

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

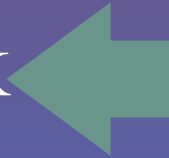
Molecular Dynamics

lattice model



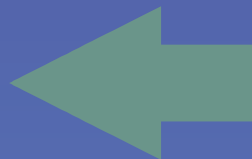
off-lattice model

triblock and diblock
copolymers



ionic diblock copolymers

very short-range
potential

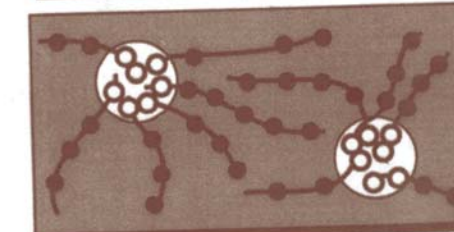
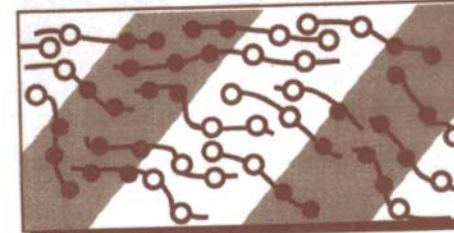
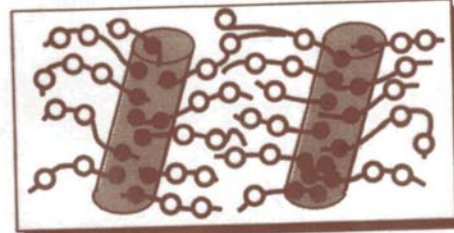
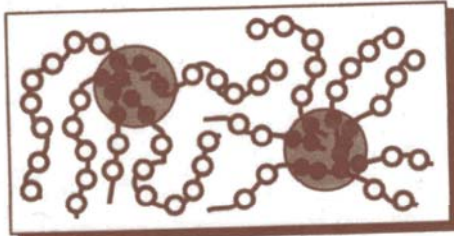
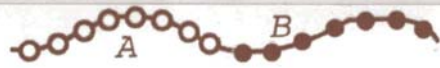


long-range electrostatic
potential

more coarse-grained



less coarse-grained



Spheres of B in A

Cylinders of B in A

Layers

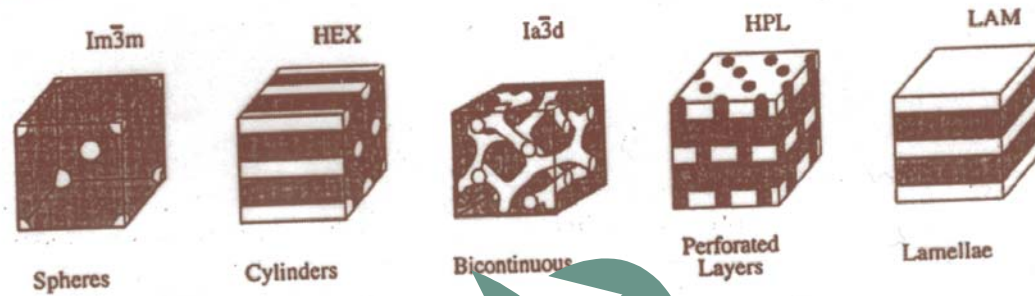
Cylinders of A in B

Spheres of A in B

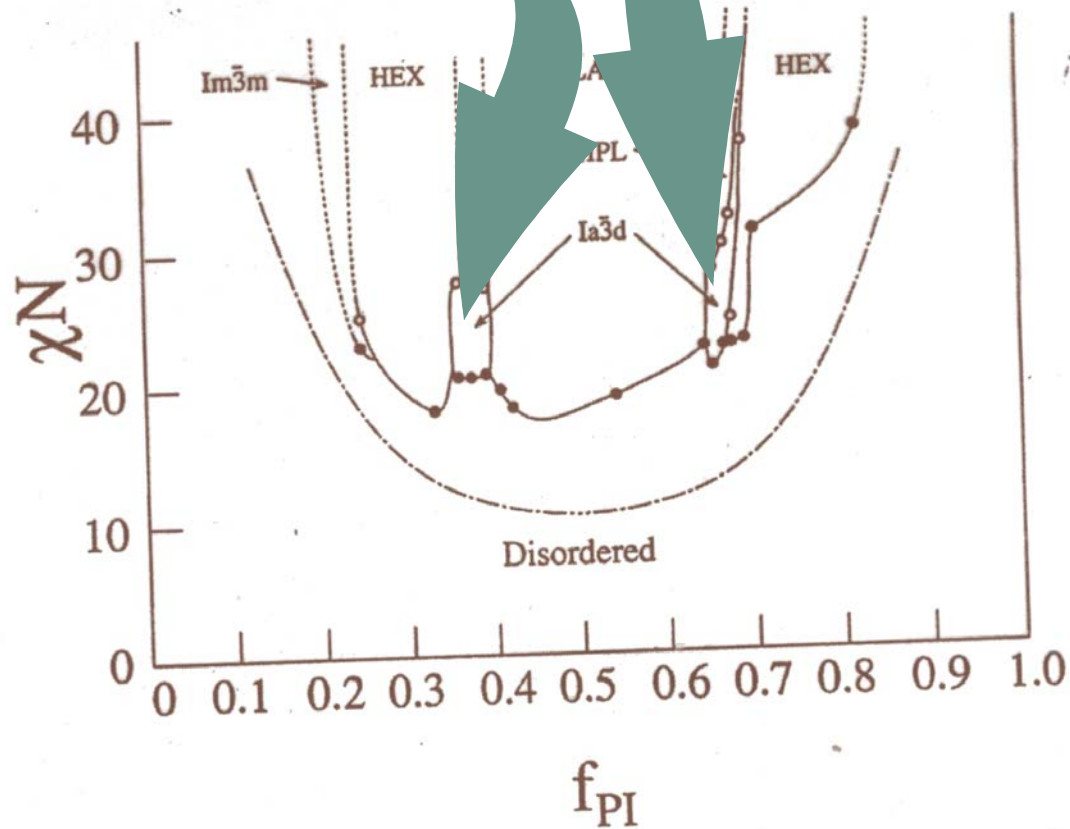
Diblock copolymer phase diagram

Macromolecules, Vol. 28, No. 26, 1995

8804 Khandpur et al.



$\chi \sim \chi$



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

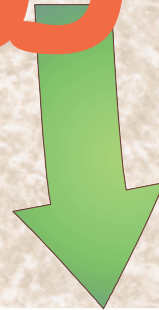
Applications of Block Copolymers

- “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

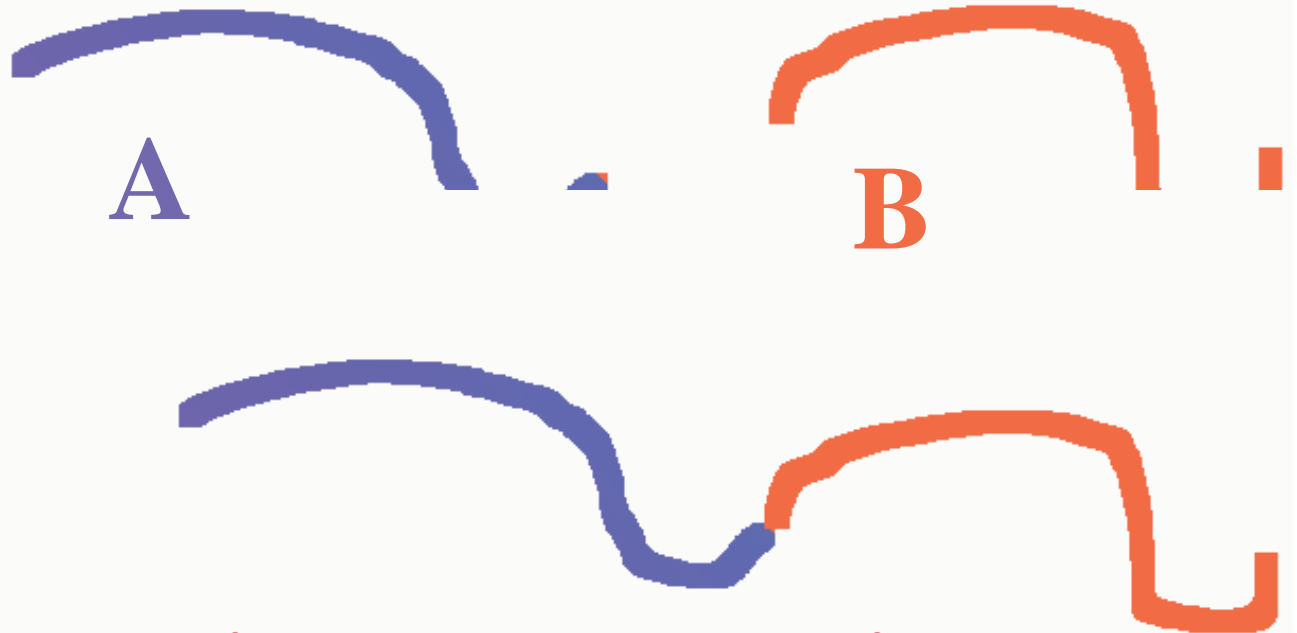


$$f_m = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B$$

$$\phi_A + \phi_B = 1$$

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

$$\chi = \frac{z}{2kT} [\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}]$$

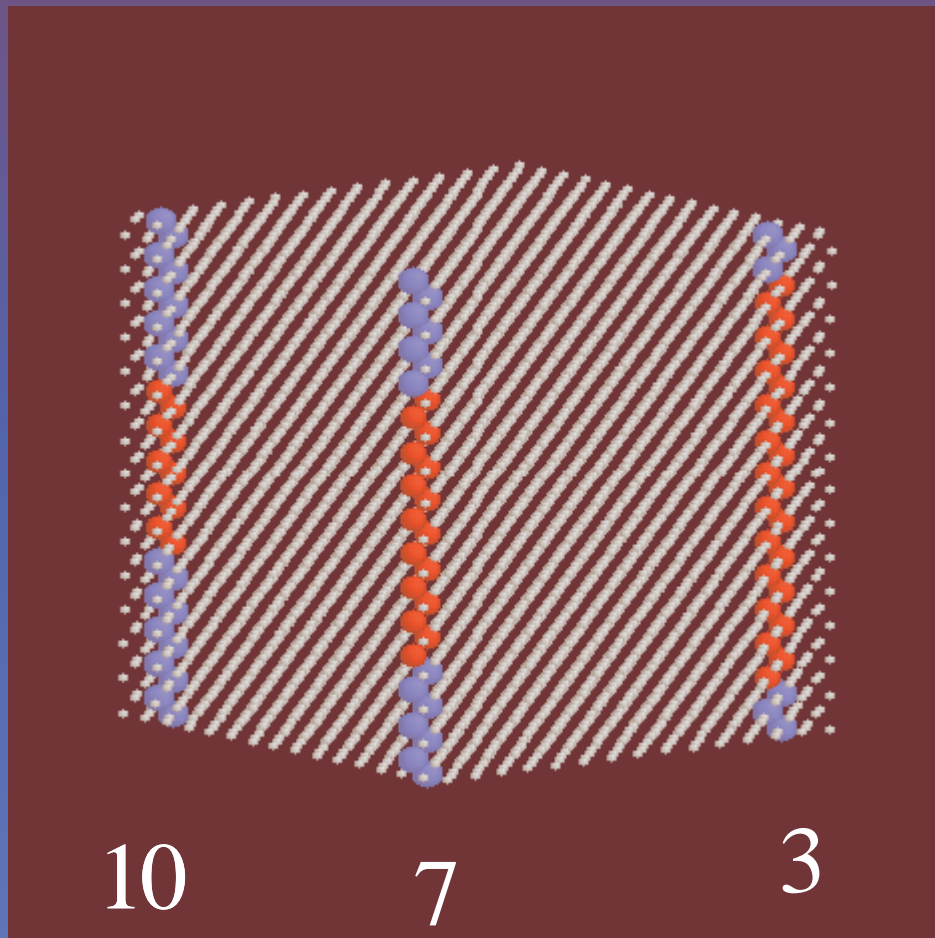


Macrophase and microphase separation

Reduced Temperature, T^*/N

- ϵ - interaction energy between A and B
- $T^* = kT/\epsilon$
- $\chi = (z - 2)/T^*$
- 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

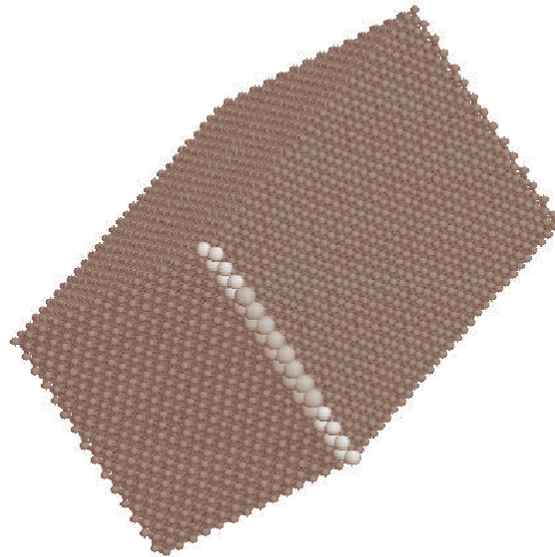
■ 3-24-3

■ 30 x 30 x 30

■ 60 x 30 x 30

■ 60 x 60 x 60

Simulation box, 60x30x30



Lamellar nanostructures

$T^*/N=0.04$



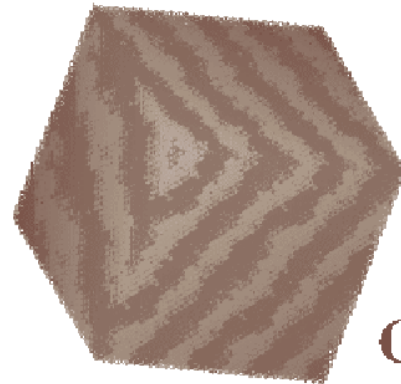
a)

$T^*/N=0.10$



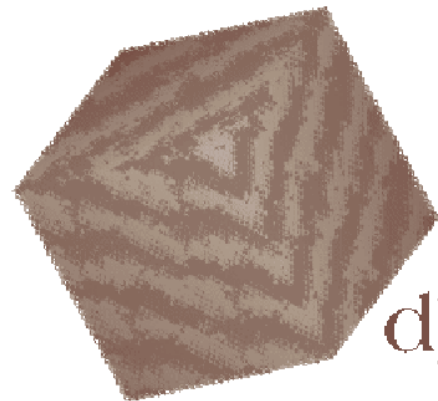
b)

$T^*/N=0.18$



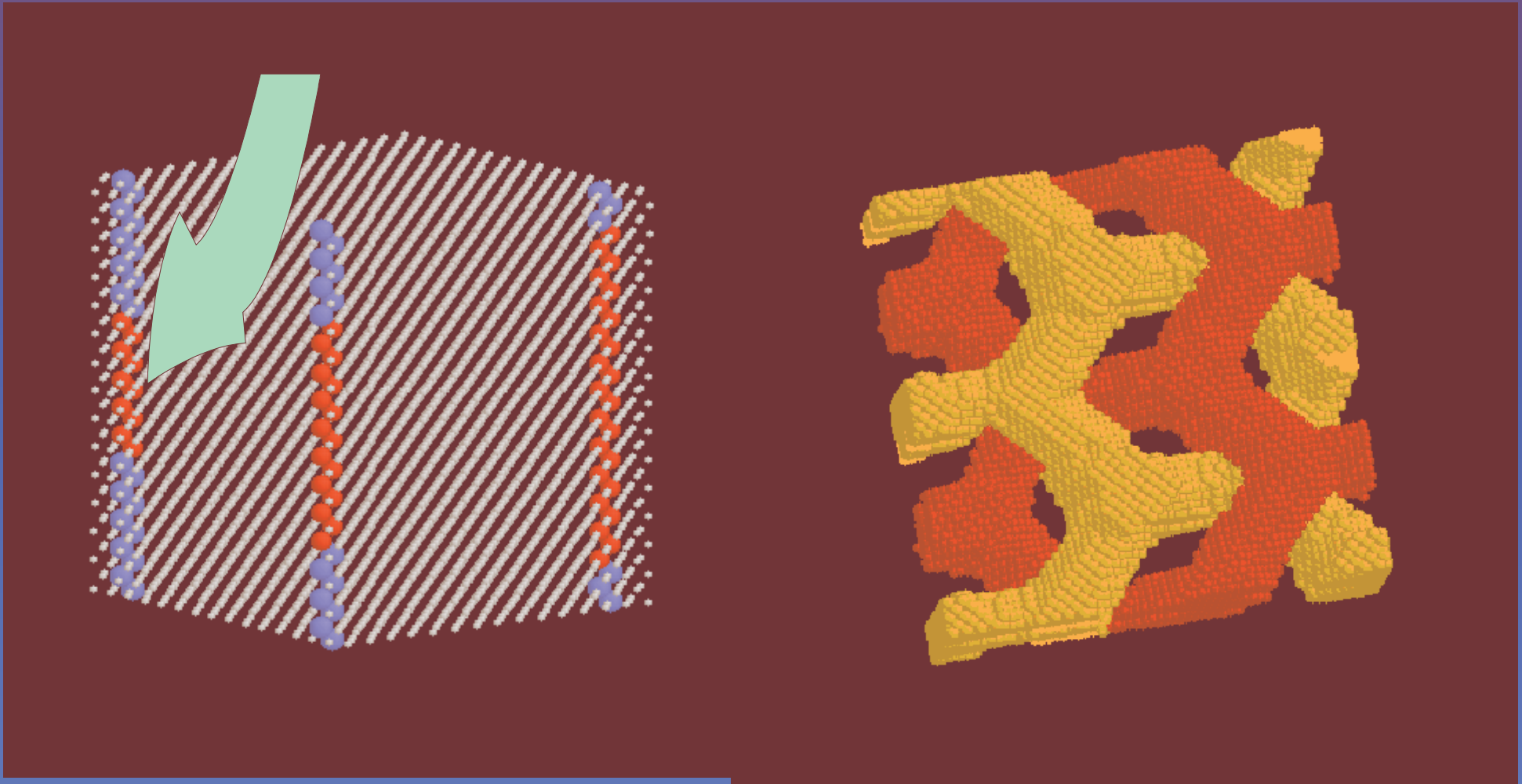
c)

$T^*/N=0.24$

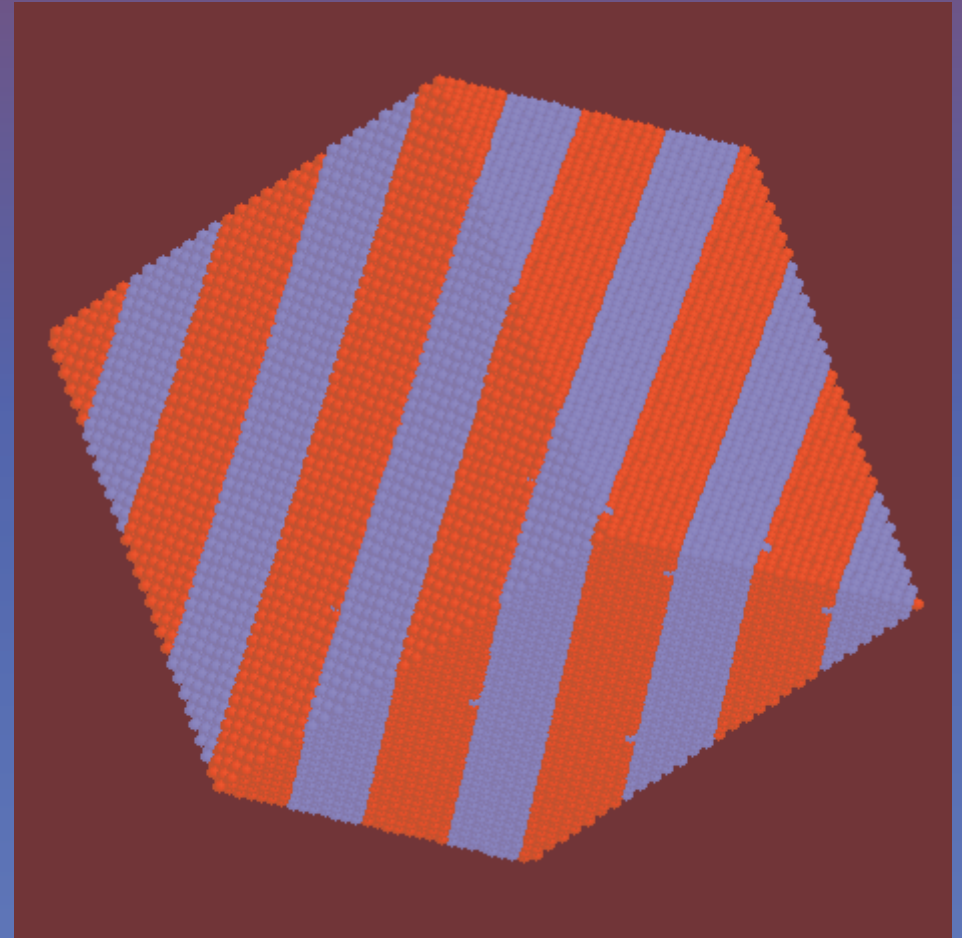
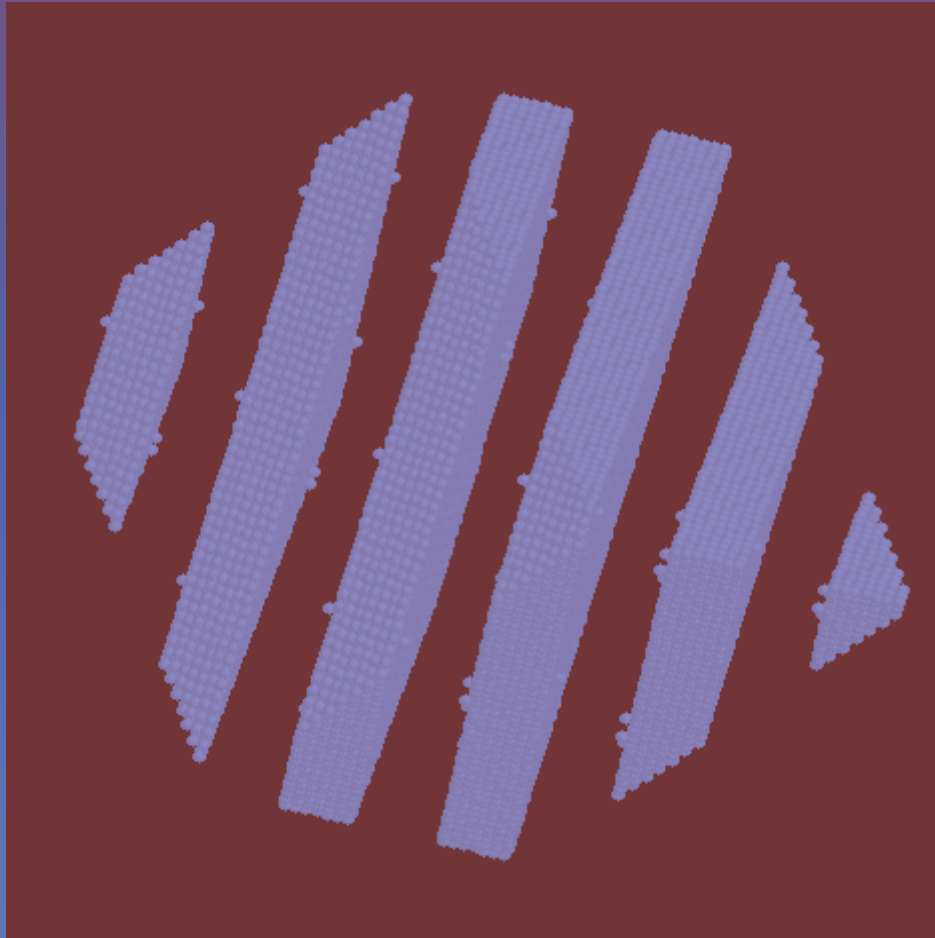


d)

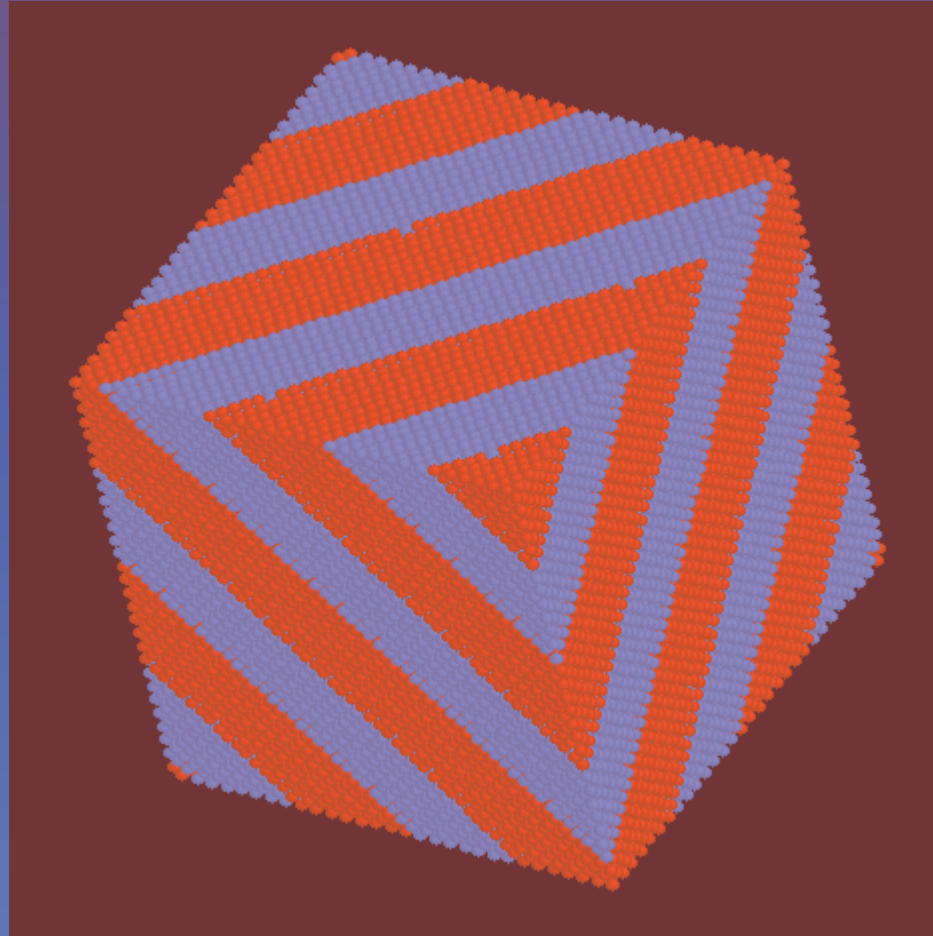
Bicontinuous nanostructure for the 10-10-10 microarchitecture, $T^*/N=0.04$



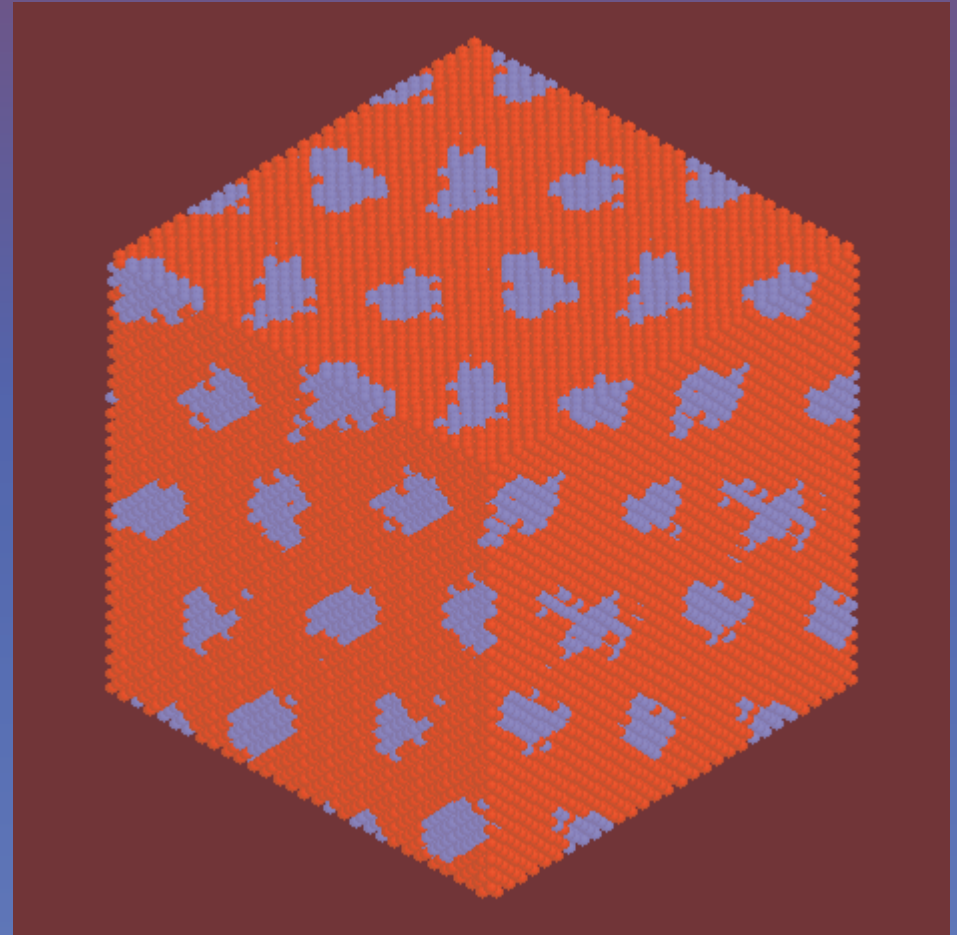
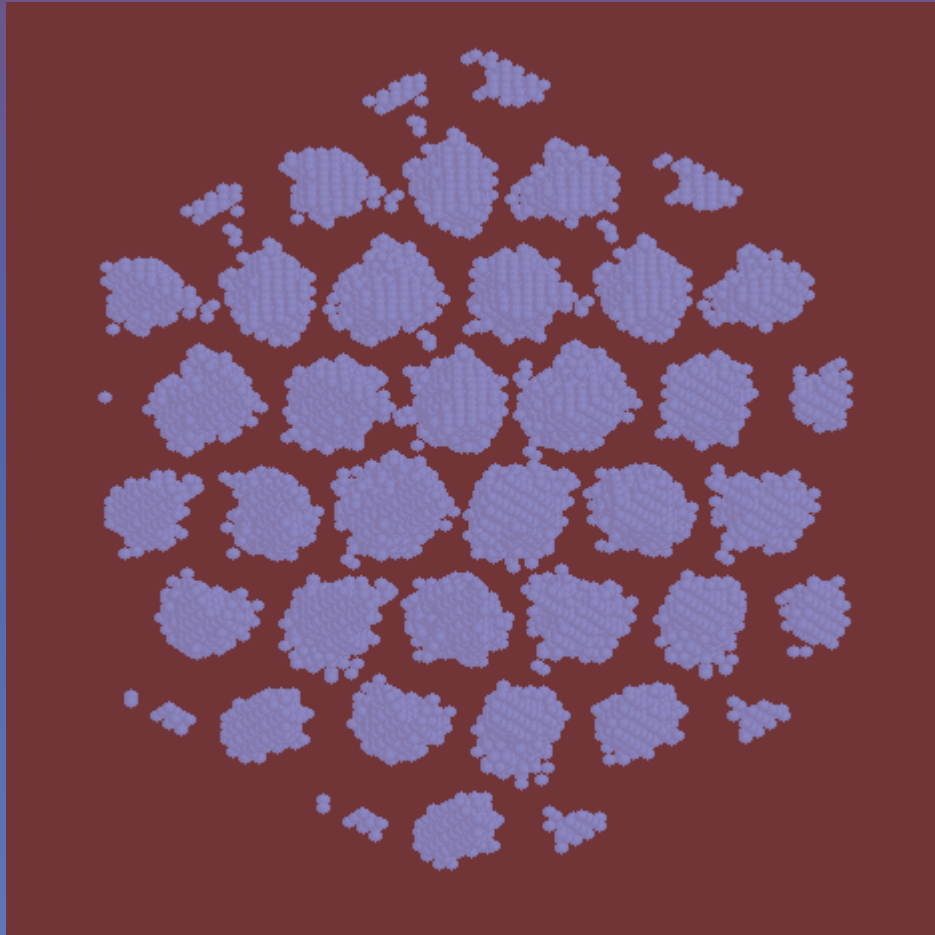
7-16-7 Microarchitecture , $T^*/N=0.04$



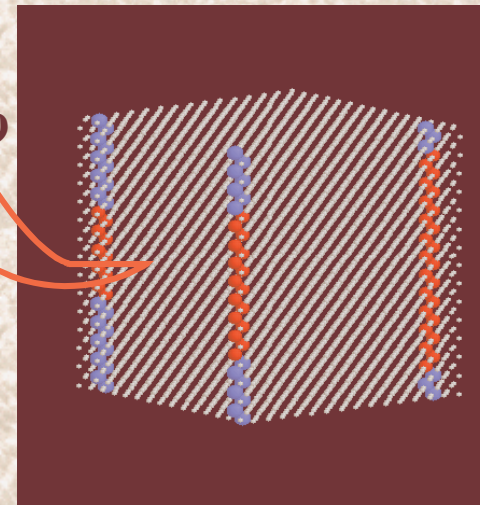
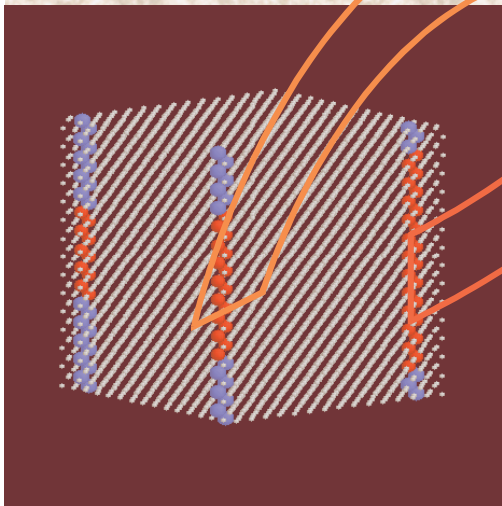
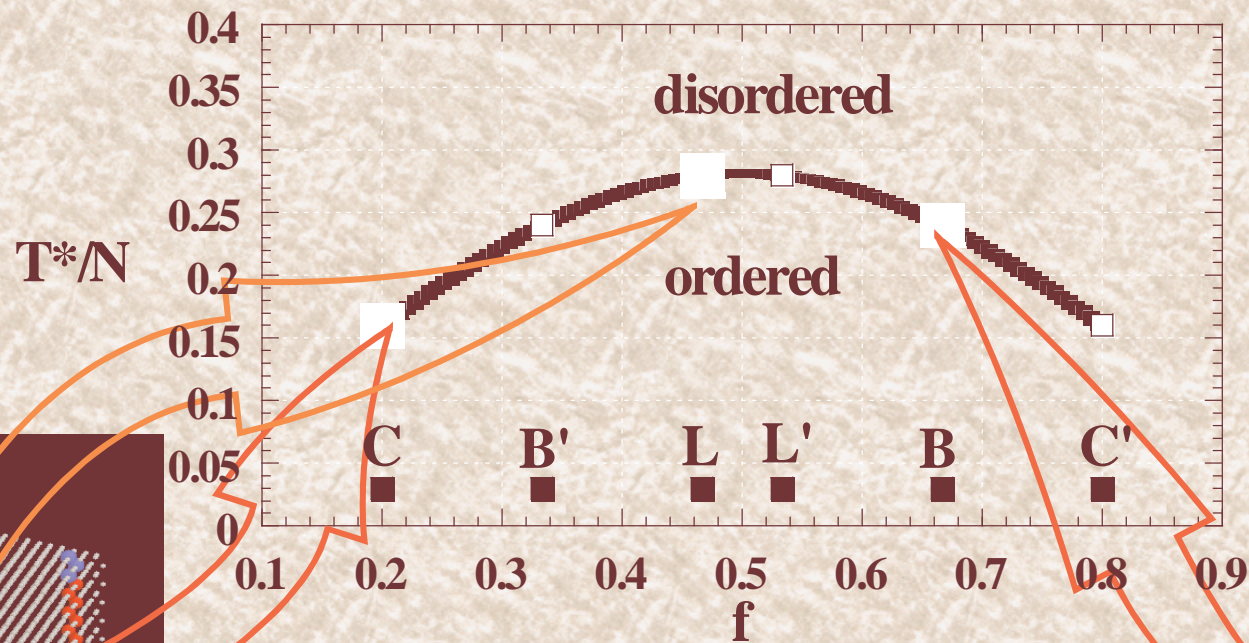
7-16-7 Microarchitecture, $T^*/N=0.04$



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



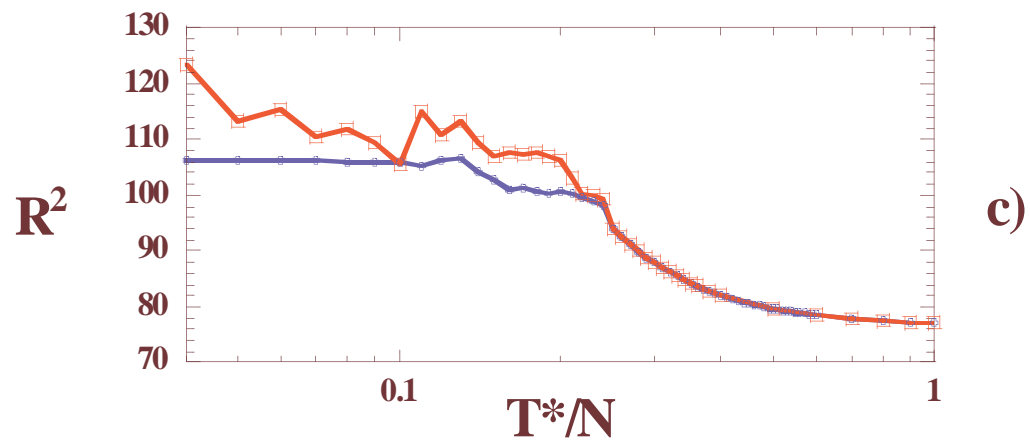
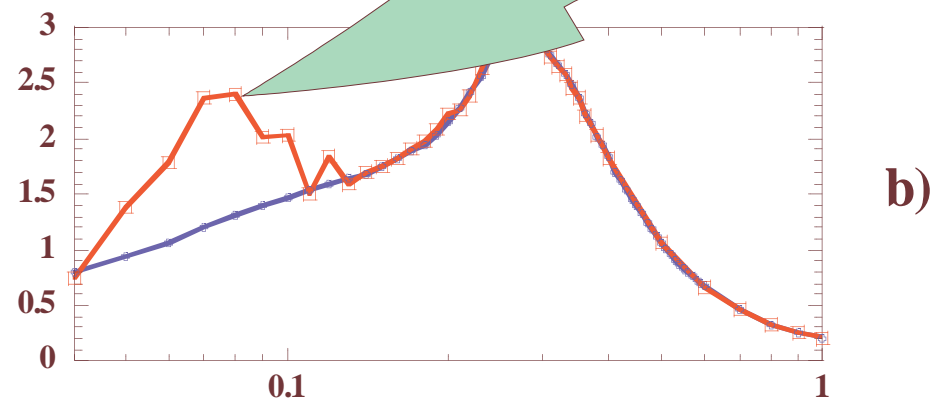
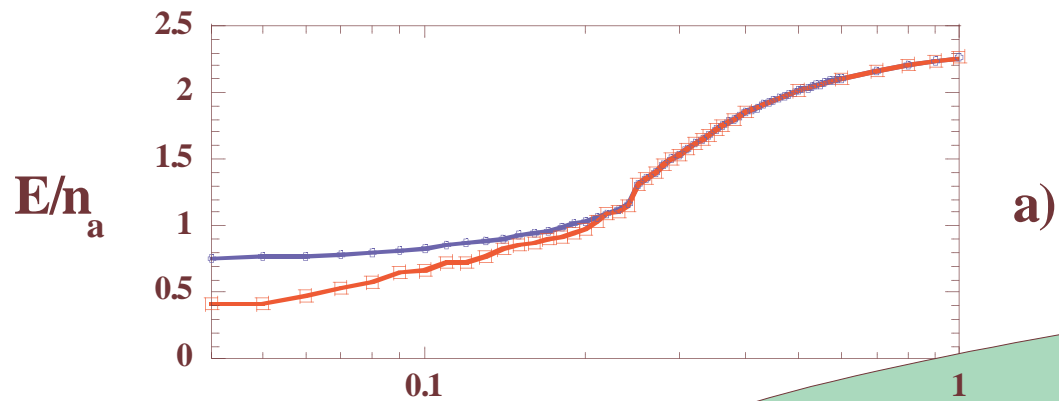
Phase diagram of the symmetric triblock copolymer melt

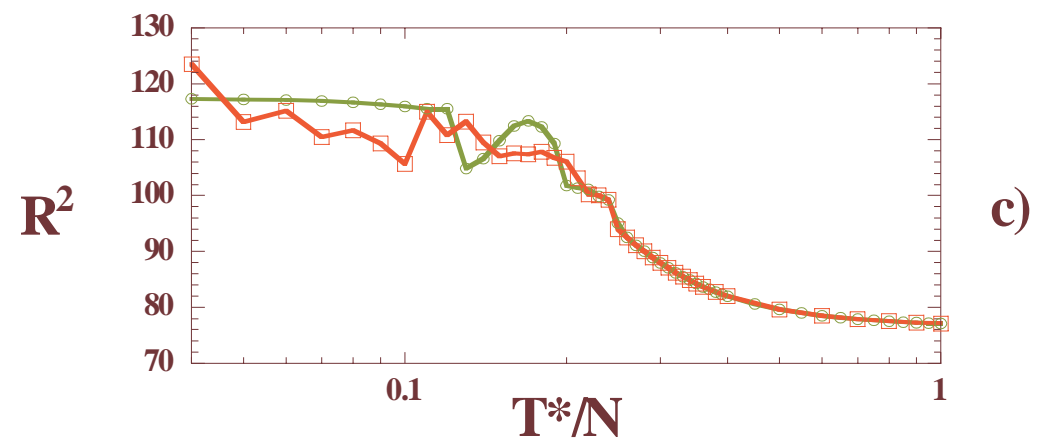
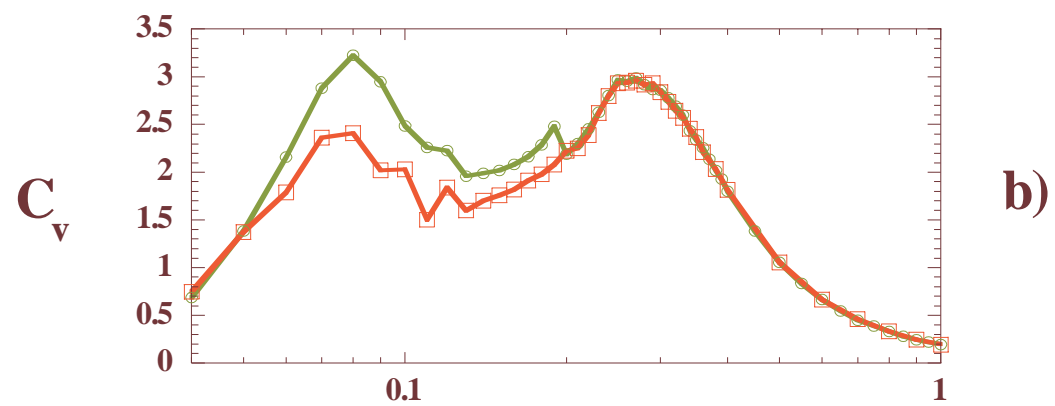
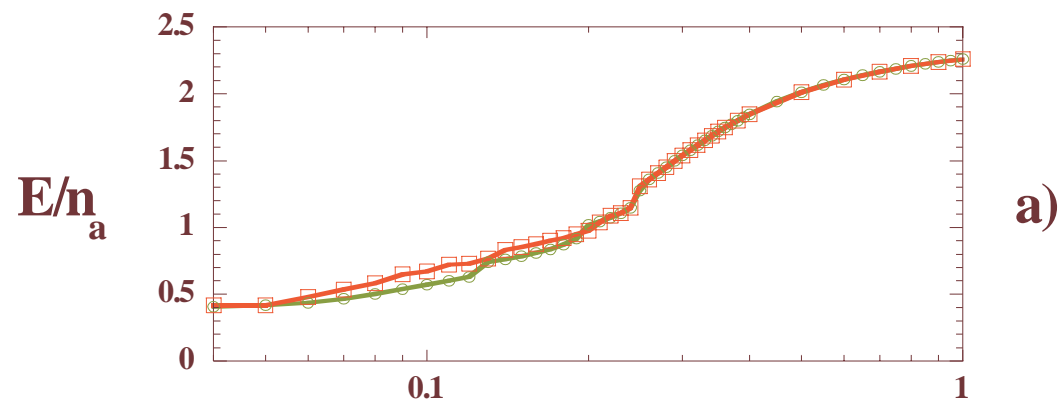


Quenching

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

Slow cooling





Lamellar nanostructures

$T^*/N=0.04$



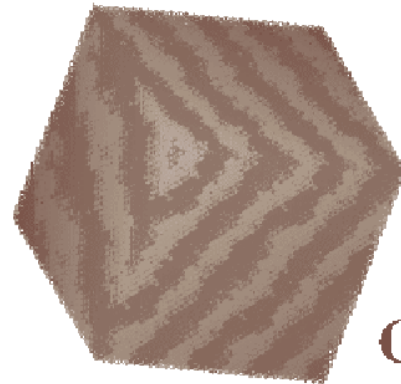
a)

$T^*/N=0.10$



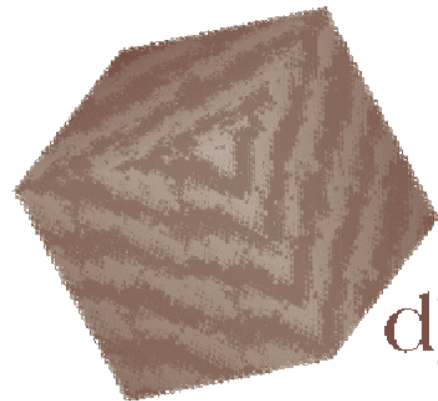
b)

$T^*/N=0.18$



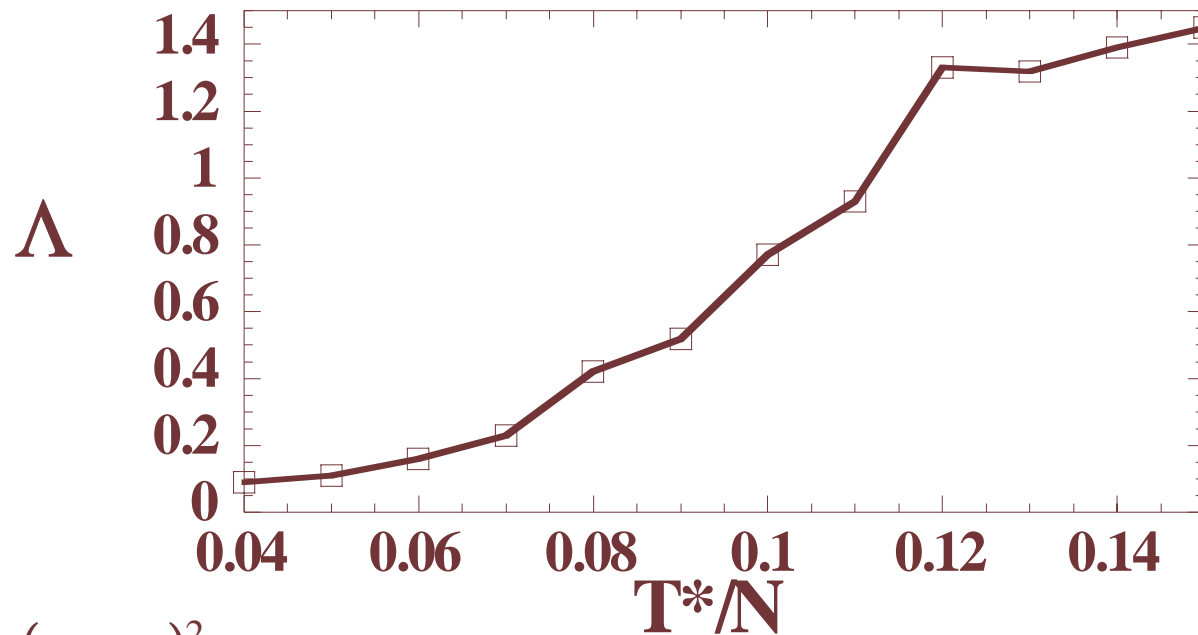
c)

$T^*/N=0.24$



d)

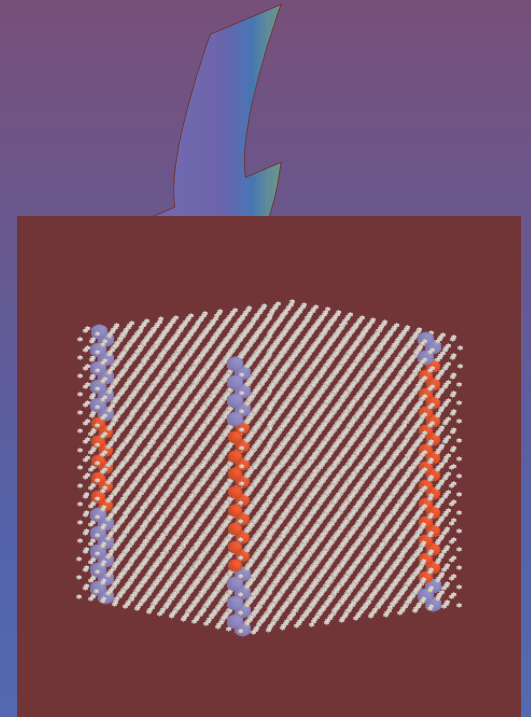
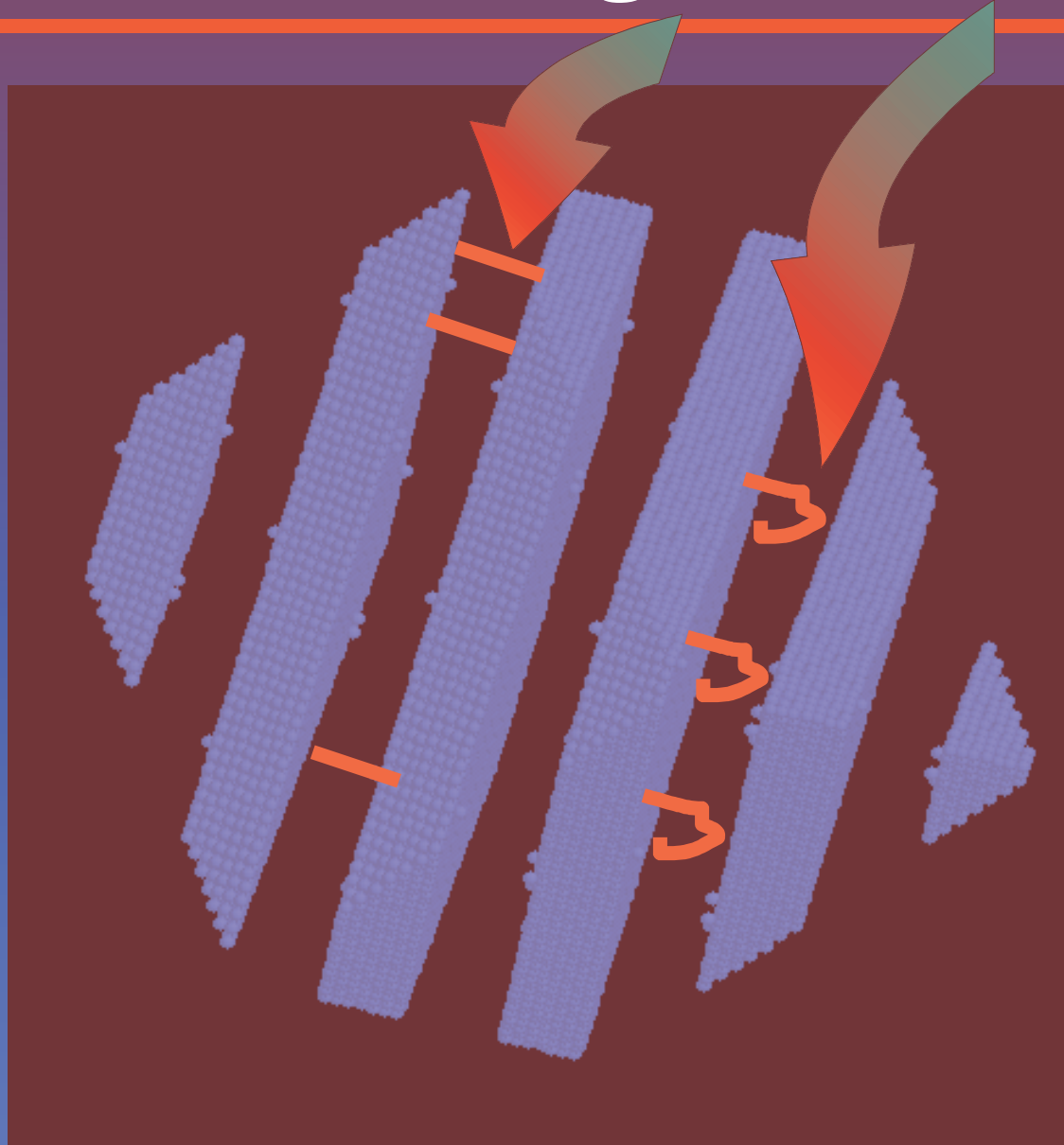
Λ parameter - low-temperature lamellar ordering



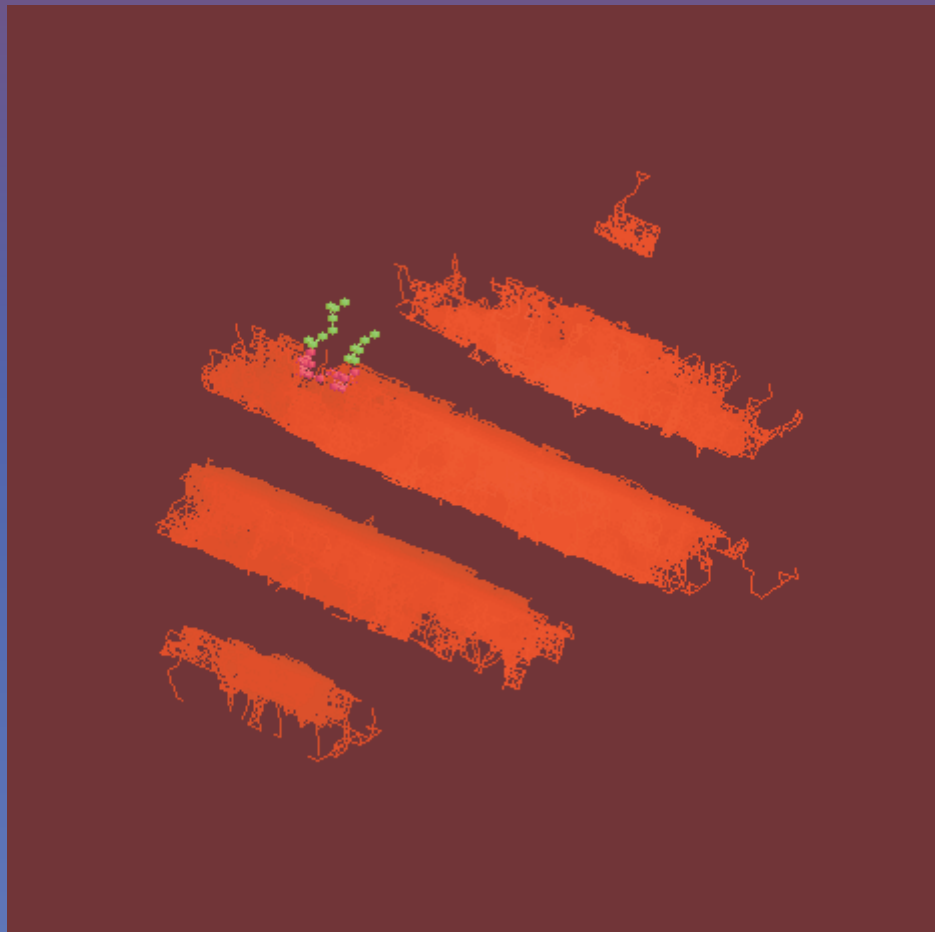
$$\Lambda = \frac{\sum_{i=1}^M (\bar{r} - r_i)^2}{M}$$

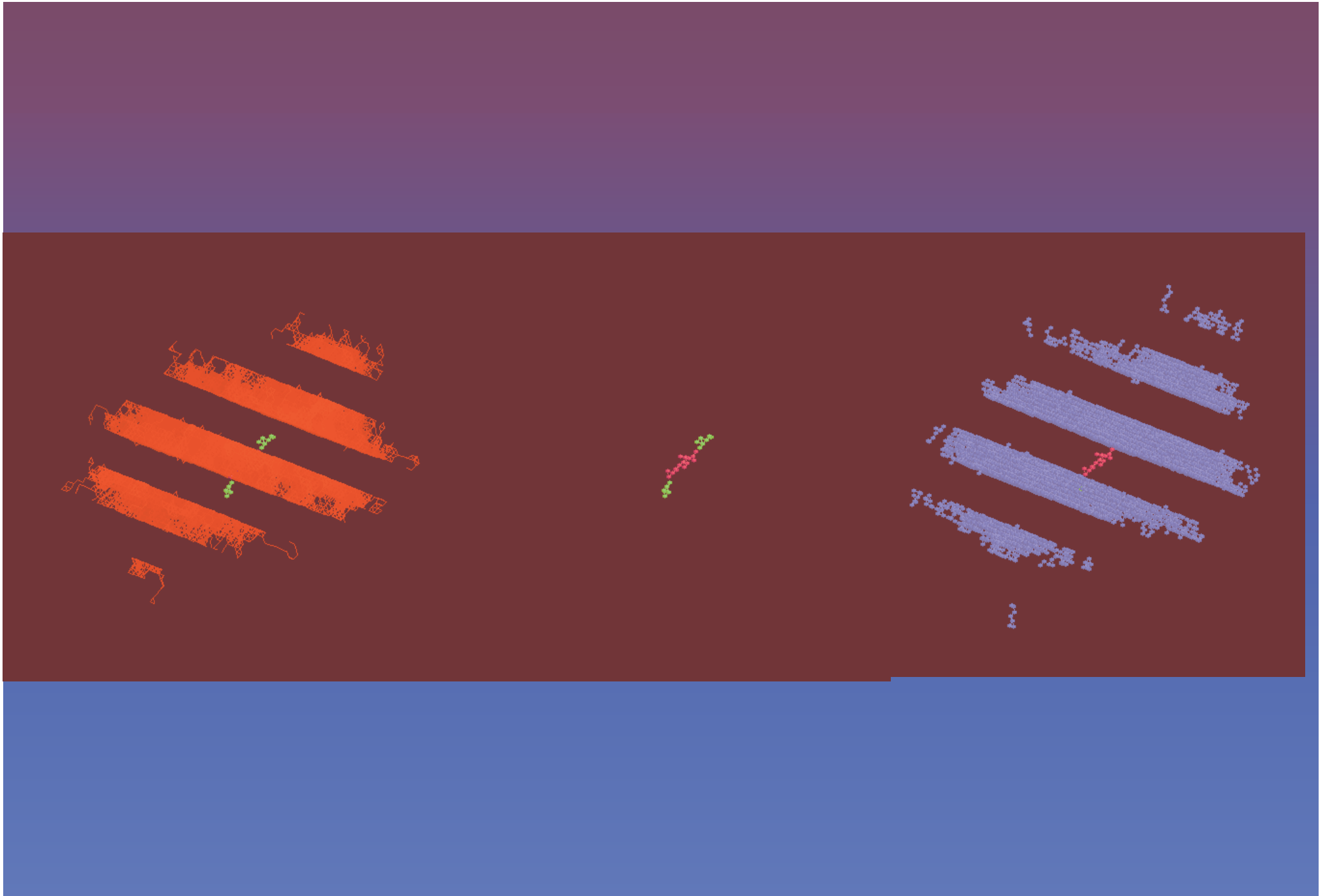
$$r_i = \vec{r}_i \bullet \vec{n}$$

Bridges and Loops



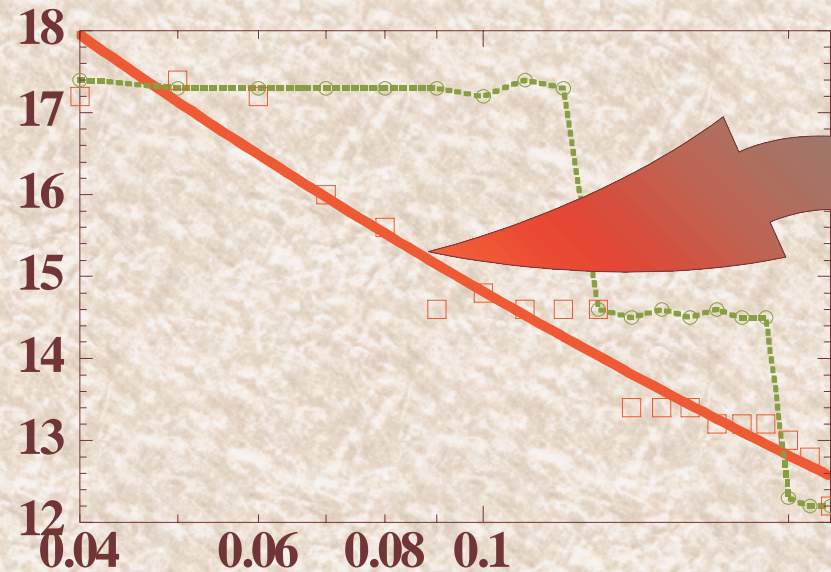
Loop





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

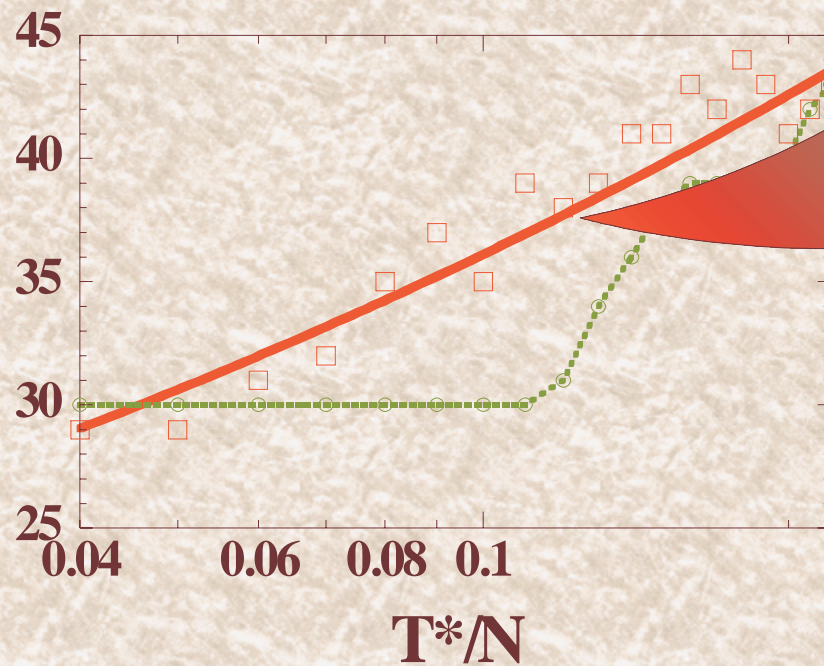
$\mu = -1/6$



$$\mu = -0.21$$

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

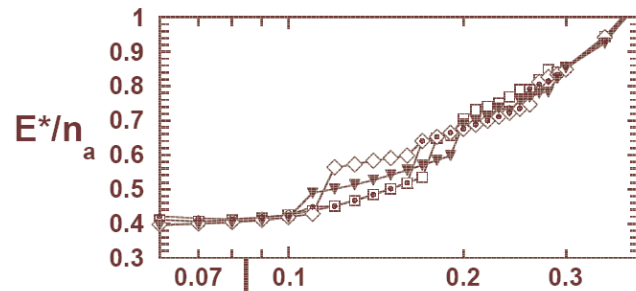
$\tau = 1/9$



$$\tau = 0.24$$

Diblock melts

8-8 microarchtekture



a)

Box sizes

30x32x30



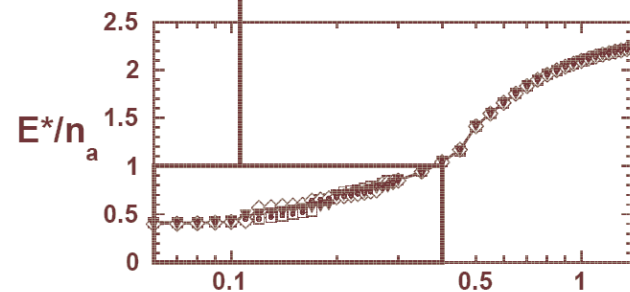
40x32x30



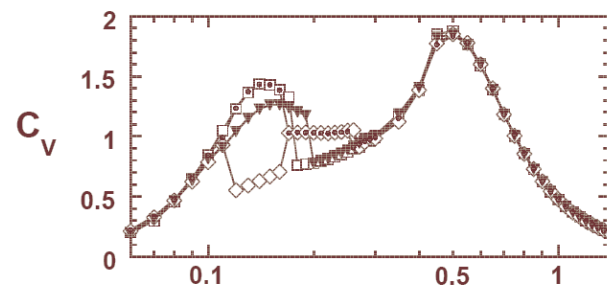
50x32x30



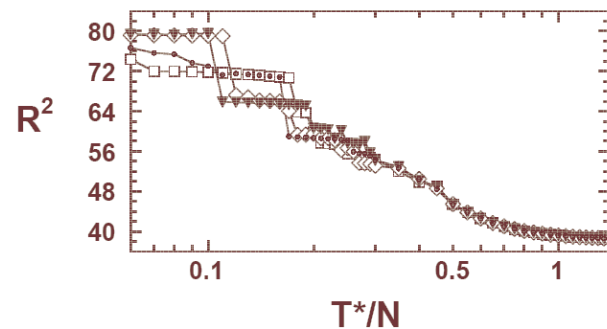
60x32x30



b)

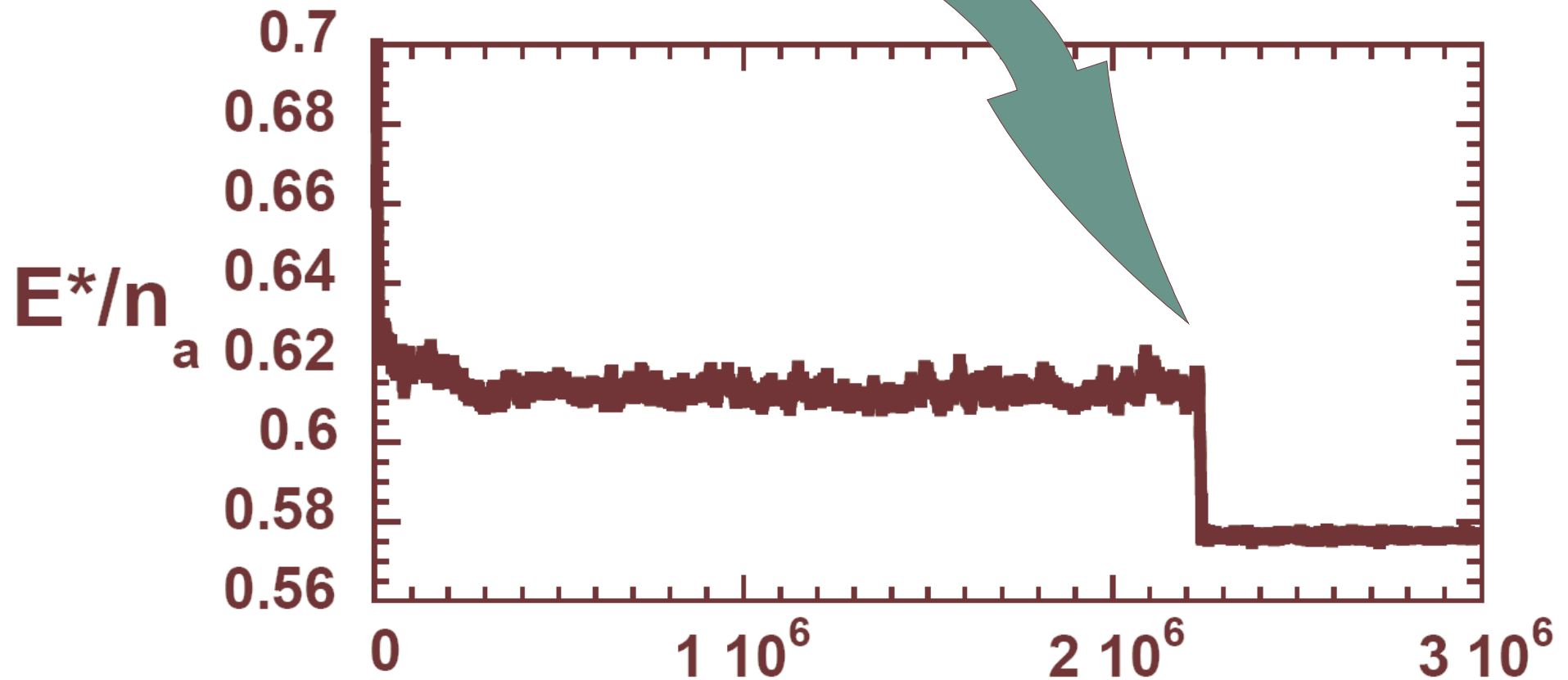


c)



d)

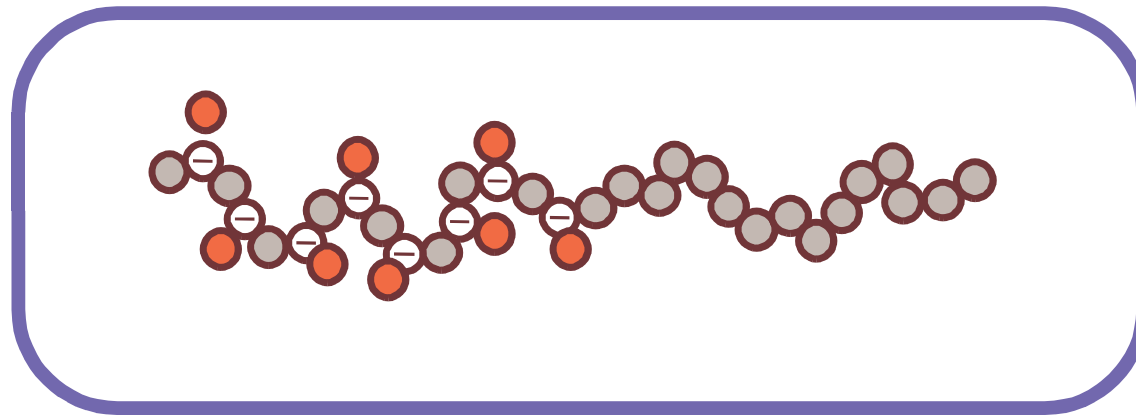
Lamellar reorientation



Monte Carlo steps

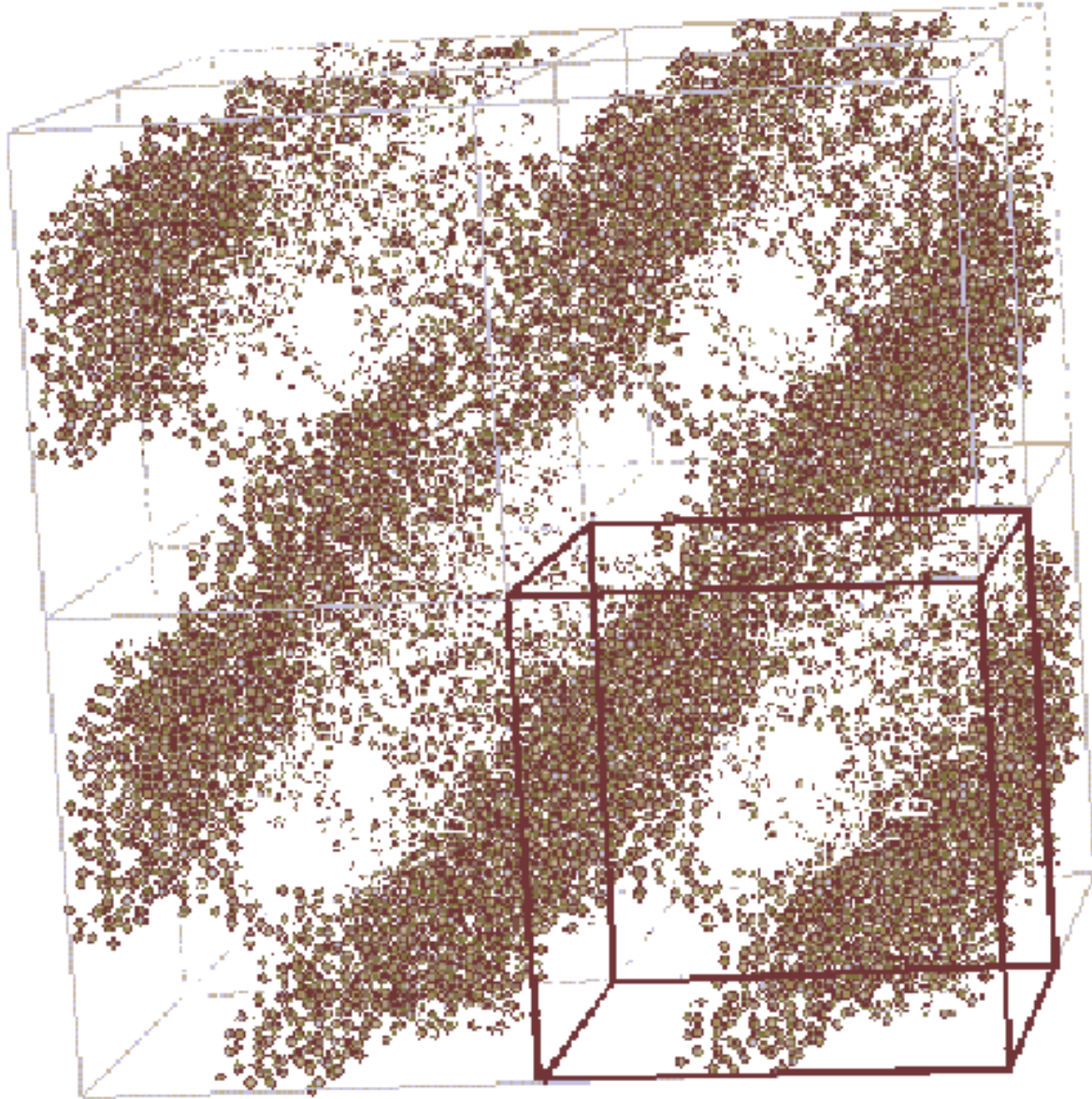
Ionic Block Copolymer

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



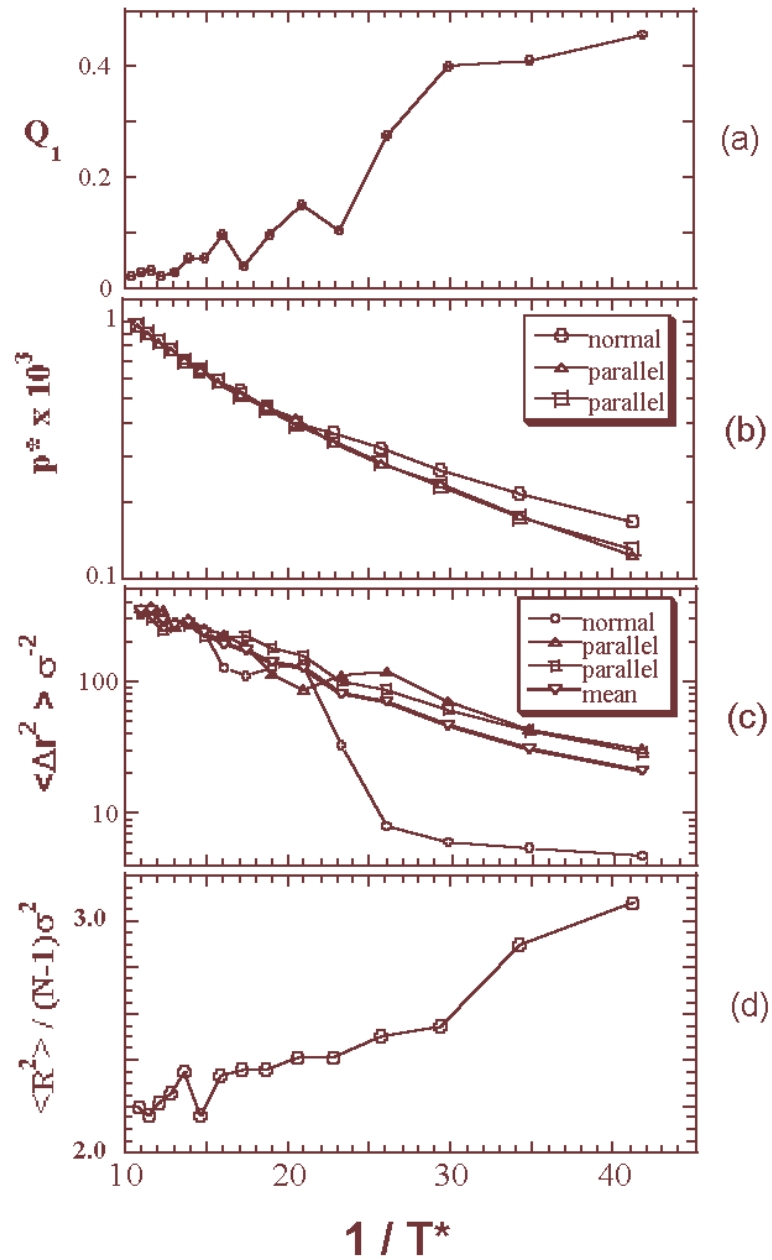
x 160

- Cations



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

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



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