Diagrams of states for single flexible-semiflexible multiblock copolymer chains in different selective solvents: Computer simulations by means of stochastic approximation Monte Carlo

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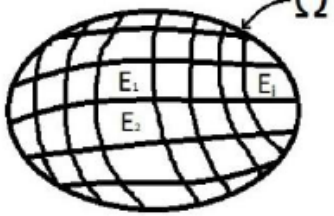
Method of simulation

Monte-Carlo algorithms of simulation

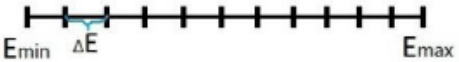
Phase space



Statistical sum of the chain

$$Z_{NVT} = \int_{\Omega} e^{-\frac{E\{\vec{x}\}}{kT}} d\Omega$$

$\{\vec{x}\}$ - conformation of the molecule



$g(E)$ - density of states function

$$\sum_{E_{min}}^{E_{max}} g(E_i) \cdot e^{-\frac{E_i}{kT}}$$

Stochastic Approximation Monte-Carlo (SAMC)

Visits all available ***macrostates*** uniformly

$\{E_{nv}, n_{st}\}$ - ***macrostate***, conformation - ***microstate***

$$p(old \to trial) = \min\left\{1, \frac{g(E_{nv}^{(old)}, n_{st}^{(old)})}{g(E_{nv}^{(trial)}, n_{st}^{(trial)})}\right\}$$ - acceptance probability

$$\ln g(E_{nv}, n_{st}) = \ln g(E_{nv}, n_{st}) + \gamma_t \cdot \left[\delta_{(E_{nv}, n_{st}),(E_{nv}^{(new)}, n_{st}^{(new)})} - \frac{1}{n}\right],$$

$$\gamma_t = \gamma_0 \cdot \min\left(1, \frac{t_0}{t}\right)$$

Advantages of SAMC

1) SAMC vs. Metropolis algorithm
2) The calculation with two-dimensional density of states function vs. the calculation with one-dimensional

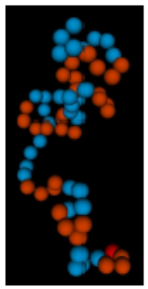
We accumulate the estimation of density of states function with certain value of monomer-monomer interaction contributions and **certain value** of stiffness energy contribution

We can calculate average values of observables for **any other** meanings of parameter ε_{st}:

$$\langle A(T)\rangle\Big|_{\varepsilon_{st}, T=fixed} = \frac{1}{Z(T)} \sum_{E_{nv}, n_{st}} \bar{A}(E_{nv}, n_{st}) \cdot g(E_{nv}, n_{st}) \cdot e^{-\frac{E_{nv} + \varepsilon_{st} n_{st}}{kT}}$$

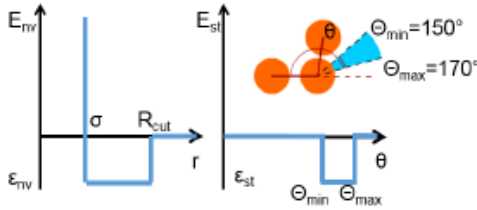
$$\langle Z(T)\rangle\Big|_{\varepsilon_{st}, T-fixed} = \sum_{E_{nv}, n_{st}} g(E_{nv}, n_{st}) \cdot e^{-\frac{E_{nv} + \varepsilon_{st} n_{st}}{kT}}$$

Model of investigated system



Snapshot for a chain with b=4

- Continuum bead-on-spring
- N=64 monomers
- Bond length **0.8σ-1.25σ**
- Flexible and semi-flexible blocks
- Block length **b=4,8,16 or 32**
- Two energy contributions:
  1) **non-valence interactions E_{nv}**
  2) **energy of stiffness E_{st}** (for semi-flexible blocks)
- R_{cut}=1.5σ
- Two types of trial moves: **local moves** and **"end-cut-and-regrow"**



$E_{nv} = \varepsilon_{ss} \cdot n_{ss} + \varepsilon_{sf} \cdot n_{sf} + \varepsilon_{ff} \cdot n_{ff}, \varepsilon_{ff} = 1$ (energy unit)

$\varepsilon_{sf} = \sqrt{\varepsilon_{ss} \cdot \varepsilon_{ff}}$ (Lorentz-Berthelot combining rules)

$E_{st} = \varepsilon_{st} \cdot n_{st}$

Full configurational energy of a chain:

$$E = \varepsilon_{ff} \cdot n_{ff} + \varepsilon_{ss} \cdot n_{ss} + \sqrt{\varepsilon_{ss}\varepsilon_{ff}} \cdot n_{sf} + \varepsilon_{st} \cdot n_{st}$$

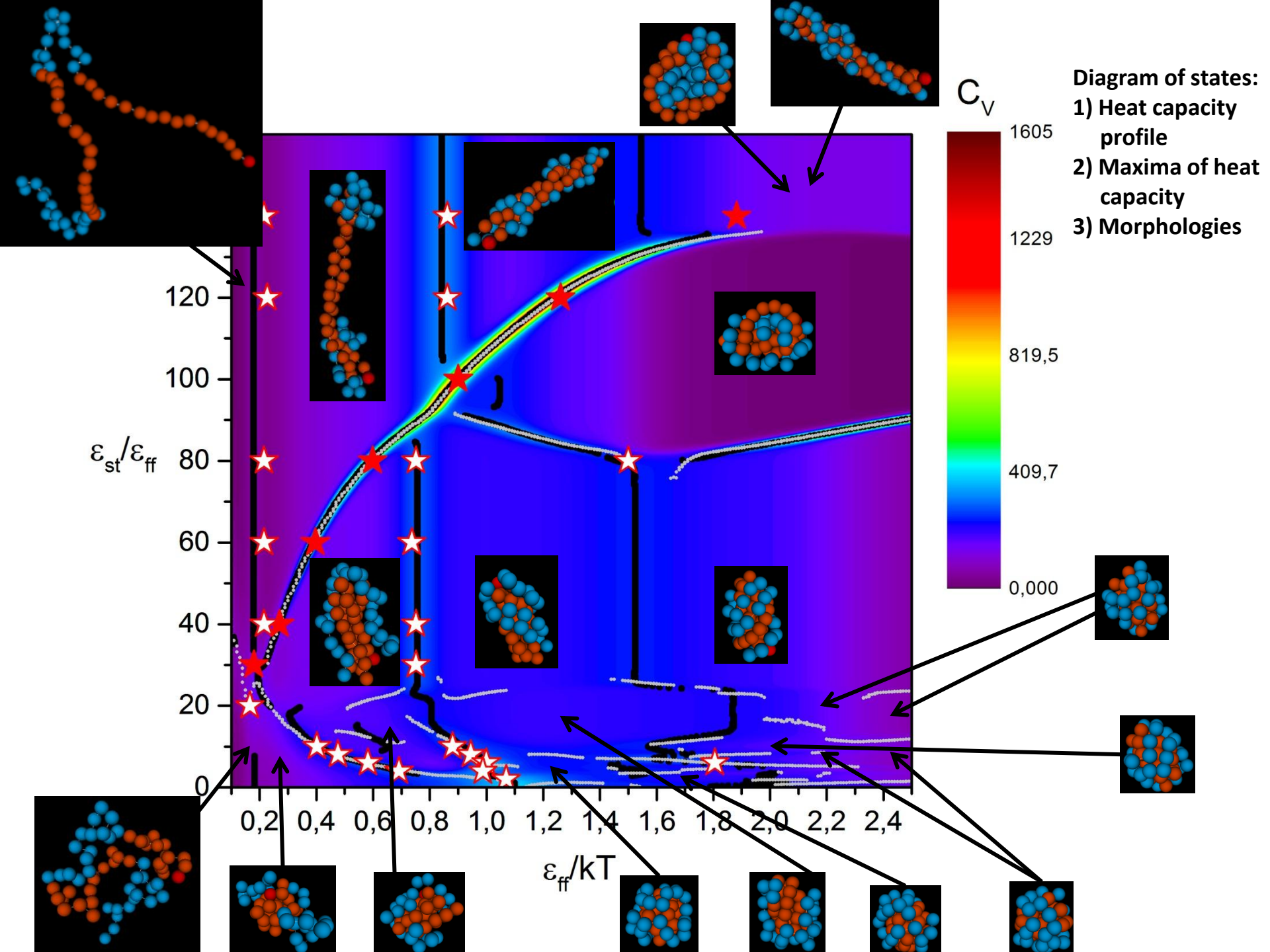


Diagram of states:
1) Heat capacity profile
2) Maxima of heat capacity
3) Morphologies
C_V
1605
1229
819,5
409,7
0,000
$\varepsilon_{st}/\varepsilon_{ff}$
0
20
40
60
80
100
120
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
1,8
2,0
2,2
2,4
ε_{ff}/kT

Analysis in microcanonical ensemble:

1) On a base of g(U)

2) On a base of g(E)