Solution to the plateau problem in the Green-Kubo formula

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(Received 17 November 2018; published 19 February 2019)

Transport coefficients appearing in Markovian dynamic equations for coarse-grained variables have microscopic expressions given by Green-Kubo formulas. These formulas may suffer from the well-known plateau problem. The problem arises because the Green-Kubo running integrals decay as the correlation of the coarse-grained variables themselves. The usual solution is to resort to an extreme timescale separation, for which the plateau problem is minor. Within the context of Mori projection operator formulation, we offer an alternative expression for the transport coefficients that is given by a corrected Green-Kubo expression that has no plateau problem by construction. The only assumption is that the Markovian approximation is valid in such a way that transport coefficients can be defined, even in the case that the separation of timescales is not extreme.

DOI: 10.1103/PhysRevE.99.022126

I. INTRODUCTION

One important objective within nonequilibrium statistical mechanics is the derivation from the microscopic laws of motion of the atoms of the governing dynamics of a set of coarse-grained (CG) variables that describe the system at a mesoscopic or macroscopic level of description [1,2]. In this quest, the projection operator technique, as described in the textbook by Grabert [3], has proved to be an extremely useful tool. As discussed there, there are essentially three different types of projection operator theories, associated to the names of Mori [4], Zwanzig [5], and Kawasaki and Gunton [6], with increasing order of generality [3]. The Kawasaki-Gunton projection operator allows one to obtain nonlinear closed equations for the averages of the coarse-grained variables. The Zwanzig projector is a special case of the Kawasaki-Gunton projector when the selected variables are, instead of the CG variables themselves, the *distribution* of the CG variables. This results in a governing equation for the probability distribution of CG variables. Finally, a Mori projector is obtained from Zwanzig projector in near-equilibrium situations [3,7]. The resulting dynamic equations in Mori theory are linear and allow one to obtain simple equations not only for the averages of the CG variables but also for their correlation functions.

The projection operator technique provides closed and exact equations for the evolution of the averages or probabilities of the CG variables with only one assumption about the initial distribution of microstates, which are assumed to be distributed with a maximum entropy ensemble [3]. The exact equations of motion of the CG variables contain a reversible term which is local in time and an irreversible integrodifferential term describing memory about the past history of the CG variables. The memory kernel is defined in microscopic terms and it involves the so-called projected dynamics which is different, in general, from the usual unprojected Hamiltonian dynamics of the system.

When the selected CG variables are such that they display a clear separation of timescales in its dynamics, then it is possible to resort to the Markovian approximation, in which the memory kernel becomes proportional to a Dirac δ function in time. Such a separation of timescales happens, in general, when the evolution of the CG variables is the result of many minuscule and fast contributions. Under the Markovian approximation, the resulting governing dynamic equations are nonlinear differential equations for the nonequilibrium averages of the CG variables in the Kawasaki-Gunton projector or stochastic differential equations (SDE) in the Mori and Zwanzig projectors. Within the Markovian approximation one obtains the transport coefficients governing the irreversible part of the dynamics in terms of the time integral of correlation functions of the time derivatives of the CG variables. These formulas for transport coefficients are the celebrated Green-Kubo formulas [8,9].

The time derivatives in the memory kernel evolve under the projected dynamics. While there are recent attempts to compute the memory kernels from molecular dynamic (MD) simulations [10–12], the usual procedure is to approximate the projected dynamics with the unprojected Hamiltonian dynamics [5]. This substitution is usually justified in the limit of very large separation of timescales.

However, one annoying problem with the substitution of the projected dynamics with the unprojected dynamics is known as the plateau problem that refers to the fact that the Green-Kubo running integrals with unprojected dynamics do not have, in general, a well-defined plateau, unless an extremely large separation of timescales exists [1,13,14], which is not always the case. This induces a degree of ambiguity into the calculation of transport coefficients through MD simulations. In a recent example, Bocquet and Barrat [15,16] encountered this problem when computing the friction coefficient entering the slip length in fluid flowing past a solid wall. We have stumbled upon the plateau problem in our own research on hydrodynamics near walls and this has led us to reconsider this problem.

In the present paper, we offer a simple nontrivial solution to the plateau problem by proposing a new corrected Green-Kubo formula for the transport coefficients based on the

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unprojected dynamics and hence directly computable in MD. This new expression for the transport coefficients reduces to the standard Green-Kubo formula in the limit of large separation of timescales but corrects it in those situations where the separation of timescales is not extreme but the Markovian approximation already holds.

The paper is distributed as follows. In Sec. II we review Mori's theory that produce the exact generalized Langevin equation for the evolution of the CG variables. Section III considers the Markovian approximation and describes the plateau problem. We give in Sec. IV a solution to the plateau problem by correcting the unprojected Green-Kubo formula. Finally, in Sec. V, we summarize the situation and discuss at the light of the previous arguments some cases where the unprojected Green-Kubo formula does not suffer from the plateau problem.

II. MORI'S GENERALIZED LANGEVIN EQUATION

In this section we present a summary of Mori's theory [4] in order to set the notation. At a microscopic level of description we assume that the system is well described by classical mechanics and that the microscopic state $z = \{\mathbf{q}_i, \mathbf{p}_i, i = 1, \dots, N\}$ is given by the set of positions and momenta of all the N atoms in the system. Hamilton's equations can be written in a very compact form as $\dot{z}_t = i\mathcal{L}z_t$, where $i\mathcal{L}$ is the Liouville operator and z_t is the trajectory in phase space with initial condition z_0. This set of first-order differential equations has as a formal solution $z_t = \exp\{i\mathcal{L}t\}z_0$.

At a macroscopic level, we have the system described with a set of M coarse-grained (CG) variables that are phase functions arranged into a column vector $\hat{A}(z)$ with components $\hat{A}_\mu(z)$, $\mu = 1, \dots, M$. The corresponding row vector is denoted by $\hat{A}^T$, where T stands for transpose. Without losing generality, we will assume that the equilibrium average of the CG variables vanish. By denoting $\hat{A}(t) = \hat{A}(z_t)$, the evolution of these functions in phase space is given by

$$\frac{d}{dt}\hat{A}(t) = \exp\{i\mathcal{L}t\}i\mathcal{L}\hat{A}(z_0). \tag{1}$$

Mori's exact generalized Langevin equation (GLE) is an evolution equation for the set of CG variables given by the following theorem [1,2,4]:

$$\frac{d}{dt}\hat{A}(t) = -LC^{-1}(0)\hat{A}(t) - \int_0^t dt'\Gamma(t-t')C^{-1}(0)\hat{A}(t') + F^+(t), \tag{2}$$

where the following matrices have been introduced:

$$\begin{aligned} L &= \langle \hat{A}i\mathcal{L}\hat{A}^T\rangle \\ C(0) &= \langle \hat{A}\hat{A}^T\rangle \\ \Gamma(t) &= \langle F^+(t)F^{+T}(0)\rangle, \end{aligned} \tag{3}$$

where $\langle\cdots\rangle$ denotes an equilibrium average,

$$\langle\cdots\rangle \equiv \int dz\rho^{\rm eq}(z)\cdots, \tag{4}$$

and $\rho^{\rm eq}(z)$ is the equilibrium ensemble. The so-called projected force is given by

$$F^+(t) = \exp\{\mathcal{Q}i\mathcal{L}t\}\mathcal{Q}i\mathcal{L}\hat{A}. \tag{5}$$

The projection operator $\mathcal{Q}$ is defined as $\mathcal{Q} = 1 - \mathcal{P}$, where $\mathcal{P}$ is Mori's projector whose effect on an arbitrary phase function $\hat{F}(z)$ is

$$\mathcal{P}\hat{F}(z) = \langle\hat{F}\rangle + \langle\hat{F}\hat{A}^T\rangle C^{-1}(0)\hat{A}(z). \tag{6}$$

The Mori projector (6) satisfies that $\mathcal{P}\hat{A} = \hat{A}$ and transforms an arbitrary function of phase space into a linear combination of the CG variables. The projected forces have zero mean and are uncorrelated from previous values of the CG variables, that is,

$$\begin{aligned} \langle F^+(t)\rangle &= 0 \\ \langle\hat{A}F^+(t)\rangle &= 0 \quad t \geqslant 0. \end{aligned} \tag{7}$$

The equilibrium time correlation matrix of the CG variables is

$$C(t) = \langle\hat{A}(t)\hat{A}^T\rangle. \tag{8}$$

If we multiply the exact equation (2) with $\hat{A}^T(z)$ and average over the equilibrium ensemble, then we obtain a closed and exact equation for the correlation matrix of the CG variables,

$$\frac{d}{dt}C(t) = -LC^{-1}(0)C(t) - \int_0^t dt'\Gamma(t-t')C^{-1}(0)C(t'). \tag{9}$$

The GLE (2) allows one to obtain not only an equation for the correlation of the CG variables but also an equation for their averages. If we multiply (2) with an initial ensemble $\rho_0(z)$ and integrate over the microstates z we obtain

$$\frac{d}{dt}a(t) = -LC^{-1}(0)a(t) - \int_0^t dt'\Gamma(t-t')C^{-1}(0)a(t'), \tag{10}$$

where the time-dependent average of the CG variables is defined as

$$a(t) = \int dz\rho_0(z)\exp\{i\mathcal{L}t\}\hat{A}(z) \tag{11}$$

and we have assumed that the average of the projected force with respect to the initial ensemble vanishes, i.e.,

$$\int dz\rho_0(z)\exp\{\mathcal{Q}i\mathcal{L}t\}\mathcal{Q}i\mathcal{L}\hat{A}(z) = 0. \tag{12}$$

Note that in deriving (2) one assumes that the dynamics is given by a time-independent Hamiltonian with a well-defined equilibrium ensemble $\rho_{\rm eq}(z)$. Therefore, both (9) and (10) describe the evolution of correlations and averages toward their equilibrium values.

III. THE MARKOVIAN APPROXIMATION

The Markovian approximation assumes that there exists a time-independent *friction matrix* M^*, that contains the transport coefficients of the CG level of description such that the linear integrodifferential term in Eq. (9) can be approximated by a memoryless term, also linear in the correlation matrix

$$\int_0^t dt'\Gamma(t-t')C^{-1}(0)C(t') \simeq M^*C^{-1}(0)C(t). \tag{13}$$

The Markov approximation (13) in the GLE (2) implies the following evolution equation for the CG variables:

$$\frac{d}{dt}\hat{A}(t) = -\Lambda^*\hat{A}(t) + F^+(t), \tag{14}$$

where the *relaxation matrix* Λ^* is defined as

$$\Lambda^* \equiv (L + M^*)C^{-1}(0). \tag{15}$$

The approximation (13) is equivalent to take

$$\Gamma(t) \approx M^*\delta^+(t), \tag{16}$$

where the Dirac δ function $\delta^+(t)$ is normalized as

$$\int_0^\infty dt\delta^+(t) = 1. \tag{17}$$

Under the Markovian approximation, Eq. (16) implies that the projected force is δ correlated in time. As a consequence, the ordinary differential equation (14) should be interpreted as an SDE for times larger than the correlation of $F^+(t)$.

By multiplying (14) with an initial ensemble $\rho_0(z)$ satisfying (12) we obtain the following Markovian equation for the averages:

$$\frac{d}{dt}a(t) = -\Lambda^* a(t). \tag{18}$$

By multiplying (14) with $\hat{A}(0)$ and averaging over initial conditions sampled from the equilibrium ensemble, one obtains the evolution equation of the correlation matrix under the Markovian approximation,

$$\frac{d}{dt}C(t) = -\Lambda^* C(t). \tag{19}$$

The form of (18) and (19) illustrates Onsager's regression hypothesis, which states that (correlations of) fluctuations decay in the same way as the averages. Equations (18) and (19) show that the transport coefficients that appear in the transport equation for the averages are the same as the transport coefficients governing the correlations of the fluctuations in equilibrium.

The solution of (19) is given by the exponential matrix,

$$C(t) = \exp\{-\Lambda^* t\}C(0). \tag{20}$$

This is the main prediction of Mori theory that states that for a linear Markovian theory the only possibility for a correlation is to decay in an exponential matrix way. This does not mean that the elements of the correlation matrix $C(t)$ decay as $e^{-\alpha t}$, because they are, in fact, the sum of many exponential terms that may lead even to quasialgebraic decays of correlations, as in the case of hydrodynamics.

We remark that the Markovian Eq. (19) cannot hold at very short times, because at $t = 0$ the exact equation (9) implies

$$\frac{d}{dt}C(0) = -L, \tag{21}$$

which is only possible in (19) if $M^* = 0$. This paradoxical result can also be obtained from Eq. (13) because if we set $t = 0$ in that equation, then we obtain again $M^* = 0$. Therefore, we expect (19) to hold only after a time $t = \tau$ larger than the decay of the memory kernel. This is a general feature of the Markovian approximation showing that correlations will decay in an exponential, Markovian way only after the time τ beyond which memory is lost. The value of τ should be explicitly measured in any procedure to validate the Markovian approximation.

The usual rationale for justifying the Markovian approximation (13) goes as follows [1,3]. The memory kernel $\Gamma(t - t')$ is given in terms of a correlation function that it is assumed to decay in a typical molecular timescale. On the other hand, it is assumed that the timescale of evolution of the CG variables is much larger than this molecular time and, therefore, within the memory integral $C(t')$ does not change appreciably and we may approximate $C(t') \simeq C(t)$. Therefore, we have

$$\int_0^t dt'\Gamma(t - t')c(t') \simeq \int_0^t dt'\Gamma(t - t')c(t) = M^+(t)c(t), \tag{22}$$

where we have introduced the *projected* Green-Kubo running integral

$$M^+(t) \equiv \int_0^t dt'\Gamma(t') = \int_0^t dt'\langle(\exp\{\mathcal{Q}i\mathcal{L}t\}\mathcal{Q}i\mathcal{L}\hat{A})\mathcal{Q}i\mathcal{L}\hat{A}^T\rangle \tag{23}$$

and the normalized correlation matrix as

$$c(t) = C^{-1}(0)C(t) \tag{24}$$

that at $t = 0$ becomes the identity matrix. The Markovian assumption relies on a separation of timescales. For some model systems (hydrodynamics of unconfined fluids [17] or Brownian particles [18]), one can justify rigorously such a separation of timescales as some parameter becomes small (wavelength or ratio of masses) and then usually the order of the limits in the parameter, time, and system size plays an important role. In the present paper, we simply assume that the Markovian approximation is a sufficiently good one. We will also consider the *unprojected* Green-Kubo running integral

$$M(t) \equiv \int_0^t dt'\langle(\exp\{i\mathcal{L}t'\}i\mathcal{L}\hat{A})\mathcal{Q}i\mathcal{L}\hat{A}^T\rangle, \tag{25}$$

where we distinguish $M(t)$ from $M^+(t)$ because the former involves the unprojected Hamiltonian dynamics $\exp\{i\mathcal{L}t\}\hat{A}$, while the later involves the projected dynamics $\exp\{\mathcal{Q}i\mathcal{L}t\}\hat{A}$. In both $M^+(t)$ and $M(t)$ we recognize a total time derivative that allows us to perform the time integral explicitly so we have the alternative forms

$$M^+(t) = \langle(\exp\{\mathcal{Q}i\mathcal{L}t\}\hat{A})\mathcal{Q}i\mathcal{L}\hat{A}^{+T}\rangle$$
$$M(t) = \langle(\exp\{i\mathcal{L}t\}\hat{A})\mathcal{Q}i\mathcal{L}\hat{A}^{+T}\rangle. \tag{26}$$

Because the projected dynamics is in general more difficult to compute than the unprojected dynamics, one usually resorts to a large separation of timescales in order to approximate the projected dynamics with the unprojected one [5,17,18]. For the Markovian approximation (13) to hold, the matrix $M^+(t)$ in (22) needs to become the time-independent matrix M^*. Note that $M^+(t)$ vanishes at $t = 0$ and after a time τ should plateau to a constant value. If one approximates $M^+(t) \simeq M(t)$, then this would require that $M(t)$ would have a plateau itself. However, this is not true because, for an ergodic system, correlations computed with the unprojected dynamics decay to zero,

$$\lim_{t\to\infty} M(t) = \lim_{t\to\infty} \langle(\exp\{i\mathcal{L}t\}\hat{A})\mathcal{Q}i\mathcal{L}\hat{A}^{+T}\rangle = \langle\hat{A}\rangle\langle\mathcal{Q}i\mathcal{L}\hat{A}^{+T}\rangle = 0. \quad (27)$$

This problem was recognized by Kirkwood as the so-called plateau problem [13,14] and limits the use of the unprojected Green-Kubo formula $M(t)$ for the calculation of transport coefficients. While $M(t)$ does not have a plateau, $M^{+}(t)$ may actually have a plateau depending essentially on the spectrum of the projected evolution operator $\exp\{\mathcal{Q}i\mathcal{L}t\}$. If $|\hat{\psi}_\mu\rangle$ are the eigenvectors of corresponding eigenvalues λ_μ of $\mathcal{Q}i\mathcal{L}$, then the operator $\exp\{\mathcal{Q}i\mathcal{L}t\}$ admits the eigendecomposition

$$\exp\{\mathcal{Q}i\mathcal{L}t\} = \sum_\mu \exp\{-\lambda_\mu t\}|\hat{\psi}_\mu\rangle\langle\hat{\psi}_\mu| \quad (28)$$

in Dirac ket and bra notation, where the inner product is defined with the equilibrium ensemble. The matrix $M^{+}(t)$ then has the form

$$M^{+}(t) = \sum_\mu \exp\{-\lambda_\mu t\}\langle\hat{A}|\hat{\psi}_\mu\rangle\langle\hat{\psi}_\mu|\mathcal{Q}i\mathcal{L}\hat{A}^{+T}\rangle. \quad (29)$$

Note that the equilibrium eigenvector $|\psi_0\rangle$ has zero eigenvalue. For the ergodic unprojected dynamics this is the only eigenvector of null eigenvalue but for the projected dynamics, the zero eigenvalue may be degenerate. In other words, the projected dynamics may have other conserved variables in addition to the Hamiltonian that render the evolution nonergodic with respect to the equilibrium measure. Assume, for example, that there is only one eigenvector $|\psi_1\rangle$ different from the equilibrium one $|\psi_0\rangle$ of null eigenvalue. Then the infinite time limit is

$$M^{*} = \lim_{t\to\infty} M^{+}(t) = \langle\hat{A}|\hat{\psi}_1\rangle\langle\hat{\psi}_1|\mathcal{Q}i\mathcal{L}\hat{A}^{+T}\rangle. \quad (30)$$

This is an expression for the transport coefficients M^* in terms of equilibrium averages. Of course, the calculation of the spectrum of $\mathcal{Q}i\mathcal{L}$, or the identification of the additional conserved quantities of the projected dynamics, is not an easy task in general but it has been carried out for a model system of a Brownian particle in a double-well potential [19]. Also, under a perturbation scheme, the time integral of the correlation of the projected force of a Brownian particle has been carried out showing a nonvanishing plateau [18]. It is believed that the projected Green-Kubo matrix $M^{+}(t)$ has a well-defined plateau in general. In summary, the projected Green-Kubo matrix $M^{+}(t)$ may have a well-defined plateau but it is difficult to evaluate it in order to get transport coefficients from direct MD simulations, while the unprojected Green-Kubo matrix $M(t)$ is easily obtained from MD simulations but it usually suffers from the plateau problem giving ambiguous values for the transport coefficients.

IV. A CORRECTED GREEN-KUBO FORMULA WITH NO PLATEAU PROBLEM

We now consider a procedure that allows one to obtain the friction matrix M^* from a modified version of the Green-Kubo formula even when no plateau exists, *provided* the dynamics is Markovian in such a way that correlations of CG variables obey (19).

The action of Mori projector operator on the phase function $i\mathcal{L}\hat{A}$ is

$$\mathcal{Q}i\mathcal{L}\hat{A} = i\mathcal{L}\hat{A} - \langle i\mathcal{L}\hat{A}\hat{A}^T\rangle\langle\hat{A}\hat{A}^T\rangle^{-1}\hat{A} = i\mathcal{L}\hat{A} + LC^{-1}(0)\hat{A} \quad (31)$$

and, therefore, the unprojected Green-Kubo matrix (25) becomes

$$M(t) = \int_0^t dt'\langle i\mathcal{L}\hat{A}(t')i\mathcal{L}\hat{A}^T\rangle + LC^{-1}(0)\int_0^t dt'\langle\hat{A}(t')i\mathcal{L}\hat{A}^T\rangle. \quad (32)$$

By using the identity $\frac{d}{dt}\hat{A}(z_t) = i\mathcal{L}\hat{A}(z_t)$ and the fact that the Liouville operator satisfies $\langle\hat{A}(t)i\mathcal{L}\hat{A}^T\rangle = -\langle i\mathcal{L}\hat{A}(t)\hat{A}^T\rangle$ we obtain

$$M(t) = \int_0^t dt'\frac{d}{dt'}\langle\hat{A}(t')i\mathcal{L}\hat{A}^T\rangle - LC^{-1}(0)\int_0^t dt'\frac{d}{dt'}\langle\hat{A}(t')\hat{A}^T\rangle. \quad (33)$$

We may integrate the time derivatives, obtaining

$$M(t) = \langle\hat{A}(t)i\mathcal{L}\hat{A}^T\rangle - \langle\hat{A}(0)i\mathcal{L}\hat{A}^T\rangle - LC^{-1}(0)\langle\hat{A}(t)\hat{A}^T\rangle + LC^{-1}(0)\langle\hat{A}(0)\hat{A}^T\rangle. \quad (34)$$

The second and fourth terms in the right-hand side cancel each other and we finally obtain

$$M(t) = -\frac{d}{dt}C(t) - Lc(t), \quad (35)$$

where the normalized correlation matrix $c(t)$ is defined in (24). This is a mathematical identity that relates the unprojected Green-Kubo matrix $M(t)$ with the correlation matrix $C(t)$ of the CG variables. It shows that $M(t)$ cannot have a plateau for an ergodic system where $\lim_{t\to\infty} C(t) = 0$.

If we now assume that the correlation function $C(t)$ obeys the Markovian dynamics (19) with (15), then Eq. (35) becomes

$$M(\tau) \simeq M^* \cdot c(\tau). \quad (36)$$

This expression shows that the unprojected Green-Kubo matrix decays as the correlation of the CG variables. Although the time integral in the left-hand side of (36) has no plateauit is still possible to infer the friction matrix M^* by multiplying (36) with the inverse of the normalized correlation, leading to

$$M^* = \int_0^\tau dt\langle\mathcal{Q}i\mathcal{L}\hat{A}(t)i\mathcal{L}\hat{A}^T\rangle c^{-1}(\tau). \quad (37)$$

This new corrected Green-Kubo formula (37) allows one to calculate the friction matrix M^* from MD simulations and does not suffer from the plateau problem by construction, provided the dynamic is Markovian. Equation (37) is the main result of the present paper. Equation (37) is conceptually pleasing as it displays in very graphical terms why the unprojected Green-Kubo integral (25) has no plateau—in fact, it decays as the correlation matrix itself. It is obvious that

(37) cannot be true at $\tau = 0$ as this would imply $M^* = 0$. However, after a time in the molecular timescales, the right-hand side of Eq. (37) should be time independent provided that the Markovian description (19) is valid. In the limit of very large separation of timescales, when $M(t)$ has a "fast-up, slow-down" structure, we may assume that the normalized correlation matrix is very close to its value at $t = 0$ which is just the identity matrix, that is, $c^{-1}(\tau) \simeq 1$. In this case, we recover from (37) the unprojected Green-Kubo prescription (25) for the transport coefficients.

In summary, Eq. (37) shows a way to infer the friction matrix M^* in the Markovian equation (14) from a time integral even when it is not possible to identify a well-defined plateau in the unprojected Green-Kubo formula (25).

The mathematics behind the derivation of (37) should not obscure the essential procedure that we have followed here. We have inferred M^* from the fact that the correlation matrix $C(t)$ obeys the Markovian equation (19). In this respect, an alternative, *entirely equivalent*, and perhaps simpler way to obtain the friction matrix M^* is by introducing the time-dependent matrix

$$\Lambda(t) \equiv -\frac{d}{dt}C(t)C^{-1}(t). \tag{38}$$

From Eq. (19), if the Markov assumption is correct, then, after a molecular time τ, $\Lambda(t)$ should become a time-independent matrix Λ^*,

$$\lim_{t\to\infty} \Lambda(t) = \Lambda^*. \tag{39}$$

Therefore, from (15) we can obtain the friction matrix as

$$M^* = -L + \Lambda^* C(0). \tag{40}$$

In some situations, however, it is preferable to obtain the friction matrix M^* from the corrected Green-Kubo expression (37) than from (40) because the Green-Kubo expression involves the time derivative $i\mathcal{L}\hat{A}$ that may induce special structure to the matrix M^*. This is the case of hydrodynamics near walls that we discuss elsewhere.

The method to obtain the matrix Λ^* from the plateau of $\Lambda(t)$ in (38) needs high-quality statistics for $C(t)$ and $\frac{d}{dt}C(t)$. The same is true for the new Green-Kubo formulas (37). In fact, $C(t)$ is an exponentially decaying matrix, and $C^{-1}(t)$ is an exponentially growing matrix. At very large times, any statistical error will be exponentially amplified. This means also that τ should be, in practice, as small as possible in order to detect a plateau value for $\Lambda(t)$ and for which statistical errors have not yet been amplified to a catastrophic level.

V. DISCUSSION

In this work, we have addressed the plateau problem that appears in the expression of transport coefficient in terms of the unprojected Green-Kubo running integrals. When the dynamic of the CG variables is Markovian, but with no extreme separation of timescales, the decay of the unprojected Green-Kubo running integral does not allow us to determine unambiguously the value of the transport coefficients. We have proposed a correction to the unprojected Green-Kubo expression that does has a well-defined infinite time limit and allows one to directly measure transport coefficients from MD simulations.

As a final remark, we note that there are situations in which the unprojected Green-Kubo running integral indeed displays a well-defined plateau. This can only happen if some of the assumptions made in the argument based on the mathematical identity (35) do not hold.

For example, if we take as CG variable the position $\mathbf{r}(t)$ of a tagged particle in a fluid, then we have the well-known mathematical identity

$$\frac{1}{2}\frac{d}{dt}\langle(\mathbf{r}(t)-\mathbf{r}(0))^2\rangle = \int_0^t dt'\langle\mathbf{v}(t)\cdot\mathbf{v}\rangle, \tag{41}$$

where $\mathbf{v}(t)$ is the velocity of the particle. This equation would correspond to (35). It is clear that because the root-mean-square displacement is a "correlation" that does not decay to zero, the infinite time integral of the right-hand side does not need to decay to zero. It actually gives a nonzero value given by the self-diffusion coefficient.

Another example can be found whenever we consider a conserved quantity. Consider, for example, the momentum density correlation function in an infinite system in Fourier space,

$$\hat{\mathbf{g}}_{\mathbf{k}} = \sum_i^N \mathbf{p}_i \exp\{i\mathbf{k}\cdot\mathbf{r}_i\}. \tag{42}$$

The correlation matrix function is

$$\mathbf{C}(k,t) = \langle\hat{\mathbf{g}}_{\mathbf{k}}(t)\hat{\mathbf{g}}_{-\mathbf{k}}\rangle. \tag{43}$$

Equation (35) now becomes

$$\partial_t C(k,t) = -\int_0^t dt'\langle i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{k}}(t)i\mathcal{L}\hat{\mathbf{g}}_{-\mathbf{k}}\rangle. \tag{44}$$

The action of the Liouville operator is well known,

$$i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{k}} = -i\mathbf{k}\cdot\hat{\boldsymbol{\sigma}}_{\mathbf{k}}, \tag{45}$$

where $\hat{\boldsymbol{\sigma}}_{\mathbf{k}}$ is the Fourier transform of the Irving-Kirkwood stress tensor. Therefore, we have

$$\partial_t C(k,t) = \mathbf{k}\cdot\boldsymbol{\Theta}(k,t)\cdot\mathbf{k}, \tag{46}$$

where the fourth-order viscosity tensor is defined as the time integral of the stress correlation function

$$\boldsymbol{\Theta}(k,t) = \int_0^t dt'\langle\boldsymbol{\sigma}_{\mathbf{k}}(t)\boldsymbol{\sigma}_{-\mathbf{k}}\rangle. \tag{47}$$

Equation (46) is what corresponds now to (35) and the argument is that because the correlation $C(k,t)$ decays, the viscosity tensor $\boldsymbol{\Theta}(k,t)$ *must* decay toward zero. This is true in general but fails for the very special value of $\mathbf{k} = \mathbf{0}$. At this value, we see that the left-hand side is zero because, for $\mathbf{k} = \mathbf{0}$, $\hat{\mathbf{g}}_{\mathbf{k}=\mathbf{0}}$ is the total momentum of the system. As we assume that the equilibrium average of the CG variables vanish, we are implicitly assuming that we are in the center-of-mass reference frame of the fluid, for which total momentum vanishes. Therefore, the right-hand side of (46) vanishes at $\mathbf{k} = 0$. At the same time, for $\mathbf{k} = 0$ the Irving-Kirkwood stress tensor becomes the total stress tensor of the fluid

$$\hat{\boldsymbol{\sigma}}^{\alpha\beta}_{\mathbf{k}=\mathbf{0}} = \sum_i \mathbf{p}_i \mathbf{v}_i + \frac{1}{2}\sum_{ij} \mathbf{r}_{ij}\mathbf{F}_{ij}, \tag{48}$$

and the isotropic fourth-order viscosity tensor $\boldsymbol{\Theta}(0,t)$ has only two independent components given by the unprojected Green-Kubo expressions for the shear and bulk viscosities. Therefore, for $\mathbf{k}=\mathbf{0}$, Eq. (46) takes the trivial form $\mathbf{0} = \mathbf{0}\cdot\boldsymbol{\Theta}(0,t)\cdot\mathbf{0}$ and $\boldsymbol{\Theta}(0,t)$ is no longer constrained to decay to zero anymore and may display a well-defined plateau, as it is observed empirically. However, for values of $\mathbf{k} \neq 0$, the resulting unprojected Green-Kubo formula for the (nonlocal) viscosities suffer necessarily from the plateau problem and require the correction presented in this paper for its actual evaluation. In forthcoming publications we will show how nonlocal transport coefficients for *discrete* hydrodynamics with and without confining walls can be unambiguously measured by using the new corrected Green-Kubo formula.

ACKNOWLEDGMENTS

We thank Aleks Donev, Rafael Delgado-Buscalioni, Friederike Schmid, Gerhard Jung, and Diego Camargo for useful discussions. This research is supported by the Ministerio de Economía y Competitividad of Spain (MINECO) under Grants No. FIS2013-47350-C5-3-R and No. FIS2017-86007-C3-3-P.

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