Complex temporal patterns in molecular dynamics: a direct measure of the phase space exploration by the trajectory at macroscopic time scales

Who? **Dmitry Nerukh**
Robert Glen

From? Cambridge

When? 16 May 2007

Logarithmic growth of the Statistical Complexity

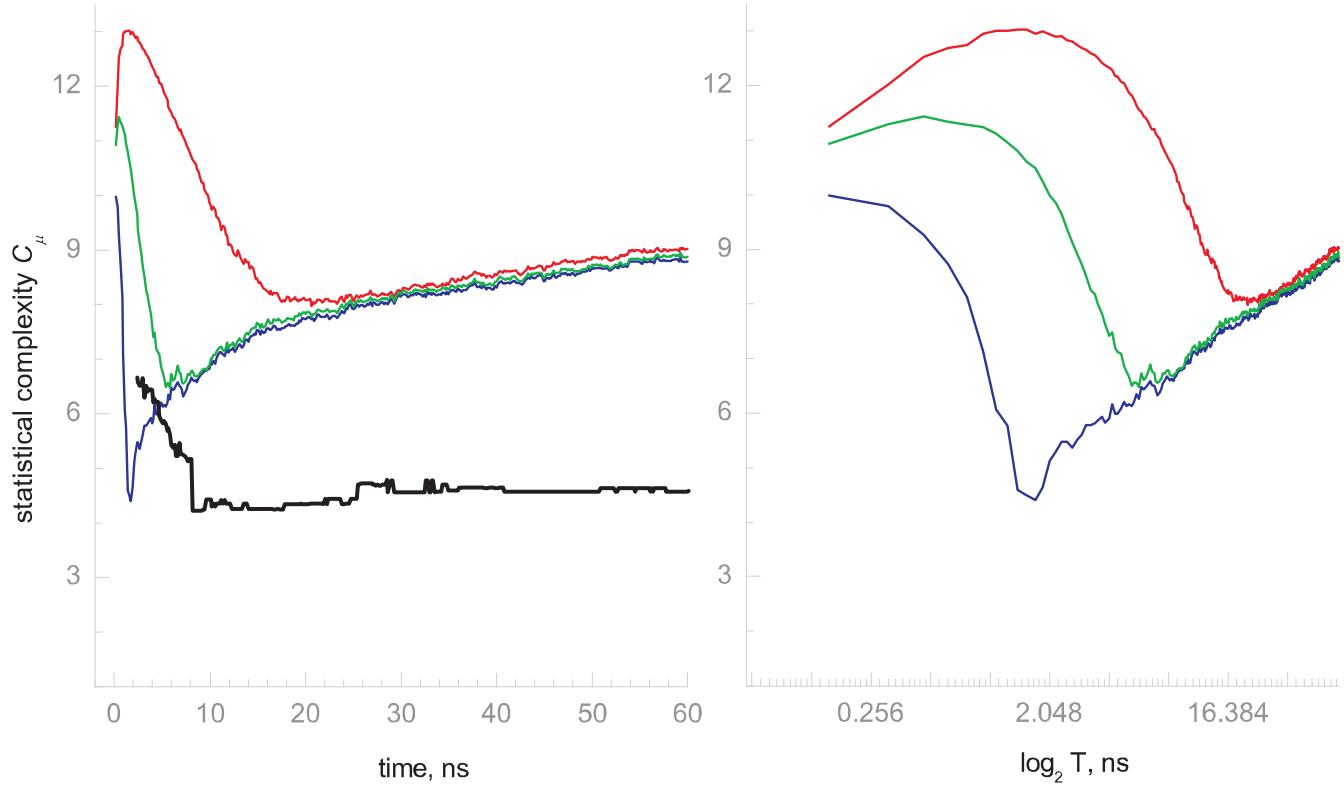

Figure: Statistical complexity against time for the hydrogen velocity signal and the surrogate.

Velocity autocorrelation

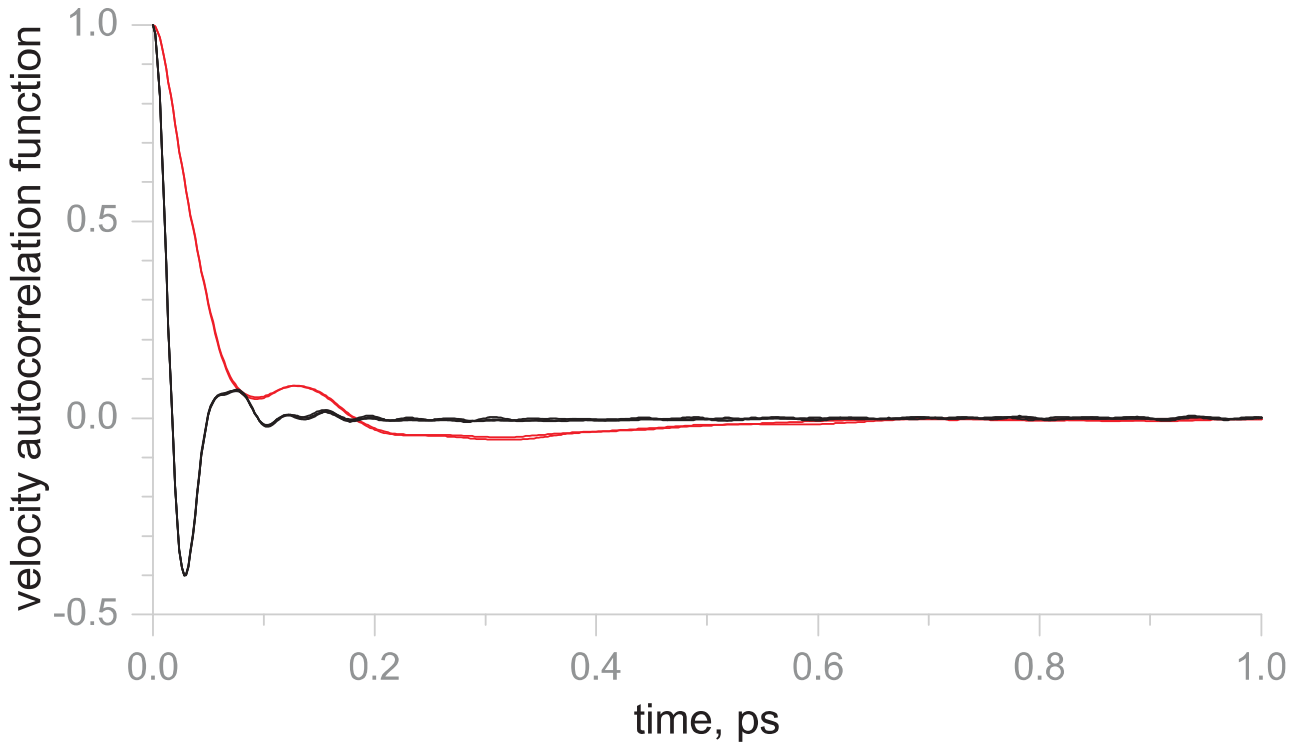

Figure: Velocity autocorrelation function for oxygen (red) and hydrogen atoms.

Spectra of the signals

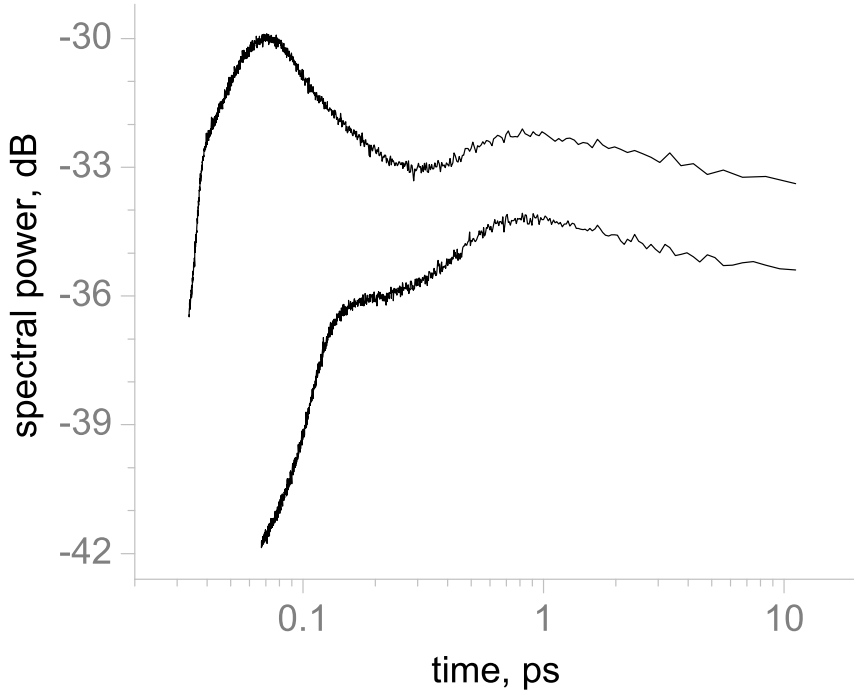

Figure: Spectra of the hydrogen and oxygen velocities. (collaboration with Vladimir Ryabov, Hakodate)

Causal states occurrences

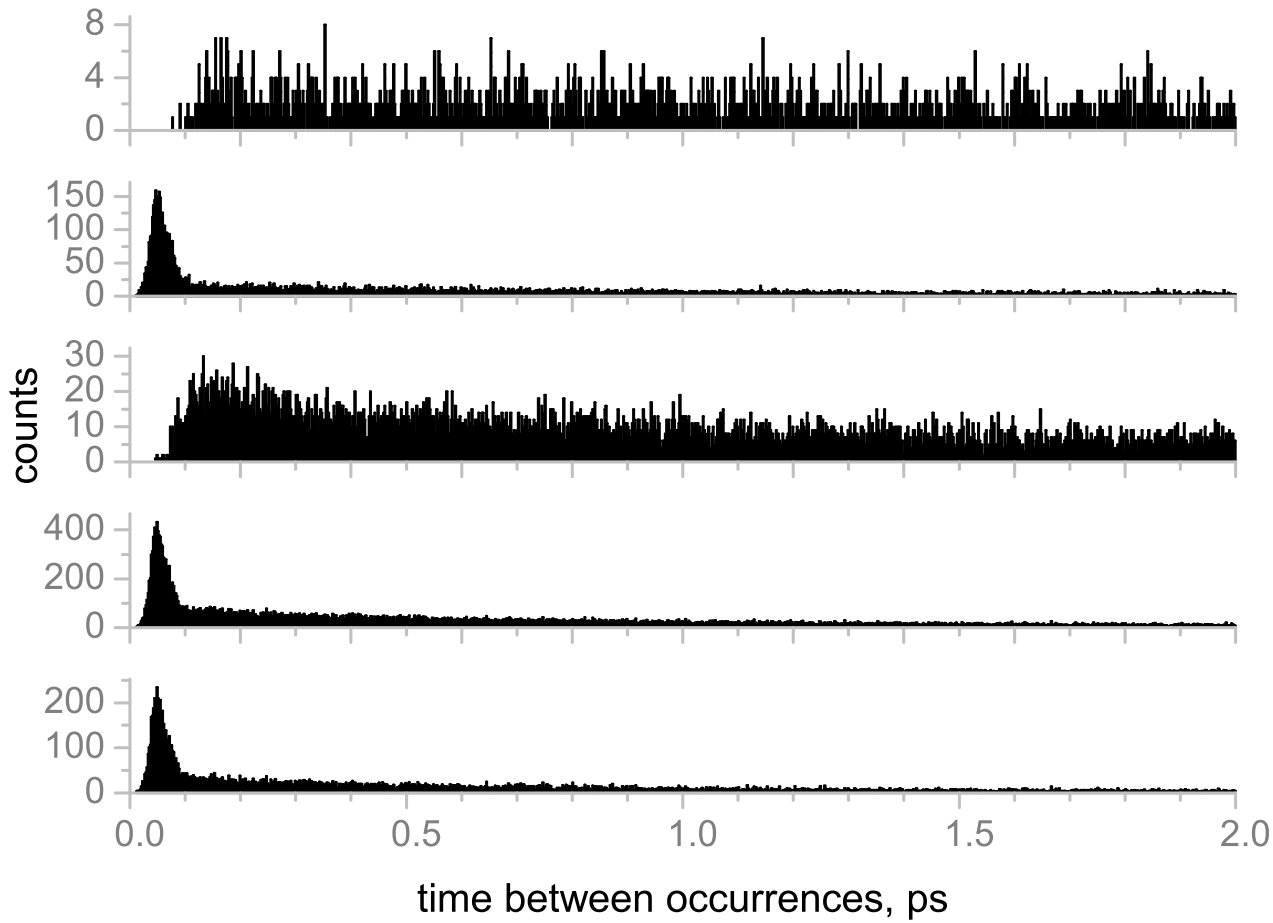

Figure: Histograms of the times between successive occurrences of five representative causal states.

Classification of the causal states

"frequent" states	About 30 states that occur with the frequency of less than 0.1ps (autocorrelation decay time): do not change with the signal length
all other states	Many less frequent states: grow with the length of the signal
surrogate signal	The same number of states as "frequent" states
"frequent" spectra	Have a maximum at 1ps

Statistical Physics meaning of Statistical Complexity

phase space points The evolution of the statistical mechanical phase space points $\mathbf{q} : \mathbf{q}_{t+1} = T\mathbf{q}_t$.

Markov dynamics Because of the determinism the dynamics $\{\mathbf{q}_t\}$ forms a Markov chain.

microstate For an ensemble a random variable representing the current microstate is $\mathbf{Q}$.

macrostate A macroscopic observed variable is a function f of the microstate $\mathbf{Q}$.

partitioning The function f partitions the phase-space into mutually exclusive and jointly exhaustive sets, on each of which f takes a unique value.

observed process The observed process is $A = f(\mathbf{Q})$ and it is not Markovian. However, a Markovian process can be constructed from the observed one by building the ϵ-machine on A. Now the sequence of the causal states $\{S_t\}$ makes a Markov chain.

$C_\mu = I[\mathbf{Q}; S]$

Shalizi and Moore show that in this setting the Statistical Complexity of S quantifies the amount of information contained in the macrostate about the microstate:

$$C_\mu = I[\mathbf{Q}; S],$$

where I is the mutual information between random variables X and Y: $I[X;Y] = H[X] - H[X|Y]$; and $H[X|Y]$ is a conditional entropy of X given Y: $H[X|Y] = -\sum P(X) \sum P(X|Y) \log_2 P(X|Y)$.

Why C_μ grows?

A situation when a single trajectory of the system with time covers the phase space: a "microstate" would consist of the areas sampled by the trajectory up to time t: $\mathbf{Q} = \mathbf{Q}(t)$.
Therefore, C_μ becomes dependent on time and now reflects the way the trajectory covers the phase space:

$$C_\mu(t) = I[\mathbf{Q}(t); S].$$

h_Q is a measure of the whole phase space

The coefficient h_Q as a measure of the growth rate:

$$C_\mu = a + h_Q \log_2 T$$

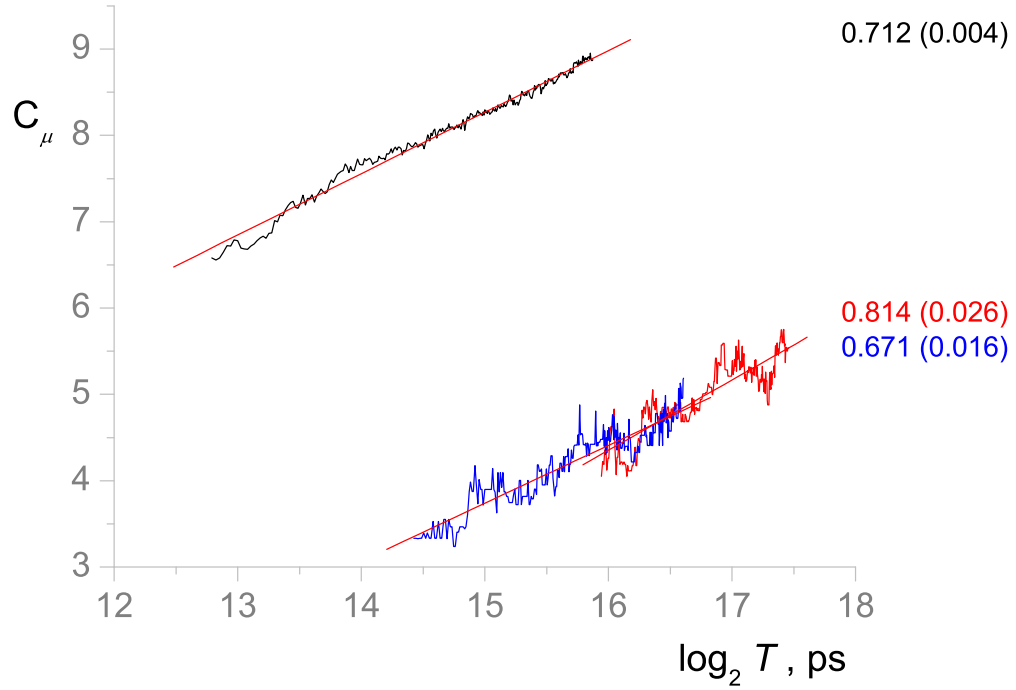

Figure: h_Q values for: black - the hydrogen velocity, red - the oxygen velocity, and blue - the instantaneous temperature.

Clusters: different dynamics

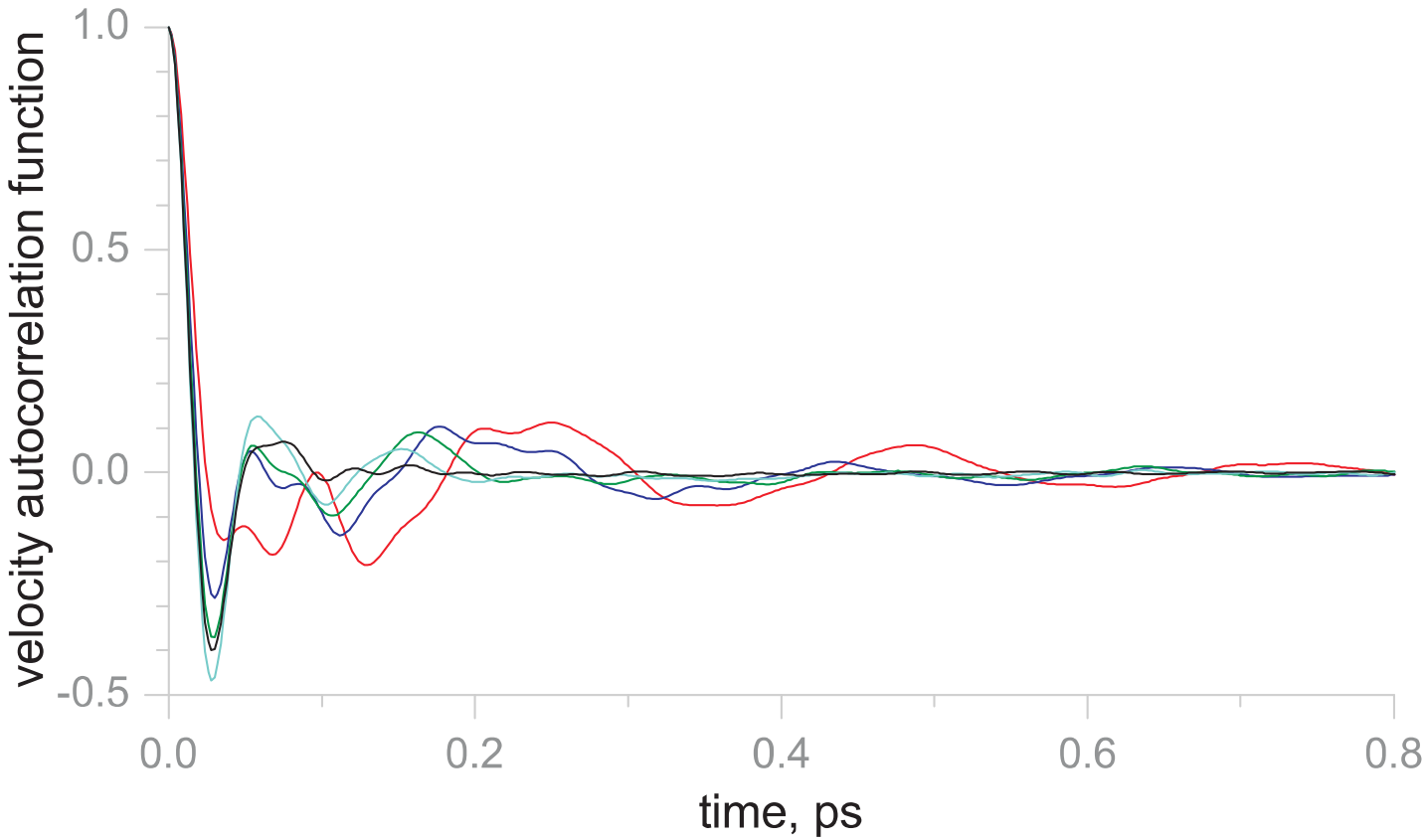

Figure: Velocity autocorrelation function for oxygen 3, 7, 15, 52, and pbc water models.

Clusters: different dynamics

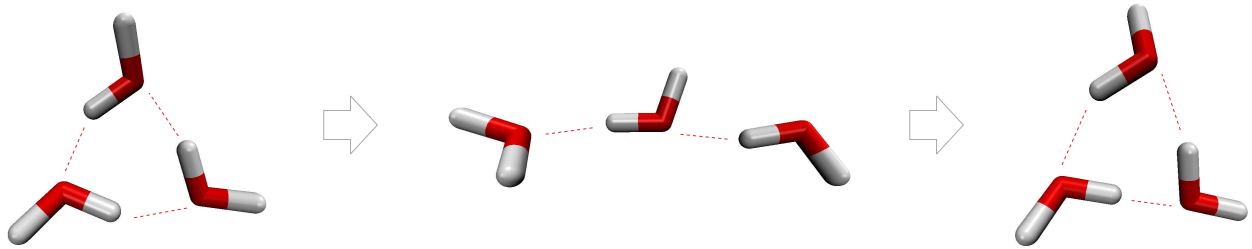

Figure: Snapshots of the 3w cluster at 0, 0.78, and 1.42 ps (relative time) illustrating the process of quick rearrangement when two molecules have only one hydrogen bond connection each.

Complexity for the clusters

"frequent" states

The number of the "frequent" states (short time dynamics) is the same

short time C_μ

The probabilities of the "frequent" states are different, however, the overall complexity, C_μ is the same

h_Q

Phase space exploration, h_Q is different, especially for 3w:

Table: h_Q values for different clusters and pbc

molecular system	h_Q
3w	0.904 ± 0.002
7w	0.675 ± 0.005
15w	0.675 ± 0.004
52w	0.703 ± 0.004
pbc	0.658 ± 0.005

Thanks

- European Commission: EC Contract Number 012835 - EMBIO
- Prof. Vladimir Ryabov

公立はこだて未来大学
FUTURE UNIVERSITY-HAKODATE