Multi-scale modelling of flow-induced crystallisation in polymers.

Richard Graham,

School of Mathematical Sciences, University of Nottingham.

Acknowledgements

Collaborators

- Daniel Read, Oliver Harlen and Chinmay Das (University of Leeds)
- Muhammad Anwar (Institute of Space Technology, Islamabad)
- Claire McIlroy (University of Lincoln)
- Peter Olmsted (Georgetown University)
- Kenny Jolley (Loughborough University)
- Matthew Hamer
- Dow Chemicals
- SCG Chemicals
- Autodesk

Funding

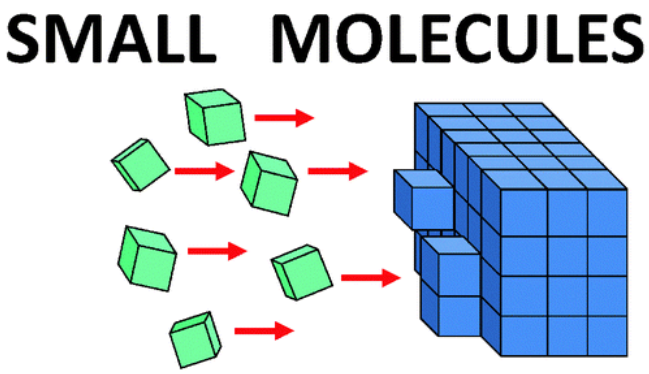
- EPSRC (EP/G048827/1) and (EP/P005403/1)
- School of Mathematical Sciences, University of Nottingham (PhD Studentship)

The University of Nottingham

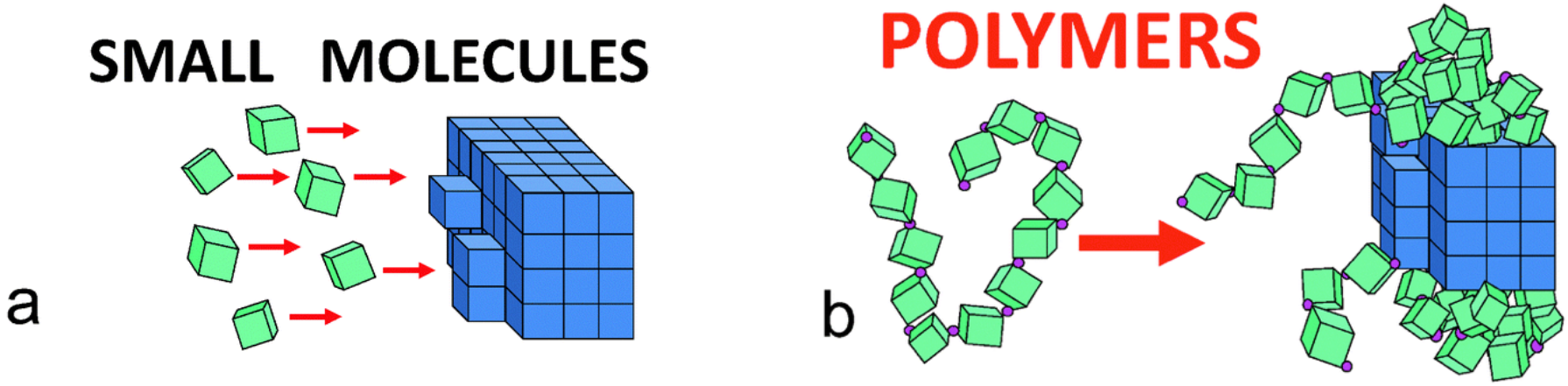
UNIVERSITY OF LEEDS

Crystallisation in polymers

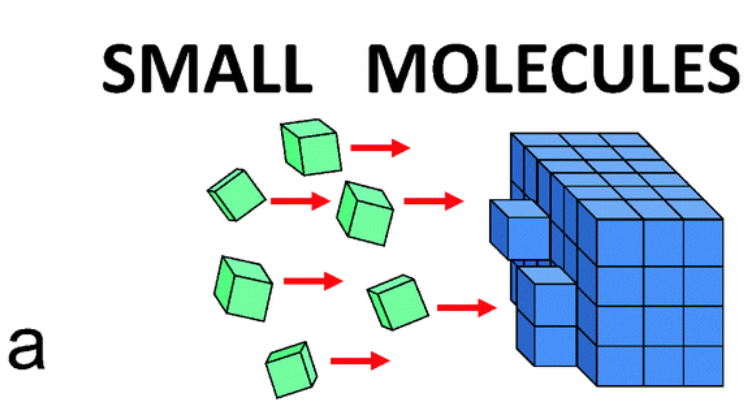
a

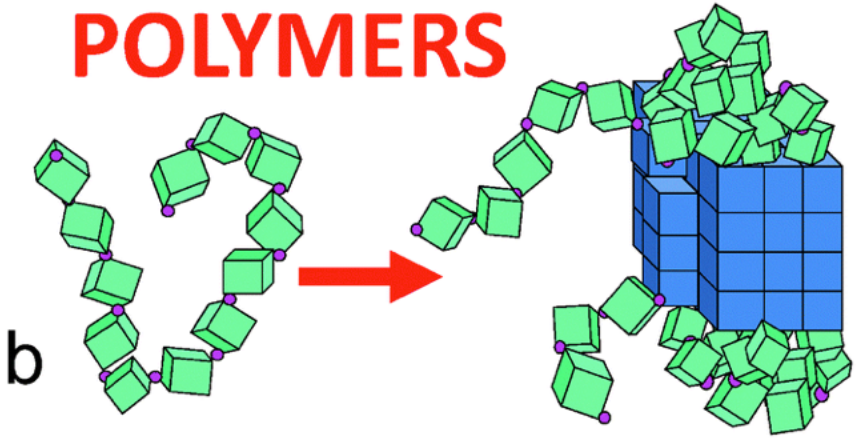


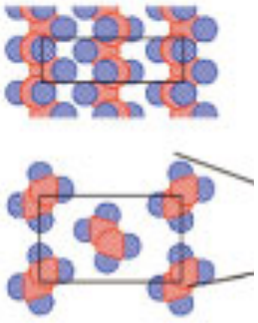
Crystallisation in polymers



Crystallisation in polymers

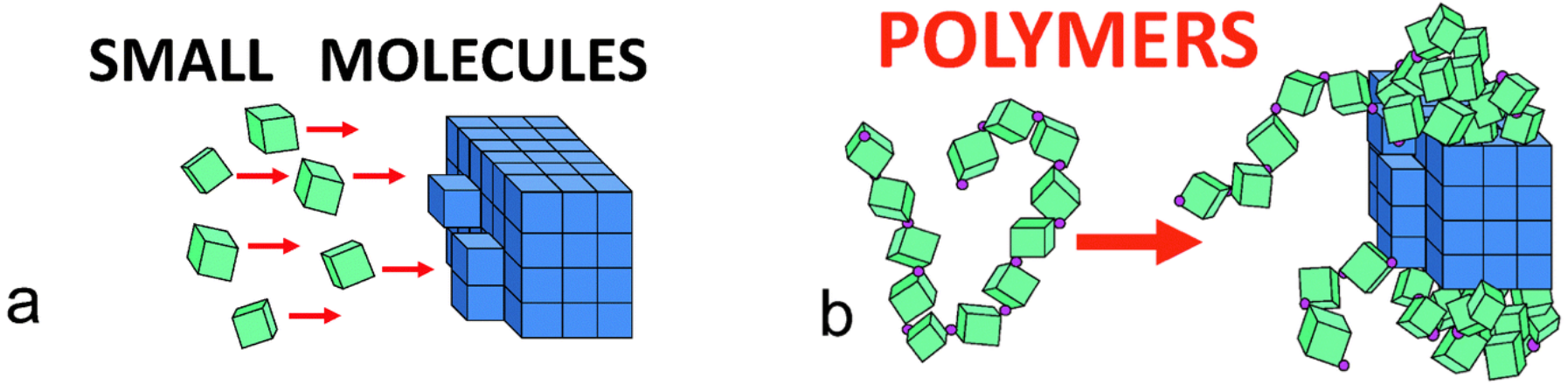


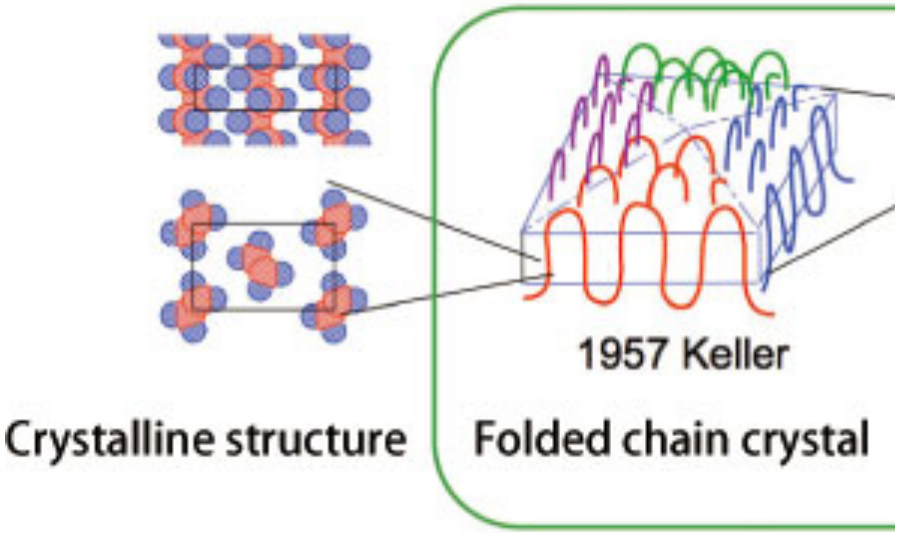




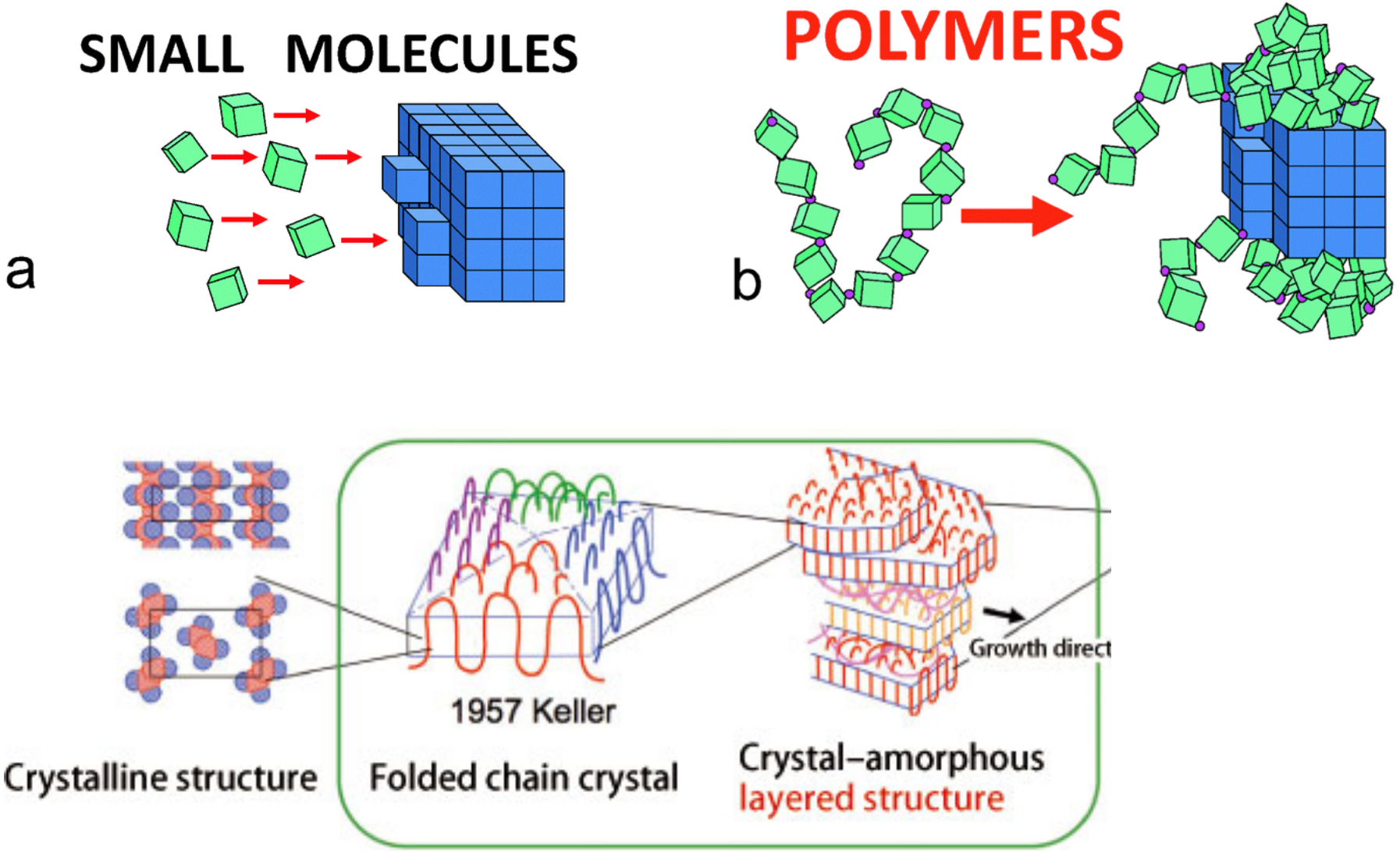
Crystalline structure

Crystallisation in polymers

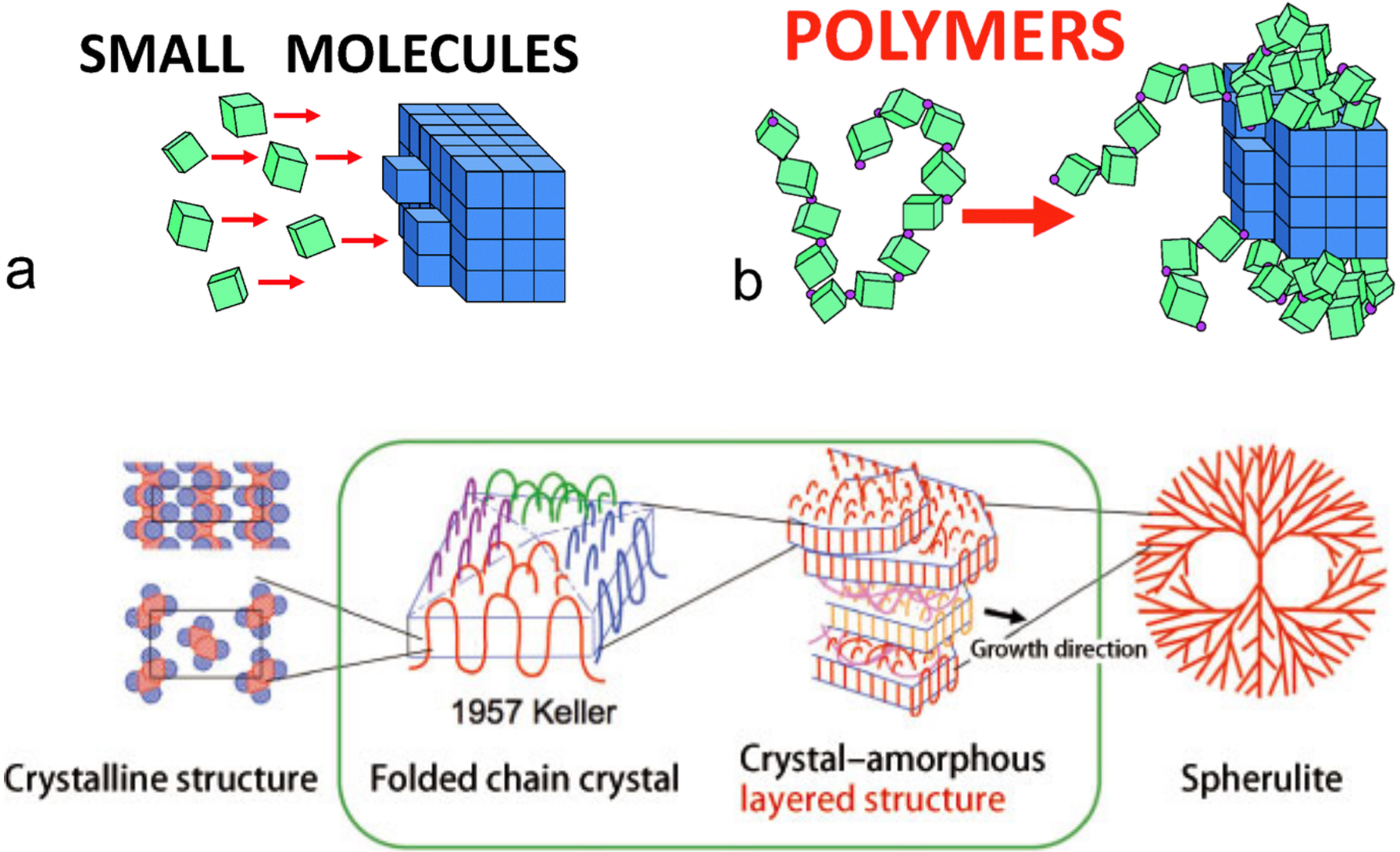




Crystallisation in polymers

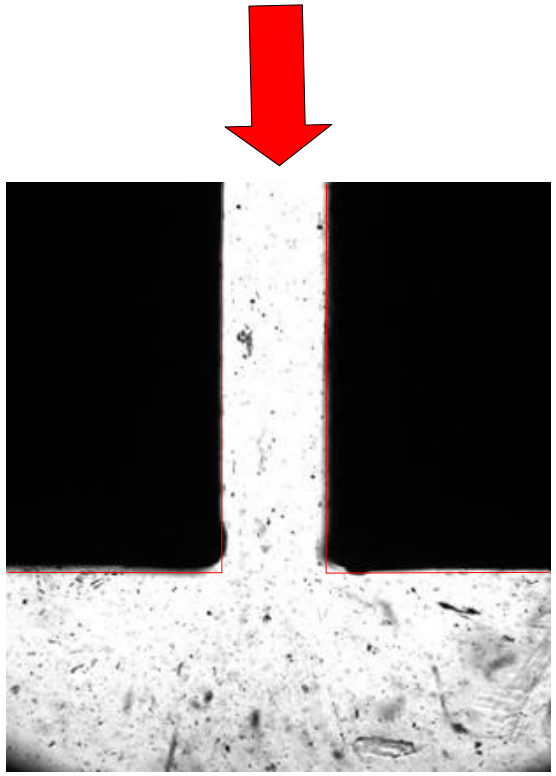


Crystallisation in polymers



Polymer crystallisation during flow

Deep slit ; T=130°C; $\dot{\gamma}_{w,app.} \approx 100\ s^{-1}$

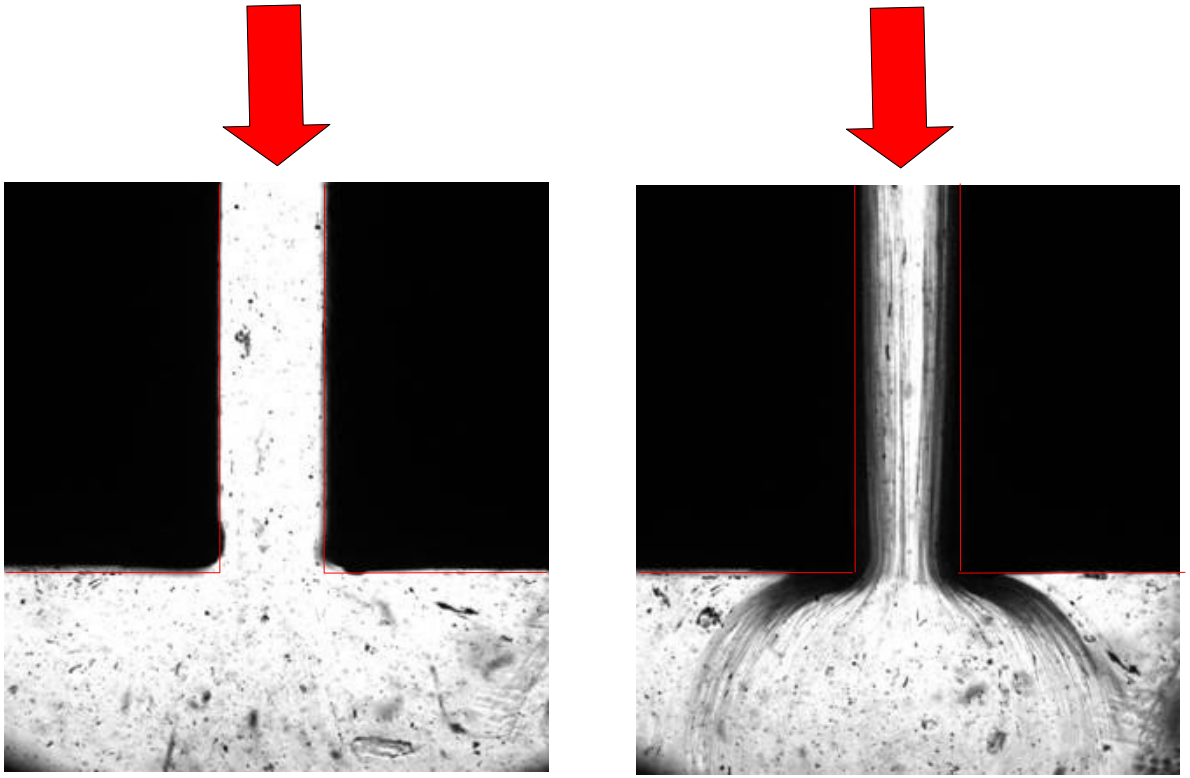


180kg/mol HDPE melt

Scelsi et al., Rheol Acta(2008).

Polymer crystallisation during flow

Deep slit ; T=130°C; $\dot{\gamma}_{w,app.} \approx 100\ s^{-1}$

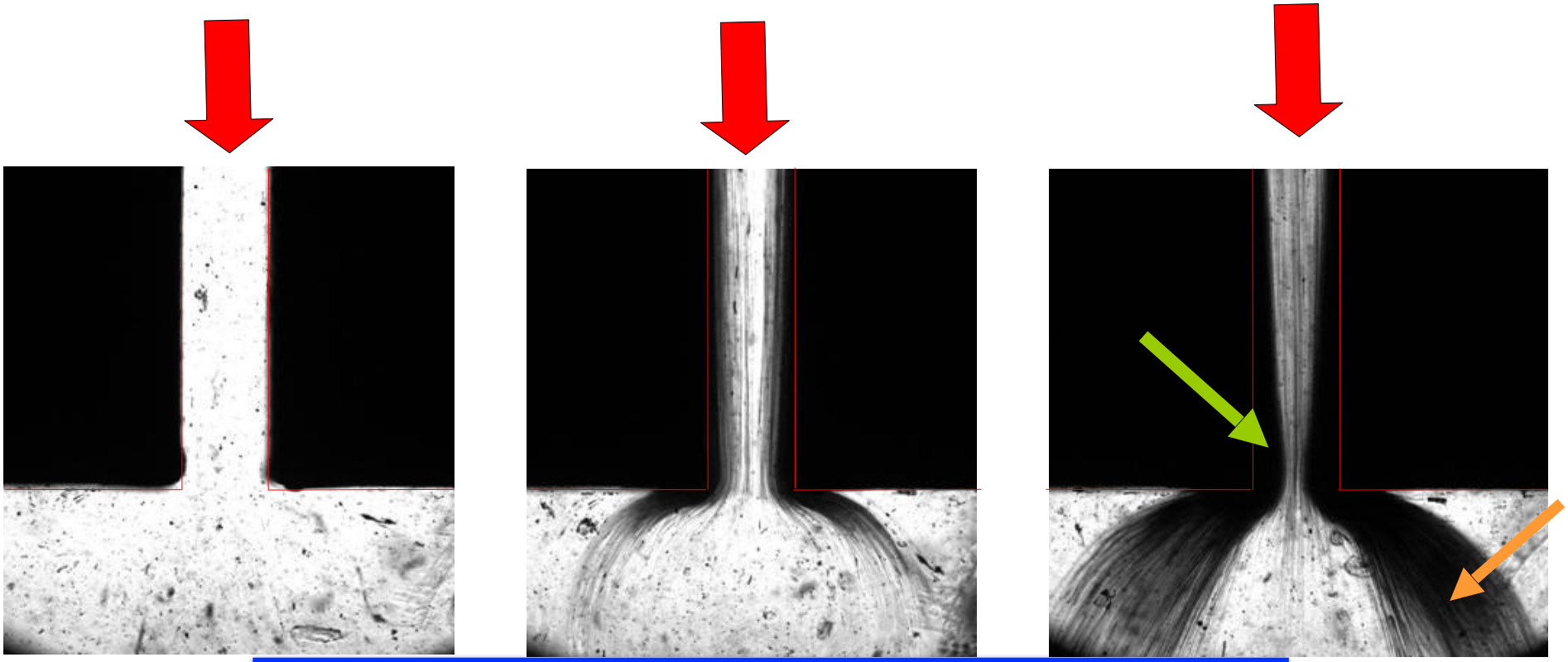


180kg/mol HDPE melt

Scelsi et al., Rheol Acta(2008).

Polymer crystallisation during flow

Deep slit ; T=130°C; $\dot{\gamma}_{w,app.} \approx 100\ s^{-1}$



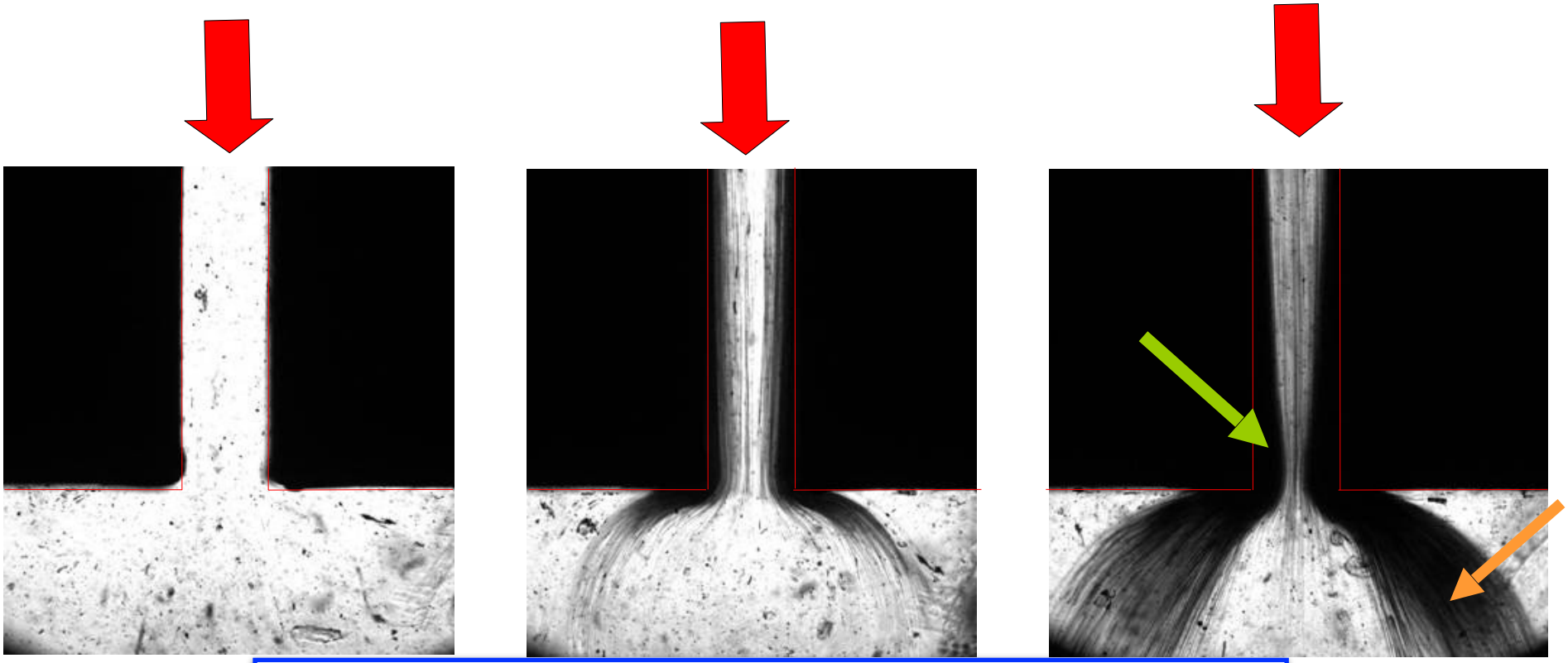
Crystallisation is enhanced in regions of strong flow

180kg/mol HDPE melt

Scelsi et al., Rheol Acta(2008).

Polymer crystallisation during flow

Deep slit ; T=130°C; $\dot{\gamma}_{w,app.} \approx 100\ s^{-1}$



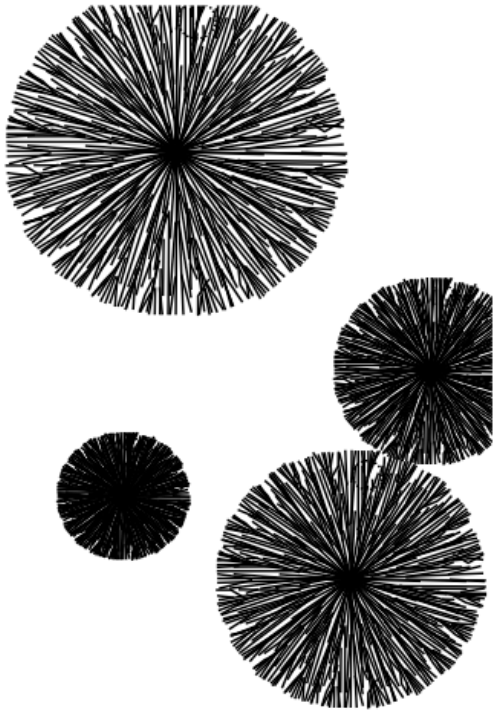
Crystallisation is enhanced in regions of strong flow

Key processing control variables are temperature, flow-rate and molecular weight

180kg/mol HDPE melt

Scelsi et al., Rheol Acta(2008).

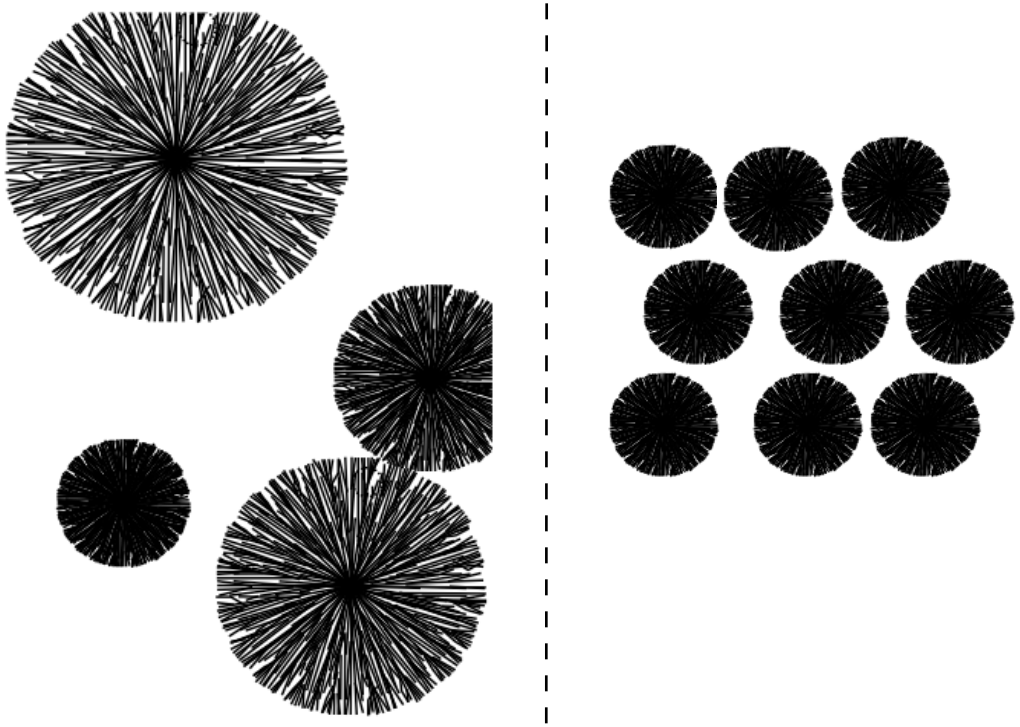
Effect of flow



Quiescent
(no flow)

Increasing flow rate

Effect of flow

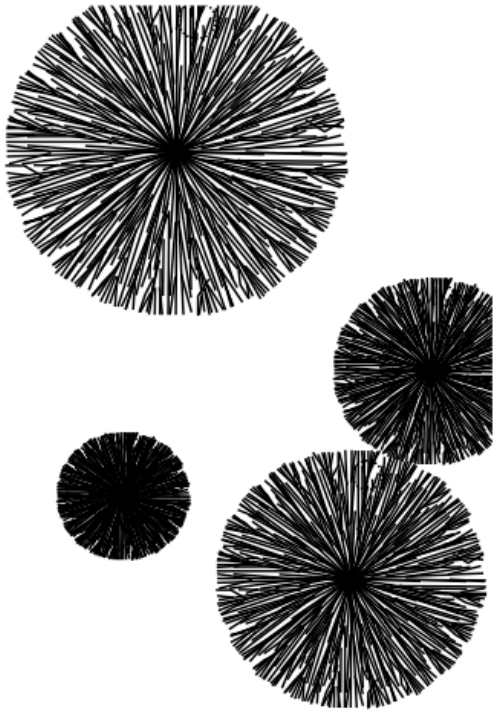


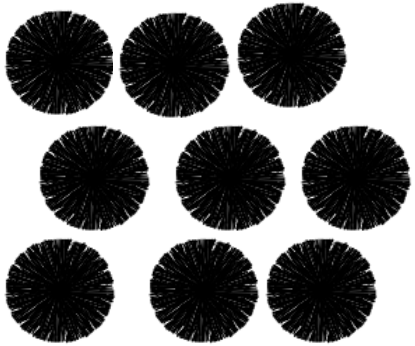
Quiescent
(no flow)

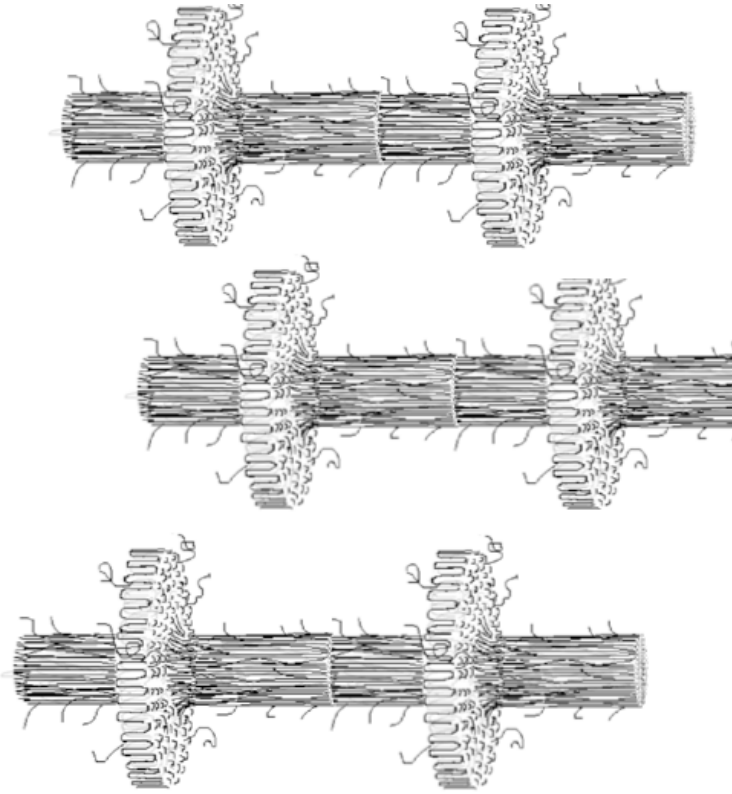
Enhanced
nucleation

Increasing flow rate

Effect of flow







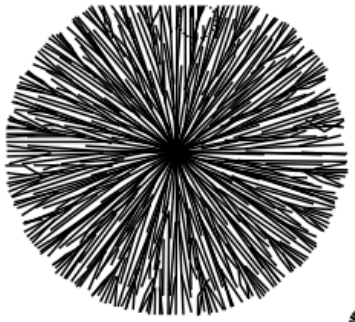
Quiescent
(no flow)

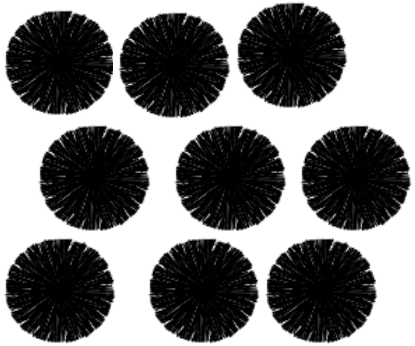
Enhanced
nucleation

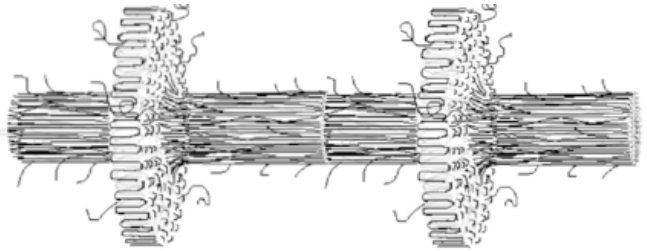
Shish
kebabs

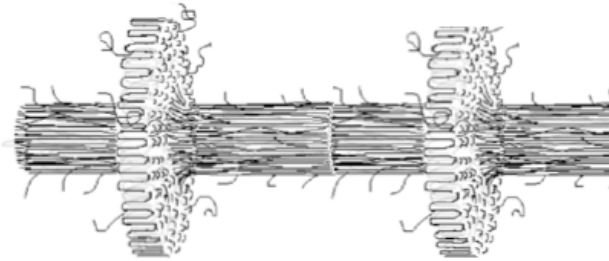
Increasing flow rate

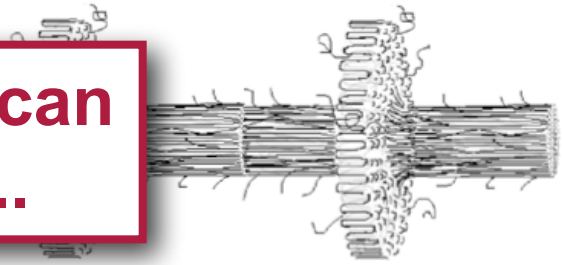
Effect of flow











Controlling crystallisation can be the difference between...

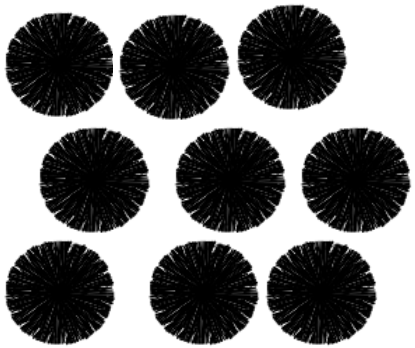
Quiescent (no flow)

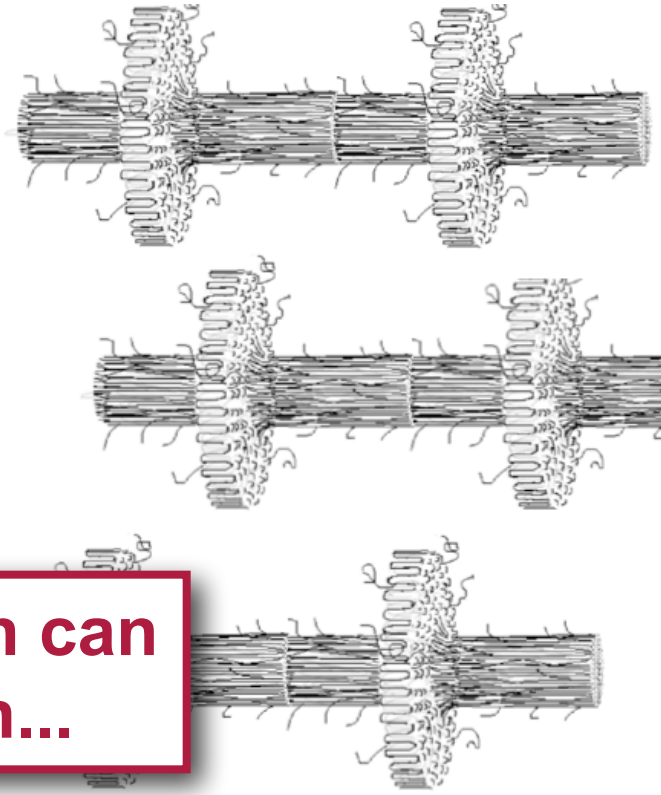
Enhanced nucleation

Shish kebabs

Increasing flow rate

Effect of flow





Controlling crystallisation can be the difference between...

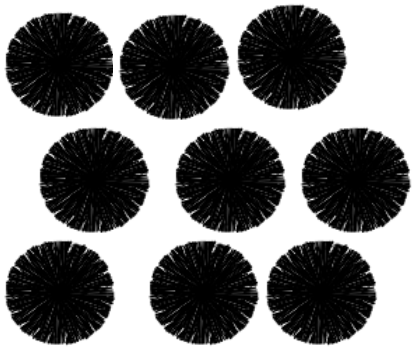
Quiescent (no flow)

Enhanced nucleation

Shish kebabs

Increasing flow rate

Effect of flow



Controlling crystallisation can be the difference between...

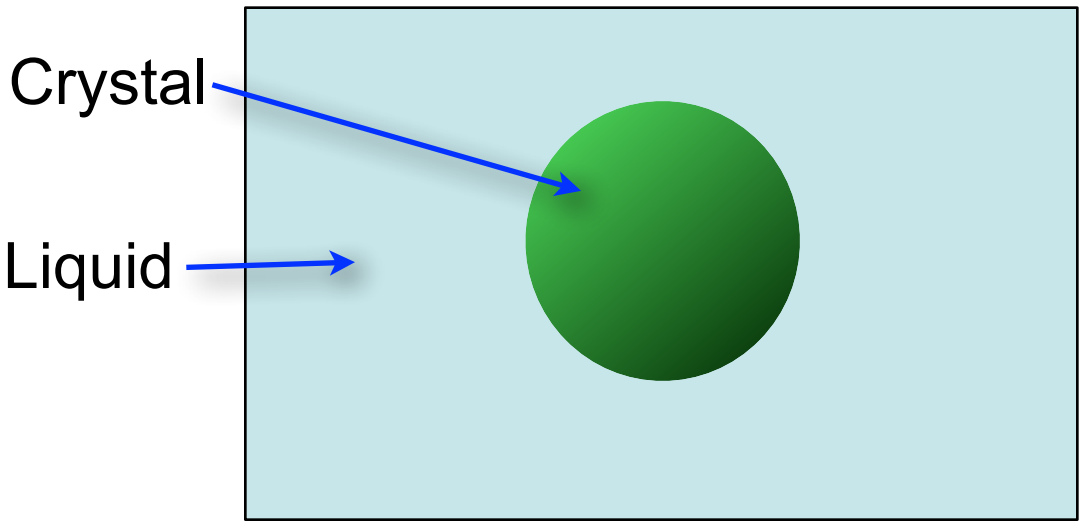
Quiescent (no flow)

Enhanced nucleation

Shish kebabs

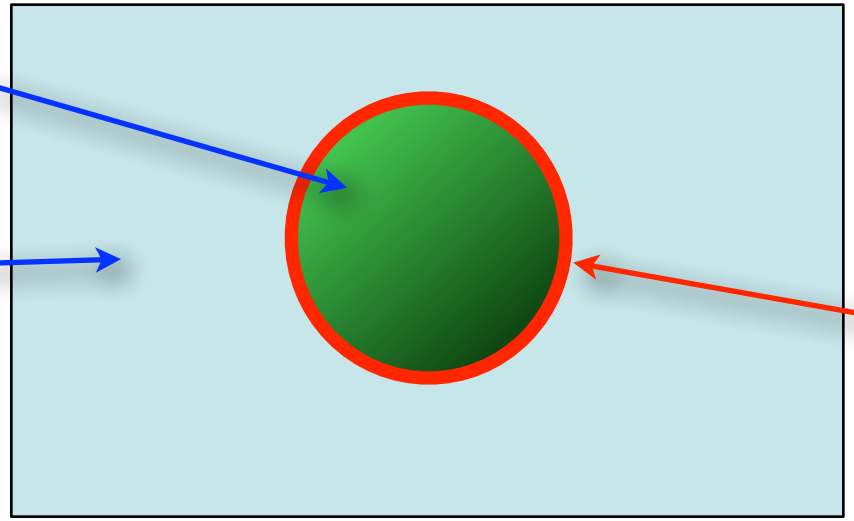
Increasing flow rate

Nucleation



Bulk crystallisation lowers the free energy

Nucleation



Bulk crystallisation lowers the free energy

... but the interface has a cost.

Bulk gain

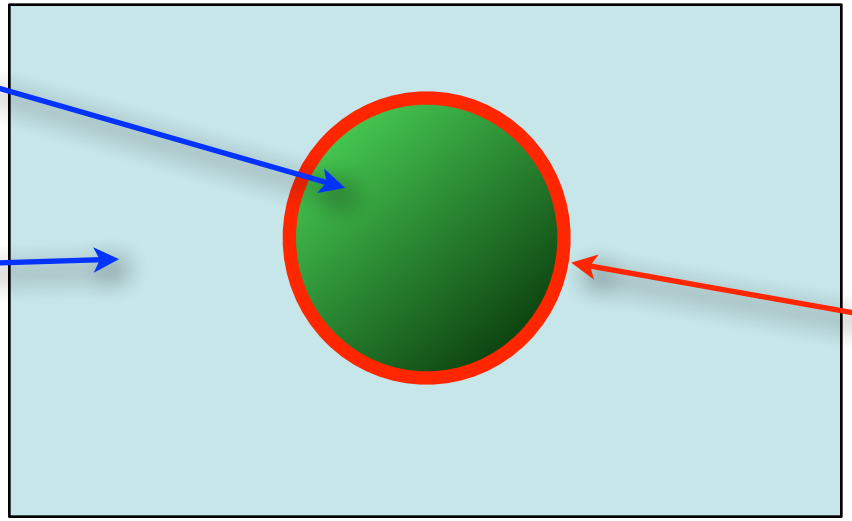
$$F = AR^2 - BR^3$$

Surface cost

F= Free energy

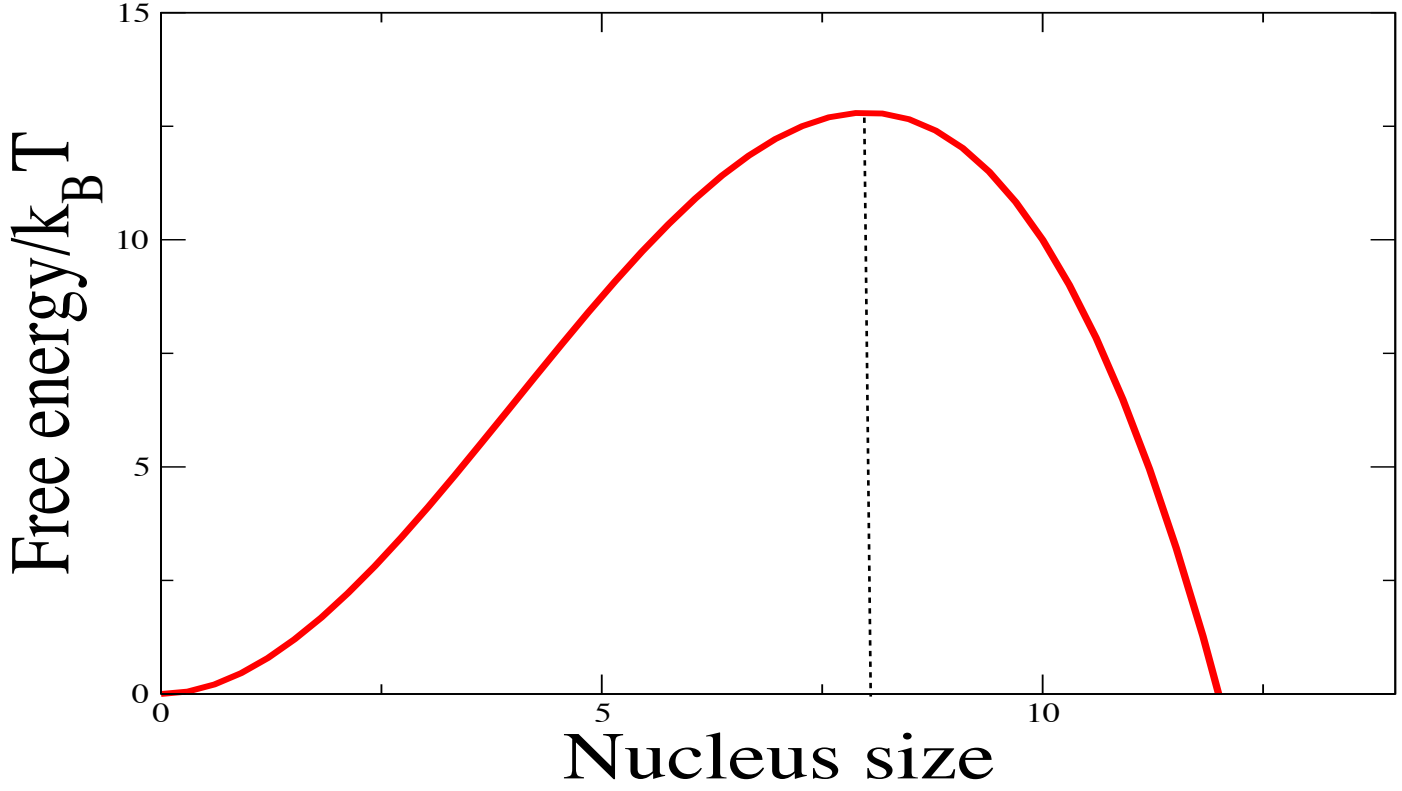
R= Nucleus radius

Nucleation



Bulk crystallisation lowers the free energy

... but the interface has a cost.



Bulk gain

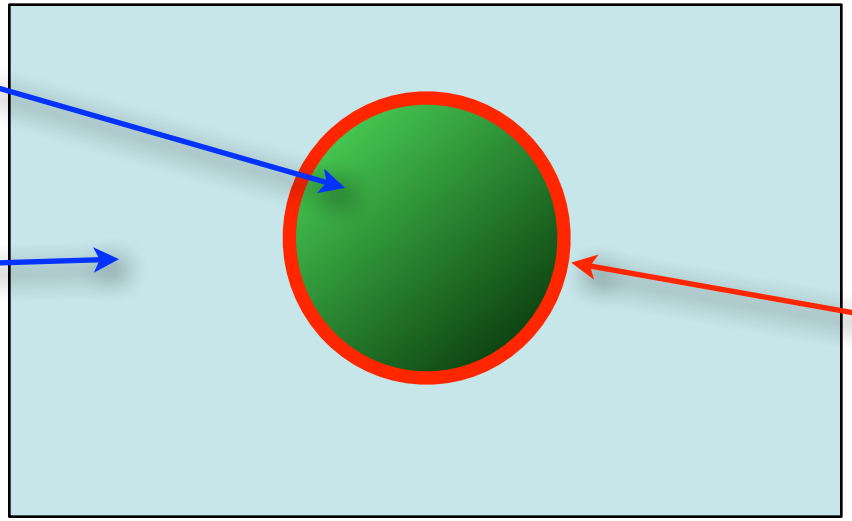
$$F = AR^2 - BR^3$$

Surface cost

F= Free energy

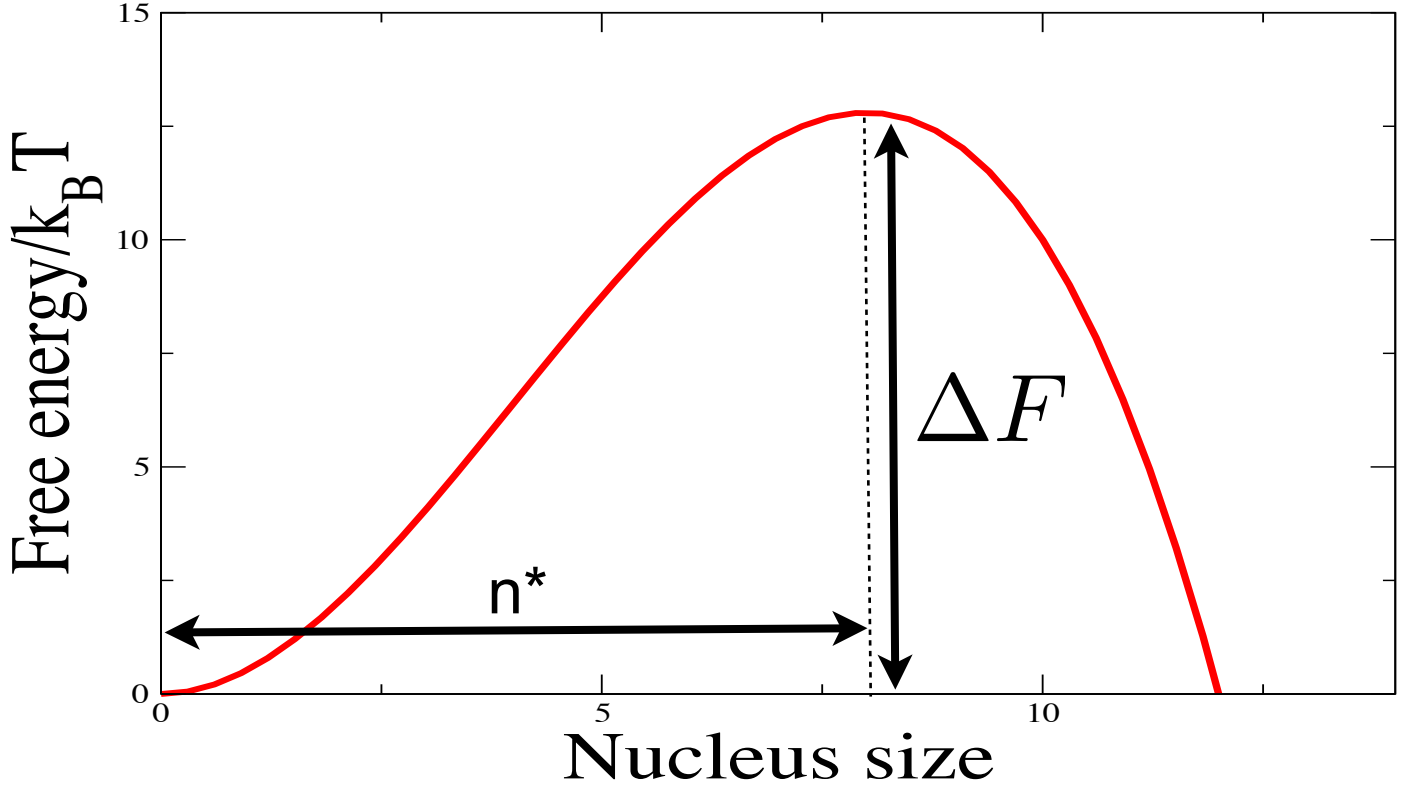
R= Nucleus radius

Nucleation



Bulk crystallisation lowers the free energy

... but the interface has a cost.



Bulk gain

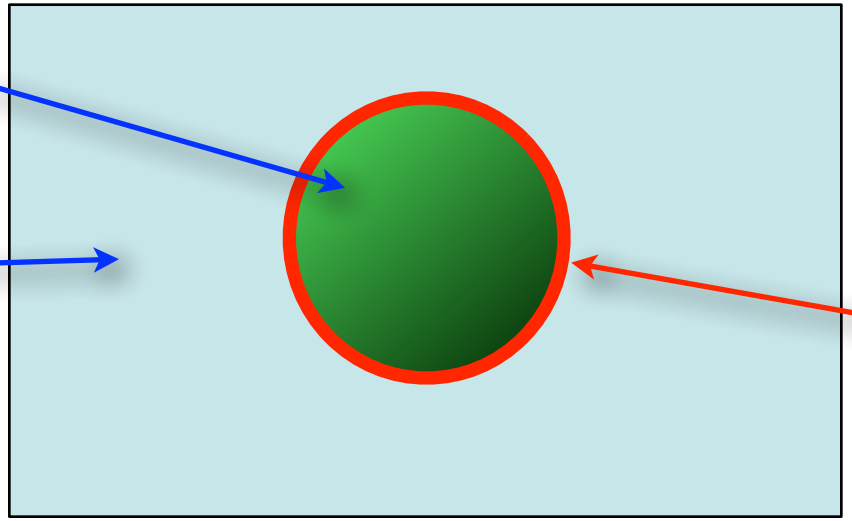
$$F = AR^2 - BR^3$$

Surface cost

F= Free energy

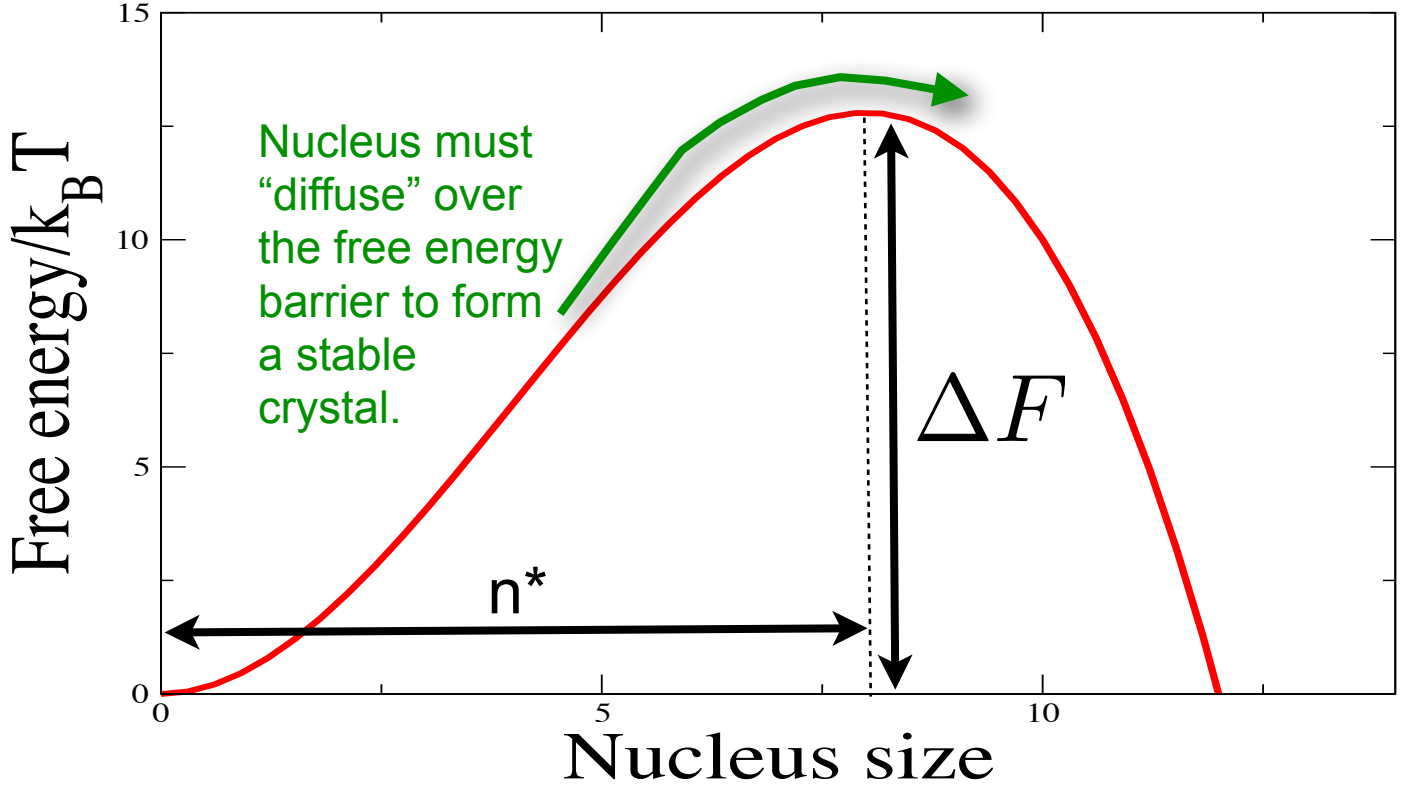
R= Nucleus radius

Nucleation



Bulk crystallisation lowers the free energy

... but the interface has a cost.



Bulk gain

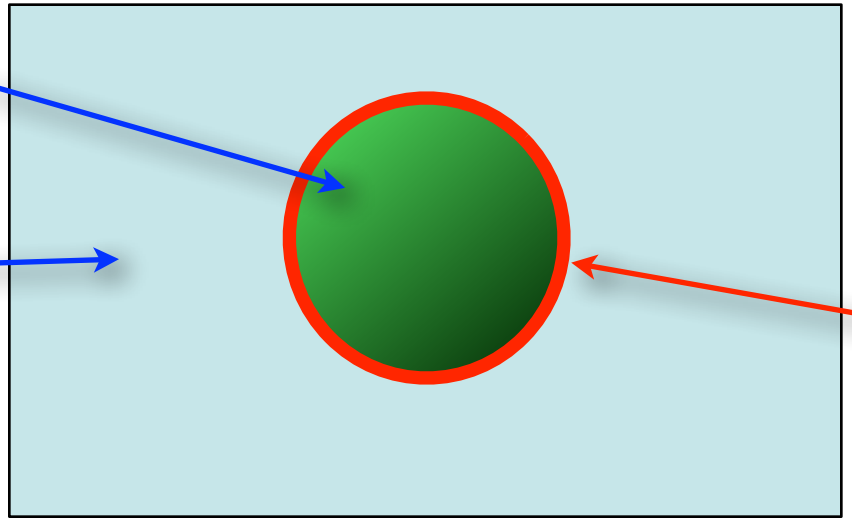
$$F = AR^2 - BR^3$$

Surface cost

F= Free energy

R= Nucleus radius

Nucleation



Bulk crystallisation lowers the free energy

... but the interface has a cost.

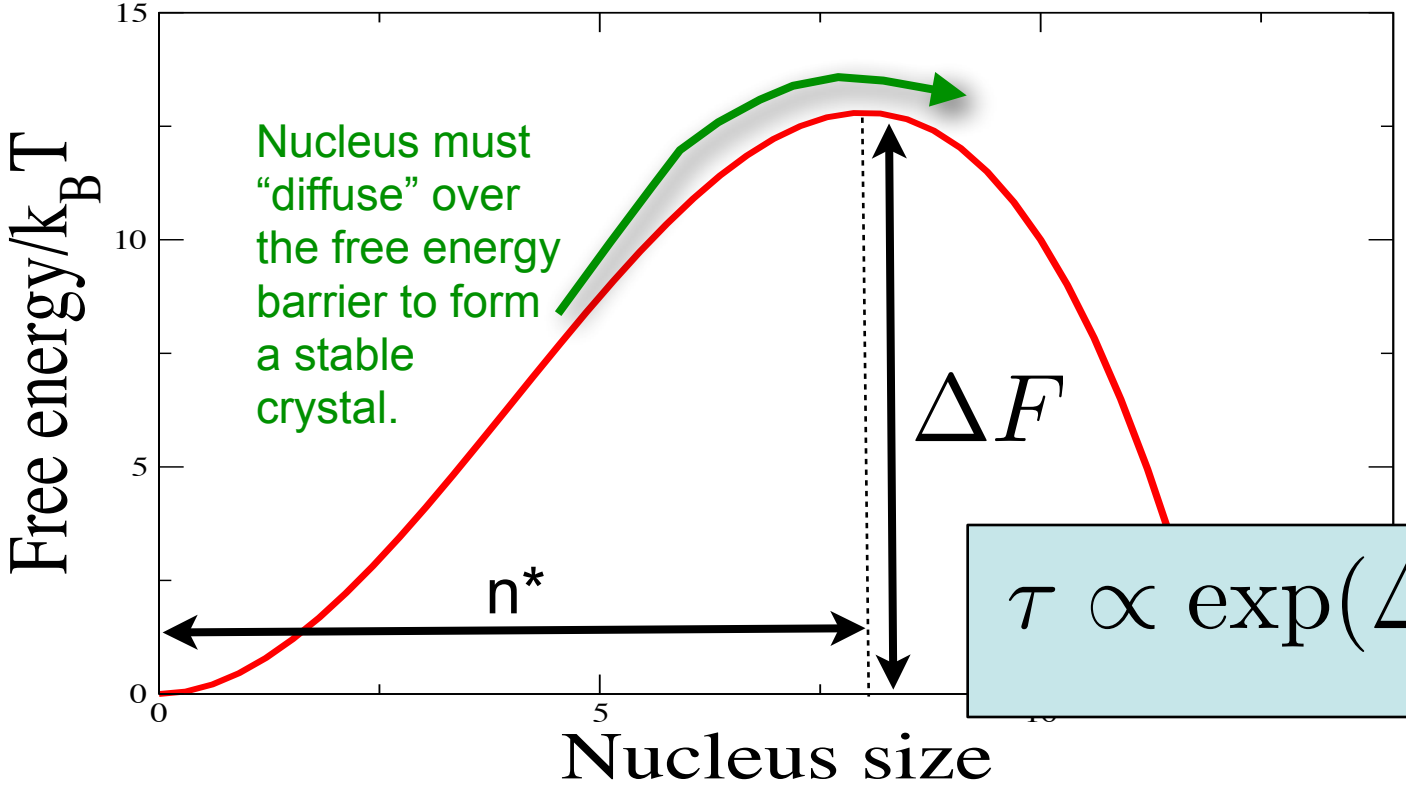
Bulk gain

$$F = AR^2 - BR^3$$

Surface cost

F= Free energy

R= Nucleus radius

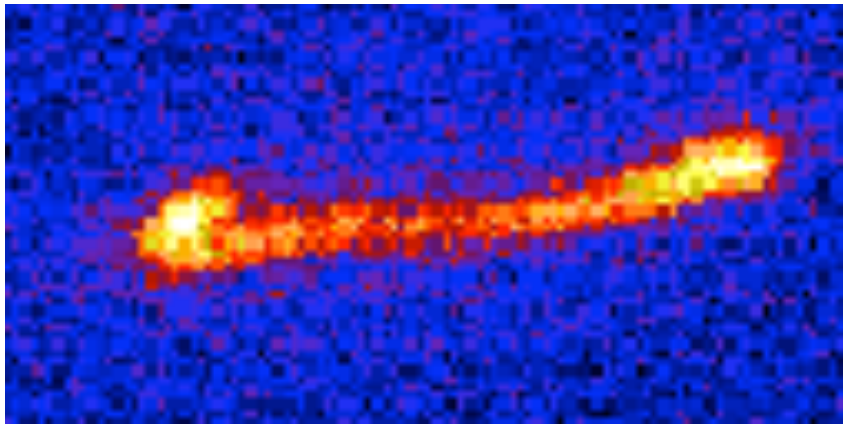


$$\tau \propto \exp(\Delta F / k_B T)$$

How rare is nucleation?

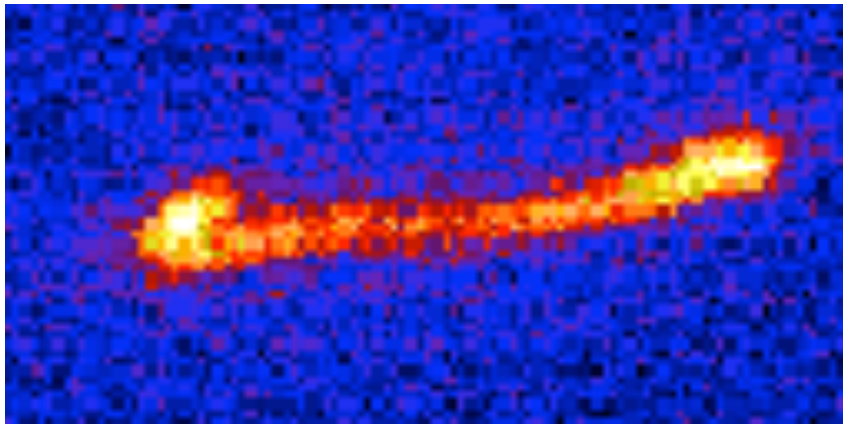
How rare is nucleation?

Polymer nucleation during flow



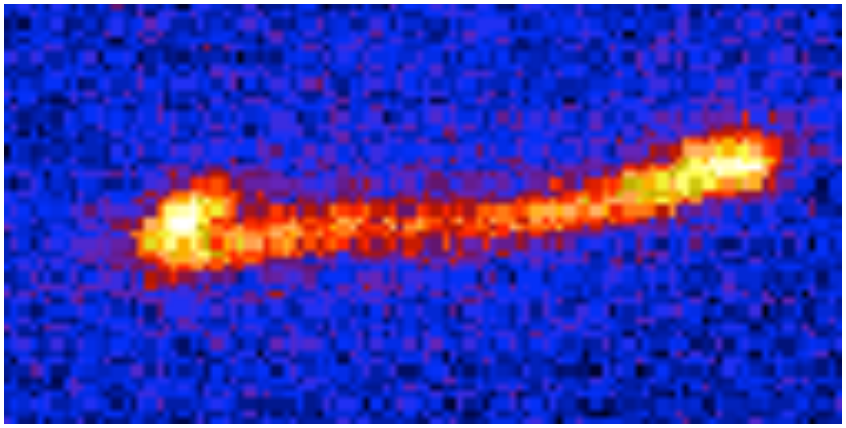
Experiments by Teixeira et al Macromolecules (2005) vol. 38 (2) pp. 581-592

Polymer nucleation during flow

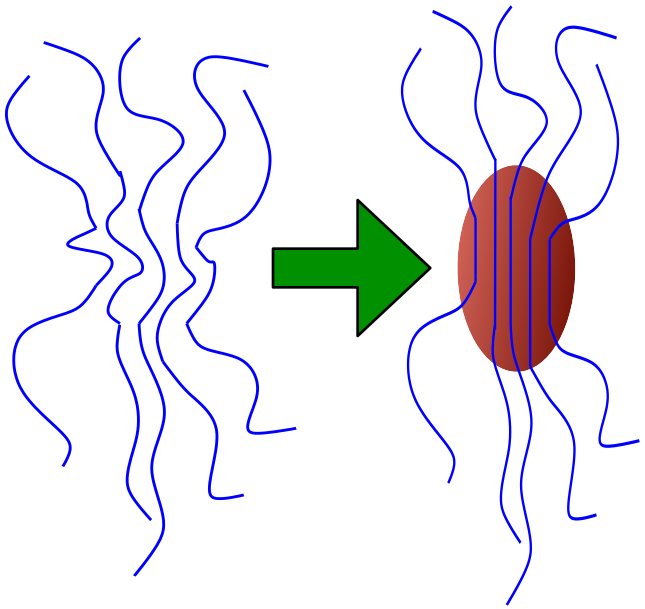


Experiments by Teixeira et al Macromolecules (2005) vol. 38 (2) pp. 581-592

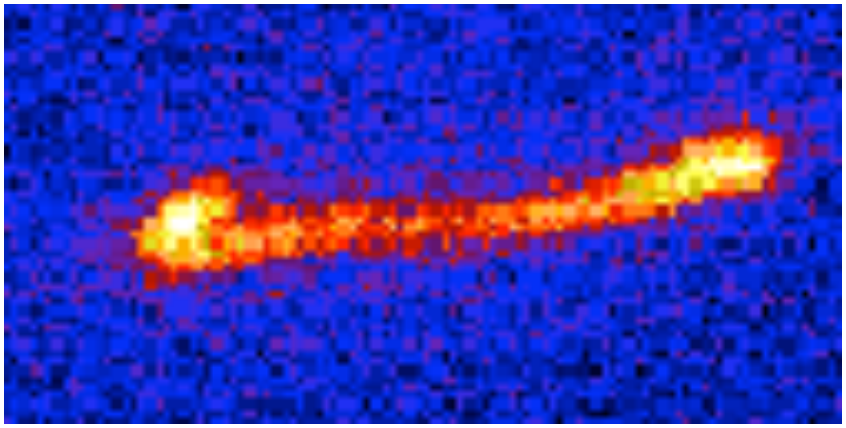
Polymer nucleation during flow



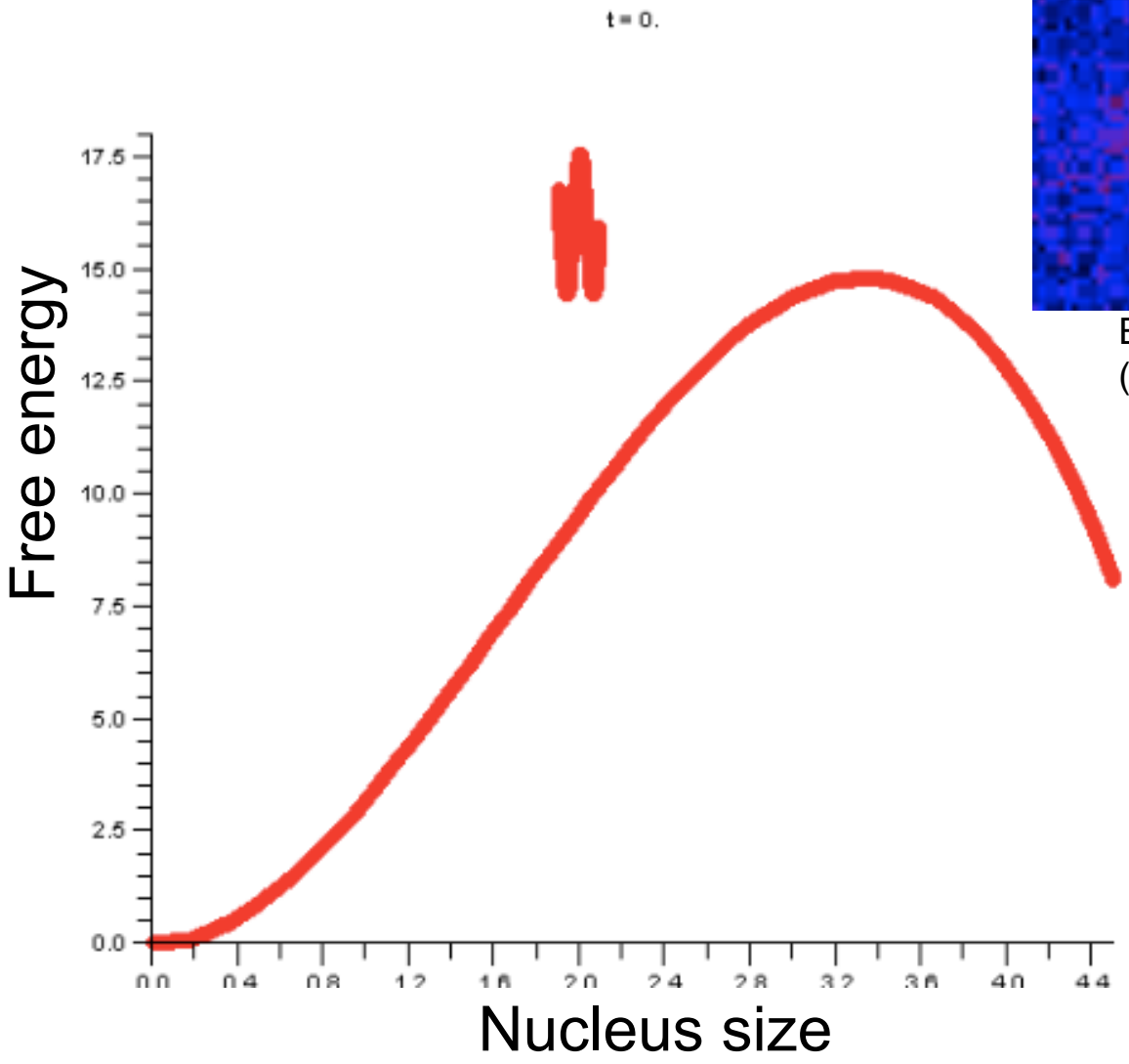
Experiments by Teixeira et al Macromolecules (2005) vol. 38 (2) pp. 581-592

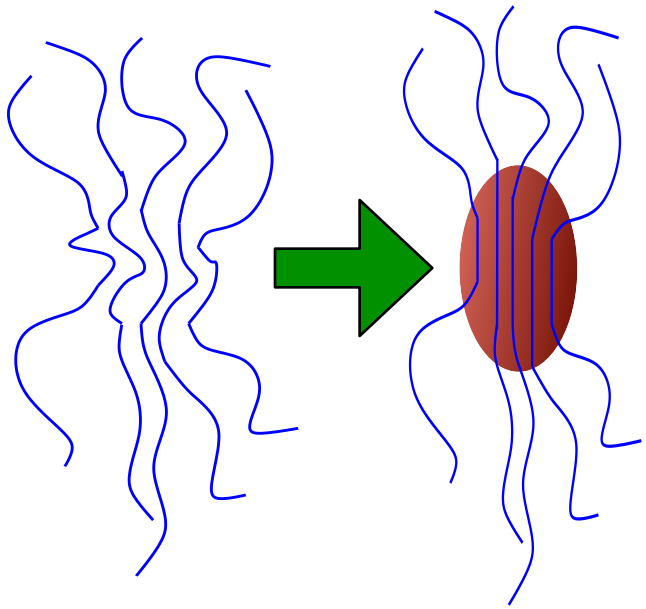


Polymer nucleation during flow

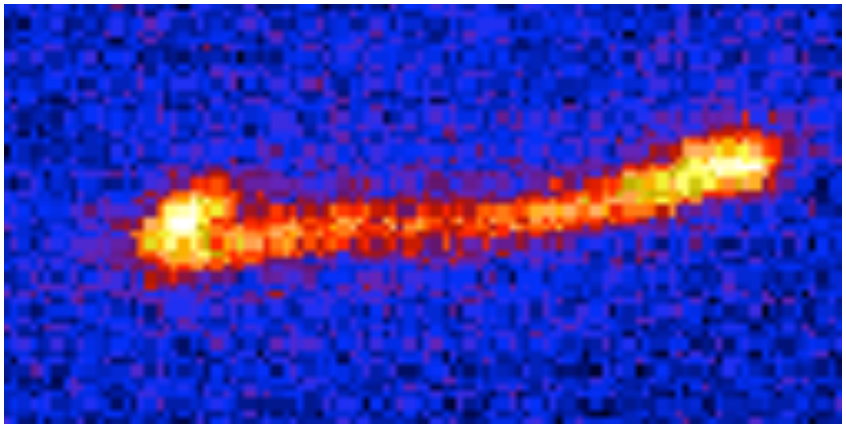


Experiments by Teixeira et al Macromolecules (2005) vol. 38 (2) pp. 581-592

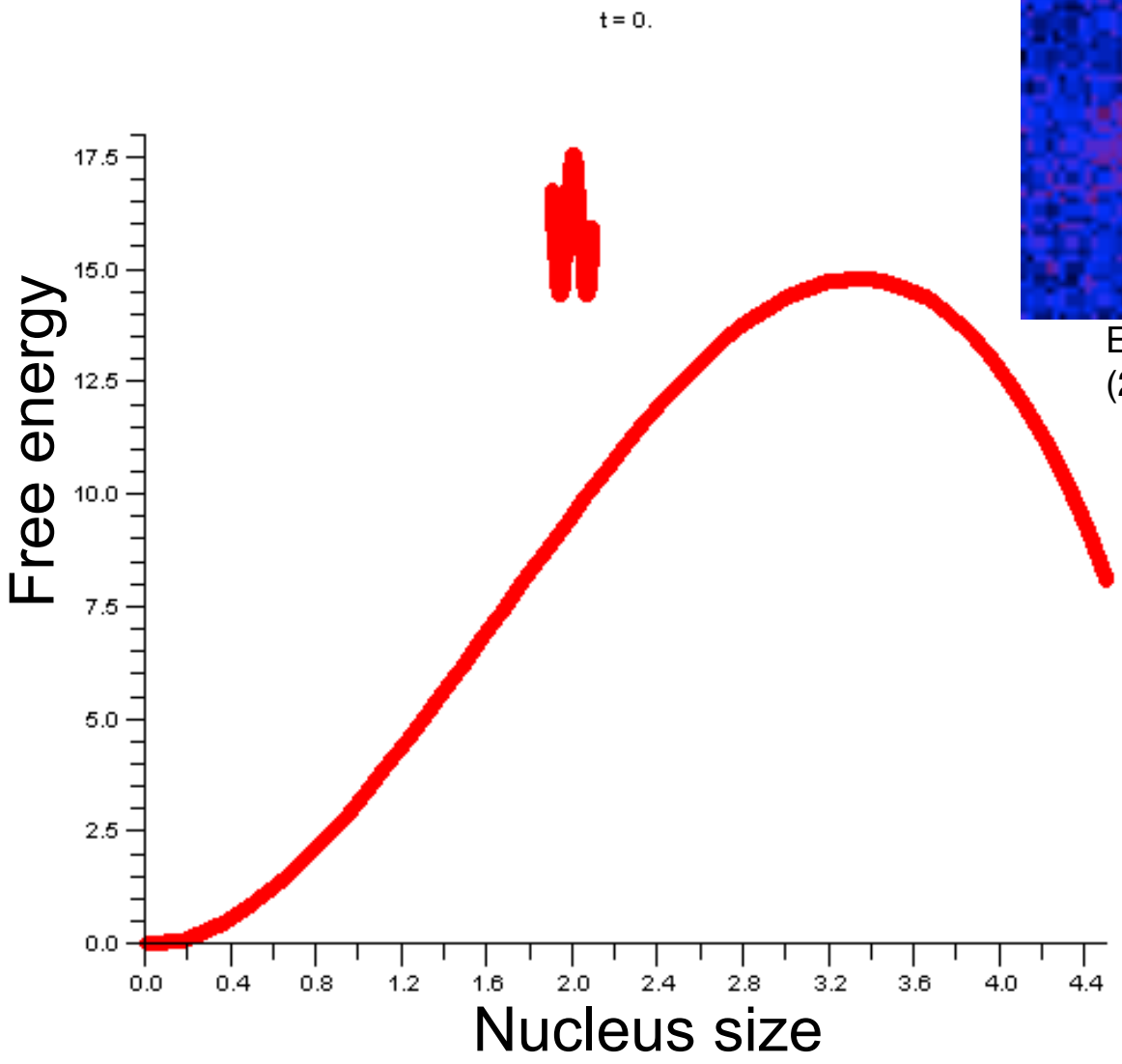


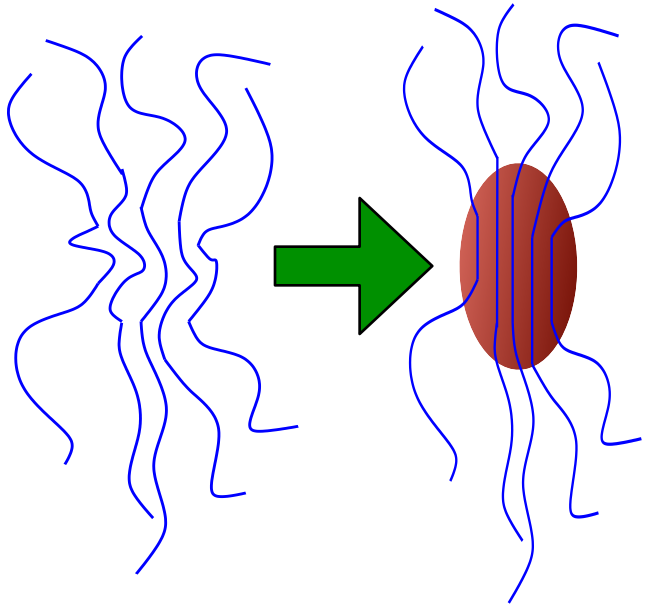


Polymer nucleation during flow



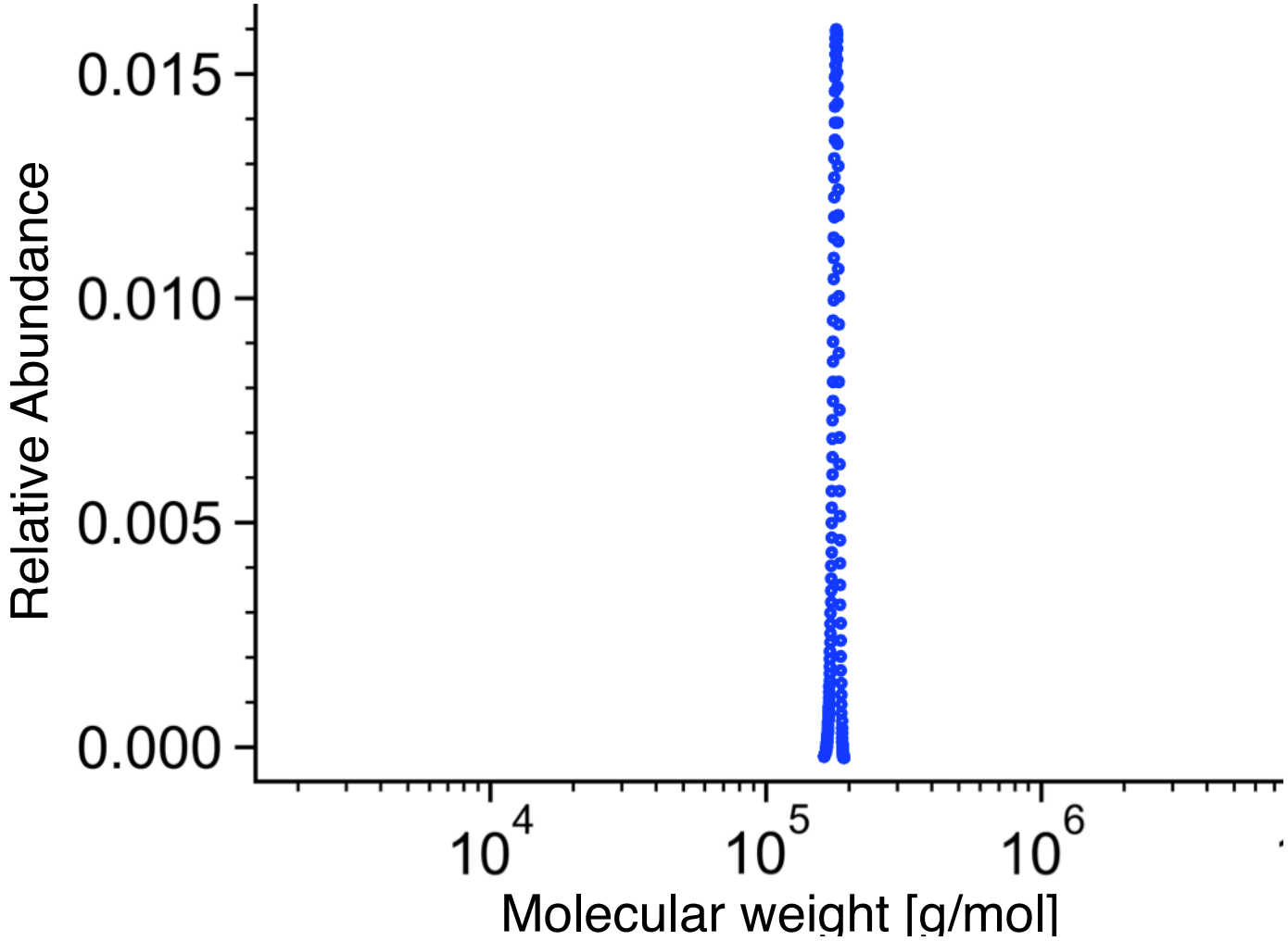
Experiments by Teixeira et al Macromolecules (2005) vol. 38 (2) pp. 581-592



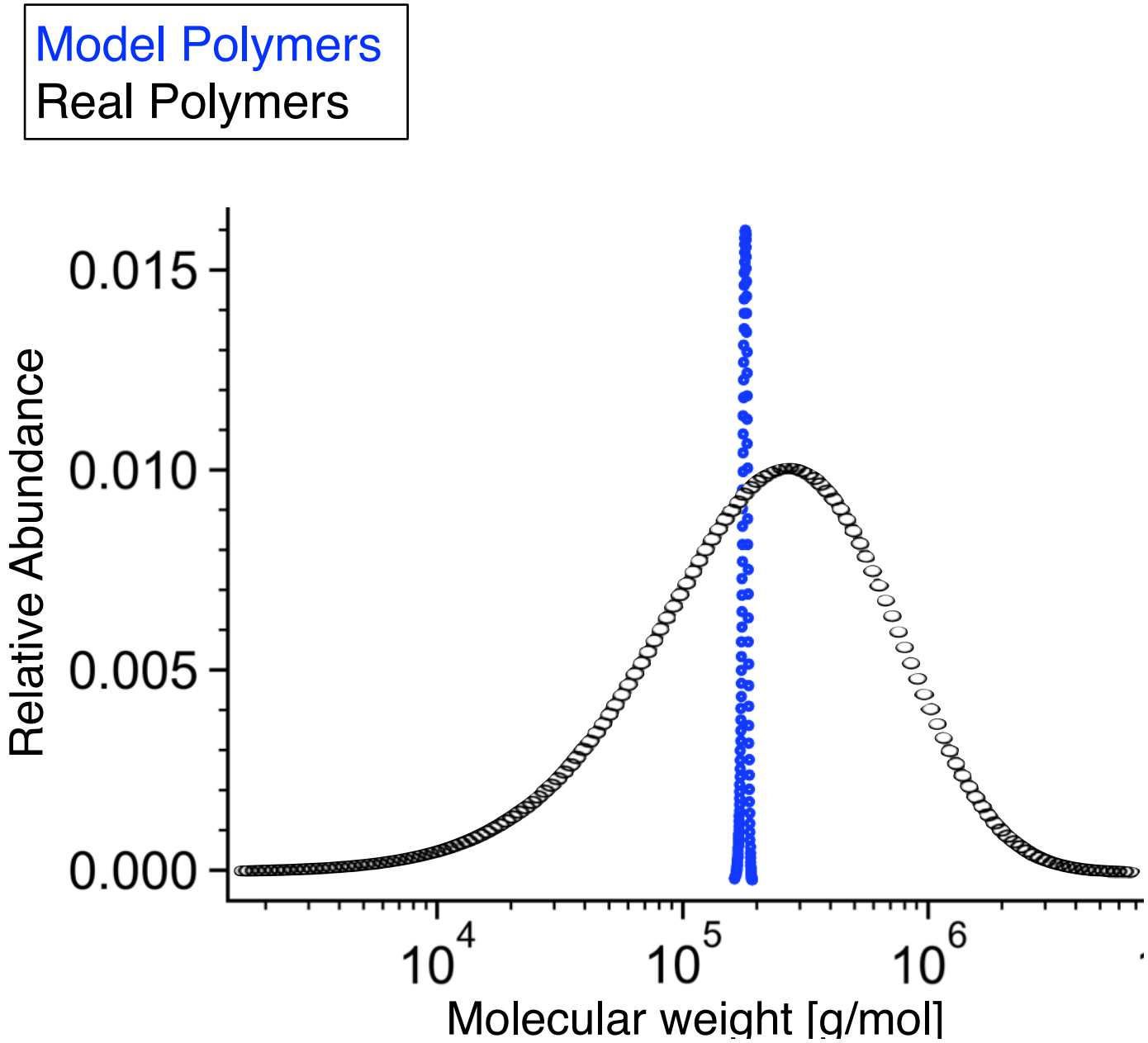


Polydispersity

Model Polymers
Real Polymers

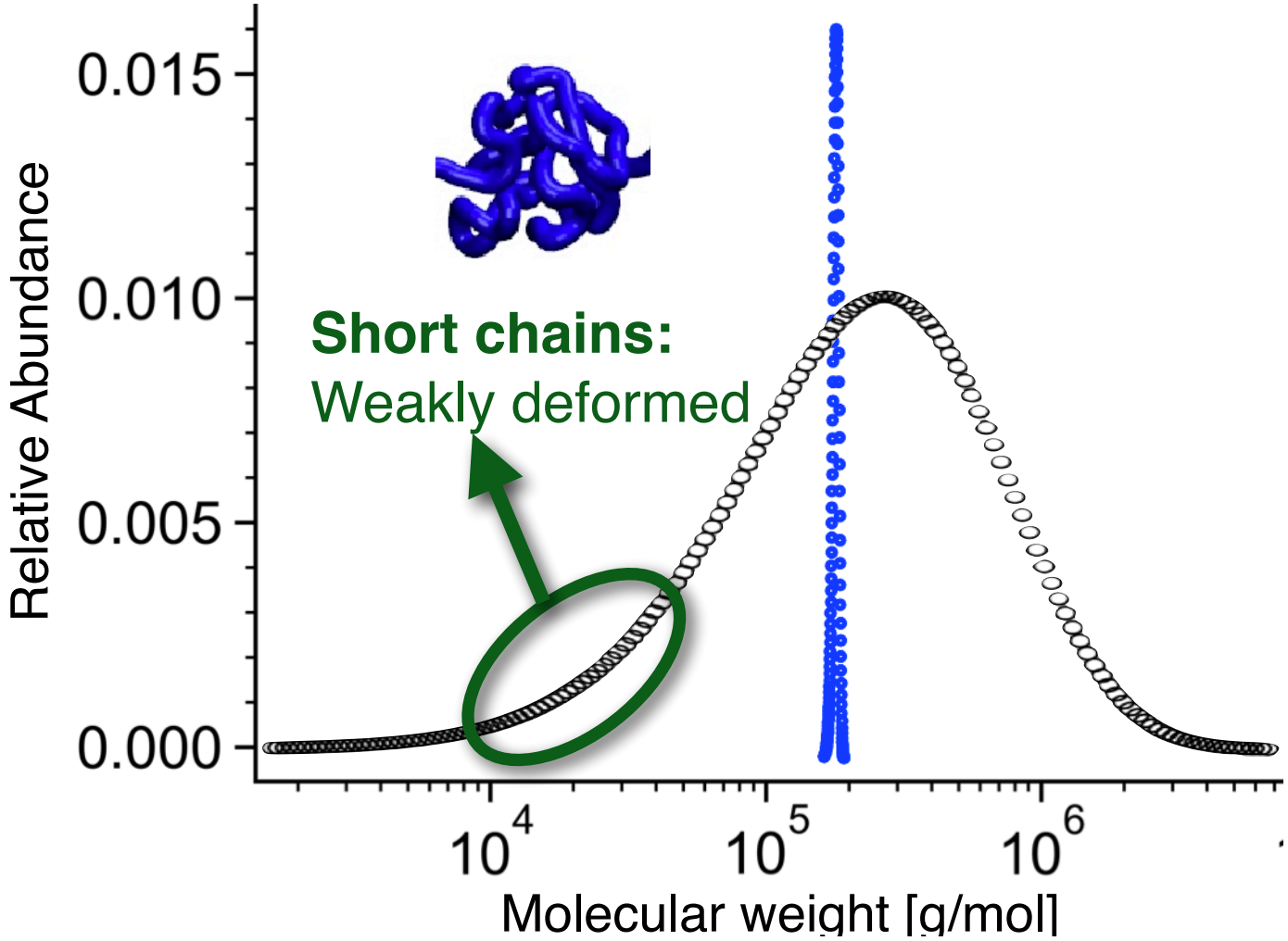


Polydispersity



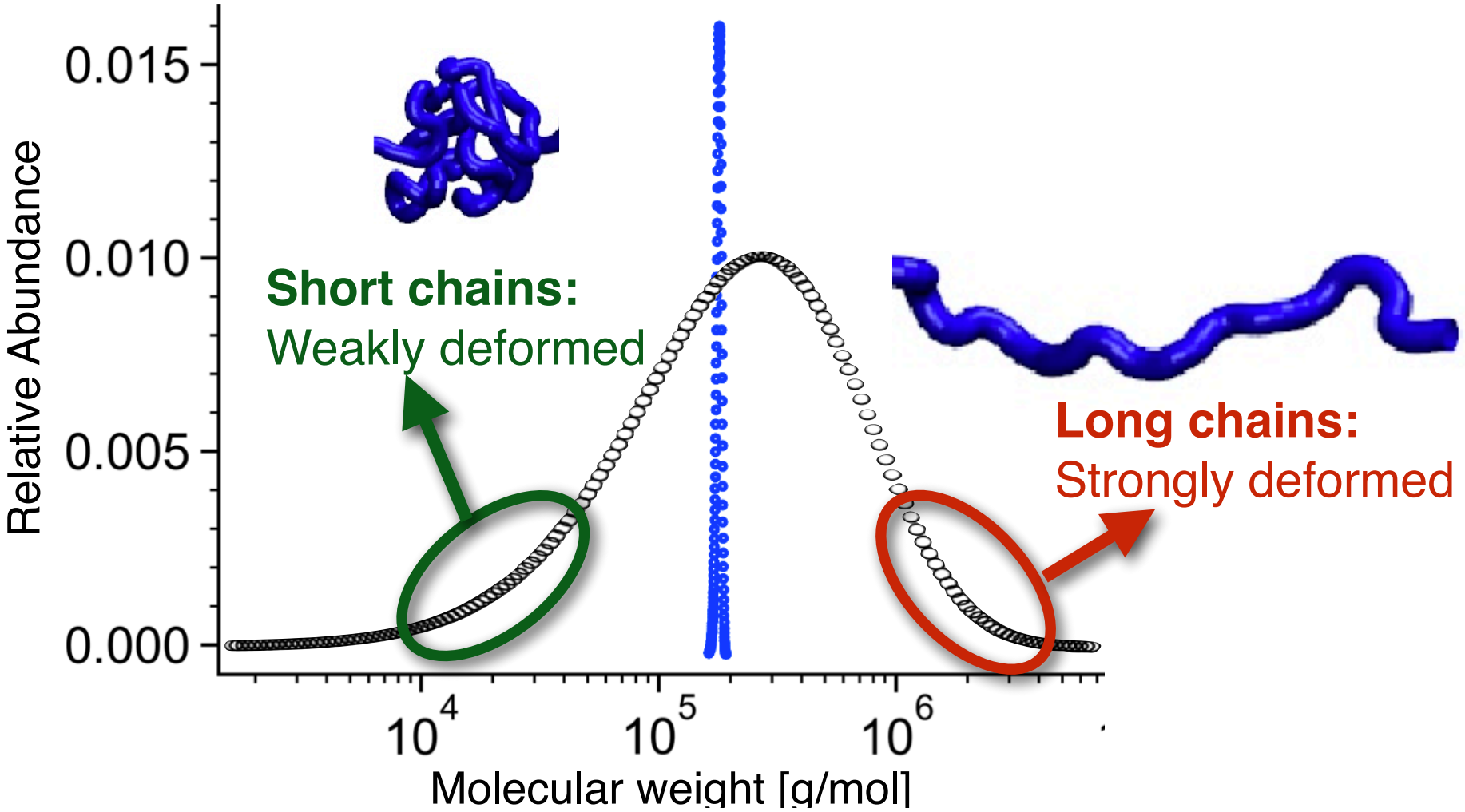
Polydispersity

Model Polymers
Real Polymers



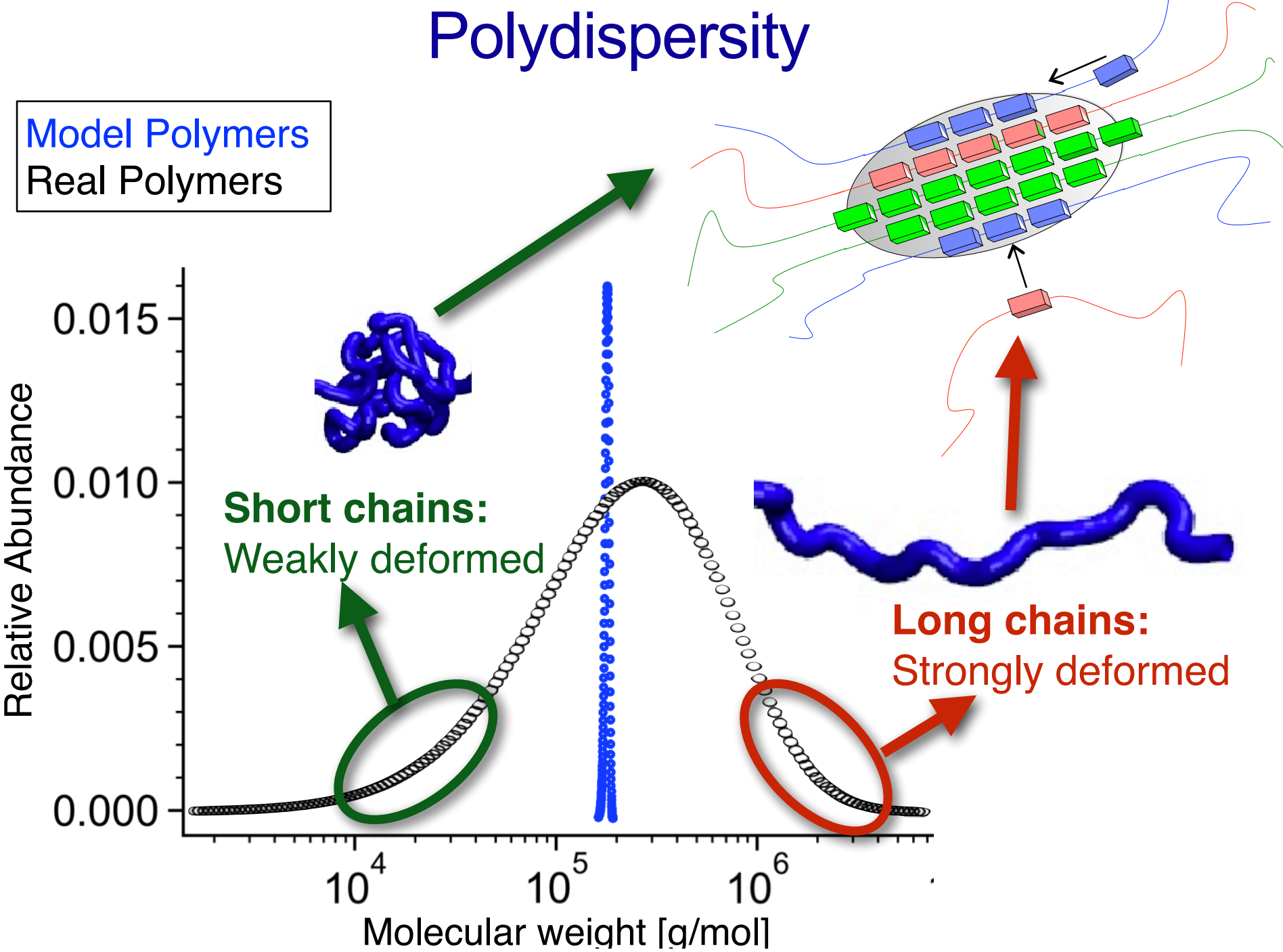
Polydispersity

Model Polymers
Real Polymers



Polydispersity

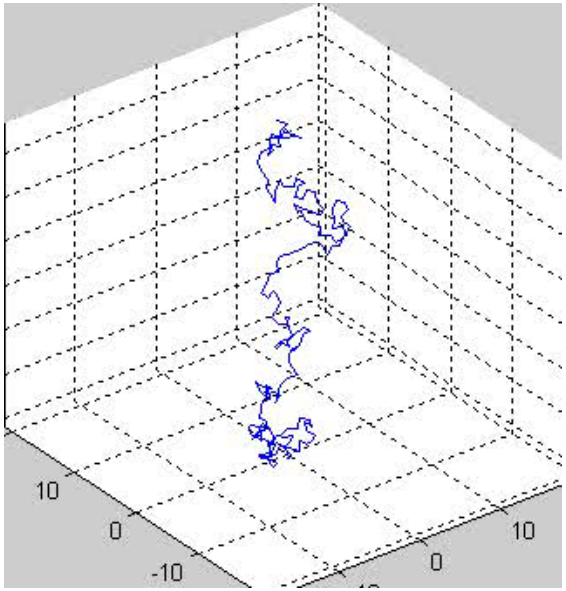
Model Polymers
Real Polymers



Two computational difficulties

Two computational difficulties

Slow diffusion

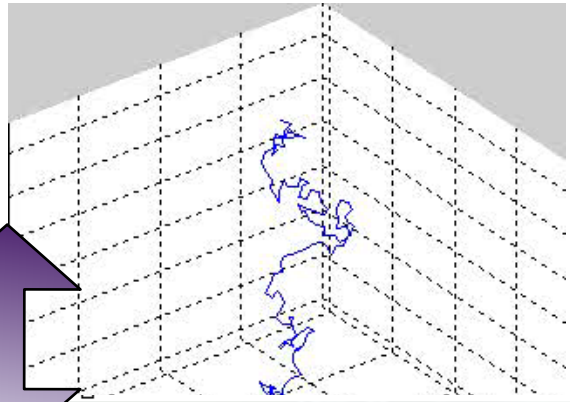


Two computational difficulties

Slow diffusion

Two computational difficulties

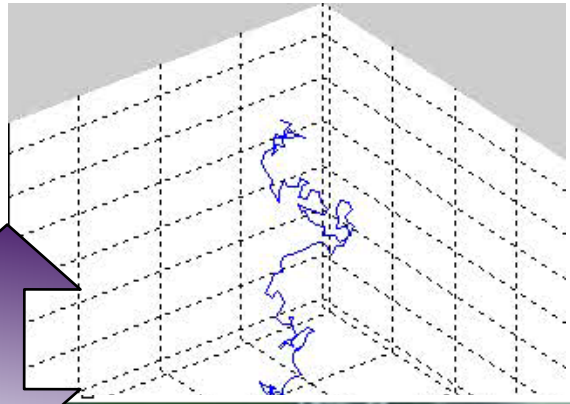
Slow diffusion



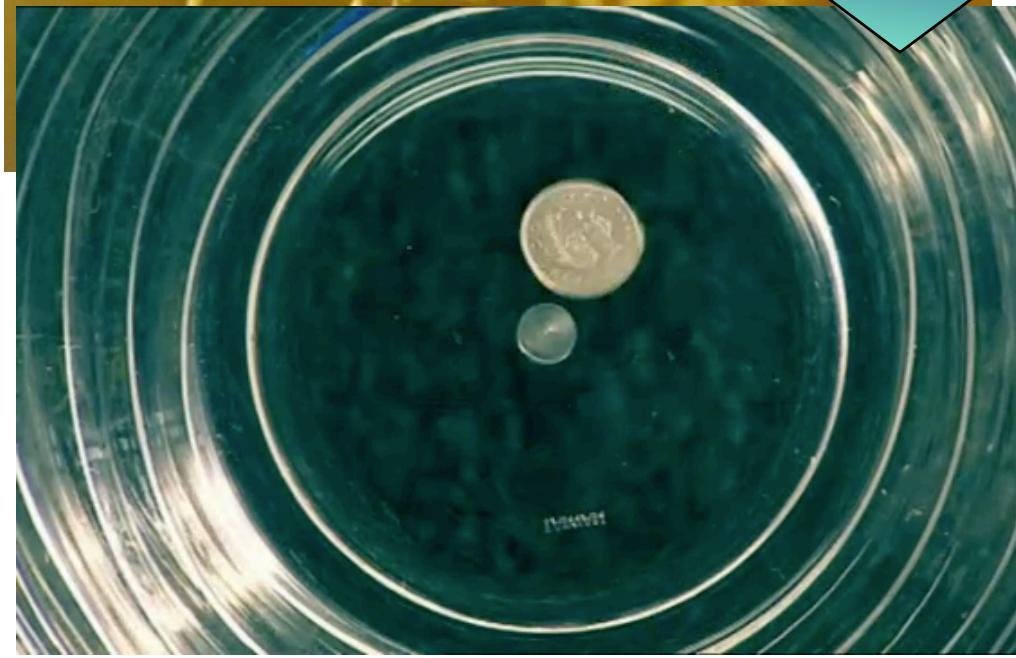
Nucleation

Two computational difficulties

Slow diffusion

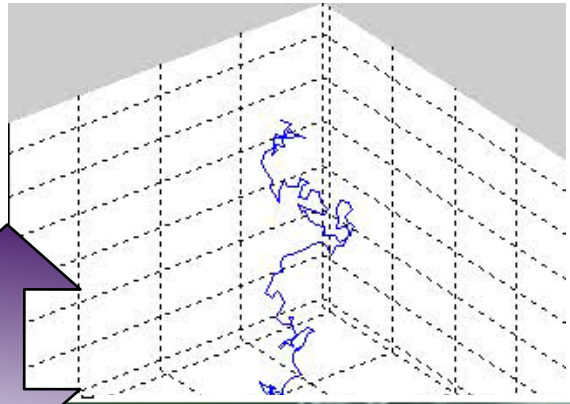


Nucleation

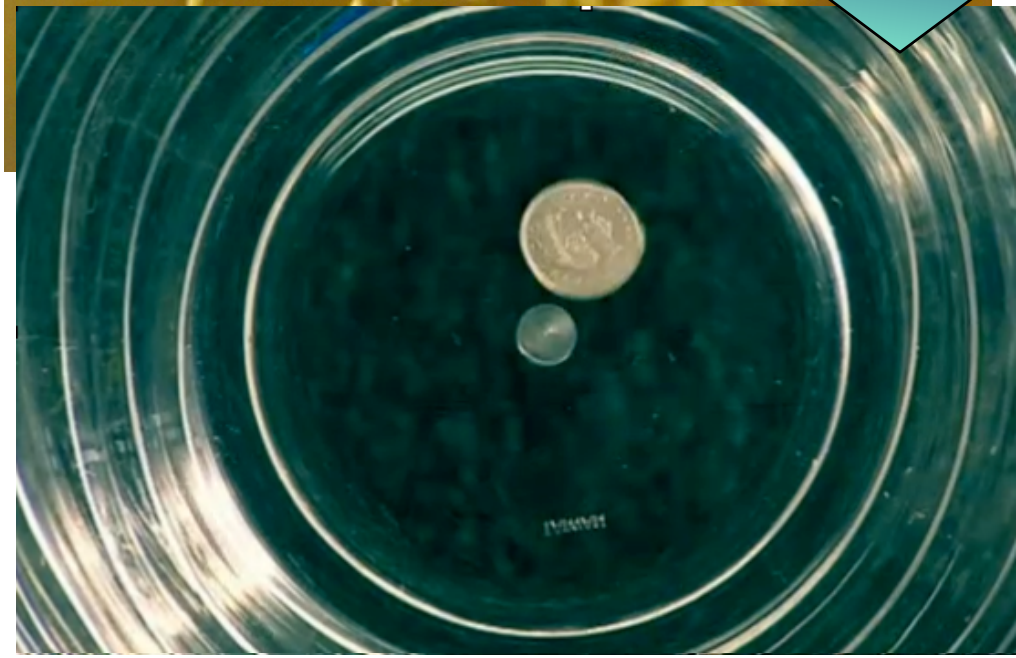


Two computational difficulties

Slow diffusion



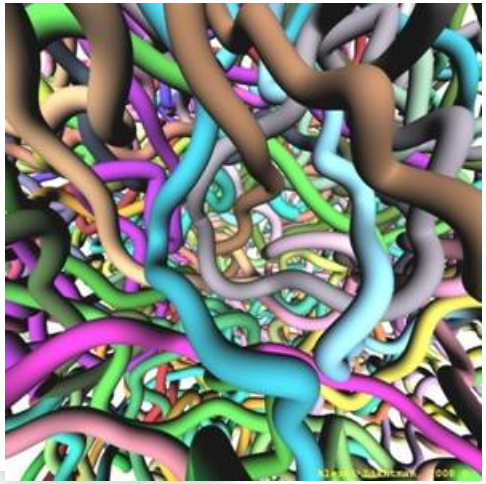
Nucleation



Multiscale modelling in flow-induced crystallisation

Increasing computational speed

Molecular dynamics simulations



Continuous description of the position and momentum of of all atoms.

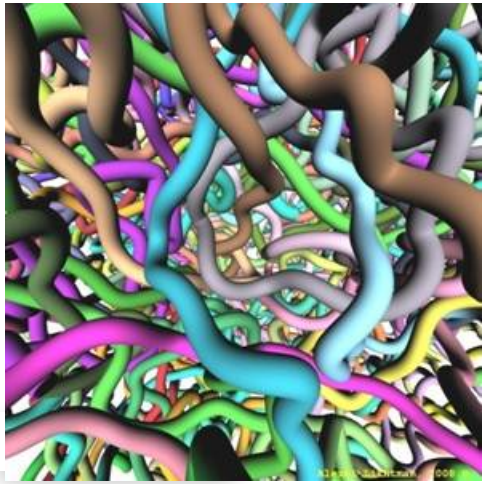
Increasing detail

Multiscale modelling in flow-induced crystallisation

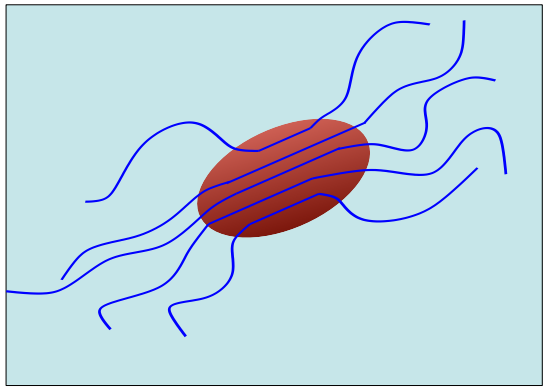
Increasing computational speed

Molecular dynamics simulations

The GO model (kinetic Monte Carlo)



Continuous description of the position and momentum of of all atoms.



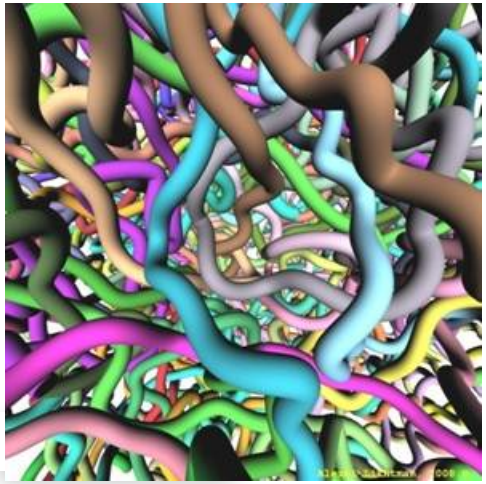
Limited resolution and discretised nucleus

Increasing detail

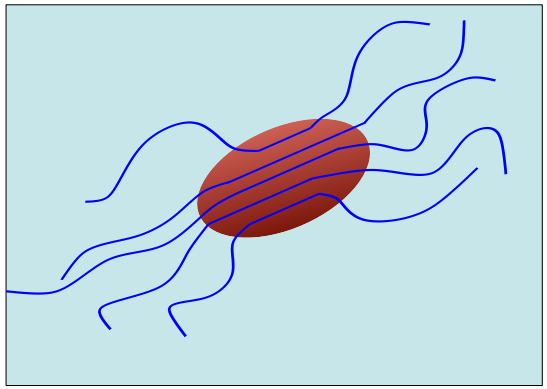
Multiscale modelling in flow-induced crystallisation

Increasing computational speed

Molecular dynamics simulations	The GO model (kinetic Monte Carlo)	Macroscale continuum models



Continuous description of the position and momentum of of all atoms.



Limited resolution and discretised nucleus

$$\dot{\phi}_3 = 8\pi\dot{N}(T),$$
$$\dot{\phi}_2 = G(T)\phi_3,$$
$$\dot{\phi}_1 = G(T)\phi_2,$$
$$\dot{\phi}_0 = G(T)\phi_1,$$
$$\dot{N} = \dot{N}_0 \exp[\eta(\lambda^2 - 1)]$$

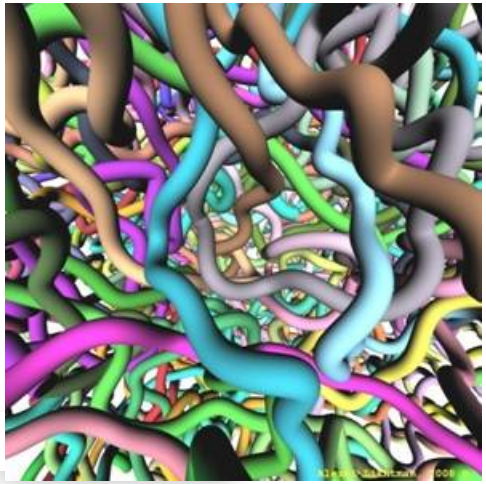
Continuum description through deterministic differential equations

Increasing detail

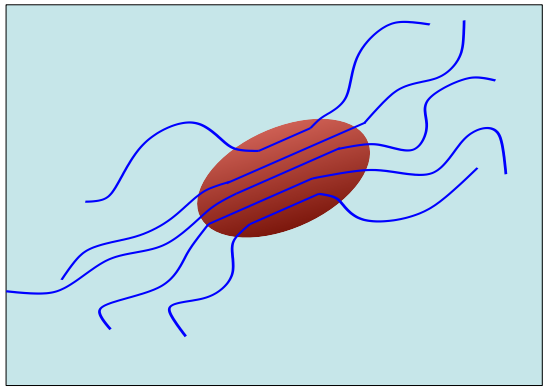
Multiscale modelling in flow-induced crystallisation

Increasing computational speed

Molecular dynamics simulations	The GO model (kinetic Monte Carlo)	Macroscale continuum models	Finite element calculations



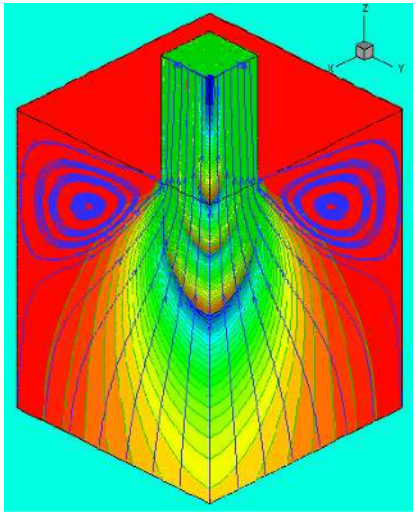
Continuous description of the position and momentum of of all atoms.



Limited resolution and discretised nucleus

$$\dot{\phi}_3 = 8\pi\dot{N}(T),$$
$$\dot{\phi}_2 = G(T)\phi_3,$$
$$\dot{\phi}_1 = G(T)\phi_2,$$
$$\dot{\phi}_0 = G(T)\phi_1,$$
$$\dot{N} = \dot{N}_0 \exp[\eta(\lambda^2 - 1)]$$

Continuum description through deterministic differential equations



Computational fluid dynamics of polymer crystallisation during processing

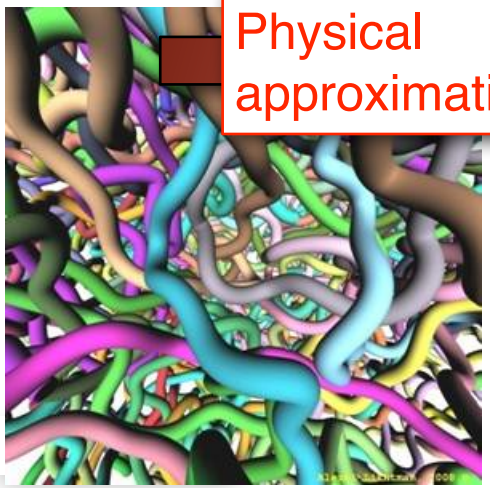
Increasing detail

Multiscale modelling in flow-induced crystallisation

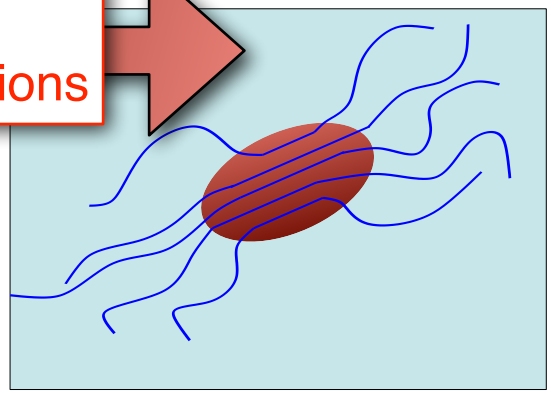
Increasing computational speed

Molecular dynamics simulations	The GO model (kinetic Monte Carlo)	Macroscale continuum models	Finite element calculations

Physical approximations



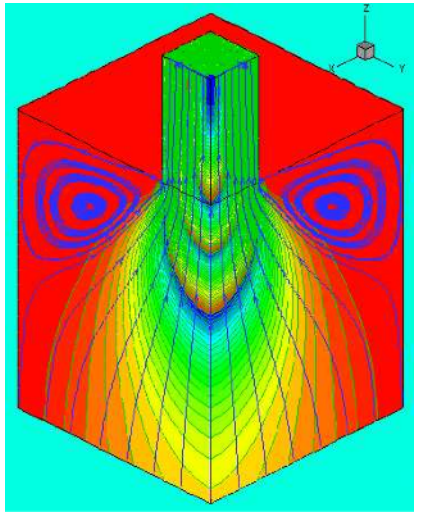
Continuous description of the position and momentum of of all atoms.



Limited resolution and discretised nucleus

$$\dot{\phi}_3 = 8\pi\dot{N}(T),$$
$$\dot{\phi}_2 = G(T)\phi_3,$$
$$\dot{\phi}_1 = G(T)\phi_2,$$
$$\dot{\phi}_0 = G(T)\phi_1,$$
$$\dot{N} = \dot{N}_0 \exp[\eta(\lambda^2 - 1)]$$

Continuum description through deterministic differential equations



Computational fluid dynamics of polymer crystallisation during processing

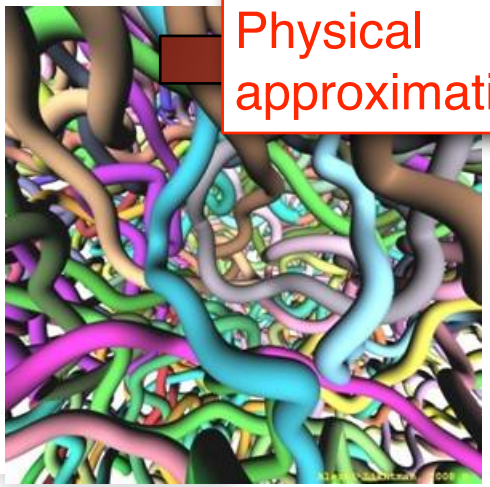
Increasing detail

Multiscale modelling in flow-induced crystallisation

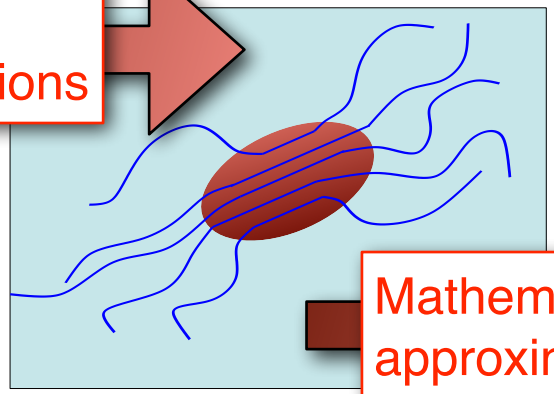
Increasing computational speed

Molecular dynamics simulations	The GO model (kinetic Monte Carlo)	Macroscale continuum models	Finite element calculations

Physical approximations



Continuous description of the position and momentum of of all atoms.

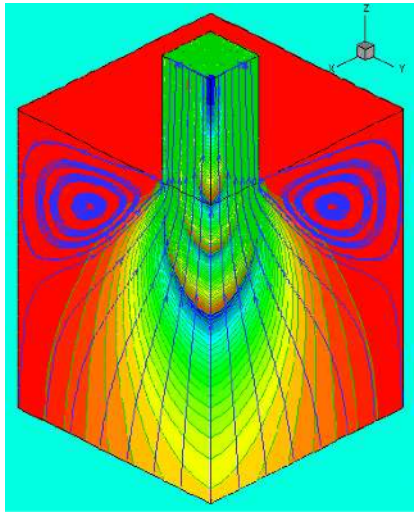


Limited resolution and discretised nucleus

Mathematical approximations

$$\dot{\phi}_3 = 8\pi\dot{N}(T),$$
$$\dot{\phi}_2 = G(T)\phi_3,$$
$$\dot{\phi}_1 = G(T)\phi_2,$$
$$\dot{\phi}_0 = G(T)\phi_1,$$
$$\dot{x}_1 = \dot{x}_0[\lambda(\lambda^2 - 1)]$$

Continuum description through deterministic differential equations



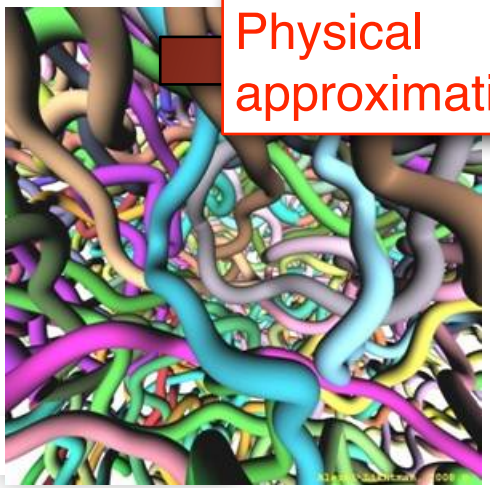
Computational fluid dynamics of polymer crystallisation during processing

Increasing detail

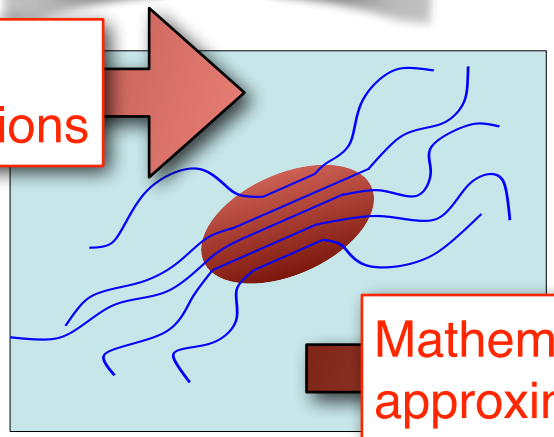
Multiscale modelling in flow-induced crystallisation

Increasing computational speed

Molecular dynamics simulations	The GO model (kinetic Monte Carlo)	Macroscale continuum models	Finite element calculations

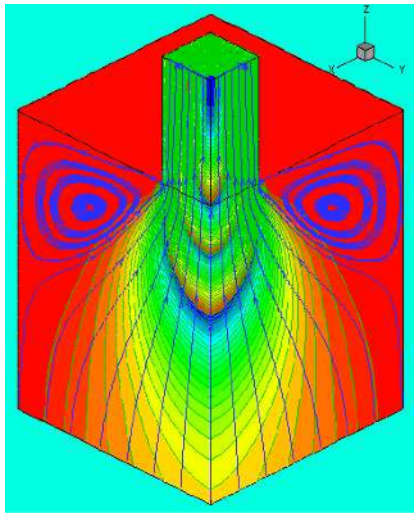


Physical approximations



Mathematical approximations

$$\dot{\phi}_3 = 8\pi\dot{N}(T),$$
$$\dot{\phi}_2 = G(T)\phi_3,$$
$$\dot{\phi}_1 = G(T)\phi_2,$$
$$\dot{\phi}_0 = G(T)\phi_1,$$
$$\dot{x}_1 = \ldots(\lambda^2 - 1)]$$



Continuous description of the position and momentum of of all atoms.

Limited resolution and discretised nucleus

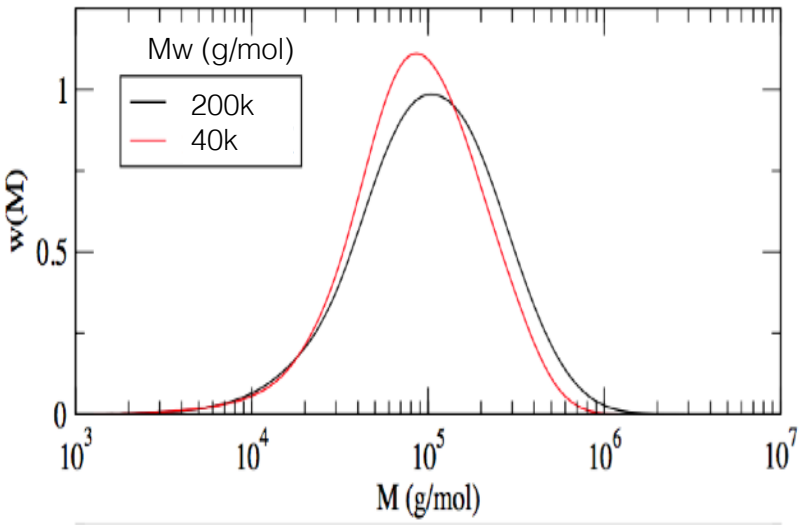
Continuum description through deterministic differential equations

Computational fluid dynamics of polymer crystallisation during ...g

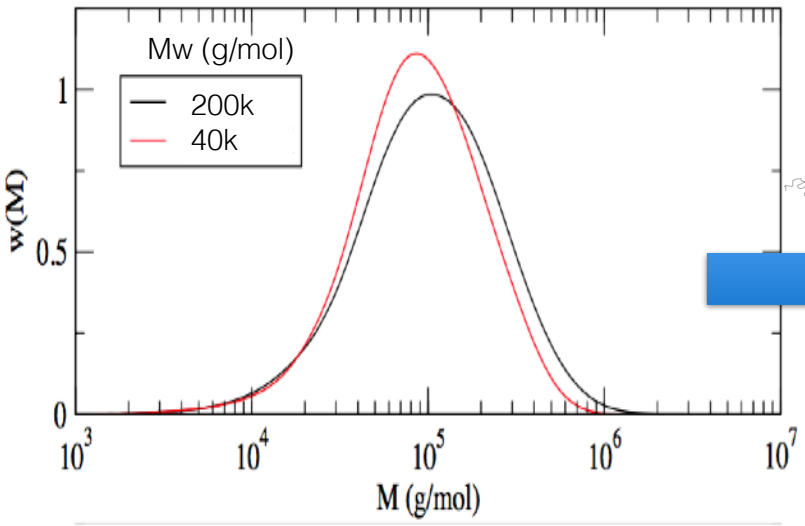
Techniques developed can assist more detailed simulations

Increasing detail

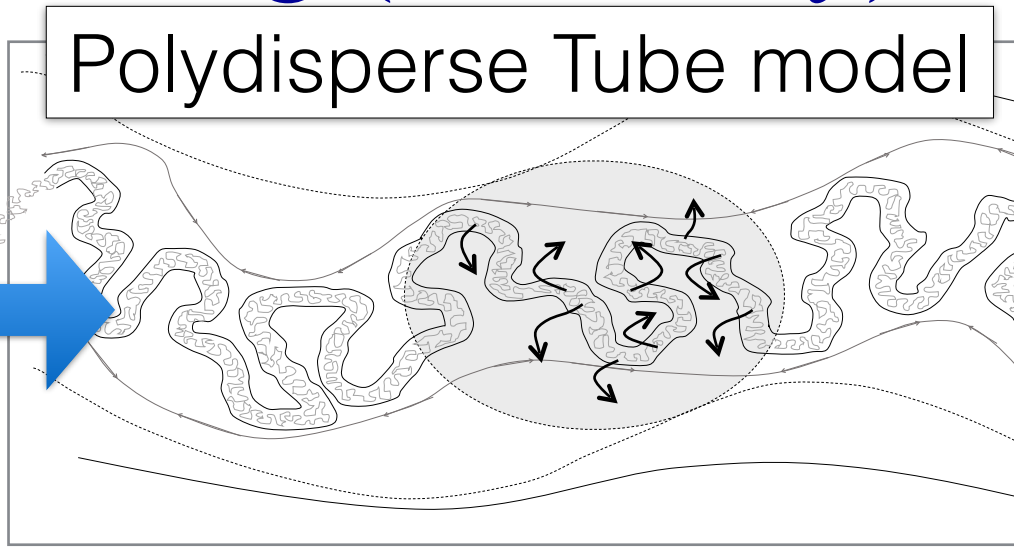
Rheological modelling (flow only)



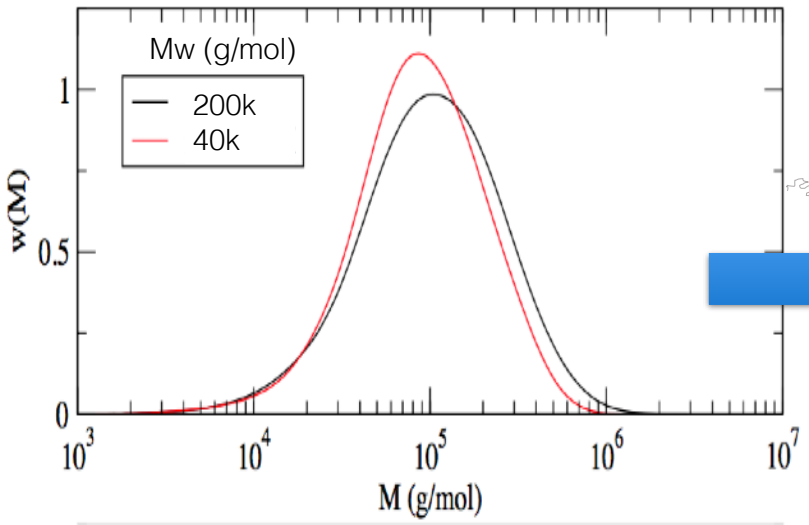
Rheological modelling (flow only)



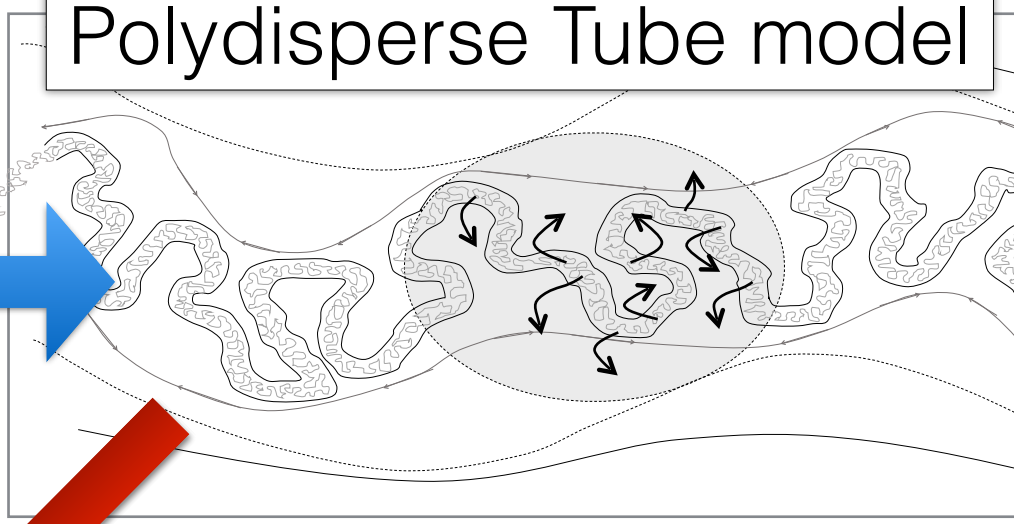
Polydisperse Tube model



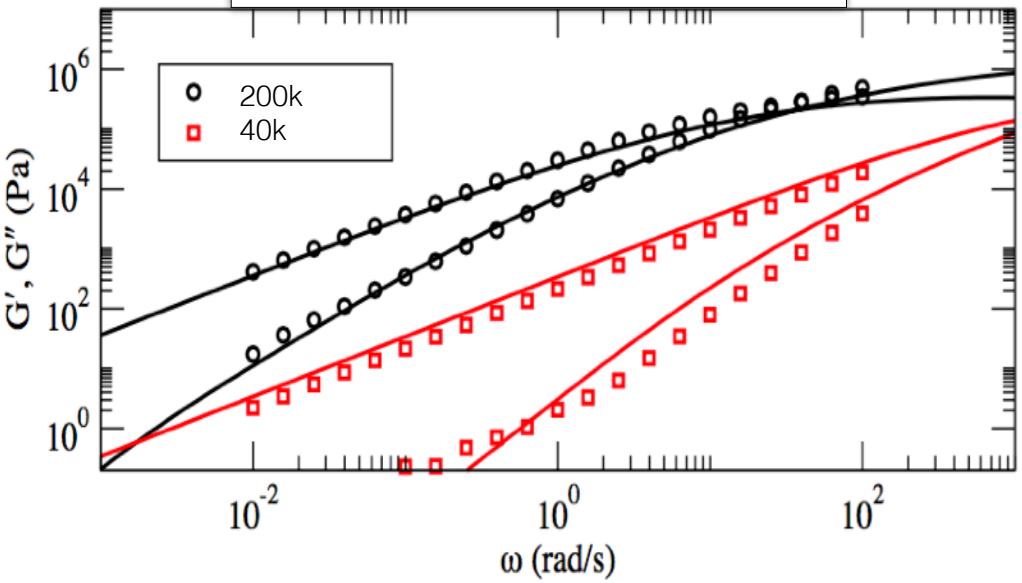
Rheological modelling (flow only)



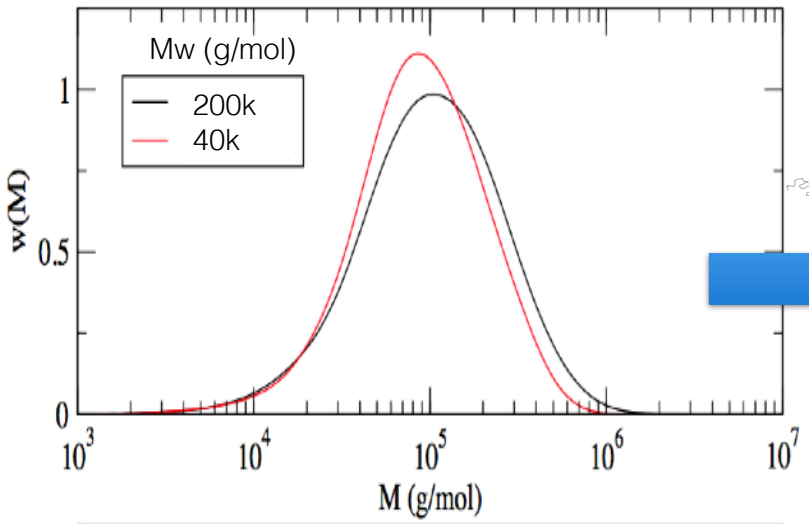
Polydisperse Tube model



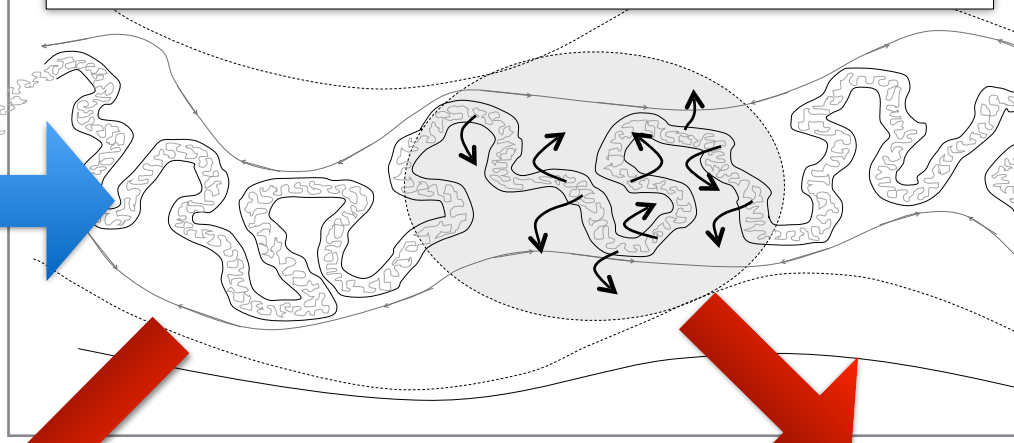
Linear rheology



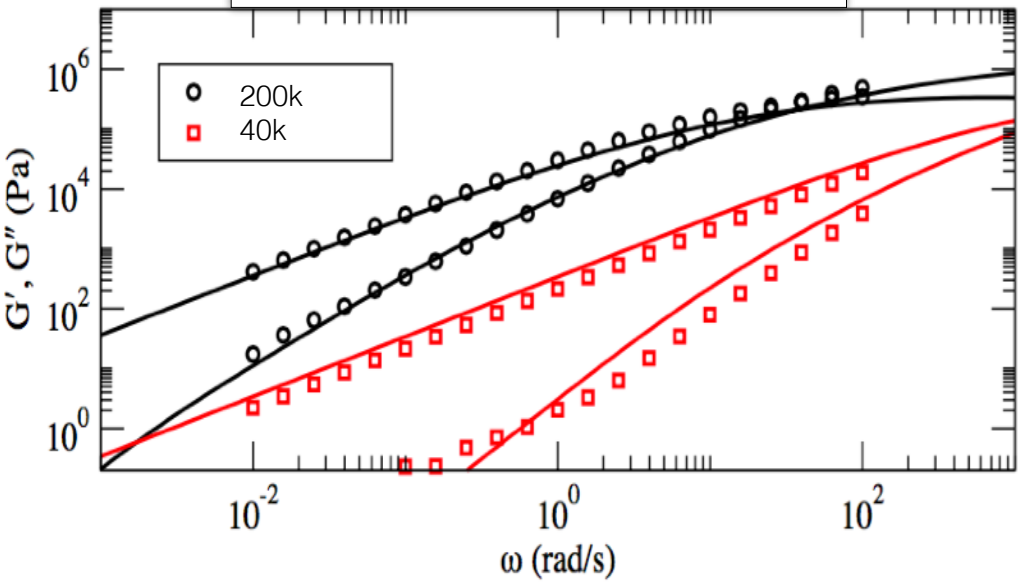
Rheological modelling (flow only)



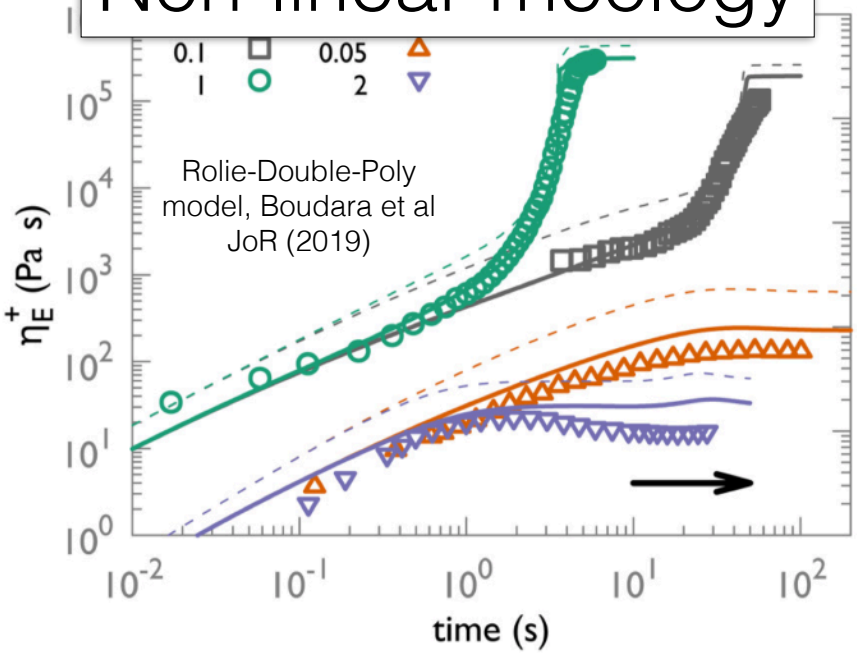
Polydisperse Tube model



Linear rheology

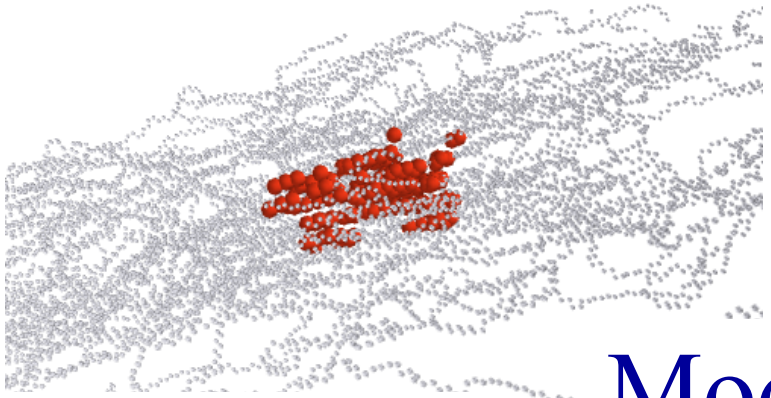


Non-linear rheology



Modelling nucleation

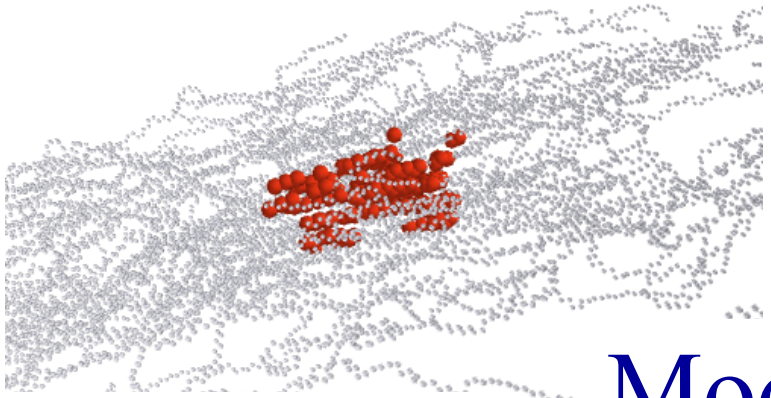
(a) Molecular dynamics



Rutledge et al (2013) & (2016)
Schilling et al (2013) & (2014)
Anwar and Graham (2019)

Modelling nucleation

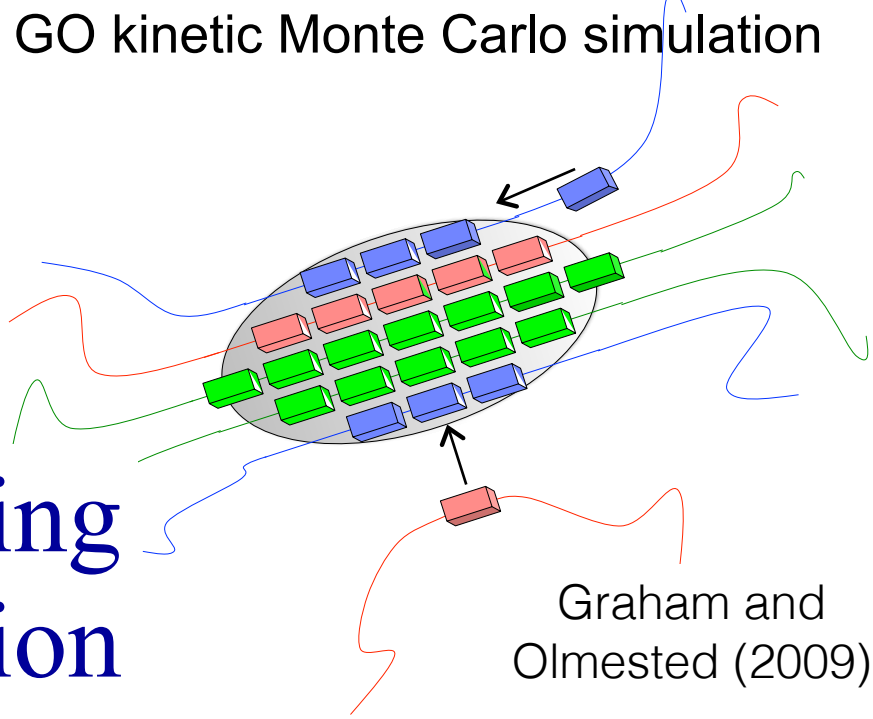
(a) Molecular dynamics



Rutledge et al (2013) & (2016)
Schilling et al (2013) & (2014)
Anwar and Graham (2019)

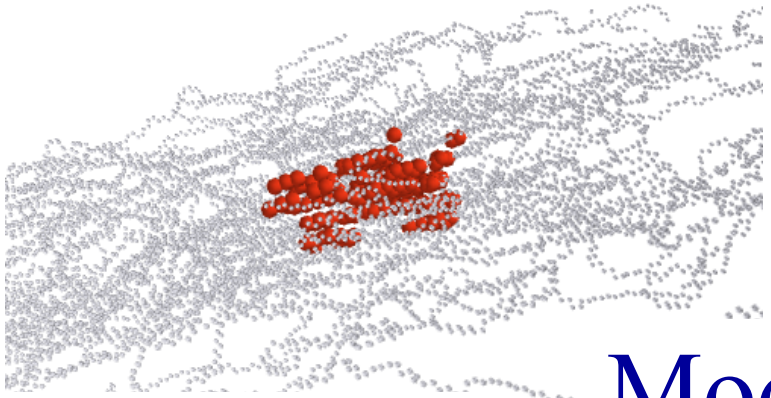
Modelling nucleation

(b) The GO kinetic Monte Carlo simulation



Graham and
Olmested (2009)

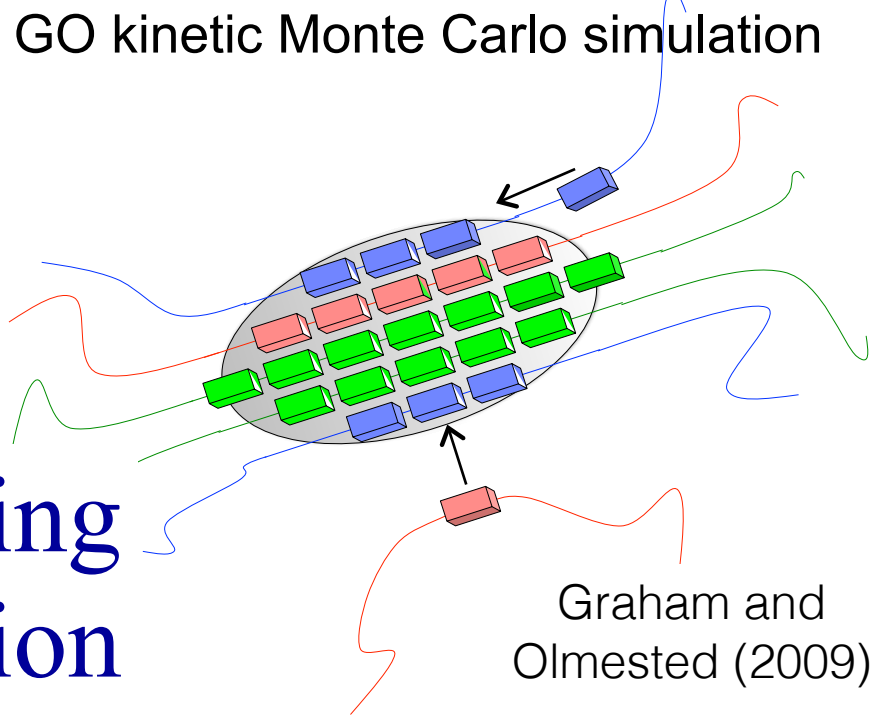
(a) Molecular dynamics



Rutledge et al (2013) & (2016)
Schilling et al (2013) & (2014)
Anwar and Graham (2019)

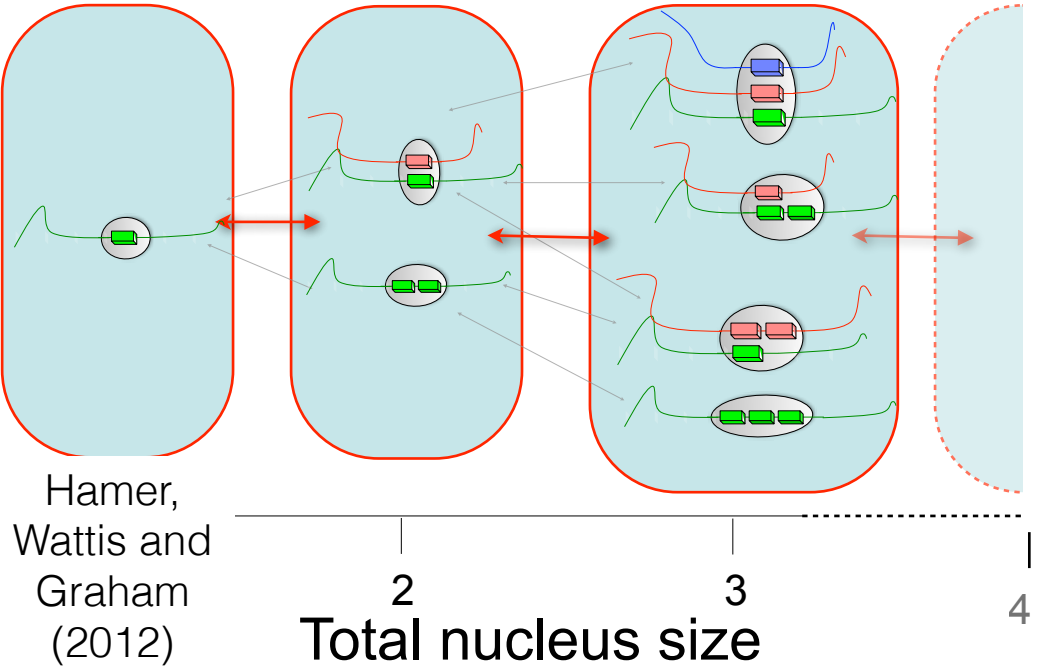
Modelling nucleation

(b) The GO kinetic Monte Carlo simulation



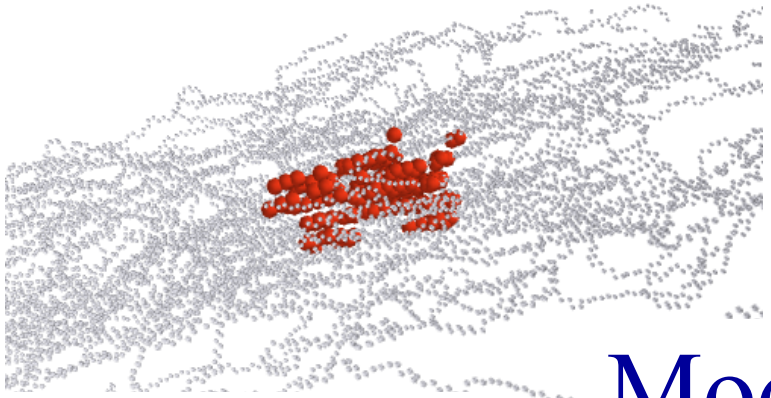
Graham and Olmested (2009)

(c) Projection to 1D



Hamer, Wattis and Graham (2012)

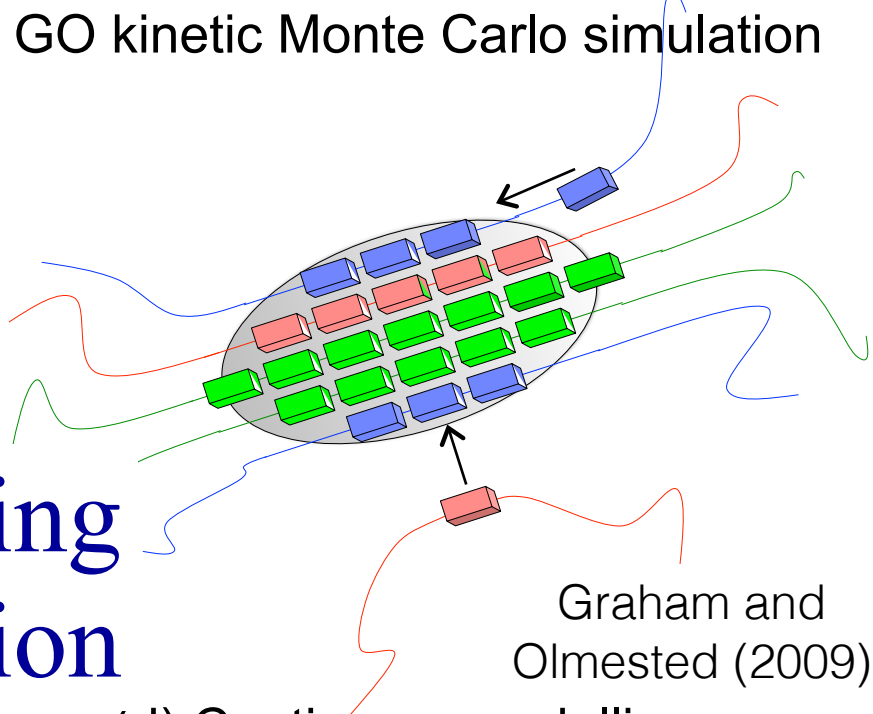
(a) Molecular dynamics



Rutledge et al (2013) & (2016)
Schilling et al (2013) & (2014)
Anwar and Graham (2019)

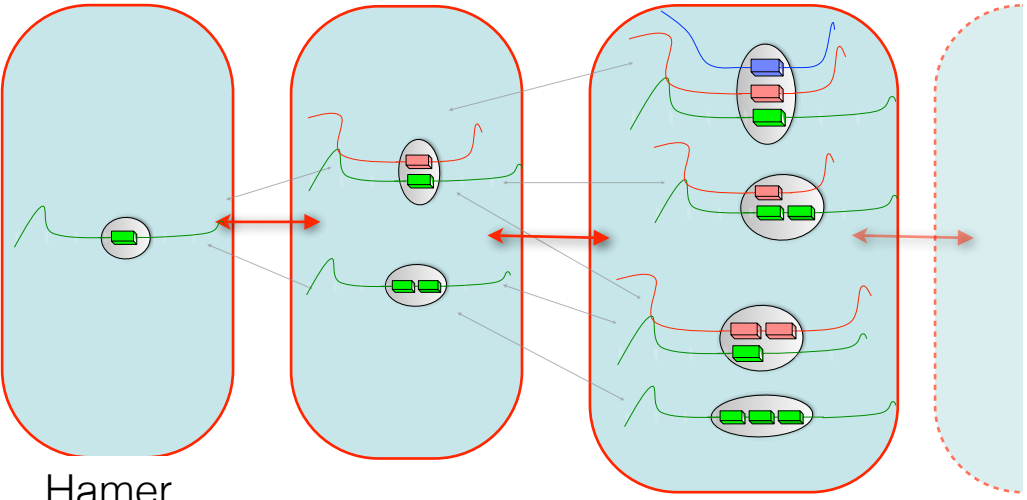
Modelling nucleation

(b) The GO kinetic Monte Carlo simulation



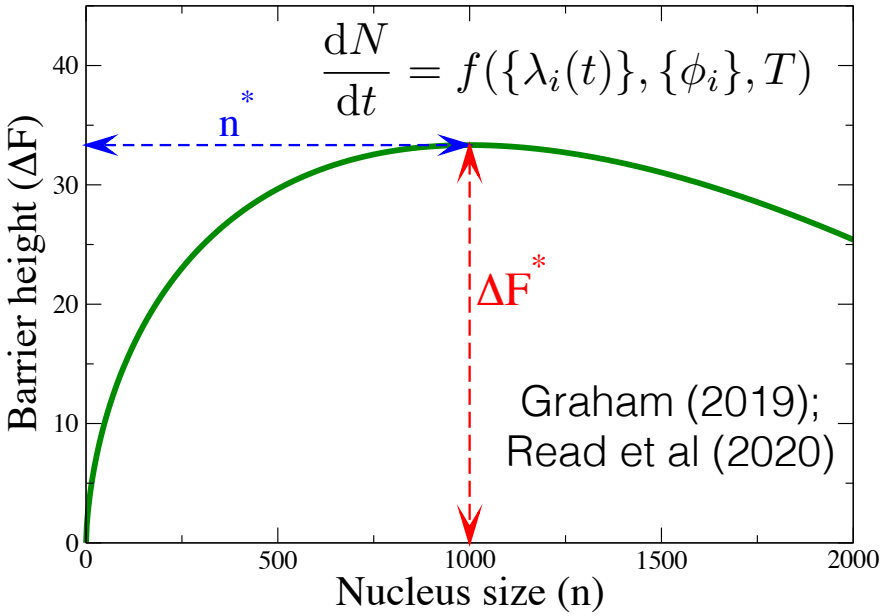
Graham and Olmested (2009)

(c) Projection to 1D



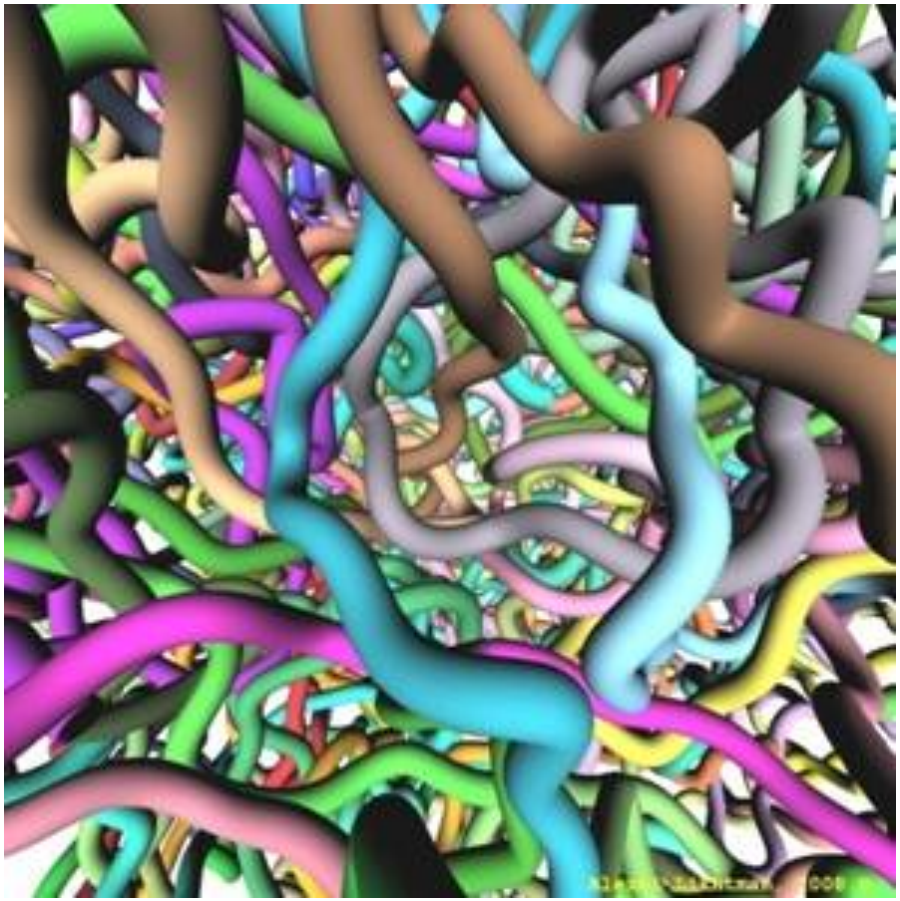
Hamer, Wattis and Graham (2012)

(d) Continuum modelling



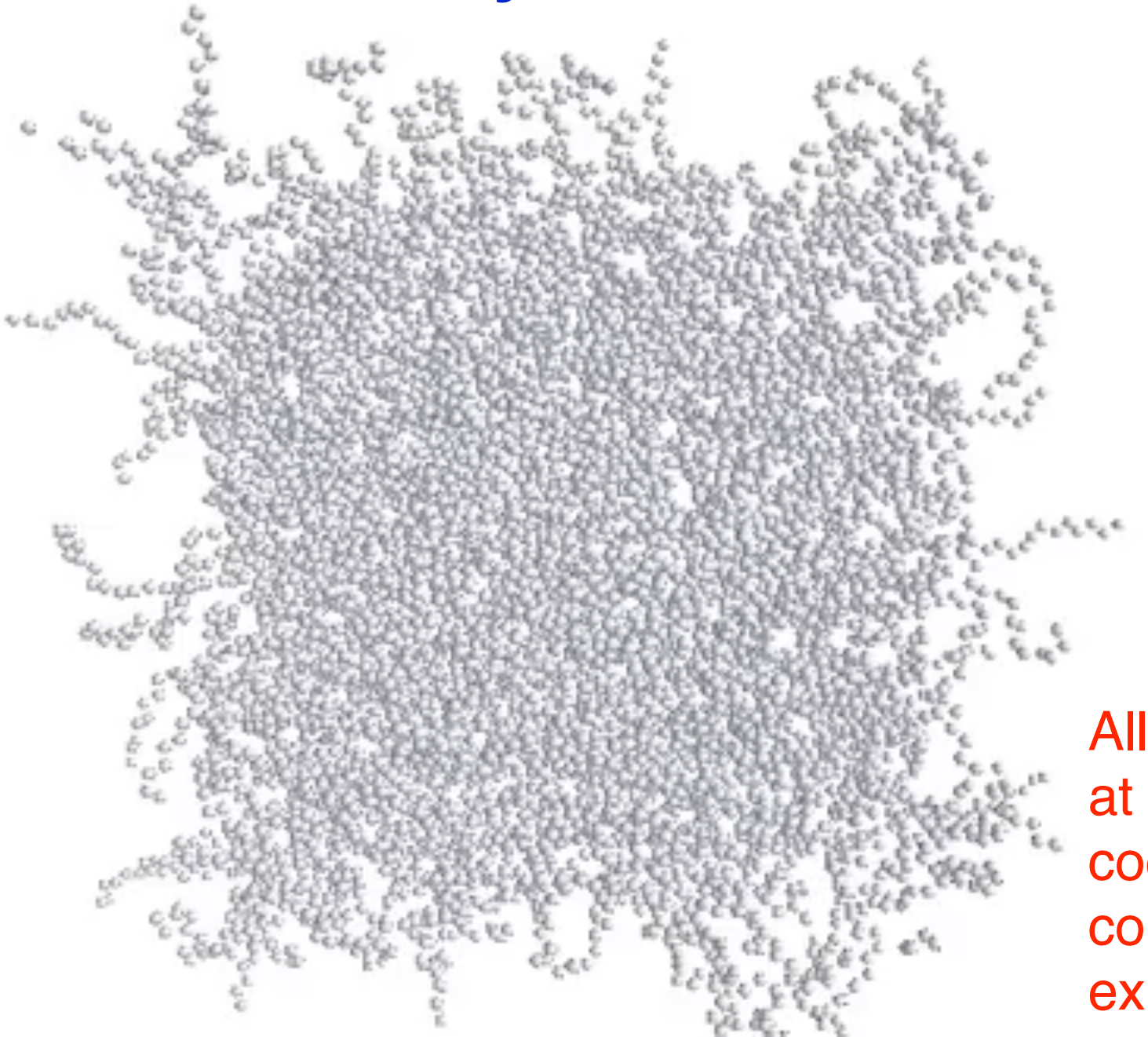
Graham (2019); Read et al (2020)

Molecular Dynamics - Monodisperse polymers



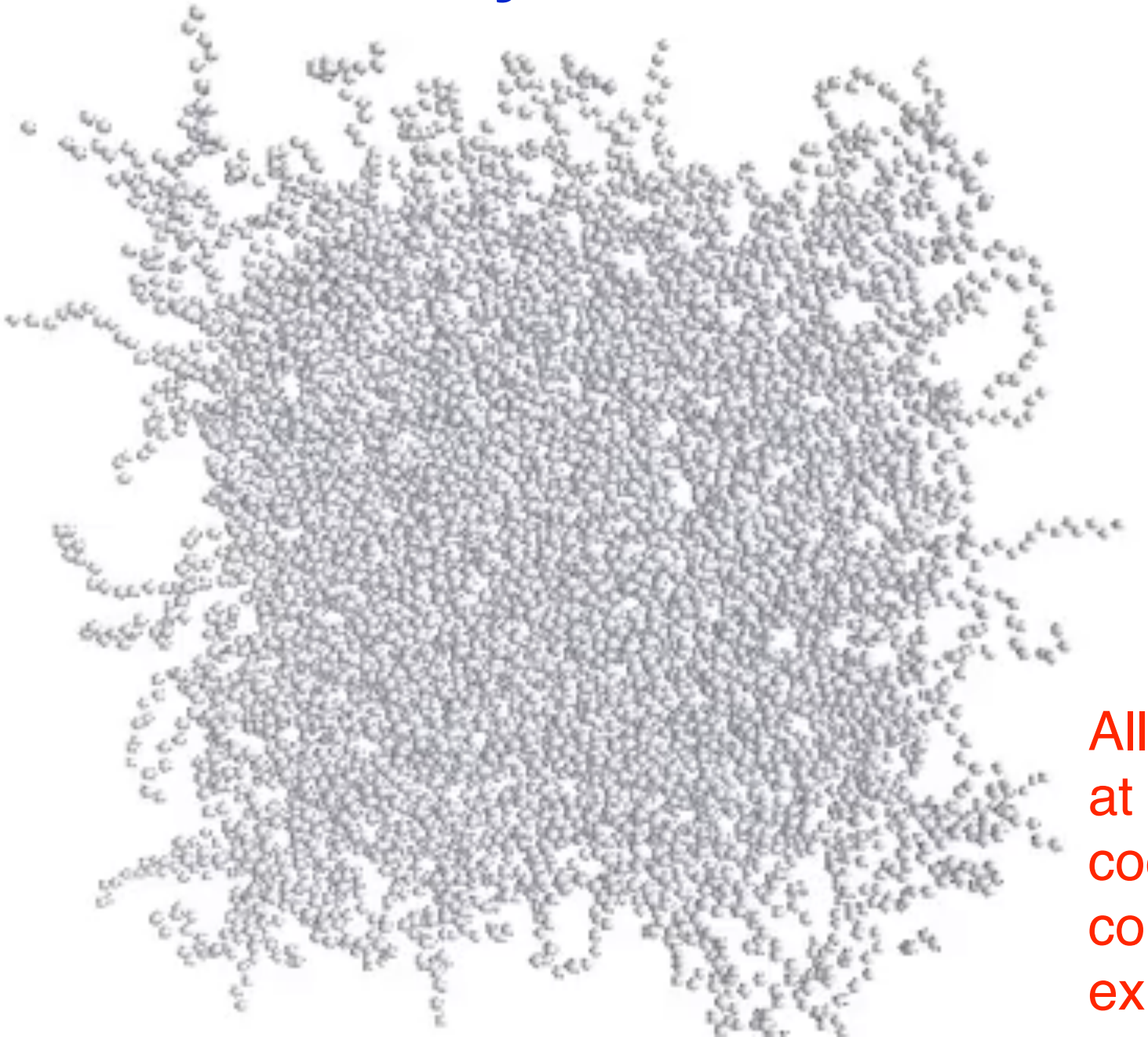
Continuous description of the position and momentum of of all atoms.

Molecular dynamics: flow & nucleation



All simulations at high under-cooling (much colder than experiments)

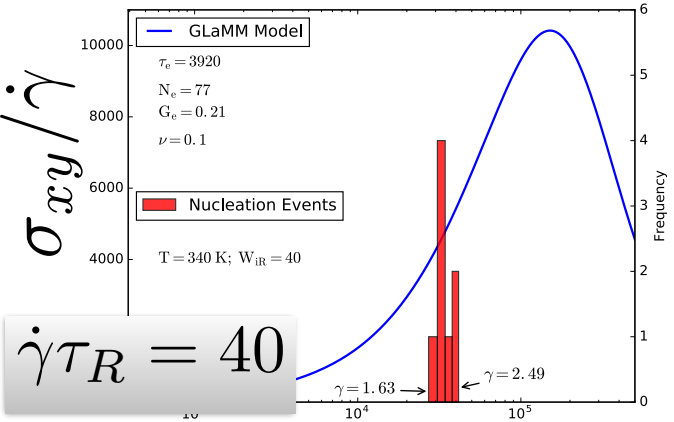
Molecular dynamics: flow & nucleation



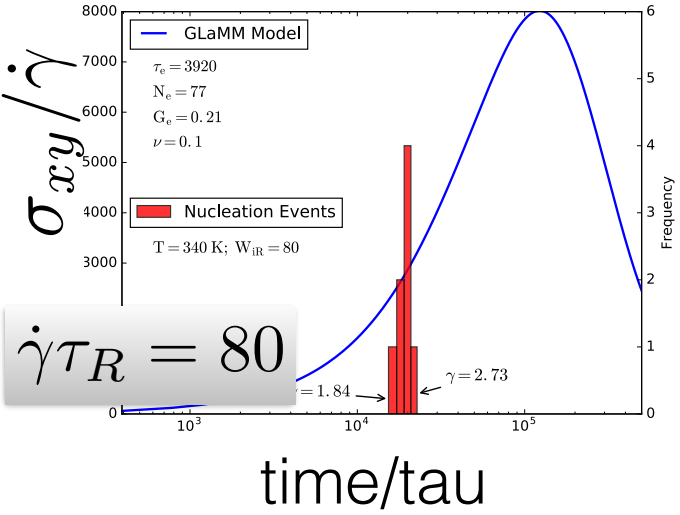
All simulations at high under-cooling (much colder than experiments)

Molecular dynamics:
The timing of nucleation events during the stress transient

$$T = 340K$$



$$\dot{\gamma}\tau_R = 40$$

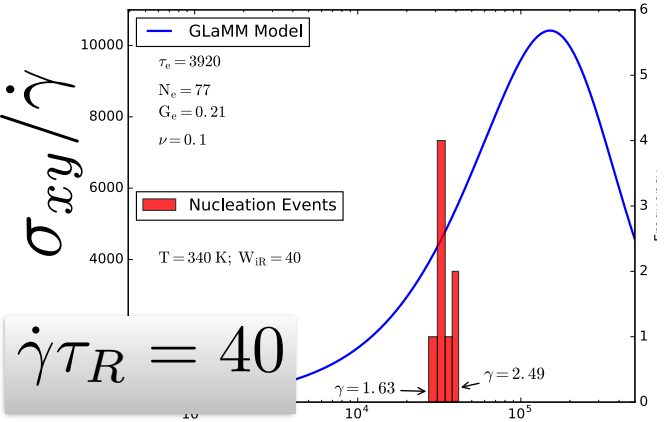


$$\dot{\gamma}\tau_R = 80$$

Anwar and Graham, J. Chem. Phys. **150**, 084905 (2019)

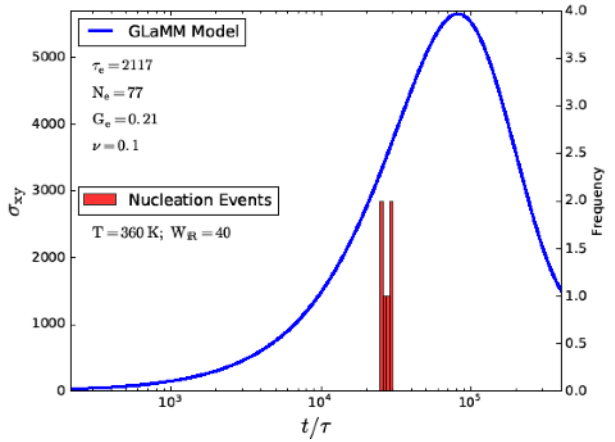
Molecular dynamics:
The timing of nucleation events during the stress transient

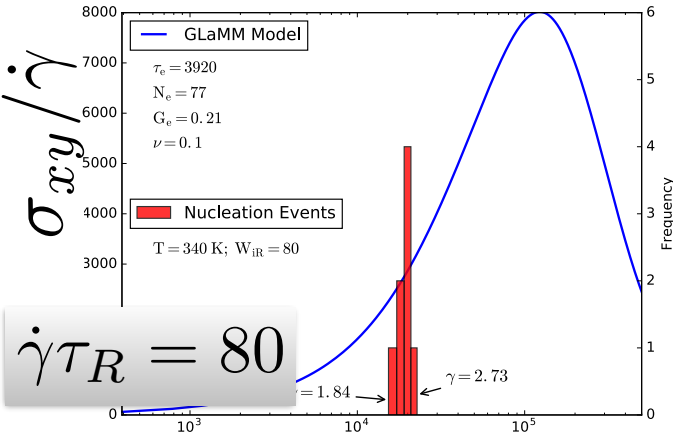
$T = 340K$



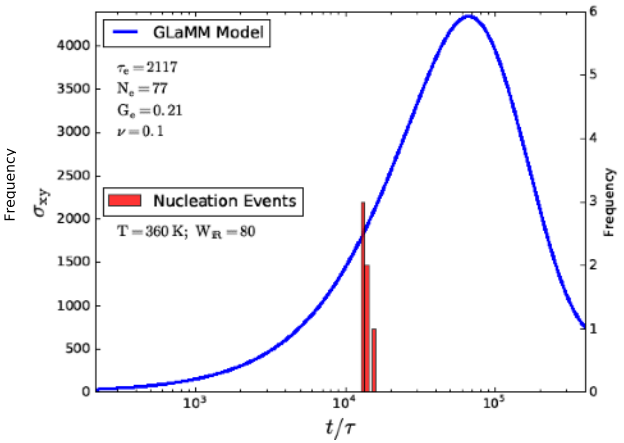
$\dot{\gamma}\tau_R = 40$

$T = 360K$





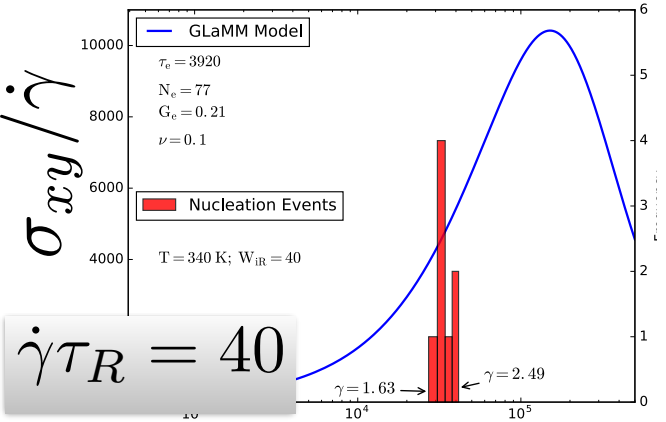
$\dot{\gamma}\tau_R = 80$



Anwar and Graham, J. Chem. Phys. **150**, 084905 (2019)

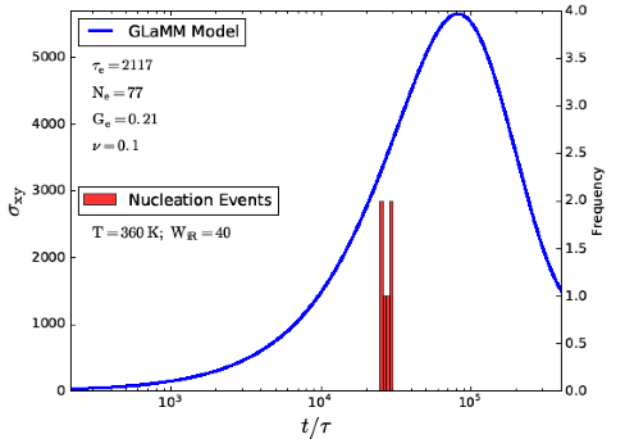
Molecular dynamics:
The timing of nucleation events during the stress transient

$T = 340K$

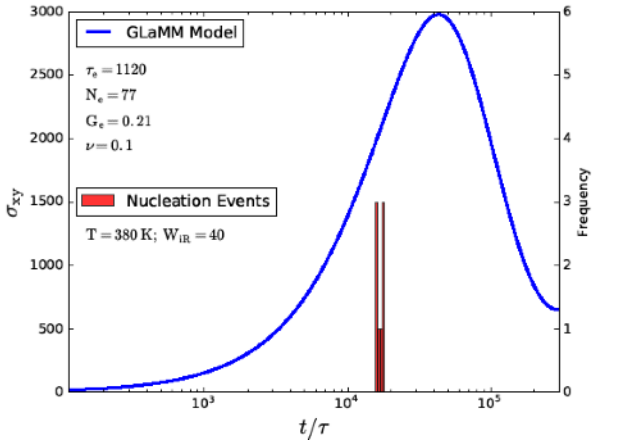


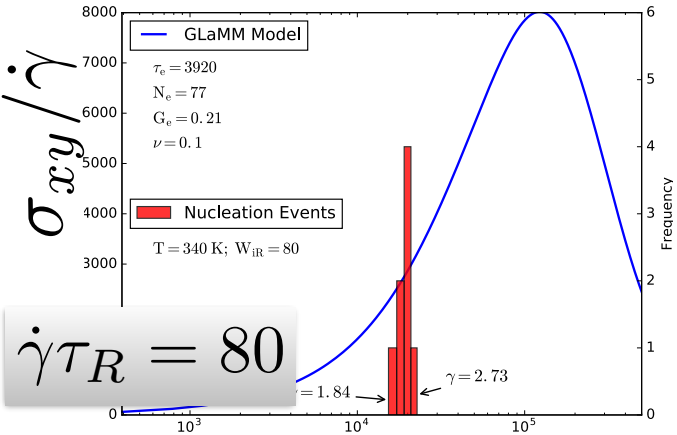
$\dot{\gamma}\tau_R = 40$

$T = 360K$

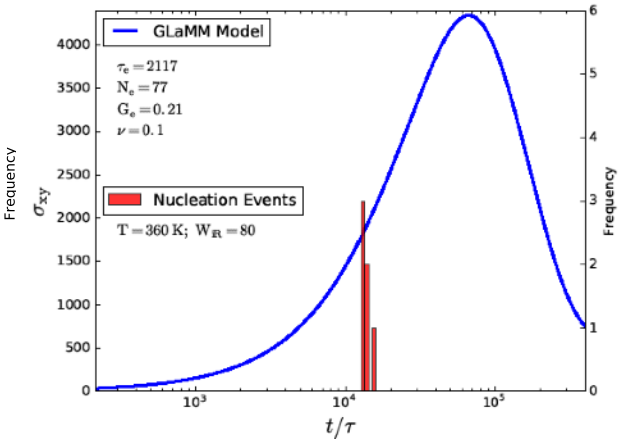


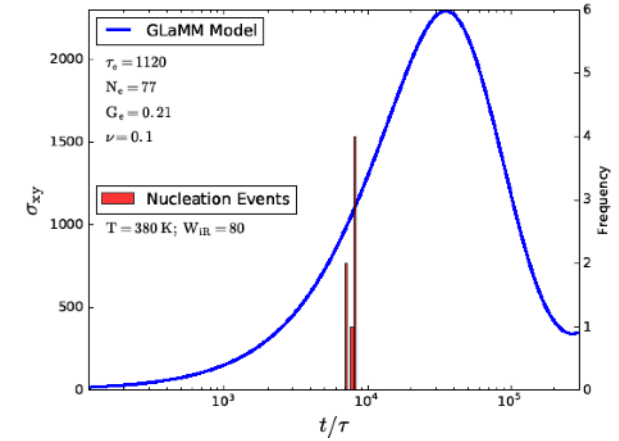
$T = 380K$





$\dot{\gamma}\tau_R = 80$

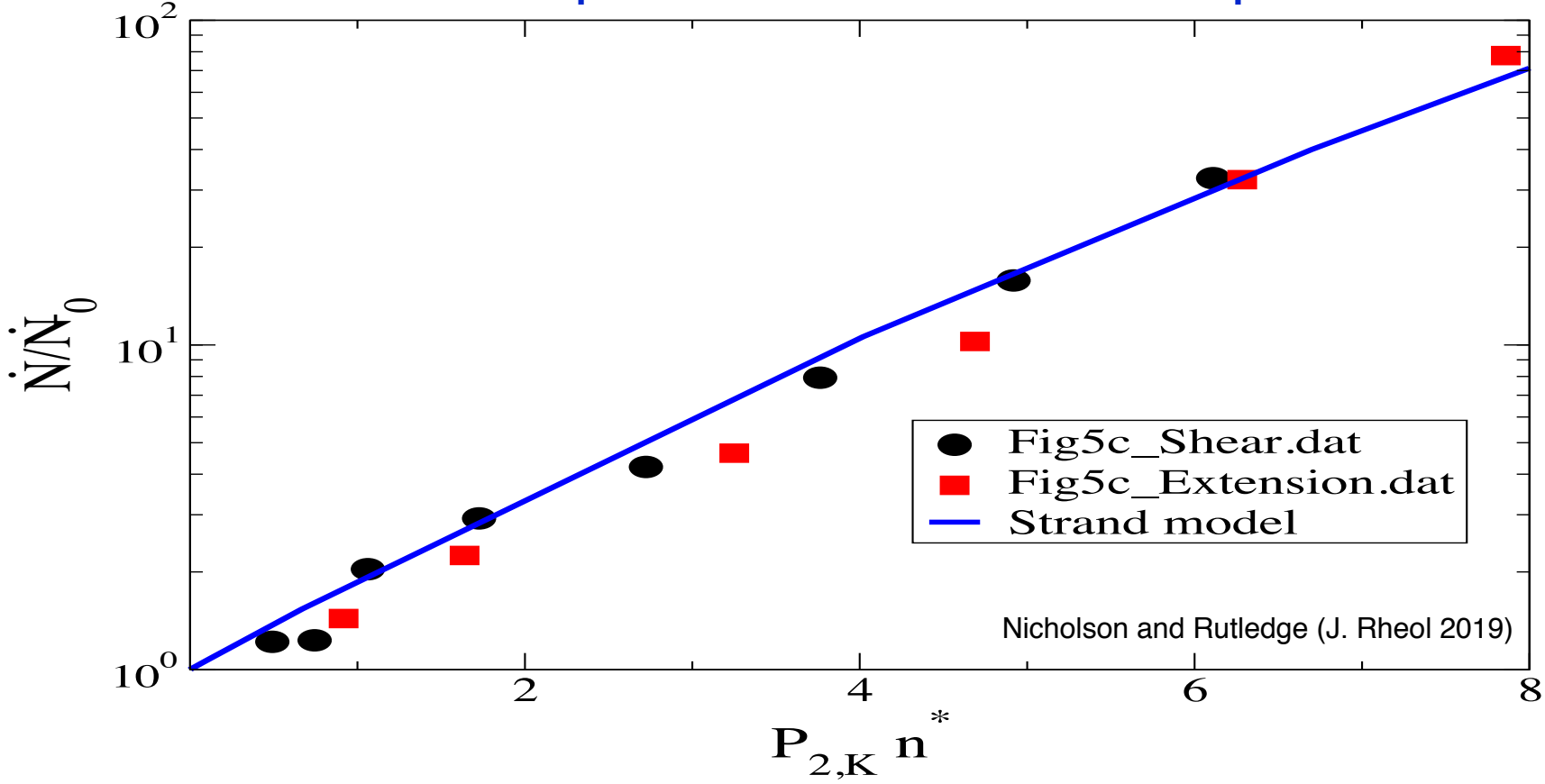




Anwar and Graham, J. Chem. Phys. **150**, 084905 (2019)

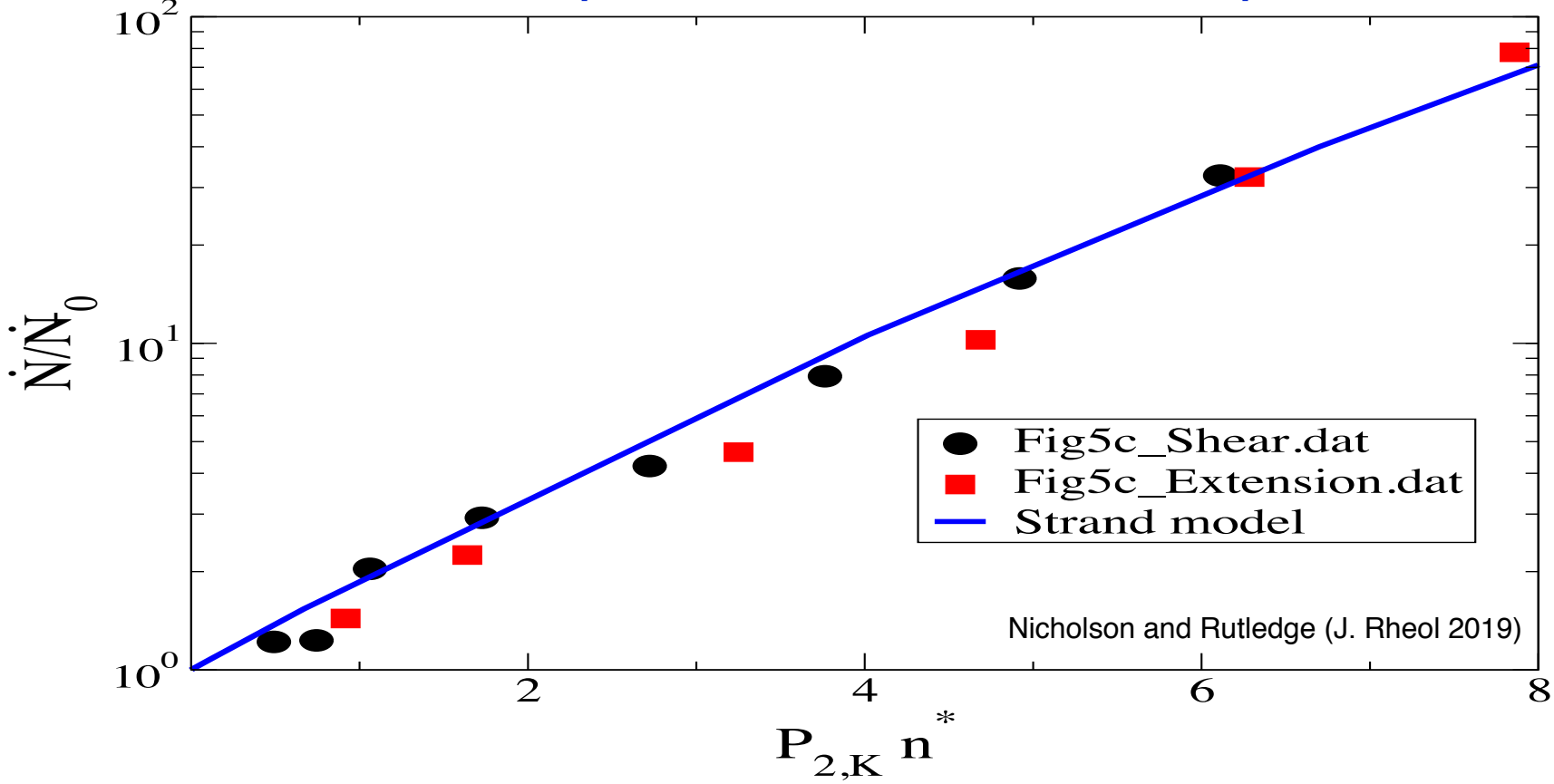
A key result from Nicholson and Rutledge

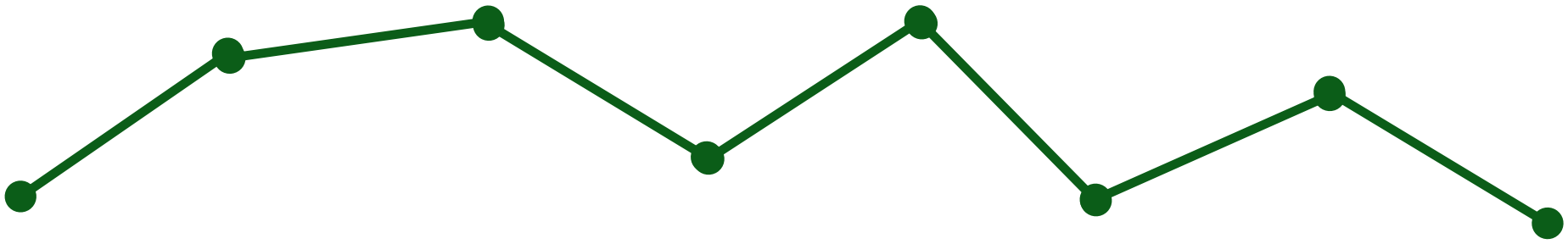
Nucleation rate is exponential in the Kuhn step nematic order



A key result from Nicholson and Rutledge

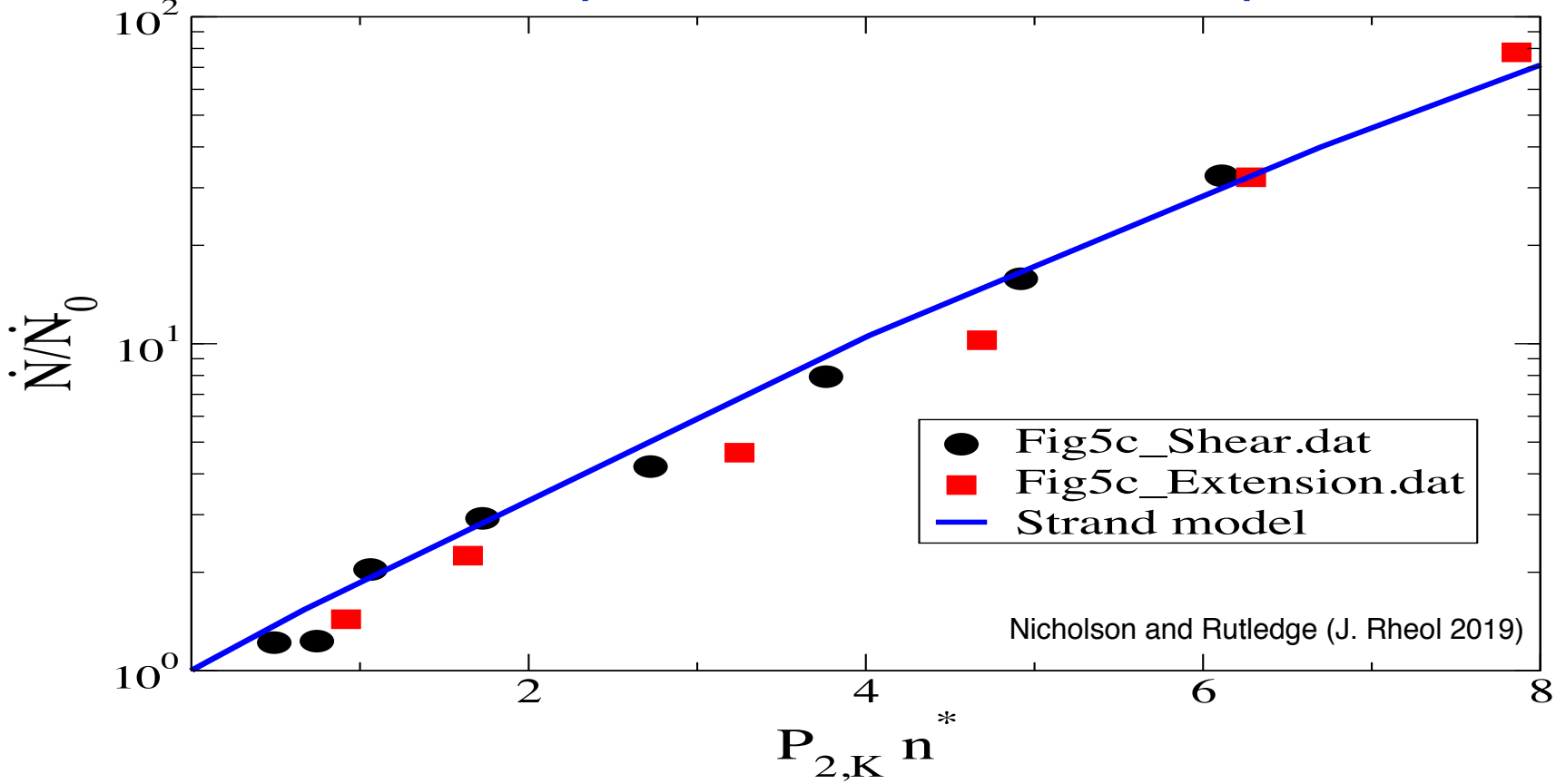
Nucleation rate is exponential in the Kuhn step nematic order

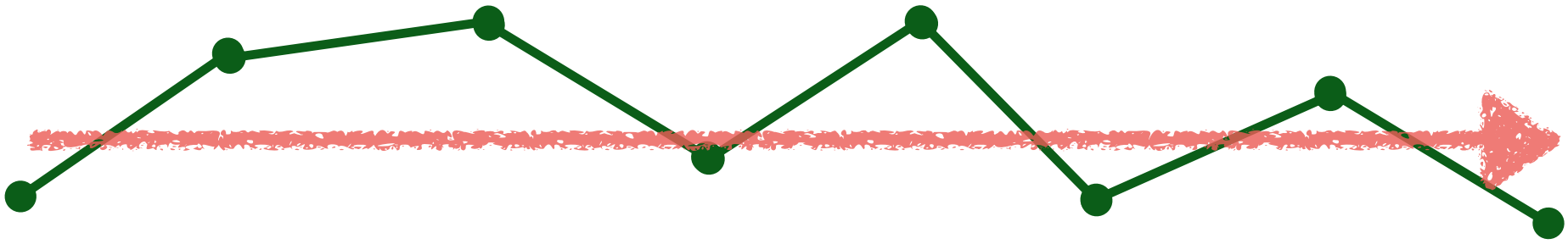




A key result from Nicholson and Rutledge

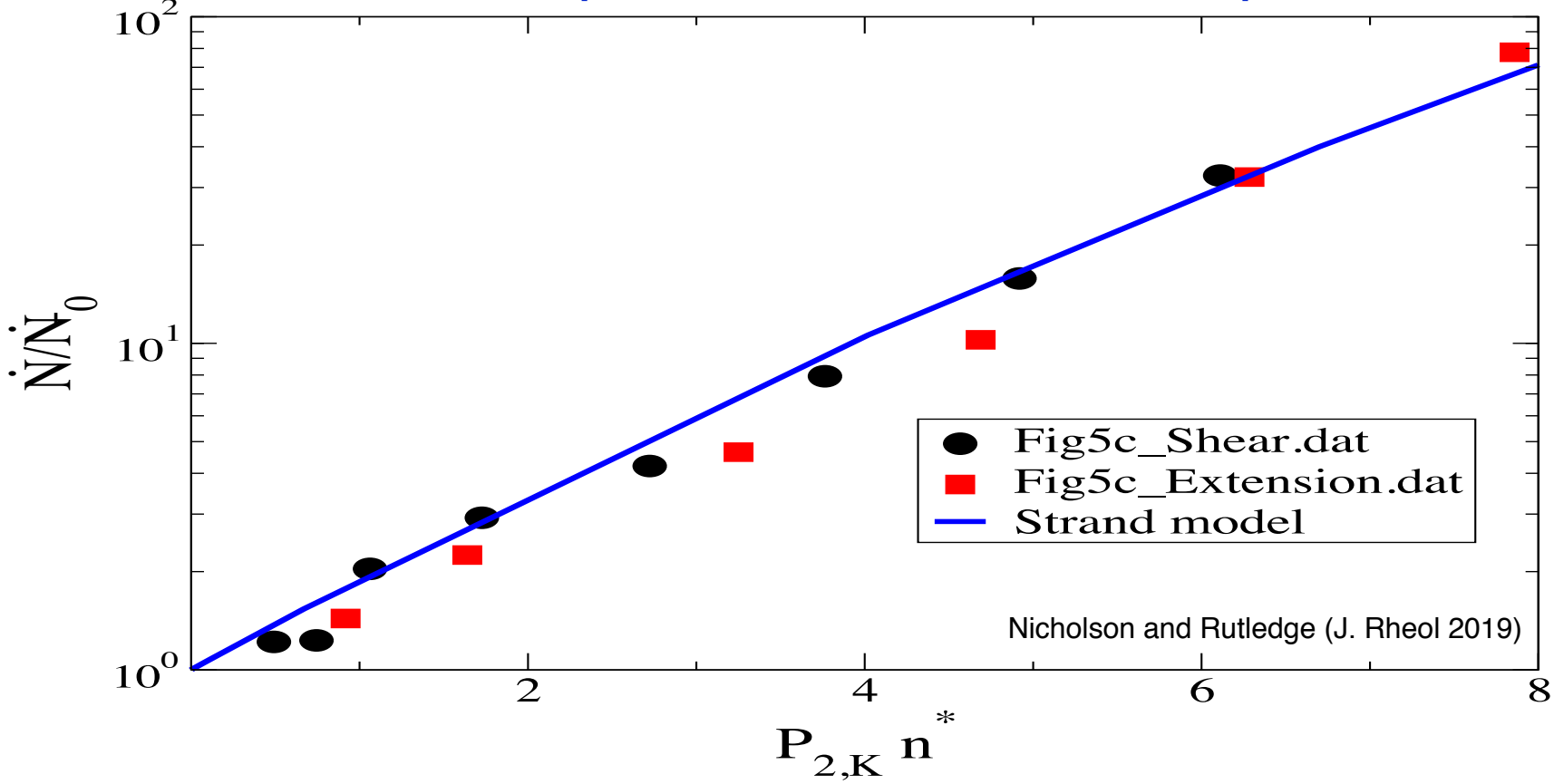
Nucleation rate is exponential in the Kuhn step nematic order

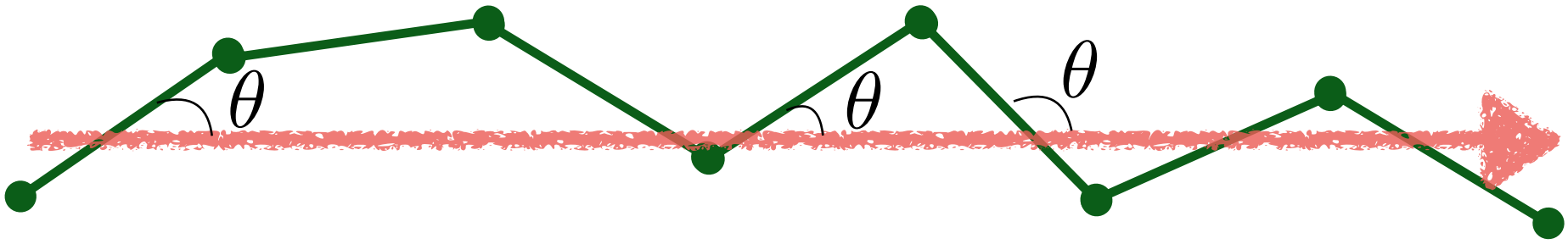




A key result from Nicholson and Rutledge

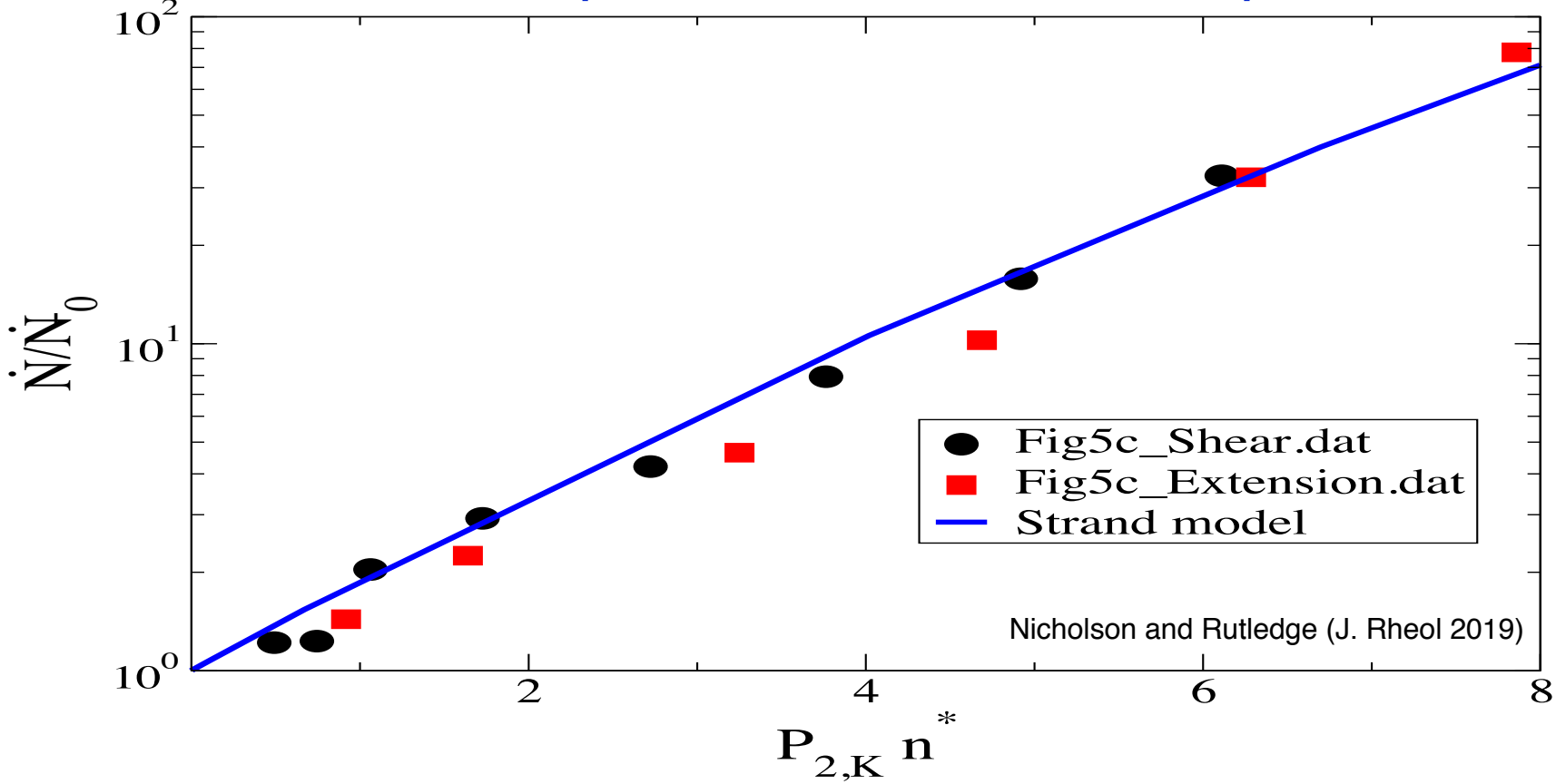
Nucleation rate is exponential in the Kuhn step nematic order



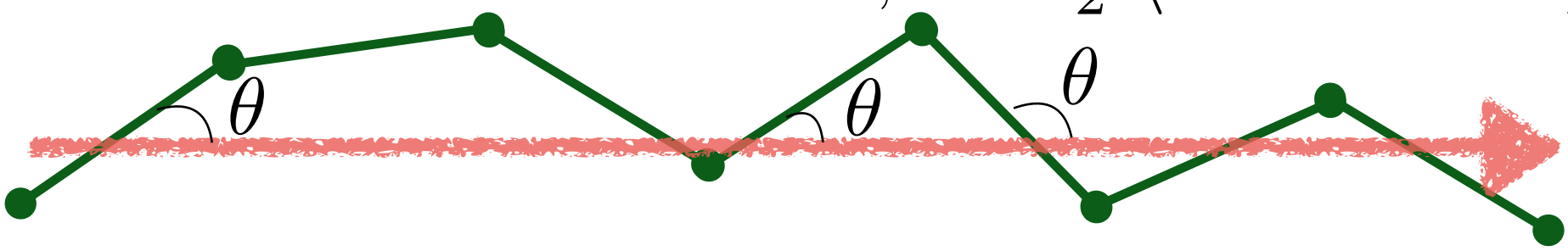


A key result from Nicholson and Rutledge

Nucleation rate is exponential in the Kuhn step nematic order

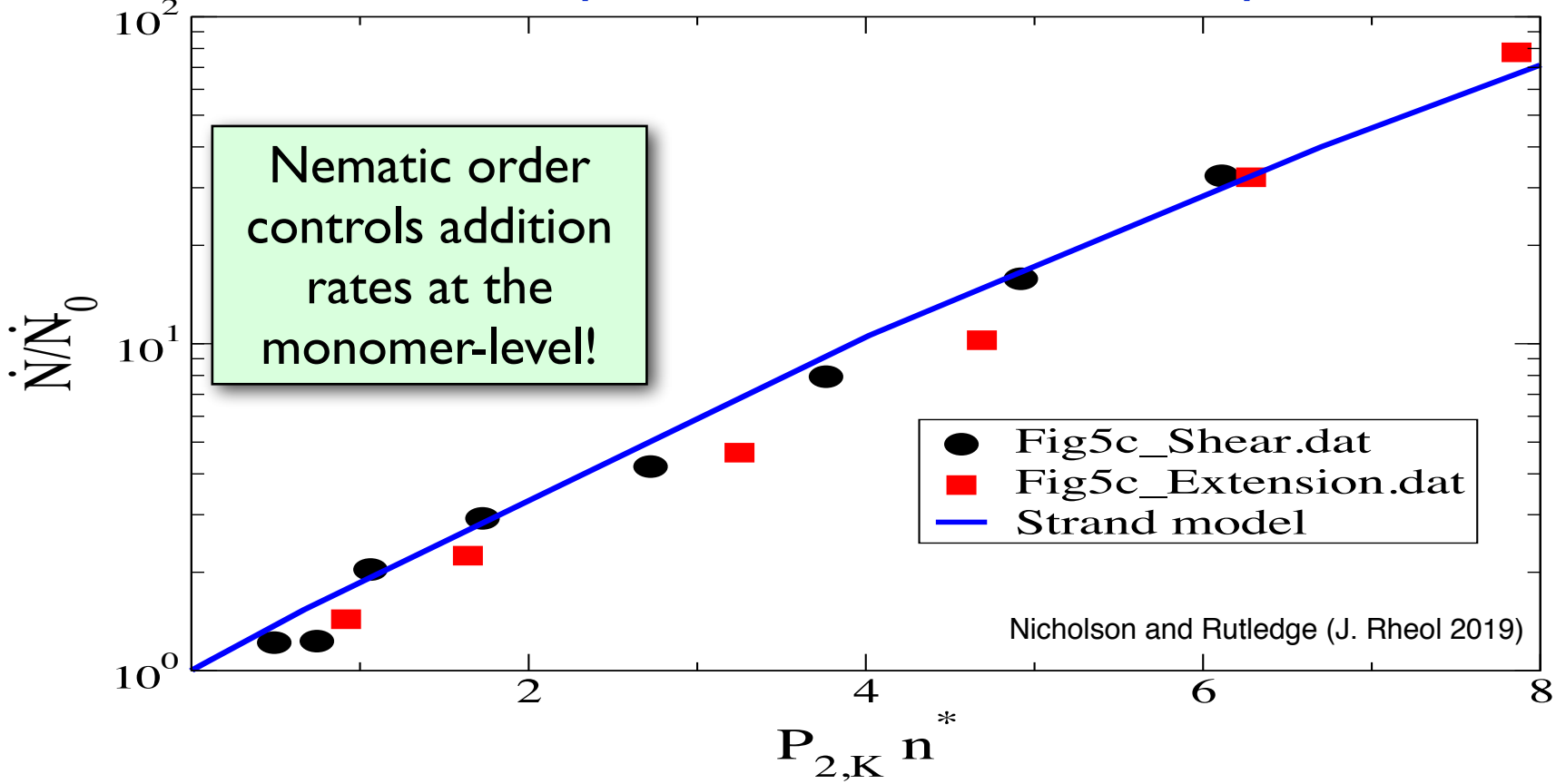


$$P_{2,K} = \frac{1}{2}\left\langle 3\cos^2\theta - 1 \right\rangle$$

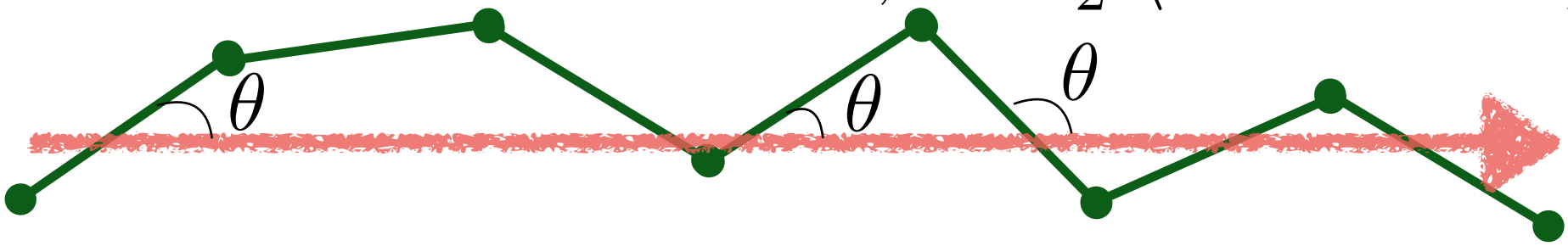


A key result from Nicholson and Rutledge

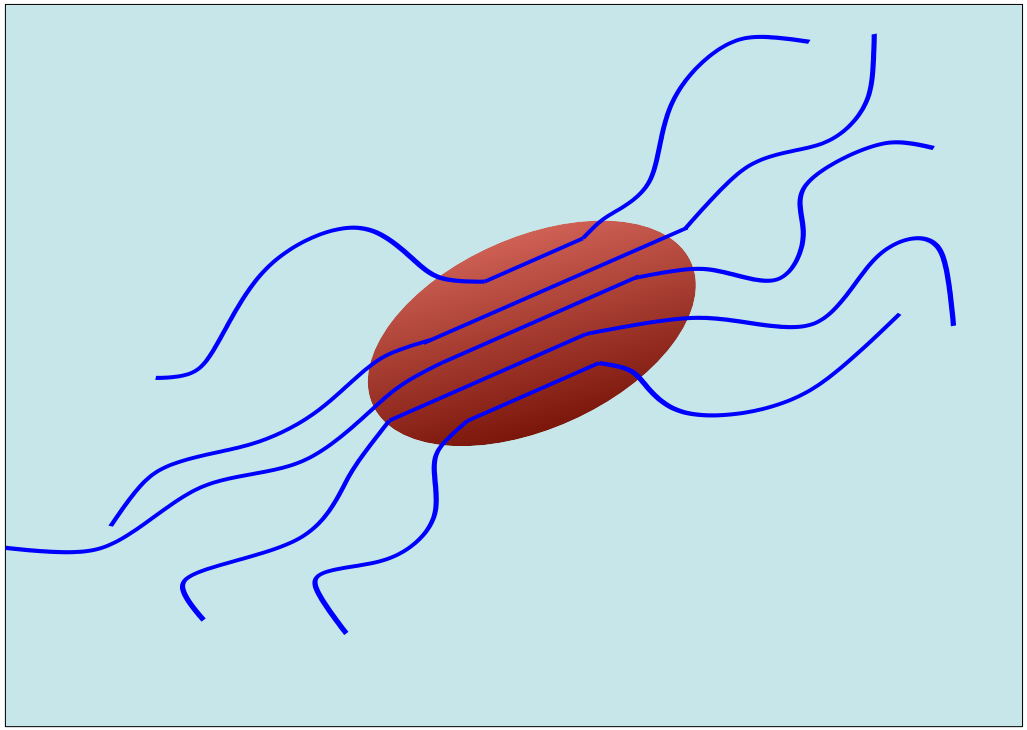
Nucleation rate is exponential in the Kuhn step nematic order



$$P_{2,K} = \frac{1}{2}\left\langle 3\cos^2\theta - 1 \right\rangle$$

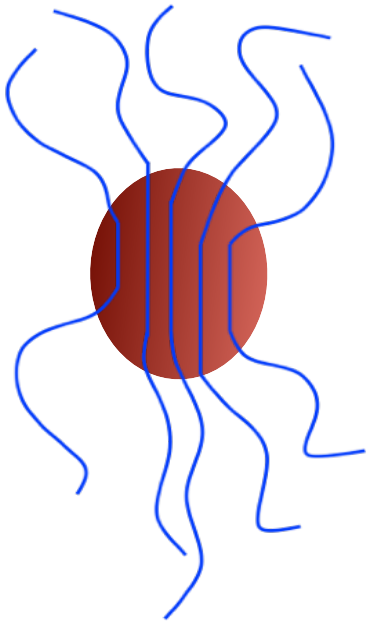


GO model (kinetic Monte-Carlo)



Limited resolution and
discretised nucleus

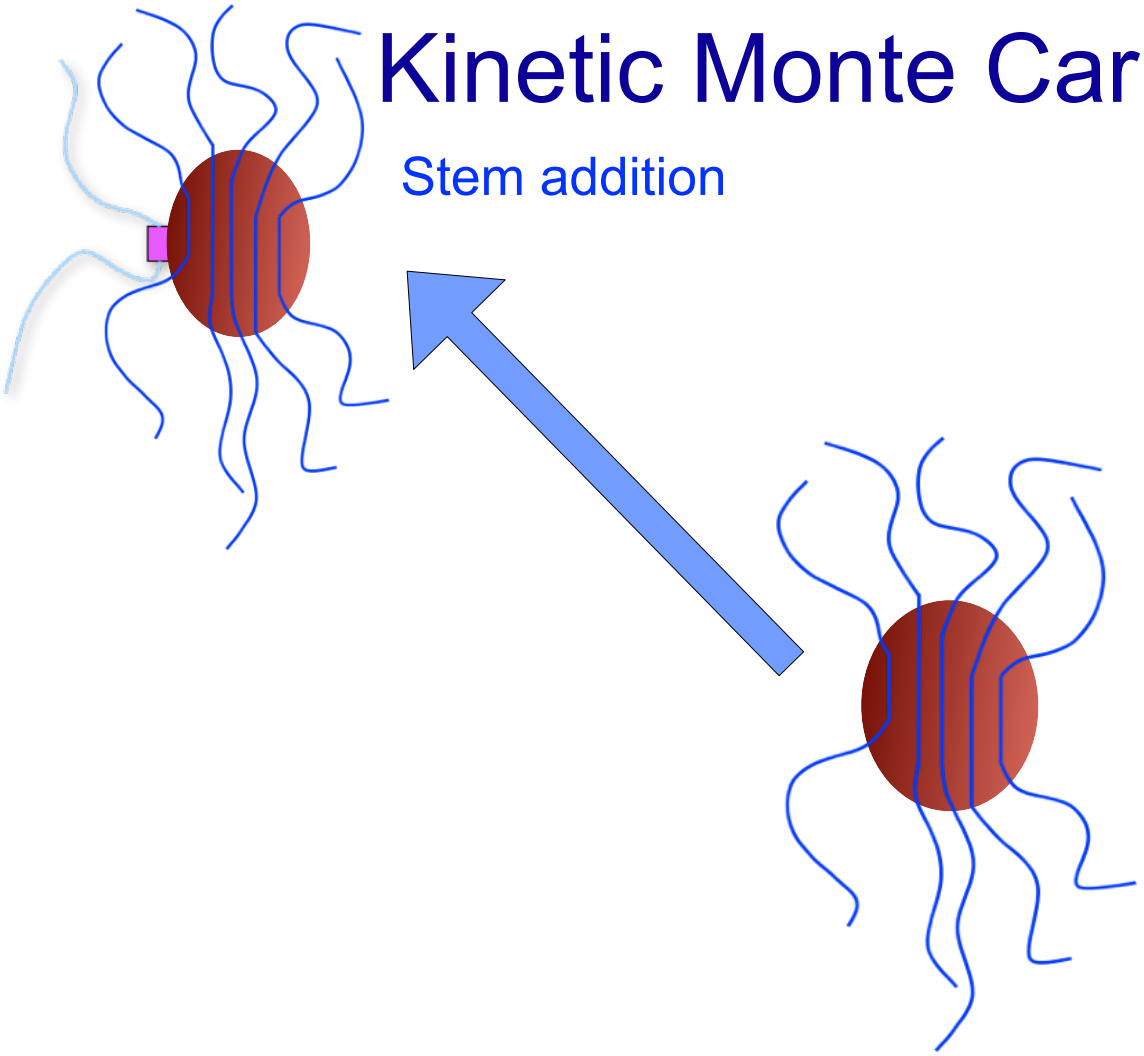
Kinetic Monte Carlo model



Graham and Olmsted,
Phys. Rev. Lett. **115**
115707 (2009)

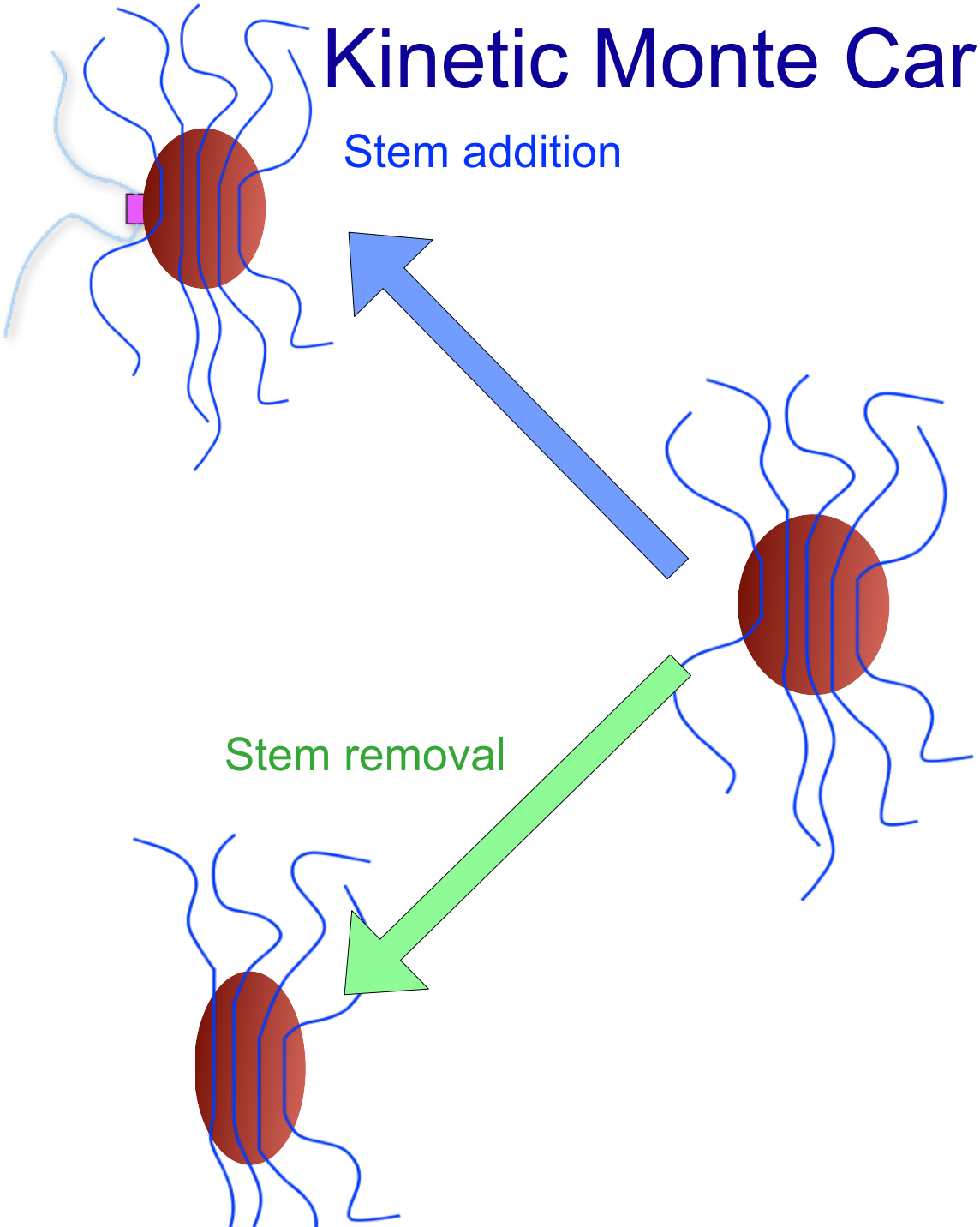
Kinetic Monte Carlo model

Stem addition



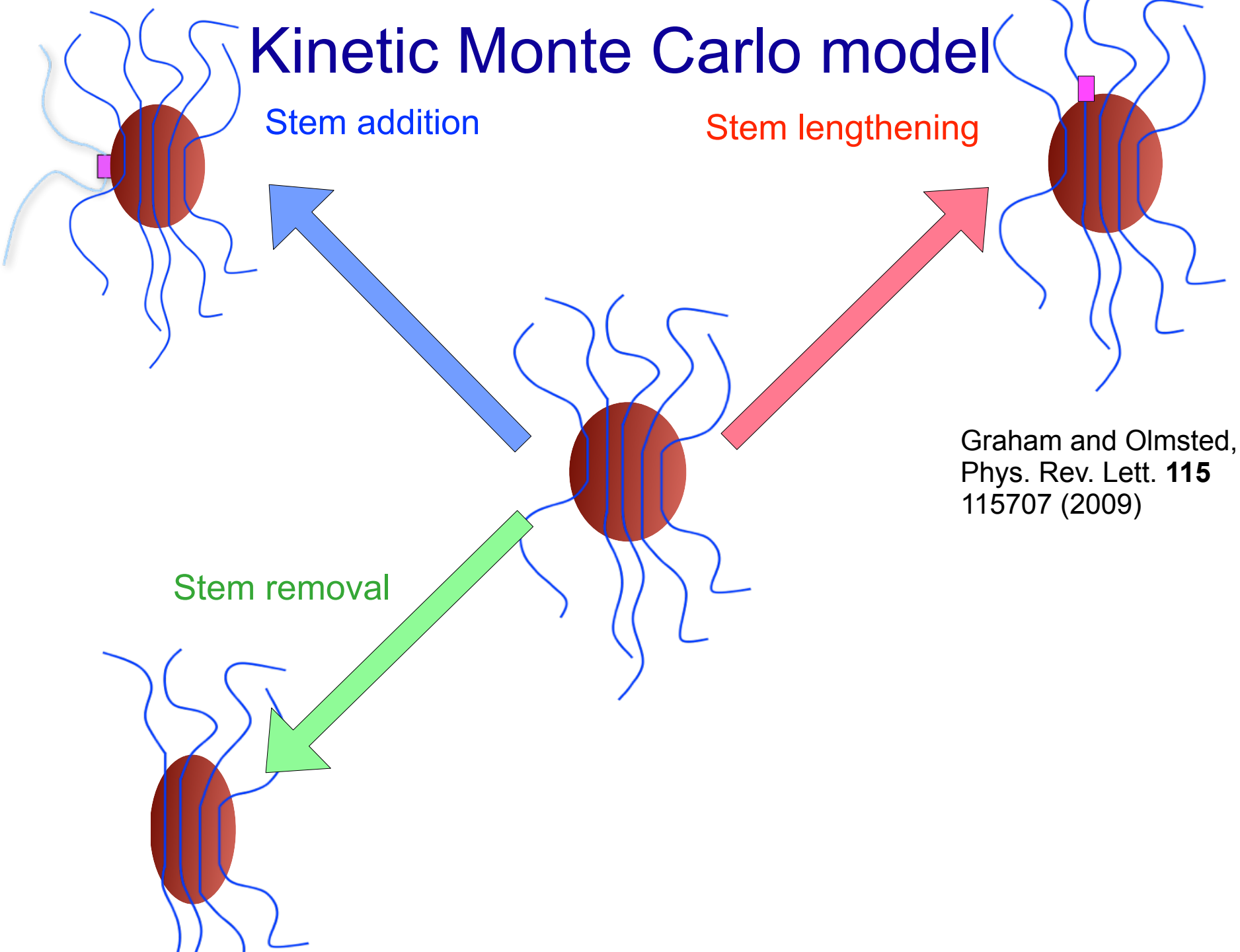
Graham and Olmsted, Phys. Rev. Lett. **115** 115707 (2009)

Kinetic Monte Carlo model



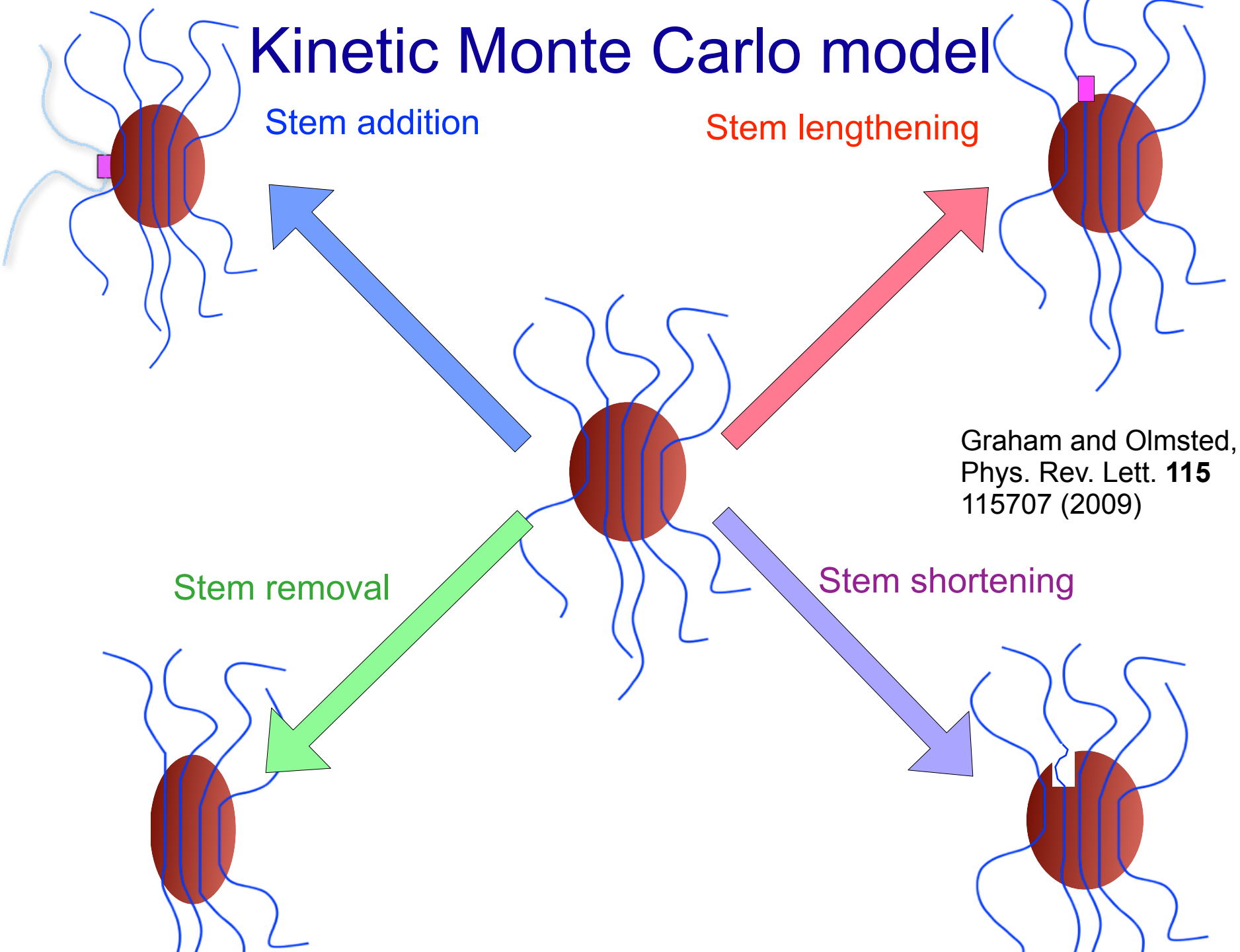
Graham and Olmsted, Phys. Rev. Lett. **115** 115707 (2009)

Kinetic Monte Carlo model



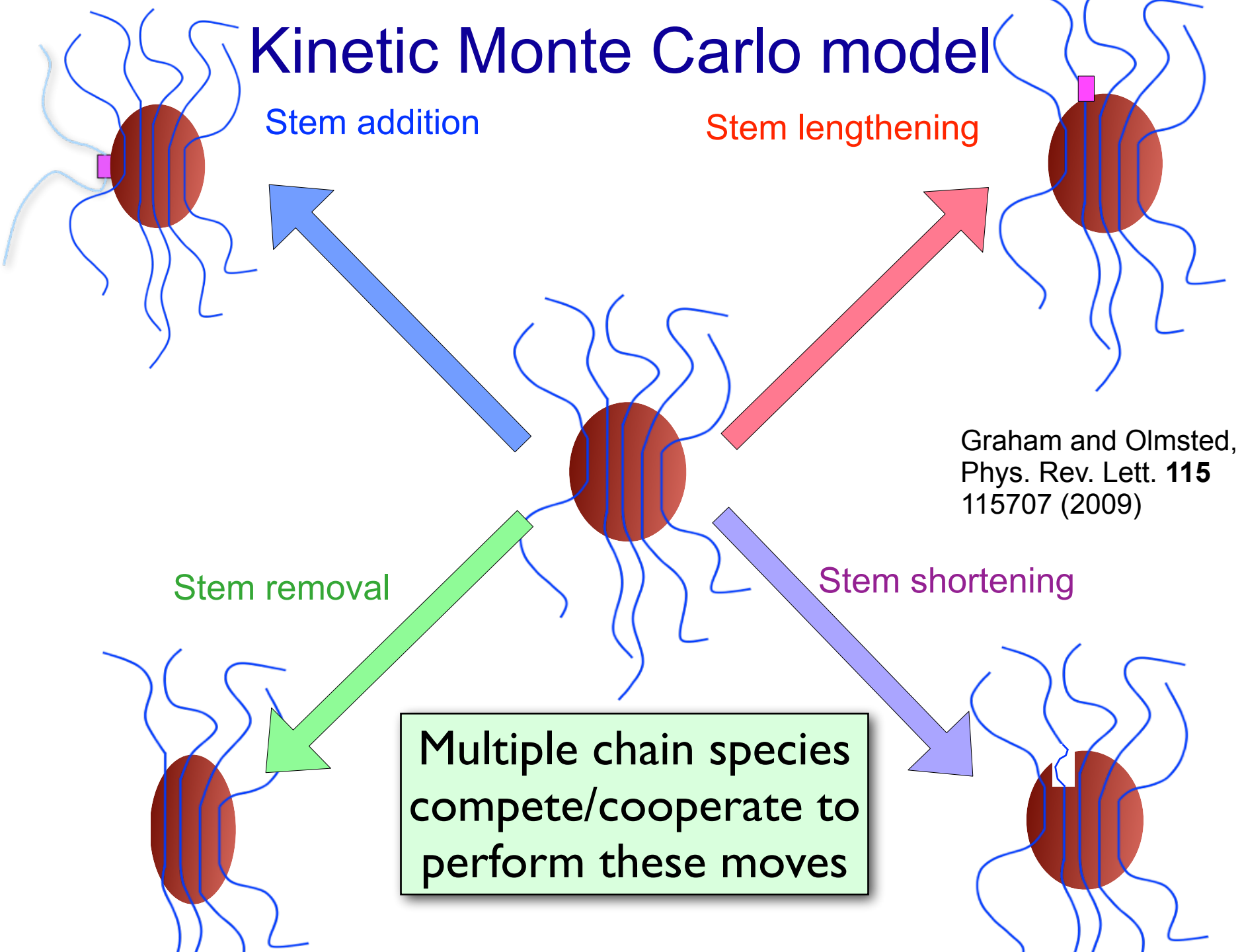
Graham and Olmsted, Phys. Rev. Lett. **115** 115707 (2009)

Kinetic Monte Carlo model



Graham and Olmsted,
Phys. Rev. Lett. **115**
115707 (2009)

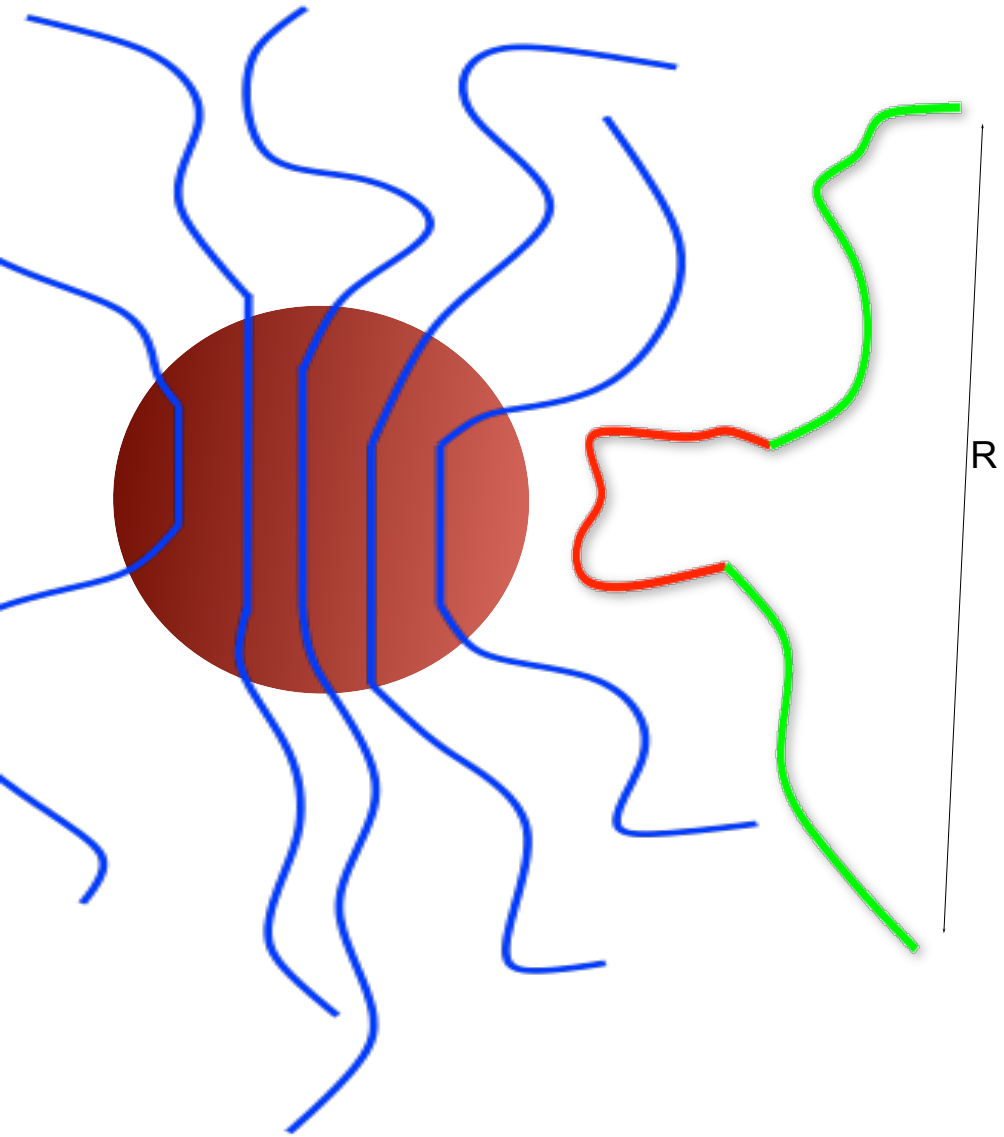
Kinetic Monte Carlo model



Graham and Olmsted, Phys. Rev. Lett. **115** 115707 (2009)

Multiple chain species compete/cooperate to perform these moves

Influence of flow - chain deformation

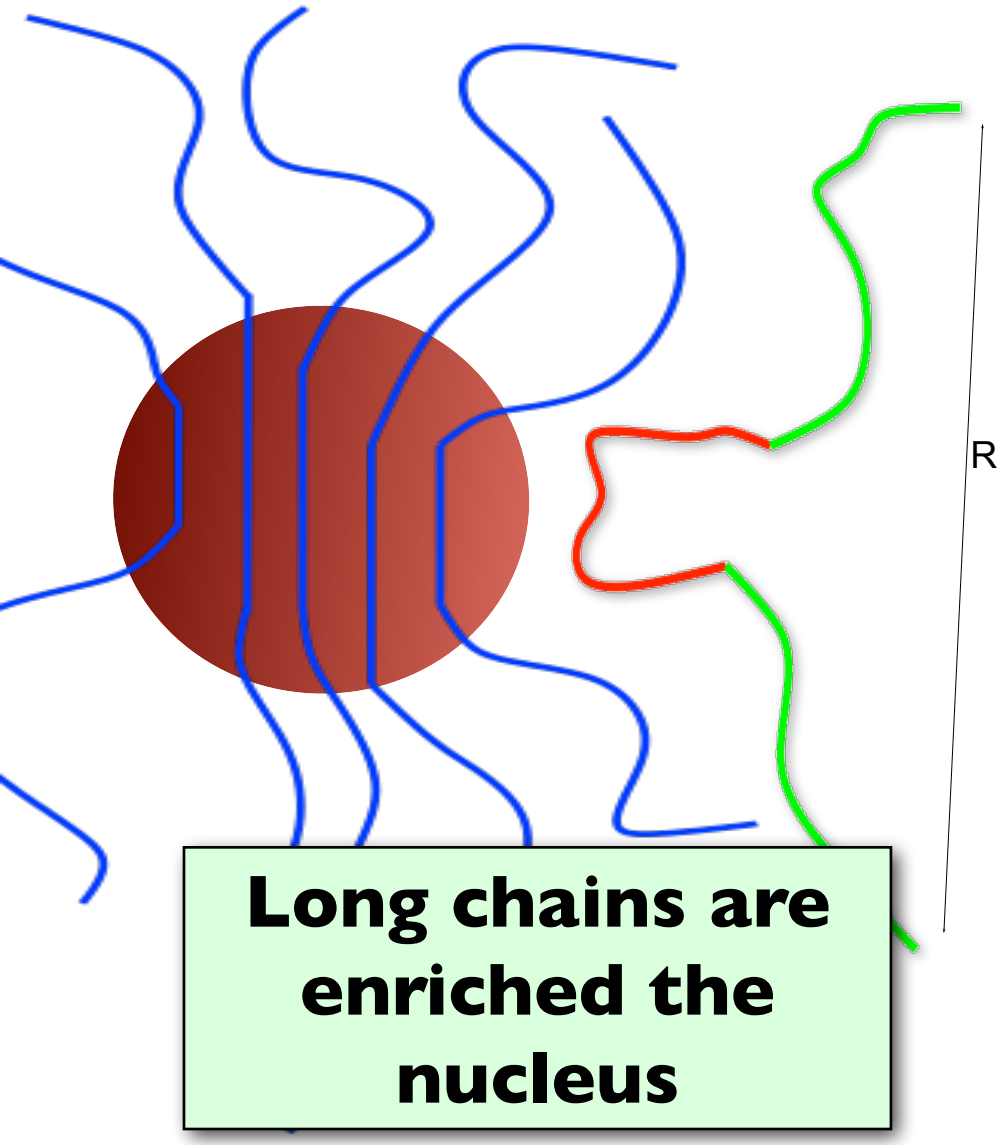


As computed by a molecular flow theory.

Flow imposes an average molecular strain, <RR>.

Graham and Olmsted, Phys. Rev. Lett. **115** 115707 (2009)

Influence of flow - chain deformation

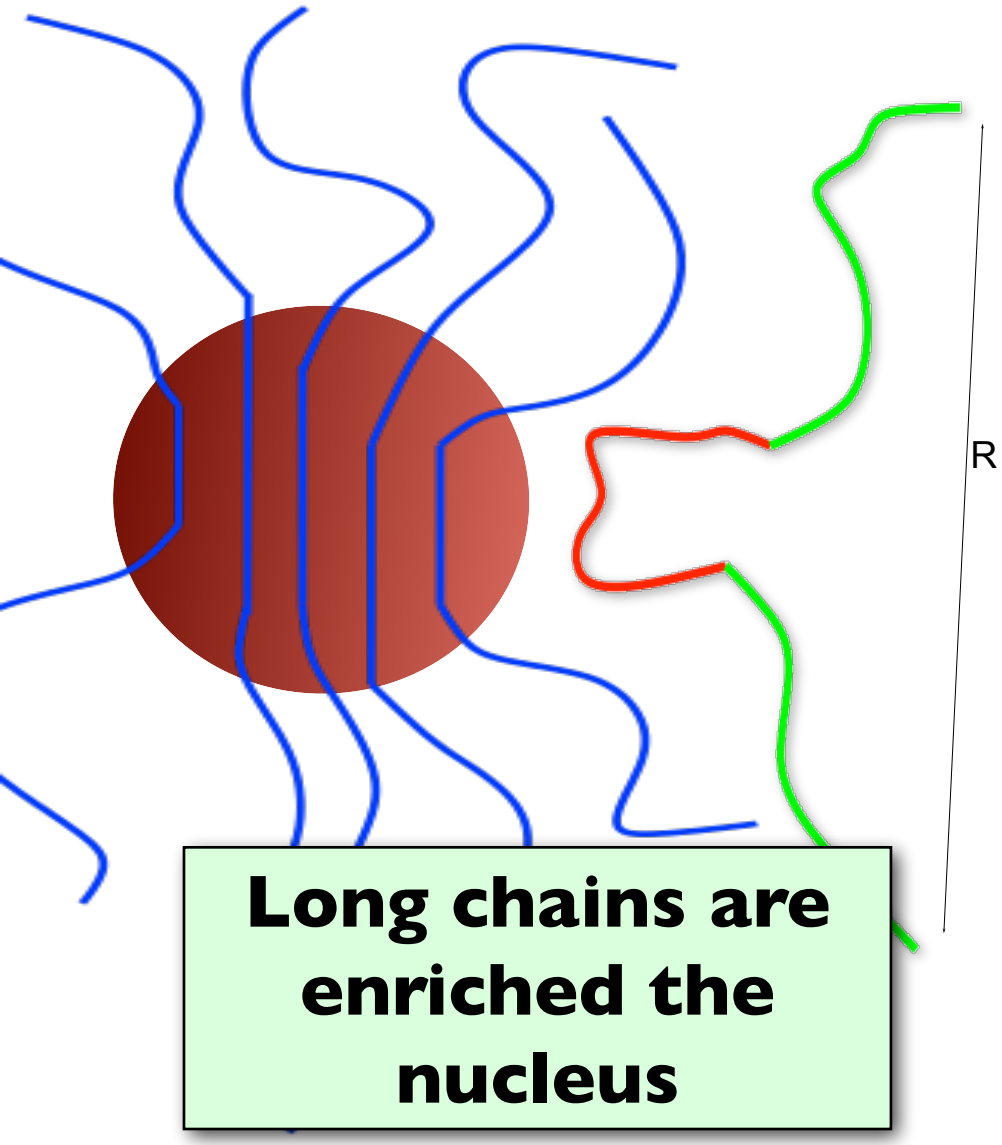


As computed by a molecular flow theory.

Flow imposes an average molecular strain, <RR>.

Graham and Olmsted, Phys. Rev. Lett. **115** 115707 (2009)

Influence of flow - chain deformation



Long chains are enriched the nucleus

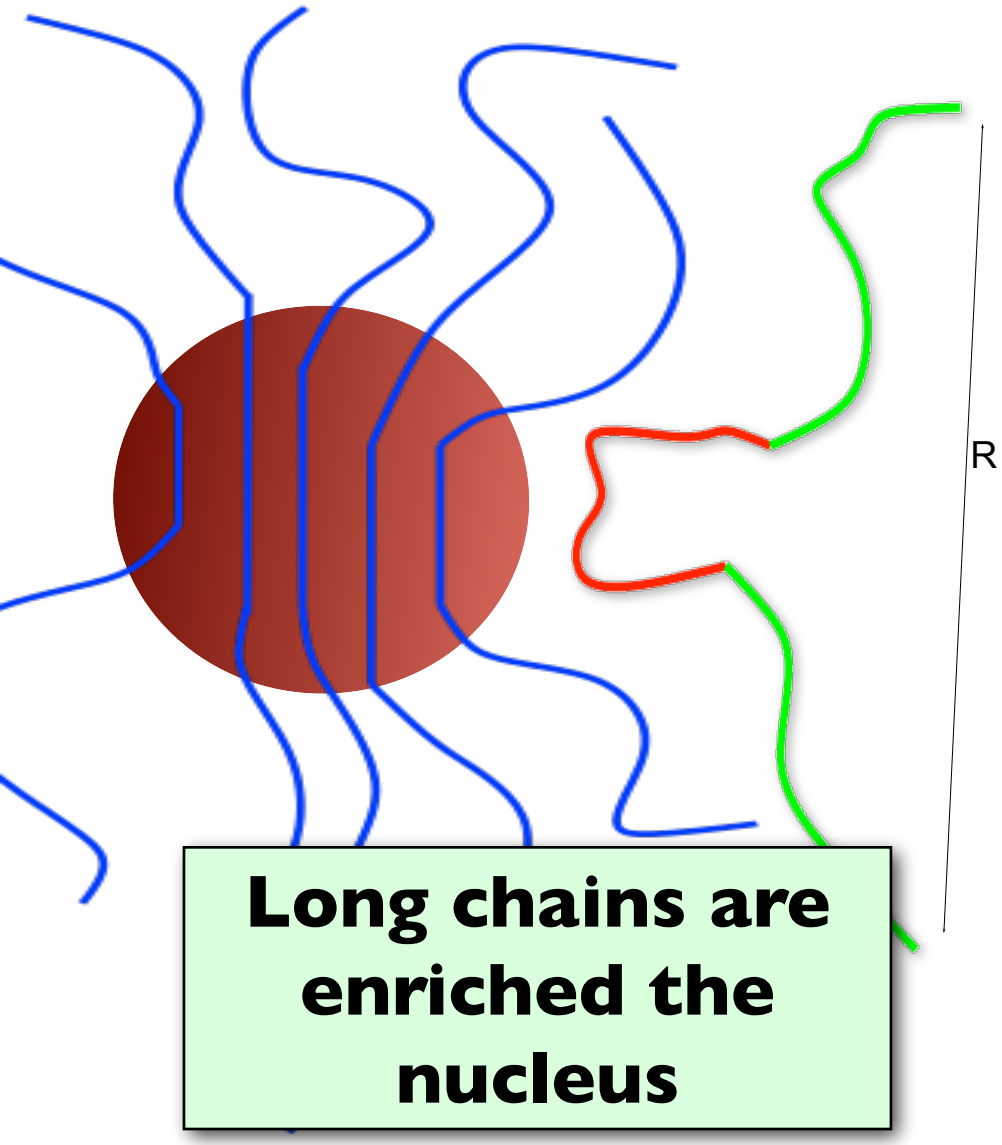
As computed by a molecular flow theory.

Flow imposes an average molecular strain, <RR>.

Monomer attachment rate: $k_i^+ \propto \exp(\Delta f_i)$

Graham and Olmsted, Phys. Rev. Lett. **115** 115707 (2009)

Influence of flow - chain deformation



Long chains are enriched the nucleus

As computed by a molecular flow theory.

Flow imposes an average molecular strain, <RR>.

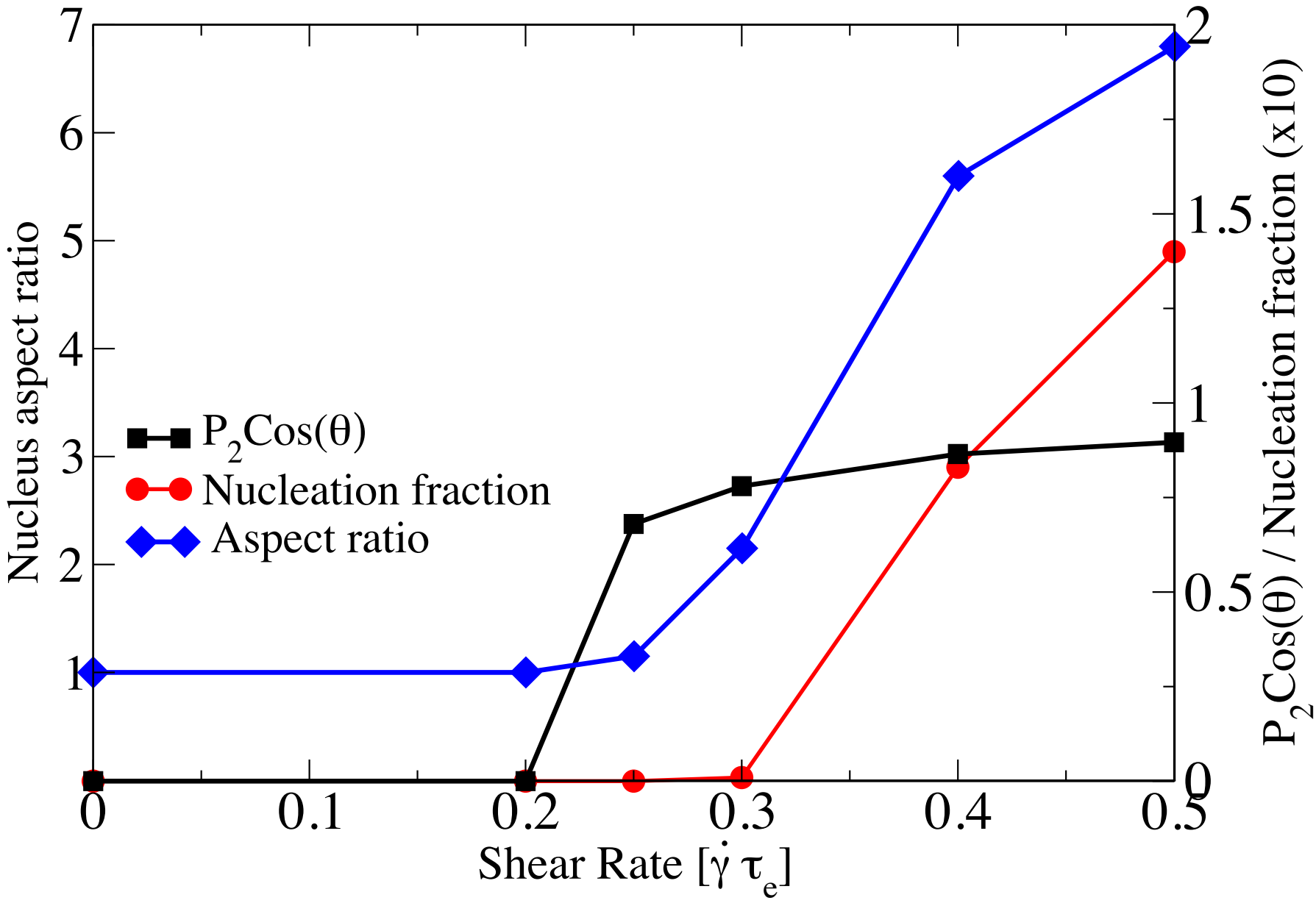
Monomer attachment rate: $k_i^+ \propto \exp(\Delta f_i)$

Free energy change on deformation: $\Delta f_i = \Gamma P_{2,K,i}$

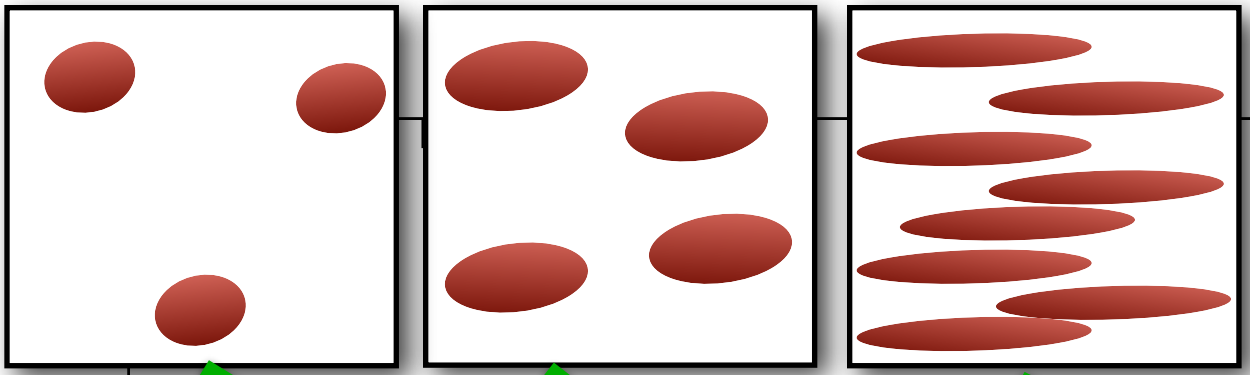
Nematic order

Graham and Olmsted, Phys. Rev. Lett. **115** 115707 (2009)

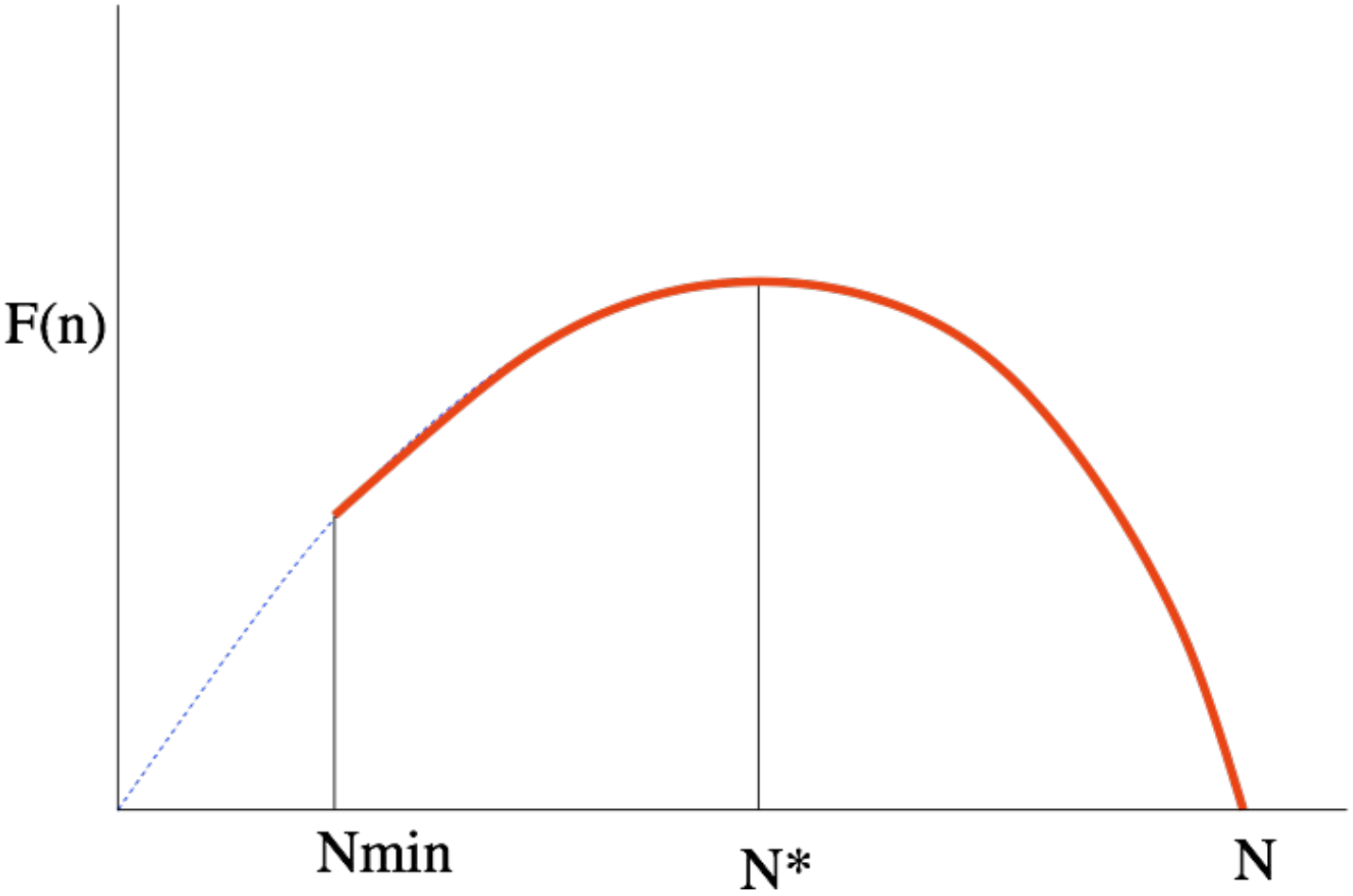
Effect of flow on nucleation



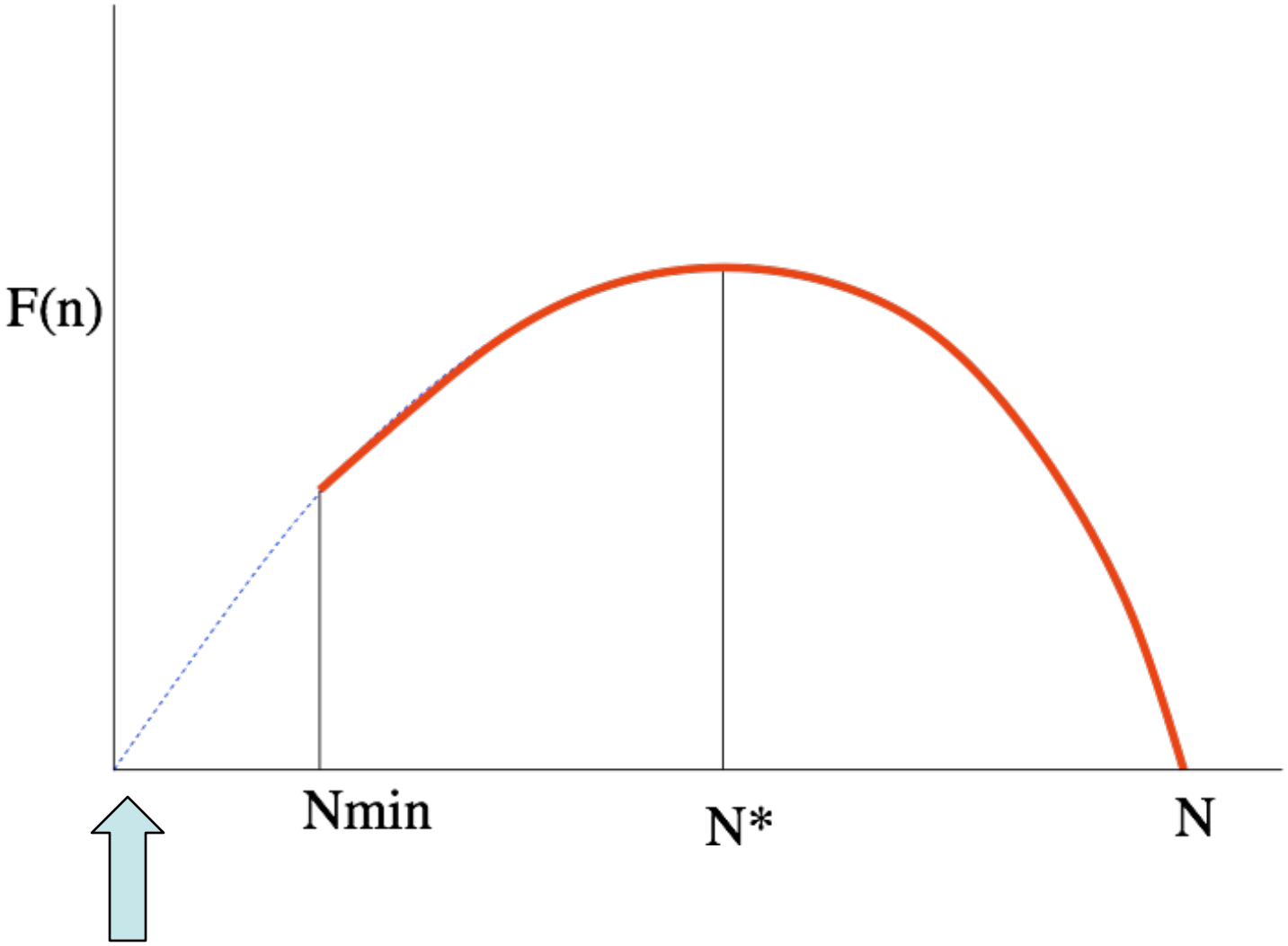
Effect of flow on nucleation



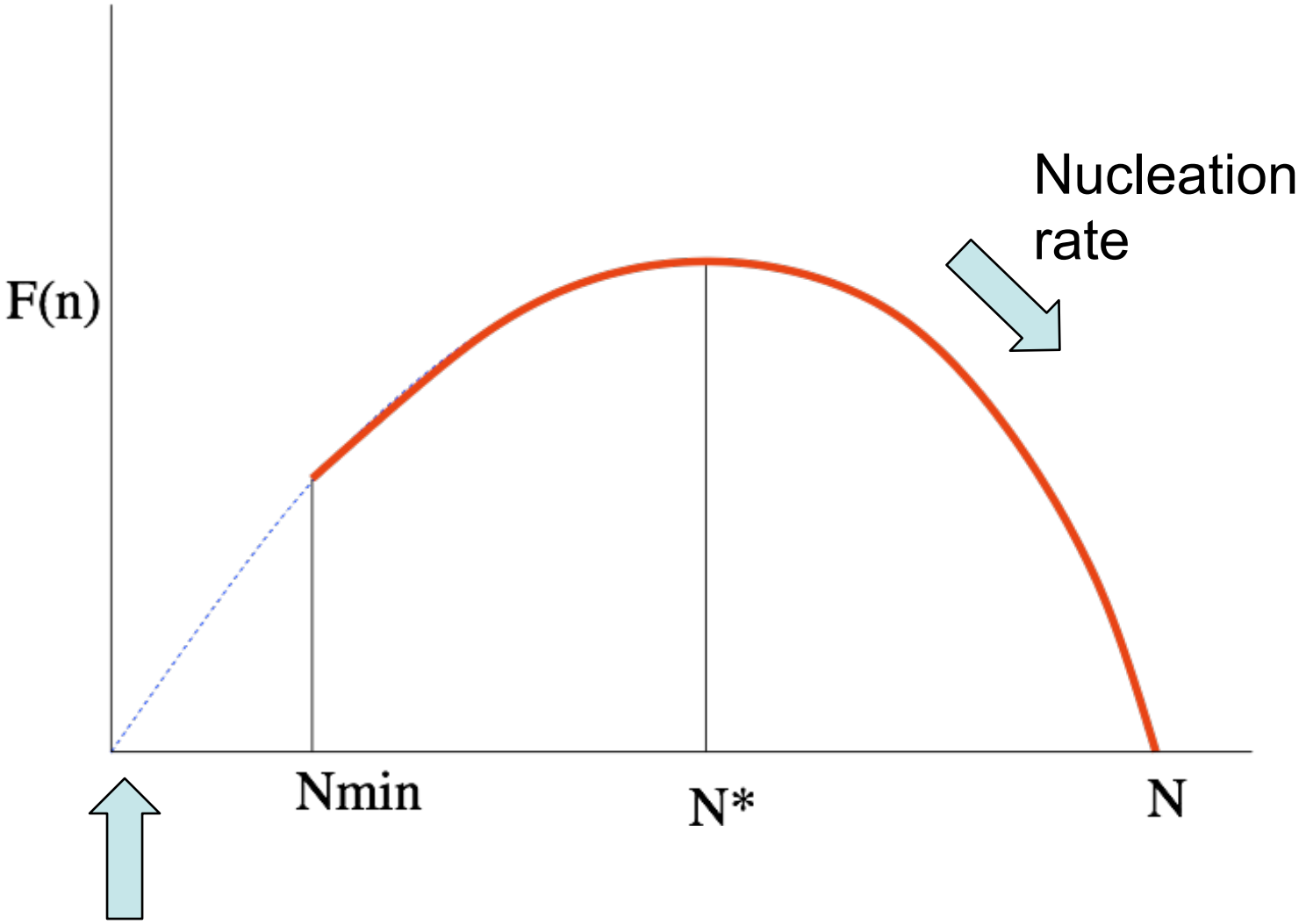
a) Faster nucleation simulation



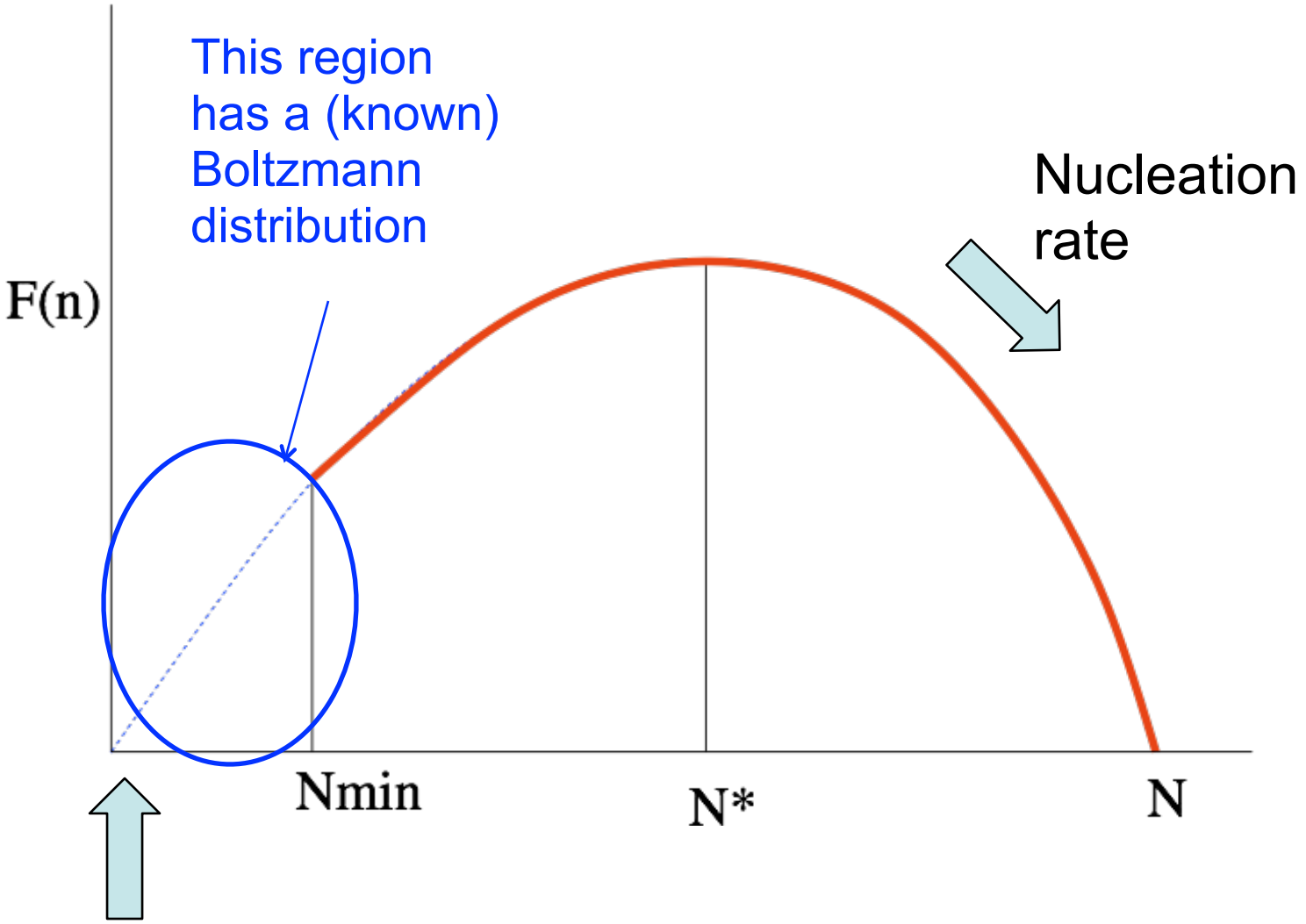
a) Faster nucleation simulation



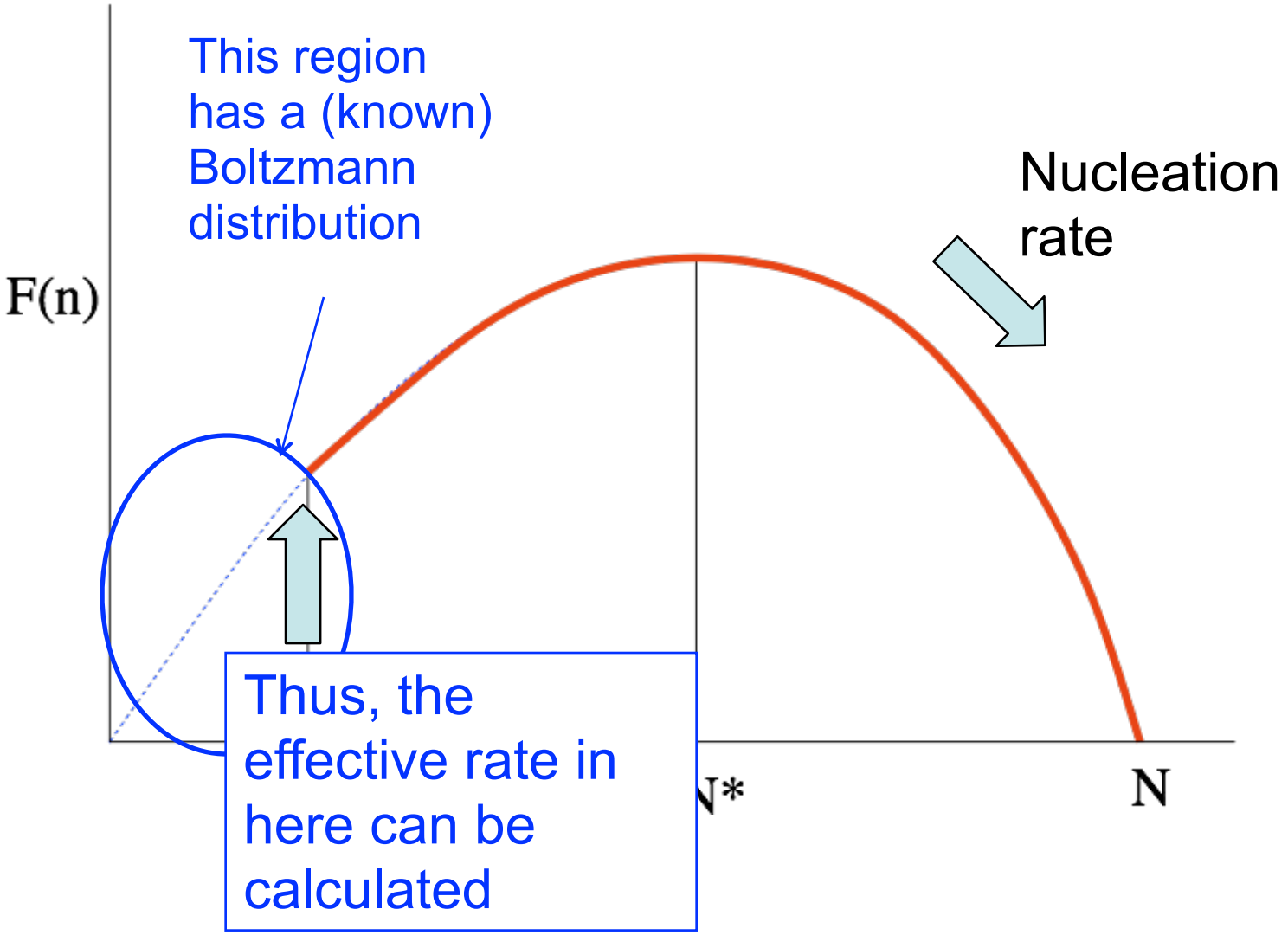
a) Faster nucleation simulation



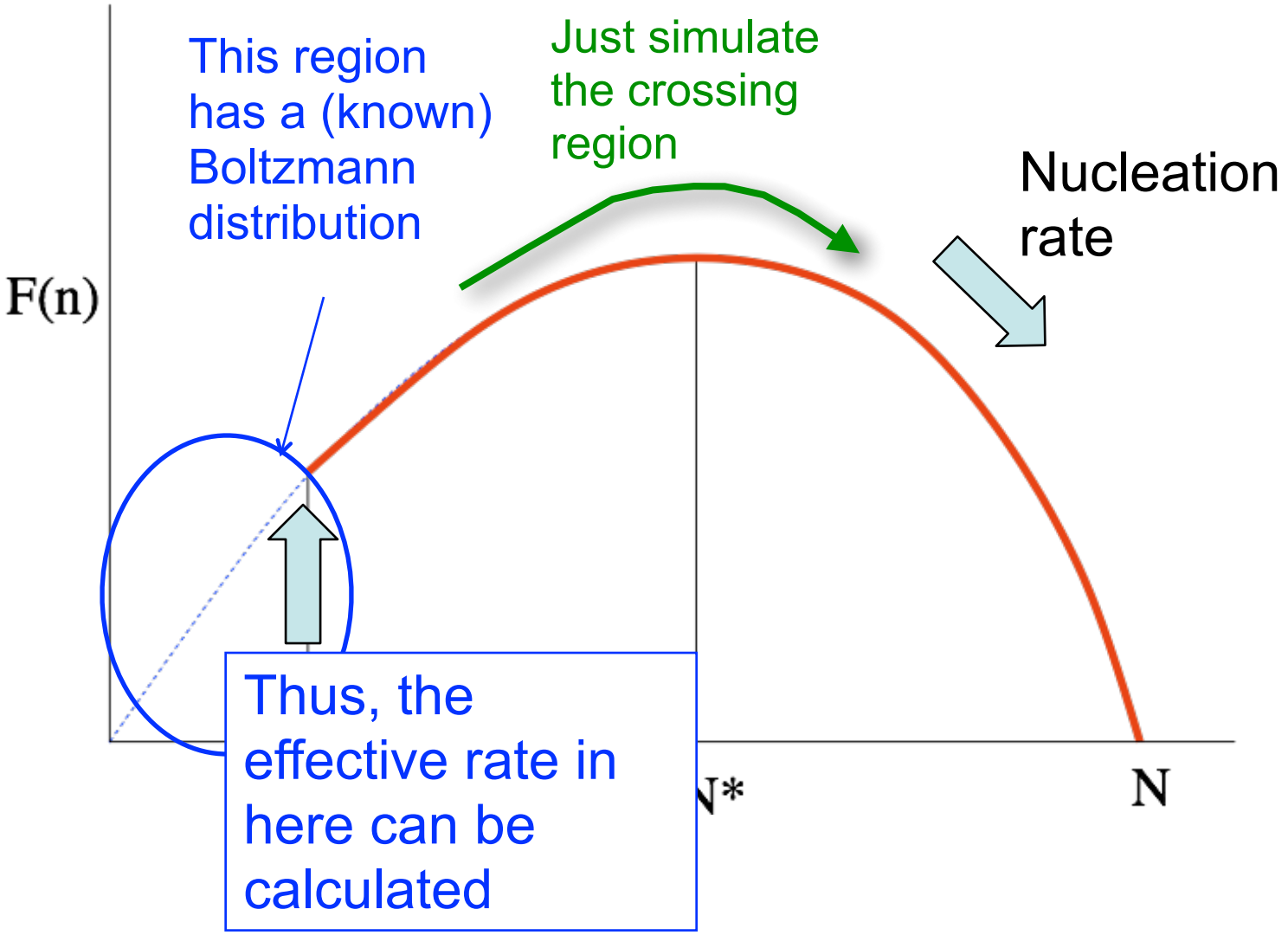
a) Faster nucleation simulation



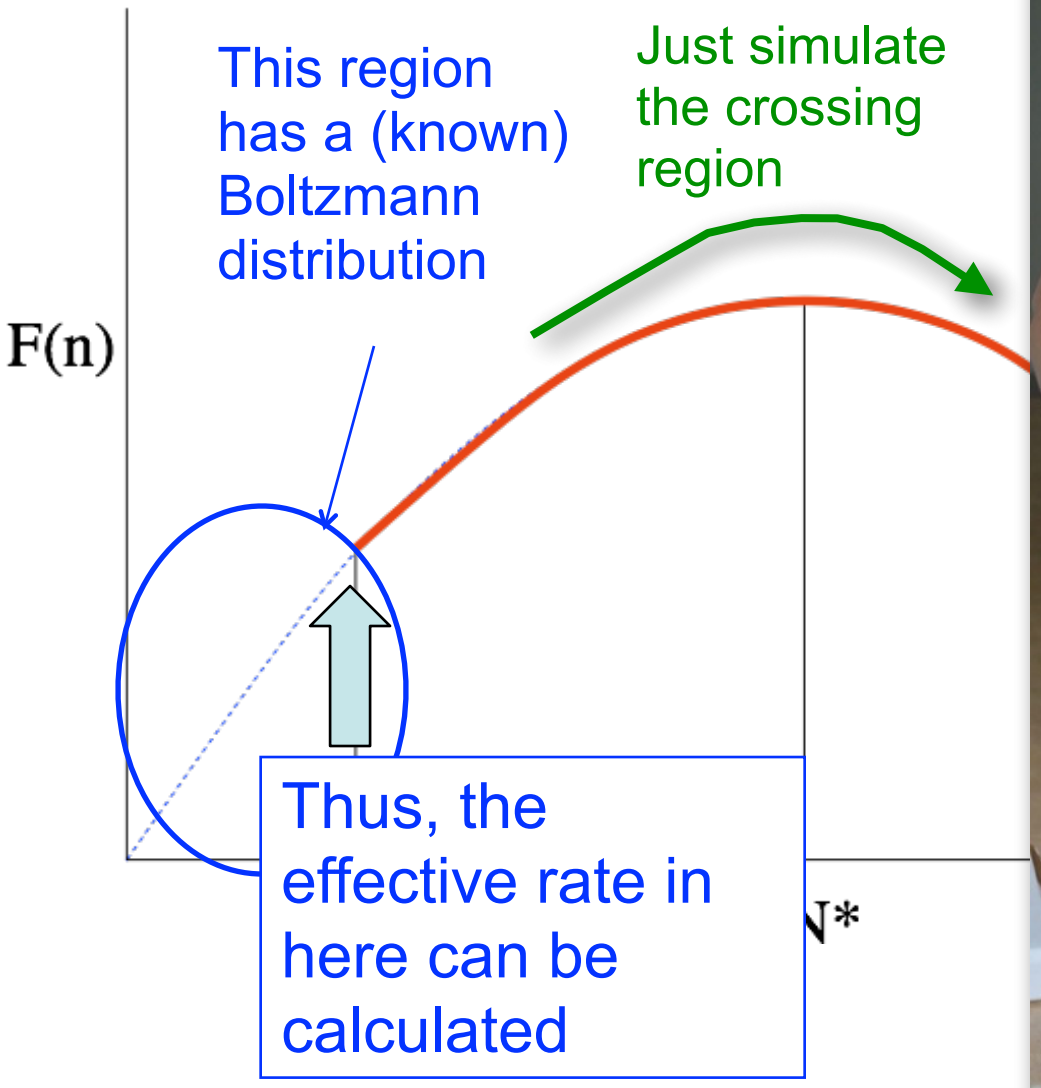
a) Faster nucleation simulation



a) Faster nucleation simulation



a) Faster nucleation simulation



a) Faster nucleation simulation

This region has a (known) Boltzmann distribution

Nucleation rate

F(n)

N*

N

Thus, the effective rate in here can be calculated

a) Faster nucleation simulation

This region has a (known) Boltzmann distribution

Nucleation rate

F(n)

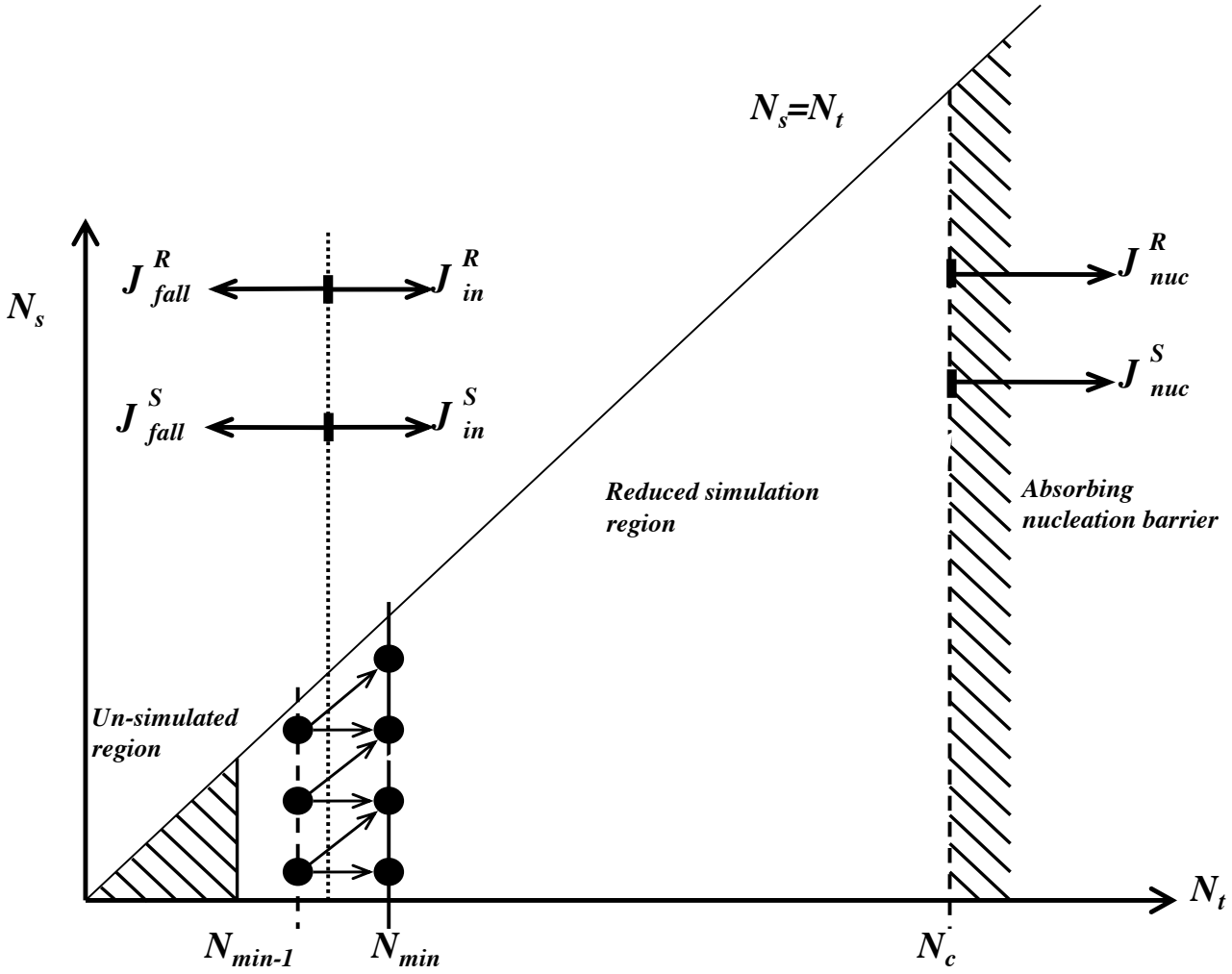
N*

N

Thus, the effective rate in here can be calculated

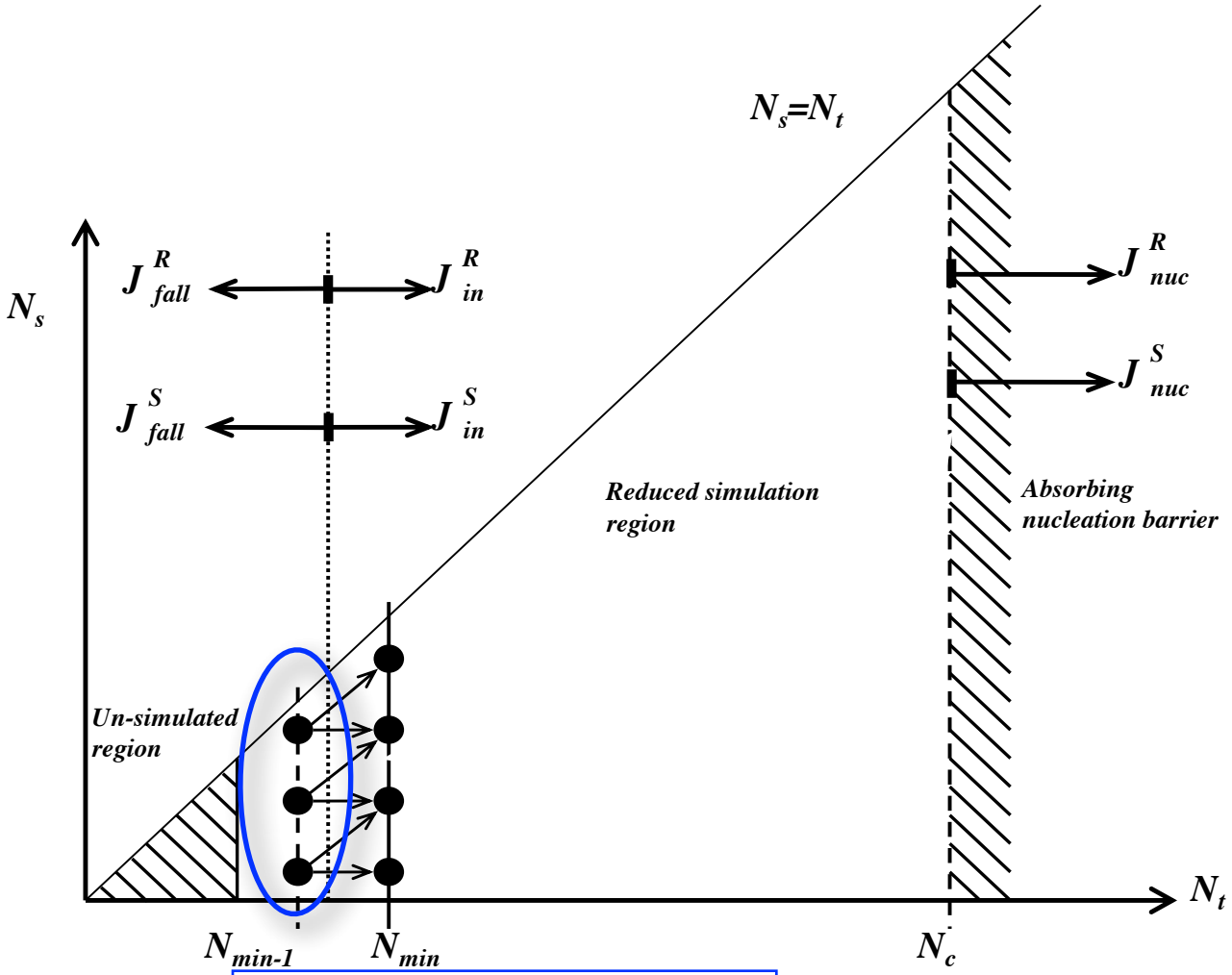
Only need to simulate the reduced barrier region (much cheaper!)

Generalisation to higher dimensions



Jolley and Graham, J. Chem. Phys **134** (16) 164901 (2011)

Generalisation to higher dimensions

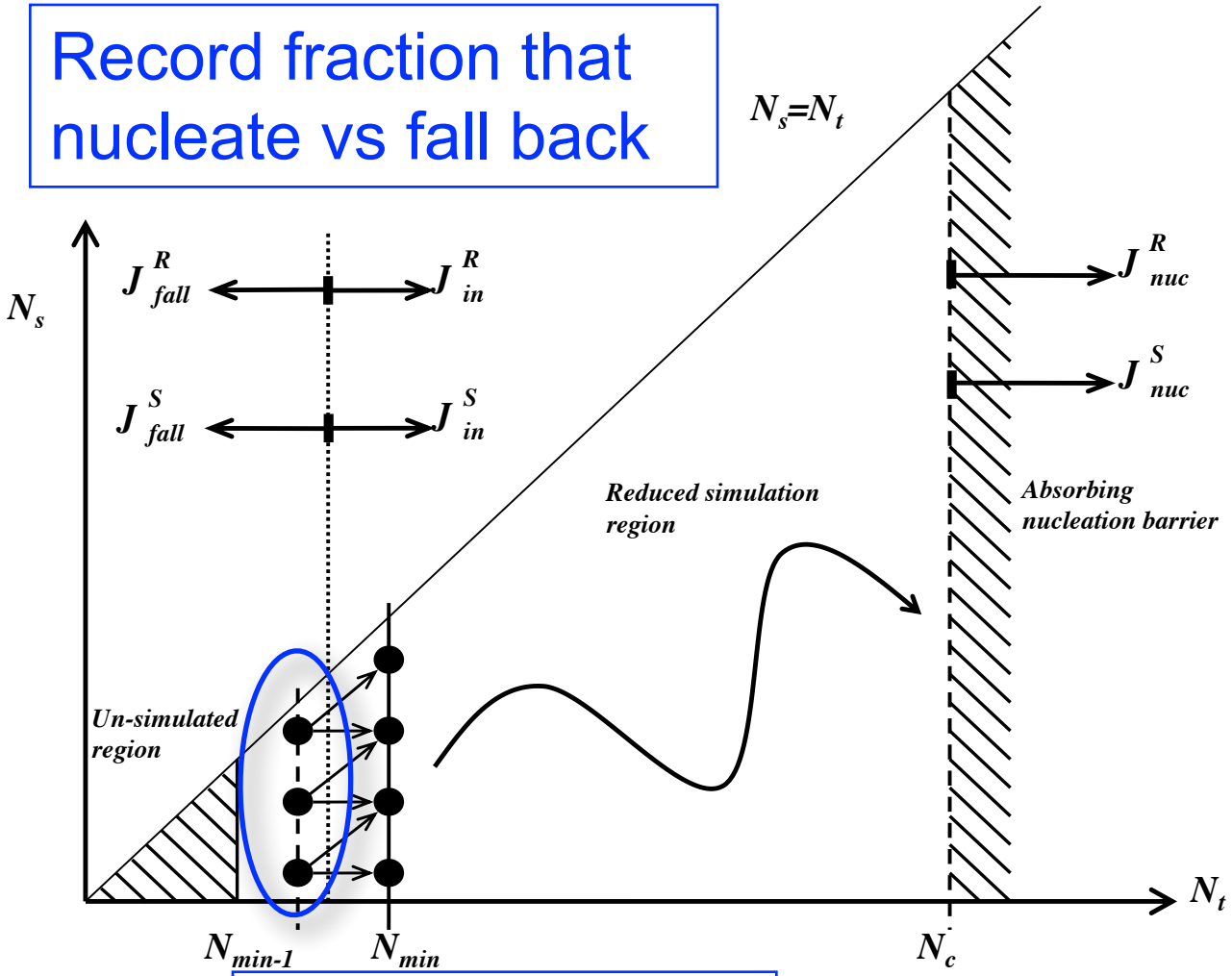


Inject nuclei with a Boltzmann distribution

Jolley and Graham, J. Chem. Phys **134** (16) 164901 (2011)

Generalisation to higher dimensions

Record fraction that nucleate vs fall back

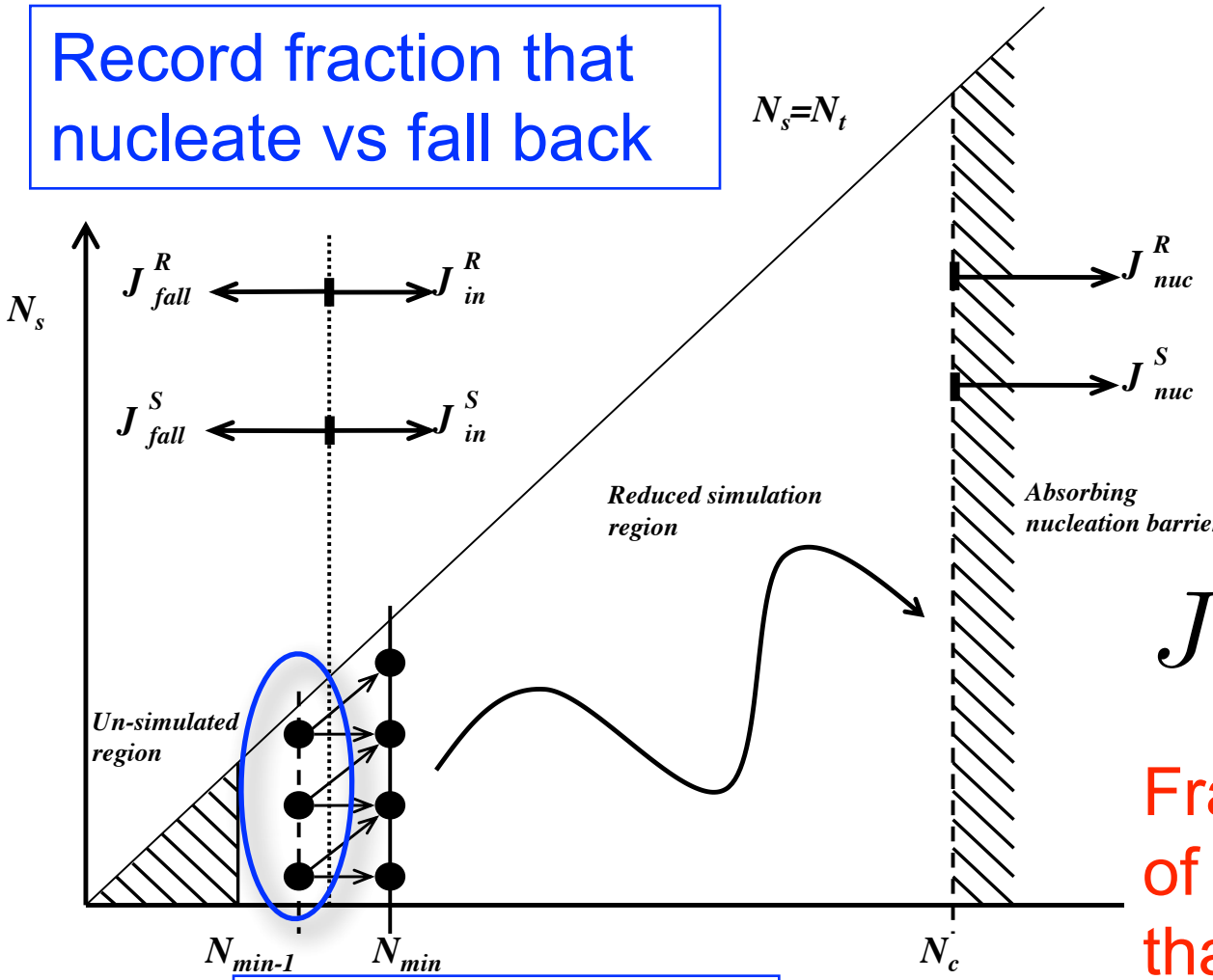


Inject nuclei with a Boltzmann distribution

Jolley and Graham, J. Chem. Phys **134** (16) 164901 (2011)

Generalisation to higher dimensions

Record fraction that nucleate vs fall back



Inject nuclei with a Boltzmann distribution

Nucleation rate

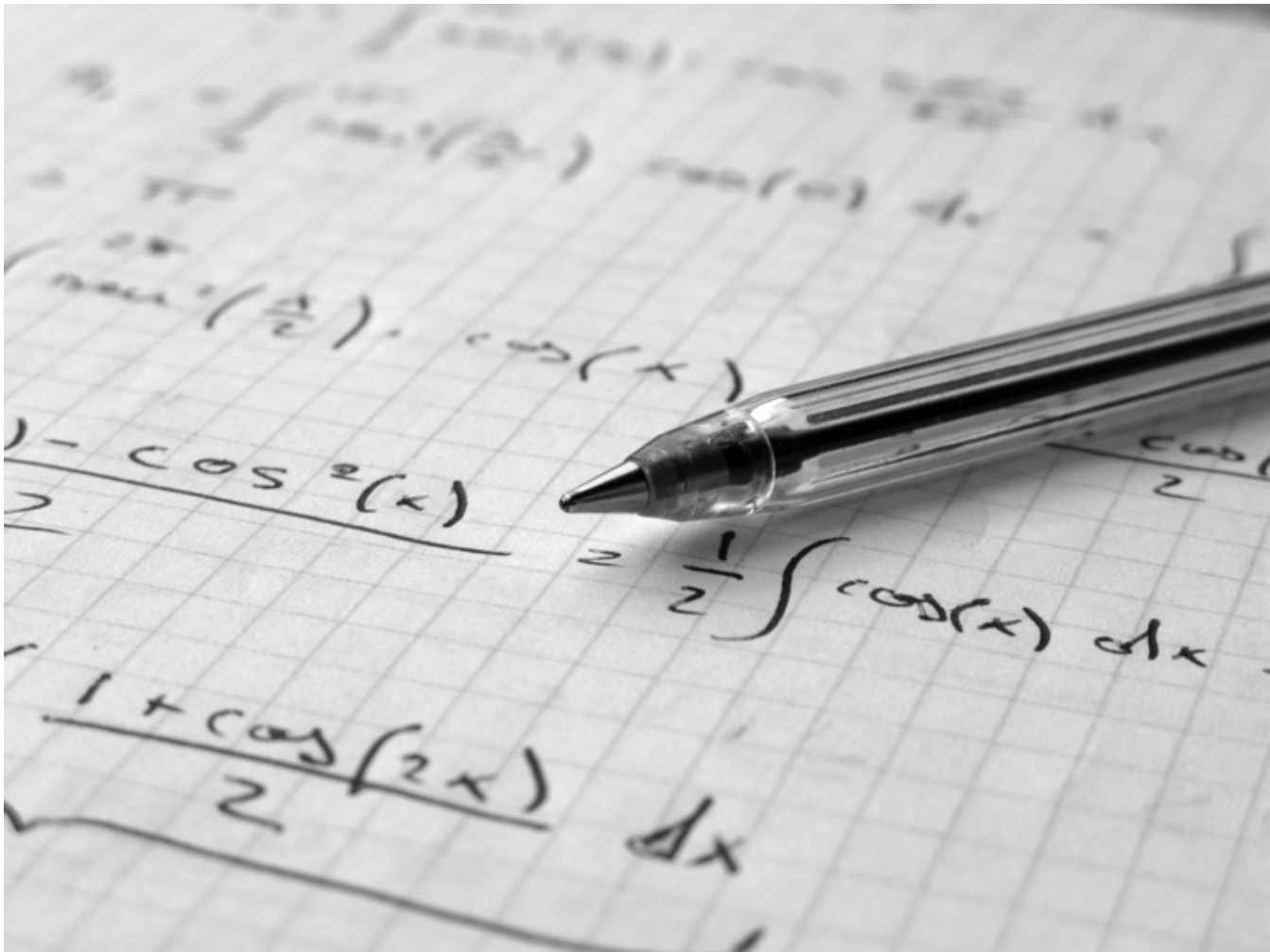
$$J_{nuc} = \phi J_{in}^{real}$$

Fraction of runs that nucleate

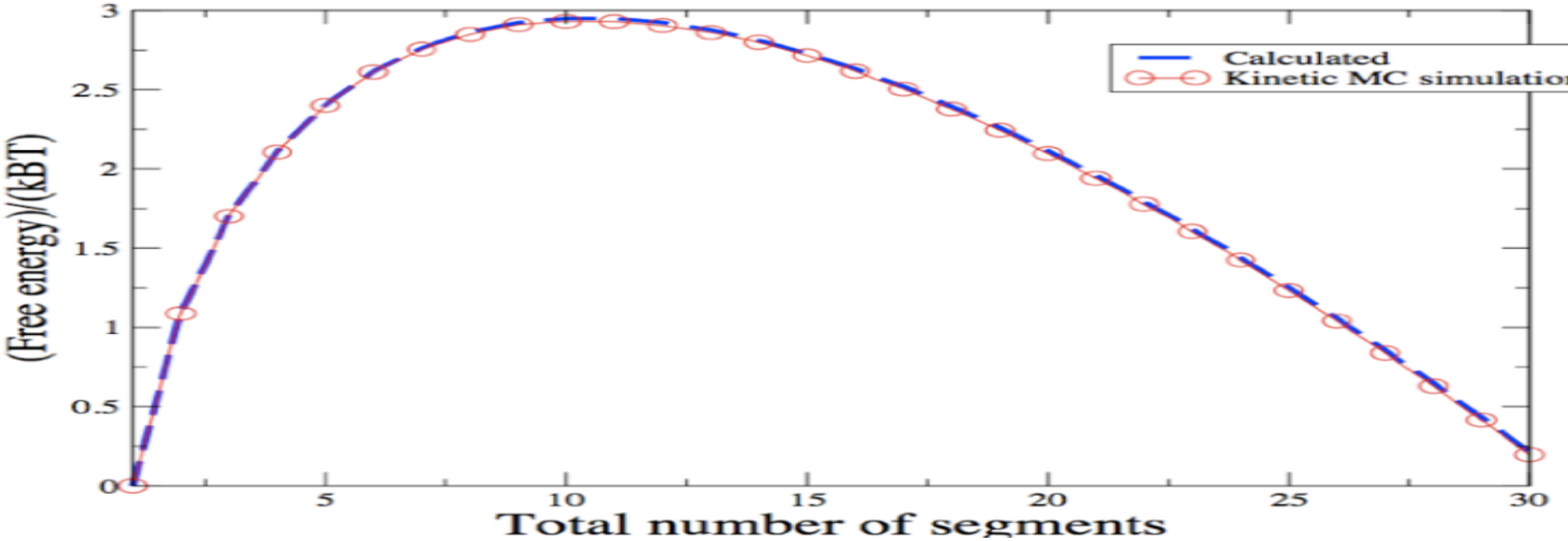
Injection rate for the full system

Jolley and Graham, J. Chem. Phys **134** (16) 164901 (2011)

Continuum model
(nearly analytic)

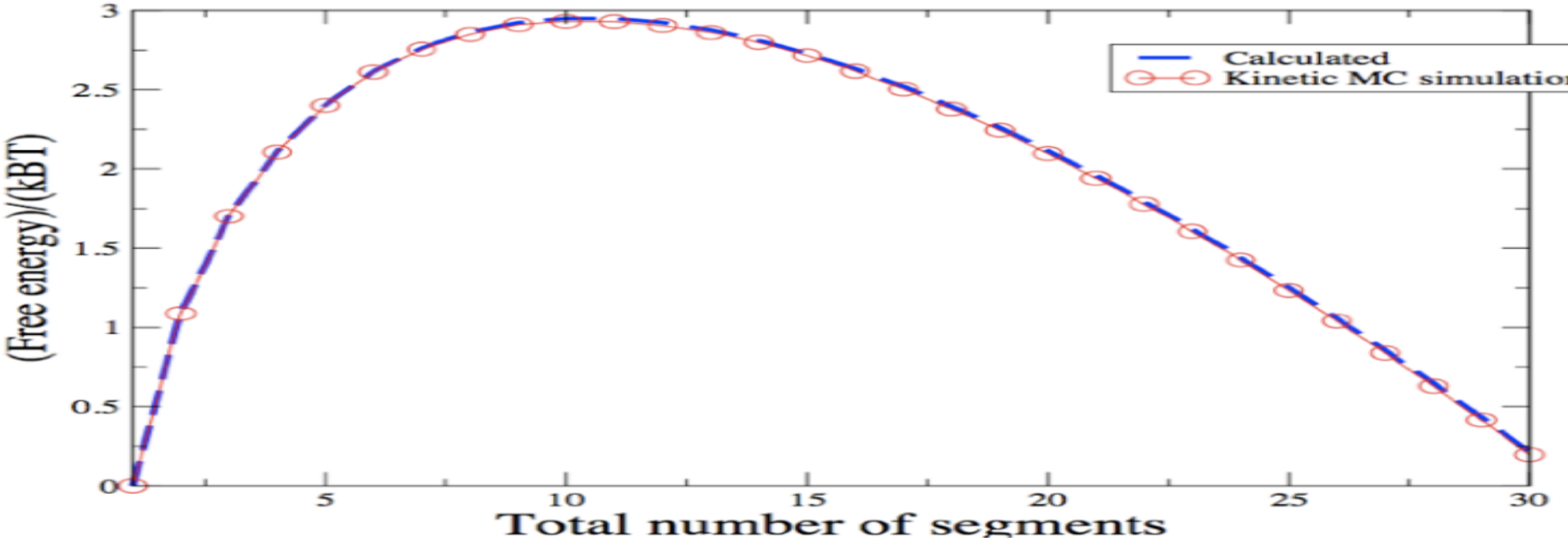


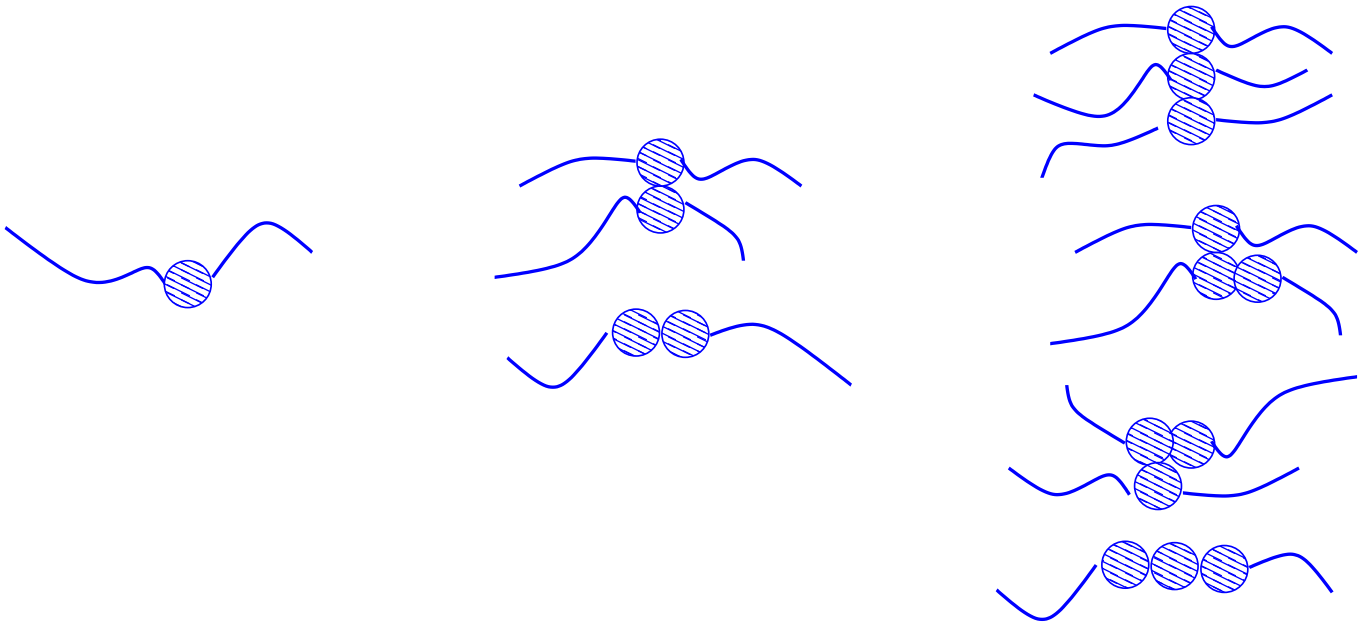
Projecting the GO model to a 1D system



Hamer, Wattis and Graham, Soft Matter **8,** 11396 (2012)

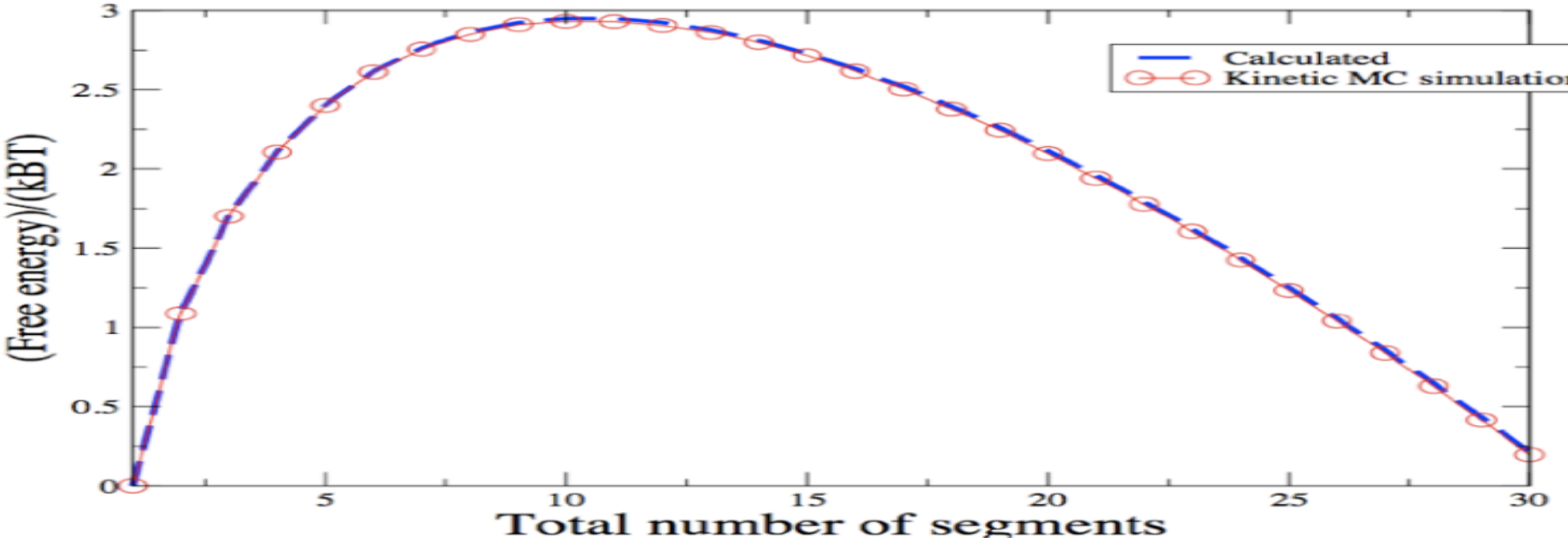
Projecting the GO model to a 1D system

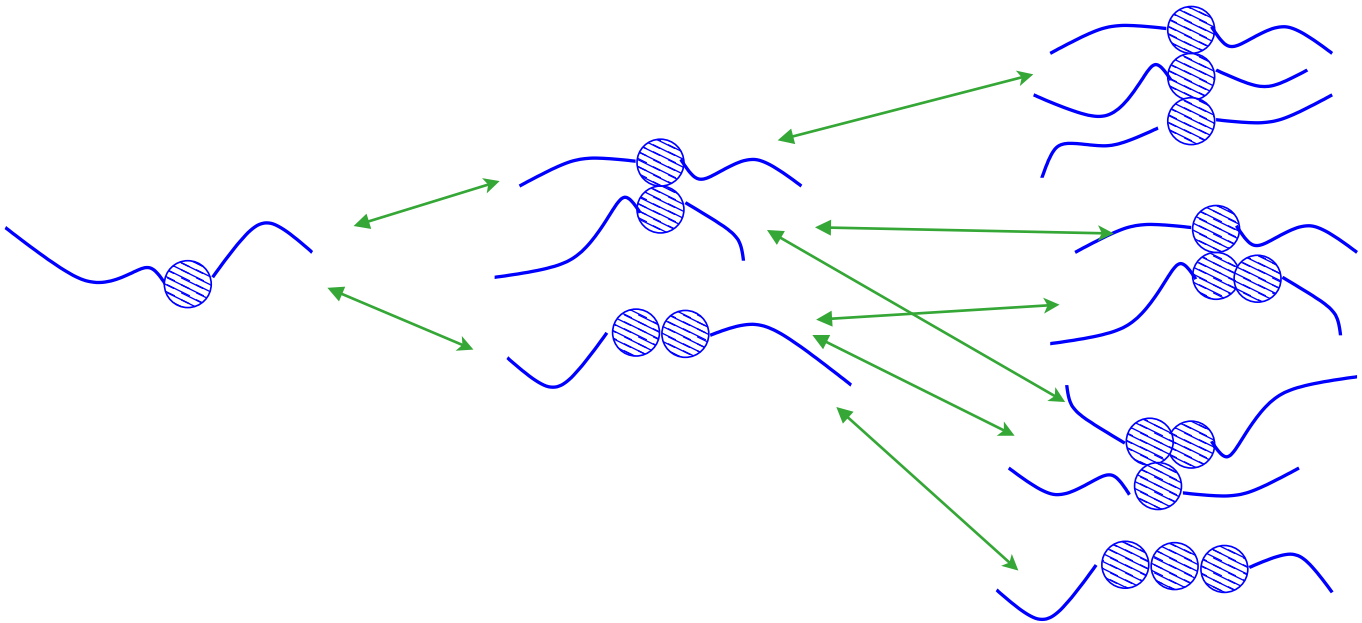




Hamer, Wattis and Graham, Soft Matter **8,** 11396 (2012)

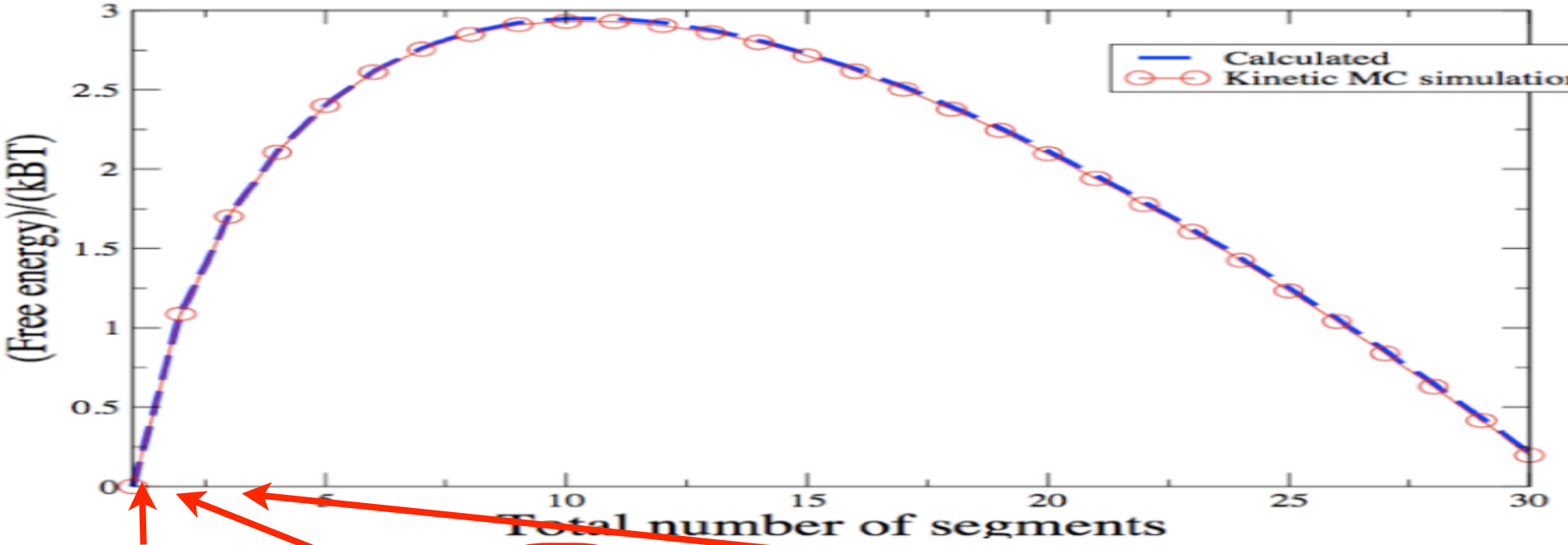
Projecting the GO model to a 1D system

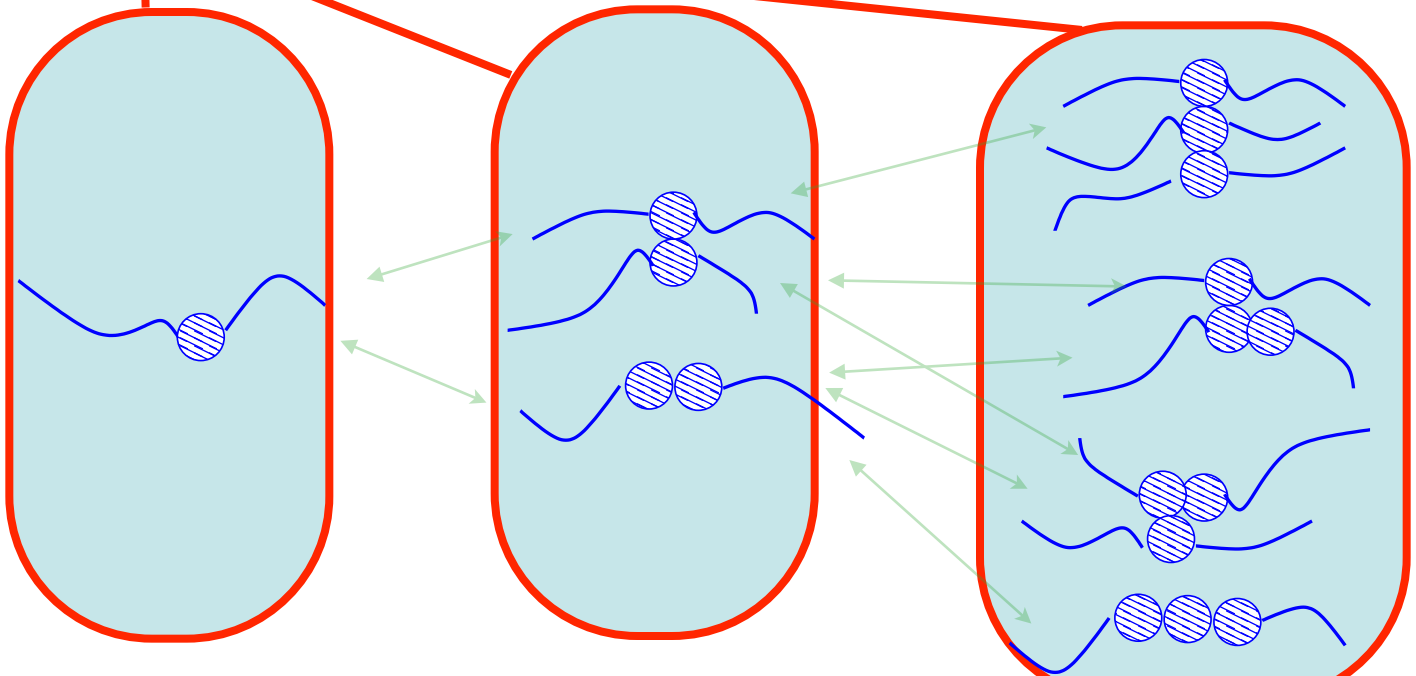




Hamer, Wattis and Graham, Soft Matter **8,** 11396 (2012)

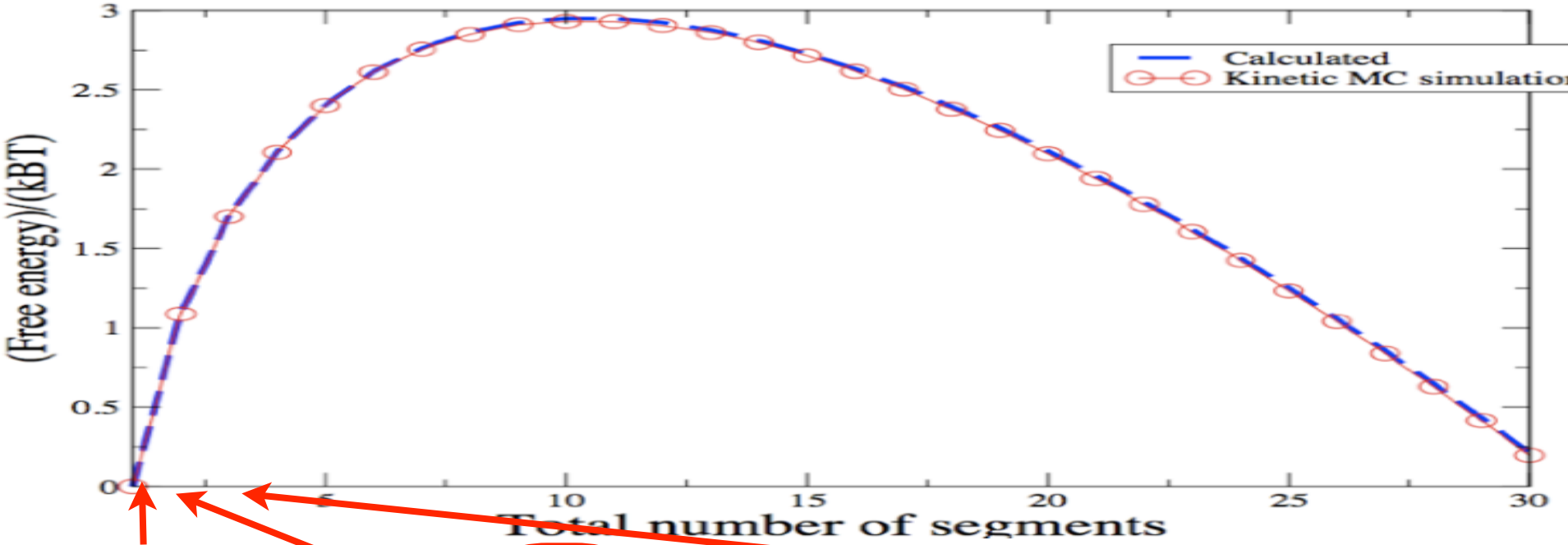
Projecting the GO model to a 1D system

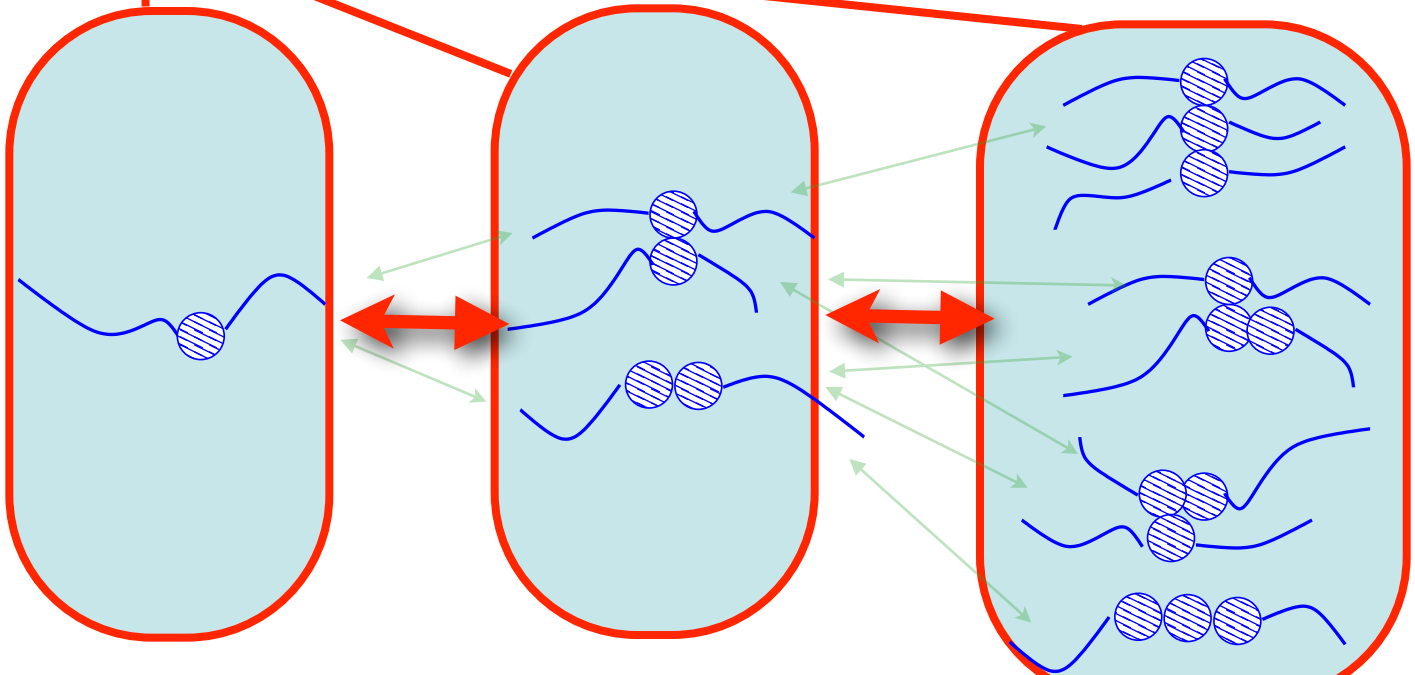




Hamer, Wattis and Graham, Soft Matter **8,** 11396 (2012)

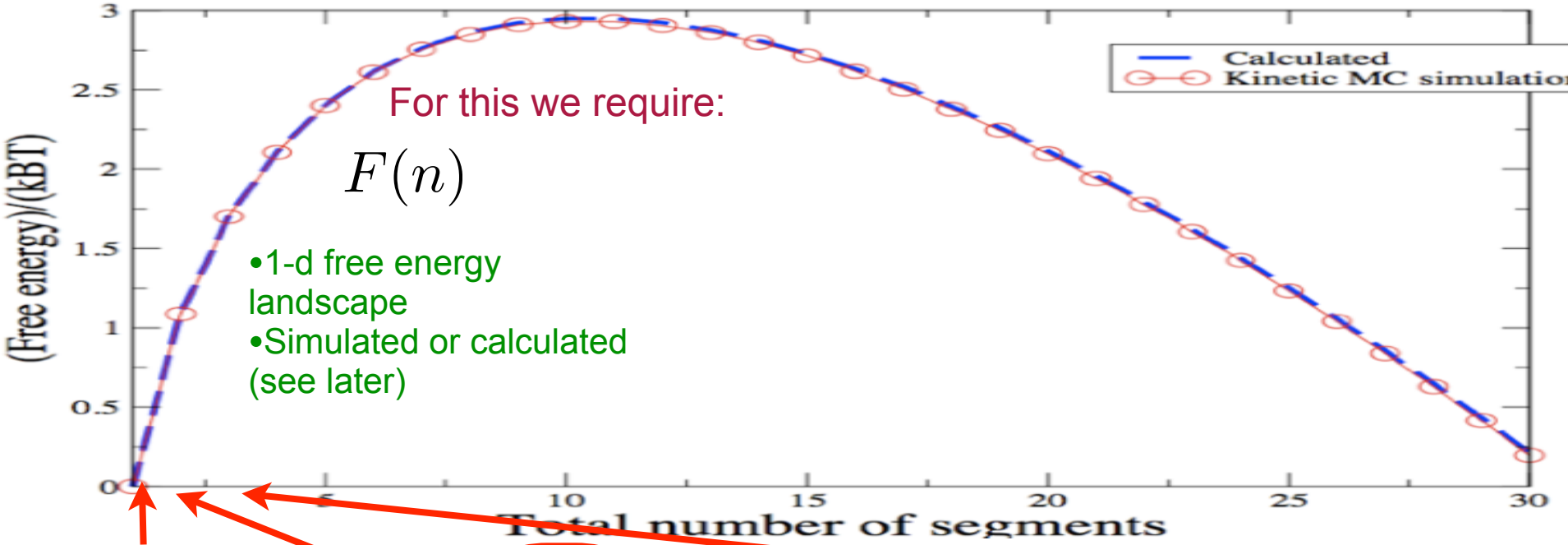
Projecting the GO model to a 1D system





Hamer, Wattis and Graham, Soft Matter **8,** 11396 (2012)

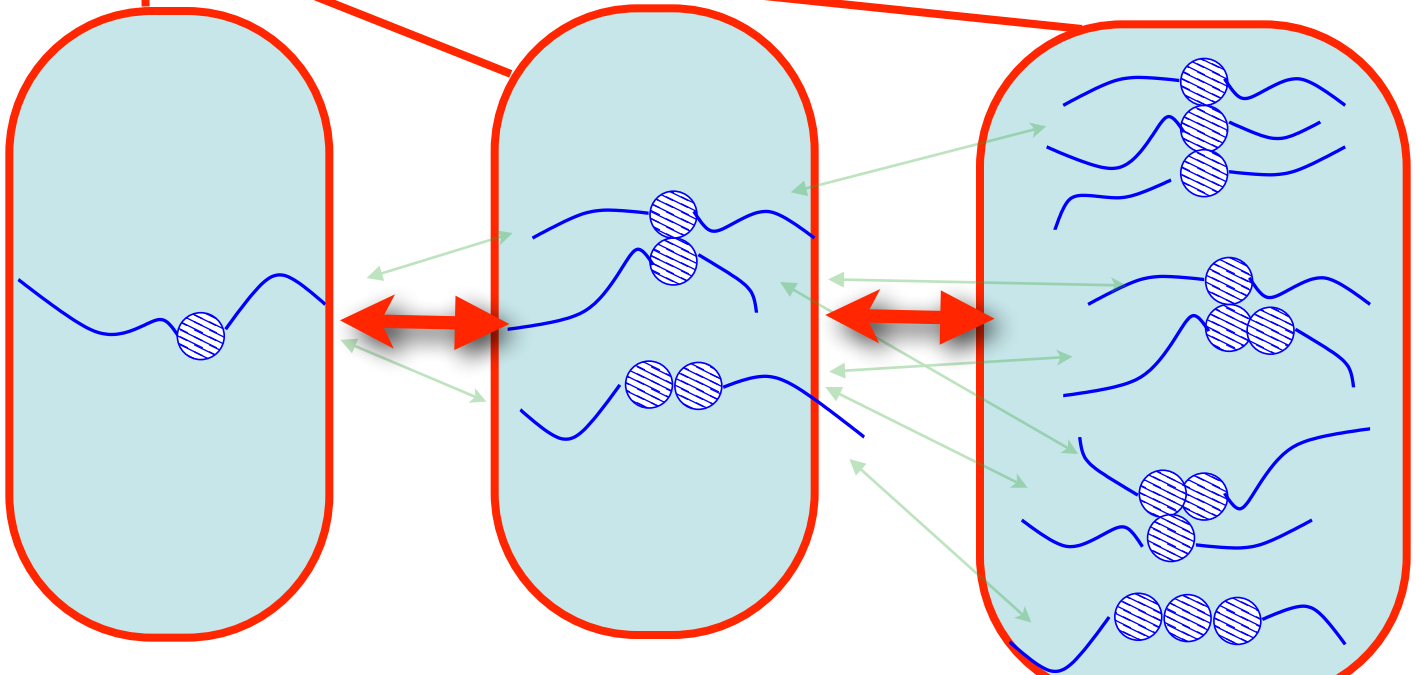
Projecting the GO model to a 1D system



For this we require:

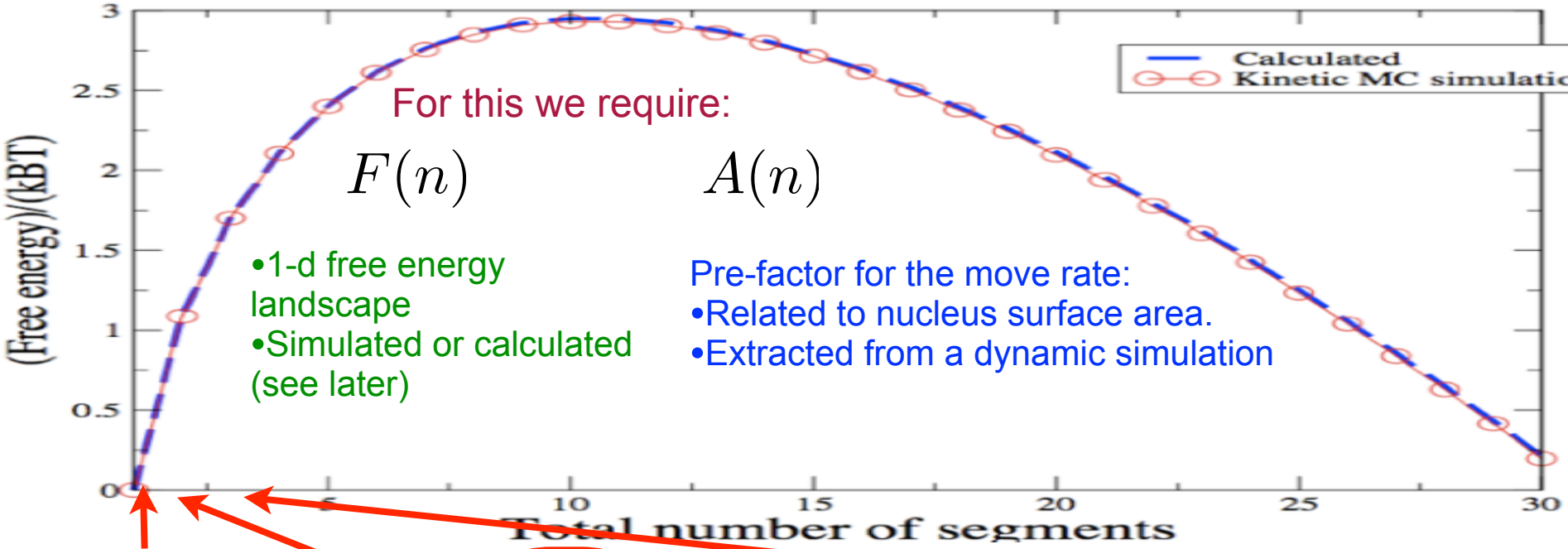
$$F(n)$$

- 1-d free energy landscape
- Simulated or calculated (see later)



Hamer, Wattis and Graham, Soft Matter **8,** 11396 (2012)

Projecting the GO model to a 1D system

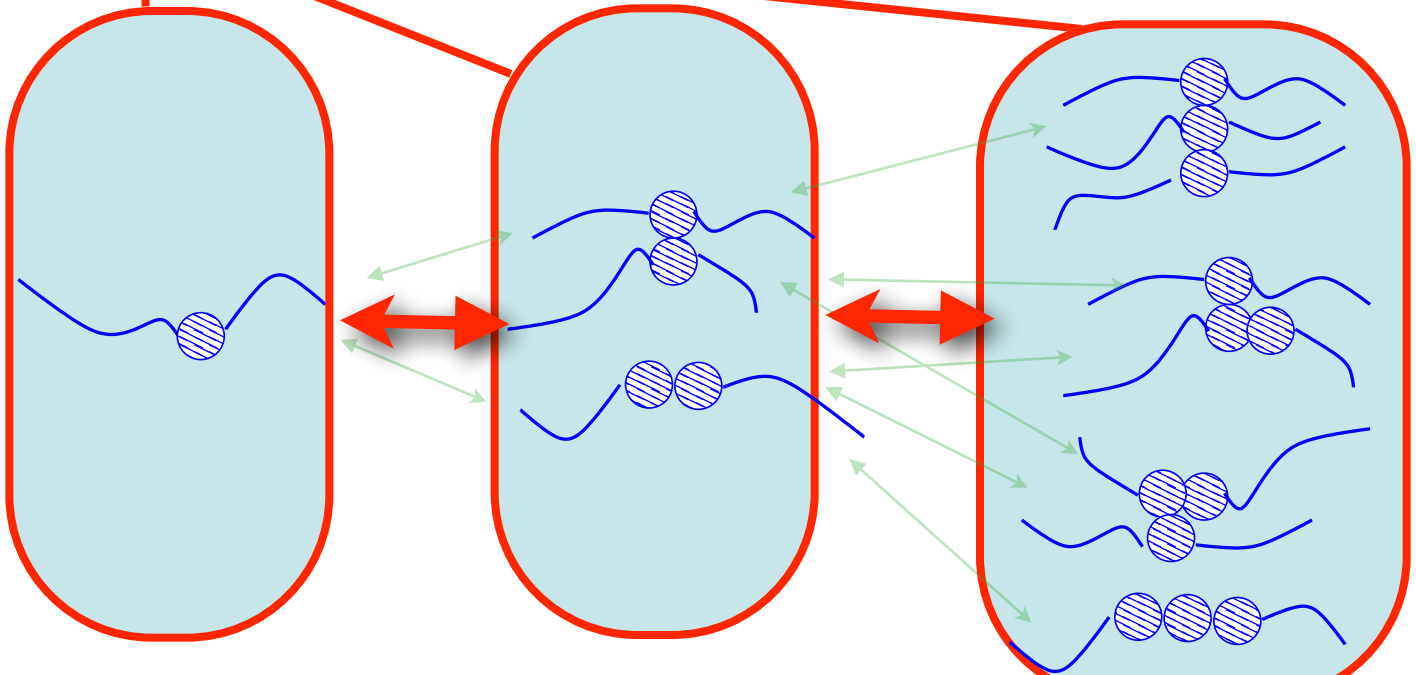


For this we require:

$F(n)$ $A(n)$

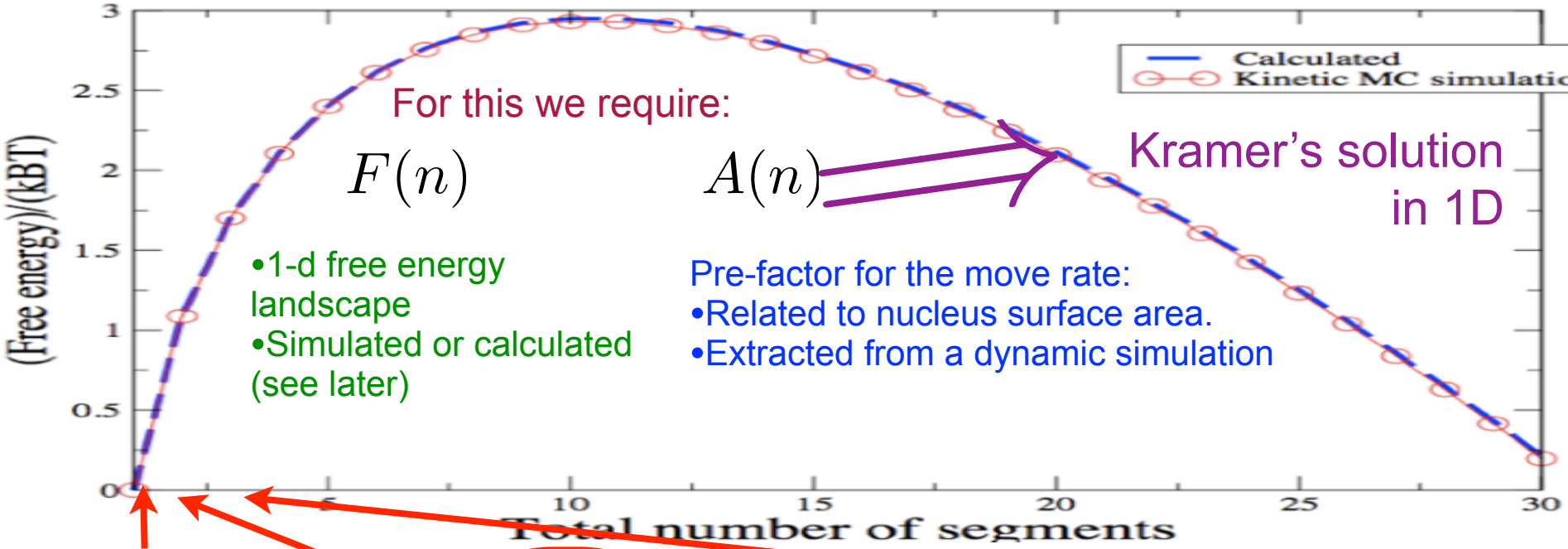
- 1-d free energy landscape
- Simulated or calculated (see later)

Pre-factor for the move rate:
- Related to nucleus surface area.
- Extracted from a dynamic simulation



Hamer, Wattis and Graham, Soft Matter **8,** 11396 (2012)

Projecting the GO model to a 1D system



For this we require:

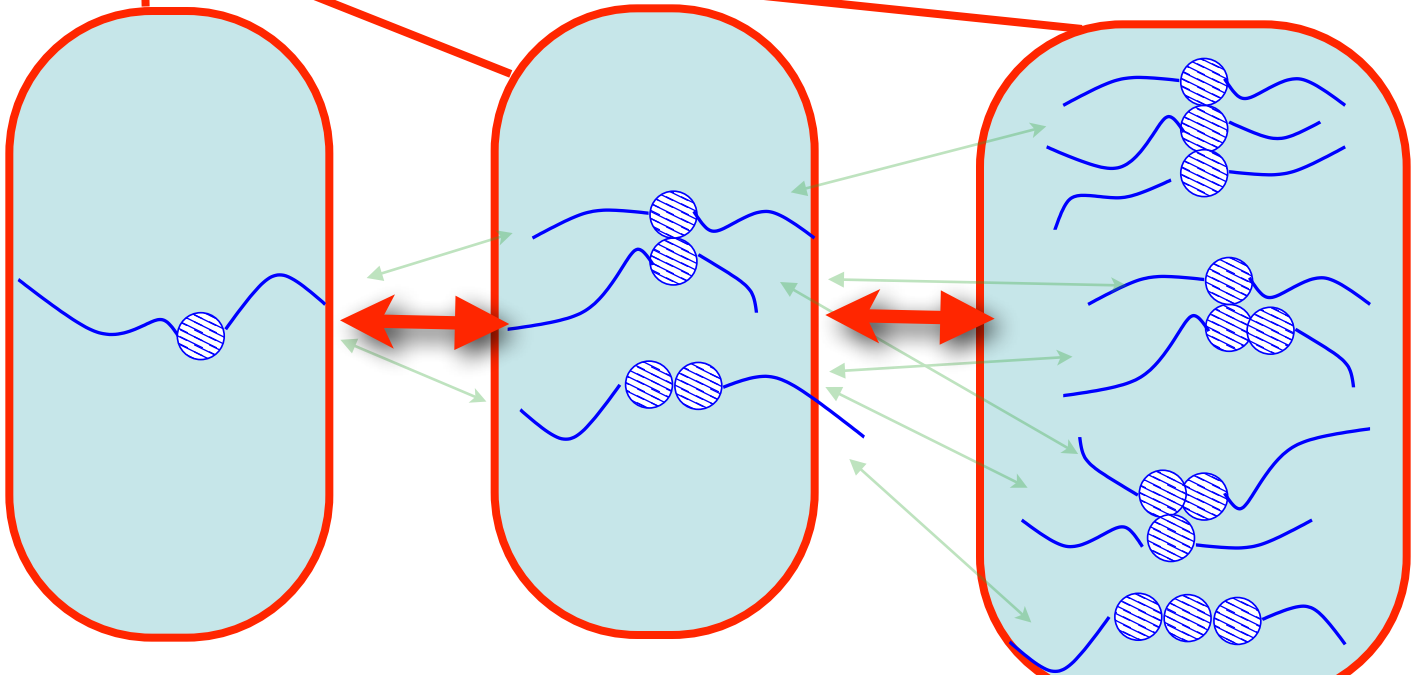
$F(n)$

$A(n)$

Kramer's solution in 1D

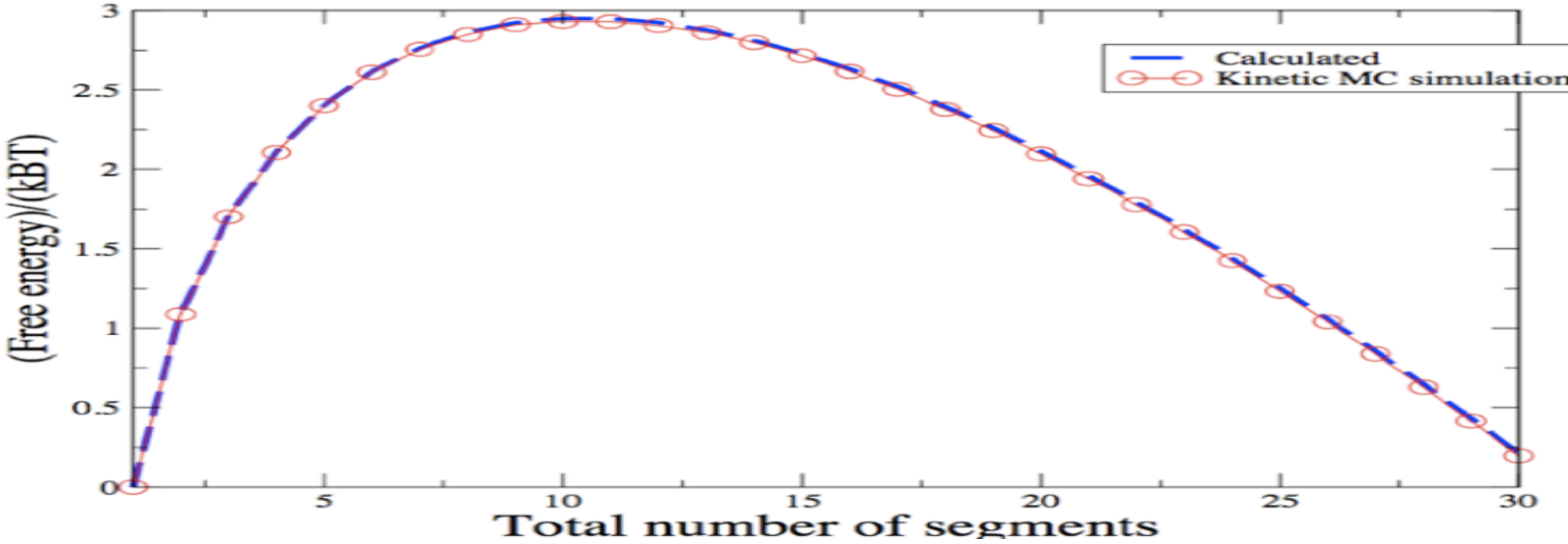
- 1-d free energy landscape
- Simulated or calculated (see later)

Pre-factor for the move rate:
- Related to nucleus surface area.
- Extracted from a dynamic simulation

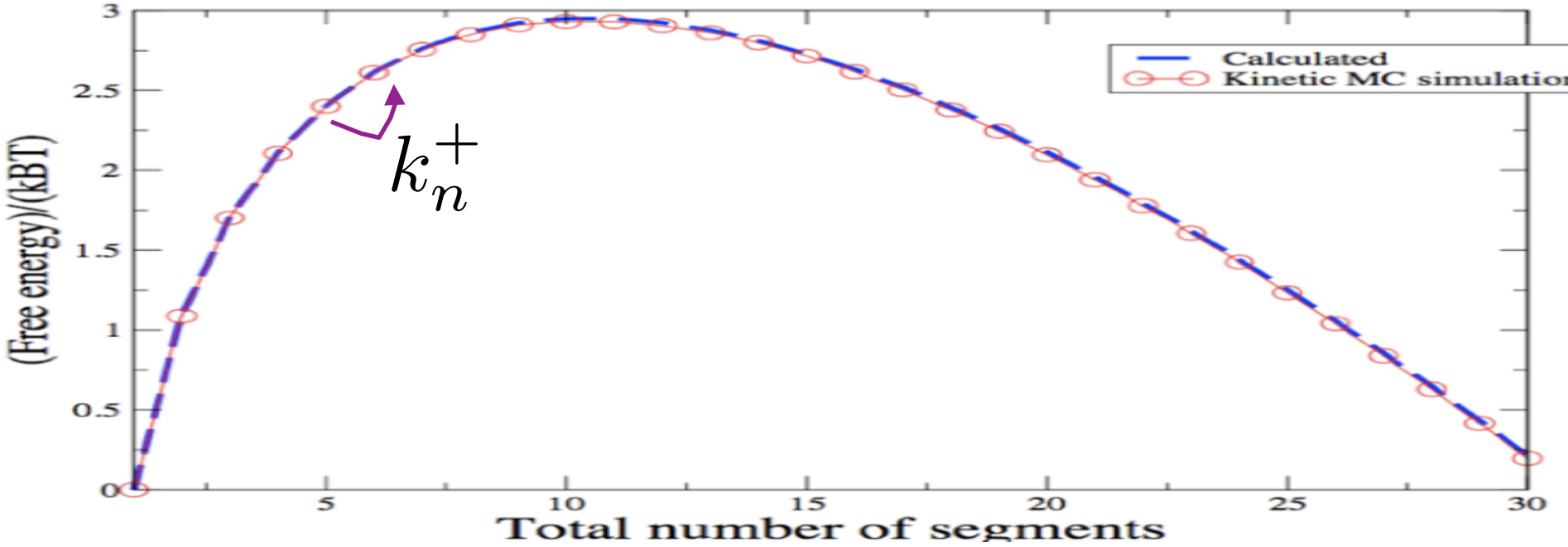


Hamer, Wattis and Graham, Soft Matter **8,** 11396 (2012)

Projecting the GO model to a 1D system

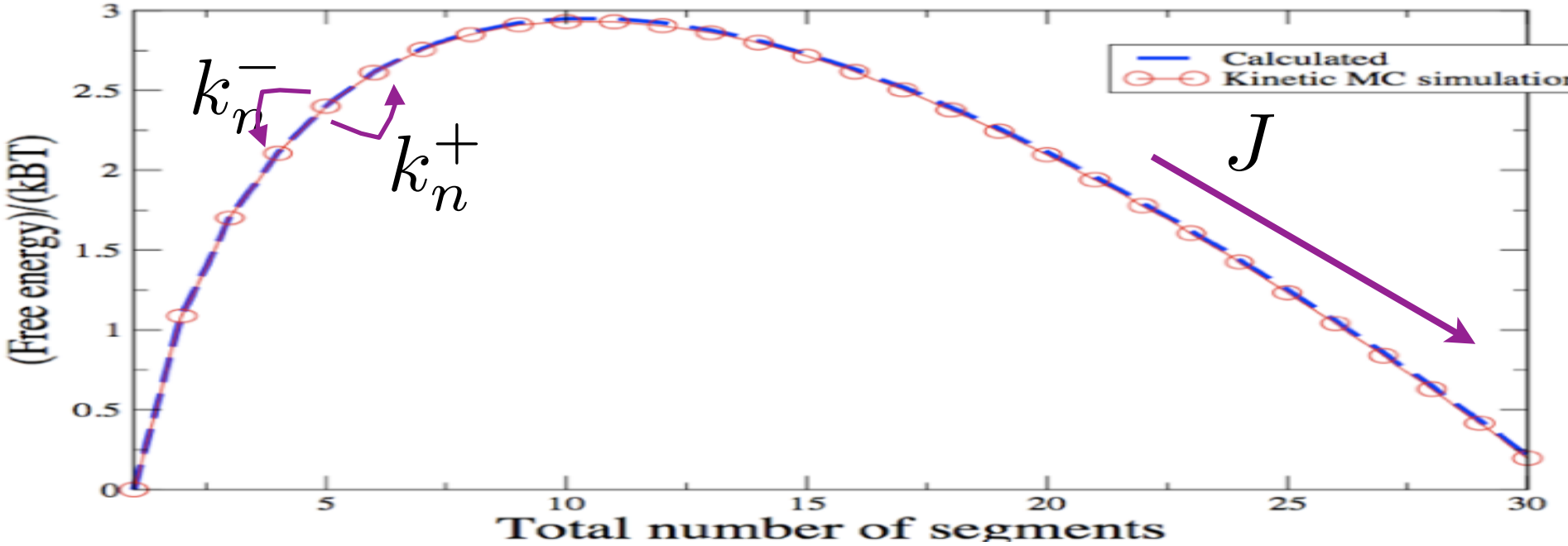


Projecting the GO model to a 1D system



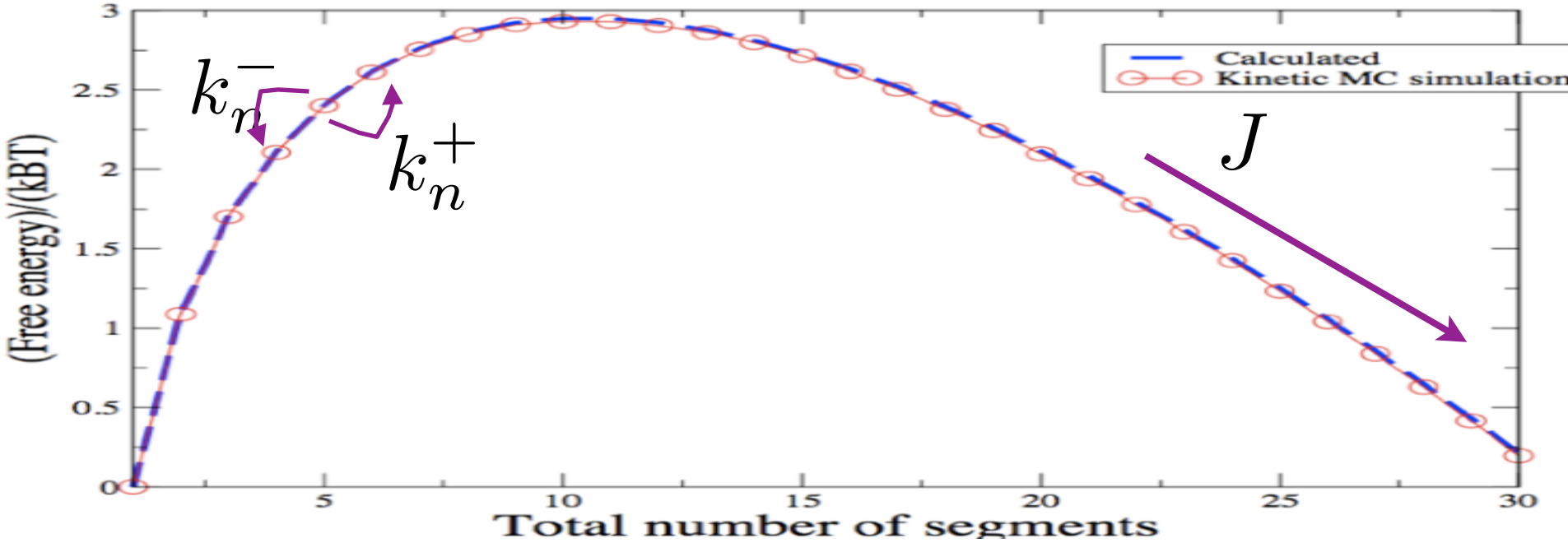
$$k_n^+ = A(n)\exp(-\Delta F(n))$$

Projecting the GO model to a 1D system



$$k_n^+ = A(n)\exp(-\Delta F(n)) \qquad k_n^- = A(n-1)$$

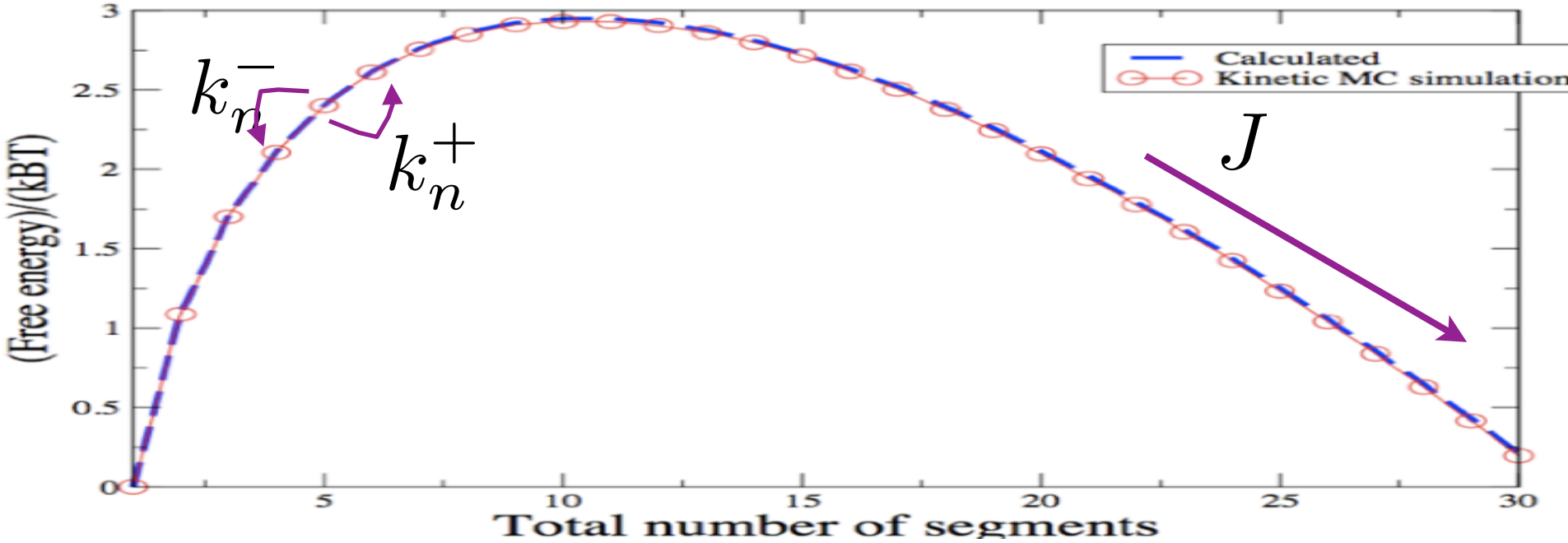
Projecting the GO model to a 1D system



$$k_n^+ = A(n)\exp(-\Delta F(n)) \qquad k_n^- = A(n-1)$$

In steady state $$J = k_n^+ P_n - k_{n+1}^- P_{n+1}$$

Projecting the GO model to a 1D system

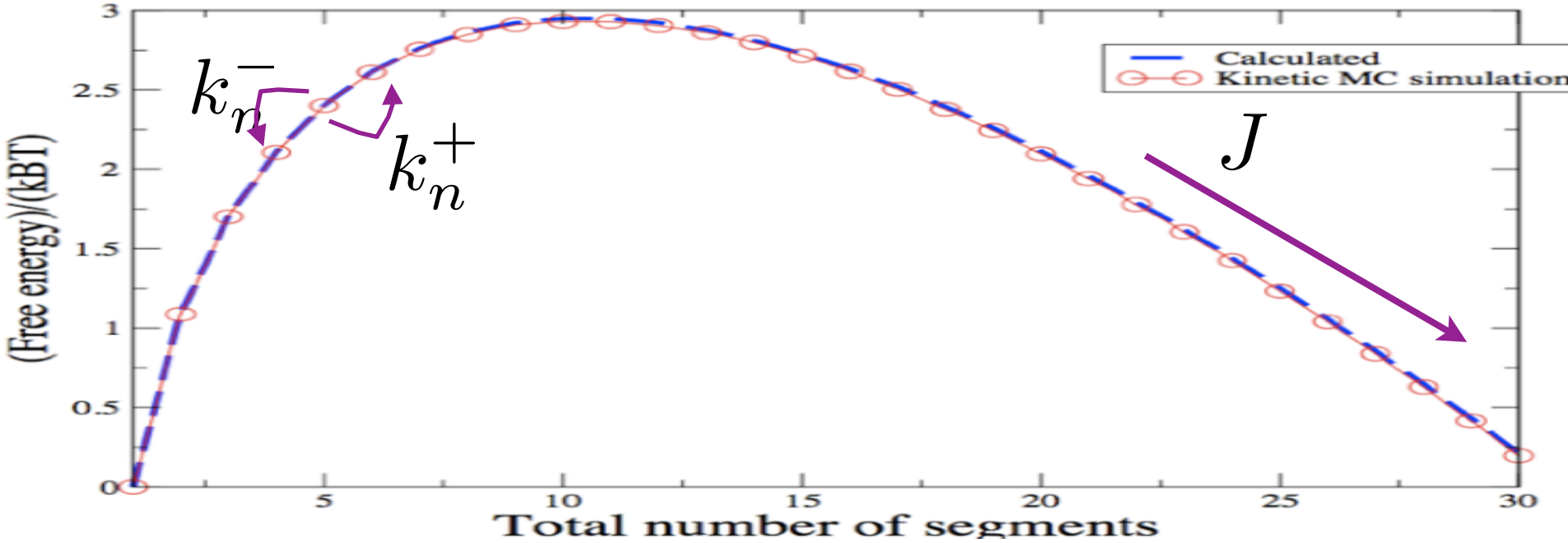


$$k_n^+ = A(n)\exp(-\Delta F(n)) \qquad k_n^- = A(n-1)$$

In steady state $$J = k_n^+ P_n - k_{n+1}^- P_{n+1}$$

$$A(n) = \frac{J}{P_n \exp(-\Delta F(n)) - P_{n+1}}$$

Projecting the GO model to a 1D system



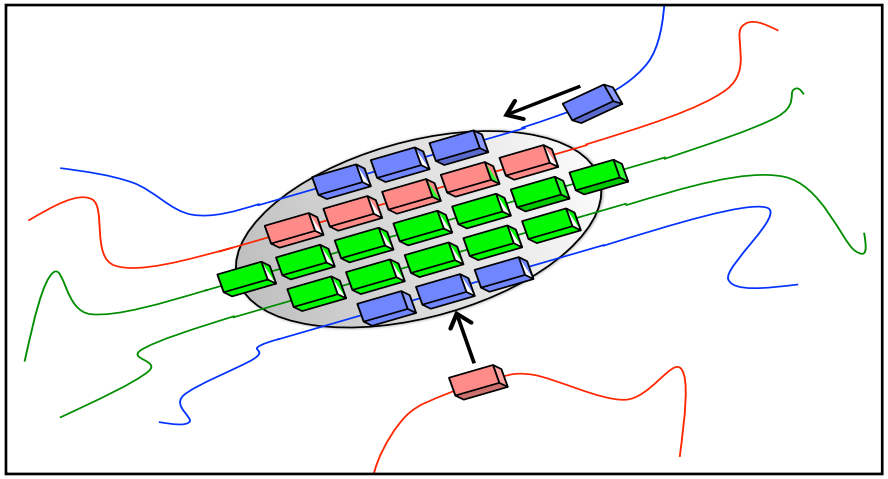
$$k_n^+ = A(n)\exp(-\Delta F(n)) \qquad k_n^- = A(n-1)$$

In steady state $$J = k_n^+ P_n - k_{n+1}^- P_{n+1}$$

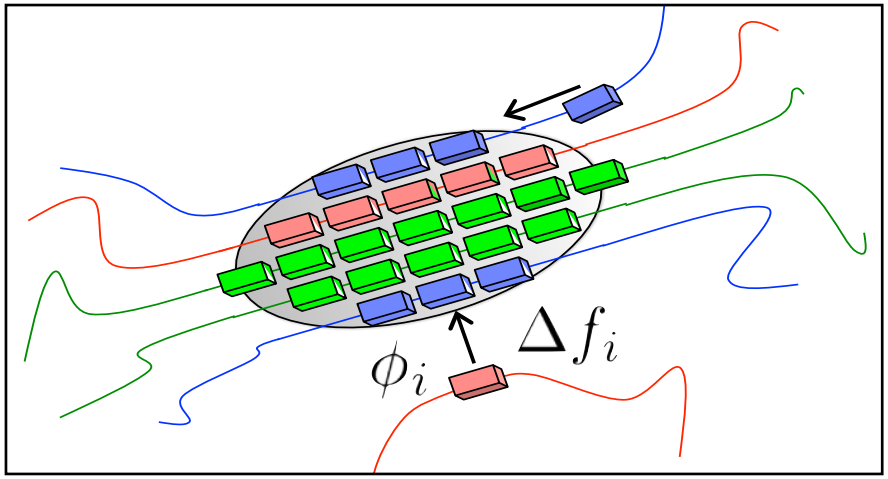
$$A(n) = \frac{J}{P_n \exp(-\Delta F(n)) - P_{n+1}}$$

Can be extracted from our simulations

Model for the barrier under flow (polySTRAND)

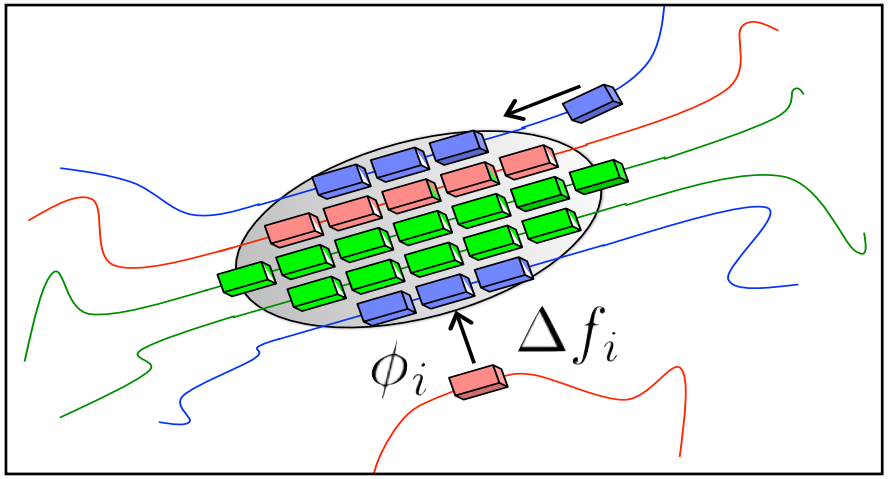


Model for the barrier under flow (polySTRAND)



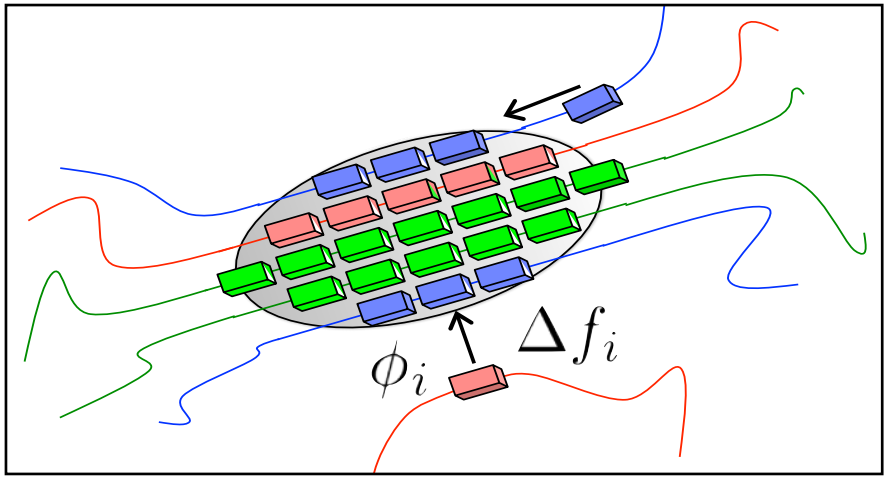
Df_i=nematic order
φ_i=melt fraction of i

Model for the barrier under flow (polySTRAND)



Df_i=nematic order
φ_i=melt fraction of i
N_T=total monomers
N_s=total stems
S=surface area

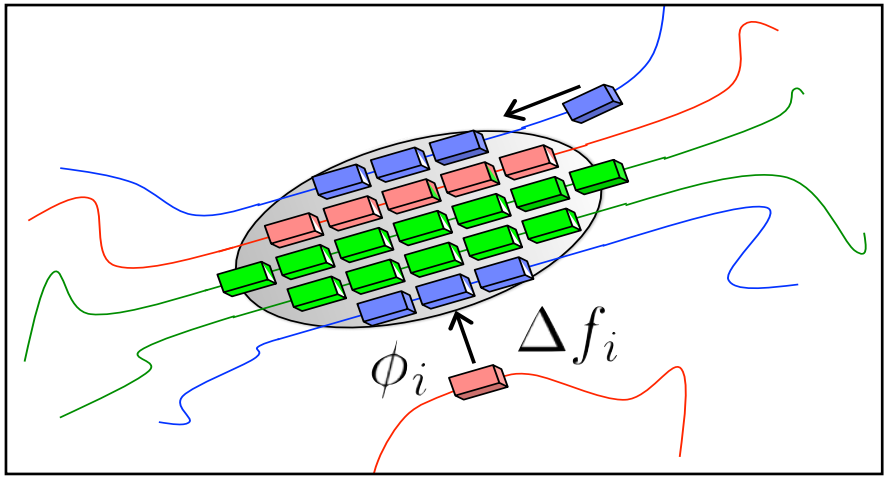
Model for the barrier under flow (polySTRAND)



Df_i=nematic order
φ_i=melt fraction of i
N_T=total monomers
N_s=total stems
S=surface area

e_B=Bulk free energy gain
μ_s=surface area cost

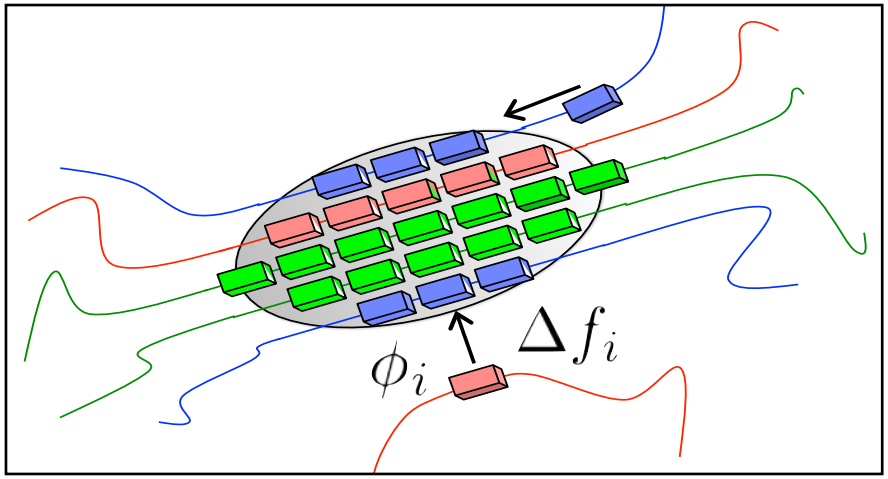
Model for the barrier under flow (polySTRAND)



Df_i=nematic order
φ_i=melt fraction of i
N_T=total monomers
N_s=total stems
S=surface area

e_B=Bulk free energy gain
μ_s=surface area cost
v_i=fraction of i monomers
w_i=fraction of i stems
q=N_T/N_S

Model for the barrier under flow (polySTRAND)



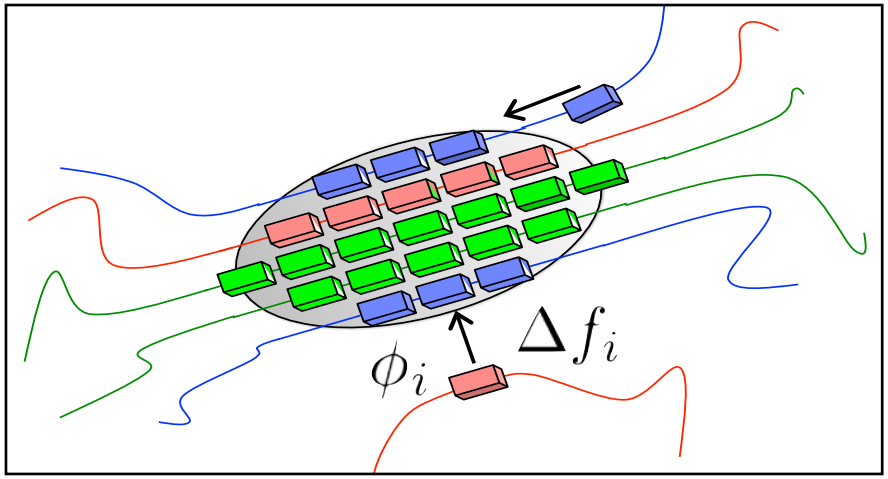
Df_i=nematic order
φ_i=melt fraction of i
N_T=total monomers
N_s=total stems
S=surface area

e_B=Bulk free energy gain
μ_s=surface area cost
v_i=fraction of i monomers
w_i=fraction of i stems
q=N_T/N_S

Nucleus free energy

$$\frac{F(N_T, N_S, \{w_i\}, \{v_i\})}{k_B T} = N_T \sum_i [q w_i (2 \log w_i - \log \phi_i) - v_i \log v_i + (v_i - q w_i) \log(v_i - q w_i) - v_i \Delta f_i]$$
$$+ N_S \log q - \epsilon_B N_T + \mu_S S(N_T, N_S).$$

Model for the barrier under flow (polySTRAND)



Df_i=nematic order
φ_i=melt fraction of i
N_T=total monomers
N_s=total stems
S=surface area

e_B=Bulk free energy gain
μ_s=surface area cost
v_i=fraction of i monomers
w_i=fraction of i stems
q=N_T/N_S

Nucleus free energy

Stem entropy change: melt→nucleus

Stem/monomer arrangement entropy

$$\frac{F(N_T, N_S, \{w_i\}, \{v_i\})}{k_B T} = N_T \sum_i [q w_i (2 \log w_i - \log \phi_i) - v_i \log v_i + (v_i - q w_i) \log(v_i - q w_i) - v_i \Delta f_i] + N_S \log q - \epsilon_B N_T + \mu_S S(N_T, N_S).$$

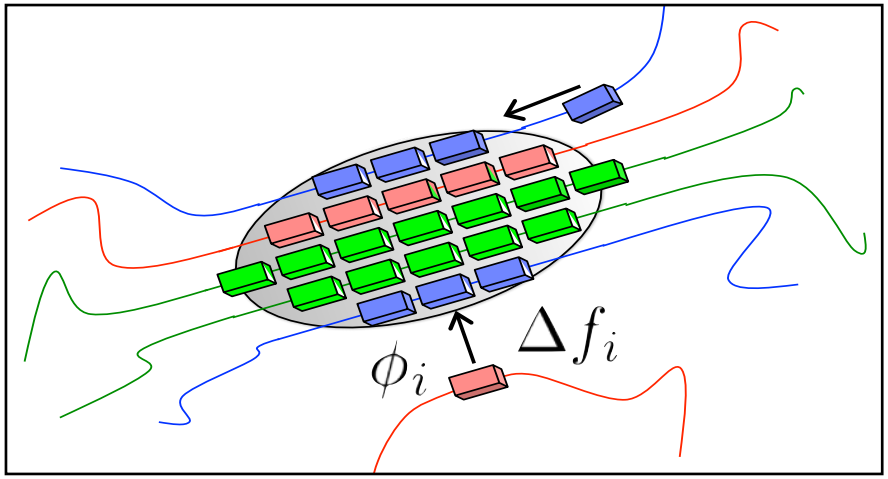
Sum over species

Flow-induced ordering

Bulk gain

Surface cost

Model for the barrier under flow (polySTRAND)



Df_i=nematic order
φ_i=melt fraction of i
N_T=total monomers
N_s=total stems
S=surface area

e_B=Bulk free energy gain
μ_s=surface area cost
v_i=fraction of i monomers
w_i=fraction of i stems
$q=N_T/N_S$

Minimise with constraint $\sum_i w_i = \sum_i v_i = 1$

Nucleus free energy

Stem entropy change: melt→nucleus

Stem/monomer arrangement entropy

$$\frac{F(N_T, N_S, \{w_i\}, \{v_i\})}{k_B T} = N_T \sum_i [q w_i (2 \log w_i - \log \phi_i) - v_i \log v_i + (v_i - q w_i) \log(v_i - q w_i) - v_i \Delta f_i] + N_S \log q - \epsilon_B N_T + \mu_S S(N_T, N_S).$$

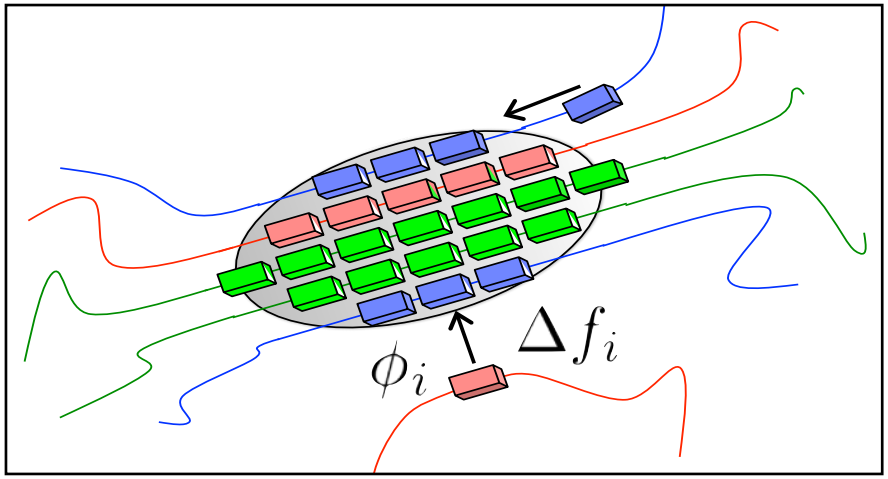
Sum over species

Bulk gain

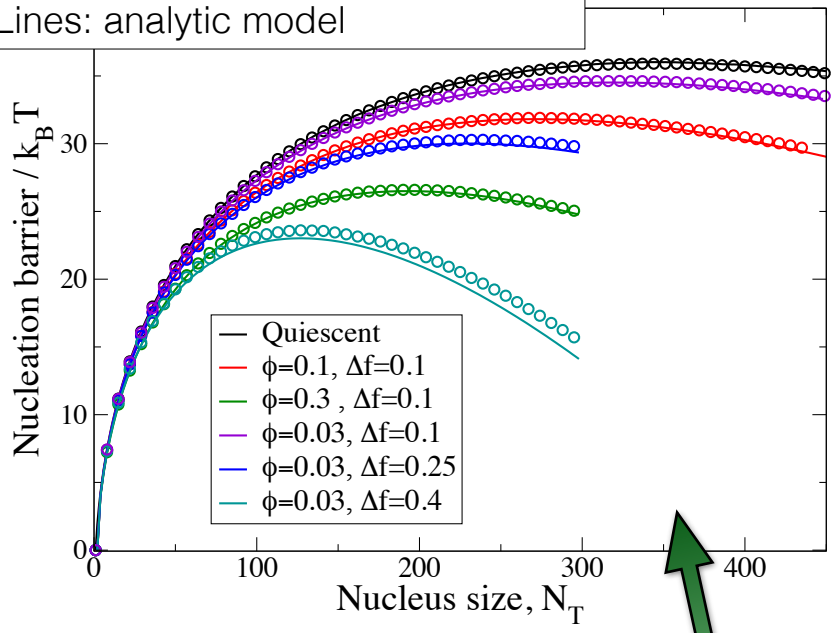
Surface cost

Flow-induced ordering

Model for the barrier under flow (polySTRAND)



Symbols: GO model simulations
Lines: analytic model



Df_i=nematic order
φ_i=melt fraction of i
N_T=total monomers
N_s=total stems
S=surface area

e_B=Bulk free energy gain
μ_s=surface area cost
v_i=fraction of i monomers
w_i=fraction of i stems
$q=N_T/N_S$

Minimise with constraint $\sum_i w_i = \sum_i v_i = 1$

Nucleus free energy

Stem entropy change: melt→nucleus

Stem/monomer arrangement entropy

$$\frac{F(N_T, N_S, \{w_i\}, \{v_i\})}{k_B T} = N_T \sum_i [q w_i (2 \log w_i - \log \phi_i) - v_i \log v_i + (v_i - q w_i) \log(v_i - q w_i) - v_i \Delta f_i]$$

$$+ N_S \log q - \epsilon_B N_T + \mu_S S(N_T, N_S).$$

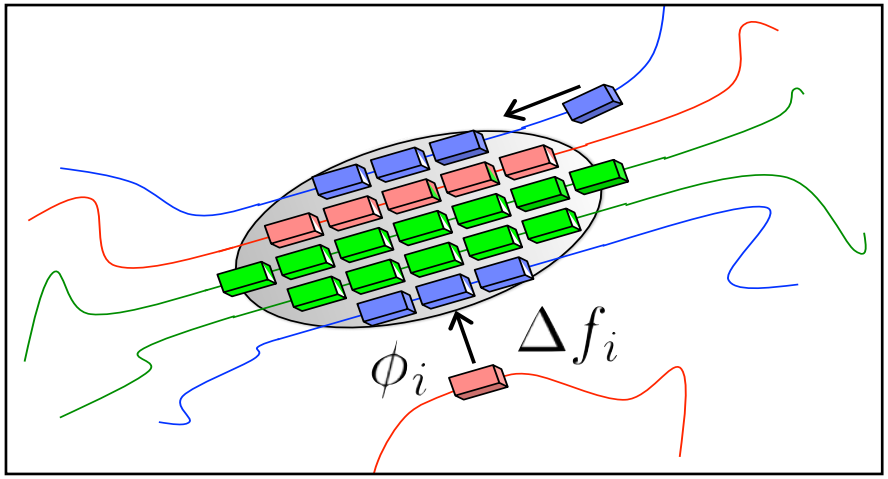
Sum over species

Bulk gain

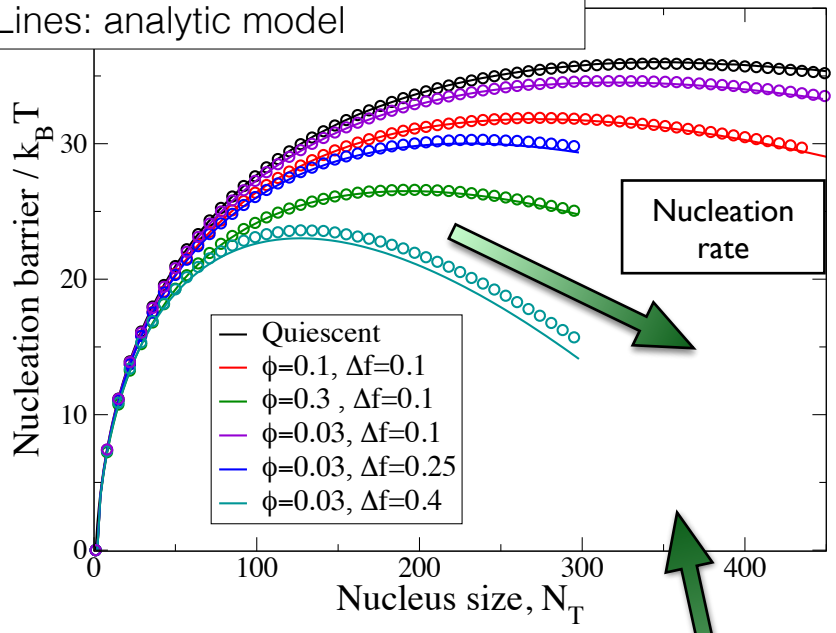
Surface cost

Flow-induced ordering

Model for the barrier under flow (polySTRAND)



Symbols: GO model simulations
Lines: analytic model



Df_i=nematic order
φ_i=melt fraction of i
N_T=total monomers
N_s=total stems
S=surface area

e_B=Bulk free energy gain
μ_s=surface area cost
v_i=fraction of i monomers
w_i=fraction of i stems
$q=N_T/N_S$

Minimise with constraint $\sum_i w_i = \sum_i v_i = 1$

Nucleus free energy

Stem entropy change: melt→nucleus

Stem/monomer arrangement entropy

$$\frac{F(N_T, N_S, \{w_i\}, \{v_i\})}{k_B T} = N_T \sum_i [q w_i (2 \log w_i - \log \phi_i) - v_i \log v_i + (v_i - q w_i) \log(v_i - q w_i) - v_i \Delta f_i] + N_S \log q - \epsilon_B N_T + \mu_S S(N_T, N_S).$$

Sum over species

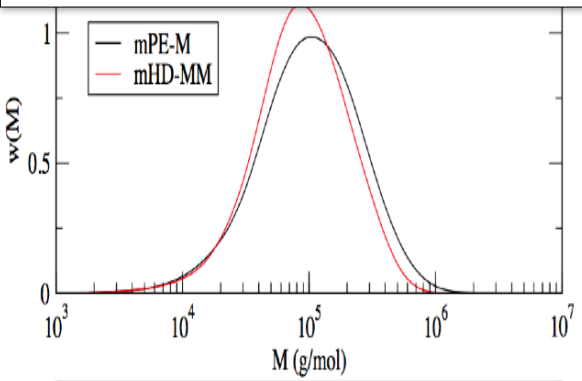
Bulk gain

Surface cost

Flow-induced ordering

Model summary

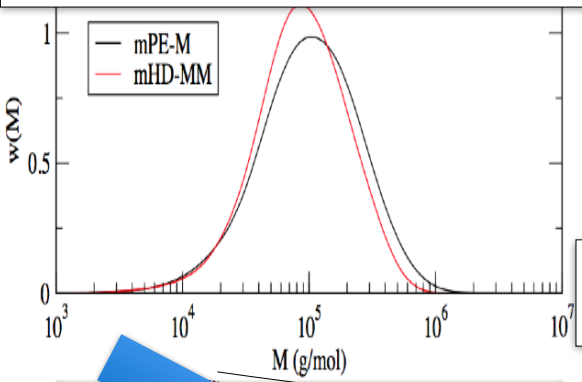
Molecular weight distribution



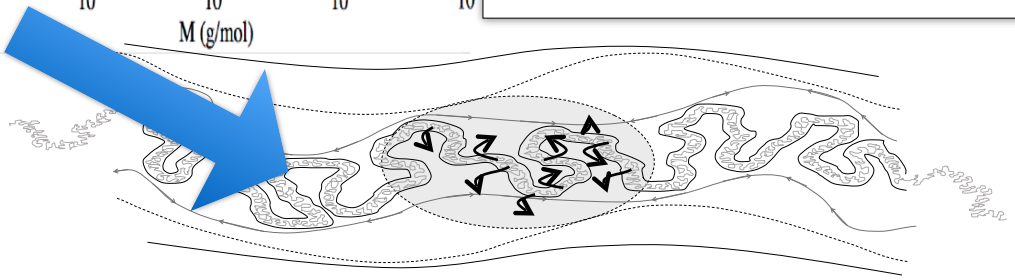
Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

Model summary

Molecular weight distribution



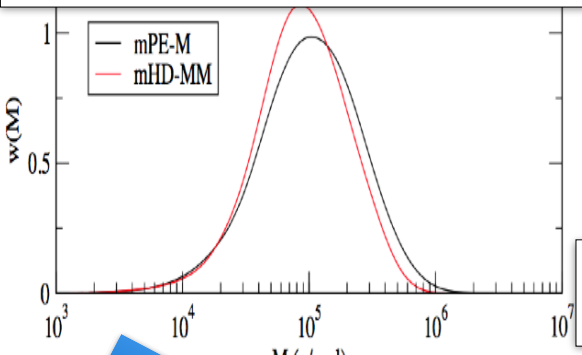
Flow model



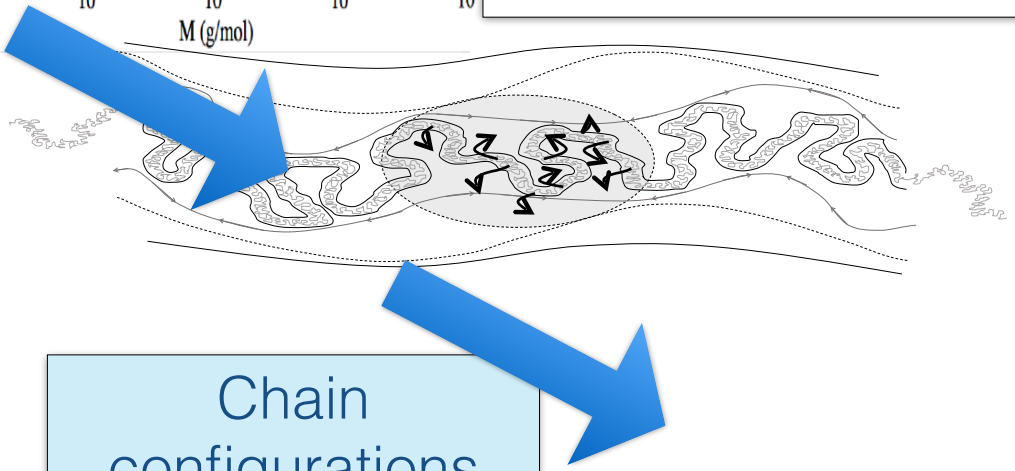
Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

Model summary

Molecular weight distribution



Flow model

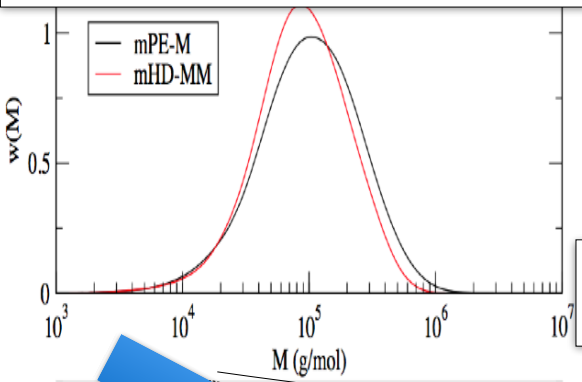


Chain configurations

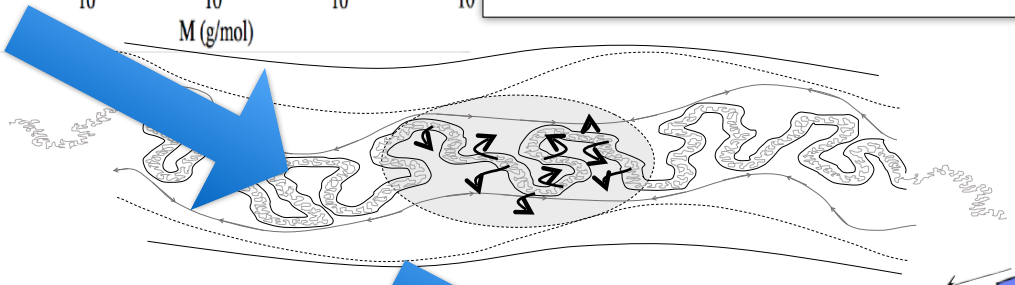
Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

Model summary

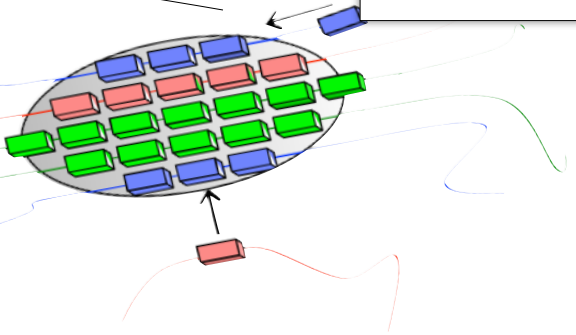
Molecular weight distribution



Flow model



STRAND model

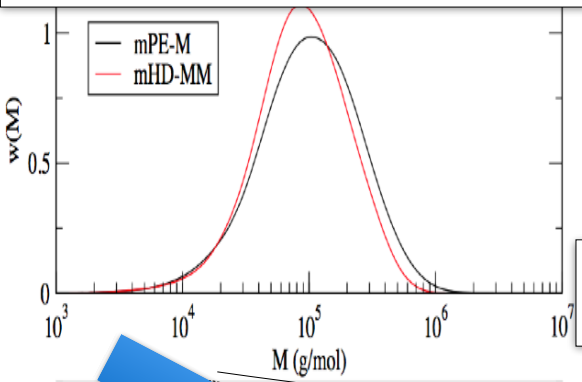


Chain configurations

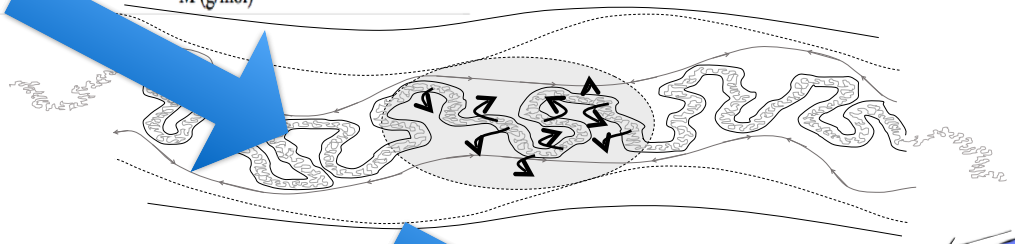
Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

Model summary

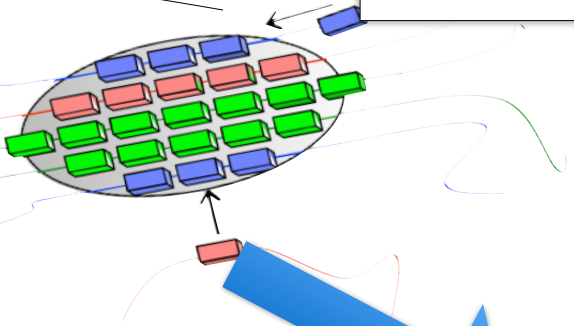
Molecular weight distribution



Flow model



STRAND model



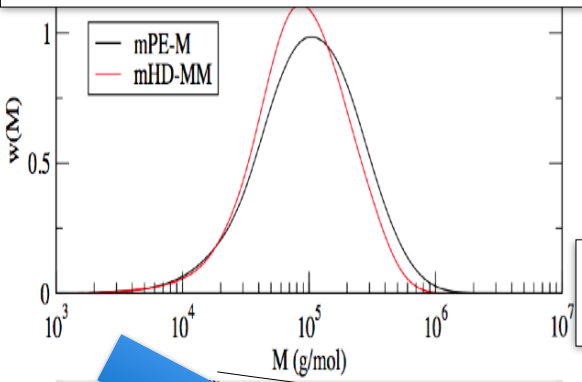
Chain configurations

Nucleation barrier

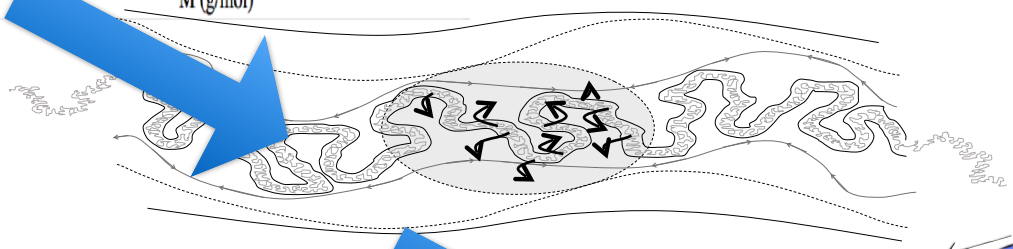
Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

Model summary

Molecular weight distribution

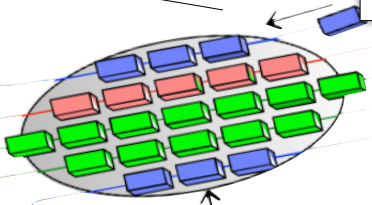


Flow model



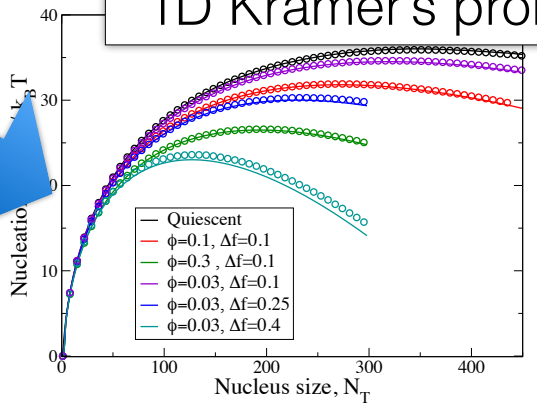
STRAND model

Chain configurations



1D Kramer's problem

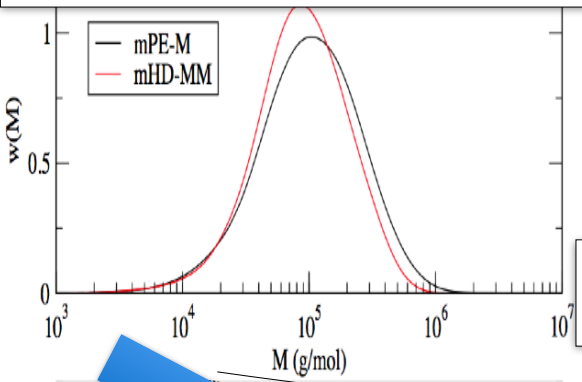
Nucleation barrier



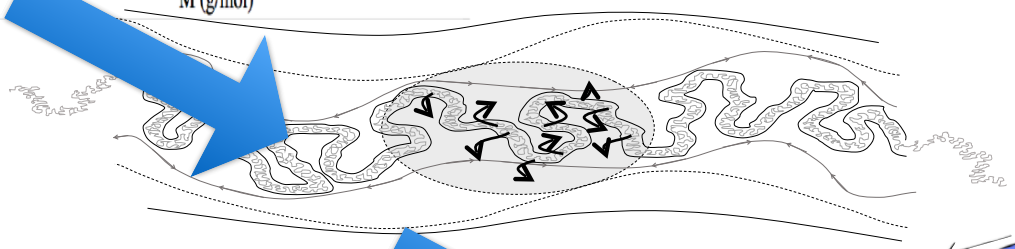
Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

Model summary

Molecular weight distribution

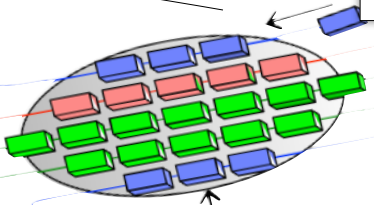


Flow model

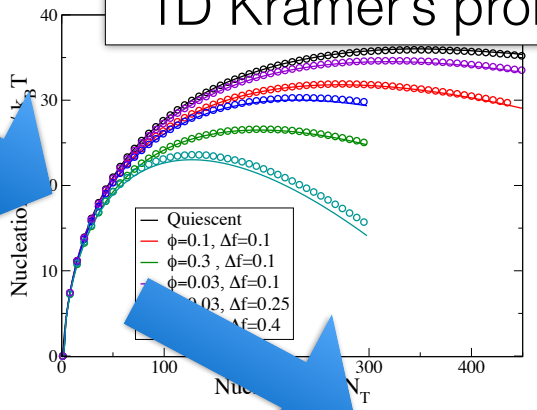


STRAND model

Chain configurations



1D Kramer's problem



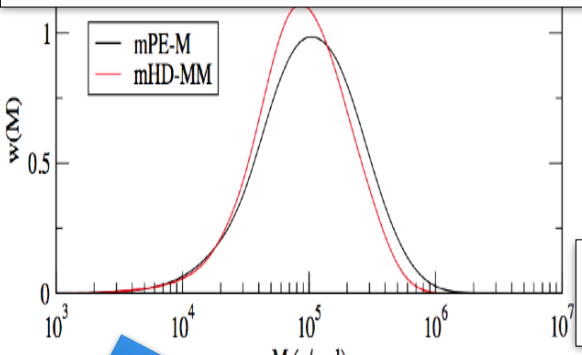
Nucleation barrier

Nucleation Rate

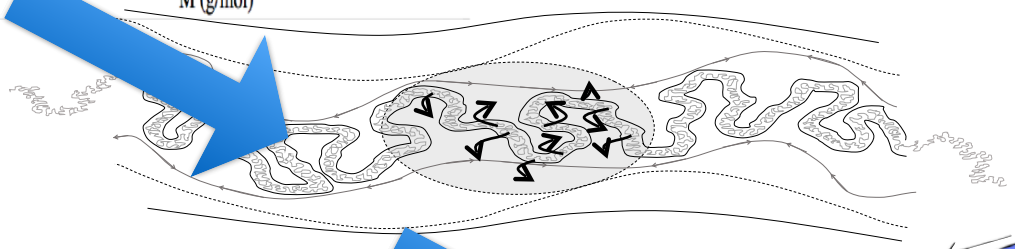
Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

Model summary

Molecular weight distribution

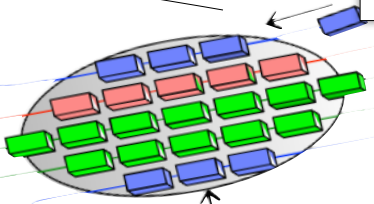


Flow model

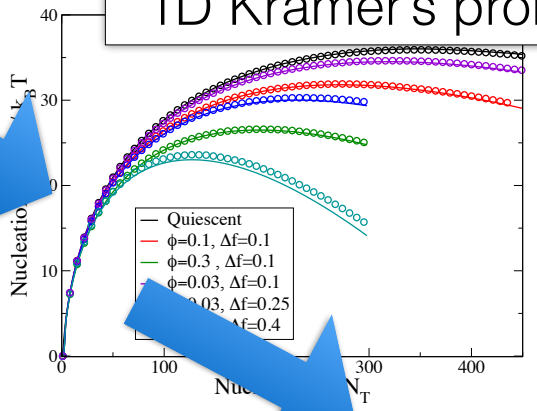


STRAND model

Chain configurations



1D Kramer's problem



Nucleation barrier

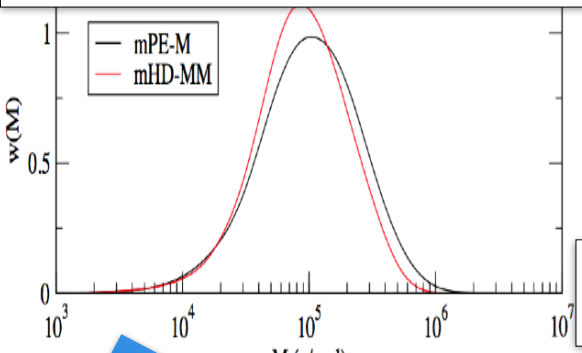
Nucleation Rate

Also predicts long chain enhancement

Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

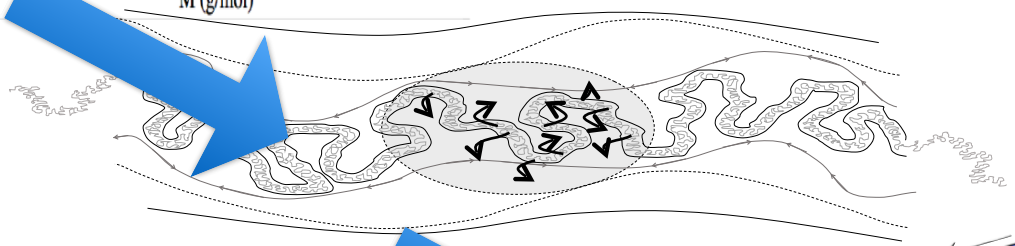
Model summary

Molecular weight distribution



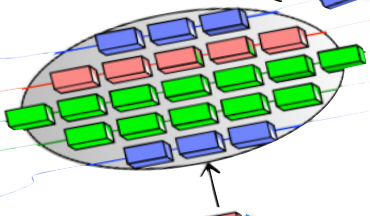
Flow model

All steps are numerically simple/ cheap - no stochastic simulation required

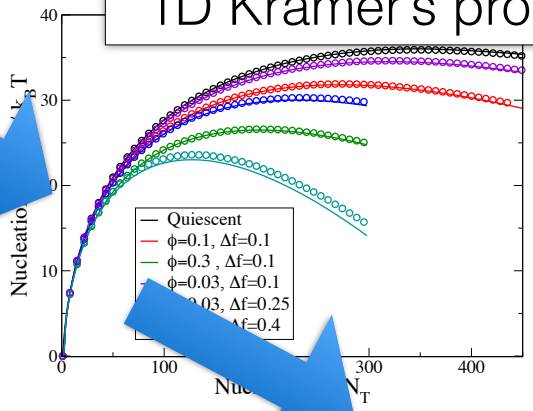


STRAND model

Chain configurations



1D Kramer's problem



Nucleation barrier

Also predicts long chain enhancement

Nucleation Rate

Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

Comparison with experiments

Direct observation of nucleation during steady shear

Continuous Shear Flow

Measurements on an isotactic polypropylene resin by Coccorullo *et al.* Macromolecules (2008) and Pantani *et al.* Macromolecules (2010)

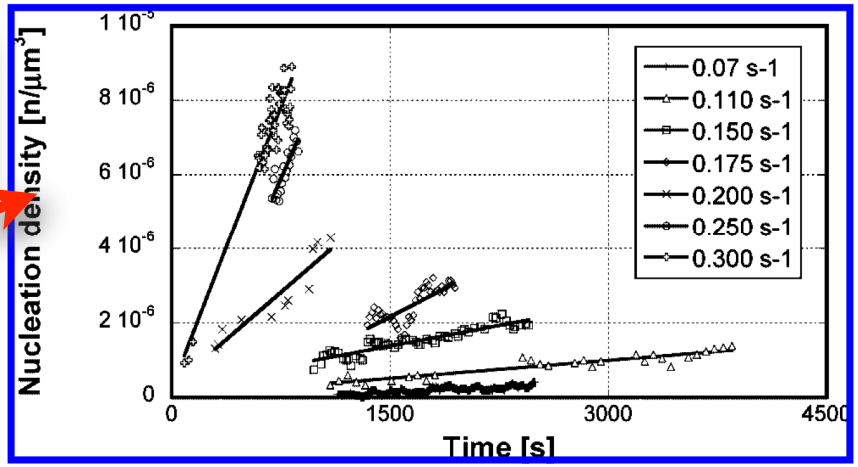
Direct observation of nucleation during steady shear

Continuous Shear Flow

Measurements on an isotactic polypropylene resin by Coccorullo *et al.* Macromolecules (2008) and Pantani *et al.* Macromolecules (2010)

Direct observation of nucleation during steady shear

Count nuclei as they appear



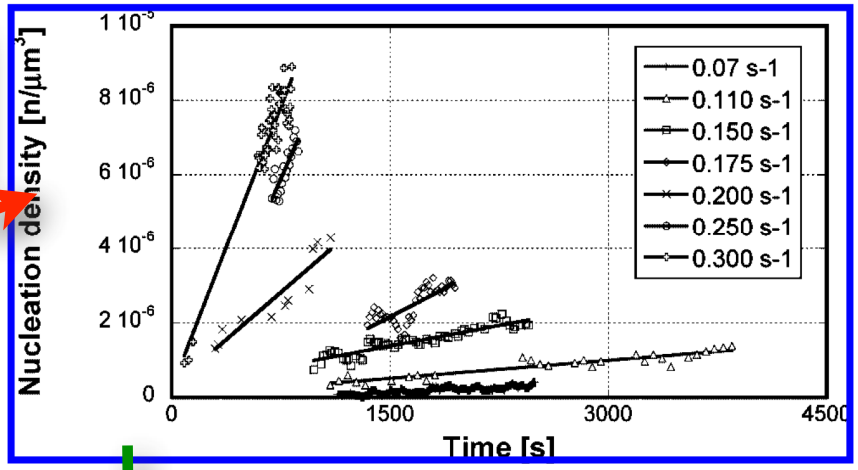
Continuous Shear Flow

Measurements on an isotactic polypropylene resin by Coccorullo *et al.* Macromolecules (2008) and Pantani *et al.* Macromolecules (2010)

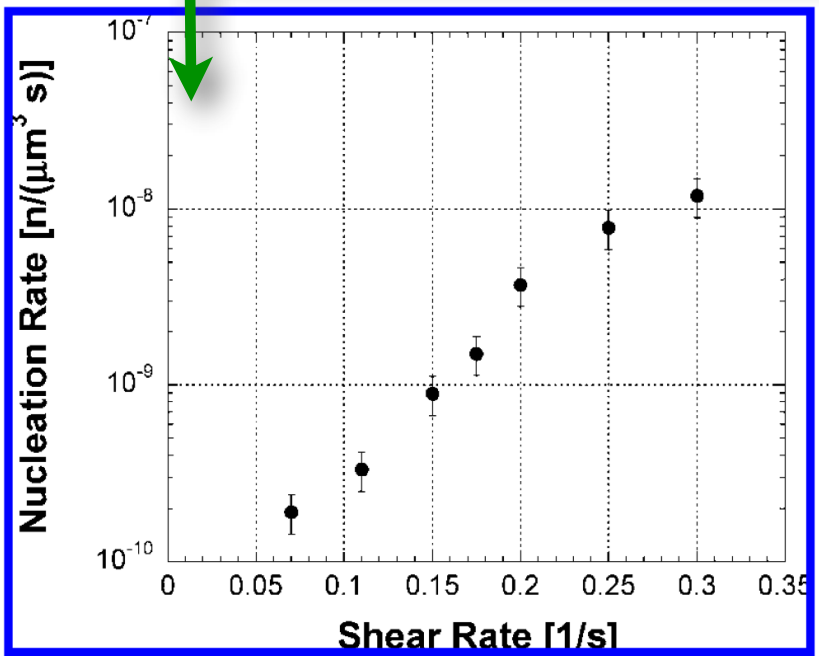
Direct observation of nucleation during steady shear

Count nuclei as they appear

Continuous Shear Flow

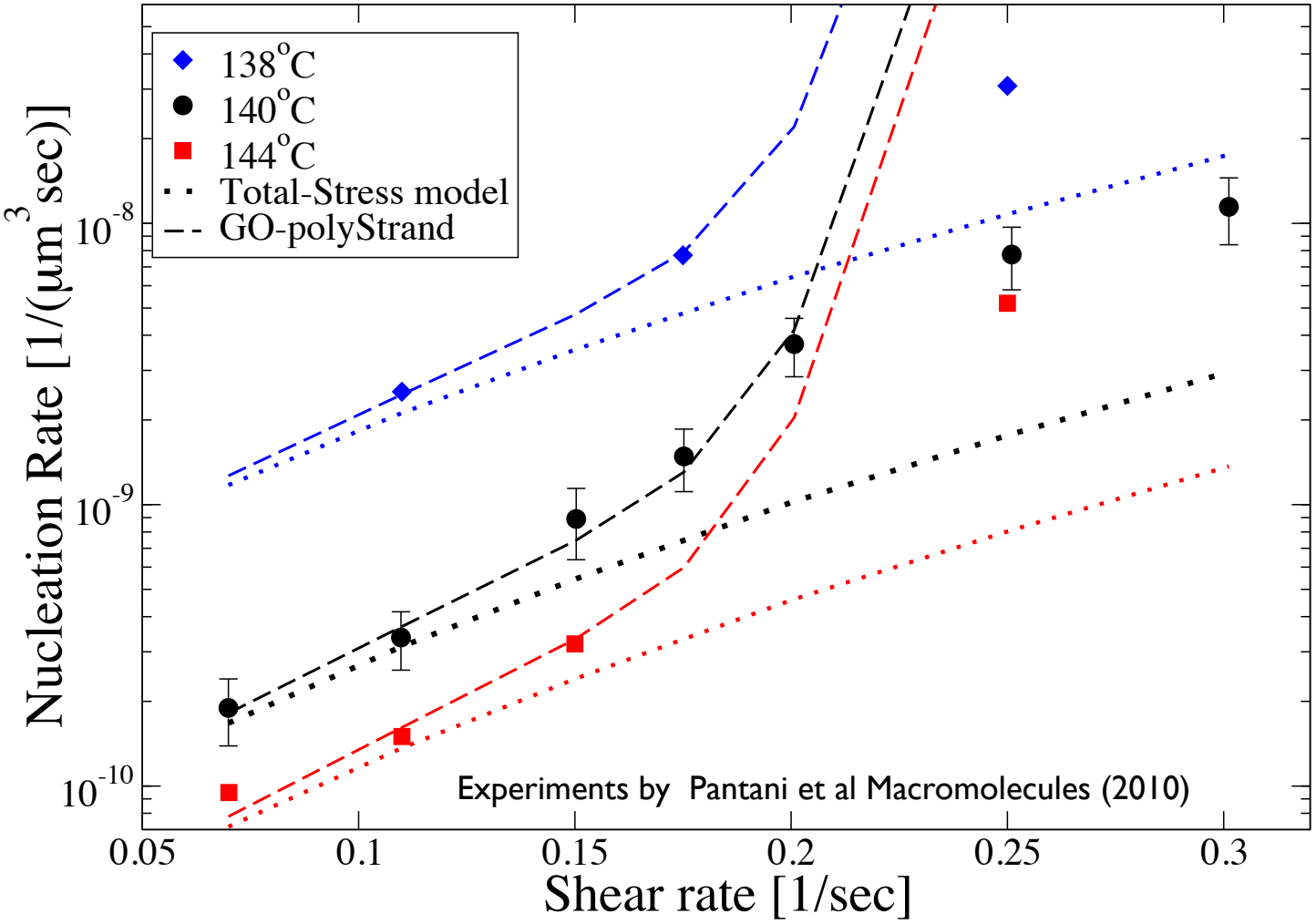


Steady nucleation rate against shear rate



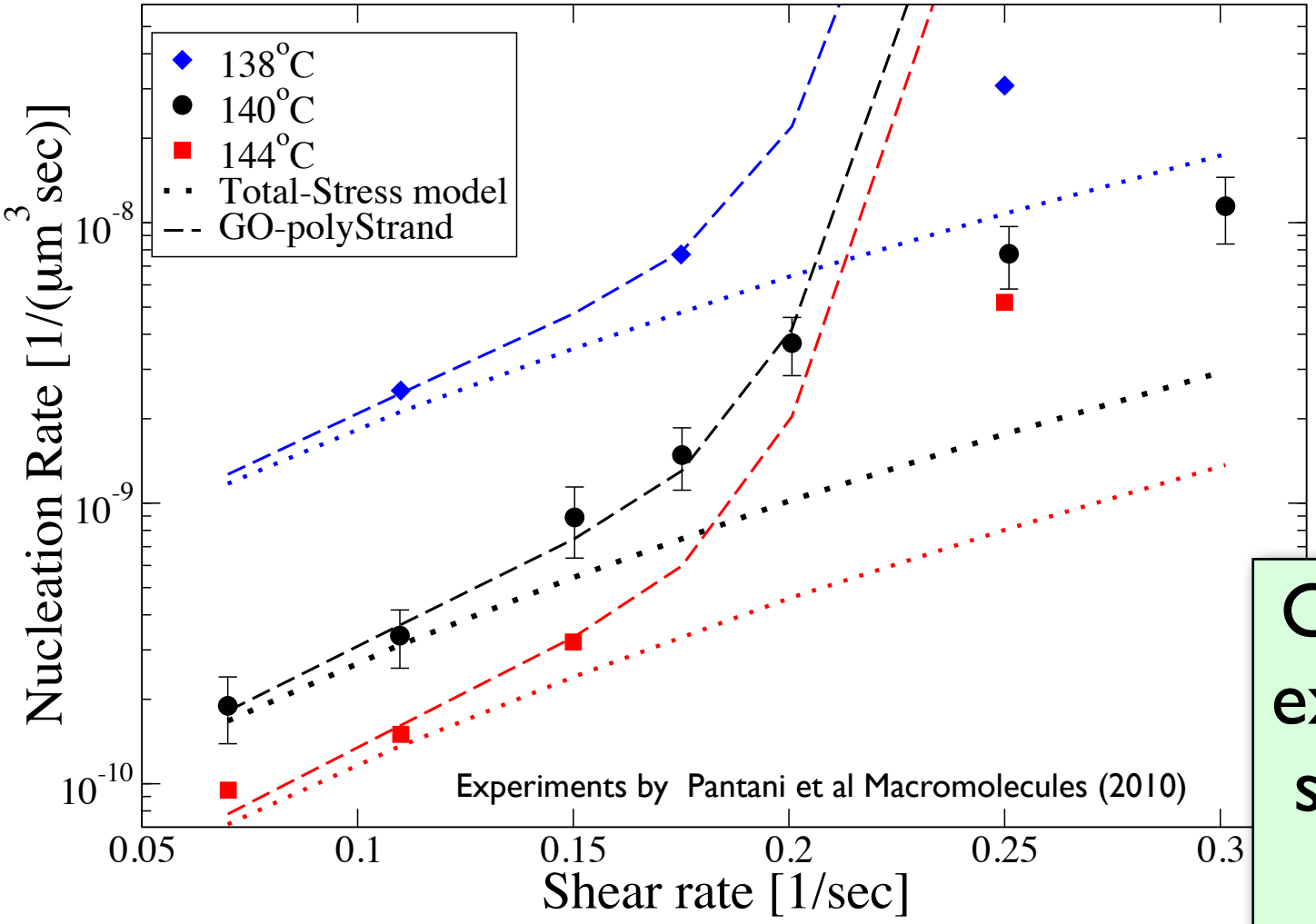
Measurements on an isotactic polypropylene resin by Coccorullo *et al.* Macromolecules (2008) and Pantani *et al.* Macromolecules (2010)

Direct observation of nucleation during steady shear



Read, McIlroy, Das, Harlen and Graham,
Phys. Rev. Lett. **124** 147802 (2020)

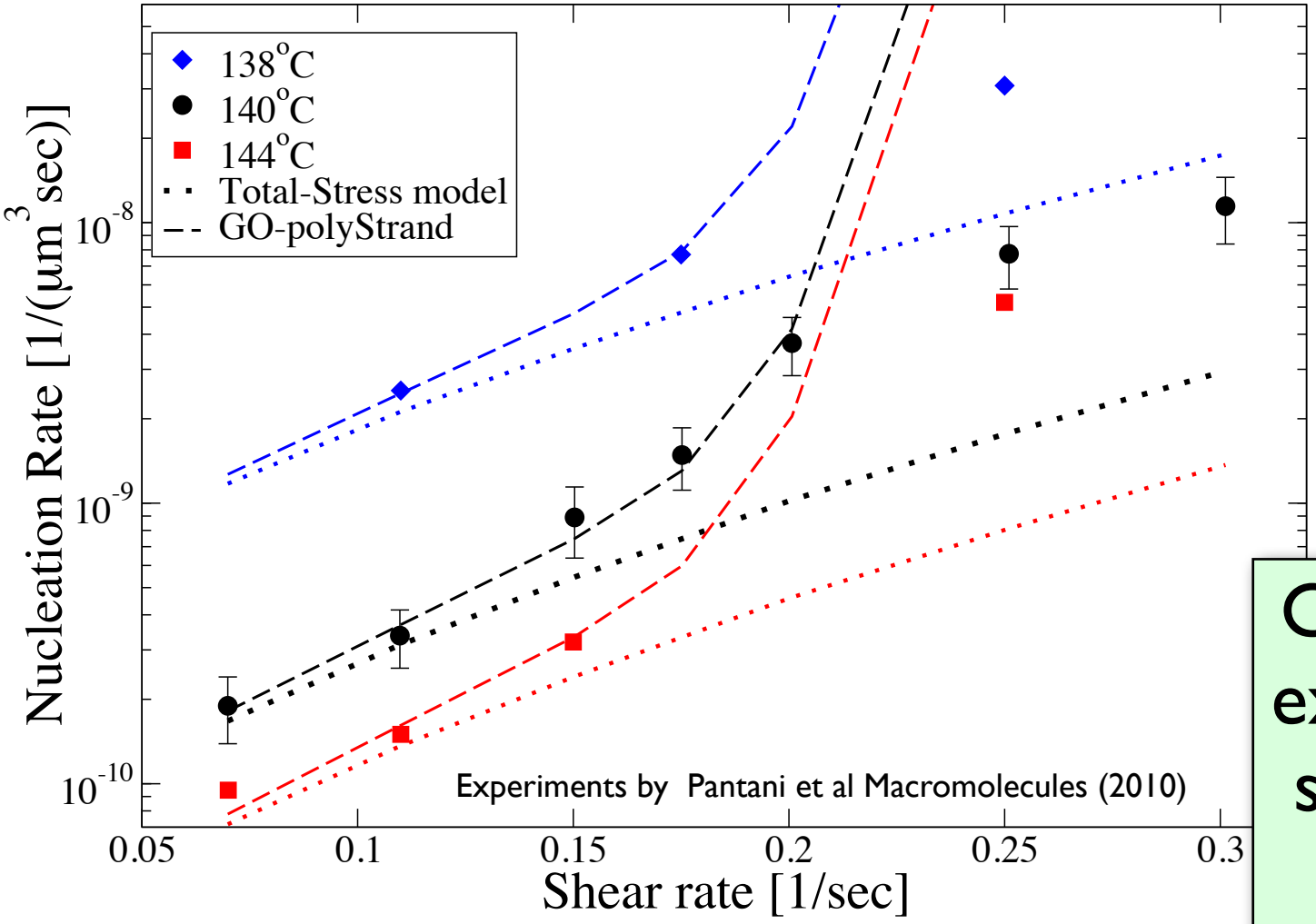
Direct observation of nucleation during steady shear



Curvature is experimental signature of long chain enhancement

Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

Direct observation of nucleation during steady shear

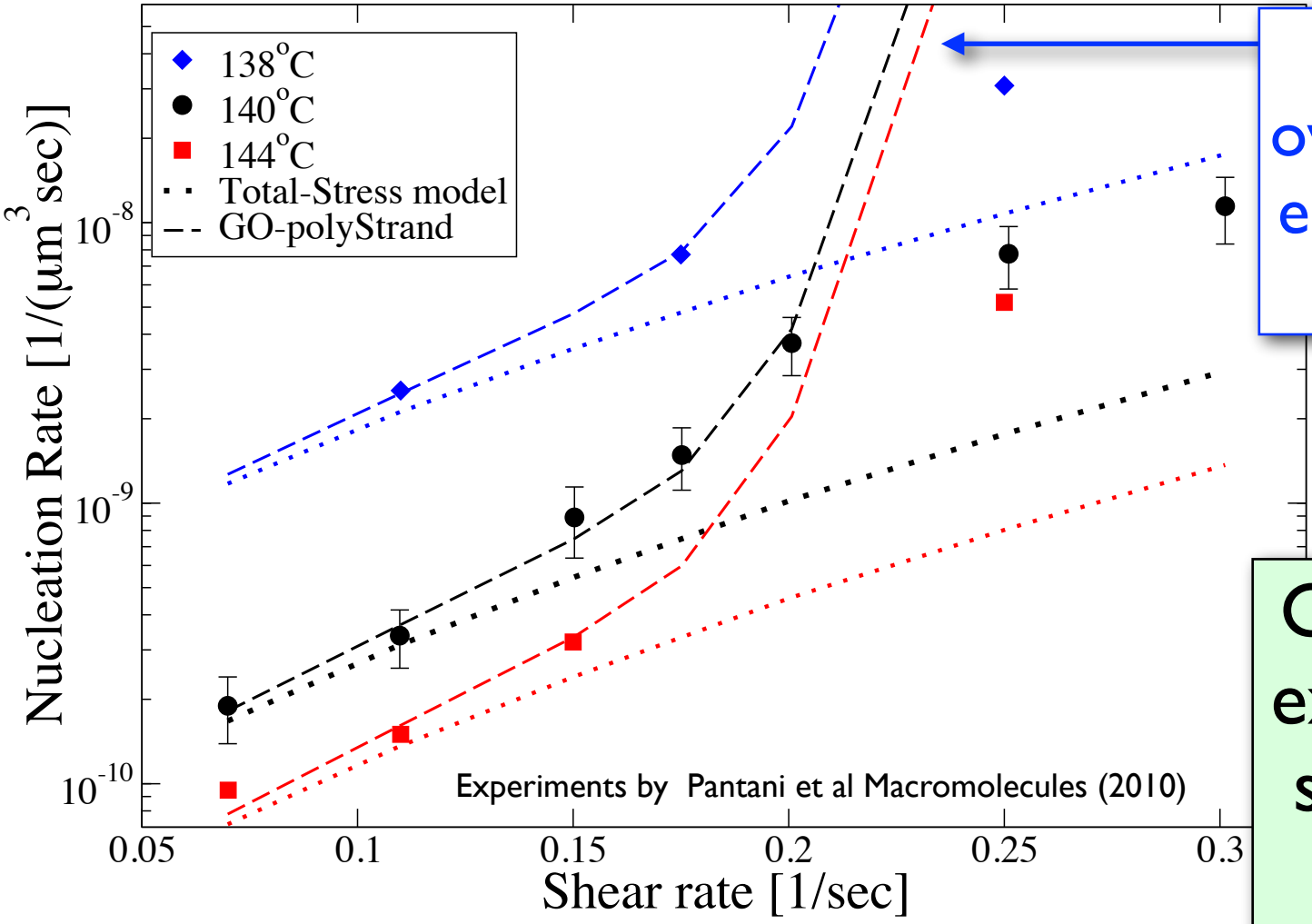


Curvature is experimental signature of long chain enhancement

Effect of temperature is successfully predicted

Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

Direct observation of nucleation during steady shear



Model overpredicts the enhancement at higher rates

Curvature is experimental signature of long chain enhancement

Effect of temperature is successfully predicted

Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

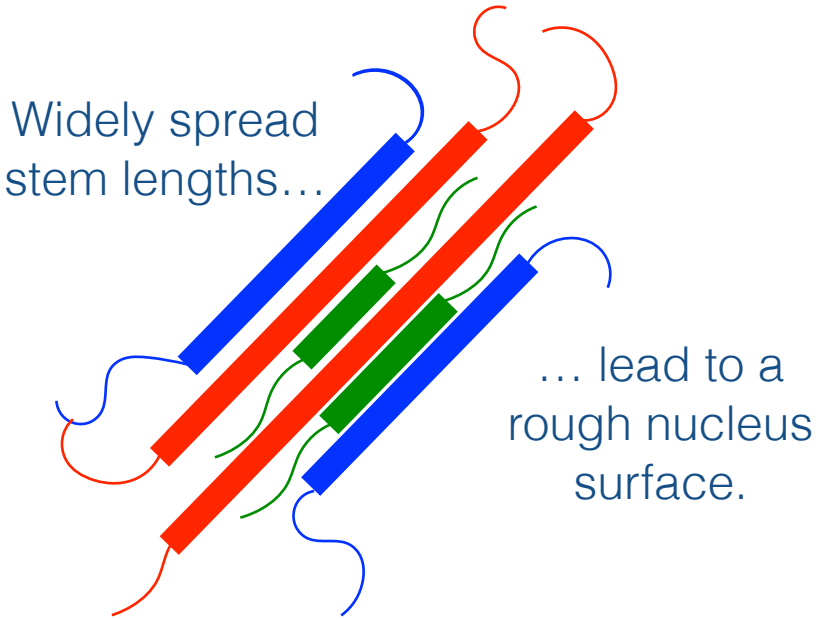
Smooth-polyStrand model

Nucleus roughness penalty

Long chain depletion

Smooth-polyStrand model

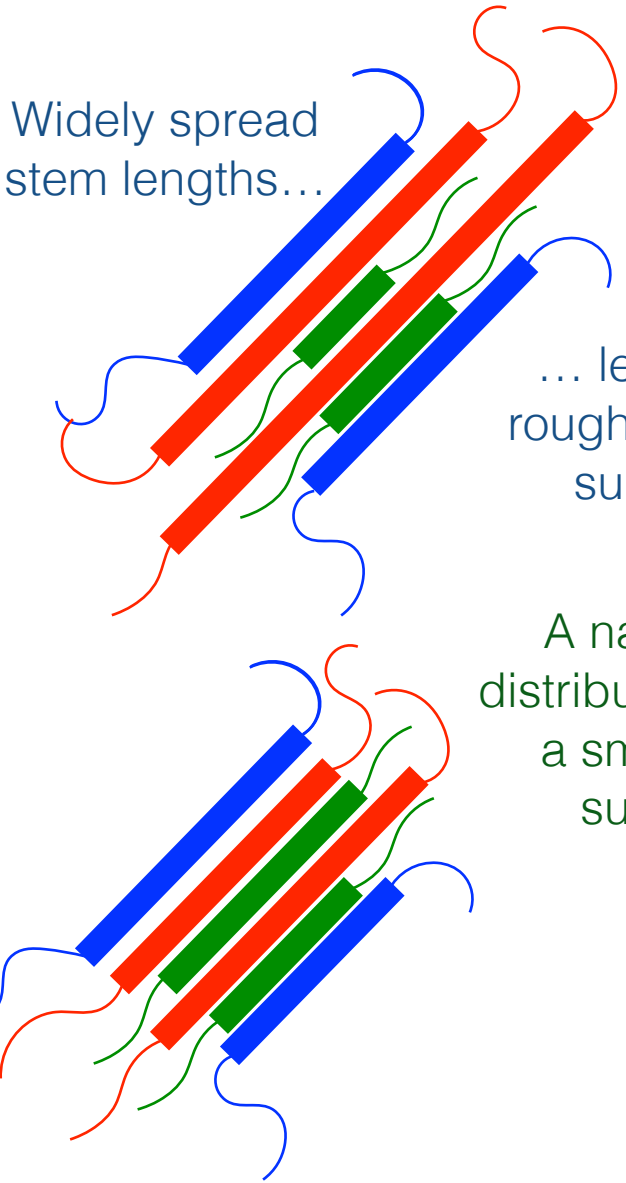
Nucleus roughness penalty



Long chain depletion

Smooth-polyStrand model

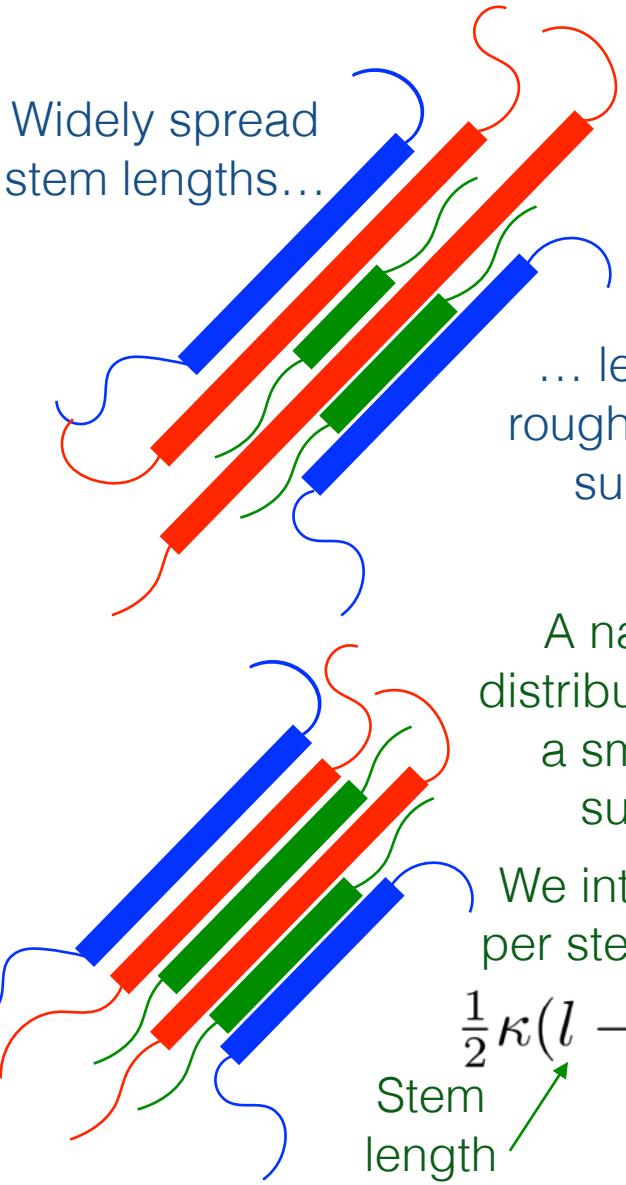
Nucleus roughness penalty



Long chain depletion

Smooth-polyStrand model

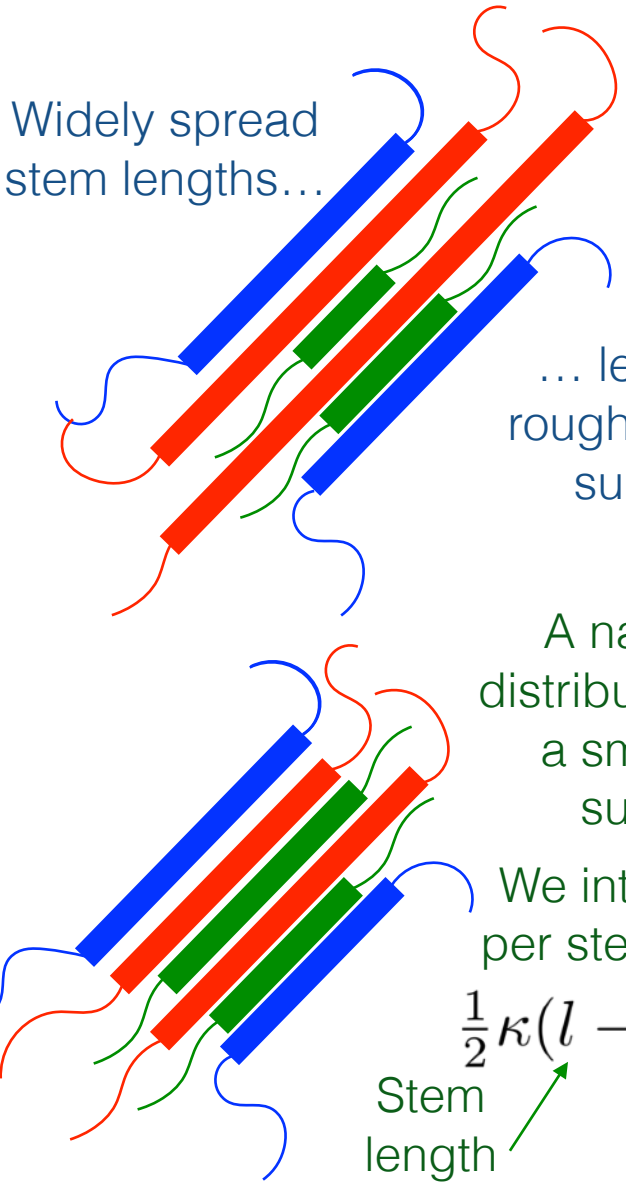
Nucleus roughness penalty



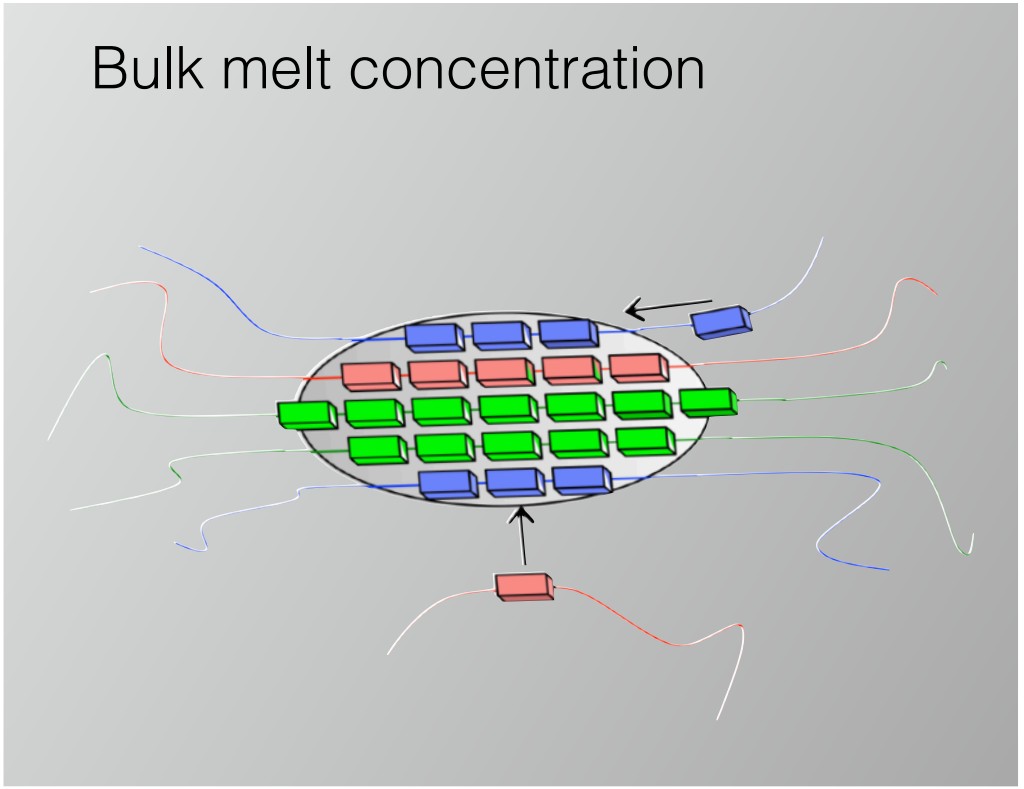
Long chain depletion

Smooth-polyStrand model

Nucleus roughness penalty

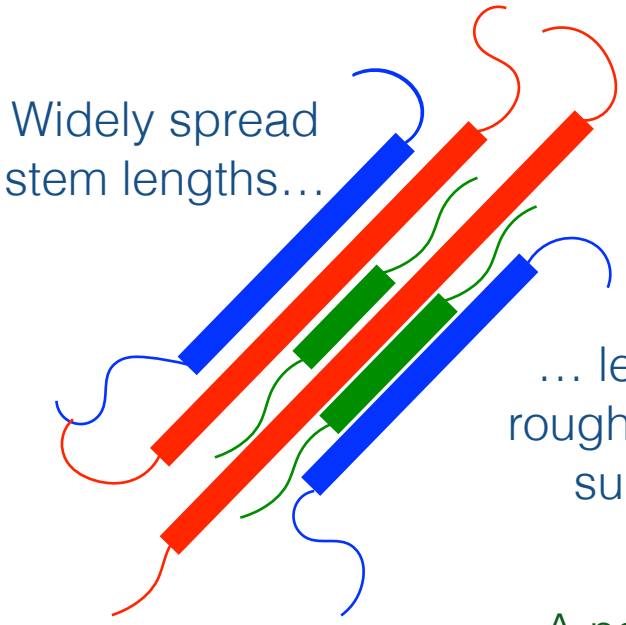


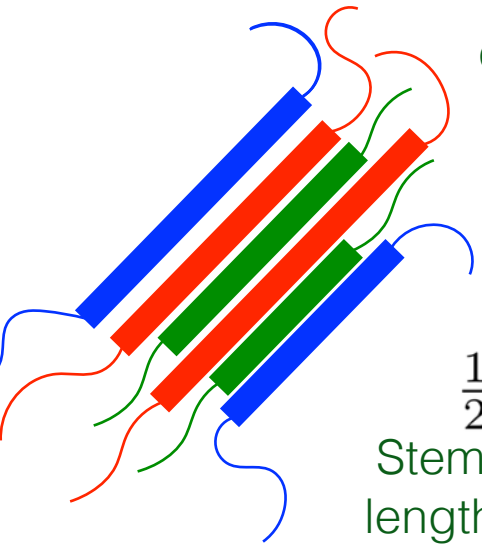
Long chain depletion



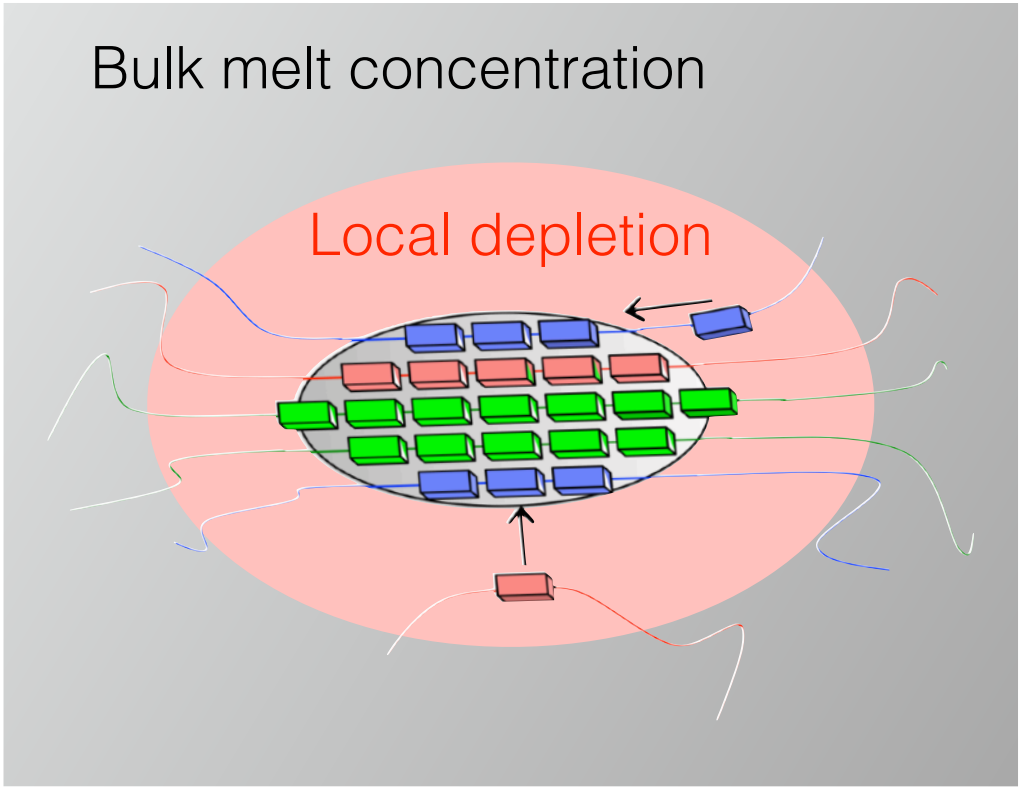
Smooth-polyStrand model

Nucleus roughness penalty



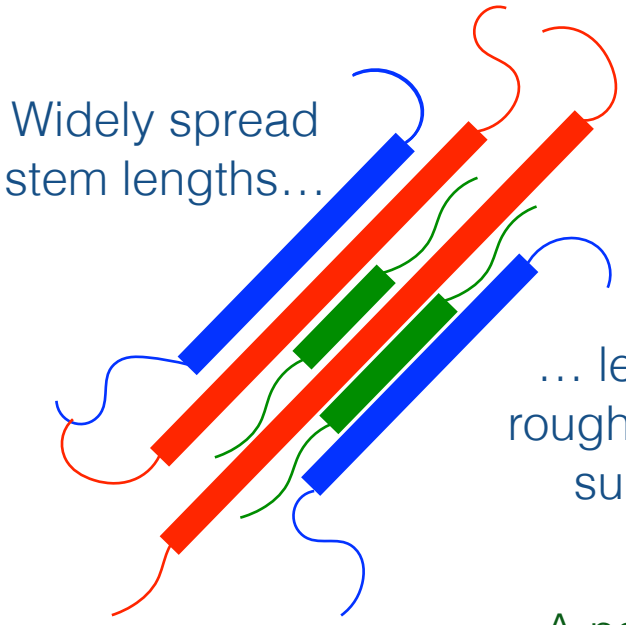


Long chain depletion



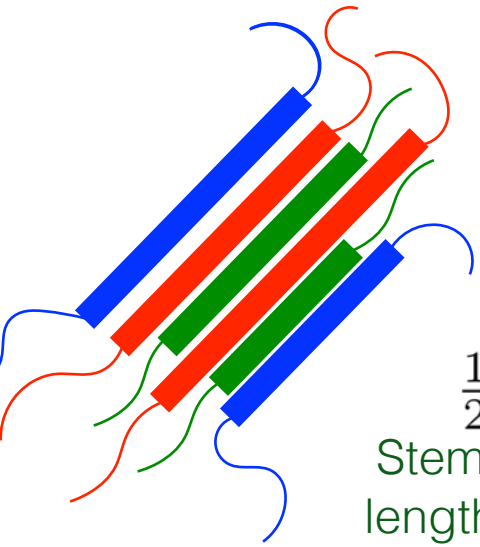
Smooth-polyStrand model

Nucleus roughness penalty



Widely spread stem lengths…

… lead to a rough nucleus surface.



A narrower distribution gives a smoother surface

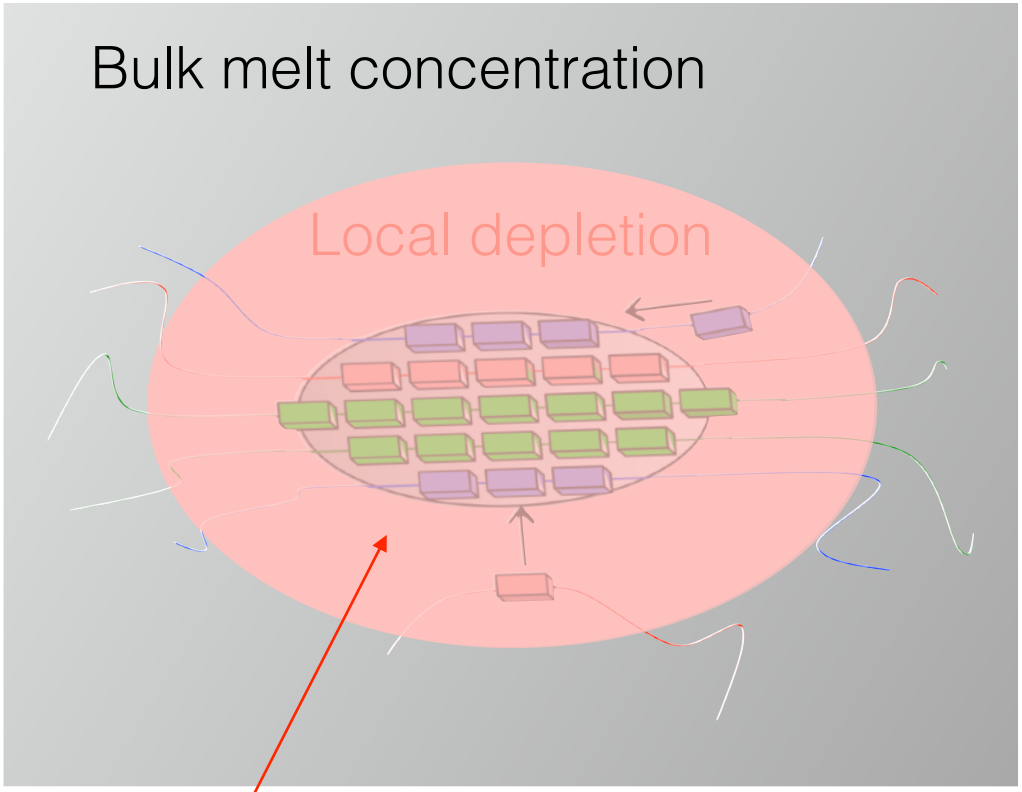
We introduce a per stem penalty

$$\frac{1}{2}\kappa(l-L)^2$$

Stem length

Average length

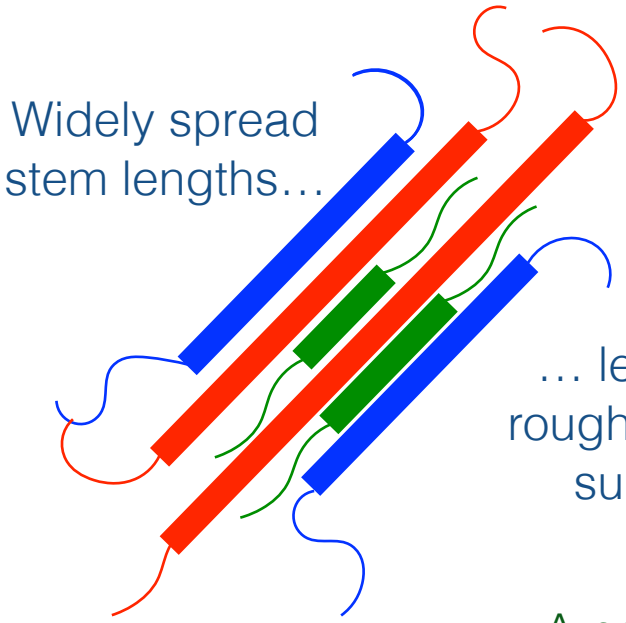
Long chain depletion

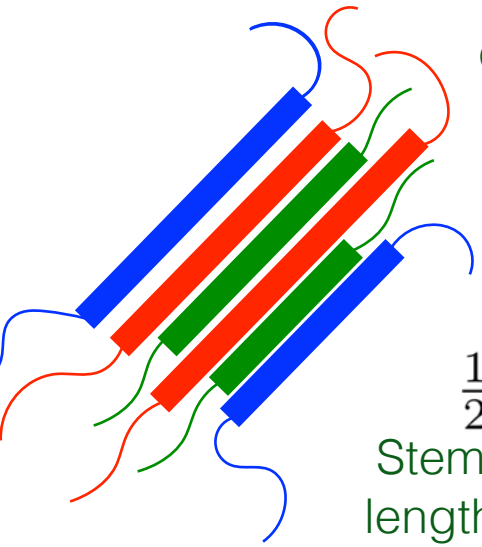


Stems are conserved over this region [nucleus + depletion region]

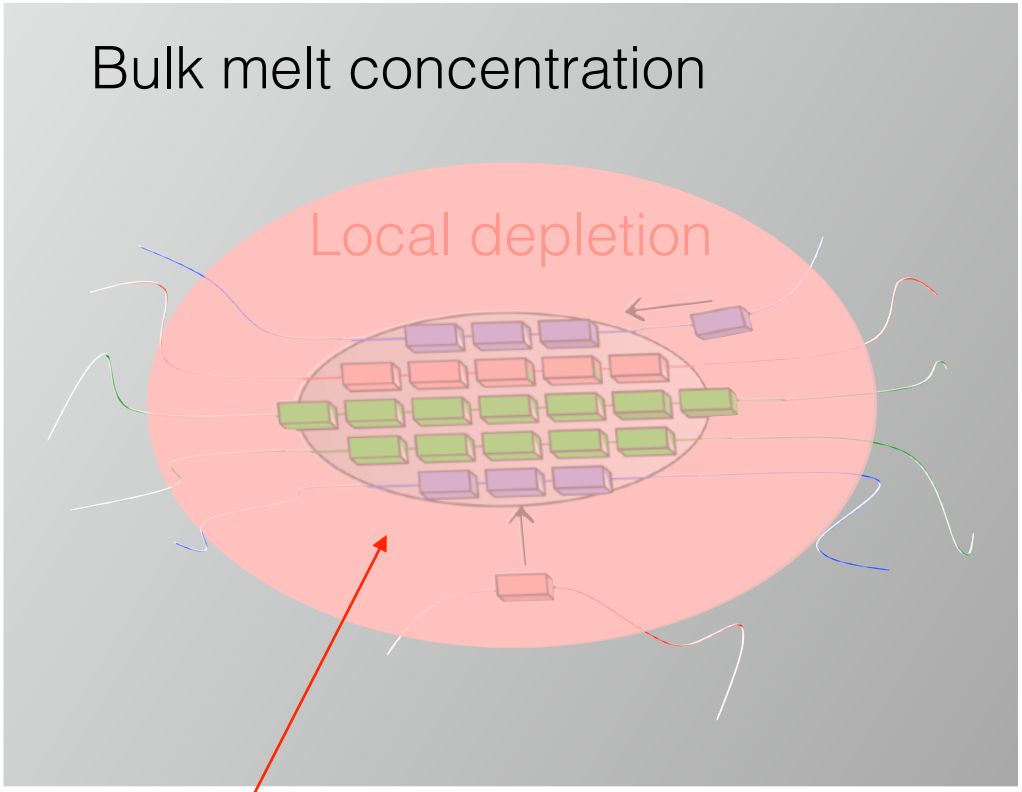
Smooth-polyStrand model

Nucleus roughness penalty





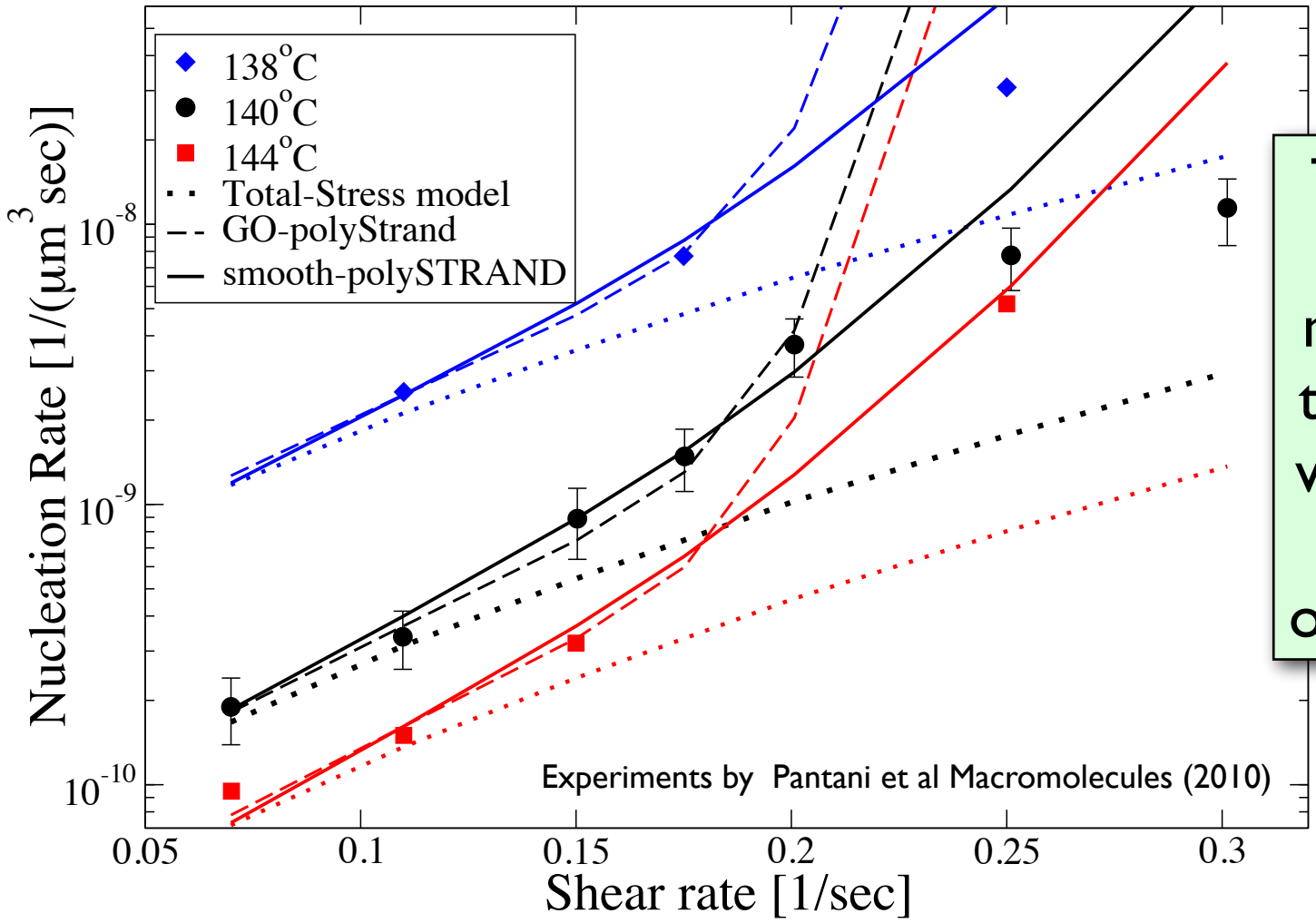
Long chain depletion



$$Q_s = Q_{s0} N_s$$

Number of available stems, Q_s, grows with nucleus size, N_s.

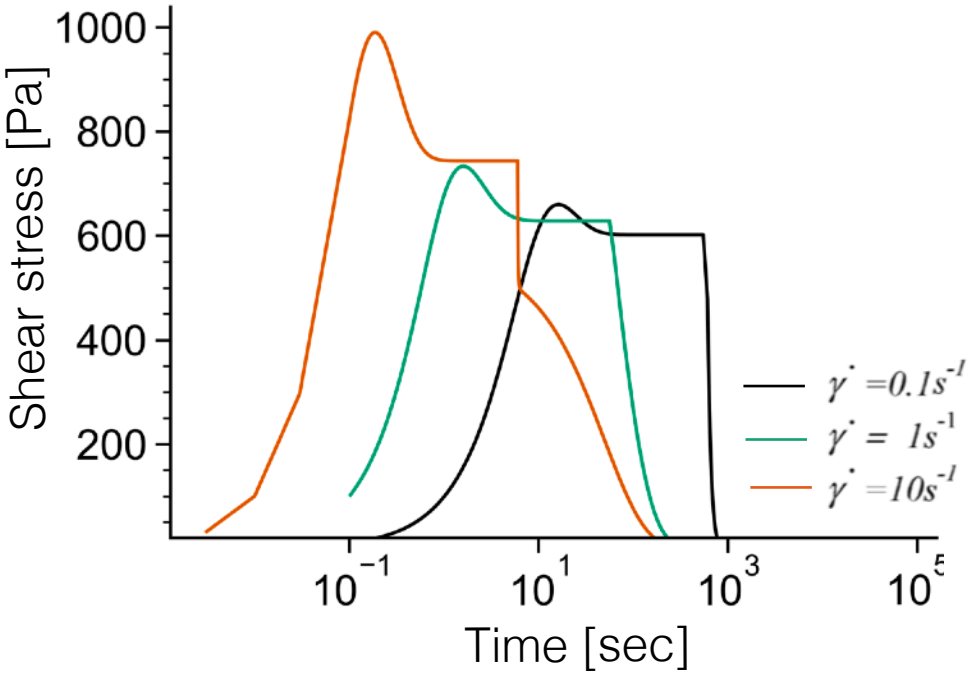
Direct observation of nucleation during steady shear



The smooth-polyStrand model retains the curvature, while relieving some of the overprediction

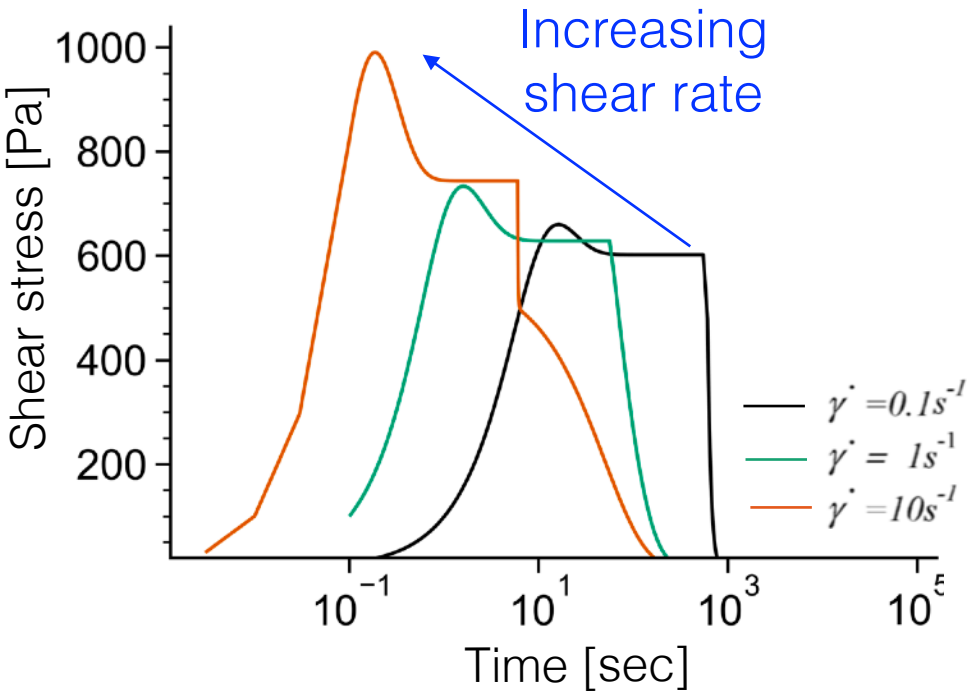
Read, McIlroy, Das, Harlen and Graham, Phys. Rev. Lett. **124** 147802 (2020)

Shear pulse experiments



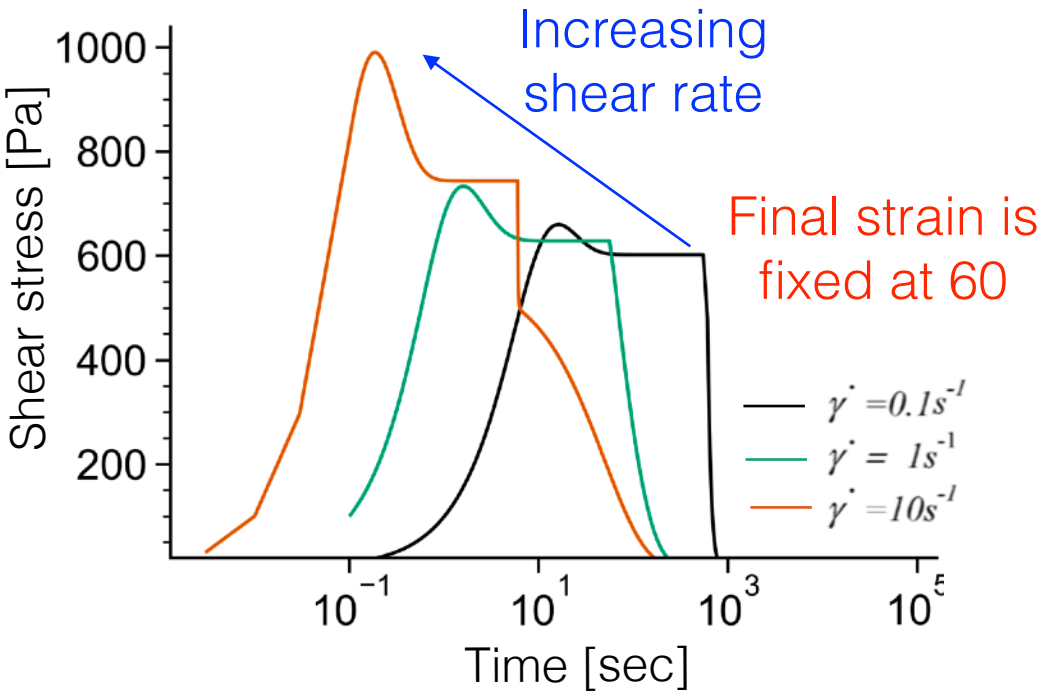
Experiments on isotactic poly(1-butene) [Mw=116-398 kg/mol] by Acierno et al Rheol Acta (2003)

Shear pulse experiments



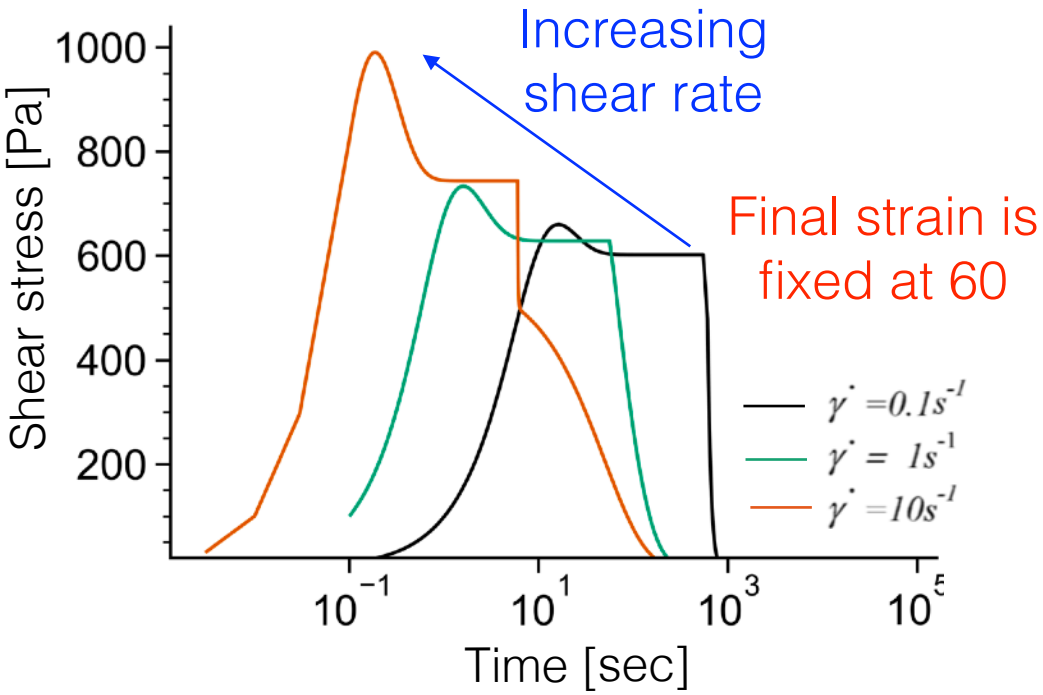
Experiments on isotactic poly(1-butene) [Mw=116-398 kg/mol] by Acierno et al Rheol Acta (2003)

Shear pulse experiments

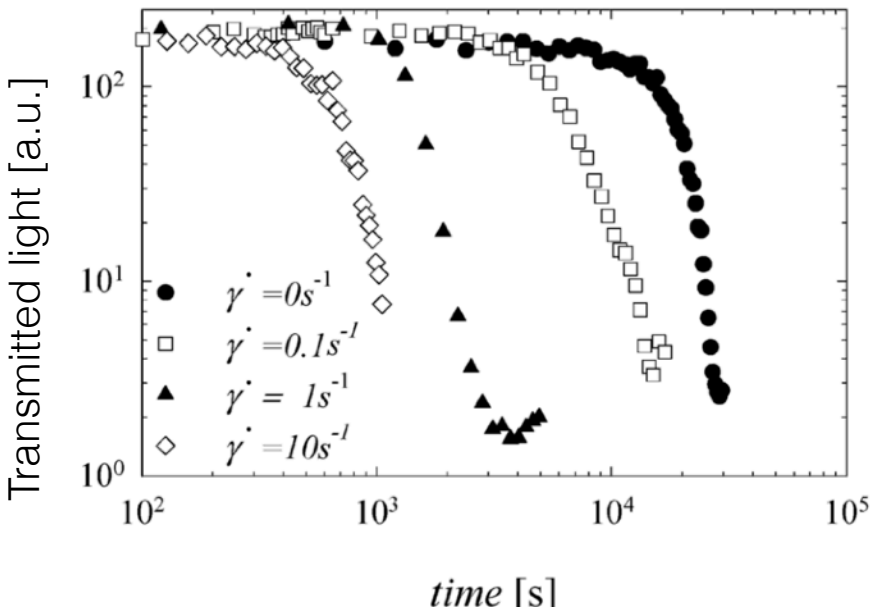


Experiments on isotactic poly(1-butene) [Mw=116-398 kg/mol] by Acierno et al Rheol Acta (2003)

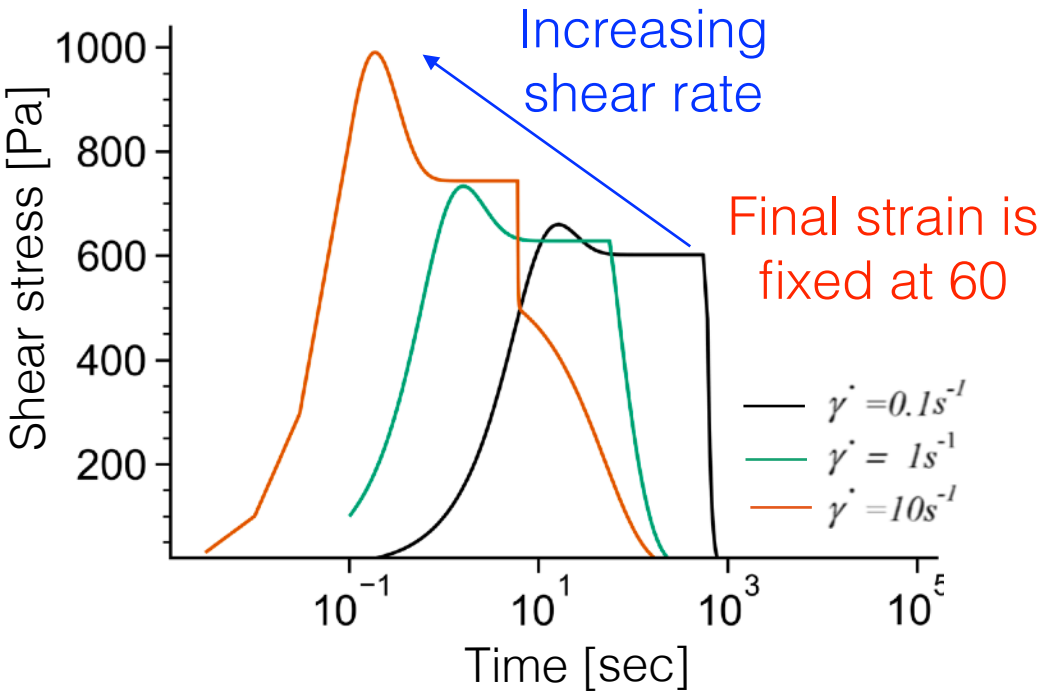
Shear pulse experiments



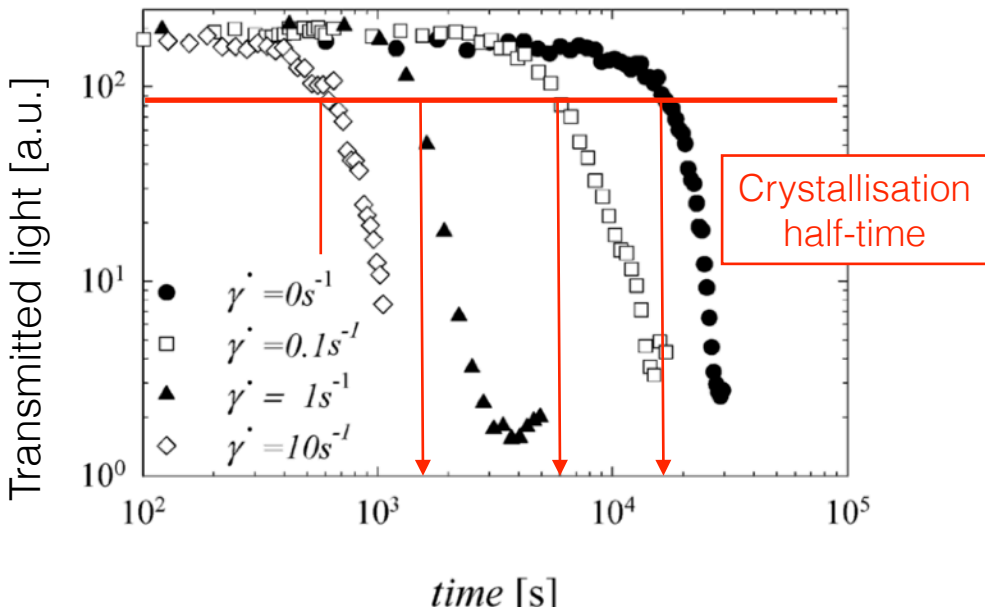
Experiments on isotactic poly(1-butene) [Mw=116-398 kg/mol] by Acierno et al Rheol Acta (2003)



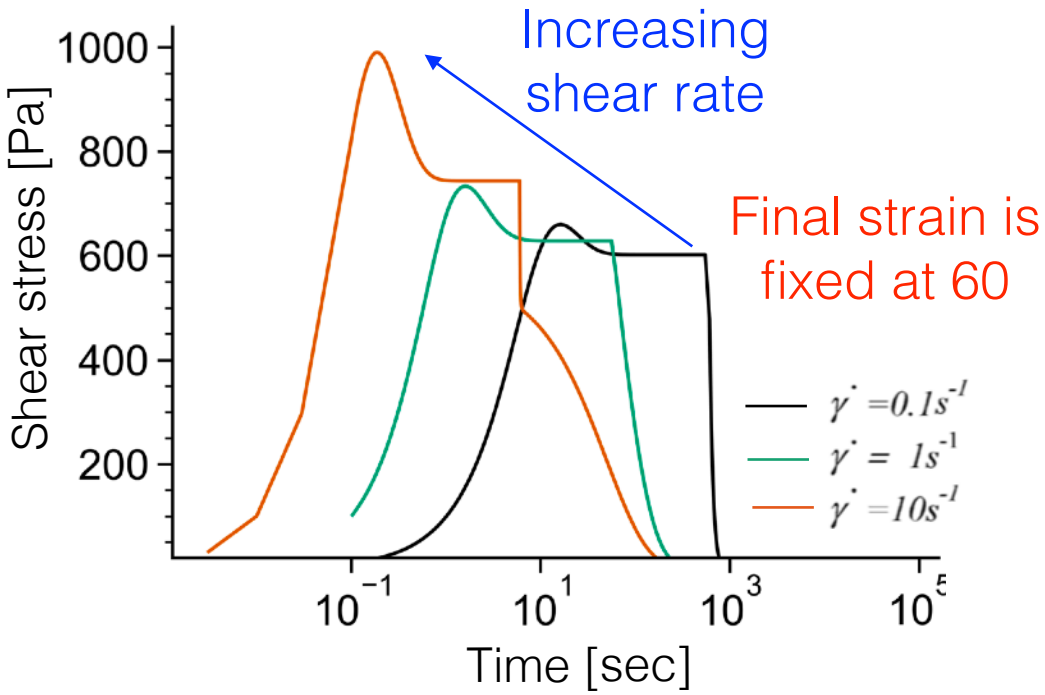
Shear pulse experiments



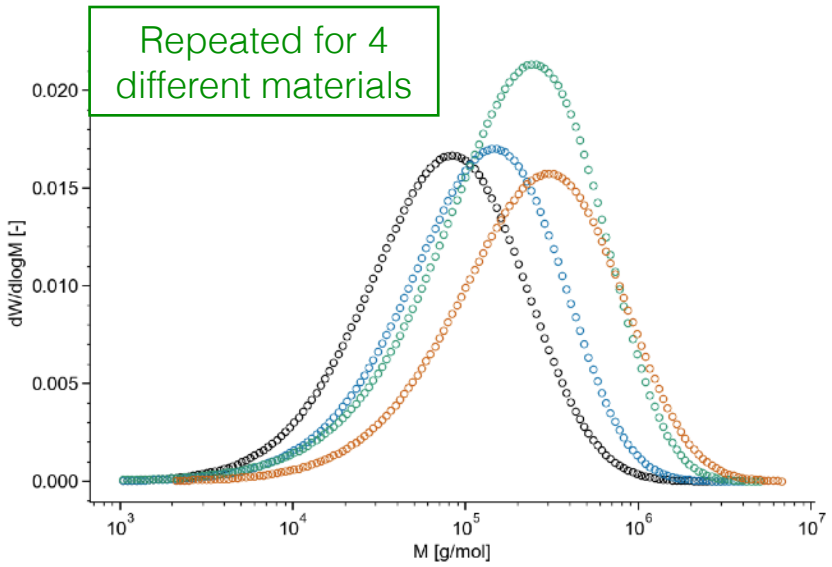
Experiments on isotactic poly(1-butene) [Mw=116-398 kg/mol] by Acierno et al Rheol Acta (2003)

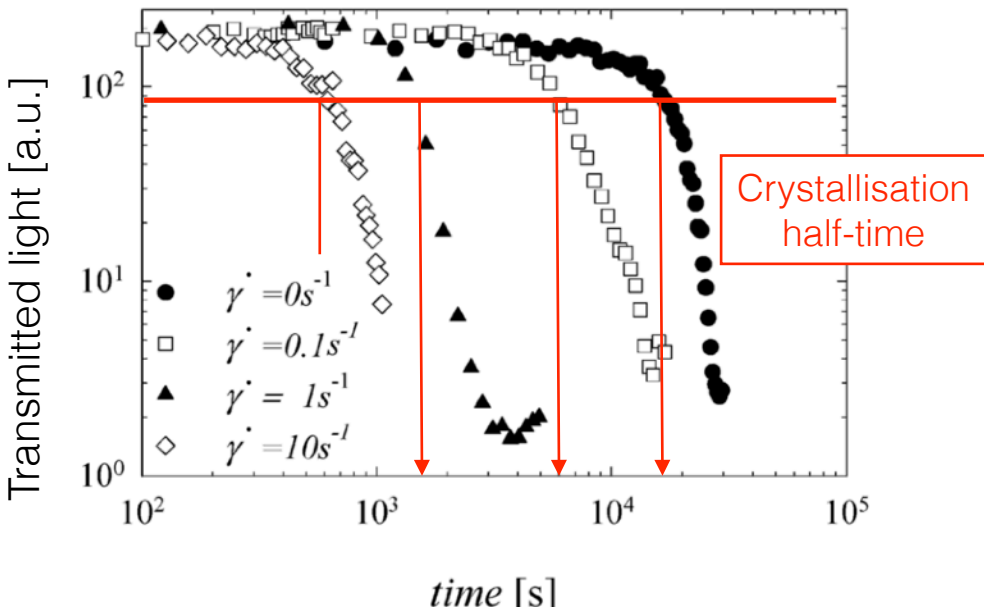


Shear pulse experiments

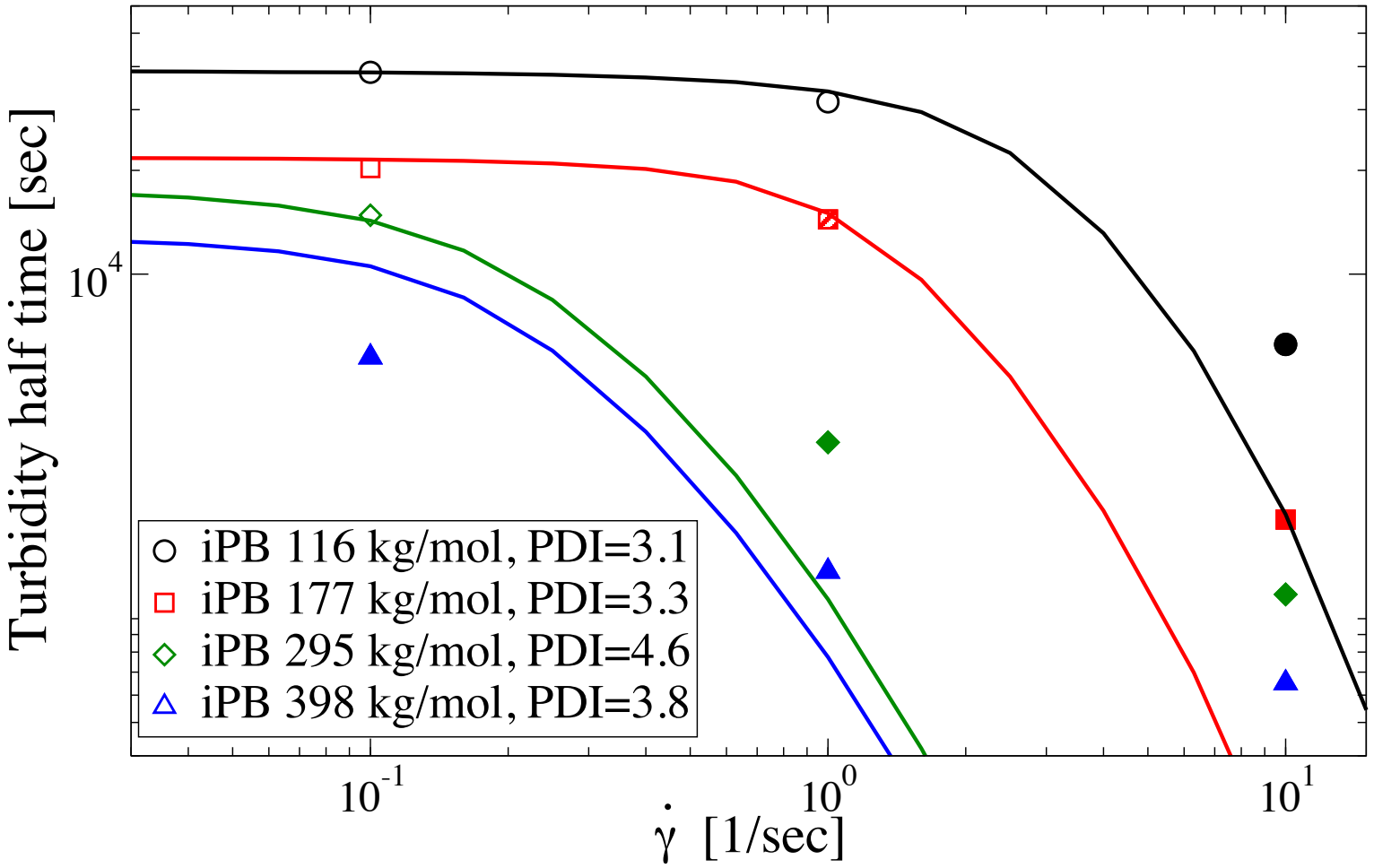


Experiments on isotactic poly(1-butene) [Mw=116-398 kg/mol] by Acierno et al Rheol Acta (2003)



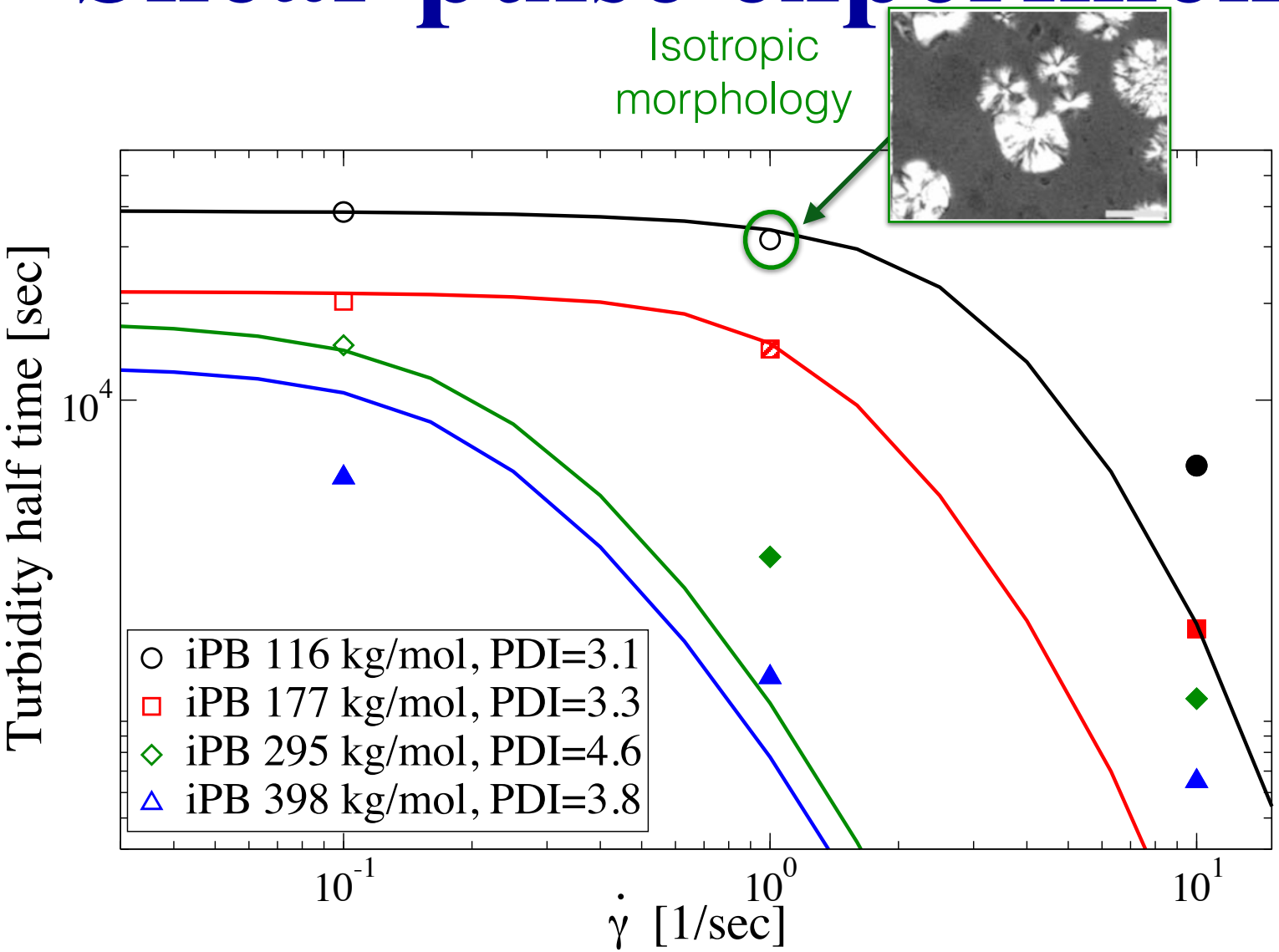


Shear pulse experiments



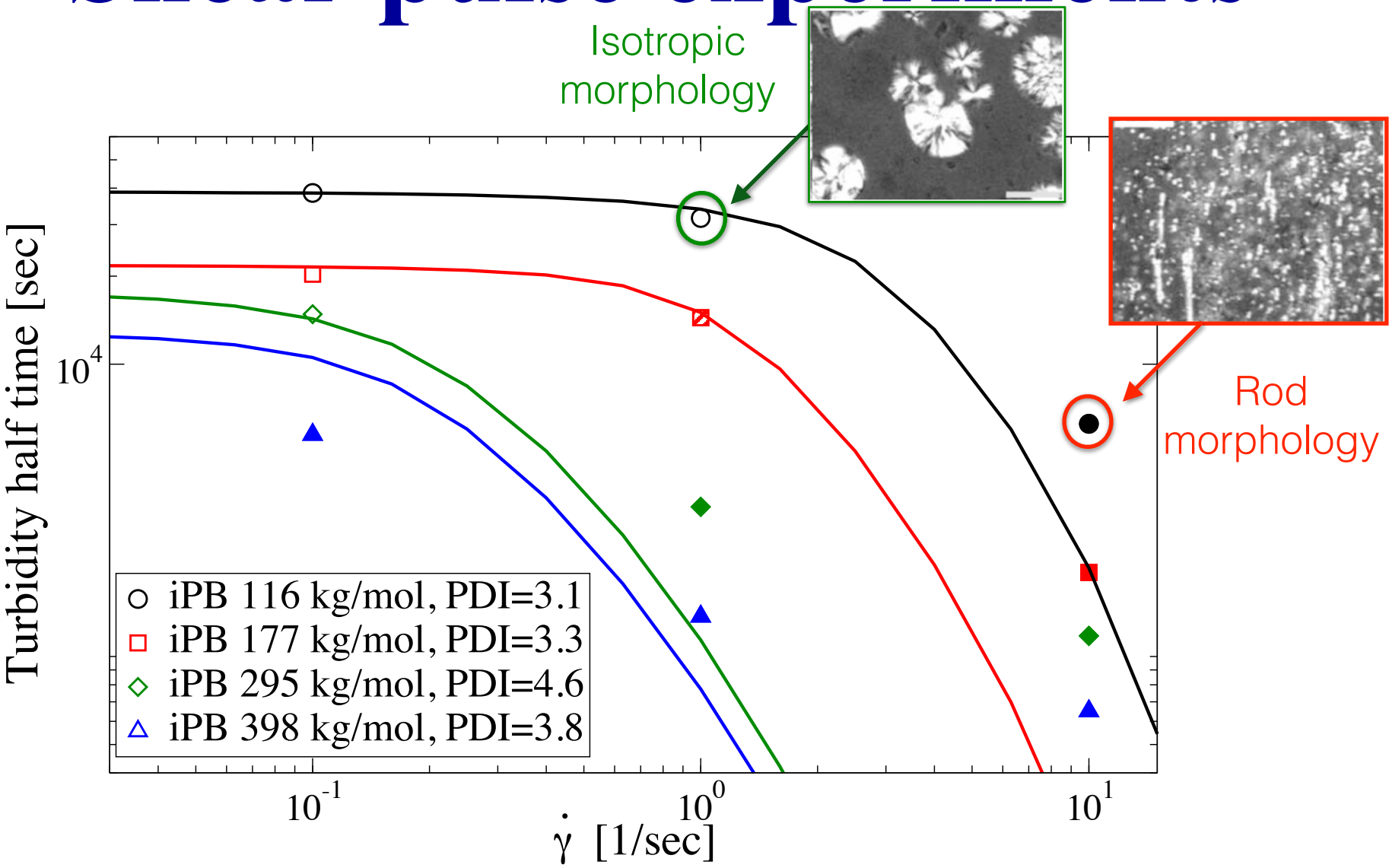
- The same FIC parameters are used for all 4 curves
- Model captures variation due to molecular weight distribution

Shear pulse experiments



- The same FIC parameters are used for all 4 curves
- Model captures variation due to molecular weight distribution

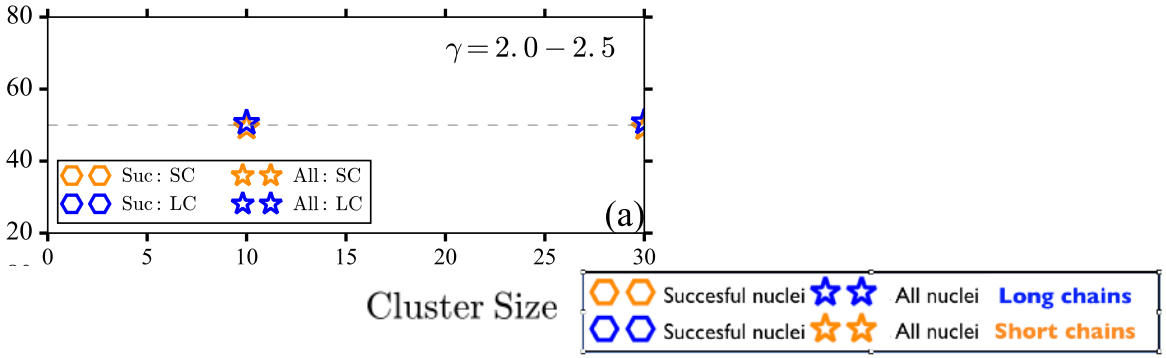
Shear pulse experiments



- The same FIC parameters are used for all 4 curves
- Model captures variation due to molecular weight distribution

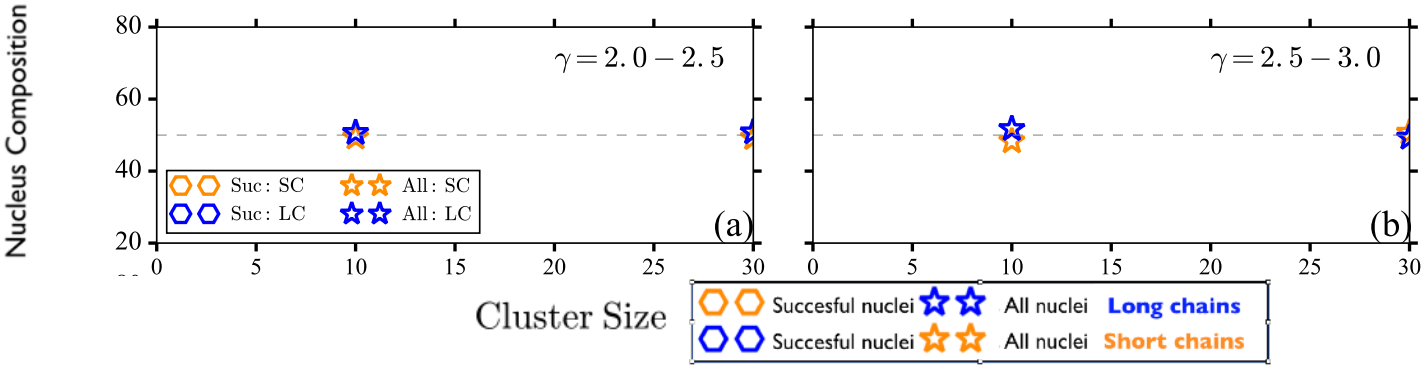
Is long chain enhancement seen in Molecular Dynamics simulations?

Nucleus Composition



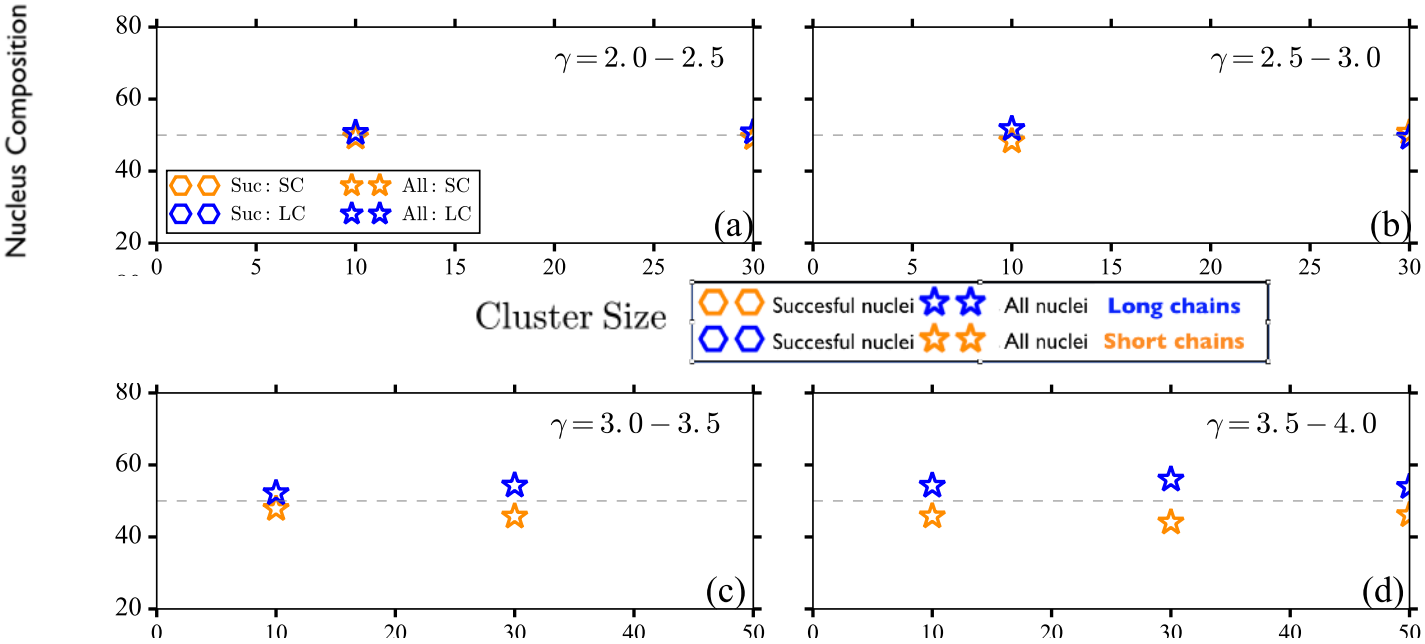
MD simulations of bidisperse PE - 50:50 C1000/C125 chains

$\dot{\gamma}\tau_{R,\mathrm{long}} = 10$



MD simulations of bidisperse PE - 50:50 C1000/C125 chains

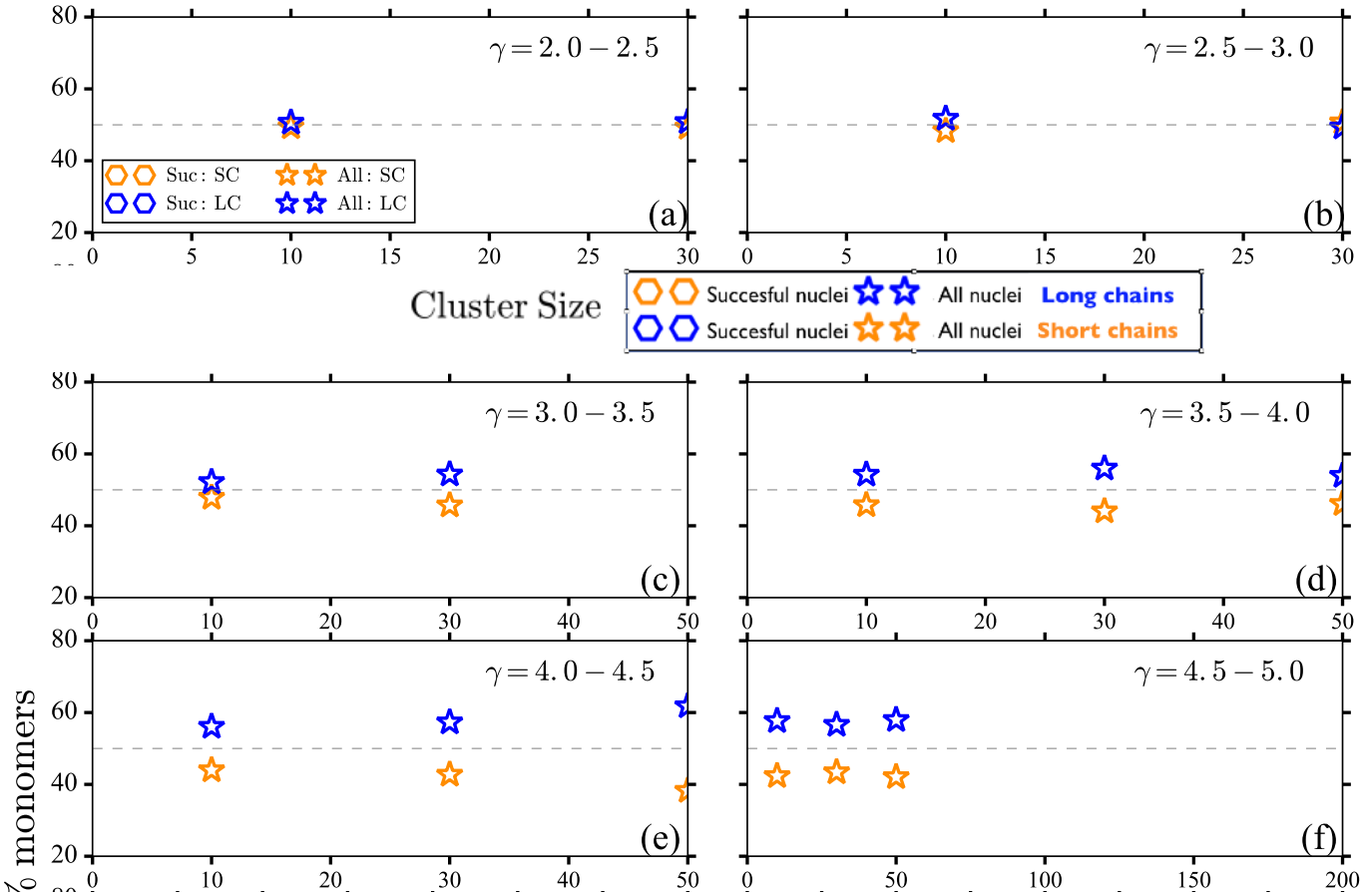
$\dot{\gamma}\tau_{R,\mathrm{long}} = 10$



MD simulations of bidisperse PE - 50:50 C1000/C125 chains

$\dot{\gamma}\tau_{R,\mathrm{long}} = 10$

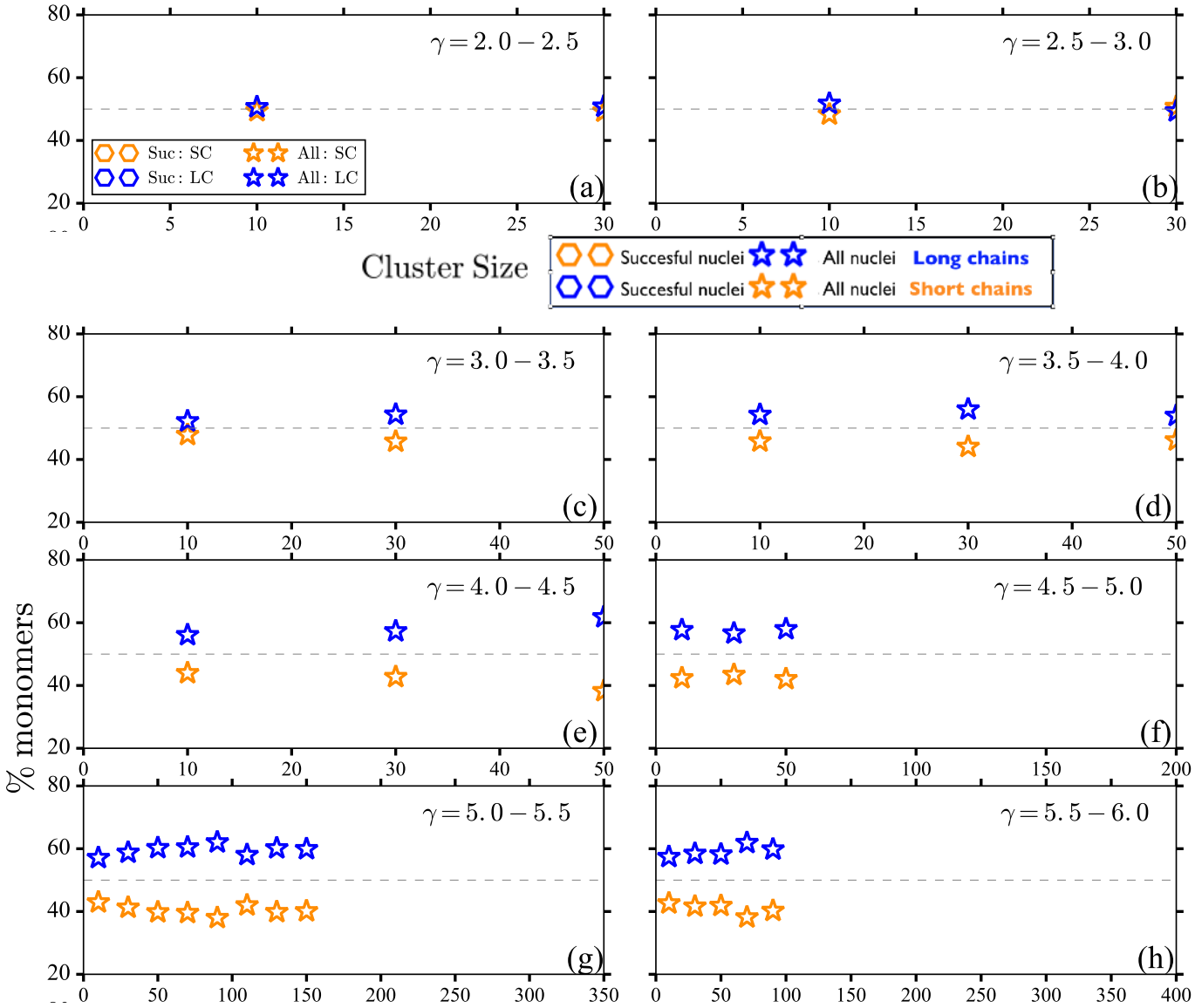
Nucleus Composition



MD simulations of bidisperse PE - 50:50 C1000/C125 chains

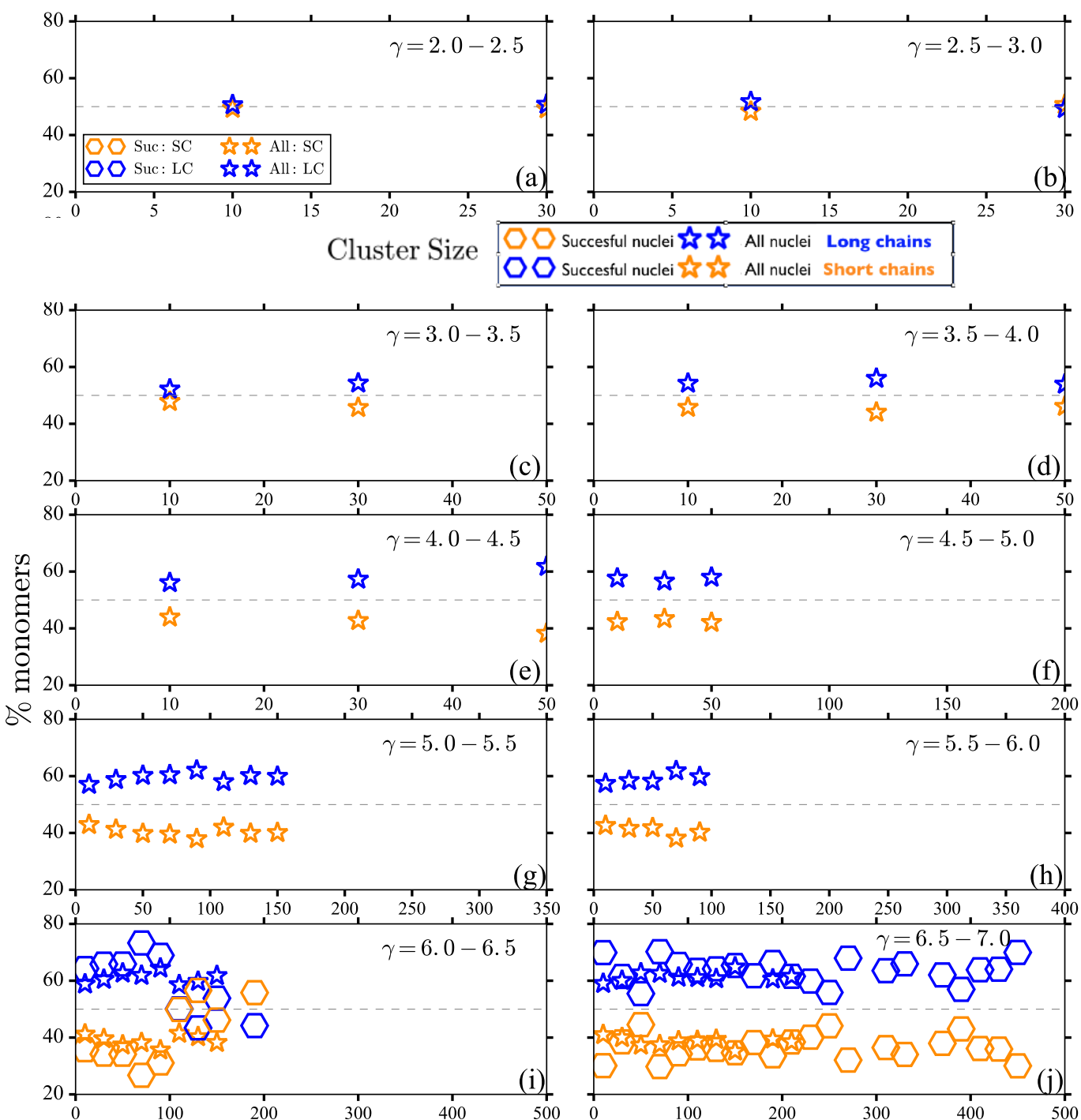
$\dot{\gamma}\tau_{R,\mathrm{long}} = 10$

Nucleus Composition



MD simulations of bidisperse PE - 50:50 C1000/C125 chains

$\dot{\gamma}\tau_{R,\mathrm{long}} = 10$

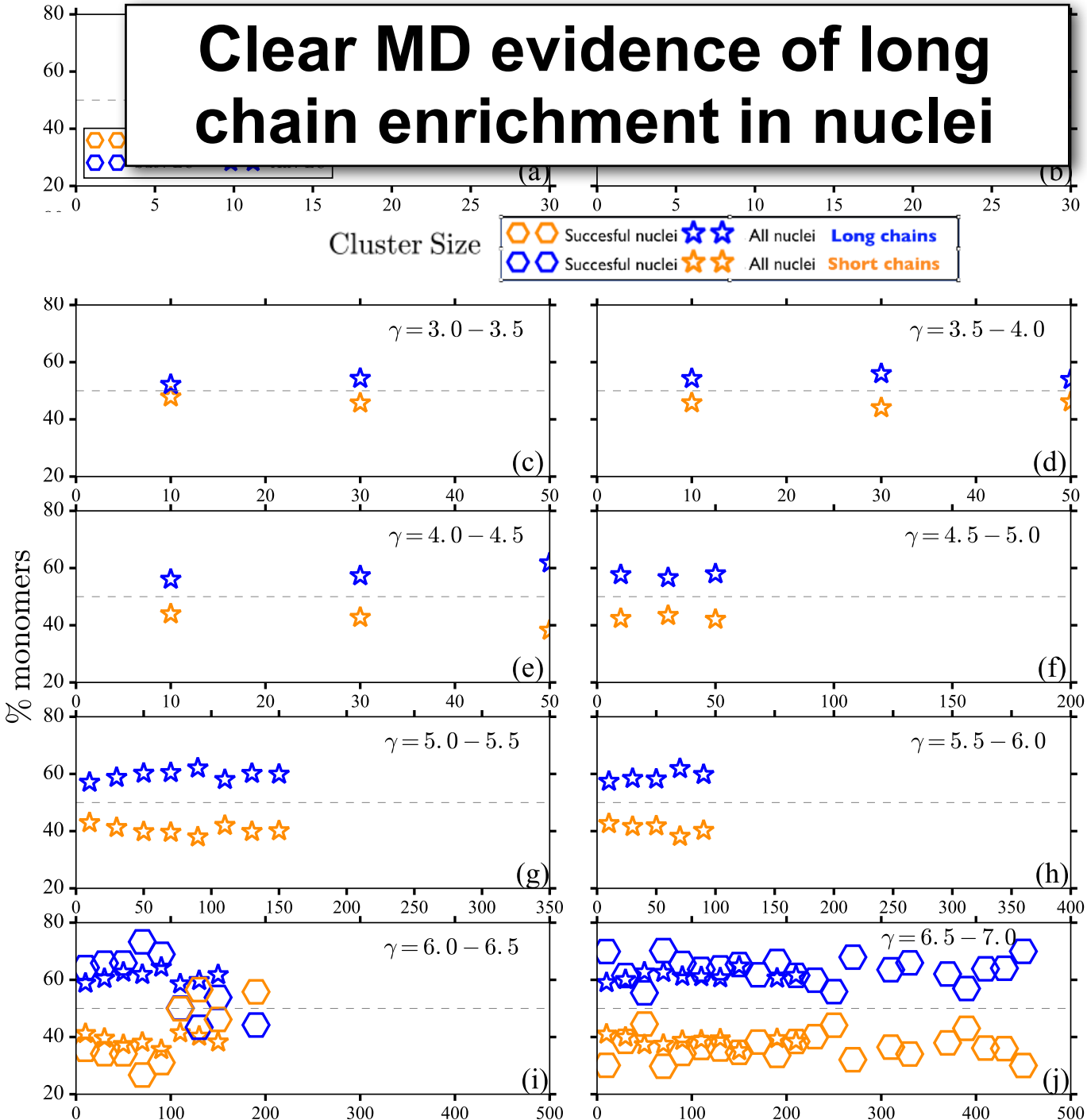


MD simulations of bidisperse PE - 50:50 C1000/C125 chains

$\dot{\gamma}\tau_{R,\mathrm{long}} = 10$

Nucleus Composition

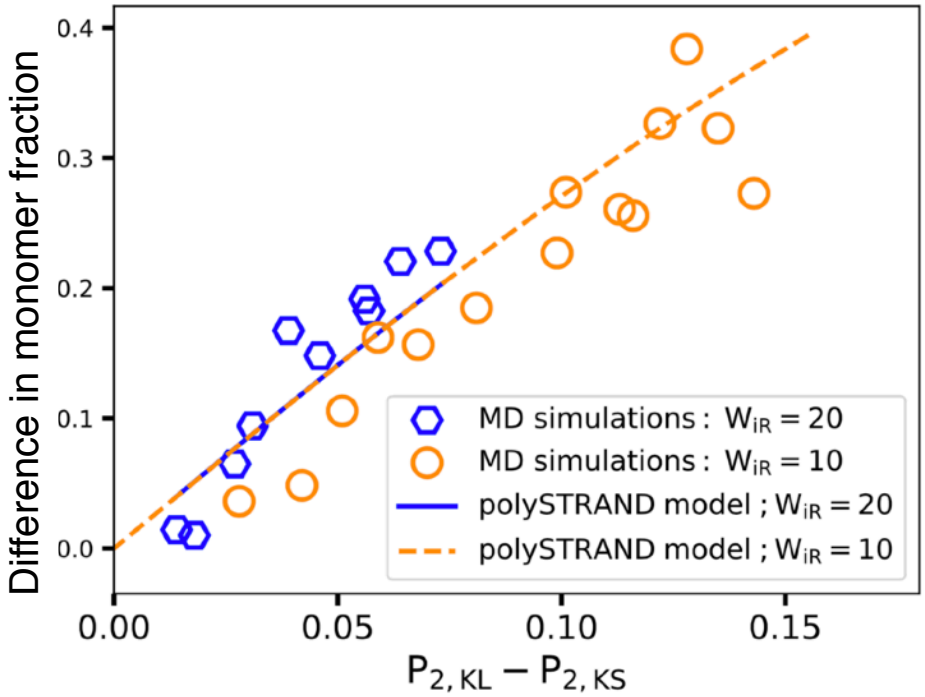
Clear MD evidence of long chain enrichment in nuclei



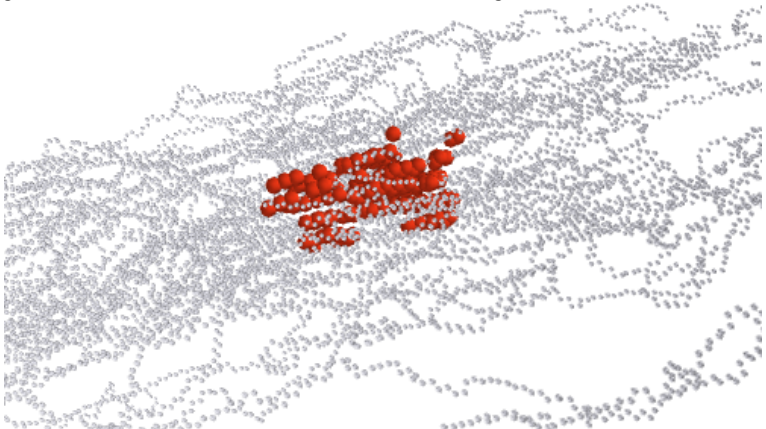
MD simulations of bidisperse PE - 50:50 C1000/C125 chains

$\dot{\gamma}\tau_{R,\mathrm{long}} = 10$

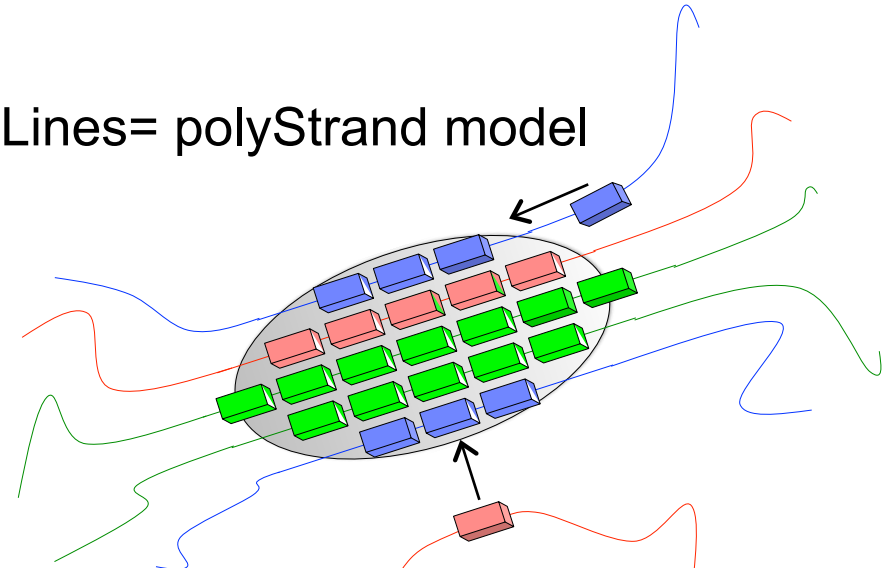
Quantifying the long chain enhancement



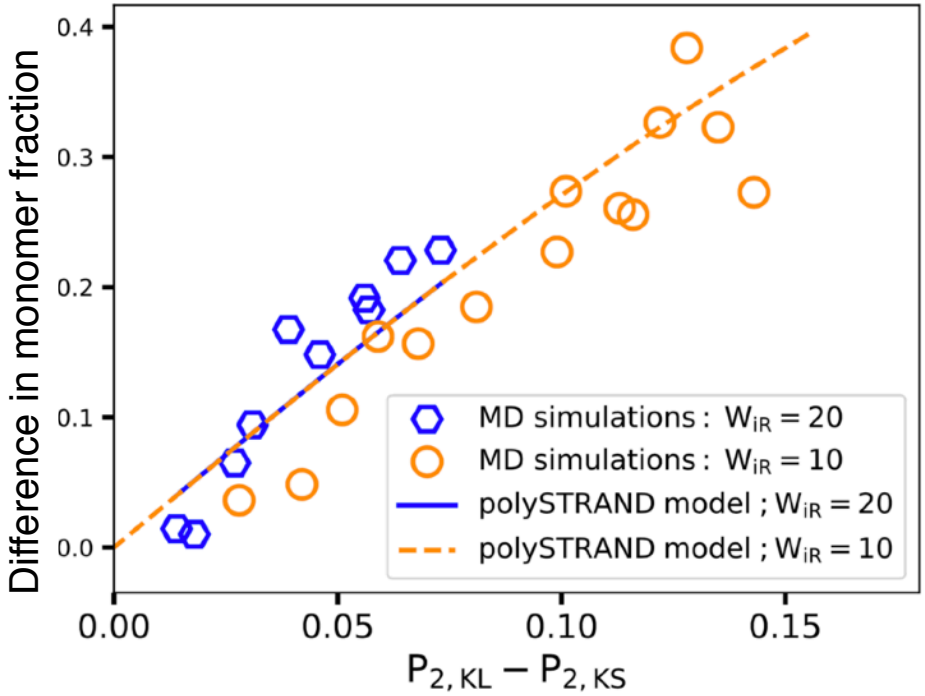
Symbols= Molecular dynamics

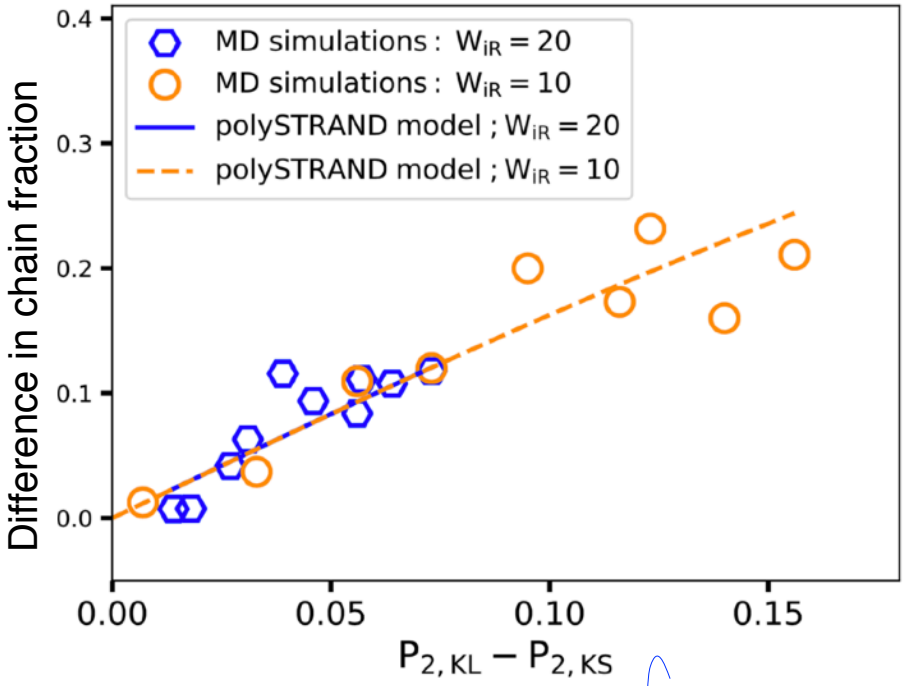


Lines= polyStrand model

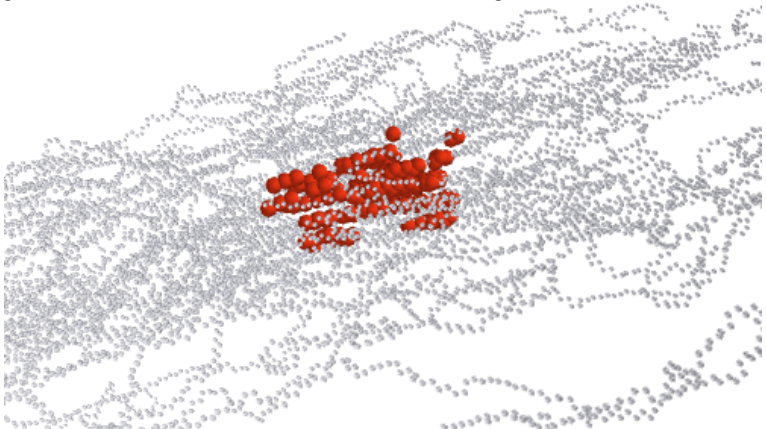


Quantifying the long chain enhancement

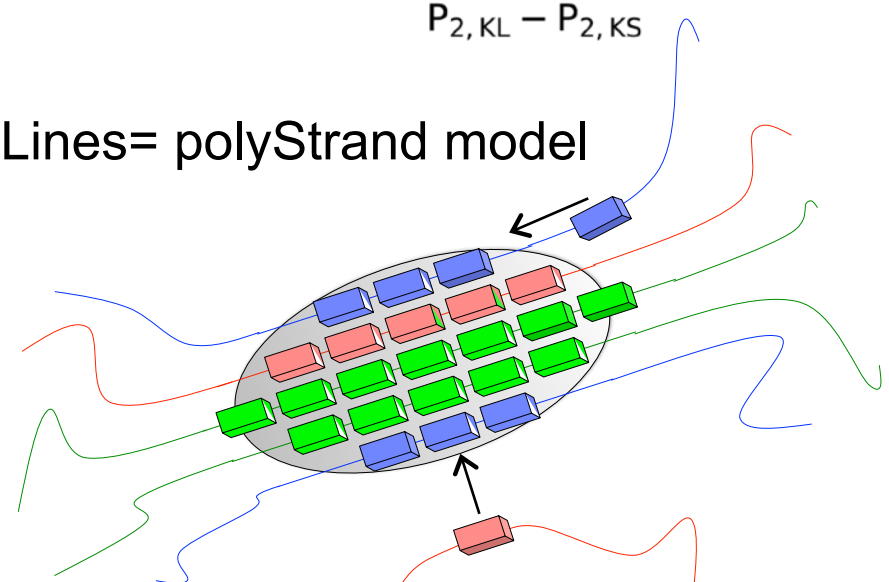




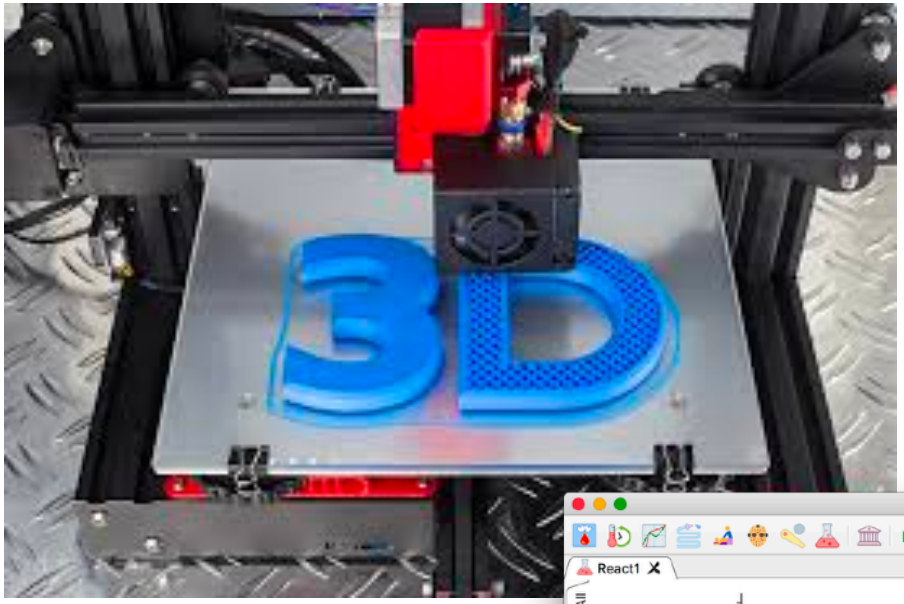
Symbols= Molecular dynamics

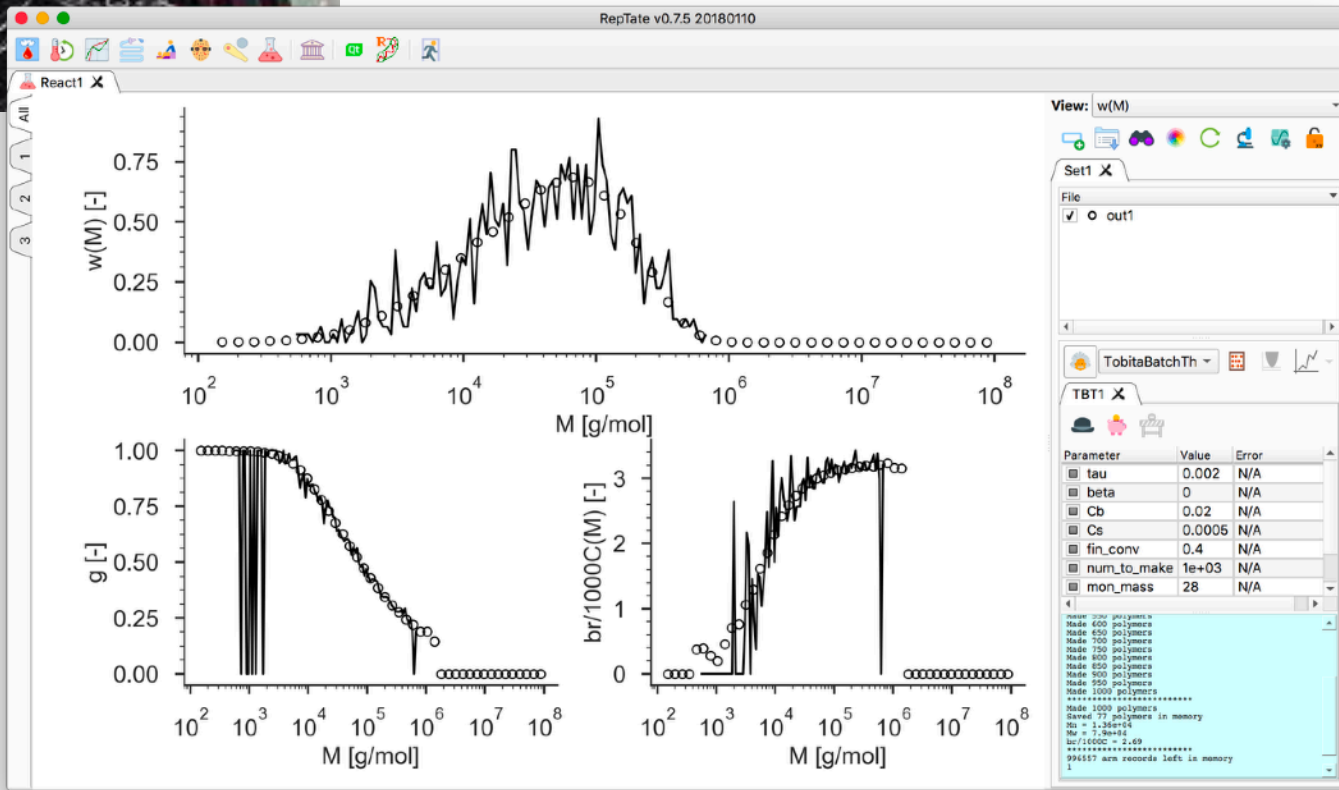


Lines= polyStrand model



Applications

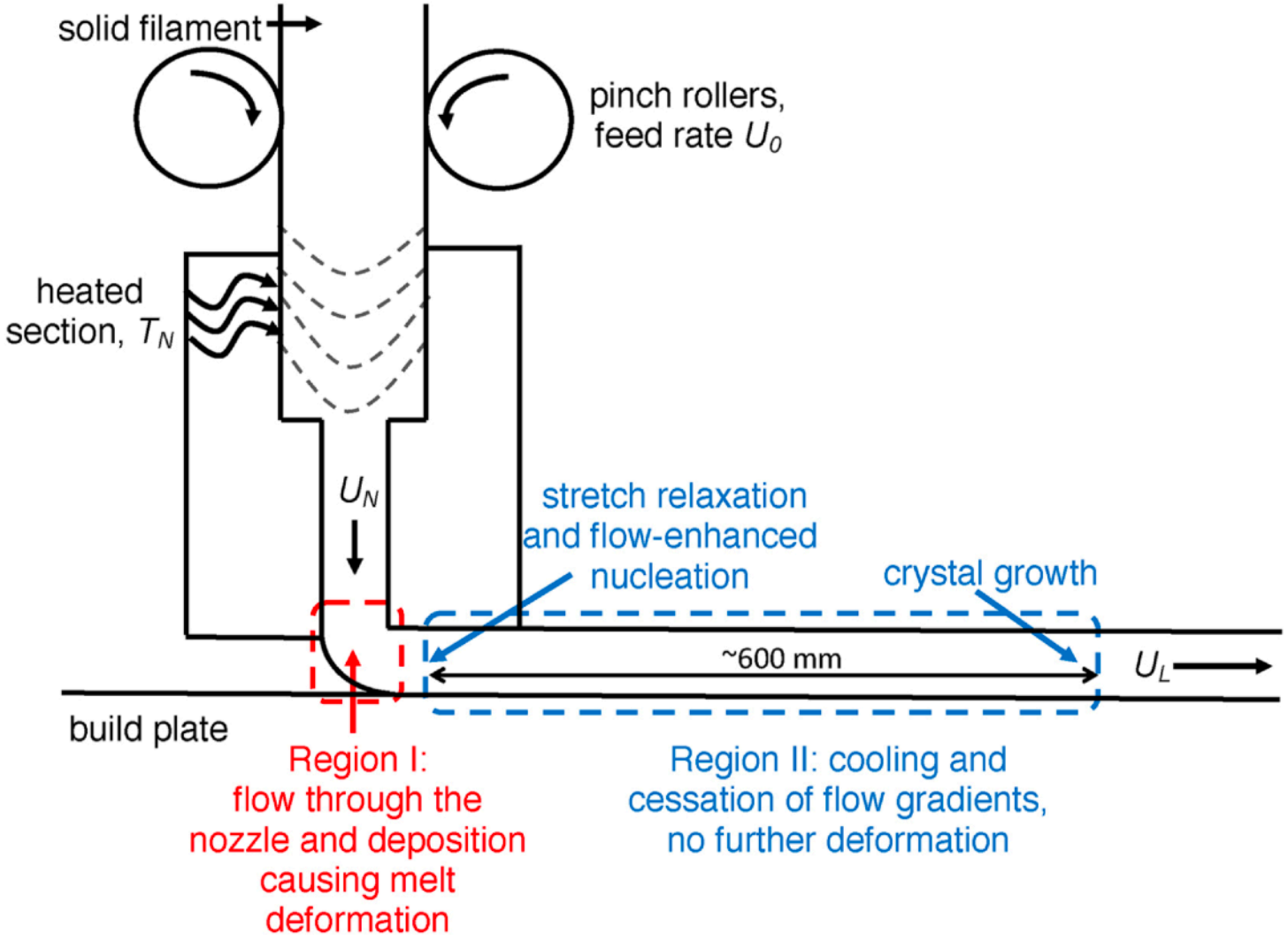




Modelling crystallisation in 3D-printing

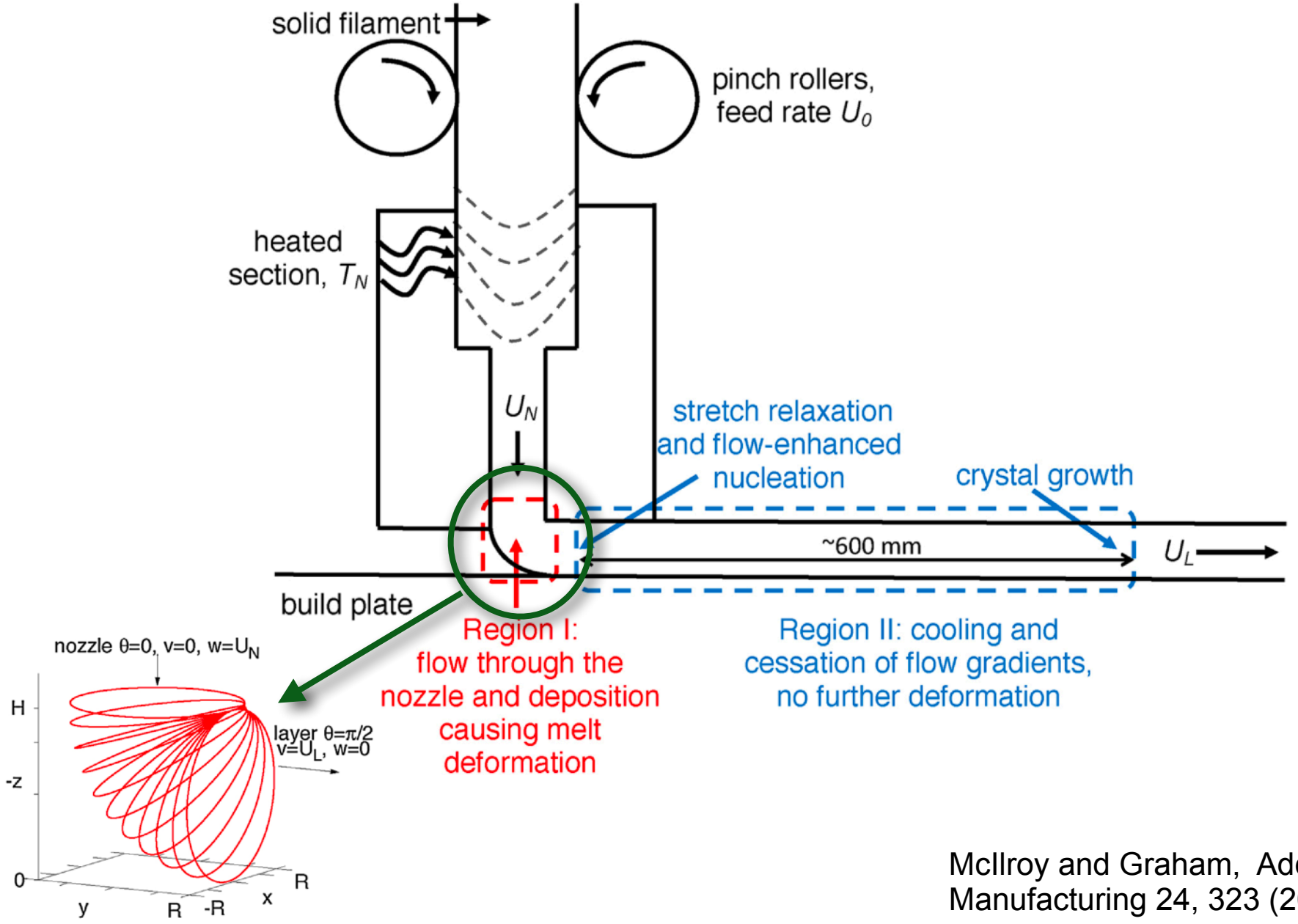
Modelling crystallisation in 3D-printing

Modelling crystallisation in 3D-printing



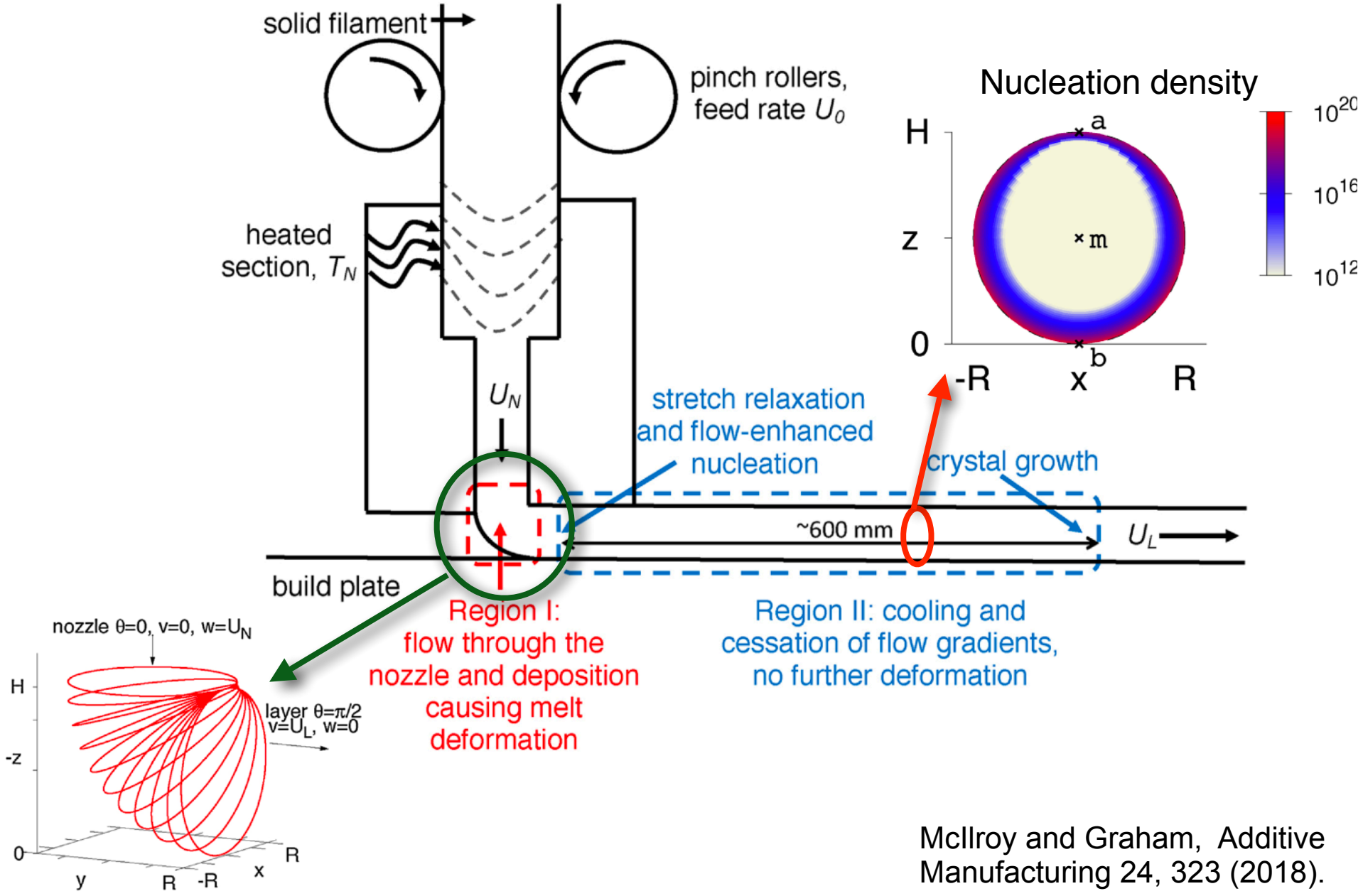
McIlroy and Graham, Additive Manufacturing 24, 323 (2018).

Modelling crystallisation in 3D-printing



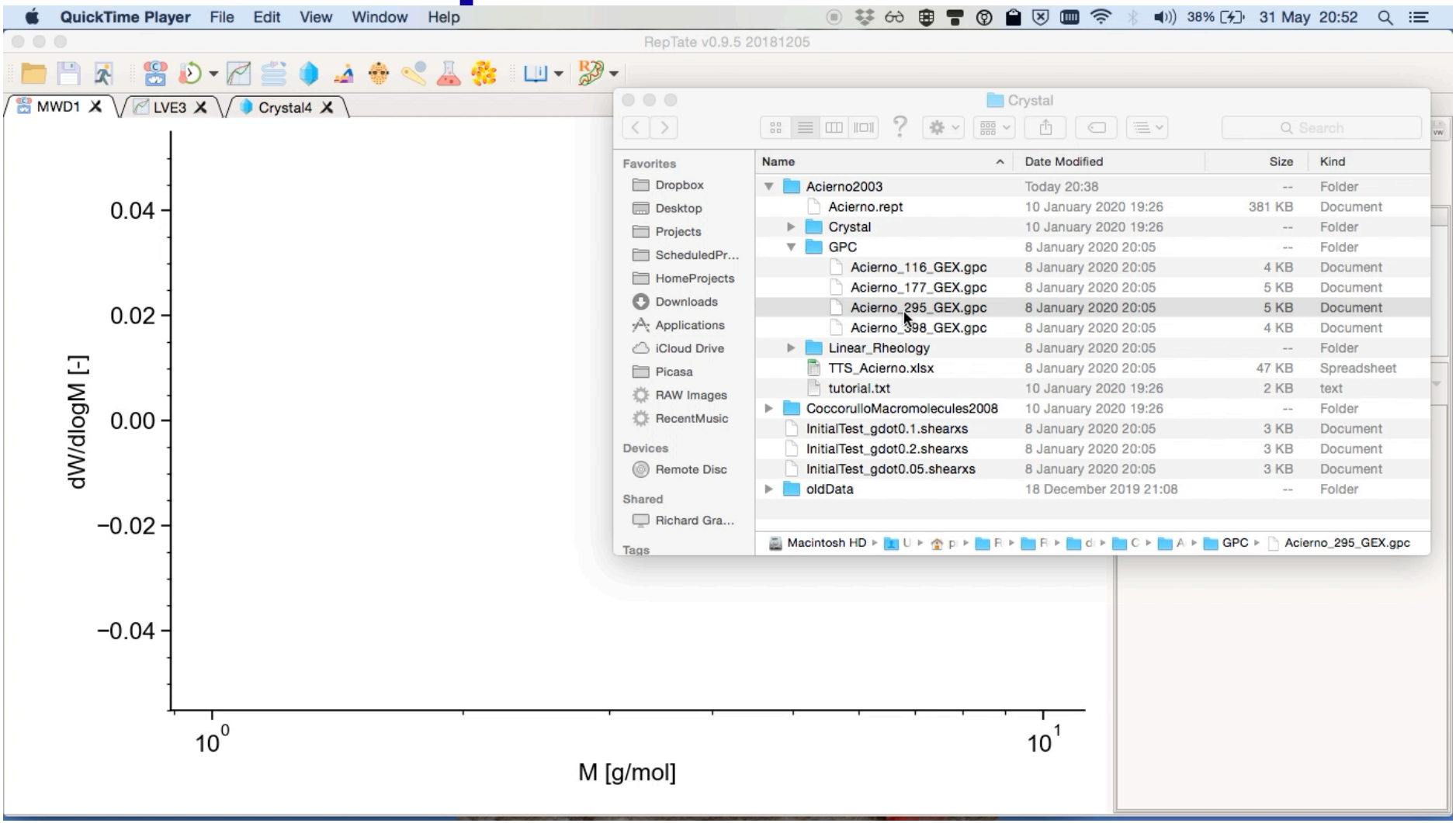
McIlroy and Graham, Additive Manufacturing 24, 323 (2018).

Modelling crystallisation in 3D-printing



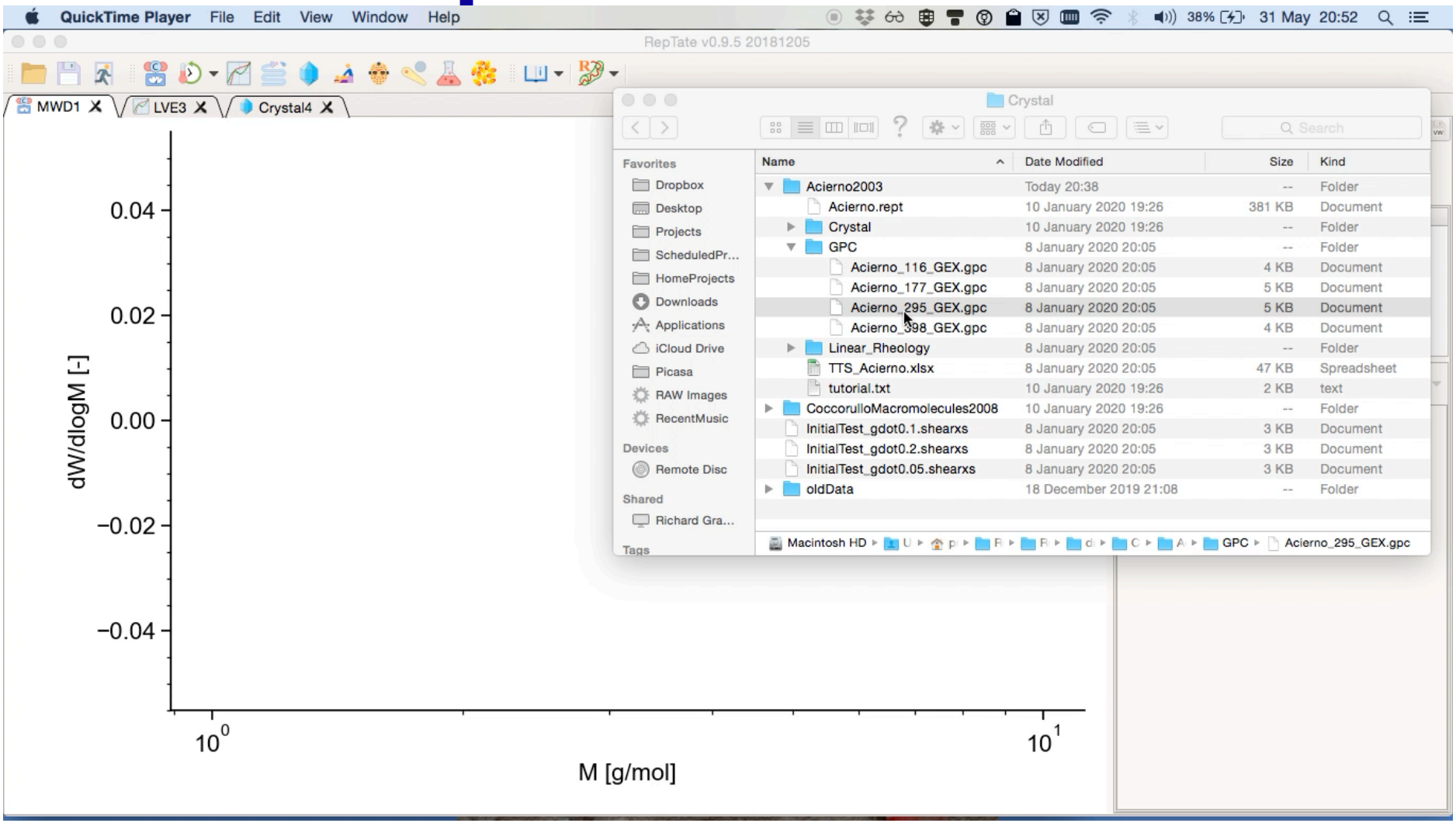
McIlroy and Graham, Additive Manufacturing 24, 323 (2018).

RepTate software



Freely available from: http://reptate.readthedocs.io/

RepTate software



Freely available from: http://reptate.readthedocs.io/

Summary

- **Flow-induced crystallisation:** In polymers flow can very strongly enhance the rate of crystallisation.
- **Modelling is challenging**: due to very wide spread of length and timescales
- **Multi-scale modelling**: MD and kinetic Monte Carlo simulations used to systematically derive a continuum model of nucleation.
- **Continuum model**: Nearly analytic expression for the nucleation rate; quantitatively consistent with MD and the GO model
- **Agreement with experiments:** Agrees with experiments. Correctly captures variation with flow rate, temperature and molecular weight.
- **Enhancement of long chains:** Model predicts long chains are over-presented in nuclei of crystallisation; confirmed in MD simulations; experimental signature identified.