Nucleation kinetics in closed systems
COST Action CM1402: From molecules to crystals – how do organic molecules form crystals?

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2-6 November 2015, Lyon, France
Institute of Physics CAS, Prague

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Introduction

**Nucleation**

- 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

![Diagram of nuclei and parent phase]

- **nuclei of a new phase** (droplet, crystal)
- **parent phase** (vapor, solution or liquid)

- 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).

Supersaturation (supercooling) increases with volume decrease.

⇒ nucleation kinetics in confined volumes
Standard nucleation model

**UNARY NUCLEATION**
(simple component system of a new phase)

\[ \begin{align*}
    k_1^+ & \quad k_2^- \\
    k_2^- & \quad k_3^+ \\
    k_3^+ & \quad k_4^- \\
    k_4^- & \quad k_5^+ \\
    \vdots & \quad \vdots
\end{align*} \]

**BINARY NUCLEATION**
(A, B components)

\[ \begin{align*}
    \begin{array}{c}
    k_B^+(0, 2) \\
    k_B^+(0, 1) \\
    k_A^+(0, 1) \\
    k_A^+(1, 0) \\
    k_B^+(1, 0)
    \end{array}
    & \quad \begin{array}{c}
    k_B^-(0, 3) \\
    k_B^-(0, 2) \\
    k_B^-(1, 1) \\
    k_B^-(1, 2) \\
    k_B^-(2, 1)
    \end{array} \\
    \begin{array}{c}
    k_A^-(1, 2) \\
    k_A^-(1, 1) \\
    k_A^-(2, 1) \\
    k_A^-(2, 0) \\
    k_A^-(3, 0)
    \end{array}
    & \quad \begin{array}{c}
    k_A^+(0, 2) \\
    k_A^+(1, 1) \\
    k_A^+(2, 0) \\
    k_A^+(2, 0) \\
    k_A^+(3, 0)
    \end{array}
\end{align*} \]
Standard nucleation model

Kinetic equations

\[ k_i^+ (k_i^-) - \text{attachment (detachment) frequencies of molecules} \]

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

\[ J_i(t) = k_i^+ F_i(t) - k_{i+1}^- F_{i+1}(t) \]  \hspace{1cm} (2)

\( F_i \) – number density of clusters of size \( i \)

\( J_i \) - cluster flux density (nucleation rate for \( i^* \))

\( k_i^+ (k_i^-) \) – attachment (detachment) frequencies

Total number of nuclei greater than \( m \): \( Z_m(t) = \sum_{i>m} F_i(t) = \int_0^t J_m(t') dt' \)

Local equilibrium:

\[ J_i = 0 \Rightarrow k_i^+ F_i^0 = k_{i+1}^- F_{i+1}^0 \Rightarrow k_{i+1}^- = k_i^+ \frac{F_i^0}{F_{i+1}^0} = k_i^+ \exp \left( \frac{W_{i+1} - W_i}{k_B T} \right) \]  \hspace{1cm} (3)
Kinetic equations

Equilibrium

\[ J_i = 0 \Rightarrow k_i^+ F_i^0 = k_{i+1}^− F_{i+1}^0 \] (4)

\[ \Rightarrow F_i^0 = F_1^0 \frac{k_1^+ k_2^+ k_3^+ \ldots k_{i−1}^+}{k_2^- k_3^- k_4^- \ldots k_i^-} \]

\( F_i^0 \) – 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: \( B_2 = N_1 \exp \left( \frac{W_1}{kT} \right) \)

\( N_1 \) – number of molecules within parent phase

Knowing \( F_i^0 \) and \( k_i^+ \Rightarrow k_i^- \) from Eq. (4).
Standard nucleation model

Classical nucleation theory (CNT)

**Initial and boundary conditions**

\[ N_1 \text{ - number of molecules (number of nucleation sites)} \]
\[ F_1(t = 0) = N_1, \quad F_{i>1}(t = 0) = 0 \]
\[ F_1(t) = N_1 \]

\( t \gg \text{induction time} \Rightarrow \)

**Stationary nucleation (steady-state):** \[ J_i(t) = J^S = \text{const.} \]

\[ J^S = \left( \sum_{i=1}^{\infty} \frac{1}{k_i^+ F_i^0} \right)^{-1} \]

exact analytical formula

\[ J^S = k_i^+ z F_i^0, \quad \text{where Zeldovich factor: } Z = \sqrt{\frac{1}{2\pi kT}} \left( -\frac{d^2 W_i}{di^2} \right)_{i=i^*} \]

\[ F_i^0 = B \exp\left( -\frac{W_i}{kT} \right); \quad B = N_1 \exp\left( \frac{W_1}{kT} \right) \]

\( k_i^+, W_i = ?; \text{ small clusters?} \)
Standard nucleation model

Stationary nucleation (steady-state)

\[ J_i = J^S = \text{const.} \quad \text{for any cluster size } i \quad (N_1 = \text{const.}) \Rightarrow \]

Boundary conditions:

\[ F_i^S \to F_i^0 \quad \text{for } i \to 1; \quad F_i^S \to 0 \quad \text{for } i \to \infty \]

\[ J^S = k_i^+ F_i^S - k_{i+1}^- F_{i+1}^S \]
Standard nucleation model

Stationary nucleation (steady-state)

\[ J_i = J^S = \text{const.} \]

for any cluster size \( i \) \((N_1 = \text{const.})\) ⇒

Boundary conditions:

\[ F_i^S \to F_i^0 \quad \text{for} \quad i \to 1; \quad \quad F_i^S \to 0 \quad \text{for} \quad i \to \infty \]

\[
J^S = k_i^+ F_i^S - k_{i+1}^- F_{i+1}^S = k_i^+ F_i^0 \frac{F_i^S}{F_i^0} - k_{i+1}^- F_{i+1}^0 \frac{F_{i+1}^S}{F_{i+1}^0} = k_i^+ F_i^0 \left( \frac{F_i^S}{F_i^0} - \frac{F_{i+1}^S}{F_{i+1}^0} \right)
\]

\[
\sum_{i=1}^{M-1} \frac{J^S}{k_i^+ F_i^0}
\]
Standard nucleation model

Stationary nucleation (steady-state)

\[ J_i = J^S = \text{const.} \]
for any cluster size \( i \) \((N_1 = \text{const.})\) \(\Rightarrow\)

Boundary conditions:

\[ F_i^S \rightarrow F_i^0 \quad \text{for} \quad i \rightarrow 1; \quad F_i^S \rightarrow 0 \quad \text{for} \quad i \rightarrow \infty \]

\[ J^S = k_i^+ F_i^S - k_{i+1}^- F_{i+1}^S = k_i^+ F_i^0 \frac{F_i^S}{F_i^0} - k_{i+1}^- F_{i+1}^0 \frac{F_{i+1}^S}{F_{i+1}^0} = k_i^+ F_i^0 \left( \frac{F_i^S}{F_i^0} - \frac{F_{i+1}^S}{F_{i+1}^0} \right) \]

\[ \sum_{i=1}^{M-1} \frac{J^S}{k_i^+ F_i^0} = \left( \frac{F_1^S}{F_1^0} - \frac{F_2^S}{F_2^0} \right) + \left( \frac{F_2^S}{F_2^0} - \frac{F_3^S}{F_3^0} \right) + \left( \frac{F_3^S}{F_3^0} - \frac{F_4^S}{F_4^0} \right) + \ldots \]
Standard nucleation model

Stationary nucleation (steady-state)

\[ J_i = J^S = \text{const.} \]

for any cluster size \( i \) \((N_1 = \text{const.})\) \( \Rightarrow \)

Boundary conditions:

\[ F_i^S \rightarrow F_i^0 \quad \text{for} \quad i \rightarrow 1; \quad \quad F_i^S \rightarrow 0 \quad \text{for} \quad i \rightarrow \infty \]

\[ J^S = k_i^+ F_i^S - k_{i+1}^- F_{i+1}^S = k_i^+ F_i^0 \frac{F_i^S}{F_i^0} - k_{i+1}^- \frac{F_{i+1}^S}{F_{i+1}^0} = k_i^+ F_i^0 \left( \frac{F_i^S}{F_i^0} - \frac{F_{i+1}^S}{F_{i+1}^0} \right) \]

\[ \sum_{i=1}^{M-1} \frac{J^S}{k_i^+ F_i^0} = \left( \frac{F_1^S}{F_1^0} - \frac{F_2^S}{F_2^0} \right) + \left( \frac{F_2^S}{F_2^0} - \frac{F_3^S}{F_3^0} \right) + \left( \frac{F_3^S}{F_3^0} - \frac{F_4^S}{F_4^0} \right) + \ldots = 1 + \frac{F_i^S}{F_i^0} \rightarrow 1 \]

for \( M \rightarrow \infty \)
Standard nucleation model

Stationary nucleation (steady-state)

\[ J_i = J^S = \text{const.} \]

for any cluster size \( i \) \( (N_1 = \text{const.}) \) \( \Rightarrow \)

Boundary conditions:

\[ F^S_i \rightarrow F^0_i \quad \text{for} \quad i \rightarrow 1; \quad F^S_i \rightarrow 0 \quad \text{for} \quad i \rightarrow \infty \]

\[ J^S = k^+_i F^S_i - k^-_{i+1} F^S_{i+1} = k^+_i F^0_i \frac{F^S_i}{F^0_i} - k^-_{i+1} \frac{F^S_{i+1}}{F^0_{i+1}} F^S_{i+1} = k^+_i F^0_i \left( \frac{F^S_i}{F^0_i} - \frac{F^S_{i+1}}{F^0_{i+1}} \right) \]

\[
\sum_{i=1}^{M-1} \frac{J^S}{k^+_i F^0_i} = \left( \frac{F^S_1}{F^0_1} - \frac{F^S_2}{F^0_2} \right) + \left( \frac{F^S_2}{F^0_2} - \frac{F^S_3}{F^0_3} \right) + \left( \frac{F^S_3}{F^0_3} - \frac{F^S_4}{F^0_4} \right) + \ldots = 1 + \frac{F^S_M}{F^0_M} \rightarrow 1
\]

for \( M \rightarrow \infty \)

\[ J^S = \left( \sum_{i=1}^{\infty} \frac{1}{k^+_i F^0_i} \right)^{-1} \]

exact analytical formula
Standard nucleation model

\( k_i^+ \) - attachment frequency

\( k_i^- \) follows from the principle of local equilibrium (3)

Crystal nucleation

Crystal phase corresponds a stable phase, liquid a metastable phase, and in between is the diffusion activation energy.


\[
\begin{align*}
k_i^+ &= R_D A_i \exp \left( -\frac{E_D}{kT} \right) \exp \left( -\frac{q(W_{i+1} - W_i)}{kT} \right) ; & q &= 0.5[1 + \text{sign}(W_{i+1} - W_i)] \\
A_i &= \gamma i^{2/3} = 4\pi r^2 \quad \text{surface area} \\
R_D &= \text{mean number of molecules striking on unit nucleus surface}
\end{align*}
\]
**Standard nucleation model**

\[ k_i^+ - attachment\ frequency \]

**Vapor \( \rightarrow \) crystal**

\[ R_D = \frac{P}{\sqrt{2\pi m_1 kT}} \quad (deposition\ rate) \]

\( P \) – vapor pressure; \( m_1 \) – molecular mass

**Melt \( \rightarrow \) crystal (unary parent phase)**


\[ R_D = N_S \left( \frac{kT}{h} \right) \]

\( N_S \) – number of nucleation sites on the nucleus surface; \( \varrho_S \) – surface density of molecules

**Solution \( \rightarrow \) crystal**

**HON:** (A) Direct-impingement control / (B) Volume-diffusion control

\[ R_D = CN_S \left( \frac{kT}{h} \right) \]

\( C \) – concentration; (A) nucleation kinetics is restrictive

**HON:** (B) HON is controlled by volume diffusion

\( R_D \) – incoming diffusion flux of monomers; (B) HON is controlled by volume diffusion
Standard nucleation model

Work of formation of clusters

Formation of phase interface is energetically disadvantageous

Homogeneous nucleation:

Capillarity approximation

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

\[ W^S = \sum_k A_k \sigma_k \quad \text{surface energy} \]

- \( i \) – cluster size (number of molecules within cluster)
- \( r \) – cluster radius; \( \sigma \) – interfacial energy; \( v_1 \) – molecular volume
- \( \Delta \mu \) – difference of chemical potentials
- \( A_k \) – surface areas; \( \sigma_k \) – corresponding interfacial energies

\[ V_{n\varrho} = im_1 \Rightarrow r(i) \]

- \( V_n \) - nucleus volume; \( \varrho \) – density of crystal phase; \( m_1 \) – molecular mass
Standard nucleation model

Work of formation of clusters

Homogeneous nucleation

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

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

$\Delta h_E$ – heat of fusion; $N_A$ – Avogadro constant; $T_E$ – equilibrium temperature; $T$ – temperature  
$k_B$ – Boltzmann constant; $S$ – supersaturation;
Standard nucleation model

Work of formation of clusters

Nucleation in polymer systems: thermodynamic aspects

Standard nucleation model

Classical nucleation theory

Classical nucleation theory (CNT): fails to explain exp. data ($W_i = ??$)

Argon Lennard-Jones nucleation – MC simulations

\[ \delta \Delta W_n = W_n - W_{n-1} \]

\[ \Rightarrow \] Down to very small cluster sizes, classical nucleation theory built on the liquid drop model can be used very accurately to describe the work required to add a monomer to the cluster!

However, erroneous absolute value for the cluster work of formation, $W_i$. 

Standard nucleation model

Confined systems

Initial and boundary conditions

\[ F_i(t = 0) = F_i^0 \quad \text{pro} \ i \leq i_0 \quad (\text{usually} \ i_0 \approx i^*/2) \]

\[ F_i^0 \] - equilibrium distribution of nuclei

\[ F_i(t = 0) = 0 \quad \text{pro} \ i > i_0 \]

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

\[ N_n \] – number of nucleation sites \((N_n = N_1 \text{ for HON})\)

CNT model (HON+HEN)

\[ N_n \gg \sum_{i>1} i F_i \]
## Standard nucleation model

### Confined systems

#### Initial and boundary conditions

\[ F_i(t = 0) = F_i^0 \quad \text{pro} \ i \leq i_0 \quad (\text{usually} \ i_0 \approx i^*/2) \]

- \( F_i^0 \): equilibrium distribution of nuclei
- \( F_i(t = 0) = 0 \quad \text{pro} \ i > i_0 \)

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

- \( N_n \): number of nucleation sites \((N_n = N_1 \text{ for HON})\)

#### CNT model (HON+HEN)

\[ N_n \gg \sum_{i > 1} iF_i \]

#### Confined system (HON)

\[ F_1(t) = N_1(t = 0) - \sum_{i > 1} iF_i(t) \]

#### Confined system (HEN)

- Free substrate surface \( \downarrow \)

\[ F_1(t) = N_n(t = 0) - \sum_{i > 1} N_i^S(t) \]

- Number of nucleation sites occupied by nuclei

\[ N_1(t) = N_T - \sum_{i > 1} iF_i(t) \]

- \( N_1 \): number of molecules within parent phase
- \( N_T \): total number of molecules within system (liquid + solid phase)

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Nucleation kinetics

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**Selected Applications**

**Homogeneous nucleation**

**HON: ethanol, V→L transition** \((T = 260 \text{ K})\)

Selected Applications
Homogeneous nucleation

Size distribution of nuclei

S=3, \( i^* = 75 \)

\[ \log_{10} F \ (m^{-3}) \]

\( S=3, \ i^* = 75 \)

\( \nu = 1 \)

11
21
31
41
51

\( F^0 \)
Selected Applications
Homogeneous nucleation

Distribution function - time dependence

$S_{ini} = 3$

$S_{ini} = 5$

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Selected Applications

Homogeneous nucleation

Distribution function - size dependence \((S_{ini} = 5)\)
Selected Applications

Homogeneous nucleation

Nucleation rate - time dependence

$S_{ini} = 3$

$S_{ini} = 5$

dimensionless time

$J/J_s$ (m$^{-3}$ s$^{-1}$)

closed system

open system

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Selected Applications

Homogeneous nucleation

Nucleation rate \((S_{ini} = 5, J_0^S = J^S \text{ at } S_{ini})\)

Open system \((S_{ini} = \text{const.})\)

Closed system

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Selected Applications

Homogeneous nucleation

Nucleation rate \( (S_{ini} = 5) \)

![Graphs showing nucleation rate with different values of initial supersaturation.](image)
Selected Applications

Homogeneous nucleation

Supersaturation

Critical size

Nucleation kinetics
Selected Applications

Homogeneous nucleation

**HON: Liquid/Solution → Solid transition**

Z. Kožíšek, CrystEngComm 15 (2013) 2269

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**Size distribution of nuclei**

**CNT**

**Encapsulated system**

\[ N_1(t) = \text{const.} \]

\[ N_1 \text{ decreases with time} \]
Selected Applications

Homogeneous nucleation

Model system: nucleation of Ni melt

DSC experiments and MC simulations [J. Bokeloh et al., PRL 107 (2011) 145701

J was obtained from a statistical evaluation of crystallization behavior during continuous cooling.
A single Ni sample was repeatedly heated up to 1773 K and subsequently cooled down to 1373 K.

sample masses: 23 µg – 63 mg

survivorship function:

\[ F_{\text{sur}}(\Delta T) = 1 - \exp\left(\int J(\Delta T) \, dt\right) \]

\[ \Delta T \Rightarrow J = \Gamma \exp\left(-\frac{\Delta W^*}{k_B T}\right) \]

- **MC simulations** show a deviation of the energy of formation \(\Delta W_i\) from CNT.
- However, the actual height of the energy barrier is in good agreement with CNT.

All system parameters are known \(\Rightarrow\) we can determine the size distribution of nuclei \(F_i\)
Homogeneous nucleation

Ni melt: \( \Delta h_E = 17.29 \text{ kJ mol}^{-1}, T_E = 1748 \text{ K}, \varrho_S = 8357 \text{ kg m}^{-3}, \sigma = \sigma_m T / T_E, \)

where \( \sigma_m = 0.275 \text{ J m}^{-2}, E = 29.085 \text{ kJ mol}^{-1} \)

\[
T = 1449 \text{ K} \Rightarrow i^* = 456
\]

\[
F_i V = 1
\]

one \( i \)-sized nucleus is formed in \( V \)

\[
F^S_{456} = 250000 \text{ m}^{-3} \Rightarrow V_1 = 1 / F^S_{i^*} = 4 \text{ cm}^3
\]

sample masses: 23 \( \mu \text{g} \) – 63 mg

\[\Rightarrow V = 7.15 \times 10^{-9} \text{ m}^3 - 2.9 \times 10^{-12} \text{ m}^3\]

In difference of experimental data, no critical nuclei are formed in Ni melt.

**Solution:** reduce the interfacial energy or take into account \( \sigma(i) \) dependency \( \Rightarrow \)

lower nucleation barrier

Maybe heterogeneous nucleation occurs?
CNT model of nucleation on active centers – one additional equation is needed


Additional equation:

\[ \frac{dZ(t)}{dt} = [N_0 - Z(t)]J^S(t) \]

\( Z(t) \) - the total number of nuclei at time \( t \)
\( N_0 \) - the number of active sites;
\( J^S \) - time dependent nucleation frequency (usually taken as fit parameter)

Our new model does not need additional equation!!

\[ \rightarrow \text{ only modification of boundary conditions} \]

Nucleation on active centers

HEN: Vapor → Solid transition

![Graph showing nucleation kinetics](image-url)
Selected Applications

Nucleation on active centers

HEN: Vapor $\rightarrow$ Solid transition


FIG. 1. Bright-field plan-view TEM images of $a$-Si thin films annealed at 873 K in nitrogen with the artificial nucleation sites, which show the evolution with the annealing time at (a) $2.0 \times 10^4$ s, (b) $3.6 \times 10^4$ s, and (c) $5.4 \times 10^4$ s. It is seen that a single dendritic crystallite grows at each artificial site, and no coalescence has occurred up to $5.4 \times 10^4$ s.
Selected Applications

Nucleation on active centers

HEN: Vapor \rightarrow \text{Solid transition}

FIG. 2. Dynamic evolution of the CSD in the controlled solid-phase crystallization of $\alpha$-Si thin films with artificial nucleation sites. Three CSDs marked with $\triangle$, $\blacksquare$, and $\bullet$ are observed in the samples shown by (a), (b), and (c) of Fig. 1, respectively. The solid lines are the theoretical predictions with the depletion of the nucleation sites taken into account.
**Selected Applications**

**Nucleation on active centers**

**HEN: polymer nucleation from melt** (polyethylene) \( \Delta T = 10.4 \, K \)


Selected Applications
Nucleation on active centers

**HEN: polymer nucleation from melt** (polyethylene)


![Graph showing experimental data](image)

\[ \sigma_{nano} \text{ (instead of } \sigma) \text{ introduced to fit } F_i^S \Rightarrow k^* = 9, \ l^* = 24.9, \ m^* = 4.5 \Rightarrow 3D \text{ model} \]
Selected Applications

Polymer nucleation on active centers (polyethylene)

Summary

Advantages

- Relatively simple model enables to determine basic characteristics of nucleation in real time.
- Model takes into account depletion of the parent phase during phase transformation.
- Model includes exhaustion of active centres (new approach to heterogeneous nucleation).

This work was supported by the Project No. LD15004 (VES15 COST CZ) of the Ministry of Education of the Czech Republic.

Thank you for your attention.
Summary

**Advantages**

- Relatively simple model enables to determine basic characteristics of nucleation in real time.

- **Model takes into account depletion of the parent phase during phase transformation.**

- Model includes exhaustion of active centres (new approach to heterogeneous nucleation).

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