Adsorption of a coarse-grained flexible polymer on nanocylinders - A Monte Carlo study

Jonathan Gross
with
Thomas Vogel and Michael Bachmann

Computational Quantum Field Theory

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Adsorption of a coarse-grained flexible polymer on nanocylinders

Outline

- Model and Simulation
- Results
- Summary and Comparison

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Model and Simulation

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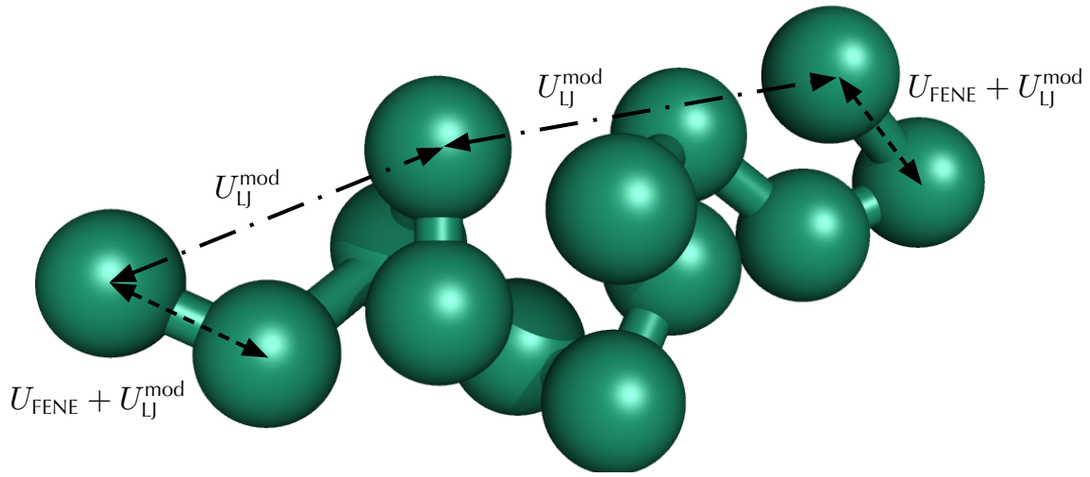
The fully flexible polymer

R. B. Bird, C. F. Curtiss, R. C. Armstrong, O. Hassager, Dynamics of Polymeric Liquids, 2nd ed., 2 vols., Wiley, New York, 1987
S. Schnabel, T. Vogel, M. Bachmann, W. Janke, Chemical Physics Letters 476 (2009) 201–204
S. Schnabel, M. Bachmann, W. Janke, Journal of Chemical Physics 131 (2009) 124904-1–9

- FENE potential to model bonds

$$U_{\text{FENE}}(r_{ii+1}) = -\frac{K}{2}R^2 \log\left[1 - \left(\frac{r_{ii+1} - r_0}{R}\right)^2\right]$$



- shifted and truncated Lennard-Jones potential between all monomers

$$U_{\text{LJ}}^{\text{mod}}(r_{ij}) = U_{\text{LJ}}(\min(r_{ij}, r_c)) - U_{\text{LJ}}(r_c) \qquad U_{\text{LJ}}(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

$$\epsilon = 1 \qquad r_0 = 0.7 \qquad \sigma = r_0/2^{1/6} \qquad K = 40 \qquad R = 0.3 \qquad r_c = 2.5\sigma$$

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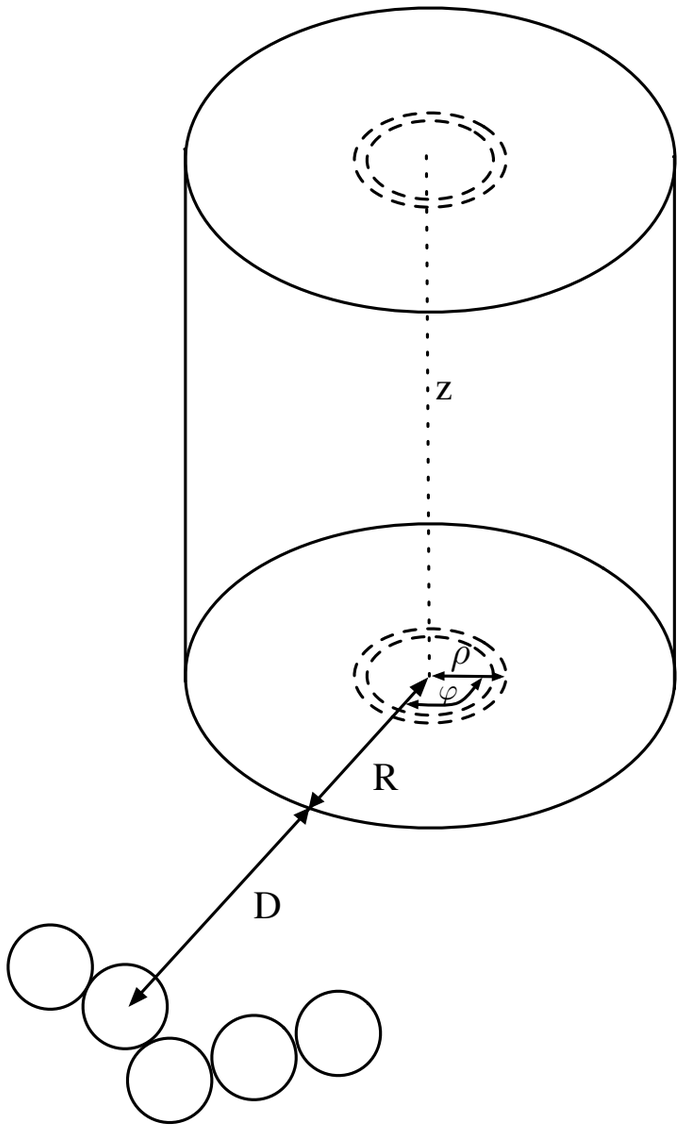
The nanocylinder



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Polymer nanodroplets adsorbed on nanocylinders: A Monte Carlo study

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$$U_{\text{cyl}}(R,D) = \varepsilon_c \pi \int_0^{2\pi} d\varphi \int_0^R \rho d\rho \left(\frac{63}{64x^{11/2}} - \frac{3}{2x^{5/2}} \right)$$

$$x = (D+R)^2 + \rho^2 - 2\rho(D+R)\cos\varphi$$

- transform 6-12-Lennard-Jones to cylindrical coordinates
- perform integration over z-axis
- potential depends on distance and radius

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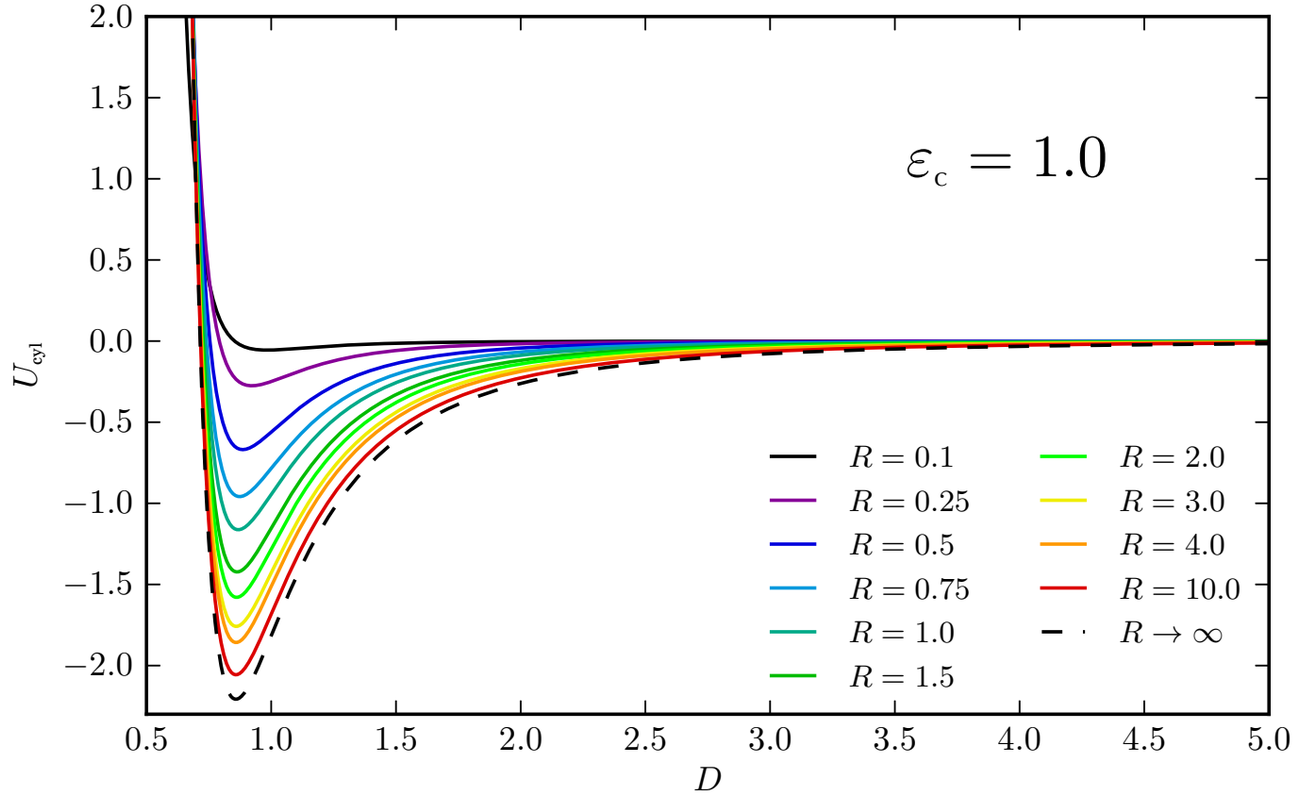
Cylinder potential for different radii

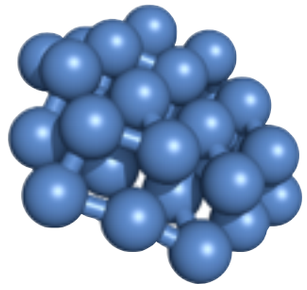


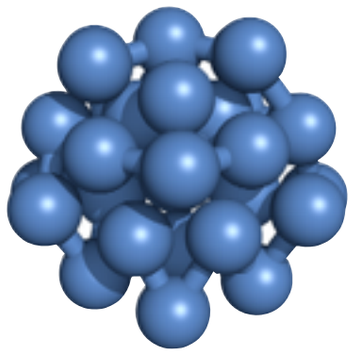
- effective attraction of the nanocylinder increases with radius
- for $R \to \infty$ cylinder surface similar to planar surface
- different nanocylinder materials controlled via ε_c

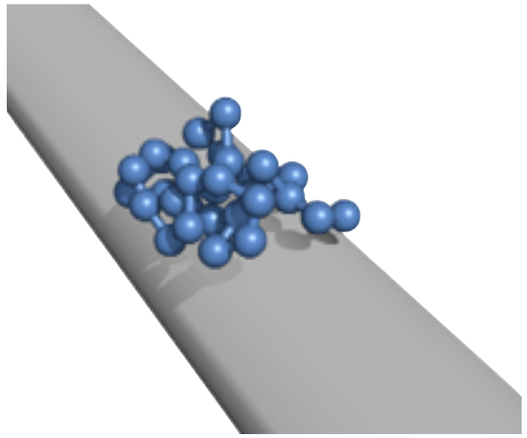
Adsorption of a coarse-grained flexible polymer on nanocylinders

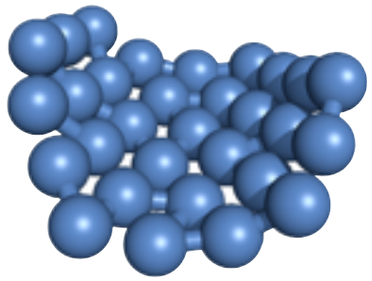
Thermodynamics

- we simulated 5 different nanocylinder materials $\varepsilon_c = \{1.0, 2.0, 3.0, 4.0, 5.0\}$
- each material with 10 different radii $R = \{0.1, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 3.0, 4.0, 10.0\}$
- parallel tempering simulations at 80 temperatures
- $5 \cdot 10^7$ MCS per replica
- polymer with 30 monomers
- construction of structural phase diagrams using canonical observables







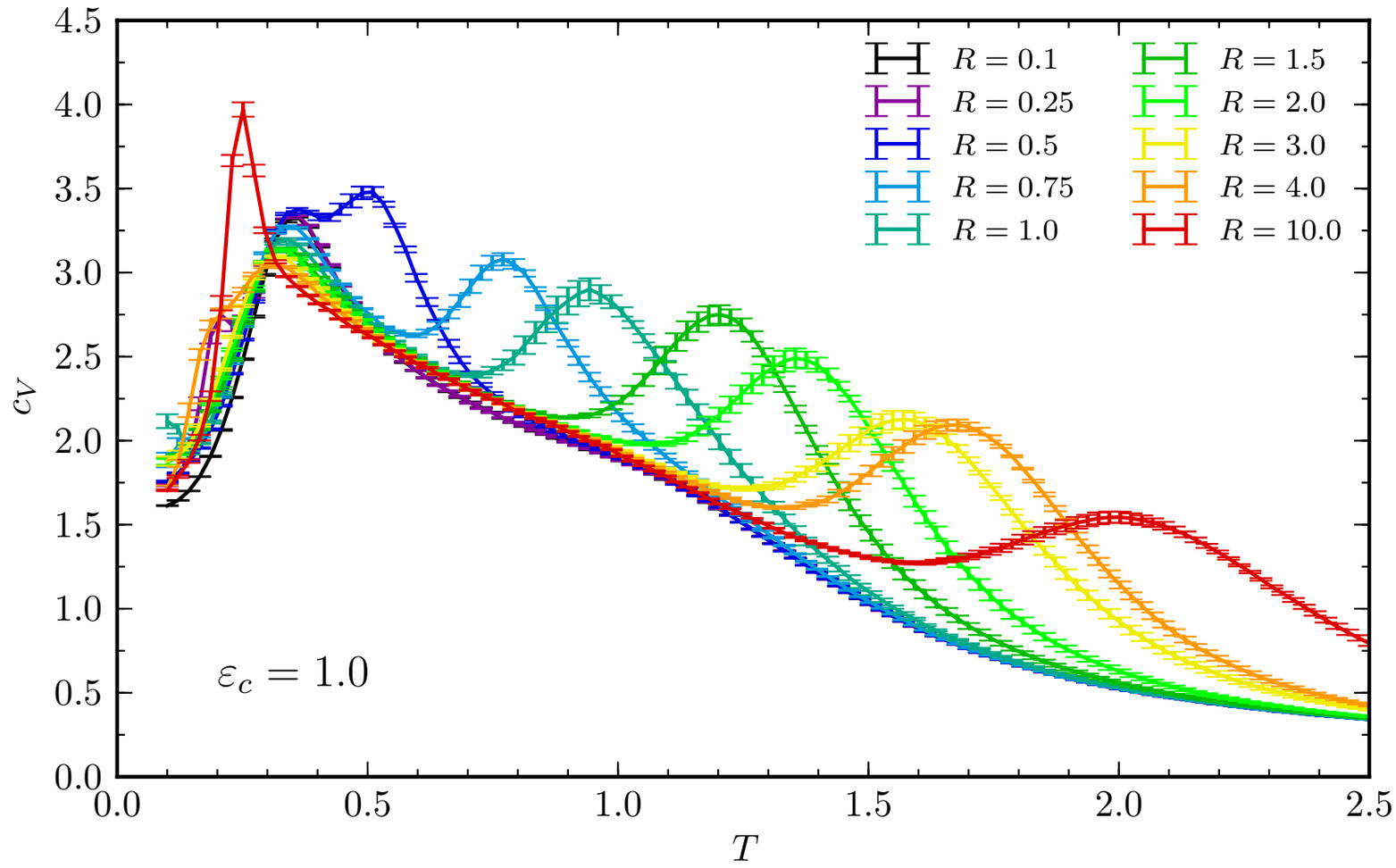


Adsorption of a coarse-grained flexible polymer on nanocylinders

Results

Adsorption of a coarse-grained flexible polymer on nanocylinders

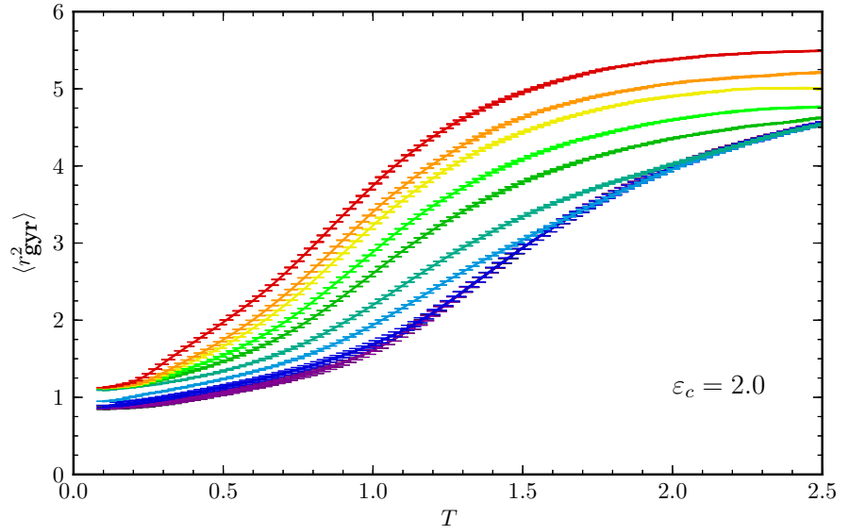
Specific heat $\frac{C_V}{N} = \frac{1}{N}\frac{\partial \langle E \rangle}{\partial T} = \frac{\beta^2}{N}(\langle E^2 \rangle - \langle E \rangle^2)$

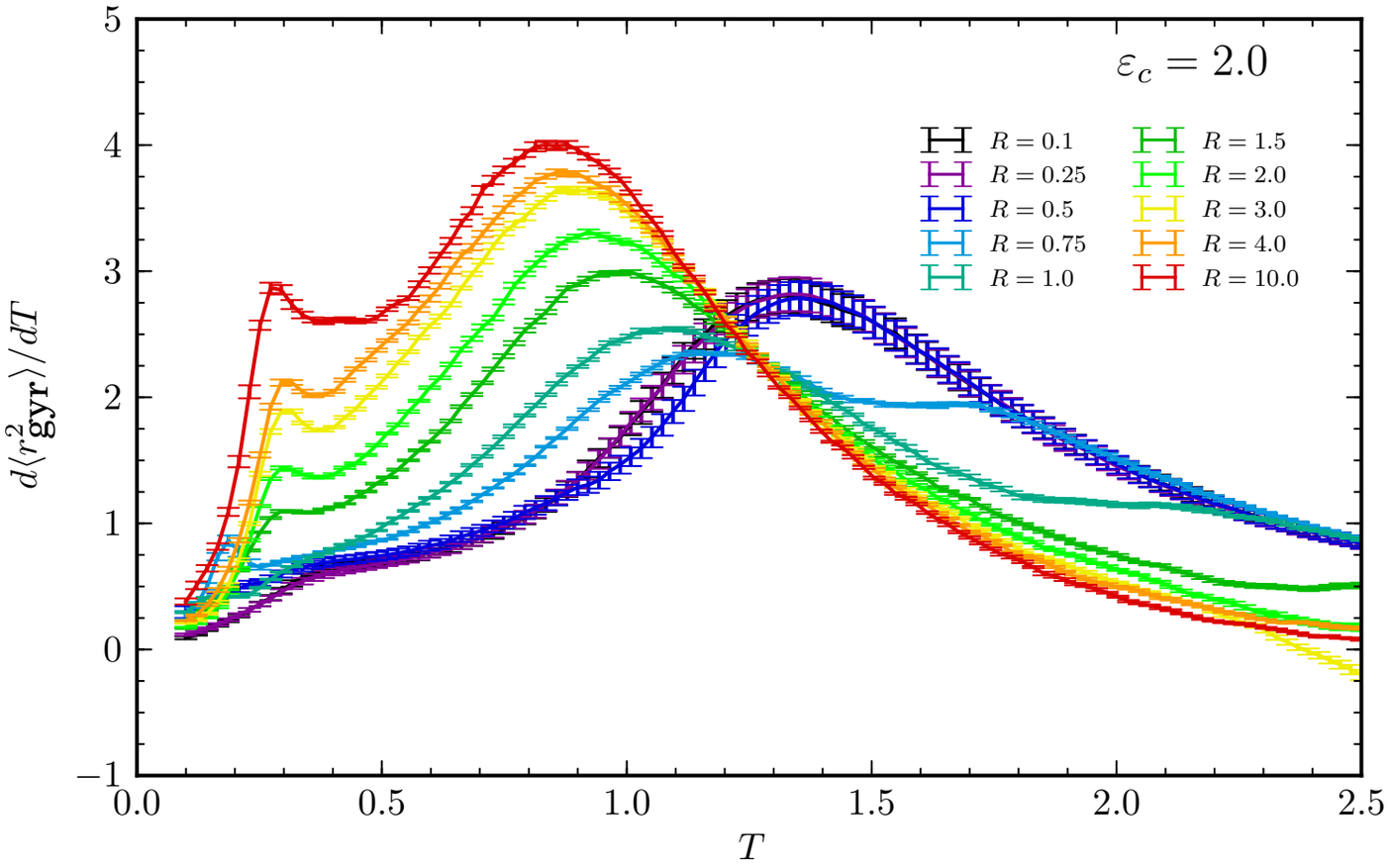


- high temperature peaks correspond to adsorption of the polymer
- peak at low temperature signals the freezing transition

Adsorption of a coarse-grained flexible polymer on nanocylinders

Radius of gyration and its thermal fluctuation





- high temperature peaks correspond to collapse of the polymer

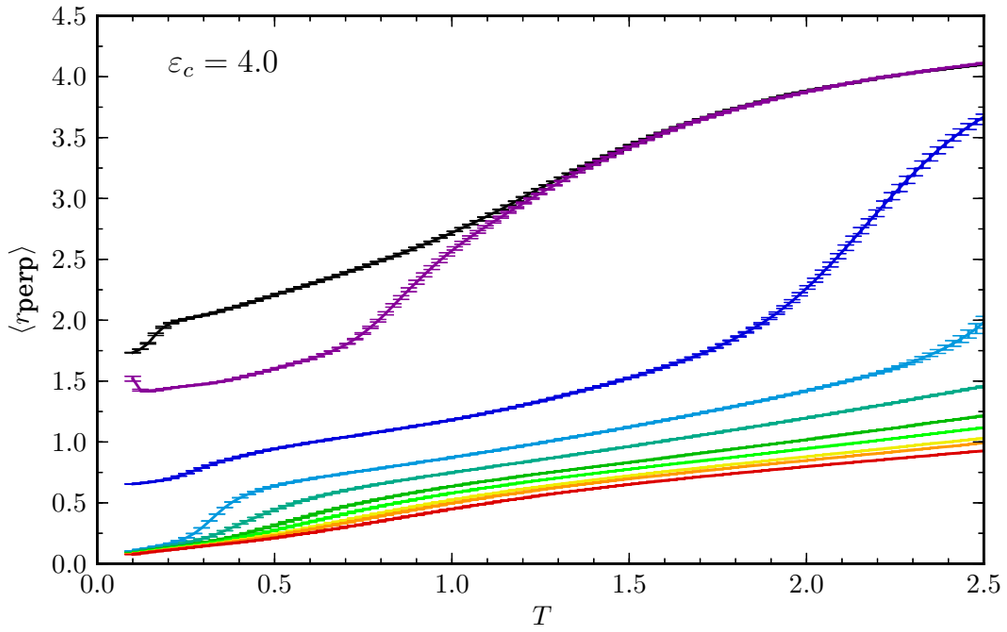
- freezing transition visible at low temperatures

- collapse transition shifts to lower temperatures for already adsorbed conformations

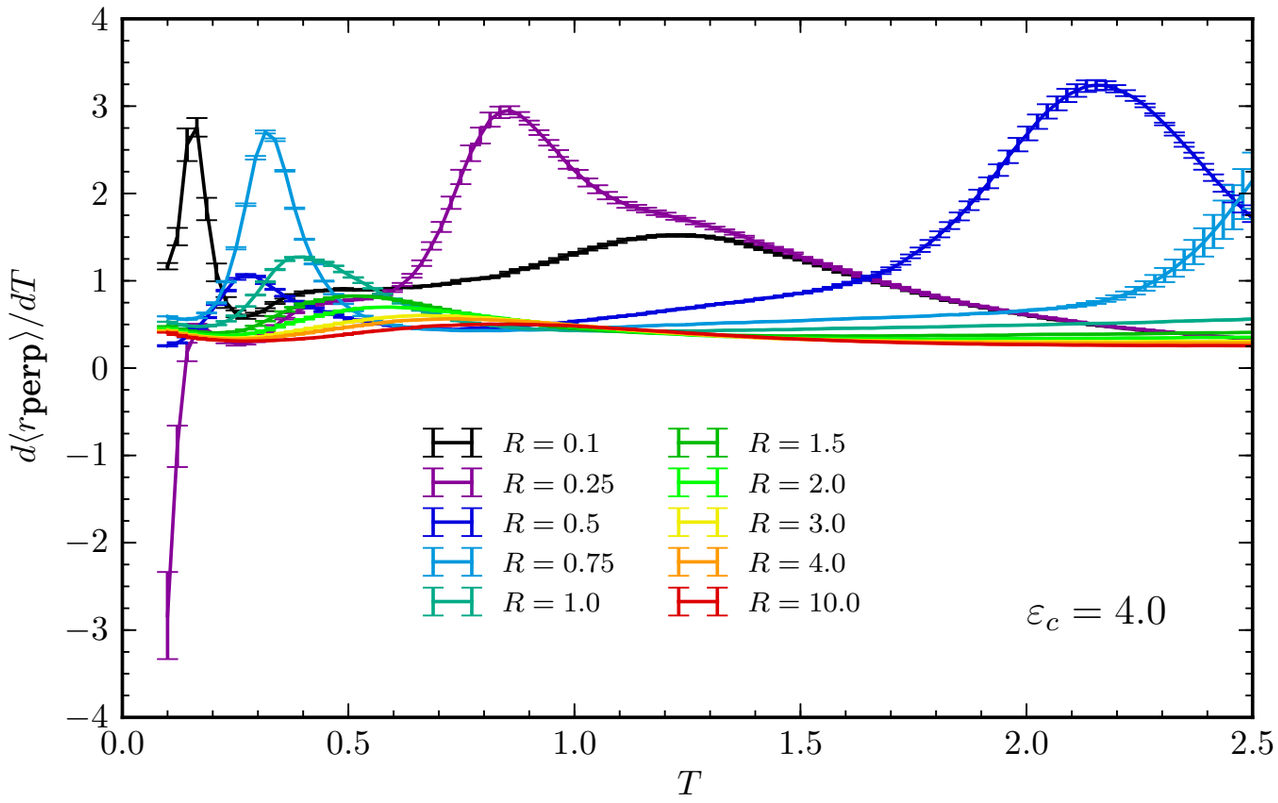
Adsorption of a coarse-grained flexible polymer on nanocylinders

Polymer extension perpendicular to the cylinder surface

$$r_{\text{perp}} = D_{\text{max}}(\mathcal{C}) - D_{\text{min}}(\mathcal{C})$$



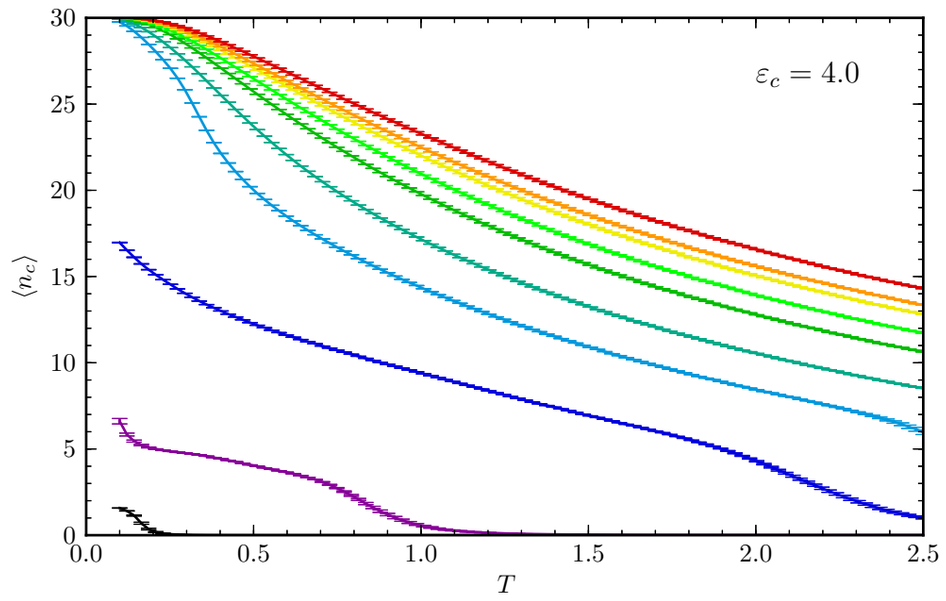
- value at lowest temperature contains information about the layering



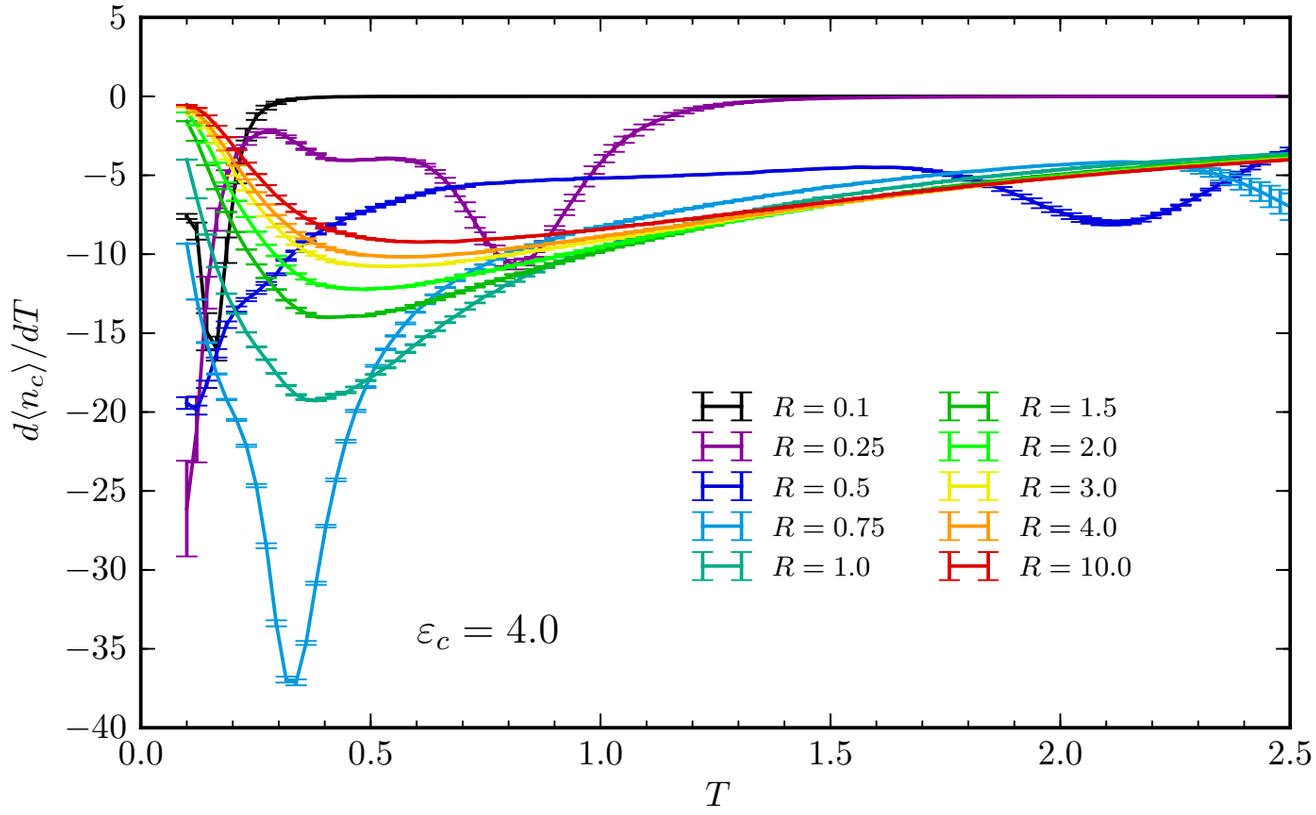
- high temperature peaks correspond to adsorption of the polymer
- peak at low temperature signals the freezing transition

Adsorption of a coarse-grained flexible polymer on nanocylinders

Number of surface contacts



- value at lowest temperature contains information about the layering



- adsorption at high temperatures
- low temperature peaks signal freezing/flattening

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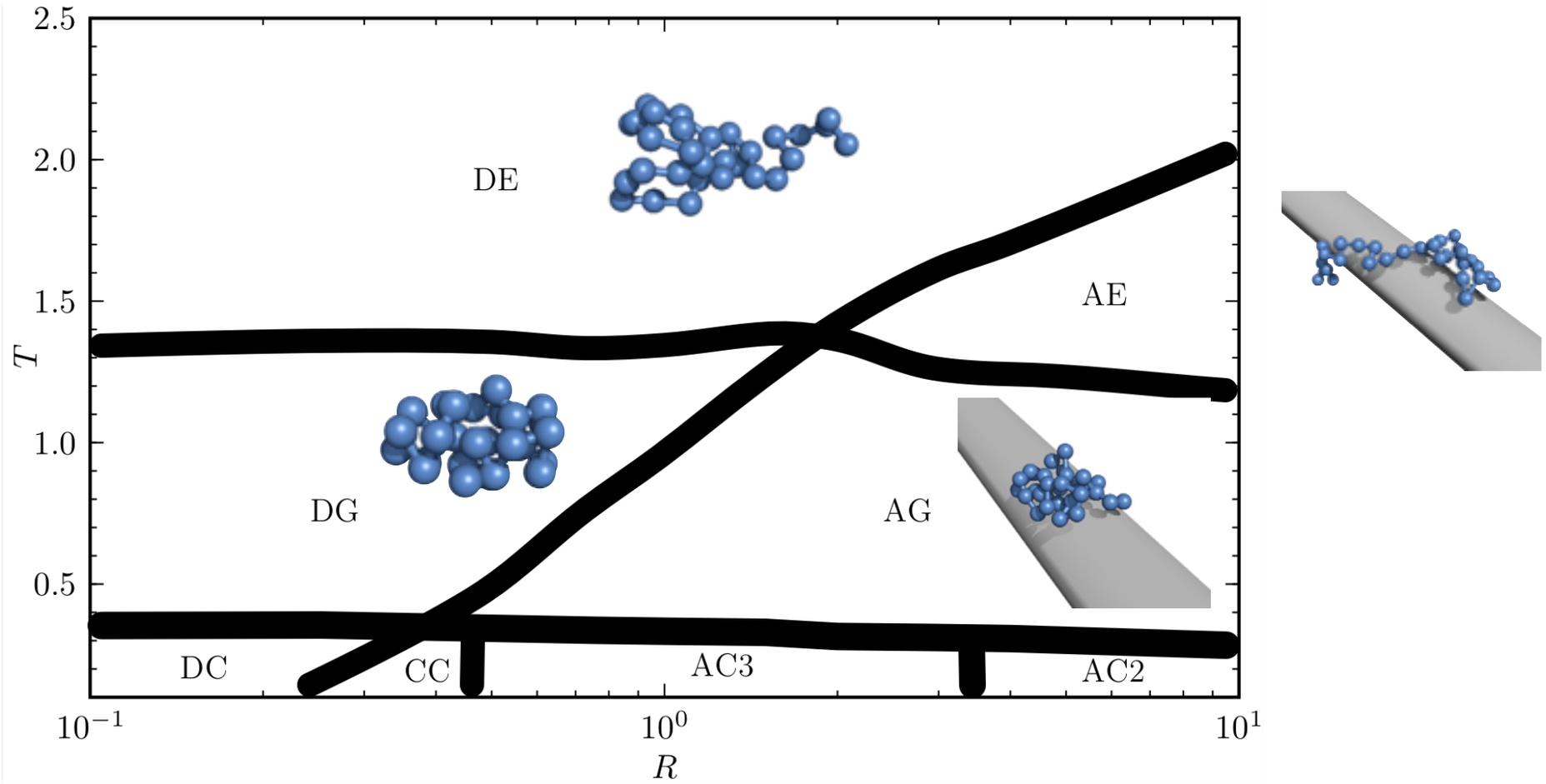
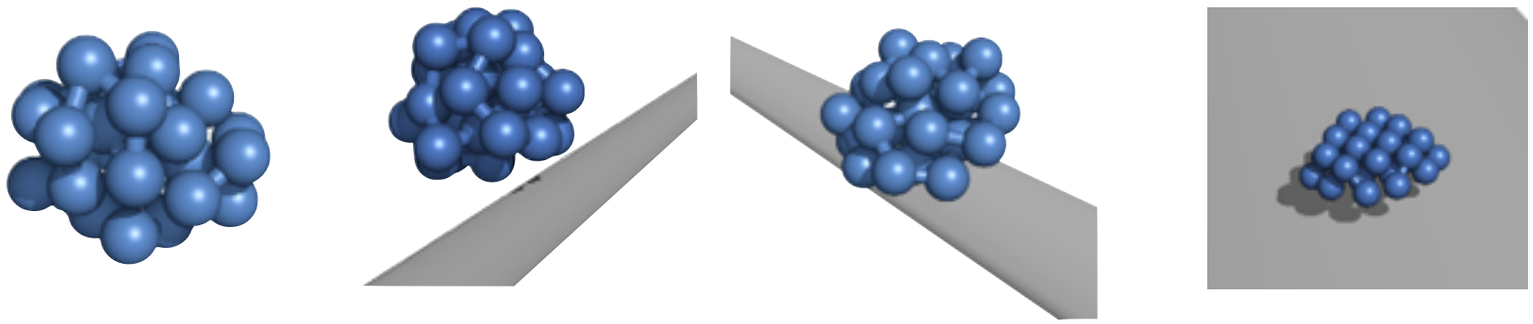
Adsorption of a coarse-grained flexible polymer on nanocylinders

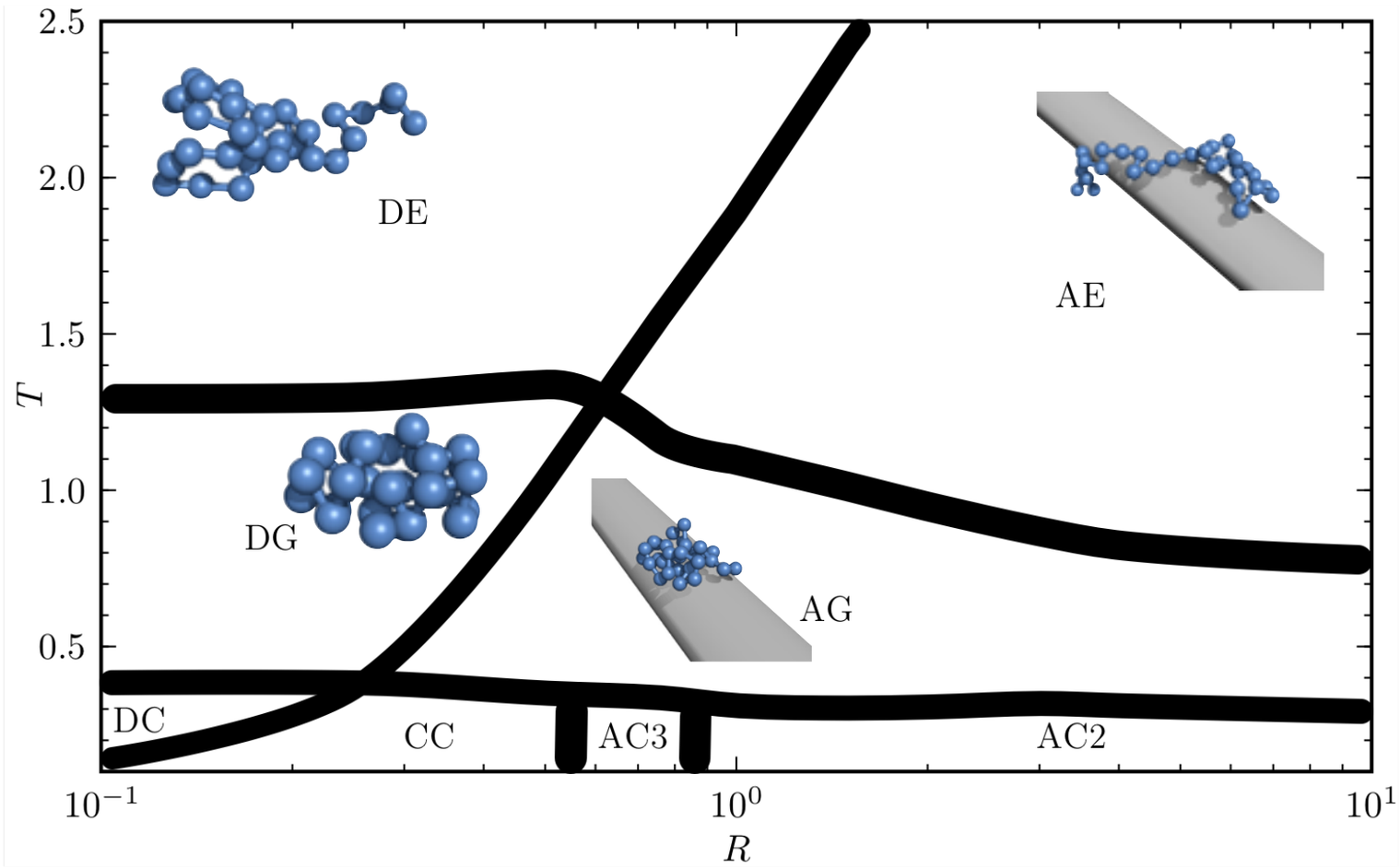
Pseudo phase diagram for $\varepsilon_c = 1.0$

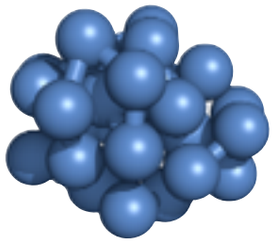


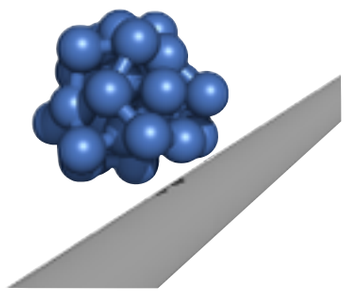


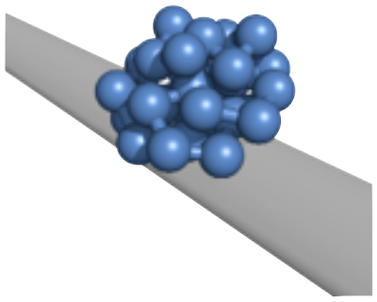
Adsorption of a coarse-grained flexible polymer on nanocylinders

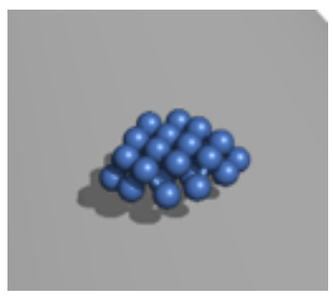
Pseudo phase diagram for $\varepsilon_c = 2.0$





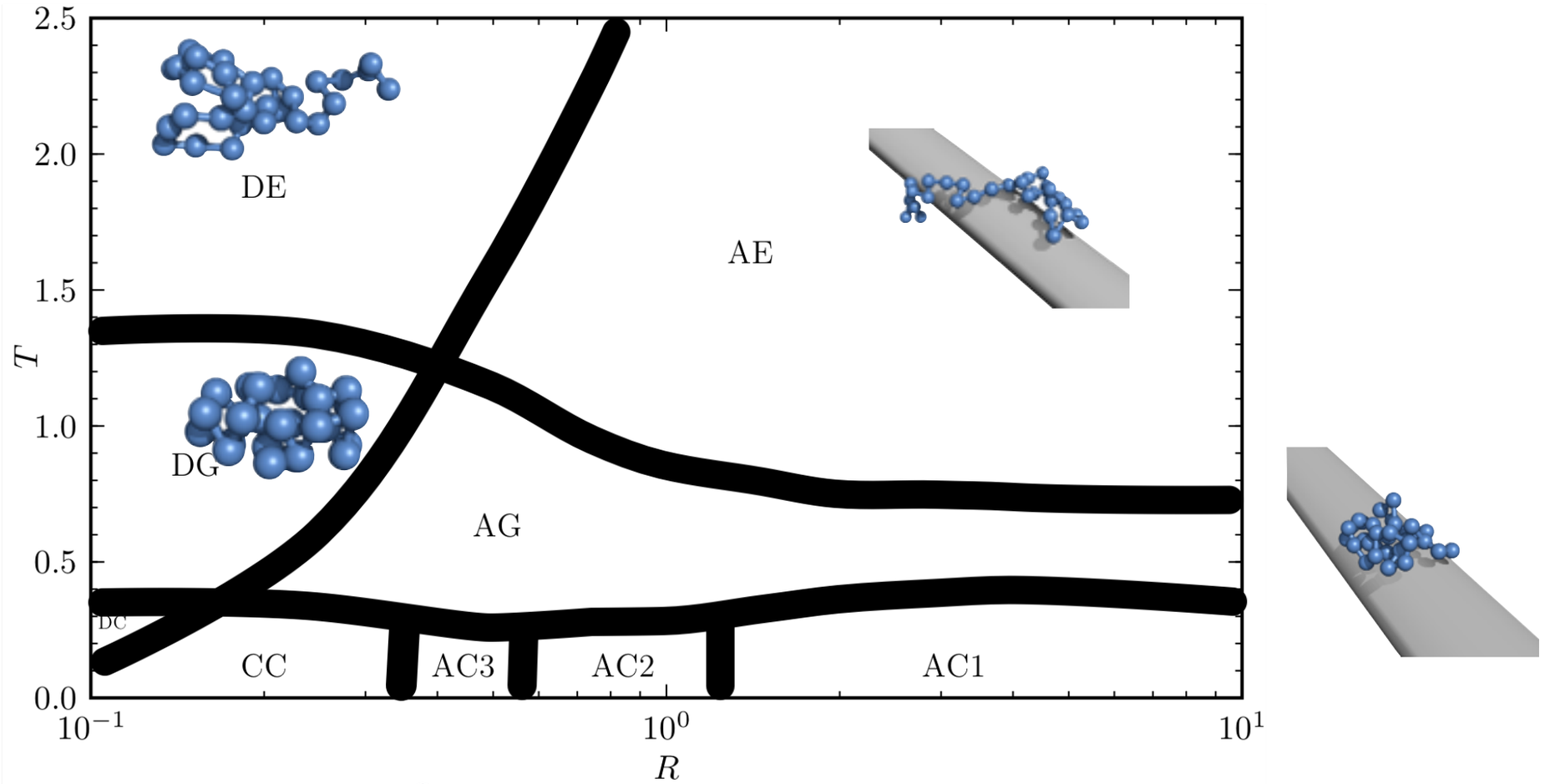


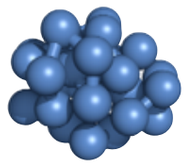


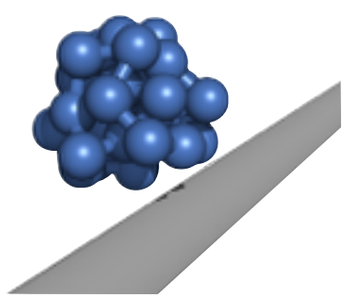


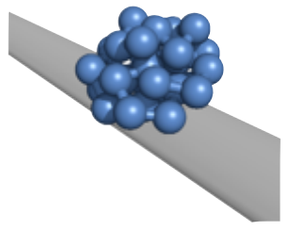
Adsorption of a coarse-grained flexible polymer on nanocylinders

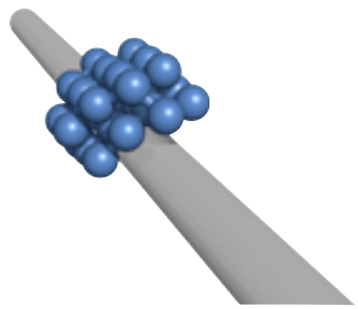
Pseudo phase diagram for $\varepsilon_c = 3.0$

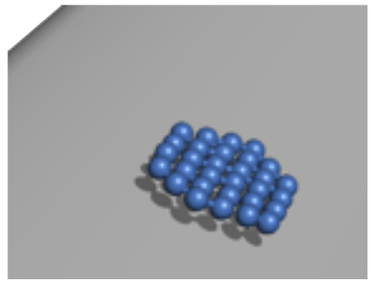






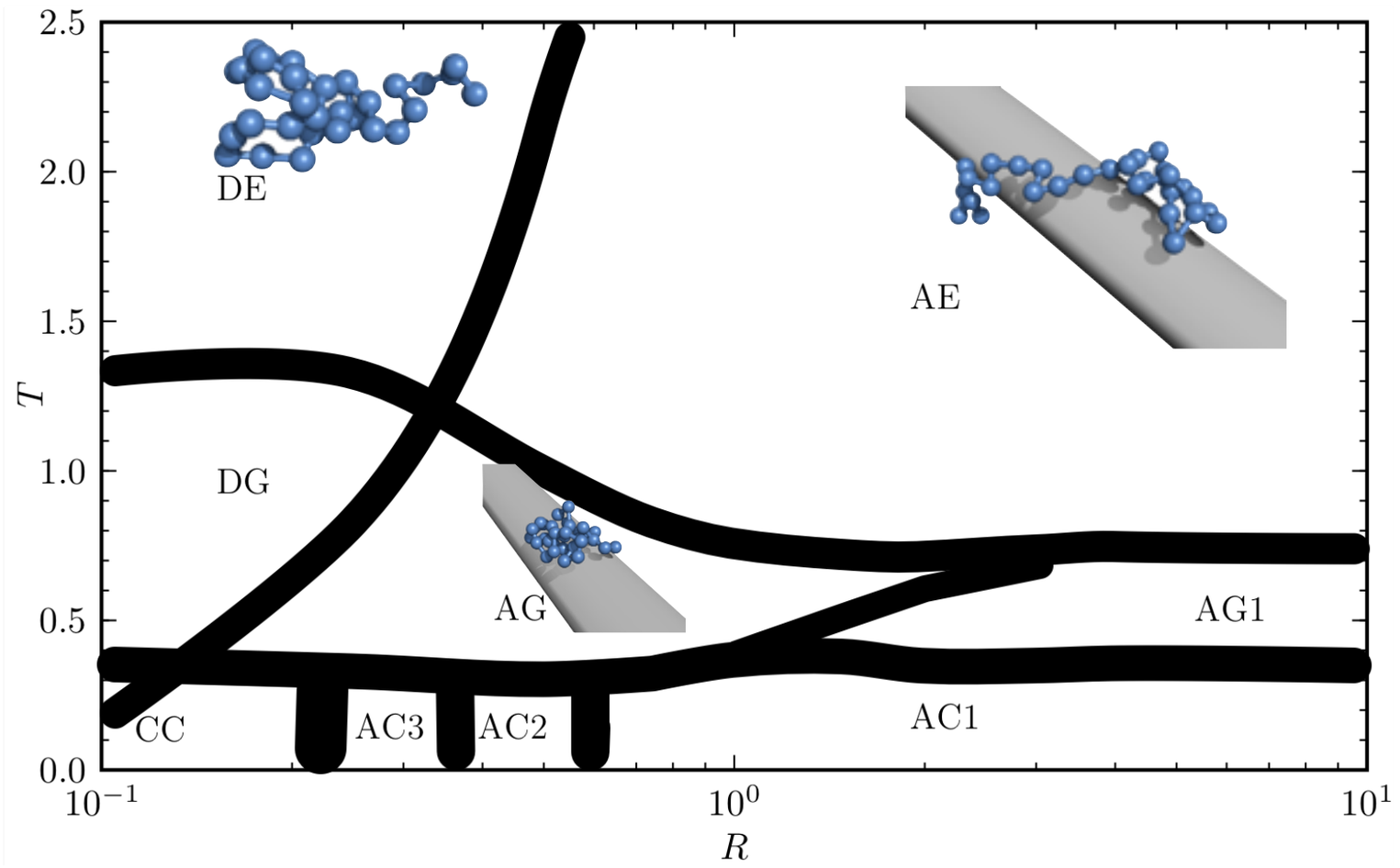


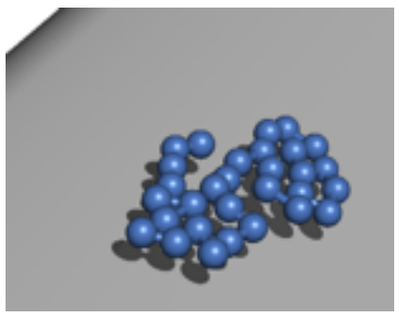


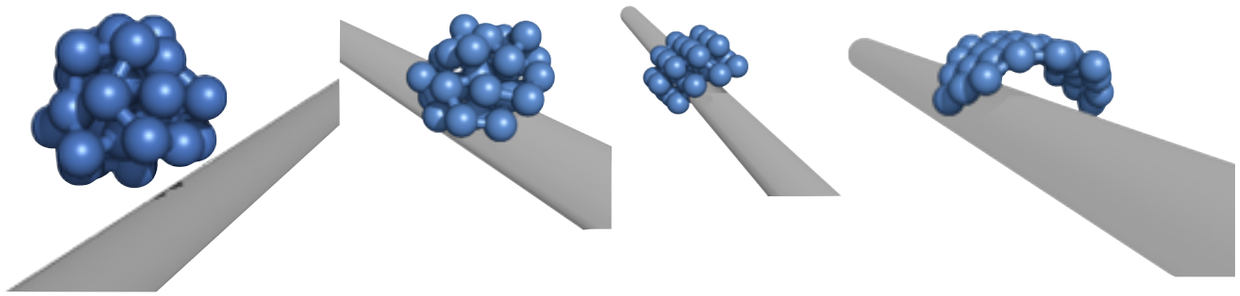


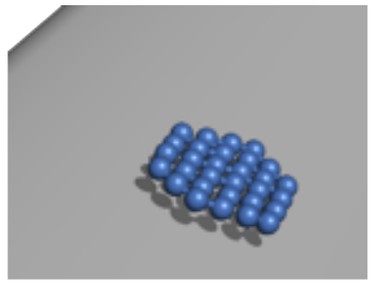
Adsorption of a coarse-grained flexible polymer on nanocylinders

Pseudo phase diagram for $\varepsilon_c = 4.0$



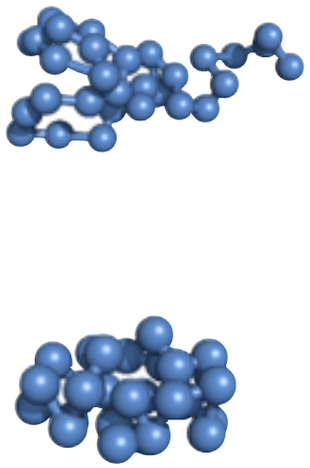


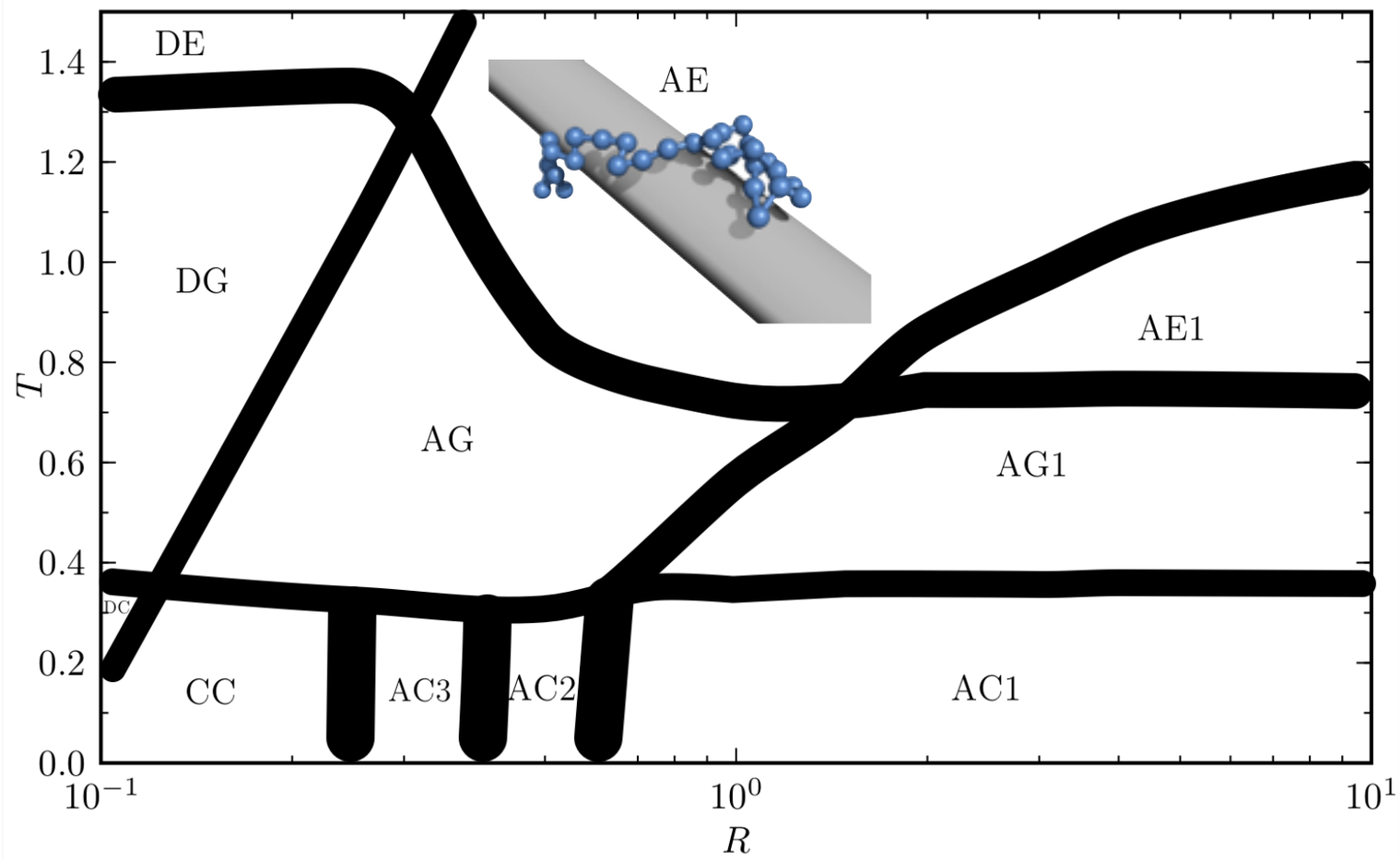


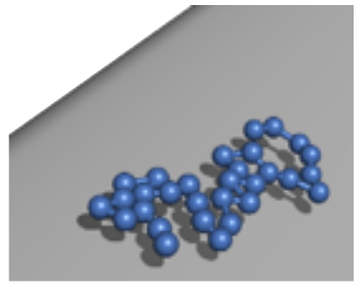


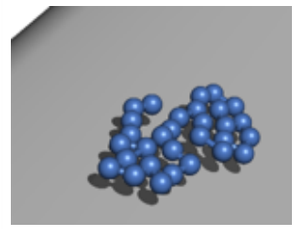
Adsorption of a coarse-grained flexible polymer on nanocylinders

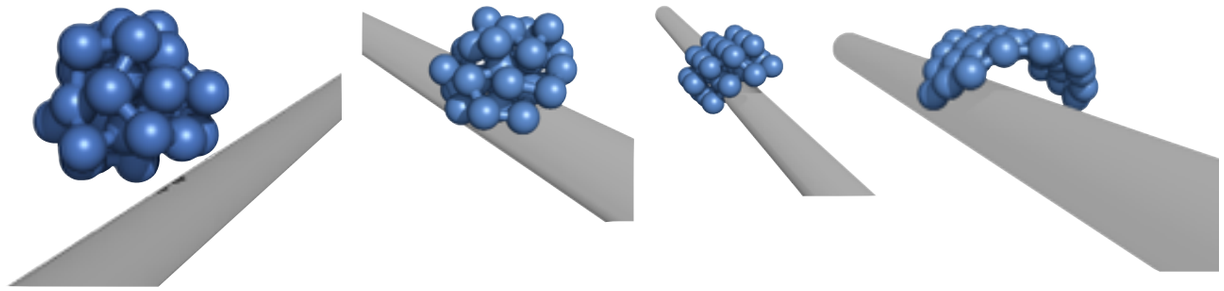
Pseudo phase diagram for $\varepsilon_c = 5.0$

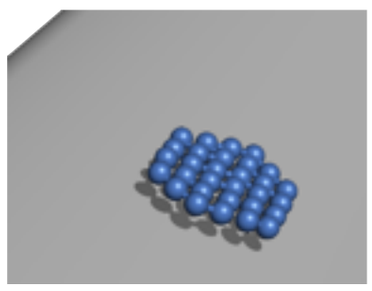












Adsorption of a coarse-grained flexible polymer on nanocylinders

Summary and Comparison

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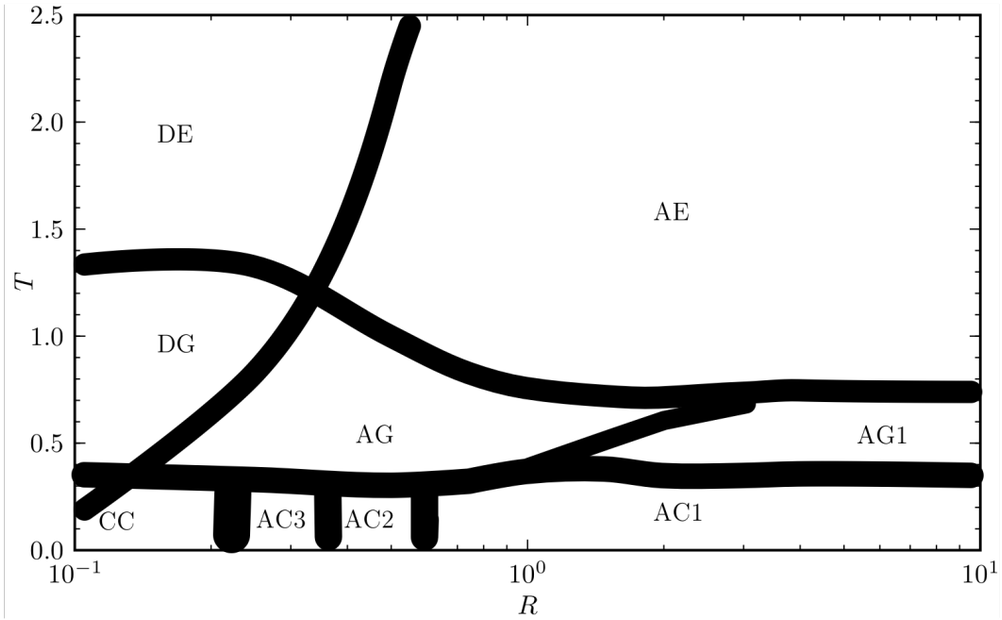
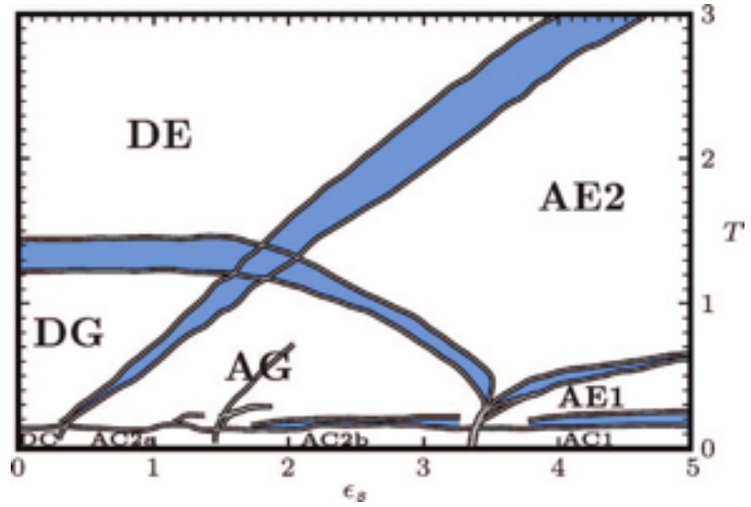
Adsorption of a coarse-grained flexible polymer on nanocylinders

Summary and Comparison

- structural phase diagrams for a 30-mer adsorbed at 5 different materials with 10 radii
- effective surface-monomer attraction proportional to cylinder radius
- multiple layered adsorbed structures identified
- desorbed structures similar to the free polymer structures





M. Möddel, M. Bachmann, W. Janke, J. Phys. Chem. B,**113**, 3314 (2009).

- phase diagram comparable to adsorption study on walls

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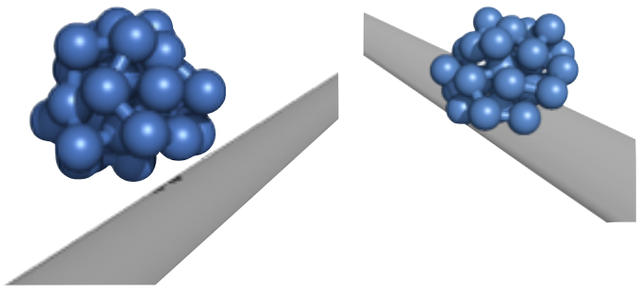
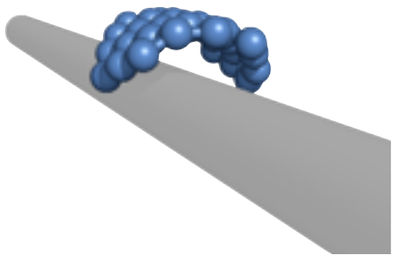
Adsorption of a coarse-grained flexible polymer on nanocylinders

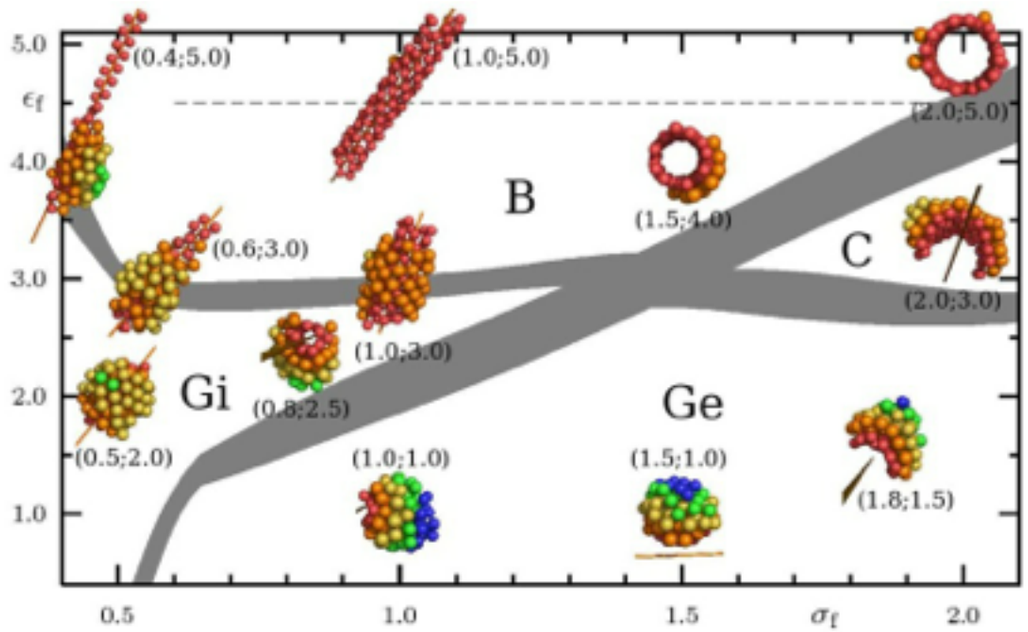
Summary and Comparison

- “exterior droplets” as in nanowire study found



- “clamshell” wrapping





T. Vogel, M. Bachmann, Phys. Rev. Lett. **104**, 198302 (2010).

- complete wrapping not found due to short chains

- no penetrated droplets, since monomer-surface attraction is very small for small radii

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Thank you for your attention.