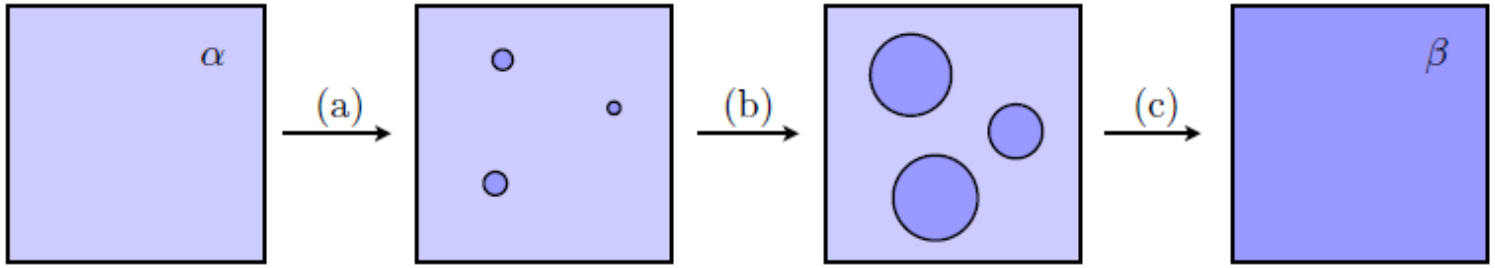
Chemical Analysis

Nucleation theory

- process leading to the formation of a new phase (solid, liquid) within metastable original phase (undercooled melt, supersaturated vapor or solution)
- first step in crystallization process; plays a decisive role in determining the crystal structure and the size distribution of nuclei



- homogeneous nucleation (HON)
  (at random sites in the bulk of a parent phase)
- heterogeneous nucleation (HEN)
  (on foreign substrate, impurities, defects, active centres)

nucleus: the smallest observable "particle" (often $\approx 1\mu m$)

Clusters of a new phase are formed on **nucleation sites** due to fluctuations and after overcoming some critical size ($< 1nm$) become **nuclei** (overcritical clusters).

Nucleation theory

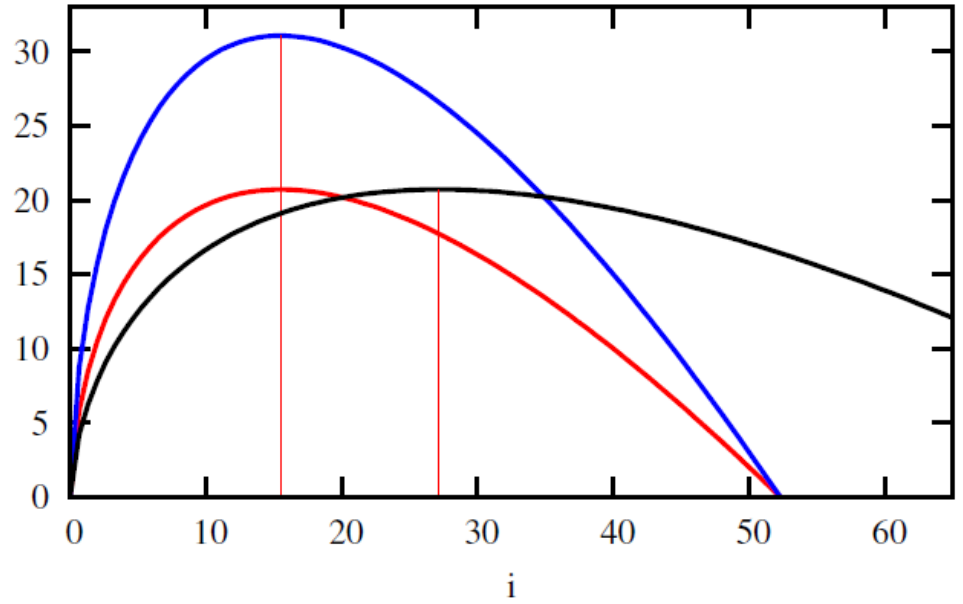
Homogeneous nucleation:

Capillarity approximation

$$W_i = -i\Delta\mu + \gamma i^{2/3} = -\frac{4\pi r^3}{3V_1}\Delta\mu + 4\pi r^2\sigma$$

$$W^S = \sum_k A_k\sigma_k \quad \text{- surface energy}$$

- i - cluster size (number of molecules within cluster)
- r - cluster radius; σ - interfacial energy; V_1 - molecular volume
- $\Delta\mu$ - difference of chemical potentials
- A_k - surface areas; σ_k - corresponding interfacial energies



$$\frac{\partial W_i}{\partial i} = 0 \quad \Rightarrow \quad i^* = \left(\frac{2\gamma\sigma}{3\Delta\mu}\right)^3; \qquad i^* \text{ – critical size; } W^* = W_{i^*} \text{ – nucleation barrier}$$

melt → crystal: $\Delta\mu = \frac{\Delta h_E}{N_A T_E}(T_E - T)$ solution → crystal: $\Delta\mu = k_B T \ln S$

Δh_E – heat of fusion; N_A – Avogadro constant; T_E – equilibrium temperature; T – temperature
k_B – Boltzmann constant; S – supersaturation;

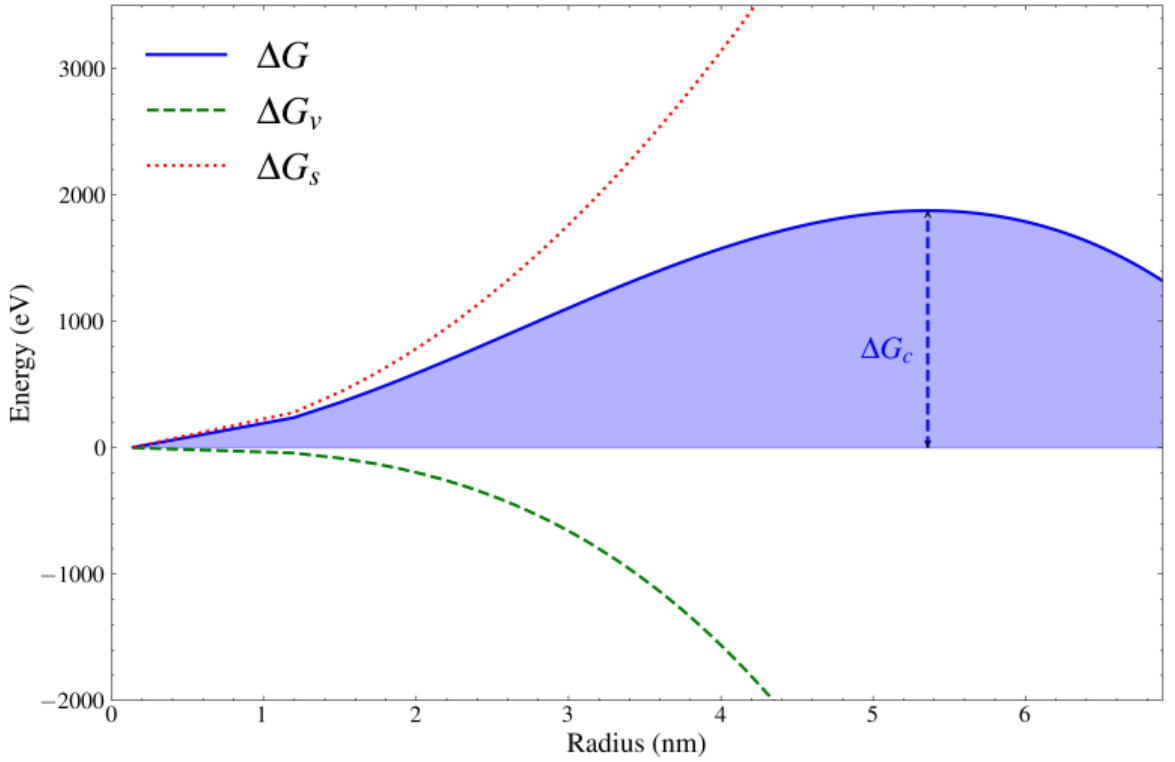
Metallic impurities: Fe

Parameter	Symbol	Value (Unit)
Temperature	T	668 K
Molar Mass	M	55.85 g/mol
Mass Density	ρ	7.87 g/cm^3
Melting Point	T_m	1538 K
Heat of Fusion	ΔH_f	11.7 kJ/mol
Surface Tension	σ	2.5 J/m^2

Table 3: Parameters for Fe

Parameter	Symbol	Value (Unit)
Critical radius	r	5.34 nm
Energy barrier	ΔG_c	3.00×10^{-16} J
Critical number of molecules	n	54722

Table 4: Critical values for Fe



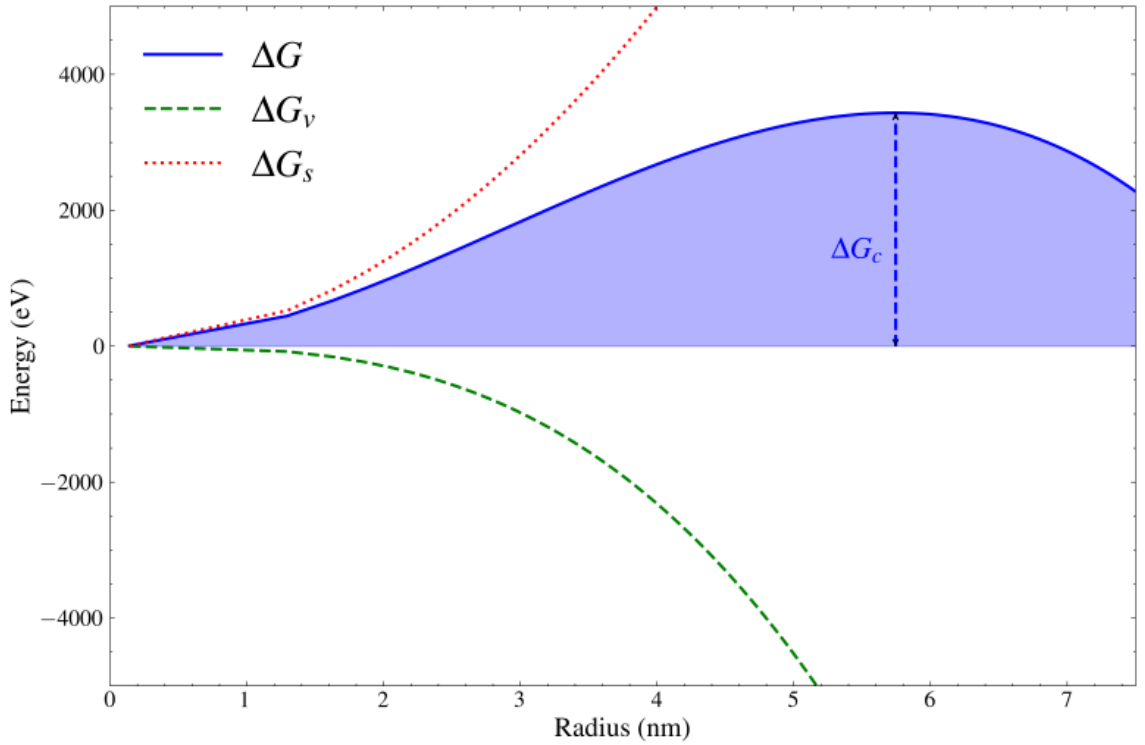
Metallic impurities: Cr

Parameter	Symbol	Value (Unit)
Temperature	T	668 K
Molar Mass	M	51.9961 g/mol
Mass Density	ρ	7.19 g/cm^3
Melting Point	T_m	2130 K
Heat of Fusion	ΔH_f	14.6 kJ/mol
Surface Tension	σ	3.98 J/m^2

Table 1: Parameters for Cr

Parameter	Symbol	Value (Unit)
Critical radius	r	5.74 nm
Energy barrier	ΔG_c	5.50×10^{-16} J
Critical number of molecules	n	66115

Table 2: Parameters for Cr



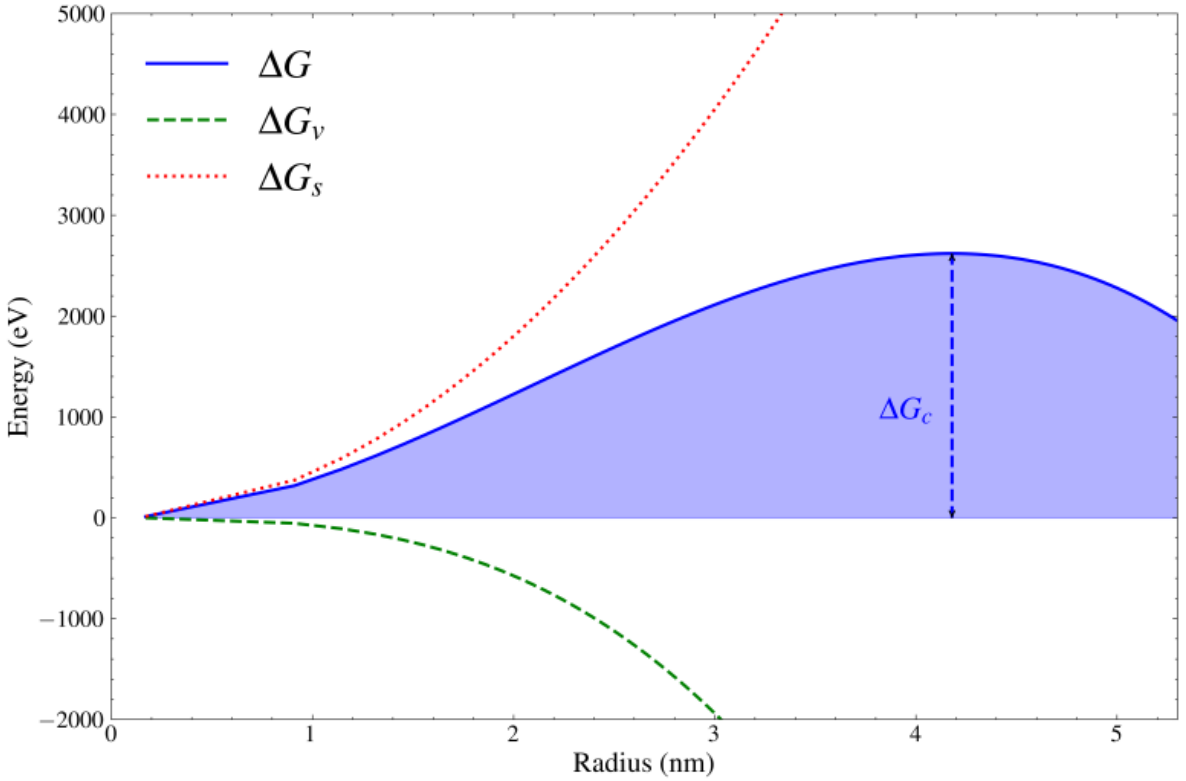
Metallic impurities: AlN

Parameter	Symbol	Value (Unit)
Temperature	T	668 K
Molar Mass	M	40.98 g/mol
Mass Density	ρ	3.26 g/cm^3
Melting Point	T_m	2200 K
Heat of Fusion	ΔH_f	49.59 kJ/mol
Surface Tension	σ	5.74 J/m^2

Table 5: Parameters for AlN

Parameter	Symbol	Value (Unit)
Critical radius	r	4.18 nm
Energy barrier	ΔG_c	4.2×10^{-16} J
Critical number of molecules	n	14646

Table 6: Critical values for AlN



Non Metallic impurities: LiH, LiD, LiT

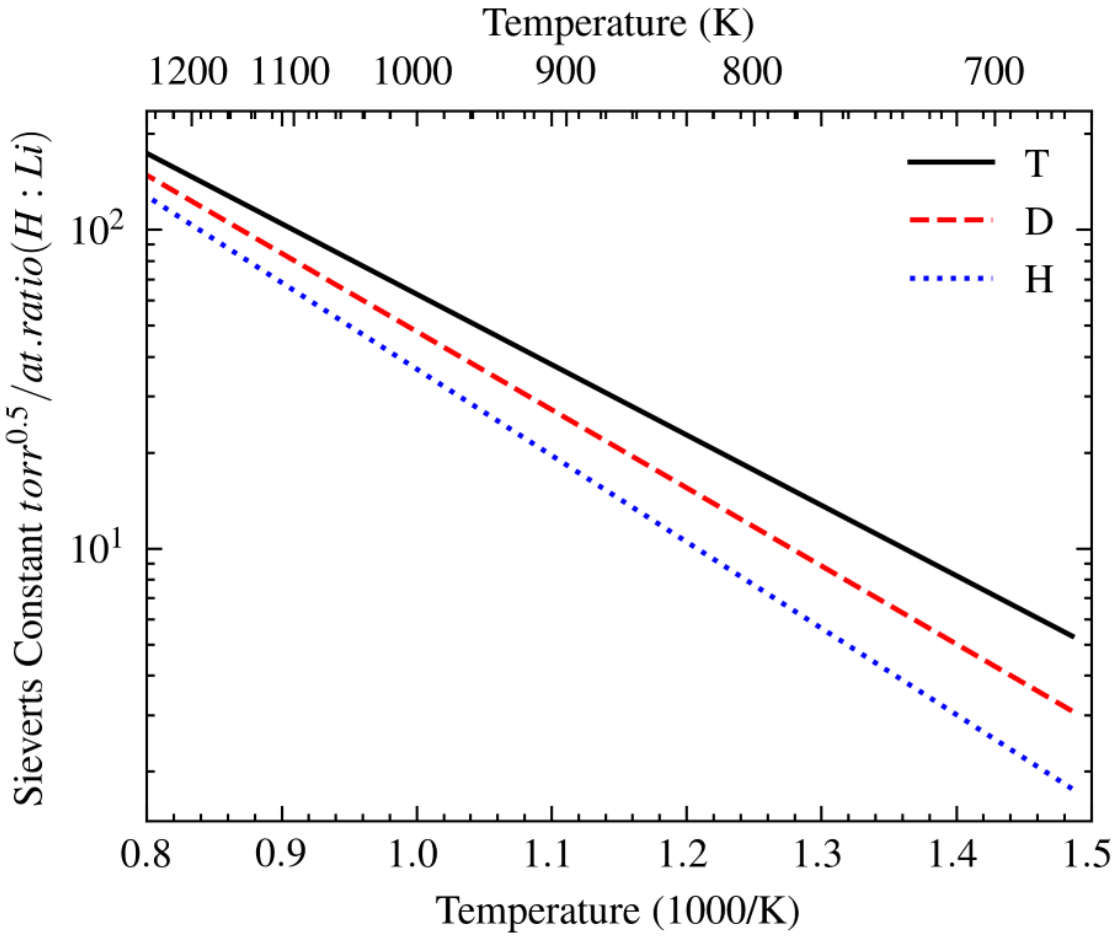
Reaction	Ratio	mol/m^3	(H:Li) Ratio
(n, Xp)	0.015	6.5×10^{-7}	9.12×10^{-6}
(n, Xd)	0.15	6.34×10^{-6}	8.96×10^{-5}
(n, Xt)	1.53	6.5×10^{-5}	9.1×10^{-4}
Neutrons/Pulse	6.2×10^{21}		

Table 7: Hydrogen nuclides production

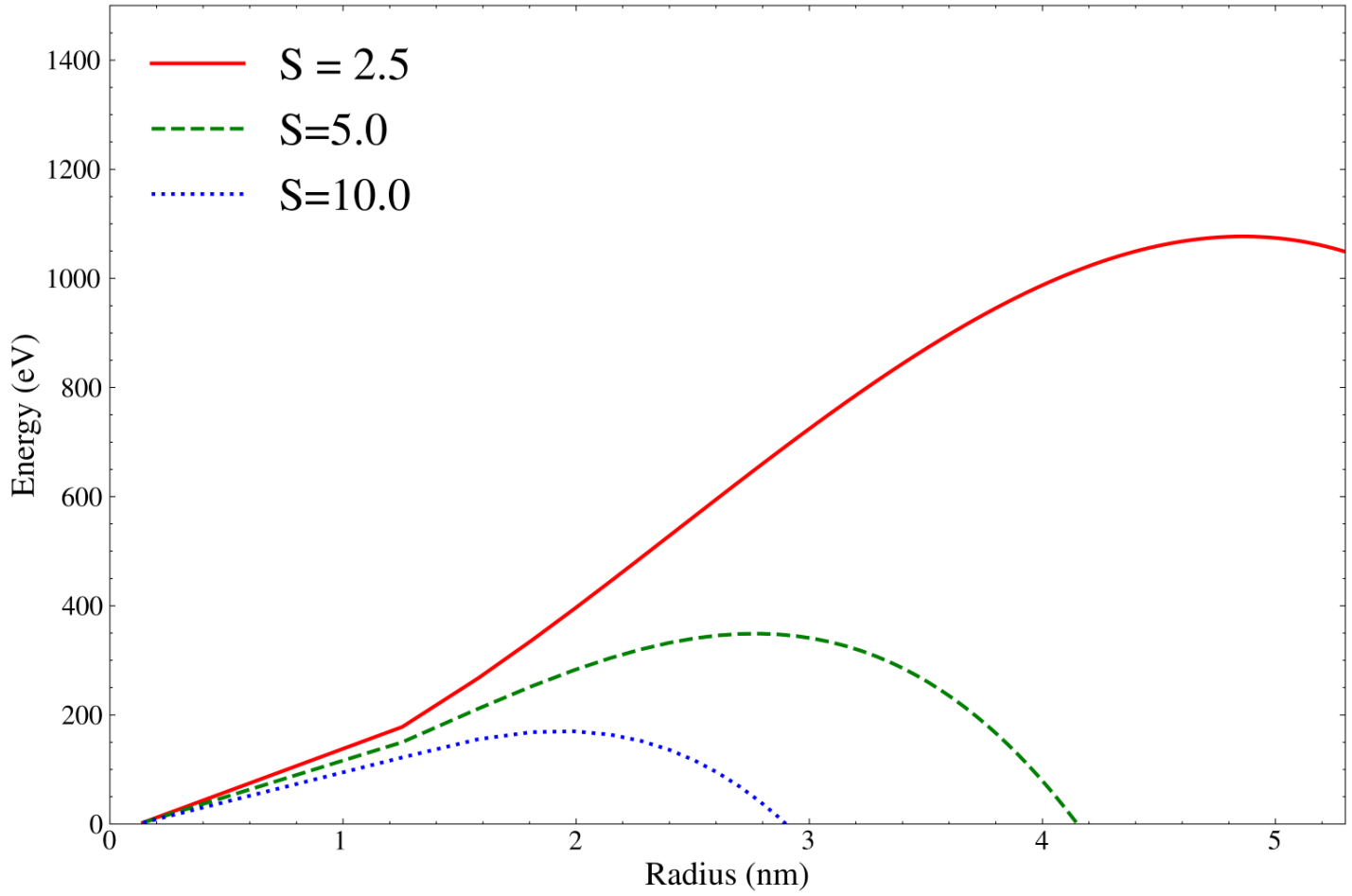
$$P^{1/2} = K \cdot C_1 \qquad \frac{p_{D_2}}{p_{H_2}} = \sqrt{2}, \quad \frac{p_{T_2}}{p_{D_2}} = \sqrt{3}$$

Nuclide	Sieverts Constant (Torr$^{0.5}$/[(H:Li)])	(H:Li) Ratio
H	1.65	0.0045
D	2.90	0.00363
T	5.02	0.00360

Table 8: Solubility of hydrogen isotopes in lithium



Non Metallic impurities: LiH, LiD, LiT



Kinetic equations

k_i^+ (k_i^-) — attachment (detachment) frequencies of molecules

$$\frac{dF_i}{dt} = k_{i-1}^+ F_{i-1} - \left[k_i^+ + k_i^-\right] F_i + k_{i+1}^- F_{i+1} = J_{i-1}(t) - J_i(t)$$

$$J_i(t) = k_i^+ F_i(t) - k_{i+1}^- F_{i+1}(t)$$

- F_i — number density of clusters of size i
- J_i - cluster flux density (nucleation rate for i^*)
- k_i^+ (k_i^-) — attachment (detachment) frequencies

F_i^0 — equilibrium number of cluster formed by i molecules. It can be shown that

$$F_i^0 = B_2 \exp\left(-\frac{W_i}{kT}\right)$$

Homogeneous nucleation, self-consistent model: $B_2 = N_1 \exp\left(-\frac{W_1}{kT}\right)$

Kinetic equations

Initial and boundary conditions

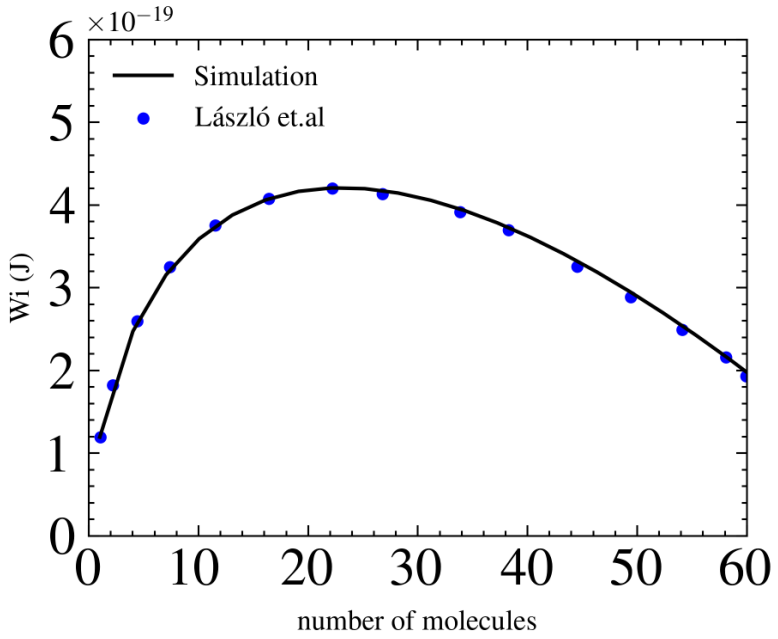
$$F_i(t=0) = F_i^0 \quad \text{for } i \le i_0 \text{ (usually } i_0 \approx i^*/2)$$

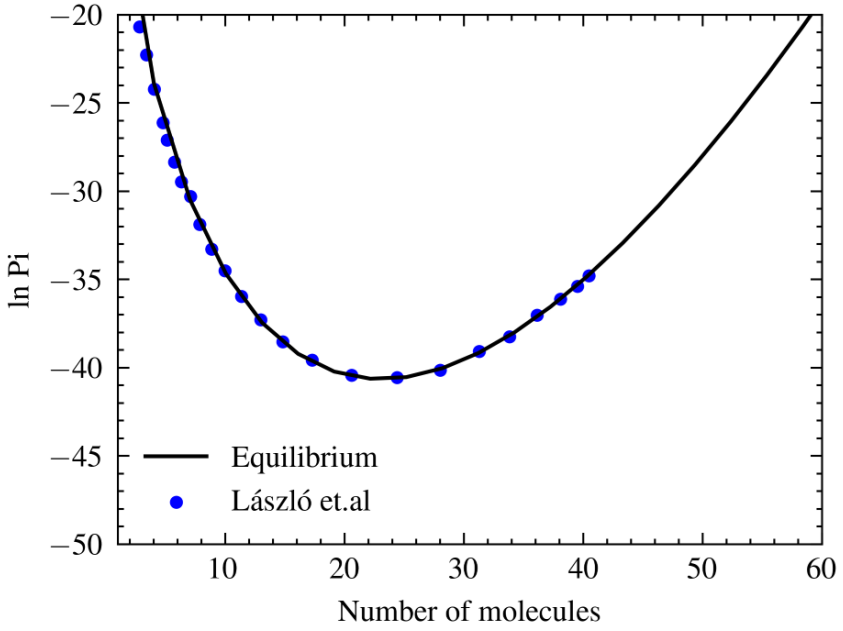
F_i^0 — equilibrium distribution of nuclei

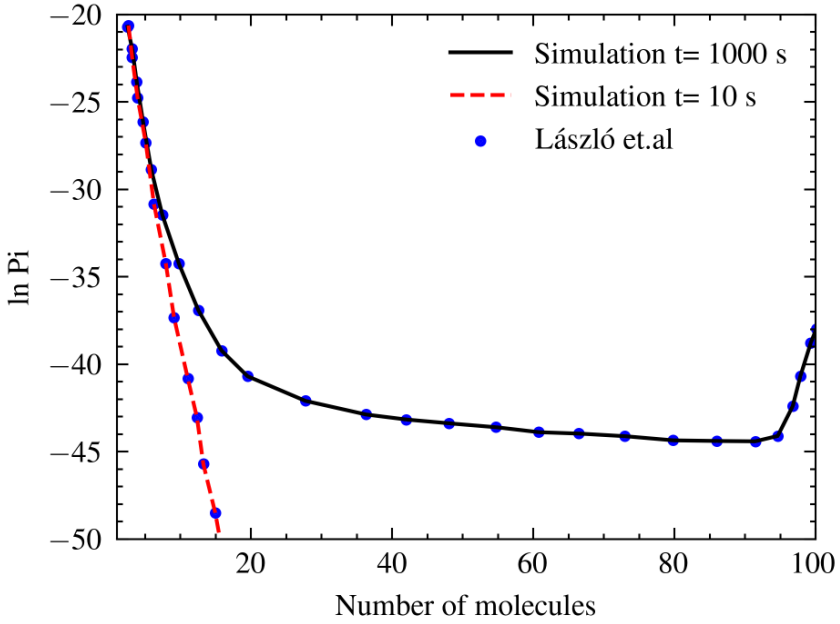
$$F_i(t=0) = 0 \quad \text{for } i > i_0$$

$$F_1(t) = F_1^0 = N_n = \text{const.}$$

N_n — number of nucleation sites ($N_n = N_1$ for HON)







Q&A

Thank you for your attention

Image from the flowing link.