

Mori-Zwanzig formalism as a practical computational tool

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An operational procedure is presented to compute explicitly the different terms in the generalized Langevin equation (GLE) for a few relevant variables obtained within Mori-Zwanzig formalism. The procedure amounts to introducing an artificial controlled parameter which can be tuned in such a way that the so-called projected dynamics becomes explicit and the GLE reduces to a Markovian equation. The projected dynamics can be realised in practice by introducing constraints, and it is shown that the Green-Kubo formulae computed with these dynamics do not suffer from the plateau problem. The methodology is illustrated in the example of star polymer molecules in a melt using their center of mass as relevant variables. Through this example, we show that not only the effective potentials, but also the friction forces and the noise play a very important role in the dynamics.

I. Introduction

The theoretical basis of non-equilibrium statistical mechanics were laid down in the middle of the 20th century by Onsager, Kirkwood, Green, Kubo, Mori, Zwanzig, and many others.¹⁻³ One of the major achievements of the theory, nowadays referred to as Mori-Zwanzig formalism, is the derivation *via* a projection operator technique of a generalized Langevin equation (GLE) which describes the non-equilibrium evolution of any set of functions defined on the phase-space of the microscopic system. These functions have been named as relevant variables, coarse-grained variables, collective variables, or collective modes in different contexts. While exact, the GLE is unfortunately difficult to use as a computational tool, for two main reasons. First, the various terms in the equation involve the so-called “projected dynamics”, which is not the real dynamics that one can calculate *e.g.* *via* molecular dynamics (MD) simulations and it is difficult to write down explicitly in general. This means that the GLE is not explicit in general. Second, even if it were explicit, the GLE is an integro-differential equation with random coefficients, and the numerical integration of such an equation is very difficult. To get around these difficulties, it is usually assumed that both the projected and the real dynamics are equivalent, and that the relevant variables are such that they evolve on a time scale much larger than the correlation time of the memory kernel so that the GLE can be rendered Markovian and turned into a standard stochastic differential equation (SDE). However, there is no clear mathematical justification for these approximations, and they often fail. For instance, they lead to the well-known “plateau problem” that requires the introduction of another *ad-hoc* approximation in which one truncates the limit of the time integrals.⁴⁻⁶ For these reasons, the GLE is not often used in practical computations. This is unfortunate considering the increasing need of formulating simplified coarse molecular models that have sufficient molecular detail and yet remain amenable to simulation.

In the present paper, we propose a procedure to make explicit the projected dynamics and formalize the Markovian approximation, and thereby derive a workable equation from the GLE. The basic idea is to alter the underlying microscopic dynamics by including an artificial parameter ε which controls the ratio between time scales of the relevant variables and the rest. In the limit as $\varepsilon \rightarrow 0$ it can be shown using limiting theorems for singularly perturbed Markov processes that the modified dynamics leads to an *exact* Markovian description for the relevant variables. Thus, by introducing the control parameter ε , we transform the problem of approximating non-rigorously a model into a problem of assessing the adequacy of a well-defined modified model to

reality. A similar strategy was used in a different context in [ref. 7](#). The construction of the modified dynamics is one of the main purposes of this paper. In particular, we show how to compute all the objects in the procedure *via* ergodic sampling of appropriately constrained molecular dynamics simulations. We also show that the resulting Green-Kubo expressions obtained in the new formulation do not suffer from the plateau problem, which is inherent to the use of the real dynamics.[4-6](#)

The procedure is subsequently applied to the coarse-graining of complex molecules. There is at present a great interest in constructing coarse-grained models in which each molecule is represented by a smaller number of degrees of freedom.[8](#) Towards this aim much attention has been paid to obtaining *coarse-grained (CG) potentials* governing the interaction of the coarse degrees of freedom. Usually, certain functional forms for the CG potentials are assumed and they are parametrized in order to obtain structural properties like the radial distribution function. Several methods have been developed in order to obtain the appropriate parameters: iterative adjustment of potential parameters starting from an approximation based on the potentials of mean force,[9,10](#) through the solution of the Ornstein-Zernike equation,[11](#) by using the inverse Monte Carlo technique,[12,13](#) by matching thermodynamic properties,[14](#) or by using directly the underlying all-atom interactions through a force matching procedure.[15,16](#) The CG potentials produce correct results for the study of equilibrium and structural properties, as they have been designed just to recover such behaviour. However, dynamic properties like diffusion or, more generally, time correlations, are not necessarily recovered from a simple molecular dynamics simulation using the CG potentials. The basic reason for this failure is that a coarse-graining procedure eliminates degrees of freedom that should appear in the coarse-grained dynamics in the form of *dissipation* and *thermal noise*, both connected through the fluctuation-dissipation theorem. The construction of CG potentials is only part of the story of coarse-graining. This has been recognized recently by considering the generalized Langevin equation for the coarse-grained variables[17](#) which includes velocity dependent friction forces and thermal fluctuations. In the present paper, we show how our procedure can be applied to the coarse-graining of star polymer molecules, by computing not only coarse-grained effective conservative forces but also dissipative friction forces. The resulting dynamic equations have the structure of dissipative particle dynamics.[18,19](#)

The remainder of this paper is organized as follows. In Sec. II we review Mori-Zwanzig theory, and re-derive and interpret the GLE. In Sec.

III we present the standard Markovian approximation which is used to turn the GLE into an SDE, and we discuss the caveats with this approximation, in particular the well-known plateau problem. In Sec. IV we introduce our procedure to modify the original dynamics and thereby obtain directly an SDE instead of a GLE in suitable limit. We also show that the coefficients in the SDE do not suffer from the plateau problem and we discuss how to compute them in practice using constrained MD simulations. In Sec. V we show how to apply the procedure to coarse-grain the dynamics of big complex molecules and in Sec. VI we consider the specific example of star polymer in a melt. Finally, in Sec. VII we give a few concluding remarks and indicate how the procedure proposed here could be generalized.

II. Review of Mori-Zwanzig theory

In this section we review Mori-Zwanzig theory by working directly with the equation of motion for the relevant variables rather than the one for the probability density function of these variables.^{3,20,21} We choose this approach because it is slightly more expeditive and, we believe, more transparent. We will work with Zwanzig's projector instead of Mori's projector.³ The former leads to a general non-linear GLE while the latter produces linear GLE. It can be shown that the linear GLE of Mori's is an approximation near equilibrium of the more general Zwanzig's GLE.³

We shall focus on systems whose microscopic state is characterized by the instantaneous positions and momenta of the N atoms of the system, $\{\mathbf{q}_i(t), \mathbf{p}_i(t)\}$ with $i = 1, \dots, N$. We denote the collection of these variables by $\mathbf{Z}(t) = (Z_1(t), \dots, Z_{6N}(t))$, which is a vector of $6N$ components. In terms of $\mathbf{Z}(t)$, the Hamiltonian dynamics of the system can be written as by

$$\frac{d\mathbf{Z}(t)}{dt} = J \frac{\partial H(\mathbf{Z}(t))}{\partial \mathbf{z}}, \quad \mathbf{Z}(0) = \mathbf{z} \quad (1)$$

where \mathbf{z} denotes the initial condition, H is the Hamiltonian and J is the symplectic matrix with a block diagonal structure with the blocks given by

$$J = \begin{pmatrix} \mathbf{0} & \mathbf{1} \\ -\mathbf{1} & \mathbf{0} \end{pmatrix} \quad (2)$$

Suppose that we are interested not in the evolution of $\mathbf{Z}(t)$ *per se*, but rather that of $\mathbf{A}(\mathbf{Z}(t))$ where $\mathbf{A}(\mathbf{z}) = (A_1(\mathbf{z}), \dots, A_M(\mathbf{z}))$ is a specific

observable, *i.e.* any set of M functions defined on phase-space. Even more specifically our aim is to calculate the statistical properties of $\mathbf{A}(\mathbf{Z}(t))$ for $t \geq 0$ for the ensemble of initial conditions $\mathbf{Z}(0) = \mathbf{z}$ satisfying $\mathbf{A}(\mathbf{z}) = \alpha$ for some fixed α and with \mathbf{z} distributed according to the equilibrium density $\rho^{\text{eq}}(\mathbf{z})$ conditional on $\mathbf{A}(\mathbf{z}) = \alpha$. Zwanzig's approach is a way to write an integro-differential equation with random coefficients whose solutions in different realizations generate the desired ensemble of $\mathbf{A}(\mathbf{Z}(t))$.

To see how this equation is derived, let us first make explicit the dependency in the initial condition \mathbf{z} in $\mathbf{A}(\mathbf{Z}(t))$ by denoting $\mathbf{A}(\mathbf{Z}(t)) \equiv \mathbf{a}(t, \mathbf{z})$. This function can be formally expressed as

$$\mathbf{a}(t, \mathbf{z}) = \exp\{tL\}\mathbf{A}(\mathbf{z}) \quad (3)$$

in which the exponential operator is defined through its Taylor series expansion and L is the Liouville operator

$$L = -\frac{\partial H}{\partial \mathbf{z}} J \frac{\partial}{\partial \mathbf{z}} \quad (4)$$

[Eqn \(3\)](#) shows that $\mathbf{a}(t, \mathbf{z})$ satisfies the following equation

$$\partial_t \mathbf{a}(t, \mathbf{z}) = L\mathbf{a}(t, \mathbf{z}), \quad \mathbf{a}(0, \mathbf{z}) = \mathbf{A}(\mathbf{z}) \quad (5)$$

Next introduce the conditional expectation operator P_α whose action to an arbitrary phase function $F(\mathbf{z})$ gives the conditional equilibrium expectation of $F(\mathbf{z})$ at $\mathbf{A}(\mathbf{z}) = \alpha$ fixed, *i.e.* the function of α defined as

$$P_\alpha F = \frac{1}{\Omega(\alpha)} \int F(\mathbf{z}) \rho^{\text{eq}}(\mathbf{z}) \delta(\mathbf{A}(\mathbf{z}) - \alpha) d\mathbf{z} \quad (6)$$

Here $\rho^{\text{eq}}(\mathbf{z})$ is the equilibrium probability density (e.g. the microcanonical density $\rho^{\text{eq}}(\mathbf{z}) = \Omega_0^{-1} \delta(H(\mathbf{z}) - E)$ where E is the energy and Ω_0 is the normalization factor, assuming that $H(\mathbf{z})$ is the only invariant of motion), and we defined

$$\Omega(\alpha) = \int \rho^{\text{eq}}(\mathbf{z}) \delta(\mathbf{A}(\mathbf{z}) - \alpha) d\mathbf{z} \quad (7)$$

$\Omega(\alpha)$ is the probability density of $\mathbf{A}(\mathbf{z})$ or, loosely speaking, “the number of microstates compatible with the macrostate $\mathbf{A}(\mathbf{z}) = \alpha$.” Let $Q_\alpha = 1 - P_\alpha$, and in [eqn \(5\)](#) use $L\mathbf{a}(t, \mathbf{z}) = L \exp\{tL\}\mathbf{A}(\mathbf{z}) = \exp\{tL\}L\mathbf{A}(\mathbf{z})$ and insert $1 = P_{\mathbf{A}(\mathbf{z})} + Q_{\mathbf{A}(\mathbf{z})}$ to transform this equation into

$$\partial_t \mathbf{a}(t, z) = \exp\{tL\} P_{\mathbf{A}(z)} L \mathbf{A} + \exp\{tL\} Q_{\mathbf{A}(z)} L \mathbf{A} \quad (8)$$

Using the Duhamel–Dyson identity

$$\exp\{tL\} = \exp\{tQ_{A(z)}L\} + \int_0^t ds \exp\{(t-s)L\}P_{A(z)}L \exp\{sQ_{A(z)}L\} \quad (9)$$

the second term at the right-hand side of [eqn \(8\)](#) can be written as

$$\partial_t \mathbf{a}(t, \mathbf{z}) = \exp\{tL\}P_{A(z)}L\mathbf{A} + \int_0^t ds \exp\{(t-s)L\}P_{A(z)}L\tilde{\mathbf{R}}(s, \cdot) + \tilde{\mathbf{R}}(t, \mathbf{z}) \quad (10)$$

where we defined

$$\begin{aligned} \tilde{\mathbf{R}}(t, \mathbf{z}) &= \exp\{tQ_{A(z)}L\}Q_{A(z)}L\mathbf{A} \\ &= Q_{A(z)} \exp\{tQ_{A(z)}L\}L\mathbf{A} \end{aligned} \quad (11)$$

and we used a dot instead of a \mathbf{z} as second argument for $\tilde{\mathbf{R}}$ in $P_{A(z)}L\tilde{\mathbf{R}}(s, \cdot)$ to stress that this term depends on \mathbf{z} only through $\mathbf{A}(\mathbf{z})$ (the same is true for $P_{A(z)}L\mathbf{A}$ but not for $\tilde{\mathbf{R}}(t, \mathbf{z})$ which is a general function of \mathbf{z}). The second term at the right-hand side of [eqn \(10\)](#) can be simplified by means of the following identity which, for clarity, we write component-wise using the indices $\mu, \nu = 1, \dots, M$ to denote the components of \mathbf{A} and \mathbf{a} and Einstein sum convention over repeated indices

$$\begin{aligned} P_\alpha L\tilde{R}_\mu(s, \cdot) &= \frac{1}{\Omega(\mathbf{a})} \int dz \rho^{\text{eq}}(z) \delta(\mathbf{A}(z) - \mathbf{a}) L \exp\{sQ_{A(z)}L\} Q_{A(z)} L A_\mu \\ &= -\frac{1}{\Omega(\mathbf{a})} \int dz \rho^{\text{eq}}(z) \left[\exp\{sQ_{A(z)}L\} Q_{A(z)} L A_\mu \right] L \delta(\mathbf{A}(z) - \mathbf{a}) \\ &= \frac{1}{\Omega(\mathbf{a})} \int dz \rho^{\text{eq}}(z) \left[\exp\{sQ_{A(z)}L\} Q_{A(z)} L A_\mu \right] [L A_\nu(z)] \frac{\partial}{\partial \alpha_\nu} \delta(\mathbf{A}(z) - \mathbf{a}) \\ &= \frac{1}{\Omega(\mathbf{a})} \frac{\partial}{\partial \alpha_\nu} \int dz \rho^{\text{eq}}(z) \delta(\mathbf{A}(z) - \mathbf{a}) [L A_\nu(z)] \left[\exp\{sQ_{A(z)}L\} Q_{A(z)} L A_\mu \right] [L A_\nu(z)] \\ &= \frac{1}{\Omega(\mathbf{a})} \frac{\partial}{\partial \alpha_\nu} \left(\Omega(\mathbf{a}) P_\alpha \left(\left[\exp\{sQ_{A(z)}L\} Q_{A(z)} L A_\mu \right] [L A_\nu] \right) \right) \\ &= M_{\mu\nu}(\mathbf{a}, s) \frac{\partial S(\mathbf{a})}{\partial \alpha_\nu} + k_B \frac{\partial M_{\mu\nu}(\mathbf{a}, s)}{\partial \alpha_\nu} \end{aligned} \quad (12)$$

Here and below the operators inside the brackets $[\cdot]$ only act on the terms at their right in these brackets and we have introduced the entropy

$$S(\mathbf{a}) = k_B \ln \Omega(\mathbf{a}) \quad (13)$$

as well as the memory matrix $M(\boldsymbol{\alpha}, t) = M^T(\boldsymbol{\alpha}, -t)$ whose components are given by the following conditional expectation

$$M_{\mu\nu}(\boldsymbol{\alpha}, t) = \frac{1}{k_B} P_{\alpha} \left([LA_{\nu}] [\exp\{tQ_A L\} Q_A LA_{\mu}] \right) = \frac{1}{k_B} P_{\alpha} \left(\bar{R}_{\nu}(t, \cdot) \bar{R}_{\mu}(0, \cdot) \right) \quad (14)$$

Inserting [eqn \(12\)](#) in [eqn \(10\)](#) and using the property that for any $f(\mathbf{A}(\mathbf{z}))$, we have $\exp\{Lt\}f(\mathbf{A}(\mathbf{z})) = f(\mathbf{a}(t, \mathbf{z}))$ and so

$$\begin{aligned} \exp\{tL\} P_{A(\mathbf{z})} LA(\mathbf{z}) &= P_{\mathbf{a}(t, \mathbf{z})} LA(\mathbf{z}), \exp\{(t-s)L\} M(A(\mathbf{z}), s) \frac{\partial S(A(\mathbf{z}))}{\partial \boldsymbol{\alpha}} \\ &= M(\mathbf{a}(t-s, \mathbf{z}), s) \frac{\partial S(\mathbf{a}(t-s, \mathbf{z}))}{\partial \boldsymbol{\alpha}}, \exp\{(t-s)L\} k_B \frac{\partial M(A(\mathbf{z}), s)}{\partial \boldsymbol{\alpha}} \\ &= k_B \frac{\partial M(\mathbf{a}(t-s, \mathbf{z}), s)}{\partial \boldsymbol{\alpha}} \end{aligned}$$

we arrive at the following equation for $\mathbf{a}(t, \mathbf{z})$

$$\begin{aligned} \partial_t \mathbf{a}(t, \mathbf{z}) &= \mathbf{v}(\mathbf{a}(t, \mathbf{z})) \\ &+ \int_0^t ds M(\mathbf{a}(t-s, \mathbf{z}), s) \frac{\partial S(\mathbf{a}(t-s, \mathbf{z}))}{\partial \boldsymbol{\alpha}} + k_B \int_0^t ds \frac{\partial M}{\partial \boldsymbol{\alpha}}(\mathbf{a}(t-s, \mathbf{z}), s) + \bar{\mathbf{R}}(t, \mathbf{z}) \end{aligned} \quad (15)$$

where $\mathbf{v}(\boldsymbol{\alpha})$ is the following conditional expectation

$$\mathbf{v}(\boldsymbol{\alpha}) = P_{\alpha} \mathbf{L} \mathbf{A} \quad (16)$$

[Eqn \(15\)](#) is a formally exact rewriting of [eqn \(5\)](#) and it may not be immediately clear what we have gained with it. Recall however that we are not interested in solving this equation for a specific initial condition $\mathbf{a}(0, \mathbf{z}) = \mathbf{A}(\mathbf{z})$ but rather for an ensemble of initial conditions \mathbf{z} satisfying $\mathbf{a}(0, \mathbf{z}) = \mathbf{A}(\mathbf{z}) = \boldsymbol{\alpha}(0)$ for some fixed $\boldsymbol{\alpha}(0)$ and with \mathbf{z} distributed according to the equilibrium density $\rho^{\text{eq}}(\mathbf{z})$ conditional on $\mathbf{A}(\mathbf{z}) = \boldsymbol{\alpha}(0)$. In this case, $\bar{\mathbf{R}}(t, \mathbf{z})$, which is the only term in [eqn \(15\)](#) which is not a function of $\mathbf{a}(s, \mathbf{z})$ for $0 \leq s \leq t$, can be interpreted as a noise term whose statistics must be consistent with [eqn \(14\)](#). With this in mind, we can introduce the shorthand notation $\mathbf{a}(t, \mathbf{z}) = \boldsymbol{\alpha}(t)$, and rewrite [eqn \(15\)](#) as an integro-differential equation with a random source term which is usually referred to as the generalized Langevin equation (GLE):

$$\begin{aligned} \frac{d\boldsymbol{\alpha}(t)}{dt} &= \mathbf{v}(\boldsymbol{\alpha}(t)) \\ &+ \int_0^t ds M(\boldsymbol{\alpha}(t-s), s) \frac{\partial S(\boldsymbol{\alpha}(t-s))}{\partial \boldsymbol{\alpha}} + k_B \int_0^t ds \frac{\partial M}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}(t-s), s) + \mathbf{R}(t) \end{aligned} \quad (17)$$

where $\mathbf{R}(t)$ is now viewed as a zero-mean random process whose statistical properties are specified by [eqn \(11\)](#) in which \mathbf{z} is random and distributed according to the equilibrium density $\rho^{\text{eq}}(\mathbf{z})$ conditional on $\mathbf{A}(\mathbf{z}) = \alpha(0)$. By solving [eqn \(17\)](#) with the initial condition $\alpha(0)$ in different realizations of $\mathbf{R}(t)$ we can then generate the exact statistics of $\mathbf{A}(\mathbf{Z}(t))$ for $t \geq 0$ along an ensemble of trajectories consistent with $\mathbf{A}(\mathbf{Z}(0)) = \alpha(0)$.

While formally exact within the statistical interpretation above, the GLE ([eqn \(17\)](#)) is unfortunately rather useless in practice. Indeed, while $\mathbf{v}(\alpha)$ and the gradient $\partial S/\partial \alpha$ are conditional expectations which can in principle be computed using constrained molecular dynamics, we cannot calculate $M(\alpha, t)$ and $\mathbf{R}(t)$ since they involve the projected dynamics associated with $Q_{\mathbf{A}(\mathbf{z})}L$ which we do not know how to generate. (Note also that the process $\mathbf{R}(t)$ is non-Gaussian in general, *i.e.* it is *not* specified completely by its correlation function in [eqn \(14\)](#).²⁰) On top of this, even if we knew how to compute $M(\alpha, t)$ and the full statistics of $\mathbf{R}(t)$, [eqn \(17\)](#) would remain very challenging to integrate numerically because of its non-Markovian character.

III. The standard Markovian approximation and its caveats

The usual way the GLE ([eqn \(17\)](#)) is made practical is *via* a set of approximations which collectively go under the name of “Markovian approximation.” This approximation is introduced as follows. Assuming that the time scale of variation of the relevant variables is much larger than the time scale of decay of the memory matrix $M(\alpha, t)$ defined in [eqn \(14\)](#), one approximates this matrix by

$$M(\alpha, t) \approx M_T(\alpha)\delta(t) \quad (18)$$

where the time-independent friction matrix $M_T(\alpha)$ is defined as

$$M_T(\alpha) = \int_0^T dt M(\alpha, t) = \int_0^T dt P_\alpha(\bar{\mathbf{R}}(t, \cdot) \otimes \bar{\mathbf{R}}(0, \cdot)) \quad (19)$$

Note that the integral is capped at a finite time T rather than extended to infinity; we will explain shortly why it is necessary to do so. Consistent with the approximation in [eqn \(18\)](#), one then assumes that the random term $\mathbf{R}(t)$ in [\(17\)](#) can be modelled as a white-noise, *i.e.* a Gaussian process with mean zero and whose correlation at $\alpha(t) = \alpha$ fixed is given

by

$$\langle \mathbf{R}_T(t) \otimes \mathbf{R}_T(s) \rangle = k_B M_T(\alpha) \delta(t - s) \quad (20)$$

Under these assumptions, the GLE (eqn (17)) becomes the stochastic differential equation (SDE)

$$\frac{d\mathbf{a}(t)}{dt} = \mathbf{v}(\mathbf{a}(t)) + M_T(\mathbf{a}(t)) \frac{\partial S}{\partial \mathbf{a}}(\mathbf{a}(t)) + k_B \frac{\partial M_T}{\partial \mathbf{a}}(\mathbf{a}(t)) + \mathbf{R}_T(t) \quad (21)$$

The Fokker-Planck equation which is mathematically equivalent to eqn (21) was derived by Zwanzig.² The only thing left open to make eqn (21) fully explicit is how to compute the friction matrix in eqn (19). This is done by assuming that the projected dynamics $\exp\{tQ_{\mathbf{A}(\mathbf{z})}L\}$ can be replaced by the real dynamics $\exp\{tL\}$ in eqn (11), *i.e.*

$$\tilde{\mathbf{R}}(t, \mathbf{z}) \approx \exp\{Lt\} Q_{\mathbf{A}(\mathbf{z})} L \mathbf{A} = L \mathbf{A}(\mathbf{Z}(t)) - \mathbf{v}(\alpha(t)) \quad (22)$$

where $\mathbf{v}(\alpha)$ is defined in eqn (16), $\mathbf{Z}(t)$ is the solution of the original Hamilton eqn (1) and we used again the shorthand notation $\alpha(t) = \mathbf{a}(t, \mathbf{z})$. The right-hand side of eqn (22) can in principle be computed using a combination of standard MD simulations (to compute $\mathbf{Z}(t)$) and constrained molecular simulation (to compute $\mathbf{v}(\alpha)$). Eqn (22) is valid for short times when the time integrals in eqn (15) can be neglected: indeed, using $\partial_t \mathbf{a}(t, \mathbf{z}) = L \mathbf{A}(\mathbf{Z}(t))$ in eqn (15) and solving this equation with the integrals set to zero for $\tilde{\mathbf{R}}(t, \mathbf{z})$ gives eqn (22). Unfortunately, eqn (22) is harder to justify at later times. In particular, this approximation is the reason why the integral in eqn (19) must be capped at a finite T : if one extends the limit of integration T in eqn (19) to infinity using the approximation (eqn (22)) for $\tilde{\mathbf{R}}(t, \mathbf{z})$, then the integral vanishes. This is the well-known plateau problem^{4,5} and the current practice is to select for the upper time of integration a time T which is large compared to the correlation time of the (unspecified) orthogonal dynamics, but small compared to the time scale of evolution of the macroscopic variables.^{3,22} This intermediate time scale is assumed to exist, at least in situations where there is a clear separation of time scales, but the specific value for T is not provided by the theory, and it is difficult to predict how the results depend on T .

In summary, both approximations eqn (18) and (22) are uncontrolled

and this clearly diminishes the confidence that one can have in [eqn \(21\)](#). In the next section, we introduce another procedure to derive an equation similar to [eqn \(21\)](#) but whose validity is easier to assess and which does not suffer from the plateau problem.

IV. Modified dynamics and Markovian limiting equation

In order to replace [eqn \(18\)](#) and [\(22\)](#) by more controlled approximations, consider the time integrals appearing in the GLE [\(eqn \(17\)\)](#) and perform the change of variables $s = \varepsilon^2 \tau$, where ε is a non-dimensional control parameter. This leads to

$$\frac{d\mathbf{a}(t)}{dt} = \mathbf{v}(\mathbf{a}(t)) + \varepsilon^2 \int_0^{t/\varepsilon^2} d\tau M(\mathbf{a}(t - \varepsilon^2 \tau), \varepsilon^2 \tau) \frac{\partial S}{\partial \mathbf{a}}(\mathbf{a}(t - \varepsilon^2 \tau)) + \varepsilon^2 k_B \int_0^{t/\varepsilon^2} d\tau \frac{\partial M}{\partial \mathbf{a}}(\mathbf{a}(t - \varepsilon^2 \tau), \varepsilon^2 \tau) + \mathbf{R}(t) \quad (23)$$

Now observe that if the following limit exists

$$\lim_{\varepsilon \rightarrow 0} \varepsilon^2 M(\mathbf{a}(t - \varepsilon^2 \tau), \varepsilon^2 \tau) \equiv m(\mathbf{a}(t), \tau) \quad (24)$$

then, in the limit as $\varepsilon \rightarrow 0$, [eqn \(23\)](#) reduces to the SDE

$$\frac{d\mathbf{a}(t)}{dt} = \mathbf{v}(\mathbf{a}(t)) + \bar{M}(\mathbf{a}(t)) \frac{\partial S}{\partial \mathbf{a}}(\mathbf{a}(t)) + k_B \frac{\partial \bar{M}}{\partial \mathbf{a}}(\mathbf{a}(t)) + \bar{\mathbf{R}}(t) \quad (25)$$

Here the friction matrix $\bar{M}(\mathbf{a})$ has the Green-Kubo form

$$\bar{M}(\mathbf{a}) = \int_0^{\infty} m(\mathbf{a}, \tau) d\tau \quad (26)$$

and (as discussed below) the random term $\bar{\mathbf{R}}(t)$ is an Itô white-noise, *i.e.* a Gaussian process with mean zero and whose correlation at $\mathbf{a}(t) = \mathbf{a}$ is given by

$$\langle \mathbf{R}(t) \mathbf{R}(s) \rangle = k_B \bar{M}(\mathbf{a}) \delta(t - s) \quad (27)$$

In view of the above, it is of great value to find out under what conditions the limit in [eqn \(24\)](#) does indeed exist. By using the definition in [eqn \(14\)](#) we may write

$$\varepsilon^2 M(\mathbf{a}(t - \varepsilon^2 \tau, \mathbf{z}), \varepsilon^2 \tau) = \frac{\varepsilon^2}{k_B} P_{\mathbf{a}(t - \varepsilon^2 \tau, \mathbf{z})} \left([\exp\{\varepsilon^2 \tau Q_A L\} Q_A L \mathbf{A}] \otimes [Q_A L \mathbf{A}] \right) \quad (28)$$

From this expression, it can be checked by direct calculation that one way to ensure that the limit [eqn \(24\)](#) exists is by assuming that the Liouville operator has the following form

$$L = L_0 + \frac{1}{\varepsilon} L_1 + \frac{1}{\varepsilon^2} L_2 \quad (29)$$

with the operators L_1, L_2 satisfying

$$\begin{aligned} P_{A(z)} L_2 &= 0 \\ P_{A(z)} L_1 P_{A(z)} &= 0 \end{aligned} \quad (30)$$

Indeed, in this case, [eqn \(28\)](#) simply becomes

$$\varepsilon^2 M(\mathbf{a}(t - \varepsilon^2 \tau, \mathbf{z}), \varepsilon^2 \tau) = \frac{1}{k_B} P_{\mathbf{a}(t)} \left([\exp\{\tau L_2\} L_1 \mathbf{A}] \otimes [L_1 \mathbf{A}] \right) + \mathcal{O}(\varepsilon) \quad (31)$$

and the limiting dynamic equation obtained from [eqn \(17\)](#) when $\varepsilon \rightarrow 0$ precisely is [eqn \(25\)](#) with the Green-Kubo friction matrix $\bar{M}(\mathbf{a})$ now given explicitly by

$$\bar{M}(\mathbf{a}) = \frac{1}{k_B} \int_0^\infty d\tau P_{\mathbf{a}} \left([\exp\{\tau L_2\} L_1 \mathbf{A}] \otimes [L_1 \mathbf{A}] \right) \quad (32)$$

and the drift term is given by

$$\mathbf{v}(\mathbf{a}) = P_{\mathbf{a}} L_0 \mathbf{A}. \quad (33)$$

While the derivation above is heuristic, it can be made rigorous using the techniques discussed in [ref. 23,24](#) (see also the Appendix in [ref. 25](#)), *i.e.* under a suitable ergodicity assumption of the dynamics associated with the operator L_2 , it can be proved that [eqn \(25\)](#) captures exactly (though in a statistical sense) the dynamics of $\mathbf{A}(\mathbf{Z}(t))$ in the limit as $\varepsilon \rightarrow 0$. This derivation also explains why the noise term $\bar{\mathbf{R}}(t)$ in [eqn \(25\)](#) is indeed a white-noise to be interpreted in Itô sense. Finally, it shows that the matrix $\bar{M}(\mathbf{a})$ does not, in general, have the plateau problem: indeed the integral in [eqn \(32\)](#) converges to a nontrivial value provided only that the dynamics associated with L_2 is mixing sufficiently fast beside being ergodic.

The next important question is in which sense is [eqn \(25\)](#) useful. Indeed for a general selection of the relevant variables $\mathbf{A}(\mathbf{z})$, the Liouville operator will not have the form given in [eqn \(29\)](#) and so it is not *a priori* clear how to derive [eqn \(25\)](#). There is a way to do so, however, based on the observation that it is always possible to decompose the Liouville operator as $L = L_0 + L_1 + L_2$ by defining

$$\begin{aligned} L_0 &= P_{A(\mathbf{z})}(L - \mathcal{R}) \\ L_1 &= Q_{A(\mathbf{z})}(L - \mathcal{R}) \\ L_2 &= \mathcal{R} \end{aligned} \quad (34)$$

and letting $P_{A(\mathbf{z})}$ be the expectation with respect to the equilibrium distribution associated with the operator \mathcal{R} . This operator, to be specified more fully later, should be similar to L , except that it leaves both the Hamiltonian *and* the relevant variables invariant, that is

$$\begin{aligned} \mathcal{R}f(H(\mathbf{z})) &= 0 \\ \mathcal{R}g(A(\mathbf{z})) &= 0 \end{aligned} \quad (35)$$

for any functions f and g . By construction, the operators L_0, L_1, L_2 in [eqn \(34\)](#) satisfy the properties in [eqn \(30\)](#). This suggests the introduction of a modified dynamic operator L^ε as in [eqn \(29\)](#)

$$L^\varepsilon \equiv L_0 + \frac{1}{\varepsilon}L_1 + \frac{1}{\varepsilon^2}L_2 \quad (36)$$

The dynamics associated with L^ε coincides with the real dynamics when $\varepsilon = 1$ and produces a dynamics of the relevant variables which is governed by the SDE [\(eqn \(25\)\)](#) when $\varepsilon \rightarrow 0$. By inserting the operators [eqn \(34\)](#) into [eqn \(32\)](#), [\(33\)](#) we obtain

$$\begin{aligned} v(\alpha) &= P_\alpha(LA) \\ \bar{M}(\alpha) &= \frac{1}{k_B} \int_0^\infty d\tau P_\alpha([\exp\{\tau\mathcal{R}\}LA] \otimes [LA]) \end{aligned} \quad (37)$$

The advantage of the above procedure, which differs from the usual prescription in that the projected dynamics $\exp\{tQ_{A(\mathbf{z})}L\}$ is approximated by $\exp\{tL_2\} \equiv \exp\{t\mathcal{R}\}$ rather than $\exp\{tL\}$, is that we have now an explicit and practical method to compute the constrained averages once we specify the operator \mathcal{R} . A natural candidate for the dynamics associated with \mathcal{R} is one which is obtained from the original Hamilton's [eqn \(1\)](#) by adding the constraint that $\mathbf{A}(\mathbf{Z}(t)) = \alpha$. How to do so in

practice in the special case when $\mathbf{A}(\mathbf{z})$ is a linear function of the positions and the momenta is straightforward and an example will be given in Sec. V. The general case when $\mathbf{A}(\mathbf{z})$ is a nonlinear function of \mathbf{z} is more complicated to handle and will be left for future work.

If we then assume that this constrained dynamics is ergodic and denote compactly by $\mathbf{Z}_{\mathcal{R}}(t) = \exp\{t\mathcal{R}\}\mathbf{z}$ the constrained trajectory with initial condition $\mathbf{Z}_{\mathcal{R}}(0) = \mathbf{z}$ with \mathbf{z} such that $\mathbf{A}(\mathbf{z}) = \alpha$ and $H(\mathbf{z}) = E$, then the conditional expectations in [eqn \(37\)](#) can be expressed as time averages

$$P_{\alpha}LA = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt LA(\mathbf{Z}_{\mathcal{R}}(t)) \quad (38)$$

and

$$\bar{M}(\alpha) = \lim_{T \rightarrow \infty} \frac{1}{k_B} \int_0^{T'} dt' \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt [LA(\mathbf{Z}_{\mathcal{R}}(t+t'))] \otimes [LA(\mathbf{Z}_{\mathcal{R}}(t))] \quad (39)$$

In practice the limits in these expressions have to be approximated but it is important to stress that this can be done to arbitrary precision by letting T and T' grow bigger, *i.e.* [eqn \(38\)](#) and [\(39\)](#) do not suffer from the plateau problem.

In summary, if we replace L by L^{ε} and let $\varepsilon \rightarrow 0$, then the dynamics of relevant variables is governed exactly by the limiting [eqn \(25\)](#) with the coefficients in this equation given explicitly by [eqn \(38\)](#) and [\(39\)](#). In doing so, the price we pay is a *modelling error*, that is, we model the original system by one whose dynamics is associated with L^{ε} in the limit as $\varepsilon \rightarrow 0$ rather than with L . In effect this amounts to accelerating the non-relevant degrees of freedom. The validity of this modeling approximation requires that the real dynamics L and the projected dynamics \mathcal{R} be similar, *i.e.* that the effect of accelerating the dynamics orthogonal to that of the variables $\mathbf{A}(\mathbf{z})$ only has a small effect in the evolution of these variables. In other words, it requires that the relevant variables $\mathbf{A}(\mathbf{z})$ be comparatively slow.

V. Coarsening big complex molecules

In this section, we show how the above methodology can be applied to the coarse-graining of a collection of big molecules by using center of mass (CoM) variables as relevant variables. We will consider later as a concrete example that these molecules are star polymers but the

framework is to a large extent independent of what kind of molecule we have, provided that they are made of many atoms and that they are isotropic. For non-isotropic molecules, further orientational information may be required in addition to the CoM variables.

We assume that the fluid system is composed by M molecules and each molecule is made of N_m atoms whose positions and momenta are \mathbf{r}_{i_μ} , \mathbf{p}_{i_μ} where the index i_μ runs from $1, \dots, N_m$, while the index μ runs from $1, \dots, M$, *i.e.* Greek indices label molecules. The Hamiltonian of the system is

$$H(z) = \sum_{\mu=1}^M \sum_{i_\mu=1}^{N_m} \frac{\mathbf{p}_{i_\mu}^2}{2m_{i_\mu}} + \phi \quad (40)$$

where m_{i_μ} is the mass of the atom i_μ and ϕ is the potential energy. The Liouville operator is given by

$$L = \sum_{\mu} \sum_{i_\mu} \frac{\mathbf{p}_{i_\mu}}{m_{i_\mu}} \frac{\partial}{\partial \mathbf{r}_{i_\mu}} + \sum_{\mu} \sum_{i_\mu} \mathbf{F}_{i_\mu} \frac{\partial}{\partial \mathbf{p}_{i_\mu}} \quad (41)$$

where $\mathbf{F}_{i_\mu} = -\partial\phi/\partial\mathbf{r}_{i_\mu}$ is the force on the atom i_μ .

At a coarse-grained level, we will represent the complex molecule by just the position \mathbf{R}_μ and momentum \mathbf{P}_μ of its center of mass. These relevant variables are the following functions of the atomic variables

$$\begin{aligned} \mathbf{R}_\mu(z) &= \frac{1}{M_\mu} \sum_{i_\mu=1}^{N_m} m_{i_\mu} \mathbf{r}_{i_\mu} \\ \mathbf{P}_\mu(z) &= \sum_{i_\mu=1}^{N_m} \mathbf{p}_{i_\mu} \end{aligned} \quad (42)$$

where $M_\mu = \sum_{i_\mu=1}^{N_m} m_{i_\mu}$ is the total mass of the molecule μ . Note that we have $L\mathbf{R}_\mu = \mathbf{P}_\mu/M_\mu$, this is, the Liouville operator applied to a relevant variable is (proportional to) a relevant variable itself. As a consequence, the conditional average of \mathbf{P}_μ conditioned to \mathbf{P}_μ and \mathbf{R}_μ is just \mathbf{P}_μ itself. This means that there are no dissipative terms (nor noise terms) in the evolution of the positions, and [eqn \(25\)](#) reduces to

$$\begin{aligned}\frac{d\mathbf{R}_\mu}{dt} &= \frac{\mathbf{P}_\mu}{M_\mu} \\ \frac{d\mathbf{P}_\mu}{dt} &= \langle \mathbf{F}_\mu \rangle + T\gamma_{\mu\nu} \frac{\partial S}{\partial \mathbf{P}_\nu} + k_B T \frac{\partial \gamma_{\mu\nu}}{\partial \mathbf{P}_\nu} + \tilde{\mathbf{F}}_\mu\end{aligned}\quad (43)$$

where we recall that the sum over repeated indices is implied. Here we use the shorthand notations $\mathbf{R} = (\mathbf{R}_1, \dots, \mathbf{R}_M)$, $\mathbf{P} = (\mathbf{P}_1, \dots, \mathbf{P}_M)$ and we denote by $\langle \cdot \rangle$ the conditional expectation $P_{(\mathbf{R}, \mathbf{P})}$ at (\mathbf{R}, \mathbf{P}) fixed. The friction tensor is defined by

$$\gamma_{\mu\nu}(\mathbf{R}, \mathbf{P}) = \frac{1}{k_B T} \int_0^\infty dt \langle \delta \mathbf{F}_\mu \exp\{t\mathcal{L}\} \delta \mathbf{F}_\nu \rangle \quad (44)$$

where $\delta \mathbf{F}_\mu = \mathbf{F}_\mu - \langle \mathbf{F}_\mu \rangle$ and \mathbf{F}_μ is the total force acting on the molecule μ :

$$\mathbf{F}_\mu = \sum_\nu \mathbf{F}_{\mu\nu} \equiv \sum_\nu \sum_{i_\nu, j_\nu} \mathbf{F}_{i_\nu j_\nu} \quad (45)$$

Here $\mathbf{F}_{i_\nu j_\nu}$ is the force that atom j_ν exerts on atom i_ν , and $\mathbf{F}_{\mu\nu}$ is the total force that molecule ν exerts on molecule μ . The entropy has the form

$$S(\mathbf{R}, \mathbf{P}) = k_B \ln \int dz \frac{1}{Z} \exp\{-\beta H(z)\} \prod_\mu \delta(\mathbf{R}_\mu(z) - \mathbf{R}_\mu) \delta(\mathbf{P}_\mu(z) - \mathbf{P}_\mu) \quad (46)$$

The momentum integrals involved in the entropy function can be performed explicitly with the result

$$S(\mathbf{R}, \mathbf{P}) = S_0 - \frac{1}{T} V(\mathbf{R}) - \frac{1}{T} \sum_\mu \frac{|\mathbf{P}_\mu|^2}{2M_\mu} \quad (47)$$

where S_0 is a constant and $V(\mathbf{R})$ is the so called effective potential defined by

$$V(\mathbf{R}) \equiv -k_B T \ln \int dz \frac{1}{Q} \exp\{\beta \phi(z)\} \prod_\mu \delta(\mathbf{R}_\mu(z) - \mathbf{R}_\mu) \quad (48)$$

This effective potential satisfies

$$-\frac{\partial V}{\partial \mathbf{R}_\mu} = \langle \mathbf{F}_\mu \rangle \quad (49)$$

which justify its name. By using [eqn \(47\)](#) in [eqn \(43\)](#), this equation reduces to

$$\begin{aligned}\frac{d\mathbf{R}_\mu}{dt} &= \frac{\mathbf{P}_\mu}{M_\mu} \\ \frac{d\mathbf{P}_\mu}{dt} &= \langle \mathbf{F}_\mu \rangle - \gamma_{\mu\nu} \frac{\mathbf{P}_\nu}{M_\nu} + k_B T \frac{\partial \gamma_{\mu\nu}}{\partial \mathbf{P}_\nu} + \tilde{\mathbf{F}}_\mu\end{aligned}\quad (50)$$

Note that we have $\sum_\nu \mathbf{F}_\nu = 0$, because of Newton's Third Law. From [eqn \(44\)](#) this implies that the friction coefficient defined in [eqn \(44\)](#) satisfies $\sum_\mu \gamma_{\mu\nu} = 0$ and, therefore,

$$\gamma_{\mu\mu} = -\sum_{\nu \neq \mu} \gamma_{\mu\nu} \quad (51)$$

While we expect that $\gamma_{\mu\mu}$ will be a positive quantity (because it is the time integral of an autocorrelation function), this equation shows that $\gamma_{\mu\nu}$ may be negative.

Using [eqn \(45\)](#) and [\(51\)](#), [eqn \(50\)](#) can be written as

$$\begin{aligned}\frac{d\mathbf{R}_\mu}{dt} &= \frac{\mathbf{P}_\mu}{M_\mu} \\ \frac{d\mathbf{P}_\mu}{dt} &= \langle \mathbf{F}_\mu \rangle + \sum_\nu \gamma_{\mu\nu} \left(\frac{\mathbf{P}_\mu}{M_\mu} - \frac{\mathbf{P}_\nu}{M_\nu} \right) + k_B T \sum_\nu \frac{\partial \gamma_{\mu\nu}}{\partial \mathbf{P}_\nu} + \tilde{\mathbf{F}}_\mu\end{aligned}\quad (52)$$

where we wrote the sums explicitly to avoid confusions (not all repeated indices are summed in [eqn \(52\)](#)). The stochastic force $\tilde{\mathbf{F}}_\mu$ can be expressed in terms of a linear combination of Wiener processes as, for example, $\mathbf{F}_\mu = \sum_\alpha B_{\mu\alpha} d\mathbf{W}_\alpha(t)/dt$ with

$$\sum_\alpha B_{\mu\alpha} B_{\nu\alpha} = 2k_B T \gamma_{\mu\nu} \quad (53)$$

This is the Fluctuation–Dissipation theorem for this problem. Note that [eqn \(52\)](#) has the structure of dissipative particle dynamics (DPD).^{18,19} These equations have also been obtained recently in [ref. 26](#) in a re-derivation of Mori–Zwanzig theory. However, an important difference with the usual DPD equations is that the effective force $\langle \mathbf{F}_{\mu\nu} \rangle$ and the friction tensor $\gamma_{\mu\nu}(\mathbf{R}, \mathbf{P})$ depend, in principle, on the CoM variables of *all* the molecules in the system and not only on $\mathbf{R}_\mu - \mathbf{R}_\nu$ as in DPD.

VI. Simulation results for a melt of star polymer

As a concrete application, we now consider a system of star polymers that form a polymer melt. A single typical molecule in the melt is shown in [Fig. 1](#).

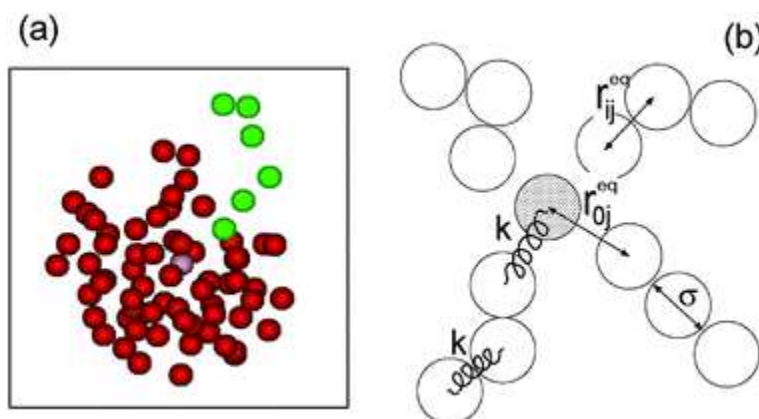


Fig. 1 (a) One of the star polymers in the polymer melt in a typical configuration. Seven monomers are coloured lighter indicating one arm and the central monomer. It has $f = 12$ arms of $m = 6$ monomers each. (b) A sketch of the star polymer model: all monomers interact with the purely repulsive Lennard-Jones potential (truncated at $r_c = 2^{1/6}\sigma$ and shifted to zero potential energy, $\phi(r_c) = 0$) with units such that $\varepsilon = 1$, $m = 1$ and $\sigma = 2.415$. Neighbour monomers are attached by springs of stiffness $k = 20\varepsilon/\sigma^2$ and move around the equilibrium distance r^{eq}_{ij} , with $r^{eq}_{ij} = 1.147\sigma$ if i and j are non-center monomers and $r^{eq}_{0j} = 1.615\sigma$, if $i (= 0)$ is the center monomer.

The star polymers have $f = 12$ arms and $m = 6$ monomers per arm. Each arm is connected to a central monomer so that the total number of monomers per polymer is $N_m = f \times m + 1$. The melt contained a collection of M polymer molecules, with typically $M = 160$. Excluded volume interactions between monomers were taken into account by the purely repulsive (truncated and shifted) Lennard-Jones potential also known as the WCA potential. Bonded interactions were modelled by

linear springs, *i.e.*, $\mathbf{F}_{ij}(\mathbf{r}_{ij}) = -k\delta r \mathbf{e}_{ij}$ where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, the unit vector $\mathbf{e}_{ij} = \mathbf{r}_{ij}/|\mathbf{r}_{ij}|$ is the unit vector along \mathbf{r}_{ij} , and $\delta r \equiv r_{ij} - r^{\text{eq}}_{ij}$, where r^{eq}_{ij} is the equilibrium distance and k is the spring constant. The values used for these parameters are reported in the caption of the polymer model sketch in [Fig. 1](#). The polymer volume fraction is $\Phi = N(\pi/6)\sigma^3/L^3$, where L is the length of the (cubic) simulation box and $N = M \times N_m$ is the total number of monomers in the system. The results presented here correspond to a semidilute state $\Phi = 0.1962$ and the simulations were done in periodic cubic boxes of size $L = 76\sigma$ yielding a monomer number density of $n = 0.314\sigma^{-3}$. Throughout the paper, results are given in Lennard-Jones units: energy, mass, length and time units being $\varepsilon = 1$, $m = 1$, $\sigma = 2.415$, $\tau = \sigma(m/\varepsilon)^{1/2}$, respectively. All simulations were carried out in the microcanonical ensemble *NVE* (care was taken to set the same total energy in every simulation); and the average temperature was $k_B T = 3.965\varepsilon$. An equilibrated configuration was initially taken from a Monte Carlo bond fluctuation model simulation.²⁷ In these configurations the monomer positions are set in a lattice. These initial configurations were equilibrated using Langevin thermostatted molecular dynamics at the desired temperature. In order to produce a set of independent initial configurations we ran a long enough MD simulation and saved one configuration per each diffusion time, typically about $(R_g^2/D)\tau$, where $R_g = 7.64\sigma$ is the gyration radius and $D \simeq 0.08\sigma^2/\tau$ the diffusion coefficient. In doing so we collected a set of 35 configurations, each one having an independent set of positions and momenta (\mathbf{R}, \mathbf{P}) of the CoM of the molecules. Starting from each of these 35 configurations we ran a short simulation (1000τ) to collect the required CoM molecular dynamics raw data. These set of short runs were carried out using the constrained dynamics discussed in Sec. IV and specified below.

First, we estimated whether we have a separation of time scales by measuring the velocity autocorrelation function of the CoM and comparing the result with the force autocorrelation function on the molecules. The former gives the time scale of the CoM velocity, which is a relevant variable. The latter provides an estimate of the typical time scale at which the memory function in the definition of the friction coefficient decays. Both autocorrelation functions are plotted in [Fig. 2](#). There is a large difference between correlation times, which leads us to believe that the CoM are indeed slow variables and that the modification of the dynamics proposed in Sec. IV should have a small impact on their dynamics. The reason is that the molecules are very massive (they contain 73 atoms). While the time scale of the velocity scales with the mass, the time scale of the force does not, because it is given by an

atomic collision time scale. Note, however, that the force in [Fig. 2](#), being the time derivative of the momentum (*i.e.* of the mass times the velocity), has also a negative part that decays slowly, in the same time scale as the velocity. This negative part of the force could invalidate the procedure proposed in Sec. IV. However, this part is responsible for the “plateau problem” and disappears with a correct treatment with the constrained dynamics. We will discuss the plateau problem by the end of this section.

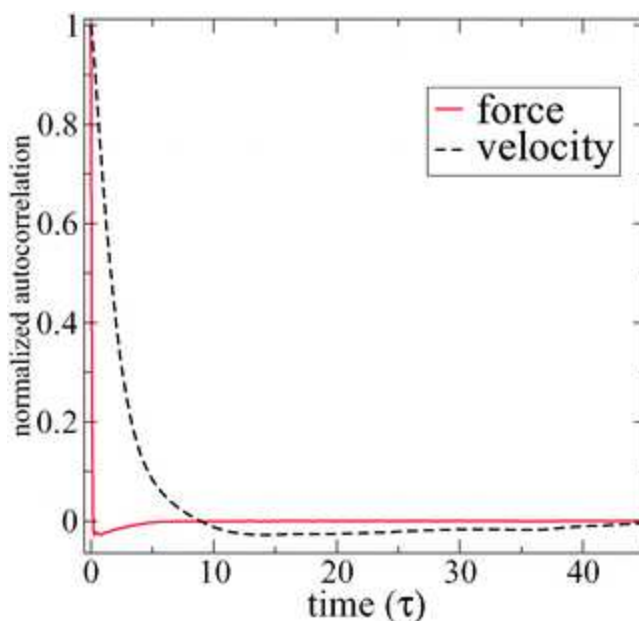


Fig. 2 The velocity autocorrelation function of the CoM and the autocorrelation function of the force on a molecule. These functions have correlation times well-separated and a Markovian behaviour is expected.

The constrained dynamics \mathcal{R} that we use in order to compute the mean force $\langle \mathbf{F}_{\mu v} \rangle$ and the friction coefficient $\gamma_{\mu v}(\mathbf{R}, \mathbf{P})$ is the following

$$\begin{aligned} \frac{d\mathbf{r}_{i_\mu}}{dt} &= \frac{\mathbf{p}_{i_\mu}}{m_{i_\mu}} - \frac{\mathbf{P}_\mu}{M_\mu}, \\ \frac{d\mathbf{p}_{i_\mu}}{dt} &= \mathbf{F}_{i_\mu} - \frac{m_{i_\mu}}{M_\mu} \mathbf{F}_\mu \end{aligned} \quad (54)$$

where \mathbf{P}_μ is the CoM momentum of molecule μ , \mathbf{F}_{i_μ} is the total force on monomer i_μ and \mathbf{F}_μ is the total force on molecule μ . Because the

constraints to maintain the positions and momenta of the CoM are linear functions, the corresponding Lagrange multipliers can be easily identified and this leads to [eqn \(54\)](#). These equations conserve the total energy, they leave the positions and momentum of the CoM invariant, and they also conserve the volume in phase space. For these reasons, this dynamic samples the constrained ensemble that appears in the definition of $\langle \mathbf{F}_{\mu\nu} \rangle$ and $\gamma_{\mu\nu}(\mathbf{R}, \mathbf{P})$, and these averages may be computed as time averages.

Consistent with [eqn \(38\)](#), by running [eqn \(54\)](#), one can compute $\langle \mathbf{F}_{\mu\nu} \rangle$ as the time average of the force $\mathbf{F}_{\mu\nu}$ that molecule ν exerts on molecule μ . In principle $\langle \mathbf{F}_{\mu\nu} \rangle$ depends on all the CoM positions \mathbf{R} . If it happens, as we expect, that the force that molecule ν exerts on molecule μ depends only on the CoM positions \mathbf{R}_μ and \mathbf{R}_ν of these two molecules and does not depend much on where the rest of molecules are located, then a pair-wise approximation should be valid. By translational and rotational symmetry we expect that the average force will be of the form

$$\langle \mathbf{F}_{\mu\nu} \rangle \approx F(R_{\mu\nu}) \mathbf{e}_{\mu\nu} \quad (55)$$

where $F(R_{\mu\nu}) = \langle \mathbf{F}_{\mu\nu} \cdot \mathbf{e}_{\mu\nu} \rangle$, $\mathbf{e}_{\mu\nu} = (\mathbf{R}_\mu - \mathbf{R}_\nu) / R_{\mu\nu}$ and $R_{\mu\nu} = |\mathbf{R}_\mu - \mathbf{R}_\nu|$. Consistent with this assumption, we computed the modulus of the average force $F(R_{\mu\nu})$ by averaging the result of $\langle \mathbf{F}_{\mu\nu} \cdot \mathbf{e}_{\mu\nu} \rangle$ over all those pairs μ, ν that are at a certain distance $R_{\mu\nu}$. The result is plotted in [Fig. 3](#). Note that it is highly improbable to find a pair at very short distances. In fact for $R_{\mu\nu} < 1.1R_g$ (the gyration radius being $R_g = 7.64\sigma$) there is no data available.

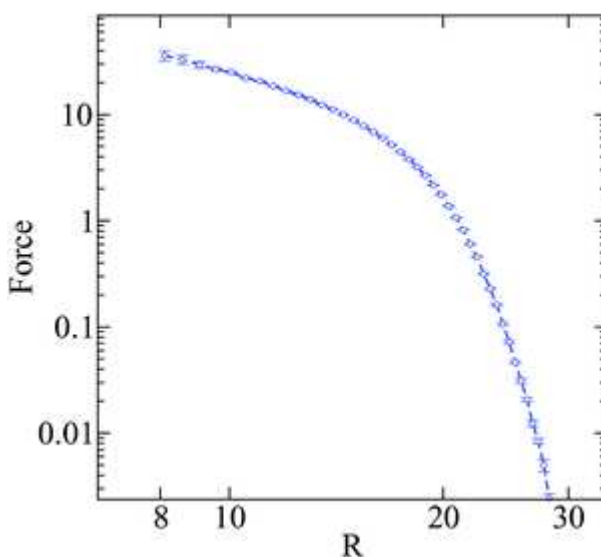


Fig. 3 The conservative force used by the present pair-wise approximation $\langle \mathbf{F}_{\mu\nu} \cdot \mathbf{e}_{\mu\nu} \rangle$ versus the distance $R_{\mu\nu}$ between center of masses of two interacting molecules. Error bars correspond to the standard error of the means of the whole set of pairs.

Next we checked that the mean transversal force, $\langle \mathbf{F}_{\mu\nu} \cdot \mathbf{e}_{\mu\nu}^\perp \rangle$ (with $\mathbf{e}_{\mu\nu}^\perp \cdot \mathbf{e}_{\mu\nu} = 0$), averaged over pairs, vanishes within statistical error. We also verified that the average force $\langle \mathbf{F}_{\mu\nu} \cdot \mathbf{e}_{\mu\nu} \rangle$ for a pair at a distance $R_{\mu\nu}$ is the same, within our statistical accuracy, for any pair of molecules at the same distance. To check this, we first measured the standard error of the mean force $\langle \mathbf{F} \cdot \mathbf{e}_{\mu\nu} \rangle$ for a given pair μ, ν that is at a distance $R_{\mu\nu}$, and averaged this error over all the pairs at that distance. If all pairs behave similarly in statistical terms, the deviation *between* pairs estimations of the mean force $\langle \mathbf{F}_{\mu\nu} \cdot \mathbf{e}_{\mu\nu} \rangle$ of pairs at a distance $R_{\mu\nu}$ should be within the single-pair error bar. We observed that this is indeed the case for all values of R , although the standard deviation *between* pairs was found to be slightly larger than the single-pair standard error. A previous computational study has found that the triplet part of the three-star force is only 11% of the pair-wise part even for a close approach of three star polymers.²⁸ A detailed *significance test* assessing, in probabilistic terms, the validity of the pair-wise hypothesis will be left for future work.

Let us turn now to the friction coefficients $\gamma_{\mu\nu}(\mathbf{R}, \mathbf{P})$. Again, one has to deal with the problem of their many arguments. Our main hypothesis is that the correlation between the forces on molecule μ and ν will depend on the positions of these two molecules but will not depend much on the positions and momenta of the rest of the molecules. We thus introduce the following functional ansatz

$$\gamma_{\mu\nu}(\mathbf{R}, \mathbf{P}) \approx -\gamma_\perp(R_{\mu\nu})(\mathbf{1} - \mathbf{e}_{\mu\nu} \mathbf{e}_{\mu\nu}^T) - \gamma_{\parallel}(R_{\mu\nu}) \mathbf{e}_{\mu\nu} \mathbf{e}_{\mu\nu}^T. \quad (56)$$

The right-hand side of this equation only depends on \mathbf{R}_μ and \mathbf{R}_ν and it is a general form for a tensor that is invariant by rotations along the axis joining the particles μ, ν . Compatibility of [eqn \(56\)](#) with [eqn \(44\)](#) then requires that

$$\begin{aligned}\gamma_{\parallel}(R_{\mu\nu}) &= -\frac{1}{k_B T} \int_0^{\infty} dt \langle (\delta F_{\mu}(t) \cdot \mathbf{e}_{\mu\nu})(\delta F_{\nu}(0) \cdot \mathbf{e}_{\mu\nu}) \rangle \\ \gamma_{\perp}(R_{\mu\nu}) &= -\frac{1}{k_B T} \int_0^{\infty} dt \langle (\delta F_{\mu}(t) \cdot \mathbf{e}_{\mu\nu}^{\perp})(\delta F_{\nu}(0) \cdot \mathbf{e}_{\mu\nu}^{\perp}) \rangle\end{aligned}\quad (57)$$

Under the assumption that the right-hand side of [eqn \(57\)](#) is the same for all the pairs that are at the same distance $R_{\mu\nu}$ as indicated by the lhs, we may average over all the pairs $\mu\nu$ that happen to be at the distance $R_{\mu\nu}$, this is

$$\gamma_{\parallel}(R_{\mu\nu}) = -\frac{1}{N_{\mu\nu}} \sum_{\mu\nu} \frac{1}{k_B T} \int_0^{\infty} dt \langle (\delta F_{\mu}(t) \cdot \mathbf{e}_{\mu\nu})(\delta F_{\nu}(0) \cdot \mathbf{e}_{\mu\nu}) \rangle \quad (58)$$

where $\sum_{\mu\nu}$ is a sum over all those pairs that are at a given distance $R_{\mu\nu}$ and $N_{\mu\nu}$ is the number of pairs at that distance. A similar procedure has been used to extract $\gamma_{\perp}(R_{\mu\nu})$. Both $\gamma_{\parallel}(R_{\mu\nu})$ and $\gamma_{\perp}(R_{\mu\nu})$ are plotted in [Fig. 4](#). Note that the transversal friction γ_{\perp} becomes slightly negative at $R_{\mu\nu} \simeq 2R_g = 15.28\sigma$, before tending to a vanishing value around $R_{\mu\nu} \simeq 25\sigma$. Most probably, this is a consequence of a dynamic aspect of depletion forces which tend to join back two neighbouring molecules as soon as they move further away the mean molecular separation due to caging effects. Note that the fact that γ_{\perp} may have a small negative part does not compromise that the full friction matrix $\gamma_{\mu\nu}$, which is a $3M \times 3M$ matrix, is positive definite (a positive definite matrix may have indeed some of its elements taking negative values).

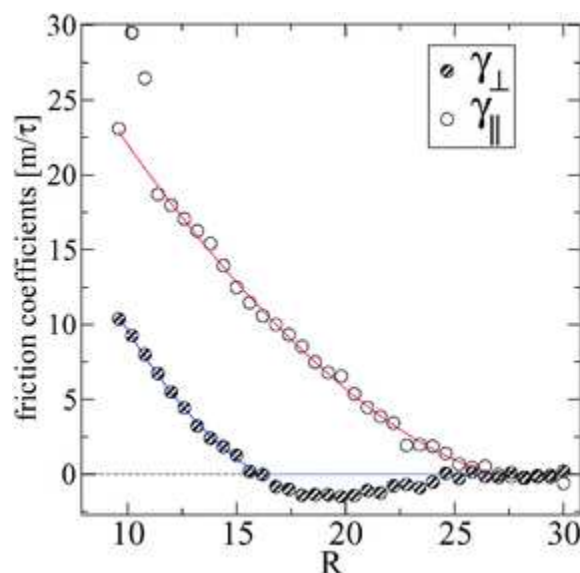


Fig. 4 The friction coefficients γ_{\perp} and γ_{\parallel} in [eqn \(44\)](#) as obtained from averaging over 35 MD runs over $T_{\text{run}} = 1000\tau$ each. Solid lines corresponds to the following fits: $\gamma_{\perp} = 44.67 - 4.68 R + 0.12 R^2$ for $R < 16.05$ and otherwise $\gamma_{\perp} = 0$ while, $\gamma_{\parallel} = 49.38 - 3.61 R + 0.11 R^2 - 3 \times 10^{-3} R^3 + 5 \times 10^{-5} R^4$ for $R < 26.84$ and zero otherwise.

Some insight on the validity of this pair-wise assumption is gained from the evaluation of the standard deviation of the force correlation appearing in the integrand of [eqn \(57\)](#), at each lagging time and CoM distance considered. Again, we compared the standard deviation of the mean *between* pairs with the average standard error obtained from one-pair estimations. Our hypothesis requires these two quantities to be similar, otherwise the mean behaviour of different pairs would be different in a significant (measurable) way. Preliminary results indicate that the pair-wise assumption works reasonably well except for short distances and times, $R < 2R_g$ and $t < 0.15\tau$. Note that intermolecular forces decorrelate only after $t > 0.1\tau$. This suggests a possible violation of the pair-wise approximation, mainly within the region of the space-time diagram where the strongest collision events take place. In particular, the star polymers considered here ($f = 12$, $m = 6$) can interpenetrate each other (*i.e.* $R_{\mu\nu} < 2R_g$) and under the present thermodynamic state $\Phi = 0.2$, may reach relatively far into each core (up to $R_{\mu\nu} \sim 1.1R_g$). This issue shall be studied in detail in a future work, which shall include proper significance tests for the pair-wise hypothesis.

Finally, let us discuss the plateau problem. In [Fig. 5](#) we compare the time integral of the autocorrelation of the force computed with the constrained dynamics and computed with the usual Hamiltonian unconstrained dynamics. We observe that the constrained dynamics produces a correlation function with a time integral that has a well-defined plateau value, while the unconstrained dynamics does not. The constrained and unconstrained dynamics produce identical results for short times. However, the justification of a well-defined value for the friction matrix, with a time integral independent of the upper limit of integration can only be achieved with the constrained simulation.

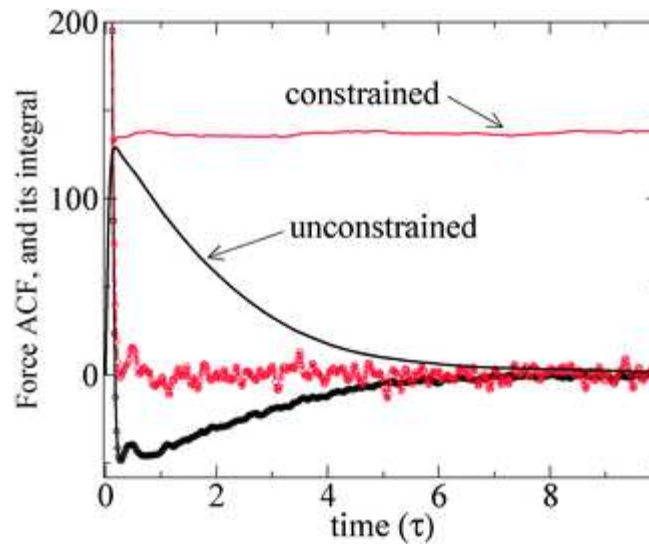


Fig. 5 The force autocorrelation $\langle \delta \mathbf{F}_\mu \cdot \delta \mathbf{F}_\mu(t) \rangle$ compared with the unconstrained $\langle \delta \mathbf{F}_\mu \cdot \delta \mathbf{F}_\mu(t) \rangle_{\text{eq}}$. Also shown are their time integrals. The unconstrained dynamics does not have a well-defined plateau, whereas the constrained dynamics allows for a good definition of the friction coefficient.

Comparison of DPD with MD simulations

As a consistency check, we now compare the simulation of the stochastic DPD [eqn \(52\)](#), with the effective forces and frictions computed microscopically, with the simulation of the original MD equations. The first issue to resolve is the fact that the effective force does not have data for short distances. We have smoothly extrapolated this force with a bell shaped function for $R_{\mu\nu} < 8\sigma$ and have checked in the simulations that the results are insensitive to the height of this function at the origin. This is because the DPD particles hardly visit the short distances that are hardly visited by the CoM in the molecular dynamics simulation. A similar situation occurs for the friction coefficients, for which there are no data at short distances. The specific extrapolated values for the friction coefficients do not affect the results.

The stochastic forces that we use in the DPD simulations are detailed in the appendix. Note that in order to obtain the amplitude $B_{\mu\alpha}(\mathbf{R})$ of the stochastic forces, we need to extract the square root, in matrix sense, of the $3M \times 3M$ friction matrix, according to the Fluctuation-Dissipation theorem in [eqn \(53\)](#). This is a computationally very expensive task in

general. However, for pair-wise forces, it is possible to find a simple solution for the stochastic forces which is a generalization of the usual stochastic forces in DPD. However, this simple solution requires that the coefficients γ_{\perp} , γ_{\parallel} be positive. For this reason, we have approximated in the DPD model the coefficient $\gamma_{\perp}(R_{\mu\nu})$ by a strictly positive function obtained by setting to zero the values of $\gamma_{\perp}(R_{\mu\nu})$ that become negative.

The observables selected to compare MD with DPD are the radial distribution function and velocity autocorrelation function for the velocity of the CoM. The former provides information on the static properties of the system while the latter gives insight about its dynamical properties. In [Fig. 6](#) the comparison of the radial distribution function computed from a DPD simulation of [eqn \(52\)](#) with the radial distribution function of the CoM computed from the MD simulation shows a reasonable agreement. For static quantities like the radial distribution function of the CoM in [Fig. 6](#), both a DPD simulation and a coarse-grained molecular dynamics (CGMD) produce identical results. The CGMD is defined as the result of setting to zero the friction (and, consistently, the stochastic force) in [eqn \(52\)](#).

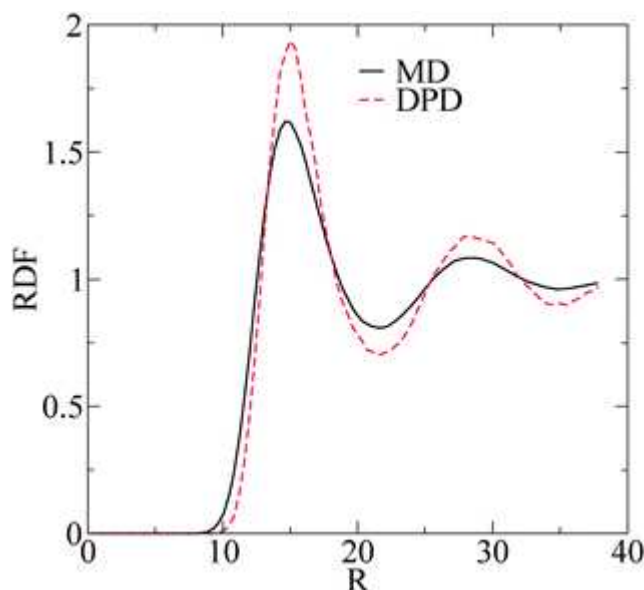


Fig. 6 The comparison of the Markovian prediction (DPD) with the MD simulation results for the radial distribution function of the CoM.

[Fig. 7](#) shows the velocity autocorrelation of the CoM computed with MD, with DPD, and with CGMD. The agreement between the MD and DPD results is very good. As it is apparent from [Fig. 7](#), the CGMD simulation based only on effective potentials provides very nonphysical

results. It is necessary to introduce also the dissipation inherent to any coarse-graining procedure in order to obtain realistic results from a coarse-grained simulation. This is one important message to retain from the present paper (see also [ref. 29](#)).

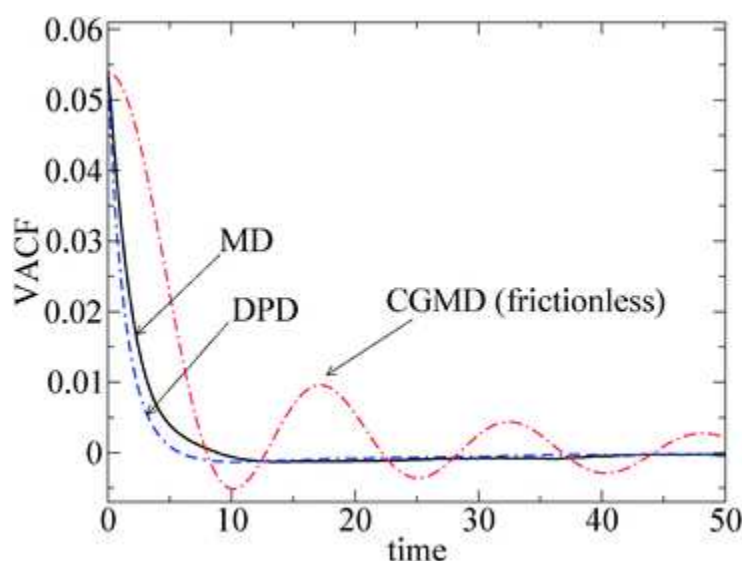


Fig. 7 The velocity autocorrelation function of the CoM computed with MD (solid line), with DPD (dashed line) and with CGMD (dotted-dashed line).

The agreement between DPD and MD simulations, although satisfactory, can be certainly improved. The discrepancies between both types of simulations should be attributed exclusively to the pair-wise approximation which is the only approximation that we have taken, apart from the Markovian approximation. The latter, as we discussed, is rather well satisfied. Of course, having the exact expressions [eqn \(44\)](#) and [eqn \(49\)](#) and a method to compute these objects from constrained simulations, opens the door to the investigation of improvements of the approximations [eqn \(55\)](#) and [eqn \(56\)](#) that we have taken in the present work.

VII. Discussion

The main objective of Mori-Zwanzig theory is to obtain the dynamic equations for a set of reduced variables. In principle, the equation for the evolution of these variables is the GLE, which is a complicated integro-differential equation with random coefficients. The GLE is not fully explicit and hence very difficult to use in practice. However, if the

relevant variables are slow, their dynamics should be approximately Markovian and, hence, one can expect that it can be captured accurately by an SDE. How to derive this SDE turns out to be non-obvious, however. In particular, the standard Markovian approximation used in the literature suffers from the plateau problem because it used the original dynamics instead of the (unknown) projected dynamics to compute the coefficients in the SDE.

In this paper we gave an operational procedure which permits to alleviate these difficulties. The procedure is based on a modification of the original dynamics which makes precise what one means by the statement that the relevant variables are slow: in fact, the procedure amounts to making all the remaining variables evolve infinitely fast compared to the relevant ones. In this limit, one can define unambiguously what the projected dynamics is, justify the Markovian approximation, and give precise estimates for the coefficients in the SDE.

Being able to derive this SDE is important for two basic reasons. First it provides *understanding* of the dynamics of the system. Second it *facilitates the simulation* of the system. The fact that complex molecules may be represented with equations with the structure of dissipative particle dynamics (DPD) is a very valuable piece of knowledge. At the same time, it is by far less expensive to simulate the system at the level of the CoM through a DPD simulation than to simulate the whole system with molecular dynamics. Both the number of computing units (*i.e.* particles) and the size of the required time steps in DPD makes the coarse simulation the method of choice if only macroscopic time scales are of interest.

One aspect of our approach should be emphasized: the coefficients appearing in the SDE (effective forces and frictions) depend, in general, on the whole set of relevant variables in a nontrivial way. From a theoretical viewpoint this feature is a plus which shows that our approach does not rely on extra assumptions on how the coefficients depend on the relevant variables. From a computational viewpoint, however, this may be an issue. Indeed, to pre-compute these coefficients we need to sample the multidimensional space of the relevant variables, which may not be feasible in practice. For instance, in the particular example of star polymers studied in Sec. VI, for every configuration of the M molecules we should have a different set of effective forces and frictions. The way we got around the multidimensional sampling of the coefficients was through the constitutive assumption of pair-wise additivity which can be made *a posteriori* to simplify the coefficients in the SDE obtained by our

procedure. Any such constitutive assumption should be checked through significance tests and before performing any comparison between microscopic and coarse-grained simulations, and in the example in Sec. VI it indeed turned out to be valid and reasonably accurate. But this clearly means that the pre-computing strategy will be limited to situations where it is possible to make sensible assumptions on the functional form of the coefficients of the SDE.

One way to go beyond the pre-computing strategy and not use any extra constitutive assumptions is to compute on-the-fly the coefficients in the SDE for the relevant variables. This fits within the framework of the heterogeneous multiscale method³⁰⁻³² and it amounts to do the following. Given the current state $\alpha(t)$ of the relevant variables, a short run of constrained simulations is performed to estimate the value of the coefficients in the SDE at value $\alpha(t)$; these estimates are then used to propagate the relevant variables by one macro-time-step to a new value $\alpha(t + \Delta t)$, and the procedure is repeated. This strategy will be doable even if the dimension of the relevant variable space is large (*i.e.* even if pre-computing the coefficients may not be an option) and still provide a serious computational gain over the vanilla MD simulation. We intend to explore this avenue in future publications.

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Appendix A: DPD stochastic forces

In this appendix we show how to formulate the stochastic forces for the DPD model. Instead of performing the square root, in matrix sense, of the $3M \times 3M$ friction matrix $\gamma_{\mu\nu}$, we rather postulate the form of the stochastic forces and demonstrate that their variances have the

structure of the friction matrix in [eqn \(56\)](#). The stochastic force is postulated to be of the form $\tilde{F}_\mu = \Sigma_\nu \tilde{F}_{\mu\nu}$, where the pair-wise stochastic force is

$$\tilde{F}_{\mu\nu} dt = (2k_B T)^{1/2} \left(\tilde{A}(r_{\mu\nu}) d\bar{W}_{\mu\nu}^S + \frac{1}{3} \tilde{B}(r_{\mu\nu}) \text{tr}[dW_{\mu\nu}^S] \mathbf{1} \right) \cdot \mathbf{e}_{\mu\nu} \quad (\text{A1})$$

where

$$d\bar{W}_{\mu\nu}^{S\alpha\beta} = \frac{1}{2} [dW_{\mu\nu}^{\alpha\beta} + dW_{\mu\nu}^{\beta\alpha}] - \frac{1}{3} \text{tr}[dW_{\mu\nu}^S] \delta_{\alpha\beta} \quad (\text{A2})$$

Here, $dW^{\alpha\beta}_{\mu\nu}$ is a matrix of independent increments of the Wiener process with the symmetries

$$dW^{\alpha\beta}_{\mu\nu} = dW^{\alpha\beta}_{\nu\mu}. \quad (\text{A3})$$

Note that $\tilde{F}_{\mu\nu} = -\tilde{F}_{\nu\mu}$ and momentum will be conserved by the stochastic forces. The matrix $dW^{\alpha\beta}_{\mu\nu}$ satisfies the Ito rule

$$dW^{\alpha\alpha'}_{\mu\mu'} dW^{\beta\beta'}_{\nu\nu'} = (\delta_{\mu\nu} \delta_{\mu'\nu'} + \delta_{\mu\nu'} \delta_{\nu\mu'}) \delta_{\alpha\beta} \delta_{\alpha'\beta'} dt. \quad (\text{A4})$$

From this equation one can easily obtain the following identities

$$\begin{aligned} \text{tr}[dW_{\mu\mu'}^S] \text{tr}[dW_{\nu\nu'}^S] &= 3(\delta_{\mu\nu} \delta_{\mu'\nu'} + \delta_{\mu\nu'} \delta_{\nu\mu'}) dt, \\ d\bar{W}_{\mu\mu'}^{S\alpha\alpha'} d\bar{W}_{\nu\nu'}^{S\beta\beta'} &= (\delta_{\mu\nu} \delta_{\mu'\nu'} + \delta_{\mu\nu'} \delta_{\nu\mu'}) \\ &\quad \times \left[\frac{1}{2} (\delta_{\alpha\beta} \delta_{\alpha'\beta'} + \delta_{\alpha\beta'} \delta_{\alpha'\beta}) \right. \\ &\quad \left. - \frac{1}{3} \delta_{\alpha\alpha'} \delta_{\beta\beta'} \right] dt, \\ \text{tr}[dW_{\mu\mu'}^S] d\bar{W}_{\nu\nu'}^S &= 0 \end{aligned} \quad (\text{A5})$$

These identities allow to show that the variance of the stochastic forces is given by

$$\tilde{F}_\mu dt \tilde{F}_\nu dt = 2k_B T (A(r_{\mu\nu}) \mathbf{1} + B(r_{\mu\nu}) \mathbf{e}_{\mu\nu} \mathbf{e}_{\mu\nu}) dt \quad (\text{A6})$$

provided that we choose

$$\begin{aligned}\tilde{A}(r_{\mu\nu}) &= (2A(r_{\mu\nu}))^{1/2} \\ \tilde{B}(r_{\mu\nu}) &= (3B(r_{\mu\nu}) - A(r_{\mu\nu}))^{1/2}\end{aligned}\tag{A7}$$

We see, therefore, that the proposed structure for the stochastic force has a variance with the structure of the friction matrix in the pair-wise approximation, [eqn \(56\)](#).

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