Phase space diffusion in molecular liquids: non-stationary random walk model

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It is commonly assumed that the *diffusion in the phase space* of simple liquids such as common solvents or small molecules in solution *is normal.* That is it is completely equivalent to the random Brownian motion, at least at the chemically relevant time scale. Here we test this hypothesis for MD simulated bulk water at room temperature (and other liquids). The standard correlation analysis and the diffusion coefficient do not reveal any differences from the normal diffusion case at the time scales greater than ≈10ps. Therefore, we utilize a novel information content analysis of very long (≈1μs) phase space trajectories using the approach of Computational Mechanics (CM) based on the analysis of Markov chains with memory [1].

For specific molecular signals x (for example, the velocity of one atom or the instant temperature) we consider the sequences $\{x_{t-l}x_{t-l+1}\dots x_t\}$ that start at times $t-l$ and end at times t, with t covering the whole simulation period and l being the length of the sequences (3-15 simulation time steps). The set of the sequences is an l-dimensional projection of the molecular phase space trajectory (this is a multi-dimensional phase space signal, even though it is obtained from a low-dimensional molecular signal). We calculate various statistics on the sequences. The results are compared to an artificial signal which is random by definition (constructed as a "surrogate", very similar to the molecular signal but a purely random one).

The conditional probabilities of the molecular signal values following each sequence $P(x_{t+1}|\{x_{t-l}x_{t-l+1}\dots x_t\})$ show that the distributions are significantly different for the surrogate and the molecular signal and converge much slower in the latter case, at the scale of up to 1μs. The analysis in the CM framework demonstrates that the CM statistic on the molecular signal *never converges* with t in contrast to the surrogate. This means that the convergence rate of the conditional probabilities for the molecular system is different compared to the surrogate, thus disproving the random, normal nature of the diffusion.

Thus, contrary to the common view we find **significant deviations from the normal diffusion** in the phase space that clearly demonstrate non-random character of the dynamics. Unlike the normal diffusion where the molecular motions along any coordinate can be described by random Gaussian processes and, hence, are equiprobable, the molecular systems exhibit preferred routes in the phase space. We find that these routes change with time leading to long-term *non-stationarity* in the atomistic trajectories. We show that this non-stationarity can be reproduced using a stochastic model by modifying the usual *random walk model* with changing in time conditional probabilities.

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[1] J. P. Crutchfield and K. Young, Phys. Rev. Lett. **63**, 105 (1989).