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Long time fluctuation of liquid water: $1/f$ spectrum of energy fluctuation in hydrogen bond network rearrangement dynamics

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The power spectrum of the potential energy fluctuation of liquid water is examined and found to yield so-called $1/f$ frequency dependence (f is frequency). This is in sharp contrast to spectra of simple liquids (e.g., liquid argon), which exhibit a near white spectrum. This indicates that there exists an extended multiplicity of hydrogen bond network relaxations in liquid water. A simple model of cellular dynamics is proposed to explain this frequency dependence. On the other hand, the cluster dynamics of argon also involves energy fluctuations of a $1/f$ type, resulting from various relaxation processes at core and surface.

I. INTRODUCTION

Liquid water is a “frustrated” system with multiple random hydrogen bond network structures. Upon the melting from ice to liquid, water absorbs the latent heat 80 cal/g, about 1.4 kcal/mol, and hydrogen bonds become partially broken (frustrated). The system starts to undergo rearrangement dynamics of the hydrogen bond network.^{1,2} This rearrangement dynamics involves collective motion of water molecules and energy fluctuations.^{3–7} It was shown that individual water molecules exhibit enormously large energy fluctuation in pico second time scale, sometimes reaching up to 20 kcal/mol, associated with these collective motions.^{3,4} The total potential energy fluctuation, a sum of these individual energy fluctuations is comparably small, due to their cancellation through the flip-flop-type energy exchanges among water molecules; individual fluctuations are mutually strongly correlated and canceled.^{4,8} Nevertheless, the magnitude of the water total energy fluctuation is larger than that most other liquids,¹ as speculated from its large heat capacity.¹

In the present work we show that the power spectrum of the potential energy fluctuation in liquid waters, yields $1/f^\alpha$ frequency dependence (where α is about 0.75), indicating the existence of multiple relaxation processes of the water hydrogen bond network. This spectrum is in strong contrast to that of simple atomic liquids, such as liquid argon, which yields nearly flat “white-noise” spectra.

Potential energy surfaces of liquids consist of numerous potential energy wells, the minima of which are termed “inherent structures.”⁹ In the course of the dynamics, the system successively visits these inherent structures (wells); the total potential energy fluctuation associated with transitions between inherent structures (inherent structure

transitions, i.e., fundamental structure changes)^{4–7,9} in liquid water has a $1/f^\alpha$ ($\alpha = 1.3$) power spectrum. The total potential energy fluctuation, which is equal to the minus of the total kinetic energy fluctuation in a microcanonical MD (molecular dynamics) simulation, represents the temperature fluctuation of the total system. It has been more or less known that liquid water exhibits a long time temperature fluctuation in MD calculations and very many steps are needed to achieve convergency in Monte Carlo (MC) simulations. The present analysis shows the existence of very long time rearrangement dynamics in liquid water. An average lifetime of individual hydrogen bonds is a few ps. But global hydrogen bond network structures are seen to persist for longer duration; liquid water involves many relaxation processes of different time scales.

A cellular-dynamical model is proposed below to simulate the energy fluctuation in water. The model is based on an assumption that the unstable interactions accumulate at some sites or regions in the network and, when instability exceeds a threshold value, the existing (stressed) network structure collapses and is stabilized by distributing the excess energy to the neighboring sites. It was indeed shown in the previous analyses for the water hydrogen bond network rearrangement dynamics^{3,4} that a few water molecules become very unstable associated with collective motions and then undergo large displacements to find new stable configurations.

Many systems have a $1/f^\alpha$ spectrum with the exponent $0 < \alpha < 2$. This is so-called ubiquitous $1/f$ or flicker noise. The problem is still incompletely understood inasmuch as the systems where $1/f$ noise can be observed are very diverse, it seems likely that a variety of mechanisms can give rise to $1/f$ noise. Excellent reviews are given by Aizawa *et al.*¹⁰ for the Hamiltonian chaos, by Dutta *et al.*¹¹ and by Weissman¹² for the thermal fluctuation phenomena and their models. Recent development is due to Bak *et al.* for

^{a)}Present and permanent address.

self-organized critical (SOC) systems such as a sandpile model.^{13–16} The basic premise of SOC models is that a large interactive system will spontaneously evolve towards a critical state in which fluctuations of all sizes are possible. We here show that liquid water, strongly interacting (hydrogen bonded) network system, is a new example which yields $1/f$ fluctuation.

The methods used are described in Sec. II. The simulation results and discussion are given in Sec. III. A cellular dynamics model for the water energy fluctuations is presented in Sec. IV. Conclusions are given in Sec. V.

II. METHOD

A standard molecular dynamics (MD) method is used for trajectory calculations. 64 (or 216) water molecules are confined in a cubic box, a periodic boundary condition, and the minimum image technique are used, as has been described in detail earlier.^{3–6} A truncated TIP2 potential is used for water intermolecular interactions.⁴ The intramolecular vibrations are not included in the calculation.

A trajectory calculations is computed for 5.4 ns for the system with 64 water molecules (100 ps for that with 216 molecules) at a temperature of 297 K. (The time units are 1 fs = 10^{-15} s, 1 ps = 10^{-12} s, 1 ns = 10^{-9} s.) The power spectrum of the total potential energy is calculated by fast Fourier transformation method (or direct Fourier transformation)

$$S(\omega) = \left| \int_{t_{\min}}^{t_{\max}} V(t) e^{i\omega t} dt \right|^2, \quad (1)$$

where $V(t) = \sum_i V_i(t)/2$ is the total potential energy of the system at time t (in 2 fs interval) and $V_i(t)$ is a potential energy of a water molecule i interacting with all other water molecules j , $V_i(t) = \sum_j V_{ij}(t)$. The trajectory is divided into several time portions, $t_{\min} - t_{\max}$, the power spectra of which are calculated with Eq. (1). These spectra are then averaged to obtain a quality spectrum and locate an onset frequency f_c where the spectrum frequency changes from of the $1/f^\alpha$ type to of another (e.g., a white-noise type; $\alpha = 0$) type. Similarly, the power spectra of the individual water molecular potential energies $V_i(t)$ are calculated. An average over arbitrary chosen molecules i ($i = 1-64$ or $1-216$) in the ensemble is taken.

For the system with 64 water molecules, structures of the initial 28 ps portion of the trajectory are quenched in a 10 fs interval by a steepest descent method to find their local minima, inherent structures and the power spectrum of their potential energies, $V(t)$ [$V_i(t)$] is analyzed.

In order to examine the effect of temperature variations, we have calculated the power spectra for two different temperatures, 250 and 390 K. We also performed 6 ns trajectory calculations for liquid argon and argon cluster with 108 atoms. The power spectra of their potential energies fluctuations are also analyzed.

III. SIMULATION RESULTS AND DISCUSSIONS

The power spectrum of a 5.4 ns trajectory for the system with 64 water molecules is shown in Fig. 1. The tra-

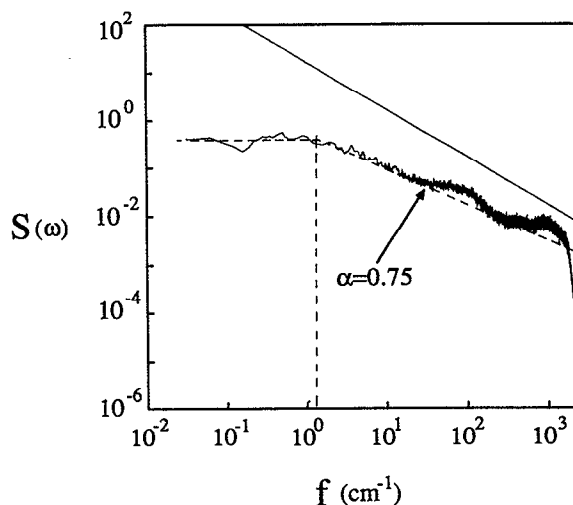


FIG. 1. The power spectrum of total system potential energy in liquid water. The system with 64 water molecules at 297 K. f is in wave number (cm^{-1}) for $f = \omega/2\pi$. A 5.4 ns trajectory is divided into six parts, which are Fourier transformed and averaged. Weak Gaussian averaging is used to smooth the spectral curve. A solid line indicates $1/f^\alpha$ with $\alpha = 1.0$, and dashed lines with $\alpha = 0$ and 0.75 . The modified TIP2 potential is used.

jectory is divided into four parts, each part for 0.9 ns duration, and the power spectra of the total potential energy fluctuations [Eq. (1)] in these parts are averaged to obtain a smooth spectrum curve. We can see there are three regimes apparent in the spectrum.^{17,18} In a frequency range, $1-1000 \text{ cm}^{-1}$, the spectrum yields the $1/f^\alpha$ ($f = \omega/2\pi$, $\alpha = 0.75$) dependence with small peaks corresponding to the normal mode vibrations of translational and librational motions around $20-1000 \text{ cm}^{-1}$.⁴ Above 1000 cm^{-1} the power drops sharply in the higher frequency, since there is no high frequency motion (note that our simulation does not include intramolecular vibrations). Below a low crossover frequency f_c around 1.5 cm^{-1} , the spectrum is of a white-noise type. There is no correlation between events (i.e., motions cause the energy fluctuation) separated longer than 20 ps. Crossover frequency (onset) of power spectra was discussed by Kaneko and Konishi for anomalous diffusion in a symplectic map lattice dynamics,¹⁸ and by Hwa for a sandpile model.¹⁷ Kaneko *et al.*¹⁸ found that the lattice dynamics yields an anomalous diffusion, power-law-type behavior involving the dynamics on the hierarchical structure of (KAM) tori, on short-time scale, but a normal diffusion on very long-time scale, longer than the time for the KAM tori breaking down. Here the time corresponding to f_c (inverse of it), about 20 ps, might be considered as a duration time of an overall hydrogen network structure in liquid water dynamics.¹⁹ It is longer than the average life time of individual hydrogen bonds, which is about a few ps. Indeed, a graphics movie of the hydrogen bond network rearrangement indicates that overall structure of a hydrogen bond network persists for a few 10 ps.

The $1/f$ -type spectrum in the frequency higher than this f_c shows that the correlation of network fluctuations decays not in a single Markovian process (the Debye-type relaxation) but through multiple processes. The number of

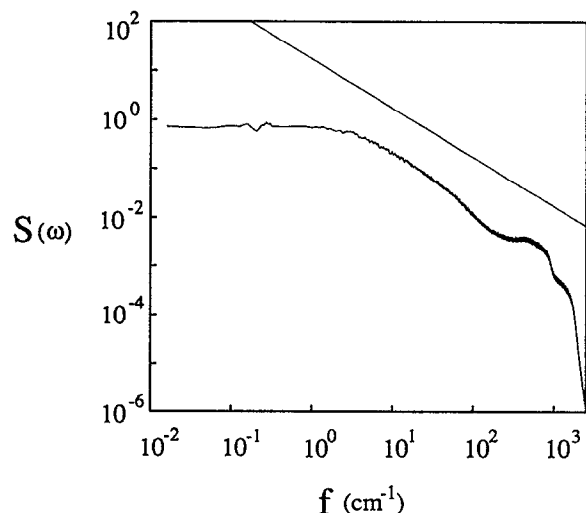


FIG. 2. The power spectrum of individual molecule potential energies in liquid water. Averaged over arbitrarily chosen 20 water molecules i . A 4.2 ns part of the trajectory is used. See also caption of Fig. 1.

molecules involved in the network rearrangement motion at each instance is very widely distributed.⁴ This wide distribution should correspond to the multiplicity of the relaxation processes; a large scale rearrangement involving many molecules is relatively infrequent and is associated with a long time relaxation process. A small scale rearrangement, on the other hand, occurs more often and is associated with a short time relaxation process. In the Appendix we propose a simple scaling relation between the rearrangement magnitude and the energy fluctuation correlation, arising from these assumptions.

The power spectrum of the individual fluctuation is shown in Fig. 2. Similarly to Fig. 1, the spectrum has a near white part in the frequency region lower than f_c and has small peaks in the high frequency region arising from the normal vibrations. In the middle part, however, the slope depends on the frequency and the spectrum is not well fitted by a straight line. An individual water molecule is confined in the surrounding hydrogen bond network in a short-time scale, thus a Markovian behavior (Debye-type relaxation) is observed, and it changes smoothly to a diffusive motion in a long-time scale.

The power spectra of the total and individual potential energy fluctuations for a larger system²⁰ with 216 water molecules [shown in Figs. 3(a) and 3(b), respectively] yield very similar frequency dependence to those for the 64 molecule system, shown in Figs. 1 and 2. Since only the 100 ps trajectory is used to obtain these power spectra, finding a location of the low frequency crossover point f_c is difficult.

The water binding structures in the trajectory for the system with 64 molecules, the same trajectory as above, are quenched to their local minima (inherent structures) in a 10 fs interval.^{5,6} Each quenching takes about 3 min in a supercomputer, near equivalent to Cray-MYP, and we have calculated 2800 quenched structures (28 ps) so far. The potential energies of these inherent structures, sequen-

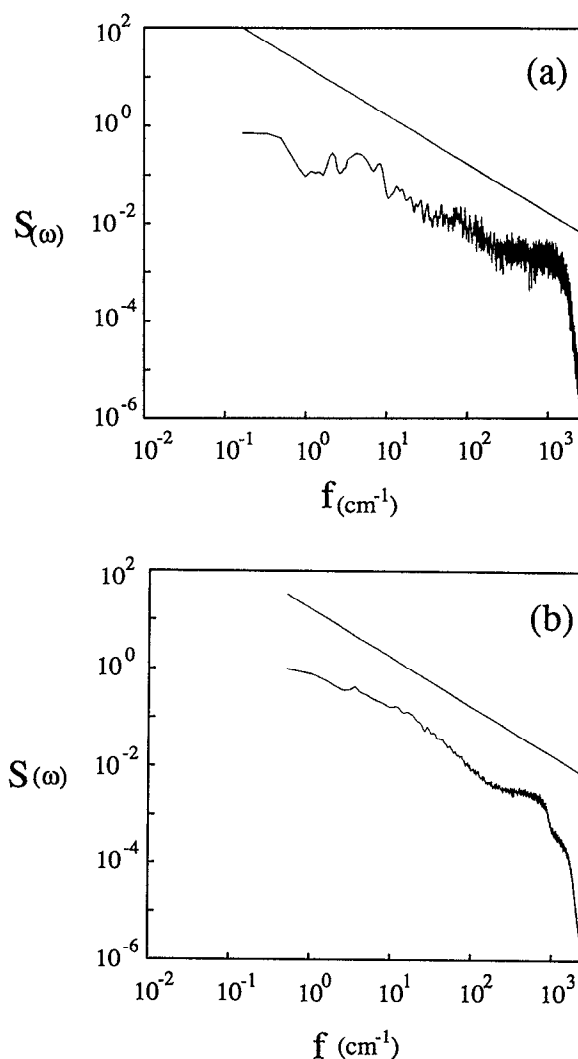


FIG. 3. The power spectra of (a) total system potential energy and (b) individual molecule potential energies in liquid water. The system with 216 water molecules at 297 K. A 100 ps trajectory. Parts of 64 ps duration are Fourier transformed in (b). Weak Gaussian averaging is used. Averaged over arbitrarily chosen 30 water molecules i and (b). f is in wave number. A solid line indicates $\alpha = 1.0$.

tially visited by the trajectory, are plotted in Fig. 4. The fluctuation of these energies is a typical $1/f$ noise. Indeed, as seen in Fig. 5(a), the power spectrum does not have the small vibrational peaks observed in Figs. 1–3 and is well fitted by the straight line with the slope with $\alpha \approx 1.3$. The spectrum of the individual energy fluctuation [Fig. 5(b)] can also be fitted by the line with the same slope $\alpha \approx 1.3$. It is not clear from the spectrum of this very short time (28 ps) energy fluctuation where the low-frequency turning point f_c exists. We employed only straight Fourier transformation of the discrete energy fluctuation data in Fig. 4, and so the spectrum obtained does not diminish in the high frequency region, unlikely as an instant structure spectrum shown in Fig. 1. Nevertheless, it is evident that the inherent structure potential energy spectrum yields a stronger $1/f$ dependence than the instant structure spectrum. It is of the interest here to find to what extent the inherent structure fluctuation reflects the real (instant) structural

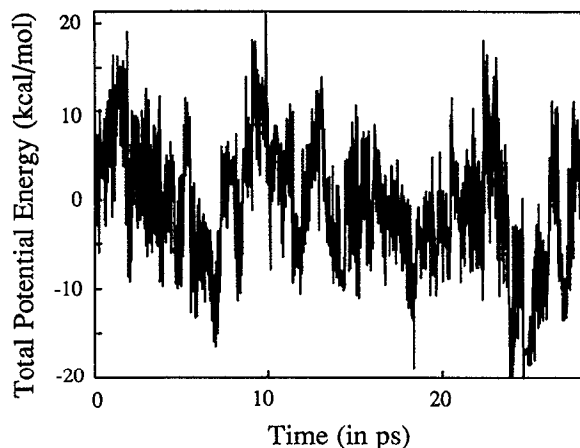


FIG. 4. The total system potential energy in inherent structures. The water structures in the first 28 ps part of the 5.4 ns trajectory (in Fig. 1) are sequentially quenched in 10 fs interval. Energy is relative to -779.7 kcal/mol.

fluctuation in the trajectory. In Fig. 6, the instant structure energy averaged over 20 fs ($\Delta t = 10$ fs)

$$\tilde{V}(t) = \frac{1}{2\Delta t} \int_{-\Delta t}^{\Delta t} V(t + \tau) d\tau \quad (2)$$

is plotted. We can see that the overall character of the energy fluctuations in the instant structures (Fig. 6) and the inherent structures (Fig. 4) are indeed very similar, although the scale of variation is smaller in the former case. The liquid dynamics in the instant structure includes diffusion from a potential well to the next well and short time vibrational relaxations, and so the spectra of its potential energy fluctuation (Figs. 1 and 2) are shifted from the inherent structure's [Figs. 5(a) and 5(b)] to yield more white and Debye-type frequency dependences. When a longer averaging time, e.g., 400 fs [$\Delta t = 200$ in Eq. (2)], is used in Eq. (2), the energy fluctuation corresponds to so-called V (vibrationally averaged) structures.^{1,3,21} Its spectrum (not shown in a figure) is similar to the inherent structure's in a certain range, about $1\text{--}100\text{ cm}^{-1}$.

The liquid argon spectra of the total and individual potential energy fluctuations are plotted in Figs. 7 and 8, respectively. We can see in Fig. 7 that total potential energy fluctuation is almost frequency independent, meaning the liquid structural change is stochastic and mostly simple diffusional.^{22(a)} As an atomic self-diffusion spectrum shows,^{22(b)} however, each atomic motion involves some vibratory component, resulting in weak frequency dependence of the individual potential energy power spectrum (Fig. 8). It is important to point out that argon clusters, on the other hand, yield strong $1/f$ frequency dependence (see Fig. 9). A cluster involves different kinds of motions for different parts, core and surface parts.^{23–25} We have recently investigated a hierarchical structure of the potential energy surfaces in clusters, and indeed found that potential energy barrier height distributions for surface displacements are very different from those for the core displacements, and characters of their motions are also

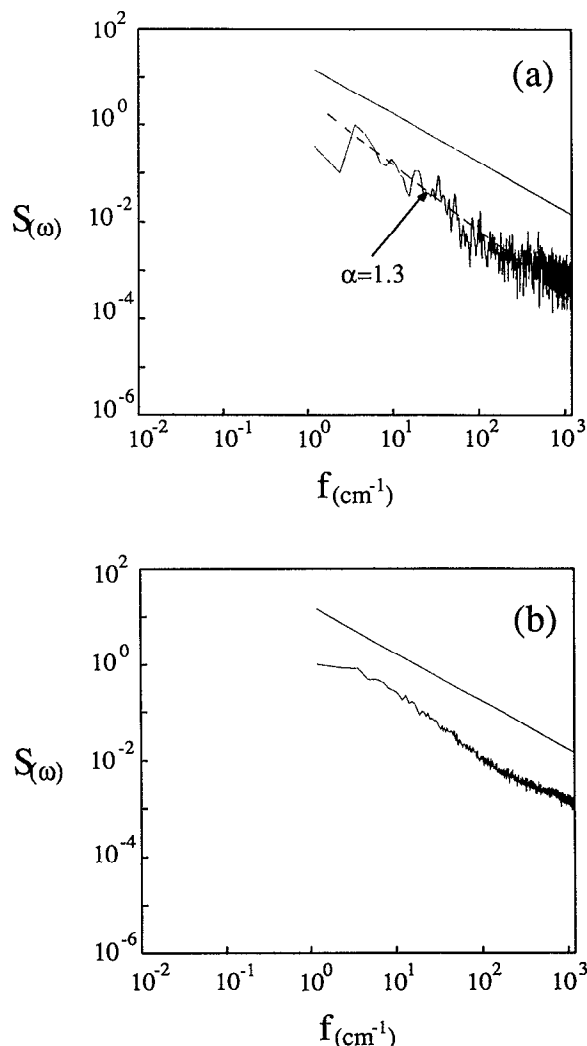


FIG. 5. The power spectra of (a) the total potential energy (Fig. 4) and (b) individual molecular potential energies in inherent structures. A solid (dashed) line indicates $\alpha = 1.0$ (1.3). Averaged over all 64 water molecules in (b). f is in wave number.

very different.²⁵ A cluster thus involves multiple relaxations and thus gives power law temporal correlations.

With lowering temperature,^{26,27} the onset f_c seems to be shifted to the lower frequency and the $1/f^\alpha$ part of the spectrum has a little steeper slope [see Fig. 10(a) at 250 K]; the water dynamics involving large hydrogen bond rearrangements becomes slower and less diffusional since the excess kinetic energy to go over potential energy barriers for these arrangements is small. Preliminary calculations for low temperature dynamics ($T < 200$ K; not shown in figure) indicate that the system motion is very stagnant, mostly vibrating around a potential energy minimum (inherent structure) and rarely making jumps to other minima.⁵ Then the power spectrum seems to have a much steeper slope $\alpha > 1.0$. Such increase of the slope with lowering temperature agrees with a cellular dynamics result shown below [Fig. 14(a)]. It is noted that the present MD calculation is of a microcanonical trajectory with a constant volume, and so the low temperature trajectory dy-

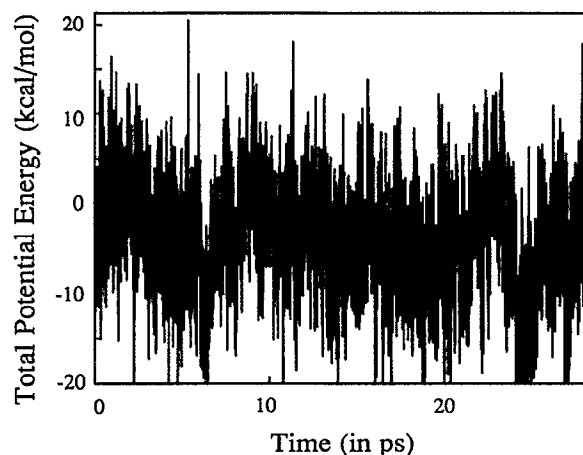


FIG. 6. The total system potential energy in the first 28 ps part of the 5.4 ns trajectory (Fig. 1). Instant structure energies averaged over 20 fs, $\Delta t = 10$ fs [Eq. (2)]. Energy is relative to -626.4 kcal/mol. See Fig. 4.

namics here does not necessarily correspond to an experimentally observed situation under a constant pressure.^{26,27} In the higher temperature [in Fig. 10(b) at 390 K], hydrogen bonds break and molecular motions become more independent, thus yielding a more white spectrum. Similar temperature dependence of the spectra is also observed in argon clusters (not shown in figures).

IV. A CELLULAR DYNAMICS MODEL FOR WATER ENERGY FLUCTUATION

The significant differences between the power spectra in liquid water and those in liquid argon must be attributed to the unique structure and dynamics of the hydrogen bond network among water molecules. When some parts of the network are strongly distorted and the energy of mol-

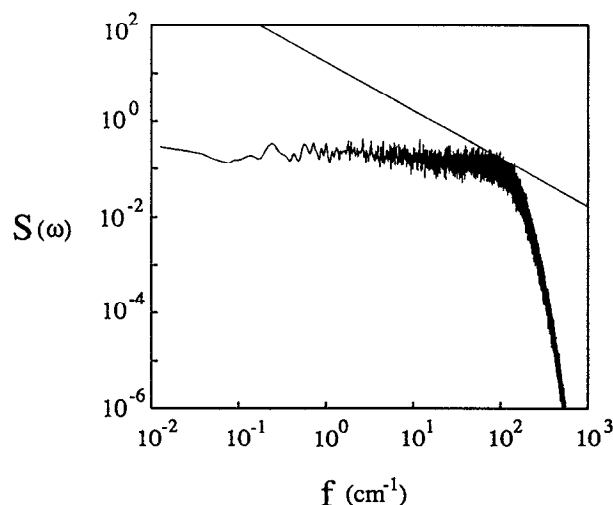


FIG. 7. The power spectrum of the total system potential energy in liquid argon. The system with 108 argon atoms at 95 K. A 6 ns trajectory is divided into two parts, which are Fourier transformed and averaged. Weak Gaussian averaging is used. A simple Lennard-Jones potential is used. f is in wave number. A solid line indicates $\alpha = 1.0$.

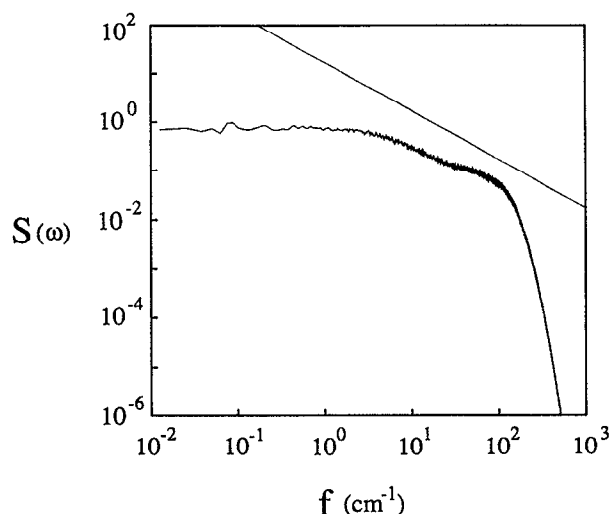


FIG. 8. The power spectrum of individual atomic potential energies in liquid argon. See caption of Fig. 7.

ecules in that region exceeds a certain limit, the elastic network distortion then turns into a plastic structural rearrangement through rotations and large displacements of unstable molecules.^{3,4} These molecules are stabilized by finding a new stable network structure. The released excess energy is often more than several kcal/mol per molecule.^{3,4} Some part of this released energy should dissipate into the thermal vibrations but the large part of it is distributed to the neighbor molecules. Then the next accumulation of distortion begins in the neighbors. In this way, the total system never reaches a uniform stable state: The concentration of unstable molecules fluctuates but does not diminish. This is reminiscent of the dynamics in random spin systems, and thus we can say that liquid water is a frustrated system.

We construct a cellular dynamics model which captures the essential features of this frustration dynamics but

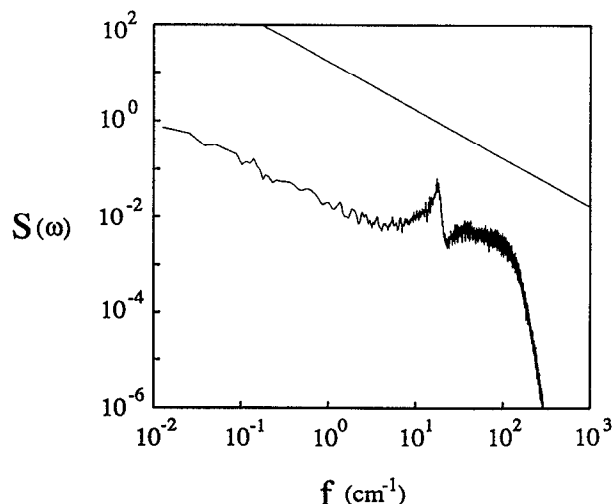


FIG. 9. The power spectrum of the total system energy in argon cluster. A cluster with 108 argon atoms at 35 K. See caption of Fig. 7.

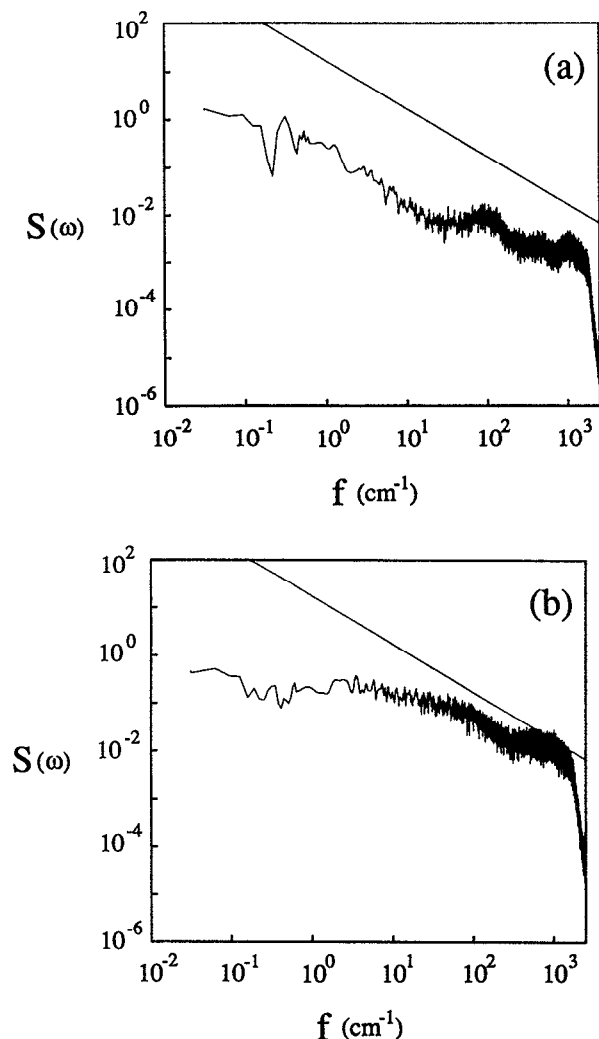


FIG. 10. The power spectra of the total system potential energies in liquid water. (a) at 250 K and (b) at 390 K. The system with 64 water molecules. A 1.2 ns trajectory is used. See caption of Fig. 1.

is designed to be as simple as possible. We consider the three-dimensional cubic lattice with the periodic boundary condition and define the "potential energy" $V_i(t)$ at each site (cell) at time t . The energy at the next time step $V_i(t + \Delta t)$ is determined by the following algorithm:

- (1) Define $E_i(t) = V_i(t) + \{\eta_i(t)\}^2$, where $\eta_i(t)$ is the Gaussian white noise, $\langle \eta_i(t) \eta_j(t') \rangle = D \delta_{ij} \delta_{tt'}$, which corresponds to the small amplitude vibration of the network.
- (2) If $E^- < E_i(t) < E^+$ for all i , then $V_i(t + \Delta t) = V_i(t)$.
- (3) If $E_i(t) \geq E^+$ at the i th site, then $V_i(t) \rightarrow V'_i(t) = V_i(t) - V_s$ and $V_j(t) \rightarrow V'_j(t) = V_j(t) + a V_s / z$, where j is the nearest neighbor or the second neighbor of i , $z = 18$ is the number of first and second neighbors, and $1-a$ is the rate of dissipation to the heat bath.

Here each site is changed in parallel. The relaxation rule (3) resembles that in the SOC models¹³ (see Fig. 11); the i th site is stabilized and the excess energy V_s is distributed

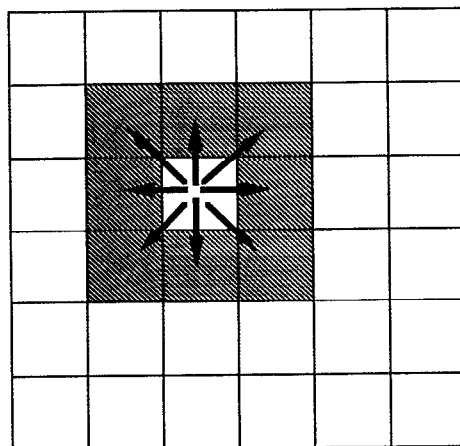


FIG. 11. The relaxation of the cell in the two-dimensional lattice. When V_i exceeds E^+ , the energy at the i th site is distributed to the first and second neighbors [rule (3)]. Actual simulation is done in three-dimensional cubic lattice.

to its neighbors. The distributed energy can trigger off the next stabilization at the neighbor sites. Thus cascaded avalanches with various size are induced. When $a = 1$, the energy is strictly conserved without dissipation. In this case avalanches with very large size are possible and in the present model which has periodic boundary conditions, some avalanches will never stop. We choose a to be $0 < a < 1$, so that every avalanche has finite size. Then the energy proportional to the avalanche size is lost into the heat bath and the system is cooled.²⁸ In order to prevent the system from dying out, the energy of the same order needs to be supplied to the system from the bath; then the system becomes "equilibrium." In usual modeling of a random process this is assured by imposing the detailed balance. We here, instead, adopt a simple rule which resembles to the rule (3)

- (4) If $E_i(t) \leq E^-$ at the i th site, then $V_i(t) \rightarrow V'_i(t) = V_i(t) + V_d$, where $V_d = E^- - E_i(t)$.

Thus sites which have lost too much energy are heated by accepting the energy from the bath. Rule (3) and rule (4) are repeatedly applied until all avalanches cease.

Then

- (5) If $E^- < V'_i(t) + \{\eta_i(t)\}^2 < E^+$ for all i , $V_i(t + \Delta t) = V'_i(t)$.

In this model the change of parameters E^+ and E^- can be absorbed by rescaling other parameters, so there are three independent parameters left, D , V_s , and a . D should be regarded as the amplitude of thermal fluctuation, $D \approx k_B T$. It should be noted that since the detailed balance is not explicitly assured in this model, the "temperature" here is used in a very loose sense. We assume that the dissipation energy is of order of thermal fluctuation; $(1-a)V_s \approx D$, and that the stabilization energy at the individual site is much larger than the thermal energy; $V_s \approx E^+ - E^- \gg D$. Calculations were carried out for $8 \times 8 \times 8$ cubic lattice. Initial values, $V_i(0)$ were chosen to be uniform random numbers between E^- and E^+ .

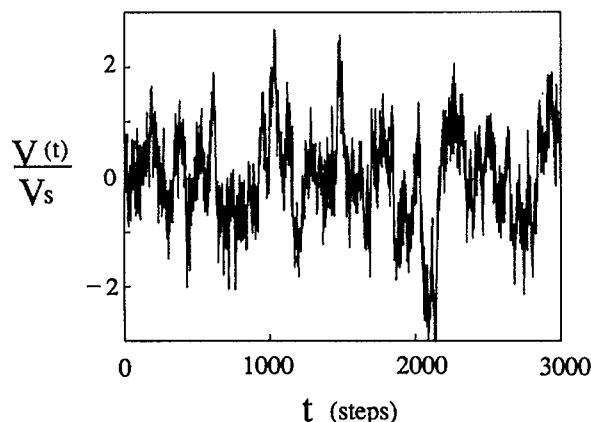


FIG. 12. The total system fluctuation $V(t)$ in the cellular dynamics model. The calculation was done in $8 \times 8 \times 8$ cubic lattice. The parameters are $E^+ = 10$, $E^- = -11$, $V_s = 20$, $D = 0.9$, and $a = 0.9$.

Results of this cellular dynamics model resembles those of the MD calculations of liquid water in many points. In Fig. 12 we show the fluctuation of the total energy $V(t) = \sum_i V_i(t)$ of this model, which is very similar to Fig. 4. In Fig. 12 the amplitude of the total energy fluctuation is of the same order as V_s , which is the amplitude of the individual energy fluctuation. The law of large number (the total fluctuation $\approx V_s \sqrt{N}$) does not hold, but individual fluctuations are mutually strongly correlated and canceled each other. Thus the flip-flop-type energy exchange plays the important role in this model as well as in the MD results.^{4,8} Figure 13 is the power spectrum of Fig. 12. Note that the energy fluctuation in the cellular dynamics here corresponds that in the inherent structures. It shows the $1/f^\alpha$ dependence with $\alpha = 1.5$, which is slightly larger than the slope $\alpha = 1.3$ in Fig. 5. The system responds to the input white noise with the non-Debye-type

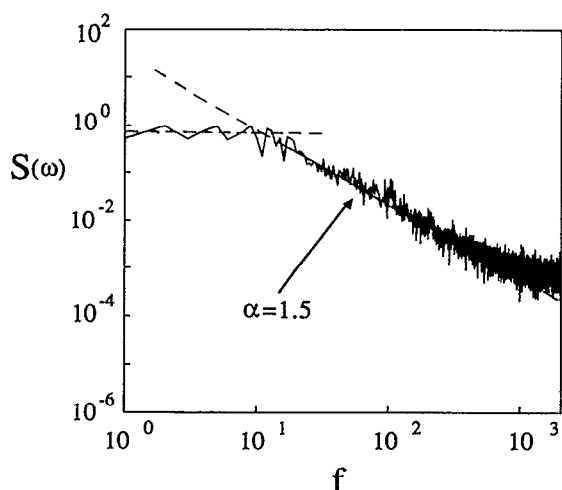


FIG. 13. The power spectrum of the total system fluctuation in the cellular dynamics model. Spectra of eight trajectories with $n = 4096$ steps are averaged. f is frequency in the unit of $1/n$. Dashed lines indicate $1/f^\alpha$ with $\alpha = 0$ and 1.5 . See caption of Fig. 12.

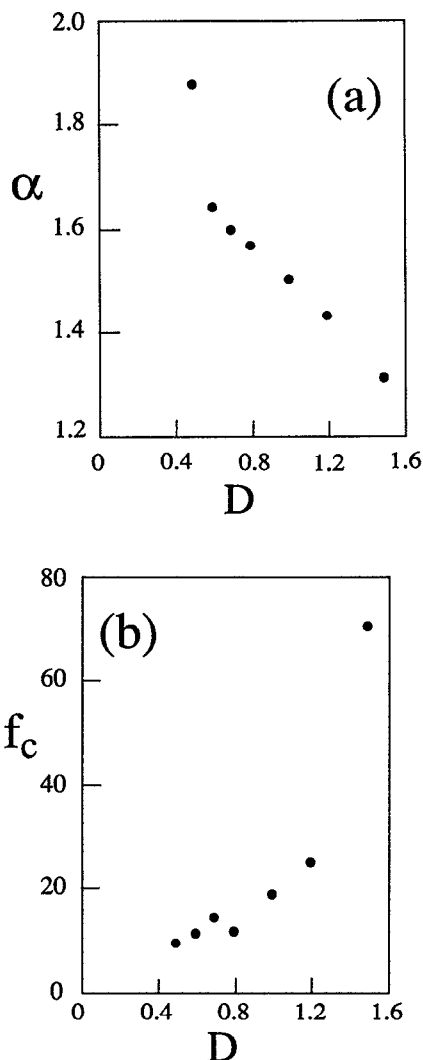


FIG. 14. Dependence of the slope α on the noise amplitude D (a) and dependence of the cutoff frequency f_c on D (b). $8 \times 8 \times 8$ cubic lattice with $E^+ = 10$, $E^- = -11$, $V_s = 20$, and $a = 0.9$.

fluctuation which has the long time correlation. These results are insensitive to the choice of $V_i(0)$. In fact, with the parameters of Fig. 12, many other choices of $V_i(0)$ we tried [e.g., $V_i(0) = (E^+ + E^-)/2$ for all i] lead to the same spectrum as Fig. 13. It seems that the state that supports the $1/f^\alpha$ fluctuations is indeed an attractor of the dynamics, with a sufficiently large basin of attraction.

The spectrum depends on the parameters in the interesting way; with decreasing D , the slope α becomes large and the turning point f_c shifts to the lower frequency side. If we regard D as temperature, this behavior agrees with the tendency observed in the MD results (see, e.g., Figs. 1 and 10). We show in Fig. 14 how α and f_c depend on D . The slope α in Fig. 14(a) jumps to near 2 at very small D . It will be interesting to examine more details to see whether this increase of α is related to the kinetic transition of the model from the liquid state to a frozen glassy state. For other parameter, α and f_c change with a or V_s value in the same way as they do with D . A choice of V_d in rule (4) (e.g., changing it to $V_d = 2$) does not affect the

basic feature of the dynamics. The present simple cellular dynamics model yields the nontrivial fluctuations which are similar to the MD results in many points and strongly suggests that the frustration dynamics and associated flip-flop-type energy exchange are essential to describe liquid water. The present thermal driven SOC model seems to yield "global equilibrium" with large energy fluctuation as shown in Fig. 12. It should be, however, improved to explicitly take account for the detailed balance to yield the definite thermal equilibrium.

V. CONCLUSIONS

We have analyzed the power spectra of the water energy fluctuations. The inherent structures sequentially visited by the system yields a near $1/f^{1.3}$ energy fluctuation, indicating there are multiple relaxation processes in liquid water. The power spectrum for the instant structures in the real trajectory becomes slightly more white, $1/f^{0.75}$, and has a crossover to a white-noise behavior. The time corresponding to this crossover frequency f_c , 10–30 ps, might be considered to be a duration time of an overall hydrogen bond network structure. More analyses are necessary to exactly define overall hydrogen bond structures and dynamics¹⁹ and to understand how the spectrum shape and crossover frequency depend on size of the system²⁰ and on character of the hydrogen bond network and others. A cellular dynamics model, thermal driven SOC model, for the liquid water energy fluctuation was proposed. The model provides a similar power spectrum to the inherent structure's and takes account for the flip-flop energy exchanges among individual molecules.

In the present study, we have only dealt with the energy fluctuations. How the dynamics involved the $1/f$ -type energy fluctuations is reflected (or not reflected) in other physical quantities such as Raman spectra²⁹ and dielectric relaxation³⁰ is yet to be investigated. An extensive investigation for a detailed mechanism of the hydrogen bond network dynamics in a long-time scale by analyzing multidimensional potential energy surfaces for the network rearrangements and their hierarchical structure should be performed and it ought to be related to the $1/f$ -type power spectra. A thermal driven SOC model, which explicitly satisfies the detailed balance, must be developed.

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APPENDIX

From the Wiener-Khinchin theorem, Eq. (1) is

$$S(\omega) = \frac{1}{\omega^2} \int \langle \dot{V}(0) \dot{V}(t) \rangle e^{i\omega t} dt, \quad (\text{A1})$$

where $\langle \cdots \rangle$ is the ensemble average and $\dot{V} = dV/dt$. Here \dot{V} should depend on the magnitude of the network structure rearrangement. We thus write $\dot{V}(t) \approx g(N)$ and N is the number of water molecules which move simultaneously with large displacements at time t . We expect $g(N) \approx N^\delta$. $\delta = 1/2$ if there is no correlation among fluctuations of N molecules and $\delta = 0$ if the energy cancellation of fluctuations is complete. Equation (A1) should be written as the superposition of various rearrangement processes

$$S(\omega) \approx \frac{1}{\omega^2} \int \sum_{N, N'} P(N) P(N, 0; N', t) g(N) g(N') e^{i\omega t} dt, \quad (\text{A2})$$

where $P(N)$ is the probability distribution that N molecules move with large displacements, and $P(N, 0; N', t)$ is the constrained probability that N molecules move with large displacements at time $t = 0$ and N' molecules move at the later time t . In the MD simulation at room temperature with 216 water molecules, $P(N)$ is peaked at around $N = 20$ and has nonnegligible values for $N > 90$.⁴ If we assume that Eq. (A2) can be written in the scaling form as

$$S(\omega) \approx \frac{1}{\omega^2} \int \sum_{N, N'} N^{-\gamma(N')} N'^{-\gamma'} F[tN^{-\beta}, t(N')^{-\beta'}] e^{i\omega t} dt, \quad (\text{A3})$$

and replace the summation with the integral, then, for the higher frequency region than the turning point, we have

$$S(\omega) \approx 1/\omega^\alpha, \quad \alpha = (1 - \gamma)/\beta + (1 - \gamma')/\beta' + 3. \quad (\text{A4})$$

In order to be consistent with the MD results, $(1 - \gamma)/\beta + (1 - \gamma')/\beta' \approx -2$.

The validity of the scaling assumption of Eq. (A3), however, has not yet been checked directly in MD calculations. Further investigation is needed to examine whether Eq. (A3) really holds, and to determine the exponents β and γ .

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