Supporting Information

Concentration and Temperature Dependences of Polyglutamine Aggregation by Multiscale Coarse-Graining Molecular Dynamics Simulations

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I. Connection between HOP and RDF

The radial distribution function (RDF) has been widely used to quantify the structural properties of materials. For aggregation studies, the advantage of heterogeneity order parameter (HOP) over RDF is that, for a given configuration, HOP provides a single

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value which can quantify the heterogeneity of this configuration, but RDF generates an array of values. Nevertheless, there does have a quantitative relationship between average HOP and RDF. The RDF for an ensemble of configuration is defined as[1]

$$g(r) = \frac{V}{N_t^2} < \sum_i \sum_{j \neq i} \delta(r - r_{ij}) > \tag{1}$$

where δ is Dirac δ-function, and $\langle \ \rangle$ indicates an ensemble average. We then define the RDF for a *single* configuration I :

$$g_I(r) = \frac{V}{N_t^2} \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \tag{2}$$

and $g(r) =< g_I(r) >$.

On the other hand, for a given configuration, the HOP h is defined by the following equation,

$$h = \frac{1}{N_t} \sum_{i=1}^{N_t} \sum_{j=1}^{N_t} \exp(\frac{-r_{ij}^2}{2\sigma^2}) \tag{3}$$

where r_{ij} is the distance between site *i* and site *j* corrected with the periodic boundary condition, N_t is the total number of sites in the same configuration, $\sigma = \frac{L}{N_t^{1/3}}$ with L the side length of the cubic simulation box. The HOP can be rewritten as,

$$h = \frac{1}{N_t} \sum_r \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \exp(-\frac{r_{ij}^2}{2\sigma^2}) = \frac{1}{\rho} \sum_r g_I(r) \exp(-\frac{r_{ij}^2}{2\sigma^2}) \tag{4}$$

where ρ is the density of the system. In the thermodynamic limit $L \to \infty$ and $N_t \to \infty$, the sum can be replaced by the integral,

$$h = \frac{1}{\rho}\int_0^{\infty} \exp(-\frac{r_{ij}^2}{2\sigma^2}) g_I(r) dV = \frac{1}{\rho}\int_0^{\infty} \exp(-\frac{r_{ij}^2}{2\sigma^2}) g_I(r) 4\pi r^2 dr \qquad (5)$$

The above equation demonstrates that the physical meaning of the average HOP is an exponentially modulated average of RDF for an individual configuration. For an ideally homogeneous configuration $g_I = 1$, according to eq 5, we obtain $h = 4\pi\Gamma(3/2) = 15.74$, which is the exact value numerically calculated[2] for an ideally homogeneous configuration when $N_t \geq 1000$.

Since the RDF can be numerically connected to the experimentally observable structure factor, the definition of HOP might help to interpret some experimental results for molecular aggregation.

II. Supplementary Figures

The original and rescaled HOP distributions at various concentrations and temperatures, the relationship between potential energy and HOP, and the instantaneous configuration energies in equilibrium are plotted below.

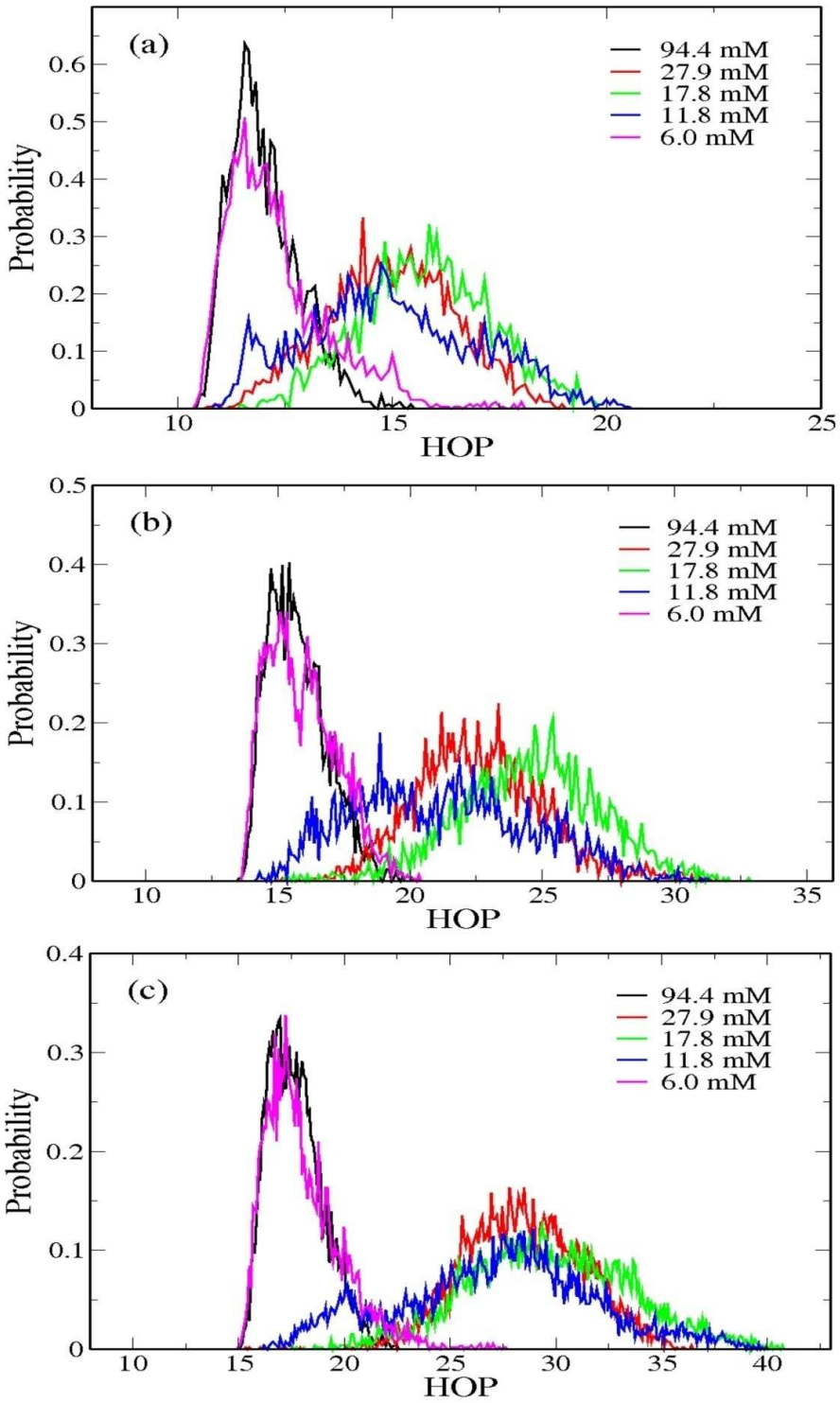

Figure S1. Distributions of HOPs at different concentrations with different simulation sizes of (a) 27, (b) 54, and (c) 81 polyglutamine molecules, respectively.

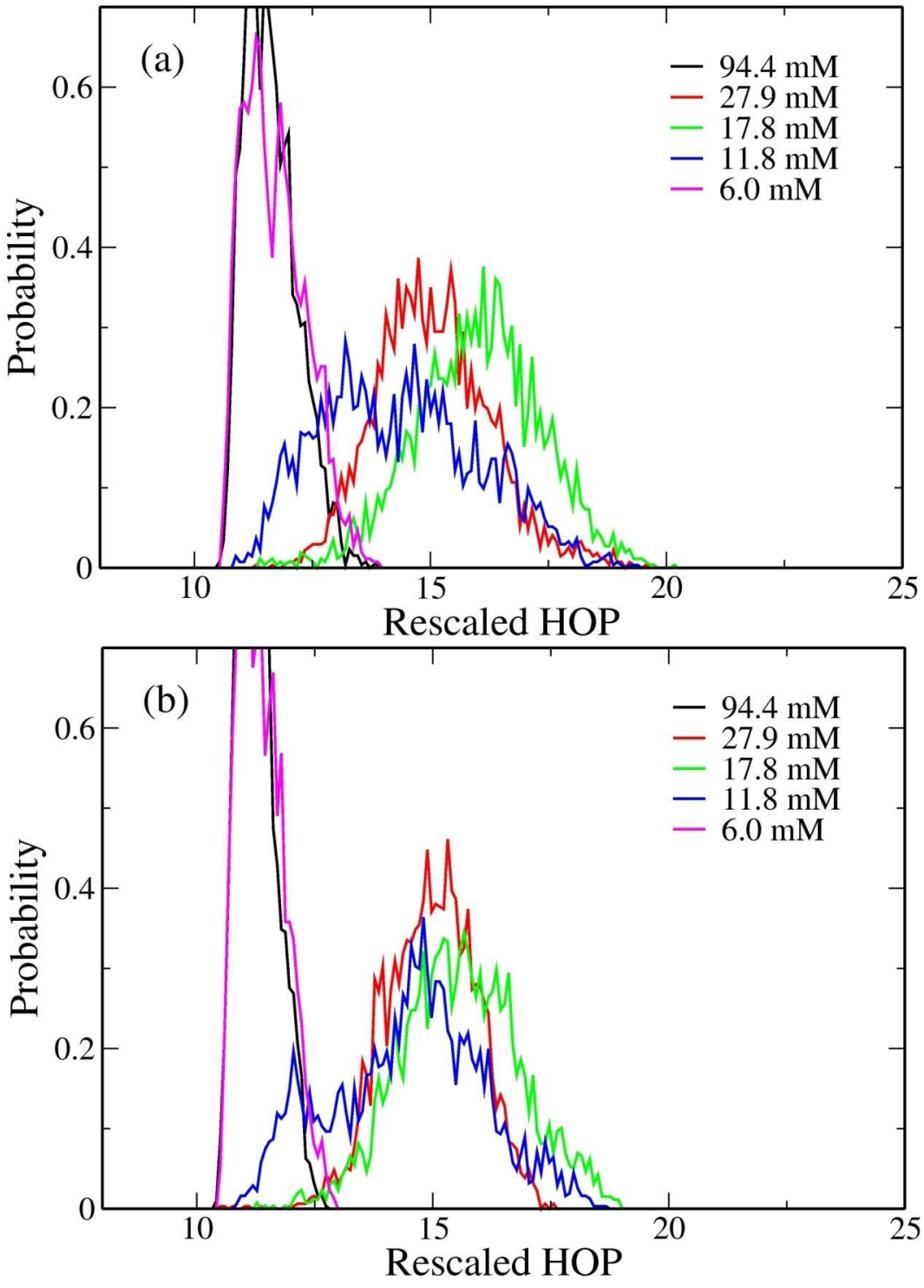

Figure S2. Distributions of rescaled HOPs at different concentrations of the systems with (a) 54 and (b) 81 polyglutamine molecules, respectively.

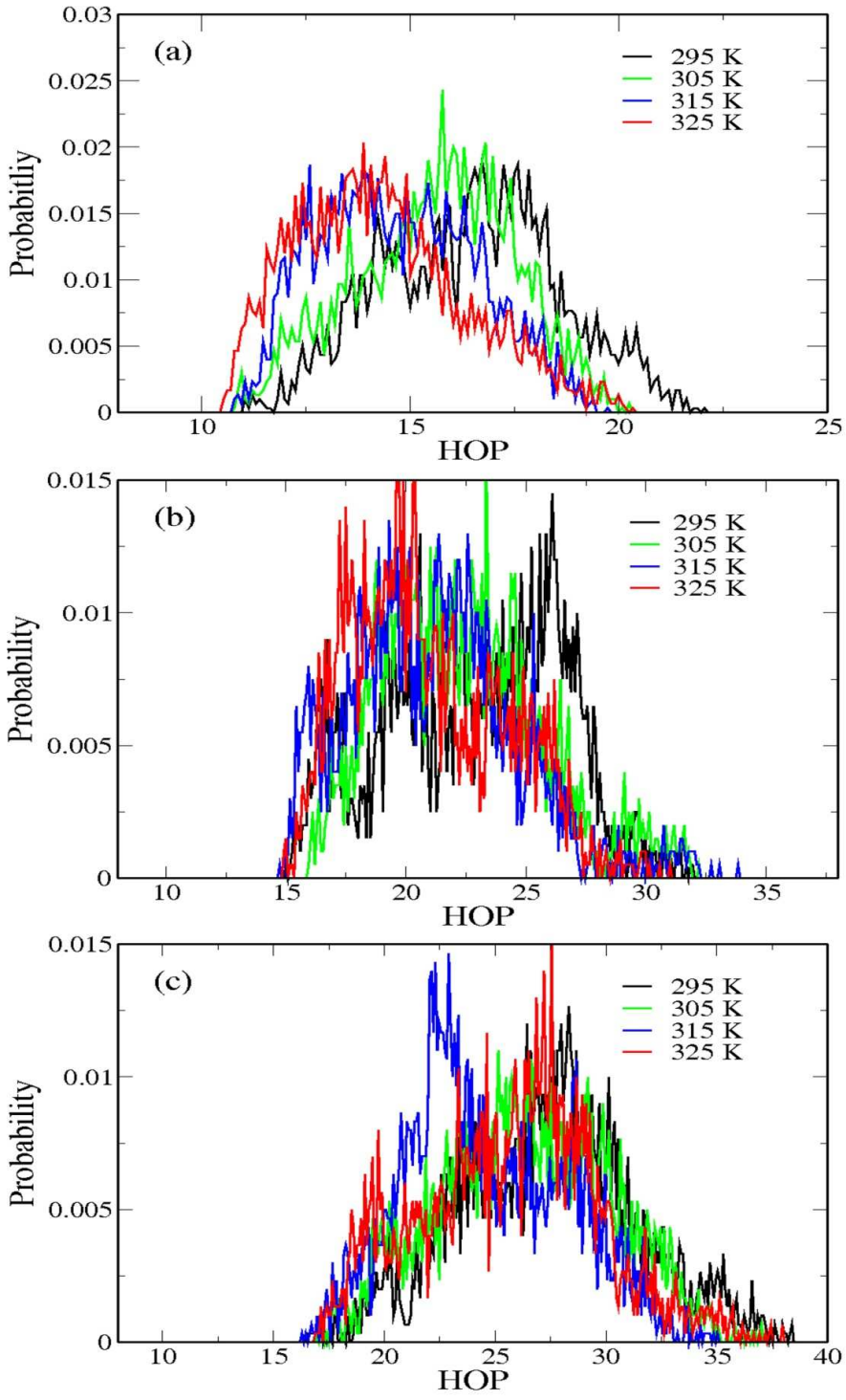

Figure S3. Distributions of HOPs at different temperatures with different simulation sizes of (a) 27, (b) 54, and (c) 81 polyglutamine molecules, respectively.

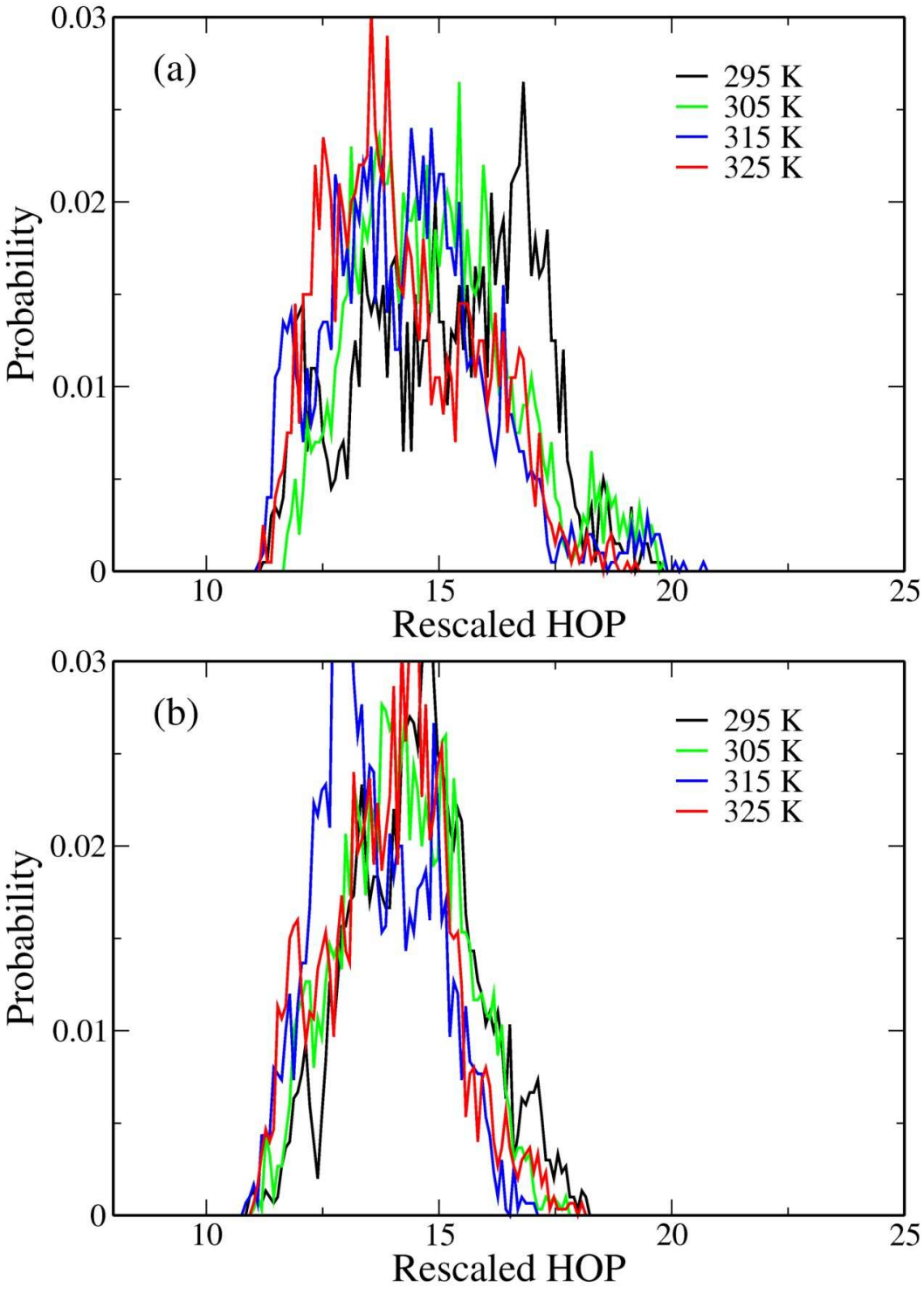

Figure S4. Distributions of rescaled HOPs at different temperatures of the systems with (a) 54 and (b) 81 polyglutamine molecules, respectively.

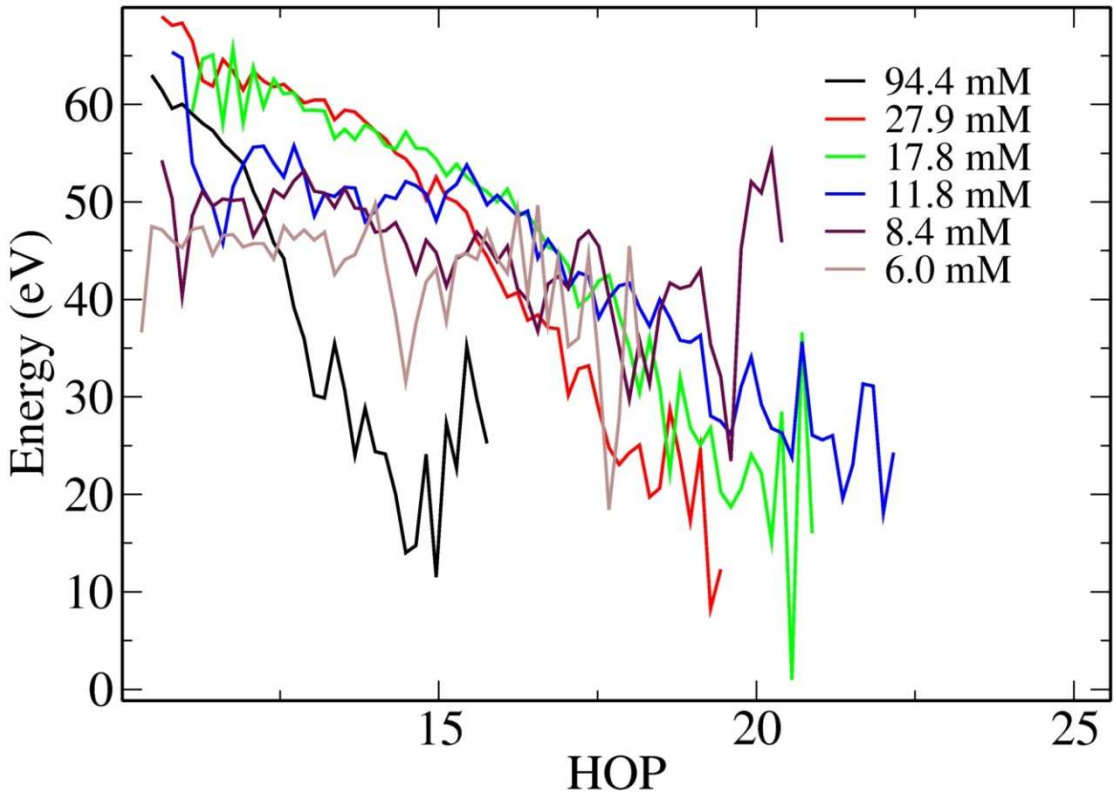

Figure S5. Configurational energy versus HOP at different concentrations with the temperature fixed at T = 310 K.

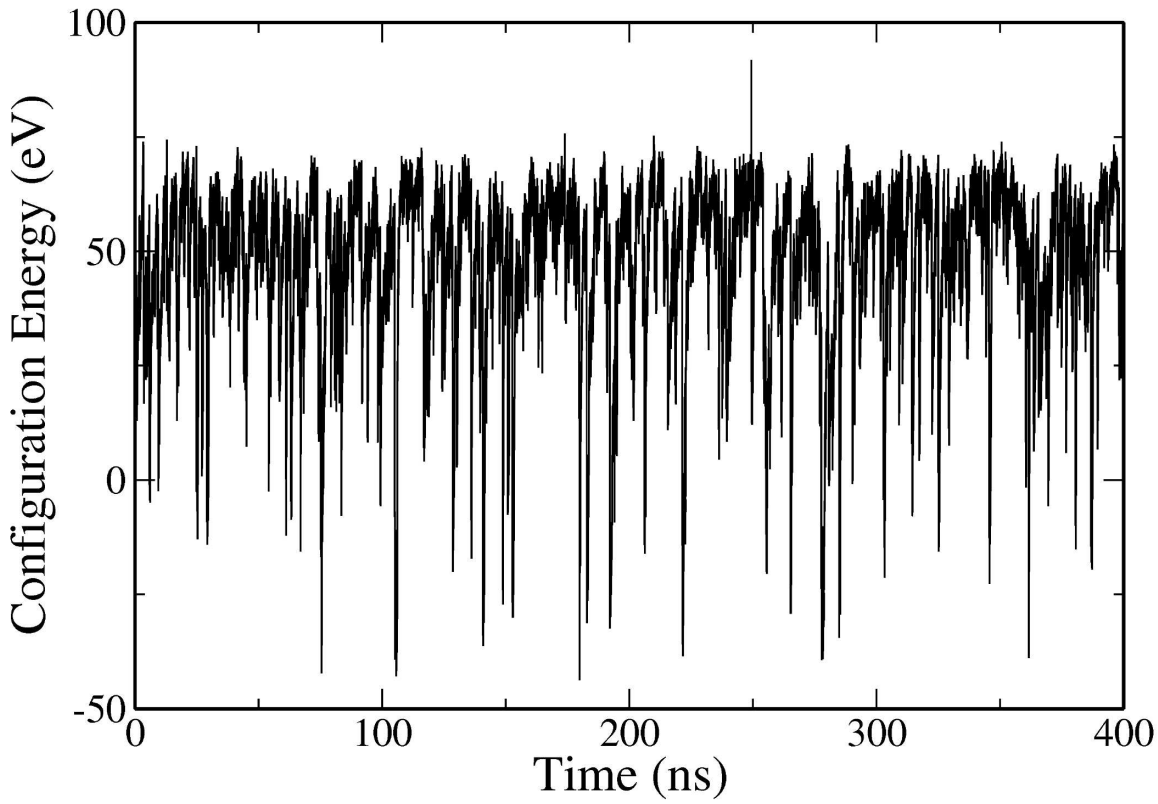

Figure S6. The instantaneous configuration energy in equilibrium for the system with 27 polyglutamines at C = 11.8 mM and T = 310 K.

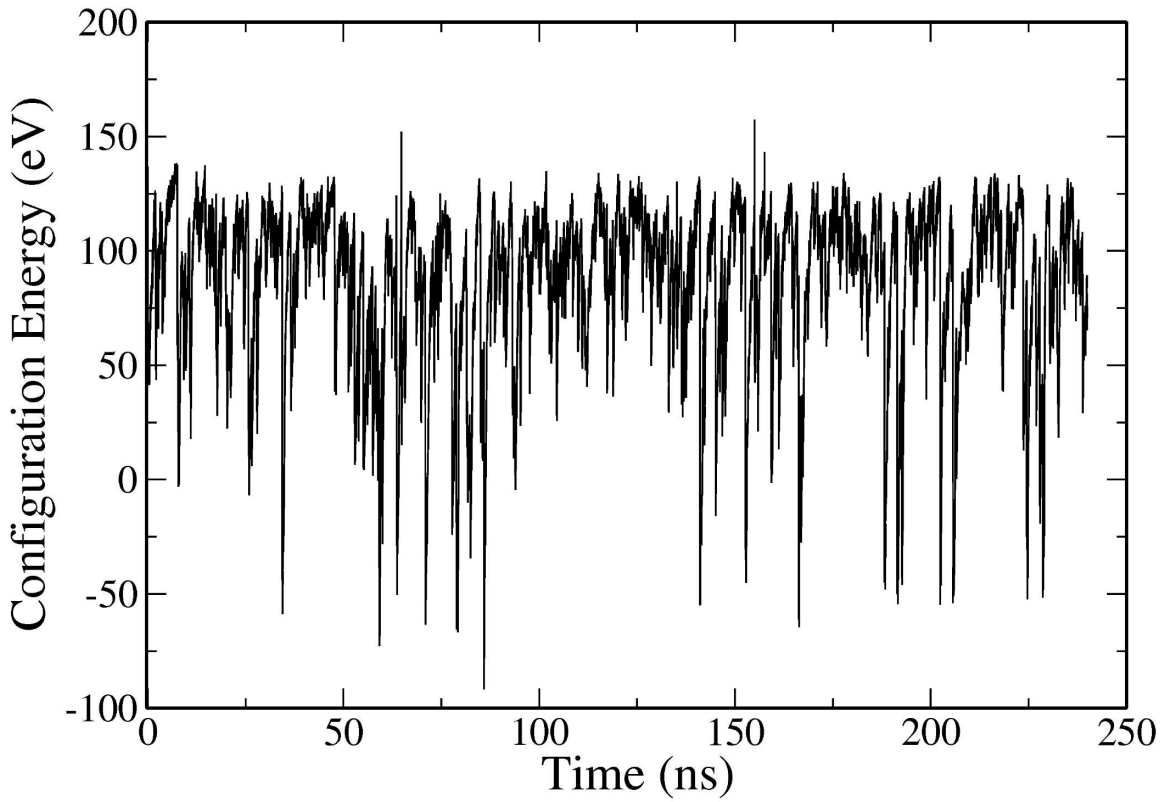

Figure S7. The instantaneous configuration energy in equilibrium for the system with 54 polyglutamines at C = 11.8 mM and T = 310 K.

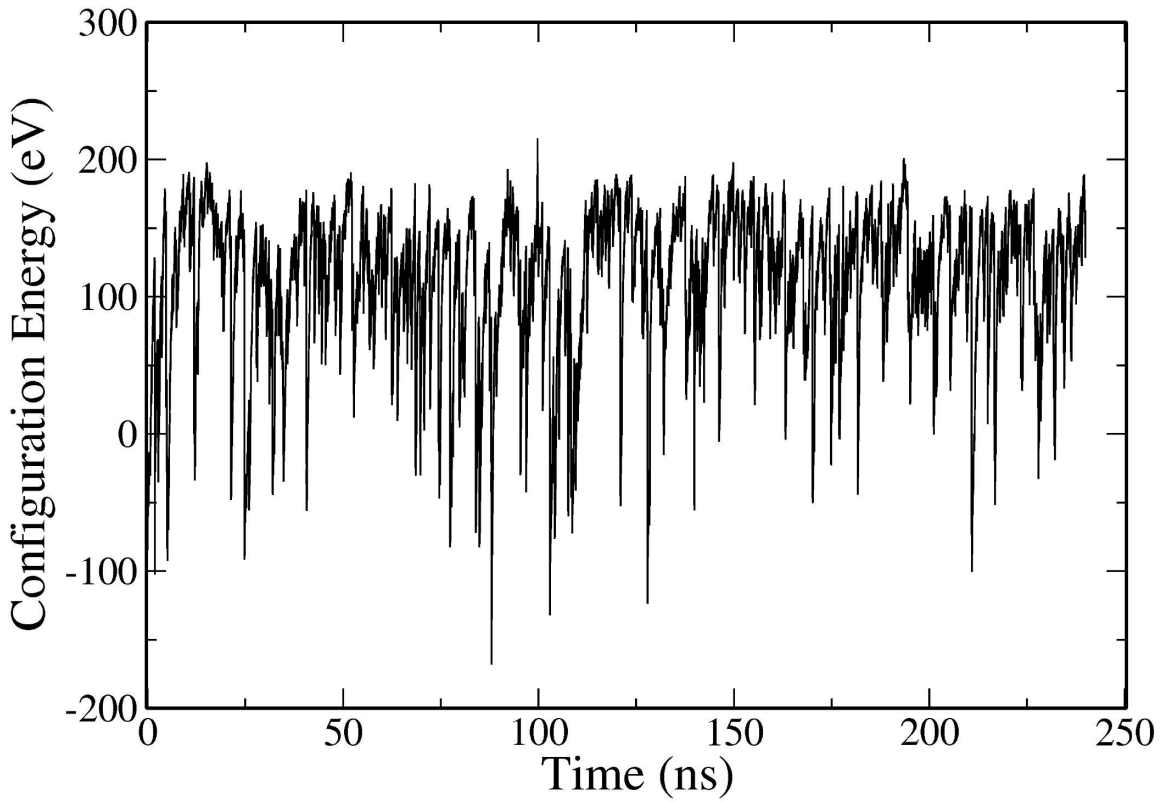

Figure S8. The instantaneous configuration energy in equilibrium for the system with 81 polyglutamines at C = 11.8 mM and T = 310 K.

REFERENCES

(1) Allen, M. P.; Tildesley, D. J. Computer Simulation of liquids; Oxford University Press: New York, 1987.

(2) Wang, Y. T.; Voth, G. A. *J. Phys. Chem. B* **2010**, *114*, 8735.