The structure of chaos in liquid water

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MD simulated classical trajectories of liquid water are considered from the chaotic dynamics point of view. By applying a sophisticated statistical procedure, called 'causal states' reconstruction, we decompose the dynamical phase space into non-overlapping elementary areas of two qualitatively different classes, characterised by the decay law for Poincare recurrence times. By an analogy with the Standard map they can be attributed to 'chaotic sea' and quasiperiodic motions in the vicinity of ('sticky') periodic islands. The proposed method of identifying the areas with sticky dynamics in the high-dimensional phase space has far reaching implications in understanding the molecular transport, including the anomalous diffusion process. It is important, for example, for elucidating general regularities underlying the complex motions of protein atoms in the process of folding or other self-organising biomolecular dynamics.

Motivation

The trajectories of atoms and molecules in liquids can be described by Newtonian ordinary differential equations of motion. Therefore, any complex patterns formed by the molecules due to their mutual interactions have geometric counterparts in the phase space defined by their coordinates and velocities. The problem of identifying and classifying the patterns as well as predicting their appearance is crucially important since they ultimately define the functionality of the systems. However, a profound difficulty in the dynamical picture of molecular systems is its high-dimensionality. Commonly used approaches from non-linear dynamics, such as Lyapunov exponents, dimensions, and entropies fail in most cases for the dimensionality higher than ≈ 10.

One of the most difficult problems in the analysis of the high-dimensional molecular trajectories is the definition of the notion of 'structure' or 'cluster' in the phase space. We address this issue in a broad statistical sense considering deviations from the uniform phase space filling by a typical trajectory as clusters. The presence of structures in the phase space of dynamical systems can be interpreted as the existence of nonuniformities in the invariant measure [J.-P. Eckmann and D. Ruelle. *Rev. Mod. Phys.*, 57:617–656, 1985]. The latter defines the probabilities of visiting various parts of the phase space by trajectories. The clusters appear in the phase space due to the presence of abundant resonances that arise as a result of nonlinear interactions between atoms. The borders of resonant areas are known to be 'sticky' in a sense that any trajectory spends a long time in their vicinity. This is in contrast to other, non-resonant areas, where the trajectories evolve randomly filling the phase space almost uniformly.

A quantitative description of the nonuniformity of the phase space covering by the trajectories can be achieved via the Poincare recurrence theory. Consider a small element $\Delta\Gamma$ of the phase space Γ of a Hamiltonian system located around the point $\mathbf{x}$. A trajectory wanders in the chaotic area visiting the element $\Delta\Gamma$ from time to time (recurring to it). Denoting the time between successive recurrences as τ the probability distribution function of recurrence times $P(\Delta\Gamma, \mathbf{x}, \tau)$ can be introduced that depends on the phase volume and the position of the element $\Delta\Gamma$, as well as the value of τ itself. If the motion is ergodic the dependence of τ on the coordinates $\mathbf{x}$ becomes inessential and one can introduce the distribution function $P(\tau) = lim_{\Delta\Gamma\to 0} P(\Delta\Gamma, \tau)/\Delta\Gamma$. For a typical chaotic trajectory the following asymptotic relation holds

$$P(\tau) = \frac{1}{\langle\tau\rangle} exp(-\tau/\langle\tau\rangle), \qquad (1)$$

where $\langle\tau\rangle$ is the average recurrence time over the distribution $P(\tau)$. Eq. (1) can be used, in principle, for distinguishing areas with chaotic motion from those close to sticky areas by introducing a partition of the phase space into non-overlapping volumes and analyzing the distributions $P(\tau)$ for each of them.

It is not clear how to create a partition in the phase space. We suggest a way of define a 'natural' partitioning that can identify different dynamics by comparing the decay times of Poincare recurrences to the defined areas.

Methodology

Molecular Dynamics simulation details

In this work, bulk water (periodic boundary conditions) consisting of 392 or 878 SPC or SPC-E molecules was simulated using the GROMACS molecular dynamics package. The temperature of the systems was kept constant at 300K using Berendsen or Nose-Hoover thermostats whose combination with various coupling constants was investigated. A sufficient equilibration was performed before collecting data for analysis. The velocity of the hydrogen atom of one of the water molecules was used. At the locations where the velocity pierces the xy plane the points of a two-dimensional map were generated and used as the original continuous signal for analysis.

We have found that the results do not depend on the parameters of molecular simulations such as the forcefield, the temperature, the type of the thermostat, the number of molecules, etc.

Defining the partition of the phase space

For an initial approximation to the phase space partition, we have chosen a symmetrical partition in one of the projections of an atom's velocity. The example of calculations with this method for the two-dimensional cross-section of our (three-dimensional) velocity data using 2, 3, 4, and 5 partition elements are shown in Fig. 1. The simulated trajectory of 1μs long resulted in approximately $3 \cdot 10^7$ data points (symbols).

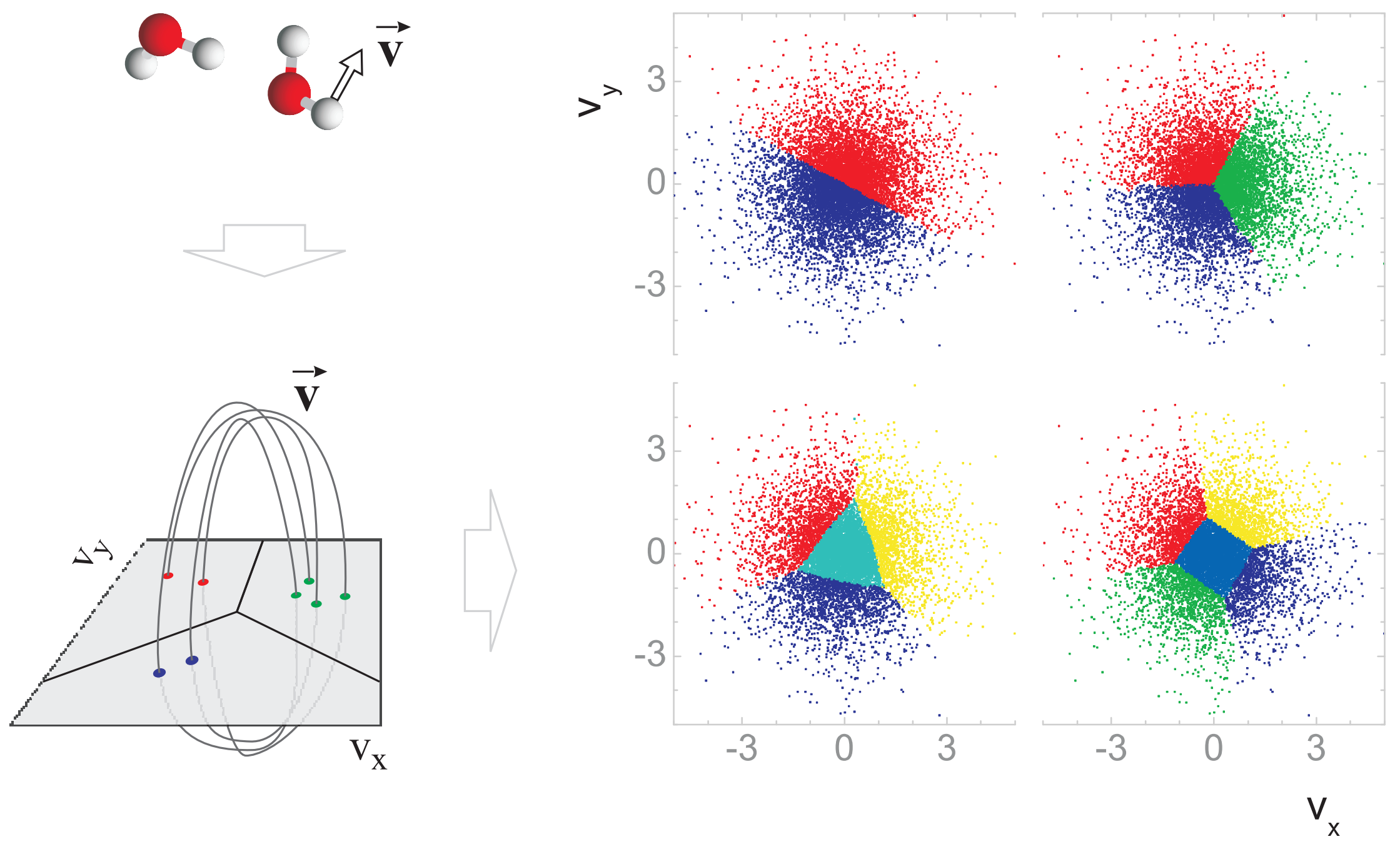

Figure 1: Symbolising MD trajectory

The methodology for **finding the required phase space partition** is 'Computational Mechanics' (CM) developed by Crutchfield *et al* [J. P. Crutchfield and K. Young. *Phys. Rev. Lett.*, 63(2):105–108, July 1989]. CM builds a statistic on infinitely long histories ('pasts') of symbols s_i representing the state of the system at times t_i, $\overleftarrow{s}_i \equiv \{\dots s_{i-2}s_{i-1}s_i\}$, by analysing the 'futures' $\overrightarrow{s}_i \equiv \{s_{i+1}s_{i+2}\dots\}$ following each past. The algorithm groups the pasts into classes called 'causal states' ϵ_j. The criterion of grouping is the equivalence of the probabilities of the futures, that is two pasts $\overleftarrow{s}_i$ and $\overleftarrow{s}_j$ are assigned to the same causal state if the distributions of their futures are the same: $P(\overrightarrow{s}|\overleftarrow{s}_i) = P(\overrightarrow{s}|\overleftarrow{s}_j)$, where $P(X|Y)$ is the probability of X given Y.

We have previously shown that the resulting causal states define a special kind of the phase space partitioning. The partitioning provides the maximal extraction of non-random information from the trajectory of the system.

Results

We compare our results on water to a well documented two-dimensional area preserving system known as the Standard map [B. V. Chirikov. *Phys. Rep.*, 52:264–379, 1979]. We used a regime when a large chaotic area contains two stability islands.

For both the water and the Standard map data the causal states demonstrate a clear separation into two classes that we call 'periodic' states (those defined by Poincare recurrence times decaying much slower compared to Eq. (1)) and 'chaotic' ones. To quantify the difference between the classes we introduce a dimensionless parameter D, equal to the discrepancy between the decay exponent λ calculated from the histogram of recurrence times and its 'normal' value $\frac{1}{\langle\tau\rangle}$ defined by the Eq. (1)

$$D = \frac{1}{\lambda\langle\tau\rangle} - 1, \qquad (2)$$

where λ is the exponent defining the shape of the distribution function

$$P(\tau) \propto exp(-\lambda\tau) \qquad (3)$$

found numerically. Large D values indicate strong discrepancy between the calculated value of the exponent in Eq. (3) and the expected value of $1/\langle\tau\rangle$.

The 'abnormal' tail in the distribution of the recurrence times can be clearly visualised for the case of the Standard map (Fig. 2a). In the case of water time series there is no apparent distinction between the two types of behaviour as it is shown in Fig. 2b. In the simplest approximation, this could be interpreted as the absence of periodic islands in the phase space of water because of the breaking of all invariant tori that occurs due to interaction between resonances in the multiple degrees of freedom system.

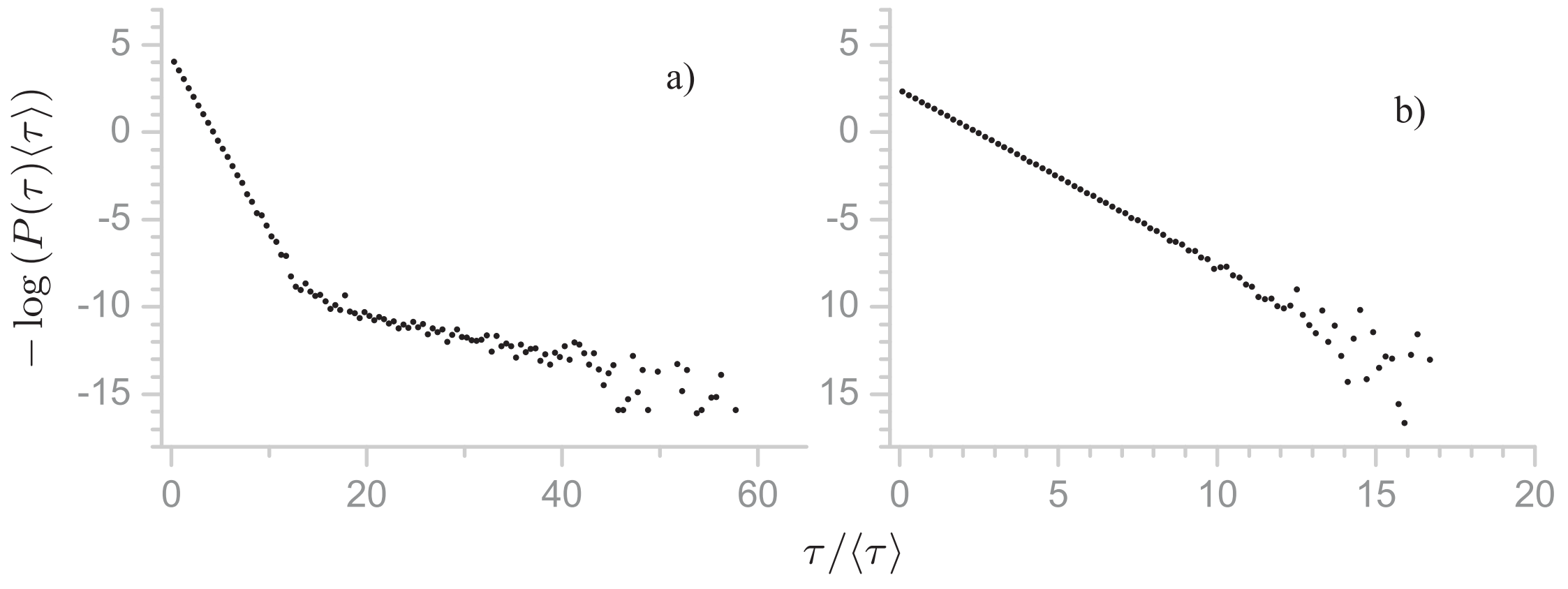

Figure 2: Distribution of Poincare return times for a) Standard map; b) water.

In Fig. 3 we plot the scatter diagrams representing the apparent clustering of the causal states into two classes with respect to the parameter D as a function of the probability $P(\epsilon_i)$ of the causal states.

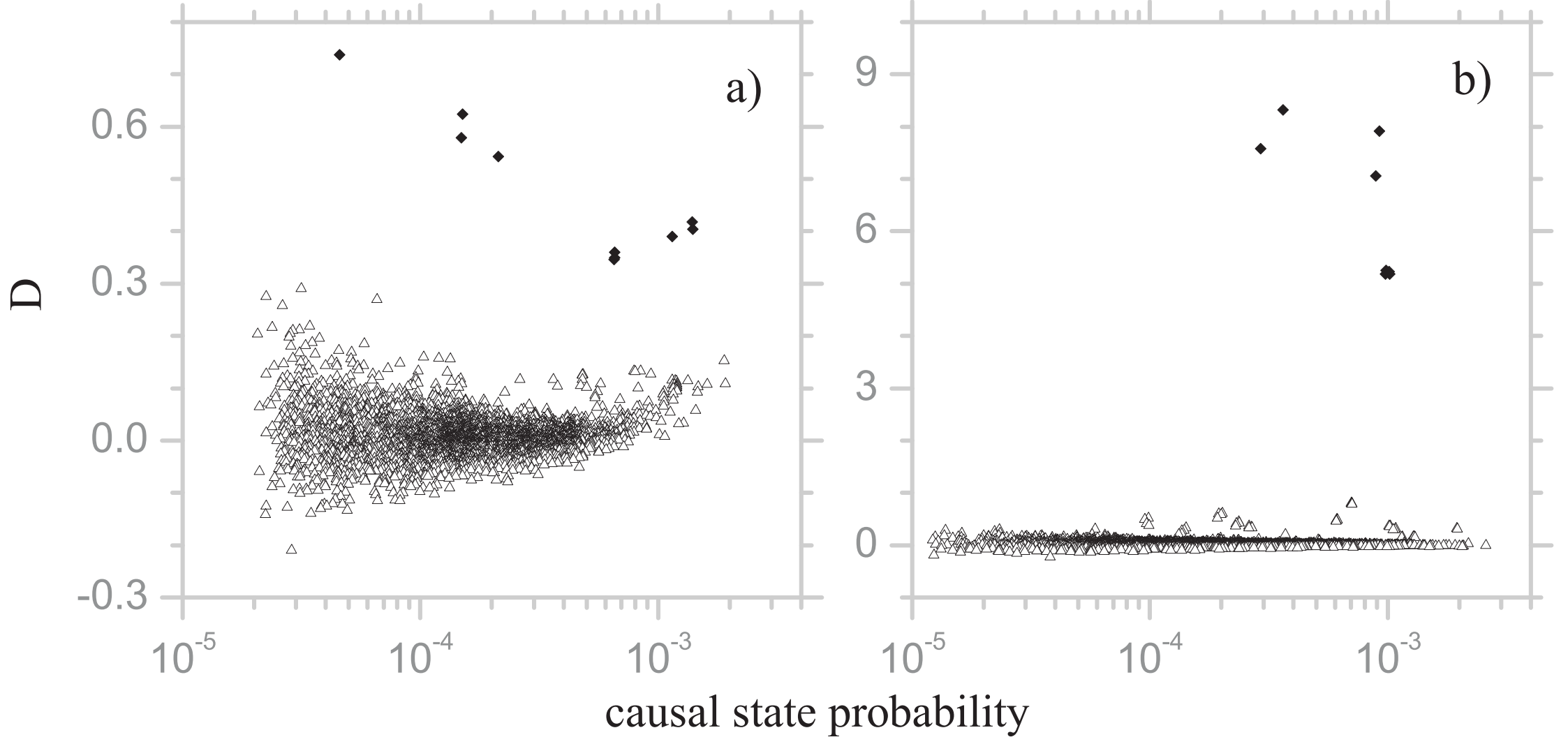

Figure 3: 'Periodic' (diamonds) and 'chaotic' states for (a) water, (b) Standard map.

Conclusions

The two classes of 'periodic' and 'chaotic' states are present in the dynamics of both water and the Standard map. The 'chaotic' states represent long term mixing processes that describe the way the system explores the phase space. The number of 'chaotic' states is high indicating the prevalence of the areas of chaotic motions (chaotic sea) over the periodic components (resonance islands), a rather typical picture previously reported only for low-dimensional dynamical systems [G.M. Zaslavsky. *Phys. Repts*, 371:461–580, 2001].