

Hydrodynamics from dissipative particle dynamics

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Starting from the stochastic differential equations corresponding to the updating algorithm of dissipative particle dynamics we derive, with a standard technique of projection operators, the hydrodynamic equations for the mass and momentum density fields. The connection of the original parameters of the model with the viscosity and speed of sound of the fluid is clarified.

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I. INTRODUCTION

The method of dissipative particle dynamics (DPD) introduced by Hoogerbrugge and Koelman [1,2] is a promising approach to the study of hydrodynamic behavior in complex geometries as in, for example, those appearing in colloidal suspensions. DPD is essentially a molecular dynamics (MD) simulation where the particles interact through direct conservative potentials *and* dissipative Brownian dashpots. The point particles are no longer regarded as molecules in a fluid but rather as representing clusters of particles that interact dissipatively. This implies a mesoscopic level of description and it is expected that the relevant hydrodynamic behavior appears with a number of particles much smaller than those required in conventional molecular dynamics [3-5].

In general, the introduction of noise and dissipation represents a coarse graining in the description of the dynamics of a system. In Brownian dynamics (BD) simulations [6], for example, an individual friction and random force is assigned to each particle of the system. BD is intended to describe colloidal suspensions in time scales large compared to molecular collision times. The effect of the solvent is coarse grained through the noise and friction forces. The macroscopic behavior of Brownian dynamics simulations is diffusive as the only conserved quantity is the total mass the system. In DPD, on the other hand, not only the mass but also the momentum is conserved in each "collision" between particles. As a consequence, the macroscopic behavior will not be diffusive but hydrodynamic, this is, there exists a transport equation for the momentum density of the fluid. It should be noted that the total energy of the system is not conserved either in BD or DPD and, therefore, there is no transport equation for the energy.

Despite the observations that the simulations pass even quantitatively some well-known hydrodynamic test, there is no rigorous theoretical justification that DPD has correct hydrodynamic behavior. In particular, it is not clear

what is the connection between the original parameters of the model and the viscosity and speed of sound of the fluid modeled. Even though some expressions are given and tested in the original references, they are based on unsystematic approximations [7,8]. For example, the viscosity of the fluid is proportional to the friction coefficient of the Brownian dashpots. This means that in the limit of zero friction the viscosity would vanish, and this cannot possibly be true: there always exists a nonzero contribution to the viscosity coming from the conservative and deterministic part of the dynamics (otherwise a MD simulation would produce zero viscosity).

We have recently formulated the stochastic differential equations and the equivalent Fokker-Planck equation that correspond to the updating algorithm proposed by Hoogerbrugge and Koelman [9]. The Fokker-Planck equation for DPD is the analog to the Liouville equation for molecular dynamics and, in fact, it reduces to the Liouville equation in the limit of zero noise and friction. The Fokker-Planck equation governs the distribution of the microscopic variables of the system, i.e., the positions and velocities of all the particles of the system. Our main interest in [9] was to discuss the equilibrium properties of the model. In particular, we found that in order to obtain the correct equilibrium distribution it is necessary to modify slightly the original algorithm. With the modified algorithm, we obtained in a natural way a fluctuation-dissipation theorem very similar to the one obtained in conventional Brownian motion. This theorem allows one to relate the amplitude of the noise to the temperature of the system.

The purpose of this paper is to formulate the equations of motion for the macroscopic hydrodynamic variables starting from the microscopic Fokker-Planck equation. We will use the standard technique of projection operators in order to obtain the equations of hydrodynamics for DPD. As our main interest is to clarify the connection of the amplitude of the noise and the friction coefficient with the sound speed and viscosity of the fluid modeled, we only need to consider linearized hydrodynamics. This allows us to use the time-independent projection operator of Mori and proceed according to the standard technique [10]. The extension to nonlinear hydrodynamics is not difficult, though.

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From a mathematical point of view, the main difference between the derivation of the macroscopic equations from the microscopic equations in DPD versus MD is in the non-Hermiticity of the Fokker-Planck operator, in contrast to the Hermitian property of the Liouville operator. For this reason we will generalize conveniently Mori's projection operator technique.

II. MICROSCOPIC DYNAMICS

The stochastic differential equations (SDE's) that govern the position \mathbf{r}_i and momentum \mathbf{p}_i of the particles in DPD are given by [9]

$$\begin{aligned} d\mathbf{r}_i &= \frac{\mathbf{p}_i}{m_i} dt, \\ d\mathbf{p}_i &= \left[\sum_{j \neq i} \mathbf{F}_{ij}^C(\mathbf{r}_{ij}) + \sum_{j \neq i} -\gamma\omega(r_{ij})(\mathbf{e}_{ij} \cdot \mathbf{v}_{ij})\mathbf{e}_{ij} \right] dt \\ &\quad + \sum_{j \neq i} \sigma\omega^{1/2}(r_{ij})\mathbf{e}_{ij} dW_{ij}, \end{aligned} \quad (1)$$

where m_i is the mass of particle i , $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij}$, $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, $\mathbf{v}_i = \mathbf{p}_i/m_i$, and $\mathbf{F}_{ij}^C(\mathbf{r}_{ij})$ is the conservative force exerted on particle i by particle j . The dimensionless weight function $\omega(r_{ij})$ provides the range of interaction of the dissipative and random forces and it is normalized in such a way that $\int \omega(r) d\mathbf{r} = V/N = n^{-1}$. The friction coefficient γ and the noise amplitude σ are subjected to the fluctuation-dissipation theorem

$$\sigma = (2k_B T \gamma)^{1/2}, \quad (2)$$

where T is the temperature of the equilibrium state towards which the system relaxes (if the boundary conditions allow for it) and k_B is Boltzmann's constant. Finally, $dW_{ij} = dW_{ji}$ are $(N-1)N/2$ independent increments of the Wiener process. To fix ideas, we will assume the Itô interpretation which implies the Itô calculus rule

$$dW_{ij} dW_{i'j'} = (\delta_{ii'} \delta_{jj'} + \delta_{ij'} \delta_{ji'}) dt, \quad (3)$$

i.e., $dW_{ij}(t)$ is an infinitesimal of order $1/2$ [11].

The above SDE's are very similar to the ones that correspond to the updating algorithm proposed by Hoogerbrugge and Koelman with a slightly different notation. However, note that we have a square root of the weight function in the random force. This is in contrast to the original algorithm and it is crucial in order to obtain the proper equilibrium ensemble [9].

The Fokker-Planck equation that is mathematically equivalent to the SDE's (1) is given by [11]

$$\partial_t \rho(z; t) = L \rho(z; t), \quad (4)$$

where z is a shorthand for the set of all positions and momenta of the particles, $\rho(z; t)$ is the probability density in phase space, and the Fokker-Planck operator is [9]

$$\begin{aligned} L \equiv & - \left[\sum_i \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i,j \neq i} \mathbf{F}_{ij}^C \cdot \frac{\partial}{\partial \mathbf{p}_i} \right] \\ & + \sum_{i,j \neq i} \gamma \omega(r_{ij}) \mathbf{e}_{ij} \cdot \frac{\partial}{\partial \mathbf{p}_i} \left[(\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) \right. \\ & \left. + k_B T \mathbf{e}_{ij} \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \right]. \end{aligned} \quad (5)$$

The first term in square brackets is the Liouville operator. The second term proportional to the friction coefficient γ takes into account the effects of the dissipation. In the absence of dissipation ($\gamma = 0$), Eq. (1) reduces to Newton's equations of motion and (4) becomes Liouville's equation. Note that the diffusion tensors accompanying the second derivatives with respect to the momentum do not depend on the momenta of the particles. This implies that the Itô and Stratonovich interpretations provide exactly the same answers [11].

It is a matter of substitution to check that the canonical equilibrium ensemble is not only a stationary solution of the Liouville equation but also a stationary solution of the Fokker-Planck equation (4), i.e., $L\rho^{eq} = 0$, where

$$\begin{aligned} \rho^{eq}(z) &= \frac{1}{Z} \exp\{-H(z)/k_B T\} \\ &= \frac{1}{Z} \exp\left\{-\left(\sum_i \frac{p_i^2}{2m_i} + V(r)\right)/k_B T\right\}, \end{aligned} \quad (6)$$

$H(z)$ is the Hamiltonian of the system, V is the potential function that gives rise to the conservative forces \mathbf{F}^C , and Z is the normalizing partition function.

We will need several operators related to the Fokker-Planck operator L . For example, if we use the SDE (1) with the aid of the calculus rule (3) in order to compute the differential df of an arbitrary function f , we will find

$$\begin{aligned} df &= \sum_i \frac{\partial f}{\partial \mathbf{r}_i} \cdot d\mathbf{r}_i + \frac{\partial f}{\partial \mathbf{p}_i} \cdot d\mathbf{p}_i \\ &\quad + \sum_{ij} \frac{1}{2} \frac{\partial^2 f}{\partial \mathbf{r}_i \partial \mathbf{r}_j} d\mathbf{r}_i d\mathbf{r}_j + \frac{1}{2} \frac{\partial^2 f}{\partial \mathbf{r}_i \partial \mathbf{p}_j} d\mathbf{r}_i d\mathbf{p}_j \\ &\quad + \frac{1}{2} \frac{\partial^2 f}{\partial \mathbf{p}_i \partial \mathbf{p}_j} d\mathbf{p}_i d\mathbf{p}_j + O(dt^{3/2}) \\ &= \tilde{L} f dt + \sum_{i \neq j} \sigma \omega^{1/2}(r_{ij}) \mathbf{e}_{ij} \cdot \frac{\partial f}{\partial \mathbf{p}_i} dW_{ij} + O(dt^{3/2}). \end{aligned} \quad (7)$$

The operator \tilde{L} is given by

$$\begin{aligned} \tilde{L} \equiv & \left[\sum_i \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i,j \neq i} \mathbf{F}_{ij}^C \cdot \frac{\partial}{\partial \mathbf{p}_i} \right] \\ & + \sum_{i,j \neq i} \gamma \omega(r_{ij}) \left[-(\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{e}_{ij} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right. \\ & \left. + k_B T \mathbf{e}_{ij} \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \right]. \end{aligned} \quad (8)$$

The relevance of \tilde{L} stems from the fact that it allows one to compute the time derivative of averages, because of the following property derived from (7):

$$\frac{d}{dt}\langle f \rangle = \langle \tilde{L}f \rangle. \quad (9)$$

Another crucial property satisfied by DPD is detailed balance. Detailed balance is satisfied if [12]

$$L\rho^{eq}\phi = \rho^{eq}\tilde{L}^\epsilon\phi \quad (10)$$

where ϕ is an arbitrary function of positions and momenta. The operator \tilde{L}^ϵ is obtained from \tilde{L} by reversing the sign of the velocities. It is a matter of some algebra to prove that DPD satisfies the detailed balance property (10).

III. MORI FORMALISM

In this section we will adapt the standard technique of projection operators to the case that the dynamic operator is not self-adjoint, as happens with L in (5). Following Ref. [10], we introduce a scalar product in order to construct a Hilbert space for the functions of phase space,

$$(\phi, \psi) \equiv \int \rho^{eq}(z)\phi(z)\psi(z)dz \equiv \text{tr}[\rho^{eq}\phi\psi]. \quad (11)$$

With this scalar product and due to detailed balance (10) the operators \tilde{L} and \tilde{L}^ϵ are adjoints of each other, i.e.,

$$(\tilde{L}\phi, \psi) = (\phi, \tilde{L}^\epsilon\psi). \quad (12)$$

As in any technique of projection operators, the first step consists in selecting the relevant variables that describe the macroscopic behavior of the system. We will denote the relevant variables by $A_i(z)$ and we will specify them in the next section. The only requirement by now is that their equilibrium value vanish. With the relevant variables one constructs a relevant ensemble of the form

$$\bar{\rho}_t(z) \equiv \frac{1}{Z} \exp\{-\beta H(z) + \beta\lambda_i(t)A_i(z)\}, \quad (13)$$

where summation over repeated indices is understood, $\beta = 1/k_B T$, and $\lambda_i(t)$ are a set of thermodynamic parameters that depend on time. They are selected in such a way that the average of A_i performed with the relevant ensemble coincides with the actual average performed with the solution of the Fokker-Planck equation (4), that is,

$$\langle A_i \rangle_t = \text{tr}[\rho_t A_i] = \text{tr}[\bar{\rho}_t A_i]. \quad (14)$$

Near equilibrium the relevant ensemble must be similar to the canonical ensemble and therefore the parameters $\lambda_i(t)$ are small, allowing for an expansion of the form

$$\bar{\rho}_t(z) = \rho^{eq}(z)[1 + \beta\lambda_i(t)A_i(z)]. \quad (15)$$

We further define the deviations from equilibrium

$$\begin{aligned} \rho_t &= \rho^{eq}[1 + \Psi_t], \\ \bar{\rho}_t &= \rho^{eq}[1 + \bar{\Psi}_t], \end{aligned} \quad (16)$$

in such a way that $\bar{\Psi}_t = \beta\lambda_i(t)A_i$. In terms of the deviations from equilibrium Eq. (14) becomes

$$\langle A_i \rangle_t = (A_i, \Psi_t) = (A_i, \bar{\Psi}_t) \quad (17)$$

which implies

$$\beta\lambda_i(t) = (A_i, A_j)^{-1}(A_j, \Psi_t), \quad (18)$$

and therefore

$$\bar{\Psi}_t = A_i(A_i, A_j)^{-1}(A_j, \Psi_t) \equiv \mathcal{P}\Psi_t \quad (19)$$

where \mathcal{P} is a projection operator that extracts the relevant part of the actual ensemble.

It is convenient to write the Fokker-Planck equation (4) in terms of the deviations from the equilibrium, that is,

$$\partial_t \Psi_t = \tilde{L}^\epsilon \Psi_t, \quad (20)$$

where the detailed balance (10) has been used. As usual, from this equation one writes equations for the relevant $\mathcal{P}\Psi_t$ and irrelevant $\mathcal{Q}\Psi_t \equiv (1 - \mathcal{P})\Psi_t$ parts and solves for the second. Substitution into the equation for the relevant part leads to

$$\partial_t \bar{\Psi}_t = \mathcal{P}\tilde{L}^\epsilon\bar{\Psi}_t + \int_0^t du \mathcal{P}\tilde{L}^\epsilon \exp\{\mathcal{Q}\tilde{L}^\epsilon(t-u)\}\mathcal{Q}\tilde{L}^\epsilon\bar{\Psi}_u. \quad (21)$$

Note that in order to write this equation conventional calculus has been used because Ψ_t is an ordinary function and (20) a usual partial differential equation. There is no need of using stochastic calculus at the level of the Fokker-Planck equation. For example, the formal solution of (20) is

$$\Psi_t = \exp\{\tilde{L}^\epsilon t\}\Psi_0 \quad (22)$$

where the operator $\exp\{\tilde{L}^\epsilon t\}$ is defined in terms of its series expansion.

From Eq. (20) one obtains an exact equation for the average of the relevant variables:

$$\begin{aligned} \frac{d}{dt}\langle A_i \rangle &= (\tilde{L}A_i, \bar{\Psi}_t) + \int_0^t du [\exp\{\tilde{L}\mathcal{Q}(t-u)\} \\ &\quad \times \tilde{L}A_i, \mathcal{Q}\tilde{L}^\epsilon A_j] \beta\lambda_j(u) \end{aligned} \quad (23)$$

where the Hermitian property of \mathcal{P} and \mathcal{Q} and detailed balance have been used.

The crucial point in any technique of projection operators is the selection of the relevant variables. In general, one tries to find variables for which the complicated memory term in (23) can be approximated by a term which is local in time (i.e., Markovian). This will be possible whenever there exists a clear separation of time scales between the relevant variables and the memory kernels, which will be the case if the relevant variables are "slow." In this case, the Markovian equation which approximates

(23) reads

$$\begin{aligned} \frac{d}{dt}\langle A_i \rangle &= (\tilde{L}A_i, \bar{\Psi}_i) \\ &+ \left[\int_0^\infty du (\exp\{\tilde{L}Qu\} \tilde{L}A_i, Q\tilde{L}^\epsilon A_j) \right] \beta \lambda_j(t) \\ &= (\tilde{L}A_i, \bar{\Psi}_i) + \mu_{ij} \beta \lambda_j(t), \end{aligned} \quad (24)$$

where the transport coefficients μ_{ij} are expressed in terms of Green-Kubo formulas, i.e., time integrals of equilibrium correlation functions.

IV. HYDRODYNAMIC VARIABLES

We are interested in the hydrodynamic behavior of a system of particles governed by DPD. For this reason the selected relevant variables would be, in principle, the microscopic mass, momentum, and energy density fields defined by

$$\begin{aligned} \delta \rho_{\mathbf{r}} &= \sum_i m \delta(\mathbf{r} - \mathbf{r}_i) - \rho_0, \\ \mathbf{g}_{\mathbf{r}} &= \sum_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i), \\ \delta e_{\mathbf{r}} &= \sum_i \left[\frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} \phi_{ij} \right] \delta(\mathbf{r} - \mathbf{r}_i) - e_0, \end{aligned} \quad (25)$$

where ρ_0 and e_0 are the equilibrium mass and energy densities of the fluid. Note that the equilibrium average of these quantities (25) vanishes.

The time derivative of the average of any phase function involves the operator \tilde{L} , because of Eq. (9). Let us consider then the effect of \tilde{L} on the hydrodynamic variables. For example,

$$\tilde{L}\rho_{\mathbf{r}} = -\nabla \cdot \mathbf{g}_{\mathbf{r}}. \quad (26)$$

In the same way, one obtains

$$\begin{aligned} \tilde{L}\mathbf{g}_{\mathbf{r}} &= -\nabla \cdot \left[\sum_i \frac{1}{m} \mathbf{p}_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i) \right. \\ &\left. + \frac{1}{2} \sum_{ij}' \mathbf{F}_{ij} \mathbf{e}_{ij} \int_0^{r_{ij}} d\alpha \delta(\mathbf{r} - \mathbf{r}_i - \alpha \mathbf{e}_{ij}) \right], \end{aligned} \quad (27)$$

where \mathbf{F}_{ij} is the total force (including conservative and dissipative parts, but not the random contribution) that particle j exerts on particle i . The prime in the summation excludes the $i = j$ terms. In (27) the generalized Taylor theorem [13,14] has been used:

$$\delta(\mathbf{r} - \mathbf{r}_i) - \delta(\mathbf{r} - \mathbf{r}_j) = -\nabla \cdot \mathbf{e}_{ij} \int_0^{r_{ij}} d\alpha \delta(\mathbf{r} - \mathbf{r}_i - \alpha \mathbf{e}_{ij}). \quad (28)$$

Both Eqs. (26) and (27) imply that the equations of motion for the mass and momentum densities are transport equations, because their derivatives are the divergence

of a flux. This implies that the small k components of these fields in Fourier space are slowly varying quantities for which local in time or Markovian equations of the form (24) exist.

On the other hand, the operator \tilde{L} applied to the energy density field leads to

$$\tilde{L}e_{\mathbf{r}} = -\nabla \cdot \tau_{\mathbf{r}}^C + \sum_{ij}' \left[\mathbf{F}_{ij}^D \cdot \mathbf{v}_i + k_B T \frac{\gamma}{m} \omega(r_{ij}) \right] \delta(\mathbf{r} - \mathbf{r}_i) \quad (29)$$

where the conservative energy flux has the form

$$\begin{aligned} \tau_{\mathbf{r}}^C &\equiv \sum_i \left[\frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} \phi_{ij} \right] \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i) \\ &+ \frac{1}{4} \sum_{ij} \frac{1}{m} \mathbf{F}_{ij}^C \cdot (\mathbf{p}_i + \mathbf{p}_j) \mathbf{e}_{ij} \\ &\times \int_0^{r_{ij}} d\alpha \delta(\mathbf{r} - \mathbf{r}_i - \alpha \mathbf{e}_{ij}) \end{aligned} \quad (30)$$

and $\mathbf{F}_{ij}^D = -\gamma \omega(r_{ij}) (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{e}_{ij}$ is the dissipative force on particle i exerted by particle j .

The physical meaning of the different terms in (29) is clear. The first divergence term represents the conserved contribution whereas the second term stands for the effects of the dissipated energy due to the friction of the dashpots and the increase in energy due to the Brownian kicks exerted on each pair of particles. This last term cannot be expressed as the divergence of a flux and, therefore, in the limit of small wave numbers in Fourier space the time derivative of the energy density field does not vanish. The energy density field is then *not* a slow variable and cannot be taken as a relevant variable.

In summary, the only relevant variables in a system of particles governed by DPD are the mass density (actually its deviations from the equilibrium density), and the momentum density field. The relevant ensemble obtained with these relevant variables will be

$$\bar{\Psi}_t = \beta \int_V d\mathbf{r} [\mu_{\mathbf{r}}(t) \delta \rho_{\mathbf{r}} + \lambda_{\mathbf{r}}(t) \cdot \mathbf{g}_{\mathbf{r}}], \quad (31)$$

where $\mu_{\mathbf{r}}(t)$ and $\lambda_{\mathbf{r}}(t)$ are the corresponding thermodynamic parameters.

We will devote the rest of this section to finding the physical meaning of these parameters. It is first necessary to consider the matrix of scalar products. In general this matrix is $M_{ij} = (A_i, A_j)$, but when specialized to the hydrodynamic variables it becomes

$$M_{ij} \rightarrow \mathbf{M}_{\mathbf{r}\mathbf{r}'} = \begin{pmatrix} M^{\rho\rho}(\mathbf{r} - \mathbf{r}') & M^{\rho\mathbf{g}}(\mathbf{r} - \mathbf{r}') \\ M^{\rho\mathbf{g}}(\mathbf{r} - \mathbf{r}') & M^{\mathbf{g}\mathbf{g}}(\mathbf{r} - \mathbf{r}') \end{pmatrix}, \quad (32)$$

where $M^{\rho\rho}(\mathbf{r} - \mathbf{r}') = (\delta \rho_{\mathbf{r}}, \delta \rho_{\mathbf{r}'})$, $M^{\rho\mathbf{g}}(\mathbf{r} - \mathbf{r}') = (\delta \rho_{\mathbf{r}}, \mathbf{g}_{\mathbf{r}'})$, $M^{\mathbf{g}\rho}(\mathbf{r} - \mathbf{r}') = (\delta \rho_{\mathbf{r}'}, \mathbf{g}_{\mathbf{r}})$, and $M^{\mathbf{g}\mathbf{g}}(\mathbf{r} - \mathbf{r}') = (\mathbf{g}_{\mathbf{r}}, \mathbf{g}_{\mathbf{r}'})$. This matrix (32) is a 4×4 matrix that has to be understood as a functional matrix with respect to the continuous indices $\mathbf{r}\mathbf{r}'$. It is straightforward to compute the

different terms,

$$\begin{aligned} M^{\rho\rho}(\mathbf{r}-\mathbf{r}') &= m\delta(\mathbf{r}-\mathbf{r}')\rho_0 + \rho_0^2\nu(|\mathbf{r}-\mathbf{r}'|), \\ M^{\rho\mathbf{g}}(\mathbf{r}-\mathbf{r}') &= M^{\mathbf{g}\rho}(\mathbf{r}-\mathbf{r}') = 0, \\ M^{\mathbf{g}\mathbf{g}}(\mathbf{r}-\mathbf{r}') &= k_B T \rho_0 \delta(\mathbf{r}-\mathbf{r}') \mathbf{1}, \end{aligned} \quad (33)$$

where $\nu(r)$ is the pair correlation function. We observe that the 4×4 matrix is diagonal. Therefore, we may interpret the thermodynamic parameters by using (18) in the form $\langle A_i \rangle_t = (A_i, A_j) \beta \lambda_j(t)$ which in our case becomes

$$\begin{aligned} \langle \delta\rho_{\mathbf{r}} \rangle_t &= \int_V d\mathbf{r}' M^{\rho\rho}(\mathbf{r}-\mathbf{r}') \beta \mu_{\mathbf{r}'}(t), \\ \langle \mathbf{g}_{\mathbf{r}} \rangle_t &= \rho_0 \lambda_{\mathbf{r}}(t). \end{aligned} \quad (34)$$

The last equation shows that $\lambda_{\mathbf{r}}(t) = \mathbf{v}(\mathbf{r}, t)$, the velocity field. On the other hand, the kernel in the first equation will decay in general in a molecular length scale for which the thermodynamic parameter $\mu_{\mathbf{r}}(t)$ seldom varies. Therefore we would approximate

$$\langle \delta\rho_{\mathbf{r}} \rangle_t = \int_V M^{\rho\rho}(\mathbf{r}') d\mathbf{r}' \beta \mu_{\mathbf{r}}(t). \quad (35)$$

The problem with this approximation is that the integral over all space of the kernel $M^{\rho\rho}(\mathbf{r})$ vanishes identically in the canonical ensemble because

$$\int_V M^{\rho\rho}(\mathbf{r}) d\mathbf{r} = \left(\int_V d\mathbf{r} \delta\rho_{\mathbf{r}}, \delta\rho_{\mathbf{r}'} \right) = (0, \delta\rho_{\mathbf{r}'}) = 0. \quad (36)$$

The proper way to obtain a local in space approximation is by considering a small spherical volume $\Omega(\mathbf{r}, r_0)$ of radius r_0 centered around \mathbf{r} and decomposing the volume integral in (34) into two integrals,

$$\begin{aligned} \langle \delta\rho_{\mathbf{r}} \rangle_t &= \int_{\Omega(\mathbf{r}, r_0)} d\mathbf{r}' M^{\rho\rho}(\mathbf{r}-\mathbf{r}') \beta \mu_{\mathbf{r}'}(t) \\ &+ \int_{V-\Omega(\mathbf{r}, r_0)} d\mathbf{r}' M^{\rho\rho}(\mathbf{r}-\mathbf{r}') \beta \mu_{\mathbf{r}'}(t). \end{aligned} \quad (37)$$

The radius r_0 of the sphere is much larger than a typical molecular separation. For $|\mathbf{r}-\mathbf{r}'| > r_0$ the kernel $M^{\rho\rho}(\mathbf{r}-\mathbf{r}')$ has a vanishingly small amplitude and this implies that the second integral in (37) is a very slowly varying function negligible compared with the first one. Under the assumption that the macroscopic field $\mu_{\mathbf{r}}(t)$ is virtually constant within molecular length scales, now it is safe to take the local approximation

$$\langle \delta\rho_{\mathbf{r}} \rangle_t = \int_{\Omega(\mathbf{r}, r_0)} M^{\rho\rho}(\mathbf{r}-\mathbf{r}') d\mathbf{r}' \beta \mu_{\mathbf{r}}(t) \equiv M^{\rho\rho} \beta \mu_{\mathbf{r}}(t). \quad (38)$$

The integrated kernel $M^{\rho\rho}$ depends on the *ad hoc* length scale r_0 and in particular $\lim_{r_0 \rightarrow \infty} M^{\rho\rho} = 0$ [i.e., when $\Omega \rightarrow V$ then Eq. (36) holds]. However, one expects that after several molecular radii $M^{\rho\rho}$ will exhibit a plateau value which will decay to zero very slowly. The situation here is very similar to that encountered in the

time domain in the definition of the friction coefficient as the time integral of the force autocorrelation function in Brownian motion theory [16]. Therefore, the particular value of the selected r_0 will not be very important, provided that it is selected within the appropriate bounds (i.e., larger than a few molecular radii and smaller than the typical macroscopic length scale of variation of the hydrodynamic fields). In Appendix A we show that the local in space approximation for $M^{\rho\rho}(\bar{\rho}-\bar{\rho}')$ can be expressed in the form [see Eq. (A6)]

$$M^{\rho\rho} = k_B T \frac{\partial}{\partial \mu} \langle \rho \rangle^{T\mu\Omega}, \quad (39)$$

where $\langle \rho \rangle^{T\mu\Omega}$ is the average mass density in the macrocanonical ensemble at constant temperature T , chemical potential μ , and volume Ω .

We finally note that from (38) the thermodynamic parameter $\mu_{\mathbf{r}}(t)$ is proportional to the deviations of the density from its equilibrium value.

V. HYDRODYNAMIC EQUATIONS

In this section we specify the general equation of motion (23) to the case of hydrodynamic variables. Because $\tilde{L}\rho_{\mathbf{r}}$ is linear in the momentum density, there is no memory term in the equation for the mass density which becomes simply the continuity equation

$$\partial_t \delta\rho(\mathbf{r}, t) = -\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{g}(\mathbf{r}, t), \quad (40)$$

where $\delta\rho(\mathbf{r}, t) \equiv \langle \delta\rho_{\mathbf{r}} \rangle_t$ and $\mathbf{g}(\mathbf{r}, t) \equiv \langle \mathbf{g}_{\mathbf{r}} \rangle_t$. Let us consider the momentum density equation next,

$$\begin{aligned} \partial_t \mathbf{g}(\mathbf{r}, t) &= (\bar{\Psi}_t, \tilde{L}\mathbf{g}_{\mathbf{r}}) + \int_0^t du \int_V d\mathbf{r}' [\exp\{\tilde{L}Q(t-u)\} \\ &\times \tilde{L}\mathbf{g}_{\mathbf{r}}, Q\tilde{L}^\epsilon \mathbf{g}_{\mathbf{r}'}] \beta \mathbf{v}(\mathbf{r}', t), \end{aligned} \quad (41)$$

where we have used that $Q\tilde{L}^\epsilon \rho_{\mathbf{r}} = 0$ to get rid of the memory term proportional to $\mu_{\mathbf{r}}(t)$. The first term in (41) will give rise to the (linearized) Euler terms in the Navier-Stokes equation whereas the second term will produce the viscosity terms. We will consider an expansion up to second order terms in gradients, because only for slowly spatially varying fields does one expect a clear separation of time scales and a Markovian approximation for the second term in (41).

A. Euler terms

In order to see this, we have to consider first the effect of the operators \tilde{L} and \tilde{L}^ϵ on $\mathbf{g}_{\mathbf{r}}$:

$$\begin{aligned} \tilde{L}\mathbf{g}_{\mathbf{r}} &= -\frac{\partial}{\partial \mathbf{r}} \cdot \sigma_{\mathbf{r}}^C - \frac{\partial}{\partial \mathbf{r}} \cdot \sigma_{\mathbf{r}}^D, \\ \tilde{L}^\epsilon \mathbf{g}_{\mathbf{r}} &= \frac{\partial}{\partial \mathbf{r}} \cdot \sigma_{\mathbf{r}}^C - \frac{\partial}{\partial \mathbf{r}} \cdot \sigma_{\mathbf{r}}^D, \end{aligned} \quad (42)$$

where the conservative and dissipative stress tensors are

defined by

$$\begin{aligned}\sigma_{\mathbf{r}}^C &= \left[\sum_i \frac{1}{m} \mathbf{p}_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i) \right. \\ &\quad \left. + \frac{1}{2} \sum_{ij} \mathbf{F}_{ij}^C \mathbf{e}_{ij} \int_0^{r_{ij}} d\alpha \delta(\mathbf{r} - \mathbf{r}_i - \alpha \mathbf{e}_{ij}) \right], \\ \sigma_{\mathbf{r}}^D &= \frac{1}{2} \sum_{ij} \mathbf{F}_{ij}^D \mathbf{e}_{ij} \int_0^{r_{ij}} d\alpha \delta(\mathbf{r} - \mathbf{r}_i - \alpha \mathbf{e}_{ij}).\end{aligned}\quad (43)$$

Therefore we will need to compute $(\bar{\Psi}_t, \sigma_{\mathbf{r}}^C)$ and $(\bar{\Psi}_t, \sigma_{\mathbf{r}}^D)$. Let us consider the last term first:

$$\begin{aligned}(\bar{\Psi}_t, \sigma_{\mathbf{r}}^D) &= \int_V d\mathbf{r}' \beta \mu_{\mathbf{r}'}(t) (\delta \rho_{\mathbf{r}'}, \sigma_{\mathbf{r}}^D) \\ &\quad + \int_V d\mathbf{r}' \beta \mathbf{v}(r', t) (\mathbf{g}_{\mathbf{r}'}, \sigma_{\mathbf{r}}^D).\end{aligned}\quad (44)$$

The first integral vanishes because it involves an equilibrium average of an odd number of momenta. The second integral would produce a third order tensor. However, the equilibrium average is isotropic and there are no third order tensors which are isotropic and symmetric in a pair of indices. Therefore this second term also vanishes. On the other hand, the conservative term is a bit more involved:

$$\begin{aligned}(\bar{\Psi}_t, \sigma_{\mathbf{r}}^C) &= \int_V d\mathbf{r}' \beta \mu_{\mathbf{r}'}(t) (\delta \rho_{\mathbf{r}'}, \sigma_{\mathbf{r}}^C) \\ &\quad + \int_V d\mathbf{r}' \beta \mathbf{v}(r', t) (\mathbf{g}_{\mathbf{r}'}, \sigma_{\mathbf{r}}^C).\end{aligned}\quad (45)$$

The last contribution to this expression vanishes because, again, it involves an odd number of integrated momenta.

$$\begin{aligned}[\exp\{\tilde{L}Q(t-u)\} \tilde{L} \mathbf{g}_{\mathbf{r}}, Q \tilde{L}^\epsilon \mathbf{g}_{\mathbf{r}'}] &= -\partial_{\mathbf{r}} \partial_{\mathbf{r}'} [\exp\{\tilde{L}Q(t-u)\} \sigma_{\mathbf{r}}^C, Q \sigma_{\mathbf{r}'}^C] + \partial_{\mathbf{r}} \partial_{\mathbf{r}'} [\exp\{\tilde{L}Q(t-u)\} \sigma_{\mathbf{r}}^C, Q \sigma_{\mathbf{r}'}^D] \\ &\quad + \partial_{\mathbf{r}} \partial_{\mathbf{r}'} [\exp\{\tilde{L}Q(t-u)\} \sigma_{\mathbf{r}}^D, Q \sigma_{\mathbf{r}'}^C] + \partial_{\mathbf{r}} \partial_{\mathbf{r}'} [\exp\{\tilde{L}Q(t-u)\} \sigma_{\mathbf{r}}^D, Q \sigma_{\mathbf{r}'}^D].\end{aligned}\quad (49)$$

Now, the cross terms D and C cancel each other due to temporal reversibility. This is shown in Appendix B. The next step is to integrate by parts the term $\partial_{\mathbf{r}'}$ and to assume that the kernels in (49) are short ranged in space, with correlation lengths much shorter than the typical length scale of variation of the velocity field, allowing for the approximation $\beta \partial_{\mathbf{r}'} \mathbf{v}(r', t) \approx \beta \partial_{\mathbf{r}} \mathbf{v}(r, t)$. By invoking also locality in time (that the correlation time of the kernels is short lived compared with the temporal scale of variation of the velocity field), we arrive finally at the following approximation for the kernel in (41):

$$\begin{aligned}\int_0^t du \int_V d\mathbf{r}' [\exp\{\tilde{L}Q(t-u)\} \tilde{L} \mathbf{g}_{\mathbf{r}}, Q \tilde{L}^\epsilon \mathbf{g}_{\mathbf{r}'}] \beta \mathbf{v}(r', t) \\ = \partial_{\mathbf{r}} (\Pi^C + \Pi^D) \partial_{\mathbf{r}} \mathbf{v}(r, t),\end{aligned}\quad (50)$$

where the following viscosity fourth order tensors are introduced:

We would attempt a local approximation for the first contribution, because the correlation function $(\delta \rho_{\mathbf{r}'}, \sigma_{\mathbf{r}}^C)$ will decay within molecular dimensions. However, the naive approximation similar to (35) will fail again and for the same reasons. Therefore the proper local approximation will be

$$(\bar{\Psi}_t, \sigma_{\mathbf{r}}^C) = \int_{\Omega(r, r_0)} (\delta \rho_{\mathbf{r}'}, \sigma_{\mathbf{r}}^C) d\mathbf{r}' \beta \mu_{\mathbf{r}}(t) \quad (46)$$

and by using (38) one finally obtains

$$(\bar{\Psi}_t, \sigma_{\mathbf{r}}^C) = \frac{\int_{\Omega(r, r_0)} (\delta \rho_{\mathbf{r}'}, \sigma_{\mathbf{r}}^C) d\mathbf{r}'}{\int_{\Omega(r, r_0)} (\delta \rho_{\mathbf{r}'}, \delta \rho_{\mathbf{r}}) d\mathbf{r}'} \delta \rho(r, t) \equiv c_0^2 \mathbf{1} \delta \rho(r, t) \quad (47)$$

where the constant c_0^2 is the isothermal speed of sound. Note that in the definition of the speed of sound there is no dependence on the friction coefficient γ . Therefore this speed of sound is exactly the same that would be obtained in a MD model. In Appendix A we show that the speed of sound (47) can be recast in the familiar form

$$c_0^2 = \left. \frac{\partial p}{\partial \rho} \right|_T \quad (48)$$

where $p(T, \rho)$ is the pressure. Note that the partial derivative is taken at constant temperature.

B. Viscosity terms

Let us arrange a bit the memory kernels of Eq. (41) by using (42).

$$\begin{aligned}\Pi^C(\mathbf{r}) &\equiv \beta \int_0^\infty du \int d\mathbf{r}' (\exp\{\tilde{L}Qu\} \sigma_{\mathbf{r}}^C, Q \sigma_{\mathbf{r}'}^C) \\ &\approx \beta \int_0^\infty du \int d\mathbf{r}' (\exp\{\tilde{L}u\} \sigma_{\mathbf{r}}^C, Q \sigma_{\mathbf{r}'}^C) \\ &= \beta \int_0^\infty du \int d\mathbf{r}' [\sigma_{\mathbf{r}}^C(u), Q \sigma_{\mathbf{r}'}^C], \\ \Pi^D(\mathbf{r}) &\equiv \beta \int_0^\infty du \int d\mathbf{r}' (\exp\{\tilde{L}Qu\} \sigma_{\mathbf{r}}^D, Q \sigma_{\mathbf{r}'}^D) \\ &\approx \beta \int_0^\infty du \int d\mathbf{r}' (\exp\{\tilde{L}u\} \sigma_{\mathbf{r}}^D, Q \sigma_{\mathbf{r}'}^D) \\ &= \beta \int_0^\infty du \int d\mathbf{r}' [\sigma_{\mathbf{r}}^D(u), Q \sigma_{\mathbf{r}'}^D].\end{aligned}\quad (51)$$

Here we have approximated the ‘‘projected dynamics’’ with the real dynamics because, by expanding the exponential in its power series, one arrives at $\exp\{\tilde{L}Qu\} = \exp\{\tilde{L}u\} + \mathcal{O}(\nabla)$. Therefore, in an expansion to second order in gradients such as the one we are considering here,

both dynamics give the same results.

We can now invoke translational invariance of the equilibrium ensemble to write

$$\begin{aligned}\Pi^C(\mathbf{r}) &= \Pi^C = \frac{1}{V} \int d^3\mathbf{r} \Pi^C(\mathbf{r}), \\ \Pi^D(\mathbf{r}) &= \Pi^D = \frac{1}{V} \int d^3\mathbf{r} \Pi^D(\mathbf{r}).\end{aligned}\quad (52)$$

The isotropy of the equilibrium ensemble implies that the fourth order tensors should be isotropic too, that is, of the form [15]

$$\begin{aligned}\Pi_{\mu\nu,\mu'\nu'}^C &= \eta^C (\delta_{\mu\mu'}\delta_{\nu\nu'} + \delta_{\mu\nu'}\delta_{\nu\mu'}) \\ &\quad + \left(\zeta^C - \frac{2}{3}\eta^C\right) \delta_{\mu\nu}\delta_{\mu'\nu'}, \\ \Pi_{\mu\nu,\mu'\nu'}^D &= \eta^D (\delta_{\mu\mu'}\delta_{\nu\nu'} + \delta_{\mu\nu'}\delta_{\nu\mu'}) \\ &\quad + \left(\zeta^D - \frac{2}{3}\eta^D\right) \delta_{\mu\nu}\delta_{\mu'\nu'},\end{aligned}\quad (53)$$

where the shear and bulk viscosities are given by

$$\begin{aligned}\eta^C &= \beta \int_0^\infty du \frac{1}{V} [\Sigma_{\mu\nu}^C(u), \mathcal{Q}\Sigma_{\mu\nu}^C], \\ \left(\zeta^C - \frac{2}{3}\eta^C\right) &= \beta \int_0^\infty du \frac{1}{V} [\Sigma_{\mu\mu}^C(u), \mathcal{Q}\Sigma_{\nu\nu}^C], \\ \eta^D &= \beta \int_0^\infty du \frac{1}{V} [\Sigma_{\mu\nu}^D(u), \mathcal{Q}\Sigma_{\mu\nu}^D], \\ \left(\zeta^D - \frac{2}{3}\eta^D\right) &= \beta \int_0^\infty du \frac{1}{V} [\Sigma_{\mu\mu}^D(u), \mathcal{Q}\Sigma_{\nu\nu}^D],\end{aligned}\quad (54)$$

where $\mu \neq \nu$ and no summation over repeated indices is implied. Here the total stress tensors are defined as

$$\begin{aligned}\Sigma^C &= \int d^3\mathbf{r} \sigma_{\mathbf{r}}^C = \sum_i \frac{\mathbf{p}_i}{m} \mathbf{p}_i + \sum_{ij} (\mathbf{r}_i - \mathbf{r}_j) \mathbf{F}_{ij}^C, \\ \Sigma^D &= \int d^3\mathbf{r} \sigma_{\mathbf{r}}^D = \sum_{ij} (\mathbf{r}_i - \mathbf{r}_j) \mathbf{F}_{ij}^D \\ &= -\gamma \sum_{ij} (\mathbf{r}_i - \mathbf{r}_j) \omega_{ij} (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{e}_{ij}.\end{aligned}\quad (55)$$

Note that η^D and ζ^D in (54) contain a factor of γ^2 coming from the two dissipative forces appearing in the time correlation. Therefore they vanish as $\gamma \rightarrow 0$.

Finally, substitution of (50) and (53) together with the Euler terms (47) into (41) leads to the Navier-Stokes equation

$$\begin{aligned}\partial_t \mathbf{g}(\mathbf{r}, t) &= -c_0^2 \nabla \delta \rho(\mathbf{r}, t) + \eta \nabla^2 \mathbf{v}(\mathbf{r}, t) \\ &\quad + \left(\zeta - \frac{2\eta}{3}\right) \nabla[\nabla \cdot \mathbf{v}(\mathbf{r}, t)]\end{aligned}\quad (56)$$

where the total shear viscosity is $\eta = \eta^C + \eta^D$ and the total bulk viscosity is $\zeta = \zeta^C + \zeta^D$.

VI. CONCLUDING REMARKS

In this paper we have formulated the hydrodynamic equations for DPD taking as starting point the microscopic Fokker-Planck equation that governs the position and velocity of the dissipative particles. We have neglected the energy density field as a proper hydrodynamic variable because it is not conserved in DPD. Its balance equation has source and dissipative terms that cannot be expressed as the divergence of a flux. Therefore, the energy is a rapidly varying function for which a proper hydrodynamic equation does not exist. On the other hand, we find transport equations for the mass and momentum density fields which have the expected form of Navier-Stokes equations. The main result of this paper is not to have found these equations, which are expected on merely physical grounds: Galilean invariance and isotropy of the microscopic equations together with conservation of mass and momentum force the equations to have the structure of Navier-Stokes equations [1]. Rather, the two main results of the derivation are the microscopic expressions for the sound speed (48) and the viscosity coefficients (54). The sound speed is given in terms of the usual thermodynamic expression. The sound speed squared is given by the derivative of the pressure with respect to the density at constant temperature. The pressure and hence the sound speed do not depend on the friction coefficient of the Brownian dashpots. This is not completely unexpected in view of the result of Ref. [9] that states that the equilibrium state of DPD is the canonical ensemble, which is independent of the friction coefficient. Being an equilibrium property of the system, it is not surprising that the sound speed does not depend on the friction coefficient. In other words, the sonic propagation is due entirely to the conservative part of the microscopic dynamics.

On the other hand, the shear and bulk viscosities are seen to have two contributions that come from the conservative and from the dissipative part of the dynamics, respectively. The dissipative contribution is proportional to the square of the friction coefficient and vanishes in a purely MD simulation, for which $\gamma = 0$. In this limit, the viscosity is given by the conservative contribution only. Both contributions are given in terms of Green-Kubo formulas. In Ref. [1] the viscosity is proportional to the friction coefficient and therefore vanishes in the limit of zero friction. This cannot be the case because it would mean that a molecular dynamics simulation would produce non-viscous behavior. Therefore such an expression can only hold for high enough friction in a way that the conservative contribution to the viscosity can be neglected. On the other hand, in view of the γ^2 factor in front of the dissipative contribution, it is not clear that the dependence of the dissipative contribution to the viscosity is simply linear as stated in Ref. [1] [if one assumes that the correlation of the stress tensor in (55) does not depend strongly on γ then the dependence should be quadratic].

We finally comment on the range of temperature for which a Newtonian description of the liquid is valid. At low temperature the noise level is very small and the fric-

tion tends to freeze the motion of the particles. In the absence of forcing boundary conditions the particles will tend to form a sort of colloidal crystal, searching for better accommodation in the potential created by the rest of the particles [8]. It is apparent that the rheological properties of such a state are likely to be different from a Newtonian viscous response. This non-Newtonian response has been actually reported in Ref. [1]. A criterion for the validity of the Navier-Stokes equations would be then that the temperature of the system should be well above the melting temperature of the dissipative crystal.

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APPENDIX A

The numerator of (47) can be written as

$$\int_{\Omega(\mathbf{r}, r_0)} (\delta\rho_{\mathbf{r}'}, \sigma_{\mathbf{r}'}^C) d\mathbf{r}' = m[\delta N(\mathbf{r}, r_0), \sigma_{\mathbf{r}}^C], \quad (\text{A1})$$

where $\delta N(\mathbf{r}, r_0)$ is the fluctuating number of particles within the region $\Omega(\mathbf{r}, r_0)$ of volume Ω and $\sigma_{\mathbf{r}}^C$ is the total stress tensor of the particles within $\Omega(\mathbf{r}, r_0)$. The ensemble average is performed with the canonical ensemble, i.e., at constant temperature T , number of particles N , and volume V . However, one expects the equivalence of averages of quantities defined for the subvolume Ω performed with the canonical ensemble and those performed with a grand canonical ensemble at constant temperature T , chemical potential μ , and volume Ω , that is,

$$m\langle \delta N(\mathbf{r}, r_0) \sigma_{\mathbf{r}}^C \rangle^{T, N, V} = m\langle \delta N(\mathbf{r}, r_0) \sigma_{\mathbf{r}}^C \rangle^{T, \mu, \Omega}. \quad (\text{A2})$$

The actual value of the chemical potential μ is such that it produces an average number of particles $\langle M \rangle$ in the volume Ω equal to $\frac{N}{V}\Omega$, in order to have the same average density inside and outside of the region $\Omega(\mathbf{r}, r_0)$. The grand canonical ensemble can be defined as an statistical average of canonical averages, that is,

$$\langle \delta N(\mathbf{r}, r_0) \sigma_{\mathbf{r}}^C \rangle^{T, \mu, \Omega} \equiv \sum_{M=0}^{\infty} P_{T, \mu, \Omega}(M) \langle \delta M \sigma_{\mathbf{r}}^C \rangle^{E, M, \Omega} \quad (\text{A3})$$

where the probability of having M particles within the volume Ω is given by

$$P_{T, \mu, \Omega}(M) = \frac{\exp -\beta\{F(T, M, \Omega) - \mu M\}}{\sum_{M=0}^{\infty} \exp -\beta\{F(T, M, \Omega) - \mu M\}}. \quad (\text{A4})$$

The free energy is defined as $F(T, M, \Omega)$

$= -k_B \ln Z(T, M, \Omega)$, where $Z(T, M, \Omega)$ is the partition function in the canonical ensemble. In this way,

$$\begin{aligned} & \sum_{M=0}^{\infty} P_{T, \mu, \Omega}(M) \langle \delta M \sigma_{\mathbf{r}}^C \rangle^{T, M, \Omega} \\ &= \sum_{M=0}^{\infty} P_{T, \mu, \Omega}(M) \delta M \langle \sigma_{\mathbf{r}}^C \rangle^{T, M, \Omega} \\ &= k_B T \frac{\partial}{\partial \mu} \sum_{M=0}^{\infty} P_{T, \mu, \Omega}(M) \langle \sigma_{\mathbf{r}}^C \rangle^{T, M, \Omega} \\ &= k_B T \frac{\partial}{\partial \mu} \sum_{M=0}^{\infty} P_{T, \mu, \Omega}(M) p(T, M, \Omega) \mathbf{1} \\ &= k_B T \frac{\partial}{\partial \mu} p(T, \mu, \Omega) \mathbf{1}, \end{aligned} \quad (\text{A5})$$

where $p(T, M, \Omega)$ is the pressure in the canonical ensemble of a system of M particles enclosed in a volume Ω at a temperature T and where $p(T, \mu, \Omega)$ is the pressure defined in the grand canonical ensemble.

We may follow the same steps for the denominator in (47), i.e.,

$$\begin{aligned} \int_{\Omega(\mathbf{r}, r_0)} (\delta\rho_{\mathbf{r}'}, \delta\rho_{\mathbf{r}'}) d\mathbf{r}' &= m\langle \delta N(\mathbf{r}, r_0) \delta\rho_{\mathbf{r}} \rangle^{T, \mu, \Omega} \\ &= k_B T m \frac{\partial}{\partial \mu} \langle \rho \rangle^{T, \mu, \Omega}, \end{aligned} \quad (\text{A6})$$

so finally the speed of sound (47) becomes

$$c_0^2 = \frac{\frac{\partial p}{\partial \mu}}{\frac{\partial \rho}{\partial \mu}} = \frac{\partial p}{\partial \rho} \Big|_T. \quad (\text{A7})$$

APPENDIX B

In this appendix we show that the cross correlations D and C in (49) cancel each other. We introduce the time reversal operator defined by

$$\mathcal{R}f(p, q) = f(-p, q) \quad (\text{B1})$$

where $f(p, q)$ is an arbitrary function of phase space. In particular we obtain

$$\begin{aligned} \mathcal{R}\sigma^C &= \sigma^C, \\ \mathcal{R}\sigma^D &= -\sigma^D. \end{aligned} \quad (\text{B2})$$

It is a matter of simple algebra to show that the time reversal operator satisfies the following properties:

$$\begin{aligned} \mathcal{R}\tilde{L}^\epsilon &= \tilde{L}\mathcal{R}, \\ \mathcal{R}\mathcal{P} &= \mathcal{P}\mathcal{R}, \\ \mathcal{R}^2 &= \mathcal{R}, \\ (\mathcal{R}f, g) &= (f, \mathcal{R}g). \end{aligned} \quad (\text{B3})$$

With these properties we arrive at the following equation:

$$\begin{aligned}
(\exp\{\mathcal{Q}\tilde{L}^\epsilon u\}\mathcal{Q}\sigma^\beta, \mathcal{Q}\sigma^\alpha) &= (\exp\{\mathcal{Q}\tilde{L}^\epsilon u\}\mathcal{Q}\sigma^\beta, \mathcal{R}^2\mathcal{Q}\sigma^\alpha) \\
&= \epsilon^\alpha \epsilon^\beta (\exp\{\mathcal{Q}\tilde{L}^\epsilon u\}\mathcal{Q}\sigma^\beta, \mathcal{Q}\sigma^\alpha) \\
&= \epsilon^\alpha \epsilon^\beta (\exp\{\mathcal{Q}\tilde{L}^\epsilon u\}\mathcal{Q}\sigma^\alpha, \mathcal{Q}\sigma^\beta)
\end{aligned}
\tag{B4}$$

where α and β denote D or C and $\epsilon^D = 1$, $\epsilon^C = -1$. Therefore,

$$(\mathcal{Q}\sigma^D, \exp\{\mathcal{Q}\tilde{L}^\epsilon u\}\mathcal{Q}\sigma^C) + (\mathcal{Q}\sigma^C, \exp\{\mathcal{Q}\tilde{L}^\epsilon u\}\mathcal{Q}\sigma^D) = 0.
\tag{B5}$$

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