Memory Function Formalisms for System Reduction in Molecular Dynamics

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Molecular dynamics (MD) [1] is a popular material simulation technique based on Newton's equations of motion for a large number of interacting particles. The power and accuracy of MD stems from the relatively fundamental nature of the processes it describes. MD consists of the numerical integration of the following system of ordinary differential equations (ODE):

$$\frac{d}{dt}q_i = \frac{1}{m_i}p_i\,, \quad \frac{d}{dt}p_i = -\nabla_{q_i}\Phi(q)\,, \quad 1 \le i \le N \tag{1}$$

Here q_i, p_i, and m_i are the position, momentum, and mass of the ith particle, respectively, and $\Phi(q)$ is the interaction potential. The number of particles N is often very large in a realistic system, which can be computationally intensive to simulate. For this reason, MD is currently confined to the description of length and time scales on the order of microns and nanoseconds, respectively [2]. It is often the case, however, that only the trajectories of some subset of the particles in (1) are needed to extract useful information from an MD simulation. In this article, we outline a technique for constructing a set of differential equations for the evolution of such a subset and present some results from a simple toy problem.

Suppose we wish to keep—without loss of generality—the first M of the particles in equation (1). We can split the variables (q_i, p_i) into two groups: (a) the resolved particles with positions and momenta $\hat{q}_i$ and $\hat{p}_i$, where $1 \le i \le M$, and (b) the discarded unresolved particles with variables denoted by $\tilde{q}_i$ and $\tilde{p}_i$, where $1 \le i \le N - M$. Via a sequence of mathematical steps too involved to reproduce here, it can be proven [3] that the $\hat{q}_i$ and $\hat{p}_i$ are governed by the following reduced system of differential equations:

$$\begin{aligned} \frac{d}{dt}\hat{q}_i &= \frac{1}{m_i}\hat{p}_i\,, \\ \frac{d}{dt}\hat{p}_i &= -\nabla_{\hat{q}_i}\varphi(\hat{q}) - \int_0^t ds\, K_i(s)\,\hat{p}(t-s) + F_i(t)\,, \quad 1 \le i \le M \end{aligned} \tag{2}$$

The derivation of this set of stochastic integro-differential equations is a generalization of the Mori-Zwanzig memory function formalism [4,5]. Here $\varphi(\hat{q})$ is known as the renormalized potential, $K_i(t)$ is a memory kernel, and $F_i(t)$ is a random force. These quantities take somewhat different forms depending on the details of the system in question and the nature of the variable splitting that is chosen, though general expressions exist for their calculation.

As a simple (yet fundamental) example to illustrate some details of the system in (2), we consider the toy problem of a fluid of identical particles at thermal equilibrium governed by the potential:

$$\Phi(q) = \sum_{i<j}^{N} u_{LJ}\left(|\, q_i - q_j \,|\right) \tag{3}$$

where u_{LJ} is the Lennard-Jones pair potential. For such a system, it can be shown that it is optimal to choose the renormalized potential as the potential of mean force of the resolved particles, namely:

$$\varphi(\hat{q}) \;\propto\; -k_B T \log\left\{ \int d\tilde{q} \exp\left(-\Phi(q)/k_B T\right) \right\} \tag{4}$$

The form of $\varphi(\hat{q})$ will then be that of a modified pair potential plus a three-body interaction, a four-body interaction, and so on. The statistical isotropy inherent in (3) implies that the memory kernel $K_i(t)$ is a scalar, and the fact that these are identical particles implies that $K_i(t) = K(t)$ is the same for all i. Furthermore, it can be proven that $K(t)$ decays relatively slowly for large t as $t^{-d/2}$, where d is the spatial dimensionality of the system. Several examples of the memory kernel for this system are shown in Fig. 1 for various M/N ratios. These were calculated from the Volterra integral equation (not shown here) that defines $K(t)$. Finally, note that in this simple equilibrium system the random force

$F_i(t)$ is a Gaussian stochastic process, and that its correlation is given by the familiar fluctuation-dissipation theorem:

$$\left\langle F_i(t+t')\cdot F_j(t')\right\rangle = d\, m\, k_B T\, K(t)\, \delta_{ij}, \tag{5}$$

though this is not necessarily the case in general.

Equations (1) and (2) are relatively straightforward to integrate numerically for reasonable values of N and M. Results for the trajectory of a single particle chosen from a full system of $N = 500$ particles are shown in Fig. 2, along with the trajectory of the single particle remaining in a reduced system of $M = 1$. Despite the fact that the environments of these two particles are profoundly different – the former interacts with 499 other particles, the latter explicitly with none – the qualitative character of their trajectories is the same. This notion can be made more quantitative by noting that both the diffusion coefficient and the velocity autocorrelation function of the two particles can be shown to be identical both in theory and simulation. Results regarding the invariance of other properties between the full and reduced systems can be both derived and verified.

The formalism outlined above has relevance to many MD applications where variable splitting may be desirable. These include systems with a significant difference in size between resolved and unresolved particles (i.e., colloidal systems), as well as systems with a large difference in time scale between different parts of the system (e.g., proteins, where high-energy bonds vibrate at a much higher frequency). Further refinement and application of such techniques in these and other contexts may have a significant impact on the type and scale of problems accessible to MD.

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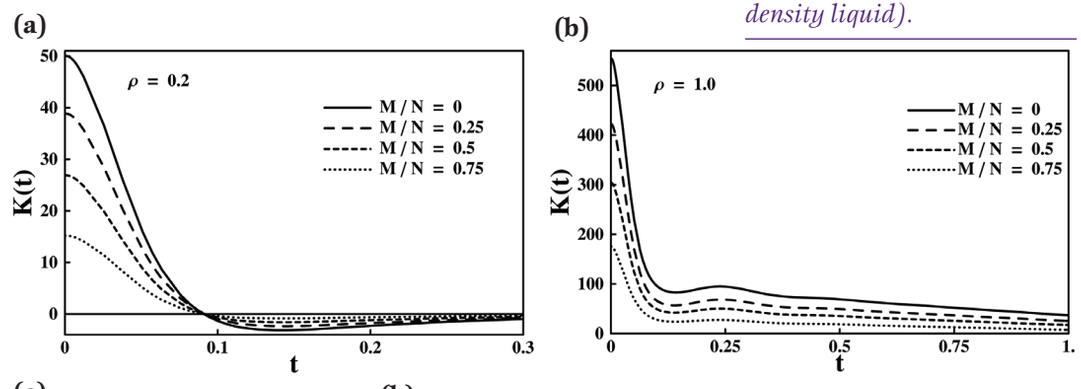

Fig. 1. Memory kernels K(t) calculated in the example system for various M/N ratios. Sets of curves for two full system dimensionless number densities ρ = N/V are shown: (a) ρ = 0.2 (low-density gas), and (b) ρ = 1.0 (high-density liquid).

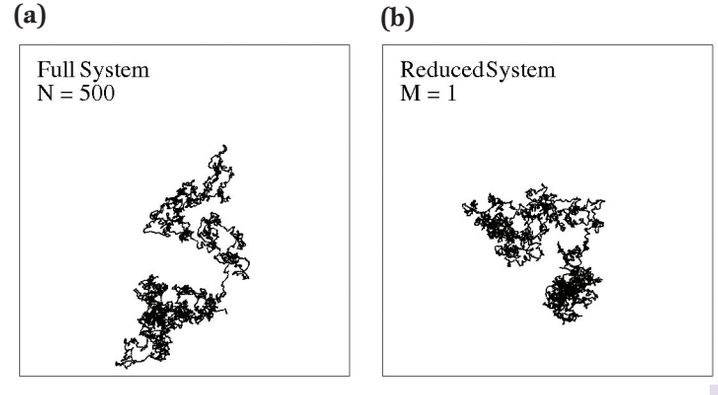

Fig. 2. Plane-projected trajectories of (left) a single particle selected from a full system of N = 500 Lennard-Jones particles, and (right) the remaining particle in a reduced system with M = 1.

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