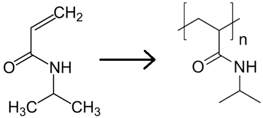
Thermodynamics of thermoresponsive polymer PNIPAM in aqueous solutions

Jakub Polak[1], Vladimir Palivec[1], Adam Kovalcik[1], Daniel Ondo[1] and Jan Heyda[1]



[1] Department of Physical Chemistry
University of Chemistry and Technology, Prague

1st Users Conference of IT4I
Tuesday, October 31, 2017

Outline

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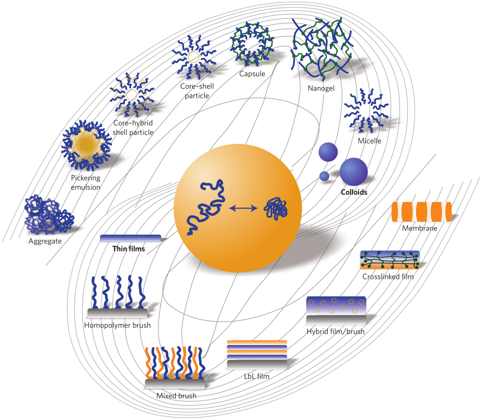
Smart Materials based on thermoresponsive polymers

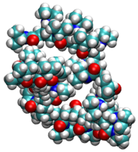


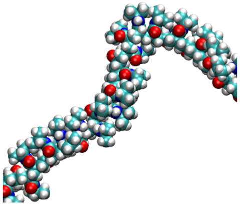
Stuart et al. *Nature Materials*, 2010, 9, pp. 101-113

- Large changes in a material property upon a application of a small external stimuli
  - Temperature, pressure, stress, moisture, light
  - Change of pH, addition of salt
- This change is revesible and controlable
  - Volume phase transition
  - Conformation (cis/trans)
  - Polarity
  - Optical properties (transparent/opaque)
  - Electrical properties ((non-)conductive)
- Near transition sensitive to another stimuli
  - $\rightarrow$ Multiresponsive materials

Computational methods

- System:
  - 1 PNIPAM chain in 6nm cubic box filled with 10k water molecules
  - Different force-fields employed and fine-tuned
  - Different chain lengths investigated
- Method and scalability:
  - **Direct MD hopeless for thermodynamics**
  - Replica Exchange MD (REMD) technique for sampling
  - 76 replicas spanning the temperature range 270-420 K
  - Equilibration ≈50-100 ns, production ≈100 ns per replica
  - Gromacs 5.1.2 package was used
  - Large number of particles → good scaling
  - 1 replica per 1 core ≈5 ns/day, 1 replica per node (24 cores) provides ≈85 ns/day
  - → **76x24=1824** cores/job (Salomon cluster)
- Analysis:
  - Coil ⇆ Globule equilibrium sampled $K = P_{coil}/P_{globule}$
  - Direct access to transition free energy, $\Delta G = -RT \ln K$





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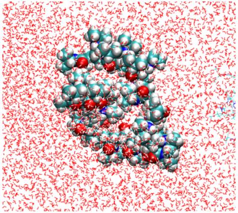

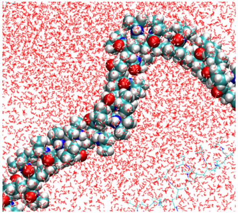

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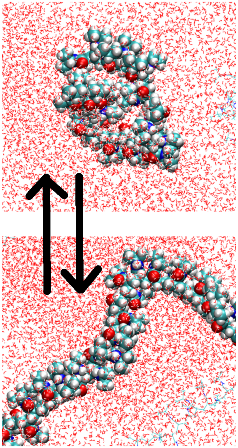

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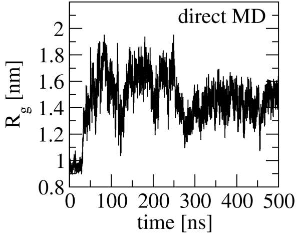
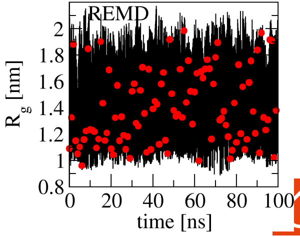
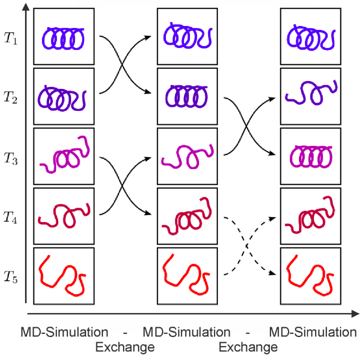
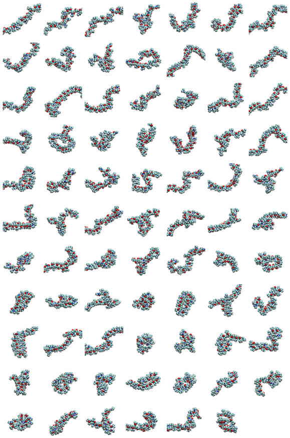




Enhanced sampling via replica exchange MD simulation





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- Frequent Monte-Carlo-like swap moves between neighbors
- Largely increased sampling of the conformational space at all Temp.
- Very suitable for thermodynamic studies (all Temp. in a single run)

Zacharias et al., J. Phys.: Condensed Matter, 2015, 27, pp. 323101

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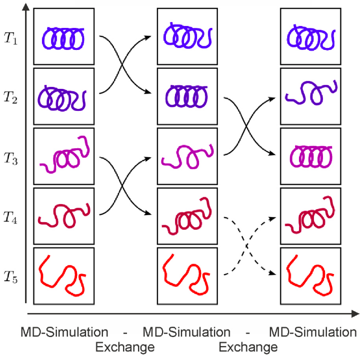

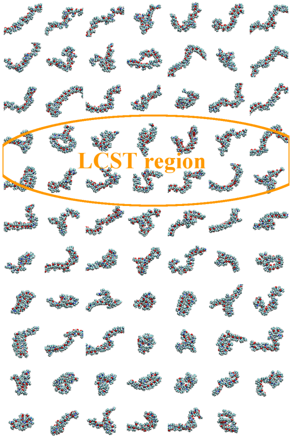

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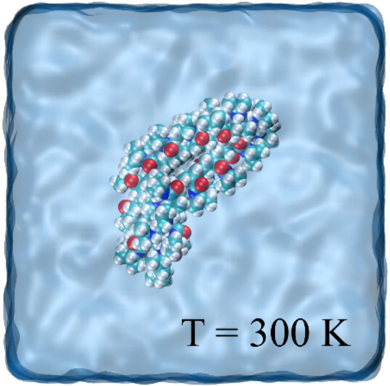
Theory: Meeting atomistic and macroscopic properties



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$$\left(\frac{\partial \Delta G}{\partial T}\right) = -\Delta S \qquad \left(\frac{\partial \Delta G}{\partial c_3}\right) = -RT\Delta\Gamma_{23}$$

$$\Gamma_{23} = \rho_3(G_{23} - G_{21}) \approx -\left(\frac{\partial \mu_2}{\partial \mu_3}\right)_{p,T,m_2} \qquad \text{(dialysis exp.)}$$

$$\Delta G(\Delta T, c_3) \simeq \Delta G(T_0) + \left.\frac{\partial \Delta G}{\partial T}\right|_0 \Delta T + \left.\frac{\partial \Delta G}{\partial c_3}\right|_0 c_3 + \ldots \quad \text{(Taylor)}$$

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- 1-water, 2-PNIPAM, 3-salt
  G_{21}, G_{23} – Kirkwood-Buff integrals (*effective exluded volume*)
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- Depleted salt affects ΔT

Algaer et al. *JPCB*, 2011, 115, pp. 13781
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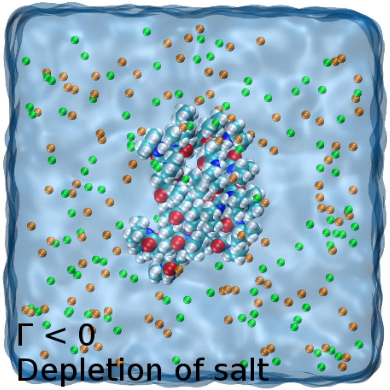

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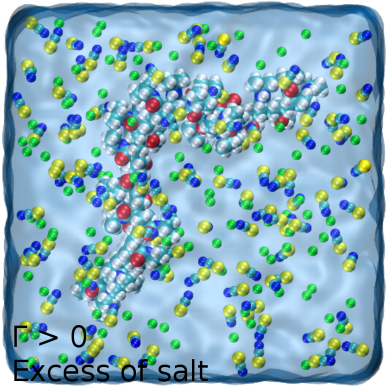

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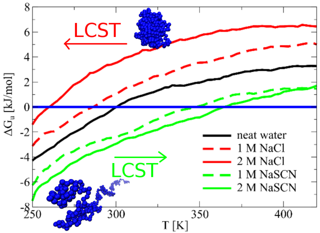
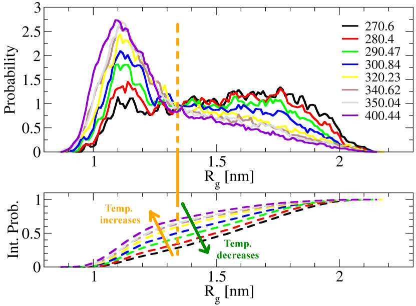
Thermodynamics from simulation perspective





- With increasing temperature the collapsed population rises
- coil $\rightleftarrows$ globule equilibrium $\Rightarrow \Delta G_U(T) = -RT \ln \frac{[C_{oil}](T)}{[G_{lobule}](T)}$
- Addition of salt may lead to swelling (NaSCN), or collapse (NaCl)
- These two stimuli (c_{salt} and ΔT) compensate at new LCST

Polak, J.; Palivec, V.; Kovalcik, A.; Ondo, D.; Heyda, J. in preparation

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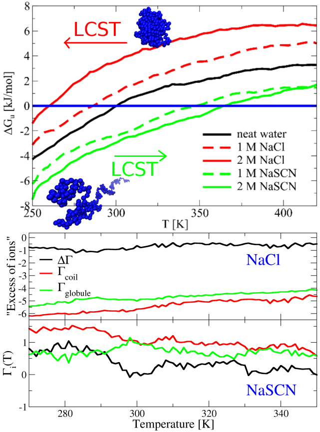

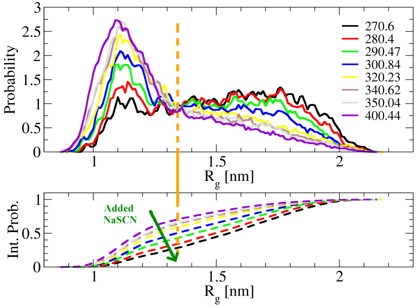

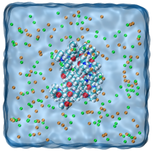

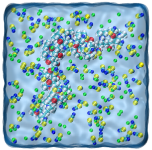

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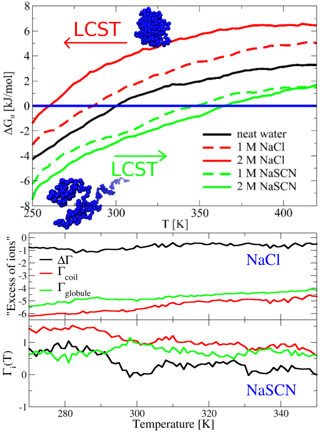

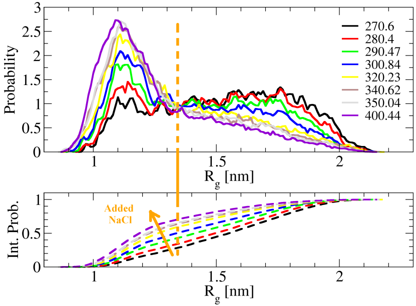

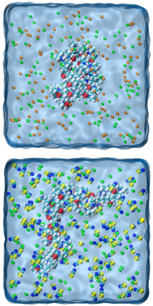

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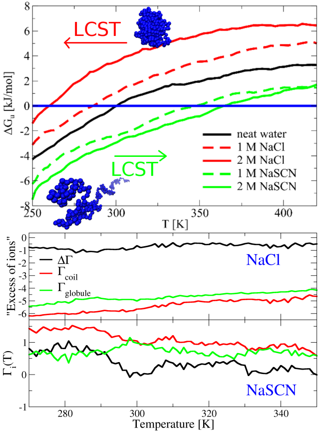

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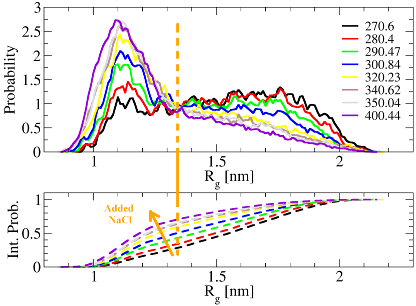

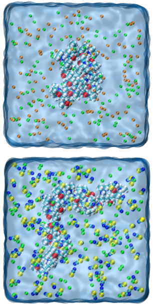

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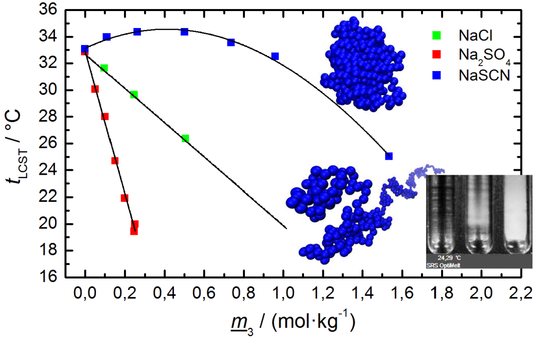

- Excluded salts cause linear decrease of LCST, i.e., cloud-point, (NaCl, Na_2SO_4)
- Salts with excess on polymer surface lead to weak nonlinear increase (NaSCN)

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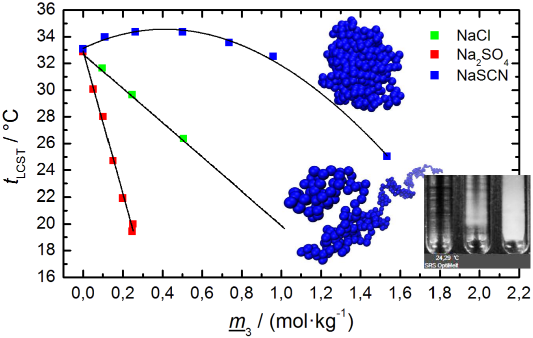

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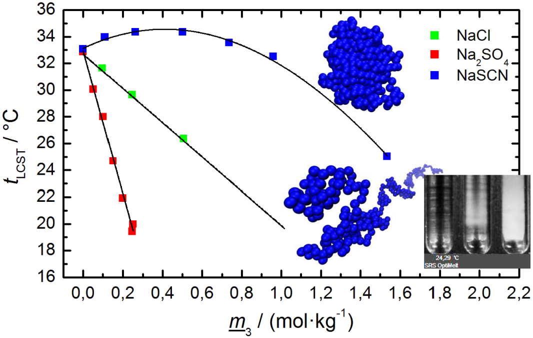

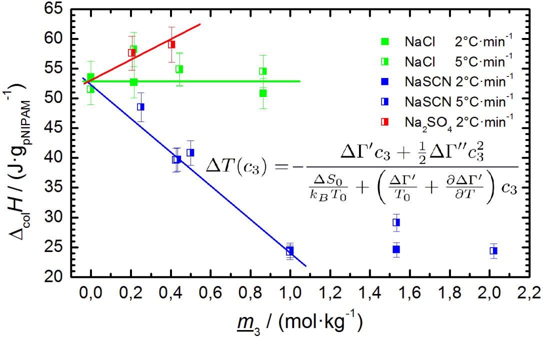

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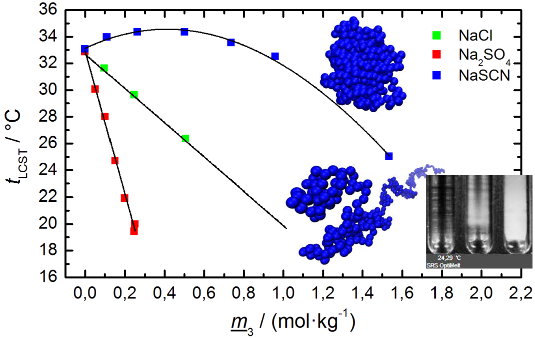

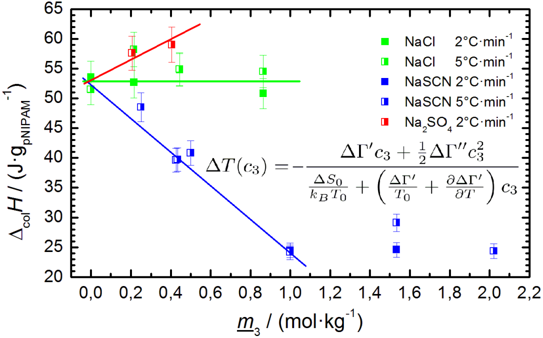

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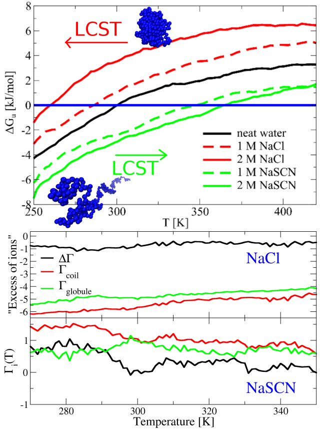
Conclusion

- Highly paralelized REMD was employed to:
  - develop reliable force-field of pNIPAM
  - investigate thermodynamic properties in water
  - investigate effect of salt on thermodynamics
  - quantify salt excess and/or depletion
- Results are complemented with experiments:
  - cloud-point measurements
  - DSC calorimetry
  - ITC calorimetry
- Outlook:
  - effect of the polymer chain length on LCST
  - role of finite polymer concentration (i.e., many chains)



Acknowledgement

- Experiments: Jakub Polak, Adam Kovalcik, Daniel Ondo (LCST, ITC, DSC)
- Simulations: Vladimir Palivec, Denis Zadrazil, Emil Pavelka– see our poster

- Czech Science Foundation, Grant 16-57654Y
- CIISB proposal at CEITEC-MU Brno (DSC, DLS, SAXS)
- IT4Innovations National Supercomputing Center – LM2015070
  - Project OPEN-7-50
  - Project OPEN-10-36

Thank you for your attention

Looking for 14 ChemJets – (flyers&info by our poster)

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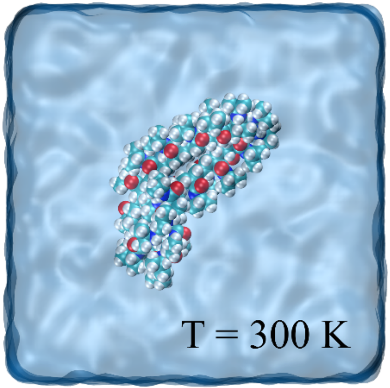

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$$\Delta\Gamma_{23} = \Gamma_{c3} - \Gamma_{g3} \;\rightarrow\; \mu_c - \mu_g = \Delta G(c_3) \quad \text{... Gibbs E.}$$

$$\Delta\Gamma(c_3, \Delta T) = \Delta\Gamma' c_3 + \frac{1}{2}\Delta\Gamma'' c_3^2$$

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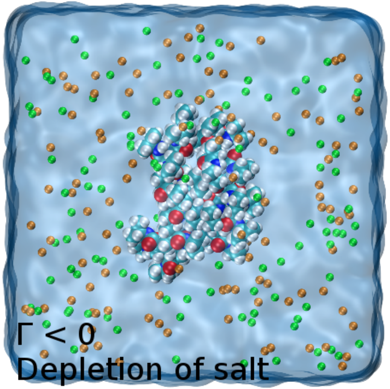
- 1-water, 2-PNIPAM, 3-salt
  G_{21}, G_{23} – Kirkwood-Buff integrals (*effective exluded volume*)
  Γ_{23} – Preferential interaction (*number of particles*)
- Depleted salt affects ΔT
- Binding salt affects ΔT and ΔH

Theory: Meeting atomistic and macroscopic properties



Algaer et al. *JPCB*, 2011, 115, pp. 13781
Heyda et al. *Macromolecules*, 2013, 46, pp. 1231
Heyda et al. *JPCB*, 2014, 118, pp. 10979

Okur et al. *JPCB*, 2017, 121, pp. 1997

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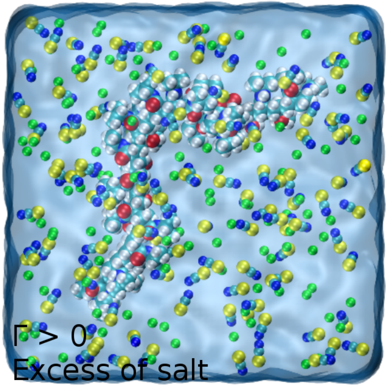

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