Markovian equations of motion for non-Markovian coarse-graining and properties for graphene blobs

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New Journal of Physics 15 (2013) 125015 (25pp)
Received 21 May 2013
Published 10 December 2013
Online at http://www.njp.org/
doi:10.1088/1367-2630/15/12/125015

Abstract. We obtain Markovian equations of motion for a many body system of interacting coarse-grained (CG) variables and additional fluxes. The investigated CG variables belong to the special family of linear combinations of atomistic degrees of freedom. The system of Markovian equations of motion approximates Mori’s exact non-Markovian generalized Langevin equation and is easy to solve by computer simulation. All parameters of the equations can be obtained from equilibrium molecular dynamics simulations of the investigated microscopic system. These parameters are either equal to the famous static covariances from Mori’s continued fraction or they represent generalized constant friction matrices. We propose two different ways to compute these friction matrices based on Mori’s continued fraction. Finally, some of the parameters are computed numerically for the special case of centre of mass

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New Journal of Physics 15 (2013) 125015
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variables in the graphene lattice and it is found that the CG variables interact with their additional fluxes in a spatially very local way.

Online supplementary data available from stacks.iop.org/NJP/15/125015/mmedia

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### 1. Introduction

The term ‘coarse-graining’ (CG) refers to a collection of methods used to reduce the number of degrees of freedom of complex atomistic systems such as polymers [1, 2], proteins [3], fluids [4–8] or combinations thereof. The motivation for doing so is straightforward: computational time can be saved or larger systems over longer time-scales can be approached by keeping only the relevant part of the information. The hope is that a few relevant variables still reproduce the relevant predictions of the complex atomistic model.

Systematically coarse-graining Hamiltonian systems containing many microscopic variables with the Mori–Zwanzig projection operator formalism [9–12] leads to non-Markovian equations of motion of the type of a generalized Langevin equation (GLE) for so-called relevant variables. In many cases, by a clever choice of relevant variables, a Markovian approximation can be justified.

A prominent mesoscale method is dissipative particle dynamics (DPD) [13, 14]. In the DPD-method it is usually assumed *a priori* that the equation of motion is Markovian and hence:

### References

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the noise is white. In general the noise is not white but coloured. Occurrences or applications of coloured noise include the bath of harmonic oscillators [15], extensions of the Kramers theory of chemical relaxation [16] or constant temperature molecular dynamics (MD) [17, 18].

DPD is often used on an empirical basis with empirically fitted parameters and no rigorous justification of the Markovianity. For simple fluids this approach is very well justified, since there is a clear separation of timescales between slow macroscopic and fast microscopic variables [10]. The Navier–Stokes equations themselves are clearly Markovian. In lattice dynamics or for the CG of large molecules, the non-Markovianity deserves further investigations and it was argued that the Markovian assumption introduces significant errors into the coarse-grained description [19–22].

The work presented here is motivated by earlier work on the development of Markovian CG models for graphene and carbon nanotubes (CNTs). Early work was based on top-down CG CNT-models assuming a priori the DPD-form of the equations of motion for centre of mass (COM) variables of groups of carbon atoms [23, 24]. In a systematic bottom-up approach for two-dimensional (2D) motion of graphene, a Markovian approximation was applied to GLEs obtained from Mori’s or Zwanzig’s projection operators [25–27]. COM-based relevant variables seemed to show not only less non-Markovian features than finite element based variables but also showed weaknesses in the reproduction of cross-correlation functions of the relevant variables or long-wavelength normal mode decay, while the reproduction of autocorrelation functions is nearly perfect. The finite element based variables obtained by the CG procedure ‘CGMD’ [28] clearly showed non-Markovian behaviour. Both choices of variables have in common that they belong to the family of linear combinations of the atomistic variables. Therefore, this work aims for the development of general CG non-Markovian equations of motion for this family of CG variables and for schemes for the approximate numerical computation of these equations.

It was already shown many times for a single scalar relevant variable that Mori’s hierarchy of non-Markovian GLEs (or equivalently the continued fraction representation) [29] can be reformulated into a system of Markovian linear equations with auxiliary variables which is much easier to solve if truncated appropriately [30, 31]. In the work of Darve et al [32], a Galerkin discretization of a generalized Fokker–Planck equation is introduced, using a set of basis functions of the relevant variables. Also this approach was applied to one single COM variable of a single protein or to a single reaction coordinate. Our aim is a formulation of a CG many body system in 2D or 3D with fewer degrees of freedom than in the microscopic description, but still with many coupled CG variables, where a direct discretization of the phase space of CG variables becomes impractical due to its high-dimensionality. For this purpose we find the equations of motion derived by Karasudani et al [33] a very useful starting point. They involve a change in perspective by extending directly the set of relevant variables entering the GLE. The additional variables that are used in this approach are exactly those that appear in Mori’s hierarchy, but now propagated with a computable dynamics described by the non-projected Liouvillian. In contrast to Mori’s continued fraction in the Laplace domain, this exact transformation provides equations that allow one to combine the two steps of truncation of the hierarchy and to find an extended Markovian system in the time domain. It is a description of the CG dynamics in the time-domain, which we eventually require, in order to implement it into a practical computational tool.

In section 2, starting from Mori’s GLE and its generalization to an infinite hierarchy of GLEs for the noises [29], we obtain useful approximations for the truncation of this hierarchy.
by constant generalized friction matrices and we derive a finite set of Markovian equations of
motion for the main relevant variables and auxiliary fluxes. The latter is achieved by making
use of Karasudani’s approach to Mori’s GLE [33]. Then, in section 3, we apply the method
to relevant variables represented by the family of linear combinations of microscopic atomistic
degrees of freedom. In this way we obtain a clear prescription for how to compute all coefficients
in the resulting set of Markovian equations from equilibrium MD simulations. Since the subject
is very algebra intensive, the main results of sections 2 and 3 are completed by a few more
details provided in the appendix and all the details of the calculations provided as supplementary
material (available from stacks.iop.org/NJP/15/125015/mmedia). Finally, section 4 gives some
basic numerical results for the special case of hexagonal COM variables constructed from the
2D in plane motion of a simple atomistic graphene model. We observe that the interaction of
the CG displacements and momenta with the auxiliary fluxes is very local in nature, i.e. the CG
momentum of a COM-blob \( \mu \) interacts mostly with its own auxiliary fluxes and with its nearest
neighbours \( \nu \) in the graphene lattice. This property is advantageous from the computational
point of view.

2. Approximating non-Markovian equations

2.1. Mori’s generalized Langevin equation (GLE)

For a set of relevant variables \( A_0(t) \) we obtain from Mori theory [12, 34] the GLE, which is a
set of exact equations of motion of the form

\[
\dot{A}_0(t) = \Omega_0 A_0(t) - \int_0^t K_0(t - t') A_0(t') \, dt' + F_1(t).
\]  

The need for the index 0 will become clear later. We use boldface notation because, in general,
we are interested in a vector \( A_0 \) containing a set of say \( M \) relevant variables, which may be
vectors themselves in a \( D \)-dimensional space with \( D > 1 \), i.e. we might write \( A_0 \equiv A_{0\mu} \equiv
A_{0\mu\alpha} \) with \( \mu = 1 \ldots M \) and \( \alpha = 1 \ldots D \). We will use Greek ‘blob’ indices such as \( \mu, \nu, \sigma \)
and Cartesian indices \( \alpha, \beta \). In order to keep the notation as simple as possible we will use
index-notation only if it facilitates readability. Hence, expressions such as \( B C, B_{\mu\mu'} C_{\mu'\nu} \) and
\( B_{\mu\alpha\mu'} C_{\mu'\alpha'\nu} \) all denote the same product of two matrices \( B \) and \( C \), with contraction of the
blob-index \( \mu' \) and the Cartesian index \( \alpha' \).

The different elements of the GLE (1) require the definition of an inner product of phase
functions \( \langle \phi, \psi^* \rangle \). We use the classical mechanics limit of Mori’s definition as an equilibrium
average [12]

\[
\langle \phi, \psi^* \rangle \equiv \int \, d\rho^eq(z) \phi(z) \psi^*(z) \equiv \langle \phi \psi \rangle
\]  

with the equilibrium ensemble

\[
\rho^eq(z) = \frac{1}{Z} \exp[\frac{-H(z)}{k_b T}].
\]  

microscopic variables \( z \), the partition function \( Z \) and the Hamiltonian \( H(z) \). The second
definition in (2) was introduced for brevity of notation. It will be used most of the time,
implicitly assuming the presence of the star which denotes the conjugate transpose in general
and in particular the conventional transpose in all cases considered in this work.
In (1) the drift $\Omega_0$, the memory function $K_0(t)$ and the random force $F_0(t)$ are given by

$$\Omega_0 = \langle L A_0 A_0 \rangle \langle A_0 A_0 \rangle^{-1},$$

$$K_0(t) = \langle F_1(t) F_1 \rangle \langle A_0 A_0 \rangle^{-1},$$

$$F_1(t) = \exp(QLt)QLA_0,$$

$$\langle F_1(t) \rangle = 0, \quad \langle F_1(t) A_0 \rangle = 0,$$

where we use the short notation for initial values, e.g. $A_0 \equiv A_0(t = 0)$. $L$ is the Liouville operator associated with the Hamiltonian $H(z)$. With the inner product, the Liouville operator is assumed to be anti-Hermitian, i.e. $\langle L \phi \psi \rangle = -\langle \phi L \psi \rangle$. $Q$ is a projection operator projecting onto the space orthogonal to the space spanned by the relevant variables $A_0(z)$. It is defined by

$$Q \equiv 1 - P$$

where $P$ is a projection operator projecting any phase space function $\psi(z(t))$ onto the space of relevant variables according to

$$P \psi(z(t)) = \langle \psi(z(t)) A_0 \rangle \langle A_0 A_0 \rangle^{-1} A_0.$$

It should be noted that Mori theory is linear. One consequence is that all nonlinearities of the Hamiltonian $H(z)$, leading to the coupling of eigenmodes, can only show up in the memory function $K_0(t)$ of the GLE (1). The linearity of the theory is essential for the manipulations presented in the following.

### 2.2. Mori hierarchy

By recursively repeating the procedure of splitting the dynamics into a relevant and an orthogonal part Mori constructed a recursive cascade of GLEs for projected forces [29]. The recursion relation reads

$$\dot{F}_j(t) = \Omega_j F_j(t) - \int_0^t K_j(t - t') F_j(t') \, dt' + F_{j+1}(t)$$

for $j \geq 0$ with the definitions

$$\Omega_j \equiv \langle \dot{F}_j F_j \rangle \langle F_j F_j \rangle^{-1},$$

$$K_j(t) \equiv \langle F_{j+1}(t) F_{j+1} \rangle \langle F_j F_j \rangle^{-1},$$

$$F_j(t) \equiv \exp(L_j t)L_j F_{j-1} = \exp(L_j t)F_j,$$

$$F_0(t) \equiv A_0(t),$$

$$\dot{F}_j = L_j F_j,$$

$$L_0 \equiv L,$$

$$L_j \equiv (1 - P_{j-1})L_{j-1} = \prod_{i=0}^{j-1} (1 - P_i) L.$$

The $j$th projection operator $P_j$ is defined by its action on a phase space function $\psi(z)$ as

$$P_j \psi(z) \equiv \langle \psi(z) F_j \rangle \langle F_j F_j \rangle^{-1} F_j$$

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in analogy to (8). This also gives $P_0 = P$. $L$ is the conventional Liouville operator introduced earlier.

The analogue of the Markovian approximation [26, 35], now applied to (9) for $j > 0$ would be

$$K_j(t) \approx \Gamma_j \delta^+(t),$$

where the right hand Dirac delta function has the property [35]

$$\int_0^\infty \delta^+(t) \, dt = 1.$$

2.3. Continued fraction representation of the GLE

Transforming the hierarchy of GLEs (9) into the Laplace domain, one obtains the recursion relation [29]

$$\Xi_j(p) = (1p - \Omega_j + \Xi_{j+1}(p) \Delta_{j+1}^2)^{-1}$$

for the correlation function $\Xi_j(t)$ defined by

$$K_j(t) \equiv \Xi_{j+1}(t)(\Delta_{j+1})^2,$$

$$\Xi_j(t) \equiv \langle F_j(t) F_j \rangle \langle F_j F_j \rangle^{-1},$$

$$\Delta_j^2 \equiv \langle F_j F_j \rangle \langle F_{j-1} F_{j-1} \rangle^{-1}$$

with Laplace variable $p$ and unit matrix $1$. This can be rewritten as a continued fraction for any $j$, for example for $j = 0$

$$\Xi_0(p) = \left[ 1p - \Omega_0 + \left[ 1p - \Omega_1 + \left[ 1p - \Omega_2 + \left[ 1p - \Omega_3 \\
+ \cdots + \left[ 1p - \Omega_j + K_j(p) \right]^{-1} \Delta_j^2 \cdots \Delta_3^2 \Delta_2^2 \right]^{-1} \right]^{-1} \right]^{-1},$$

where we have expressed the continued fraction starting from level $j + 1$ by $K_j(p) = \Xi_{j+1}(p) \Delta_{j+1}^2$ according to (21). We can directly express the memory kernel in the same way, for example for $K_1(t)$ we have

$$K_0(p) = \left[ 1p - \Omega_1 + \left[ 1p - \Omega_2 + \left[ 1p - \Omega_3 \\
+ \cdots + \left[ 1p - \Omega_j + K_j(p) \right]^{-1} \Delta_j^2 \cdots \Delta_3^2 \Delta_2^2 \right]^{-1} \right]^{-1} \Delta_1^2,$$

or, in an ambiguous but more graphic notation

$$K_0(p) = \frac{\Delta_1^2}{1p - \Omega_1 + \frac{\Delta_2^2}{1p - \Omega_2 + \frac{\Delta_3^2}{1p - \Omega_3 + \cdots + \frac{\Delta_j^2}{1p - \Omega_j + K_j(p)}}}}.$$
where the fractions must be interpreted as matrix products of the form used in (25) with prepended inverses (i.e. denominators). $K_j(p)$ represents a kernel at level $j$ and can be expressed by another continued fraction of the same form starting with $\Delta_{j+1}^2$ in the nominator. Now it can immediately be seen that the Markovian approximation of (18) at level $j$ amounts to set $K_j(p) \approx \Gamma_j$, i.e. to a constant friction matrix in the Laplace domain. This corresponds to the well known horizontal truncation of the continued fraction [36] and it is the essential approximation that we have to make. We do not believe that the dynamics on level $j$ is generally Markovian. But, nonetheless, the representation of the essential object, which is the memory function $K_0(p)$, improves, the more we go down in the continued fraction expansion, by including more and more additional static equilibrium properties $\Delta_j^2$ and $\Omega_j$ as determined from the microscopic system. Furthermore, as shown in the following section, we choose $\Gamma_j$ in two ways that are both consistent with the continued fraction representation of $K_0(p)$.

2.4. Approximations for the friction $\Gamma_j$ based on continued fractions

In this work we focus on the family of relevant variables $A(z) = \{X(x), P(p)\}$ where the $X(x)$ are linear combinations of the microscopic displacements $x$ only and the $P(p)$ are linear combinations of the microscopic momenta $p$ only. Since $x$ and $p$ are statistically independent, so are then, due to the linear dependence, also $X$ and $P$. The same is true for variables proportional to higher even and odd time-derivatives of $X$ in general. This is equivalent to saying that odd time-derivatives of $\langle X(t)X \rangle$ vanish at $t = 0$, i.e. that all relevant correlation functions are even functions of time. This is the reason why, for the chosen family of relevant variables, the $\Omega_j$ vanish for $j \geq 1$ as shown in appendix B.

This leads to simplified continued fractions for $\Xi_0(p)$ and $K_0(p)$ which read

\[
\Xi_0(p) \approx \left[1p - \Omega_0 + \left[1p + \left[1p + \left[1p + \cdots + \left[1p + \Gamma_j \right]^{-1} \Delta_j^2 \cdots \right]^{-1} \Delta_j^2 \right]^{-1} \Delta_j^2 \right]^{-1} \right],
\]

(27)

\[
K_0(p) \approx \left[1p + \left[1p + \left[1p + \cdots + \left[1p + \Gamma_j \right]^{-1} \Delta_j^2 \cdots \right]^{-1} \Delta_j^2 \right]^{-1} \Delta_j^2 \right]^{-1} \Delta_j^2,
\]

(28)

where we have already made the Markovian approximation (18), i.e. $K_j(p) \approx \Gamma_j$. Now, making a long-time approximation in (27), i.e. setting $p = 0$ and solving for $\Gamma_j$ leads to

\[
\Gamma_{2m} \approx \prod_{i=0}^{m-1} \Delta_{2(m-i-1)}^2 \left(\Xi_0^{-1} + \Omega_0\right) \prod_{i=1}^{m-1} \Delta_{2i-1}^{-2},
\]

\[
\Gamma_{2m-1} \approx \prod_{i=1}^{m} \Delta_{2(m-i)+1}^2 \left(\Xi_0^{-1} + \Omega_0\right)^{-1} \prod_{i=1}^{m-1} \Delta_{2i}^{-2},
\]

(29)

with $\Xi_0 \equiv \Xi_0(p = 0)$. Note that

\[
\Xi_0(p = 0) = \int_0^\infty \langle A(t)A \rangle \, dt,
\]

(30)
which is the only time-integral we have to compute, regardless of the level \( j \). For the first few friction matrices the explicit expressions are

\[
\begin{align*}
\Gamma_0 & \approx \Xi_0^{-1} + \Omega_0, \\
\Gamma_1 & \approx \Delta_1^2 (\Xi_0^{-1} + \Omega_0)^{-1}, \\
\Gamma_2 & \approx \Delta_2^2 (\Xi_0^{-1} + \Omega_0) \Delta_1^{-2}, \\
\Gamma_3 & \approx \Delta_1^2 \Delta_2^2 (\Xi_0^{-1} + \Omega_0)^{-1} \Delta_2^{-2}, \\
\Gamma_4 & \approx \Delta_2^2 \Delta_3^2 (\Xi_0^{-1} + \Omega_0) \Delta_1^{-1} \Delta_3^{-2}.
\end{align*}
\]

Making the same long-time approximation in (28) gives

\[
\begin{align*}
\Gamma_{2m} & \approx \prod_{i=0}^{m-1} \Delta_{2(m-i-1)}^2 K_0 \prod_{i=1}^{m-1} \Delta_{2i-1}^{-2}, \\
\Gamma_{2m-1} & \approx \prod_{i=1}^{m} \Delta_{2(m-i)+1}^2 K_0^{-1} \prod_{i=1}^{m-1} \Delta_{2i}^{-2}
\end{align*}
\]

with \( K_0 \equiv K_0(p = 0) \). Note that

\[
K_0(p = 0) = \int_0^{\infty} \langle F_1(t) F_1 \rangle dt \langle AA \rangle^{-1}
\]

is the standard Markovian approximation for \( K_1(t) \) for the special case \( j = 0 \) which contains projected dynamics and is hence not easily computable from MD in contrast to (30). We immediately see that the expressions (36) become identical to the expressions (29) for the approximation \( K_0 \approx \Xi_0^{-1} + \Omega_0 \). We can improve on this ‘diffusive limit’ by using the approximation \( F_1(t) = \exp(QLt) F_0 \approx \exp(Lt) F_0 = A(t) - \Omega_0 A(t) \equiv \delta F(t) \). Then the matrix resulting from the integral

\[
K_0(p = 0) \approx \int_0^t \langle \delta F(t) \delta F \rangle dt \langle AA \rangle^{-1}
\]

is to be inserted into (36), giving a second way to approximate the friction matrix. Both equations (30) and (38) are closures for the determination of \( \Gamma_j \), which are consistent with the Mori theory of continued fractions.

2.5. Equivalent system of linear equations

Besides an approximation for \( \Gamma_j \) we need a convenient way to solve the truncated form of the GLE hierarchy (9) by time integration. For this purpose it is convenient to convert the integro-differential GLE into a system of ordinary differential equations. Our starting point will be a reformulation introduced by Karasudani et al [33] which involves a change in perspective by considering a slightly different set of relevant variables \( A(z(t)) \). This set is

\[
A(z(t)) \equiv A(t) = [A_0(t), A_1(t), \ldots, A_m(t)]^T
\]

with

\[
A_j(t) \equiv \exp(Lt) A_j, \quad A_j \equiv F_j.
\]
Note that, with this definition, \( A_j = L_j A_{j-1} = L_j F_{j-1} = F_j \), but \( A_j(t) \neq F_j(t) \) since the propagator of \( A_j(t) \) contains the conventional Liouville operator \( L \) while the propagator of \( F_j(t) \) contains the projected Liouville operator \( L_j \) as defined in (16).

Then, a new projection operator \( \mathcal{P} = \mathcal{P} \) is associated with this new extended set of relevant variables projecting now onto the subspace spanned by the extended vector \( A = A(t = 0) \). The projection operator is defined by

\[
\mathcal{P} \psi(z(t)) \equiv \langle \psi(z(t)) | A \rangle \langle AA \rangle^{-1} A.
\]

(41)

The vector \( A \) represents an orthogonal set because it follows from the definition (12) that the \( A_i \) are orthogonal, i.e. \( \langle A_i A_j \rangle = \langle F_i F_j \rangle = \delta_{ij} \). With this orthogonality one can show that

\[
\mathcal{P} = \sum_{k=0}^{m} P_k, \quad \mathcal{Q} = 1 - \mathcal{P} = 1 - \sum_{k=0}^{m} P_k = \prod_{k=0}^{m} Q_k
\]

(42)

and obtains the GLE

\[
\dot{A}(t) = \Omega A(t) - \int_0^t K(t - t') A(t') \, dt' + \tilde{F}(t),
\]

(43)

with the building blocks \[33\]

\[
\Omega = \begin{pmatrix}
\Omega_0 & -1 & 0 & \ldots & 0 \\
\Delta_1^2 & \Omega_1 & -1 \\
0 & \Delta_2^2 & \ddots & \ddots & 0 \\
\vdots & \ddots & \ddots & \ddots & \ddots \\
0 & \ldots & 0 & \Delta_m^2 & \Omega_m
\end{pmatrix}
\]

(44)

\[
\tilde{F}(t) = (0, \ldots, 0, F_{m+1}(t))
\]

(45)

and

\[
K(t) = \begin{pmatrix}
0 & \ldots & \ldots & 0 \\
\vdots & \ddots & \ddots & \vdots \\
\vdots & \ddots & 0 & 0 \\
0 & \ldots & 0 & K_m(t)
\end{pmatrix}
\]

(46)

with \( \Omega_j, F_j(t), K_j(t) \) and \( \Delta_j^2 \) given, respectively, by (10), (12), (21) and (23). Therefore, the GLE with these building blocks represents a linear system of equations of motion for \( A_0(t) = \{ X(t), P(t) \} \) and \( j \)th order fluxes \( A_j(t) \) with \( j = 1..m \), where only the \( m \)th order flux evolves according to a non-Markovian GLE. To this GLE and its memory kernel \( K_m(t) \), both approximations can be applied which have been discussed previously in section 2.4, because \( K_m(t) = \langle F_{m+1}(t) F_m(t) \rangle \) is the very same \( m \)th memory kernel from the conventional Mori-hierarchy as described in section 2.2.

We approximate the constant friction matrix \( \Gamma_m \) by (29), or by (36) (with (38)). The calculation of the first few \( \Delta_j^2 \) can be found in appendix C.
3. Linear combinations of atomistic variables

3.1. Coarse-grained variables

We consider the atomic positions and momenta \( z \equiv \{ r_i, p_i \} \) of \( i = 1..N \) atoms as microscopic variables. On the CG level we focus on relevant variables of the family \( A_0(z) \equiv A_{\mu 0}(z) \equiv \{ X_\mu, P_\mu \} \). \( X_\mu \) is a generalized CG displacement and \( P_\mu \) is a generalized CG momentum defined by

\[
X_\mu \equiv \sum_i f'_{\mu i} x_i, \tag{47}
\]

\[
P_\mu \equiv \sum_i f_{\mu i} p_i = \sum_i f_{\mu i} m_i v_i = \sum_i f_{\mu i} m_i x_i, \tag{48}
\]

where \( x_i = r_i - r_{i0} \) is the displacement of atom \( i \) from its equilibrium position \( r_{i0} \) and \( m_i \) is its mass. The blob index \( \mu \) runs over \( \mu = 1..M, \, M < N \) so that \( f_{\mu i}, f'_{\mu i} \) are rectangular matrices of constant weighting coefficients. Since we assume these matrices to behave like a diagonal matrix in the Cartesian indices \( \alpha, \beta \), we omit to write them in boldface if applied to a vector.

Specific instances of these matrices are for example

\[
f'_{\mu i} = \frac{m_i}{M_\mu} \theta_{\mu i}, \quad f_{\mu i} = \theta_{\mu i} \tag{49}
\]

for COM variables [25] where the entries of the matrix \( \theta_{\mu i} \) take the value 1 if atom \( i \) is in blob \( \mu \) and zero otherwise, and

\[
M_\mu = \sum_i m_i f_{\mu i} \tag{50}
\]

is the total mass of blob \( \mu \). One atom \( i \) may also contribute to more than one CG variable \( \mu \). This is for example the case in the CGMD method [27, 28]. The most general requirements on \( f_{\mu i}, f'_{\mu i} \) are

\[
\sum_i f'_{\mu i} = 1, \quad \sum_{\mu} f_{\mu i} = 1. \tag{51}
\]

In the special case of (49), \( f_{\mu i} \) is just a scaled version of \( f'_{\mu i} \), i.e.

\[
f_{\mu i} = \frac{m_i}{M_\mu} f'_{\mu i}. \tag{52}
\]

That this relationship and (50) are also meaningful for all other physically useful linear combinations of microscopic variables (47, 48) follows from the additional requirement that the total COM of the microscopic and of the CG system should in general be consistent. Particularly COM-variables using (49) fulfil this requirement by construction. In general, if we write (47) as

\[
X_\mu = \sum_i \frac{m_i}{M_\mu} f_{\mu i} x_i, \tag{53}
\]

then multiplication with \( M_\mu \), summation over \( \mu \) and division by the total mass \( M_{\text{tot}} \) gives exactly the desired relation for the displacements

\[
\frac{1}{M_{\text{tot}}} \sum_{\mu} M_\mu X_\mu = \frac{1}{M_{\text{tot}}} \sum_i \sum_{\mu} f_{\mu i} m_i x_i = \frac{1}{M_{\text{tot}}} \sum_i m_i x_i \tag{54}
\]
with
\[ M_{\text{tot}} \equiv \sum_i m_i = \sum_i m_i \sum_{\mu} f_{\mu i} = \sum_{\mu} M_\mu \] (55)

and because of (50) and (51). For the total momentum of the system we sum (48) over all \( \mu \) and get the desired relation \( \sum_{\mu} P_\mu = \sum_i p_i \), again by using (51). Then (48) can be rewritten as
\[ P_\mu = M_\mu \sum_i f'_{\mu i} v_i \equiv M_\mu V_\mu = M_\mu \dot{X}_\mu \equiv \mathcal{M}_{\mu\nu} V_\nu, \] (56)

where \( v_i = \dot{x}_i \) and (47) have been used. Here we have introduced the diagonal matrix
\[ \mathcal{M}_{\mu\nu} \equiv M_\mu \delta_{\mu\nu} \delta_{\alpha\beta} \] (57)

allowing us to use the short matrix notation \( P = MV \) without indices if we wish.

3.2. Mori GLE for coarse-grained variables

By inserting those definitions we formally get
\[ \dot{A}_0(t) = \mathbf{\Omega}_0 A_0(t) - \int_0^t K_0(t - t') A_0(t') \, dt' + F_1(t), \] (58)

with
\[ \mathbf{\Omega}_0 \equiv \begin{pmatrix} \Omega_{0XX} & \Omega_{0XP} \\ \Omega_{0PX} & \Omega_{0PP} \end{pmatrix}, \] (59)

\[ K_0(t) \equiv \begin{pmatrix} K_{0XX}(t) & K_{0XP}(t) \\ K_{0PX}(t) & K_{0PP}(t) \end{pmatrix}, \] (60)

\[ F_1(t) \equiv \left( F_1^X(t) \quad F_1^P(t) \right)^T. \] (61)

Equation (56) assures that the time derivative of the displacement is proportional to a relevant variable. Since \( F_1^X \) contains only the contributions from the irrelevant variables we have \( F_1^X = 0 \) and as a consequence of the fluctuation–dissipation relation (5) also \( K_{0XX}(t) = K_{0XP}(t) = K_{0PX}(t) = 0 \). Further we get \( \Omega_{0XX} = 0 \) and
\[ \Omega_{0XP}^{X\mu} = \langle V_{\mu} P_{\mu'} \rangle \langle P_{\mu'} P_{\mu} \rangle^{-1} = \frac{1}{M_\mu} \langle P_{\mu} P_{\mu'} \rangle \langle P_{\mu'} P_{\mu} \rangle^{-1} = \frac{1}{M_\mu} \delta_{\mu\nu} \] (62)

by using (47) and (48) and \( \langle v_i v_j \rangle = k_B T \delta_{ij} \delta_{\alpha\beta} / m_i \). Similarly we also get for the equation of motion for the CG momentum
\[ \Omega_{\mu'\nu}^{PX} = \langle L P_{\mu} X_{\mu'} \rangle \langle X_{\mu'} X_{\nu} \rangle^{-1} = -\langle P_{\mu} L X_{\mu'} \rangle \langle X_{\mu'} X_{\nu} \rangle^{-1} \]
\[ = -\langle P_{\mu} V_{\mu'} \rangle \langle X_{\mu'} X_{\nu} \rangle^{-1} = -k_B T M_{\mu'\mu} \frac{1}{M_{\mu'}} \langle X_{\mu'} X_{\nu} \rangle^{-1}, \] (63)

where we defined a generally non-diagonal mass matrix
\[ M_{\mu\nu} \equiv \frac{1}{k_B T} \langle P_{\mu} P_{\nu} \rangle = \sum_i f_{\mu i} m_i f_{\nu i} \delta_{\alpha\beta}. \] (64)
We also have
\[ \Omega_0^{PP} = \langle L P P \rangle (P P)^{-1} = 0. \] (65)

The only non-vanishing memory term reads for \( t \geq t' \)
\[ K_0^{PP} (t - t') = \langle F_1^P (t - t') F_1^P \rangle (P P)^{-1} = \frac{1}{k_B T} \langle F_1^P (t - t') F_1^P \rangle M^{-1}. \] (66)

In summary the exact equations of motion are
\[ \dot{X}_\mu = P_\mu /M_\mu, \] (67)
\[ \dot{P}_\mu = \Omega^{PX}_{\mu \nu} X_\nu - \int_0^t K_{\mu \nu}(t - t') P_\nu (t') \, dt' + F_\mu^P (t), \] (68)

where \( \Omega_0^{PX} \) is given by (63) and \( K_0^{PP} (t - t') \) is given by (66).

3.3. Linear system of equations for the CG variables and auxiliary variables

Applying the scheme described in section 2.5 to our choice of CG variables, the whole system of equations (43) can be written in the form
\[ \dot{A} (t) = \Omega A (t) - \Gamma A (t) + \bar{F} (t). \] (69)

The vector of relevant variables contains \( 2D(m + 1) \) entries, i.e.
\[ A = (A_0, A_1, \ldots, A_m)^T \]
with
\[ A_0 = \{ A_0^X, A_0^P \} = \{ X, P \} = \{ \{ X_\mu \}, \{ P_\mu \} \}, \] (70)
\[ A_1 = \{ A_1^X, A_1^P \} = \{ Q_0 L X, Q_0 L P \} = \{ 0, Q_0 L P \}, \] (71)
\[ A_2 = \{ A_2^X, A_2^P \} = \{ Q_0 Q_1 L A_1^X, Q_0 Q_1 L A_1^P \} = \{ 0, Q_0 Q_1 L A_1^P \}. \] (72)

\[ \ldots \]
\[ A_m = \{ A_m^X, A_m^P \} \equiv \left\{ 0, \left( \prod_{k=0}^{m-1} Q_k \right) L A_{m-1}^P \right\}. \] (73)

The \( X \)-components of \( A_1 \) to \( A_m \) vanish because the \( X \)-component of \( A_1 \) projects the time-derivative \( X \) with \( Q_0 \). But for the chosen family of CG variables \( X \) is always proportional to \( P \) according to (67). \( P \) is another CG-variable, i.e. lying in the subspace spanned by \( A_0 \). Then, any projection of \( P \) by a projector \( Q_j \) is orthogonal to \( A_0 \) and must vanish.

The matrix \( \Omega \) is given by (44) where each of the blocks \( \Omega_j, \Delta_j^2, -1 \) or \( 0 \) is a square matrix of rank \( 2 \times D \times M \), and there are \( (m + 1) \times (m + 1) \) such blocks. We have
\[ \Omega_0 = \begin{pmatrix} 0 & \Omega_0^{XP} \\ \Omega_0^{PX} & 0 \end{pmatrix} \] (74)

with \( \Omega_0^{XP} \) and \( \Omega_0^{PX} \) given in (62) and (63), respectively. For \( j \geq 1 \) we have
\[ \Omega_j = \begin{pmatrix} 0 & 0 \\ 0 & \Omega_j^{PP} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}. \] (75)
The block $\Omega_j^{PP}$ vanishes for our choice of $A$ as shown in appendix C. The other blocks vanish due to the vanishing $A_j^\Delta$. Note that the vanishing of $\Omega_j$ does not imply that the rows of the matrix $\Omega$ in equation (44) are empty. They contain $\Delta_j^2$ and $-1$ matrices which read

$$\Delta_j^2 = \begin{pmatrix} 0 & 0 \\ 0 & \Delta_j^{2PP} \end{pmatrix}, \quad 1 = \begin{pmatrix} 0 & 0 \\ 0 & 1^{PP} \end{pmatrix}. \quad (76)$$

For the first few levels $j$ an explicit calculation in terms of covariances of CG variables and their derivatives at $t = 0$ gives (for details see appendix C)

$$\Delta_1^{2PP} = \langle FF \rangle \langle PP \rangle^{-1} - \langle PV \rangle \langle XX \rangle^{-1} M^{-1}, \quad (77)$$

$$\Delta_2^{2PP} = \langle FF \rangle \langle PP \rangle^{-1} \Delta_1^{-2PP}
= (\langle FF \rangle - \langle FF \rangle \langle PP \rangle^{-1} \langle FF \rangle) \langle PP \rangle^{-1} \Delta_1^{-2PP}, \quad (78)$$

$$\Delta_3^{2PP} = \langle FF \rangle \langle PP \rangle \left( \Delta_2^{2PP} \Delta_1^{-2PP} \langle PP \rangle \right)^{-1}
= (\langle FF \rangle - \langle FF \rangle \langle BB \rangle - B_2^T \langle FF \rangle + B_2 \langle FF \rangle B_2^T
- \Delta_2^{2PP} \langle PP \rangle \langle XX \rangle^{-1} \langle VP \rangle \Delta_2^{2PP}) \left( \Delta_2^{2PP} \Delta_1^{-2PP} \langle PP \rangle \right)^{-1} \quad (79)$$

with $F \equiv \dot{P}$, and $B_2 \equiv \langle FF \rangle \langle PP \rangle^{-1} + \Delta_2^{2PP}$. The matrix $\Gamma$ is the constant friction approximation of (46), i.e.

$$\Gamma = \begin{pmatrix} 0 & \ldots & \ldots & 0 \\ \vdots & \ddots & \vdots \\ \vdots & 0 & 0 \\ 0 & \ldots & 0 & \Gamma_m \end{pmatrix}, \quad \Gamma_m$$

where we can obtain $\Gamma_m$ from one of the previously introduced approximations (29), or (36) (with (38)). Again, only the $PP$-component does not vanish and the random force $\dot{F}(t)$ is given by (45) where only the $D$ $P$-components of $F_{m+1}(t)$ are non-zero. The non-trivial part of the Markovian fluctuation–dissipation relation is then

$$K_m^{PP}(t-t') = \langle F_m^{PP}(t) F_{m+1}(t') \rangle \langle F_m^{PP} F_{m+1}^{PP} \rangle^{-1} \approx \Gamma_m^{PP} \delta(t-t') = 2m \delta(t-t'), \quad (81)$$

where we can model the stochastic increment produced by the random force $F_m^{PP}(t)$ as white noise, i.e. as a linear combination of Wiener processes such as

$$dF_m^{PP}(t) = C_m^{PP} dW_{m+1}^{PP}(t), \quad (82)$$

where $dW_{m+1}^{PP}(t)$ is a $D \times M$ vector of independent Wiener increments with the property

$$dW_{m+1}^{PP} dW_{m+1}^{PP} = \delta_{\mu \nu} \delta_{\alpha \beta} dt \equiv 1^{PP} dt. \quad (83)$$

New Journal of Physics 15 (2013) 125015 (http://www.njp.org/)
and $C_{m+1}^{PP}$ is a constant $D \times M \times D \times M$ square matrix. Insertion of (82) into (81), time integration with Ito calculus, and using (83) gives

$$C_{m+1}^{PP} C_{m+1}^{PP^T} = 2\Gamma_m \langle F_m^P F_m^P \rangle = 2^{m} k_B T \left( \prod_{k=1}^{m} \Gamma_k \right) M, \quad (84)$$

which is a fluctuation–dissipation theorem relating the noise amplitudes $C_{m+1}^{PP}$ to the friction matrix $\Gamma_m$. The second equality follows from the recursive relation (81) and

$$\langle F_1^P F_1^P \rangle = 2\Gamma_1 \langle P_0^F P_0^F \rangle = 2\Gamma_1 \langle P_0^P P_0^P \rangle = 2k_B T \Gamma_1 M, \quad (85)$$

where the mass matrix $M$ was defined in (64). If $C_{m+1}^{PP}$ is symmetric then $C_{m+1}^{PP} C_{m+1}^{PP^T} = C_{m+1}^{PP} C_{m+1}^{PP}$ and (84) requires the computation of a matrix square root.

In summary the equations of motion can be simplified and written in the form of stochastic differential equations as follows:

$$(dX(t) \quad dP(t) \quad dA_1^P(t) \quad dA_2^P(t) \quad \cdots \quad dA_{m-1}^P(t) \quad dA_m^P(t))^T$$

$$= \left( \begin{array}{cccccc} 0 & \Omega_0^{XP} & 0 & \ldots & \ldots & 0 \\ \Omega_0^{XP} & 0 & -1^{PP} & \ldots & \ldots & \vdots \\ 0 & \Delta_1^{2,PP} & 0 & -1^{PP} & \ldots & \vdots \\ \vdots & \vdots & \Delta_2^{2,PP} & 0 & \ldots & \vdots \\ \vdots & \vdots & \vdots & \Delta_{m-1}^{2,PP} & 0 & -1^{PP} \\ 0 & \ldots & \ldots & 0 & \Delta_m^{2,PP} & \Gamma_m^{PP} \end{array} \right) \left( \begin{array}{c} X(t) \\ P(t) \\ A_1^P(t) \\ A_2^P(t) \\ \vdots \\ A_{m-1}^P(t) \\ A_m^P(t) \end{array} \right) dt$$

$$+ \left( \begin{array}{c} 0 \\ 0 \\ \vdots \\ \vdots \\ \vdots \\ 0 \\ 0 \end{array} \right) + \left( \begin{array}{c} 0 \\ 0 \\ \vdots \\ \vdots \\ \vdots \\ 0 \\ 0 \end{array} \right) dW_{m+1}^P(t), \quad (86)$$

where the $0$ are either vectors of length $D \times M$ or square matrices of rank $D \times M$. Equation (86) is the main result of this paper. It is valid for general CG displacements and momenta representing linear combinations of microscopic variables. All objects in (86) are computable from equilibrium MD simulations.
Figure 1. Left: honeycomb lattice of C-atoms and sketch of the CG with hexagonal COM blobs containing 24 atoms. The dashed lines show one blob with 96 C-atoms. Right: illustration of the forces $F_{ij}(r_{ij})$ and $F_{ijk}(\alpha_{ijk})$ used in the graphene model.

4. Application to centre of mass blobs in graphene

We particularise the general equation (86) and consider here as an example the in-plane 2D motion of the graphene honeycomb lattice (cf figure 1). Before writing down the specific instances of the matrices in (86) and computing some of them by MD simulation we first have to define the atomistic model.

4.1. Microscopic model

The dynamics of the graphene model is described by Hamilton’s equations of motion for the set of microscopic variables $\{r_i, p_i\}$, where $m_i$ is the mass, $r_i$ the position and $p_i$ the momentum of C-atom $i$.

For the sake of simplicity, instead of more realistic potentials such as the Brenner bond order potential [37], we use a simple 2D potential of the same form as already used in [27]. The interaction potential between C-atoms is assumed to have the form $U = U_s + U_a$. The pair potential $U_s$ models a harmonic spring and is defined as

$$U_s = \sum_{P_{ij}} U_{ij}^s, \quad U_{ij}^s = \frac{1}{2} k_s (r_{ij} - r_0)^2,$$  \hfill (87)

where $k_s > 0$ is a stiffness constant, $r_0$ is the equilibrium bond-length, $r_{ij} = |r_i - r_j|$, $e_{ij} = r_{ij} / r_{ij}$, $r_{ij} = r_i - r_j$ and $P_{ij}$ denotes all those and only those pairs of nearest-neighbour C-atoms $i$ and $j$ that are bonded and assumed to interact by the given potential. The angular potential $U (\alpha_{ijk})$ is defined as

$$U_s = \sum_{T_{ijk}} U_{ijk}^a, \quad U_{ijk}^a = \frac{1}{2} k_a (\cos \alpha_{ijk} - \cos \alpha_0)^2,$$  \hfill (88)

where $T_{ijk}$ denotes all those and only those triplets of neighbouring C-atoms $\{i, j, k\}$ that are connected as shown in figure 1 and assumed to interact by the angular potential. The equilibrium
angle is $\alpha_0 = 2\pi/3$ and
\[
\cos(\alpha_{ijk}) = \frac{r_{ij} \cdot r_{kj}}{r_{ij}r_{kj}}.
\]
(89)

Here, $k_3$ is a second stiffness constant for angular changes.

The simulation units and parameters of the microscopic model are chosen in the same way as in [27]. The unit of length $l^*$ is fixed by setting $l^* \equiv r_0 \approx 0.142$ nm in graphene. The unit of mass is $m^* \equiv m_C$ where $m_C \approx 2 \times 10^{-26}$ kg is the mass of one C-atom. The unit of time is chosen as $t^* \equiv (m_C/k_3)^{1/2}$, which amounts to set the value of $k_3 = 1$ in the selected units. The angular spring constant $k_3 = 0.12$ is found by requiring the model to reproduce the ratio of transverse to longitudinal in-plane speeds of sound $c_T/c_L \approx 0.633$ based on measured values from [38, 39]. We then get $t^* \approx 5.18$ fs. The unit of temperature is $T^* \equiv m_Cc_0^2/k_Bt^2 \approx 1.09 \times 10^9$ K. MD-simulations are performed in the (N, V, E)-ensemble at a temperature of $T = 2.74 \times 10^{-4}$ (corresponding to $T \approx 298$K). Typically, the system is equilibrated for a sufficiently long time, of the order of $10t^*$ and data are collected subsequently. The used time step in all MD-simulations is $\Delta t = 0.005t^*$.

4.2. Coefficient matrices

In the following we list the specific forms of the matrices $\Delta^{PP}_{j,\mu \nu}$ for $j = 1, 2, 3$ for COM-blobs of equal mass $M_{cg}$. They are obtained by noticing that the momentum covariance becomes diagonal, i.e. $\langle P_\mu P_\nu \rangle = M_{cg}k_BT\delta_{\mu\nu}$. Then, also the mass matrix $M_{\mu \nu}$ is diagonal and identical to $M_{\mu \nu}$, i.e. $M_{\mu \nu} = M_{\mu \nu} = M_{cg}\delta_{\mu\nu}$. These replacements have to be performed in the general results given earlier and in the appendix and supplementary material (available from stacks.iop.org/NJP/15/125015/mmedia) where the detailed calculations can be found. Then we obtain
\[
\Delta^{PP}_{1,\mu \nu} = (F_\mu F_\sigma)\langle P_\sigma P_\nu \rangle^{-1} - \frac{1}{M_{cg}^2} \langle P_\mu P_\sigma \rangle \langle X_{\sigma} X_{\nu} \rangle^{-1}
\]

\[
 = \frac{1}{M_{cg}} \left( \frac{1}{k_BT} \langle F_\mu F_\nu \rangle - k_BT \langle X_{\mu} X_{\nu} \rangle^{-1} \right),
\]
(90)

\[
\Delta^{PP}_{2,\mu \nu} = (\langle \dot{F_\mu} \dot{F_\sigma} \rangle - \langle F_\mu F_\sigma \rangle \langle P_\mu P_\sigma \rangle^{-1} \langle F_\sigma F_\sigma \rangle \langle P_\sigma P_\eta \rangle^{-1}) \Delta^{2,PP}_{1,\eta \nu}
\]

\[
 = \frac{1}{M_{cg}k_BT} \left[ \langle \dot{F_\mu} \dot{F_\sigma} \rangle - \frac{1}{M_{cg}k_BT} \langle F_\mu F_\sigma \rangle^2 \right] \Delta^{2,PP}_{1,\sigma \nu},
\]

\[
\Delta^{PP}_{3,\mu \nu} = \left[ (\dot{F}_\mu \dot{F}_\nu) - (\dot{F}_\mu \dot{F}_\sigma)B_{2,\sigma \mu'} - B_{2,\mu \sigma} (\dot{F}_\sigma \dot{F}_\mu') + B_{2,\mu \sigma} (F_\sigma F_\eta)B_{2,\eta \mu'} \right]
\]

\[-\Delta^{2,PP}_{2,\mu \sigma} \langle P_\sigma V_\eta \rangle \langle X_\eta X_{\eta'} \rangle^{-1} \langle V_\eta' P_\chi \rangle \Delta^{2,T,PP}_{2,\chi,\mu'}\]

\[
\times \langle P_\mu P_\sigma \rangle^{-1} \Delta^{2,PP}_{1,\sigma \nu'} \Delta^{2,PP}_{2,\nu \nu'}
\]

\[
 = \frac{1}{M_{cg}k_BT} \left[ (\dot{F}_\mu \dot{F}_\nu) - (\dot{F}_\mu \dot{F}_\sigma)B_{2,\sigma \mu'} - B_{2,\mu \sigma} (\dot{F}_\sigma \dot{F}_\mu') + B_{2,\mu \sigma} (F_\sigma F_\eta)B_{2,\eta \mu'} \right]
\]

\[-(k_BT)^2 \Delta^{2,PP}_{1,\mu \sigma} \Delta^{2,PP}_{2,\sigma \mu'} \Delta^{2,PP}_{1,\mu' \nu} \Delta^{2,PP}_{2,\nu \nu'}
\]
(92)
Figure 2. xx- and yy-entries of the matrices $\Delta^2_1$ ((a), (b)) and $\Delta^2_2$ ((c), (d)) versus the blob-distances for pairs of COM-blobs aligned along the x-axis containing the nearest neighbour or y-axis containing the second-nearest neighbour. (a), (c): $N_{cg} = 96$. (b), (d): $N_{cg} = 24$. The symbols represent the actual matrix entries and the lines only serve for guiding the eye.

with

$$B_{2,\mu\nu} \equiv \frac{1}{M_{cg} k_B T} \langle F_\mu F_\nu \rangle + \Delta_{PP} \mu\nu.$$ 

Similarly for each of the two approximations for the friction matrices $\Gamma_{jPP}$, the COM-blob expressions can be found, which also require the $\Delta_{jPP}$ given above.

4.3. Numerical computation of some coefficient matrices

We show numerical results for the $PP$-components of $\Delta^2_1$ and $\Delta^2_2$ for a system of 10368 C-atoms that we coarse-grain into 108 hexagonal COM-blobs with $N_{cg} = 96$ C-atoms and 432 COM-blobs with $N_{cg} = 24$ C-atoms (cf figure 1). $\Delta^2_1$ is a crucial part of all approximations of the non-Markovian hierarchy (86) with $m > 0$. It couples the momentum of blob $\mu$ to the first auxiliary variable of blob $\nu$. $\Delta^2_2$ couples the first to the second auxiliary variable. Therefore $\Delta^2_{1,2}$ are good representatives of the characteristic properties of the approximated memory in the equations of motion of the COM-blobs. A full analysis of the CG equations of motion will be presented in a forthcoming paper.

Figure 2 shows plots of the Cartesian xx- and yy-entries of the matrices $\Delta^2_{\mu\nu1}$ and $\Delta^2_{\mu\nu2}$ for pairs of blobs $\mu$ and $\nu$ aligned along the x- or y-axis versus their distance $R_{\mu\nu}$, for $N_{cg} = 96$ (left) and for $N_{cg} = 24$ (right). At a coarse-graining ratio of $N_{cg} = 96$, the resulting periodically arranged 108 blobs have neighbours at four different non-zero distances on the x-axis and three on the y-axis. In the system of 432 blobs with $N_{cg} = 24$, we have neighbours at nine different non-zero distances on the x-axis and six on the y-axis.

It can be observed that the coupling of the momentum $P_\mu$ of a blob $\mu$ to the auxiliary fluxes $A_{\nu1}(t)$ (by $\Delta^2_1$) and of $A_{\mu1}(t)$ to $A_{\nu2}(t)$ (by $\Delta^2_2$) is very local, i.e. the coupling to $A_{\nu=\mu,j}(t)$ is very dominant and only the absolute values of the coupling coefficients to the nearest blob-neighbour are significantly larger than zero. One difference between $\Delta^2_{\mu\nu1}$ and $\Delta^2_{\mu\nu2}$ is the sign of the yy-entry of the nearest neighbour coupling (along the x-axis). At the moment we can not provide any explanation for this observation, but, as can be seen from the plots, this change in sign occurs consistently for both $N_{cg} = 96$ and 24. In general, neighbours in y-direction do not seem to influence the blobs significantly. We attribute this behaviour to the nature of the
lattice of the hexagonal blobs, which are directly aligned in the $x$- but not in the $y$-direction (cf figure 1). The local behaviour suggests a nearest neighbour approximation in order to gain computational efficiency when computing the equations of motion (86) numerically.

5. Summary and discussion

We obtained Markovian equations of motion for a general many body system of interacting CG displacements $X(t)$, momenta $P(t)$ and additional fluxes $A_j(t)$. As CG variables we considered the family of linear combinations of atomistic degrees of freedom. The goal was to coarse-grain the system as a whole instead of picking out individual variables of interest such as distinguished atoms or modes. The system of Markovian equations of motion approximates Mori’s exact non-Markovian GLE and is easier to solve by computer simulation since it is linear and memory-less. All parameters of the equations can be obtained from equilibrium MD simulations of the investigated microscopic system. These parameters are the static covariances $\Delta_j^2$ known from Mori’s continued fraction and generalized constant friction matrices $\Gamma_j$. We proposed two different ways to compute the friction matrices, which require the computation of relatively few static covariances (mostly the $\Delta_j^2$ up to the desired level $j = m$) and only one and the same time integral, independently of the level $j = m$. A detailed comparison of these approaches will be presented in a forthcoming paper.

Additionally, suitable criteria for the truncation of the hierarchy must be numerically investigated. On a general ground, the most obvious criterion is whether and how fast time-correlation functions computed from the CG model, such as the CG momentum correlation function, converge to their counterparts computed from the microscopic dynamics. More specifically, we can subdivide the behaviour of time correlation functions into short time behaviour and long time behaviour. For the former, by including a certain number of $\Delta_j^2$ parameters, the presented approach allows a direct control of the number of frequency moments (or ‘sum rules’ [36]) that should be reproduced by the CG model. The essential criterion with respect to the long time behaviour is to test the reproduction of decay rates of eigenmodes, i.e. of macroscopic transport coefficients.

In this work, we presented numerical results for the special case of COM variables in the graphene lattice that indicate that the CG variables interact with their additional fluxes in a spatially very local way, following the local definition of the COM-variables themselves. This property is useful for efficient numerical computation. We also know from previous work that, on one hand, the time evolution of COM-variables seems to be more Markovian than for example for finite element (FE) based variables [25, 27]. On the other hand, COM-variables show weaknesses in reproducing dispersion relations. Therefore we are also investigating the application of the presented general non-Markovian coarse-graining scheme to the special case of FE variables which also represent linear combinations of atomistic degrees of freedom. Therefore, the general results presented here allow one to address a huge variety of molecular systems such as atomic lattices, proteins, polymers or fluids, with one or more of the preferred linear CG variables in that field.

A true separation of timescales at level $j$, i.e. the strict validity of a Markovian approximation at this level, can be expected for example for lattices with a phononic bandgap. In this case we might wish to represent the bands below the bandgap in a CG model. Either we directly choose the respective normal modes as the relevant variables, which could lead to a purely Markovian model, or alternatively to these global collective variables, we might stick to
a smaller number of spatially local COM-blobs with auxiliary variables as internal degrees of freedom, and search for a level $j$ which separates the fast from the slow dynamics. It should be kept in mind that the presence of nonlinearities in the lattice is mandatory. Otherwise, the modes do not couple and there is no relaxation to equilibrium, which renders Mori–Zwanzig theories non-applicable. Nonlinearity is thereby necessary but not sufficient [40]. Other systems where a separation of timescales might be identified, are large proteins coarse-grained into a few still large substructures. The auxiliary variables could again represent relevant internal degrees of freedom of these substructures. But even for systems without any separation of time-scales, we may expect that higher approximation levels $j$ reproduce more features of the memory function, and hence give a better approximation to the non-Markovian behaviour.

A further issue to be investigated is the requirements on the accuracy of time-integration. The described methods require the calculation of correlations of higher-order time derivatives of the relevant variables, which translates into the computation of higher-order time derivatives of the microscopic variables. This may pose a problem for standard second order accurate integrators, e.g. of Verlet-type, as we have used up to now. For the time being we have partially circumvented this potential numerical problem by calculating the required derivatives analytically, which was possible for the simple microscopic interaction potential used here. But this is of course not an option for general potentials and for arbitrary truncation levels. In addition it does not improve the time-integration itself. Therefore it is worth while to compare the results with those obtained with higher order symplectic integrators (cf e.g. [41]).

An alternative to Mori’s projector based on equilibrium averages is Zwanzig’s general nonlinear theory where the projectors are defined by constrained averages. The drift term or the memory function are then objects depending on the whole phase space of relevant variables. For practical computations, this makes modelling assumptions indispensable. In the work by Hijón et al [42], it was reasonable to assume pairwise interactions for a molecular liquid. This can not be directly transferred to lattices that are the main focus of the present work. In addition, the connection to the Mori-hierarchy is not obvious. A promising starting point that begins from the Mori hierarchy and goes a step into Zwanzig’s direction seems to be the work of Dygas et al [43] and of Grigolini [44]. Dygas et al [43] use a GLE where they multiply the memory kernel with a state-dependent factor. The authors show a Markovian system of equations with auxiliary variables derived from this extended GLE. Their approach is based on Grigolini’s work [44] who derived a GLE for non-additive fluctuations which allows one to describe a multiplicative process. It is worth investigating whether this approach can lead us to a useful nonlinear Markovian system of equations with auxiliary variables.

Acknowledgments

The authors acknowledge funding by the University of Freiburg through the German excellence initiative. DK thanks the UNED in Madrid for its kind hospitality and acknowledges funding by the DFG via the project KA 3482/2 *Simulation graphenbasierter Nanoresonatoren: Systematische Reduktion von Freiheitsgraden*. PE is grateful for the support of BIFI and the Ministry of Science and Innovation through project FIS2010-22047-C05-03. Additionally, we gratefully thank the bwGRiD project\(^7\) for the computational resources.

\(^7\) bwGRiD (www.bw-grid.de), member of the German D-Grid initiative, funded by the Ministry for Education and Research (Bundesministerium fuer Bildung und Forschung) and the Ministry for Science, Research and Arts Baden-Wuerttemberg (Ministerium fuer Wissenschaft, Forschung und Kunst Baden-Wuerttemberg).

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Appendix A. The $A_j = F_j$

Some of the equations we refer to in this appendix can be found in appendix D which we provide as supplementary material (available from stacks.iop.org/NJP/15/125015/mmedia). From [29] we know

$$F_{j,m}(0) = L_m F_{j,m-1}$$

(A.1)

with

$$L_m = \prod_{k=0}^{m-1} Q_k L = \prod_{k=0}^{m-1} (1 - \mathcal{P}_k) L = \left(1 - \sum_{k=0}^{m-1} \mathcal{P}_k \right) L,$$

(A.2)

since $\mathcal{P}_j \mathcal{P}_k = 0$ for all $j \neq k$. The first few projections $\mathcal{P}_0$, $\mathcal{P}_1$ and $\mathcal{P}_2$ are defined by their action on a phase space function $G_\mu$ according to

$$\mathcal{P}_0 \psi = \langle \psi A_0 \rangle \langle A_0 A_0 \rangle^{-1} A_0,$$

(A.3)

$$\mathcal{P}_1 \psi = \langle \psi A_1 \rangle \langle A_1 A_1 \rangle^{-1} A_1,$$

(A.4)

$$\mathcal{P}_2 \psi = \langle \psi A_2 \rangle \langle A_2 A_2 \rangle^{-1} A_2$$

(A.5)

with $A_j = F_j$. By this we obtain

$$A_1 = F_1 = L_1 A_0 = (1 - \mathcal{P}_0) LA_0 = LA_0 - \Omega_0 A_0.$$  

(A.6)

Further

$$L_1 F_1 = (1 - \mathcal{P}_0) L (LA_0 - \Omega_0 A_0)$$

$$= L^2 A_0 - \Omega LA_0 - (L^2 A_0 A_0) (A_0 A_0)^{-1} A_0 + \Omega (LA_0 A_0) (A_0 A_0)^{-1} A_0$$

$$= L^2 A_0 - \Omega LA_0 - \Omega \Omega A_0 + \Omega \Omega A_0$$

$$= L^2 A_0 - \Omega LA_0 + \Omega^2 A_0.$$  

(A.7)

The last equality is shown in (C.5).

For $A_2 = F_2$ we get

$$A_2 = F_2 = L_2 A_1 = (1 - \mathcal{P}_1 - \mathcal{P}_0) LA_1$$

$$= L A_1 - \frac{\langle LA_1 A_1 \rangle \langle A_1 A_1 \rangle^{-1} A_1 - \langle LA_1 A_0 \rangle \langle A_0 A_0 \rangle^{-1} A_0}{\Omega_1}$$

$$= L^2 A_0 - \Omega_0 LA_0 + \Delta_1^2 A_0,$$

(A.8)

since all $\Omega_j$ vanish for $j \geq 1$ as shown in appendix B. We also need

$$L_2 F_2 = (1 - \mathcal{P}_1 - \mathcal{P}_0) LA_2$$

$$= L A_2 - \frac{\langle LA_2 A_1 \rangle \langle A_1 A_1 \rangle^{-1} A_1 - \langle LA_2 A_0 \rangle \langle A_0 A_0 \rangle^{-1} A_0}{\Delta_2^1}$$

$$= L^3 A_0 - \Omega_0 L^2 A_0 + B_1 LA_0 - \Delta_2^2 \Omega_0 A_0$$  

(A.9)

with

$$B_1 = \Delta_1^2 + \Delta_2^2.$$  

(A.10)

We already took into account that all $\Omega_j$ vanish and used (C.9) and (D.81).
For $A_3 = F_3$ we get
\[
A_3 = F_3 = L_3 A_2 = (1 - P_2 - P_1 - P_0) L A_2 \\
= LA_2 - \langle LA_2 A_2 \rangle \langle A_2 A_2 \rangle^{-1} A_2 - \langle LA_2 A_1 \rangle \langle A_1 A_1 \rangle^{-1} A_1 \\
- \langle LA_2 A_0 \rangle \langle A_0 A_0 \rangle^{-1} A_0 \\
\equiv L^3 A_0 - \Omega_0 L^2 A_0 + B_1 L A_0 - \Delta_2^3 \Omega_0 A_0, \tag{A.11}
\]
where $\Omega_j = 0$ for $j \geq 1$ was used. We further need
\[
L_3 F_3 = (1 - P_2 - P_1 - P_0) L A_3 \\
= LA_3 - \langle LA_3 A_2 \rangle \langle A_2 A_2 \rangle^{-1} A_2 - \langle LA_3 A_1 \rangle \langle A_1 A_1 \rangle^{-1} A_1 \\
- \langle LA_3 A_0 \rangle \langle A_0 A_0 \rangle^{-1} A_0 \\
\equiv L^4 A_0 - \Omega_0 L^3 A_0 + B_1 L^2 A_0 - \Delta_2^2 \Omega_0 L A_0 - \beta_2 (L^2 A_0 - \Omega_0 L A_0 + \Delta_2^2 A_0) \\
= L^4 A_0 - \Omega_0 L^3 A_0 + (B_1 - \beta_2) L^2 A_0 + (\beta_2 - \Delta_2^2) \Omega_0 L A_0 - \beta_2 \Delta_2^2 A_0, \tag{A.12}
\]
where the vanishing of $\gamma_1$ and $\delta_0$ is shown in (D.85) and (D.90), respectively, and $\beta_2$ is given in (D.71).

**Appendix B. The matrices $\Omega_1$, $\Omega_2$ and $\Omega_3$ vanish**

Some of the equations we refer to in this appendix can be found in appendix D which we provide as supplementary material (available from stacks.iop.org/NJP/15/125015/mmedia). To keep the notation simple we will omit the index 0 for the CG variables from here on and write $A(t) \equiv A_0(t) = \{X(t), \dot{X}(t), P(t), \dot{P}(t)\}$ and $LA(t) = \{\dot{X}(t), \ddot{X}(t), \dot{P}(t), \ddot{P}(t)\}$. We will also write $\Omega \equiv \Omega_0$. There is
\[
\Omega_1 = \langle LF_1 F_1 \rangle \langle F_1 F_1 \rangle^{-1} = 0, \tag{B.1}
\]
where
\[
\langle F_1 F_1 \rangle = \begin{pmatrix} 0 & 0 \\ 0 & \langle F_1 F_1 \rangle^{PP} \end{pmatrix} \tag{B.2}
\]
is calculated in detail in (D.12) and $\langle LF_1 F_1 \rangle$ vanishes as shown in (D.14). Then, $\Omega_1 = 0$ under the following interpretation: in fact $\langle F_1 F_1 \rangle = 0$, hence it is not invertible and $\Omega_1$ not computable. Recalling that we have already shown in (66) that ultimately the only relevant non-zero part of the memory kernel is the $PP$-component, we can interpret the inverses of the form $\langle F_1 F_1 \rangle^{-1}$ as a pseudoinverse, resulting in inverses of zero $XX$-subblocks to be set to zero. In this way, $\Omega_1$ is well defined and indeed $\Omega_1 = 0$. This procedure will therefore be applied here and for similar cases in the following. One such case is also
\[
\Omega_2 = \langle LF_2 F_2 \rangle \langle F_2 F_2 \rangle^{-1} = 0, \tag{B.3}
\]

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where \( \langle F_2 F_2 \rangle \) has been calculated in (D.28) and \( \langle LF_2 F_2 \rangle \) vanishes as shown in (D.30). This leads to \( \Omega_2 = 0 \) if \( (F_2 F_2)^{-1} \) is computed as a pseudoinverse as discussed above for \( (F_1 F_1)^{-1} \). Further

\[
\Omega_3 = \langle L F_3 F_3 \rangle (F_3 F_3)^{-1} = 0,
\]

where \( \langle F_3 F_3 \rangle \) has been calculated in (D.56) and \( \langle LF_3 F_3 \rangle \) vanishes as shown in (D.70). This leads to \( \Omega_3 = 0 \) if \( (F_3 F_3)^{-1} \) is computed as a pseudoinverse as discussed above for \( (F_1 F_1)^{-1} \).

**Appendix C. Calculation of the \( \Delta^2_j \)**

Some of the equations we refer to in this appendix can be found in appendix D which we provide as supplementary material (available from stacks.iop.org/NJP/15/125015/mmedia).

### C.1. Calculation of \( \Delta^2_1 \)

Mori’s definition is

\[
\Delta^2_1 = \langle F_1 F_1 \rangle (F_0 F_0)^{-1},
\]

with

\[
(F_0 F_0)^{-1} = (A_0 A_0)^{-1},
\]

given in (D.2) and \( \langle F_1 F_1 \rangle \) calculated in (D.12). Inserted into (C.1) this gives

\[
\Delta^2_1 = \begin{pmatrix}
0 & 0 \\
0 & \Delta^{2pP}_1
\end{pmatrix}
\]

with

\[
\Delta^{2pP}_1 = \langle FF \rangle (PP)^{-1} - \langle PP \rangle (XX)^{-1} M^{-1}
\]

and \( F \equiv \dot{P} \). The following relation is also worth noting:

\[
\Delta^2_1 = \langle F_1 F_1 \rangle (F_0 F_0)^{-1} \\
= \left(-\langle L^2 A_0 A_0 \rangle - \langle L A_0 A_0 \rangle \Omega_0^T - \Omega_0 \langle A_0 L A_0 \rangle + \Omega_0 \langle A_0 A_0 \rangle \Omega_0^T \right) (A_0 A_0)^{-1} \\
= \Omega_0 - \Omega'
\]

with \( \Omega' \) given in (D.93).

### C.2. Calculation of \( \Delta^2_2 \)

Mori’s definition is

\[
\Delta^2_2 = \langle F_2 F_2 \rangle (F_1 F_1)^{-1},
\]

where \( \langle F_1 F_1 \rangle \) has been calculated in (D.12) and \( \langle F_2 F_2 \rangle \) in (D.28). Then we get

\[
\begin{pmatrix}
0 & 0 \\
0 & \Delta^{2pP}_2
\end{pmatrix}
\]
with

\[ \Delta_{2}^{PP} = \langle F_{2}F_{2} \rangle \langle F_{1}F_{1} \rangle^{-1} = \langle F_{2}F_{2} \rangle \langle PP \rangle^{-1} \Delta_{1}^{-2PP} \]

\[ = (\langle \dot{F} \dot{F} \rangle - \langle FF \rangle \langle PP \rangle^{-1} \langle FF \rangle) \langle PP \rangle^{-1} \Delta_{1}^{-2PP}. \]  
(C.8)

It can also be shown that

\[ \Delta_{2}^{2} = \langle F_{2}F_{2} \rangle \langle F_{1}F_{1} \rangle^{-1} = -\langle LF_{2}F_{1} \rangle \langle F_{1}F_{1} \rangle^{-1}. \]  
(C.9)

### C.3. Calculation of \( \Delta_{3}^{3} \)

Mori’s definition is

\[ \Delta_{3}^{3} = \langle F_{3}F_{3} \rangle \langle F_{2}F_{2} \rangle^{-1}, \]  
(C.10)

where \( \langle F_{2}F_{2} \rangle \) is given by (D.28) and \( \langle F_{3}F_{3} \rangle \) in (D.56), which is

\[ \langle F_{3}F_{3} \rangle = \begin{pmatrix} 0 & 0 \\ 0 & \langle F_{3}F_{3} \rangle^{PP} \end{pmatrix}. \]  
(C.11)

with

\[ \langle F_{3}F_{3} \rangle^{PP} = \langle \dot{F} \dot{F} \rangle - \langle \dot{F} \dot{F} \rangle B_{2}^{T} - B_{2} \langle \dot{F} \dot{F} \rangle + B_{2} \langle FF \rangle B_{2}^{T} - \Delta_{2}^{3} \langle PV \rangle \langle XX \rangle^{-1} \langle VP \rangle \Delta_{2}^{3T} \]  
(C.12)

and with

\[ B_{2} \equiv \langle FF \rangle \langle PP \rangle^{-1} + \Delta_{2}^{2}. \]  
(C.13)

Then

\[ \Delta_{3}^{3} = \langle F_{3}F_{3} \rangle \langle F_{2}F_{2} \rangle^{-1} = \langle F_{3}F_{3} \rangle \langle AA \rangle^{-1} \Delta_{1}^{-2} \Delta_{2}^{-2} = \begin{pmatrix} 0 & 0 \\ 0 & \Delta_{3}^{PP} \end{pmatrix}. \]  
(C.14)

with

\[ \Delta_{3}^{PP} = \langle F_{3}F_{3} \rangle^{PP} \langle PP \rangle^{-1} \Delta_{1}^{-2PP} \Delta_{2}^{-2PP}. \]  
(C.15)

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