Polymer nucleation on active centers

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Introduction

Praha, Czech Republic
New measurements of nucleation in polymer systems

**Nucleation kinetics near critical size was first time measured**

- **2003**
  - Nucleating agent was added to increase nucleation rate of polyethylene.

2D model of polymer nucleation, analysis of the total number of supercritical nuclei.
New measurements of nucleation in polymer systems

2007

K. Okada, K. Watanabe, I. Wataoka, A. Toda, S. Sasaki, K. Inoue, M. Hikosaka:

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First experimental data on size distribution of nuclei near critical size!!

⇒ New view to nucleation kinetics on active centers
**Introduction**

**Nucleation** → process leading to the **formation of a new phase** (solid, liquid) within metastable original phase (undercooled melt, supersaturated vapor or solution)

**First models:** formation of droplets from supersaturated vapor

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

- **homogeneous nucleation**
- **heterogeneous nucleation**
  - 2D, 3D nucleation
  - nucleation on active centers (special case)

→ model of nucleation kinetics for vapor–liquid transition

**Thermodynamic aspects**

**Work of formation of clusters:** $W_i = -i \Delta \mu + \gamma \sigma i^{2/3}$

- $i$: cluster size, i.e., number of monomers (molecules, atoms, repeating units) within cluster
- $\Delta \mu$: difference in chemical potentials of both phases
- $\sigma$: interfacial energy; $\gamma$: form factor

**Spherical shape:** $\Rightarrow \frac{4}{3} \pi r^3 \varrho = im_1$

- $r$: cluster radius; $\varrho$: density; $m_1$: monomer mass

**Surface energy:** $4\pi r^2 \sigma = \gamma \sigma i^{2/3}$
Chemical potentials

**Formation of droplets** (vapor → liquid transition):

\[
\Delta \mu = k_B T \ln S; \quad S = \frac{P}{P^0} = \frac{N}{N^0}
\]

- \( k_B \) = Boltzmann constant; \( T \) = temperature; \( S \) = supersaturation
- \( P \) = pressure; \( P^0 \) = saturation pressure
- \( N \) = number of monomers
- \( N^0 \) = number of monomers in saturated vapor

**Crystal nucleation from melt** (liquid → solid transition):

\[
\Delta \mu = \frac{\Delta h_E}{N_A T_E} (T_E - T)
\]

- \( \Delta h_E \) = heat of fusion
- \( N_A \) = Avogadro constant; \( T_E \) = equilibrium temperature
MODEL

In both cases:

\[ F_i^0 = A \exp \left( -\frac{W_i}{k_B T} \right) \]

\( i^* \) - critical size; \( W_{i^*} \) - nucleation barrier

Equilibrium number density of clusters:

\( A \) - preexponential factor
MODEL

Frenkel: $A = N \Rightarrow F_i^0$ does not satisfy self-consistency!!

$$F_i^0 = A \exp \left( - \frac{W_i}{k_B T} \right) \neq N$$


Usually:

$$A = N \exp \left( - \frac{\Delta \mu + \gamma \sigma}{k_B T} \right)$$
Coalescence is neglected
attachment (resp. detachment) of single molecules plays dominant role in nucleation and growth process

Nucleation starts at any monomer (nucleation center) in the bulk of the supersaturated mother phase

$k_i^+ (k_i^-)$ – attachment (detachment) frequencies of molecules
Model

Kinetic equations

\[
\frac{dF_i}{dt} = k_{i-1}^+ F_{i-1} - [k_i^+ + k_i^-] F_i + k_{i+1}^- F_{i+1}
\]
Model

Kinetic equations

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

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

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

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

Total number of nuclei greater than \( m \)

\[ Z_m(t) = \sum_{i > m} F_i(t) = \int_0^t J_m(t') dt' \]
Model

Transient frequencies

Vapor $\rightarrow$ Liquid

\[ k_i^+ = \frac{P}{\sqrt{2\pi m_1 k_B T}} \gamma i^{2/3} \]

Liquid $\rightarrow$ Solid

\[ k_i^+ = \varrho_S \left( \frac{k_B T}{h} \right)^{\gamma i^{2/3}} \exp \left( -\frac{E}{k_B T} \right) \exp \left( -\frac{q\Delta g_i}{k_B T} \right) \]

\[ \Delta g_i = W_{i+1} - W_i; \quad q = \frac{1}{2} \left[ 1 + \text{sign}(\Delta g_i) \right] \]

$\varrho_S$ - surface density of monomers; $h$ - Planck constant
$E$ - activation energy of diffusion across the phase interface

Equilibrium: $J_i = 0 \Rightarrow k_i^+ F_i^0 = k_{i+1}^- F_{i+1}^0$
Model

Transient frequencies

**Vapor → Liquid**

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\( \varrho_S \) - surface density of monomers; \( h \) - Planck constant

**Equilibrium:** \( J_i = 0 \Rightarrow k_i^+ F_i^0 = k_{i+1}^- F_{i+1}^0 \)

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

– local equilibrium principle
Model

Nucleation on active centers – one additional equation is needed


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

\( Z(t) \) - 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)
Model

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New model does not need additional equation!!
→ only modification of boundary conditions


Model

**Initial and boundary conditions**

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

\[ N_T = \sum_{i=1}^{i_0} iF_i^0 \quad \text{total number of molecules (active centers)} \]

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

\[ F_1 \gg \sum_{i>1} iF_i(t) \implies F_1 = \text{const.} \quad \text{standard model} \]
Model

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\[ F_1(t) = N_T - \sum_{i>1} F_i(t) \]

\[ F_1^0 \quad \text{- number of nucleation sites} \]
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\[ F_1(t) = N_T - \sum_{i>1} F_i(t) \quad \text{standard model} \]

\[ F_1^0 \quad \text{- number of nucleation sites} \]

\[ F_1(t) = N_T - \sum_{i>1} i F_i(t) \quad \text{closed system} \]
Model

Initial and boundary conditions

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\[ F_1^0 \quad \text{- number of nucleation sites} \]

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

\[ \text{Kinetic equations are the same for homogeneous (heterogeneous) nucleation, nucleation on active centers (nucleation agent added)} \]
Data analysis

**2D MODEL**

Nucleation agent

Parameters: $E/(k_B T) = 29.3$, $N_0 = 4.99 \times 10^{17} \text{ m}^{-3}$


$i^* = 567$
Data analysis

Work of formation of nuclei

$$\Delta G = -klm\Delta \mu + 2lm\sigma + 2km\sigma_e + kl\Delta \sigma$$

where $\Delta \sigma = \sigma_{CL} + \sigma_{AC} - \sigma_{AL}; \ i = klm$

$\Delta \mu (\sigma$) - difference of chemical potentials (interfacial energy)

per one particle (repeating unit)

$$\Delta \mu = \frac{\Delta h_E}{N_A T_E} (T_E - T)$$

$\Delta h_E$ - heat of fusion; $T_E$ - equilibrium temperature; $N_A$ - Avogadros constant

$$\frac{\partial \Delta G}{\partial k} = \frac{\partial \Delta G}{\partial l} = \frac{\partial \Delta G}{\partial m} = 0$$


$\sigma_{macro} \Rightarrow k^* = 9.8; \ l^* = 118; \ m^* = 0.57 \ \Rightarrow \ 2D \ MODEL$
Data analysis
New experimental data

Data analysis

Experimental data

Log_{10} F(i, t) vs t (min)

i=20
940
6900
Data analysis


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Data analysis

\[ F_{20}^{\text{exp}}(t \geq \tau) = c_N F_{20}(t \geq \tau) \Rightarrow c_N - \text{control volume} \]
Data analysis
Work of formation of nuclei

**3D MODEL**


\[
\begin{align*}
k^* &= \frac{4\sigma}{\Delta\mu}; \quad l^* = \frac{4\sigma_e}{\Delta\mu}; \quad m^* = \frac{2\Delta\sigma}{\Delta\mu}.
\end{align*}
\]

\(\sigma_{nano} \Rightarrow k^* = 9, l^* = 24.9, m^* = 4.5 \Rightarrow 3D\ model\)

**Assumption:** form of nuclei \(\approx\) critical nucleus form

\[
\begin{align*}
k &= k^* \frac{\sigma}{\sigma_e}; \quad l = l^* \frac{\sigma}{\sigma_e}; \quad m = m^* \frac{2\sigma}{\Delta\sigma}.
\end{align*}
\]

\(\Rightarrow \Delta G = -i\Delta\mu + \beta i^{2/3}; \quad i = klm; \quad \beta = 3^{3/2} 4\sigma\sigma_e\Delta\sigma\)

\[i^* = \frac{32\sigma\sigma_e\Delta\sigma}{\Delta\mu}\]
Liquid – solid:

\[ k_i^+ = \varrho \sigma \left( \frac{k_B T}{\hbar} \right)^{\gamma i^{2/3}} \exp \left( -\frac{E}{k_B T} \right) \exp \left( -\frac{q \Delta g_i}{k_B T} \right) \]

\[ k_i^+ = 2\text{Im} \left( \frac{k_B T}{\hbar} \right) \exp \left( -\frac{E}{k_B T} \right) \exp \left( -\frac{q \Delta g_i}{k_B T} \right) \]

\[ k_i^+ = \sqrt[3]{\frac{4\sigma e \Delta \sigma}{\sigma^2}} i^{2/3} \left( \frac{k_B T}{\hbar} \right) \exp \left( -\frac{E}{k_B T} \right) \exp \left( -\frac{q \Delta g_i}{k_B T} \right) \]
Data analysis - 3D model

\[ G(i) = -i \Delta \mu + \beta i^{(2/3)} \]

\[ \Delta \mu = 0.032 \]
\[ \beta_{macro} = 0.44 \]
\[ \beta_{nano} = 0.38 \]
Data analysis - 3D model

\[ F_i = A \exp\left(-\frac{G_i}{kT}\right) \]

\[ A = 1000 \]

\[ \sigma_{macro}, \sigma_{nano} \]

98 min
Data analysis - 3D model

2D - 3D models

2D: 98 min
3Dmacro: 98 min
3Dnano: 98 min
98 data

\[ \log_{10} F \]

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$E/(k_B T) = 28.75; \quad N_0 = 2.5 \times 10^{16} \quad c_N = 2.4 \times 10^{-13}$
Data analysis - 3D model

3D model: nano parameters, \( i^* = 487, cn = 24 \times 10^{-14} \)

\[ \log_{10} F (F^*cn \text{ in m}^{-3}) \]

\( t \text{ (min)} \)

Graph showing the relationship between \( \log_{10} F (F^*cn \text{ in m}^{-3}) \) and \( t \) (minutes) for different values of 20, 940, 6900.
Data analysis - 3D model

\[ \text{try: } i = 500, 630 \Rightarrow E, N_0 \]

3D: nano parameters, \( i^* = 487, i_{\text{exp}} = 500, 630 \)
It seems that \( f(t) \) does not reach its stationary value, but **slowly increases with time**! How to explain such behavior? Any model gives stationary state or decrease in the number density \( F \) (decrease of active centers with time).

- \( \sigma(r) = \sigma_\infty/(1 + 2\delta/r) \) – but \( F \to F^S \)
- \( E = E(i) \) – but \( F \to F^S \)
- \( G(i) \) - approximation, but even if one knows \( G \) exactly, \( F \to F^S \)

It seems that there is only one possibility how to explain small increase in \( F \) with time. Measured \( F \) probably corresponds to

**nucleation on active centers + homogeneous nucleation**
Heterogeneous + homogeneous nucleation

Schematic plot: homog. + heterog. nucleation

- heterogeneous
- homegeneous
- both

Time (s): 0, 50, 100, 150, 200, 250, 300, 350, 400

F100: 0, 5, 10, 15, 20, 25, 30
Conclusions

- **3D model** with $\sigma_{nano}$ gives better coincidence with experimental data than 2D model
- Measured data of the number density of nuclei, $F$, corresponds probably to nucleation on nucleation agent + homogeneous nucleation

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- **3D model** with $\sigma_{nano}$ gives better coincidence with experimental data than 2D model

- **Measured data** of the number density of nuclei, $F$, corresponds probably to nucleation on nucleation agent + homogeneous nucleation

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