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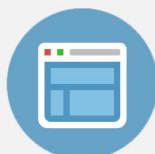
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Molecular dynamics algorithms and hydrodynamic screening

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In this paper molecular dynamics simulations of a system of Brownian particles in an explicit bath of solvent particles are considered. Generalized algorithms (Langevin simulations), in which *both* the Brownian particles and the solvent particles are artificially coupled to a heat bath, are analyzed for their dynamical properties on long length scales. Although such a dynamic is clearly unphysical, its analysis is useful for two reasons: The Langevin algorithm is frequently applied in an *ad hoc* fashion, and the deviation of its dynamical properties from the physical Hamiltonian case can be made arbitrarily small by choosing a sufficiently weak coupling to the heat bath. By a direct application of the Mori–Zwanzig projection operator formalism it is shown that the violation of global momentum conservation results in an artificial screening of the hydrodynamic interactions, with a screening length proportional to the inverse square root of the friction constant of the algorithm. The result is formally similar to expressions given in phenomenological theories of hydrodynamic screening in semidilute polymer solutions.

I. INTRODUCTION

Molecular dynamics (MD) simulations nowadays are a powerful tool for analyzing the properties of classical statistical mechanical systems. The approach is, in principle, very attractive: Simply solving Newton's equations of motion numerically provides us, *per definition*, both with correct static averages in the microcanonic ensemble, as well as with correct dynamical correlation functions (provided that the system has sufficient ergodicity properties).

However, there has been a growing trend in the community to modify the equations of motion, e.g., by coupling the system to an additional degree of freedom,^{1,2} or to a heat bath by means of a Langevin type of simulation.^{3–7} This is usually done in order to run the simulation in a different thermodynamic ensemble, which may be more suitable for the system in consideration. Sometimes, however, one is simply forced to introduce such modifications to overcome the inherent instability of microcanonical MD algorithms, which is due to the discretization errors induced by the finite time step. This problem is particularly severe for systems with long relaxation times that require long runs, and was practically encountered by the author in the context of a MD simulation of a long polymer chain in a solvent.⁸ The results of this simulation will be presented in a subsequent publication.⁸

A modification of Newton's equations usually poses no problem as far as static properties are concerned: As soon as the algorithm generates a well-defined thermodynamic ensemble, one can rely on the equivalence of ensembles in the thermodynamic limit of infinite system size. However, the dynamical properties of the system may be changed drastically—which means no less than giving up one advantage of the MD method as compared to Monte Carlo simulations.

The purpose of this paper is to demonstrate how transport theory can be used to estimate the influence of modifications of algorithms on the dynamical correlation functions. While the approach is, in principle, rather general, attention will be focused on the hydrodynamic interaction of Brownian particles immersed in a system of solvent particles, the latter being taken into account explicitly in the simulation. We compare a strictly microcanonical MD with a standard Langevin simulation, where each particle (Brownian particle *and* solvent particle) is artificially coupled to friction and noise independently. It should be emphasized that we take an “algorithmic” standpoint of view: We do not ask about a physical origin of the friction and noise of the algorithm, but rather view it as introduced by the programmer in an *ad hoc* fashion, as has been common practice in many studies. Such a dynamic is obviously unphysical, but since the correct Hamiltonian dynamics is recovered in the limit of vanishing friction constant (see below), it is interesting to quantitatively study the deviations from the correct behavior for small friction constants. However, it should be noticed that a choice of too small a friction constant results in a loss of those properties for which the heat bath was originally introduced: The stabilization effect takes place on too long a time scale, and the system thermalizes too slowly.

The important point is that one does not only have to discuss these modifications on a local scale (i.e., in practice, ask for the shift in the particle friction coefficient due to algorithmic noise), but also on the global hydrodynamic scale, where the effects are much more crucial: The algorithmic noise introduces an unphysical violation of global momentum conservation, resulting in a modification of the Navier–Stokes equation and its Green's function, the Oseen tensor.

In Sec. II, the standard Mori–Zwanzig projection operator formalism^{9–11} is straightforwardly generalized to the case of stochastic dynamics. The formula derived there is

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then used in Sec. III to calculate the autocorrelation function of the transversal part of the velocity flow field, as is usually done to derive the linearized incompressible Navier–Stokes equation. This finally yields an expression for the hydrodynamic interaction tensor, following the approach given in the book by de Gennes.¹² It turns out that the Langevin noise changes the $1/r$ Oseen behavior to a screened Yukawa-like interaction with a screening length,

$$l = \sqrt{\frac{\eta}{\xi n}}, \quad (1)$$

where η is the shear viscosity, n is the particle number density, and ξ is the friction constant by which every particle is coupled to the heat bath. This result is formally very similar to analogous expressions derived in phenomenological theories for the hydrodynamic screening of semidilute polymer solutions.¹³ The practical consequence (Sec. IV, conclusions) is that *modified MD algorithms must be used with great care when data are interpreted to analyze dynamical properties* of the system. In particular, dramatic effects are always to be expected if hydrodynamic effects are important and the algorithm changes global conservation laws.

II. THE MORI-ZWANZIG PROJECTION OPERATOR FORMALISM

The approach and notation of this section is rather close to that of Ref. 9.

We assume that the stochastic dynamics of the simulation is described by a Langevin equation, or, equivalently, by a Fokker–Planck process¹⁴ on a state space with state variables \mathbf{x} . The equation of motion, in the Fokker–Planck picture, then reads as

$$\frac{\partial}{\partial t} P(\mathbf{x}, t | \mathbf{x}_0, 0) = -i\mathcal{L}(\mathbf{x})P(\mathbf{x}, t | \mathbf{x}_0, 0), \quad (2)$$

where $P(\mathbf{x}, t | \mathbf{x}_0, 0)$ is the conditional probability density for a transition from \mathbf{x}_0 at time 0 to \mathbf{x} at time t , and $-i\mathcal{L}$ is the dynamical operator,

$$-i\mathcal{L} = -\sum_i \frac{\partial}{\partial x_i} D_i^{(1)}(\mathbf{x}) + \sum_{ij} \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} D_{ij}^{(2)}(\mathbf{x}). \quad (3)$$

$D^{(1)}$ is the drift coefficient vector resulting from the deterministic part, while $D^{(2)}$ describes the stochastic part. Note that the case of deterministic dynamics (e.g., microcanonical MD) is included as the special case $D^{(2)}=0$. The simple probability density $\rho(\mathbf{x}, t)$ for the occurrence of state \mathbf{x} at time t satisfies the same equation of motion,

$$\frac{\partial}{\partial t} \rho(\mathbf{x}, t) = -i\mathcal{L}(\mathbf{x})\rho(\mathbf{x}, t), \quad (4)$$

which, in equilibrium, is

$$-i\mathcal{L}\rho = 0. \quad (5)$$

A molecular dynamics simulation that couples all particles of mass m to a viscous background by a friction constant ξ is specified by the operator

$$-i\mathcal{L} = -i\mathcal{L}_H - i\mathcal{L}_N, \quad (6)$$

with

$$-i\mathcal{L}_H = -\sum_i \left(\frac{\partial}{\partial \mathbf{r}_i} \cdot \frac{\mathbf{p}_i}{m} + \frac{\partial}{\partial \mathbf{p}_i} \cdot \mathbf{F}_i \right) \quad (7)$$

and

$$-i\mathcal{L}_N = \sum_i \left(\frac{\partial}{\partial \mathbf{p}_i} \cdot \frac{\xi}{m} \mathbf{p}_i + \xi k_B T \frac{\partial}{\partial \mathbf{p}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right), \quad (8)$$

acting on the phase space of positions \mathbf{r}_i and momenta \mathbf{p}_i . \mathcal{L}_H describes the Hamiltonian part of the dynamics, \mathbf{F}_i being the force acting on particle i , while \mathcal{L}_N is the noise part that fixes the temperature T —the equilibrium distribution function is just the canonical one:

$$\rho = Z^{-1} \exp(-\beta \mathcal{H}), \quad (9)$$

where Z is the partition function, $\beta = 1/k_B T$, and \mathcal{H} is the Hamiltonian. Strictly deterministic dynamics is recovered in the case $\xi = 0$.

The Mori–Zwanzig formalism is a convenient method to derive dynamical equations for the equilibrium time correlation functions of slowly fluctuating dynamical variables, which we shall denote with $A_i(\mathbf{x})$ (functions on the state space). In a somewhat sloppy notation, we use $A_i(t)$ for $A_i[\mathbf{x}(t)]$, i.e., for the value A_i has at time t because the system is in state \mathbf{x} at that time. The Laplace transform of the correlation function then reads as

$$\begin{aligned} C_{ij}(z) &:= \int_0^\infty dt e^{izt} \langle A_i^*(0) A_j(t) \rangle = \int_0^\infty dt e^{izt} \int d\mathbf{x} \int d\mathbf{x}_0 A_i^*(\mathbf{x}_0) A_j(\mathbf{x}) P(\mathbf{x}, t | \mathbf{x}_0, 0) \rho(\mathbf{x}_0) \\ &= \int_0^\infty dt e^{izt} \int d\mathbf{x} \int d\mathbf{x}_0 A_j(\mathbf{x}) A_i^*(\mathbf{x}_0) e^{-i\mathcal{L}t} \delta(\mathbf{x} - \mathbf{x}_0) \rho(\mathbf{x}_0) \\ &= \int_0^\infty dt e^{izt} \int d\mathbf{x} [e^{+i\mathcal{L}t} A_j(\mathbf{x})] A_i^*(\mathbf{x}) \rho(\mathbf{x}) \\ &= \int d\mathbf{x} \rho(\mathbf{x}) A_i^*(\mathbf{x}) i(z + \mathcal{L}^\dagger)^{-1} A_j(\mathbf{x}) = \langle A_i | i(z + \mathcal{L}^\dagger)^{-1} | A_j \rangle. \end{aligned} \quad (10)$$

Here we have made use of the formal solution of Eq. (2) and introduced the scalar product,

$$\langle X|Y\rangle = \int dx X^*(x)Y(x)\rho(x). \quad (11)$$

\mathcal{L}^\dagger is the adjoint operator to \mathcal{L} , not with respect to the scalar product $\langle X|Y\rangle$, but with respect to the standard scalar product with unit weight function.

Denoting the inverse matrix of $\langle A_i|A_j\rangle$ with α_{ij} ,

$$\sum_j \alpha_{ij}\langle A_j|A_k\rangle = \delta_{ik}, \quad (12)$$

$$\mathcal{P} := \sum_{ij} \alpha_{ij}|A_i\rangle\langle A_j| \quad (13)$$

is the projection operator onto the space of the slow variables, while

$$\mathcal{Q} := 1 - \mathcal{P}, \quad (14)$$

projects onto the orthogonal space. Now the operator identity

$$(\mathcal{L} + \mathcal{Y})^{-1} = \mathcal{L}^{-1} - \mathcal{L}^{-1}\mathcal{Y}(\mathcal{L} + \mathcal{Y})^{-1}, \quad (15)$$

allows the rewriting

$$\begin{aligned} (z + \mathcal{L}^\dagger)^{-1} &= [(z + \mathcal{L}^\dagger\mathcal{Q}) + \mathcal{L}^\dagger\mathcal{P}]^{-1} \\ &= (z + \mathcal{L}^\dagger\mathcal{Q})^{-1} - (z + \mathcal{L}^\dagger\mathcal{Q})^{-1}\mathcal{L}^\dagger\mathcal{P} \\ &\quad \times (z + \mathcal{L}^\dagger)^{-1}. \end{aligned} \quad (16)$$

Insertion into Eq. (10) yields, after using

$$\begin{aligned} (z + \mathcal{L}^\dagger\mathcal{Q})^{-1}|A_j\rangle &= \frac{1}{z} \left[1 - \frac{\mathcal{L}^\dagger\mathcal{Q}}{z} + \left(\frac{\mathcal{L}^\dagger\mathcal{Q}}{z}\right)^2 \right. \\ &\quad \left. - + \dots \right] |A_j\rangle = \frac{1}{z} |A_j\rangle, \end{aligned} \quad (17)$$

$$\begin{aligned} C_{ij}(z) &= \frac{i}{z} \langle A_i|A_j\rangle - i \sum_{kl} \alpha_{kl} \langle A_i| (z + \mathcal{L}^\dagger\mathcal{Q})^{-1} \\ &\quad \times \mathcal{L}^\dagger|A_k\rangle \langle A_l| (z + \mathcal{L}^\dagger)^{-1} |A_j\rangle. \end{aligned} \quad (18)$$

Furthermore, one can expand

$$C_{ii}(0) = - \frac{\langle A_i|A_i\rangle^2}{\langle A_i|i\mathcal{L}^\dagger|A_i\rangle + \int_0^\infty dt \langle A_i|i\mathcal{L}^\dagger\mathcal{Q} \exp(i\mathcal{L}^\dagger t) \mathcal{Q} i\mathcal{L}^\dagger|A_i\rangle}. \quad (22)$$

III. THE DIFFUSION TENSOR

We consider the Brownian motion of a system of slow particles immersed in a solvent. In such a system so-called “hydrodynamic interactions” occur, which means that the stochastic displacements of the Brownian particles are correlated because of fast momentum transport through the solvent from one Brownian particle to the other. For this reason, the concept of a diffusion constant for a single Brownian particle has to be generalized to a diffusion ten-

$$\begin{aligned} (z + \mathcal{L}^\dagger\mathcal{Q})^{-1} &= \frac{1}{z} - \frac{1}{z} \mathcal{L}^\dagger\mathcal{Q} (z + \mathcal{L}^\dagger\mathcal{Q})^{-1} \\ &= \frac{1}{z} - \frac{1}{z} \mathcal{L}^\dagger\mathcal{Q} (z + \mathcal{L}^\dagger\mathcal{Q})^{-1} \mathcal{Q} \\ &= \frac{1}{z} - \frac{1}{z} \mathcal{L}^\dagger\mathcal{Q} [(z + \mathcal{L}^\dagger) - \mathcal{L}^\dagger\mathcal{P}]^{-1} \mathcal{Q} \\ &= \frac{1}{z} - \frac{1}{z} \mathcal{L}^\dagger\mathcal{Q} (z + \mathcal{L}^\dagger)^{-1} \mathcal{Q} \\ &\quad - \frac{1}{z} \mathcal{L}^\dagger\mathcal{Q} (z + \mathcal{L}^\dagger)^{-1} \mathcal{L}^\dagger\mathcal{P} \\ &\quad \times (z + \mathcal{L}^\dagger\mathcal{Q})^{-1} \mathcal{Q}. \end{aligned} \quad (19)$$

This expression is inserted in Eq. (18). The first term yields an expression in which the dynamical operator \mathcal{L}^\dagger acts on the slow variables A_i once, while the second term yields an expression of second order in $\mathcal{L}^\dagger A_i$. The third term is of third order, and hence is omitted in an approximation that is valid in the low-frequency, long-time limit. The advantage of this procedure is that the operator $(z + \mathcal{L}^\dagger\mathcal{Q})^{-1}$ is replaced by $(z + \mathcal{L}^\dagger)^{-1}$, which describes the true dynamics. The approximate memory equation then reads as

$$\begin{aligned} -izC_{ij}(z) &= \langle A_i|A_j\rangle + \sum_{kl} \alpha_{kl} \langle A_i|i\mathcal{L}^\dagger|A_k\rangle C_{lj}(z) \\ &\quad + \sum_{kl} \alpha_{kl} \langle A_i|i\mathcal{L}^\dagger\mathcal{Q} i(z + \mathcal{L}^\dagger)^{-1} \\ &\quad \times \mathcal{Q} i\mathcal{L}^\dagger|A_k\rangle C_{lj}(z). \end{aligned} \quad (20)$$

We now consider an important special case: All the occurring matrices are diagonal (the A_i are statistically and dynamically uncorrelated), and $z=0$, i.e., we study the Green-Kubo integral,

$$C_{ii}(0) = \int_0^\infty dt \langle A_i^*(0)A_i(t)\rangle. \quad (21)$$

Equation (20) then immediately yields

or $D_{ij}^{\alpha\beta}$, which gives the correlation of the displacement in the α direction of particle i to that in the β direction of particle j (the greek letters denote Cartesian indices). The Green-Kubo formula for this tensor is

$$D_{ij}^{\alpha\beta} = \int_0^\infty dt \langle v_i^\alpha(0)v_j^\beta(t)\rangle, \quad (23)$$

v_i denoting the velocity of the i th Brownian particle. Following de Gennes,¹² we replace this, for $i \neq j$, by

$$D_{ij} = D(\mathbf{r}_j - \mathbf{r}_i), \quad (24)$$

with

$$D(\mathbf{r}) = \int_0^\infty dt \langle \mathbf{u}(0,0) \mathbf{u}(\mathbf{r},t) \rangle, \quad (25)$$

where $\mathbf{u}(\mathbf{r},t)$ is the velocity flow field of the *pure* solvent (products of vectors are always meant as tensor product; scalar products are denoted by an over dot). This approximation should be reasonable for sufficiently high dilution, the physical picture being that the Brownian particles follow the motion of the surrounding fluid.

We can assume that the dominant contribution of this integral is due to long-wavelength transversal hydrodynamic modes—the latter because, at high densities, the fluid is nearly incompressible.

Let us suppose the fluid consists of N identical particles confined to a box of size $V = L^3$ with periodic boundary conditions. Then the expansion of the velocity field with respect to modes is

$$\begin{aligned} \mathbf{u}(\mathbf{r},t) &= \frac{V}{N} \sum_i \frac{\mathbf{p}_i}{m} \delta(\mathbf{r} - \mathbf{r}_i) \\ &= \sum_{\mathbf{k}} \sum_{\lambda} u_{\mathbf{k}\lambda} \boldsymbol{\epsilon}_{\lambda}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}), \end{aligned} \quad (26)$$

where $\mathbf{k} = (2\pi/L)\mathbf{n}$ runs over the reciprocal lattice vectors of the box (\mathbf{n} is an integer vector). $\boldsymbol{\epsilon}_{\lambda}$ ($\lambda = 1, 2, 3$) are polarization unit vectors with $\boldsymbol{\epsilon}_1 \cdot \mathbf{k} = \boldsymbol{\epsilon}_2 \cdot \mathbf{k} = \boldsymbol{\epsilon}_1 \cdot \boldsymbol{\epsilon}_2 = 0$, $\boldsymbol{\epsilon}_3 = \mathbf{k}/|\mathbf{k}| = \hat{\mathbf{k}}$. Hence the tensor

$$\boldsymbol{\epsilon}_1 \boldsymbol{\epsilon}_1 + \boldsymbol{\epsilon}_2 \boldsymbol{\epsilon}_2 = 1 - \hat{\mathbf{k}} \hat{\mathbf{k}} \quad (27)$$

projects onto the transversal modes. The Fourier expansion is inverted by

$$u_{\mathbf{k}\lambda} = \frac{1}{Nm} \sum_i \mathbf{p}_i \cdot \boldsymbol{\epsilon}_{\lambda}(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{r}_i), \quad (28)$$

and the diffusion tensor is written as

$$\begin{aligned} D(\mathbf{r}) &= \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{\lambda=1}^2 \sum_{\lambda'=1}^2 \boldsymbol{\epsilon}_{\lambda'}(\mathbf{k}') \boldsymbol{\epsilon}_{\lambda}(\mathbf{k}) \\ &\quad \times \exp(i\mathbf{k} \cdot \mathbf{r}) \int_0^\infty dt \langle u_{\mathbf{k}'\lambda'}^*(0) u_{\mathbf{k}\lambda}(t) \rangle. \end{aligned} \quad (29)$$

Here only transversal modes have been taken into account.

Now, since the modes are statically uncorrelated,

$$\langle u_{\mathbf{k}\lambda} | u_{\mathbf{k}'\lambda'} \rangle = \frac{k_B T}{Nm} \delta_{\mathbf{k}\mathbf{k}'} \delta_{\lambda\lambda'}, \quad (30)$$

it is reasonable to assume that they remain uncorrelated for $t > 0$ as well. This reduces the above expansion to

$$D(\mathbf{r}) = \sum_{\mathbf{k}} (1 - \hat{\mathbf{k}} \hat{\mathbf{k}}) \exp(i\mathbf{k} \cdot \mathbf{r}) \int_0^\infty dt \langle u_{\mathbf{k}\lambda}^*(0) u_{\mathbf{k}\lambda}(t) \rangle, \quad (31)$$

where λ can be chosen as 1 or 2. The remaining Green-Kubo integral is evaluated approximately using Eq. (22). Assuming that every solvent particle is, by choice of the programmer, artificially coupled to a viscous background,

we consider as a dynamical operator that of a molecular dynamics simulation with noise, Eqs. (6)–(8), whose adjoint is

$$\begin{aligned} +i\mathcal{L}^\dagger &= \sum_i \left(\frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} - \frac{\xi}{m} \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right. \\ &\quad \left. + \xi k_B T \frac{\partial}{\partial \mathbf{p}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right). \end{aligned} \quad (32)$$

One easily obtains

$$\begin{aligned} i\mathcal{L}_H^\dagger |u_{\mathbf{k}\lambda}\rangle &= \frac{1}{Nm} \sum_i \left(-\frac{i}{m} (\mathbf{k} \cdot \mathbf{p}_i) [\mathbf{p}_i \cdot \boldsymbol{\epsilon}_{\lambda}(\mathbf{k})] \right. \\ &\quad \left. + \mathbf{F}_i \cdot \boldsymbol{\epsilon}_{\lambda}(\mathbf{k}) \right) e^{-i\mathbf{k} \cdot \mathbf{r}_i} =: |\sigma_{\mathbf{k}\lambda}\rangle, \end{aligned} \quad (33)$$

$$i\mathcal{L}_N^\dagger |u_{\mathbf{k}\lambda}\rangle = -\frac{\xi}{m} |u_{\mathbf{k}\lambda}\rangle, \quad (34)$$

$$\langle u_{\mathbf{k}\lambda} | i\mathcal{L}_H^\dagger |u_{\mathbf{k}\lambda}\rangle = \langle u_{\mathbf{k}\lambda} | \sigma_{\mathbf{k}\lambda}\rangle = 0, \quad (35)$$

$$\mathcal{D} i\mathcal{L}^\dagger |u_{\mathbf{k}\lambda}\rangle = \mathcal{D} i\mathcal{L}_H^\dagger |u_{\mathbf{k}\lambda}\rangle = |\sigma_{\mathbf{k}\lambda}\rangle, \quad (36)$$

and

$$\begin{aligned} \langle u_{\mathbf{k}\lambda} | i\mathcal{L}^\dagger \mathcal{D} &= \langle -i\mathcal{D} \hat{\mathcal{L}} u_{\mathbf{k}\lambda} | \\ &= -\langle i\mathcal{D} \mathcal{L}_H^\dagger u_{\mathbf{k}\lambda} | \\ &= -\langle \sigma_{\mathbf{k}\lambda} |. \end{aligned} \quad (37)$$

In the previous equation, we have made use of $-i\hat{\mathcal{L}}$, which is defined as the adjoint operator of $+i\mathcal{L}^\dagger$ with respect to the scalar product, as defined in Eq. (11). For this operator one easily finds, e.g., by explicit partial integration,

$$\hat{\mathcal{L}}_H = \mathcal{L}_H^\dagger \quad (38)$$

and

$$\hat{\mathcal{L}}_N = -\mathcal{L}_N^\dagger, \quad (39)$$

which is very natural since \mathcal{L}_H^\dagger describes the phase-space volume-conserving Hamiltonian dynamics, while \mathcal{L}_N^\dagger describes the dissipation that drives the system into thermal equilibrium.

Combining the above results, one obtains

$$\begin{aligned} &\int_0^\infty dt \langle u_{\mathbf{k}\lambda}^*(0) u_{\mathbf{k}\lambda}(t) \rangle \\ &= \left(\frac{k_B T}{Nm} \right)^2 \left(\frac{\xi k_B T}{Nm^2} + \int_0^\infty dt \langle \sigma_{\mathbf{k}\lambda}^*(0) \sigma_{\mathbf{k}\lambda}(t) \rangle \right)^{-1}. \end{aligned} \quad (40)$$

In order to simplify the notation, we now choose the special case $\mathbf{k} = k\hat{\mathbf{e}}_z$ and $\boldsymbol{\epsilon}_{\lambda} = \hat{\mathbf{e}}_x$. A long-wavelength approximation is introduced by expanding $\sigma_{\mathbf{k}\lambda}$ up to linear order in \mathbf{k} . Using Newton's third law ($\sum_i \mathbf{F}_i = 0$), one finds

$$\sigma_{\mathbf{k}\lambda} = -\frac{ik}{Nm} \sum_i \left(F_i^x z_i + \frac{1}{m} p_i^x p_i^x \right). \quad (41)$$

Hence, the remaining Green-Kubo integral is nothing else than the definition of the shear viscosity η .¹⁵

$$\int_0^\infty dt \langle \sigma_{kl}^*(0) \sigma_{kl}(t) \rangle = \frac{k^2}{N^2 m^2} V k_B T \eta. \quad (42)$$

Therefore the diffusion tensor reads as

$$D(\mathbf{r}) = \frac{k_B T}{V \eta} \sum_{\mathbf{k}} (1 - \hat{k} \hat{k}) \frac{\exp(i\mathbf{k} \cdot \mathbf{r})}{\kappa^2 + k^2}, \quad (43)$$

with

$$\kappa^2 = \frac{\xi n}{\eta}. \quad (44)$$

Here n denotes the particle number density N/V . This result explicitly shows that a screening length $l = \kappa^{-1}$ occurs.

The final step is the explicit calculation of the \mathbf{r} dependence of the diffusion tensor. This can be done easily only in the continuum limit $L \rightarrow \infty$, where one has

$$D(\mathbf{r}) = \frac{1}{(2\pi)^3} \frac{k_B T}{\eta} \int d^3 \mathbf{k} (1 - \hat{k} \hat{k}) \frac{\exp(i\mathbf{k} \cdot \mathbf{r})}{\kappa^2 + k^2}. \quad (45)$$

The angular integration is done by using the expansions¹⁶

$$1 - \hat{k} \hat{k} = \frac{2}{3} + \sum_{m=-2}^2 K_m Y_{2m}(\hat{k}) \quad (46)$$

and

$$\exp(i\mathbf{k} \cdot \mathbf{r}) = 4\pi \sum_{lm} i^l j_l(kr) Y_{lm}^*(\hat{k}) Y_{lm}(\hat{r}), \quad (47)$$

where K_m are constant tensors, j_l is the spherical Bessel functions, and Y_{lm} is the spherical harmonics. Using the orthogonality of the latter, one obtains

$$D(\mathbf{r}) = \frac{4\pi}{(2\pi)^3} \frac{k_B T}{\eta} \int_0^\infty k^2 dk \left(\frac{2}{3} j_0(kr) - j_2(kr) \sum_{m=-2}^2 K_m Y_{2m}(\hat{r}) \right) \frac{1}{\kappa^2 + k^2} \quad (48)$$

or

$$D(\mathbf{r}) = \frac{4\pi}{(2\pi)^3} \frac{k_B T}{\eta r} \int_0^\infty \frac{x^2 dx}{\kappa^2 r^2 + x^2} \left(\frac{\sin x}{x} (1 - \hat{r} \hat{r}) + \frac{x \cos x - \sin x}{x^3} (1 - 3\hat{r} \hat{r}) \right). \quad (49)$$

The remaining integrals are tabulated,¹⁷ the final result being

$$D(\mathbf{r}) = \frac{k_B T}{4\pi \eta r} \left[e^{-\kappa r} (1 - \hat{r} \hat{r}) + \left(\frac{e^{-\kappa r}}{\kappa r} - \frac{1}{\kappa^2 r^2} (1 - e^{-\kappa r}) \right) \times (1 - 3\hat{r} \hat{r}) \right]. \quad (50)$$

For small distances, this has the form

$$D(\mathbf{r}) = \frac{k_B T}{8\pi \eta} \frac{e^{-\kappa r}}{r} [(1 + \hat{r} \hat{r}) + (1 - 3\hat{r} \hat{r}) O(\kappa r)], \quad (51)$$

demonstrating the expected Yukawa-like behavior. In particular, in the case of purely Hamiltonian dynamics ($\kappa = 0$), the standard Oseen form,

$$D(\mathbf{r}) = \frac{k_B T}{8\pi \eta r} (1 + \hat{r} \hat{r}), \quad (52)$$

is recovered.

However, for large distances the diffusion tensor according to Eq. (50) decays like r^{-3} , indicating, at first glance, that the screening is much weaker than expected. However, this is not really true, since the slowly decaying part is traceless. Looking, e.g., at the standard Kirkwood formula for the center-of-mass diffusion constant of a polymer chain of N monomers,¹⁸

$$D = \frac{D_0}{N} + \frac{1}{3N^2} \sum_{i \neq j} \text{Tr} \langle D_{ij} \rangle, \quad (53)$$

one immediately sees that it is the *trace* that matters (D_0 is the monomer diffusion coefficient).

From Eq. (50), one obtains

$$\frac{1}{3} \text{Tr} D(\mathbf{r}) = \frac{k_B T}{6\pi \eta r} \exp(-\kappa r), \quad (54)$$

which is a purely Yukawa-like decay.

IV. CONCLUSIONS

The present calculation has shown in a direct and explicit way how the modification of a standard microcanonical MD algorithm to a Langevin simulation screens hydrodynamic interactions. It has also shown the underlying physical mechanism, which is the destruction of momentum conservation. Indeed, in the purely Hamiltonian case the long-range k^{-2} behavior is a direct consequence of momentum conservation: The Taylor expansion of σ_{kl} , Eq. (41), does not contain a constant term because of Newton's third law.

The practical consequence is that the Langevin algorithm is not applicable for simulating a system of Brownian particles in an explicit bath of solvent particles. The effect is small enough only for very small friction, which, in practice, means that one might run a microcanonical simulation as well. One might also think about refined Langevin schemes that do not exhibit the screening effect, but the development of such algorithms is beyond the scope of the present investigation.

The expression we find for the hydrodynamic screening length is, apart from a numerical prefactor, the same as is obtained in phenomenological approaches, attacking the problem of hydrodynamic screening in semidilute polymer solutions.¹³ However, the symbols have a different meaning: While in our calculation n and ξ denote the density and friction coefficient of solvent particles, they mean monomer concentration and monomeric friction coefficient in Ref. 13. It is, therefore, doubtful whether the formal analogy has more of a common root than the modification of the Navier-Stokes equation due to dissipation.

In principle, similar considerations should apply for other modifications of MD algorithms, too. One must always expect strong effects on hydrodynamic properties as soon as the simulation method modifies the conservation laws. But even if this is not the case, a calculation along the lines of the present one should always be useful. The practical question that then arises is how amenable the specific algorithm is to formal analysis. The Langevin case is certainly a particularly easy one, since it generates a very simple (the canonic) ensemble, which makes the evaluation of the occurring scalar products trivial.

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