeyron equation.

First order phase transitions are characterized by latent heat produced.

Second order phase transitions: both  $g$  and 1st derivatives are cont but second derivatives are not,,, no latent heat.

Application of Clausius-Clapeyron equation.

consider liquid vapor, find vapor pressure in equilibrium with liquid.

Simplifying assumption:

- $\Delta V = V_{vap} - V_{liq} \approx V_{vap} \rightarrow V_{liq} \ll V_{vap}$
- $PV = RT$
- Assume  $l \neq l(T)$

$$\frac{dP}{dT} = \frac{l}{T} \frac{1}{V_{vap}} = \frac{l}{T} \frac{P}{RT} = \frac{lP}{RT^2}$$

$$\frac{dp}{p} = \frac{l}{RT^2} dt$$

$$P = P_0 e^{-l/RT}$$