Aggregation of semiflexible polymers under constraints

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Marco Mueller, Philipp Schierz, Martin Marenz and Wolfhard Janke

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Universität Leipzig, Germany

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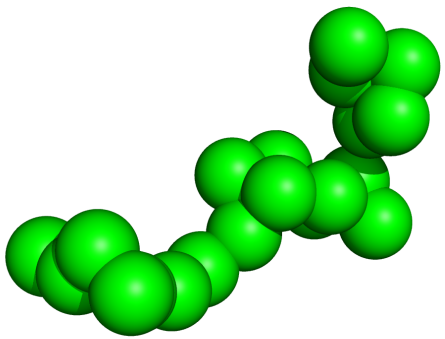
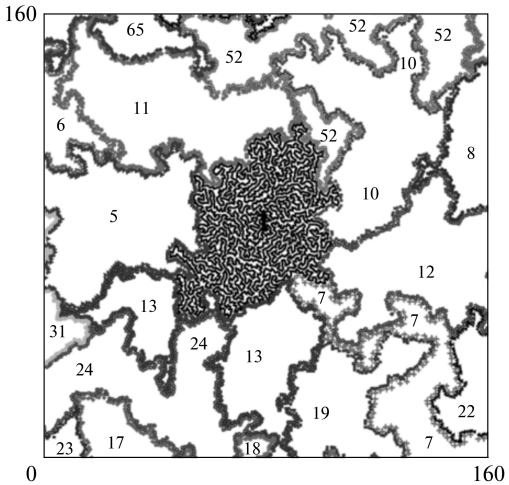
Setting the scope

single



isolated

many



melts*

*taken from Schulmann et al., Polymer Science **55**, 181 (2013).

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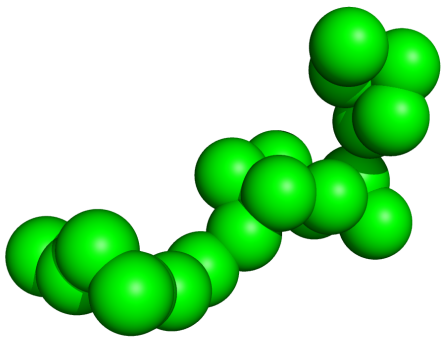
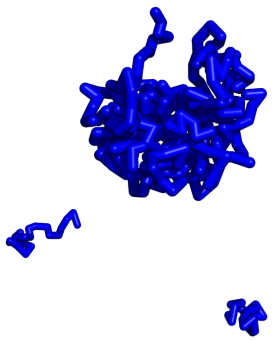


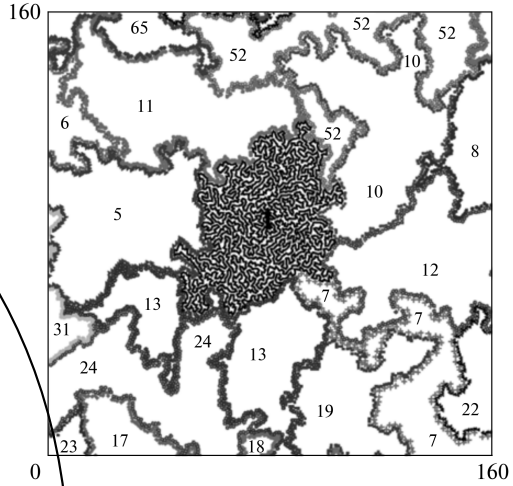
isolated

few



mesoscopic

many



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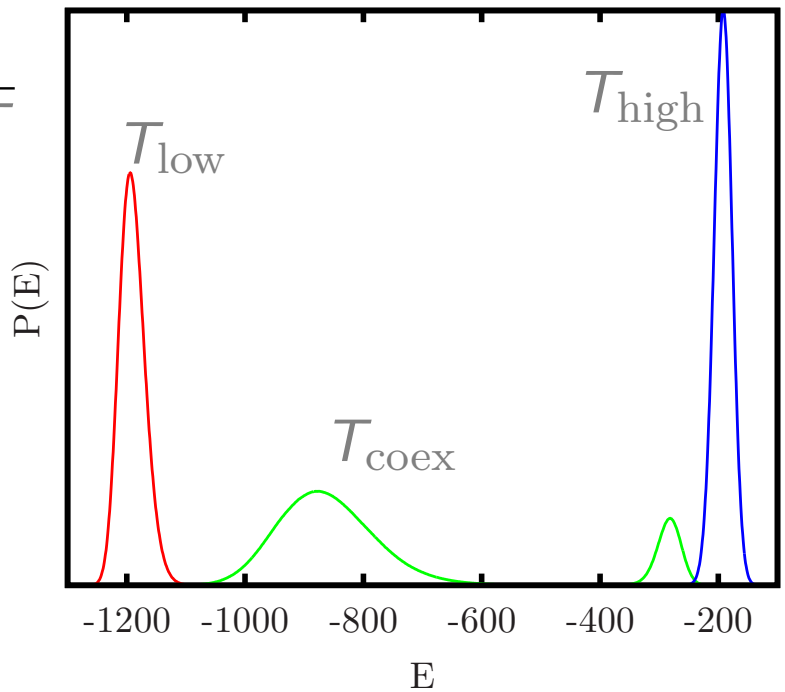
Method: Multicanonical Markov Chain Monte Carlo[1]

Attempt to cover full temperature range with a single simulation.

$$Z_{\mathrm{can}} = \sum_E \Omega(E) e^{-\beta E}, \quad \beta = \frac{1}{k_B T}$$



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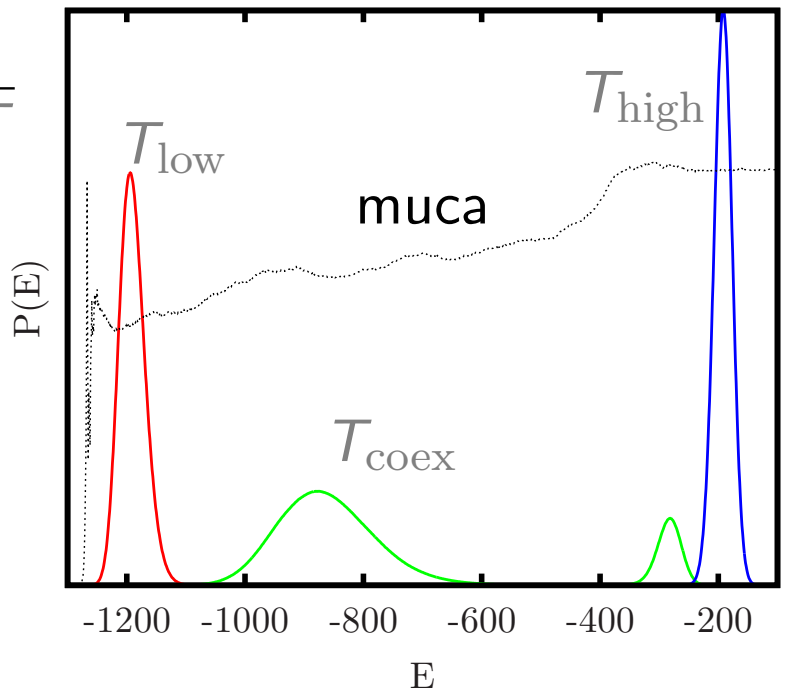
$$\downarrow$$

$$Z_{\mathrm{muca}} = \sum_E \Omega(E) W(E)$$



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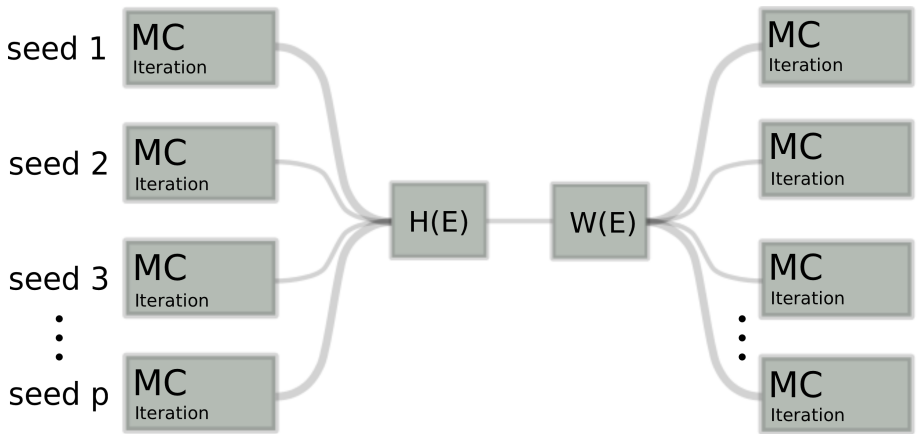
Parallel MUCA[2]

Distribute the time-consuming iteration process onto independent Markov Chains



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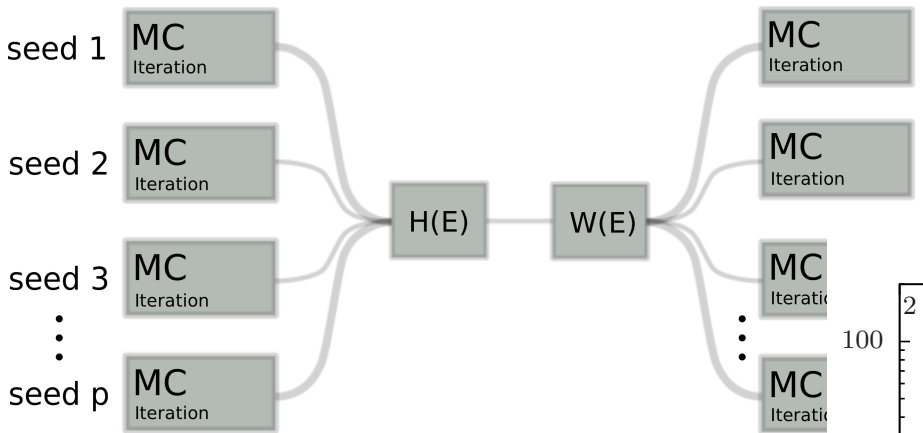

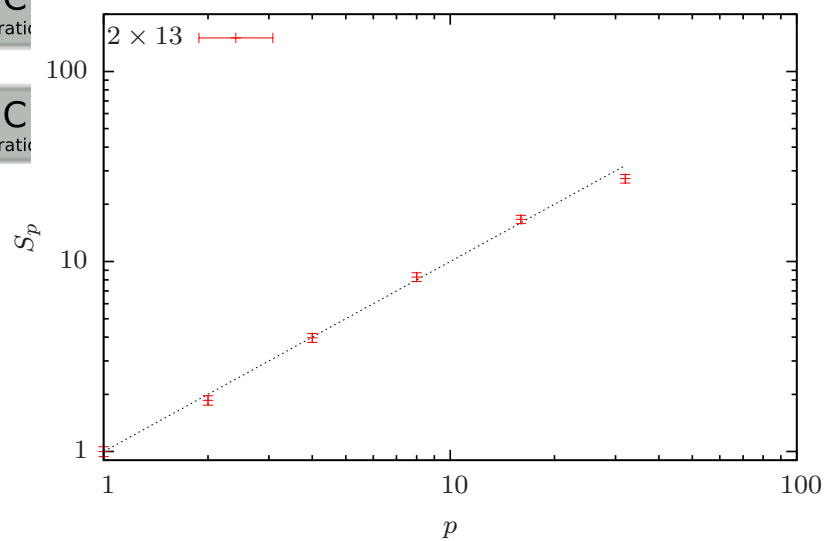

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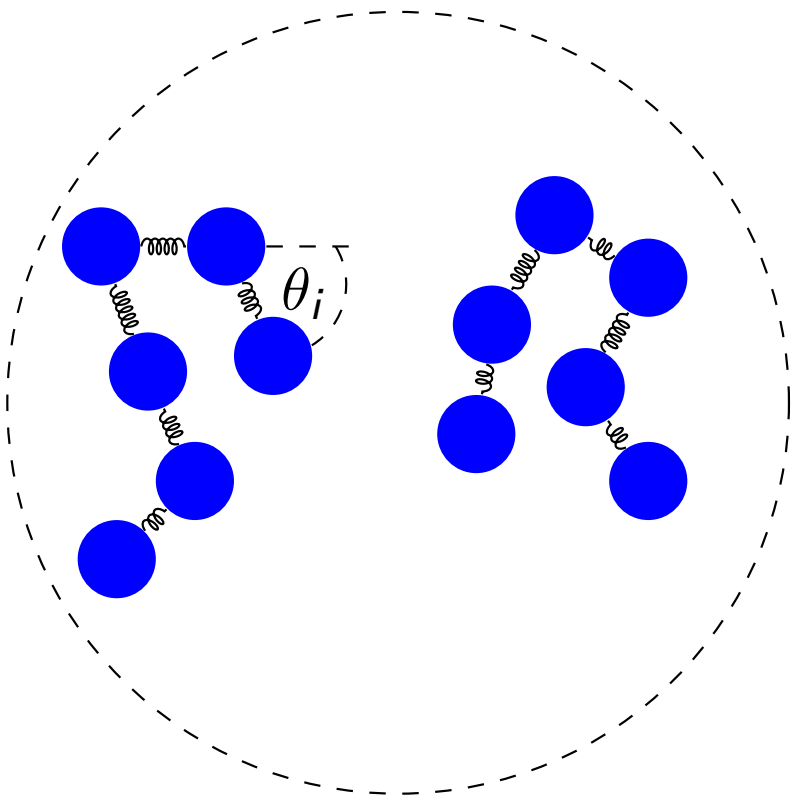
Semiflexible Homopolymers



Energy contributions:

- non-bonded (LJ):

$$\sum_{i,j} 4\epsilon \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right)$$

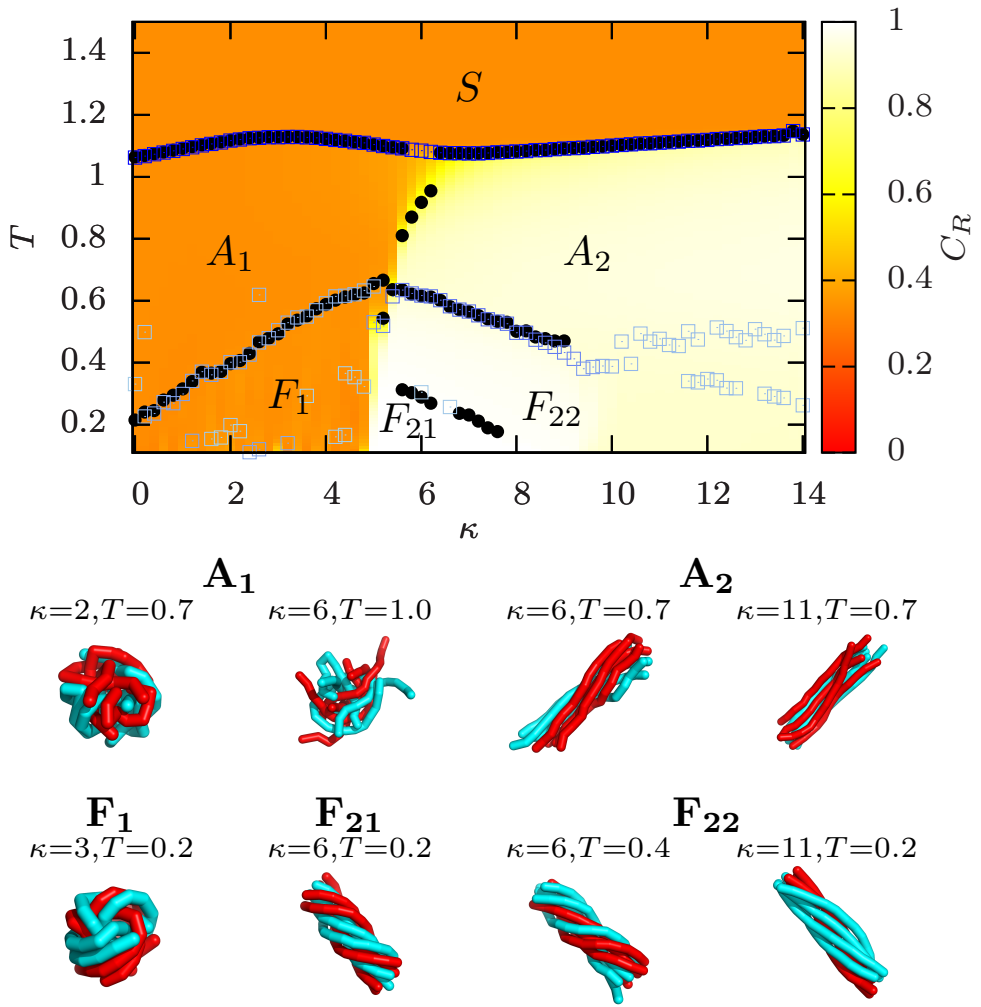
- bonded (FENE):

$$\sum_i -\frac{K}{2} R^2 \ln \left(1 - \left(\frac{r_{i,i+1} - r_0}{R} \right)^2 \right)$$

- bending (WLC):

$$\sum_i \kappa (1 - \cos \theta_i)$$

Effect of Stiffness for 8 polymers $(N = 13)$[3]



$$C_R = \frac{2}{M(M-1)} \sum_{i<j} \left(\hat{\mathbf{R}}_i \hat{\mathbf{R}}_j \right)^2$$

Structural motifs range from amorphous aggregates to polymer bundles.

$$\rho = MN/L^3 = 0.001$$

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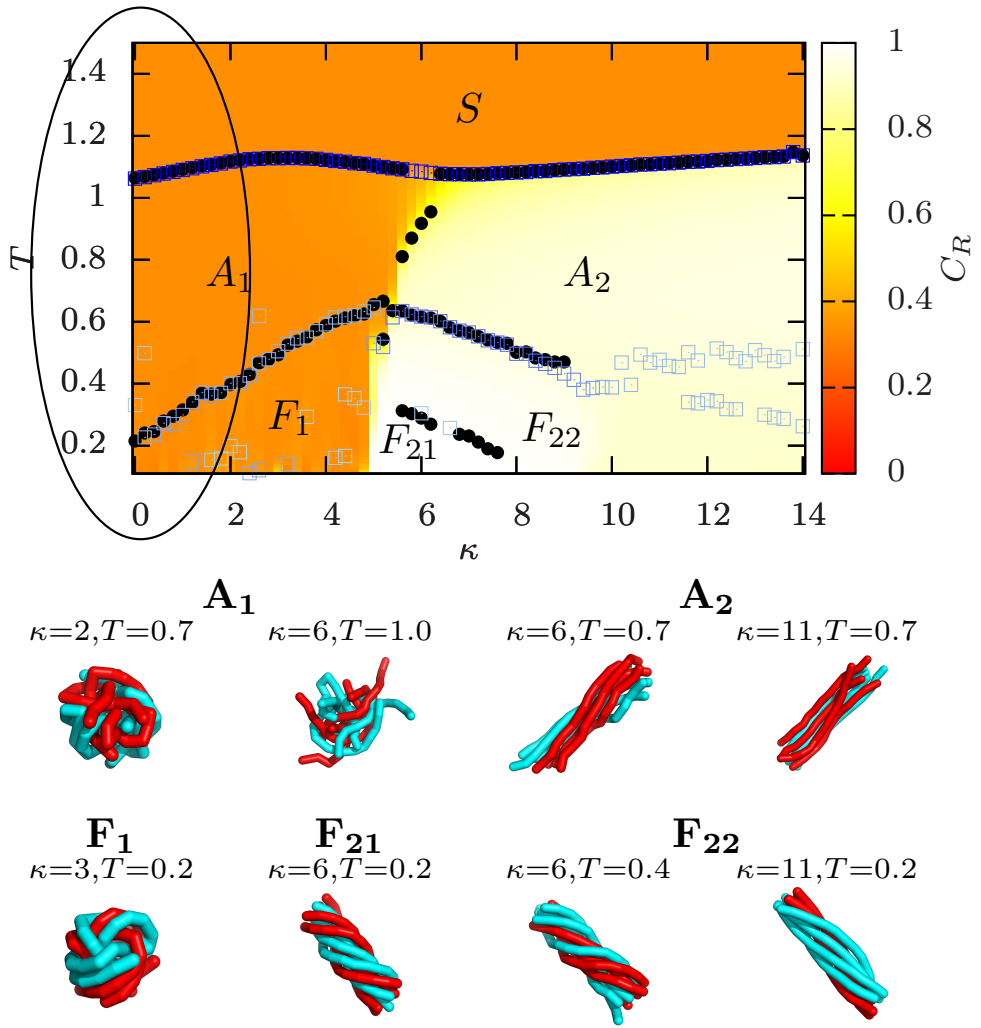

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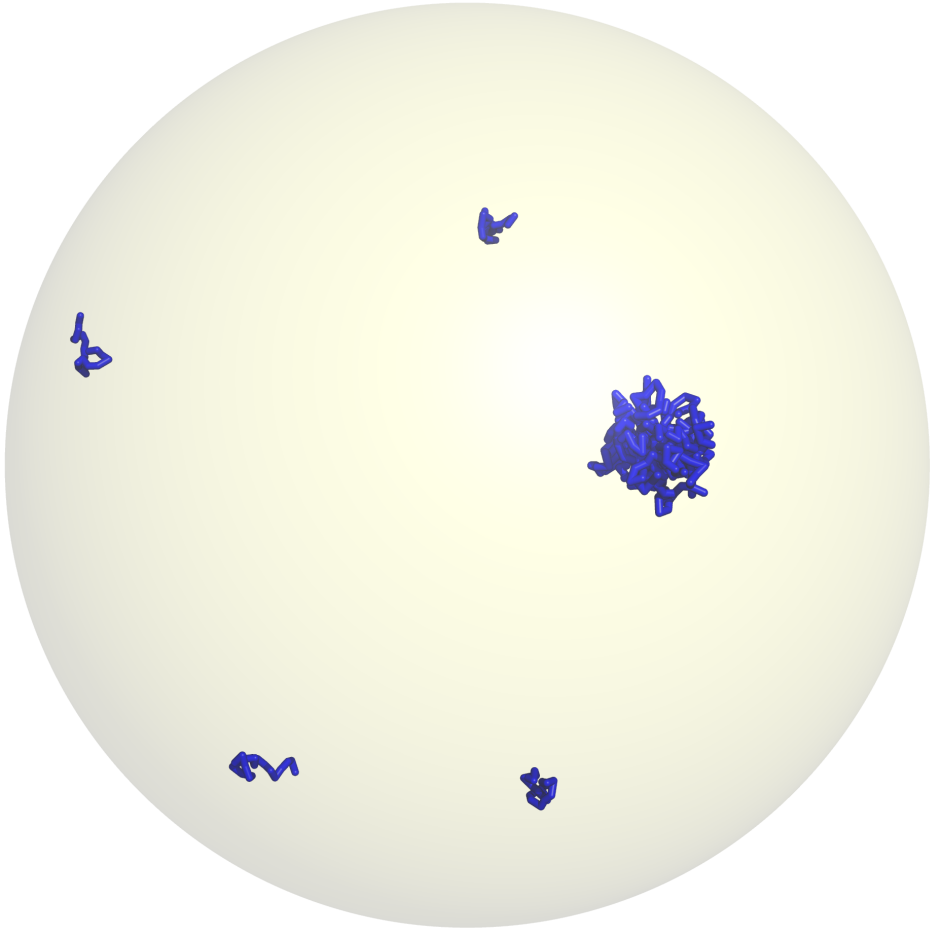
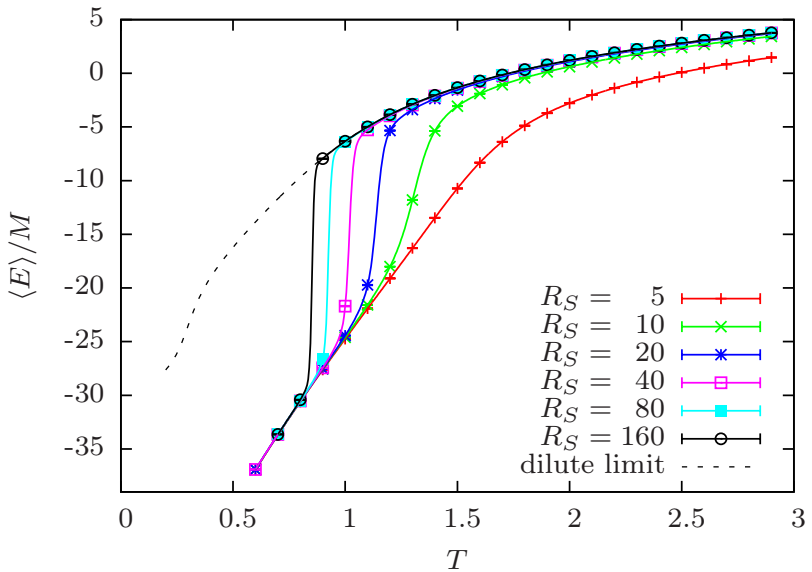
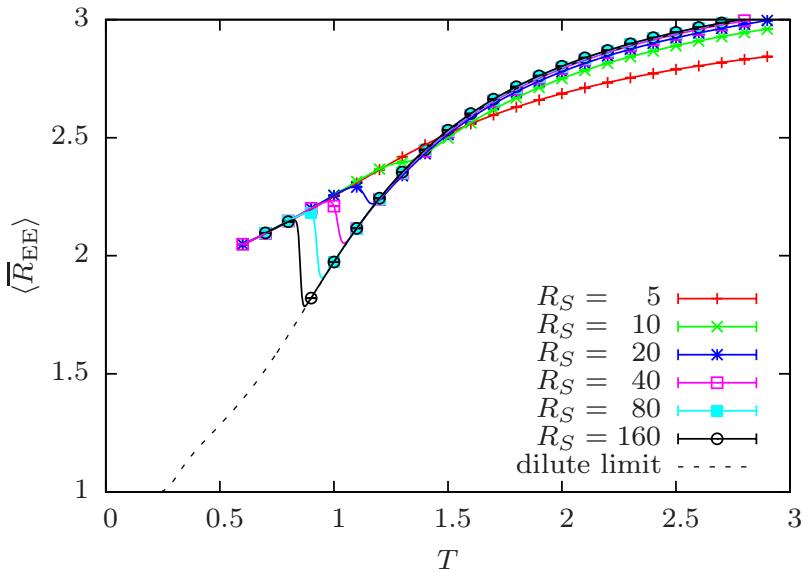


Isolated Chain approximation[4]

Flexible ($\kappa = 0$, 8×13):





$R_S \to \infty$: isolated chain approximation for $T = 0$.

volume fraction of multi-polymer system: $\Phi = NM \left(\frac{r_0}{2}\right)^3 / R_S^3$

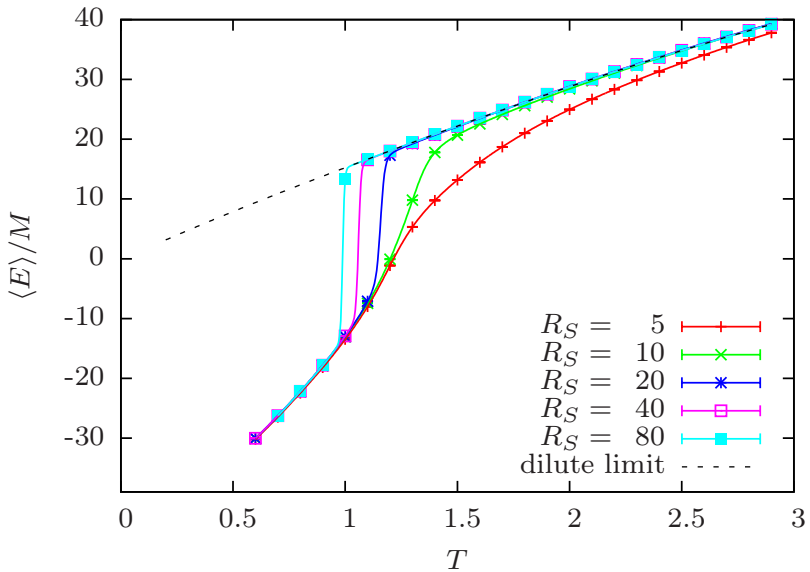
intrinsic volume fraction of single coil: $\Phi^* \simeq \frac{N\left(\frac{r_0}{2}\right)^3}{R_{\mathrm{EE}}^3}$, $R_{\mathrm{EE}} \simeq r_0 N^\nu$

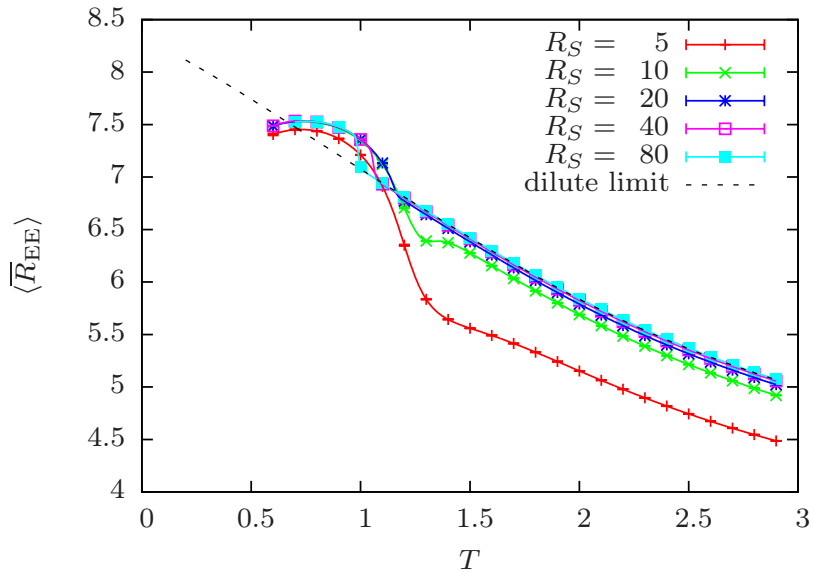
semi-dilute: $R_S^c \simeq r_0 M^{1/3} N^\nu \approx 6.3$

[4] J.Z., M. Mueller, P. Schierz, M. Marenz, and W. Janke, J. Chem. Phys **141**, 114908 (2014).

Isolated Chain approximation[4]

Stiff ($\kappa = 9$, 8×13):





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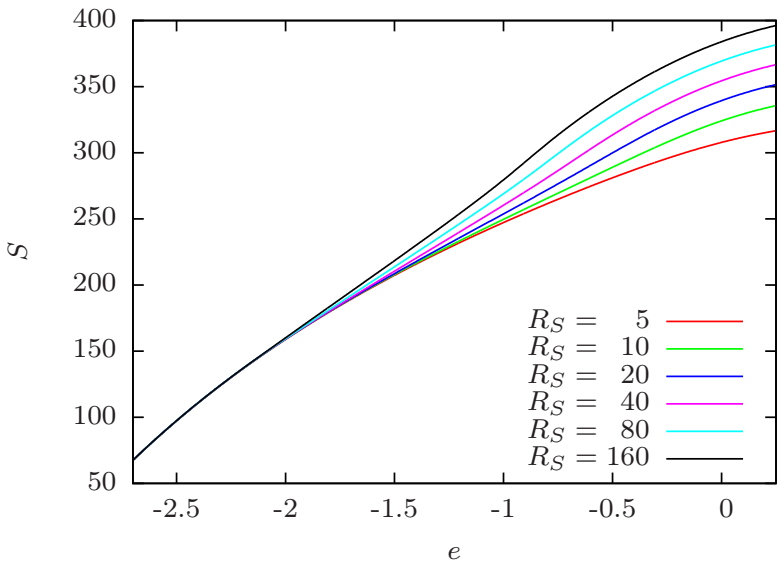
Relation between aggregation temperature and density[4]



Gibbs Construction:

$$\beta_{\mathrm{agg}} = \frac{S(E_{\mathrm{sep}}) - S(E_{\mathrm{agg}})}{\Delta E}.$$

Ideal gas approximation:

$$S(E_{\mathrm{sep}}) \sim \ln\left[\left(\frac{4\pi}{3}R_S^3\right)^M\right] \propto M \ln R_S$$

Assume $\Delta E = M\Delta e$ and $S(E_{\mathrm{sep}}) >> S(E_{\mathrm{agg}})$

$$\beta_{\mathrm{agg}}(R_S) \sim \ln R_S + \mathrm{const} \sim -a_1 \ln \rho + a_2.$$[5]

[4] J.Z., M. Mueller, P. Schierz, M. Marenz, and W. Janke, J. Chem. Phys **141**, 114908 (2014).

[5] R. Ni, S. Abeln, M. Schor, M. A. C. Stuart, and P. Bolhuis, Phys. Rev. Lett. **111**, 058101 (2013).

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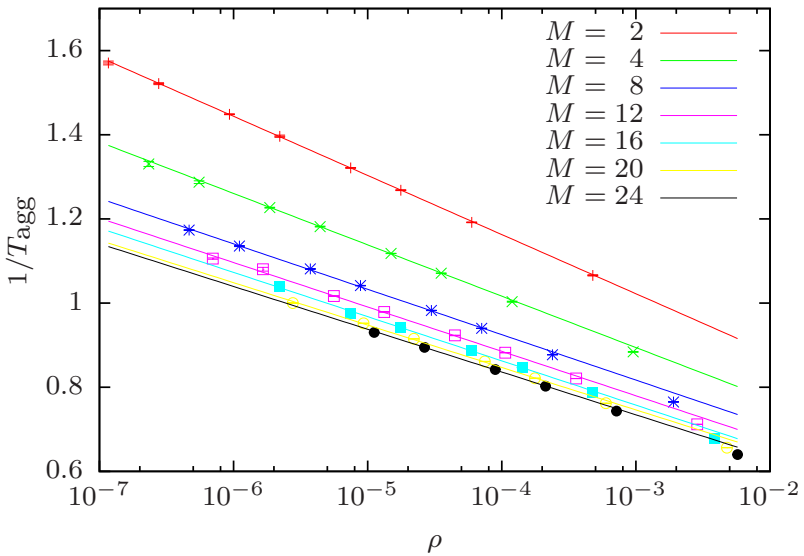

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Finite-size corrections for M^4

Assume a large fraction of polymers in aggregate with $R_{\mathrm{gyr}} \sim M^{1/3}$.
Due to surface effects of aggregate, expect finite-size corrections of order R^{-1}

$$T_{\mathrm{agg}}(M, \rho) \propto \left(1 + s(\rho) M^{-1/3} + \mathcal{O}\left(M^{-2/3}\right)\right),$$

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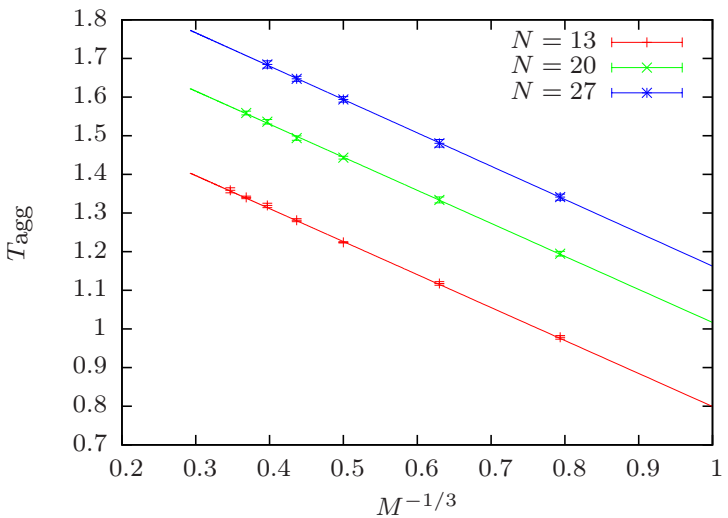

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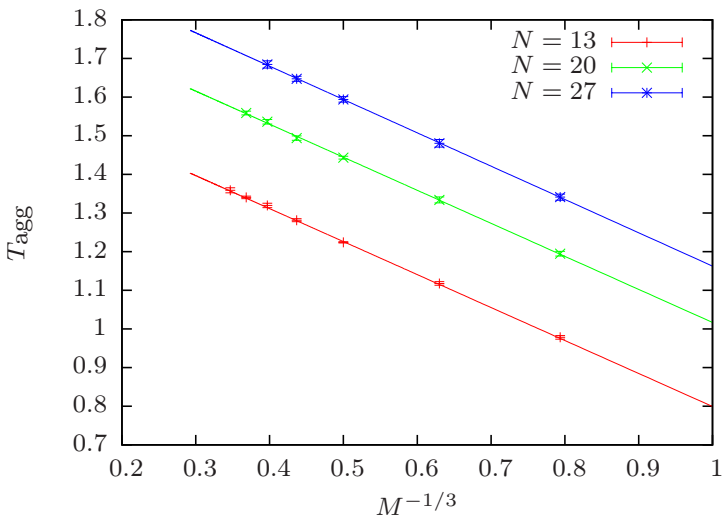

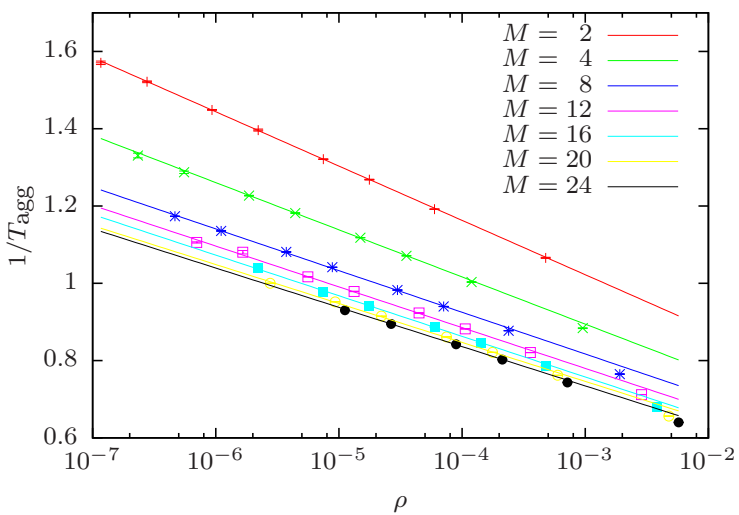

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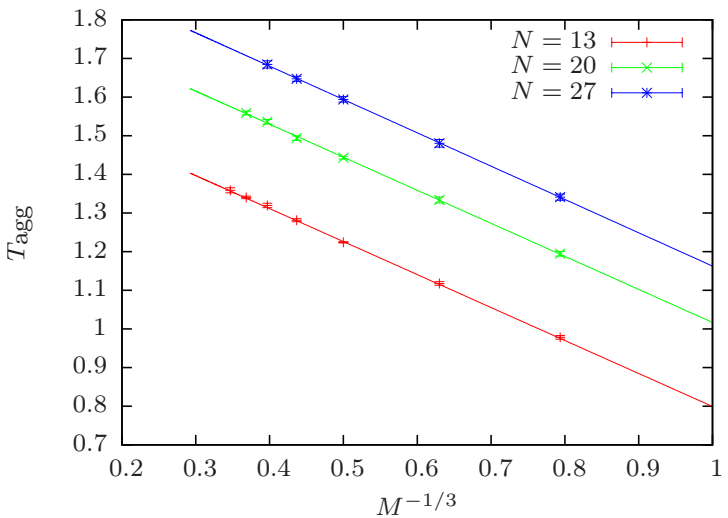

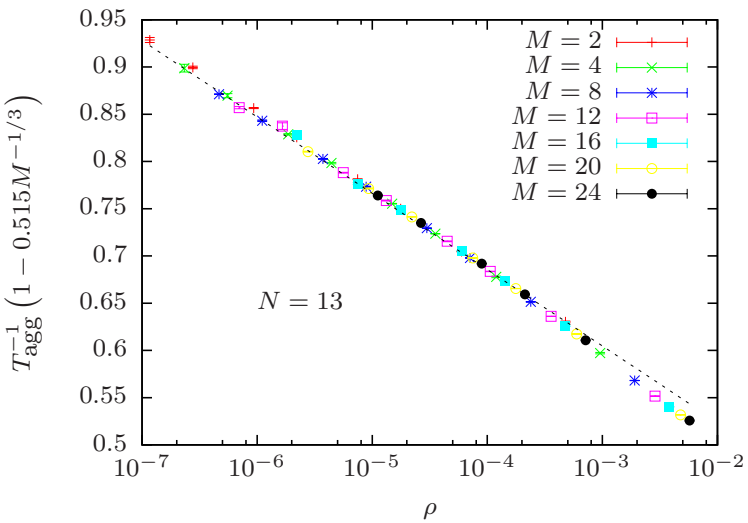

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Summary

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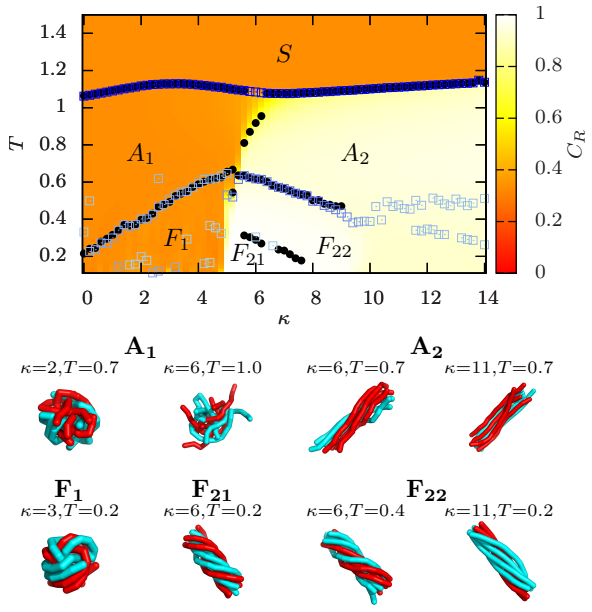

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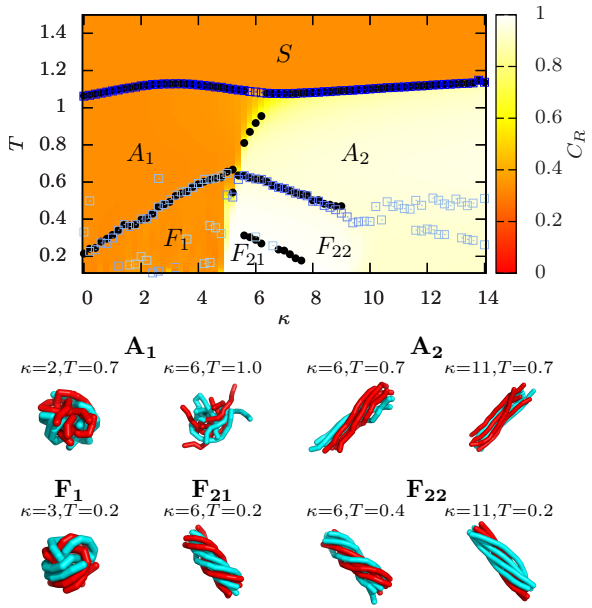
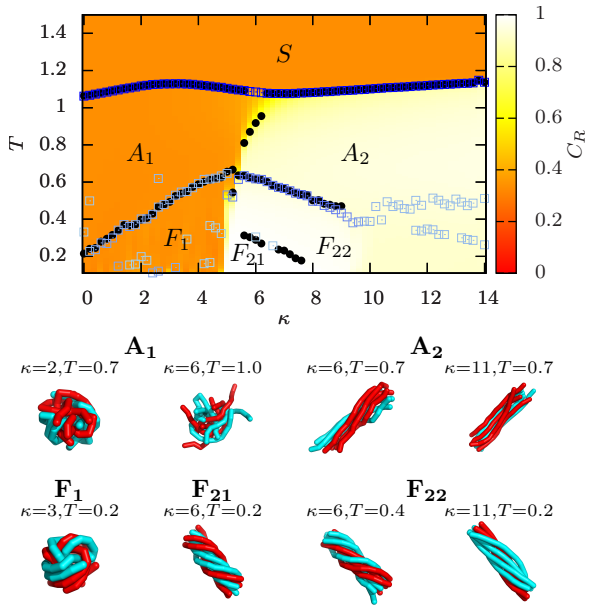
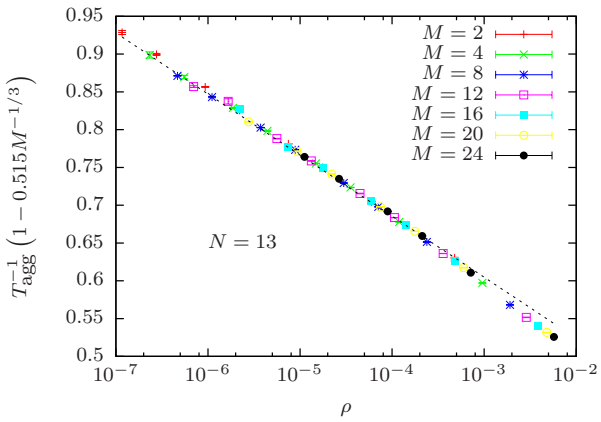


Summary

- Key role of stiffness on polymer aggregation
- Competition between collapse and aggregation yields lower temperature bound for isolated chain approximation
- General relation between aggregation temperature and density in the mesocopic regime.





Acknowledgments

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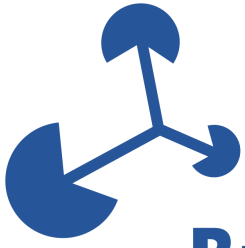

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