

Polymer Crystallization: New Concepts and Implications

(M. Muthukumar)

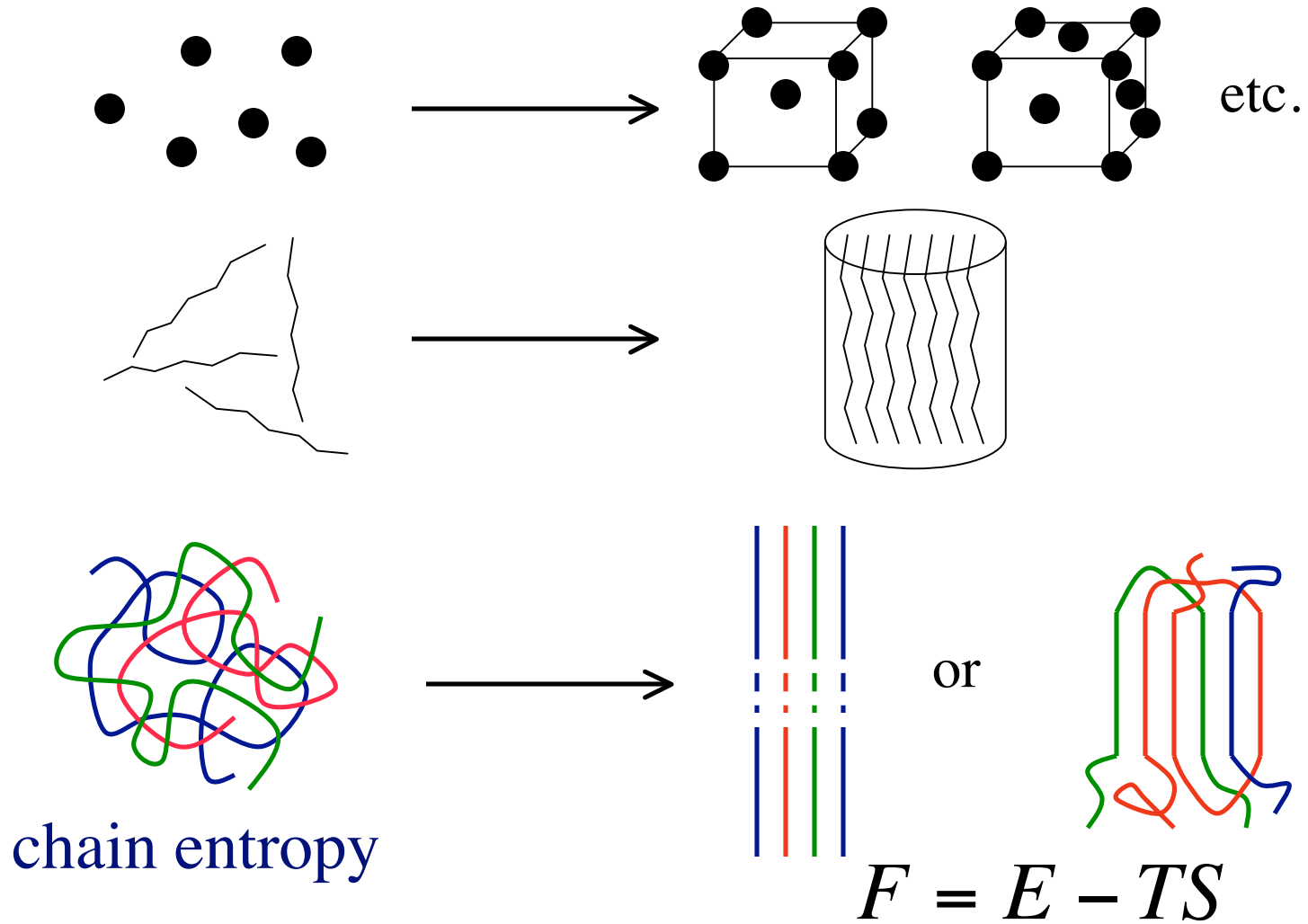
Nucleation, Aggregation and Growth
Bengaluru

July 26- July 30, 2010

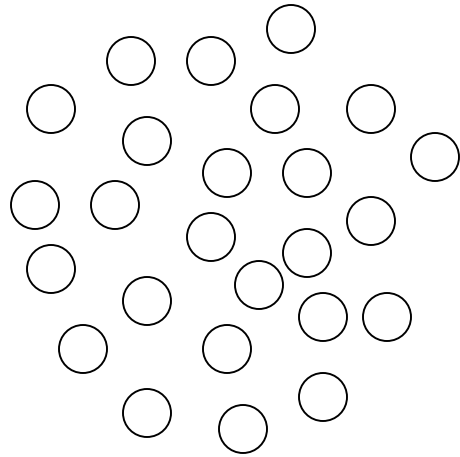


PS&E *UMass - Amherst*

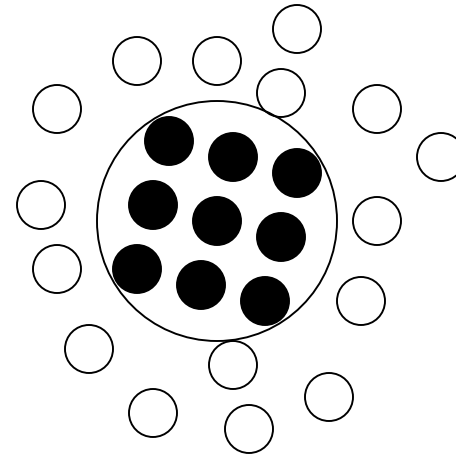
What distinguishes **polymers** from small molecules, colloidal particles, and oligomers?



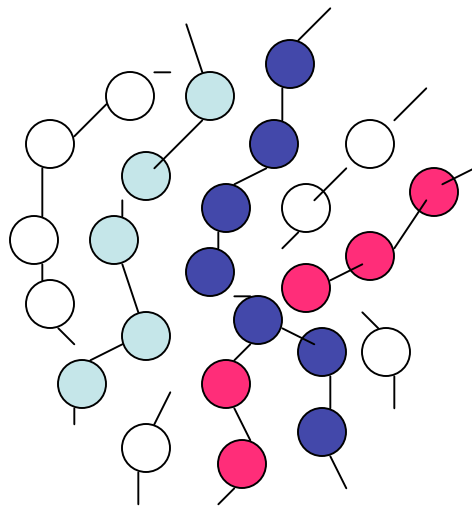
(Is TS negligible?)



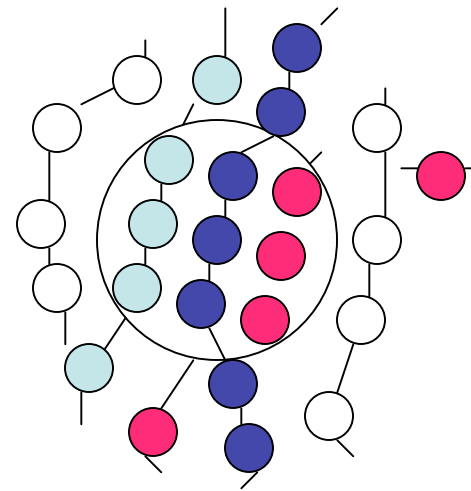
Monomeric liquid



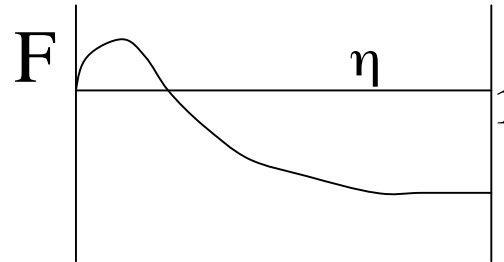
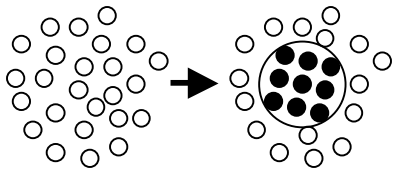
Nucleation



Polymeric liquid

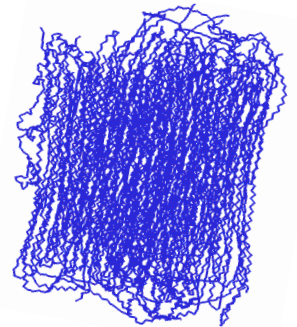
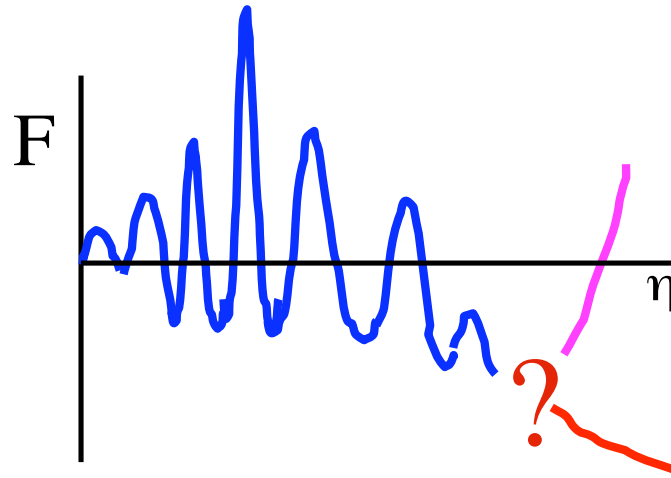
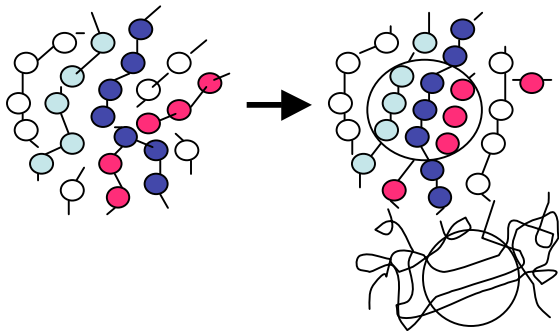


Small molecules:



(η = degree of crystallinity, lamellar thickness,..)

Polymer molecules:



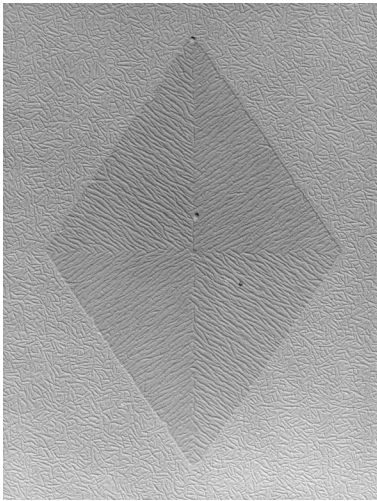
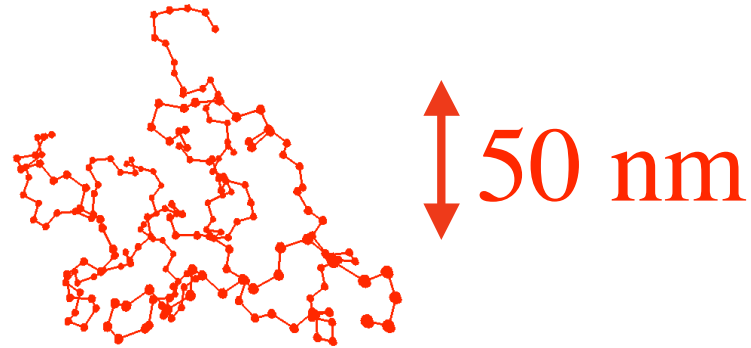
Conformational entropy

Entropic Frustration

$$F = E - T S$$

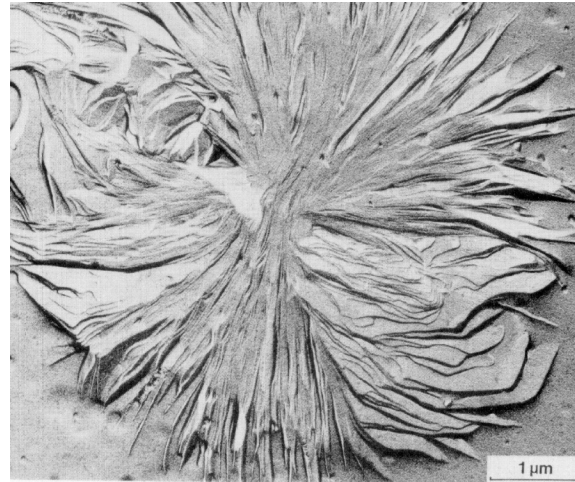
Semicrystallinity = equilibrium ?
Semicrystallinity = kinetics ?

Crystallization of flexible polymers

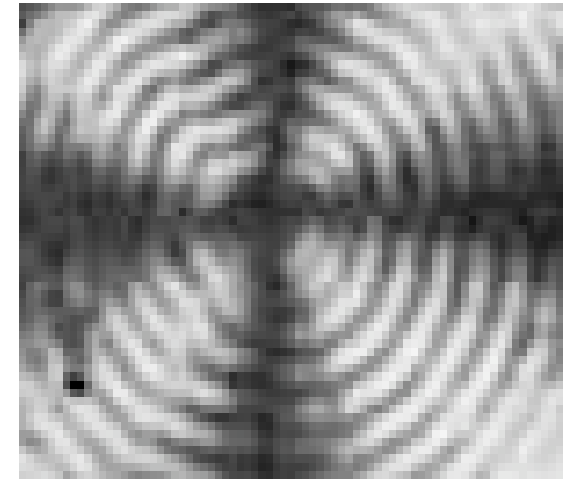


Lamella

L ~10 nm



Spherulites



GIGANTIC CHIRALITY
in polyethylene crystals
(ACHIRAL molecules)

B. Lotz and S.Z.D. Cheng, *Polymer*, 46, 577 (2005)

H. K. Storks, JACS, 60, 1753 (1938):

“..macromolecules are folded back and forth upon themselves..”

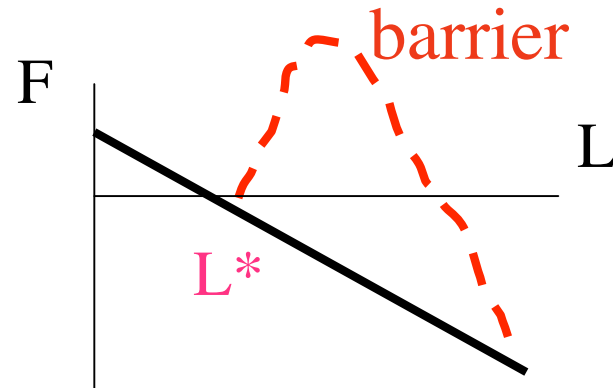
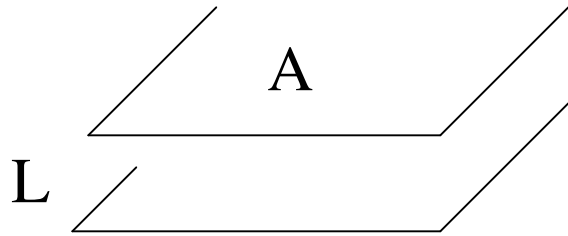
G. Strobl, “The Physics of Polymers” (1997):

“..is governed by kinetic criteria rather than by equilibrium thermodynamics”

CLASSICAL VIEW

A. Lamellar Thickness:

(L = lamellar thickness)



$$F = -(\Delta F) A L + 2 \sigma A$$

bulk interface

$$L^* = (2 \sigma / \Delta F) \sim (1/\Delta T)$$

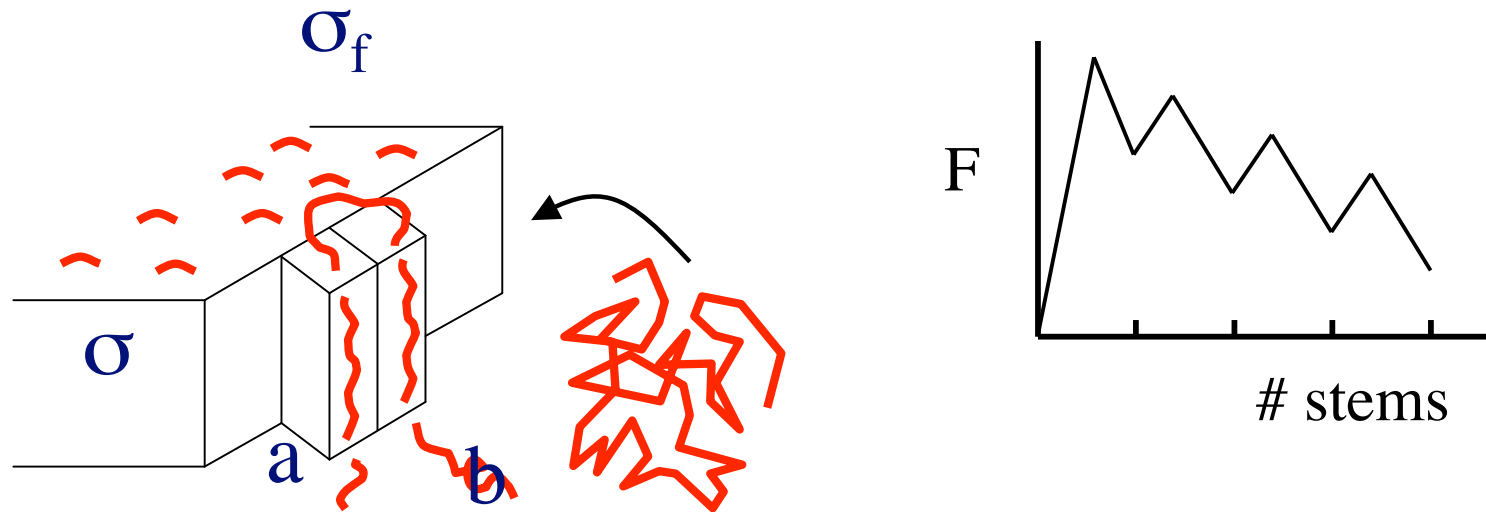
$$\Delta T = T_m - T_c$$

- * First viable state kinetically stabilized
- * Eventual extended chain dimension

CLASSICAL VIEW

B. Lamellar Growth:

Lauritzen-Hoffman Theory (1960)



Rate of growth: $G \sim \exp[-1/T(\Delta T)]$
(2d-Nucleation)

Central Issues

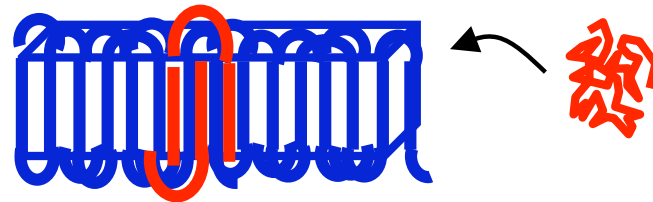
1. Primordial stage of polymer crystallization

2. Spontaneous selection of lamellar thickness $L \ll$ extended chain dimension
 $\sim 10^{-2} \times$ current equilibrium arguments

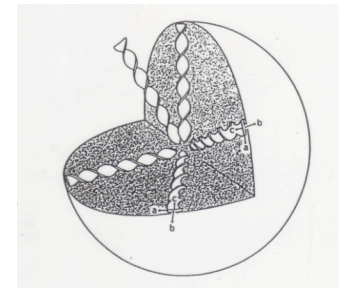
\Rightarrow “KINETICALLY CONTROLLED”

Interlude from any stable MESOMORPHIC states?

3. Kinetics at growth front



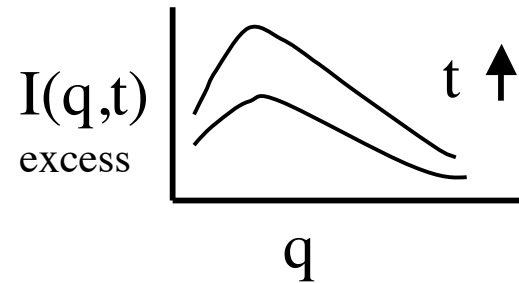
4. Origin of chiral symmetry breaking



5. Composition fluctuations on crystallization kinetics

1. Primordial stage of polymer crystallization

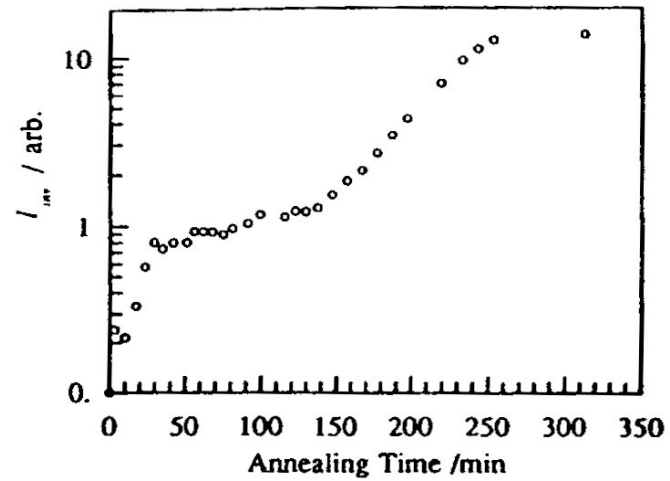
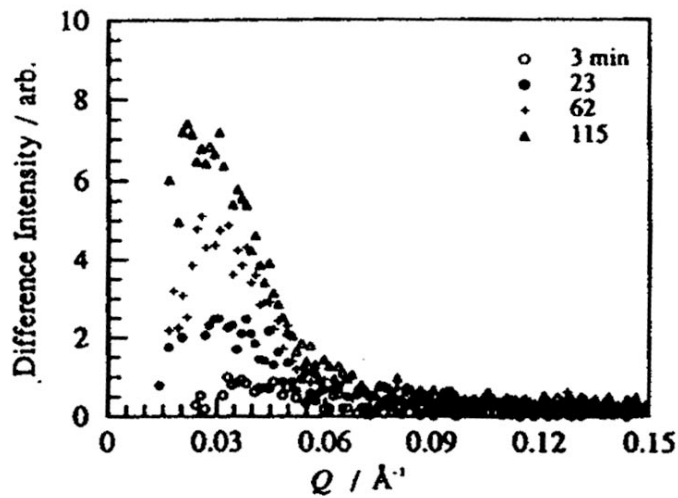
Density fluctuations **before**
crystalline signature



Postulate

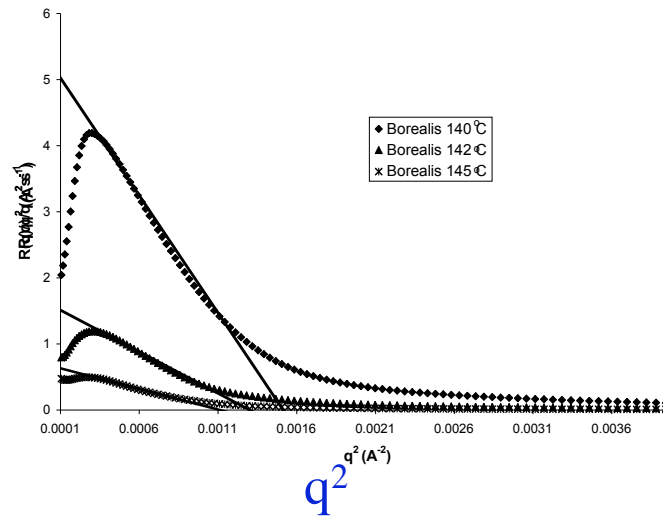
Spinodal Decomposition into
inter-connected polymer-rich and polymer-poor phases,
instead of
Nucleation-Growth

Scattered Intensity at Early Times



M. Imai et al. *Macromolecules* 1994, 27, 7103.(PET)

Rate: R_q/q^2



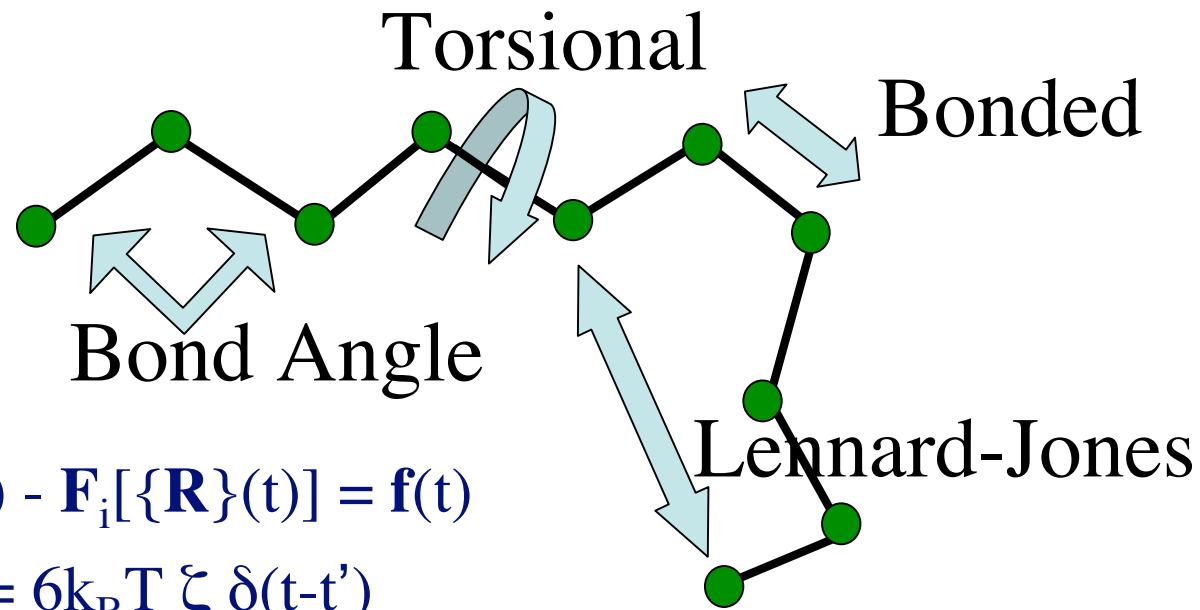
Spinodal Mode

A.J. Ryan and collaborators (I-PP)

Acknowledgments

I. Langevin Dynamics Simulations

C. Liu, P. Welch, I. Dukovski, J. Zhang



$$m_i \mathbf{a}_i(t) + \zeta \mathbf{v}_i(t) - \mathbf{F}_i[\{\mathbf{R}\}(t)] = \mathbf{f}(t)$$
$$\langle \mathbf{f}(t) \cdot \mathbf{f}(t') \rangle = 6k_B T \zeta \delta(t-t')$$

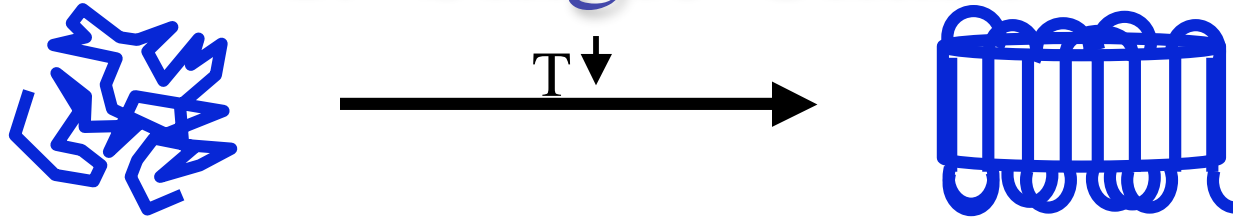
II. Statistical Mechanics

A. Kundagrami, M.K. Mitra, Y. Hatwalne

$$e^{-F/k_B T} = \int e^{-H}$$

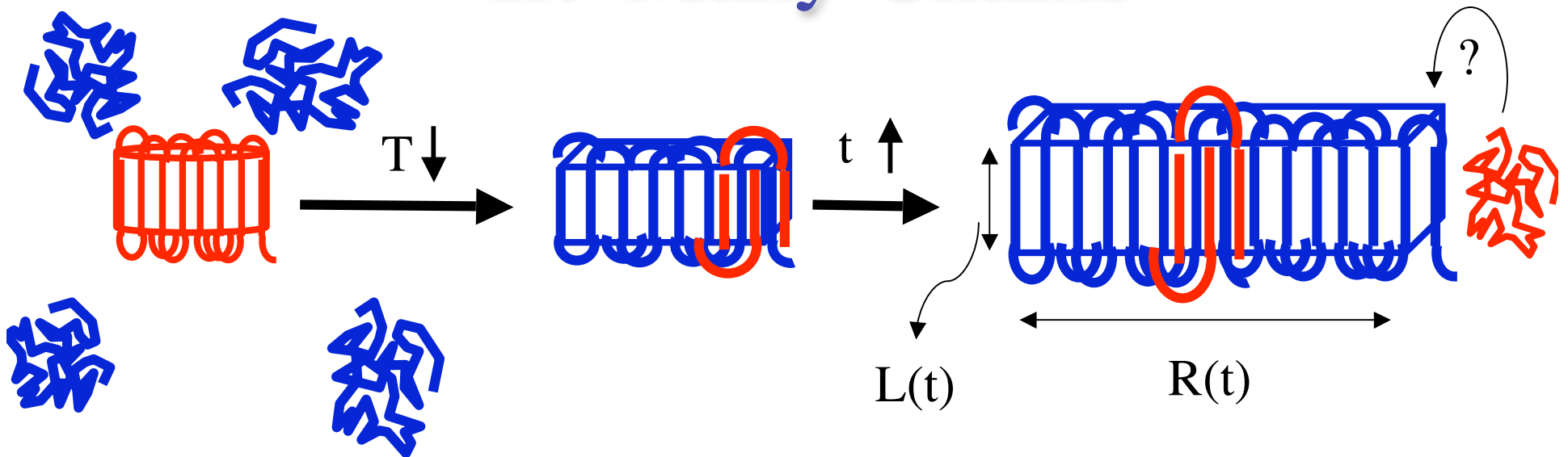
Free energy Coarse-grained Hamiltonian

I. Single Chain



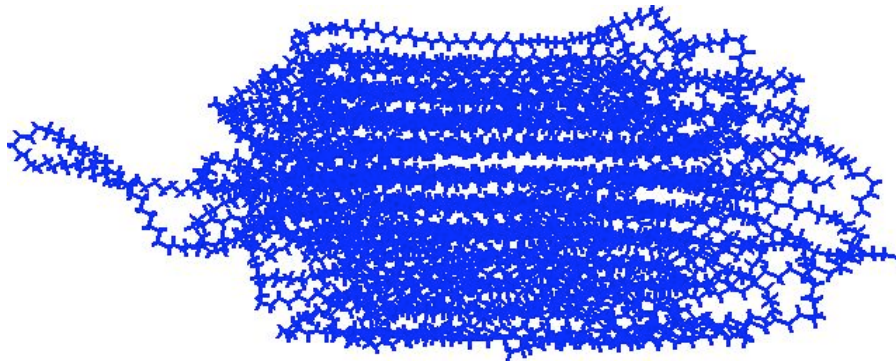
*Molecular Nature of Kinetics *Free Energy Landscape

II. Many Chains

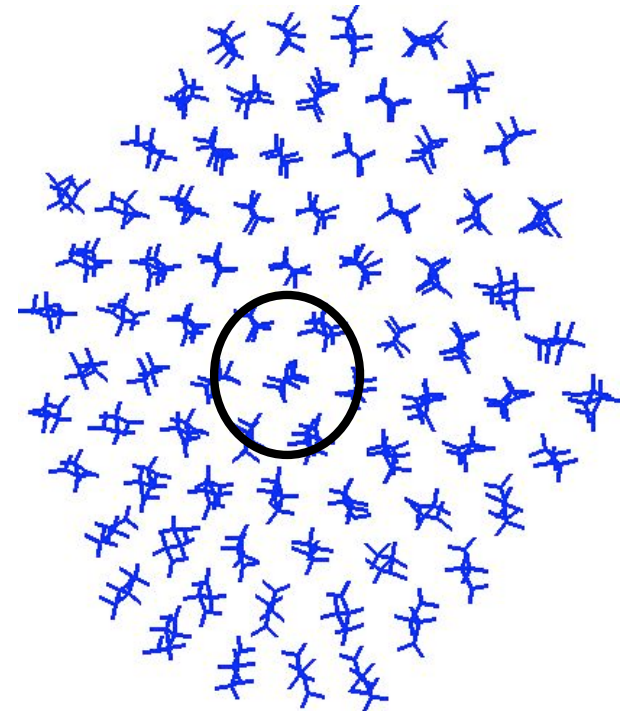


Atomistic Polyethylene

(20 Chains)

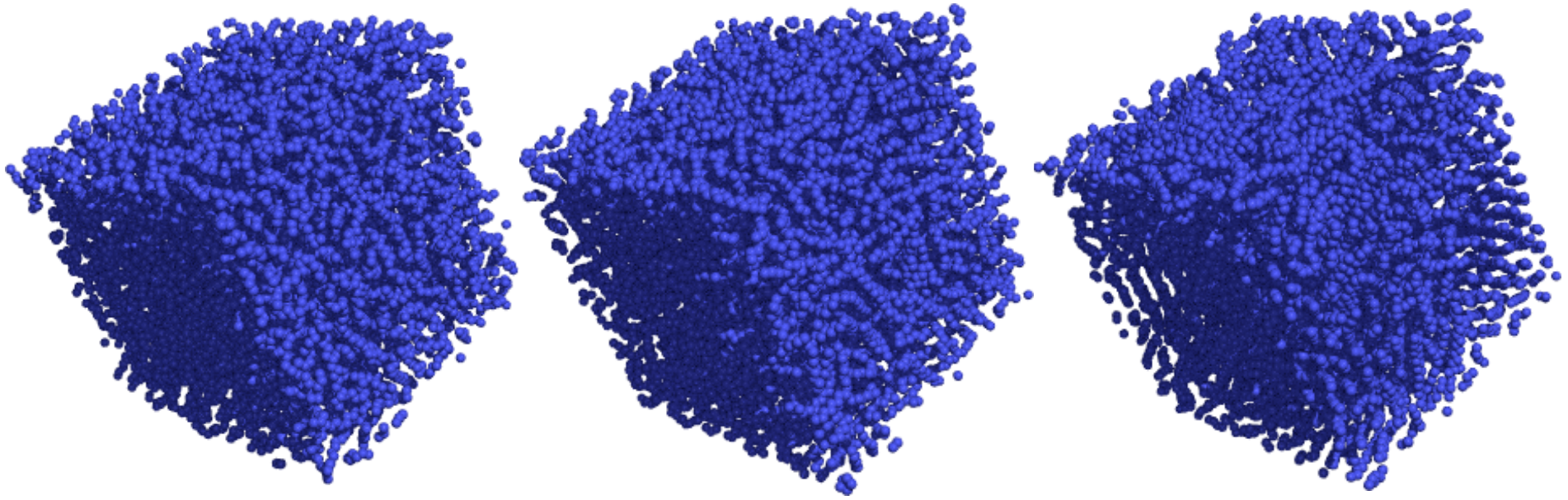


Hexagonal Chain Packing
Orthorhombic Chain Tilt



(N=12,040)

Crystallization (Vol. Fraction = 0.5)



$t < 0$
 $kT/\varepsilon = 20$

$t = 20$
 $kT/\varepsilon = 9$

$t = 6860$
 $kT/\varepsilon = 9$

$\Delta T = 2$ $N=200$ 75 chains $N_t = 15,000$

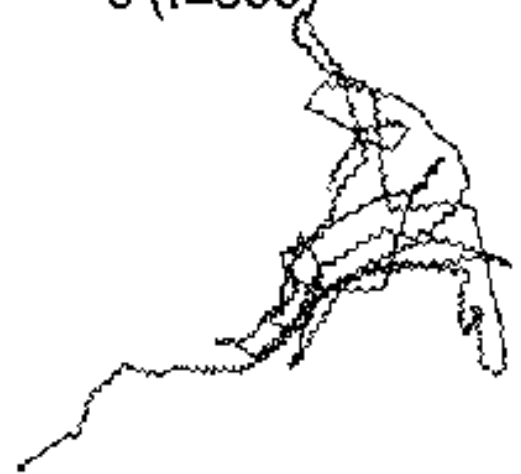
a (t=0)



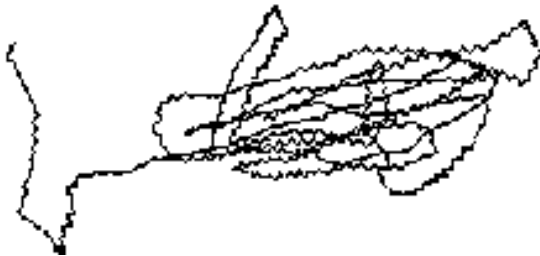
b (t=200)



c (t=600)



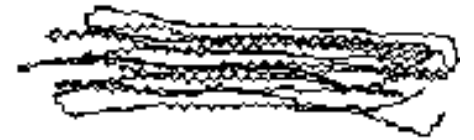
d (t=1000)



e (t=5000)

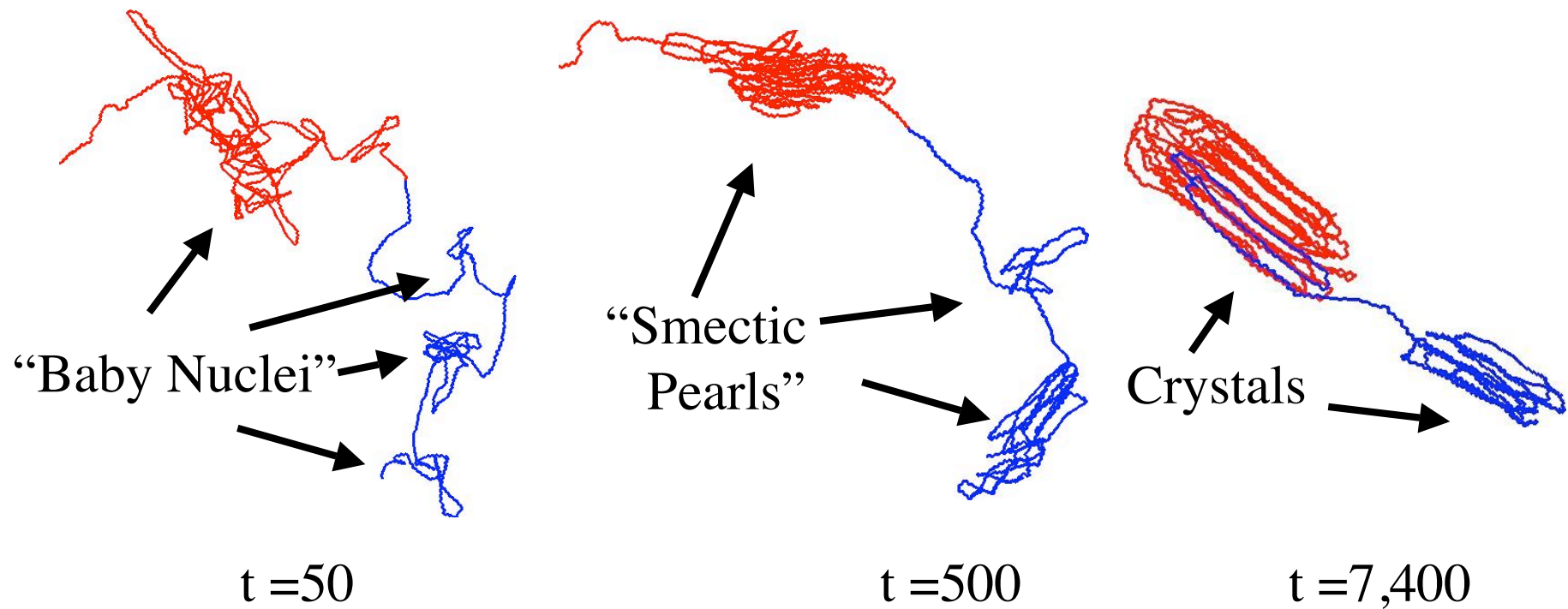


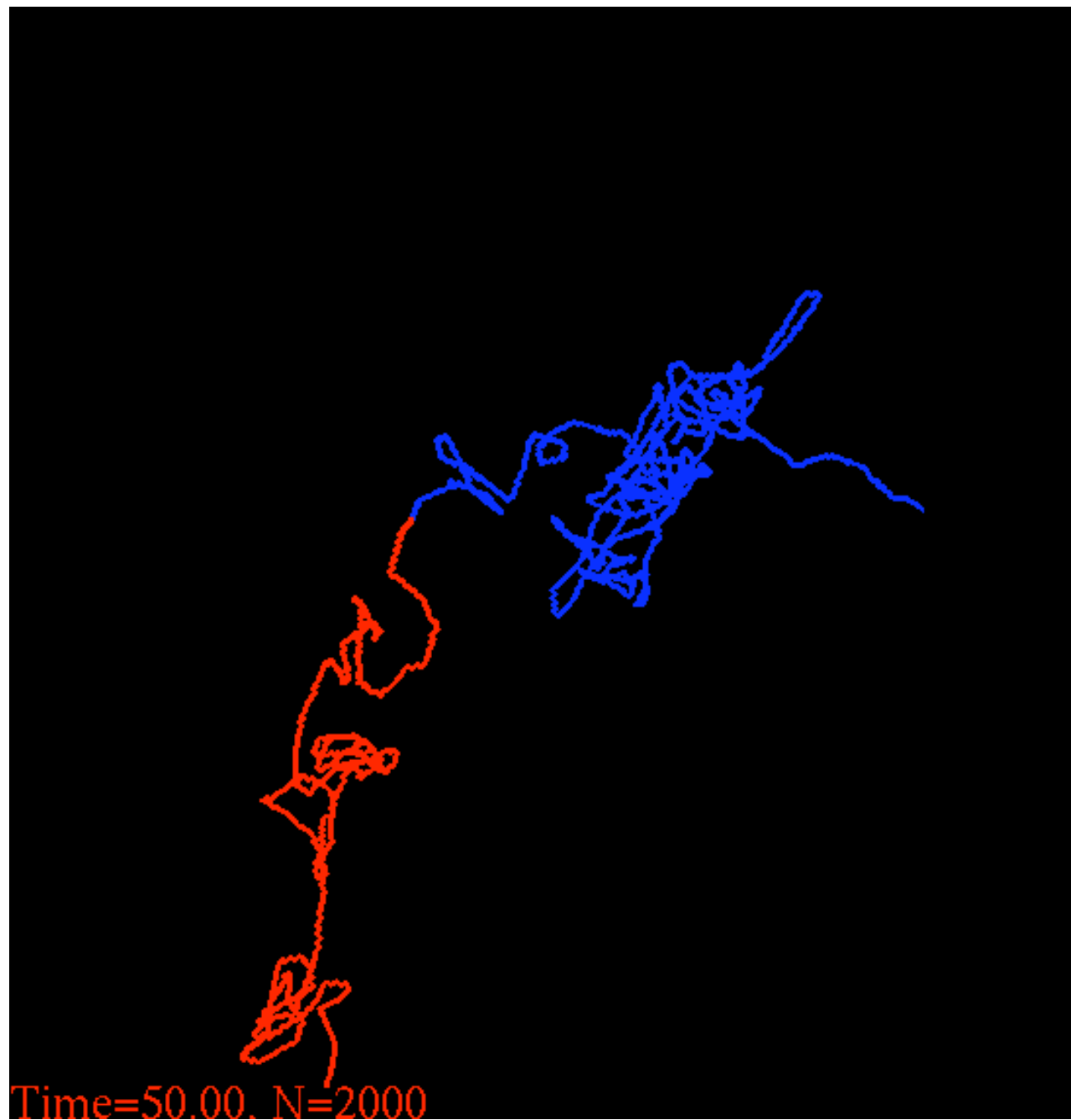
f (t=10200)



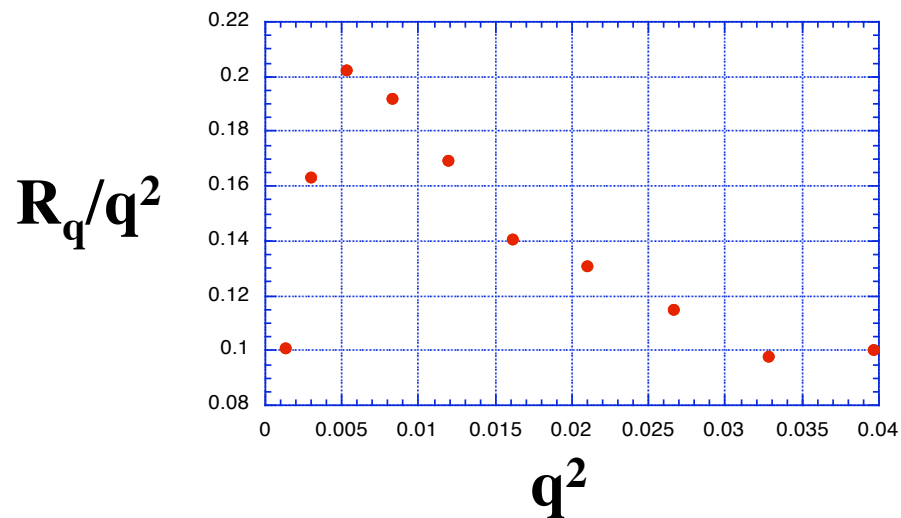
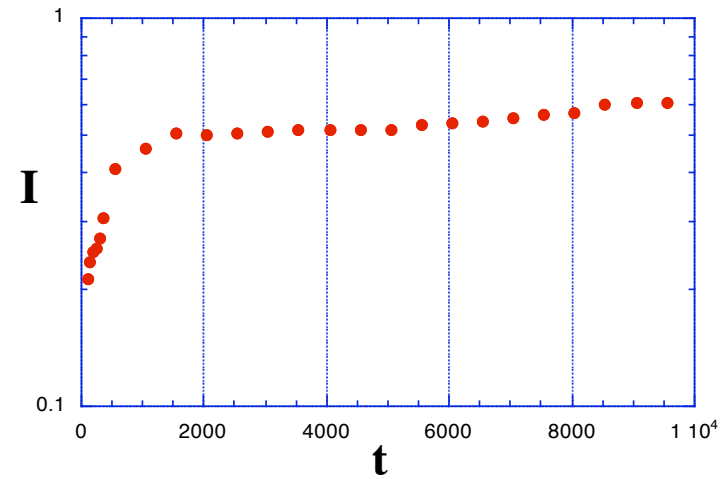
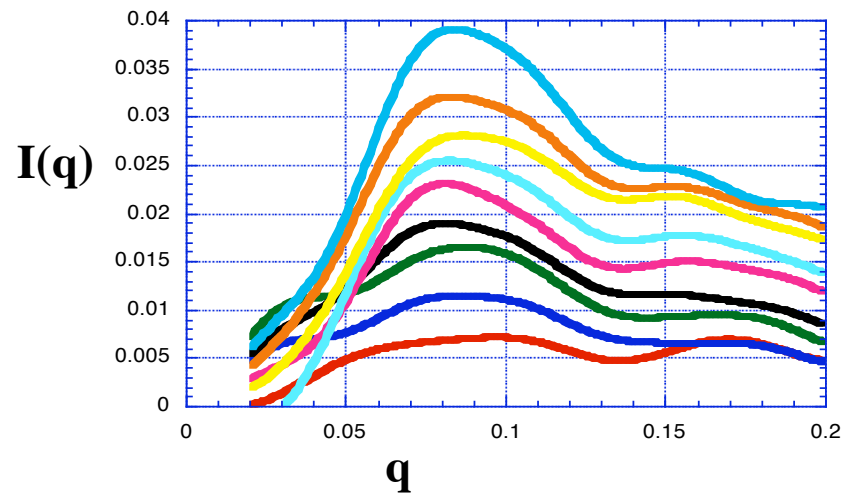
local stiffness versus attraction

Early Stage=Nucleation&Growth





Simulation Results



MM and P. Welch, *Polymer* **2000**, *41*, 8833.

Growth of density fluctuations

$$\Psi = \rho_c - \rho_a$$

$$F \sim \sum_q [-(\Delta T) + q^2 + 1/q^2] |\Psi_q|^2$$

quench
depth

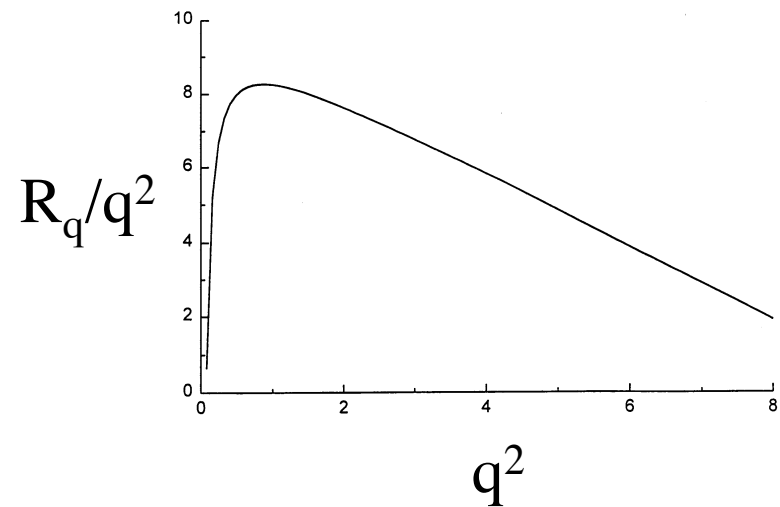
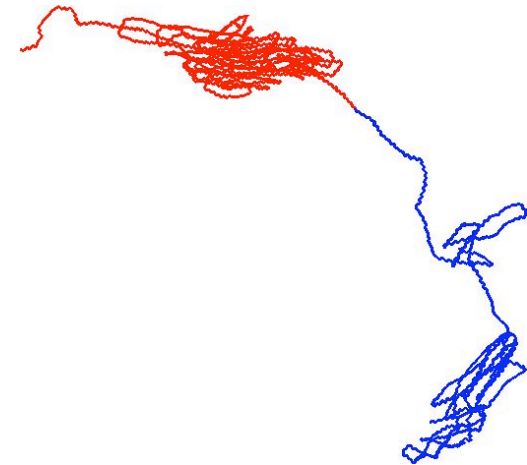
crystal-amorphous
interface

chain
connectivity

$$\partial \Psi_q / \partial t \sim -q^2 [-(\Delta T) + q^2 + 1/q^2] \Psi_q$$

$$\Psi_q(t) \sim \exp(R_q t)$$

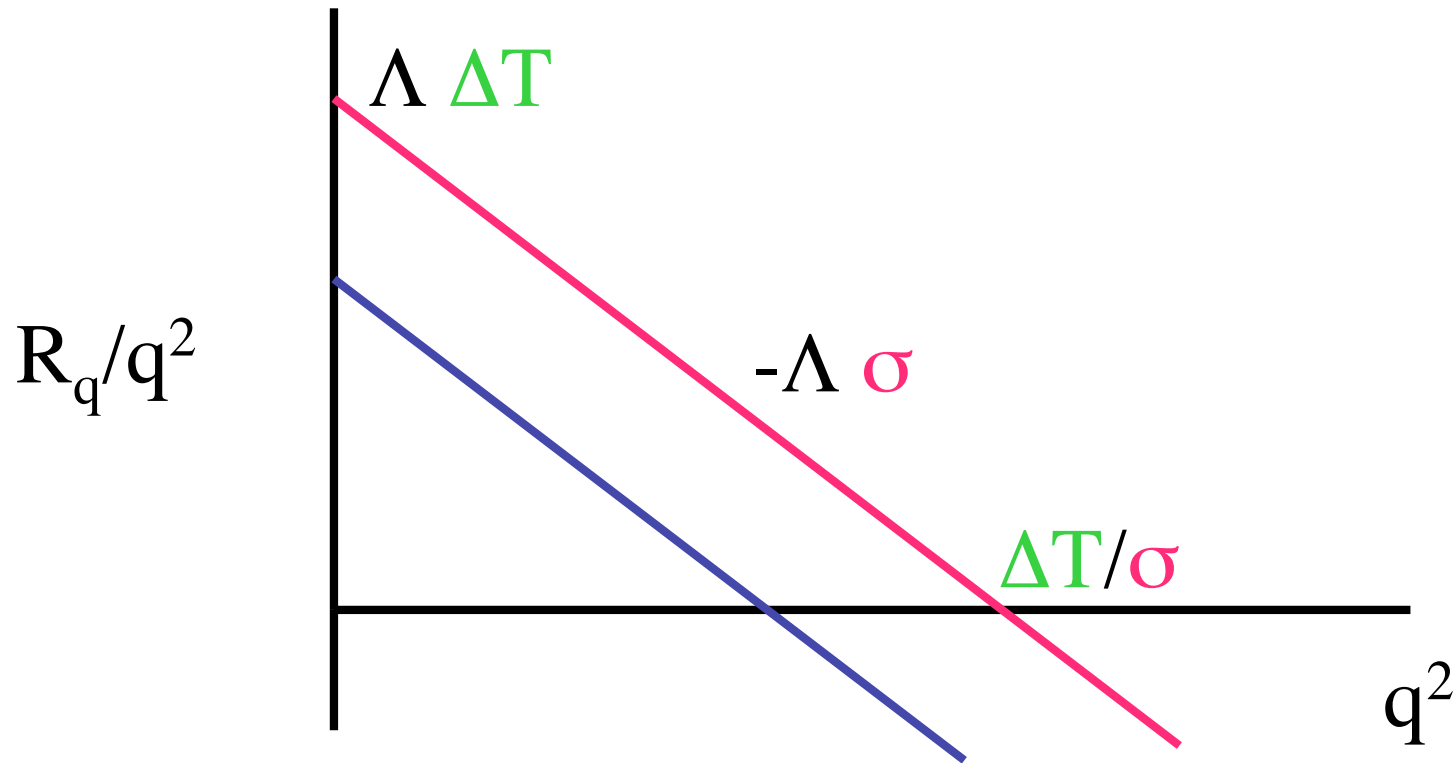
$$R_k/q^2 = \Delta T - q^2 - 1/q^2$$

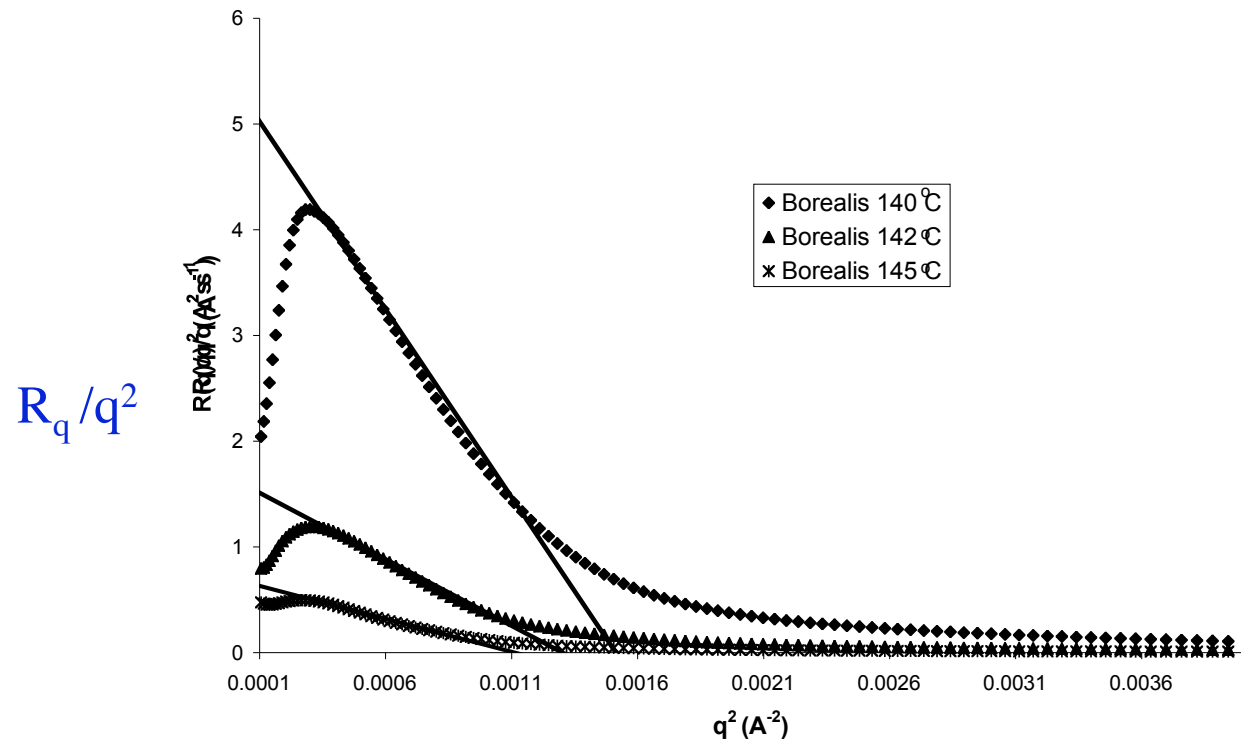


Spinodal Decomposition

$$F \sim \sum_{\mathbf{q}} [-(\Delta T) + \sigma q^2] |\Psi_{\mathbf{q}}|^2$$

$$\begin{aligned} \partial \Psi_{\mathbf{q}} / \partial t &= -\Lambda q^2 [-(\Delta T) + \sigma q^2] \Psi_{\mathbf{q}} \\ &= R_{\mathbf{q}} \Psi_{\mathbf{q}} \end{aligned}$$





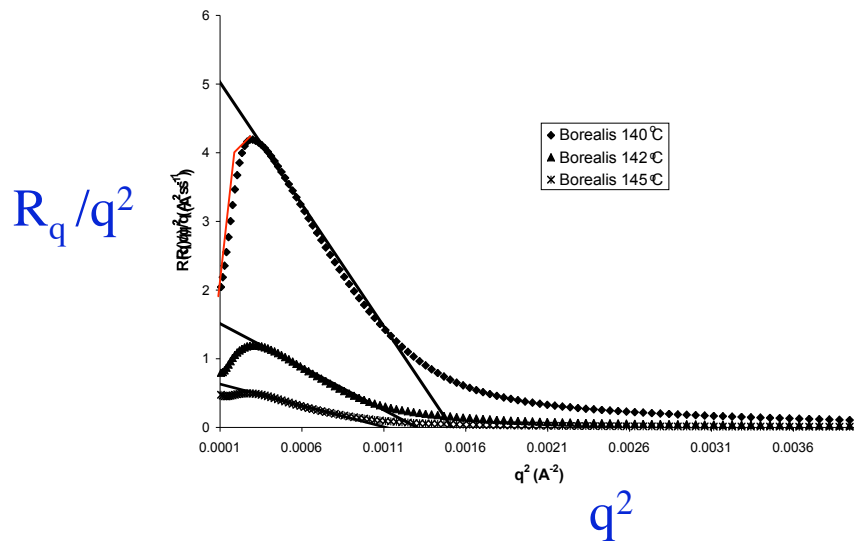
A.J. Ryan and collaborators (I-PP)

Early stage of polymer crystallization

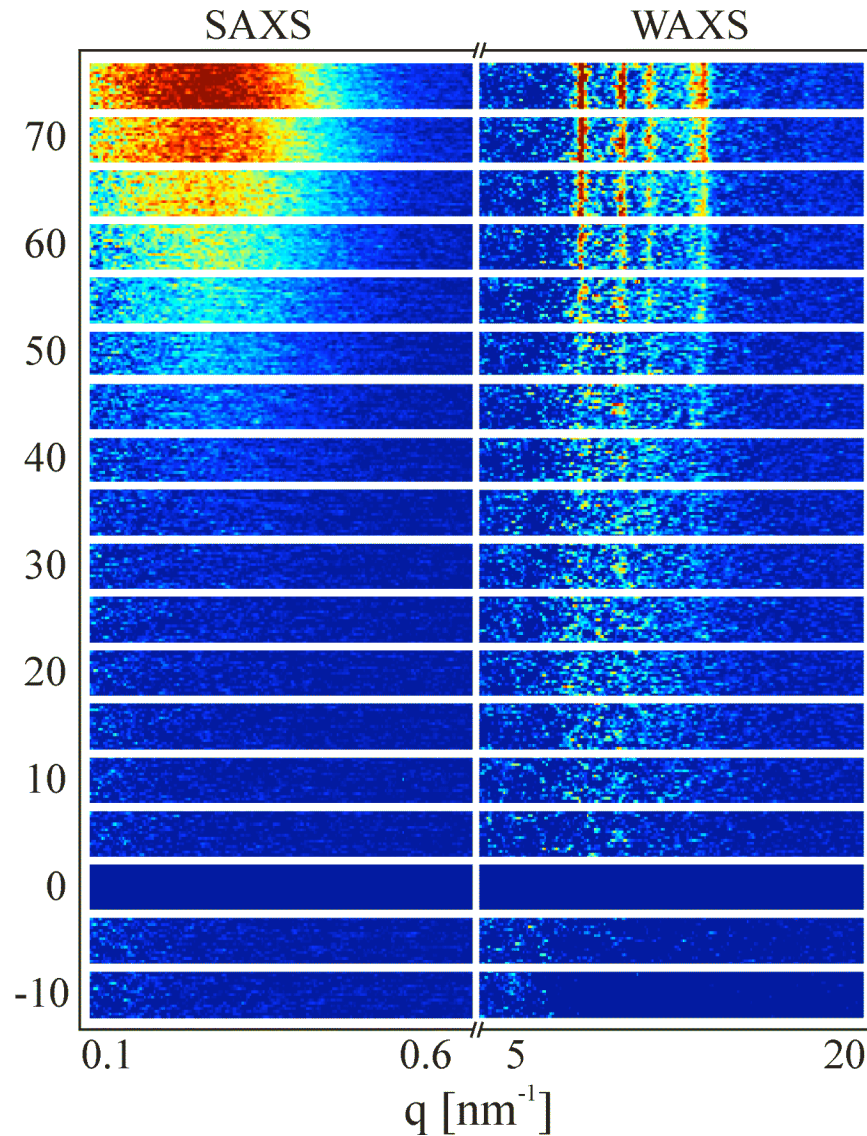
P. Panine *et al.*, Polymer (2008)

Isotactic polypropylene

Melt is cooled rapidly (80 °C/min) from 210 °C to the crystallization temperature (145 °C)

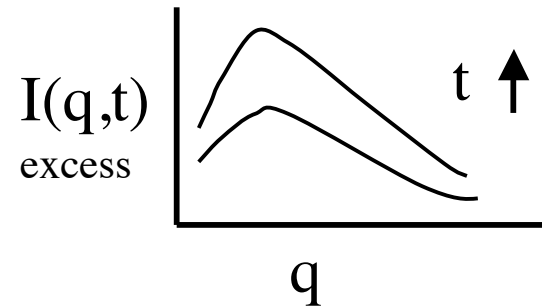


A.J. Ryan and collaborators (I-PP)



Conclusion #1

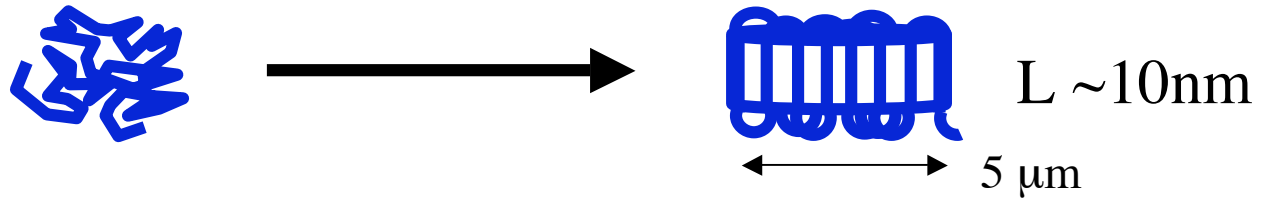
Early stage of polymer crystallization:



Initial stage of crystallization is **NUCLEATION** with each chain participating in several nuclei.

NOT spinodal decomposition

Further support from R. Alamo (FTIR) and
C. Schick (ultrafast cold crystallization)

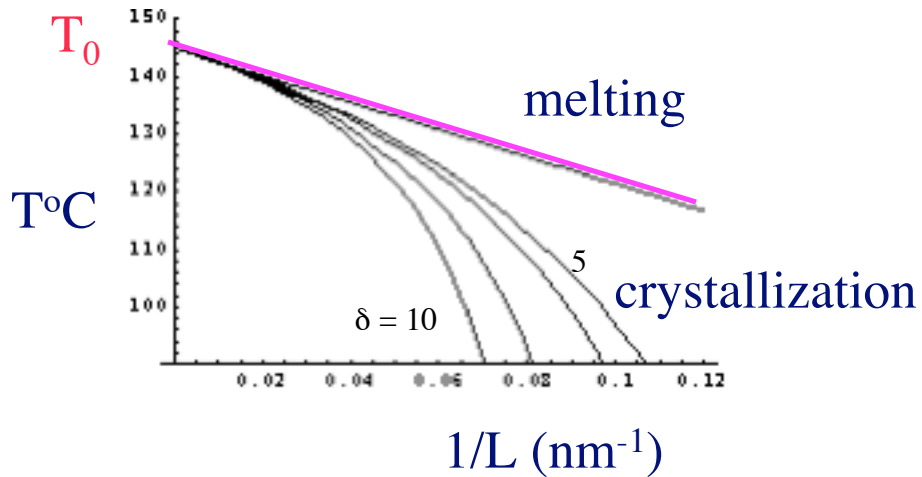


2. Spontaneous selection of lamellar thickness

(L ≪ extended chain dimension)

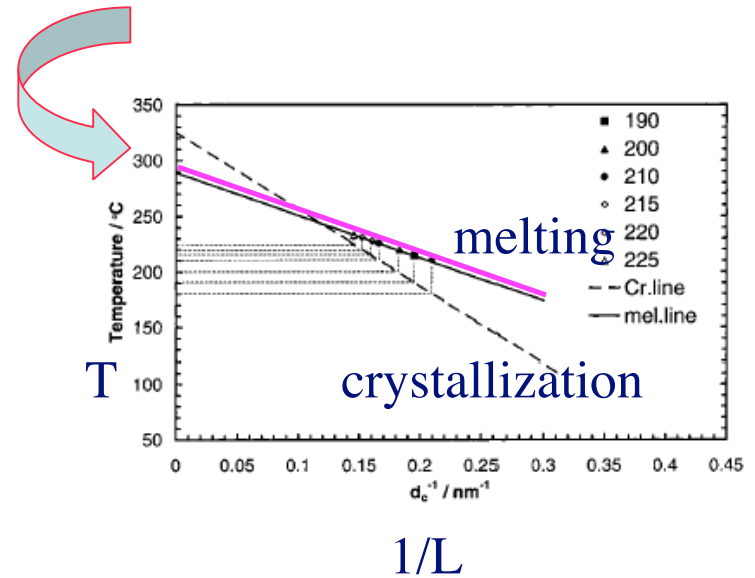
⇒ “KINETICALLY CONTROLLED”

Lauritzen-Hoffman

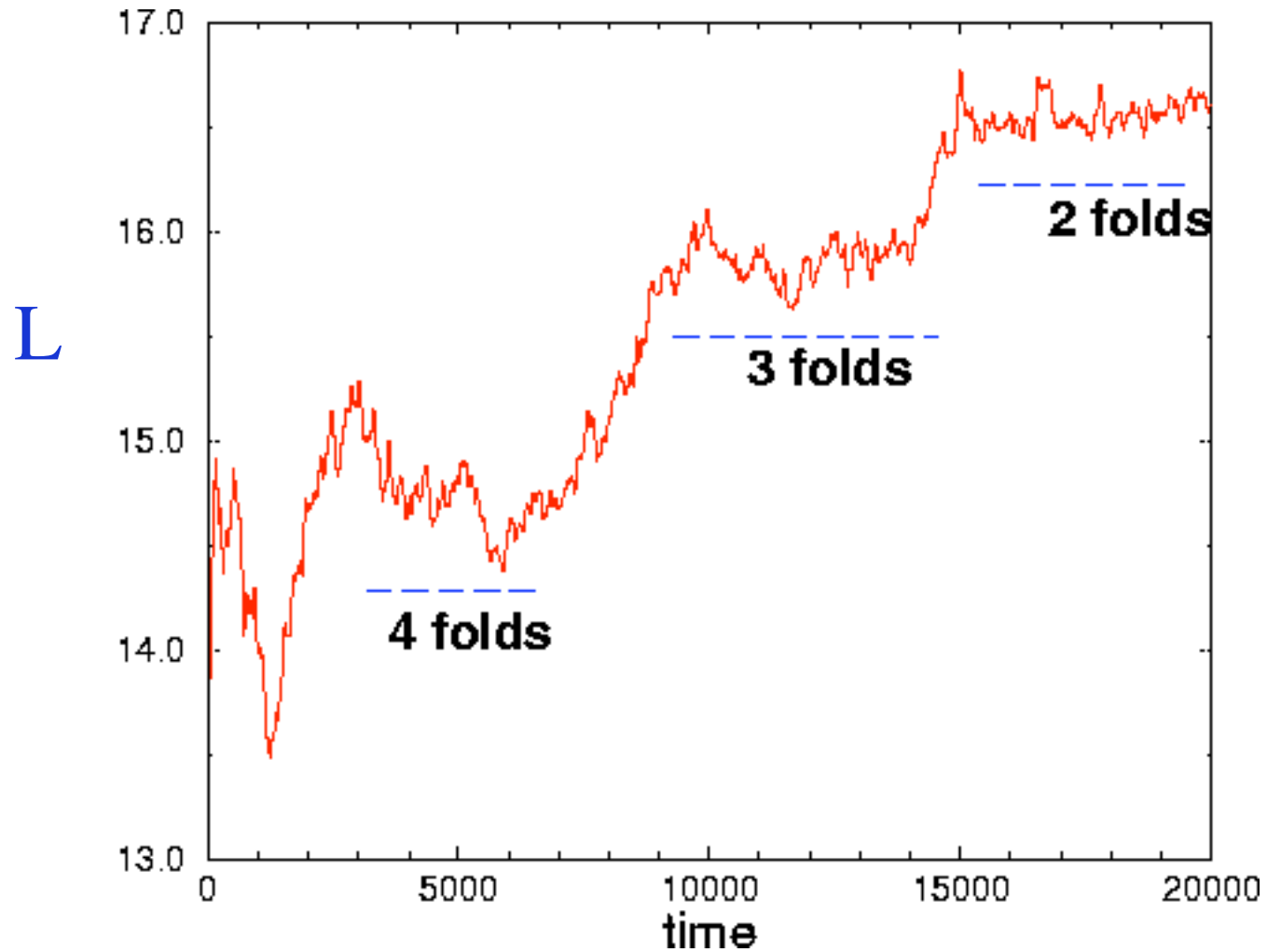


$$L = \frac{2\sigma_f T_0}{\Delta h(T_0 - T)} + \delta$$

Interlude from
MESOMORPHIC states?



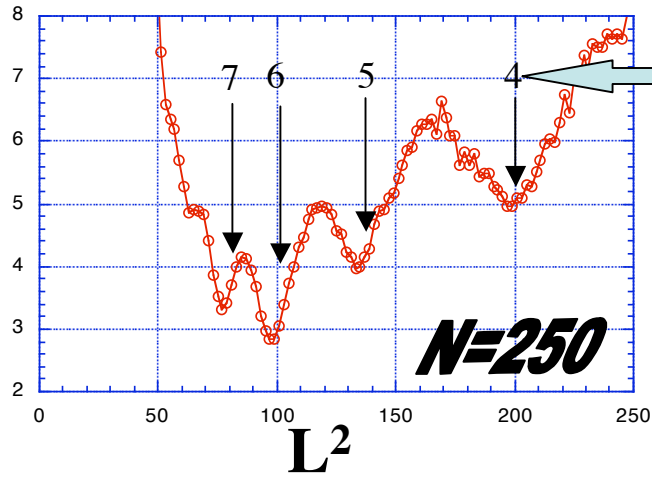
(Strobl)



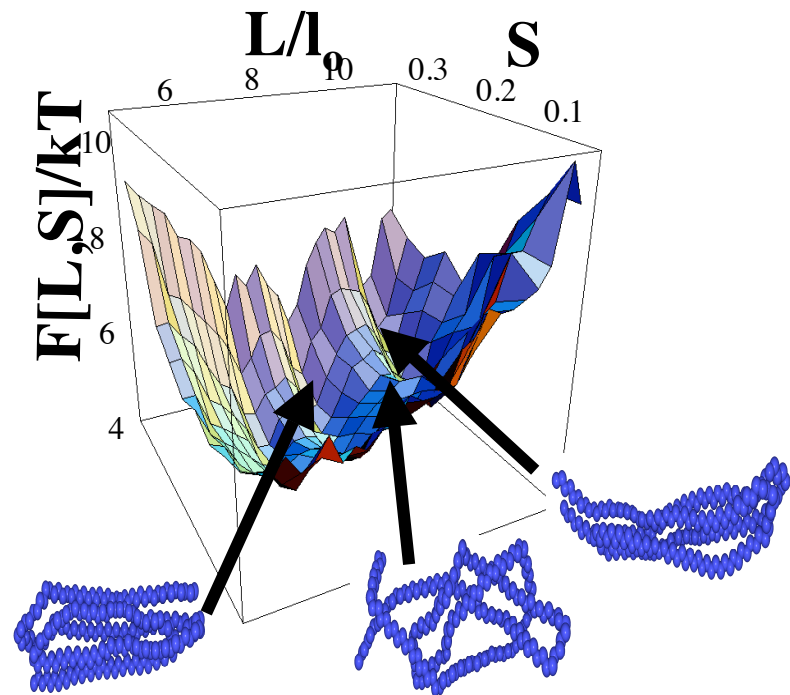
“Quantization of Lamellar Thickness”
(Agrees with Keller’s experiments)

Simulations

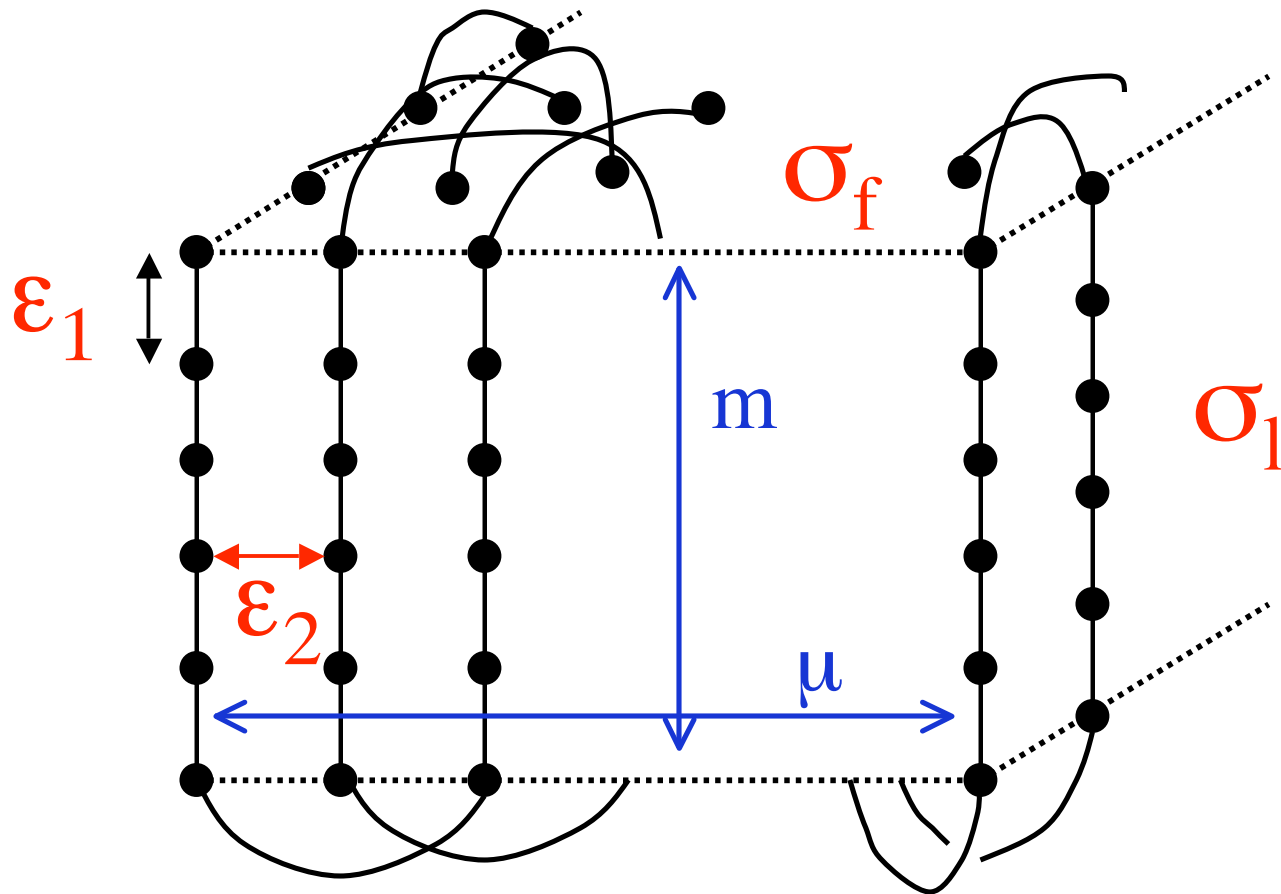
Free Energy



Number of Stems



~40 Beads/Stem



ϵ_1 =chain stiffness energy

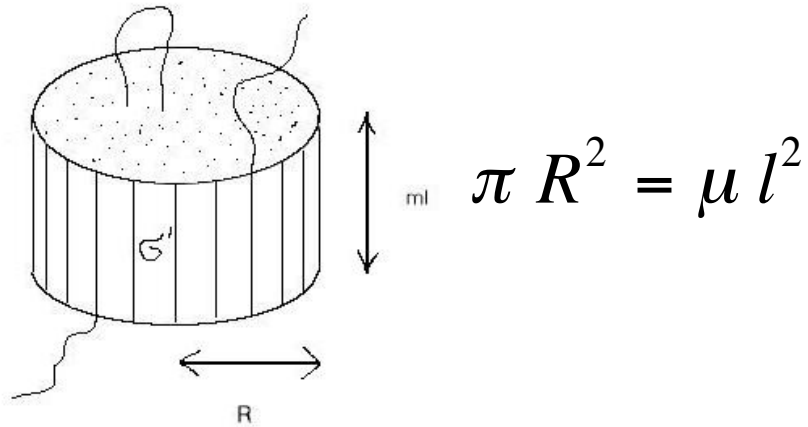
ϵ_2 =interaction energy of
non-bonded neighbors

m =lamellar thickness

μ =number of stems/chain

$$\frac{F}{k_B T} = f_{bulk}\left(T = \frac{1}{\epsilon_2}, \epsilon = \frac{\epsilon_1}{\epsilon_2}, m, \mu, N\right)$$

$$+ f_{loops}(m, \mu, N) + f_{surface}(\sigma_l, \sigma_f)$$



Let one chain have μ stems with $(\mu-1)$ loops and two tails.

$$\frac{F_{m,\mu}}{k_B T} = \underbrace{-\mu m \varepsilon}_{\text{bulk energy}} + \underbrace{\sigma \mu^{1/2} m}_{\text{lateral surface energy}} - \underbrace{\ln(Z_{m,\mu})}_{\text{chain entropy}}$$

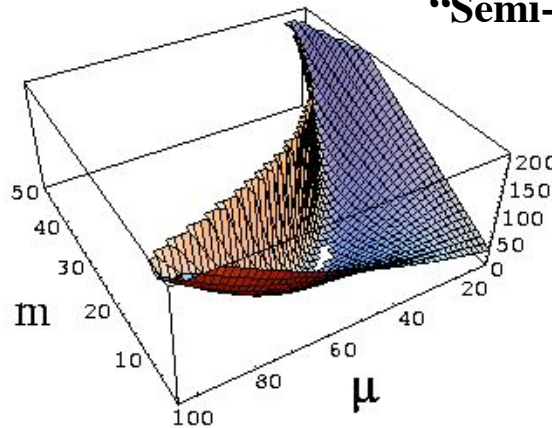
Field Theory:

MM, *Phil.Trans.Roy.Soc.*,
361A, 539 (2003)

$$Z_{m,\mu} = \oint \frac{dE}{2\pi i} e^{E(N-\mu m)} g_{tail}^2(E) g_{loop}^{\mu-1}(E; l_c)$$

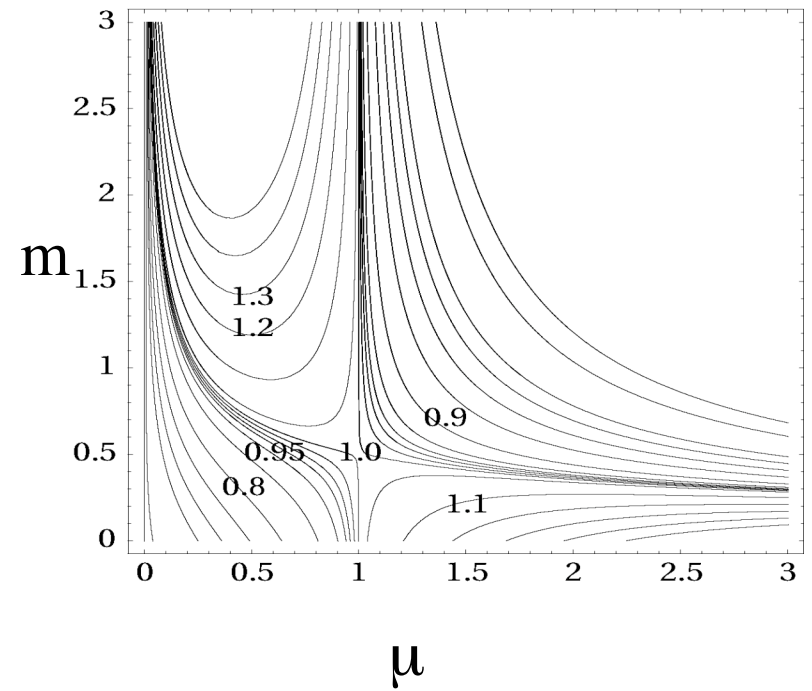
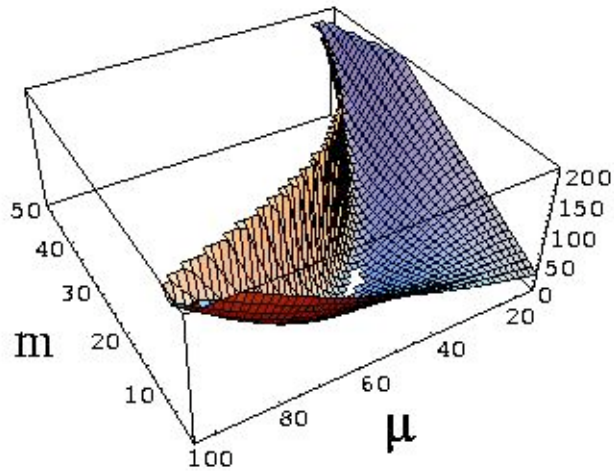
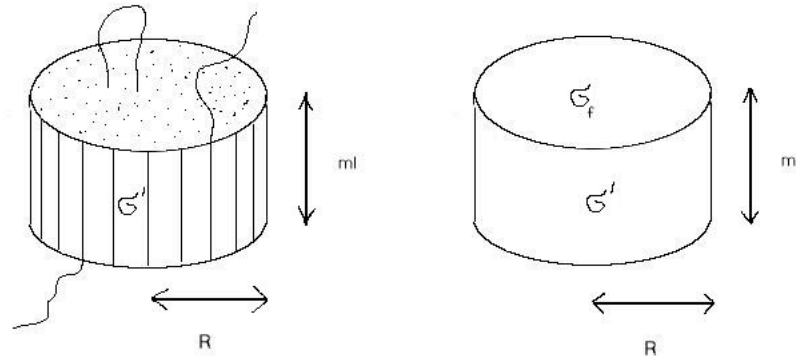
↙
↗
 “Semi-infinite space”

⇒ Finite thickness is Equilibrium

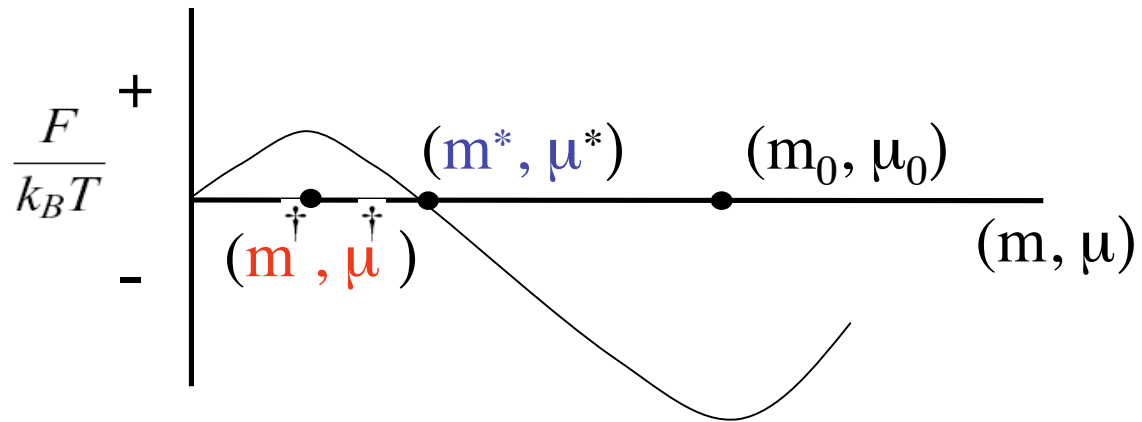
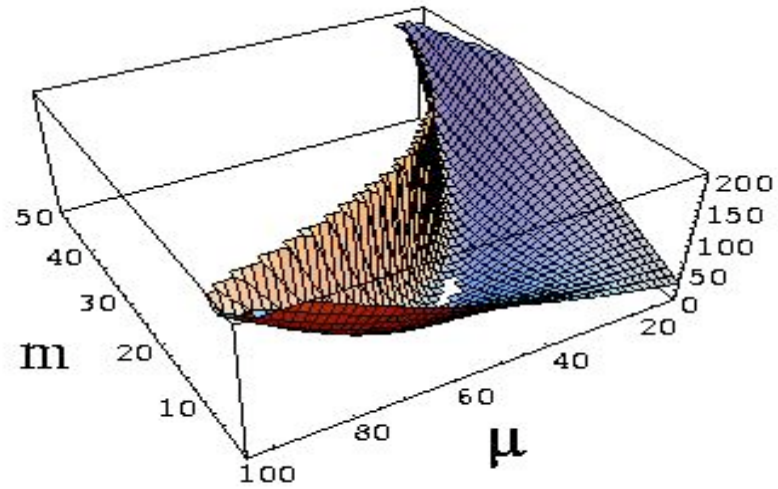


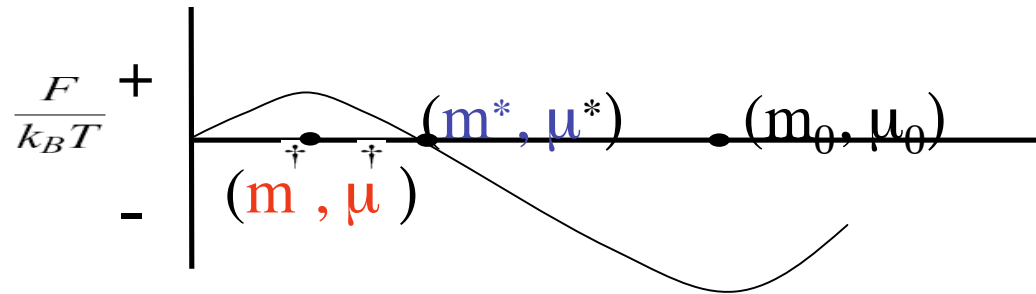
$$N = 1000, \quad \varepsilon = 1, \quad \sigma = 5, \quad l_c / l = \sqrt{32/3}$$

THEORY

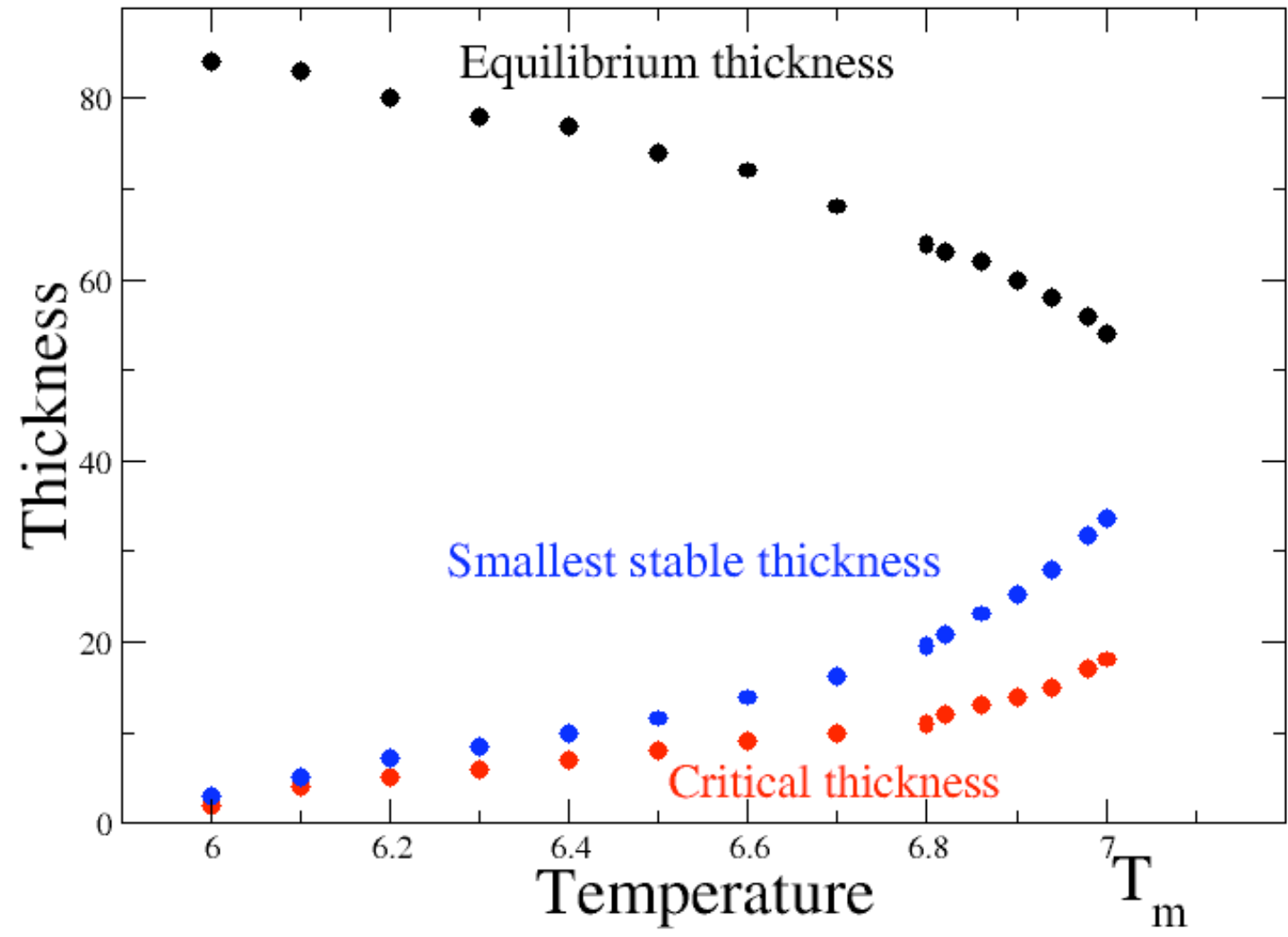


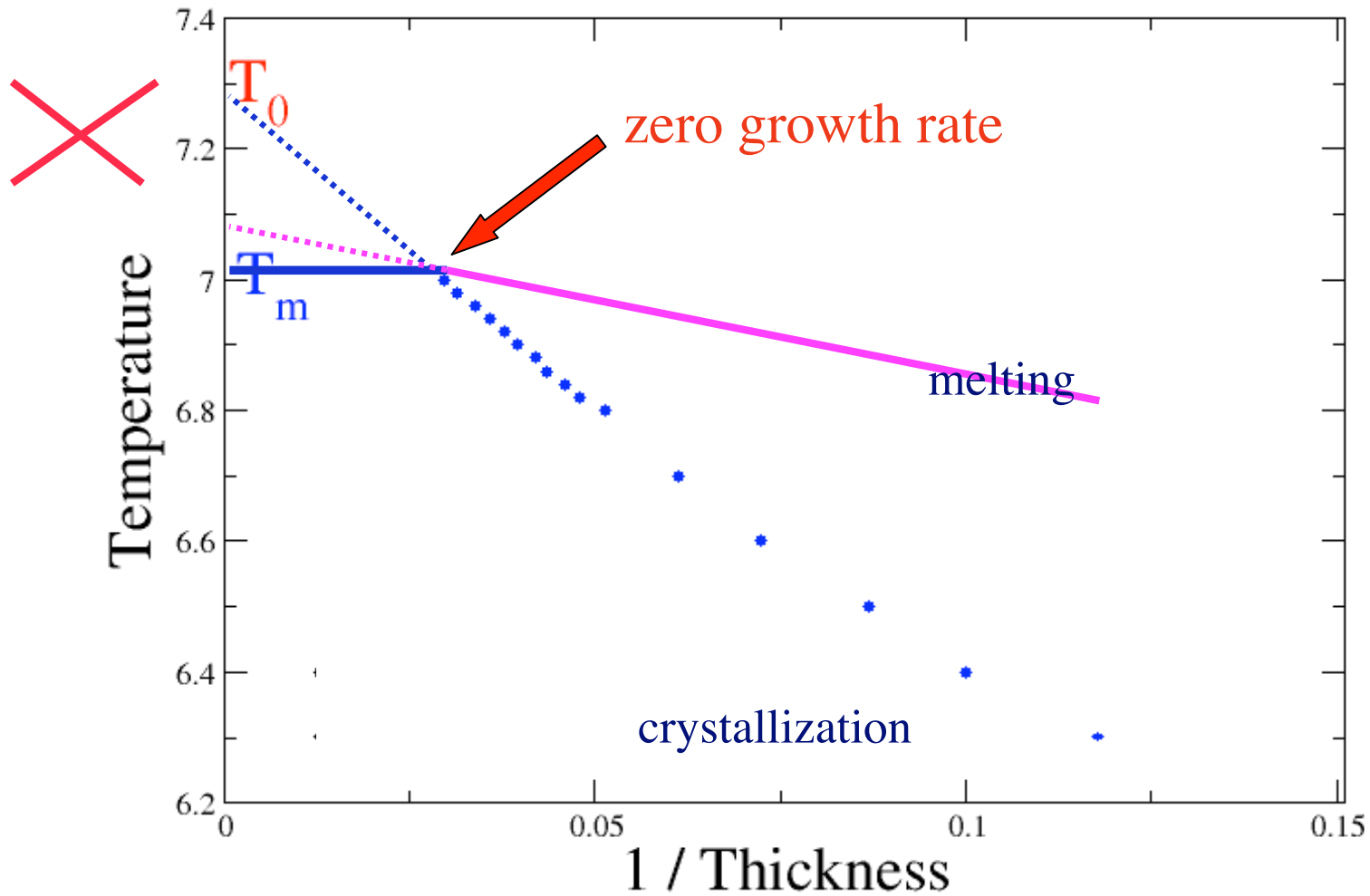
MM, *Phil.Trans.Roy.Soc.*, **361A**, 539 (2003)





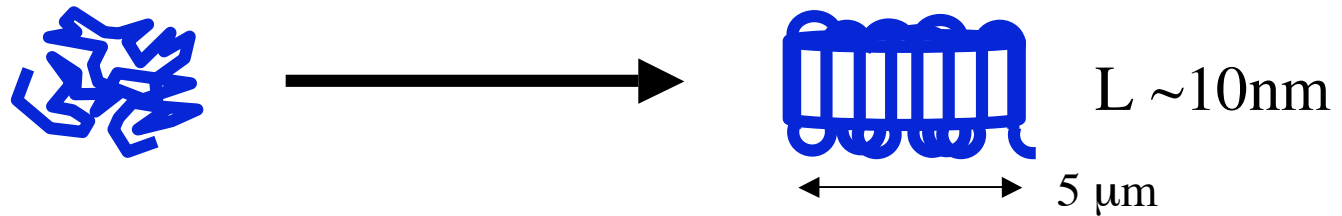
$N = 10,000$





(Experimentally confirmed by Ungar, Rastogi, Strobl,...)

Conclusion #2



1. Spontaneous selection of lamellar thickness

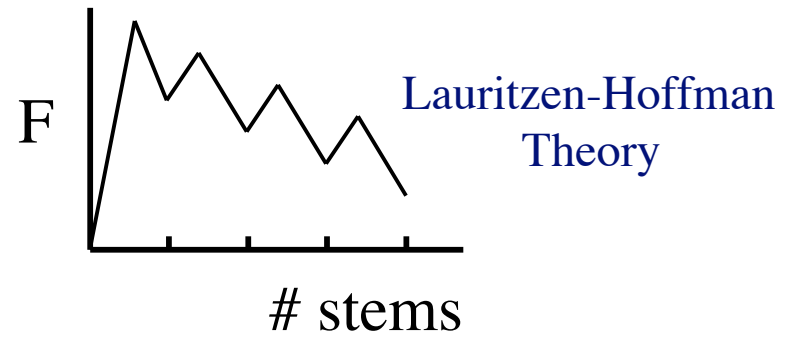
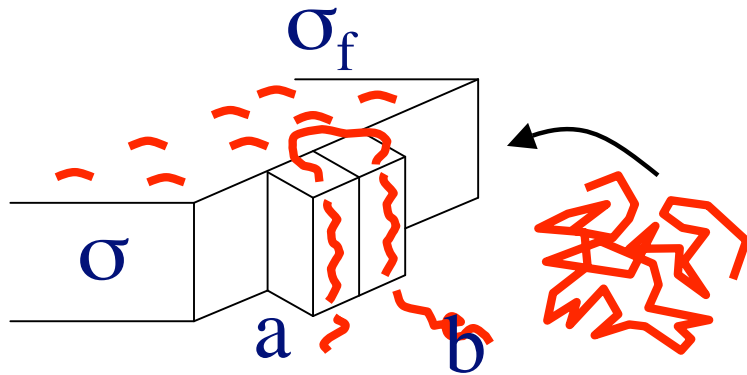
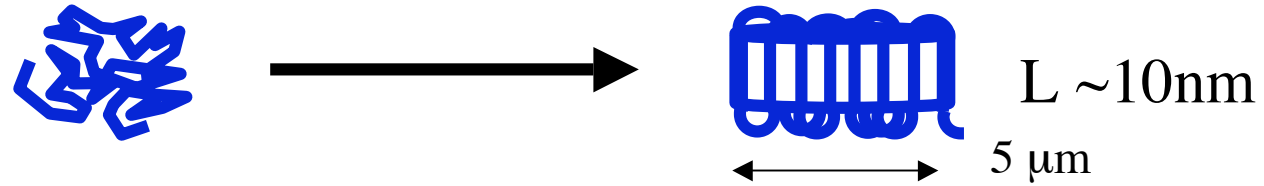
($L \ll$ extended chain dimension)

\Rightarrow “KINETICALLY CONTROLLED”

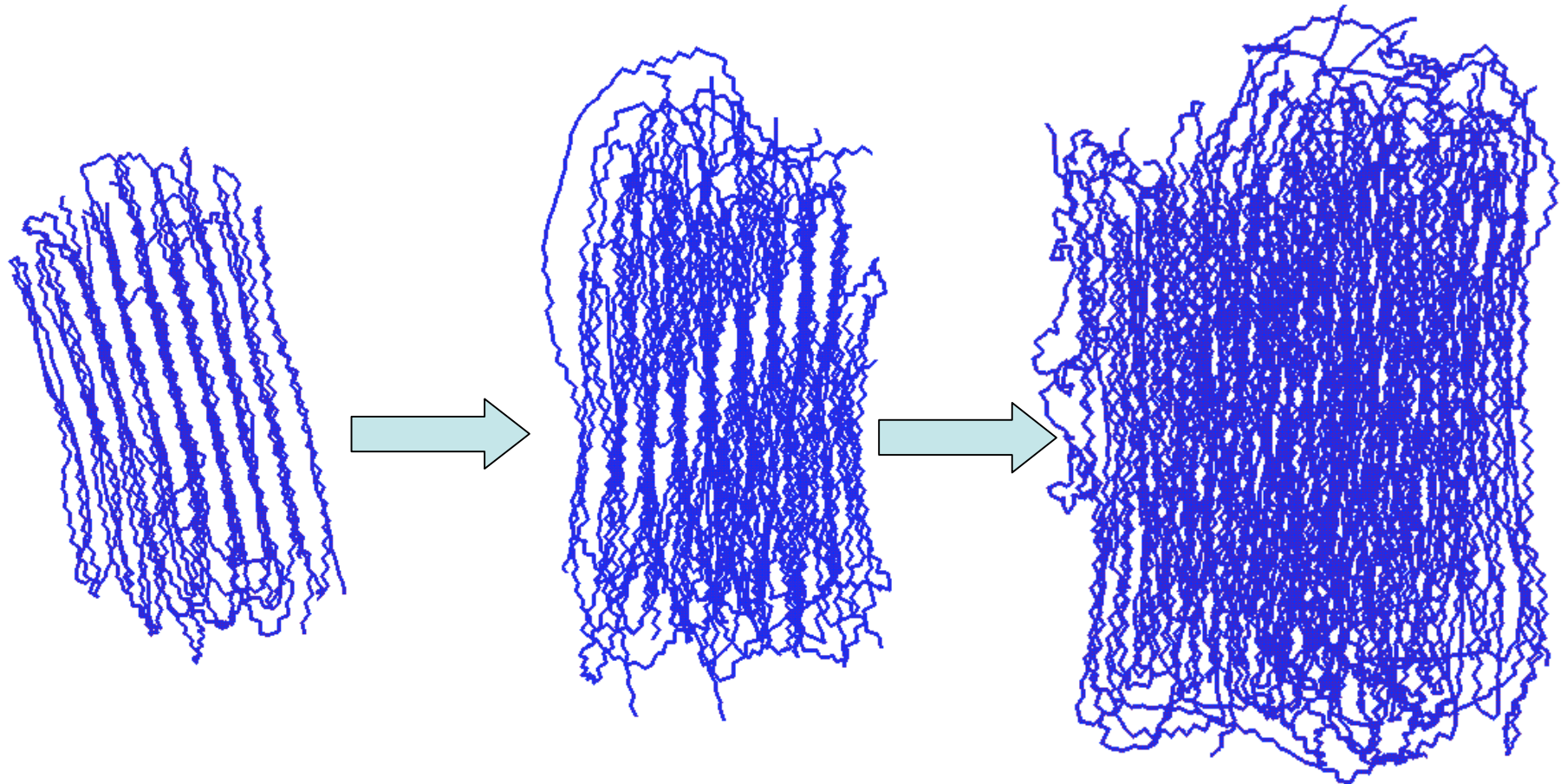
Lamellae evolve through several metastable states to reach an **EQUILIBRIUM** thickness much smaller than the extended chain dimension.

2. No stable mesomorphic phase for flexible chains

3. Kinetics at growth front



Multi-Chain Study



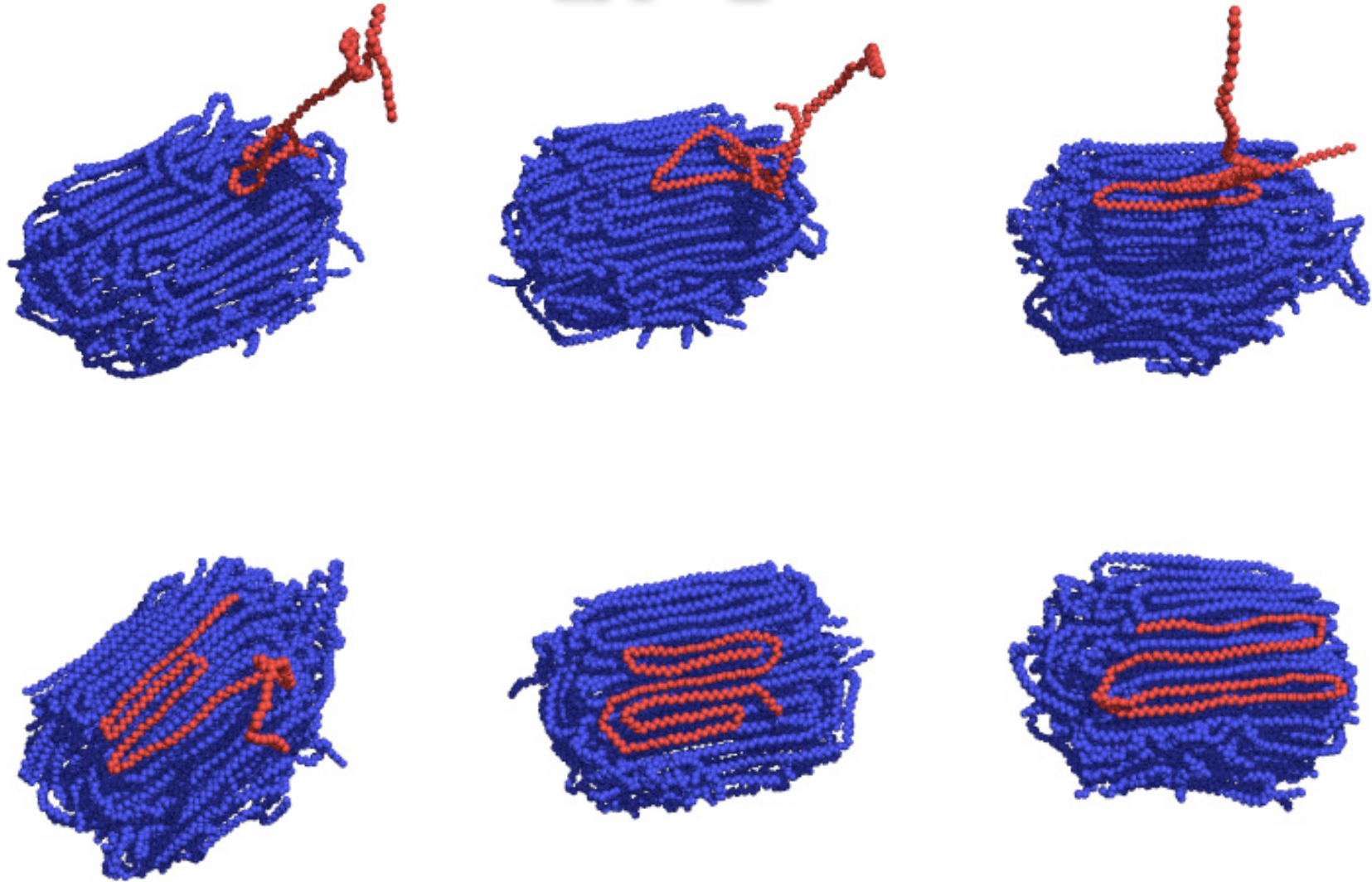
10

20

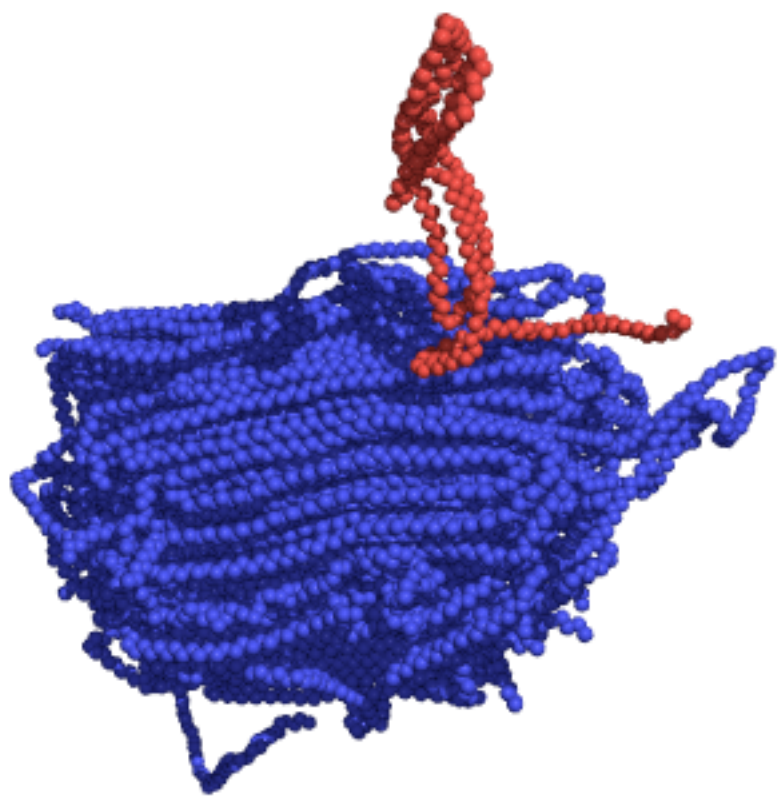
40

Addition to the Growth Front

$\Delta T=2$

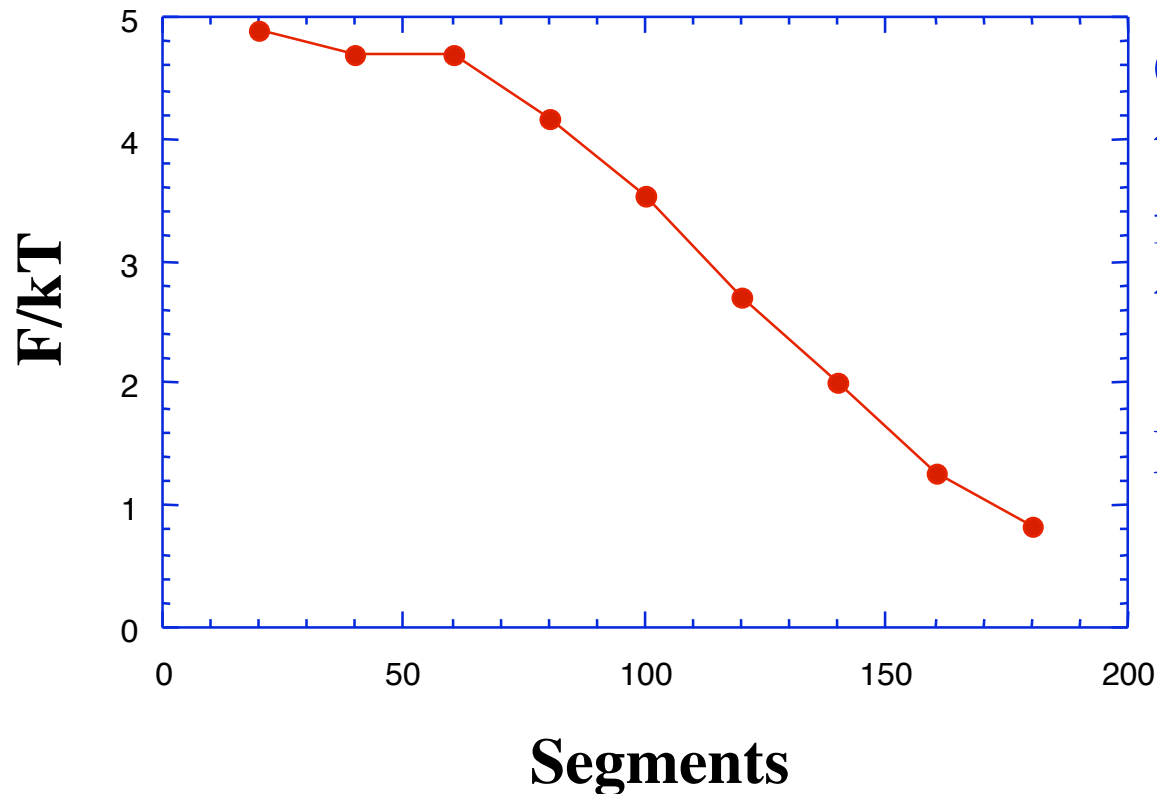


Welch and Muthukumar, *Phys. Rev. Lett.*, **87**, 218302-1 (2001)



Free Energy

“Lamellar growth is chain **ADSORPTION**”



Our Estimate of
the Free Energy
for Segment Addition
to the Growth Front

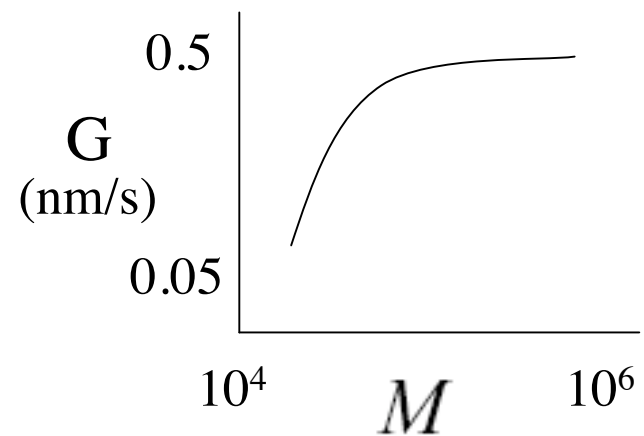
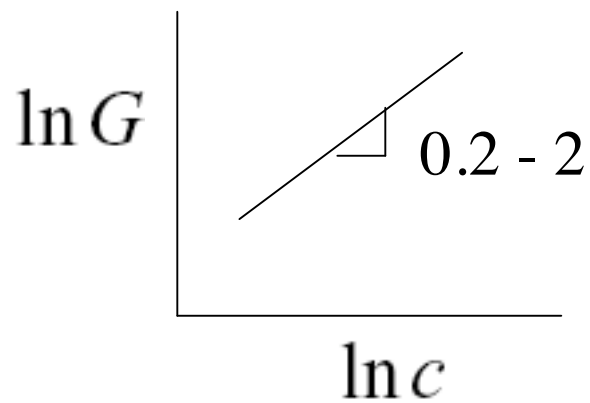
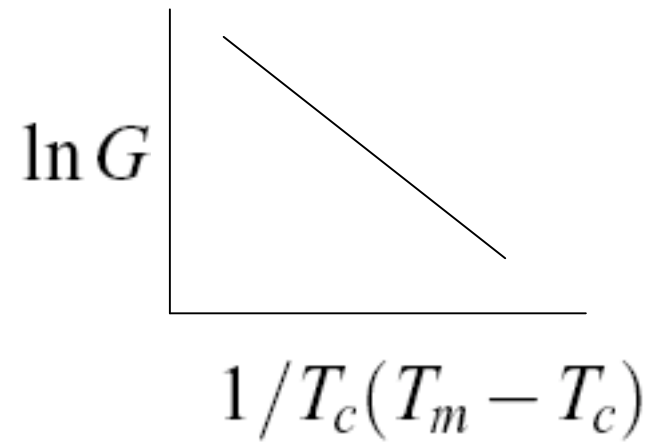
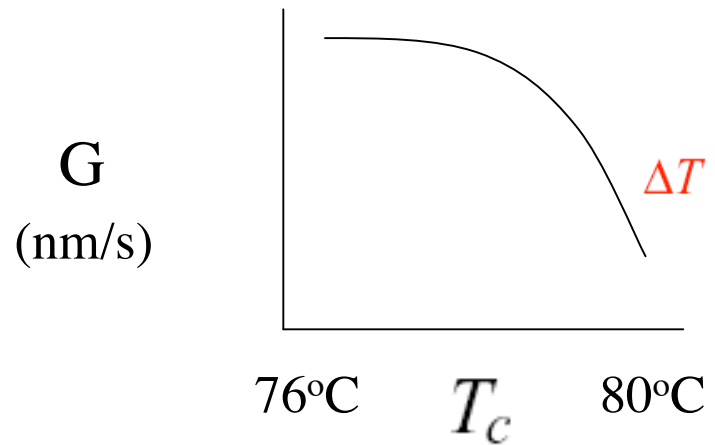
No Barrier is Observed

Based on ~4500 Samples

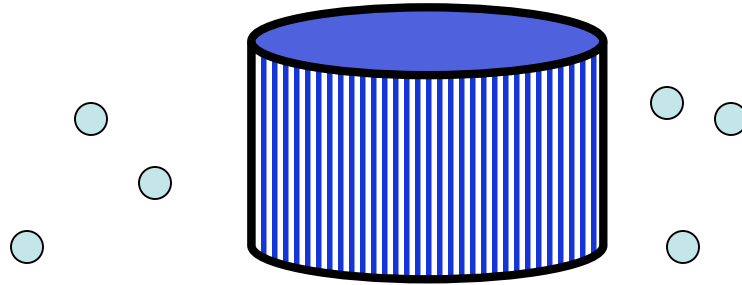
Welch and Muthukumar, *Phys. Rev. Lett.*, **87**, 218302-1 (2001)

Phenomenology

Kinetics at GROWTH FRONT



Surface Growth (small molecules):



Growth rate:

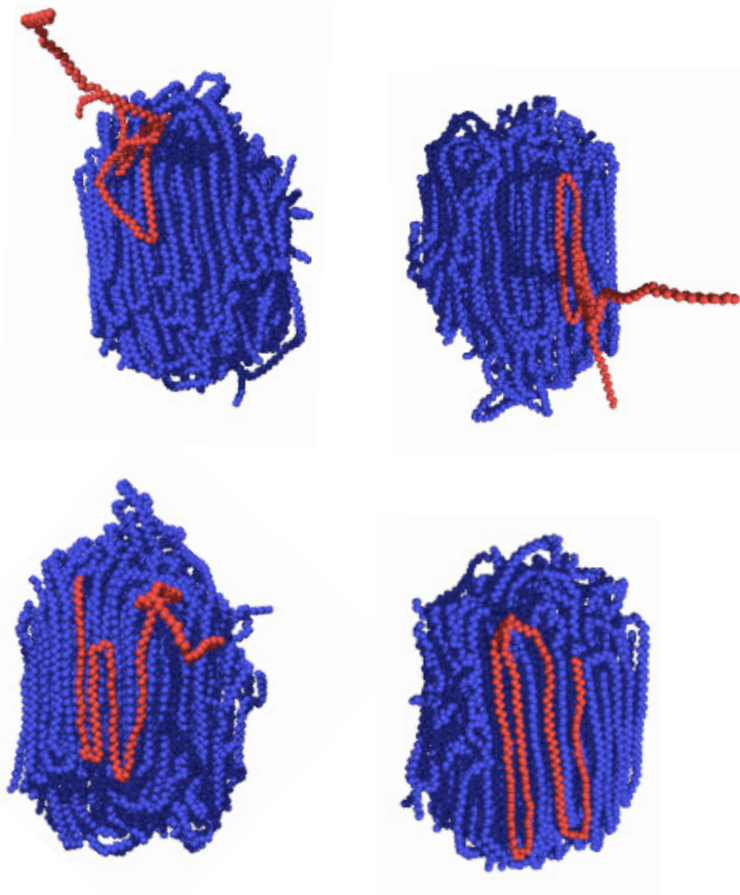
$$G \sim C \left[1 - e^{-\frac{(\Delta H)(\Delta T)}{kT_m T}} \right]$$

adsorption desorption

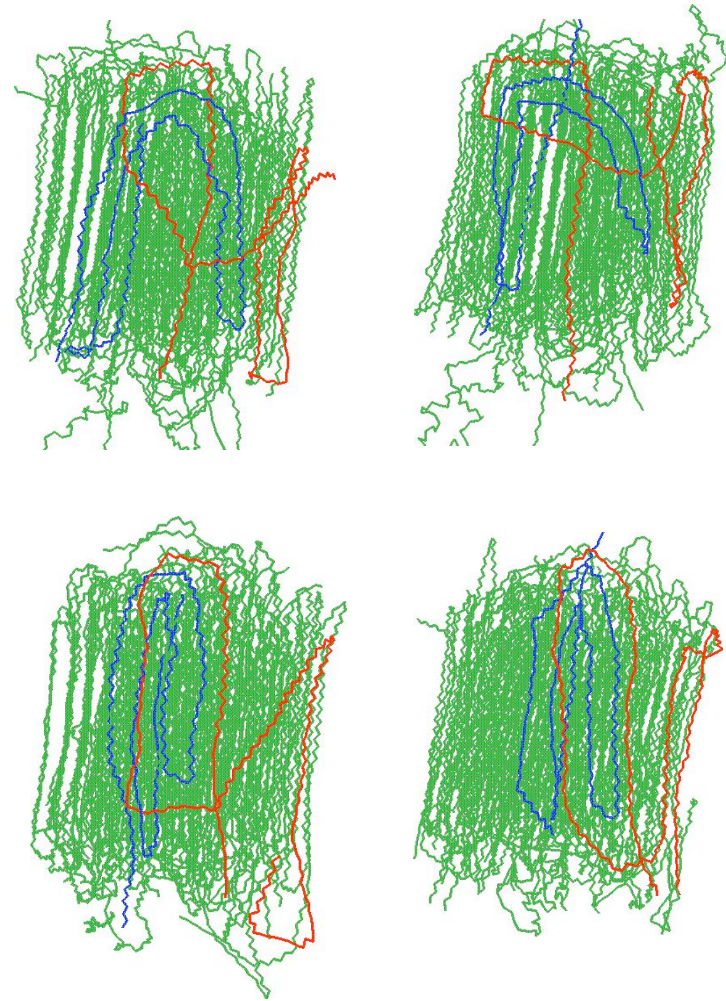
(Detailed Balance)

$$G \sim \Delta T, \quad T_c \longrightarrow T_m$$

Dilute

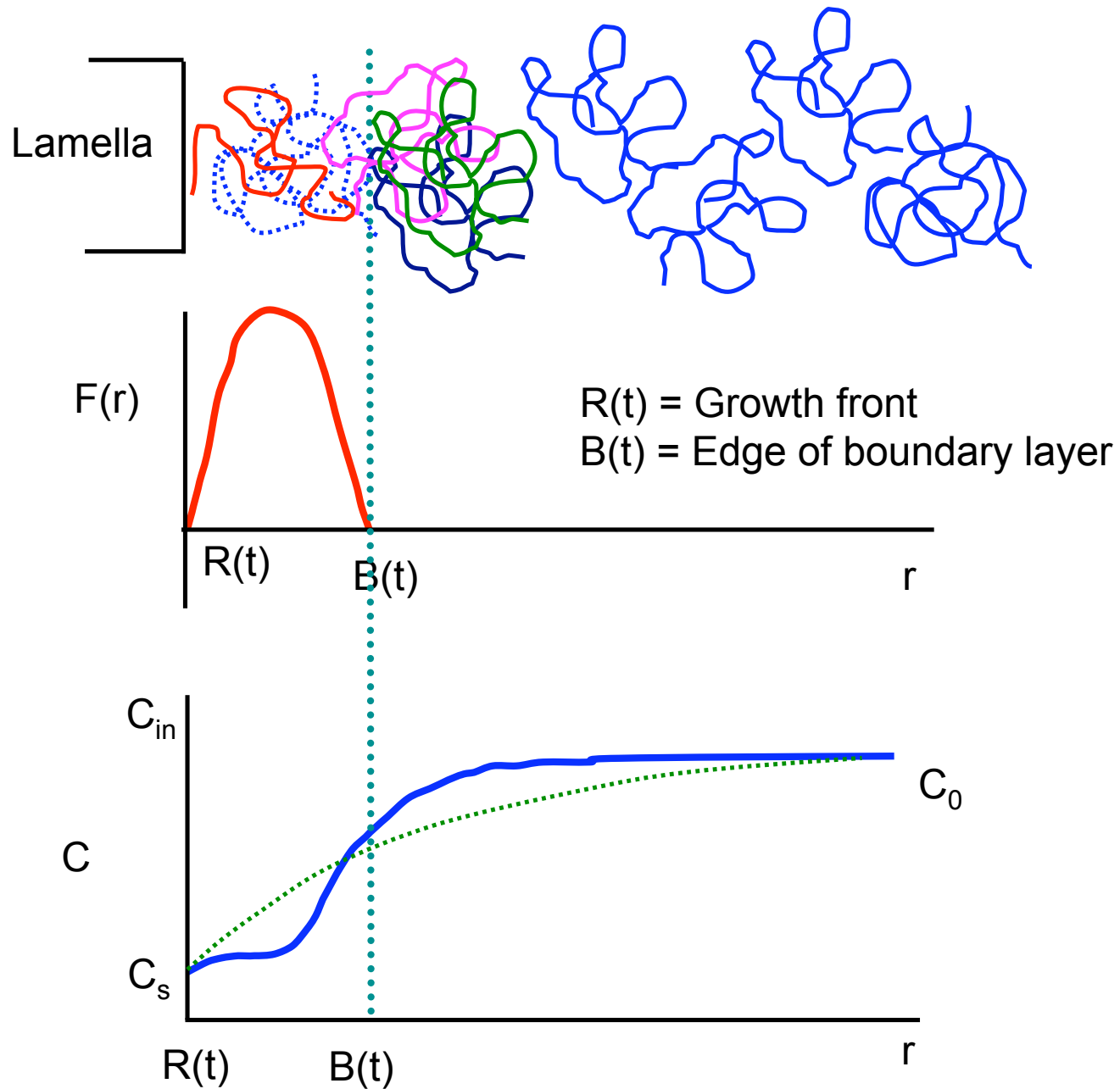


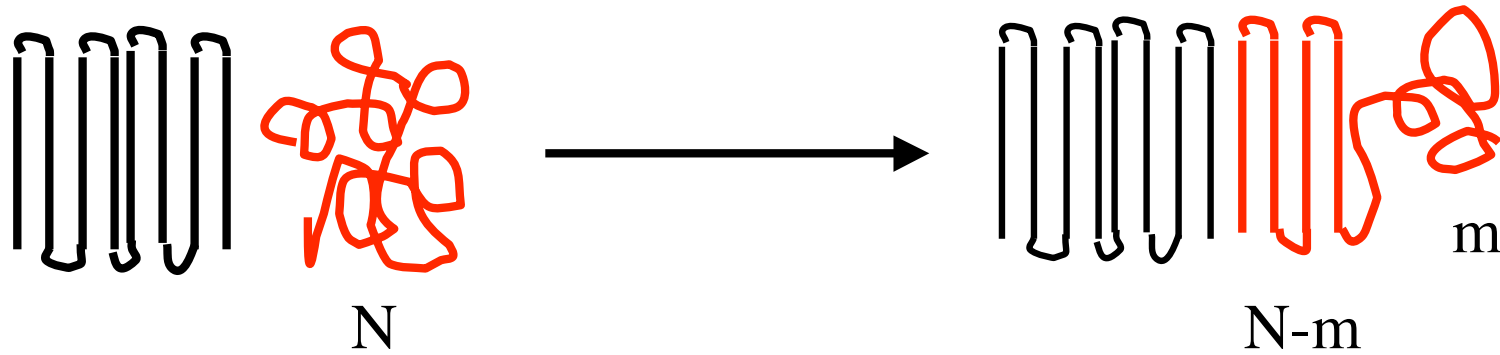
Concentrated



ENTROPIC BARRIER

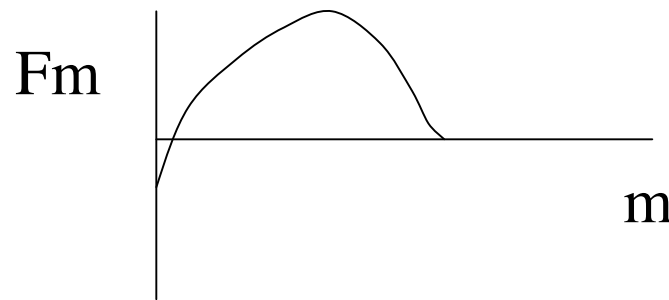
Entropic Barrier and Jamming





$$F_m = -(N - m)\Delta F + \sigma\sqrt{N - m} + (1 - \gamma)\ln m$$

[MM, *Phil.Trans.Roy.Soc.*, **361A**, 539 (2003)]



$$G \sim C K \left[1 - e^{-\frac{(\Delta H)(\Delta T)}{kT_m T}} \right]$$

(Barrier)

$$F^* \sim \frac{1}{\Delta T}$$

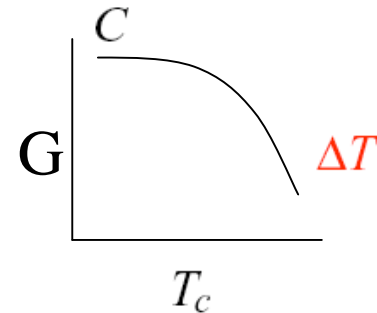
$$G \sim C \frac{D_{in}}{D} e^{-\frac{\alpha}{T\Delta T}} \left[1 - e^{-\frac{(\Delta H)(\Delta T)}{kT_m T}} \right]$$

Kinetics at Growth Front



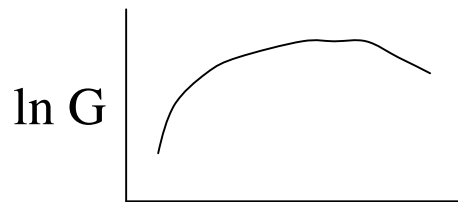
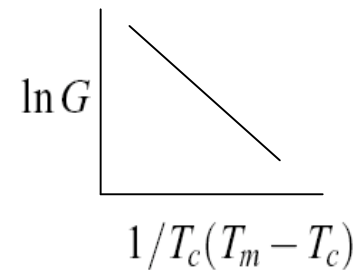
No barrier:

$$G \sim C \left[1 - e^{-\frac{(\Delta H)(\Delta T)}{kT_m T}} \right]$$



Barrier:

$$G \sim C \frac{D_{in}}{D} e^{-\frac{\alpha}{T\Delta T}} \left[1 - e^{-\frac{(\Delta H)(\Delta T)}{kT_m T}} \right]$$



$$G \sim C^\gamma M^{-\mu}$$

ln M

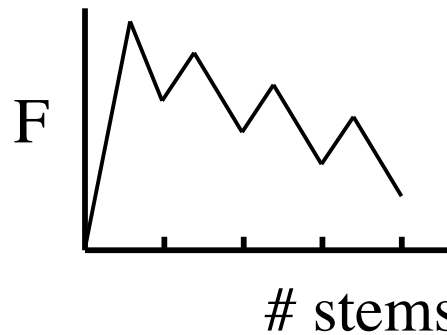
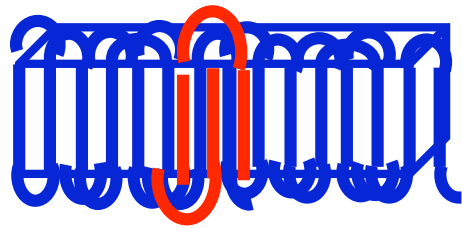
A. Kundagrami and MM, *J. Chem. Phys.* 126, 144901 (2007)

J. Zhang and MM, *J. Chem. Phys.* 126, 234904 (2007)

M.K. Mitra and MM (unpublished)

Conclusion #3

Kinetics at growth front



Lauritzen-Hoffman
Theory

Lamellar growth is chain **ADSORPTION**
with cooperative dynamics of **all** chains

Boundary layer controls the crystallization kinetics

Central Issues

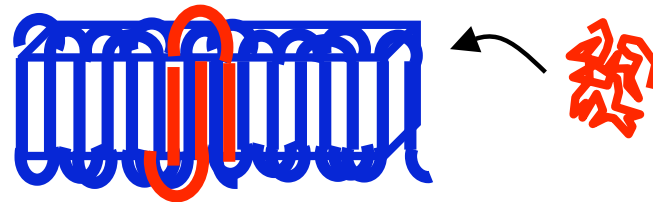
1. Primordial stage of polymer crystallization

2. Spontaneous selection of lamellar thickness $L \ll$ extended chain dimension
 $\sim 10^{-2} \times$ current equilibrium arguments

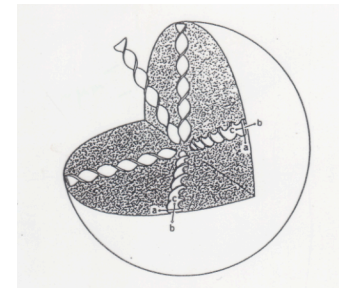
\Rightarrow “KINETICALLY CONTROLLED”

Interlude from any stable MESOMORPHIC states?

3. Kinetics at growth front

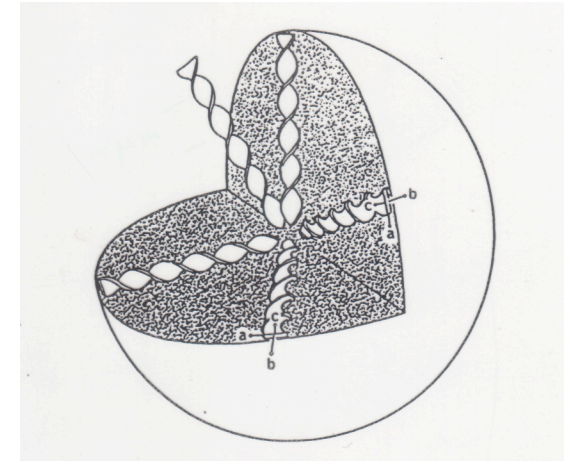
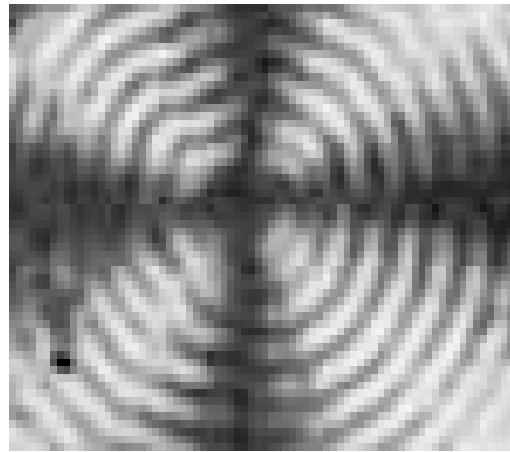
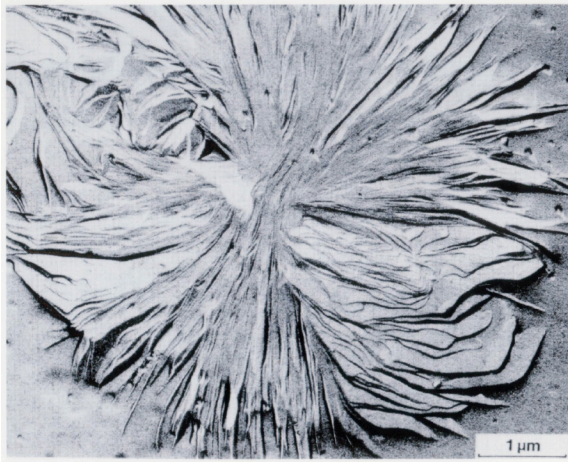


4. Origin of chiral symmetry breaking



5. Composition fluctuations on crystallization kinetics

Banded Spherulites

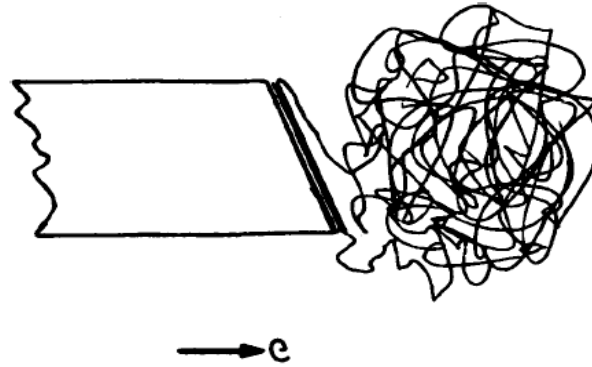


GIGANTIC CHIRALITY
in polyethylene crystals
(ACHIRAL molecules)

(Both right-handed and left-handed spherulites)

Banded Spherulites

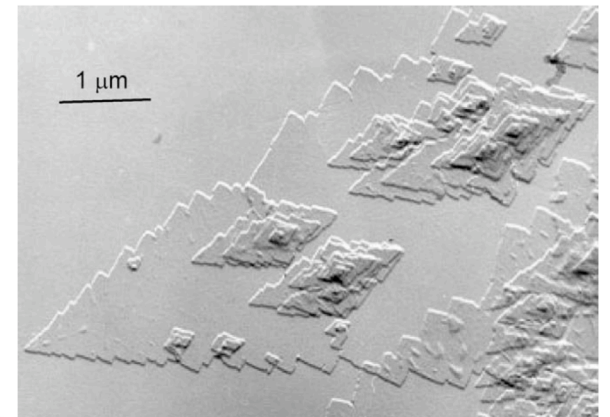
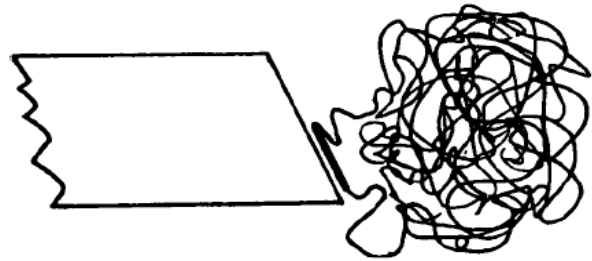
Keith-Padden:



crowding
at tilted growth front



surface stress

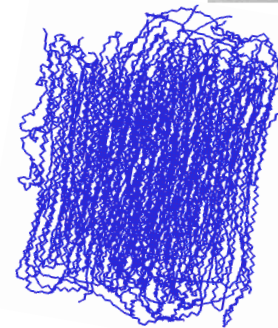


Bassett *et al.*:

DISLOCATIONS

Hatwalne-MM

DISCLINATIONS



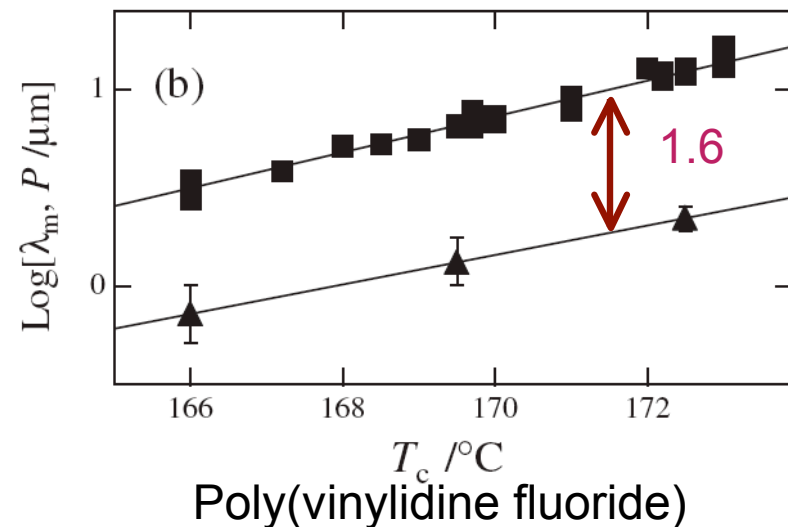
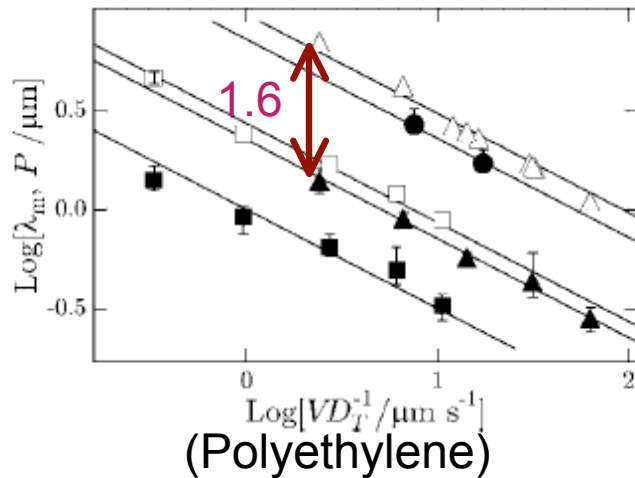
Conclusion #4

Disclinations + Finite size = Spontaneous Chiral Symmetry Breaking (even for ACHIRAL molecules)

Natural selection of ring period and lamellar width:

$$\text{Ring period} = \frac{\pi}{2} (\text{width})$$

A. Toda (Hiroshima University):



A. Toda *et al.* Macromolecules 41, 2484 (2008); Polymer J, 40, 905 (2008)

Central Issues

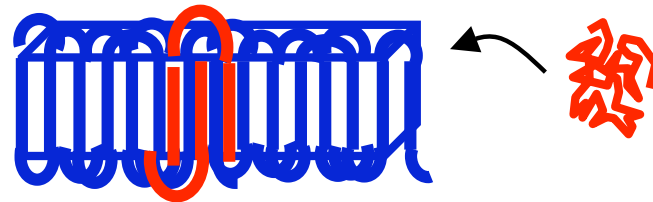
1. Primordial stage of polymer crystallization

2. Spontaneous selection of lamellar thickness $L \ll$ extended chain dimension
 $\sim 10^{-2} \times$ current equilibrium arguments

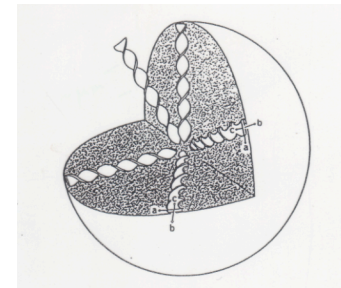
\Rightarrow “KINETICALLY CONTROLLED”

Interlude from any stable MESOMORPHIC states?

3. Kinetics at growth front



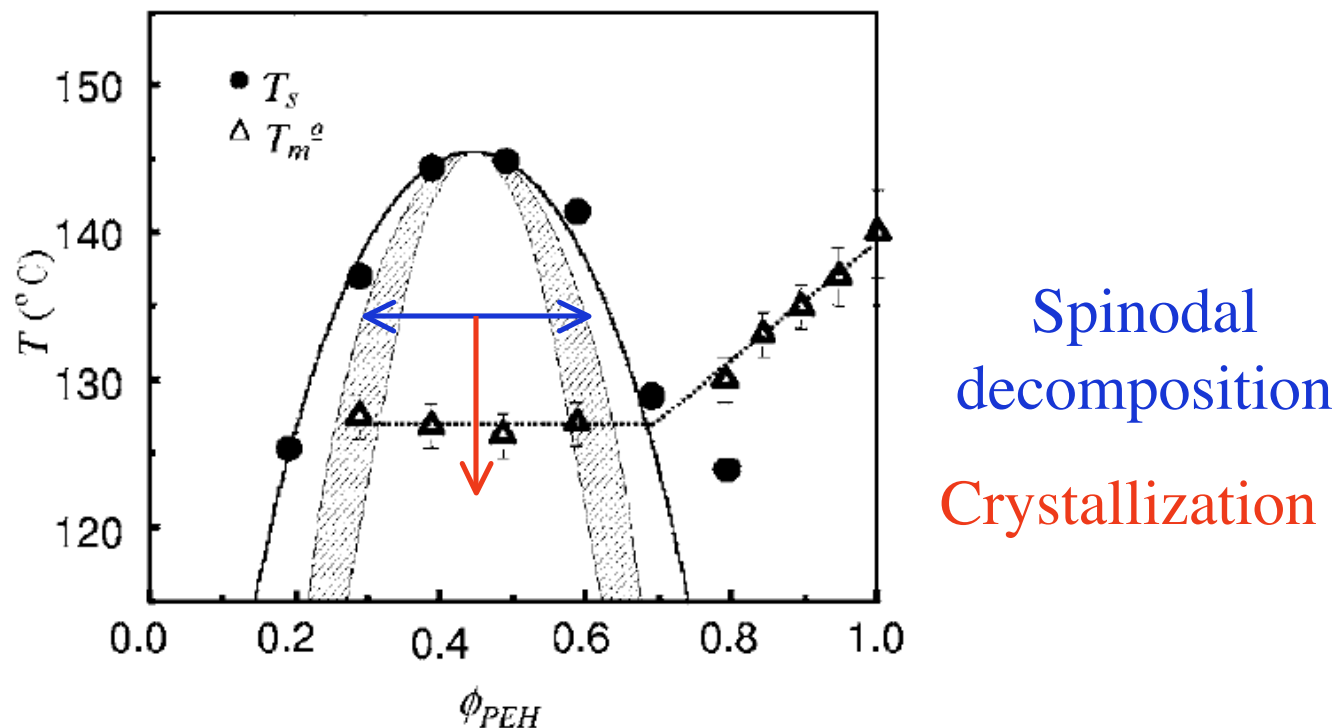
4. Origin of chiral symmetry breaking



5. Composition fluctuations on crystallization kinetics

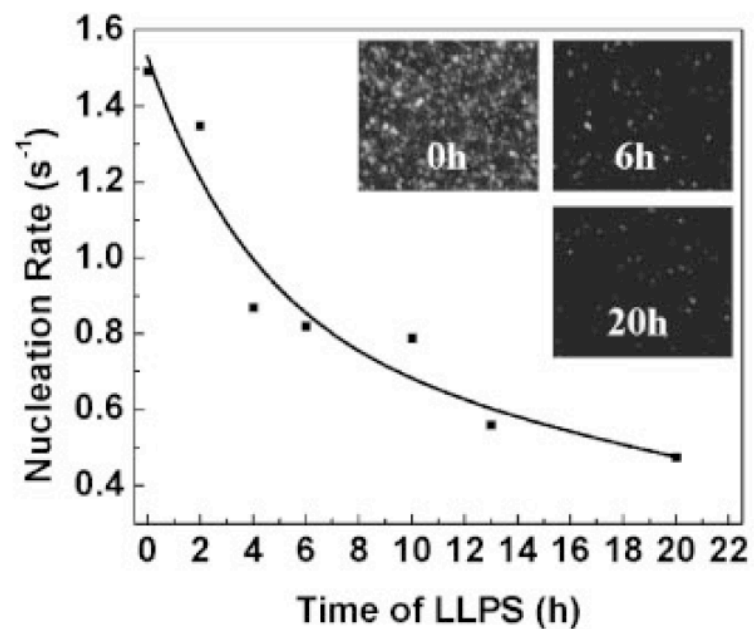
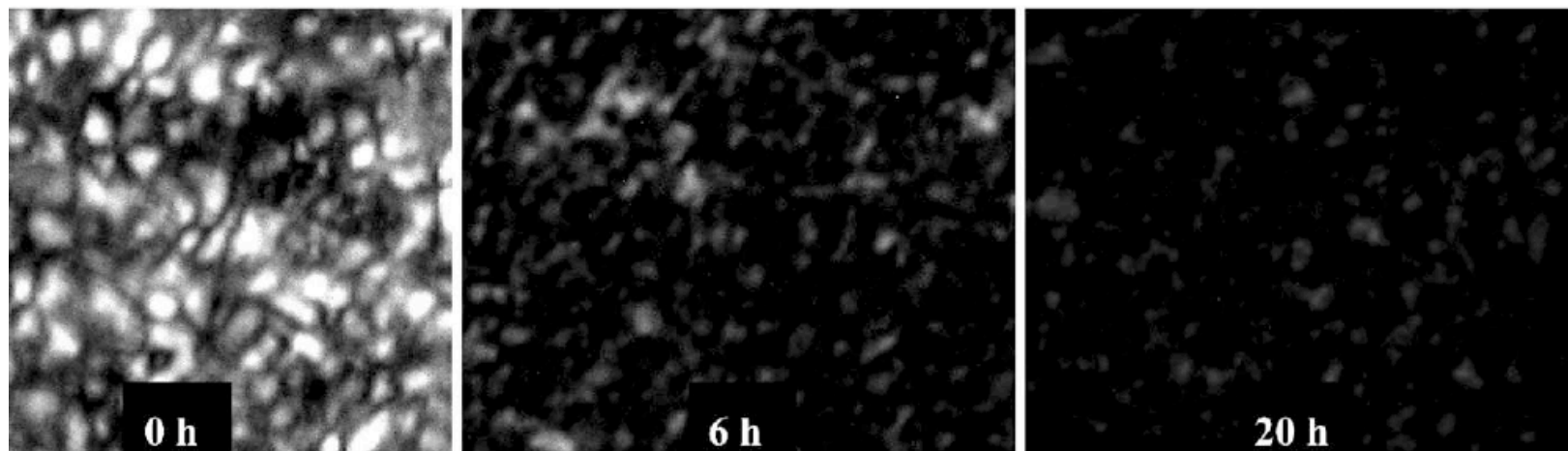
5. Composition fluctuations on crystallization kinetics

X. Zhang, ..., C.C. Han: *Macromol. Rapid Commun.* **26**, 1285 (2005);
J. Chem. Phys. **125**, 024907 (2006).



Blend of poly(ethylene-co-hexene) and poly(ethylene-co-butene)

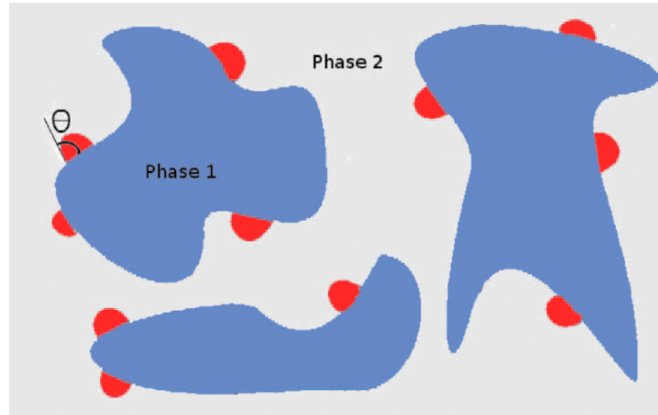
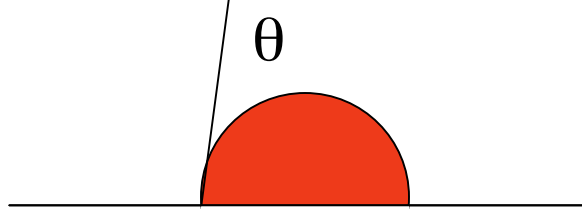
40/60 PEH/PEB, $T_c = 112^\circ\text{C}$ for 60s, after LLPS at 135°C



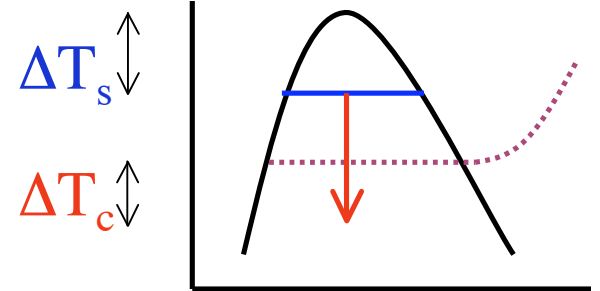
40/60 PEH/PEB, $T_c = 117.8^\circ\text{C}$ for 120s, after LLPS at 135.8°C

$$L(t) \sim \frac{t^\gamma}{(\Delta T_s)^\delta}$$

$$\delta = \frac{1}{3} = \gamma \quad \text{late regime}$$



M.K. Mitra and MM,
JCP, 132, 184908 (2010)



$$\text{Nucleation barrier: } \Delta G_c = \frac{\sigma^3 T_m^2}{(\Delta H)^2 (\Delta T_c)^2} f(\theta)$$

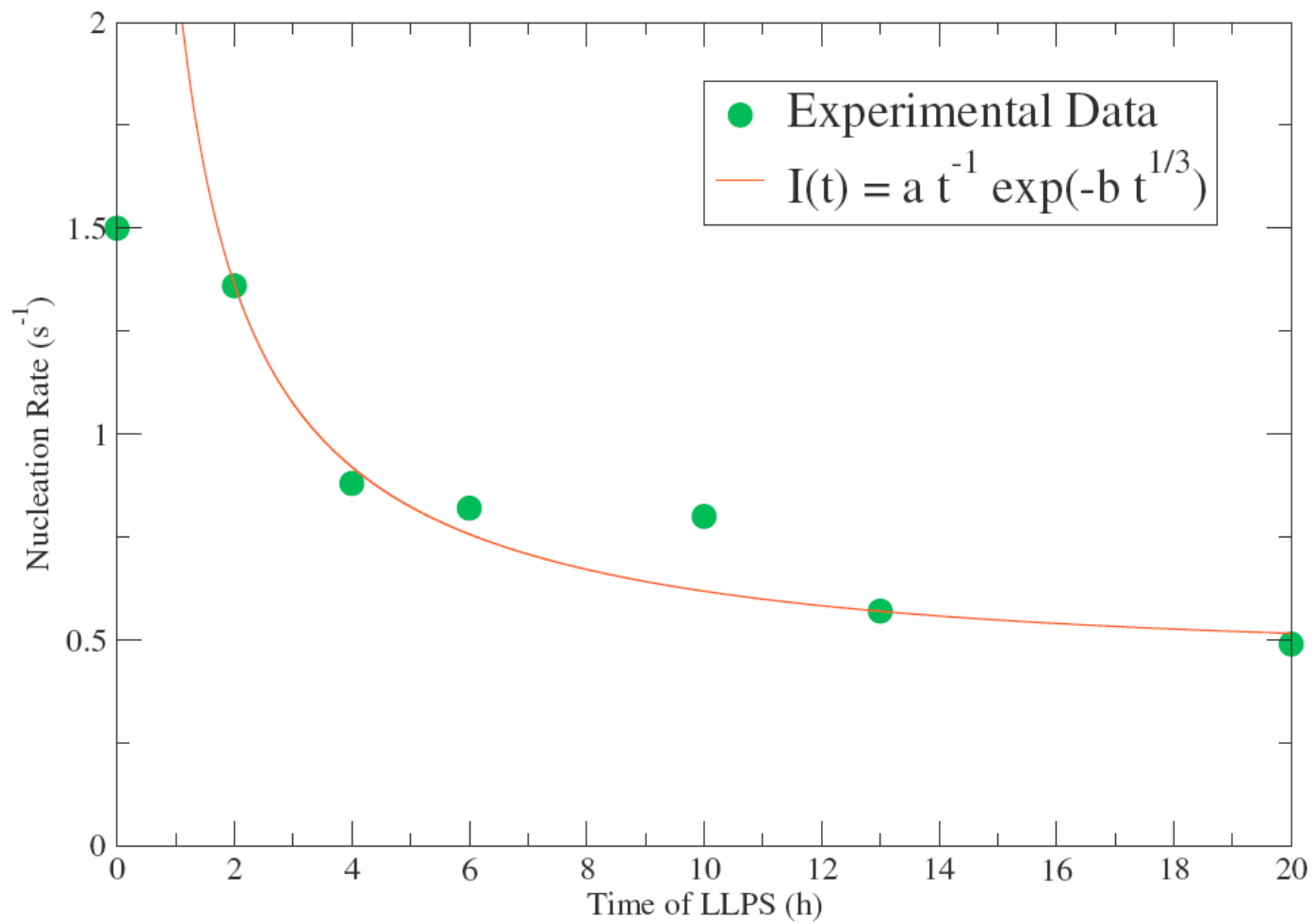
$$\text{Heterogeneous nucleation rate: } I_0 \sim e^{-\Delta G_c / k_B T}$$

$$\text{Competitive nucleation rate in a domain: } I_d = I_0 e^{-I_0 t / m}$$

$$\text{Maximum number of nuclei in a domain: } m \sim \frac{L^2(t)}{r_c^2 \sin^2 \theta}$$

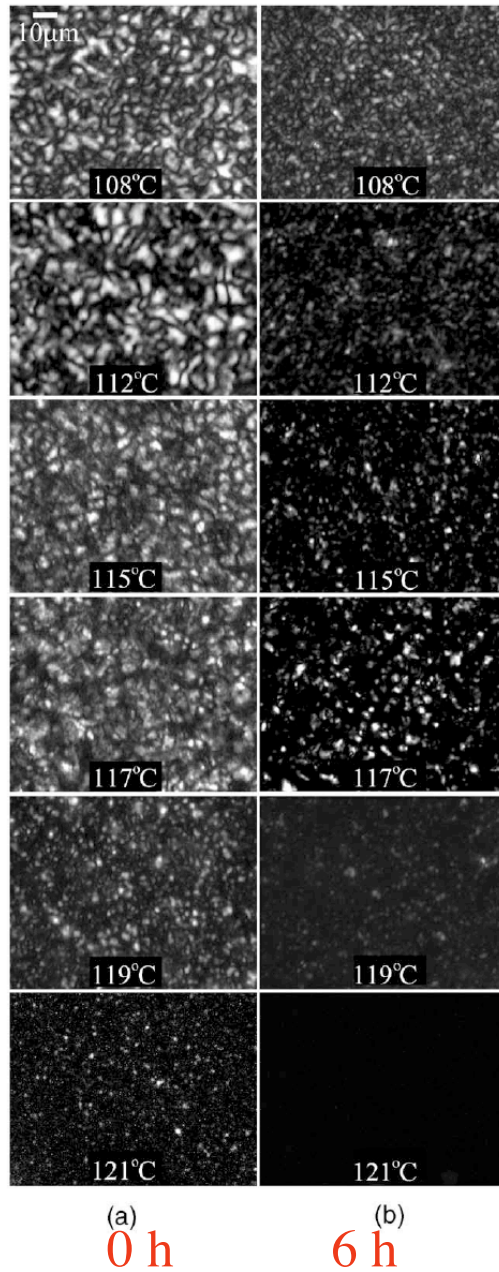
$$\text{Number of domains: } 1/L^3(t)$$

$$\text{Overall nucleation rate: } \frac{1}{L^3(t)} e^{-I_0 t / m} \sim (\Delta T_s)^{3\delta} t^{-3\gamma} e^{-\left[\frac{1}{(\Delta T_c)^2} (\Delta T_s)^{2\delta} t^{1-2\gamma} \right]}$$



Effect of crystallization T
(4 min)

LLPS
at 135°C



Effect of spinodal T
(T_c = 117°C for 120s)

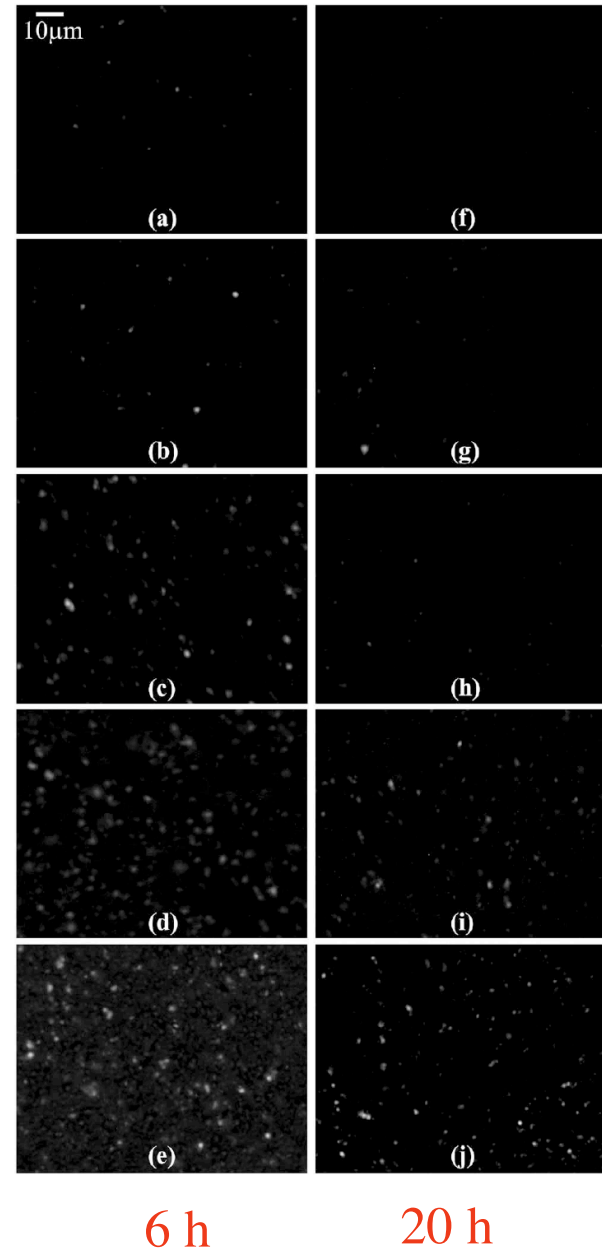
130°C

133°C

135°C

138°C

140°C



Conclusion #5

5. Effect of composition fluctuations

More heterogeneous nucleation at lesser extent of SD

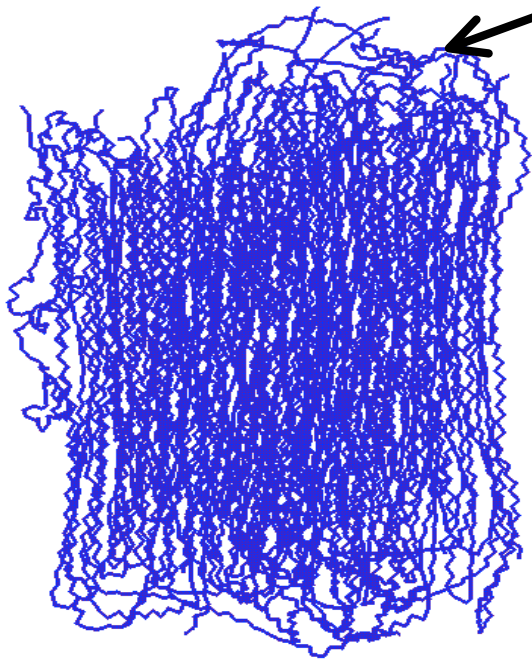
Deeper spinodal quench, less nucleation

Deeper crystallization quench, better nucleation

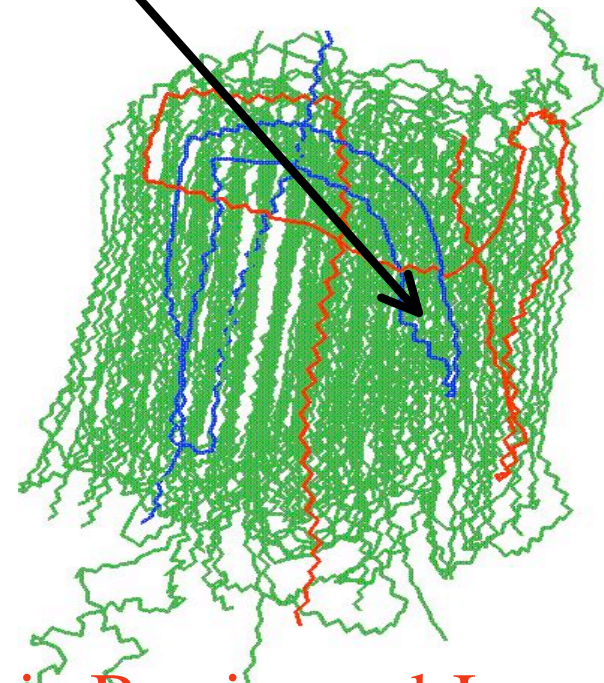
(Consistent with experiments from C. C. Han)

Polymer Crystallization: Entropically Controlled

$$F = E - TS$$



Folded Chain Crystal

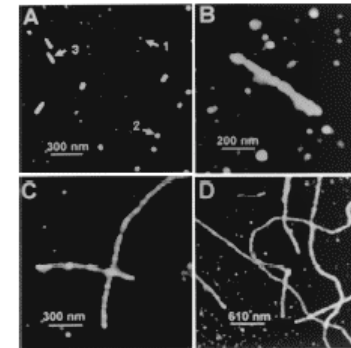


Entropic Barrier and Jamming
at growth front

Shifting Paradigms in Polymer Crystallization

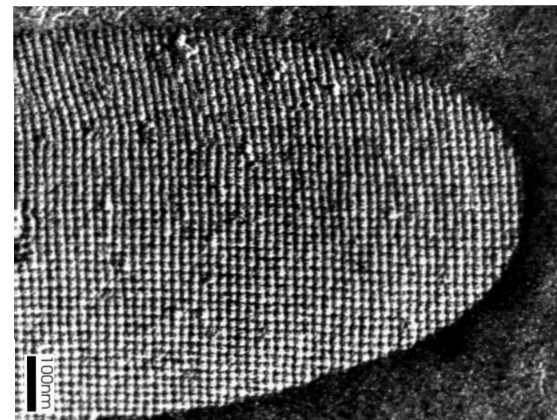
1) Amyloid fibrils

DAEFRHDSGYEVHHQLLVFFAEDVGSNLGAIIGLMVGGVVIA

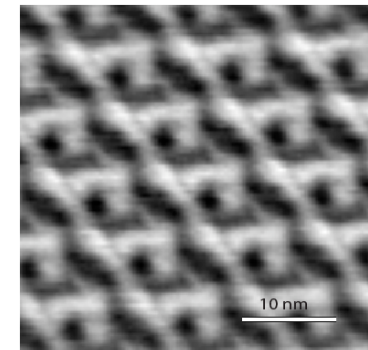


2) Bacterial walls

MAYQPKSYRKFVATTATAAMVASAVPVVSAASFTDVAPQYKDAIDFLVST
 GATKGGKTETKFGVYDEITRLDAAVILARVLKLDVDNAKDAGFTDVPKDRAY
 VNALVEAGVLNGKAPGKFGAYDPLTRVEMAKIIANRYKPKADDVKLPFTDV
 NDTWAPYVKALYKYEVTGKGTPTSTFGAYQNITRGDFAQFVYRAVNINAVPEI
 VEVTAVNSTTVKVTFTNTQIADVDFTNFADNGLTGTKATLSRDKKSEVVVNK
 PFTRNQEYTTITATGIKNLKGETAKELTGKFWVSQDVAVTVALNNSSLKVGEE
 SGLTVKDDGDVVGAKVELTSSNTNIVVSSGEVSVSAAKVTAVKPGTADV
 TAKVTLPDGVVLTNTFKVTVEVPVQVQNGGFTLVNLSNAPQNTVAFNKA
 EKVTSMFAGETKTVMYDTKNGDPETKPVDFKDATVRSLNPIIATAAINGSE
 LLVTANAGQSGKASFVETFKDNTKRTFTVDVKKDPVLQDIKVDATSVKLSDE
 AVGGGEVGVNQKTIKVSADVQYGKEIKFGTKGKVTVTNTTEGLVIKINVNSD
 NTIDFDSGNSATDQFVVVATKDKIVNGKVEVKYFKNASDTPPTSTKTITVNVV
 NVKADATPVGLDIVAPSEIDVNPANTASTADVDFINFESVEIYTLDSNGNRLK
 KVTPTATTLVGTNDYVEVNGNVLQFGNDELTLTSSSTVNVDTVADGITKRI
 PVKYINSASVPASATVATSPVTVKLNSSDNDLTFEELIFGVIDPTQLVKDEDIN
 EFAIVSKAAKNDGYLYNKPLVTVKDASGKVIPTGANVYGLNHADATNGNIWFD
 EEQAGLAKKFSVDVHFDVDFSLANVVKTGSGTVSSSPSLSDAIQLTNSGDV
 SFTLVIKSIYVKGADKDDNNLLAAPVSVNVTVTK



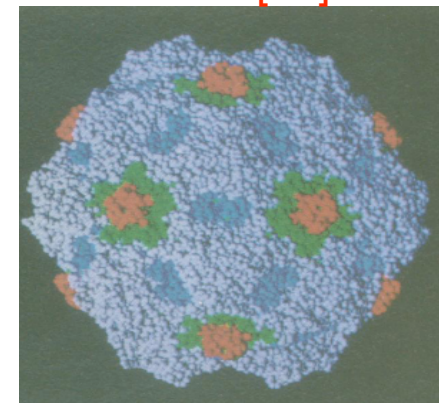
S-layers



3) Viruses

GVGVSTGSYDNQTHYRFLGDGWVEITALATRLVHLMPLSENRYCRIRV
 HNTTDSVLGNMALDDAHEQIWTPWSLVDANAWGVWLQPSDWQYIC
 NTMSQLNLVSLDQEIFNVLLTVTEQDSGGQAILIYNNDLTACMMVAVD
 SNNILPYTPAANSMETLGFYPWLPTIASPYRYFFCVDRDLSTYENQEG
 TIEHNVMGTPPLGMNSQFFTIENTQQITLLRTGDEFATGTYFFDTNPVLLT
 HTWQTNRQLGQPPLLSTFPEADTDAGTLTAQGSRHGATQMEVNVWVSE
 AIRTRPAQVGFQCPHNDFEASRAGPFAAPLVPADVQGMREANGSVR
 YSYGLQHGENWAAHGPAPERIYTWDETNFGSGRDRDGFQISAPLVVP
 PPLNGILTANPIGTLNDIHFNSNVFNSYGPLTTFSHPSPVYPQQGIWDEL
 DLEHLPRLHITAPFVCLNAPGNAPGQMLVRLGPNLTDQYDPNGATLSRIVTYG
 TFFWLGLLTMRALLRANTTWNVPVYQVSVEDNGNSYMSVTLWLPTATGN
 MQSVPLITRPVARNY

Parovirus[T1]



Why aren't we made of spheres or cubes?

$$F = E - T S$$



fixed

Need candidates where F can be changed dramatically and reversibly at fixed temperature

