Simulation in Equilibrium

Gun Woo Park

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Preliminary

Instantaneous Pressure Function

Let $\mathscr{P} = [\mathscr{P}_{ij}]$ be a deviatoric part for isotropic instantaneous pressure function is given by the virials:

$$V\mathscr{P} = \sum_{i=1}^{N_{tot}} \mathbf{r}_i \mathbf{F}_i, \tag{1}$$

where N_{tot} be the number of total chains in the box, $\mathbf{r}_i$ be the relative position vector for i-th chain in the system (i.e., connector vector for the chain), and $\mathbf{F}_i$ be a force exerted on the subjected chain.

Because the instantaneous stress tensor is given by $-\mathscr{P}$, we have

$$\tau_{xy} = -\frac{1}{V} \sum_{i=1}^{N_{tot}} x\left[\mathbf{r}_i\right] y\left[\mathbf{F}_j\right]. \tag{2}$$

Preliminary (cont.)

Shear Relaxation Modulus and Viscosity

For given instantaneous shear stress, τ_{xy}, the shear relaxation modulus is given by its autocorrelation function (ACF), C:

$$G(t) = C_{\tau_{xy}}(t). \tag{3}$$

The shear viscosity is expressed by

$$\eta = \frac{V}{k_B T} \int_0^\infty G(t)dt. \tag{4}$$

Autocorrelation Function

Basics for Correlation Function

The correlation function between two time dependent functions, f and g, are given by

$$Corr[f, g] = \langle f(\xi) g(\xi + t) \rangle_\xi, \tag{5}$$

where $\langle \cdots \rangle_\xi$ denote average over ξ.

The autocorrelation function, C_f, (without normalization) is given by

$$C_f(t) = Corr[f, f](t) \left(\equiv \langle f(\xi) f(\xi + t) \rangle_\xi \right). \tag{6}$$

Practical Form for Discrete ACF

Let the time is discretized based on time index, i and j, the practical form for ACF is given by

$$C_f(i\Delta t) = \frac{1}{N-i}\sum_{j=0}^{N-i-1} f(j\Delta t)f((i+j)\Delta t) \tag{7}$$

where N is maximum number and Δt is time between each time index.

It is frequently used the same time lag for the ACF by

$$C_f(i\Delta t) = \frac{1}{N-M}\sum_{j=0}^{N-M-1} f(j\Delta t)f((i+j)\Delta t) \tag{8}$$

with $M \leq N/2$.

ACF for Correlated Data

Let $K\Delta t$ be the fully uncorrelated time for given $f(t)$, the ACF using block average is expressed by

$$C_f(i\Delta t) = \frac{1}{N_B}\sum_{j=0}^{N_B-1} f(jK\Delta t)f((i+jK)\Delta t), \tag{9}$$

where $N_B \leq \frac{N/2}{K}$.

Association Distribution (β)

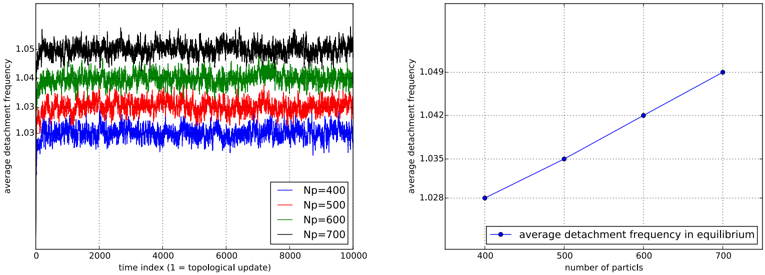


Figure 1: Average detachment frequency with respect to time index for topological update (left) and its average over equilibrium time index vs. number of particles (right).

Association Distribution ($\sqrt{\langle \mathbf{r}^2 \rangle}$)

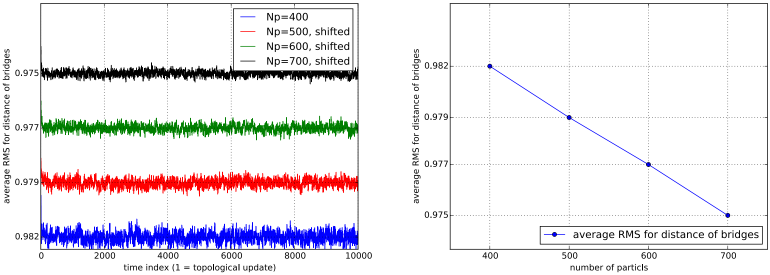
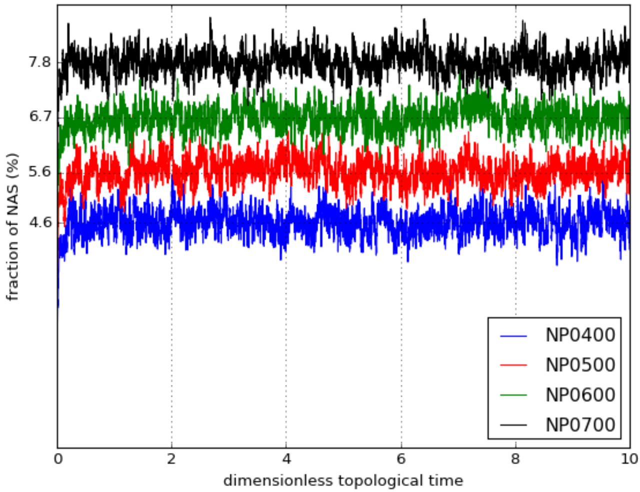
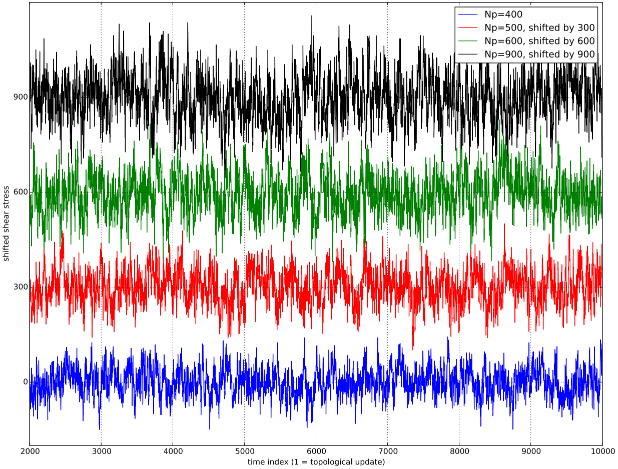


Figure 2: Average RMS for distance of bridges with respect to time index for topological update (left) and its average over equilibrium time index vs. number of particles (right).

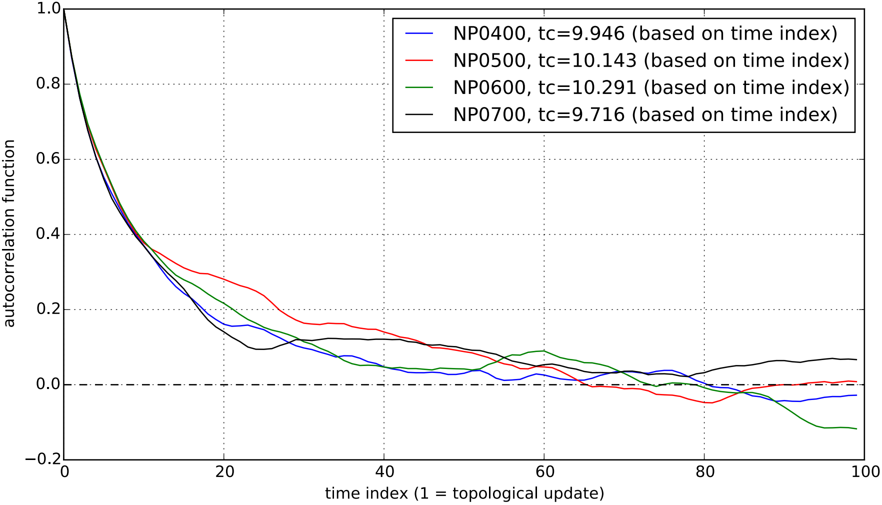
Equilibrium Check



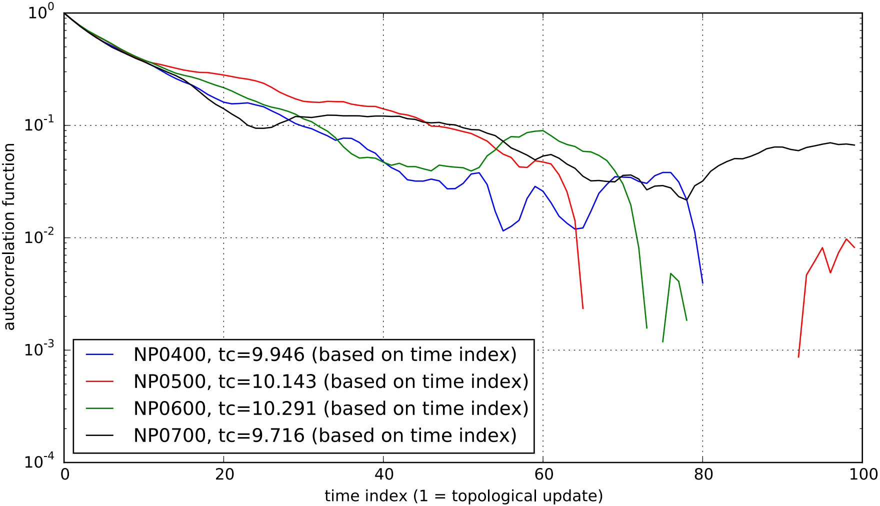
Shear Stress



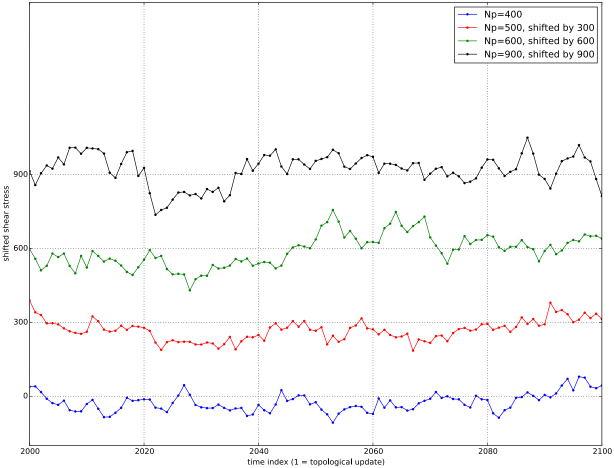
ACF with all time account (linear)



ACF with all time account (semilog)



Shear Stress (recall, detail)



Autoregressive Models

Need to study, but basics are simple: to remove short correlation. For instance, AR(1) is the autoregressive model with the first order, which means the correlation part is only depends on the previous part. The general approaches for lagged correlation function typically extract AR(1) (or AR(k) for general) mode. There is systematic protocol to treat these data.