Volterra equations to compute memory kernels and projected cross-correlation functions from molecular dynamics

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Because usual stochastic systems such as complex fluids have a large number of degrees of freedom, we use the projection operation techniques of statistical mechanics in which only a few observables are chosen to describe the system's evolution. The dynamics of such coarse-grained, or macroscopic, variables are separated from the dynamics of the other "irrelevant" microscopic variables that comprise the formers' environment. This is accomplished in the Langevin equation by dividing the coarse-grained dynamics into two components: a random one that sums up the interactions with the environment, and a dissipative one that represents the response of the macroscopic variables to their environment. The Markovian assumption is made, in which the dynamics of microscopic degrees of freedom occur on a negligible timescale in comparison to the typical one of macroscopic dynamics. Such an assumption is removed in the Mori-Zwanzig equation which becomes important as the separation of timescales is incomplete. Those memory effects are quantified by memory kernels or, more generally, by projected time correlation functions if one is also interested in decomposing memory kernels or in the coupling between different macroscopic variables. Despite the difficulty of such a task, the calculation of memory kernels from microscopic dynamics can be performed reliably and efficiently by inverting the Volterra equations obtained from the Generalized Langevin Equation (GLE) [1]. The simple yet efficient method based on the inversion of Volterra equations has, however, only been applied to the computation of the memory kernel appearing in the GLE. The first numerical method allowing to decompose of the memory kernel, or more generally to compute projected correlation functions, has been proposed quite recently by Carof et al. [2] and is based on the reconstruction of the random force, which obeys an "orthogonal" dynamics. This method is, however, difficult to implement and computationally very expensive.

Starting from the orthogonal dynamics of any given set of variables with respect to the projection variable used to derive the Mori-Zwanzig equation, I show that a set of coupled Volterra equations is obtained that relate the projected time correlation functions between all the variables of interest [3]. This set of equations can be solved using standard numerical inversion methods for Volterra equations, leading to a very convenient yet efficient strategy to obtain any projected time correlation function or contribution to the memory kernel entering a GLE. Also, I provide a very simple derivation of the orthogonal dynamics of any variable.

Using this strategy, the memory kernel related to the diffusion of tagged particles in a bulk Lennard-Jones fluid is accurately investigated up to the long-term regime to show that the repulsive-attractive cross contribution to memory effects represents a small but non-zero contribution to the self-diffusion coefficient. Furthermore, all the memory kernel's components follow the same scaling in the long-term regime, which corresponds to the one predicted by the hydrodynamics.

References

[1] Berne & Harp, Adv. Chem. Phys. (1970).
[2] Carof et al., J. Chem. Phys. 140, 124103 (2014).
[3] Obliger, J. Chem. Phys., just accepted (2023).