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Inhomogeneous multiscale dynamics in harmonic lattices

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We use projection operators to address the coarse-grained multiscale problem in harmonic systems. Stochastic equations of motion for the coarse-grained variables, with an inhomogeneous level of coarse graining in both time and space, are presented. In contrast to previous approaches that typically start with thermodynamic averages, the key element of our approach is the use of a projection matrix chosen both for its physical appeal in analogy to mechanical stability theory and for its algebraic properties. We show that thermodynamic equilibrium can be recovered and obtain the fluctuation dissipation theorem *a posteriori*. All system-specific information can be computed from a series of feasible molecular dynamics simulations. We recover previous results in the literature and show how this approach can be used to extend the quasicontinuum approach and comment on implications for dissipative particle dynamics type of methods. Contrary to what is assumed in the latter models, the stochastic process of all coarse-grained variables is not necessarily Markovian, even though the variables are slow. Our approach is applicable to any system in which the coarse-grained regions are linear. As an example, we apply it to the dynamics of a single mesoscopic particle in the infinite one-dimensional harmonic chain. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1829253]

I. INTRODUCTION

The processes underlying the properties of materials and biological assemblies often span a range of length and time scales. In understanding and predicting their behavior, it would be desirable to start from an atomistic description which could be capable of exhibiting the continuum and macroscopic behavior of the system. Molecular dynamics (MD) alone is presently incapable of bridging scales of such orders of magnitude. Coarse-graining schemes that tackle different aspects of this broad problem are currently an active area of research. Of particular interest is the possibility to follow the system dynamically and not just obtain its thermodynamic properties.

A number of ''mesoscale'' dissipative particle dynamics (DPD) type methods, for example, introduce particlelike variables in continuous equations and associate with them conservative, dissipative, and random forces.[1,2] The origin and appropriate functional form of these forces is still not fully resolved.[3,4] A different approach that aims to avoid these equations altogether relies on exploiting through efficient numerical integration techniques a large number of short MD simulations.[5] Another level of complexity is introduced when the system needs to be inhomogeneously coarse grained. One of the most successful methods under this category, the quasicontinuum,[6] involves no explicit time nor finite temperature. A generalization has been attempted but the dynamics have been introduced *ad hoc*.[7] One of the main remaining challenges in such methods remains the reflections at boundaries between regions of different level of description.[8] Coarse-grained dynamics that can systematically describe the system at different scales in both time and space remain a challenge. A general scheme that prescribes the form of the equations to be used based on an equivalent footing or framework is currently lacking.

We have used the projection operator approach of Mori and Zwanzig[9] to obtain the dynamical equations of an inhomogeneous multiscale system. To illustrate this, we solve exactly the multiscale inhomogeneous problem for harmonic systems. In this regard, harmonic systems, apart from their obvious adequacy as a first approximation for solids, provide an excellent framework to probe these ideas. The projector operator approach has been used extensively in the past. One of the main drawbacks has been the evaluation of the formal expressions obtained by the theory. By using an algebraic projection and in analogy to mechanical stability, we obtain functional forms of the forces that can be computed by a series of short molecular dynamics simulations. The key point of our approach is that we avoid altogether the first step of averaging and obtain the thermodynamic equilibrium properties *a posteriori*. The mechanical analogy has been first introduced in the literature by Deutch and Silbey for a single particle in a lattice.[10] In that respect, our results can be considered a generalization of their work. We also recover as a special case the results of Adelman and Doll for atom/solid surface scattering in harmonic lattices.[11] Additionally, the formalism provides a connection to the quasicontinuum method with explicit time and finite temperature. Finally, we comment on the form of the random forces and memory kernels that are usually assumed in other mesoscale dissipative dynamics type of methods.

The paper is organized as follows: In Sec. II we introduce the system and the coarse-grained scheme. In Sec. III we describe the equations for the coarse-grained variables using the Mori formalism. In Sec. IV we introduce a different projection matrix and rederive the theory using that inner

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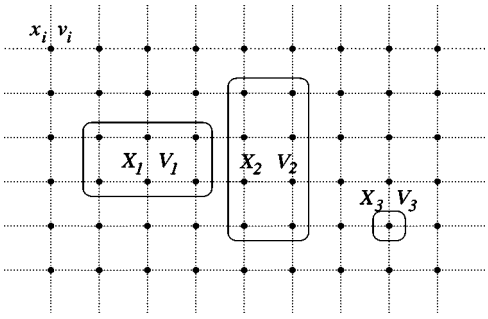

FIG. 1. Example of a coarse-graining scheme in a 2D harmonic system.

product, which allows us to obtain closed expressions for the results in Sec. IV and a numerical procedure to compute them in Sec. V. In Sec. VI we propose a simulation procedure to study the dynamics. We apply the theory developed in the previous sections to study the coarse-grained dynamics of a single mesoscopic particle in the infinite one-dimensional (1D) harmonic chain in Sec. VII. Finally, Sec. VIII provides a short summary and conclusions.

II. SYSTEM DETAILS AND COARSE-GRAINING SCHEME

We consider a harmonic system of dimension d consisting of N particles of mass m_i. We will assume that the interaction between any two particles only depends on the distance between them. The Hamiltonian of this system is

$$\mathcal{H}=\sum_{\mu=1}^{d}\left(\sum_{i}\frac{1}{2}m_i v_{i,\mu}^2+\frac{1}{2}\sum_{i,j}x_{i,\mu}A_{ij}x_{j,\mu}\right), \tag{1}$$

where $x_{i,\mu}$ and $v_{i,\mu}$ are the μ components of the deviation from the equilibrium position and velocity of the particle i, respectively, and A_{ij} is a symmetric matrix that satisfies the stability condition

$$\sum_{i}A_{ij}=0. \tag{2}$$

The variables of interest are the coordinates and velocities of the center of mass of each of the coarse-grained regions of the system

$$X_{k,\mu}=\frac{1}{M_k}\sum_{i}^{k}m_i x_{i,\mu}, \quad V_{k,\mu}=\frac{1}{M_k}\sum_{i}^{k}m_i v_{i,\mu}, \tag{3}$$

where $M_k=\Sigma_i^k m_i$ is the total mass of the coarse-grained region or particle k. The number of oscillators in each region is allowed to vary in accordance with the desired coarse-graining level. For example, if we are interested in keeping the atomistic level in one part of the system, the corresponding regions contain only one oscillator and the coarse-grained variables are just the coordinates and velocities of the original oscillators. At the same time, not every oscillator need to be related to a coarse-grained particle. We may be interested in coarse-graining completely a part of the system comprising many oscillators. In that case no index k is associated with such region. We present in Fig. 1 an example of an inhomogeneous coarse-graining scheme.

III. MORI THEORY

The equations of motion for these variables can be obtained in a straightforward manner by using the Mori projection operator formalism.[9] The equations are obtained by projecting onto the subspace spanned by the relevant variables. The projection operator is determined by the choice of the inner product (B,C) in the Hilbert space of all functions $B(x,v)$ and $C(x,v)$ of phase space coordinates.[9] It is customary to choose canonical equilibrium averages $(B,C)=\langle BC\rangle_{\mathrm{eq}}$, where

$$\langle B(x,v)\rangle_{\mathrm{eq}}=\frac{\int d^N x d^N v B(x,v)e^{-\mathcal{H}/k_B T}}{\int d^N x d^N v e^{-\mathcal{H}/k_B T}}, \tag{4}$$

k_B being the Boltzmann constant and T the temperature. We then obtain the following linear generalized Langevin equations:

$$\frac{dX_k(t)}{dt}=V_k(t), \tag{5}$$

$$M_k\frac{dV_k(t)}{dt}=-\sum_{l}\left[\Lambda_{kl}X_l(t)+\int_0^t d\tau\Phi_{kl}(\tau)V_l(t-\tau)\right]+R_k(t), \tag{6}$$

where Λ_{kl} is a renormalized matrix force, $\Phi_{kl}(t)$ a memory kernel, and $R_k(t)$ a force which contains the information of the nonrelevant variables we have left out. We have dropped the spatial labels μ in these expressions for clarity, because the Hamiltonian we are using here does not provide any coupling between the different components.

The explicit expressions for the unknown quantities in Eq. (6) involve complicated functions containing formal projection operators. However, the following information can be obtained relatively easily (see Chap. 8 of Ref. 9): the force $R_k(t)$ satisfies

$$\langle R_k(t)\rangle=0 \tag{7}$$

and

$$\langle R_k(t)R_l(0)\rangle=k_B T\Phi_{kl}(t), \tag{8}$$

where $\langle\cdots\rangle$ denotes averages over a statistical ensemble of the initial conditions that is close to equilibrium. Equation (8) is called the non-Markovian fluctuation-dissipation theorem. It guarantees that the system admits the thermodynamic equilibrium solution.

The advantage of this approach is that it provides us with equations of motion where the forces are decomposed in three parts. The first two are functions of the relevant variables $X(t)$ and $V(t)$ alone, and can be identified with conservative and dissipative type force terms, respectively. The force $R_k(t)$ can be considered as a random force. Therefore, the equations can be cast inside the theory of stochastic processes. While the physical interpretation of these equations is clear, the main problem resides in finding both closed forms of these expressions for Λ_{kl} and $\Phi_{kl}(t)$ as well as ways of actually computing them in practice. This is not an easy task

even in the case of linear systems. For example, with this projection method, we find the matrix Λ_{kl} as the inverse of the matrix $\langle X_{l'}X_l\rangle_{\rm eq}/k_BT$, i.e.,

$$\sum_{l'}\Lambda_{kl'}\frac{\langle X_{l'}X_l\rangle_{\rm eq}}{k_BT}=\sum_{l'}\frac{\langle X_kX_{l'}\rangle_{\rm eq}}{k_BT}\Lambda_{l'l}=\delta_{kl}. \tag{9}$$

This inverse matrix is generally difficult to compute. Special care is required as can be seen by noting that the individual elements $\langle X_l^2\rangle_{\rm eq}$ do not exist in the thermodynamic limit $(N\to\infty)$ because of translational invariance.

IV. MORI THEORY WITH A SPECIAL INNER PRODUCT

A. The mechanical analog: Random forces

The expressions in the preceding section have been obtained by using equilibrium averages as the inner product. Although with this approach we obtained straightaway Eqs. (5)–(9), it is not clear how one can proceed further.

A better insight is gained if we use instead an inner product with the following properties:

$$(x_{i,\mu},x_{j,\nu})=(v_{i,\mu},v_{j,\nu})=\delta_{ij}\delta_{\mu\nu}m_i^{-1},\quad (x_{i,\mu},v_{j,\nu})=0. \tag{10}$$

Using this inner product, the projection operator formalism produces the equivalent equations of the preceding section. Specifically, we recover Eq. (5) and a modified equation for the time derivative of $V(t)$, Eq. (6) that now involves a memory kernel related to the time convolution of the position $X(t)$. Integrating by parts this integral we arrive at

$$M_k\frac{dV_k(t)}{dt}=-\sum_l\left[A^{kl}X_l(t)+\int_0^t d\tau\beta_{kl}(\tau)V_l(t-\tau)+\beta_{kl}(t)X_l(0)\right]+\hat{R}_k(t), \tag{11}$$

where we have written $A^{kl}=\Sigma_i^k\Sigma_j^l A_{ij}$. We now need to compute the random force $\hat{R}_k(t)$ and the memory kernel function $\beta_{kl}(t)$. The latter is connected to the former by the projection operators formalism as

$$\beta_{kl}(t)=-\int_0^t d\tau[\mathcal{L}\hat{R}_k(\tau),X_l(0)]M_l, \tag{12}$$

where $\mathcal{L}$ is the Liouville[9] operator of the system. We later relate each quantity to those of the preceding section [see Eq. (6)].

The random force is in general a complicated function of the initial coordinates and velocities of the system. In harmonic systems, however, it can be expressed as a linear function of the initial conditions (see Sec. 8.5 of Ref. 9). This will further allow us to establish a mechanical force analogy with a reference mechanical system in which the coarse-grained variables are held fixed.

We start by assuming

$$\hat{R}_k(t)=\sum_i q_i^k(t)m_ix_i(0)+r_i^k(t)m_iv_i(0). \tag{13}$$

Consistency requires that the time dependent coefficients are given by $r_i^k(t)=\int_0^t d\tau q_i^k(\tau)$ and the set of equations

$$m_i\ddot{q}_i^k(t)=-\sum_j\hat{A}_{ij}q_j^k(t), \tag{14}$$

$$m_iq_i^k(0)=-\sum_j^k[(I-\hat{P})A]_{ij},\quad \dot{q}_i^k(0)=0, \tag{15}$$

where the dot denotes time derivative,

$$\hat{A}=(1-\hat{P})A(1-\hat{P}^t) \tag{16}$$

and $\hat{P}$ is a projection matrix defined by

$$\hat{P}_{ij}=\frac{m_i}{M_{k(i)}}\delta_{k(i),k(j)}, \tag{17}$$

where $k(i)$ denotes the index of the group in which the oscillator i belongs and $\hat{P}^t$ the transposed matrix.

Note that if $x=(x_1,x_2,\ldots)$ is the vector formed by all oscillators' coordinates, $\hat{P}^tx=X$ gives a vector whose components are the centers of mass of the coarse-grained particles. In addition, if i or j belongs to a region that has been totally coarse grained, then $\hat{P}_{ij}=0$. Thus, if both i and j belong to such regions, then $\hat{A}_{ij}=A_{ij}$.

It is easy to show that the new force matrix $\hat{A}$ is symmetric and satisfies the stability condition (2). Therefore, $q^k(t)$, and thus the random forces $\hat{R}_k(t)$, are expressed in terms of the mechanical problem (14)–(15). In fact, using the algebra we present below, we can show that the random forces can be further written as

$$\hat{R}_k(t)=-\sum_i^k\left(\sum_j A_{ij}[\hat{x}_j(t)+\hat{v}_j(t)]\right), \tag{18}$$

where $\hat{x}(t)$ and $\hat{v}(t)$ are the solution of the mechanical problem (14) with the initial conditions $\hat{x}(0)=(I-\hat{P}^t)x(0)$ and $\hat{v}(0)=(I-\hat{P}^t)v(0)$. This is a generalization of the results presented in Ref. 10 for a single particle in a lattice.

The mechanical problem generated by $\hat{A}$ is related to the original mechanical problem of the underlying lattice but instead the center of mass of the coarse-grained particles are fixed, as illustrated by the fact that the following property is obeyed at all times:

$$\hat{P}^tq^k(t)=\hat{P}Mq^k(t)=0, \tag{19}$$

where $M_{ij}=\delta_{ij}m_i$ is the mass matrix.

Note that if initially there is no disorder in the coarse-grained lattice, i.e., there are only collective initial deviations from equilibrium, then $\hat{R}_k(t)=0$ at all times. This is a crucial property of linear systems that will allow us to compute the relevant magnitudes of the coarse-grained theory from simple simulations.

The solution of Eqs. (14)–(15) can be formally written as

$$q^k(t)=\mathrm{Re}(e^{i\Omega t})q^k(0), \tag{20}$$

where Ω is the frequency matrix given by $\Omega^2=M^{-1}\hat{A}$ and i is the imaginary unit. Equation (19) is a consequence of $\hat{A}\hat{P}^t=0$, which implies $\Omega\hat{P}^t=0$. Thus, the subspace generated by $\hat{P}^t$ corresponds to eigenvectors of $\hat{A}$ with zero eigenvalues, each one corresponding to every coarse-grained par-

ticle. As a consequence, neither Ω nor $\hat{A}$ possess an inverse. However, since both matrices are diagonalizable ($\hat{A}$ is symmetric and Ω is Hermitian with the scalar product $xy=x^tMy$), we can define the pseudoinverse Ω^{-1} so that

$$\Omega^{-1}\Omega=\Omega\Omega^{-1}=I-\hat{P}^t, \quad \Omega^{-1}P^t=0. \tag{21}$$

Then, the pseudoinverse $\hat{A}^{-1}=(\Omega^{-1})^2M^{-1}$ turns out to be symmetric.

B. Memory kernel

We have obtained the random forces through the transformation to an equivalent mechanical system. We can now tackle the kernel $\beta_{kl}(t)$, which using Eqs. (13) and (12), can be written as

$$\beta_{kl}(t)=\sum_j \int_0^t d\tau \int_0^\tau d\tau' q_j^k(\tau')A_i^l \tag{22}$$

where $A_i^l=\Sigma_j^l A_{ij}$. In the limit $t\to\infty$, each $q_i^k(t)$ decays to zero as the initial perturbation (15) is propagated to the boundaries of the system by elastic waves. However, since Eq. (22) involves a double time integral, in general $\beta_{kl}(t)$ does not decay to zero with time. A better representation is obtained by calculating the integrals in Eq. (22) using Eq. (20), which leads to

$$\beta_{kl}(t)=\Phi_{kl}(t)-\Phi_{kl}(0), \tag{23}$$

where

$$\Phi_{kl}(t)=-\sum_j A_j^l[\hat{A}^{-1}Mq^k(t)]_j \tag{24}$$

with the following properties

$$\sum_l \Phi_{kl}(t)=0 \quad \text{and} \quad \Phi_{kl}(t)=\Phi_{lk}(t). \tag{25}$$

This kernel is expected to vanish as $t\to\infty$ in the thermodynamic limit ($N\to\infty$), in which case the boundaries are removed. Note that we have used the same letter to name this kernel and the one we obtained in Sec. III using equilibrium averages as the inner product. We will show in Sec. IV C that they are indeed the same.

We can now return to the generalized Langevin equation (11), which becomes

$$M_k\frac{dV_k(t)}{dt}=-\sum_l [A^{kl}-\Phi_{kl}(0)]X_l(t) - \sum_l \int_0^t d\tau\Phi_{kl}(\tau)V_l(t-\tau) - \sum_l \Phi_{kl}(t)X_l(0)+\hat{R}_k(t). \tag{26}$$

Equation (26) is the generalization to the present arbitrary inhomogeneous coarse graining of the results of Adelman and Doll for atom/solid surface scattering in harmonic solids.[11]

Note that with the identifications

$$\Lambda_{kl}=A^{kl}-\Phi_{kl}(0) \tag{27}$$

and

$$R_k(t)=-\sum_l \Phi_{kl}(t)X_l(0)+\hat{R}_k(t), \tag{28}$$

Eq. (26) is just Eq. (6).

Finally, note that Eqs. (25) and (2) imply the following expected property of the conservative force

$$\sum_l \Lambda_{kl}=0. \tag{29}$$

C. Fluctuation-dissipation theorems

Using the explicit expressions (13) and (24), and the integration formula for Gaussian distributions, we readily obtain

$$\langle\hat{R}_k(t)\hat{R}_l(0)\rangle_{\hat{A}}=k_BT\Phi_{kl}(t), \tag{30}$$

where $\langle\cdots\rangle_{\hat{A}}$ denotes averages over the initial conditions with the canonical distribution $\hat{\rho}(x,v)\propto\exp(-\hat{\mathcal{H}}/k_BT)$, where $\hat{\mathcal{H}}$ has the same form as the Hamiltonian of Eq. (1), but with $\hat{A}$ instead of A. This is the version of the fluctuation dissipation theorem that appears in Ref. 11. We show in Appendix A that the averages taken with $\langle\cdots\rangle_{\hat{A}}$ in Eq. (30) are the same as the constrained averages $\langle\cdots\rangle_{X_0=0}$ defined by the canonical distribution with the center of mass of the "coarse-grained" particles X_0 fixed at their equilibrium values ($X_0=0$), providing a physical meaning to the fluctuation-dissipation equation (30). Nevertheless, note that Eq. (30) does not hold for general constrained averages

$$\langle B(x,v)\rangle_{X_0}=\frac{\int d^Nxd^Nv B(x,v)e^{-\mathcal{H}/k_BT}\delta(\hat{P}^tx-X_0)}{\int d^Nxd^Nv e^{-\mathcal{H}/k_BT}\delta(\hat{P}^tx-X_0)}, \tag{31}$$

with X_0 different from their equilibrium values.

For our purposes it is more convenient to invoke the standard form of the fluctuation-dissipation theorem, involving the random force $R_k(t)$

$$\langle R_k(t)R_l(0)\rangle_{\text{eq}}=k_BT\Phi_{kl}(t), \tag{32}$$

where the averages are taken with the full equilibrium distribution using A. We can prove Eq. (32) straightaway by using the following algebraic identity:

$$\hat{A}^{-1}=\hat{A}^{-1}A\hat{P}^tA^{-1}\hat{P}A\hat{A}^{-1}+\hat{A}^{-1}A\hat{P}^tA^{-1}(I-\hat{P}) + (I-\hat{P}^t)\hat{A}^{-1}A\hat{P}^tA^{-1}+(I-\hat{P}^t)A^{-1}(I-\hat{P}), \tag{33}$$

where A^{-1} is the pseudoinverse of A defined in similar fashion to Eq. (21) by $A^{-1}A=AA^{-1}=I-P_T$. $(P_T)_{ij}=1/N$ is the projector on the translational mode [given by Eq. (2)], the only zero frequency mode in regular lattices.

Using a similar algebra it can be readily shown that the conservative force Λ_{kl} defined by Eq. (27) is the same as the force we obtained in Sec. III, defined by Eq. (9). Alternatively, we can prove this by taking the limit $T\to0$ in Eqs. (6) and (26). Since $V_k(t)\to0$ in that limit and both equations are exact for any initial condition, they must contain necessarily the same conservative force.

Finally, note that if we write Eq. (5) as

$$\int_0^t d\tau V_l(t-\tau) = X_l(t) - X_l(0), \tag{34}$$

multiply this equation by an arbitrary constant γ_{kl} and add it to Eq. (6) we obtain

$$M_k \frac{dV_k(t)}{dt} = -\sum_l \left[\bar{\Lambda}_{kl} X_l(t) + \int_0^t d\tau \bar{\Phi}_{kl}(\tau) V_l(t-\tau) \right] + \bar{R}_k(t), \tag{35}$$

where $\bar{\Lambda}_{kl} = \Lambda_{kl} + \gamma_{kl}$, $\bar{\Phi}_{kl} = \Phi_{kl} - \gamma_{kl}$, and $\bar{R}_k = \Sigma_l \gamma_{kl} X_l + R_k$. Therefore, by changing γ_{kl} we can obtain an infinite number of different equations of motion, all with a random force $\bar{R}$ satisfying the fluctuation-dissipation formula (30) (though with Φ instead of $\bar{\Phi}$). However, the corresponding kernel $\bar{\Phi}_{kl}$ at long times converges to $-\gamma_{kl}$, resulting in an artificial nondecaying memory effect. Furthermore, R_k (as well as $\hat{R}_k$) does not satisfy the standard fluctuation-dissipation formula (32). In fact, in general the fluctuations of those random forces diverge in the unconstrained thermodynamic equilibrium due to translational invariance. Therefore, we will refer in the following to the Langevin equation given by Eq. (6) or equivalently Eq. (26).

V. A FEW IMPORTANT RESULTS

The expression (24) we obtained for the memory kernel is still too formal for most practical situations. In this section we present a few exact results that will facilitate its calculation both analytically and numerically.

A. Velocity autocorrelation function

Let us consider the velocity autocorrelation matrix

$$C_{kl}(t) = \langle V_k(t) V_l(0) \rangle_{\text{eq}}. \tag{36}$$

Multiplying Eq. (6) by $V_l(0)$ and taking equilibrium averages we obtain a set of differential equations without noise

$$M_k \frac{dC_{kl}(t)}{dt} = -\sum_{l'} \int_0^t d\tau [\Lambda_{kl'} + \Phi_{kl'}(t-\tau)] C_{l'l}(\tau), \tag{37}$$

which together with the initial condition $C_{kl}(0) = \delta_{kl} M_k k_B T$ determine $C_{kl}(t)$. Alternatively, if we know $C_{kl}(t)$ we can derive $\Phi_{kl}(t)$ from these equations.

In Appendix B we take advantage of this relationship to show that if $C_{kl}(t)$ presents a discontinuity in its derivative at time t, then the memory kernel presents a Dirac-delta singularity at the same time t. To be more precise,

$$\Phi_{kl}(t) = -\left[\frac{\dot{C}_{kl}(0)}{C_{ll}(0)} \delta(t) + \sum_r \frac{\Delta \dot{C}_{kl}(t_r)}{C_{ll}(0)} \delta(t-t_r) \right] + \varphi_{kl}(t), \tag{38}$$

where $\Delta \dot{C}_{kl}(t_r) = \dot{C}_{kl}(t_r^+) - \dot{C}_{kl}(t_r^-)$, t_r denotes the times where $\dot{C}_{kl}(t)$ is discontinuous, and $\varphi_{kl}(t)$ is an otherwise smooth function. This property will become useful when we consider coarse graining in the time scale in Sec. VII.

The above results are general and not particular to linear systems. However, in harmonic systems there is a simpler way to compute the autocorrelation matrix. In fact,

$$C_{kl}(t) = V_k(t) V_l(0), \tag{39}$$

where $V_k(t)$ is the velocity of the coarse-grained particle k in the system starting from the following initial conditions:

$$x_i(0) = 0 \quad \text{and} \quad v_i(0) = \delta_{k(i),l} V_l(0), \tag{40}$$

with $V_l(0)^2 = M_l k_B T$. This method exploits the fact that the noise $R_k(t)$ vanishes with this particular choice of the initial conditions, as shown in Sec. IV A.

B. Numerical calculation of the kernel and conservative forces

Note that Eqs. (15) and (19) imply that if the group k contains only one oscillator, and it is connected through the force matrix A with other single-oscillator groups, then $q_i^k(t) = 0$ for all i and hence $\Phi_{kl}(t) = R_k(t) = 0$ at all times. Thus, in a region where we have kept the atomistic description, the generalized Langevin equation (6) reduces to the original Newton's equation.

Therefore, the problem is reduced to computing the conservative forces Λ_{kl} and the kernels $\Phi_{kl}(t)$ for those coarse-grained particles that belong to actual coarse-grained regions or in the proximities of them. Because of Eq. (27), we just need to calculate the memory kernel $\Phi_{kl}(t)$. This can be done by solving Eq. (14) numerically. Then, by using Eq. (22) we can obtain $\beta_{kl}(t)$. This involves a double numerical integration. The long time limit of $\beta_{kl}(t)$ gives $\Phi_{kl}(0)$, from which we can determine Λ_{kl} and $\Phi_{kl}(t)$.

Alternatively, we can use the more direct method of Cai *et al.*[8] In this approach we run a molecular dynamics simulation of the harmonic system starting from the following initial condition:

$$x_i(0) = \epsilon \delta_{k(i)l} \quad \text{and} \quad v_i(0) = 0. \tag{41}$$

Next, the center of mass of the coarse-grained particles is kept fixed by means of an external force on each oscillator $F_{k(i)}$. Therefore, Eq. (26) becomes

$$\sum_i^k F_{k(i)}(t) - [\Lambda_{kl} + \Phi_{kl}(t)] \epsilon = 0. \tag{42}$$

By determining the external force required to keep the center of mass fixed we can obtain the conservative forces and the memory kernel. This method is also applicable to situations in which the harmonic character is a first-order approximation of a more complex system.

The methods above provide us with a numerical representation of $\Phi_{kl}(t)$ at a high accuracy. This is numerically "exact" in the microscopic time scale. However, the kernel is likely to display a highly oscillatory behavior when we look at it on a coarser time scale. In order to obtain a reasonable smooth function in the mesoscopic time scale we need to coarse grain in time further. We can do that as follows: let us call δ and $\Delta \gg \delta$ the basic time steps in the microscopic and mesoscopic time scales, respectively. One im-

mediate approach would be to calculate the coarse-grained kernel $\Phi_{kl}(t)$ at the center of the mesoscopic interval j as a simple time integral:

$$\overline{\Phi}(t_j)=\frac{1}{\Delta}\int_{t_j-\Delta/2}^{t_j+\Delta/2} d\tau\Phi(\tau), \tag{43}$$

with $t_j=\Delta(j+1/2)$. However, the set of data $\overline{\Phi}(t_j)$ is going to depend strongly on the particular choice we have made of the exact location of the mesoscopic times t_j. For example, if we look at $\overline{\Phi}(t_j+\delta)$, defined as in Eq. (43) but integrating from $t_j-/\Delta/2+\delta$ to $t_j+/\Delta/2+\delta$ instead, we may obtain a very different value due to the high oscillatory behavior of the raw data. Nevertheless, we can define instead the coarse-grained kernel at t_j as the average of all these possible values inside that time step Δ. This is equivalent to calculating the following convolution:

$$\overline{\Phi}(t)=\int d\tau\Phi(\tau)\theta(t-\tau), \tag{44}$$

where

$$\theta(t)=\frac{2}{\Delta}\left(1-|t|\frac{2}{\Delta}\right)H\left(1-|t|\frac{2}{\Delta}\right), \tag{45}$$

and $H(x)$ is the Heaviside unit-step function. By applying Eq. (44) two times, we are able to reproduce the analytical results for the example we present in Sec. VII.

VI. AN "*AB INITIO*" METHOD FOR THE SIMULATION OF THE DYNAMICS

Once we know $\Phi_{kl}(t)$ numerically we can simulate the dynamics by using a DPD-like algorithm. If we assume that the stochastic process $R_k(t)$ is Gaussian (which is justified as long as we consider small deviations from equilibrium), then it is determined by the first moments: (7) and (8). In this case, we can exploit the properties (25) to generate the set of correlated variables $R_k(t)$ by using a set of independent Gaussian variables $\xi_{kl}=-\xi_{lk}$, so that $R_k(t)=\Sigma_{l\neq k}\xi_{kl}$ and

$$\langle\xi_{kl}(t)\xi_{k'l'}(0)\rangle_{\mathrm{eq}}=k_BT\Phi_{kl}(t)(\delta_{kl'}\delta_{lk'}-\delta_{kk'}\delta_{ll'}). \tag{46}$$

This is the essential ingredient used in DPD to preserve momentum conservation. In fact, since Eqs. (29) and (25) imply

$$\Lambda_{kk}=-\sum_{l\neq k}\Lambda_{kl} \quad \text{and} \quad \Phi_{kk}(t)=-\sum_{l\neq k}\Phi_{kl}(t), \tag{47}$$

respectively, we can write Eq. (6) in the form

$$M_k\frac{dV_k(t)}{dt}=\sum_{l\neq k}\left\{-\Lambda_{kl}[X_l(t)-X_k(t)] - \int_0^t d\tau\Phi_{kl}(t-\tau)[V_l(\tau)-V_k(\tau)]+\xi_{kl}(t)\right\}, \tag{48}$$

which very much resembles the DPD equations of motion. However, the first question that arises is whether we can consider $\Phi_{kl}(t)$ as Dirac-delta functions, as customary in DPD. It is frequently argued that they can be considered so because the coarse-grained variables are slow compared to the atomic time scales. This would imply that the full stochastic process $\{X(t),V(t)\}$ would be Markovian in the relevant time scale. We will show next that this should not be assumed.

VII. AN EXAMPLE: COARSE-GRAINING IN THE 1D HARMONIC CHAIN

Let us illustrate the above results with a simple example: the dynamics of a single coarse-grained particle or blob formed by n consecutive oscillators in the one-dimensional infinite harmonic chain. For simplicity we set all intrinsic parameters of the chain to unity (the mass of each oscillator, the elastic constant, and the equilibrium spacing between them). Let us denote with X and V the relevant variables (now scalar magnitudes) of the single blob. Due to translational invariance, the conservative force Λ on the blob vanishes. This can be shown by using $\langle X^2\rangle\to\infty$ in Eq. (9). Therefore, the generalized Langevin equation (6) becomes

$$n\frac{dV(t)}{dt}=-\int_0^t d\tau\Phi(\tau)V(t-\tau)+R(t). \tag{49}$$

We now use the method proposed in Sec. V A to compute the memory kernel. The autocorrelation function can be obtained by studying the dissipation of an initial velocity perturbation consisting of all oscillators at rest at the equilibrium positions except the ones in the blob, which start instead with velocity V_0. The time dependent velocity $V(t)$ of the coarse-grained particle can be computed directly from the exact solution of the infinite 1D harmonic chain, which is expressed in terms of Bessel functions,

$$V(t)=V_0\sum_{i=1}^{n}\sum_{j=1}^{n}J_{2|i-j|}(2t), \tag{50}$$

or from the macroscopic displacement field $u(x,t)$,[12] which verifies the wave equation

$$\frac{\partial^2u}{\partial t^2}=\frac{\partial^2u}{\partial x^2}. \tag{51}$$

This equation can be solved easily by standard methods, and the velocity is obtained by integrating $\partial u(x,t)/\partial t$ over the blob's region. Both methods provide the same result for large n,

$$V(t)\sim V_0(1-t/n)H(1-t/n). \tag{52}$$

Note that $V(t)$ changes in a time scale of order $\sim n$. We already see from Eq. (52) that the velocity autocorrelation decay is not exponential but linear, which is an indication that the stochastic process is non-Markovian. We can solve Eq. (49) by using Laplace transforms.[13] This is done in Appendix C. By changing to the proper time scale $t^*=t/n$, with $\Phi^*(t^*)=n\Phi(nt^*)$, we obtain

$$\int_0^\infty dt^*\Phi^*(t^*)=2, \tag{53}$$

and

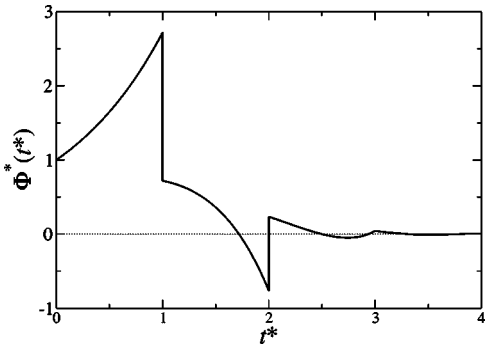

FIG. 2. Scaled memory kernel $\Phi^*=n\Phi$ as a function of $t^*=t/n$ (without the Dirac deltas at $t^*=0$, 1) for a coarse-grained particle in a 1D harmonic chain.

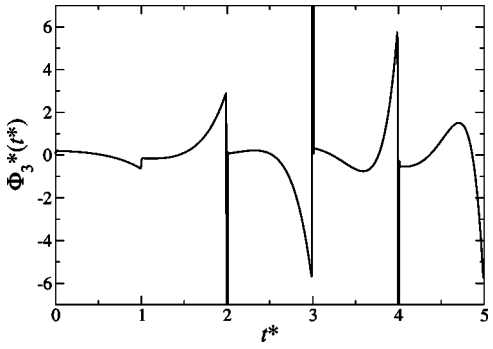

FIG. 3. Memory kernel connecting two coarse-grained particles separated by two blobs in the 1D harmonic chain.

$$\Phi^*(t^*)=\delta(t^*)-\delta(t^*-1)+e^{t^*}-H(t^*-1)e^{t^*-1}(t^*+1)+\sum_{k=2}^{\infty}H(t^*-k)e^{t^*-k}(-1)^k\frac{(t^*-k)^{k-2}}{(k-2)!}\times\left(\frac{(t^*-k)^2}{k(k-1)}+\frac{2(t^*-k)}{k-1}+1\right). \tag{54}$$

Note that the Dirac deltas appear as a consequence of the time scale change. At the microcospic time scale the autocorrelation function (50) does not present discontinuities in its time derivative.

We have plotted in Fig. 2 the memory kernel (without the Dirac-delta functions) given by Eq. (54). We have also calculated numerically this kernel by using the method of Sec. V B. Both results are indistinguishable in the plot. It is clear that the kernel has not decayed completely in the time scale of $V(t)(t^*\sim 1)$, and thus we cannot approximate it with a single Dirac delta and the random term as white noise, even in the limit $n\to\infty$.

This phenomenon is general and has implications beyond this particular example. The reason for this long-lived kernels is that the time scale of $V_k(t)$ is given by the dissipation, which in harmonic systems is due to wave propagation, and the decay time scale of the kernels is on the same time scale. This is clear from Eqs. (14)–(15). In the mesoscopic limit $\hat{A}$ tends to A, and $q_i^k(t)$ tends to the solution of the mechanical problem consisting of an initial perturbation around the edge of the coarse-grained region k. Thus, $\Phi_{kl}(t)$ will not appreciably decay at least until the elastic waves have removed the perturbation, which will be about the time it takes for the sound to cross the mesoscopic region, i.e., a mesoscopic time. This is a memory effect that occurs inside the coarse-grained particles, causing the whole process to be non-Markovian. Therefore, we cannot consider the kernels or the autocorrelation function of the random forces Dirac-delta functions, such as in DPD.

In Ref. 14, Español justified the DPD method by studying the equation of motion of an infinite number of coarse-grained particles in the one-dimensional harmonic chain. In contrast to the example discussed above, now the infinite harmonic chain is partitioned into an infinite number of blobs, each one formed by n consecutive oscillators, which is more closely related to the customary coarse-graining scheme in DPD. However, this work relies on the Markovian assumption for the dynamics, which we have shown to be unjustified. We present in Fig. 3 the scaled memory kernel $\Phi_3^*=n\Phi_3$ connecting two coarse-grained particles k and l separated by two coarse-grained particles, i.e., $|k-l|=3$, as computed from a molecular dynamics simulation with blobs of size $n=10\,000$. As before, the raw data has been coarse grained in time with a mesoscopic time step $\Delta^*=\Delta/n=0.01$. It is clearly seen that the kernel is on the mesoscopic time scale $t^*=t/n$, as expected. In fact, by applying the theory of Sec. V A we obtain that this kernel contains three Dirac-delta functions at different mesoscopic times, $2\delta(t^*-3)-\delta(t^*-2)-\delta(t^*-4)$ (recognizable in Fig. 3 as lines going out of scale), around $t^*=3$, which is the time it takes the sound to propagate from one blob to the other. We report the corresponding analytical expressions of this problem and the genelarization to higher dimensions elsewhere.

VIII. CONCLUSIONS

We have applied projection operators to the coarse-grained multiscale problem in harmonic systems with an inhomogeneous level of coarse graining. The customary approach of using equilibrium averages as inner product produces the right generalized Langevin equation, but the explicit expressions are difficult to calculate. Using an alternative inner product we have been able to provide explicit expressions for the conservative forces, the memory kernels and the random forces, in terms of a mechanical analog. Based on these expressions, we have shown that the memory kernels and the velocity autocorrelation functions can be computed in linear systems from a single molecular dynamics simulation. These results represent a generalization of previous analytical work on harmonic lattices involving the derivation of a series of algebraic properties.

In addition, a method that resembles DPD has been proposed and is applicable to any system in which the coarse-grained region is linear. This can also be seen as a natural extension of the quasicontinuum method to account for finite temperature and dynamics. Moreover, we have shown that the memory kernels and also the autocorrelation function of the random forces used in the simulations should not be considered as Dirac-delta functions, as customary in most approaches, without justification. Instead, the proposed simulations would need to include the computation of the time

convolutions involving memory kernels. In order to account for the fluctuation-dissipation theorem, the random forces need to be generated using a colored noise algorithm. Otherwise, one risks that the system simulated does not tend to the thermodynamic equilibrium. Methods addressing this issue exist in the literature,[15,16] however, further work is required to test their efficiency in these particular problems.

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APPENDIX A: CONSTRAINED AVERAGES

Starting from Eq. (13) we obtain

$$\begin{aligned}\langle \hat{R}_k(t)\hat{R}_l(0)\rangle_{\hat{A}} &= q^k(t)^t M\langle xx^t\rangle_{\hat{A}} M q^l(0)\\ &= q^k(t)^t M(1-\hat{P}^t)\langle xx^t\rangle_{\hat{A}}(1-\hat{P})Mq^l(0)\\ &= q^k(t)^t M\langle (x-X)(x-X)^t\rangle_{\hat{A}} M q^l(0).\end{aligned} \tag{A1}$$

Let us now consider the variable change from x to center mass coordinates $X=\hat{P}^t x$ plus a number of relative coordinates which we will represent using vectorial notation as ξ. Each variable ξ_i can be defined as the difference between the component x_i of the oscillator i and a fixed reference oscillator inside the same group. Then, the quantity $B(x)=(x-X)(x-X)^t$ as a function of $\{X,\xi\}$ does not depend on the center of mass coordinates X, i.e., it is a function of ξ alone: $B(x+\lambda X)=B(x)$ for all λ and x. We show next that for any function with the same property, $\langle B(x)\rangle_{\hat{A}} = \langle B(x)\rangle_{X_0=0}$.

Equation (16) implies

$$x^t A x = x^t \hat{A} x - X^t A X + 2x^t A X, \tag{A2}$$

being $x^t\hat{A}x$ a function of ξ alone. Therefore, using this expression and changing variables we obtain

$$\begin{aligned}\langle B(x)\rangle_{X_0=0} &= \frac{\int d^N x B(x)\exp(-x^t A x/2k_BT)\,\delta(\hat{P}^t x)}{\int d^N x \exp(-x^t A x/2k_BT)\,\delta(\hat{P}^t x)}\\ &= \frac{\int d^N x B(x)\exp(-x^t \hat{A} x/2k_BT)\,\delta(\hat{P}^t x)}{\int d^N x \exp(-x^t \hat{A} x/2k_BT)\,\delta(\hat{P}^t x)} = \frac{\int dX d\xi B(x)\exp(-x^t \hat{A} x/2k_BT)\,\delta(X)}{\int dX d\xi \exp(-x^t \hat{A} x/2k_BT)\,\delta(X)}\\ &= \frac{\int d\xi B(x)\exp(-x^t \hat{A} x/2k_BT)}{\int d\xi \exp(-x^t \hat{A} x/2k_BT)} = \frac{\int dX d\xi B(x)\exp(-x^t \hat{A} x/2k_BT)}{\int dX d\xi \exp(-x^t \hat{A} x/2k_BT)} = \langle B(x)\rangle_{\hat{A}}.\end{aligned} \tag{A3}$$

APPENDIX B: SINGULARITIES IN THE MEMORY KERNEL

Let us consider the Fourier transform of the autocorrelation function

$$c_{kl}(\omega) = \int_0^\infty dt e^{-i\omega t} C_{kl}(t) \tag{B1}$$

and analogously for the memory kernel $\phi_{kl}(\omega)$. In this representation, Eq. (37) becomes

$$\sum_{l'} \phi_{kl'}(\omega)c_{l'l}(\omega) = M_k[C_{kl}(0) - i\omega c_{kl}(\omega)] - \sum_{l'} \Lambda_{kl'}\frac{c_{l'l}(\omega)}{i\omega}. \tag{B2}$$

Assume $\dot{C}_{kl}(t)$ is discontinuous at the times $t=t_1,t_2,\ldots$. Then, the asymptotic behavior of $c_{kl}(\omega)$ in the limit $\omega\to\infty$ can be obtained by integration by parts[17]

$$c(\omega) \sim \frac{C(0)}{i\omega} - \frac{1}{\omega^2}\left[\dot{C}(0) + \sum_r \Delta\dot{C}(t_r)e^{-i\omega t_r}\right], \tag{B3}$$

where $\Delta\dot{C}(t_r) = \dot{C}(t_r^+) - \dot{C}(t_r^-)$. Inserting this expression in Eq. (B2) we obtain

$$\sum_{l'} \phi_{kl'}(\omega)c_{l'l}(\omega) \sim -\frac{M_k}{i\omega}\left[\dot{C}(0) + \sum_r \Delta\dot{C}(t_r)e^{-i\omega t_r}\right]. \tag{B4}$$

On the other hand, since $\phi(\omega)$ should be bounded in the limit $\omega\to\infty$, we also have

$$\sum_{l'} \phi_{kl'}(\omega)c_{l'l}(\omega) \sim \phi_{kl}(\omega)M_k\frac{C_{ll}(0)}{i\omega}. \tag{B5}$$

Combining both expressions

$$\phi_{kl}(\omega) \sim -\frac{1}{C_{ll}(0)}\left[\dot{C}(0) + \sum_r \Delta\dot{C}(t_r)e^{-i\omega t_r}\right], \tag{B6}$$

in the limit $\omega\to\infty$. The inverse transform is given by Eq. (38).

APPENDIX C: CALCULATION OF THE MEMORY KERNEL

The Laplace transform of the autocorrelation function $V(s)$ is obtained from Eq. (52) as

$$v(s)=\int_0^\infty dt^* e^{-st^*}V(t^*)=V_0\frac{e^{-s}+s-1}{s^2}. \tag{C1}$$

Using the properties of the Laplace transform,[18] we can solve Eq. (49) for the Laplace transform of the memory kernel $\phi^*(s)$,

$$\phi^*(s)=\frac{V_0-sv(s)}{v(s)}=\frac{s(e^s-1)}{1+e^s(s-1)}. \tag{C2}$$

The limit $s\to 0$ gives the time integral of $\Phi^*(t^*)$,

$$\phi^*(0)=\int_0^\infty dt^*\Phi^*(t^*)=2. \tag{C3}$$

Let us define $\hat{\Phi}^*$ as the scaled memory kernel without the singularities (Appendix B)

$$\hat{\Phi}^*(t^*)=\Phi^*(t^*)-[\delta(t^*)-\delta(t^*-1)]. \tag{C4}$$

Then,

$$\hat{\phi}^*(s)=\frac{(e^s-1)^2}{e^s+e^{2s}(s-1)}. \tag{C5}$$

We can rewrite this expression as

$$\hat{\phi}^*(s+2)=\frac{1-2e^{-(s+2)}+e^{-2(s+2)}}{(s+1)\left(1+\dfrac{e^{-(s+2)}}{s+1}\right)}, \tag{C6}$$

and then use the Taylor expansion $(1+x)^{-1}=\Sigma_{k\geqslant 0}(-1)^k x^k$ with $x=\exp(-s-2)/(s+1)$, to obtain

$$\hat{\phi}^*(s)=(s-1)^{-1}-e^{-s}[(s-1)^{-2}+2(s-1)^{-1}]+\sum_{k\geqslant 2}(-1)^k e^{-sk}(s-1)^{-k-1}[1+2(s-1)+(s-1)^2]. \tag{C7}$$

This expression can be inverted easily term by term by using the inverse Laplace transform formulas of $(s+a)^{-n}$ and $\exp(-s\tau)f(s)$.[18] The final expression is given by Eq. (54).

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