Formal derivation of dissipative particle dynamics from first principles

David Cubero* and Sophia N. Yaliraki†

Department of Chemistry, South Kensington Campus, Imperial College London, London SW7 2AZ, United Kingdom

(Received 13 January 2005; revised manuscript received 20 May 2005; published 13 September 2005)

We show that the Markovian approximation assumed in current particle-based coarse-grained techniques, like dissipative particle dynamics, is unreliable in situations in which sound plays an important role. As an example we solve analytically and numerically the dynamics of coarse-grained harmonic systems by using first principle methods. Harmonic lattices are paradigmatic for the kind of memory effect discussed here because elastic wave propagation is the only dissipation mechanism in these systems. We have recently used projector operators to formally derive the stochastic equations of motion for inhomogeneous harmonic lattices [8]. We use these results as a starting point in order to evaluate here for the first time the required memory kernels, analytically in one dimension and numerically in two and three dimensions.

Consider a coarse-grained harmonic system by partitioning the volume into mesoscopic regions $k$. We define the coarse-grained particles by choosing the set of all center of mass coordinates $X_l$ and velocities $V_l$ of all particles inside each region $k$ as the relevant variables. Then, by using Mori’s projection operator theory [9], the following equation of motion for the coarse-grained variables is obtained [8]:

$$M_k \frac{dV_k(t)}{dt} = -\sum_l \left( \Lambda_{kl} X_l(t) + \int_0^t d\tau \Phi_{kl}(\tau)V_l(t-\tau) \right) + R_k(t),$$

(1)

where $M_k$ is the mass of each coarse-grained particle; $\Lambda_{kl}$ is a conservative force matrix, $\Phi_{kl}(t)$ is a memory kernel defining dissipation; and $R_k(t)$ is a random force satisfying $\langle R_k(t) \rangle = 0$ and the fluctuation-dissipation theorem $\langle R_k(t)R_l(0) \rangle = k_B T \Phi_{kl}(t)$, where $k_B$ is the Boltzmann constant and $T$ is the temperature. In these last equations the averages are taken with an initial distribution close to thermal equilibrium. Total momentum conservation implies that $\sum_r \Phi_{kl}(t) = \sum_r R_r(t) = 0$, so that if we decompose each random force as a sum of independent variables $R_k(t) = \sum_{\ell \neq k} \xi_{kl}$, we can rewrite (1) in a form that resembles the equation of motion of a DPD system.
Imagine that at the intermediate time very different from the former case shown in Fig. 1 clearly see that the values of the coarse-grained variables are not in their equilibrium positions with zero velocity except for cooperative. Now consider that initially all coarse-grained particles are in their equilibrium positions with zero velocity except for a small amount of thermal noise.

At the macroscopic level, the displacement field \( u(x,t) \) is defined as the deviation from equilibrium of the particles expressed as

\[
\begin{align*}
\tilde{\partial}_t^2 u &= v^2 \tilde{\partial}_x^2 u, \\
\tilde{\partial}_t^2 &= v^2 \tilde{\partial}_x^2,
\end{align*}
\]

where \( v \) is the speed of sound in the material. The general solution to this equation is given by

\[
\begin{align*}
u(x,t) = f(x-vt) + g(x+vt),
\end{align*}
\]

with \( f(x) \) and \( g(x) \) travelling to right and left, respectively. Note that the ratio \( t_\tau = t/v \) defines a mesoscopic time scale because \( l \) is mesoscopic. Now consider that initially all coarse-grained particles are in their equilibrium positions with zero velocity except one, which we label as \( k=0 \). In Fig. 1(a) we have plotted the corresponding fields \( u(x,0) \) (solid line) and \( \tilde{\partial}_t^2 u(0,t) \) (dashed line). Assume that the fluctuations are small enough so that the fronts are not destroyed. Then Figs. 1(b) and 1(c) show the profiles after a time \( \tau_\tau/2 \) and \( \tau_\tau \), respectively. Now imagine that at the intermediate time \( t=\tau_\tau/2 \) we change the velocity field \( \tilde{\partial}_t^2 u \) so that the set of coarse-grained variables \( \{X_k, V_k\} \) remains the same, as shown in Fig. 1(b) (dashed line). Figure 1(d) shows the profiles after a time \( \tau_\tau/2 \). We can clearly see that the values of the coarse-grained variables are very different from the former case shown in Fig. 1(c), even though they had the same values at \( t=\tau_\tau/2 \). Therefore, the knowledge of the values at a previous instant is not sufficient. Instead, we need to know the complete profiles of \( u \) and \( \tilde{\partial}_t^2 u \) at a given time \( \tau_\tau \), equivalently, the complete previous history of \( \{X_k, V_k\} \) to specify the present state.

The arising memory kernels are the consequence of the perturbations traveling inside the coarse-grained particles by sound propagation. This phenomenon is due to the space discretization introduced by the coarse graining and we expect it to be present even if we consider fluctuations, higher dimensions, or take into account anharmonic effects, as long as the mesoscopic time scale associated with sound propagation is comparable with the relevant time scale of the mesoscopic particles. If \( \tau_\tau \) is much shorter than other characteristic times associated with distinct dissipation mechanisms present in the system, then the memory kernels due to sound propagation would collapse in the longer time scales and the previous discussion no longer applies. However, in situations in which sound propagation plays an important role, the coarse-grained variables must change in the same scale given by \( \tau_\tau \) in order to account properly for it, which implies the effect described above.

As an example, let us consider a d-dimensional cubic harmonic lattice with only first neighbor interactions. Units are defined so that the mass of each oscillator, the force constants, and the equilibrium spacings are set to unity. We coarse-grain the system by grouping the oscillators into cubic clumps, each containing \( n^d \) oscillators. It was shown in Ref. [8] that the conservative force \( \Lambda_{ij} \) is the inverse of the matrix \( \langle X_i X_j \rangle_{eq} = k_B T \). In harmonic systems, the mesoscopic time scale that characterizes the dynamics of the coarse-grained particles is given by wave propagation only, which in our units is \( \tau_\tau = n \). Therefore, by changing to \( t' = t/n \), with \( V'_k = V_k/dt' = n V_k \), Eq. (1) becomes

\[
\frac{dV'_k}{dt'} = -\sum_l \left[ \Lambda^*_{kl} \frac{X_l}{n} + \int_0^{t'} d\tau \Phi_{kl}(\tau) V'_j(t' - \tau) \right] + R'_k, \tag{3}
\]

where \( \Lambda^*_{kl} = n^{2-d} \Lambda_{kl}, \Phi^*_{ij} = n^{2-d} \Phi_{ij} \), and \( R'_k = n^{2-d} R_k \). Since we have set all internal parameters to unity, we expect all variables in Eq. (3), and, in particular, \( \Lambda^*_{kl} \) and \( \Phi^*_{ij} \), are on the order of \( O(1) \), even in the mesoscopic limit \( n \to \infty \). The analytic and simulation results we present later confirm this scaling in all three relevant physical dimensions, i.e., \( d=1, 2, \) and 3.

To continue analytically, we restrict ourselves temporarily to the one-dimensional (1-D) case. Let us consider a finite chain of \( N \) oscillators with fixed ends and then take the thermodynamic limit \( (N \to \infty) \) at the end of the calculations. The force matrix for the oscillators in this system is given by

\[
\Lambda_{ij} = 2 \delta_{ij} - 1 - (\delta_{i+1,j} + \delta_{i-1,j}).
\]

Using the analytical expression for the inverse matrix \( \Lambda^*_{ij} = \min(i,j)[1 - \max(i,j)/(N+1)] \) [11], we obtain

\[
\frac{\langle X_i X_j \rangle_{eq}}{k_B T} = -\frac{n^2 - 1}{6n} \delta_{ij} \frac{[1 + 2 \min(k,l)n - n]}{2} \times \left( 1 - \frac{1 + 2 \max(k,l)n - n}{2(N+1)} \right).
\]

Next, we invert this matrix in two steps. First we multiply it...
by \( A \), which leads to a tri-diagonal matrix \( S_{kl} = \sum_{\ell}(X_{k}X_{l})_{\ell}A_{\ell}/k_{B}T = a\delta_{ij} + b(\delta_{i,j+1} + \delta_{i,j-1}) \), with \( a = 1/3n + 2n/3 \) and \( b = (n^2-1)/6n \). Strictly speaking, the first and last columns of \( S \) do not follow that tri-diagonal form, but this is irrelevant in the thermodynamic limit. Now we invert the matrix \( S \) by using the form \( S_{ij}^{-1} = C_{ij}^{t-l} \), which leads to \( C = 1/\sqrt{a^2-4b} \) and \( v = -(a/b)^2 - 4 \). The fact that \( a/b > 2 \) for any \( n \) guarantees that \( |v| < 1 \) and consequently \( S^{-1} \) vanishes at the boundaries. The force matrix is then given by \( \Lambda = \Lambda \times S^{-1} \), resulting in

\[
\Lambda_{kl} = \sqrt{\frac{3}{2 + n^2} \left( \frac{6n^2}{n^2 - 1} - \frac{2\sqrt{3n\sqrt{2 + n^2}}}{n^2 - 1} \delta_{kl} \right)} \times \left( -1 \right)^{|k-l|} \left( \frac{1 + 2n^2 - \sqrt{3n\sqrt{2 + n^2}}}{n^2 - 1} \right)^{|k-l|}.
\]

(5)

In the mesoscopic limit \( (n \to \infty) \), it reduces to [14]

\[
\Lambda_{kl} \approx \frac{2\sqrt{3}}{n} (3 + \sqrt{3} \delta_{kl}) (-1)^{|k-l|} (2 - \sqrt{3})^{|k-l|}.
\]

(6)

Note that since \( |2 - \sqrt{3}| < 1 \), Eq. (6) predicts an exponential decay of the conservative force, in contrast with the standard linear decay used in DPD simulations [2].

Let us now turn our attention to the memory kernels. The autocorrelation matrix \( C_{kl}^{t-l}(t) = \langle V_k^t(t) V_l^0(0) \rangle_{eq} \) satisfies the same equation as \( V_k^t \), Eq. (3), but without the random force [9]. Taking the Laplace transforms \( \Phi(s) = \int_0^\infty dt^* \exp(-s t^*) \Phi(t^*) \), \( c(s) = \int_0^\infty dt^* \exp(-s t^*) C(t^*) \), we arrive at

\[
\sum_{t^*} \phi_{kl}(s) c_{kl}(s) = C_{kl}(0) - s c_{kl}(s) - \sum_{t^*} \Lambda_{kl} s c_{kl}(s),
\]

(7)

where \( C_{kl}(0) = \delta_{kl} k_B T / M_l \). The autocorrelation matrix can also be readily calculated in the mesoscopic limit using the macroscopic wave equation [8], leading to

\[
C_{kl}^{t-l}(t) = C_{kl}(0)(1 + \delta_{kl}) g(t^* - |k-l|)/2,
\]

(8)

where \( g(x) = (1-|x|)H(1-|x|) \) and \( H(x) \) is the Heaviside unit step function. Therefore, we can compute the kernels by inverting the autocorrelation matrix

\[
c_{kl}(s) = \frac{C_{kl}(0)}{s^2} \left( \delta_{kl} e^{-s} + s - 1 + e^{-s(1+|k-l|)} \left( e^{-s} - 1 \right)^2 / 2 \right) \left( 1 - \delta_{kl} \right).
\]

(9)

We do that in two steps. First we multiply \( c \) by the intermediate matrix \( R_{kl} = \cos(h) \delta_{kl} - (1/2)(\delta_{k,l+1} + \delta_{k,l-1}) \). The resulting matrix is tri-diagonal and can be inverted using the same method we applied for the conservative force. The final result for the memory kernel is

\[
\phi_{kl}(s) = \frac{s^2 \left[ -\left( s \sinh(s) + \mu(s) \right) \left[ \sinh(s) \right] \left[ 1 - \cosh(s) \right] + \delta_{kl} \mu(s) \right]}{s - s \sinh(s) \mu(s)}.
\]

(10)

where

\[
\mu(s) = \sqrt{s \cosh(s) - 1} \left[ s + s \cosh(s) - 2 \sinh(s) \right],
\]

(11)

and

\[
\phi_{k,l} = \frac{s^2 \left[ -\left( s \sinh(s) + \mu(s) \right) \left[ \sinh(s) \right] \left[ 1 - \cosh(s) \right] + \delta_{kl} \mu(s) \right]}{s - s \sinh(s) \mu(s)}.
\]

(12)

FIG. 2. Memory kernels \( \phi_{kl}(t^*) \) in one dimension.

\[
\xi(s) = \frac{\sinh(s) - s \cosh(s) + \mu(s)}{s - \sinh(s)},
\]

(13)

We can extract from (10) is the friction coefficient that would be used in a DPD theory,

\[
\int_0^\infty dt^* \Phi_{kl}(t^*) = \lim_{s \to 0} \phi_{kl}(s) = 0,
\]

(14)

which vanishes here for all \( k \) and \( l \). This result could be explained by the absence of real “dissipation” effects in harmonic systems like thermal conduction [12]. Additionally, due to the discontinuities in the time derivative of the autocorrelation function (8), we expect that the memory kernels contain several Dirac delta functions, as we have also seen numerically [8]:

\[
\Phi_{kl}(t^*) = -\delta(t^* - |k-l| + 1) - \delta(t^* - |k-l| - 1) + 2 \delta(t^* - |k-l| + \phi_{kl}(t^*)).
\]

We can observe that the kernels are very slow decaying, having a significant magnitude at the end of the plot. In fact, we can use (10) to show that the absolute value of the kernel \( |\phi_{kl}(t^*)| \) is non-
tegrable. This is a consequence of the fact that the analytic
continuation of $\phi_0(s)$ presents an infinite number of singular-
ities on the imaginary axis ($s=i\omega$ with real $\omega$).

We have calculated numerically the memory kernels in
higher dimensions. Figure 3 shows the first memory kernels
of a two-dimensional system with square clumps containing
$(400)^2$ oscillators. The data have been smoothed out with a
mesoscopic time step of $\Delta^*=0.05$. The behavior of the ker-
nels is very similar to that of the one-dimensional case. The
first two kernels (solid and dashed lines) display the same
Dirac deltas (conditioned in the figure by the convolution
time step $\Delta^*$), as predicted by Eq. (14) in the one-
dimensional case. Additionally, we present in Fig. 4 the re-
results of a three-dimensional system with cubic clumps con-
taining $(95)^3$ oscillators and $\Delta^*=0.1$. Because the length of
the clumps is too small to allow for a smooth representation
of the kernels, we have also plotted in Fig. 4 the analogous
results (dotted and dash-dotted lines) of a one-dimensional
system with a similar clamp size of 100 oscillators per group
and $\Delta^*=0.1$. The behavior of the kernels remains similar.

The presence of the memory kernels, and the correspond-
ing colored noise forces [13], would render the simulation of
the dissipative particles dynamics impractical due to com-
puter memory limitations. A more promising approach would
be to add new internal variables to the description so the
process becomes Markovian. However, it is not clear if this
can be done using a finite number of new internal variables.
The thermodynamic variables (local density and internal en-
ergy) used in Refs. [4,5] would not account for the internal
memory effect we have described in this work. This can be
seen by considering a velocity perturbation traveling inside
the coarse-grained particles. The center of mass, the local
volume, and the internal energy of the coarse-grained par-
ticle would only be affected by the perturbation when it
reaches the boundaries of the particle. On the other hand,
a particle-based method could still be used if we regard them
as virtual particles carrying energy, instead of representing
portions of the system. In any case, the formalism used or the
assumptions made would need to be closely related or
checked at the microscopic level.

D. C. thanks J. Casado-Pascual for helpful discussions.
This work has been partially supported by a grant from the
European Union and the EPSRC.

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