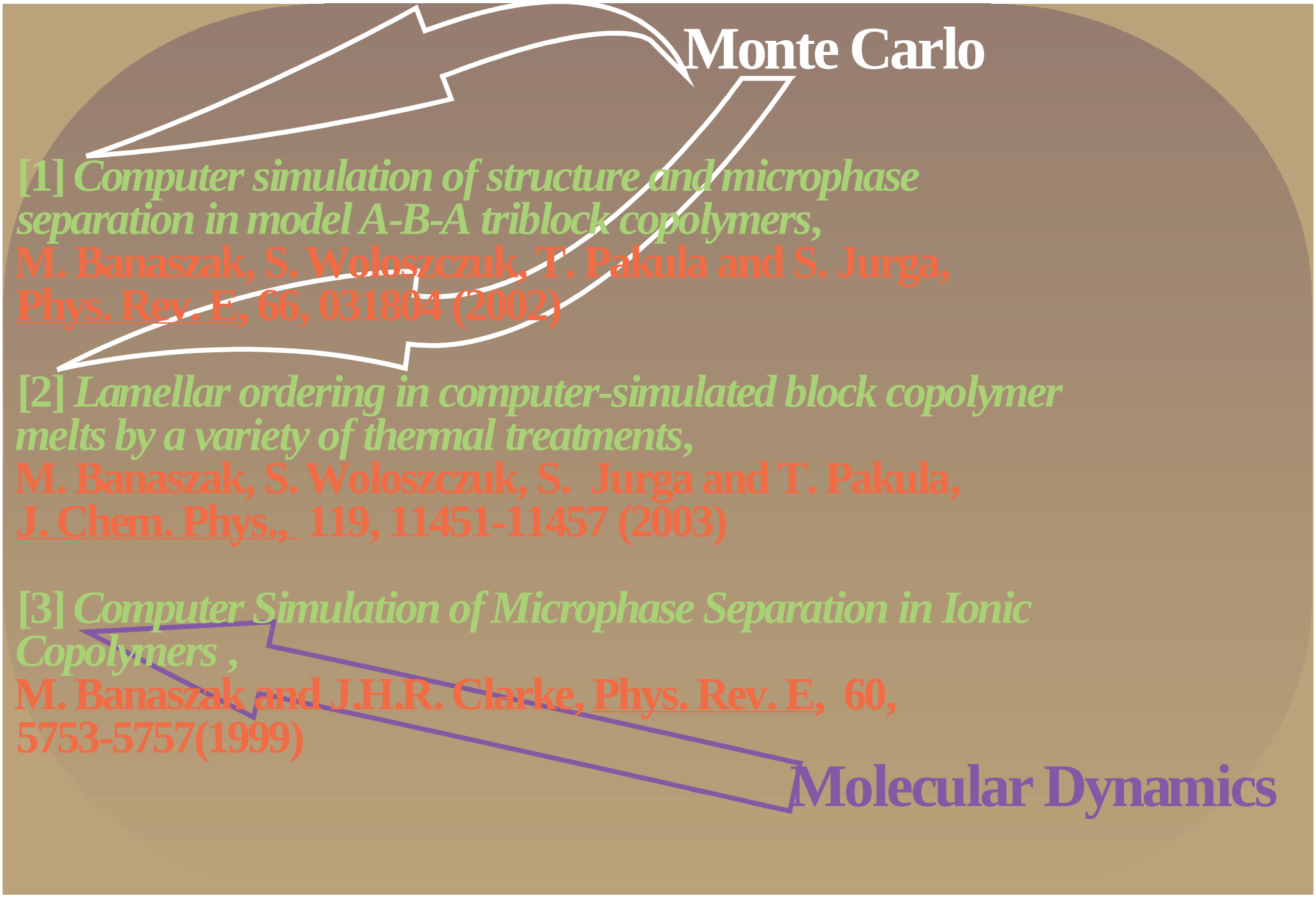
Computer Simulation of Self-Organization in Block Copolymers

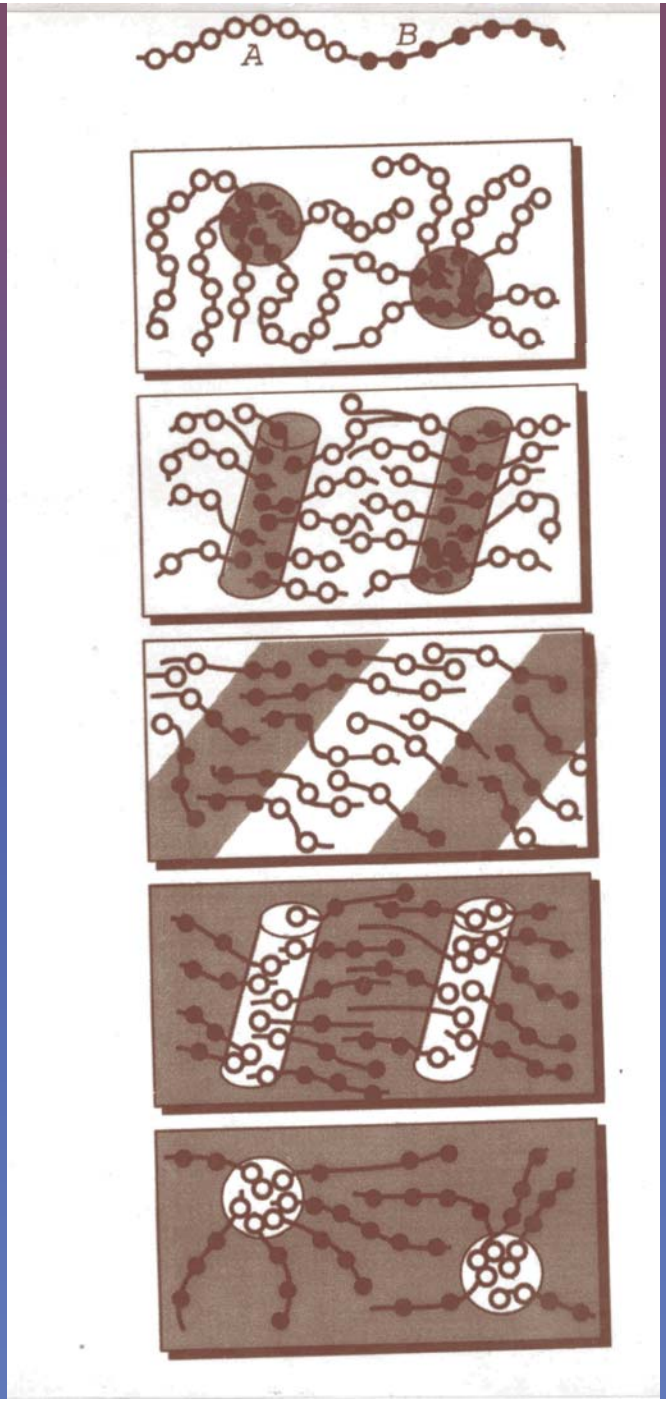
- Background
- Method
- Results

The Physics of Block Copolymers, Ian W. Hamley, Oxford University Press, 1998

Block Copolymers: Past Successes and Future Challenges, Timothy P. Lodge, *Macromol. Chem. Phys*. 2003, **204**, pp 265-273


Monte Carlo
[1] Computer simulation of structure and microphase separation in model A-B-A triblock copolymers,
M. Banaszak, S. Woloszczuk, T. Pakula and S. Jurga,
Phys. Rev. E, 66, 031804 (2002)
[2] Lamellar ordering in computer-simulated block copolymer melts by a variety of thermal treatments,
M. Banaszak, S. Woloszczuk, S. Jurga and T. Pakula,
J. Chem. Phys., 119, 11451-11457 (2003)
[3] Computer Simulation of Microphase Separation in Ionic Copolymers ,
M. Banaszak and J.H.R. Clarke, Phys. Rev. E, 60, 5753-5757(1999)
Molecular Dynamics

Monte Carlo		Molecular Dynamics
lattice model	←	off-lattice model
triblock and diblock copolymers	←	ionic diblock copolymers
very short-range potential	←	long-range electrostatic potential
more coarse-grained	←	less coarse-grained



Spheres of B in A

Cylinders of B in A

Layers

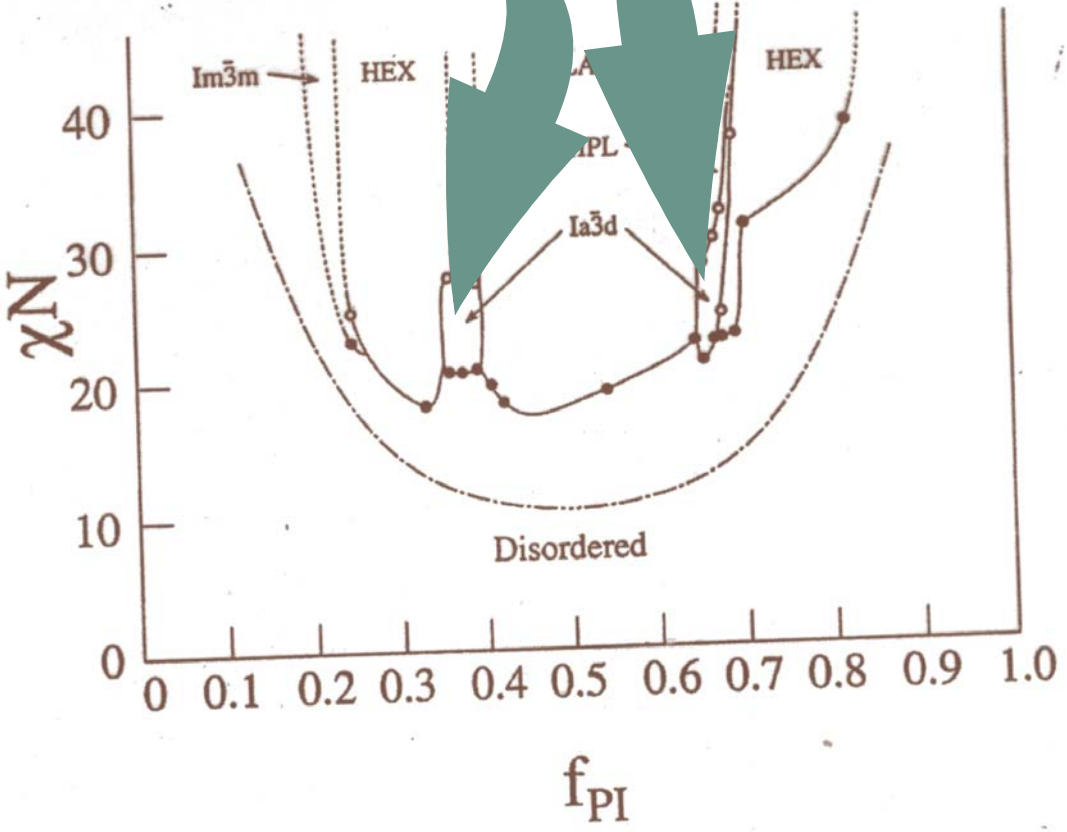
Cylinders of A in B

Spheres of A in B

Diblock copolymer phase diagam

Macromolecules, Vol. 28, No. 26, 1995

$\chi \sim \frac{1}{T}$



Block copolymers are important self-assembling materials for the following reasons:

- Precise (and continuous) control over lengthscales - from 5 to 50 nm
- Control over morphology- L, C, G and S for diblocks and over 30 for triblocks
- Possibility of selecting the polymer for each block
- Quantitative prediction of equilibrium structures - SCMF

Applications of Block Copolymers

- "Old" - retain important features of their constituent homopolymers, do not take advantage of any particular nanostructure
- "New" - depend on long-range organization and orientation of the nanostructure

Challenges

- Synthesis and preparation of materials
- New nanostructures (theory and simulation)
-

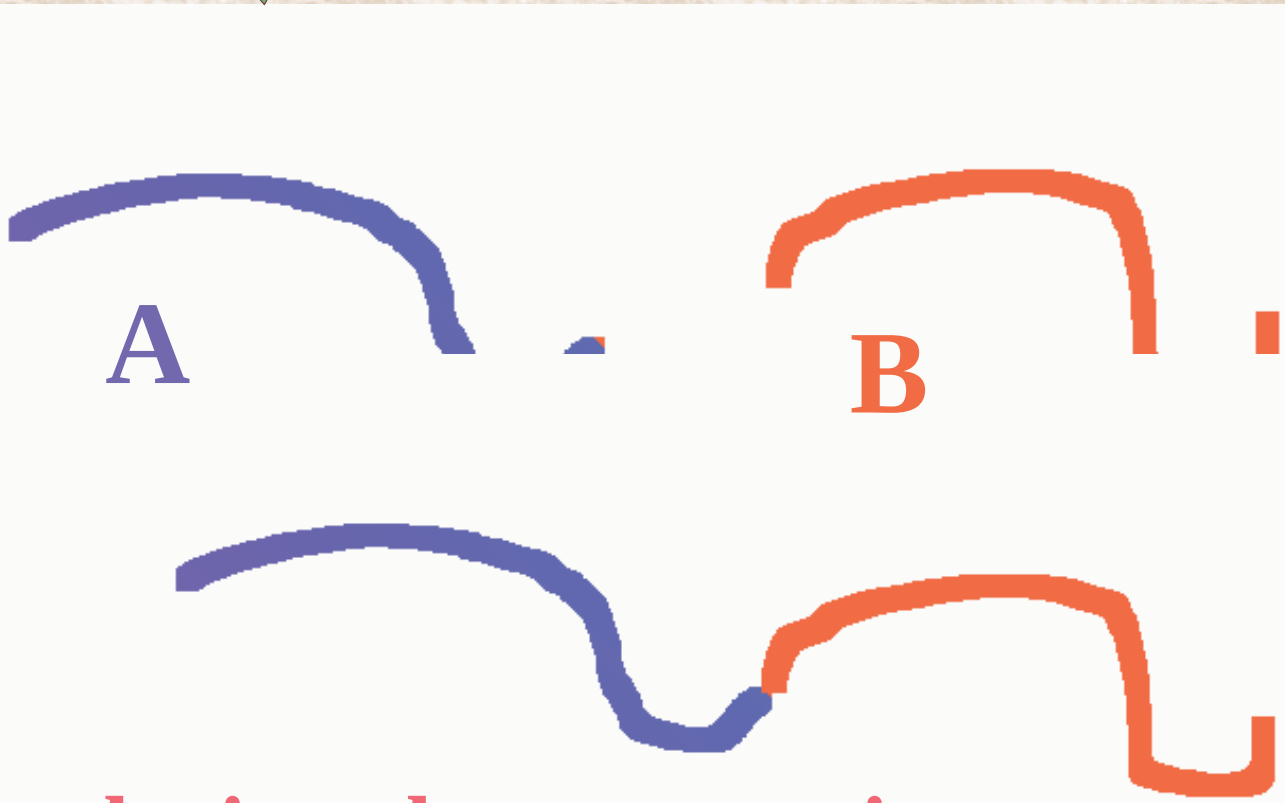
Flory-Huggins Theory

$$f_m = \frac{\phi_A}{N_A}\ln\varphi_A + \frac{\phi}{}$$

$$\varphi_A + \varphi_B = 1$$

$$-\varepsilon_{AA}, -\varepsilon_{AB}, -\varepsilon_{BB}$$

$$\chi = \frac{z}{2kT}\left[\varepsilon_{AA} + \varepsilon_{}\right.$$

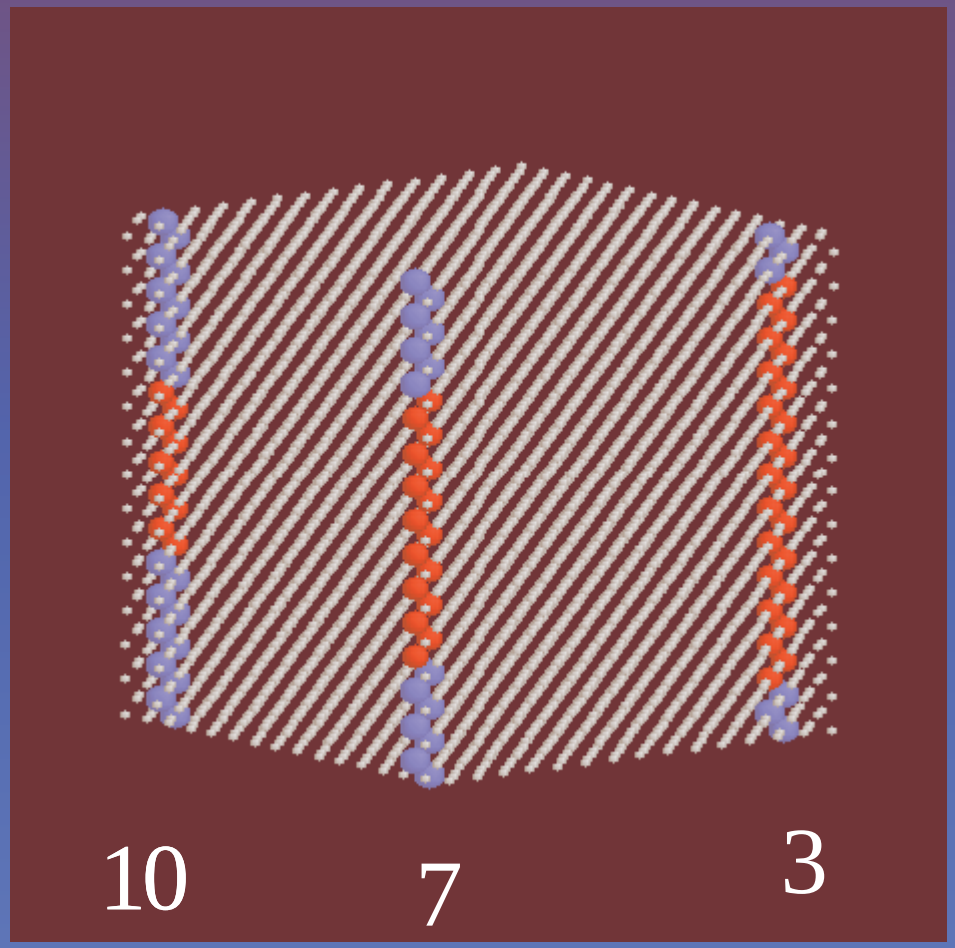


Macrophase and microphase separation

Reduced Temperature, T*/N

- ε - interaction energy between A and B
- $T^* = kT/\varepsilon$
- $\chi = (z-2)/T^*$
- Leibler's RPA theory (mean field)
  - < Flory interaction χ parameter
  - < N - copolymer chain length (number of monomeric units)
  - < $N\chi = 10.5$ - ODT for symmetric diblocks
  - < T*/N - the copolymer reduced temperature

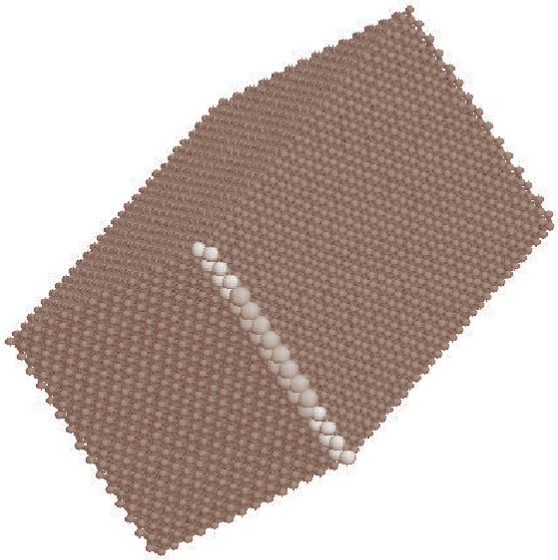
Triblock microarchitectures



- 10–10–10
- 7–16–7
- 3–24–3

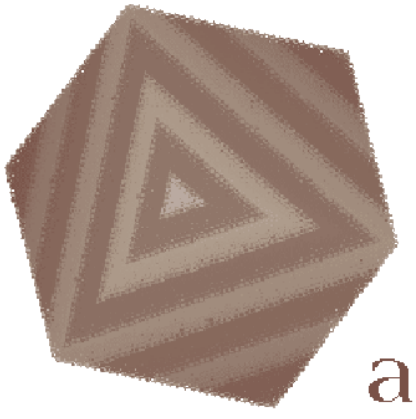
- 30 x 30 x 30
- **60 x 30 x 30**
- 60 x 60 x 60

Simulation box, 60x30x30



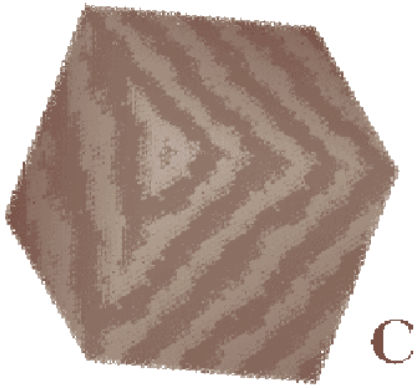
Lamellar nanostructures

T*/N=0.04



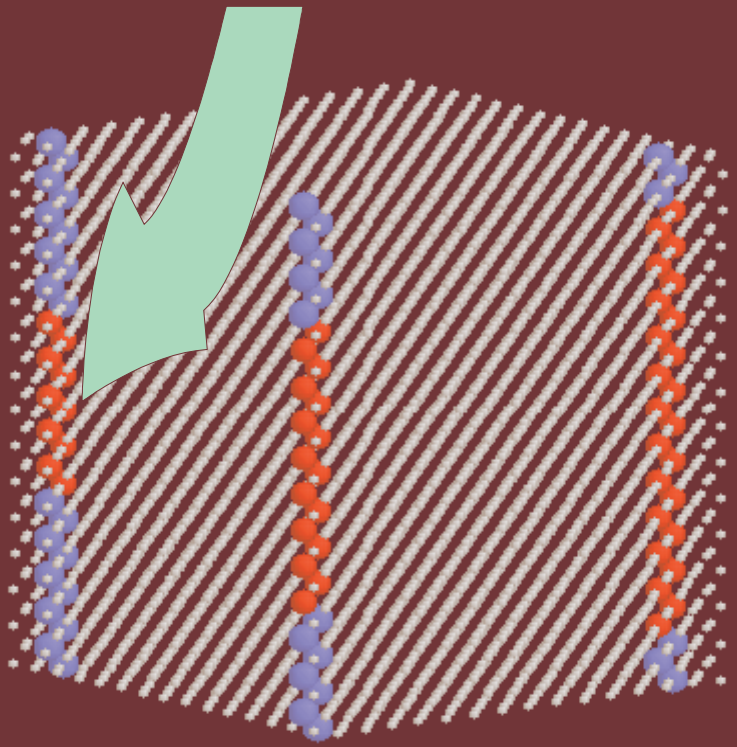
T*/N=0.10

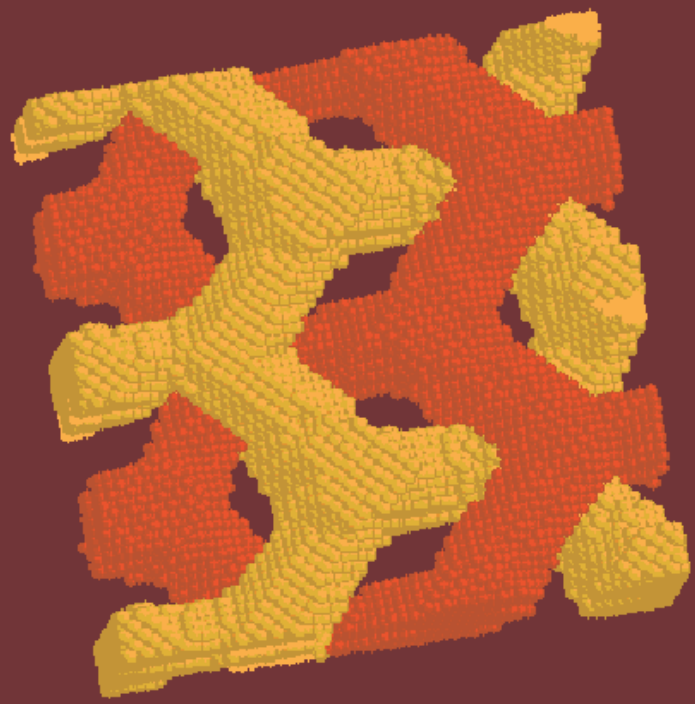
T*/N=0.18



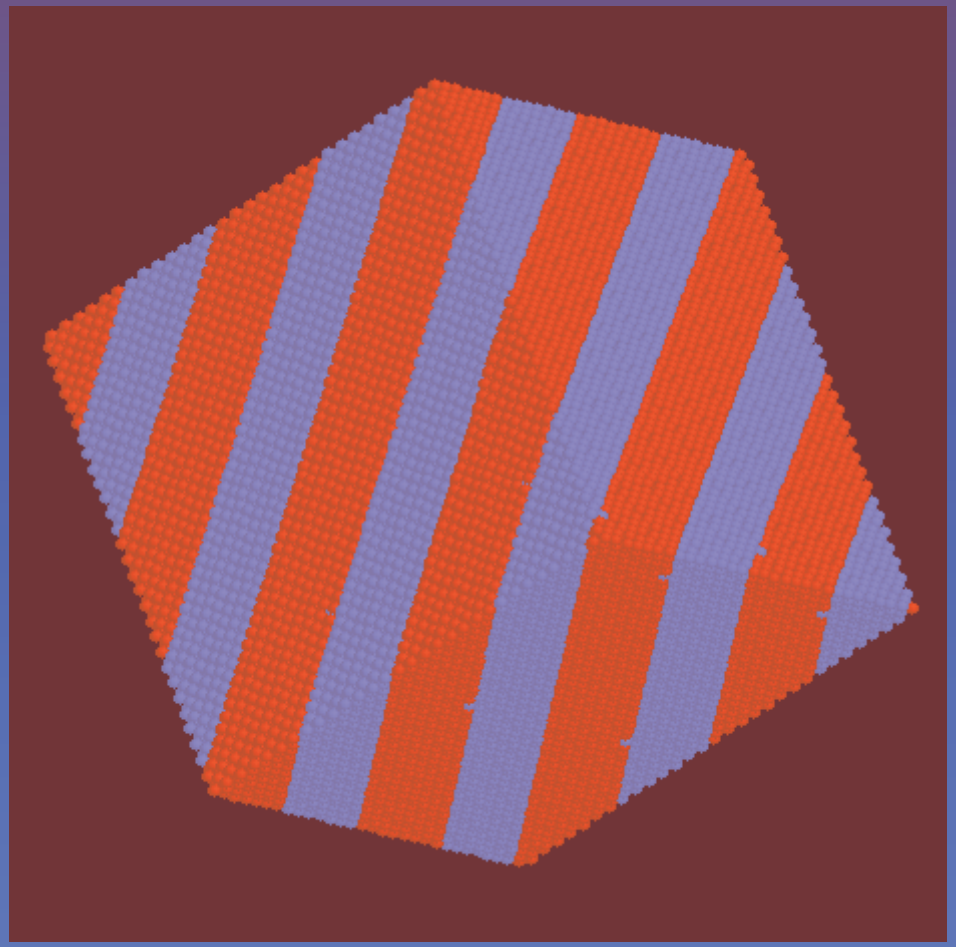
T*/N=0.24

Bicontinuous nanostructure for the 10-10-10 microarchitecture, T*/N=0.04

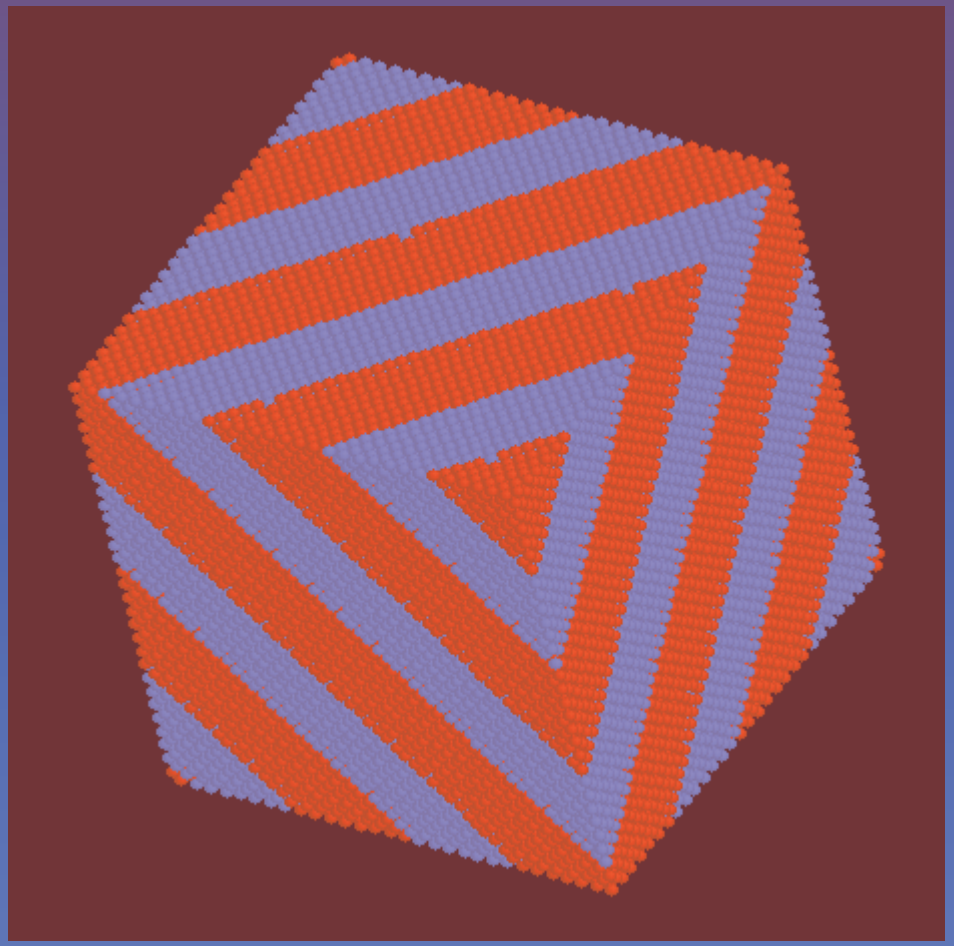




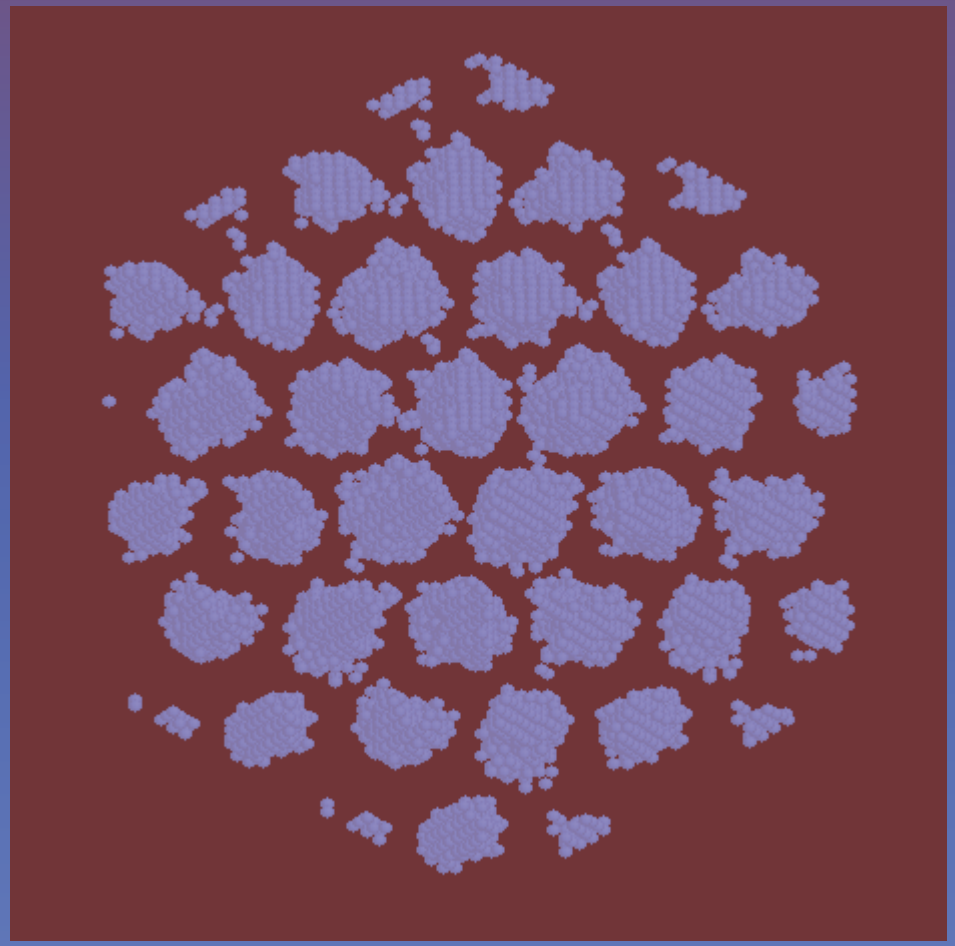
7-16-7 Microarchitecture , T*/N=0.04

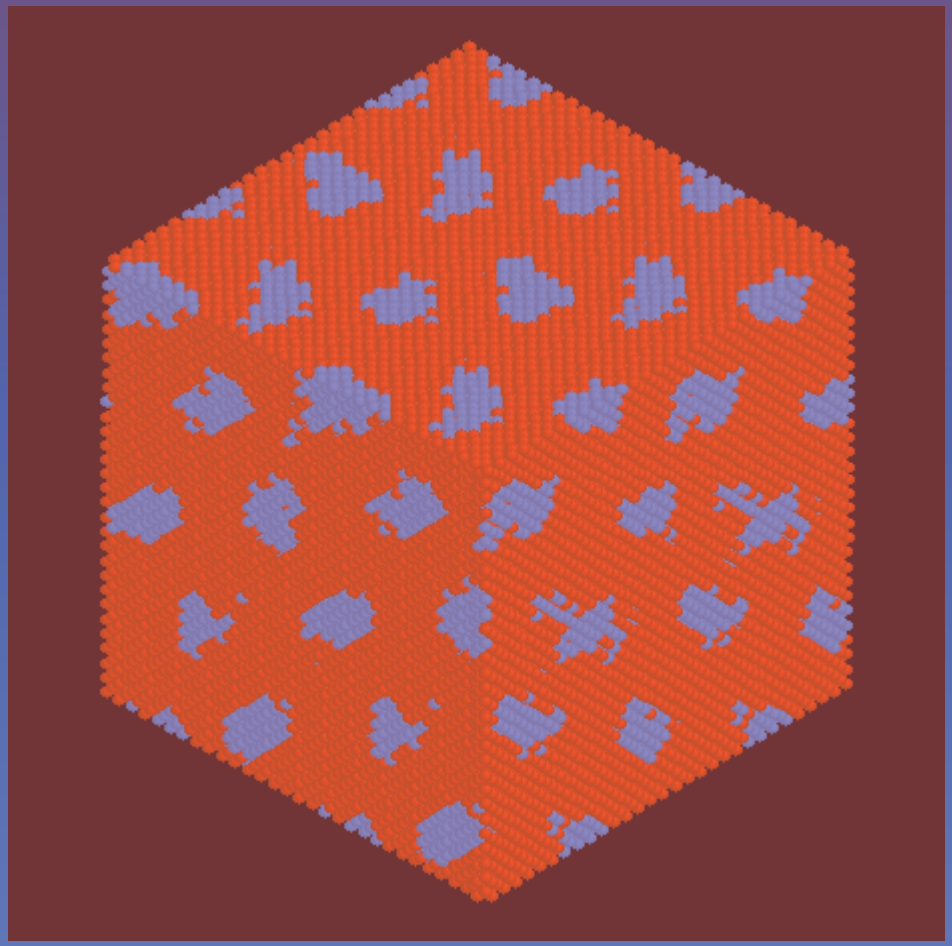


7-16-7 Microarchitecture, T*/N=0.04

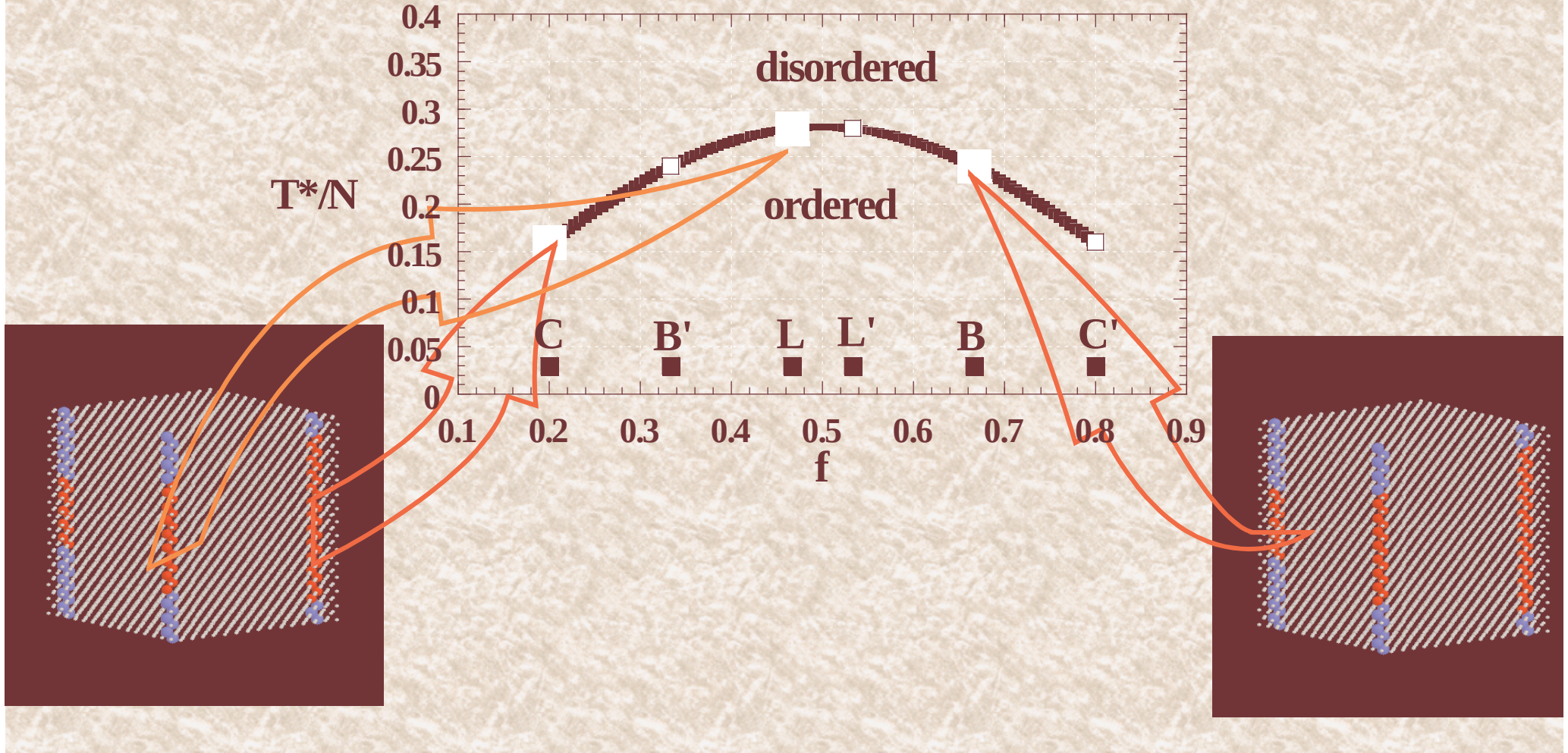


3-24-3 Microarchitecture, T*/N=0.04





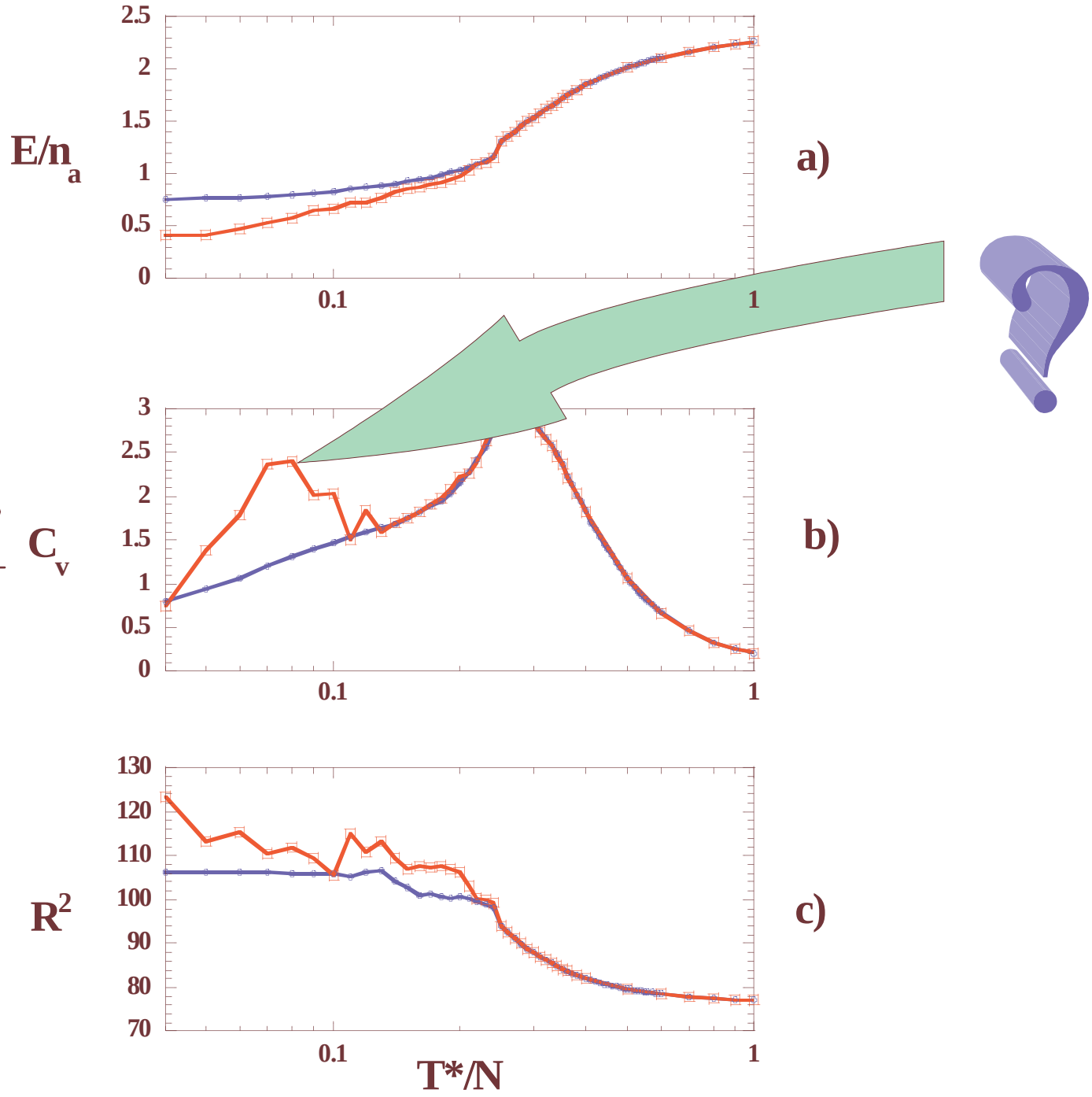
Phase diagram of the symmetric triblo copolymer melt

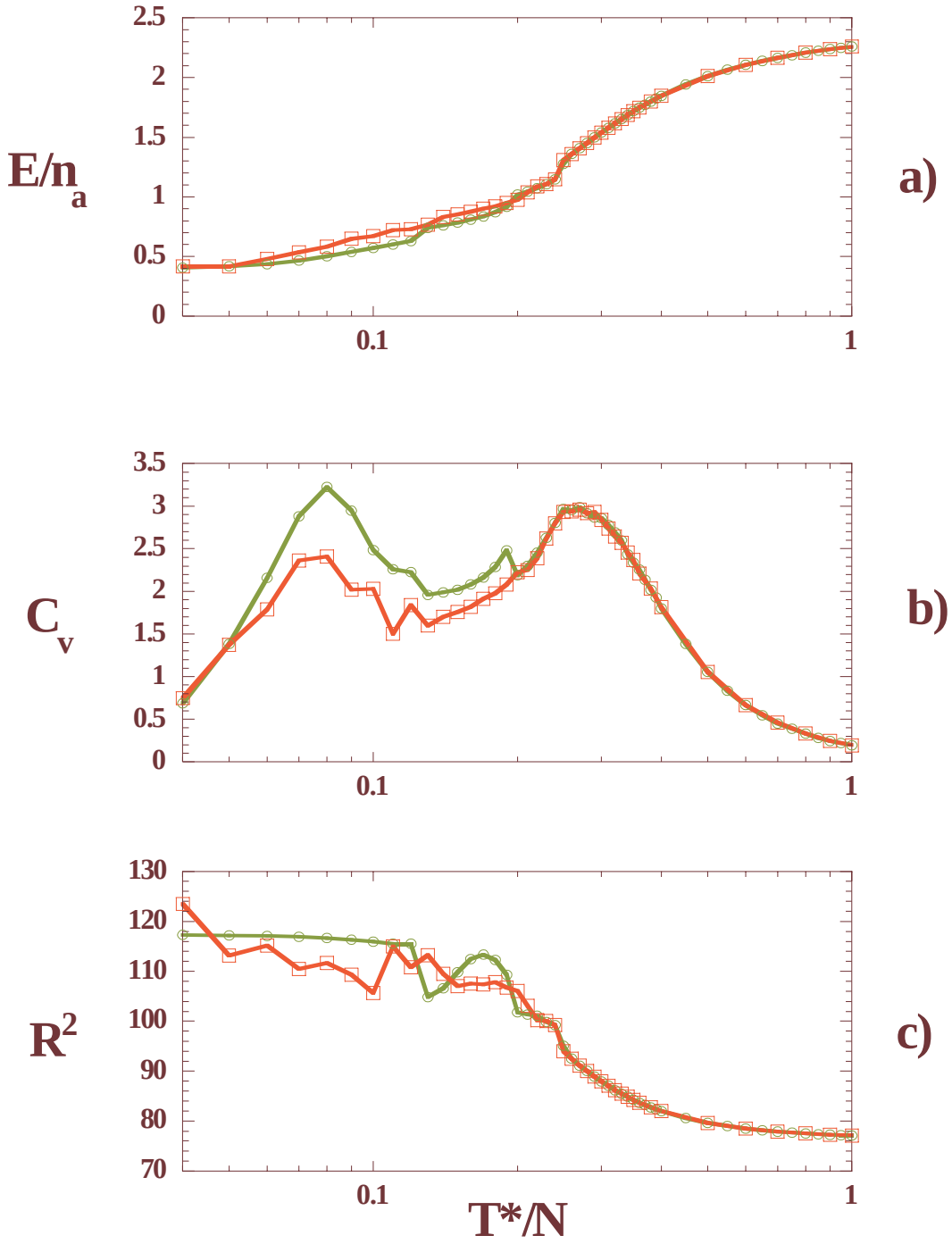


Quenching

$$C_v = \frac{\left\langle \left(E^* - \left\langle E^* \right\rangle \right)^2 \right\rangle}{n_c T^{*2}}$$

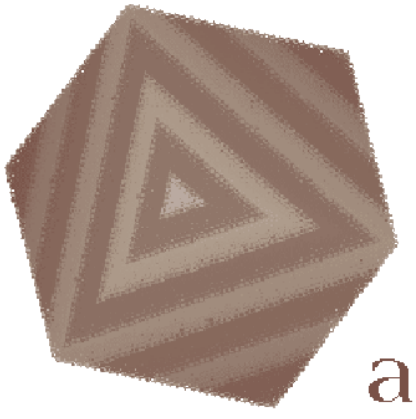
Slow cooling




E/n_a
2.5
2
1.5
1
0.5
0
0.1
1
a)
C_v
3.5
3
2.5
2
1.5
1
0.5
0
0.1
1
b)
R^2
130
120
110
100
90
80
70
0.1
1
T*/N
c)

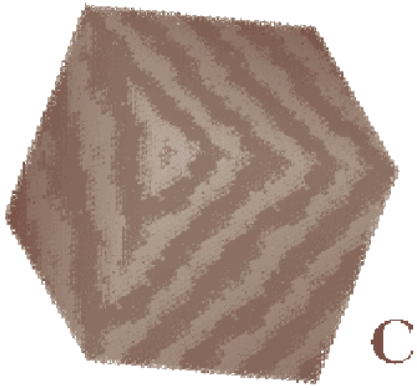
Lamellar nanostructures

T*/N=0.04



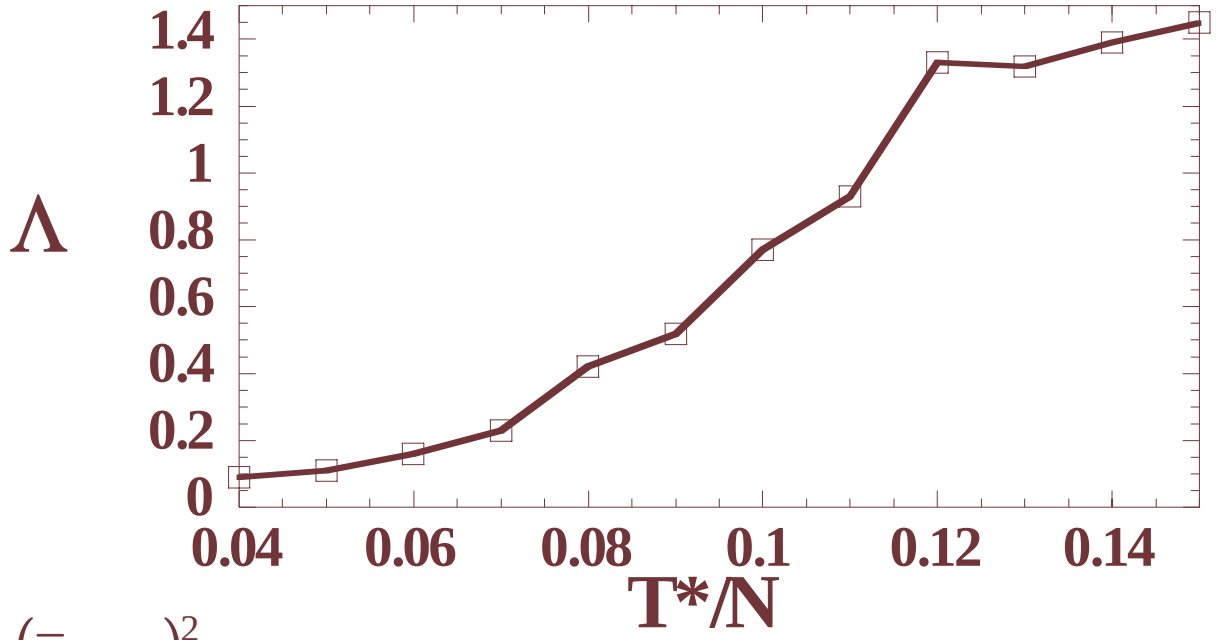
T*/N=0.10

T*/N=0.18



T*/N=0.24

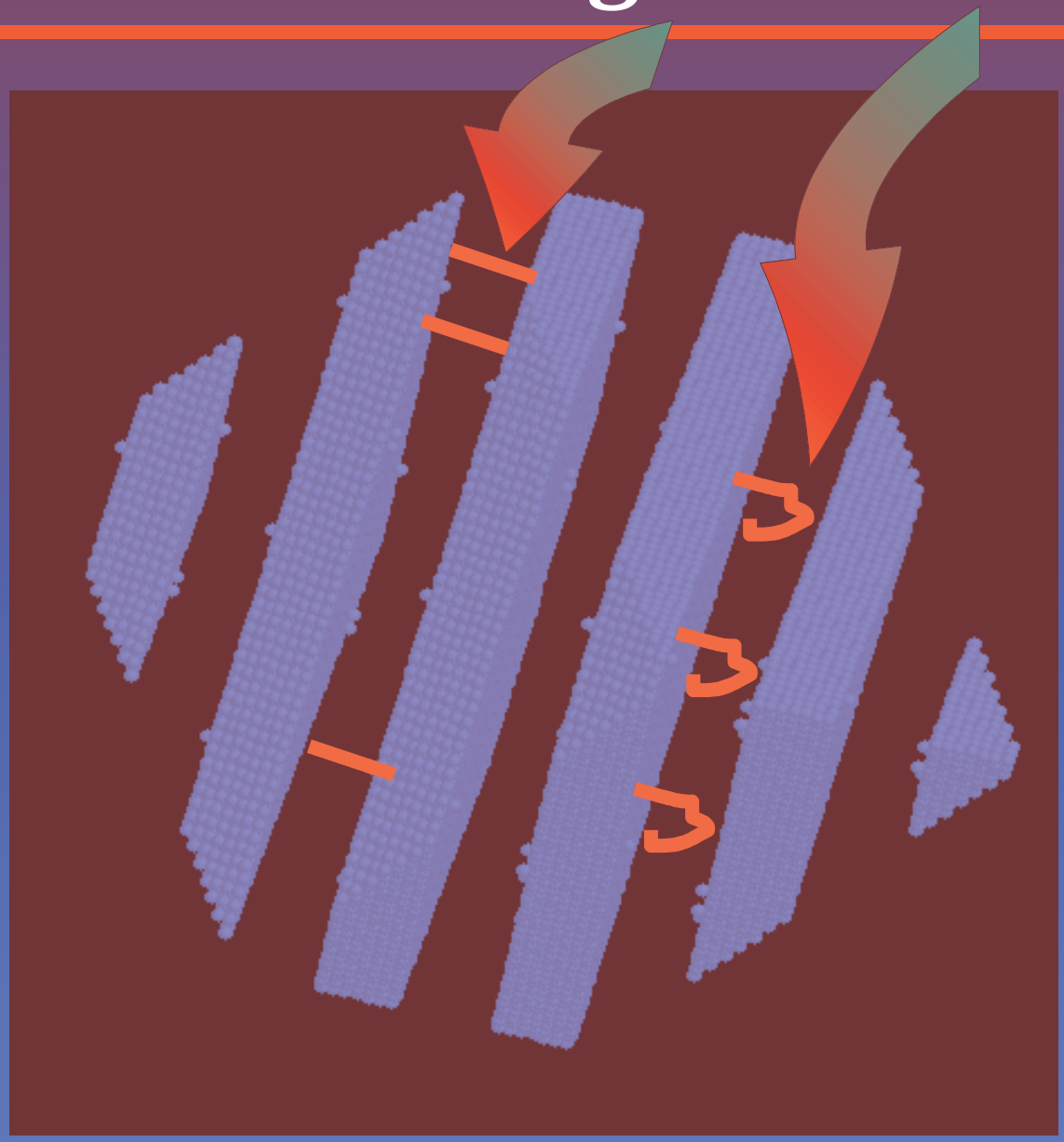
Λ parameter - low-temperature lamellar ordering

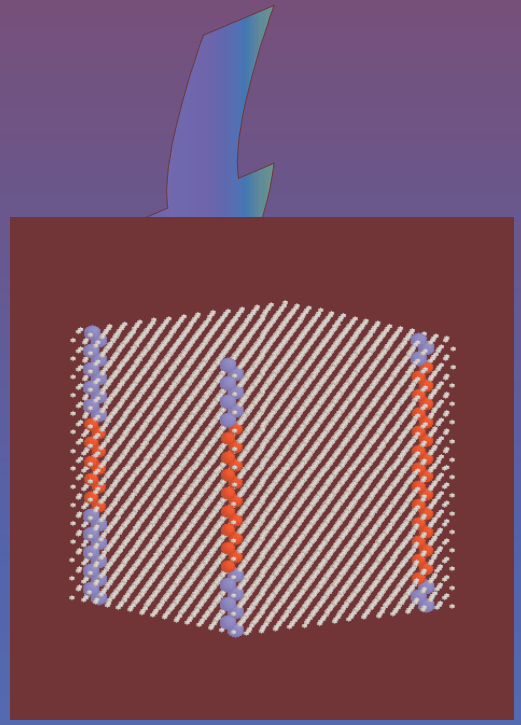


$$\Lambda = \frac{\sum_{i=1}^{M} \left(\bar{r} - r_i\right)^2}{M}$$

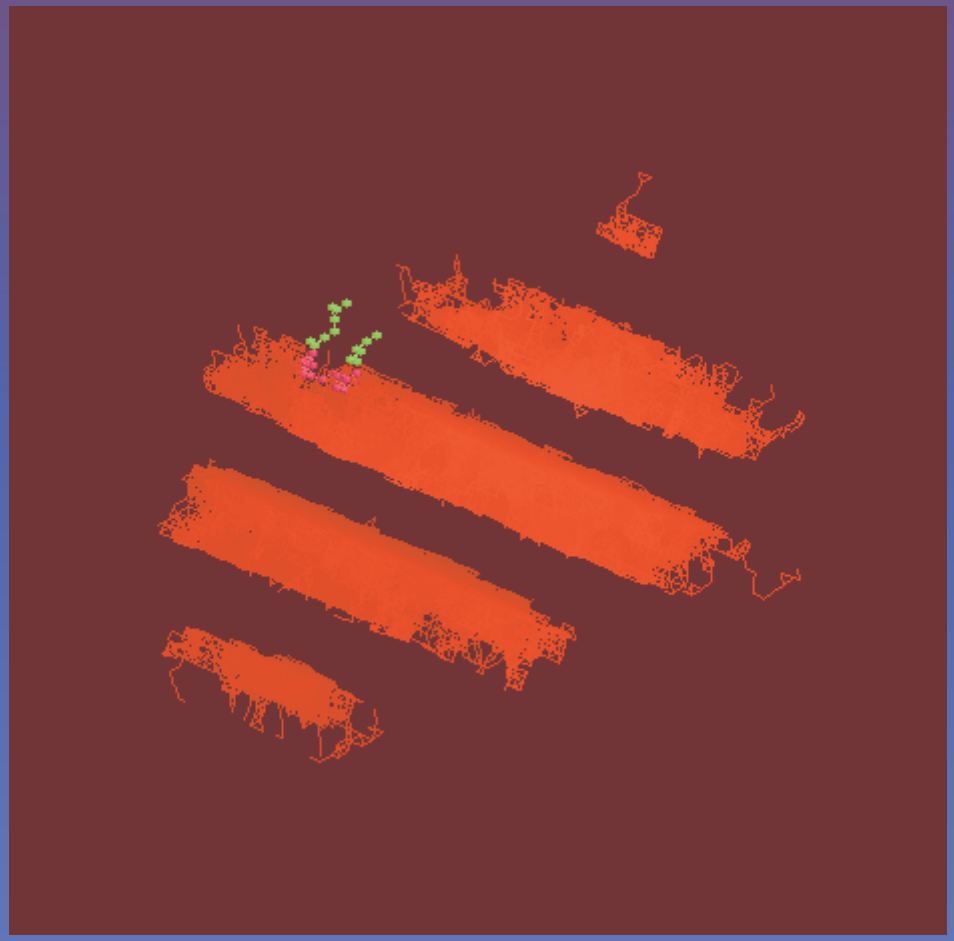
$$r_i = \vec{r}_i \bullet \vec{n}$$

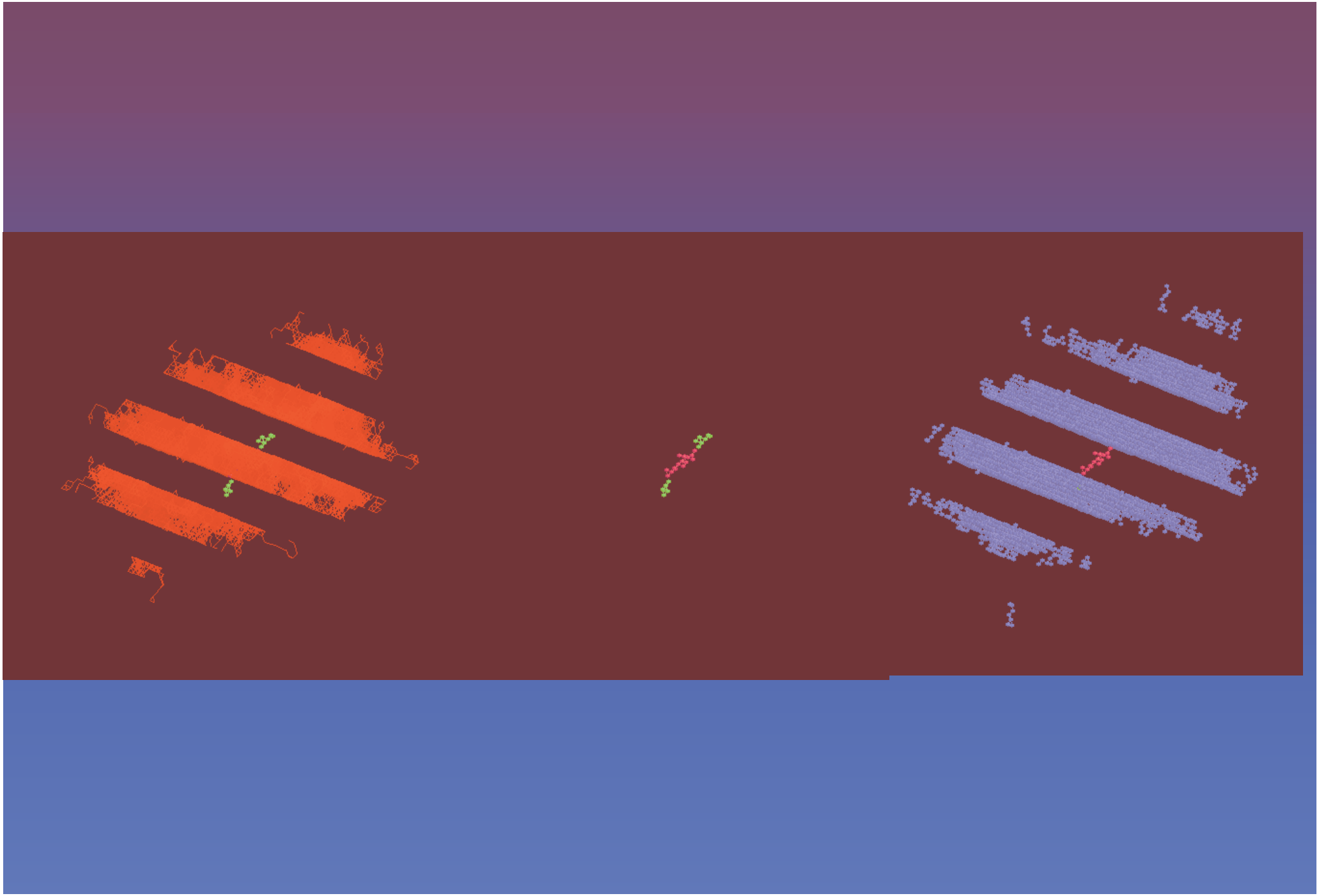
Bridges and Loops





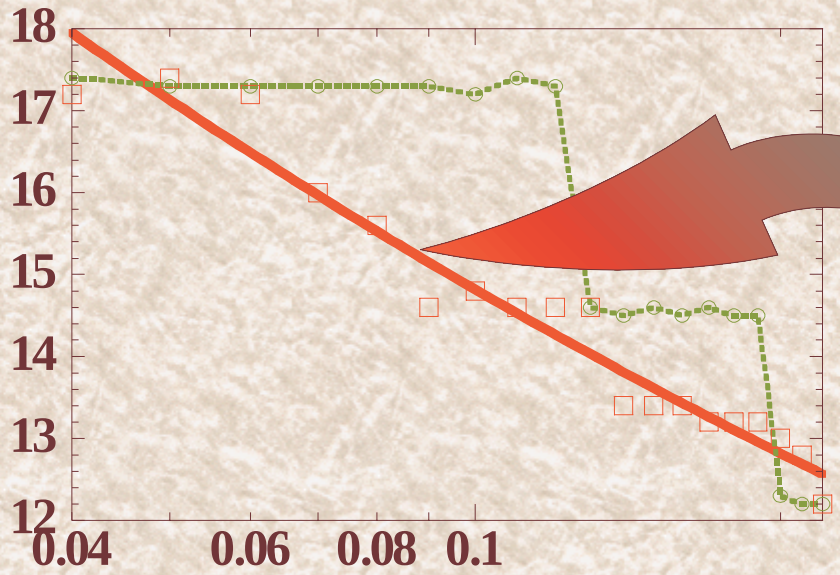
Loop





$D \sim T^{*\mu}$

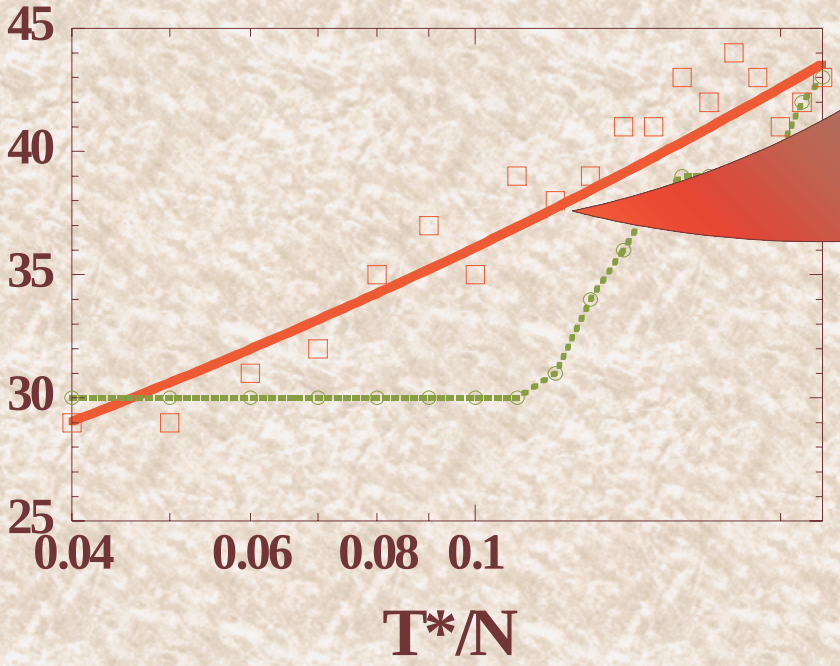
$\mu = -1/6$



$\mu = -0.21$

$\Phi \sim T^{*\tau}$

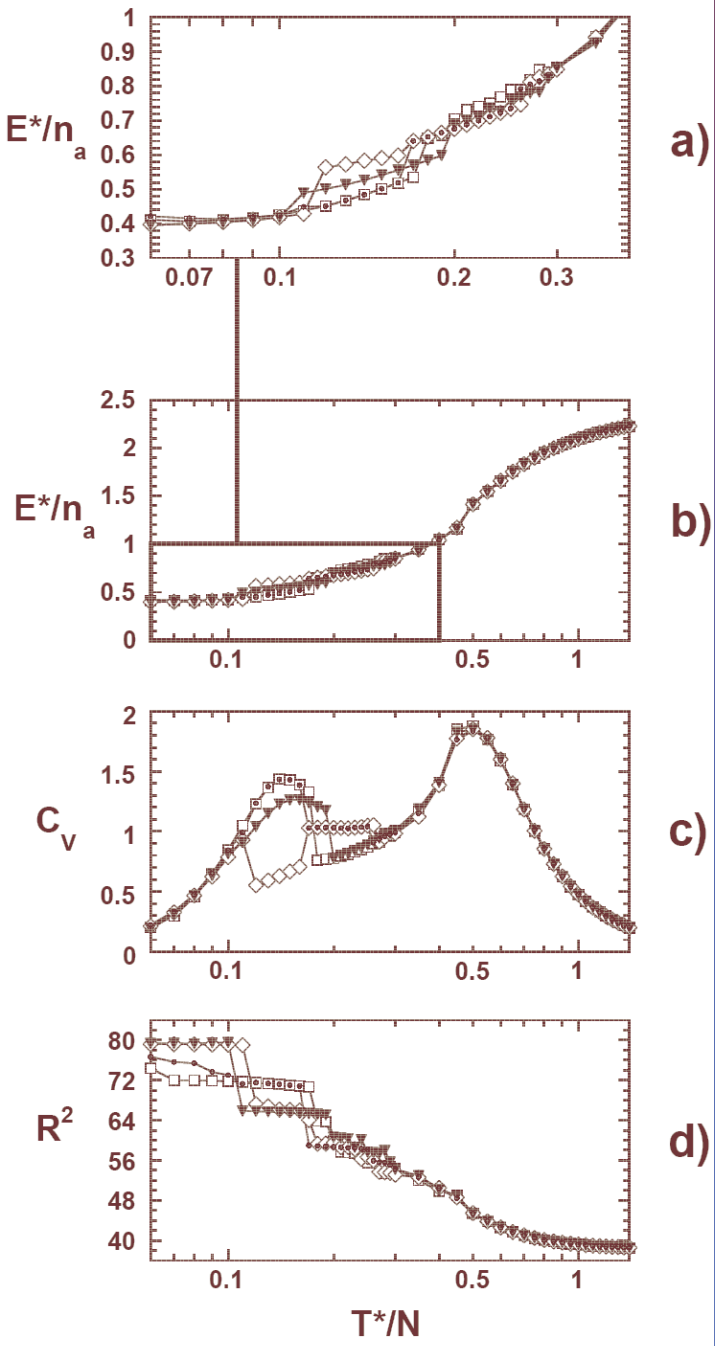
$\tau = 1/9$



$\tau = 0.24$

Diblock melts

8-8 microarchtekture



Box sizes

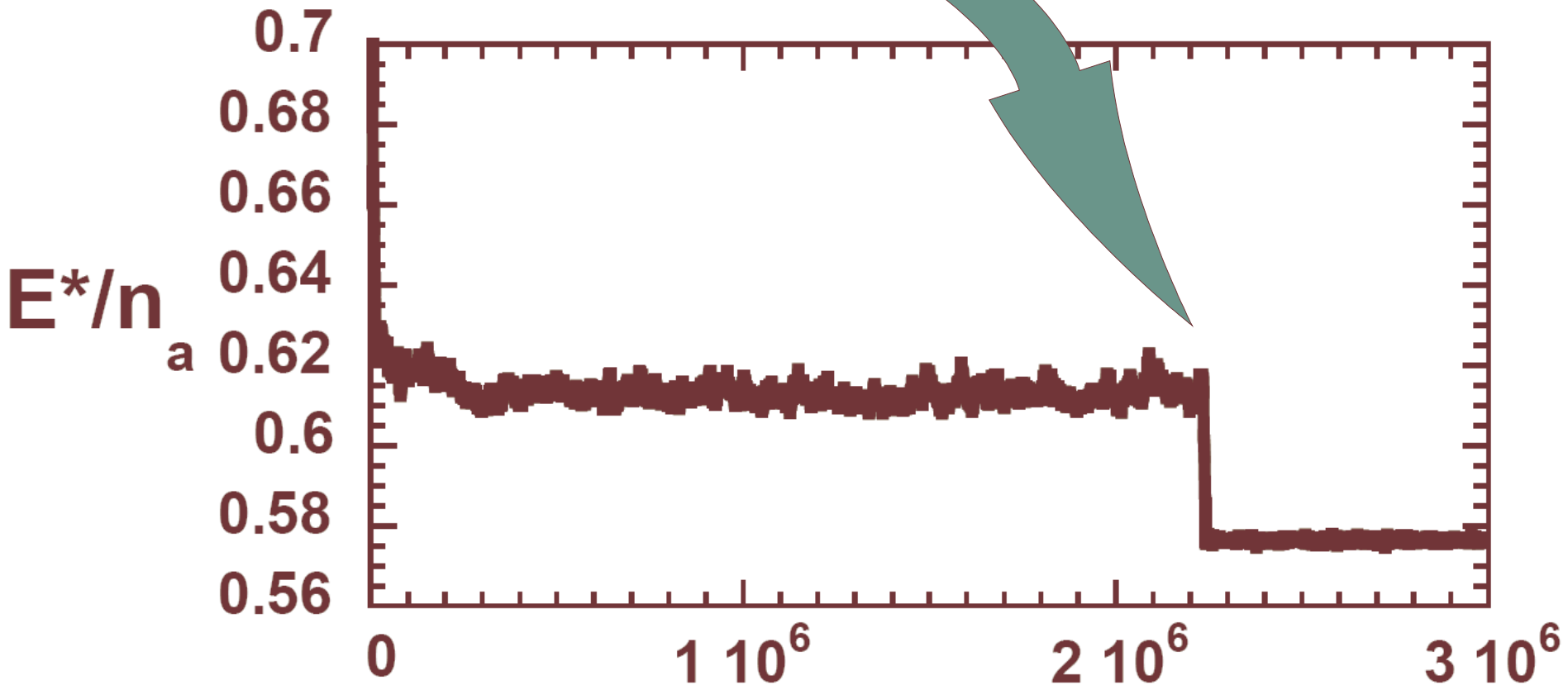
30x32x30 □

40x32x30 "

50x32x30 –

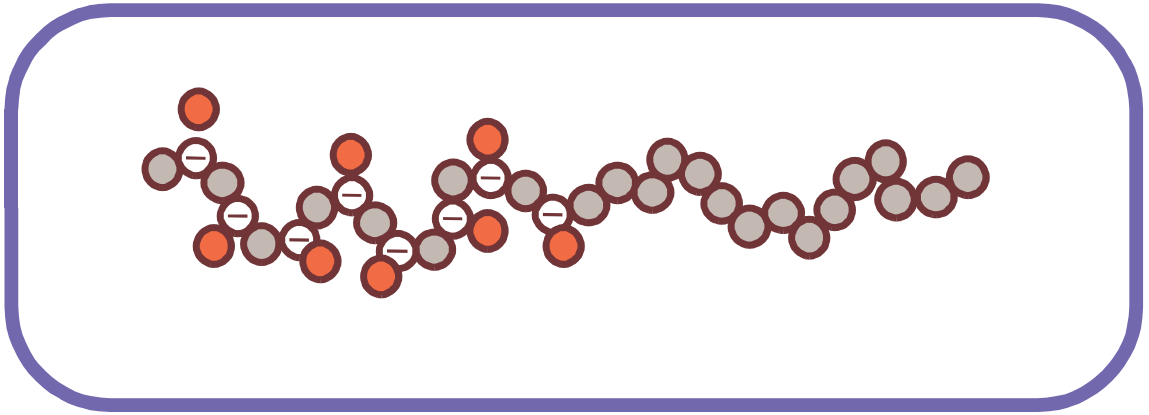
60x32x30 •

Lamellar reorientation



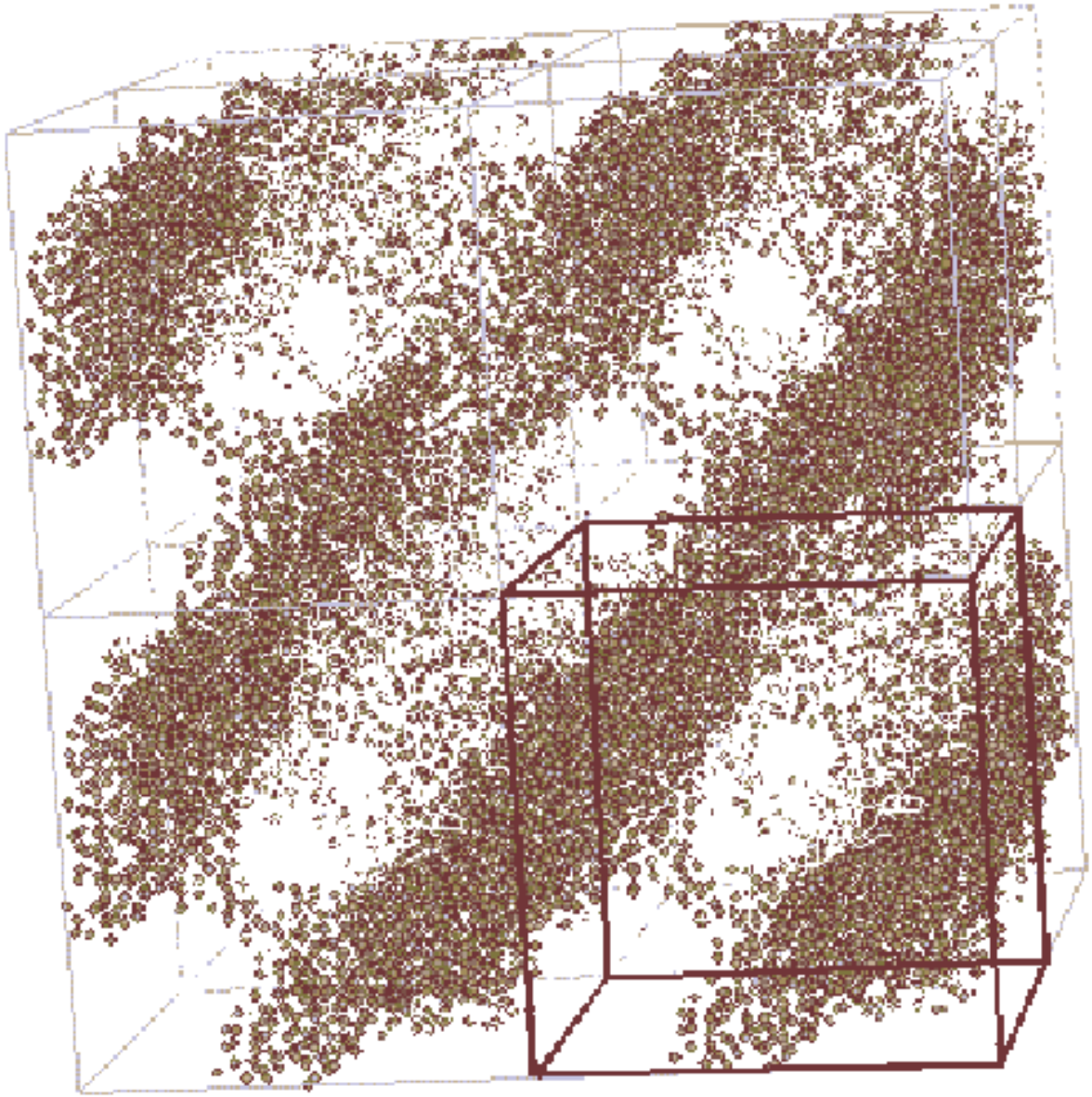
Ionic Block Copolymer

$$\phi_{WCA}(r_{ij}) = 4\varepsilon((\sigma/r_{ij})^{12}-(\sigma/r_{ij})^{6}) + \varepsilon \qquad r_{ij} < 2^{1/6}\sigma$$



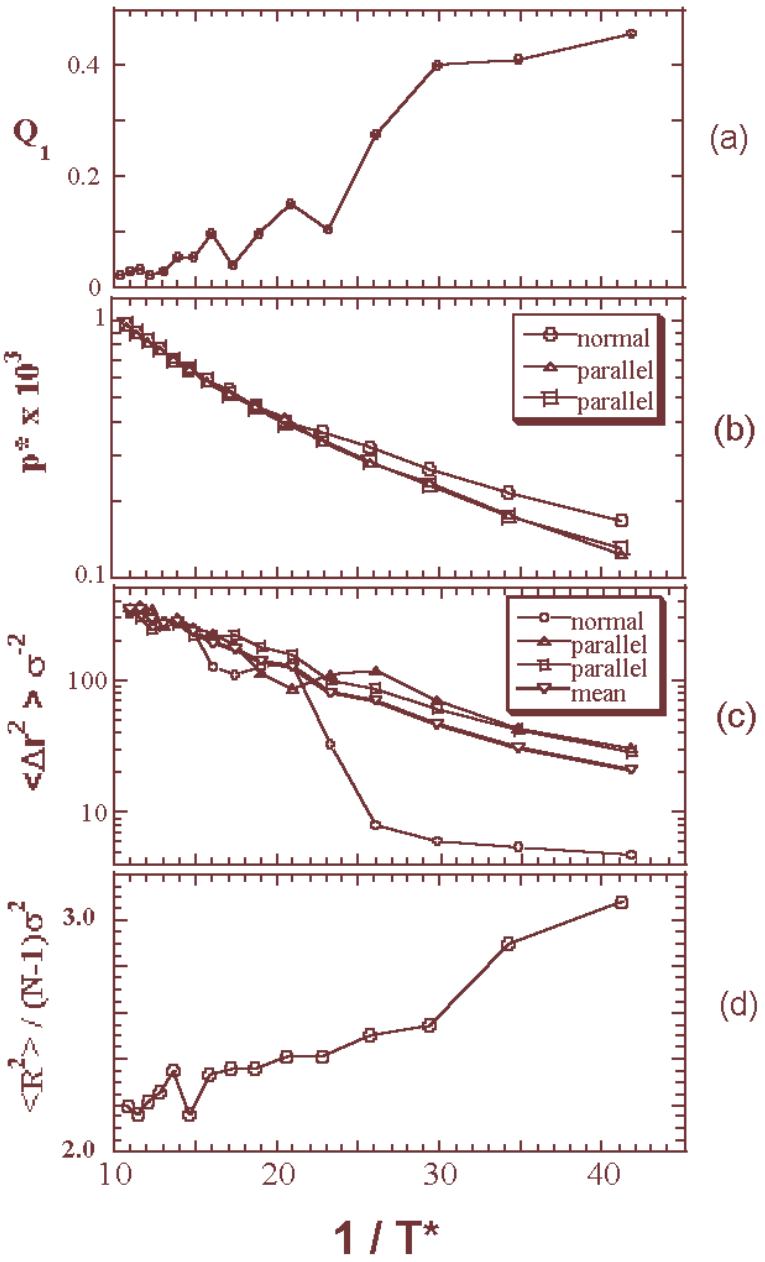
x 160

- **Cations**



$$T^* = kT / E_\sigma$$

$$E_\sigma^{ij} = \left(\frac{q_i \, q_j \, e^2}{4\pi\varepsilon_o \, \varepsilon_R \, \sigma} \right)$$



Conclusion

- MD simulation for triblock and diblock copolymers
- Microphase separation as a function of pressure
- Experimental search for low-temperature ordering effects in block copolymer melts
- New efficient algorithms for copolymer simulations