Autocorrelation Study for a Coarse-Grained Polymer Model

Kai Qi and Michael Bachmann
The Center for Simulational Physics
The University of Georgia

Talk given at the 14th Leipzig Workshop - 28/11/2013

Outline

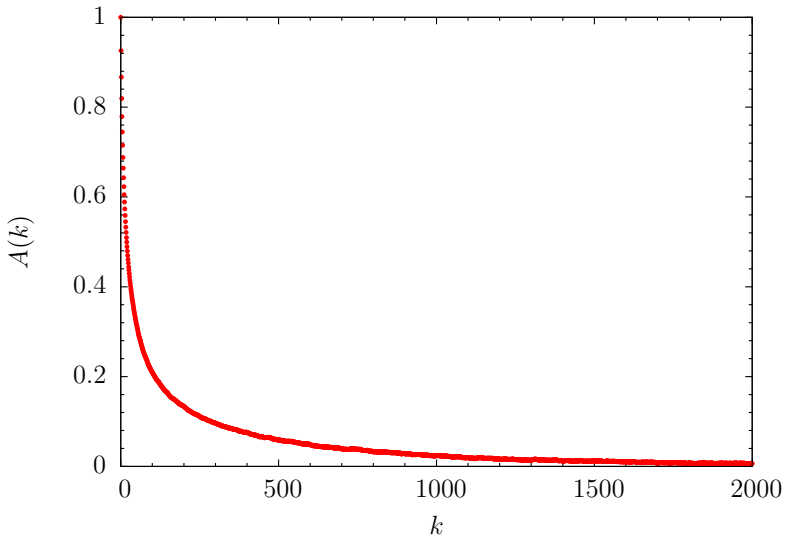
Autocorrelation Function and Autocorrelation Time

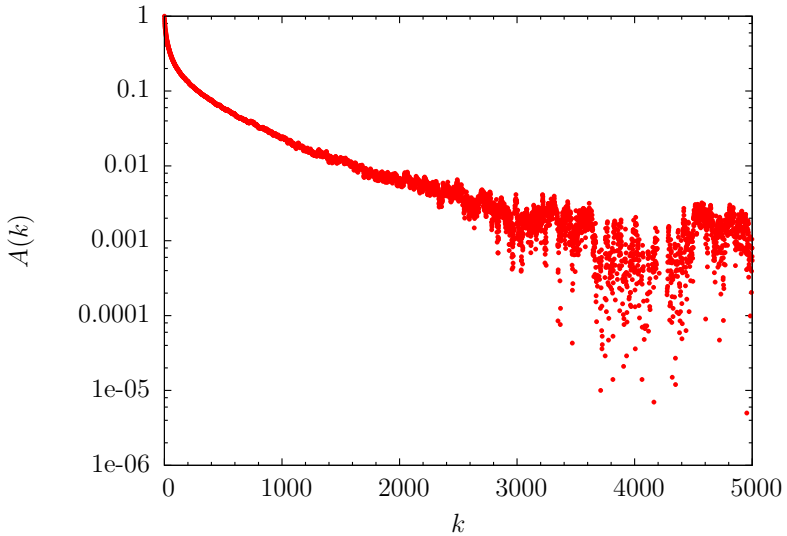
Autocorrelation Function:

- $A(k) = \frac{\langle O_m O_{m+k} \rangle - \langle O_m \rangle^2}{\langle O_m^2 \rangle - \langle O_m \rangle^2}$
  where O is an observable, m indicates any point in the time series
- Describe the correlation between two measurements with time displacement k

Exponential Autocorrelation Time:

- $A(k) \overset{k \to \infty}{\longrightarrow} e^{-k/\tau_{O,\text{exp}}}$
- $\tau_{O,\text{exp}}$ is the exponential autocorrelation time
- For large k, behavior is non-exponential. (statistics issue)





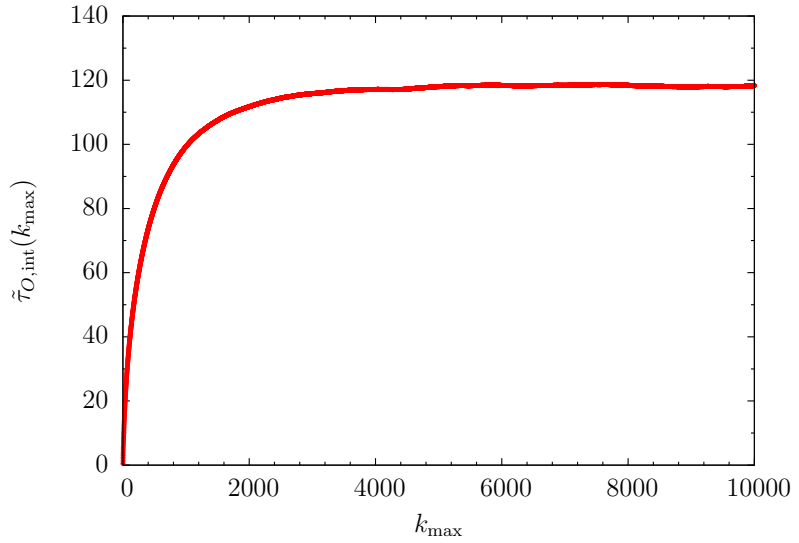
Integrated Autocorrelation Time:

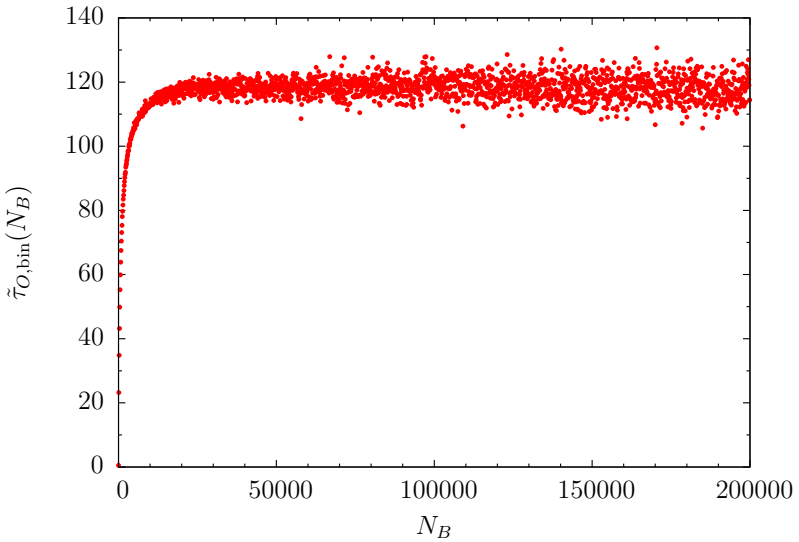
- $\tilde{\tau}_{O,\mathrm{int}}(k_{\max}) = \frac{1}{2} + \sum_{k=1}^{k_{\max}} A(k)$
- Since $A(k) \overset{k\to\infty}{\longrightarrow} 0$, the estimator will finally converge to a constant.

Binning Analysis:

- $\tilde{\tau}_{O,\mathrm{bin}}(N_B) = N_B \tilde{\sigma}^2_{\overline{O}^B,c}/2\tilde{\sigma}^2_O$

  where N_B is the binning block size, $\tilde{\sigma}^2_{\overline{O}^B,c}$ is the variance of an individual binning block average and $\tilde{\sigma}^2_O$ is the variance of an individual measurement
- As N_B increases, $\tilde{\tau}_{O,\mathrm{bin}}$ will converge to $\tilde{\tau}_{O,\mathrm{int}}$.





Model

- **Number of Monomers:** $N_m = 30, 55$
- **Energy for Conformation ζ:**

$$E(\zeta) = \sum_{i=1}^{N-2} \sum_{j=i+2}^{N} V_{\mathrm{LJ}}^{\mathrm{mod}}(r_{ij}) + \sum_{i=1}^{N-1} V_{\mathrm{FENE}}(r_{ii+1})$$

Non-bonded Lennard-Jones Potential:

$$V_{\mathrm{LJ}}^{\mathrm{mod}}(r_{ij}) = V_{\mathrm{LJ}}(r_{ij}) - V_{\mathrm{LJ}}(r_c)$$

with

$$V_{\mathrm{LJ}}(r_{ij}) = 4\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

where $\sigma = r_0/2^{1/6}$ $(r_0 = 1)$ and cut off distance $r_c = 2.5\sigma$

FENE Potential:

$$V_{\mathrm{FENE}}(r_{ii+1}) = -\frac{K}{2}R^2 \ln\left[1 - \left(\frac{r_{ii+1} - r_0}{R}\right)^2\right]$$

where $R = 3/7$ and $K = 19.6$

- **Quantities:**

Energy: $\langle E \rangle$

Number of Contacts: $\langle N_c \rangle$

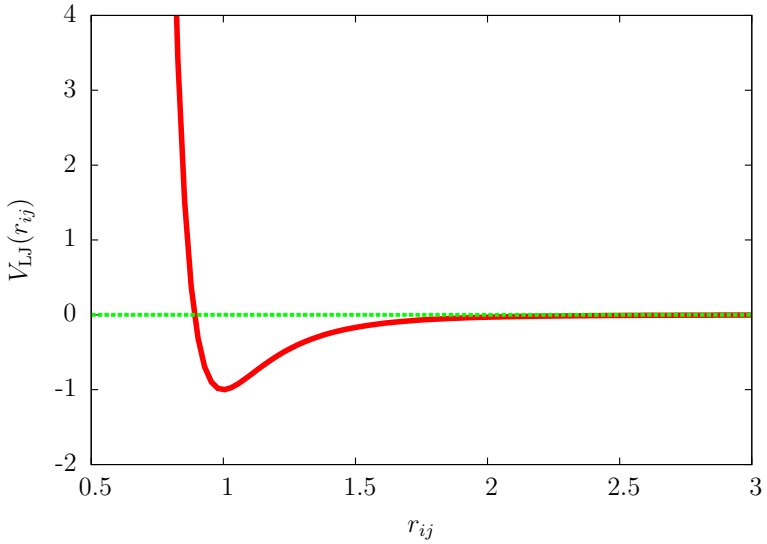
Square of End to End Distance:

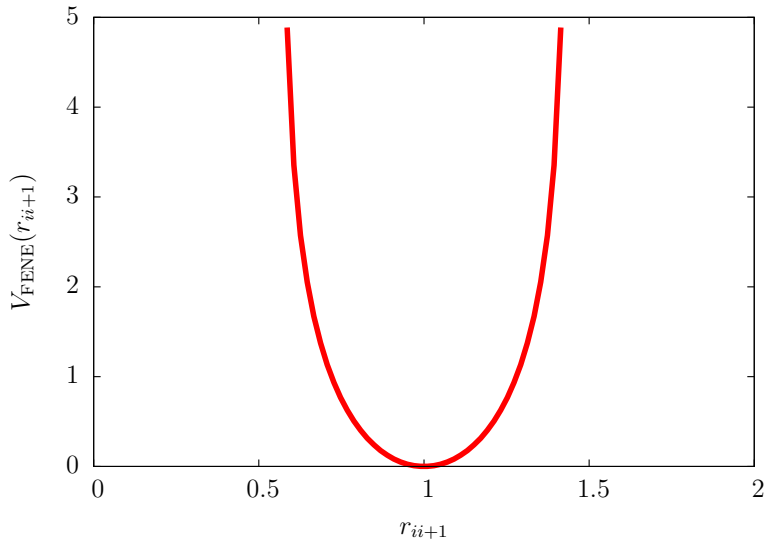
$$\langle R_{ee}^2 \rangle = \langle (\vec{r}_{N_m} - \vec{r}_1)^2 \rangle$$

Square of Radius of Gyration:

$$\langle R_{gyr}^2 \rangle = \langle \frac{1}{N_m} \sum_{i=1}^{N_m} (\vec{r}_i - \vec{r}_{c.o.m.})^2 \rangle$$

($\vec{r}_{c.o.m.}$ is the position of the center of mass)

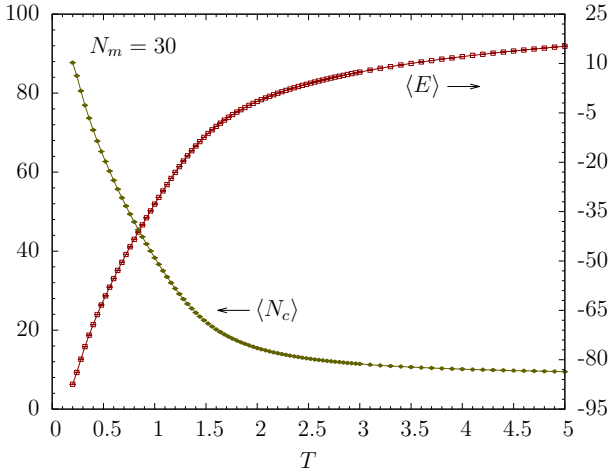


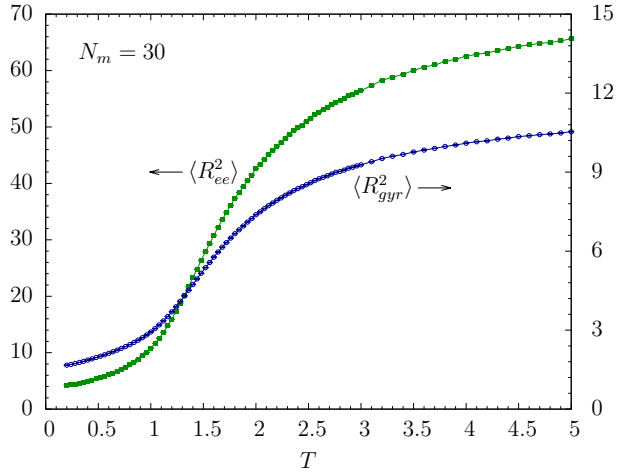


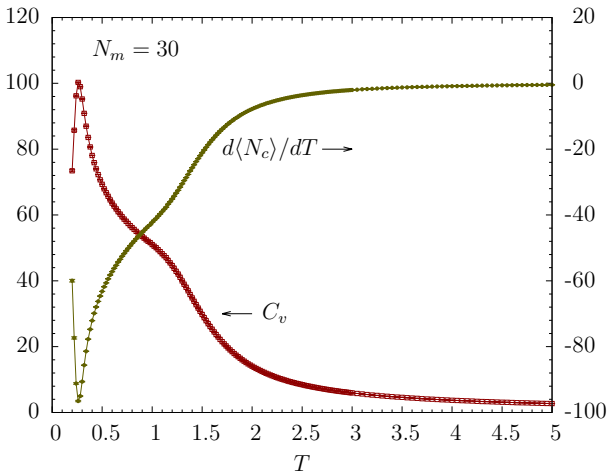
Algorithm

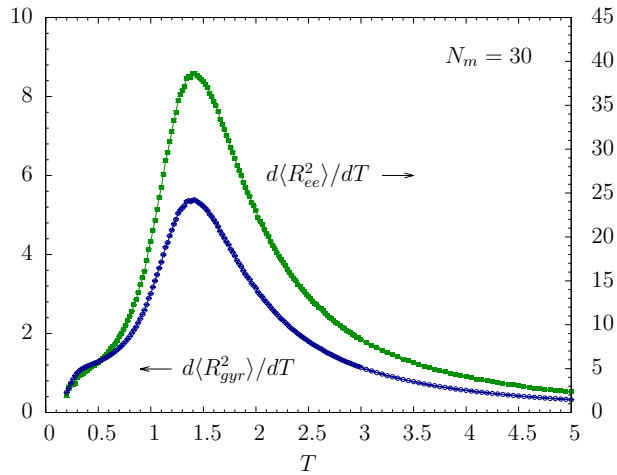
- **Algorithm:**
  Metropolis Monte Carlo method
- **Update Method:**
  random local displacements of single monomers (i.e., random move in a small cubic box with edge length $d = 0.3r_0$)
- **Reasons:**
  Metropolis algorithm works in canonical ensemble and generates the true physical distribution (Boltzmann distribution).
  Displacement update is similar to the Brownian motion process.

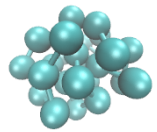
"Phase" Transitions for a 30-mer



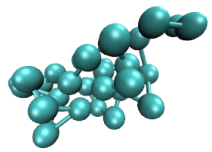




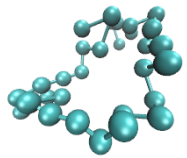




"solid" phase



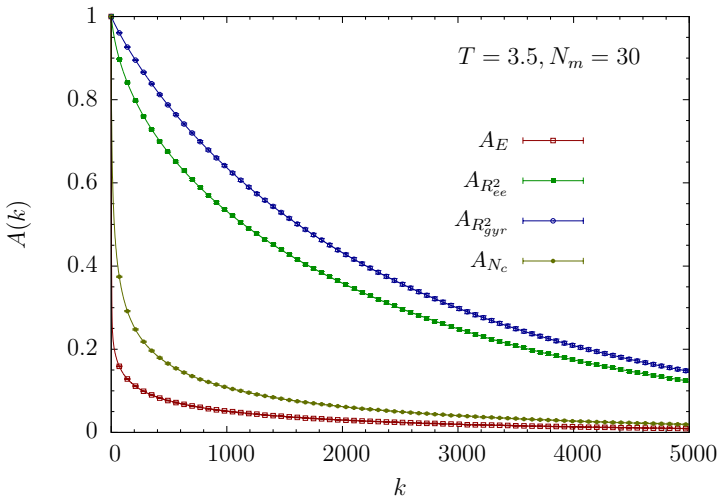
globular phase ("liquid")



random-coil phase ("gas")

- $T \approx 0.28$, globular phase $\longleftrightarrow$ "solid" phase (freezing transition, 2nd order "phase" transition)
- $T \approx 1.4$, random-coil phase $\longleftrightarrow$ globular phase (collapse transition, 2nd order "phase" transition)

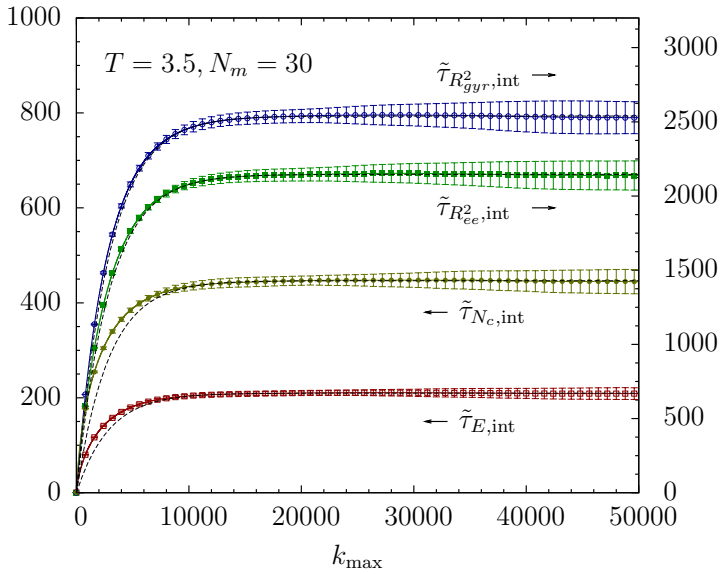
Autocorrelation Times for a 30-mer and a 55-mer

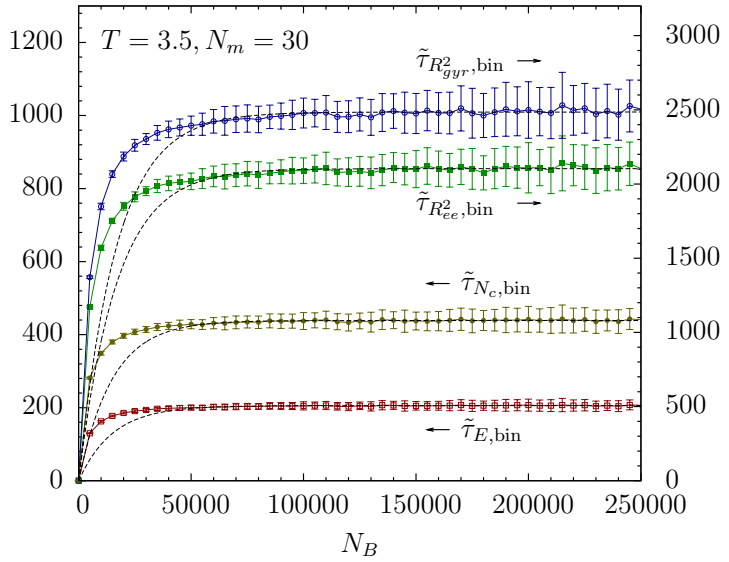


- calculate autocorrelation times at 17 temperatures
- Curve fitting:

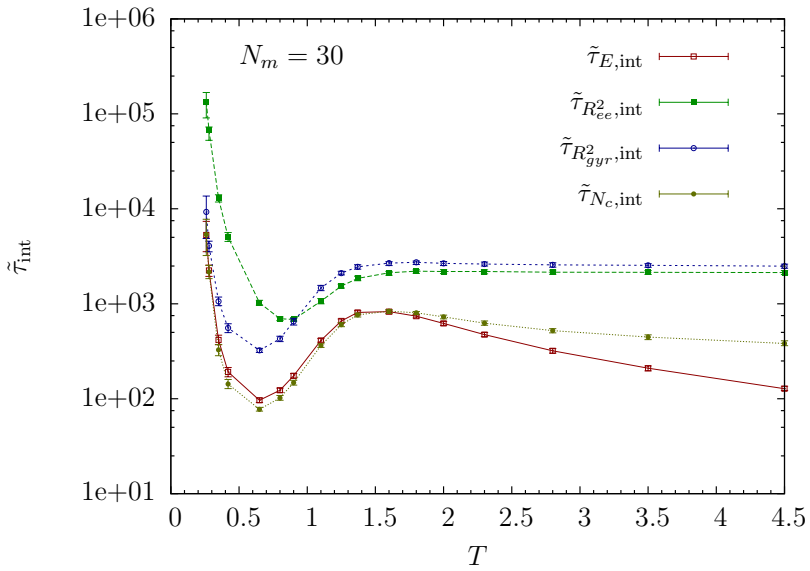
$$f_O(x) = \tau_O^f(1 - e^{-x/x^f})$$

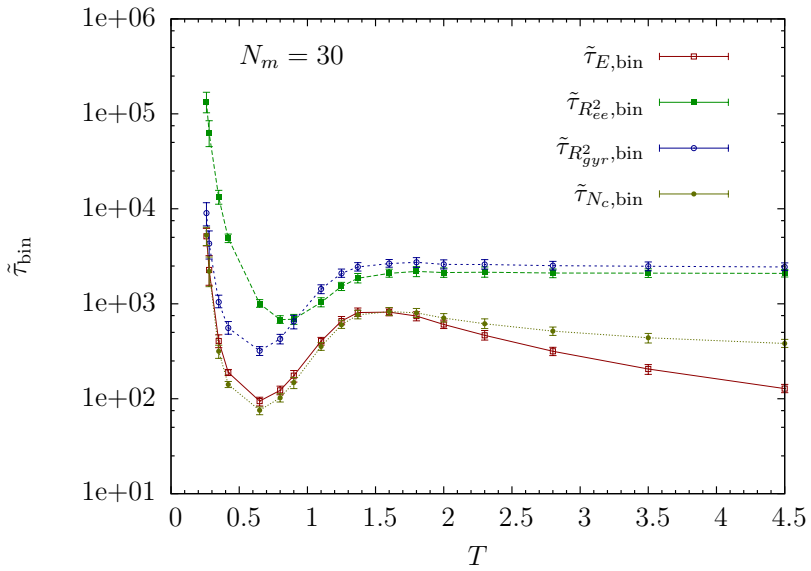
where x is $N_B/k_{\max}$; τ_O^f and x^f are two fit parameters





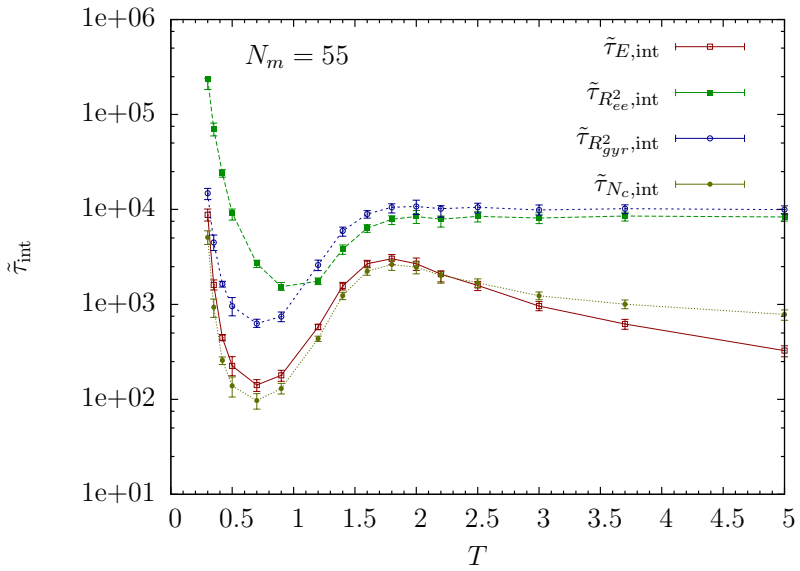
30-mer case:

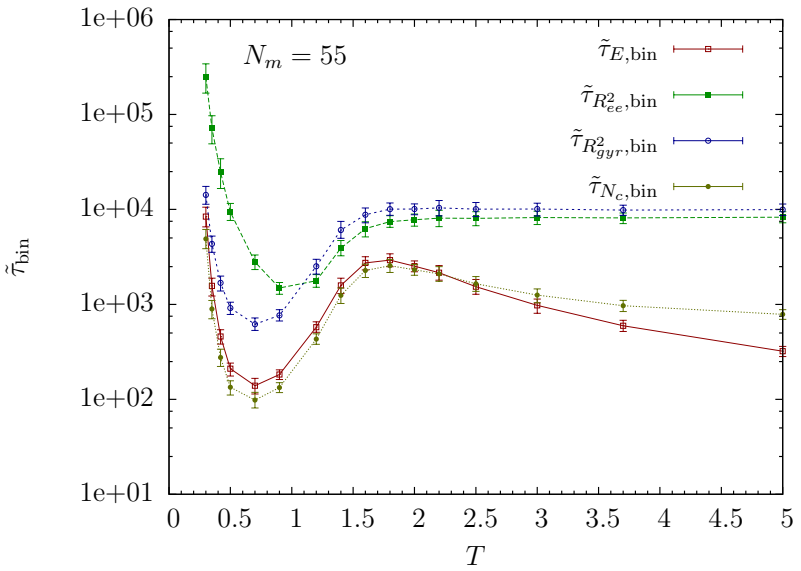




- Autocorrelation time curves estimated from two methods are identical.
- Autocorrelation times diverge near $T = 0.3$ (freezing transition); slowing down occurs at $T \approx 1.4$ (collapse transition).

55-mer case:





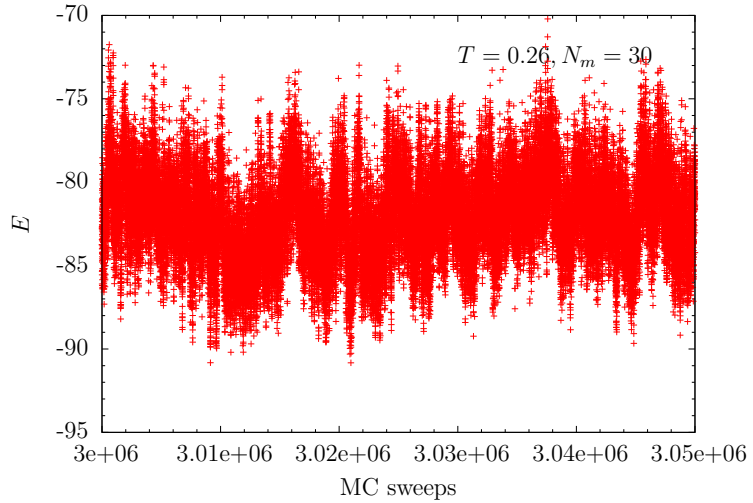
- The same curves appear in the 55-mer case except that all the values become larger.

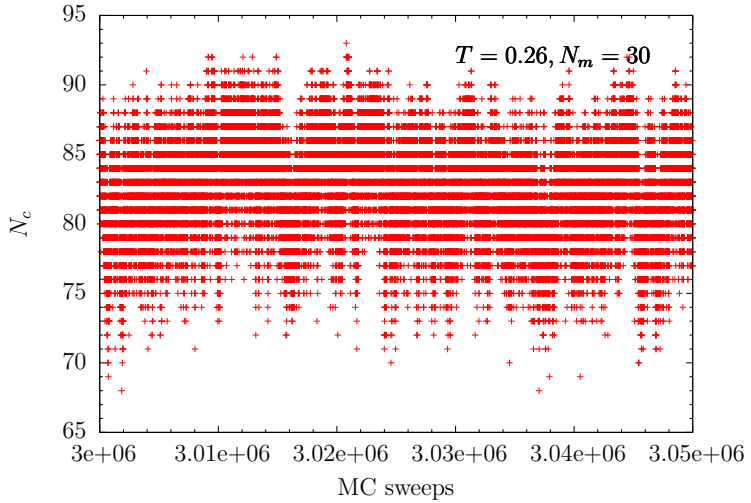
Summary

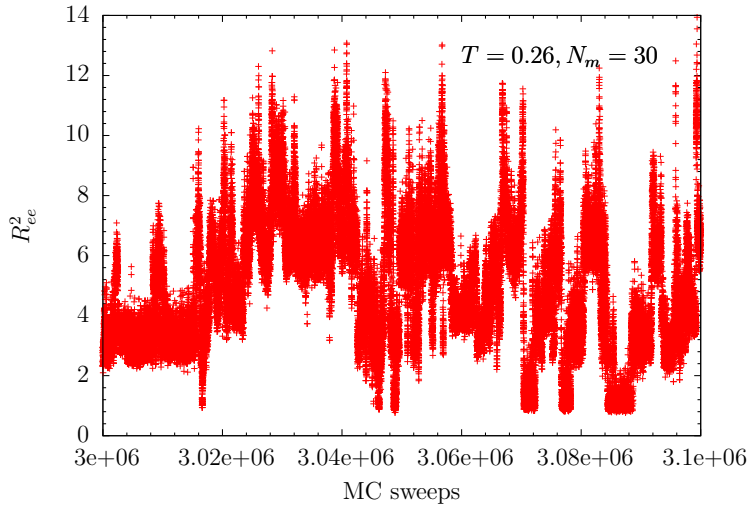
- We use Metropolis algorithm combined with displacement update to do the simulation for a coarse-grained flexible polymer model.
- By using two methods, we've constructed the $\tilde{\tau}_{\mathsf{int}}$ vs. T and $\tilde{\tau}_{\mathsf{bin}}$ vs. T graphs.
- Due to slowing down, an extremal autocorrelation time can be considered as an indicator for the collapse transition.
- This is particularly useful for finite systems, where response quantities do not necessarily exhibit clear indications for pronounced thermal activity.

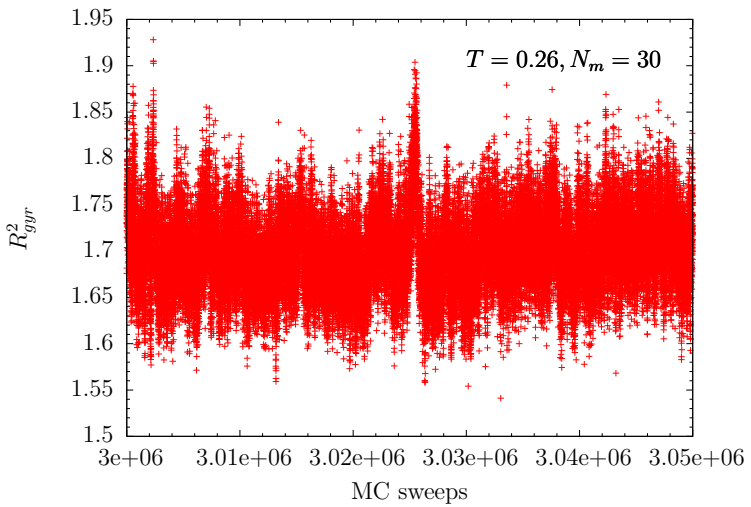
K. Qi and M. Bachmann, *Autocorrelation Study for a Coarse-Grained Polymer Model*, preprint.

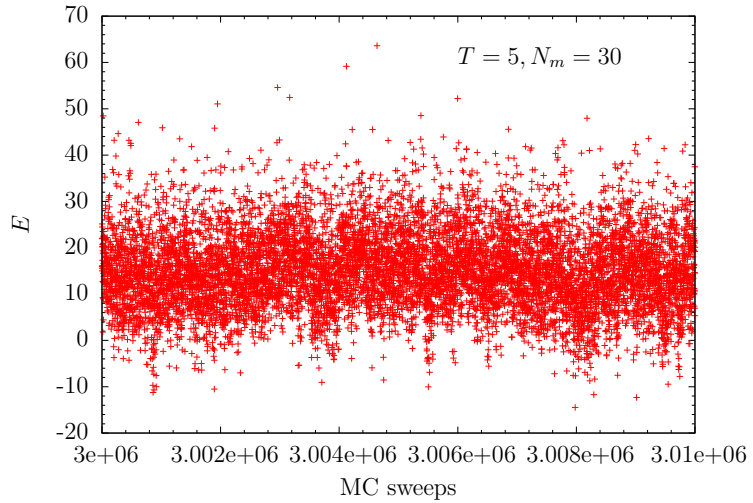
Thank you! Questions?

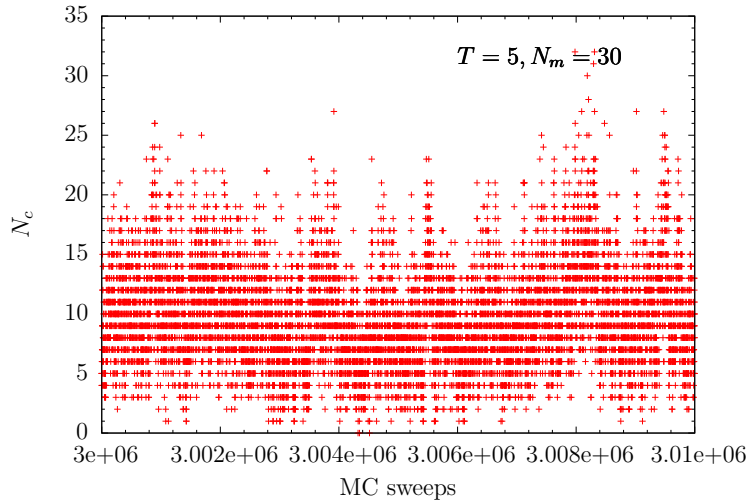

$T = 0.26, N_m = 30$
E
MC sweeps

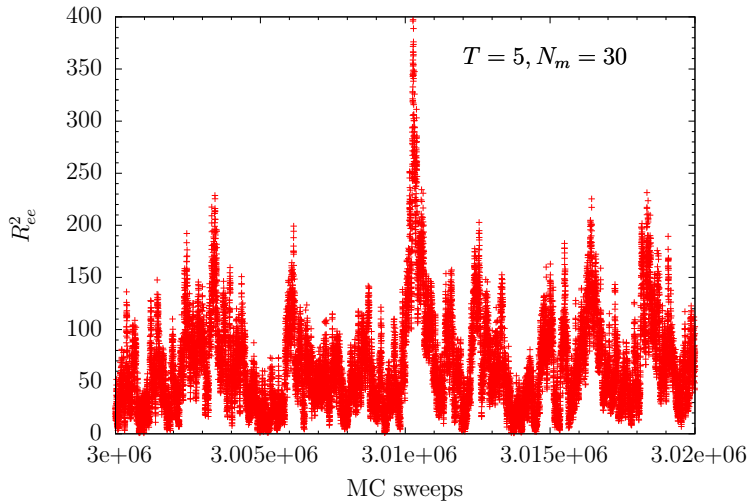

$T = 0.26, N_m = 30$
N_c
MC sweeps

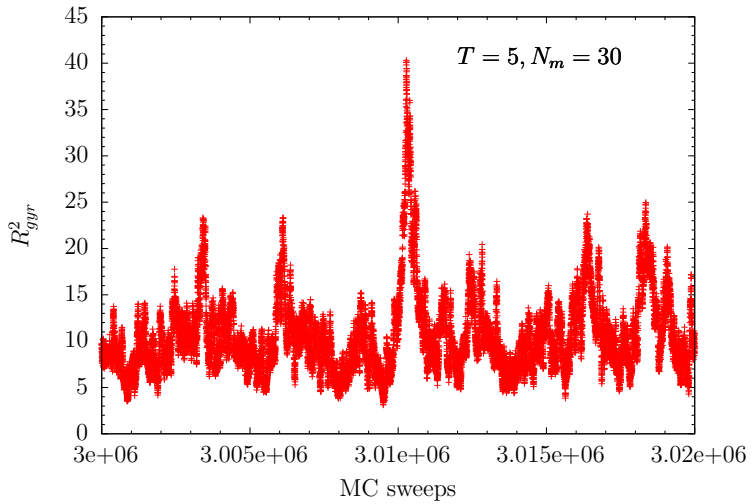

$T = 0.26, N_m = 30$
R^2_{ee}
MC sweeps


$T = 0.26, N_m = 30$
R^2_{gyr}
MC sweeps


$T = 5, N_m = 30$
E
MC sweeps


$T = 5, N_m = 30$
N_c
MC sweeps


$T = 5, N_m = 30$
R^2_{ee}
MC sweeps


$T = 5, N_m = 30$
R^2_{gyr}
MC sweeps