

The 14th International Summer School on Crystal Growth

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The Classical Nucleation Model

-- Entire Process of Crystal Growth and
Application to Chirality Conversion--

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- Introduction
- The Classical Nucleation Model (tutorial with many equations!)
- Steady State Nucleation (tutorial with many equations)
- Evolution from Nucleation to Ripening (numerical result)
- An application: Chirality Conversion of Crystals by Grinding (related to Viedma's lecture)
 - Generalized CNM with grinding
- Summary

Crystallization from beginning to end in a closed system

Nucleation of tiny crystallites

Many small clusters
High supersaturation



Growth of crystals

Clusters grow
Drop of supersaturation

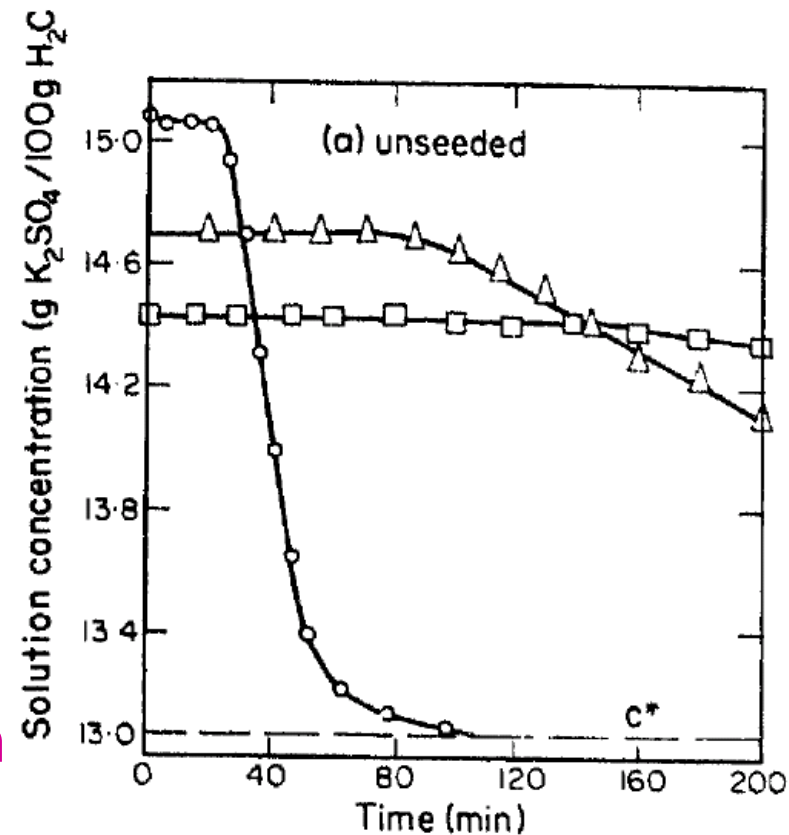


Ripening of crystals

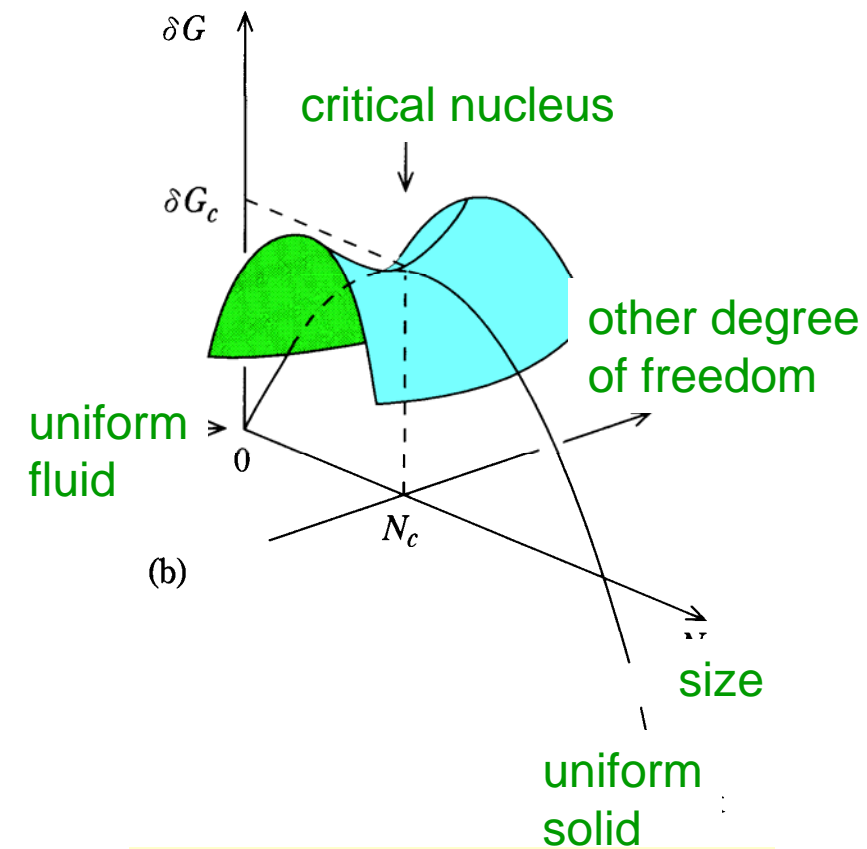
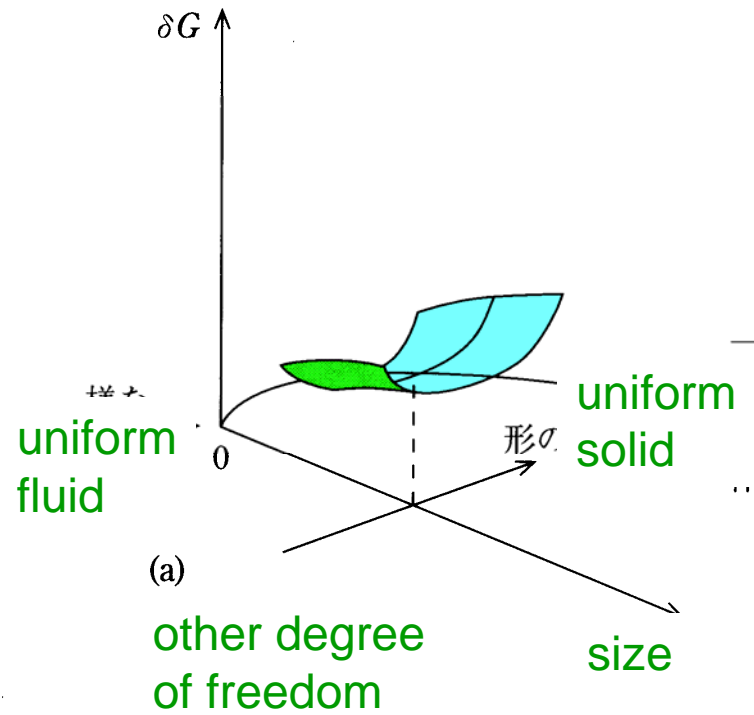
Few large clusters
Supersaturation approaches zero

How does supersaturation in a solution change during the entire process of crystallization?

- Basic question but few serious studies
- An old experiment \Rightarrow
- Old empirical laws:
von Weimarn's laws(1925)
 1. Larger crystals precipitate under lower supersaturation
 2. At a certain time the mean crystal size shows a maximum as a function of supersaturation
- Theory?



Free energy of a solid cluster in undersaturation and in supersaturation



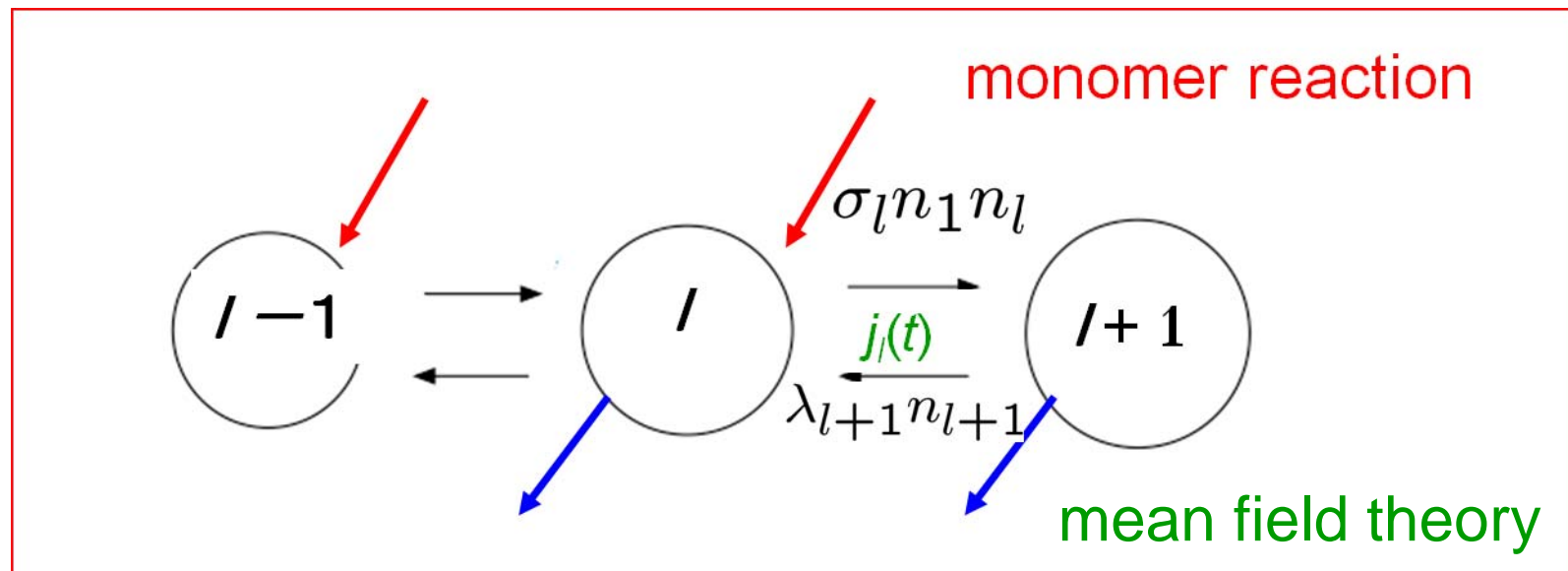
saturated or undersaturated state

を
supersaturated state

Becker-Doering model (Szilard-Farkas model) classical nucleation model (CNM)

- **Distribution of cluster size** $n_l(t)$

$$\frac{\partial n_l(t)}{\partial t} = n_1(t)n_{l-1}(t)\sigma_{l-1} - n_1(t)n_l(t)\sigma_l + n_{l+1}(t)\lambda_{l+1} - n_l(t)\lambda_l$$

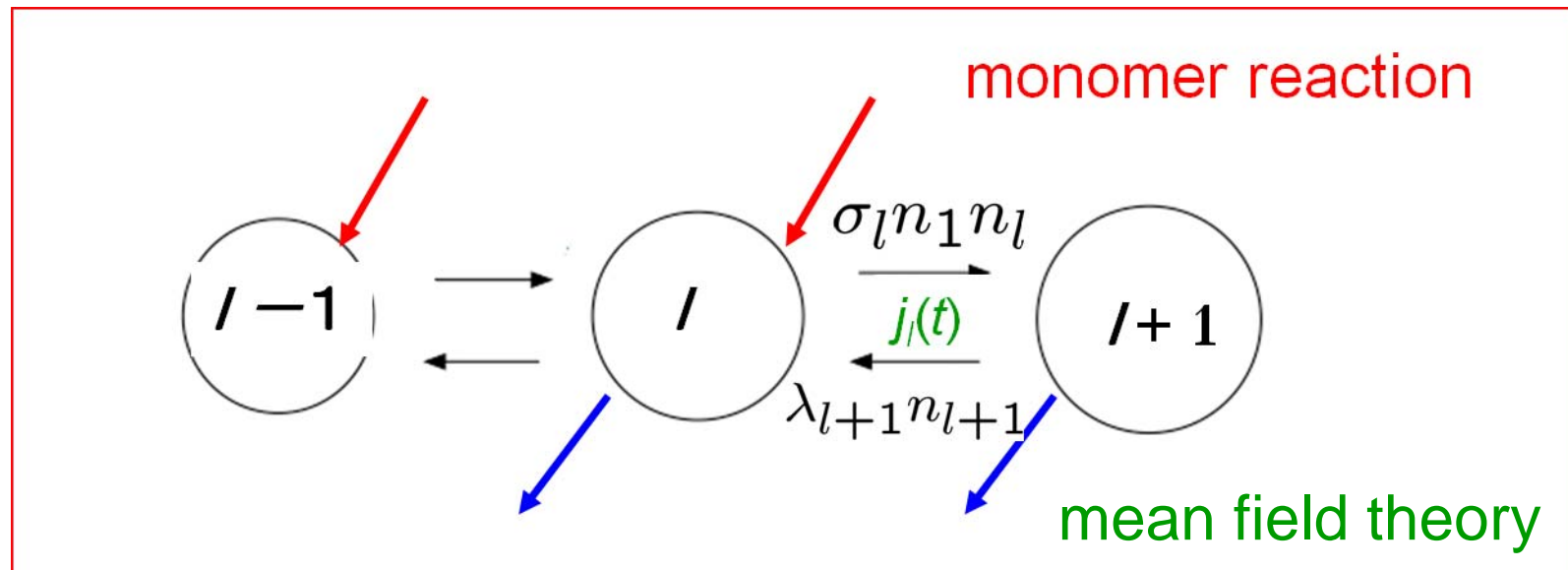


Becker-Doering model (Szilard-Farkas model) classical nucleation model (CNM)

- Distribution of clusters $n_l(t)$: number of l -mers

$$\frac{\partial n_l}{\partial t} = j_{l-1} - j_l$$

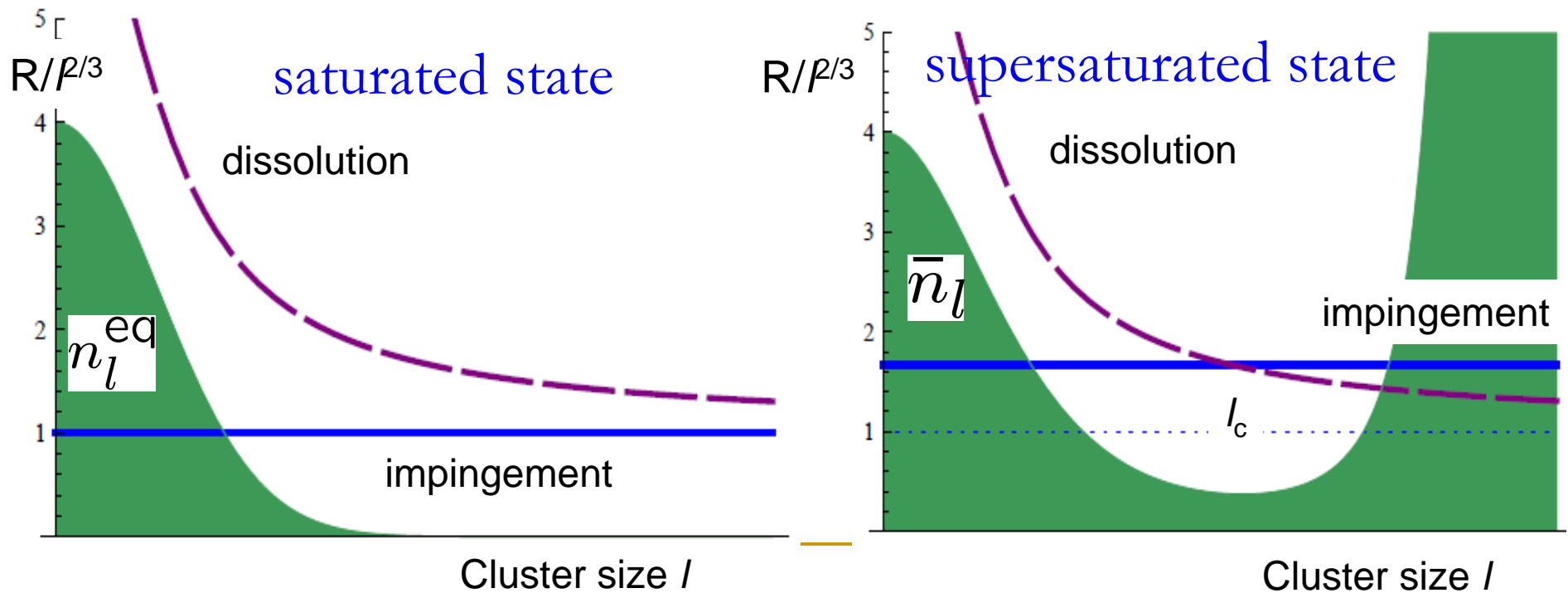
- Current $j_l(t)$ in the size space



Equilibrium and supersaturated states in the classical nucleation model

- Impingement and dissolution (evaporation)
- Distribution of cluster size $n_l(t)$

Rates per unit surface area



Classical nucleation model

- Growth factor σ_l is proportional to $l^{2/3}$ (uniform environment)

$$\sigma_l = al^{2/3}$$

- The decay rate λ_l is determined by the **detailed balance condition**

$$\sigma_l n_1^{\text{eq}} n_l^{\text{eq}} = \lambda_{l+1} n_{l+1}^{\text{eq}}$$

and the equilibrium distribution (at saturation)

$$n_l^{\text{eq}} = n_1^{\text{eq}} e^{-G_l^{\text{eq}}/k_B T} = n_1^{\text{eq}} \exp[-\bar{\alpha}(l^{2/3} - 1)]$$

$$\bar{\alpha} = (4\pi)^{1/3} (3\Omega)^{2/3} \frac{\alpha}{k_B T}$$

as

$$\lambda_l = \sigma_{l-1} n_1^{\text{eq}} \exp[\bar{\alpha}l^{2/3} - \bar{\alpha}(l-1)^{2/3}]$$

Classical nucleation model

- Growth factor σ_l

$$\sigma_l = al^{2/3}$$

- The decay rate λ_l

$$\lambda_l = \sigma_{l-1} n_1^{\text{eq}} \exp [\bar{\alpha} l^{2/3} - \bar{\alpha} (l-1)^{2/3}]$$

- For simulation we use the asymptotic form with $l \gg 1$

$$\lambda_l = al^{2/3} n_1^{\text{eq}} \left(1 + \frac{2\bar{\alpha}}{3} \frac{1}{l^{1/3}} \right).$$

Analytical study is possible.

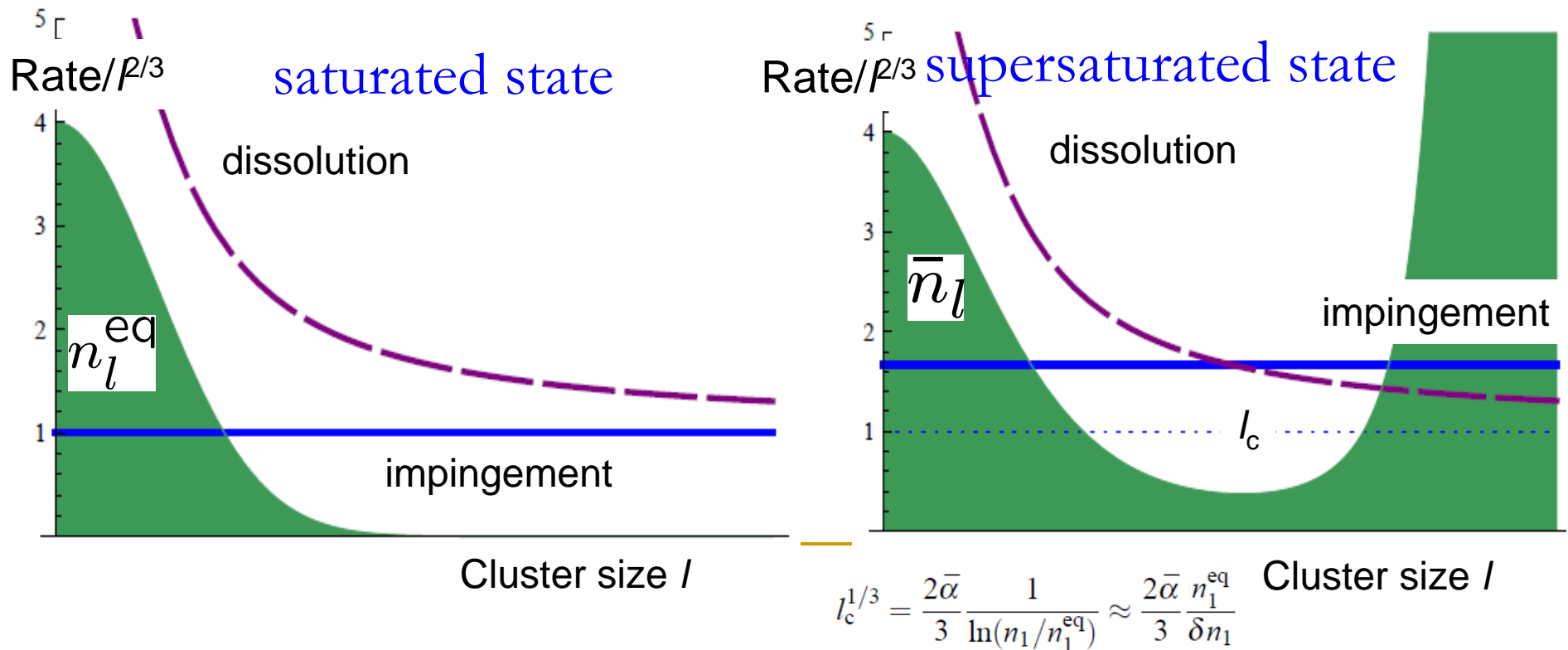
Nucleation is easier.

Direct numerical calculation is possible in a very limited regime.

Equilibrium and supersaturated states in the classical nucleation model

- Impingement and dissolution (evaporation)
- Distribution of cluster size $n_l(t)$

Rates per unit surface area

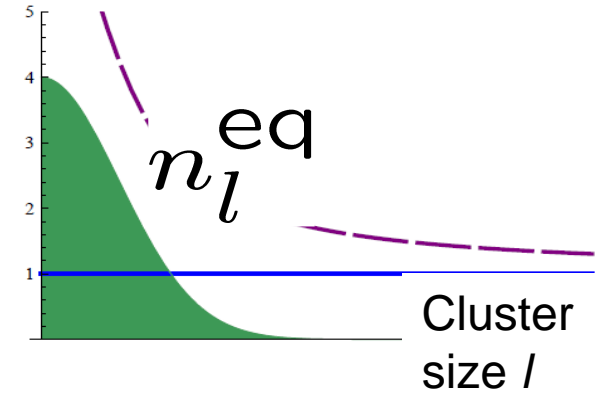


Classical nucleation model

- At saturation equilibrium

$$\sigma_l n_1^{\text{eq}} n_l^{\text{eq}} = \lambda_{l+1} n_{l+1}^{\text{eq}}$$

$$n_l^{\text{eq}} = (n_1^{\text{eq}})^l \frac{\sigma_1 \sigma_2 \cdots \sigma_{l-1}}{\lambda_2 \lambda_3 \cdots \lambda_l}$$



- In an undersaturated state

$$n_1 < n_1^{\text{eq}}$$

$$\Delta\mu < 0$$

$$\Delta\mu = k_B T \ln \frac{n_1}{n_1^{\text{eq}}}$$

$$\sigma_l n_1 \bar{n}_l = \lambda_{l+1} \bar{n}_{l+1}$$

$$\bar{n}_l = n_1^l \frac{\sigma_1 \sigma_2 \cdots \sigma_{l-1}}{\lambda_2 \lambda_3 \cdots \lambda_l} = \left(\frac{n_1}{n_1^{\text{eq}}} \right)^l n_l^{\text{eq}}$$

$$\bar{n}_l = e^{l\Delta\mu/k_B T} n_l^{\text{eq}} = n_1 \exp\left(-\frac{G_l}{k_B T}\right)$$

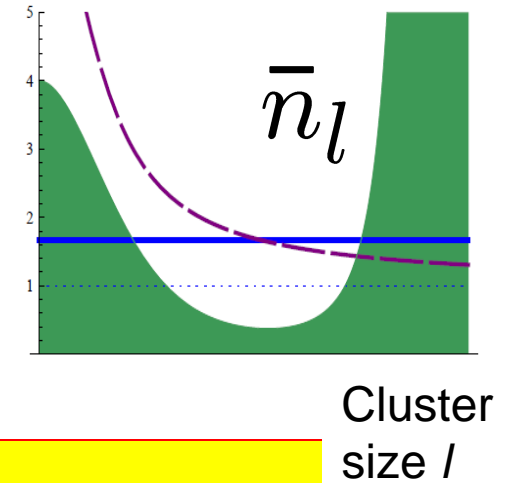
$$G_l = -l\Delta\mu + G_l^{\text{eq}} = -l\Delta\mu + \bar{\alpha}(l^{2/3} - 1).$$

Classical nucleation model

- At saturation equilibrium

$$\sigma_l n_1^{\text{eq}} n_l^{\text{eq}} = \lambda_{l+1} n_{l+1}^{\text{eq}}$$

$$n_l^{\text{eq}} = (n_1^{\text{eq}})^l \frac{\sigma_1 \sigma_2 \cdots \sigma_{l-1}}{\lambda_2 \lambda_3 \cdots \lambda_l}$$



- In a supersaturated state

$$n_1 > n_1^{\text{eq}}$$

$$\sigma_l n_1 \bar{n}_l = \lambda_{l+1} \bar{n}_{l+1}$$

$$\Delta\mu > 0$$

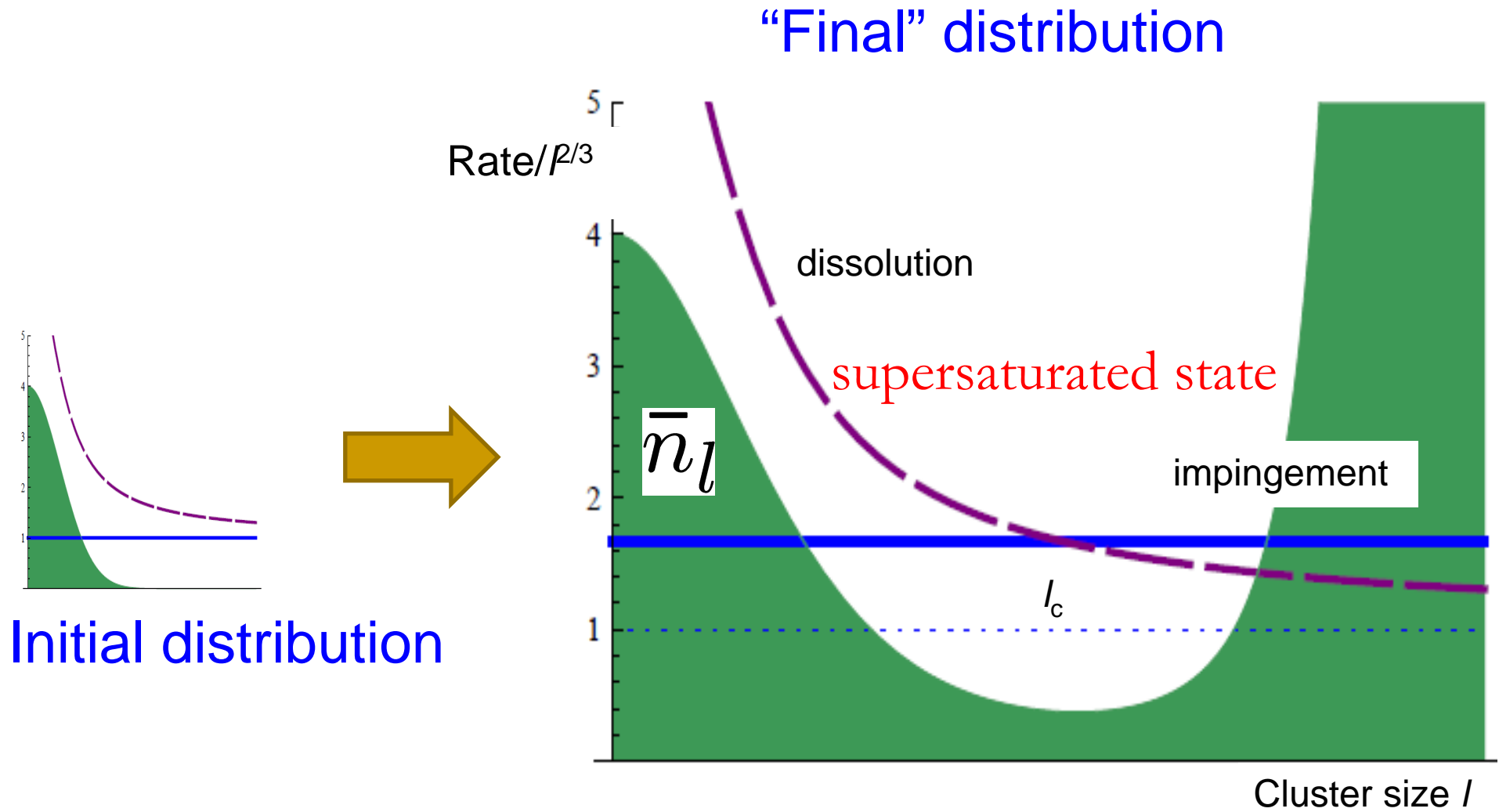
$$\Delta\mu = k_B T \ln \frac{n_1}{n_1^{\text{eq}}}$$

$$\bar{n}_l = n_1^l \frac{\sigma_1 \sigma_2 \cdots \sigma_{l-1}}{\lambda_2 \lambda_3 \cdots \lambda_l} = \left(\frac{n_1}{n_1^{\text{eq}}} \right)^l n_l^{\text{eq}}$$

$$\bar{n}_l = e^{l\Delta\mu/k_B T} n_l^{\text{eq}} = n_1 \exp\left(-\frac{G_l}{k_B T}\right)$$

$$G_l = -l\Delta\mu + G_l^{\text{eq}} = -l\Delta\mu + \bar{\alpha}(l^{2/3} - 1).$$

Nucleating state in the CNM



$$l_c^{1/3} = \frac{2\bar{\alpha}}{3} \frac{1}{\ln(n_1/n_1^{\text{eq}})} \approx \frac{2\bar{\alpha}}{3} \frac{n_1^{\text{eq}}}{\delta n_1}$$

Steady state nucleation rate with $n_1 > n_1^{\text{eq}}$

- If steady state is realized, **current in the size space is constant**

$$j_l^{\text{SS}} = \sigma_l n_1^{\text{SS}} n_l^{\text{SS}} - \lambda_{l+1} n_{l+1}^{\text{SS}}$$

$$n_1^{\text{SS}} = \text{const}, \quad n_{\infty}^{\text{SS}} = 0$$

- The decay coefficient may be expressed in terms of σ and \bar{n}_l (using $\sigma_l n_1 \bar{n}_l = \lambda_{l+1} \bar{n}_{l+1}$) and the steady current is calculated as

$$\frac{1}{j_l^{\text{SS}}} = \sum_{l'=1}^{\infty} \frac{1}{n_1 \sigma_{l'} \bar{n}_{l'}}$$

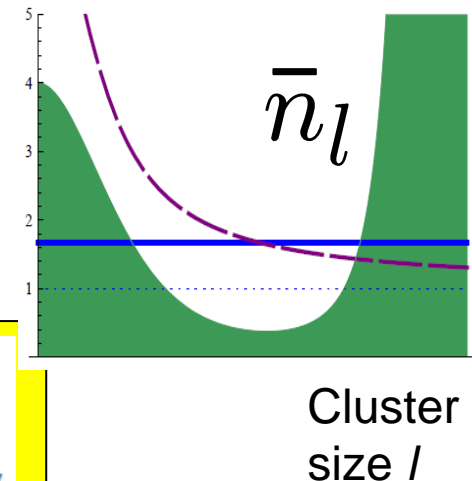
Steady state nucleation rate $n_1 > n_1^{\text{eq}}$

- The formula of steady current $\frac{1}{j_l^{\text{ss}}} = \sum_{l'=1}^{\infty} \frac{1}{n_1 \sigma_{l'} \bar{n}_{l'}}$ is evaluated by the saddle point method.

$1/\bar{n}_l$ has a strong peak at the critical size

- Steady nucleation rate is

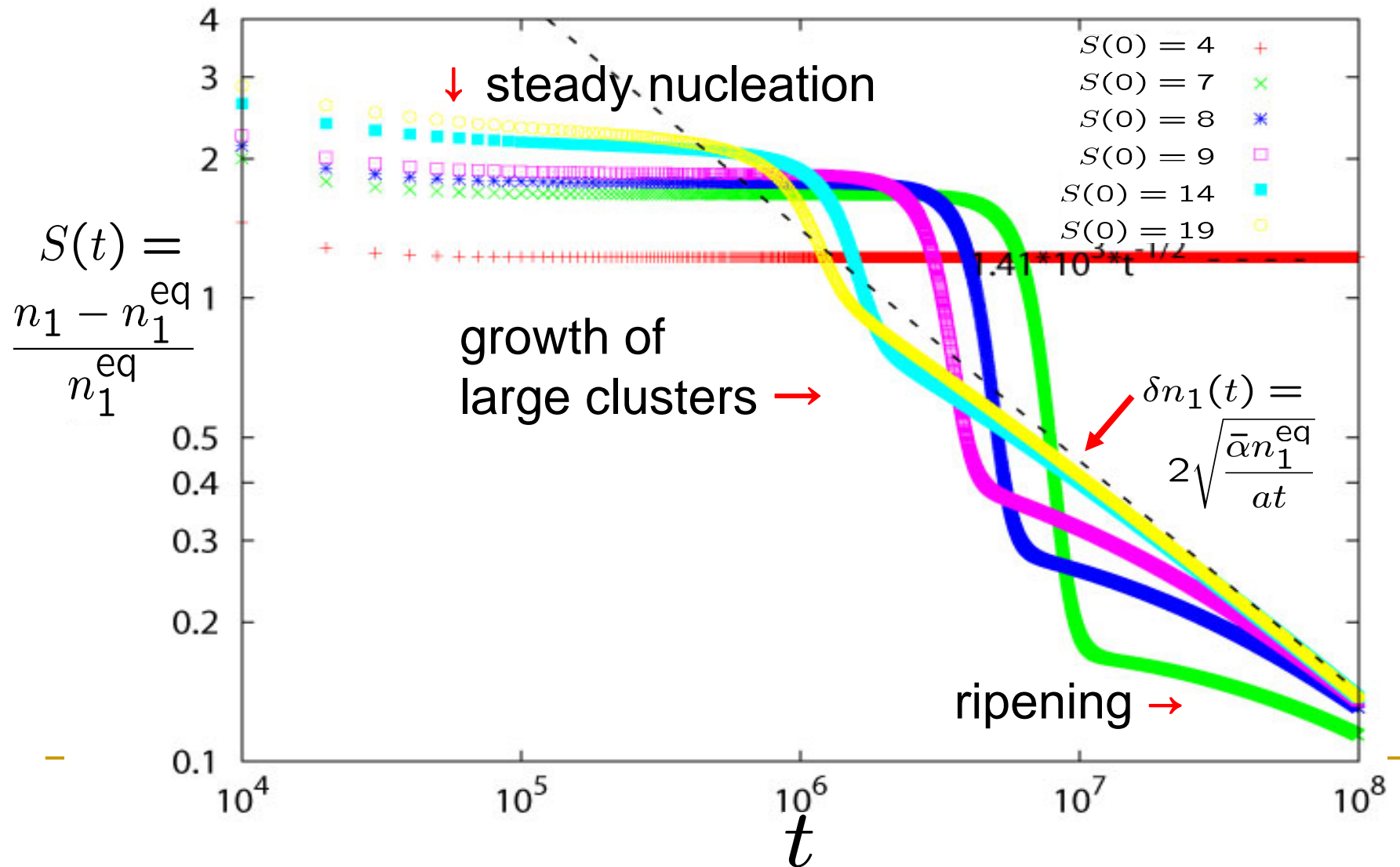
$$j^{\text{ss}} \approx n_1 \sigma_{l_c} \sqrt{-\frac{G''_{l_c}}{2\pi k_B T}} n_1 e^{-G_{l_c}/k_B T}$$



$$G_l = -l\Delta\mu + G_l^{\text{eq}} = -l\Delta\mu + \bar{\alpha}(l^{2/3} - 1).$$

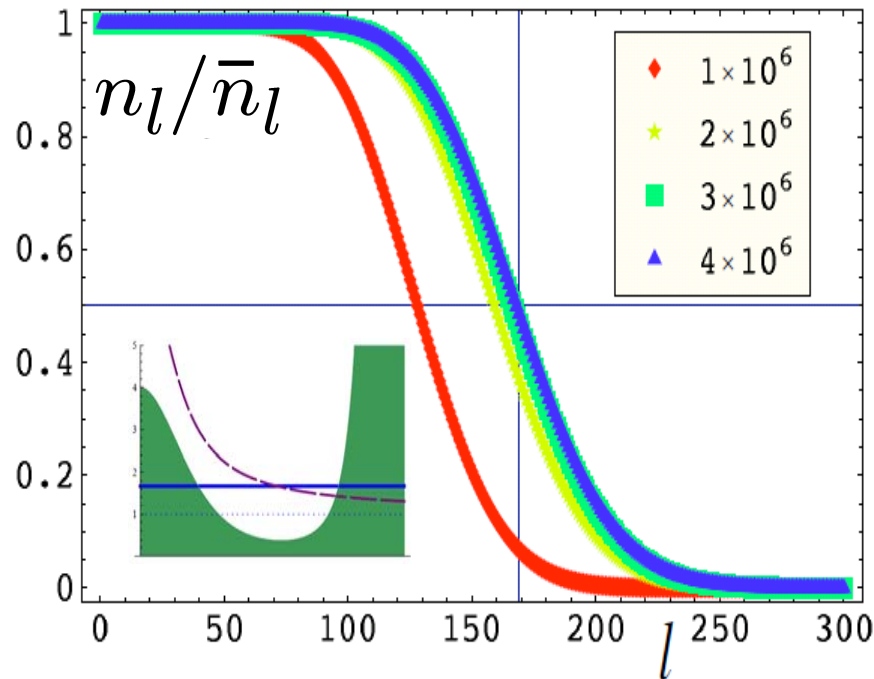
**Numerical integration of the CNM
with various initial supersaturation**

Change of supersaturation $S(t)$ with various initial supersaturation $S(0)$

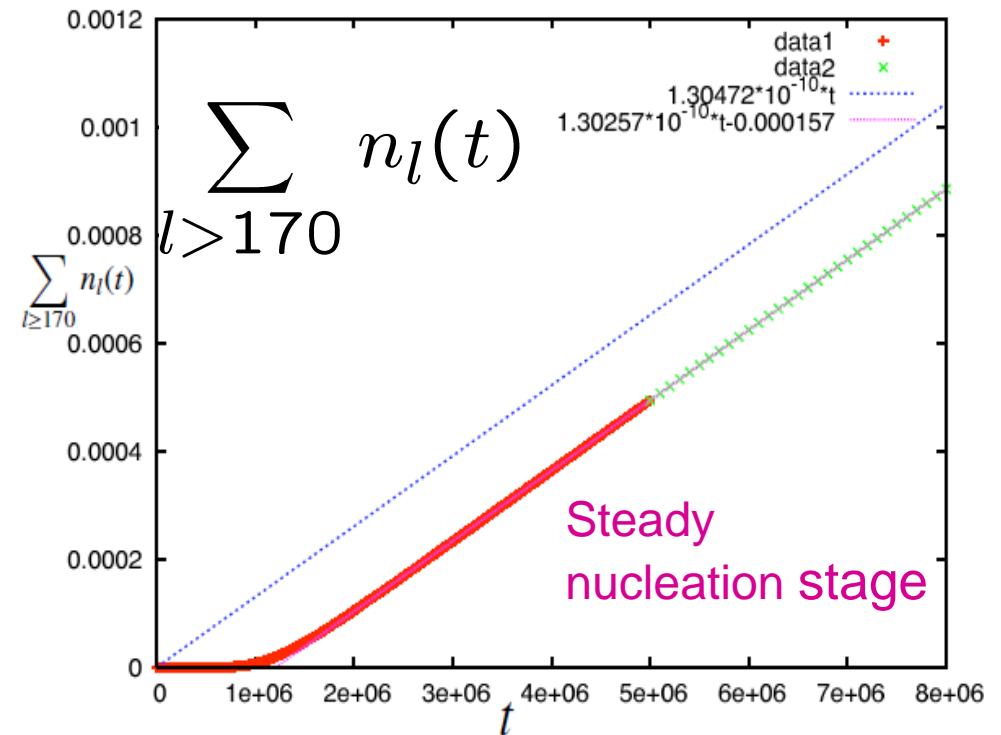


Steady nucleation stage for “low” supersaturation with $S(0)=4$

- The classical nucleation theory works well.
 - Waiting time and the steady nucleation rate



change of distribution

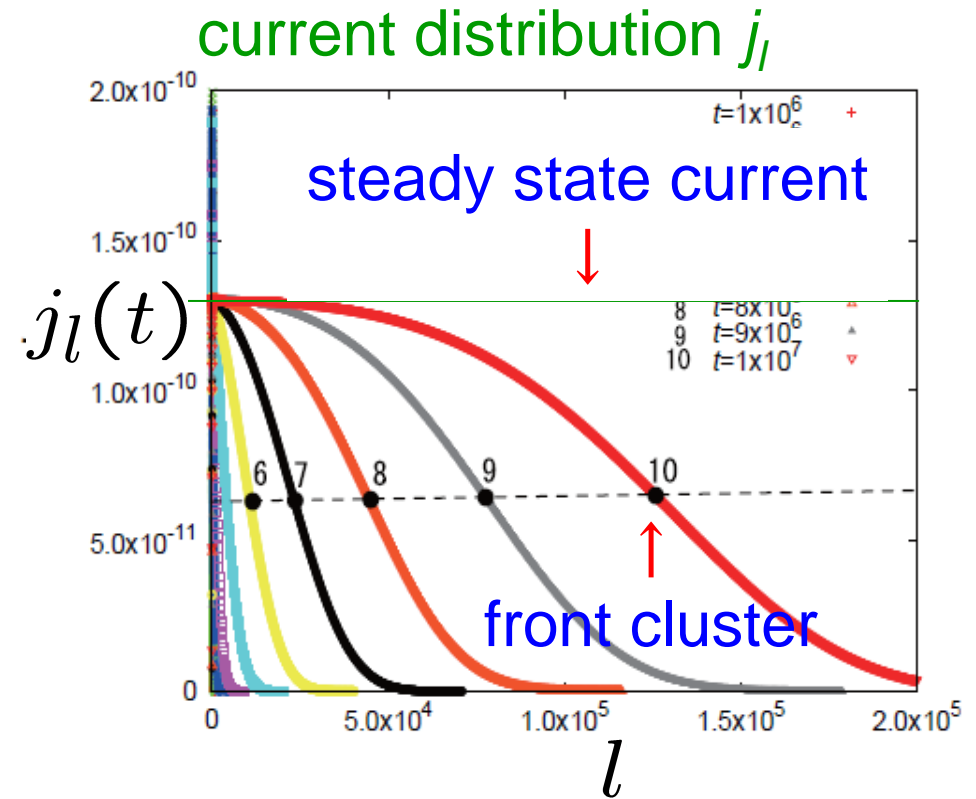
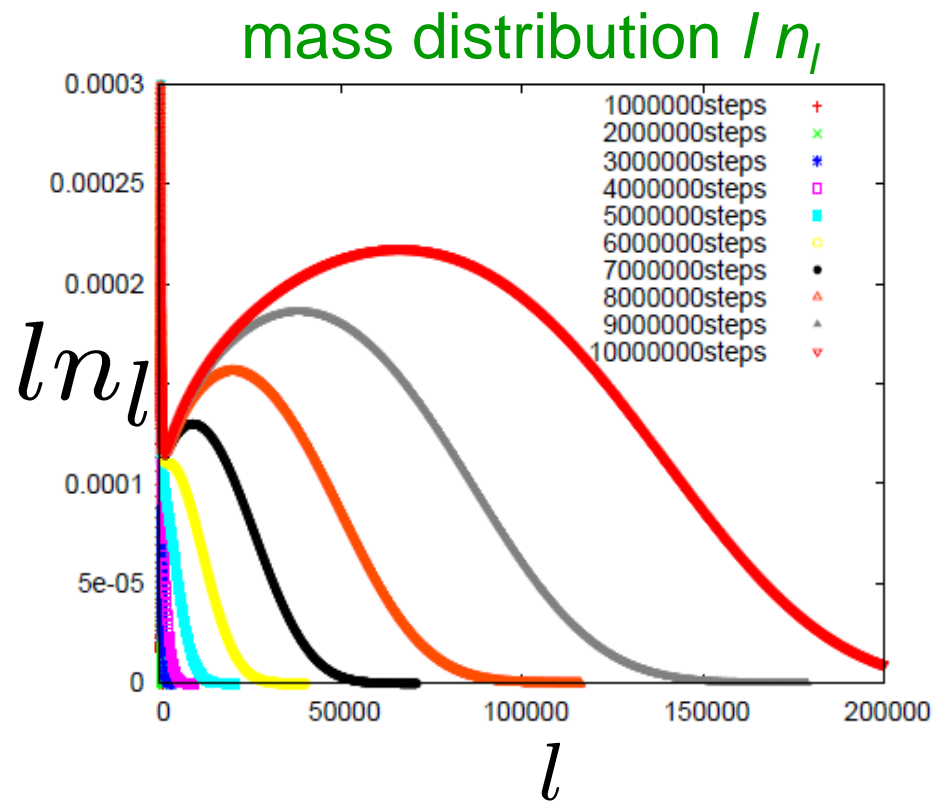


number of clusters larger than l_c

Steady nucleation stage

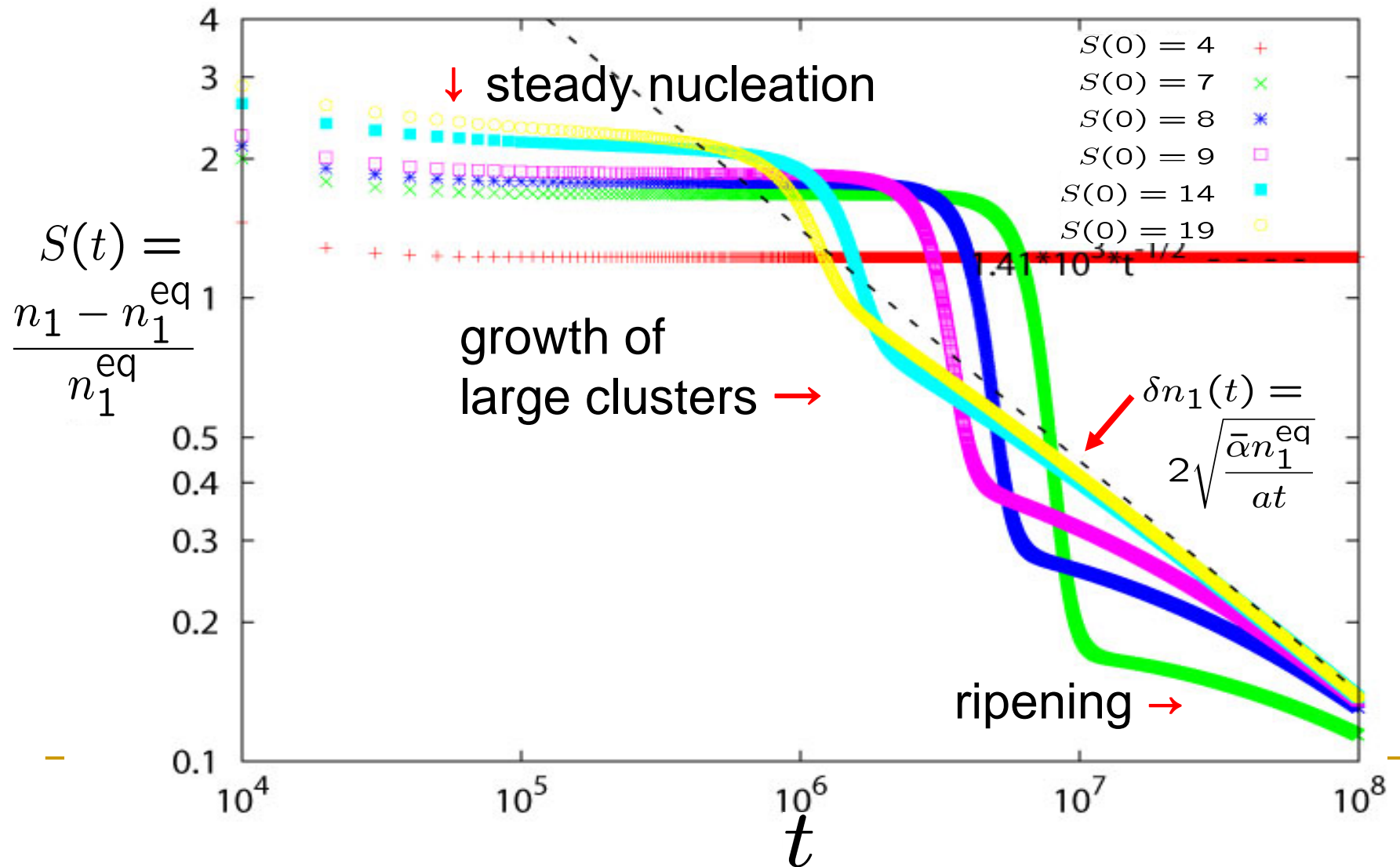
Change of the cluster distribution and the current

- Initial stage of steady nucleation with $S(0)=4$



j_l : monomer mass consumed for the growth of a l -atom clusters.

Change of supersaturation $S(t)$ with various initial supersaturation $S(0)$



Free growth stage

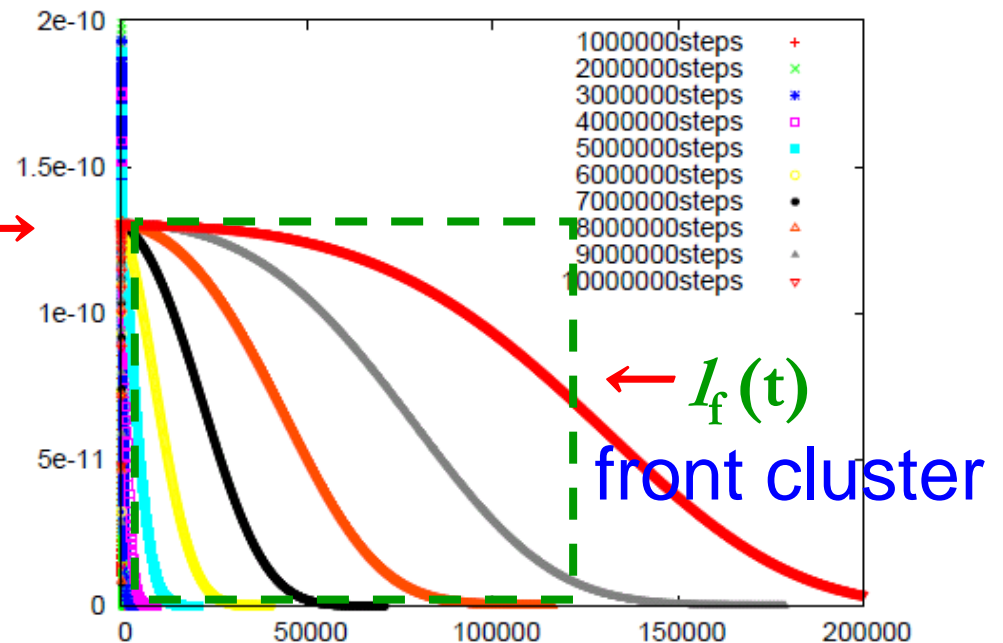
Change of the monomer number and the current

- Decrease in monomers is determined by j

$$\frac{dn_1(t)}{dt} = - \int_1^{\infty} j_l(t) dl \approx j^{SS} l_f(t)$$

current distribution j_l

steady state rate j^{SS}



Free growth stage

A model for change of monomer number

- In the steady nucleation stage

$$\frac{dn_1(t)}{dt} = - \int_1^{\infty} j_l(t) dl \approx j^{SS} l_f(t)$$

- Change of monomer number during growth of clusters

$$\frac{dn_1(t)}{dt} = -j^{SS} \frac{\delta n_1(t)}{\delta n_1^{SS}} (l_f(t) - l_c(t))$$

- Growth front of cluster size distribution

$$l_f^{1/3}(t) = (l_c^{SS})^{1/3} + \frac{a}{3} \int_{\tau}^t \delta n_1(t') dt'$$

- Size of the critical cluster

$$l_c^{1/3}(t) = \frac{2\bar{\alpha}}{3\Delta\mu} = \frac{2\bar{\alpha}}{3} \frac{n_1^{eq}}{\delta n_1(t)}$$

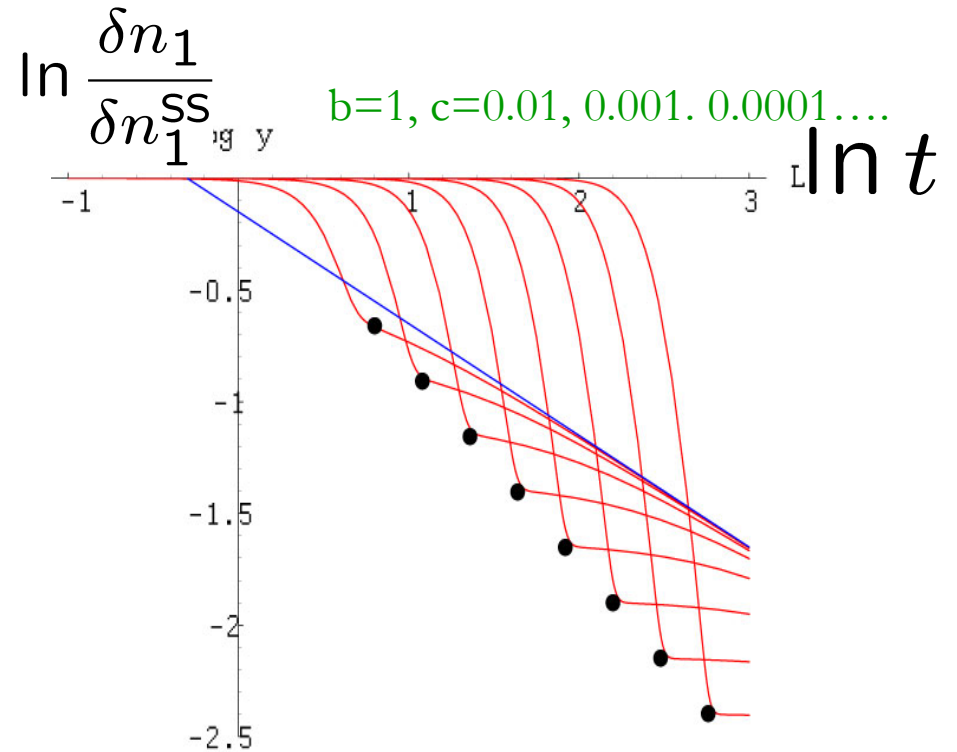
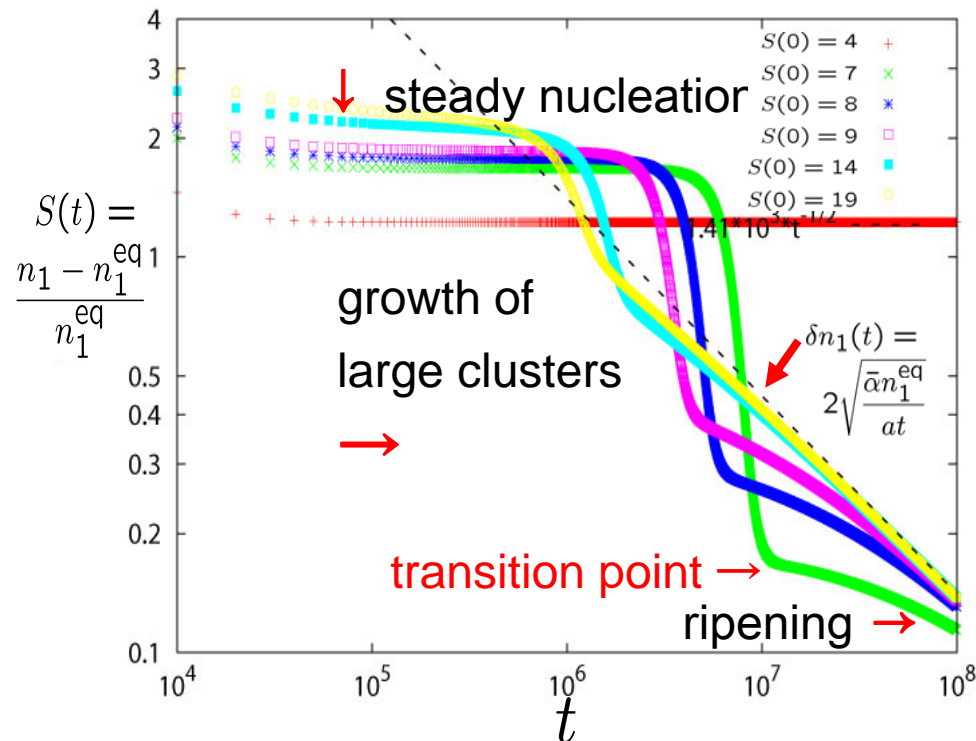
Decrease of monomers
Increase of the critical size

Free growth stage

Change of supersaturation

$$\frac{d^2 Z}{dT^2} = -\frac{dZ}{dT} \left[Z^3 - \left(\frac{b}{c}\right)^3 \left(\frac{dZ}{dT}\right)^{-3} \right] \quad \dot{Z} = \frac{\delta n_1}{\delta n_1^{SS}}$$

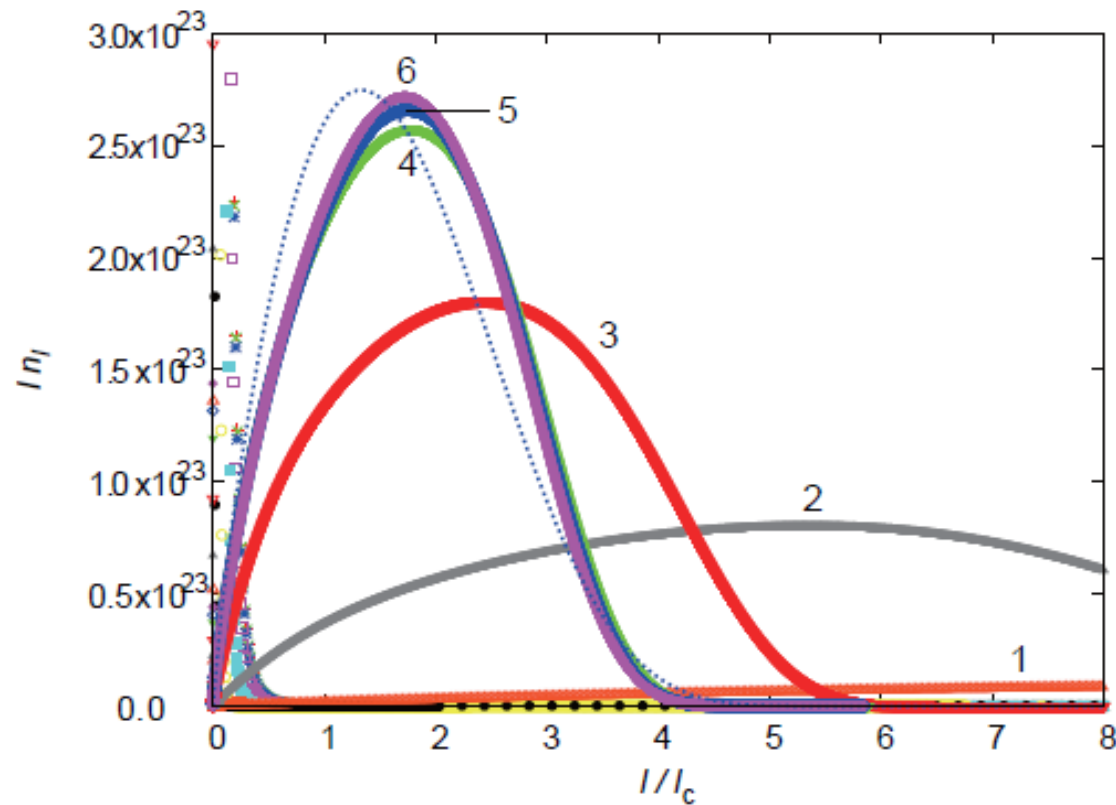
- Transition point to the late stage (t_x)



The asymptotic form is the same as the exact result except for a factor 2.

The transition point to ripening

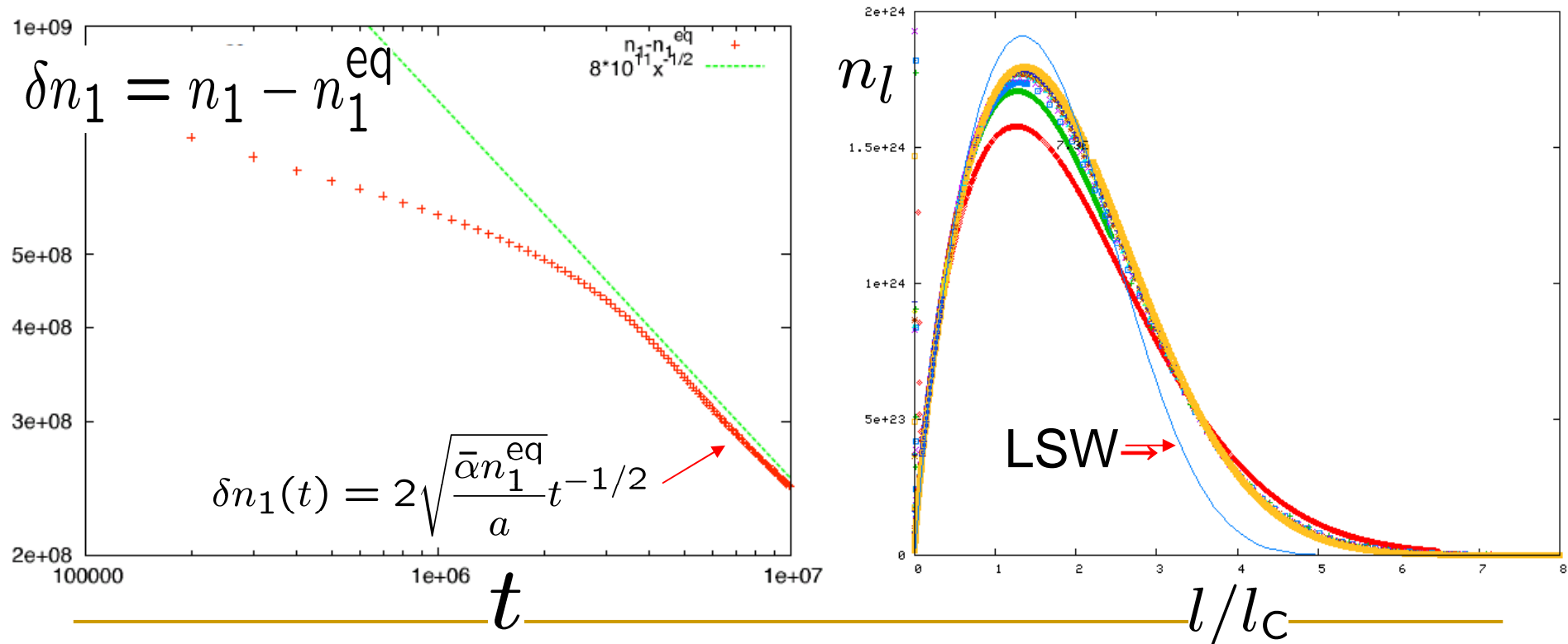
- After the transition point, the shape of the distribution is similar to the Lifshitz-Slyozov-Wagner (LSW) shape.



Ripening stage

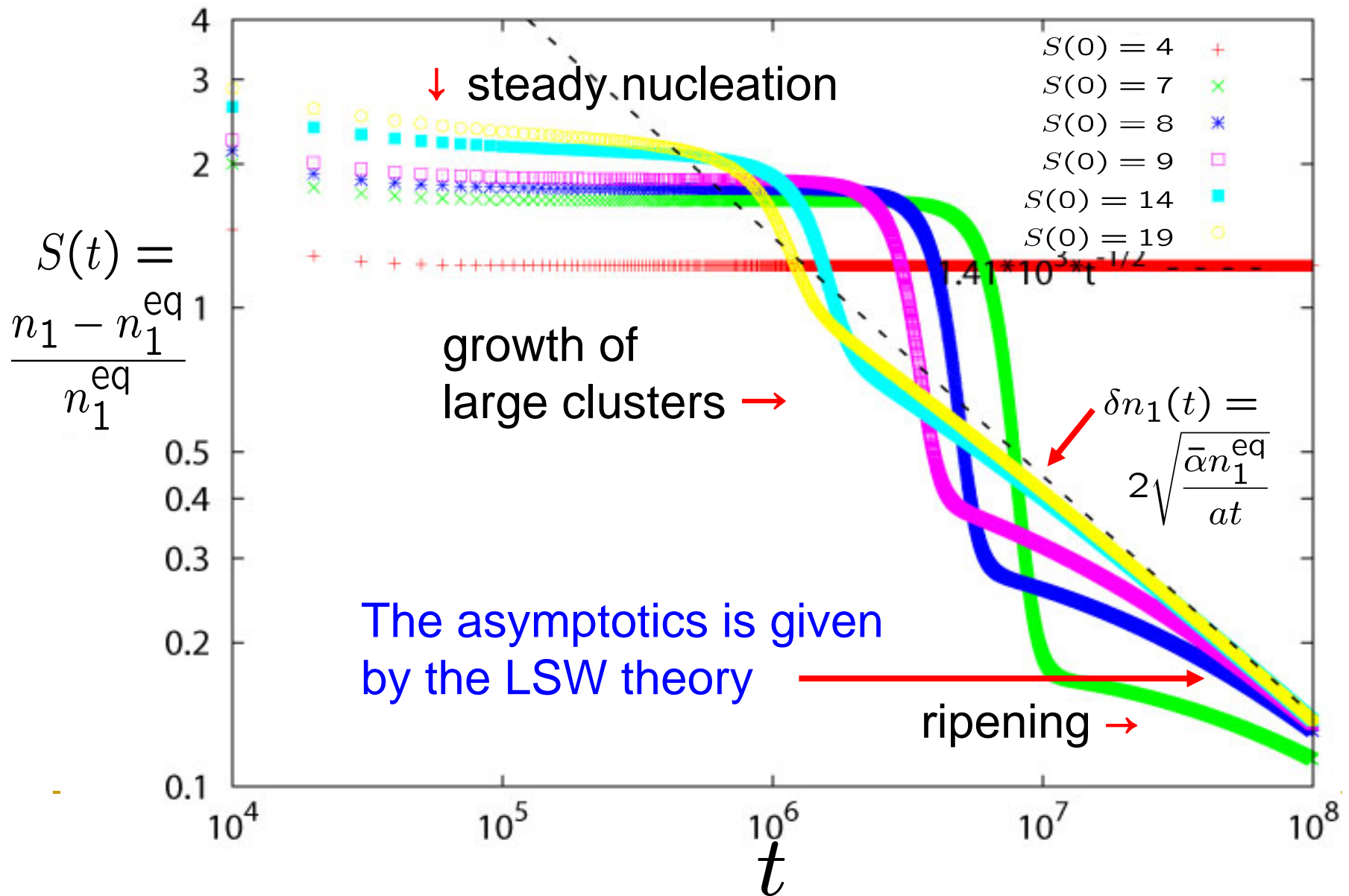
Change of distribution with $S(0)=49$

Supersaturation approaches the asymptotic form soon.
The distribution approaches the LSW form extremely slowly.



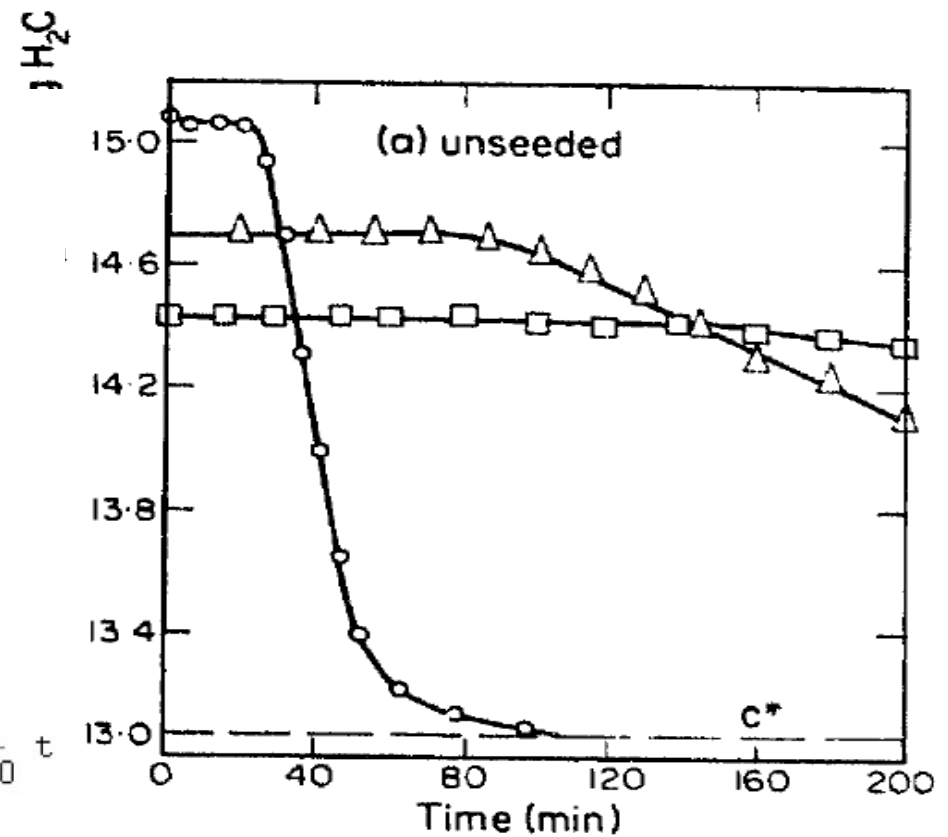
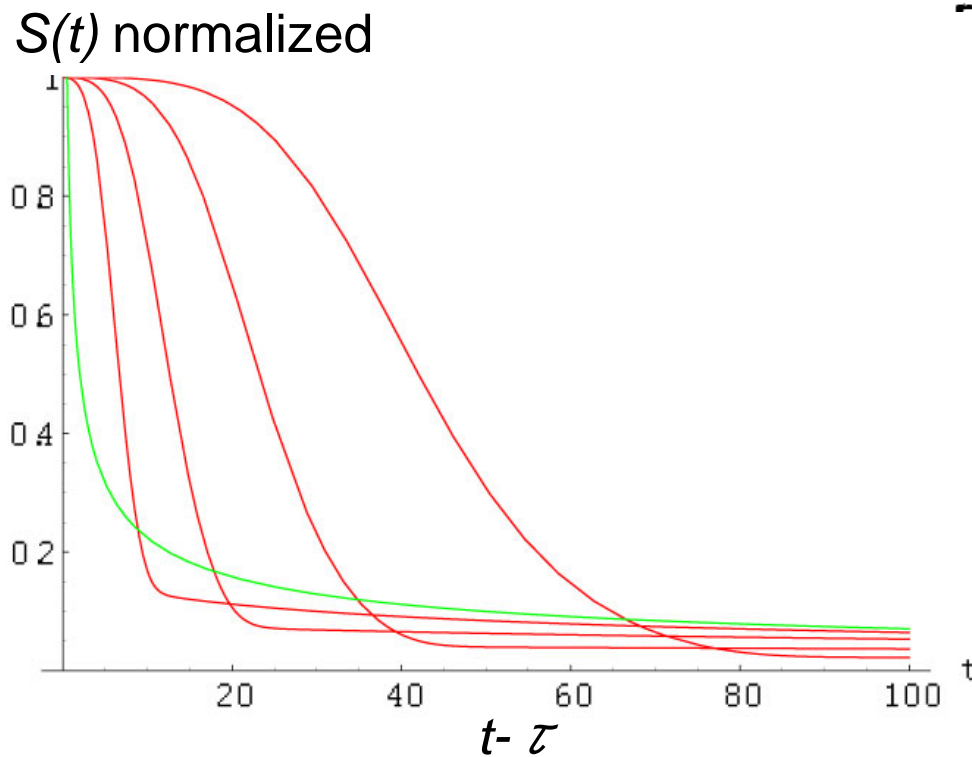
The initial distribution is nonomers only: $n_1(0)=N$

Change of supersaturation for various $S(0)$



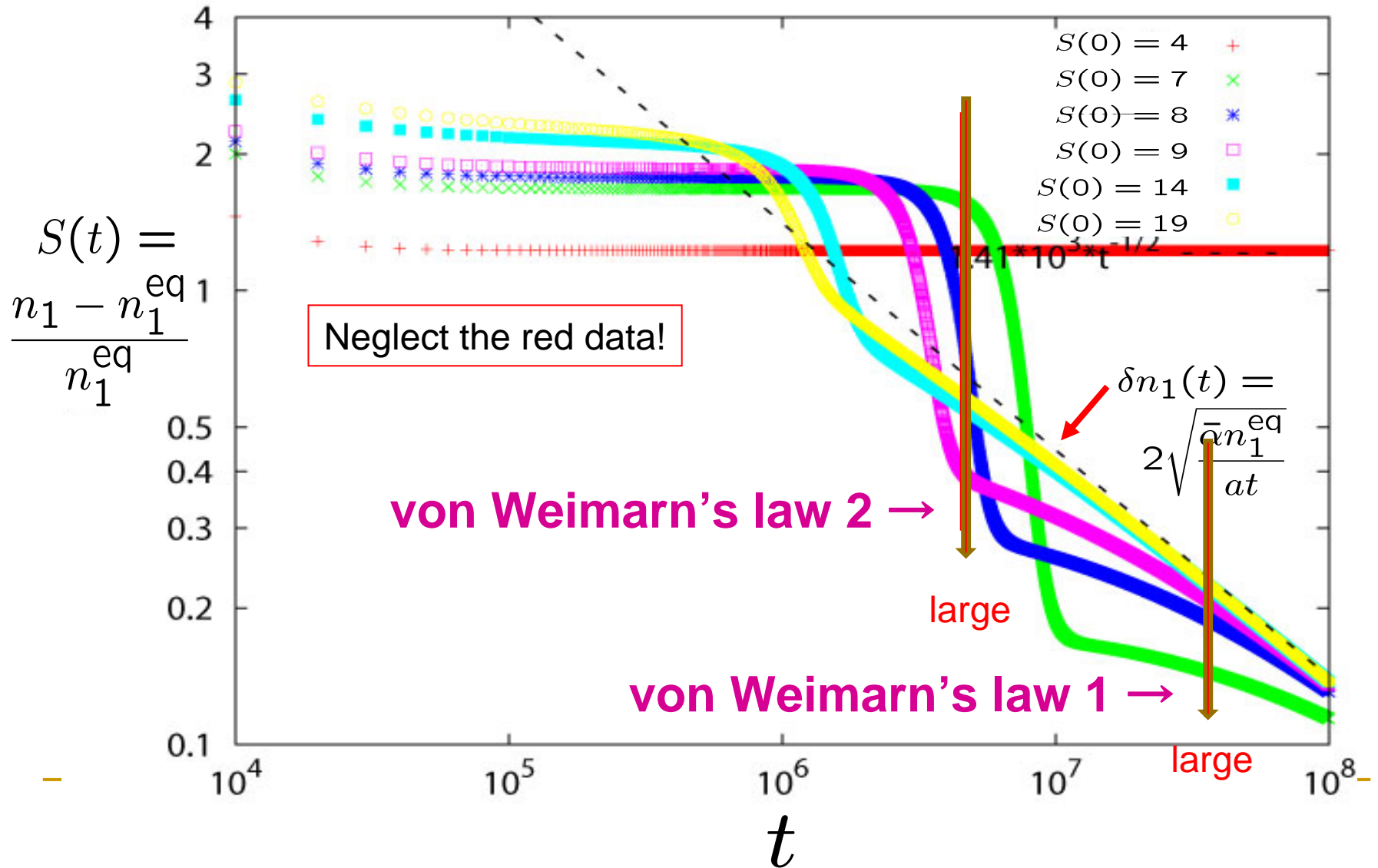
Change of supersaturation in linear scale

- The one variable model and the experiment



J. Garside, C. Gaska, J. W. Mullins:
J. Cryst. Growth **13/14** (1972) 510

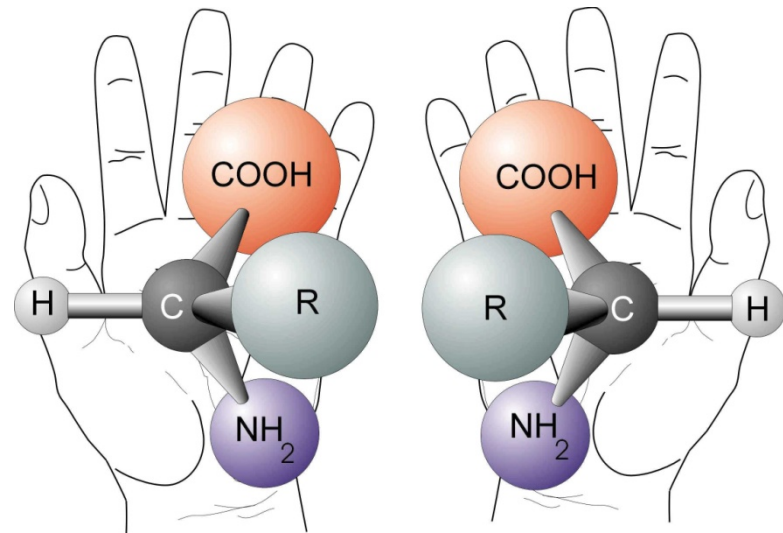
von Weimarn's laws



An application:
the generalized Classical
Nucleation Model for chirality
conversion with grinding

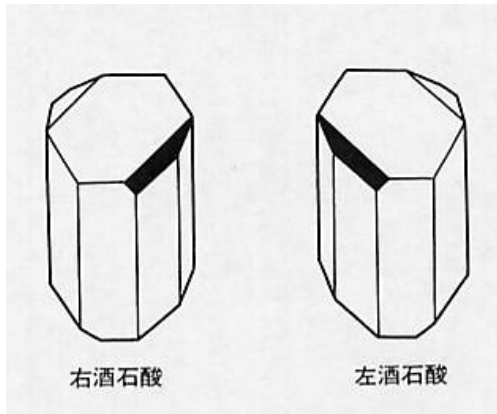
Enantiomorph of molecules

Left (levorotatory) amino acids and right (dextrorotatory) sugar in life



- Crystals of **chiral molecules**

tartaric acid (2,3-dihydroxy butanedioic acid)

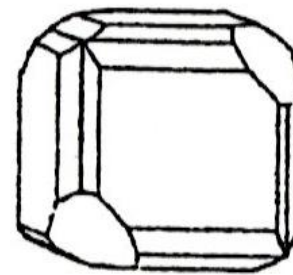
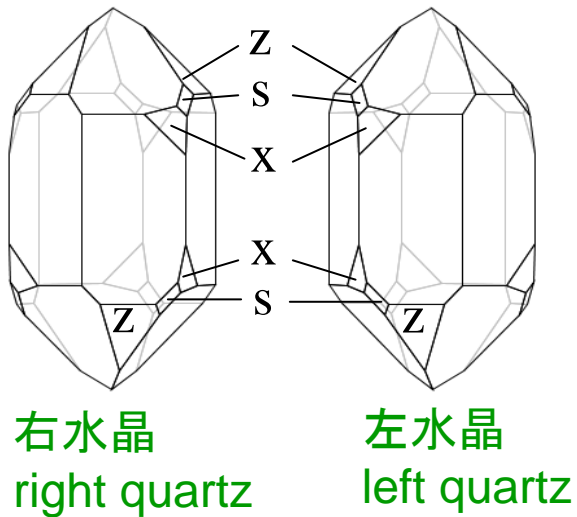


tartaric acid crystals by Waizumi

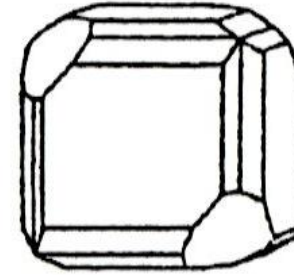
Enantiomorph of crystals



- SiO_2 (quartz)
Low temperature quarts :
 $P3_121$ and $P3_221$



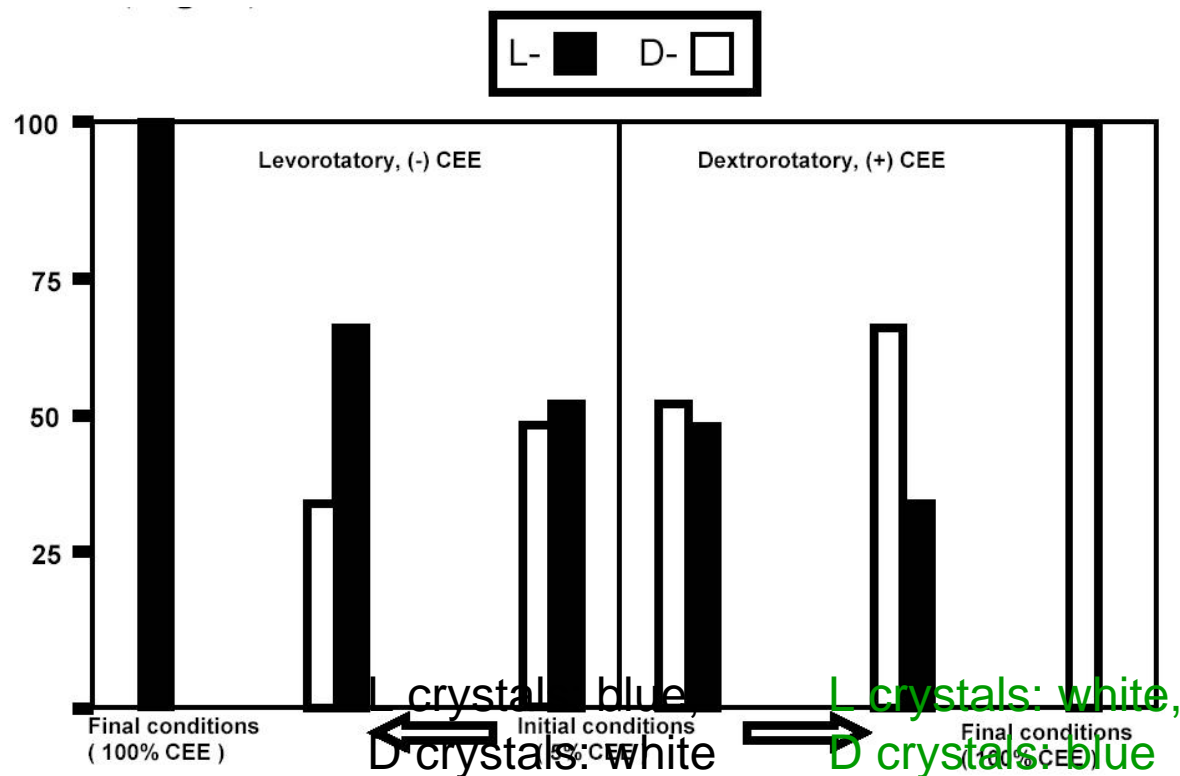
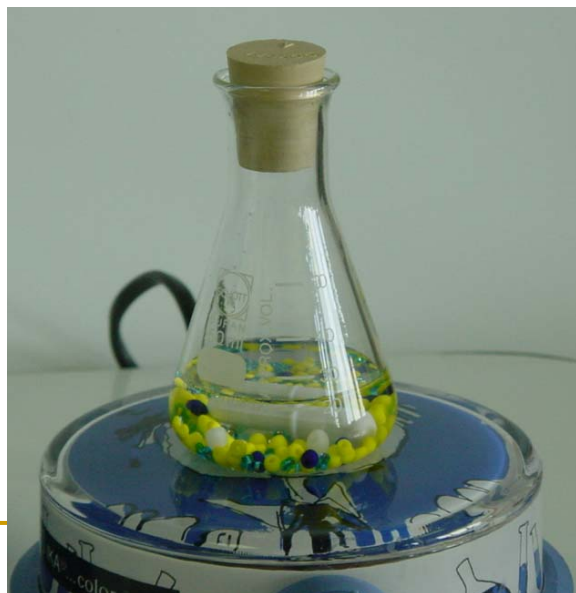
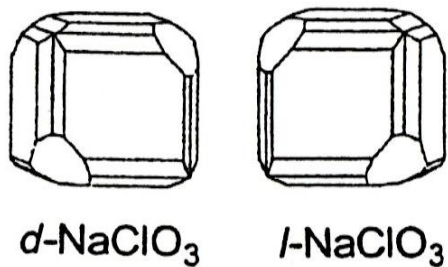
d- NaClO_3



l- NaClO_3

Chiral crystals are made of achiral molecules.

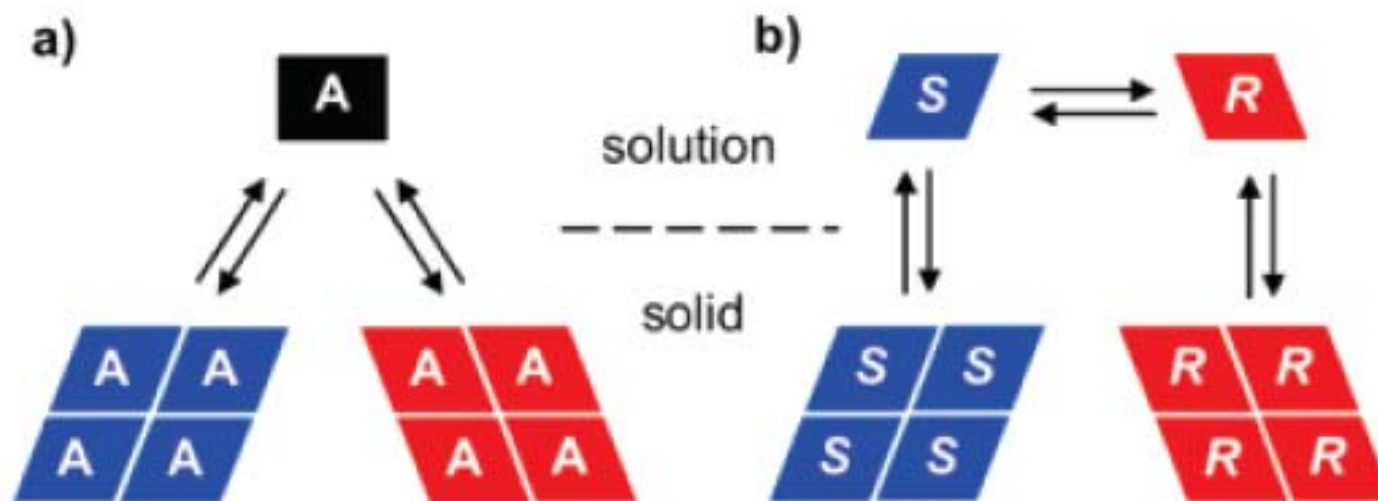
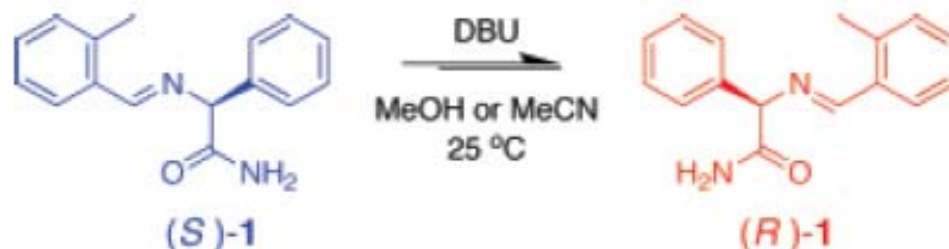
Viedma's experiment: homochirality of NaClO_3 via **chirality conversion**



C. Viedma: Phys. Rev. Lett. **94**, 065504 (2005)

Chirality conversion of organic molecules by grinding crystals

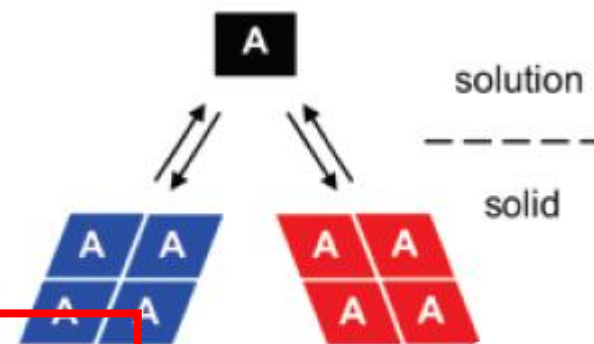
The imine of 2-methylbenzaldehyde and phenylglycinamide racemizes rapidly in solution with added organic base DBU in MeOH.



W.L. Noorduin, T. Izumi, A. Millemaggi, M. Leeman, H. Meekes, W.J.P. Van Enkevort, R. M. Kellogg, B. Kaptein, E. Vlieg, D.G. Blackmond: *J. Am. Chem. Soc.* **130** (2008) 1158

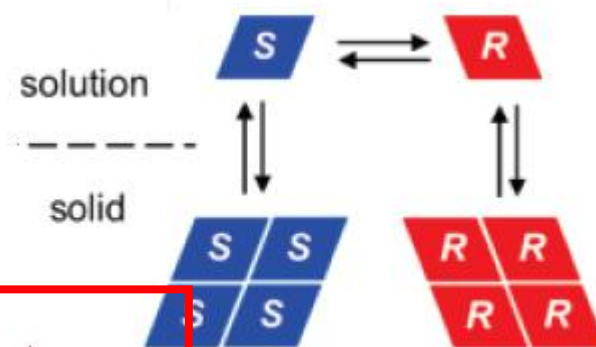
Generalized CNM with direct crystallization of clusters and grinding: **achiral molecules**

- Growth of crystals with monomers and **dimers**
- Decay of the largest clusters by grinding



Generalized CNM with direct crystallization of clusters and grinding: **chiral molecules**

- **Monomers change chirality**
- **Growth of crystals with monomers and dimers**
- **Decay of the largest clusters by grinding**



Generalized CNM with direct crystallization of clusters and grinding: **achiral molecules**

Change of number of l -mer clusters with Right and Left chirality

$$\begin{aligned} \frac{dn_l^{R,L}}{dt} = & \sigma_{l-1} n_1 n_{l-1}^{R,L} - \sigma_l n_1 n_l^{R,L} && \leftarrow \text{monomer growth} \\ & + \sigma_{l-2}^d n_2^{R,L} n_{l-2}^{R,L} - \sigma_l^d n_2^{R,L} n_l^{R,L} && \leftarrow \text{dimer growth} \\ & - (\lambda_l + \lambda_l^d) n_l^{R,L} + \lambda_{l+1} n_{l+1}^{R,L} + \lambda_{l+2}^d n_{l+2}^{R,L} && \leftarrow \text{monomer/dimer decay} \\ & + (\text{term proportional to } \lambda^{gr} n_{l_{\max}}^{R,L}). && \leftarrow \text{grinding} \end{aligned}$$

σ and λ satisfy the detailed balance condition:

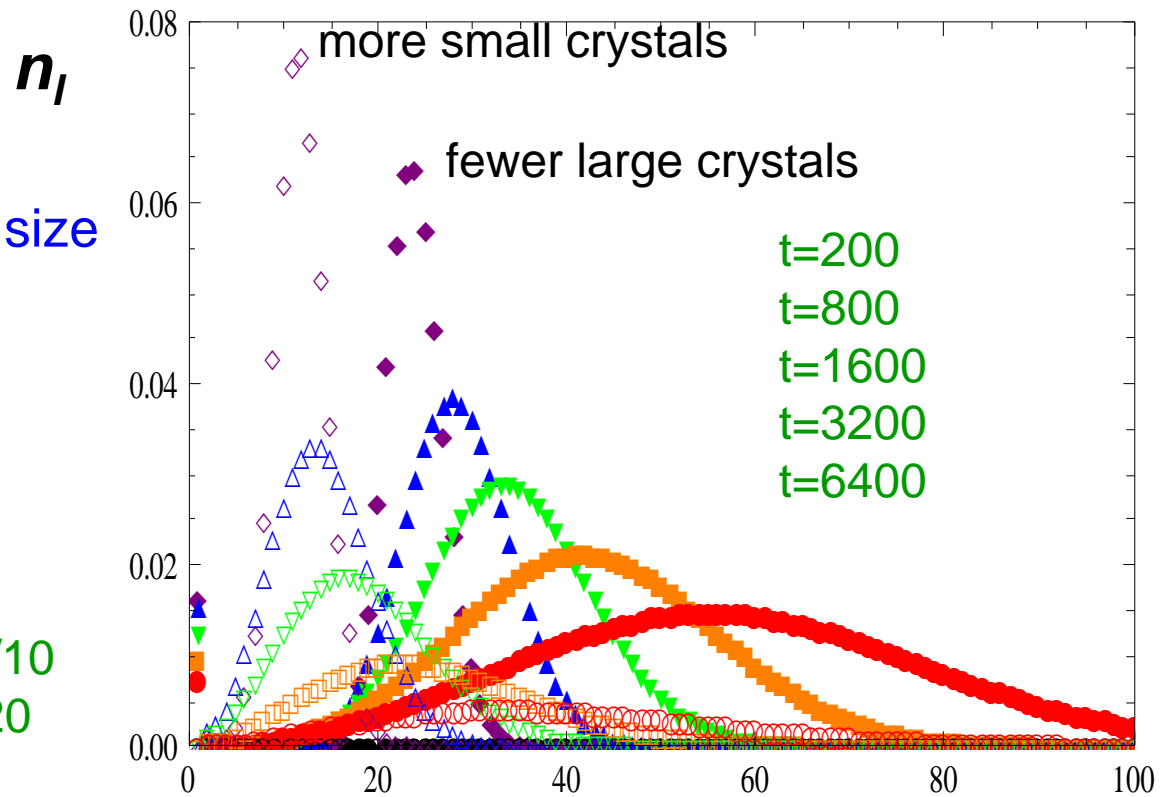
$$\sigma_l = a l^{2/3} \quad \lambda_l n_l^{R,L} = \sigma_{l-1} n_1^{\text{eq}} \exp [\bar{\alpha} l^{2/3} - \bar{\alpha} (l-1)^{2/3}] n_l^{R,L}$$

Generalized CNM without grinding

Without grinding Ostwald ripening causes chirality conversion (possible only in a small system).

Change of the cluster size distribution

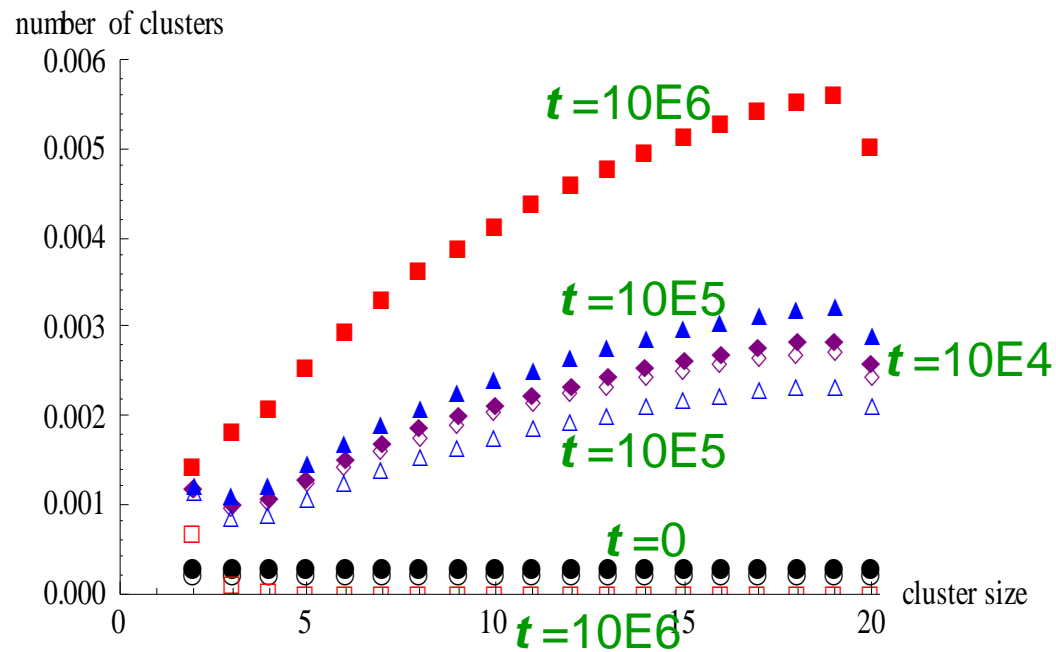
At $t = 0$:
 $n^L(l=10) = 0.45/10$
 $n^R(l=20) = 0.4/20$



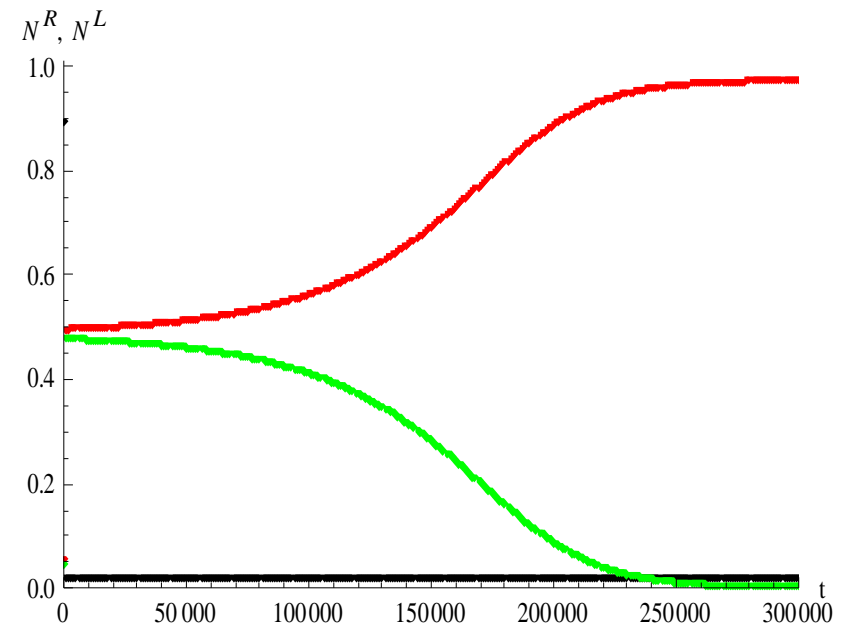
Generalized CNM with direct crystallization of clusters and **with grinding**

The exponential amplification of chirality imbalance proceeds **without change of the shape of distribution.**

Change of size distribution



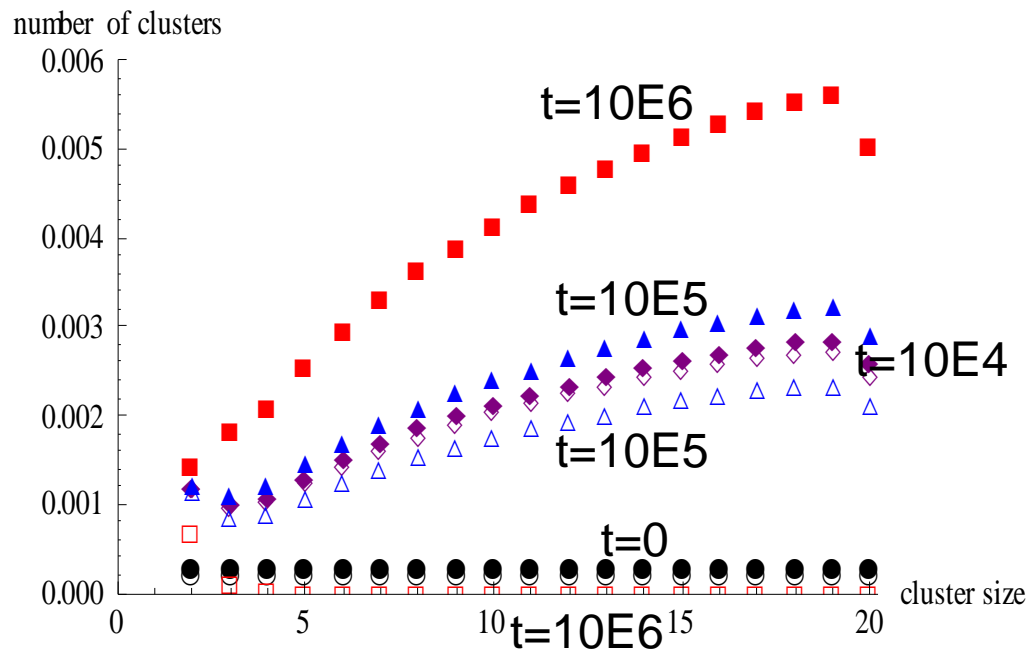
Number of R and L molecules



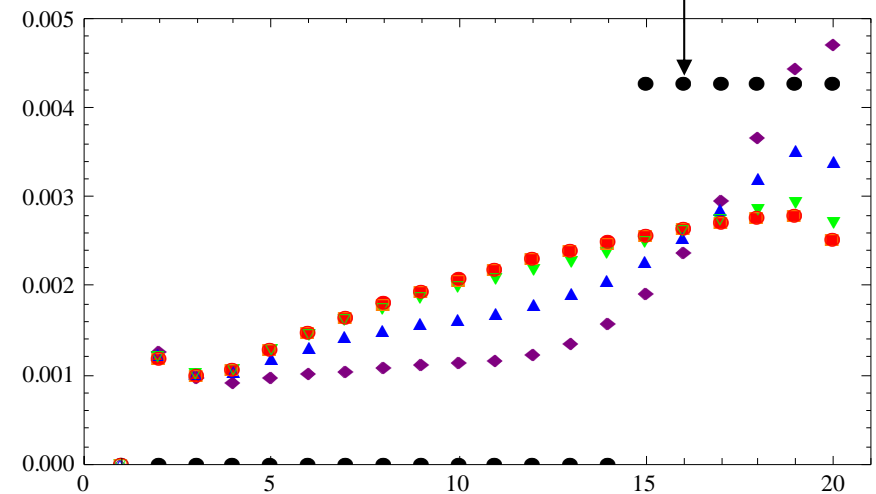
Generalized CNM with direct crystallization of clusters and **with grinding**

“Any” chiral-symmetric distribution becomes the unstable racemic distribution.

Change of size distribution



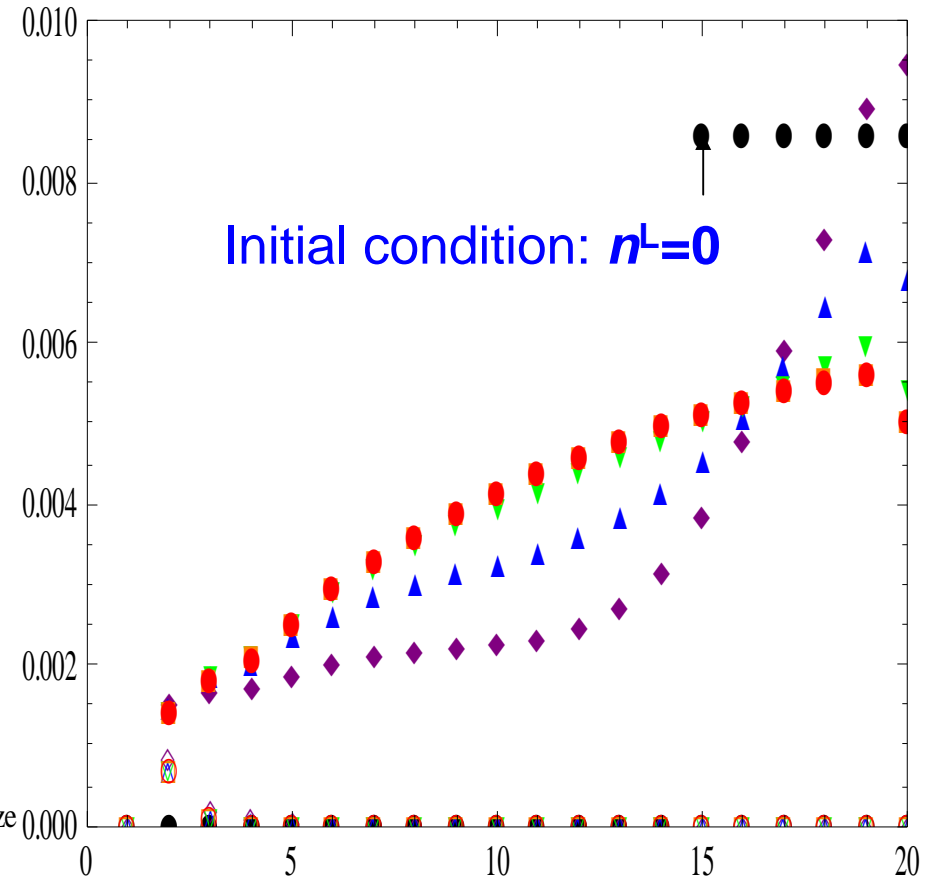
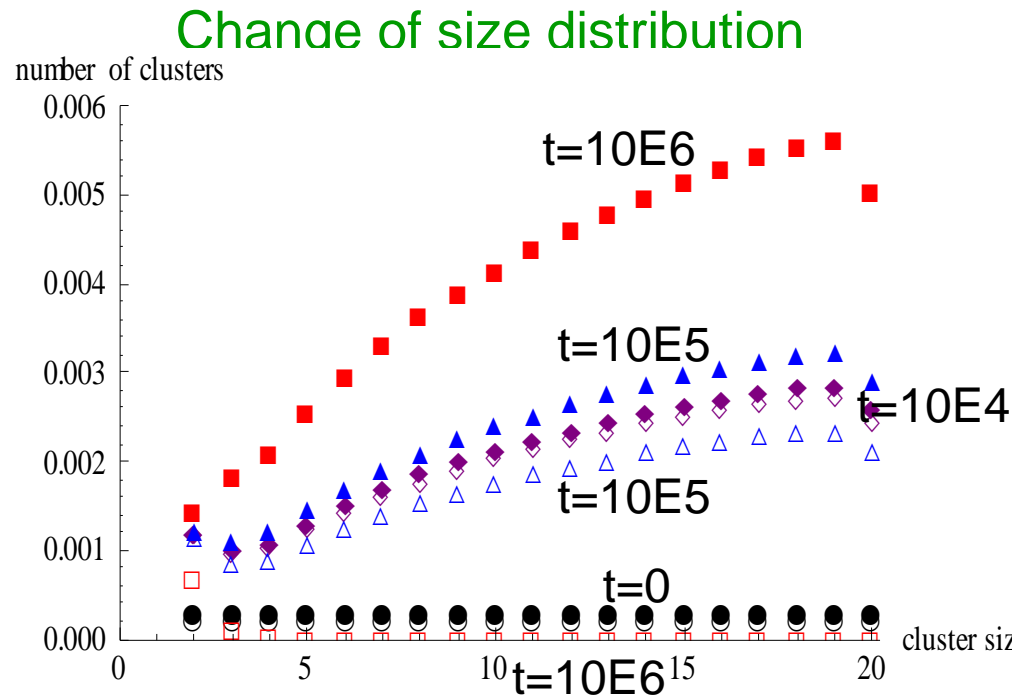
Initial condition: $n^R = n^L$



Unstable racemic “equilibrium” state

Generalized CNM with direct crystallization of clusters and **with grinding**

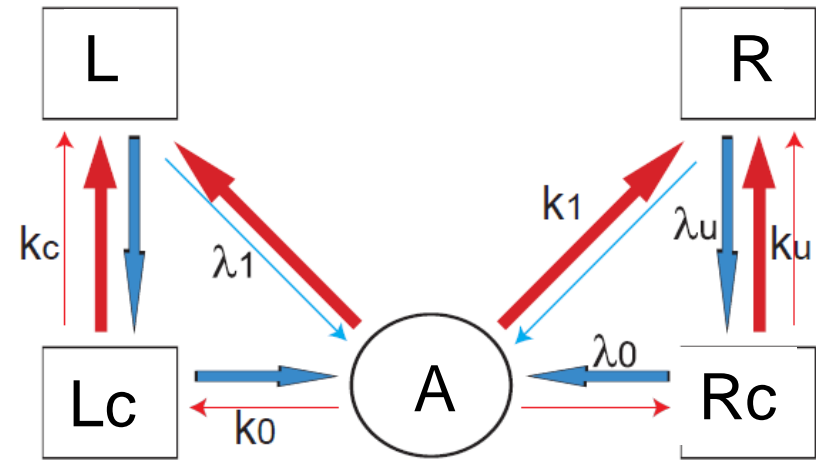
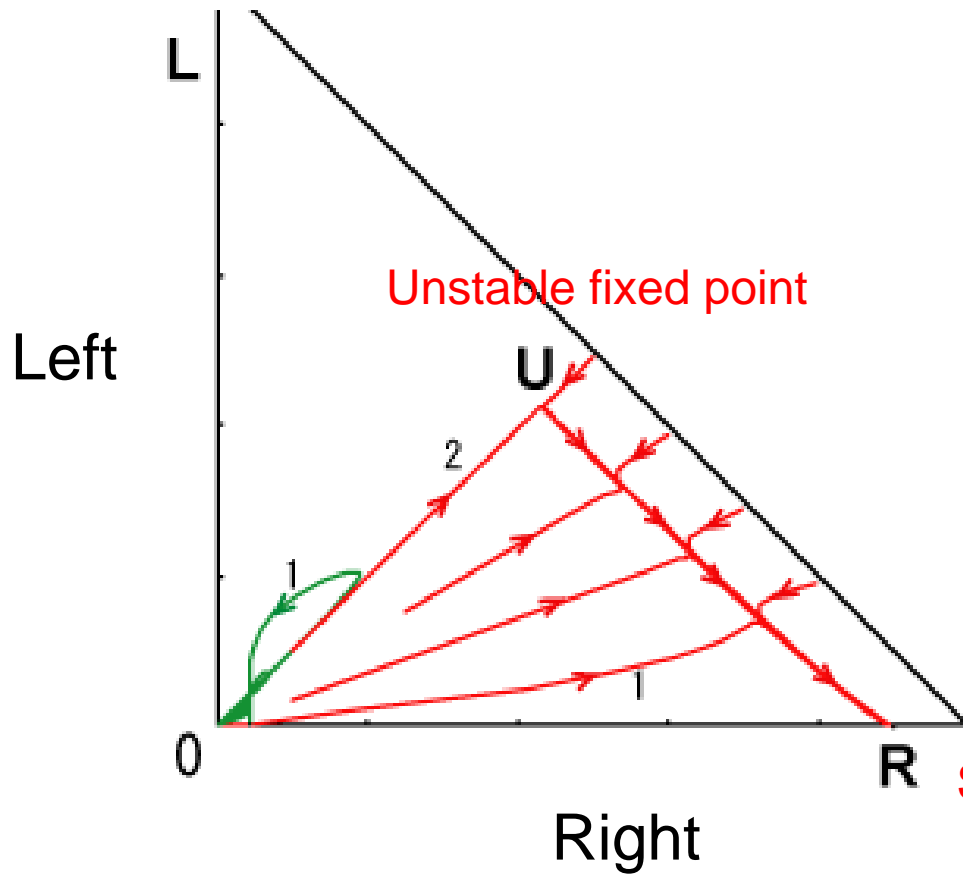
“Any” homochiral distribution becomes the stable chiral distribution. ↓



Stable chiral “equilibrium” state

Flow in a space of R and L masses

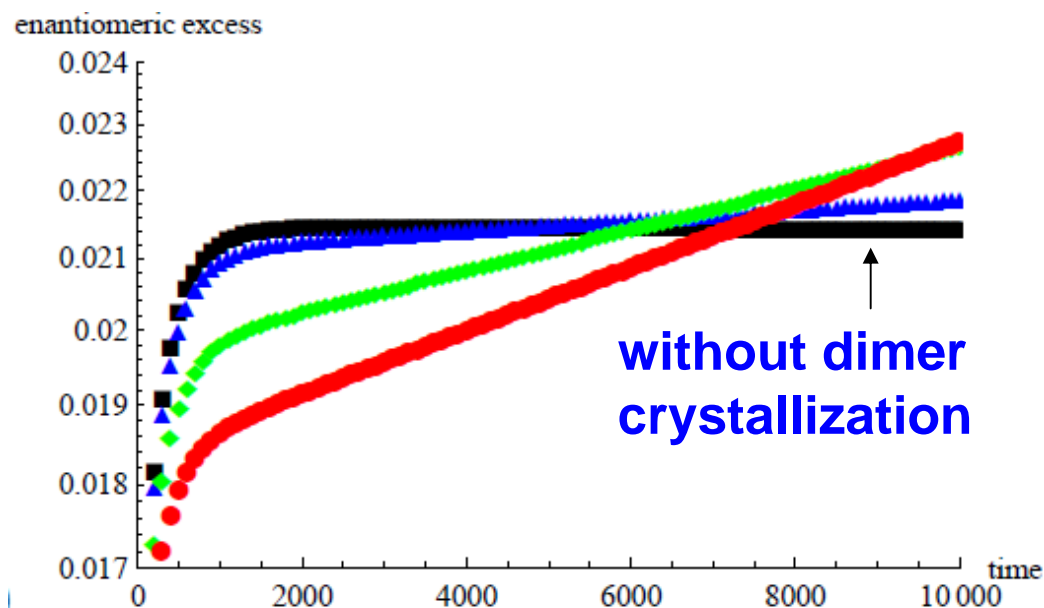
Stable fixed point



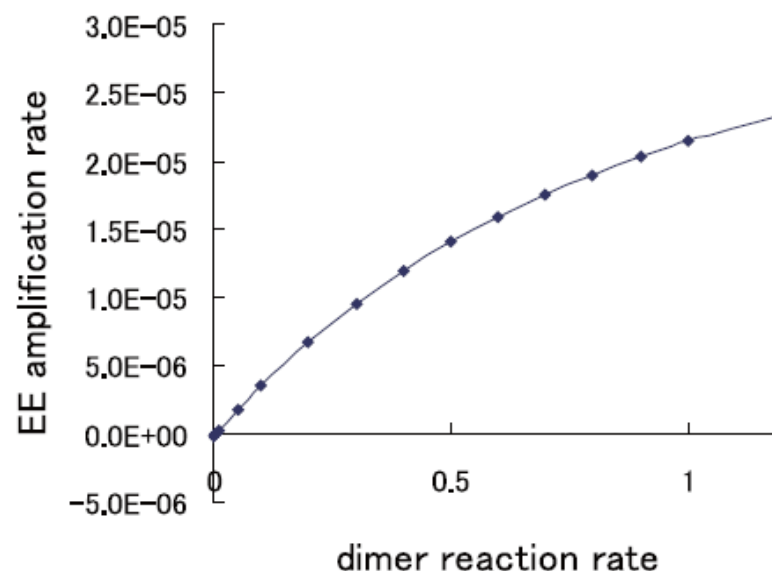
Stable fixed point

Effect of direct crystallization of dimers

Change of enantiomeric excess



EE amplification rate vs dimer reaction rate



EE amplification is proportional to the dimer crystallization rate

Summary

- The classical nucleation model (SFBD model) describes not only nucleation but also transient behavior to ripening qualitatively.
von Weimarn's law is demonstrated.
- The generalized CNM with direct crystallization of clusters with grinding can explain recently discovered chirality conversion by grinding.

Thank you for your attention.

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