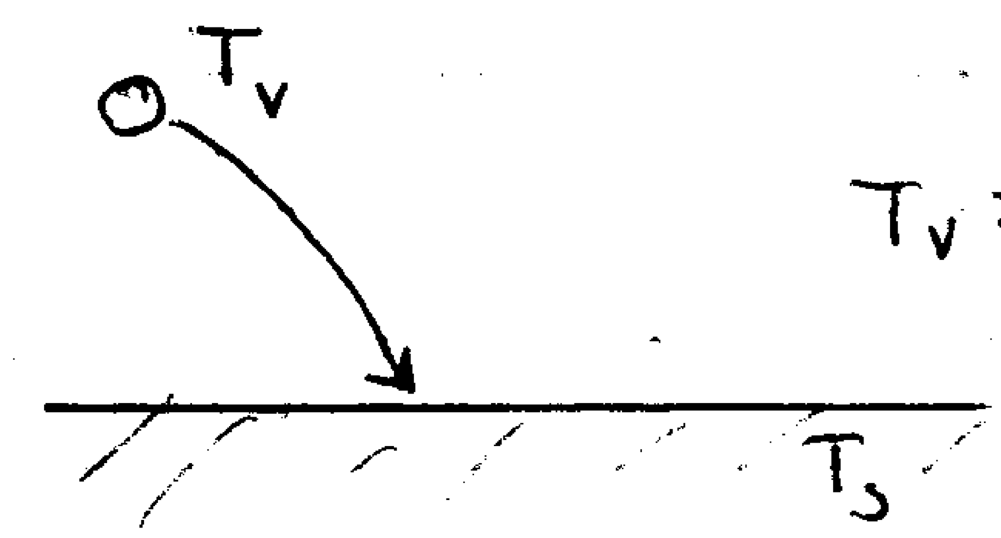
SURFACE NUCLEATION



- Monomer arrival at surface

$$\Phi_{evap} = \frac{\alpha_e \cdot N_A (P_e - P_{chamber})}{\sqrt{2\pi MRT}} \quad \left[\frac{\text{atoms}}{\text{cm}^2 \cdot \text{sec}}\right]$$

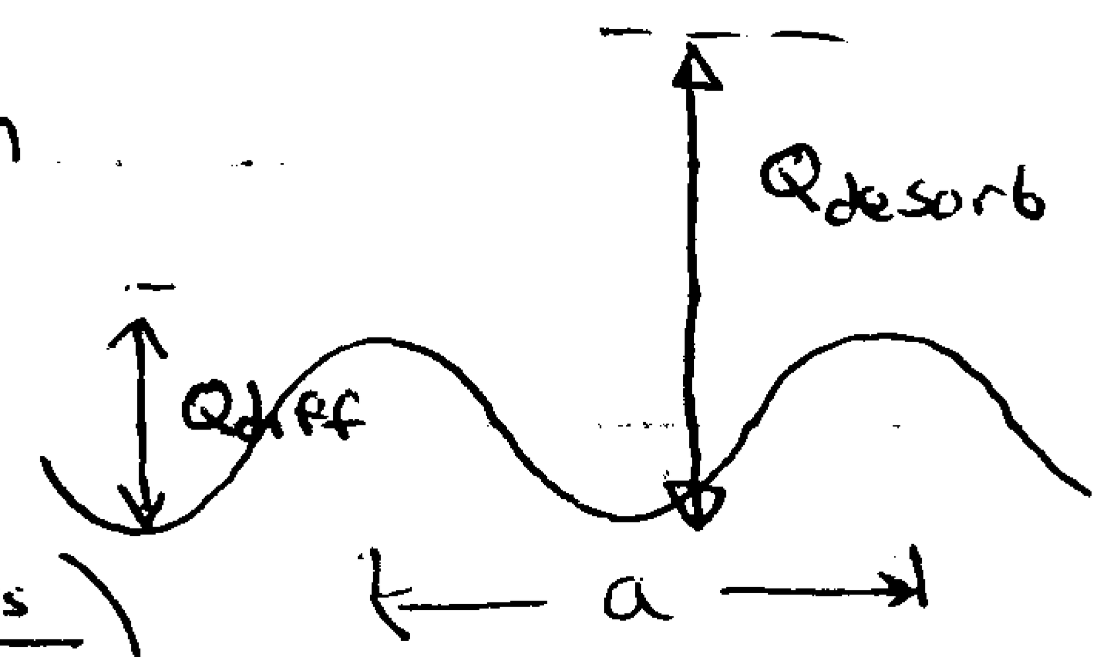
$$\Phi_{IN} = \Phi_{evap} \frac{\cos\phi \cos\theta}{\pi r^2} = \frac{C \cdot P_v}{\sqrt{2\pi m k T}}$$

(Rule of thumb $1 \left[\frac{ML}{sec}\right]$ @ $P_v = 10^{-6}$ Torr)

Monomer loses thermal energy to substrate $T_v \rightarrow T_s$

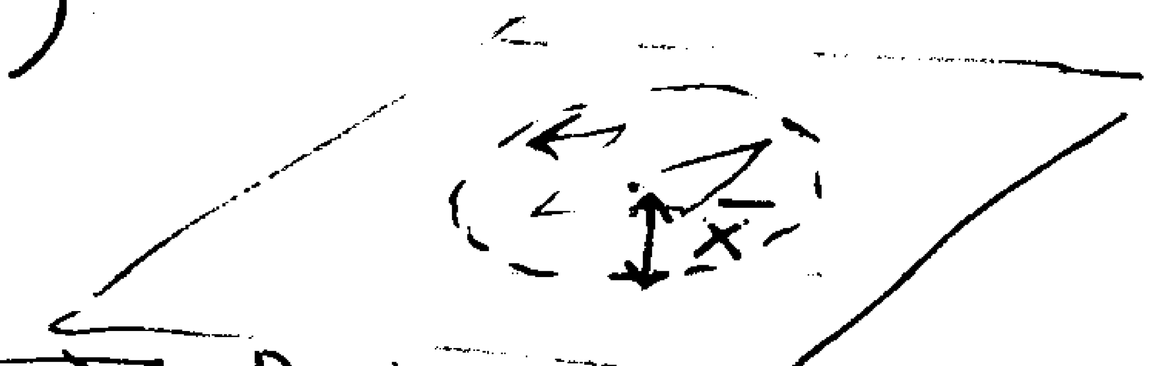
- Random walk via surface diffusion

$$\tau_s = \frac{1}{\nu} \exp\left(\frac{Q_{desorb}}{kT}\right)$$ Mean residence time



$$\bar{X} = \sqrt{2 D_s \tau_s} = \sqrt{\frac{2 D_s}{\nu}} \exp\left(\frac{Q_{DES}}{2kT}\right)$$

$$D_s = a^2 \nu \exp\left(\frac{-Q_{DIF}}{kT}\right)$$



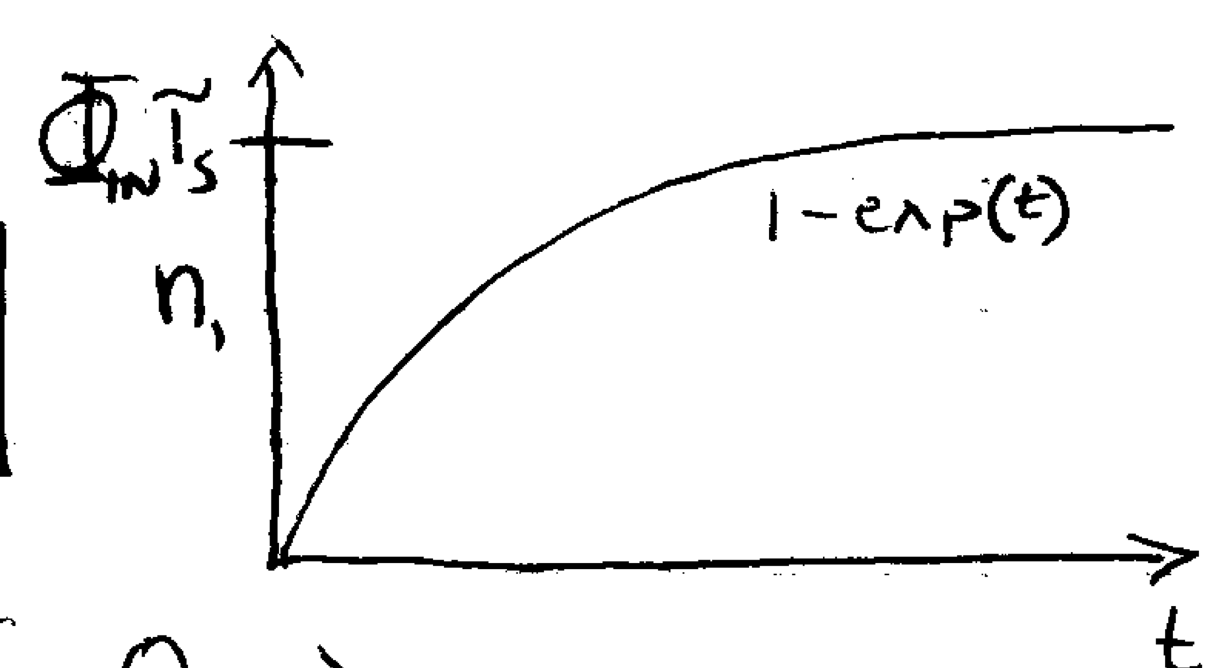
Regim visited by adatom during walk

SUBSTITUTING: $$\boxed{\bar{X} = \sqrt{2}\, a \exp\left(\frac{Q_{DES} - Q_{DIFF}}{2kT}\right)}$$

(TYPICALLY $Q_{DES} = 1-5\,eV$, $Q_{DIFF} = 0.5-1.0\,eV$)

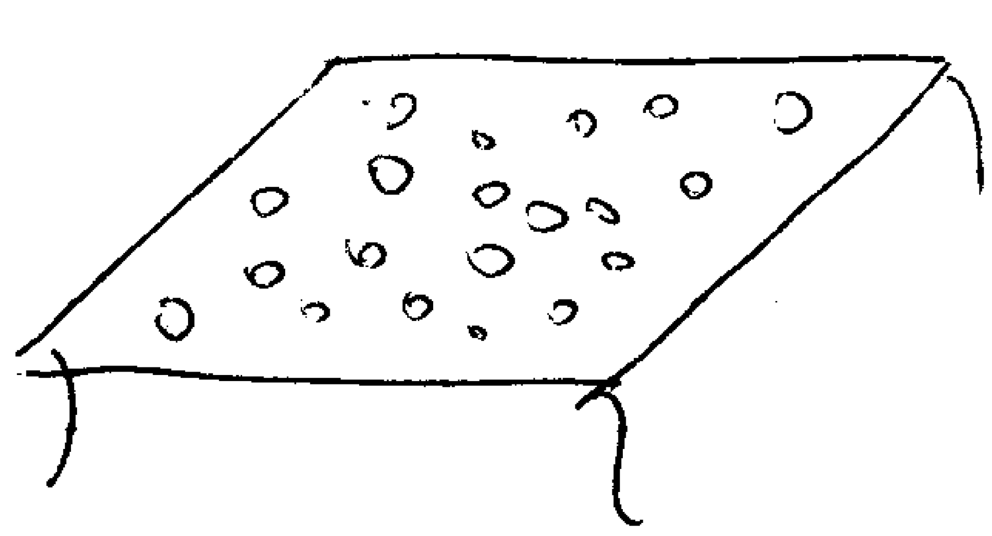
- CONCENTRATION OF ADATOMS

$$n_1 \left[\frac{\text{atoms}}{\text{cm}^2}\right] = \Phi_{in} \tau_s \left[1 - \exp\left(\frac{-t}{\tau_s}\right)\right]$$



- AT EQUILIBRIUM

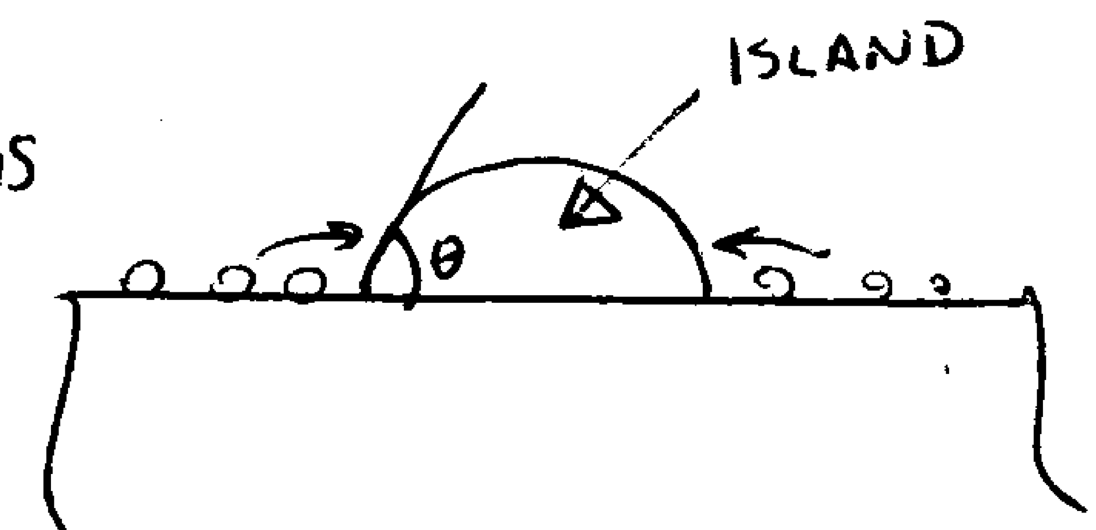
$$\Phi_{IN} = \Phi_{OUT} = n_1 \nu \exp\left(-\frac{Q_{DES}}{kT}\right) \rightarrow \boxed{n_1 = \Phi_{IN} \cdot \tau_s}$$



- 2D 'Gas' of adatoms on surface
- Driving energy to chemisorb, cluster → go into solid phase

CASE 1 CLASSICAL NUCLEATION THEORY

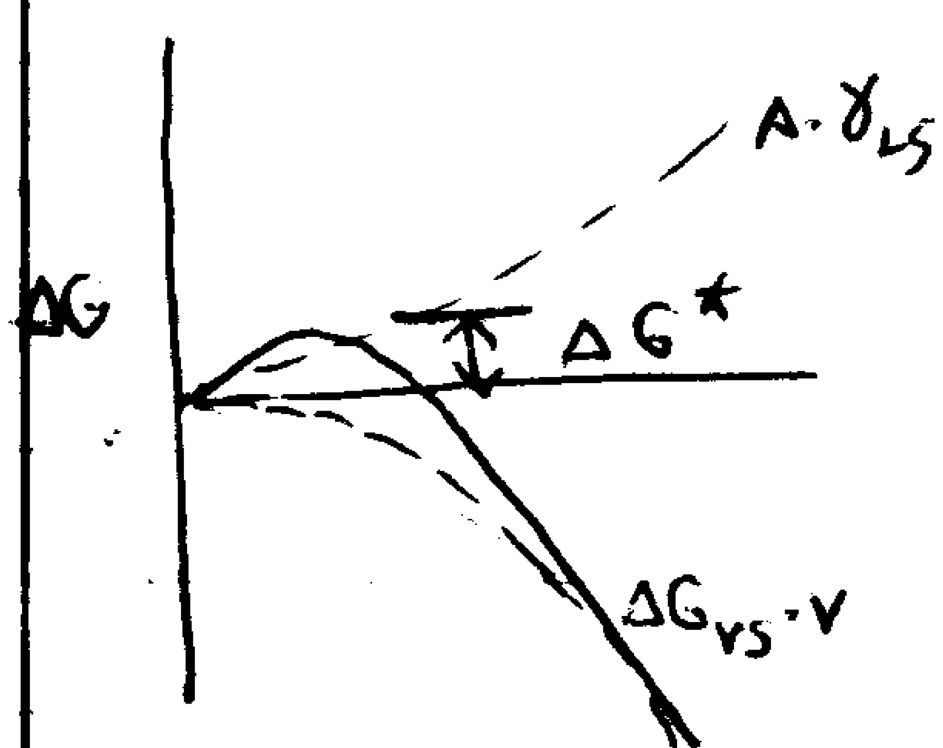
- Adatoms can coalesce via fluctuations to build critical sized island



$Q_{DES} \sim Q_{CONDENSATION\ (TO\ SOLID)}$

$$\Delta G_{HET} = \left(\frac{4}{3}\pi r^3 \Delta G_{SV} + 4\pi r^2 \gamma_{SV}\right) S(\theta)$$

$$S(\theta) = \frac{1}{2}(2+\cos\theta)(1+\cos\theta)^2$$



- CRITICAL RADIUS r^* (or n^*) ← # of atoms

  $r > r^*$ grows, $r < r^*$ shrinks

- CRITICAL BARRIER FOR NUCLEATION

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma_{SV}^3}{(\Delta G_{SV})^2} S(\theta)$$

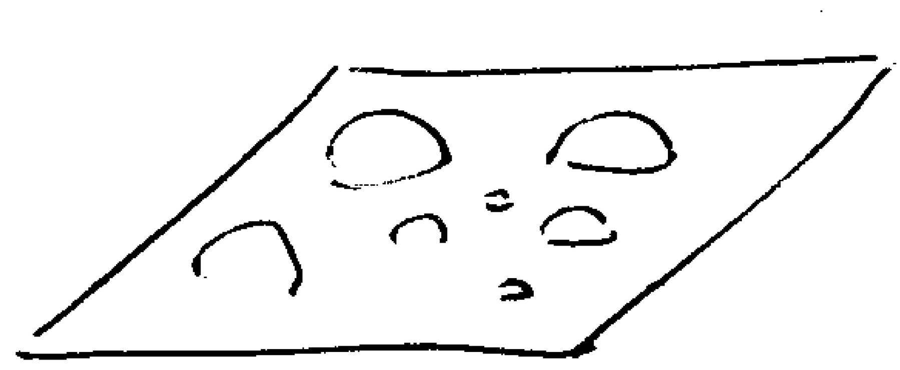
- Nucleation rate:

$$J = \underbrace{n_0 \exp\left[\frac{-\Delta G^*}{kT}\right]}_{\text{critical nuclei}} \cdot \nu_1 \cdot a^* \exp\left[\frac{-Q_{COND}}{kT}\right]$$

$$= Z\, n_0 \exp\left[\frac{-\Delta G^*}{kT}\right] \cdot \frac{kT}{h} \cdot (2\pi r^* \cdot n_1 \sin\theta) \exp\left[\frac{-Q_{DIFF}}{kT}\right]$$

Z: Zeldovich constant 10^{-2}; $\frac{kT}{h}$: jump frequency; $2\pi r^* \cdot n_1 \sin\theta$: adatoms around base of island; Q_{DIFF}: assume diffusion-like barrier.

- Implications



  - Predicts random arrangement of subcritical clusters
  - Select few will reach n^* and then be stable

- Depends on assumption of hemispherical cap model where $n^* \gg 1$

  Means that driving force for nucleation is small $Q_{COND} \sim Q_{DES}$.

- Low Φ_{in}, high $T_{SUBSTRATE}$

CASE 2 — STATISTICAL (ATOMISTIC) NUCLEATION THEORY

$$\Delta G_i^* = \Delta E_i^* + i^* kT \ln\left(\frac{n_o}{n_1}\right)$$

(n_o → sites; n_1 → adatoms)

(Energy to form critical cluster of i^* atoms)

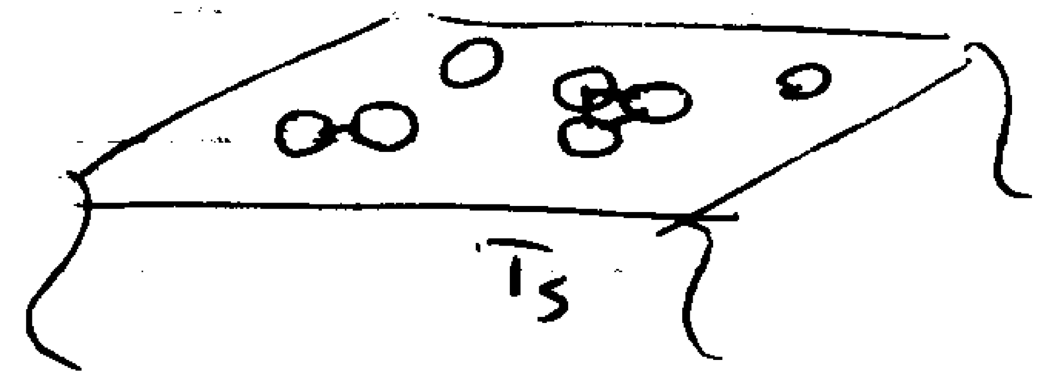
$$\frac{n_i^*}{n_o} = \left(\frac{n_1}{n_o}\right)^{i^*} \exp\left(-\frac{E_i^*}{kT}\right)$$

(Area density of critical clusters)

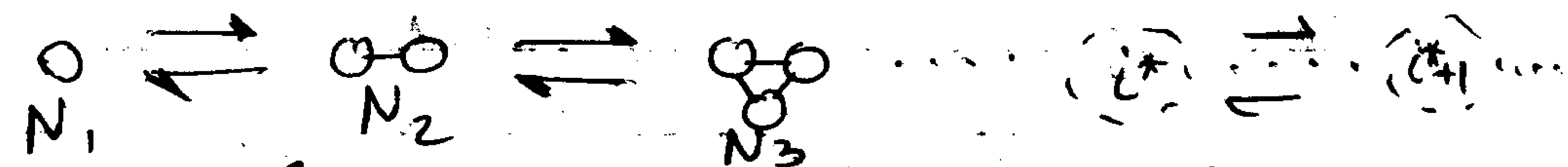
$$J = \Phi_{IN} a^2 n_o \left(\frac{\Phi_{IN}}{\nu n_o}\right)^{i^*} \exp\left[\frac{(i^*+1)Q_{DES} - Q_{DIF} + E_i^*}{kT}\right]$$

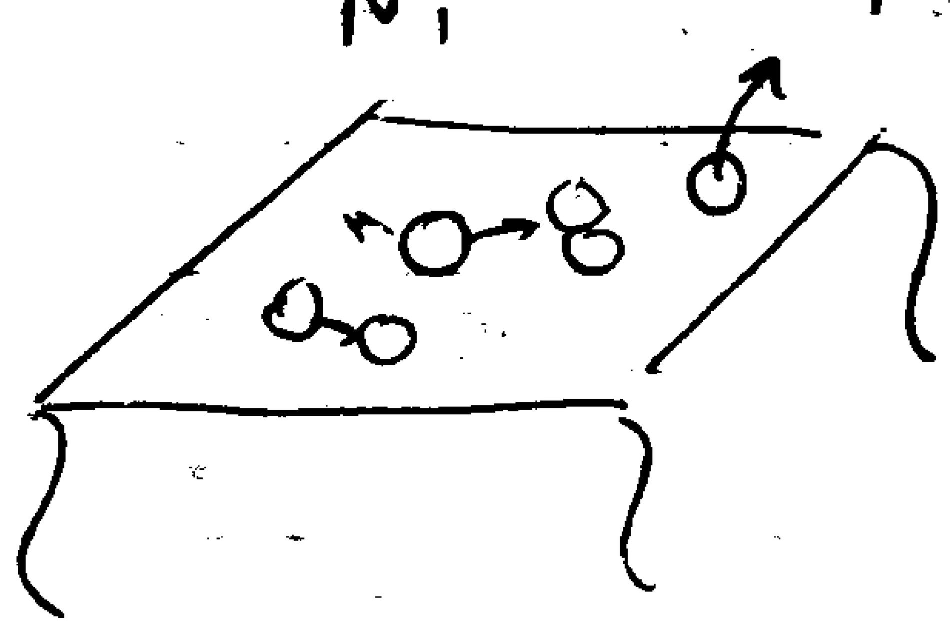
(Q_{DES}: relates to T_s (concentration); Q_{DIF}: jump onto cluster; E_i^*: assemble i^*)

- But this is not the whole picture –
  - Real deposition conditions have high Φ_{IN}, low T_s
  - So $i^* \Rightarrow 2$ (or even 1!!)
  - Hemispherical nucleation model is not really valid.



- Atomistic Reactions {Zinsmeister, Venables}





Events possible for adatom

1. Find another adatom $i \to 2$ $\quad w_{ij}$
2. Attach to island $i \to i+1$
3. Dissociate from cluster $i \geq 2$ $\quad \beta_i$
4. Desorb $\quad \frac{1}{\tau_s}$
5. Collision with arriving atom $\quad \sigma_1$

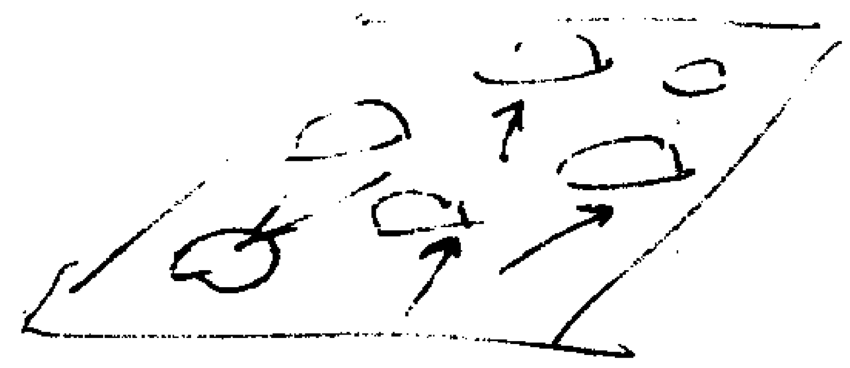
$$\frac{dN_1}{dt} = \underbrace{q'}_{\text{arriving}} + \underbrace{\sum_{i>1} N_i \beta_i}_{\text{dissociation}} - \underbrace{\frac{N_1}{\tau_s}}_{\text{desorb}} - N_1 \sum_{i>1} w_{ij} N_i - N_1 q' \sigma_1$$

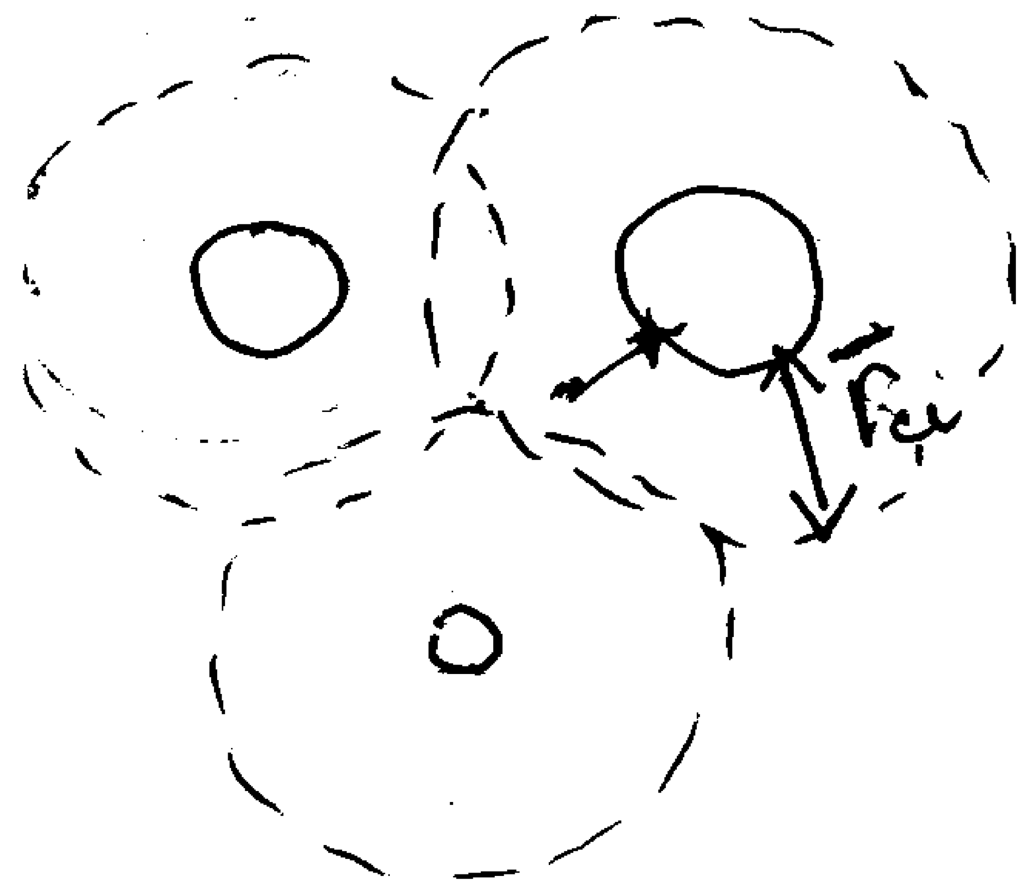
$$\frac{dN_2}{dt} = \underbrace{\frac{1}{2} w_{11} N_1^2}_{\text{become dimer}} + \underbrace{N_1 q_1' \sigma_1}_{\text{become dimer (1+2)}} + \underbrace{\sum_{i>2} N_i \beta_i}_{\text{dissociate pair from large cluster}} - w_{12} N_1 N_2 - \underbrace{N_2 q' \sigma_2}_{\text{direct 2-3}} - \underbrace{N_2 \alpha_2}_{\text{dissociate}}$$

Ⓑ MOBILITY $\omega\left[\frac{cm^2}{sec}\right]$

$G \propto \frac{1}{\omega^{1/3}}$, $d_{max} \propto \omega^{1/9}$

- As mobility ↑, Fewer, but larger islands





- $r_c(i)$ is capture radius
  $r_c \sim \bar{X}$.
- IF SPACING goes below $\sim 2\bar{X}$ then no more nucleation
  adatoms always go to island

Ⓒ TEMPERATURE T_s

- As T_s ↑, τ_s ↓ so concentration ↓ bigger islands, less density G ↓
- As T_s ↑ $D = a^2 \nu \exp\left(-\frac{Q_{DIF}}{kT}\right)$ mobility ↑
  (A few large islands)
- As T_s ↓ mobility ↓ (many small islands)