Contents

Chapter 1

Basic Approaches for Brownian Motion

$$\frac{\partial \mathbf{r}}{\partial t} = \frac{1}{\zeta}\mathbf{F}^{(s)}, \tag{1.1}$$

$\mathbf{F}^{(s)}$

$$\mathbf{r}(t+\delta t)=\mathbf{r}(t)+\delta\mathbf{r}, \tag{1.2}$$

$\delta \mathbf{r}$

$$\delta \mathbf{r} = \frac{1}{\zeta} \int_{t}^{t+\delta t} \mathbf{F}^{(s)}(t')dt'. \tag{1.3}$$

1.1 Wiener Process for Random Force Contribution

$$\mathbf{W}(t) = \mathscr{W}\left[\mathbf{F}^{(s)}(t')\right] \equiv \int_0^t \mathbf{F}^{(s)}(t')dt', \tag{1.4}$$

$$\delta \mathbf{r}$$

$$\zeta \delta \mathbf{r} = \mathbf{W}(t + \delta t) - \mathbf{W}(t) \equiv \Delta \mathbf{W}(\delta t). \tag{1.5}$$

$$\langle(\Delta\mathbf{W}(\delta t))^2\rangle = 2\zeta k_B T\delta t \quad \text{with } \Delta\mathbf{W}(\delta t) \sim \mathscr{N}(0, 2\zeta k_B T\delta t), \tag{1.6}$$

$$\mathcal{N}(\mu, \sigma^2)$$

μ

σ^2

1.2 Non-dimensionalization

R_0

l_c

R_0

$$t_c = \frac{\zeta R_0^2}{k_B T}. \tag{1.7}$$

$$[t_c] = \frac{[\zeta][R_0^2]}{[k_B T]} = \frac{M \cdot T^{-1} L^2}{M \cdot L^2 \cdot T^{-2}} = T. \tag{1.8}$$

$$\tilde{\mathbf{R}} \sim \mathcal{N}(0,1)$$

$$\Delta \mathbf{W} = \sqrt{2\zeta k_B T \delta t}\,\tilde{\mathbf{R}}. \tag{1.9}$$

$$\tilde{\mathbf{R}}$$

$$[-\sqrt{3}, \sqrt{3}]$$

$$(\sqrt{3}+\sqrt{3})^2/12 = 1$$

$$\tilde{\mathbf{r}}(\tilde{t} + \delta\tilde{t}) = \tilde{\mathbf{r}}(\tilde{t}) + \sum_{i,j} \tilde{\mathbf{F}}^{(r)}(\tilde{\mathbf{r}}_i, \tilde{\mathbf{r}}_j)\delta\tilde{t} + \tilde{\mathbf{F}}^{(s)}\sqrt{\delta\tilde{t}}, \tag{1.10}$$

$$\tilde{\mathbf{F}}^{(r)}(\tilde{\mathbf{r}}_i, \tilde{\mathbf{r}}_j) = -C\left(1 - \tilde{\mathbf{r}}_{ij}^2\right)\frac{\tilde{\mathbf{r}}_{ij}}{\tilde{r}_{ij}} \tag{1.11}$$

$$\tilde{\mathbf{F}}^{(s)} = \sqrt{2}\tilde{\mathbf{R}} \tag{1.12}$$

$$\tilde{\mathbf{F}}^{(s)} = \sqrt{2 \times 12}\tilde{\mathbf{R}}'. \tag{1.13}$$

1.3 Simulation Results

1.3.1 Notes

$$\lim_{\delta t \to 0} \frac{\delta \mathbf{r}}{\delta t} \sim \lim_{\delta t \to 0} \frac{1}{\sqrt{\delta t}} \to \infty. \tag{1.14}$$

1.3.2 Mean-square displacement

$$D = k_B T / \zeta$$

$$t_c = \frac{R_0^2}{D}. \tag{1.15}$$

$$\lim_{t\to\infty} \langle (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2 \rangle_i = 2N_D D t, \tag{1.16}$$

N_D

$$\lim_{\tilde{t}\to\infty} \langle \big(\tilde{\mathbf{r}}_i(\tilde{t}) - \tilde{\mathbf{r}}_i(0)\big)^2 \rangle_i = 2N_D\tilde{t}. \tag{1.17}$$

$$2N_D = 4$$

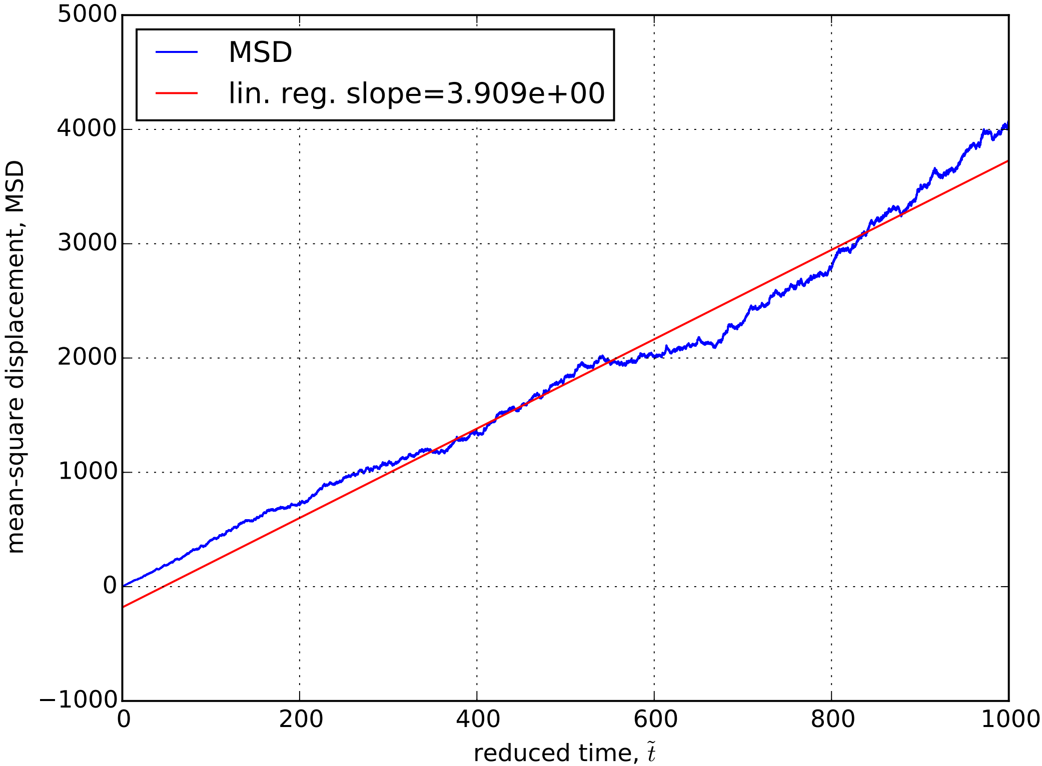


Figure 1.1: MSD for pure Brownian simulation with 1000 reduced time. The blue line represent MSD profile while the red line is linear regression for it. Notice that the slope on here is 3.909 that is similar to the 4 by theoretical interpretation.

Chapter 2

Brownian Motion with Repulsive Potential

2.1 Basic Fomular

$$\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$$

$$|\mathbf{r}_{ij}|$$

$$R_0$$

$$\mathbf{F}^{(r)}(\mathbf{r}_i, \mathbf{r}_j) = \mathbf{F}^{(r)}(\mathbf{r}_{ij}) = -C\frac{k_B T}{R_0}\left(1 - \frac{\mathbf{r}_{ij}^2}{R_0^2}\right)\hat{\mathbf{r}}_{ij} \tag{2.1}$$

R_0

C

$$C = \frac{9}{\pi} n_p^2 N^{0.2} \tag{2.2}$$

n_p

N

$$\frac{\partial \mathbf{r}}{\partial t} = \frac{1}{\zeta} \left(\sum \mathbf{F}^{(r)} + \mathbf{F}^{(s)} \right) , \tag{2.3}$$

$$\mathbf{F}^{(r)}$$

$$\mathbf{F}^{(s)}$$

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \frac{1}{\zeta}\sum \mathbf{F}^{(r)}(t)\delta t + \delta\mathbf{r}, \tag{2.4}$$

$$\delta \mathbf{r}$$

2.2 Non-dimensionalization with prefactor C

$$t_c = \frac{\zeta R_0^2}{k_B T} \frac{1}{C}, \tag{2.5}$$

$$R_0$$

$$\tilde{\mathbf{r}}(\tilde{t} + \delta\tilde{t}) = \tilde{\mathbf{r}}(\tilde{t}) + \sum_{i,j} \tilde{\mathbf{F}}^{(r)}(\tilde{\mathbf{r}}_i, \tilde{\mathbf{r}}_j)\delta\tilde{t} + \tilde{\mathbf{F}}^{(s)}\sqrt{\delta\tilde{t}}, \tag{2.6}$$

$$\tilde{\mathbf{F}}^{(r)}(\tilde{\mathbf{r}}_i, \tilde{\mathbf{r}}_j) = -\left(1 - \tilde{\mathbf{r}}_{ij}^2\right) \frac{\tilde{\mathbf{r}}_{ij}}{\tilde{r}_{ij}} \tag{2.7}$$

$$\tilde{\mathbf{F}}^{(s)} = \sqrt{\frac{2}{3}}\tilde{\mathbf{R}} \tag{2.8}$$

$$U(\mathbf{r}_i, \mathbf{r}_j) = U(\mathbf{r}_{ij}) = \frac{1}{3}\left(1 + \tilde{\mathbf{r}}_{ij}\right)^2 (2 + \tilde{\mathbf{r}}_{ij}). \tag{2.9}$$

C

$$C \sim 5900$$

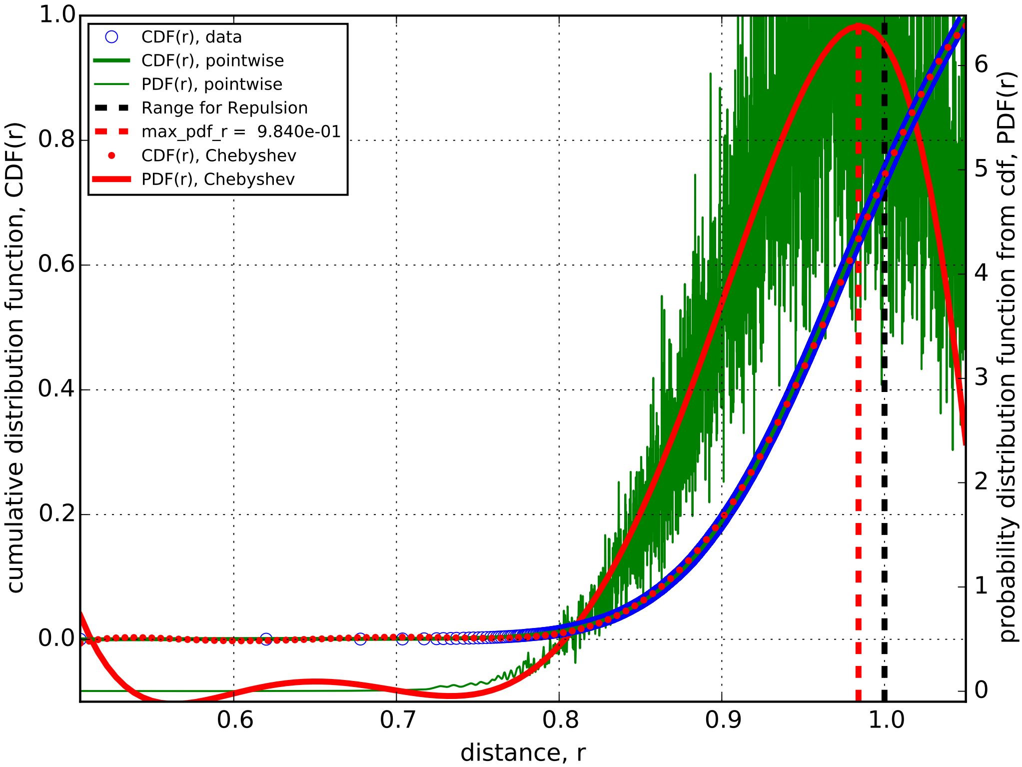
$\sim 1/77$

2.3 Simulation Results

2.3.1 Note

2.3.2 Trajectory Analysis

2.3.3 Distance and Energy Distribution



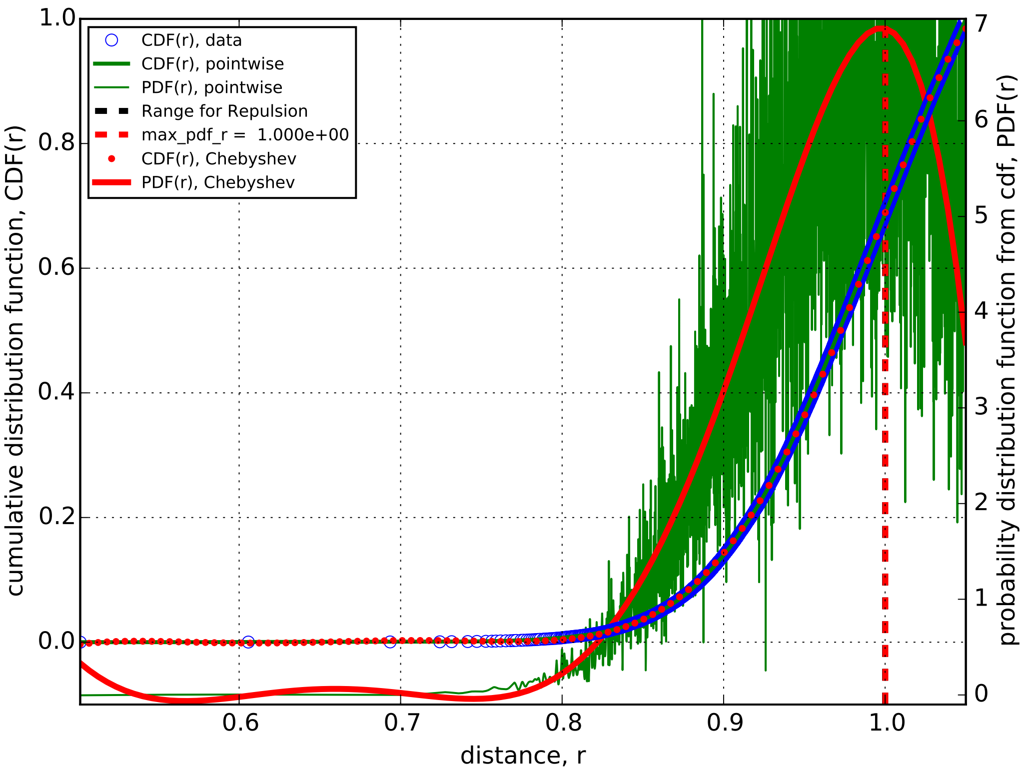


Figure 2.1: Cumulative distribution and probability distribution function for NP = 100 (up) and NP = 80 (down). The red color represent the regression, green color represent the interpolation for piece-wise cubic spline, and blue circle represent cumulative distribution from data.

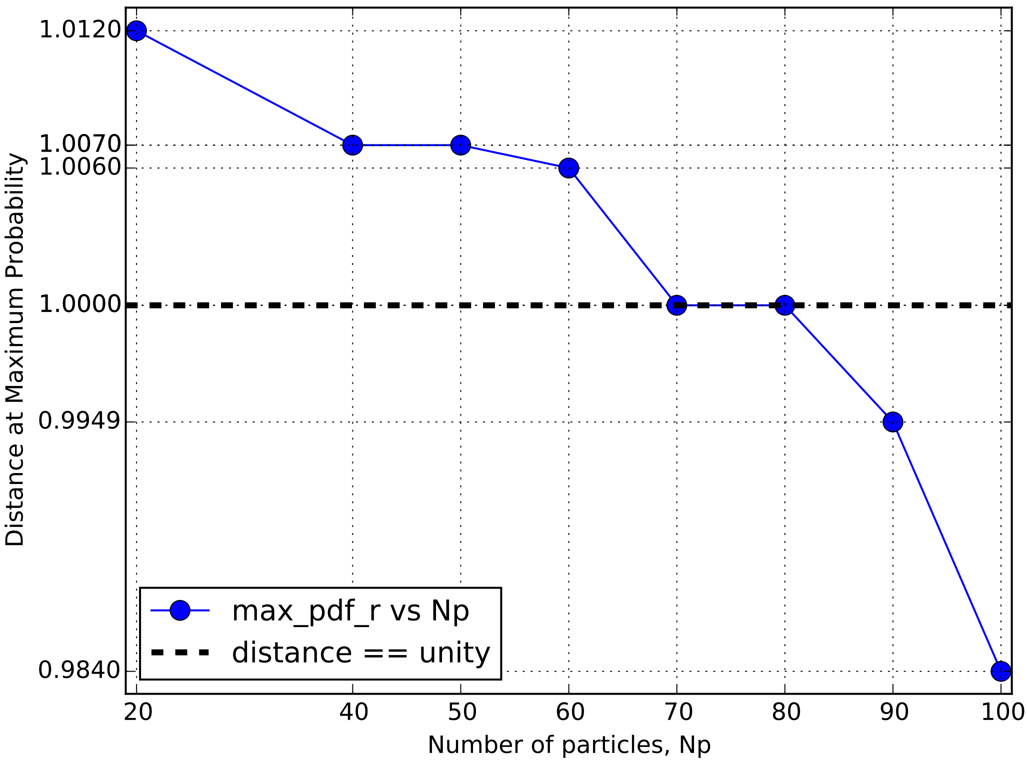


Figure 2.2: Maximum probability distance due to number of particles.

Chapter 3

Brownian Dynamics for Associative System

3.1 Evolution Equations for Associative System

$$\frac{\partial \mathbf{r}}{\partial t} = \frac{1}{\zeta} \left(\sum_i \sum_{\substack{j>i, \\ j \in \mathscr{C}_i}} \mathbf{F}^{(c)}(\mathbf{r}_i, \mathbf{r}_j) + \sum_i \mathbf{F}_i^{(r)} + \mathbf{F}^{(s)} \right), \tag{3.1}$$

$\mathscr{C}_i$

3.1.1 Gaussian Connector

$$U^{(c)}(\mathbf{r}_i, \mathbf{r}_j) = U^{(c)}(\mathbf{r}_{ij}) = \frac{N_D}{2} k_B T \frac{\mathbf{r}_{ij}^2}{R_0^2}, \tag{3.2}$$

$$\mathbf{F}^{(c)}(\mathbf{r}_i, \mathbf{r}_j) = N_D k_B T \frac{\mathbf{r}_{ij}}{R_0^2}. \tag{3.3}$$

$$\tilde{U}^{(c)}(\tilde{\mathbf{r}}_{ij}) = \frac{N_D}{2}\tilde{\mathbf{r}}_{ij}^2, \tag{3.4}$$

$$\tilde{\mathbf{F}}^{(c)}(\tilde{\mathbf{r}}_{ij}) = N_D\tilde{\mathbf{r}}_{ij}. \tag{3.5}$$

3.1.2 Finite Extensible Connector

$$U = -k_B T n \left\{ \log \left[4\pi \sinh \left(\frac{fb}{k_B T} \right) \right] - \log \left(\frac{fb}{k_B T} \right) \right\}, \tag{3.6}$$

n

b

$$\mathscr{L}^{-1}$$

$$f = \frac{k_B T}{b} \mathscr{L}^{-1} \left(\frac{r}{nb} \right). \tag{3.7}$$

$$\mathscr{L}^{-1}(\lambda) = \lambda\frac{3-\lambda^2}{1-\lambda^2} + O(\lambda^6). \tag{3.8}$$

3

$$f = \frac{k_B T}{b} \frac{3 \frac{r}{nb}}{1 - (r/nb)^2}. \tag{3.9}$$

3

r

R_M

R_0

$$U(\mathbf{r}) = -\frac{N_D}{2} k_B T \left(\frac{R_M}{R_0}\right)^2 \log\left(1 - \frac{\mathbf{r}^2}{R_M^2}\right) \tag{3.10}$$

$$\mathbf{F}(\mathbf{r}) = k_B T \frac{R_M}{R_0^2} \frac{N_D \frac{\mathbf{r}}{R_M}}{1 - \frac{\mathbf{r}^2}{R_M^2}}. \tag{3.11}$$

$$F_{\mathbf{F}}(\mathbf{r}) = F_N \mathbf{F}_G(\mathbf{r}), \tag{3.12}$$

$$\mathbf{F}_G$$

F_N

$$F_N = \frac{1}{1 - \frac{\mathbf{r}^2}{R_M^2}}. \tag{3.13}$$

$$\tilde{U}(\tilde{\mathbf{r}}) = -\frac{N_D}{2}\left(\frac{R_M}{R_0}\right)^2 \log\left(1 - \frac{\tilde{\mathbf{r}}^2}{(R_M/R_0)^2}\right), \tag{3.14}$$

$$\tilde{\mathbf{F}}(\tilde{\mathbf{r}}) = \left(\frac{1}{1 - \frac{\mathbf{r}^2}{(R_M/R_0)^2}}\right)\tilde{\mathbf{F}}_G(\tilde{\mathbf{r}}) \equiv \tilde{F}_N \tilde{\mathbf{F}}_G(\tilde{\mathbf{r}}). \tag{3.15}$$

$$\tilde{F}_N$$

$$\tilde{F}_N = \frac{1}{1 - \frac{\mathbf{r}^2}{(R_M/R_0)^2}} = F_N. \tag{3.16}$$

$$R_M/R_0 = 11$$

3.2 Implementation for Association

Z_k

3.2.1 Equilibration for Each Association Step

$$N_b(m)$$

m

$$\bar{N}_b(m_K) = \frac{1}{K} \sum_{k=1}^{K} N_b(m_k). \tag{3.17}$$

$$\bar{N}_b(m_K) - \bar{N}_b(m_{K-1}) = \frac{1}{K}\sum_{k=1}^{K} N_b(m_k) - \frac{1}{K-1}\sum_{k=1}^{K-1} N_b(m_k) \tag{3.18}$$

$$= \frac{1}{K(K-1)}\left[(K-1)\sum_{k=1}^{K} N_b(m_k) - K\sum_{k=1}^{K-1} N_b(m_k)\right] \tag{3.19}$$

$$= \frac{1}{K(K-1)}\left[(K-1)N_b(m_K) - \sum_{k=1}^{K-1} N_b(m_k)\right]. \tag{3.20}$$

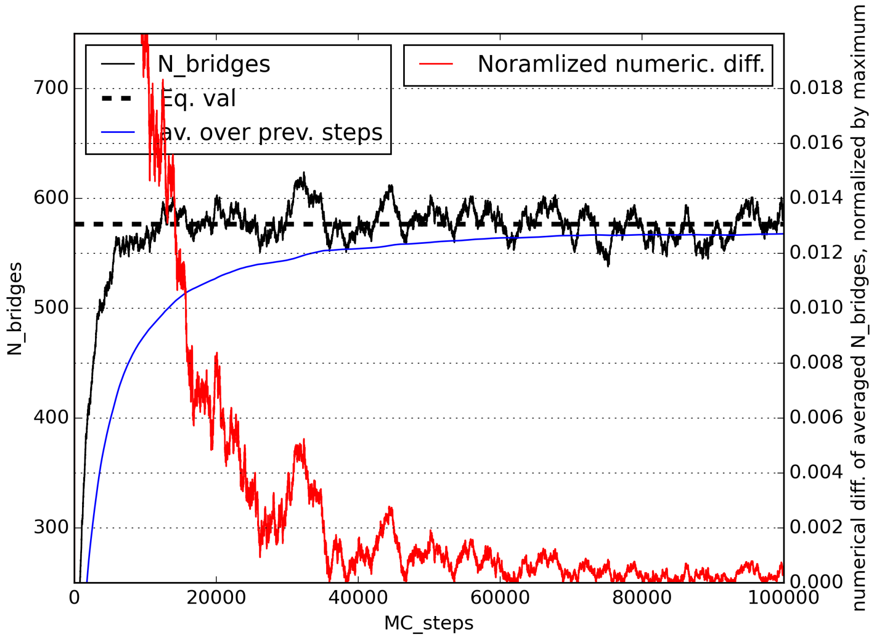


Figure 3.1: Identification of equilibrium for association steps. The black line represent the number of bridges of each MC step, blue line is the number of bridges averaged over previous time, and the red line is normalized difference value without smoothing. To be safe side, slight smoothing process is applied by using several steps.

3.2.2 Probability to Select Chain in Beads

n_p

$$2n_p$$

U

Z_k

$$Z_k = \sum_{i=1}^{2n_p} \exp\left(\beta U(\mathbf{r}_i, \mathbf{r}_{\mathscr{C}_k(i)})\right), \tag{3.21}$$

$$\beta = (k_B T)^{-1}$$

$$\mathscr{C}_k(i)$$

$$\exp(-\beta H)$$

$$H = T - V$$

Z_1

$\mathscr{C}_1(i)$

$i \in [1, n_p]$

Z_1

$2n_p$

3.2.3 Behaviour of Selected Chain

N_B

$$p_k(\{\mathbf{r}\} \equiv \exp\left(-\beta U(\{\mathbf{r}\} - \mathbf{r}_k)\right), \tag{3.22}$$

U

$$\{\mathbf{r}\} = \{\mathbf{r}_0, \mathbf{r}_1, \cdots, \mathbf{r}_{N_B}\}$$

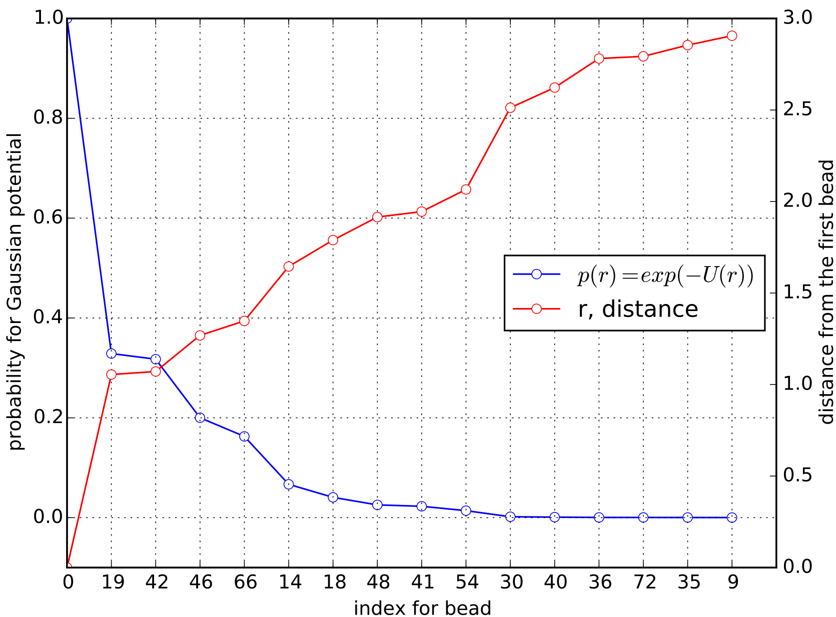


Figure 3.2: Example for the probability of chain extension using Gaussian connector. The data is sampling from 80 beads system and only account for repulsive potential (no association). The variables are dimensionless. The red color represent distance from the first bead (index is 0), and the blue color represent probability using Boltzmann factor.

3.2.4 Allowance for Number of Chain Ends per Bead

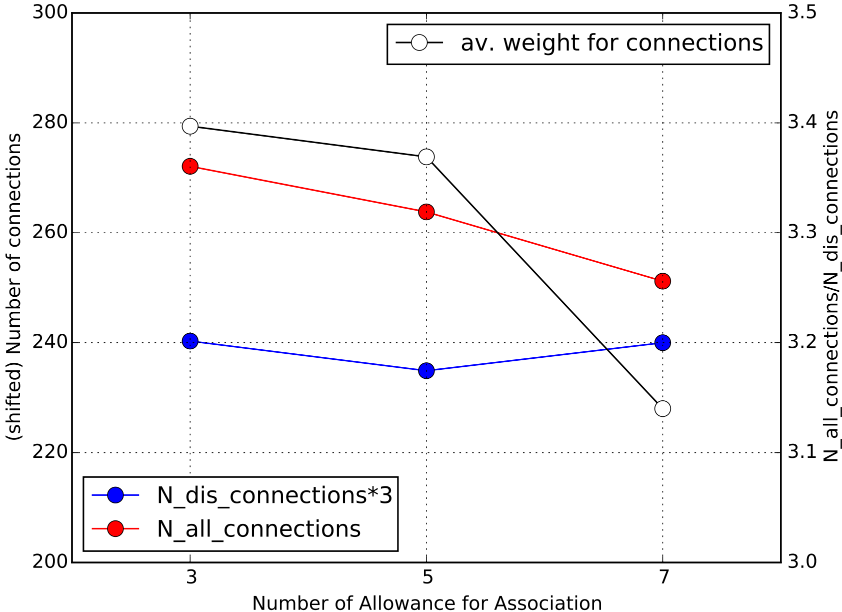


Figure 3.3: Effects of number of allowance for fluctuating attached chain ends per bead. N_dis_connections state number of distinguashable connections, i.e., all different pairs of association, and N_all_connections means number of all bridge chains. The right axis is the ratio between this two counted numbers, which refer intensity per bridge chains.

3.3 Simulation Results

3.3.1 Clustering

10^2

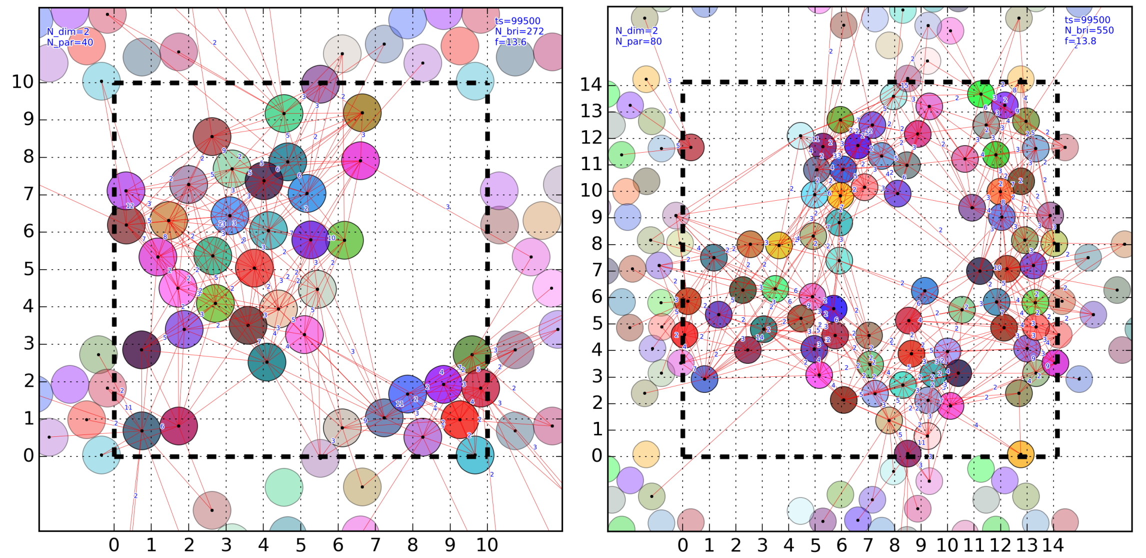


Figure 3.4: Builded cluster during simulation. Both system has the same concentration but different box size.

3.3.2 Isotropic for connecting vector

$$\boldsymbol{\sigma} = 3\nu k_B T \bar{f} \langle \tilde{\mathbf{R}} \tilde{\mathbf{R}} \rangle, \tag{3.23}$$

ν

$\bar{f}$

$\langle \mathbf{RR} \rangle$

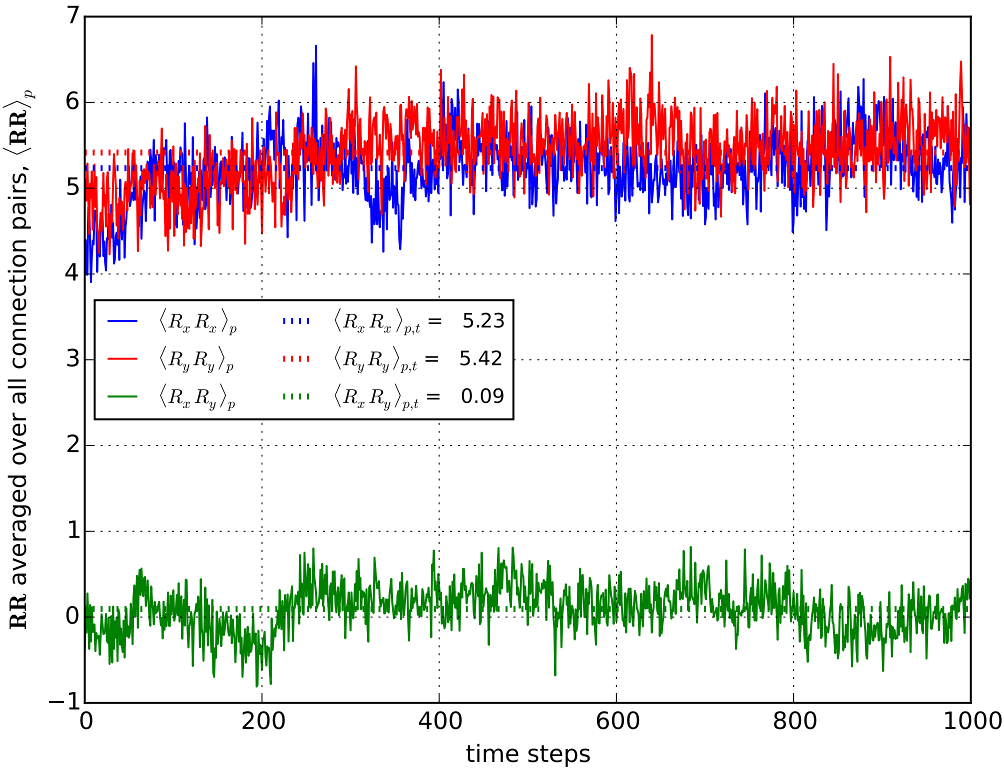


Figure 3.5: Measured $\langle \mathbf{RR} \rangle_p$ for 80 beads per 200 area system. The diagonal components are almost identical while the off-diagonal components are negligible, which is the sign for isotropy.

3.3.3 Size Effects

Appendix A

Finite Extensibility

Appendix B

Time Correlated Data

B.1 Stationary State Variable

A

A

$$A = \langle \mathscr{A} \rangle_t$$

A

A

B.2 Regression

Appendix C

Regression Scheme

C.1 Regression by Chebyshev Polynomial

ξ

$$[-1, 1]$$

$$\sum_{n=0}^{\infty} T_n(\xi) t^n = \frac{1 - t\xi}{1 - 2t\xi + t^2}, \tag{C.1}$$

T_n

$$T_0(\xi) = 1 \tag{C.2}$$

$$T_1(\xi) = \xi \tag{C.3}$$

$$T_{n+1}(\xi) = 2xT_n(\xi) - T_{n-1}(\xi). \tag{C.4}$$

$$y = f(\xi)$$

$\xi \in [-1, 1]$

$$y = \lim_{N \to \infty} \sum_{n=0}^{N} a_n T_n(\xi). \tag{C.5}$$

N

$$\chi = \sum_{\alpha=1}^{M} \left[y_\alpha - \sum_{n=0}^{N} a_n T_n(\xi_\alpha) \right]^2 , \tag{C.6}$$

y_α

α

ξ_α

ξ

$$\sum_{k=0}^{N} \left[\sum_{\alpha=1}^{M} T_n(\xi_\alpha) T_k(\xi_\alpha) \right] a_k = \sum_{\alpha=1}^{M} y_\alpha T_n(\xi_\alpha) \quad \text{for } n \in [0, N]. \tag{C.7}$$

$$\mathbf{a} = \{a_1, \cdots, a_M\}$$

N

C.2 Typical Polynomial Expression

$$y = f(x)$$

N

$$y=\sum_{n=0}^{N} c_n x^n=\sum_{n=0}^{N} b_n \xi^n, \tag{C.8}$$

ξ

$$\xi = \frac{2(x - x_c)}{x_{max} - x_{min}} \tag{C.9}$$

$$x_c = \frac{1}{2}(x_{max} + x_{min})$$

ξ

a

b

$$T_k^{(n)}$$

k

ξ

$$T_0^{(n+1)} = -T_0^{(n)} \tag{C.10}$$

$$T_{n+1}^{(n+2)} = 2T_n^{(n+1)} \tag{C.11}$$

$$T_{n+2}^{(n+2)} = 2T_{n+1}^{(n+1)} \tag{C.12}$$

$$T_k^{(n+2)} = 2T_{k-1}^{(n+1)} - T_k^{(n)} \quad \text{for } 1 \leq k \leq n, \tag{C.13}$$

$$T_0^{(0)} = 1$$

$$T_0^{(1)} = 0$$

$$T_1^{(0)} = 1$$

b

α

$$b_n = \sum_{k=n}^{N} T_n^{(k)} a_k, \tag{C.14}$$

$$c_n = \sum_{k=n}^{N} \left(\frac{2}{\Delta x} \right)^k \left(\begin{array}{c} k \\ n \end{array} \right) (-x_c)^{k-n} \, b_k, \tag{C.15}$$

$$\Delta x = x_{max} - x_{min}$$

$$y = \sum_{n=0}^{N} c_n x^n, \tag{C.16}$$

C.3 Overhead for Recursion

Appendix D

Cumulative Distribution and Probability Distribution Function

Y

Y

Y

$$\mathscr{F}(r)$$

$$P(r)$$

$$P(r) = \frac{d}{dr}\mathscr{F}(r). \tag{D.1}$$

$$dx_i = x_i - x_{i-1}$$

$$dy_i = y_i - y_{i-1}$$

Appendix E

Software architecture

E.1 GNU's scientific library as Front-End for Mathematical Calculations

E.2 Math Kernel Library (MKL) as interface between Front- and Back-End

E.3 Personally developed MATRIX class as Back-End

A

B

C

$$\mathbf{A} \cdot \mathbf{B} + \mathbf{C}$$

C

E.4 Parsing Test Conditions

E.5 Periodic Boundary Condition

E.5.1 Minimum Image Convention

E.5.2 Applying Periodic Boundary Condition for Trajectory

Appendix F

Parallel Computing

Appendix G

Post-Processing

G.1 Plotting and Making Move for Trajectory File

G.2 Trajectory Conversion

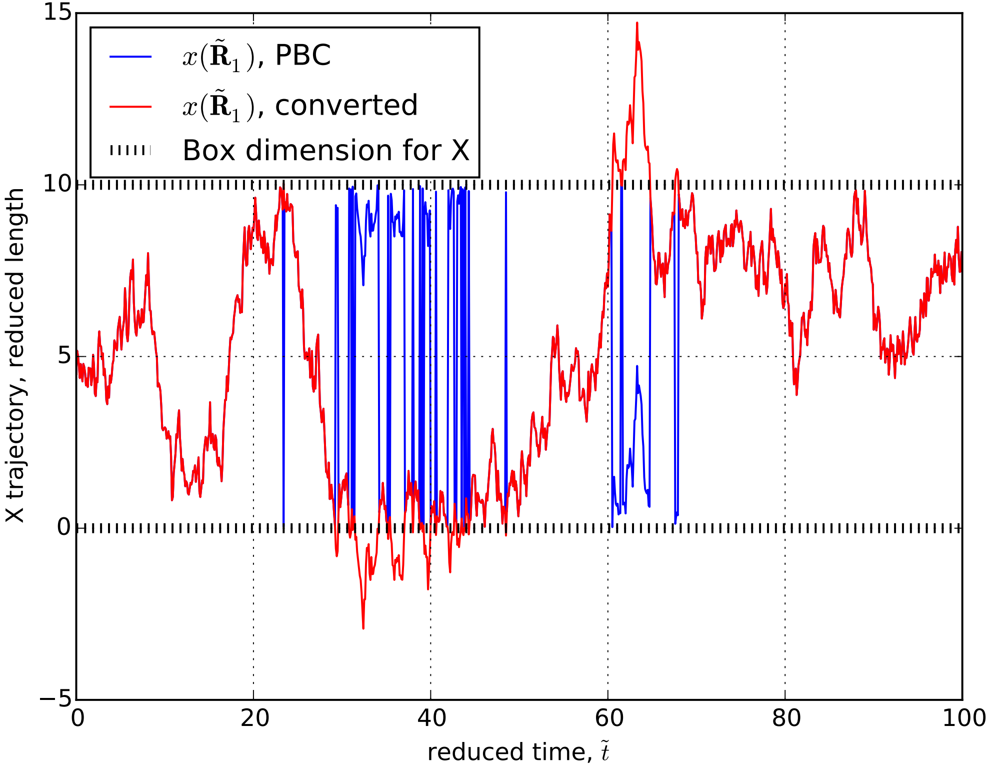


Figure G.1: Test results for trajectory conversion. Blue color represent the trajectory using periodic boundary condition (PBC) and the red color represent the converted data. The test is done using pure Brownian motion with 100 reduced time step, and trajectory is involved only for x-coordinate of the first beads among 100 beads on the system.

G.3 Pair Correlation Distribution

$\rho(\mathbf{r}_1, \mathbf{r}_2$

G.3.1 Basic Definition started with Canonical Ensemble

$$(N, V, T)$$

Z

$$Z = \int d\mathbf{r}_1, \cdots d\mathbf{r}_N \exp\left(-\beta U\right), \tag{G.1}$$

β

$$P(\mathbf{r}_1, \cdots, \mathbf{r}_N) d\mathbf{r}_1 \cdots d\mathbf{r}_N = \frac{\exp(-\beta U)}{Z} d\mathbf{r}_1 \cdots d\mathbf{r}_N. \tag{G.2}$$

$$P^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n) = \frac{1}{Z} \int \exp\left(-\beta U\right) d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N, \tag{G.3}$$

$n < N$

(n)

P

$$N - n$$