# Supporting Information

# Oligomeric "Catastrophe Machines" with Thermally Activated Bistability and Stochastic Resonance

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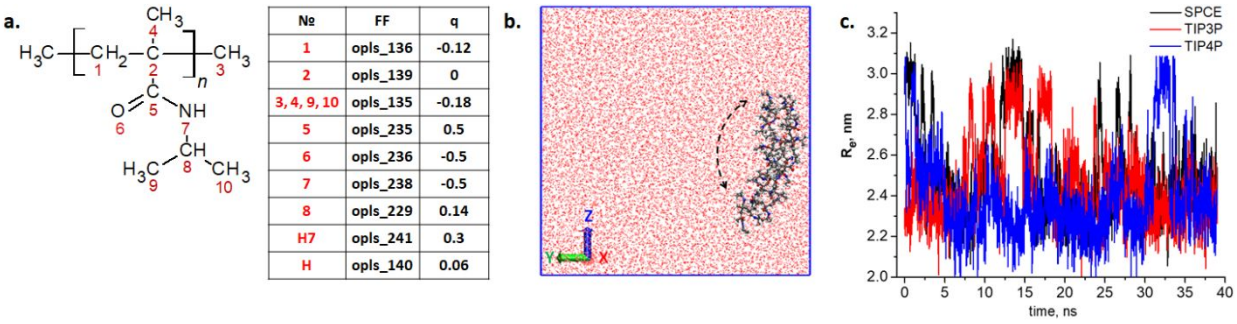
**S1.** *Simulation protocol*

Morphology simulations were performed using the GROMACS simulation package. Because all of the Lennard–Jones parameters were taken from the OPLS-AA force field, the combination rules and a fudge-factor of 0.5 were used for the 1–4 interactions. Details of the parameters used for non-bonded interactions are presented in Figure S1a. Long-range electrostatic interactions were treated using a smooth particle mesh Ewald technique. All calculations were performed in the NVT ensemble using the canonical velocity-rescaling thermostat, as implemented in the GROMACS simulation package.

The simulation was started from a random initial configuration. To reach an equilibrated morphology, the simulation was first initialized using 16,742 water molecules and one NIPMAm oligomer in a syndiotactic configuration that was 30 monomeric units long. These molecules were modeled inside a box with the dimensions of 5.0 × 3.0 × 3.0 nm, which was first exposed to a thermal bath at 290 K for 50 ns with a simulated time step of 0.001 ps (n=5 independent trajectories). The simulation was repeated in a larger box (8.0 × 8.0 × 8.0 nm), which confirmed that the results were not influenced by the simulation box size. An image of the larger simulation box (8.0 × 8.0 × 8.0 nm) is shown in Figure S1b.

To study how the oligomers respond to a power load, the system simulation was continued for an additional 150 ns (n=2 independent trajectories). The model error was estimated using the full

width at 50% of the distribution curve maximum. To show that the results are independent of the specific water model, different water models were tested (SPCE, TIP3P, TIP4P). There was no significant difference in the spontaneous oscillations of the end-to-end distance $R_e$ under the critical load ($F = 400\ pN$; Figure S1c).




| № | FF | q |
|---|---|---|
| 1 | opls_136 | -0.12 |
| 2 | opls_139 | 0 |
| 3, 4, 9, 10 | opls_135 | -0.18 |
| 5 | opls_235 | 0.5 |
| 6 | opls_236 | -0.5 |
| 7 | opls_238 | -0.5 |
| 8 | opls_229 | 0.14 |
| H7 | opls_241 | 0.3 |
| H | opls_140 | 0.06 |

**Figure S1**. a) Non-bonded interaction parameters from the OPLS-AA force field that was used in the simulation; b) the YZ-plane of the simulation box (8.0 × 8.0 × 8.0 nm, 50,888 particles); c) oscillations of the end-to-end distance $R_e$ for various water models (SPCE, TIP3P, and TIP4P).

The simulation workflow was as follows:

1) An "open" conformation of oligo-30s-NIPMAm was obtained by equilibration of the oligomer at a temperature of 290 K. This configuration of oligo-30s-NIPMAm was oriented in the YZ plane and fixed in the X-dimension.

2) The center of mass for the first monomeric unit in the oligomeric chain was fixed using a spring potential of $k = 100\ kJ/molnm^2$. No other specific constraints for bond length or atom positions were applied.

3) The longitudinal (compressing) load $F$ was applied to the center of mass for the last monomer unit and directed toward the attraction point, which was located at the center of mass for the first monomeric unit along the vector connecting the left and right ends of the molecule. Note that the

orientation of this vector changed over time because the first monomeric unit was fixed while the 30th monomeric unit could move.

4) To study stochastic resonance, an oscillating force was realized by setting a charge (+1) at one end of the oligomer and a compensative charge (–1) at the other end. An external oscillating electrical field $E = E_0 \cos \omega t$ was directed along the compressive force $F$. The period of the harmonic electrical field was close to the period of random fluctuation $T = 5ns$ and the amplitude $E_0 = 0.2V / nm$.

5) The lateral load $G$ was applied to the center of mass for the 16th monomer unit (the middle part of the oligo-NIPMAm). Hysteresis (in Figure 4a) was observed when some lateral load was added to the system under critical compression. In this case the region of the vibration (stochastic resonance) depends on increasing or decreasing of lateral load.

6) To represent the stochastic resonance, the time dependencies of the end-to-end distance were plotted under a compressing force $F$ and a lateral force $G$ that were fixed near the critical values.

**S2.** *Vibration mechanism*

To test whether spontaneous vibrations were caused by reversible switching of hydrogen bonds (HBs) between the oligomer–water configuration and the oligomer–oligomer configuration, the number of HBs between the oligomer and water molecules along the chain was quantified. The number of HBs correlated with the oligomer vibrations only for HBs located close to the oligomer bending area (Figure S2). Near all of the critical points $F_c$, $G_1$, and $G_2$, we observed pronounced spontaneous vibrations for both the oligomer and the HBs, which were synchronized in antiphase with high correlation coefficients of −0.92 and −0.90, respectively (Figures S2a–c). The spontaneous vibrations were absent far from the critical points, and the time series $R_e(t)$ did not correlate with the HB time series (Figures S2d–f).

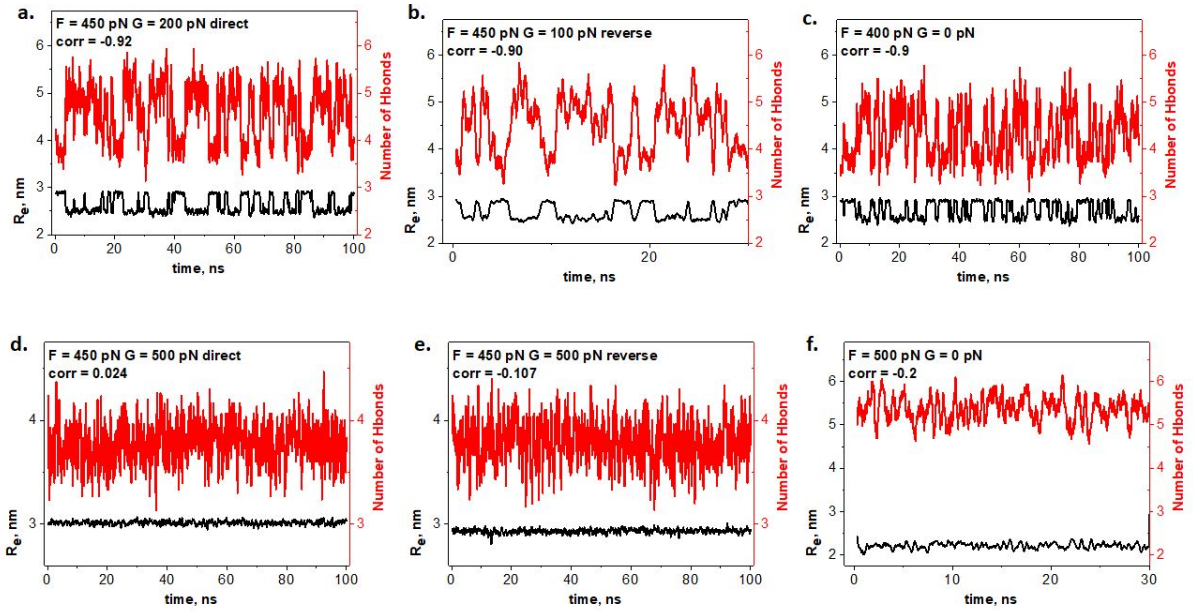



**Figure S2.** The time series for $R_e(t)$ and HBs that are near or far from the critical lateral loads. The values for the power loads $F$ and $G$ are indicated on the panels. "Direct" and "reverse" correspond to "direct way" and "reverse way", respectively, as indicated in Figure 4a. a–c) Low-frequency vibrations of $R_e(t)$ (black curves; left axes) strongly correlate with HB switching (red curves; right axes). d–f) No correlations between $R_e(t)$ and HBs far from the critical lateral loads were observed.

## **S3.** *Stochastic resonance*

Figure S3 shows the $R_e(t)$ trajectories in the stochastic resonance regime initiated by a harmonic electrical field that was applied to oligo-30s-NIPMAm *(for details, see SI1)* with different frequencies under the critical longitudinal compression $F_c$. The oligomer responded to the oscillating force with a consistent frequency (the period of oscillation of the oligomer correlated with the period of oscillation of the applied force). Frequency $\omega$ and amplitude $E_0$ of the harmonic electrical field ranged from 10–400 MHz and 0.01–1.00 V/nm, respectively, demonstrating that the stochastic resonance occurs across a wide range of parameters for the oscillating force.

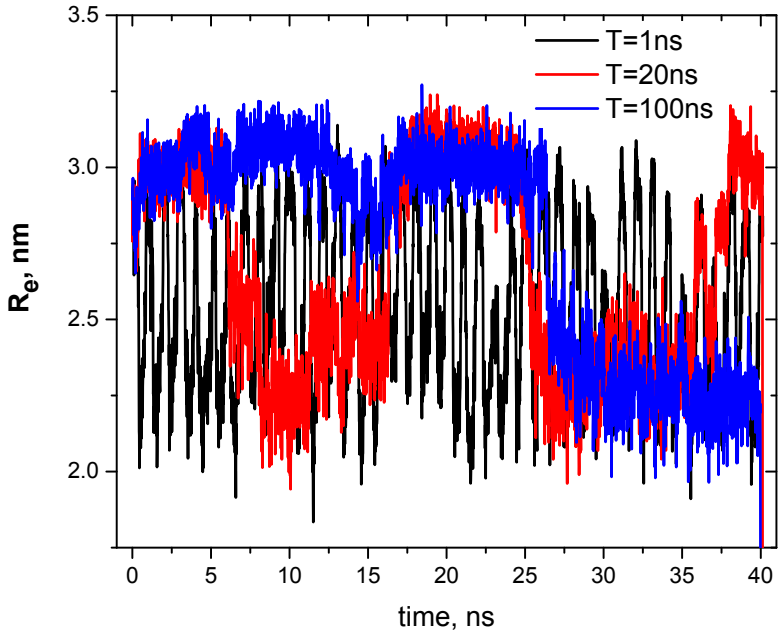



**Figure S3.** Oligo-30s-NIPMAm stochastic resonance initiated by an oscillating longitudinal force $F$ ($G = 0$) with different periods T of oscillation, as follows: the black curve represents T=1 ns, the red curve represents T=20 ns, and the blue curve represents T=100 ns.