Electronic Supporting Information for:

Colored Spectrum Characteristics of Thermal Noise on the Molecular Scale

Zhi Zhu^{1,2}, Nan Sheng¹, Haiping Fang¹, Rongzheng Wan^{1*}

¹Division of Interfacial Water and Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, P.O. Box 800-204, Shanghai 201800, China

²University of Chinese Academy of Sciences, Beijing 100049, China

*E-mail: wanrongzheng@sinap.ac.cn

Method Section

Molecule	Atom	Charge (e)	σ_i (nm)	ϵ_i (kJ/mol)
H ₂ O	Н	0.4238	0.00000	0.00000
	0	-0.8476	3.16557e-01	6.50194e-01
СН₃ОН	С	0.1450	3.50000e-01	2.76144e-01
	H (3)	0.0400	2.50000e-01	1.25520e-01
	0	-0.6830	3.12000e-01	7.11280e-01
	H (1)	0.4180	0.00000	0.00000
NH ₃	Ν	-1.0200	3.42000e-01	7.11280e-01
	Н	0.3400	0.00000	0.00000
H ₂ S	Н	0.2350	0.00000	0.00000
	S	-0.4700	3.70000e-01	1.04600e+00
CH4	С	-0.2400	3.50000e-01	2.76144e-01
	Н	0.0600	2.50000e-01	1.25520e-01
Ne	Ne	0.0000	2.78000e-01	2.88696e-01

Table S1. The potential parameters of the molecules which we used in simulations for the OPLSAA force field.

Table S1 shows the potential parameters of water, methanol, ammonia, hydrogen sulfide, methane and neon molecules in OPLSAA force field.

The mixing rules between two types of atom for Lennard-Jones interaction are as following:

$$\sigma_{ij} = (\sigma_{ii}\sigma_{jj})^{\frac{1}{2}}, \qquad \epsilon_{ij} = (\epsilon_{ii}\epsilon_{ij})^{\frac{1}{2}},$$

where σ is the van der Waals radius of atom and ϵ is the well depth of atom.



Figure S1. The power spectrum comparison of thermal noise associated with molecular rotation between the employ of NPT ensemble (black line) and the employ of NVT ensemble (red line).

Figure S1 shows the power spectrum comparison of thermal noise associated with molecular rotation for water molecule between the employ of NPT ensemble and the employ of NVT ensemble, we can see that their spectrums are consistent. This means the ensembles and the normal fluctuation of pressure have on effect on our conclusions.



Figure S2. The power spectrum comparison of thermal noise associated with molecular rotation between the employ of rigid water model (black line) and the employ of flexible water model (red line).

Figure S2 shows the power spectrum comparison of thermal noise associated with molecular rotation for water molecule between the employ of rigid water model and the employ of flexible water model, we can see that their spectrums are consistent on the qualitative. This means our conclusions are not dependent on the water models.



Figure S3. (a) The power spectrum comparison of thermal noise associated with molecular rotation between the bulk water system of $3 \times 3 \times 3$ nm (black line) and the bulk water system of $5 \times 5 \times 5$ nm (red line). (b) The power spectrum comparison of thermal noise associated with molecular rotation between the bulk water system of $3 \times 3 \times 3$ nm with one methanol solute molecule (black line) and the bulk water system of $5 \times 5 \times 5$ nm with four methanol solute molecules (red line).

Figure S3(a) shows the power spectrum comparison of thermal noise associated with molecular rotation for water molecule between in the bulk water system of $3 \times 3 \times 3$ nm and in the bulk water system of $5 \times 5 \times 5$ nm, we can see that their

spectrums are consistent. Figure S3(b) shows the power spectrum comparison of thermal noise associated with molecular rotation for methanol molecule between in the solvent system of $3 \times 3 \times 3$ nm with one methanol solute molecule and in the solvent system of $5 \times 5 \times 5$ nm with four methanol solute molecules, we can see that their spectrums are consistent. Thus, our conclusions are established for the bigger system with more solute molecules under the condition of little dissolved.



Figure S4. The power spectrum comparison of thermal noise associated with molecular rotation between the time steps employ of 0.1 fs (black line), 0.5 fs (red line) and 1 fs (blue line).

Figure S4 shows the power spectrum comparison of thermal noise associated with molecular rotation for water molecule between the time step employ of 1 fs, 0.5 fs and 0.1 fs, we can see that their spectrums are consistent. This means our conclusions are insensitive to the time steps.

Thus, our conclusions, the power spectrum of thermal noise associated with molecular rotation for polar solute molecules resemble white noise in the low frequency domain, 1/f noise in the intermediate frequency domain, red noise in the high frequency domain, are insensitive to the ensembles, water models, system sizes, and time steps.

Results and Discussion Section



Figure S5. (a) The autocorrelation functions of fluctuating forces (total forces) for whole solute molecules in the solvent. (b) The time integrals of the autocorrelation functions for the total forces on the whole solute molecules.

Theory predicts that the time autocorrelation function of the total force for the whole molecule should produce zero integral. Since stationary stochastic process can shift the time origin by any amount without affecting the correlation function, the integral of force autocorrelation function can represent as:

$$\lim_{t \to \infty} \int_{0}^{t} < F(0) \cdot F(t') > dt' = \lim_{t \to \infty} \int_{0}^{t} < F(t) \cdot F(t') > dt', \qquad (1)$$

where F(0) and F(t) are the total force of the whole molecule at time 0 and t, <> denotes the ensemble average.

The integral of F is proportional to the variation of the translational velocity for the whole molecule:

$$\int_{0}^{t} F(t')dt' = [v(t) - v(0)] \cdot m$$
, (2)

where v(t) and v(0) is the translational velocity of the whole molecule at time 0 and *t*, m is the mass of the whole molecule.

To take advantage of equation (2), equation (1) becomes:

$$\lim_{t \to \infty} \int_{0}^{t} < F(t) \cdot F(t') > dt' \lim_{t \to \infty} \frac{1}{2} \cdot < \frac{d(v^{2}(t) + v^{2}(0) - 2v(0) \cdot v(t))}{dt} > \cdot m^{2},$$
(3)

According to the equipartition of energy theorem:

$$\langle v(t) \cdot v(t) \rangle = \frac{3kT}{m},$$
(4)

where k is the Boltzmann constant, T is the temperature.

To take advantage of equation (4), equation (3) becomes

$$\lim_{t \to \infty} \int_{0}^{t} < F(0) \cdot F(t') > dt' = -\lim_{t \to \infty} \frac{d < (v(0) \cdot v(t) >)}{dt} \cdot m^{2}$$
(5)

As expressed by Green-Kubo formula

$$D = \lim_{t \to \infty} \frac{1}{3} \cdot \int_{0}^{t} < v(0) \cdot v(t') > dt',$$
(6)

where D is the diffusion coefficient of molecule. Since D is a constant, the autocorrelation function of the translation velocity for the whole molecule must be convergent to zero:

$$\lim_{t \to \infty} \langle v(0) \cdot v(t) \rangle = 0.$$
(7)

To take advantage of equation (7) and (5), equation (1) becomes

$$\lim_{t \to \infty} \int_{0}^{t} < F(0) \cdot F(t') > dt' = 0.$$
(8)

Our results also confirmed this prediction as shown in Figure S5. Figure S5(a) shows the time autocorrelation functions of the total forces that the whole solute molecules received; Figure S5(b) shows the integrals of the time autocorrelation functions of those forces, they can produce zero.