Nucleation kinetics at various conditions

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Contents

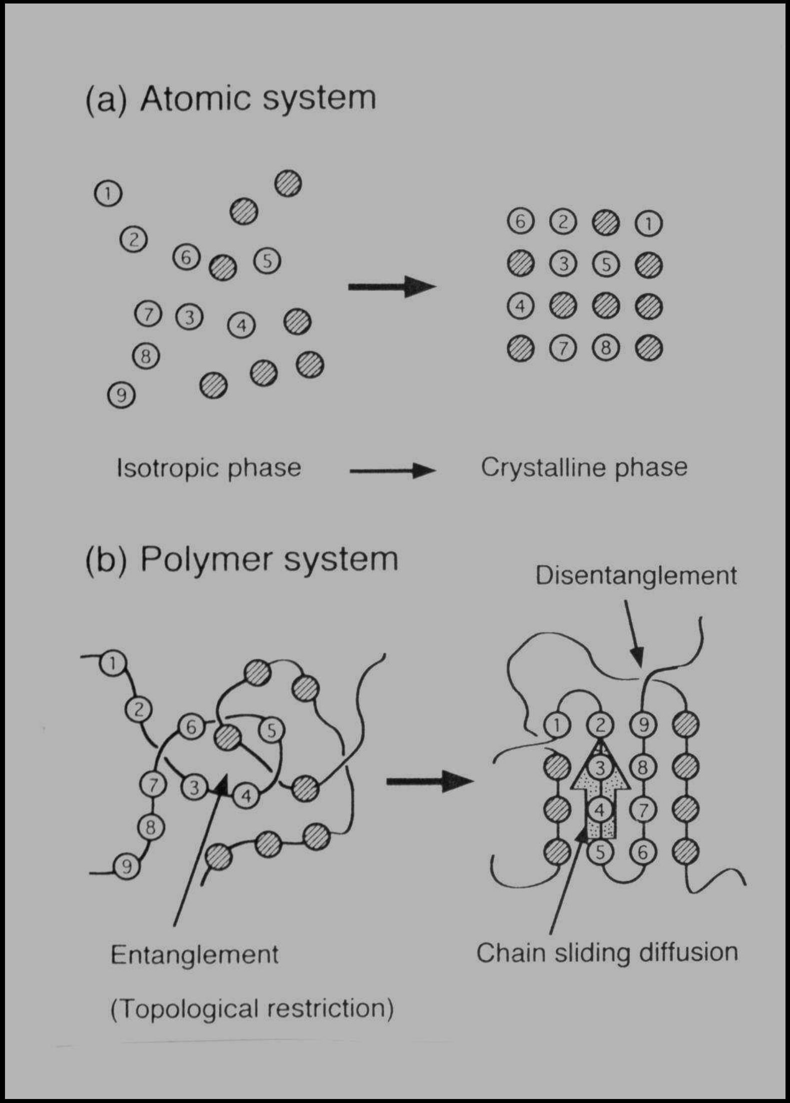
Introduction

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

at

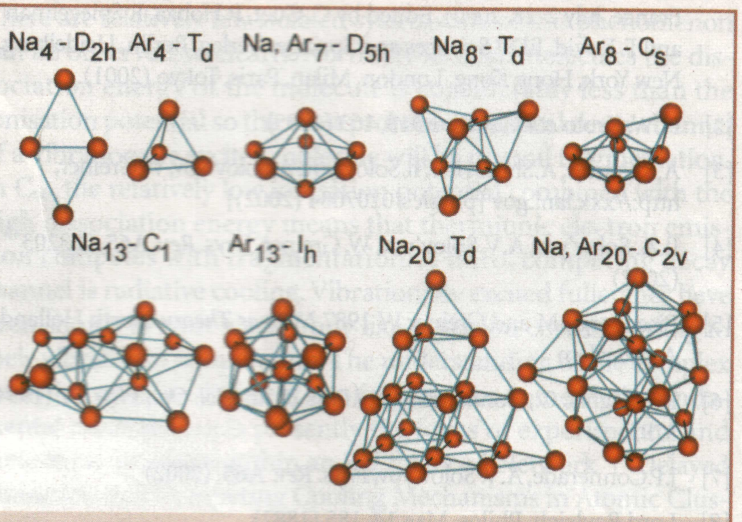
- random sites in the bulk of a mother phase **(homogeneous nucleation)**
  special case: nucleation in closed systems
- on substrate, surface of ampule, impurities, etc. **(heterogeneous nucleation)**
  special case: nucleation on active centers

Introduction

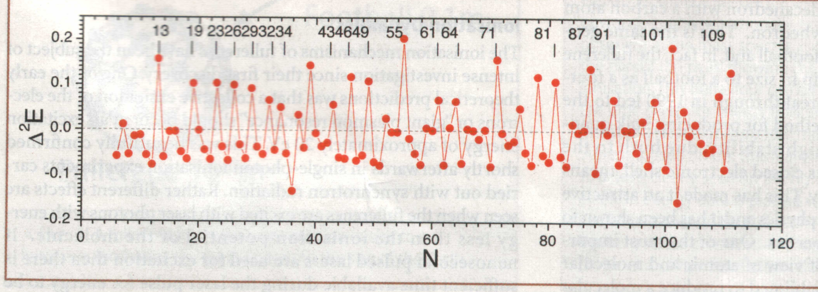


M. Nishi et al.: Polymer Journal 31 (1999) 749.

Introduction



▲ Fig. 2: Geometries and the point symmetry groups of some *Na* and *Ar* ACs calculated in [3, 4].



▲ Fig. 3: Second differences in binding energies calculated for for *Ar* ACs in [3].

europhysics news NOVEMBER/DECEMBER 2002 201

Jean-Patrick Commerade: *The science of clusters: An emerging field, Europhysics news 33/6 (2002) 200.*

Motivation

Cooperation with experimental groups (Hiroshima Univ., etc.)

- **Nucleation in microemulsions**
  Microemulsion $\rightarrow$ thermodynamically stable dispersion of one liquid phase into another (oil-in-water, water-in-oil)
  Droplet diameter about 100 nanometers
  Theoretical approaches — problem to explain measurements
  (Only thermodynamical aspects of nucleation in close systems, no connection with kinetics of formation of a new phase.)

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  (Nucleation agent is added to the melt)

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$\Longrightarrow$

- Nucleation in closed systems
- Nucleation on active centers

Thermodynamical aspects

Energy of formation of nuclei:

$$\Delta G(n) = G_{NP}(n) - G_{MP}(n) = \Delta G_V(n) + \Delta G_S(n)$$

Critical size n^*:

$$\frac{\partial \Delta G(n)}{\partial n} = 0 \Rightarrow n^*$$

Capillarity approximation:

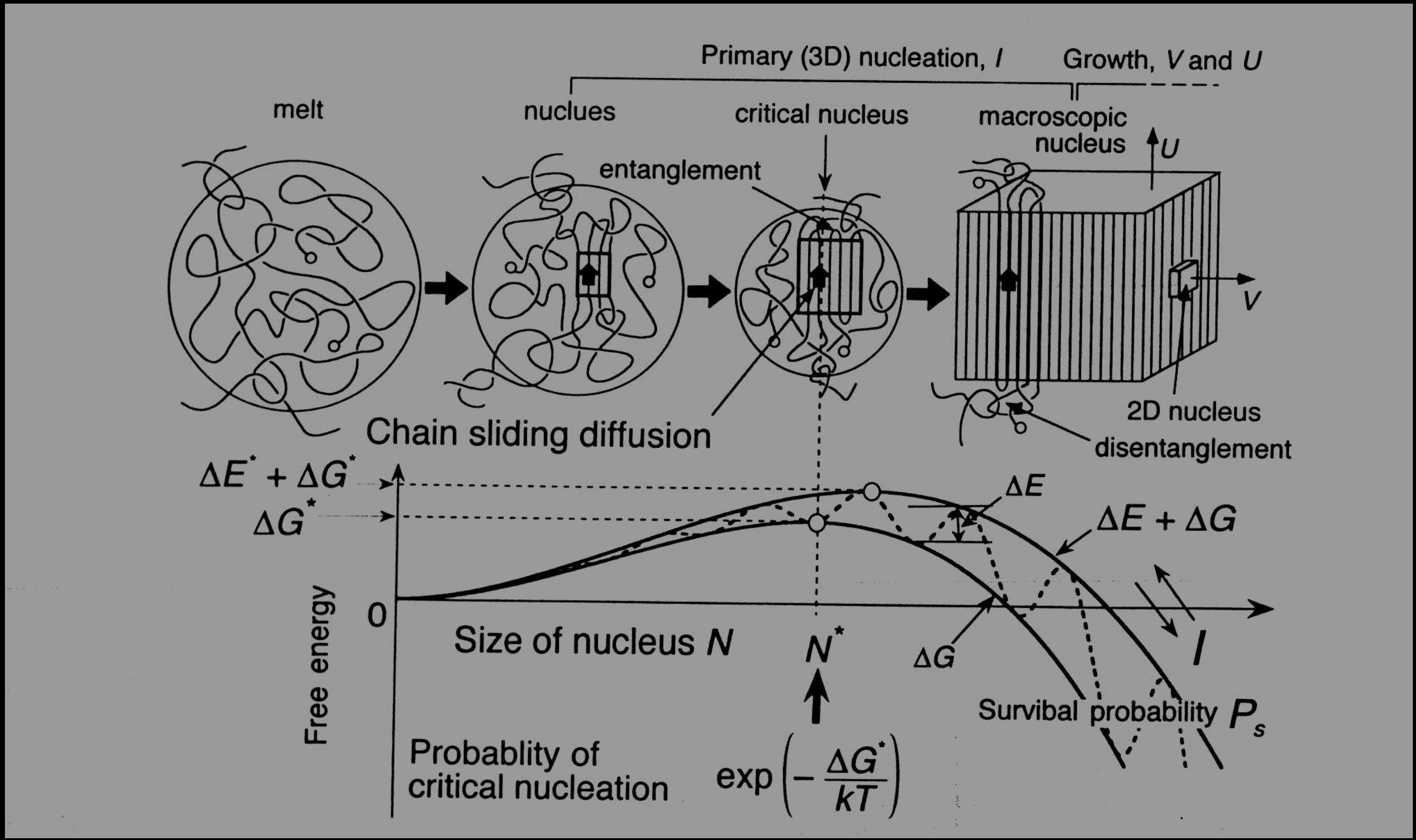
$$\Delta G(n) = -n\Delta\mu + \sigma S_n$$

For $S_n = \gamma n^{2/3} \Rightarrow$

$$n^* = \left(\frac{2\gamma\sigma}{3\Delta\mu}\right)^3$$

Thermodynamical aspects

Polymer systems



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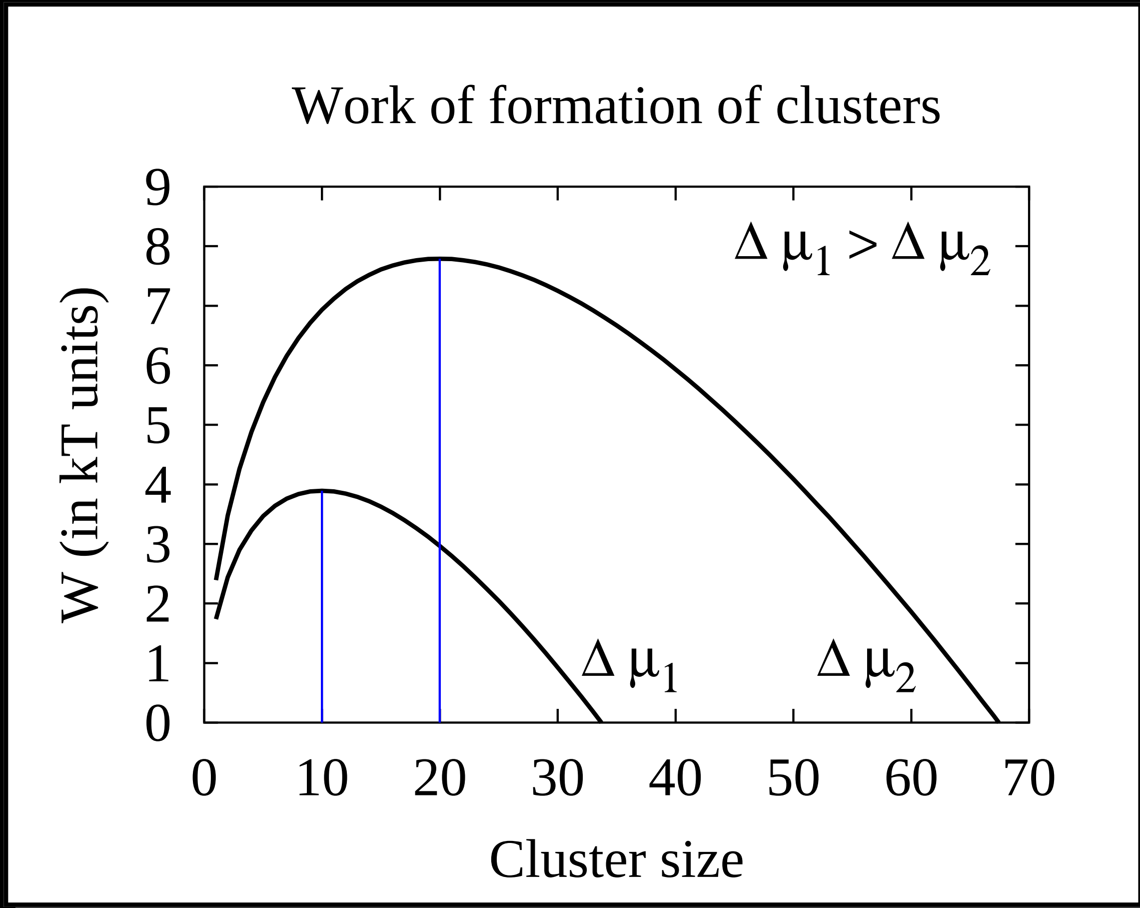
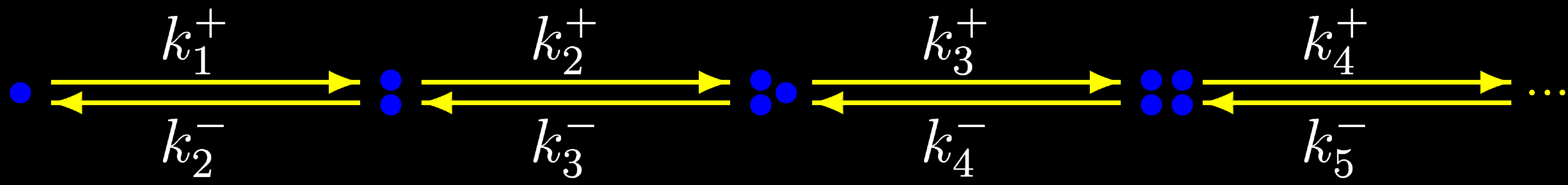
Thermodynamical aspects



$J^S = const. \exp\left(-\frac{\Delta G^*}{kT}\right)$ nucleation rate

Nucleation kinetics



k_n^+ (k_n^-) – attachment (detachment) frequencies of molecules

- **Coalescence is neglected**
  attachment (resp. detachment) of *growth units* plays dominant role in nucleation and growth process
- **Nucleation starts at any nucleation center (monomer, active center) in the bulk of supersaturated mother phase**

Basic equations

$$\frac{dF_n}{dt} = J_{n-1}(t) - J_n(t)$$

where cluster flux density (nucleation rate for n^*)

$$J_n(t) = k_n^+ F_n(t) - k_{n+1}^- F_{n+1}(t)$$

Total number of nuclei greater than m

$$Z_m(t) = \sum_{n>m} F_n(t) = \int_0^t J_m(t')dt'$$

F_n – number density of nuclei of size n

Basic equations

Initial and boundary conditions

$$F_{n>1}(t=0)=0$$

$$F_{n\to\infty}(t)=0$$

$N_1(\equiv F_1)$ – number of nucleation centers

$$\boxed{N_1 \gg \sum_{n>1} nF_n(t) \Longrightarrow N_1 = const.}$$ (open system)

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$$N_1(t) = N_0 - \sum_{n>1} F_n(t)$$ (active centers)

Transient frequencies

Vapor → Liquid

$$k_n^+ = \frac{P}{\sqrt{2\pi mkT}} S_n$$

Vapor → Solid

$$k_n^+ = \frac{P}{\sqrt{2\pi mkT}} S_n \exp\left(-\frac{E}{kT}\right)$$

Liquid → Solid

$$k_n^+ = \varrho_S \left(\frac{kT}{h}\right) S_n \exp\left(-\frac{E}{kT}\right) \exp\left(-\frac{q\Delta g_n}{kT}\right)$$

$$\Delta g_n = \Delta G_{n+1} - \Delta G_n; \quad q = \frac{1}{2}[1 + \mathrm{sign}(\Delta g_n)]$$

ϱ_S - surface density of monomers

Avrami model

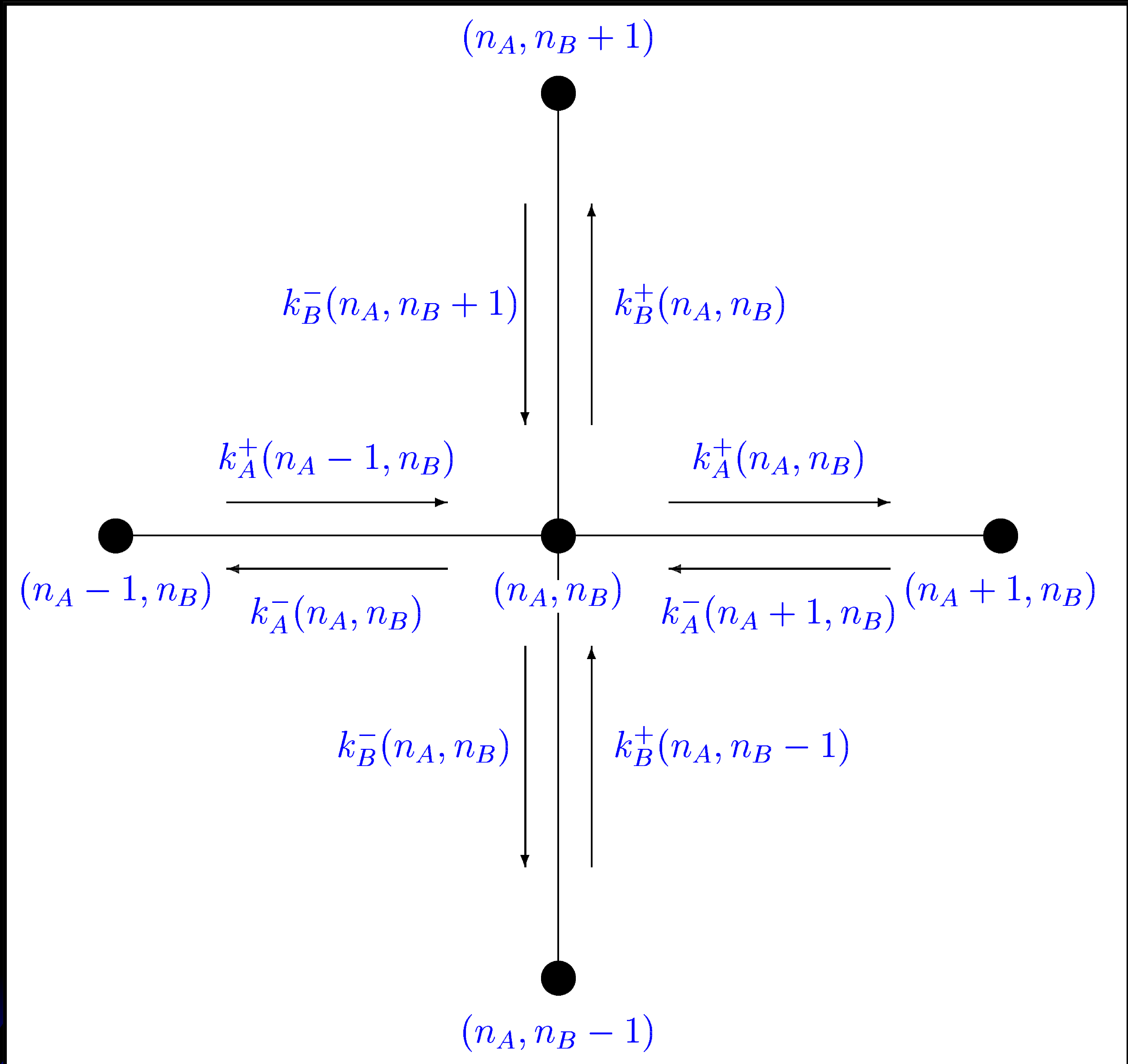
$$\frac{dN(t)}{dt} = J_A(t)[N_0 - N(t)]$$

$N(t)$ – total number of nuclei
$J_A(t)$ – time dependent nucleation rate per active center

$$N(t) = N_0 \left[1 - \exp\left(- \int_0^t J_A(t')dt' \right) \right]$$

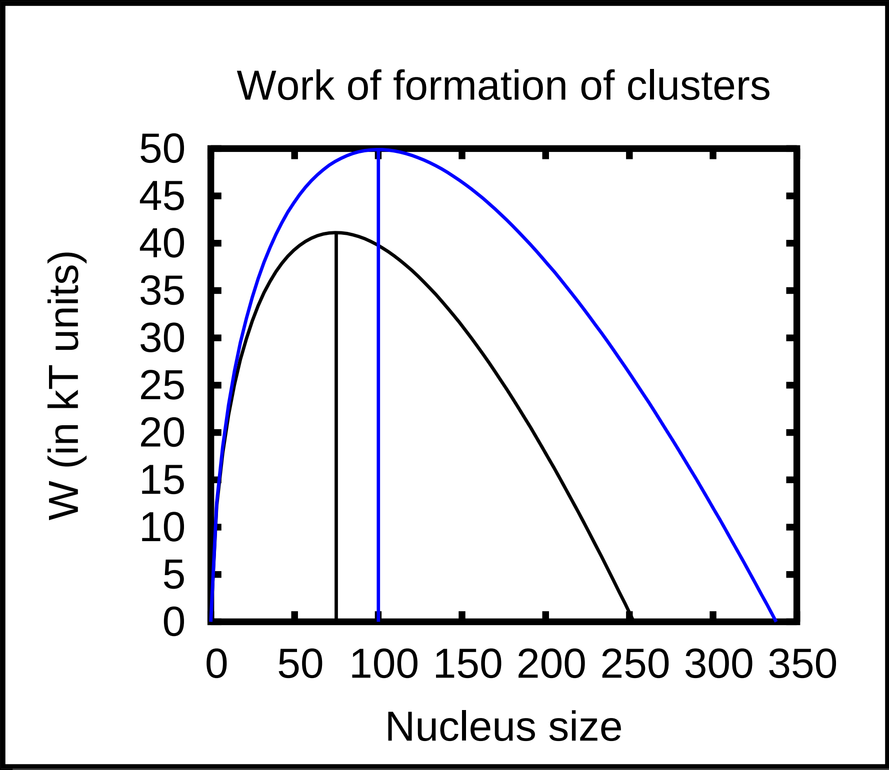
$$F_1^0 = N_0$$

Binary nucleation

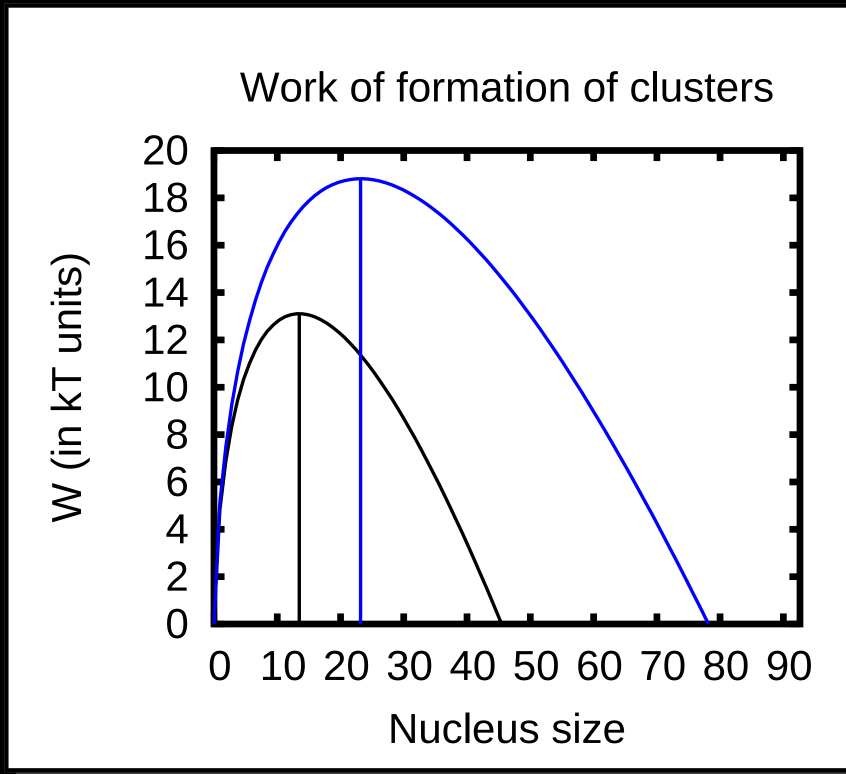


Closed systems

S=3



S=7



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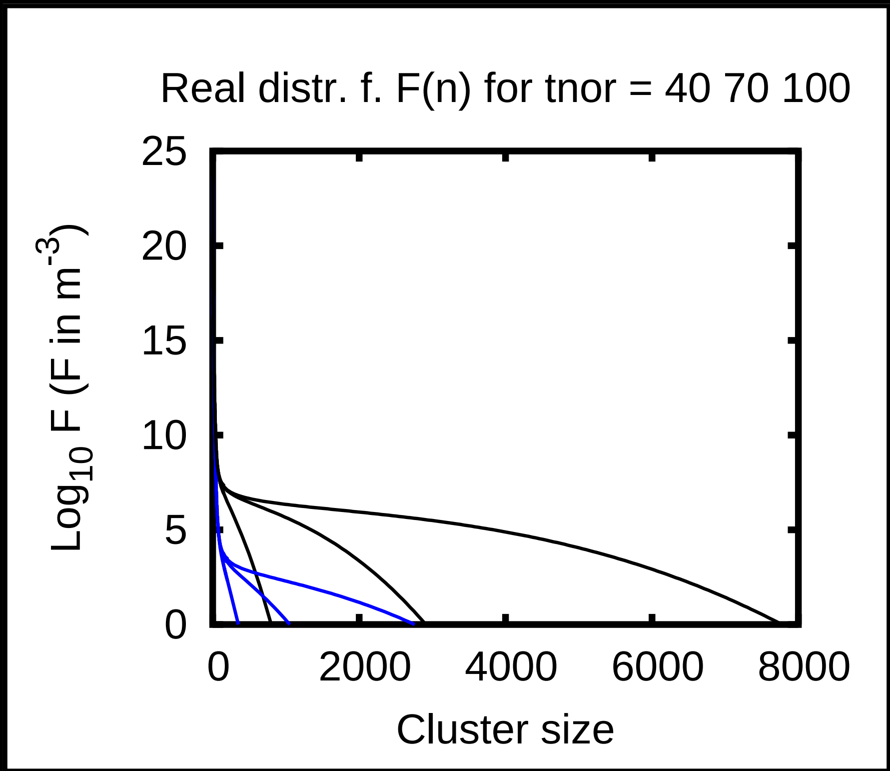

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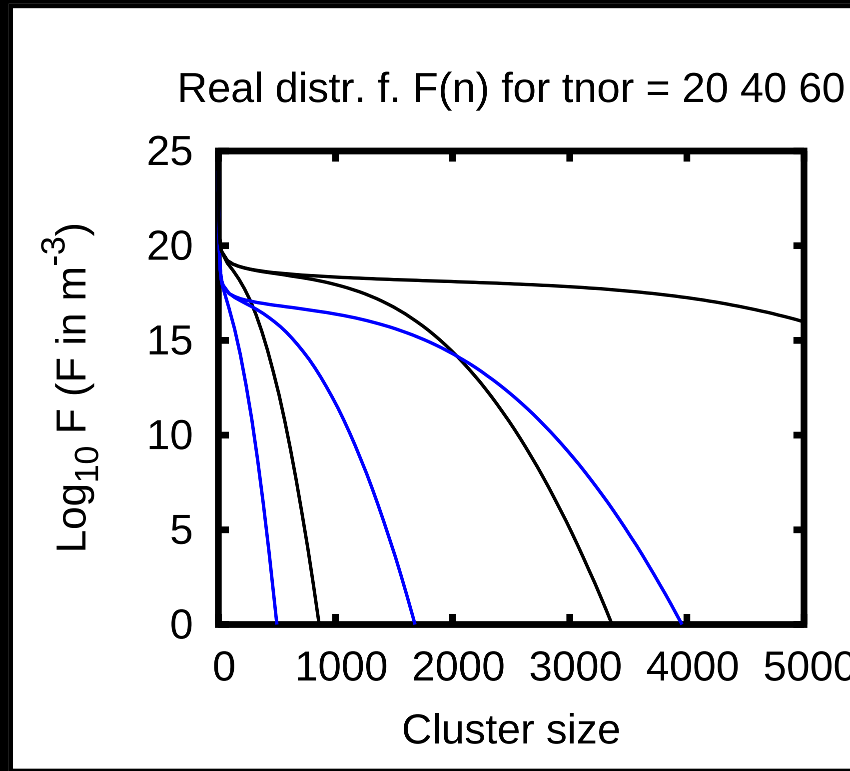

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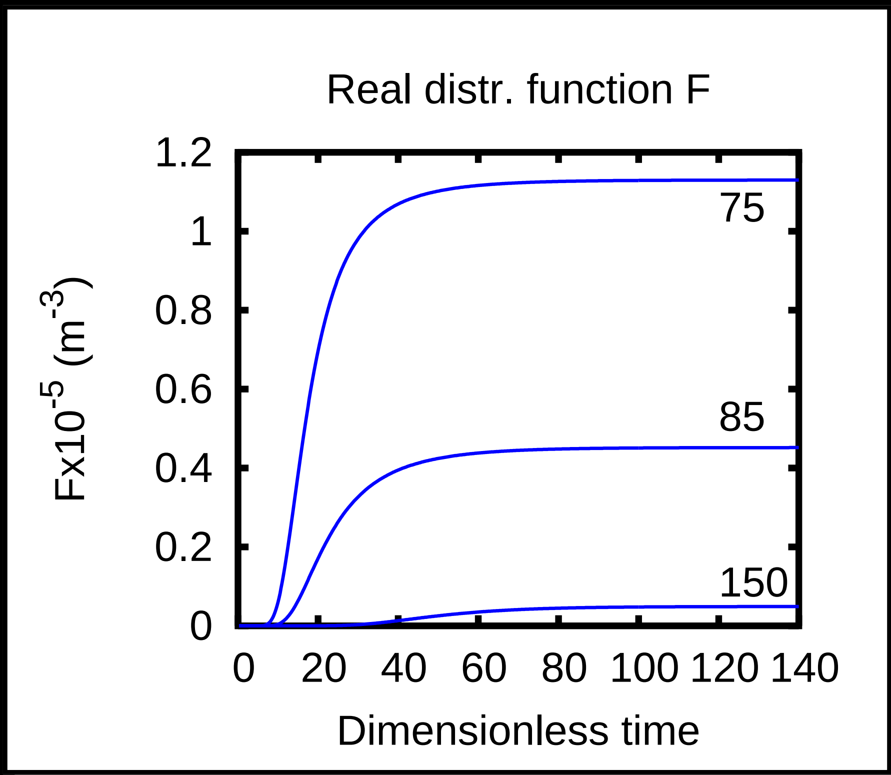

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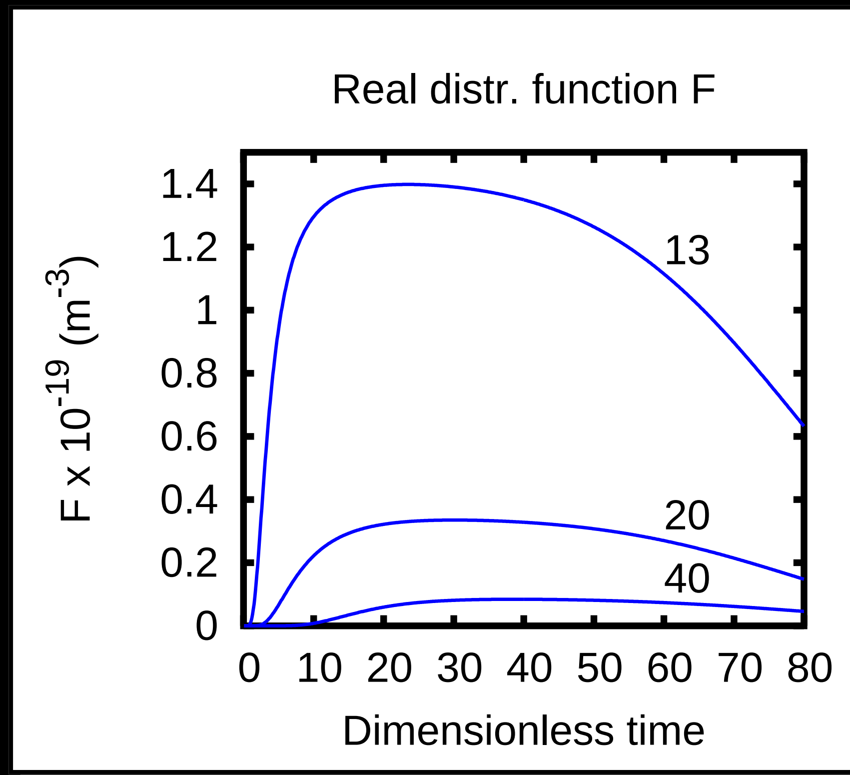

Closed systems

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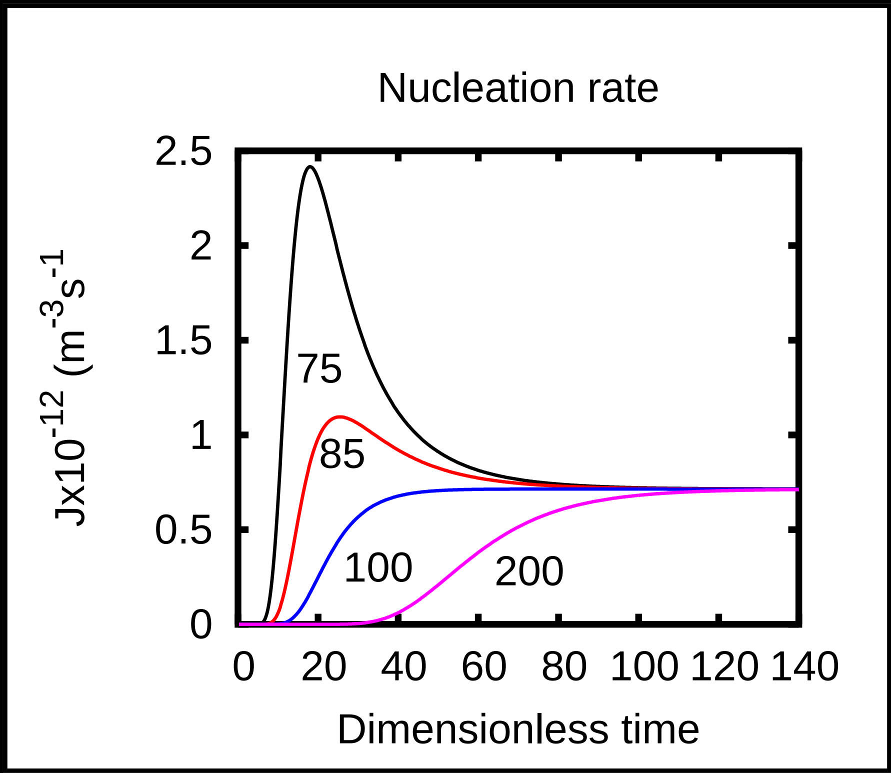

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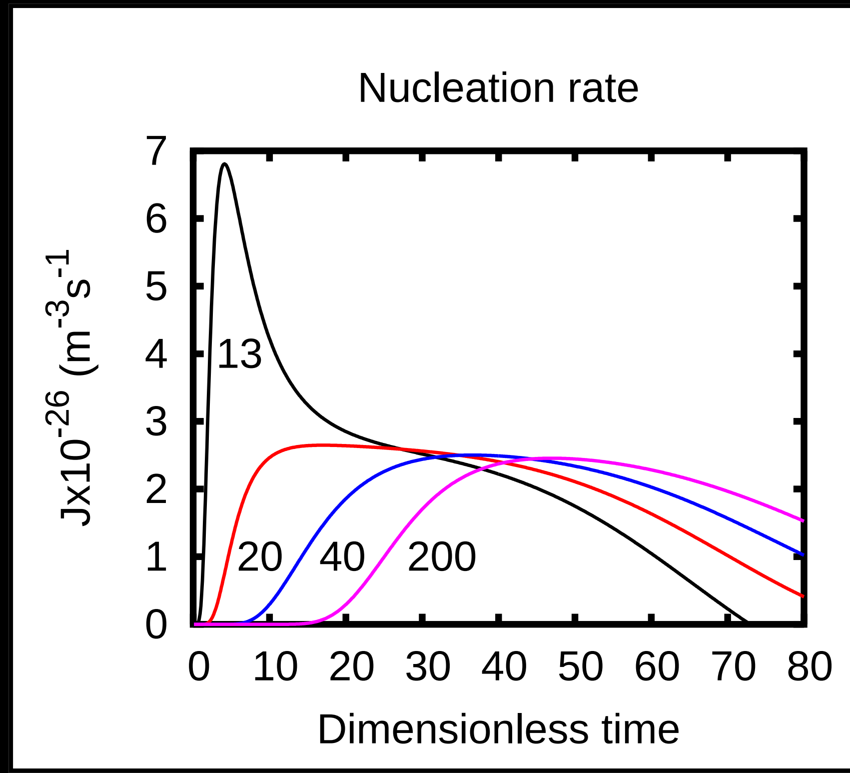

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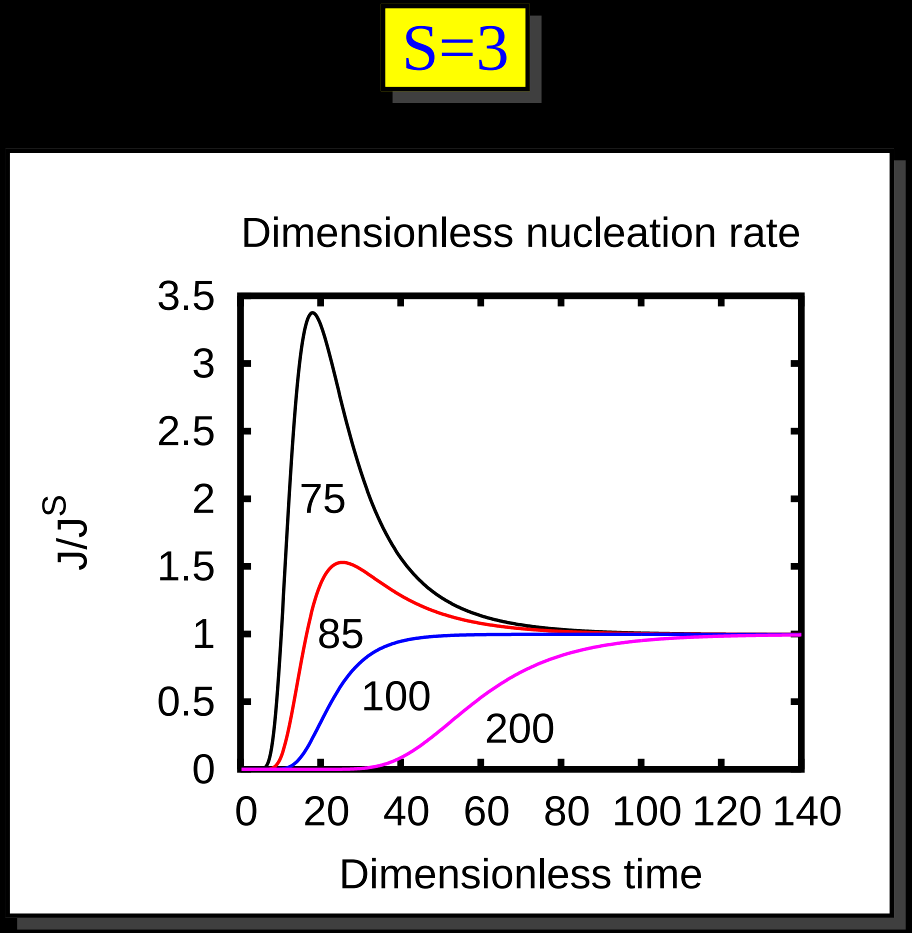

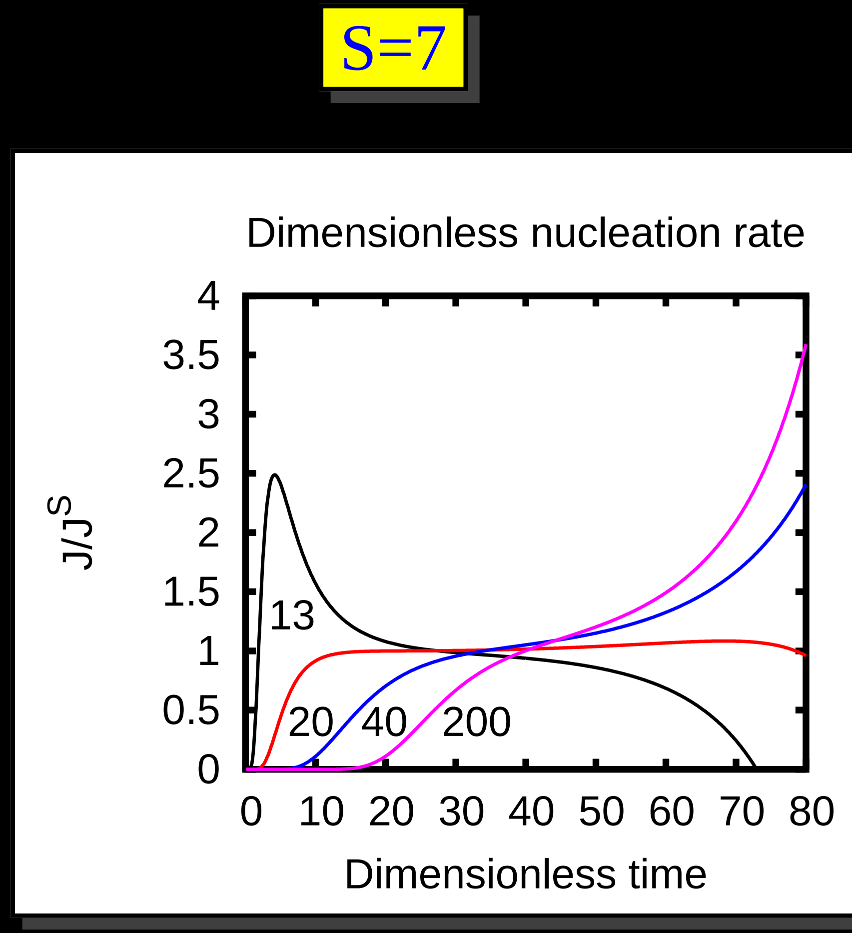

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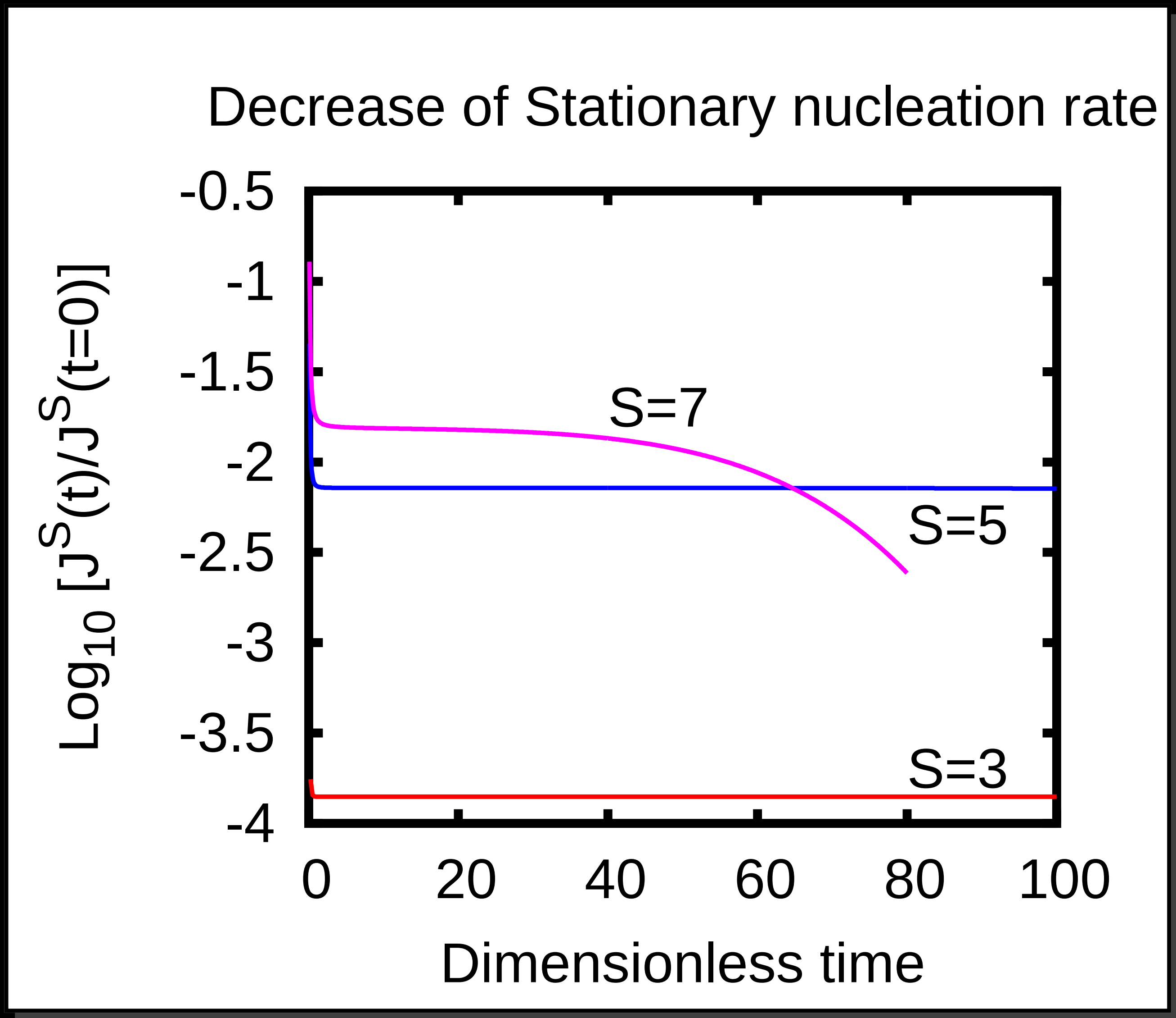

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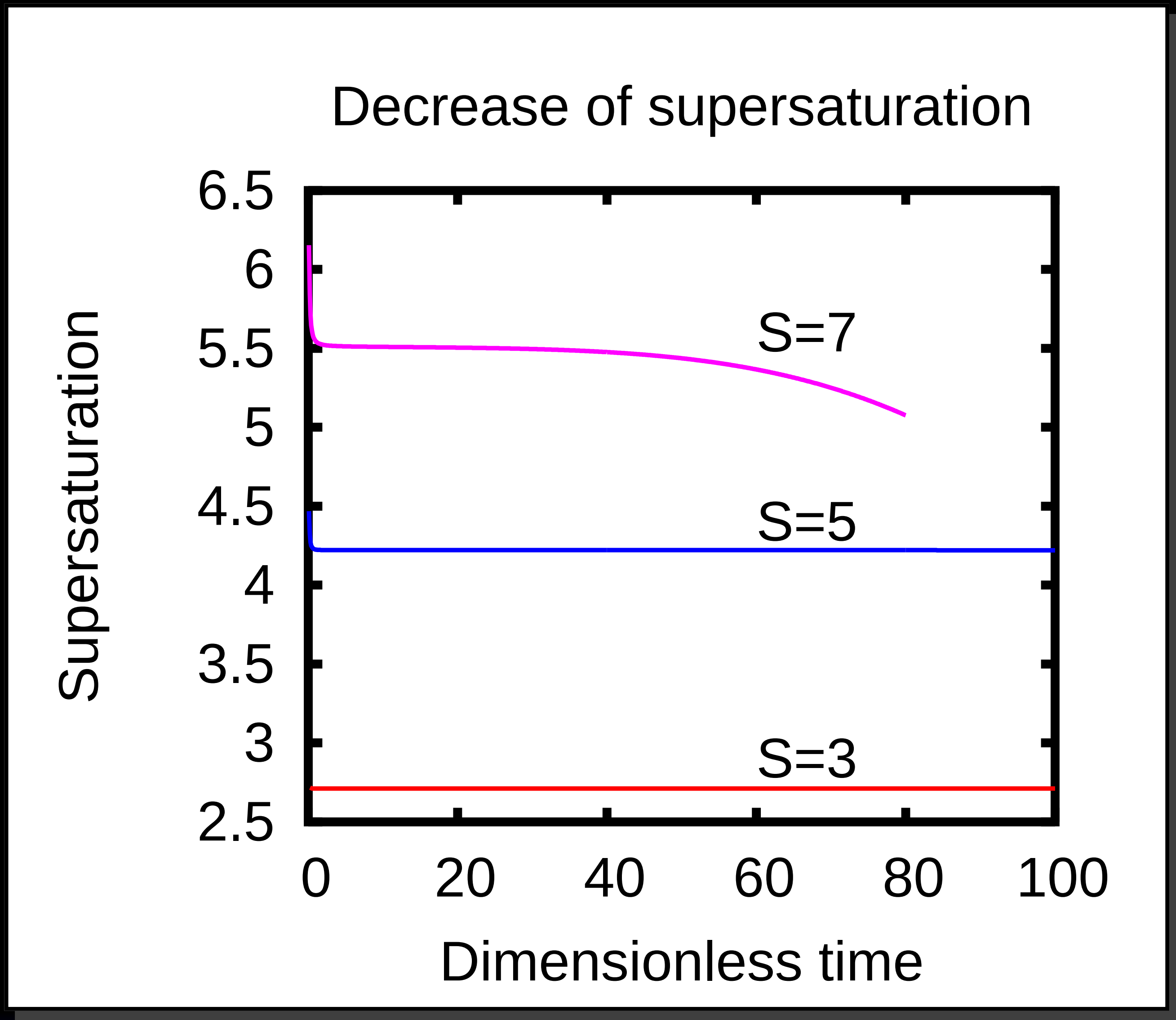
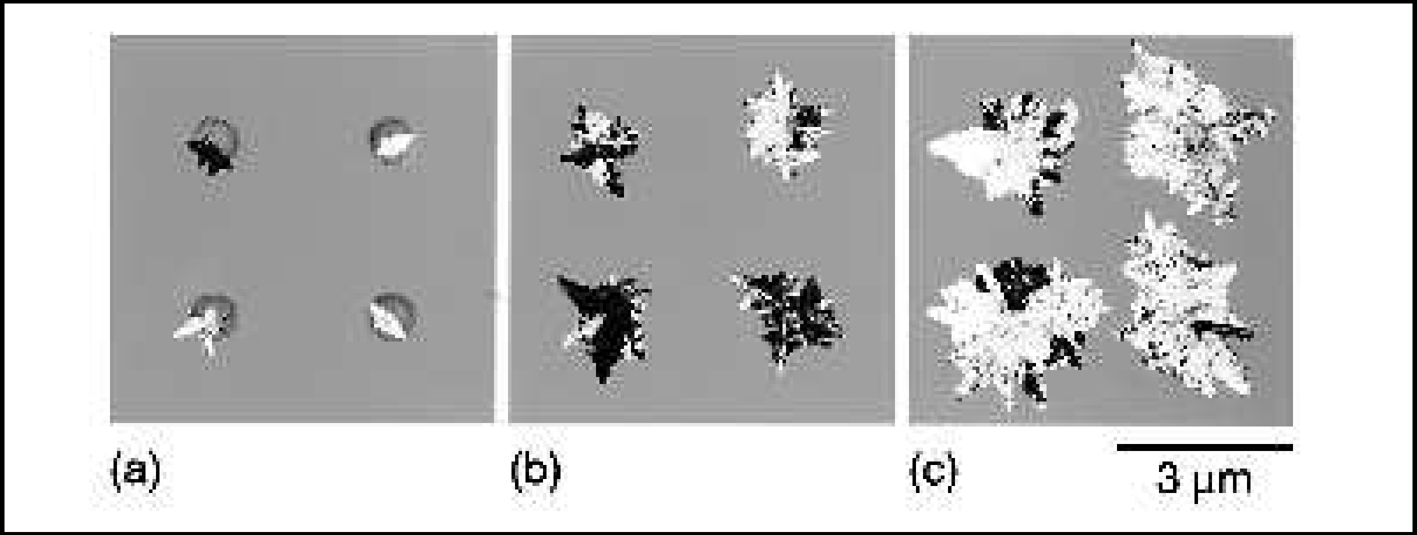


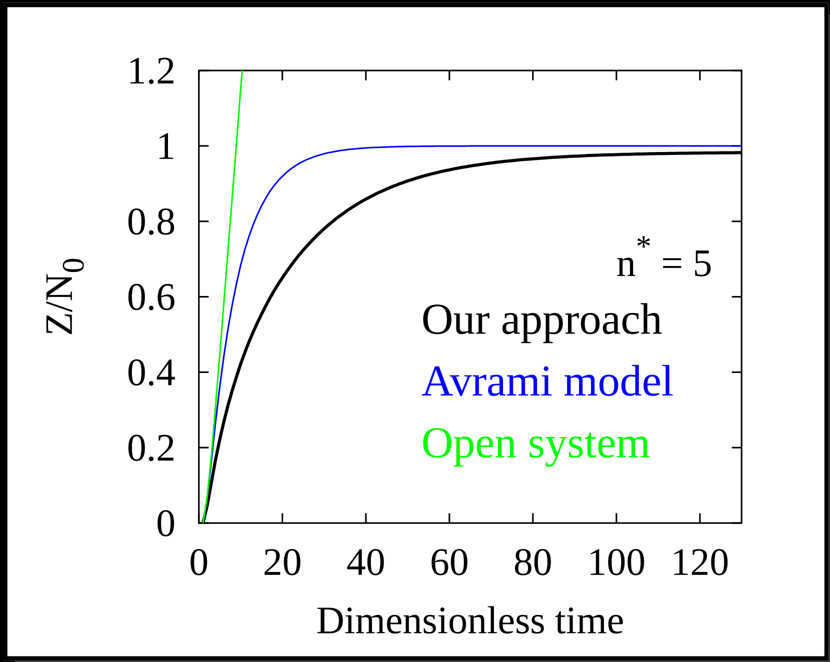
Nucleation on active centers

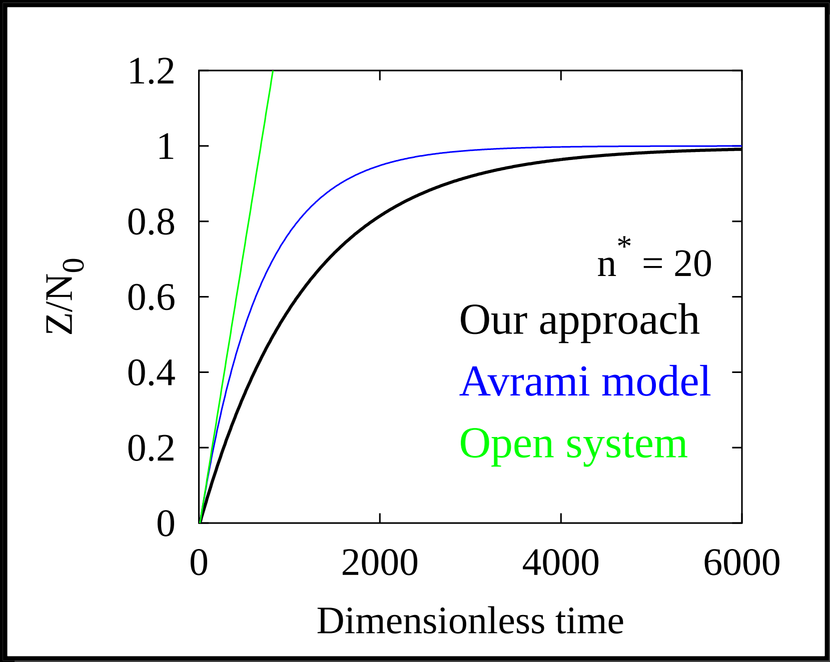


H. Kumomi and F. G. Shi: Phys. Rev. Lett. 82 (1999) 2717.

Nucleation on active centers

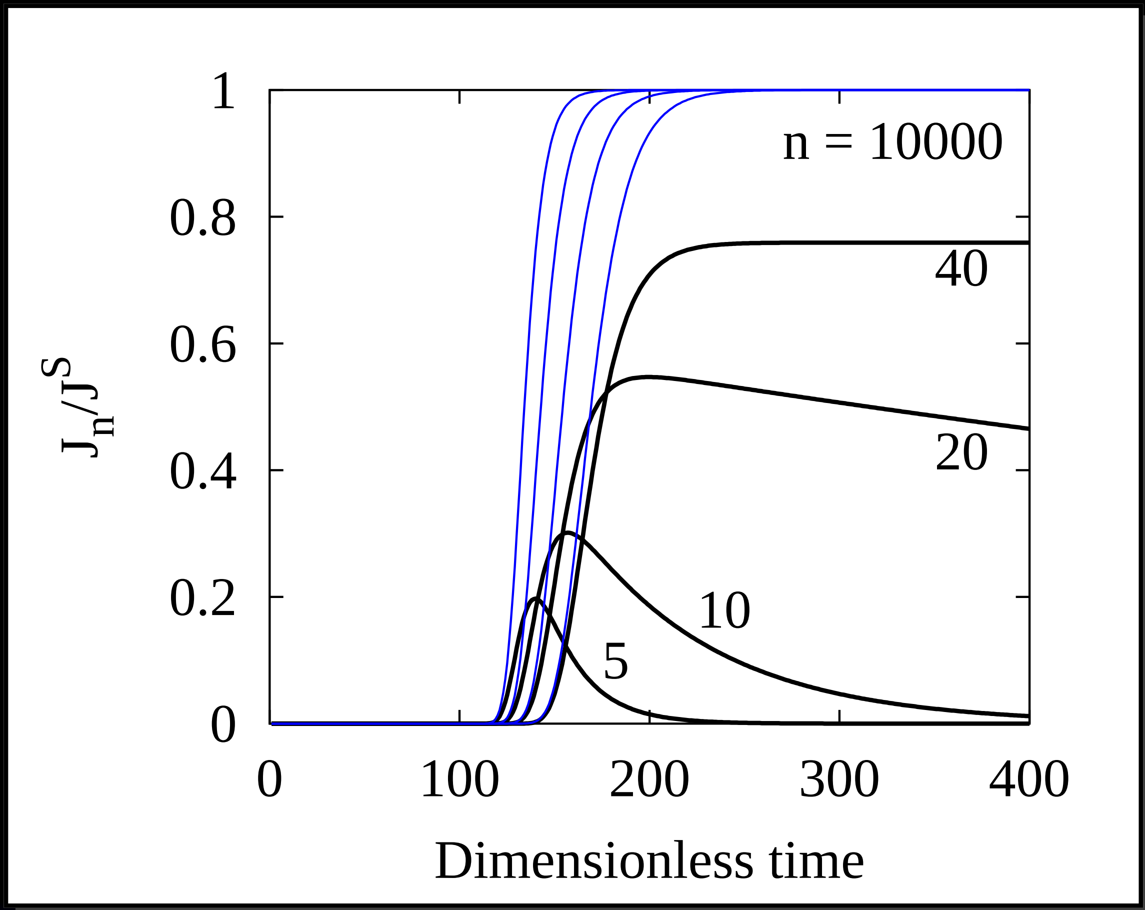
Total number of supercritical nuclei





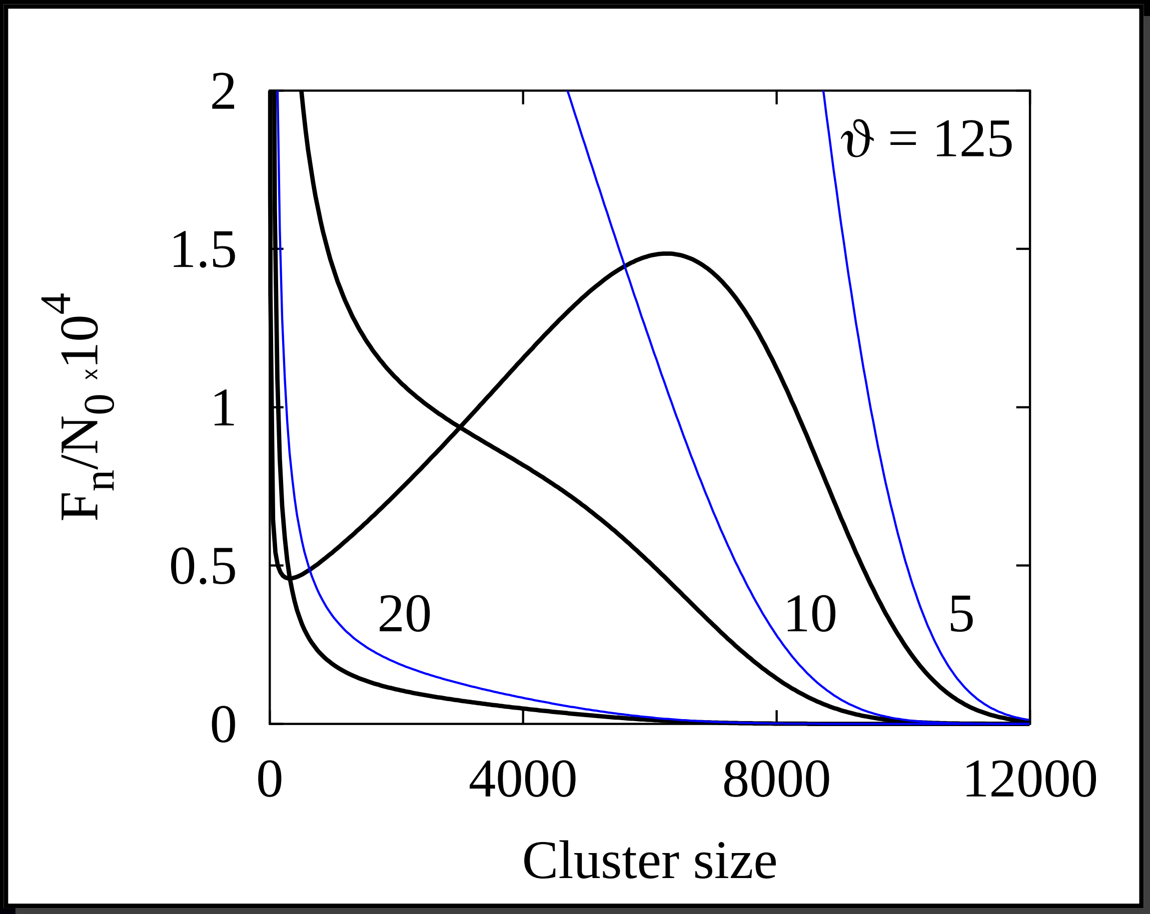
Nucleation on active centers

Nucleation rate



Nucleation on active centers

Size distribution



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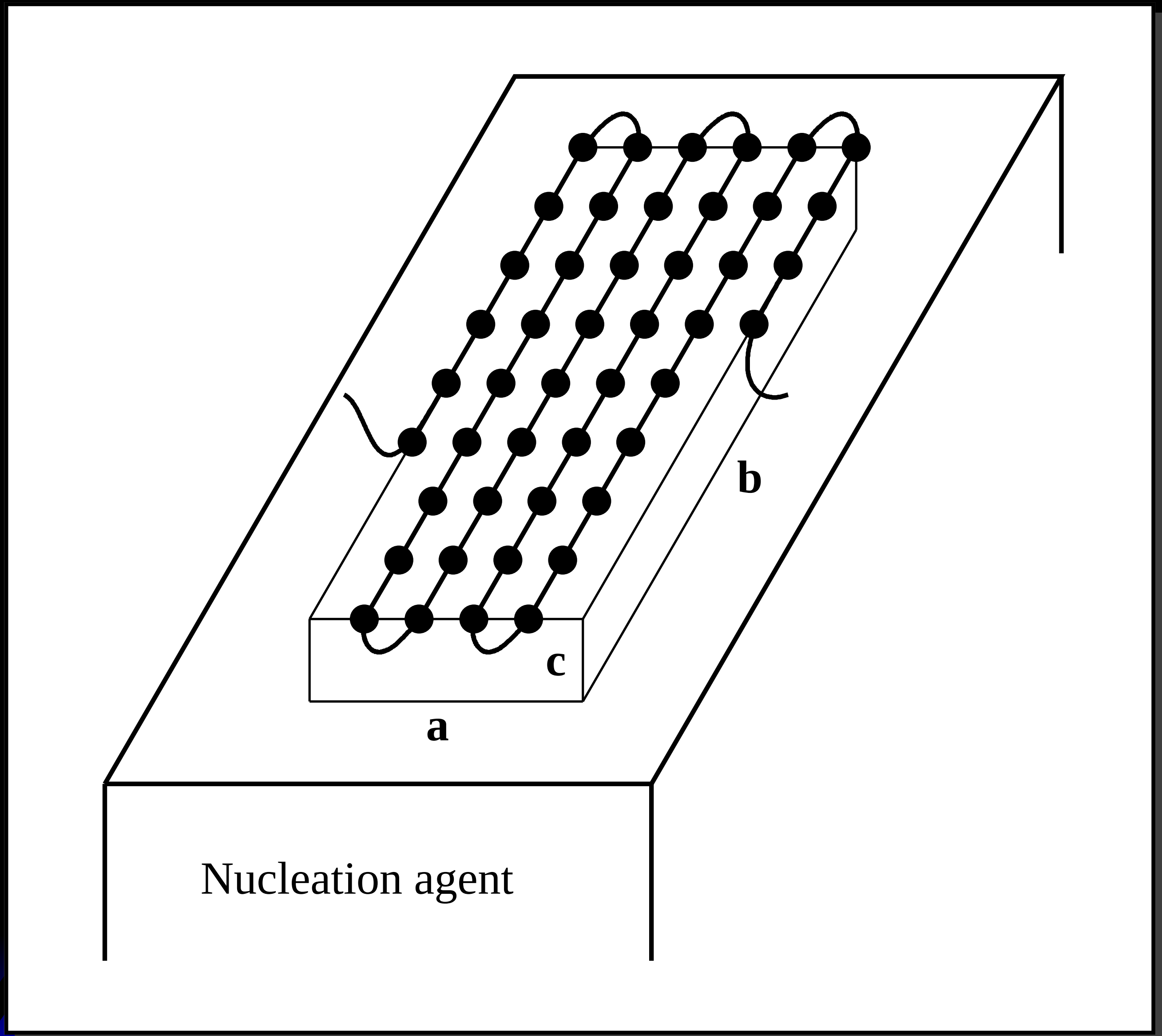

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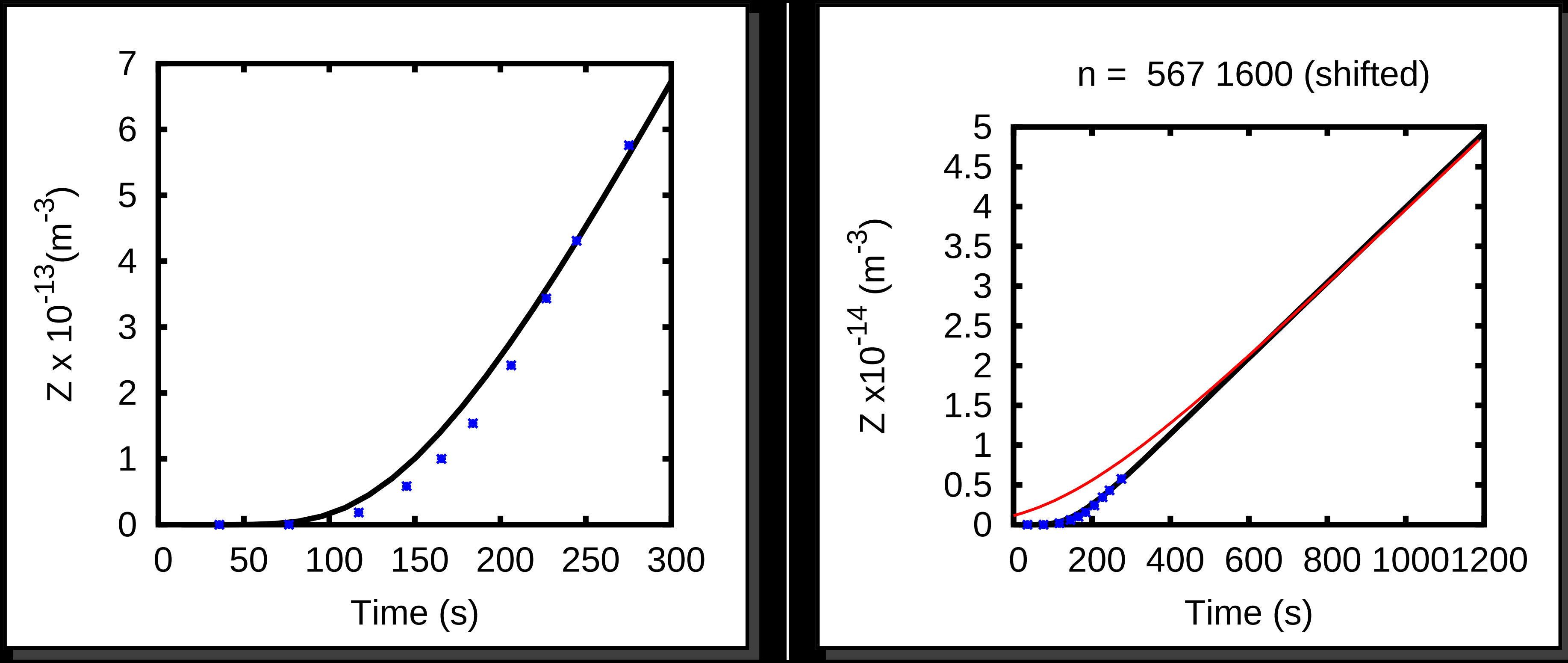

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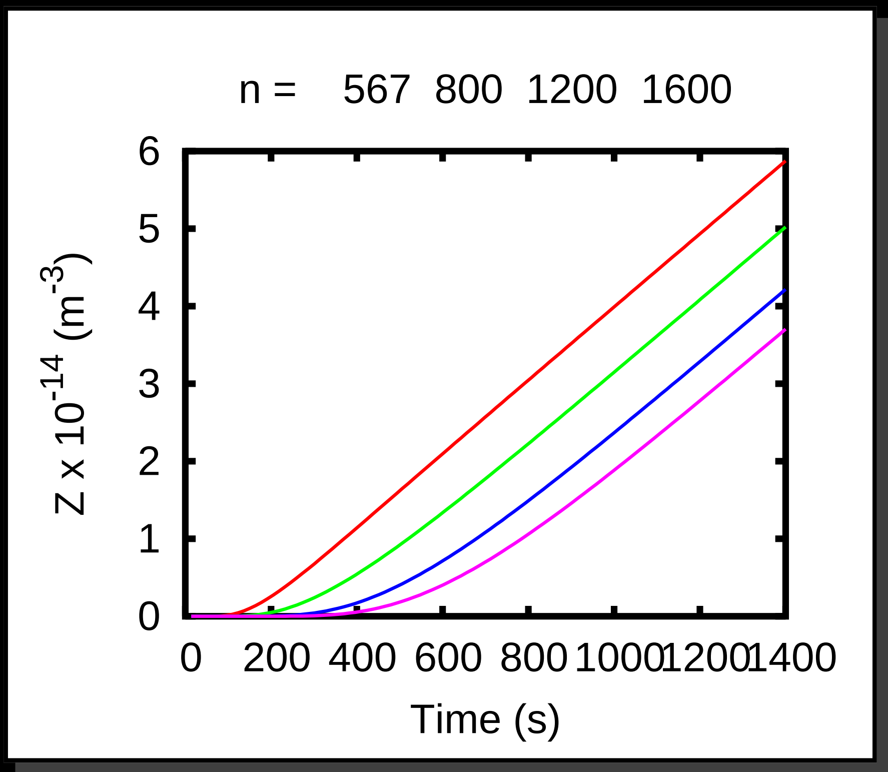

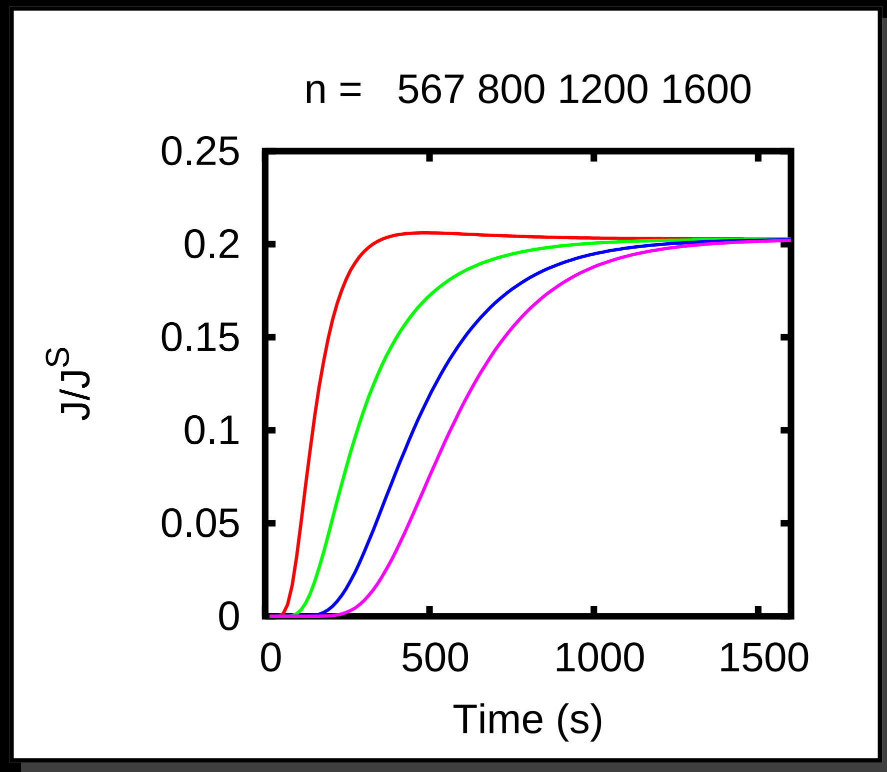

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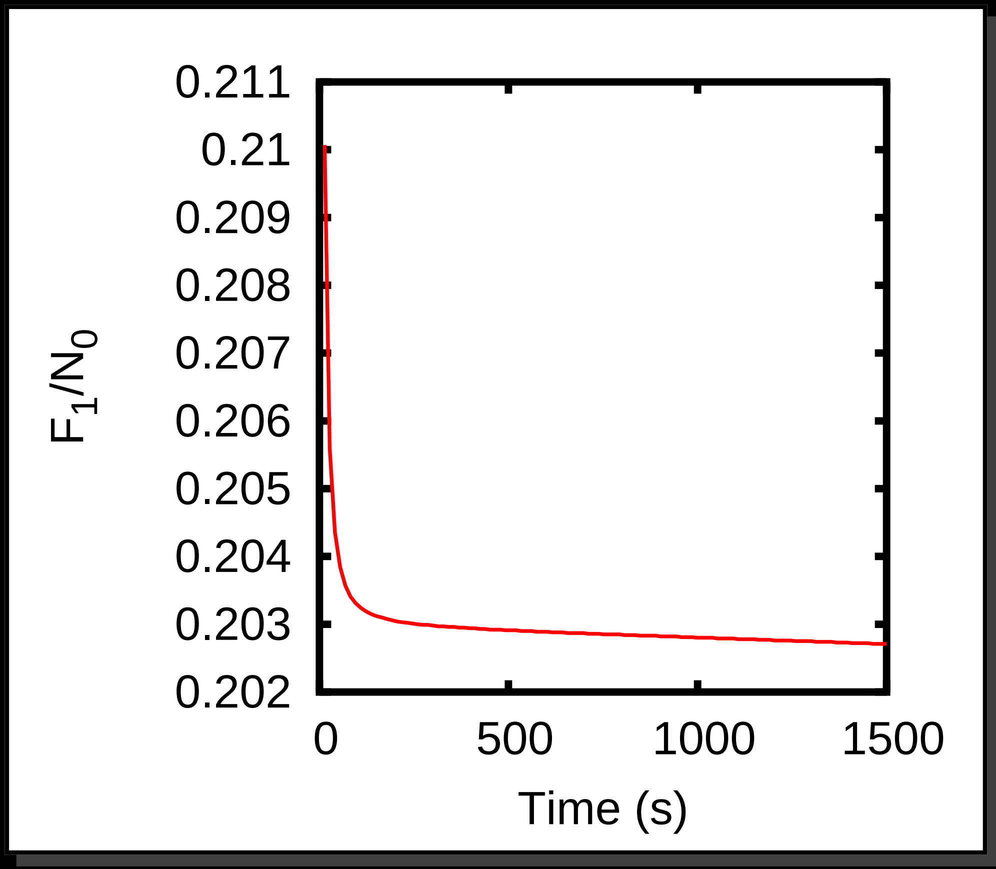

Conclusions

Closed systems

- At low supersaturations quasistationary regime is reached.
- At higher supersaturations formation of nuclei is fully nonstationary process.
- Standard approaches based only on thermodynamics can not describe nucleation in close systems.

Nucleation on active centers

- Modified standard kinetic model including the depletion of the active centers fits well nucleation of FCC polyethylene at low supersaturation.