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Single molecular signals reveal microsecond long time correlations in bulk liquids

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Single molecular experiments open up a fundamentally new perspective in understanding the dynamical properties of molecular systems. The signals from individual molecules obtained in the experiments allow the investigation of dynamical processes normally masked by the ensemble averaging of conventional techniques. Most recent results demonstrate first evidences of such non-ergodicity in, for example, the experimental single molecular diffusion [Y He, *Phys. Rev. Lett.*, **101**, 058101]. It is, therefore, very important to develop theoretical approaches for quantifying unusual dynamical properties of single molecular signals.

In this work we demonstrate the existence of microsecond long time correlations in bulk liquids. We analyse the dynamics of MD simulated water and other liquids using statistical description of the trajectories. Instead of standard two point linear correlation measures, for example, the velocity autocorrelation function $1/T\sum_t^T \mathbf{v}_t \cdot \mathbf{v}_{t+\tau}$, we analyse the *sequences* of the velocity values $\{\ldots \mathbf{v}_{t-2}\mathbf{v}_{t-1}\mathbf{v}_t\}$. Specifically, we investigate the conditional probabilities of the next value of $\mathbf{v}$ for a given sequence, Fig. 1.

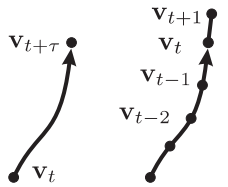

Fig. 1 Standard velocity autocorrelation (left) and our analysis of "sequences"

It can be shown that for long enough sequences it is sufficient to represent the values of the velocities using only few discrete symbols (we here used three symbols: 0, 1, and 2). Thus, the dynamics represented using the probabilities can be easily visualised by plotting the conditional probabilities of finding 0 or 1 for the sequences of a fixed length, for example $P\left(0\,|\,\{\mathbf{v}_{t-8}\ldots\mathbf{v}_t\}\right)$ and $P\left(1\,|\,\{\mathbf{v}_{t-8}\ldots\mathbf{v}_t\}\right)$. Most surprisingly we have found that these conditional probabilities *do not converge at all times* feasible in standard MD simulations even for homogeneous liquids such as bulk water or argon.

A rigorous statistical analysis of this phenomenon (using Computational Mechanics by Crutchfeld *et al* [*Phys. Rev. Lett.*, **63**, 105 (1989)]) proves that all molecular signals (we tried, among others, the atoms coordinates, velocities, and their combinations such as the instant temperature) exhibit substantial non-stationarity at the times of hundreds of nanoseconds when all possible non-stationary processes are believed to settle and reach the limiting values.

Our results provide the evidences of **previously unknown, extremely long time scale processes in completely homogeneous molecular systems that can only be revealed from the analysis of single molecular signals**. The connection of our theoretical results to particular experimental techniques is the subject of our current work.