

# Langevin Equations for Fluctuating Hydrodynamics

Notes by Aleksandar Donev, CIMS

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## 1 Fluctuating Hydrodynamics

We illustrate the general formalism by showing how isothermal compressible fluctuating hydrodynamics for a single-component fluid can be written in the augmented Langevin form. A similar calculation is presented in Ref. [1] though in indicial form and also the Hamiltonian part of the fluid dynamics is not discussed. The case of an incompressible fluid is substantially more complicated to fit into a Hamiltonian framework [2, 3] and not much is gained in the process for our purposes, so we do not discuss it here. The case when the total energy is included as a coarse-grained variable and one considers an isolated instead of a system in contact with a thermal bath is discussed extensively in the book [4]. In particular, it is demonstrated there that fluctuating hydrodynamics can be put in a Hamiltonian framework that fits in the GENERIC formalism.

### 1.1 Single-Component Fluid

For an Eulerian description of an isothermal compressible fluid  $\mathbf{x}(t) = (\rho(\mathbf{r}, t), \mathbf{v}(\mathbf{r}, t))$ , or, if an incompressibility constraint is added ( $\rho = \text{const.}$ ), then the degrees of freedom are further reduced to just the velocity. Of course one can use the conserved momentum density  $\mathbf{j} = \rho\mathbf{v}$  fields as variable instead of velocity, though it does not seem crucial here. The equations that we want to obtain in the end are the usual Landau-Lifshitz equations,

$$\begin{aligned}\partial_t \rho &= -\nabla \cdot (\rho \mathbf{v}) \\ \rho(\partial_t \mathbf{v}) &= -\rho \mathbf{v} \cdot \nabla \mathbf{v} - \nabla P + \nabla \cdot (\eta \nabla \mathbf{v}) + \nabla \cdot [(2k_B T \eta) \mathbf{W}(t)].\end{aligned}\tag{1}$$

The Hamiltonian (total energy) is

$$H = \int \left[ \rho \frac{v^2}{2} + \epsilon(\rho) \right] d\mathbf{r},\tag{2}$$

where  $\epsilon(\rho)$  is the internal energy of the fluid (at constant temperature), with

$$\frac{\partial H}{\partial \rho} = \frac{v^2}{2} + \frac{d\epsilon}{d\rho} \text{ and } \frac{\partial H}{\partial \mathbf{v}} = \rho \mathbf{v}.\tag{3}$$

Note the thermodynamic relation [5]

$$\rho \frac{d\epsilon}{d\rho} = \rho \epsilon' = \epsilon + P,$$

where  $P$  is the pressure, relating gradients of  $\partial H / \partial \rho$  to gradients of pressure via

$$\nabla \epsilon' = \rho^{-1} \nabla P.\tag{4}$$

### 1.1.1 Dissipative and Fluctuating Dynamics: Diffusion

We will assume the usual form of the viscous dissipation. Ignoring for a moment the bulk viscosity terms, one suitable form of the operator  $\mathbf{B}$  in (??) is

$$\mathbf{B} = \begin{bmatrix} 0 \\ \rho^{-1} \nabla \cdot \boldsymbol{\eta}^{1/2} \end{bmatrix} = \begin{bmatrix} 0 \\ \mathbf{B}_v \end{bmatrix}, \quad (5)$$

where in general the fourth-order positive-definite viscosity tensor  $\boldsymbol{\eta}$  may depend on density. This gives the well-known viscous term in the velocity equation,

$$(\mathbf{B}_v \mathbf{B}_v^*) \frac{\partial H}{\partial \mathbf{v}} = \rho^{-1} \nabla \cdot (\boldsymbol{\eta} \nabla \mathbf{v}) = \rho^{-1} \nabla \cdot \left[ \boldsymbol{\eta} (\nabla \mathbf{v} + \nabla^T \mathbf{v}) + \left( \kappa - \frac{2}{d} \boldsymbol{\eta} \right) (\nabla \cdot \mathbf{v}) \mathbf{I} \right]$$

along with a corresponding divergence of a stochastic stress contribution ala Landau-Lifshitz for the fluctuating part. Since  $\boldsymbol{\eta}$  does not depend on velocity (for Newtonian fluids), there is no additional drift term,

$$\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{M} = \mathbf{0}.$$

### 1.1.2 Non-dissipative Dynamics: Advection

For a compressible fluid with periodic boundaries, the reversible generator of the Navier-Stokes equations is given in Ottinger's book [4] [to get this form certain integrations by part are carried out by ignoring boundary terms, see (7.150)],

$$\mathbf{L} = \begin{bmatrix} 0 & -\nabla \cdot \\ -\nabla & \boldsymbol{\omega} \rho^{-1} \end{bmatrix}. \quad (6)$$

For more general boundary conditions one should be more careful with the boundary conditions. The skew-adjointness of  $\mathbf{L}$  is evident because the vorticity tensor

$$\omega_{jk} = \frac{\partial v_k}{\partial r_j} - \frac{\partial v_j}{\partial r_k}$$

is antisymmetric, and it is well-known that the divergence and gradient operators are negative adjoints of each other. Also note that the reciprocity relation (??) is obeyed because the velocity-velocity coupling ( $\epsilon_k \epsilon_j = 1$ ) involves  $\boldsymbol{\omega}$  and thus changes sign upon time reversal, while the velocity-density coupling ( $\epsilon_k \epsilon_j = -1$ ) does not change sign.

For the density equation,  $\mathbf{L} \cdot \frac{\partial H}{\partial \mathbf{x}}$  gives the familiar  $-\nabla \cdot (\rho \mathbf{v})$  term. From equations (3) and (4) we get the familiar pressure-gradient term in the velocity equation. The advective term  $-\mathbf{v} \cdot \nabla \mathbf{v}$  in the velocity equation comes from  $\boldsymbol{\omega} \mathbf{v} = -(\nabla \times \mathbf{v}) \times \mathbf{v}$  and the vector identity

$$\mathbf{v} \cdot \nabla \mathbf{v} = \nabla \left( \frac{v^2}{2} \right) + (\nabla \times \mathbf{v}) \times \mathbf{v}.$$

The only remaining part is to look at the divergence of  $\mathbf{L}$ , that is, the compressibility of ideal fluid flow in (Eulerian) phase space. The only possible contribution comes because the vorticity tensor  $\boldsymbol{\omega}$  depends on velocity. However, because this dependence is linear in the spatial derivatives of velocity, the functional derivative [5] vanishes,

$$\frac{\delta \boldsymbol{\omega}[\mathbf{v}(\mathbf{r})]}{\delta \mathbf{v}} = \mathbf{0} \text{ giving } \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{L} = \mathbf{0},$$

again ignoring boundary terms. These are however rather formal arguments, since even defining an equilibrium distribution requires an appropriate measure of phase space volume, and the familiar Lebesgue measure does not generalize to infinite-dimensional spaces. The usual argument out of this fundamental difficulty is to first apply a truncation (e.g., a cutoff wavenumber) or discretization (e.g., finite-volume averaging) procedure to the SPDEs and then study the resulting semi-discrete system of SDEs. Such an approach requires introducing a discrete free-energy function and ensuring that the discretization/truncation preserves the Hamiltonian structure of the reversible dynamics, which is usually rather non-trivial.

### 1.1.3 Conserved Variables

In discretizations it is preferred to use conserved variables, specifically, the momentum density  $\mathbf{g} = \rho \mathbf{v}$  instead of velocity. Using the coarse-grained variables  $\mathbf{x}(t) = (\rho(\mathbf{r}, t), \mathbf{g}(\mathbf{r}, t))$ , the reversible part of the dynamics is generated by [see (2.60) in [4], and also [5]],

$$\mathbf{L} = \begin{bmatrix} 0 & -\frac{\partial}{\partial \mathbf{r}} \cdot \rho \\ -\rho \frac{\partial}{\partial \mathbf{r}} & \mathbf{L}_g \end{bmatrix},$$

where we use the notation  $\partial/\partial \mathbf{r} \equiv \nabla$  to make it easier to distinguish differential operators acting on everything to the left versus those acting on a particular field. In these variables the counterpart of the vorticity tensor is defined by

$$\mathbf{L}_g \cdot \mathbf{v} = -\nabla \cdot (\mathbf{v} \mathbf{g}) - (\nabla \mathbf{v}) \cdot \mathbf{g} \text{ or } (\mathbf{L}_g)_{jk} = -\frac{\partial}{\partial r_k} g_j - g_k \frac{\partial}{\partial r_j}. \quad (7)$$

In these variables the dissipative/fluctuating dynamics is generated by

$$\mathbf{B} = \begin{bmatrix} 0 \\ \nabla \cdot \boldsymbol{\eta}^{1/2} \end{bmatrix} = \begin{bmatrix} 0 \\ \mathbf{B}_g \end{bmatrix}. \quad (8)$$

Since  $\mathbf{L}_g$  depends on  $\mathbf{g}$  there may be a nonzero compressibility in phase space  $\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{L}$  and thus an additional drift. In order to calculate  $\frac{\partial}{\partial \mathbf{g}} \cdot \mathbf{L}_g$  we write  $\mathbf{L}_g$  in integral form, without carrying out an integration by parts to convert it into a local differential operator as done in (7),

$$(\mathbf{L}_g)_{jk} = \int d\mathbf{r}' \left[ \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial r_j} g_k(\mathbf{r}) - g_j(\mathbf{r}') \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial r'_k} \right]$$

From this representation we see that there is no additional drift term necessary since [c.f. (2.13) in [6]],

$$\frac{\partial}{\partial \mathbf{g}} \cdot \mathbf{L}_g = \mathbf{0}.$$

Putting the pieces together gives the stochastic conservation laws suggested by Landau and Lifshitz,

$$\begin{aligned} \partial_t \rho &= -\nabla \cdot \mathbf{g} \\ \partial_t \mathbf{g} &= -\nabla \cdot (\mathbf{v} \mathbf{g}) - \nabla P + \nabla \cdot (\boldsymbol{\eta} \nabla \mathbf{v}) + \nabla \cdot \left[ (2k_B T \boldsymbol{\eta})^{1/2} \boldsymbol{\mathcal{W}} \right]. \end{aligned} \quad (9)$$

As discussed in Section (??), the choice of variables matters. One has to decide whether the coarse-grained Hamiltonian is (2) or

$$H = \int \left[ \frac{g^2}{2\rho} + \epsilon(\rho) \right] d\mathbf{r}. \quad (10)$$

The transformation from  $\mathbf{x} = (\rho, \mathbf{g})$  to  $\tilde{\mathbf{x}} = (\rho, \mathbf{v})$  has a non-constant Jacobian due to the nonlinearity,

$$\mathbf{J} = \begin{bmatrix} \mathbf{I} & \mathbf{0} \\ -\rho^{-1}\mathbf{v} & \rho^{-1} \end{bmatrix}, \text{ so that } \ln |\mathbf{J}| = -\Delta V^{-1} \int \ln \rho \, d\mathbf{r},$$

where  $\Delta V^{-1}$  is a coarse-graining volume, making it clear that the free-energy correction due to curvature is non-extensive. If we assume that the “natural” variable is  $\mathbf{g}$  and the coarse-grained free energy functional is (10), then (??) says that the transformed free energy functional is

$$\tilde{H}[\rho, \mathbf{v}] = \int \left[ \rho \frac{v^2}{2} + \epsilon(\rho) - \Delta V^{-1} k_B T \ln \rho \right] d\mathbf{r}.$$

It is not hard to show that the transformed  $\mathbf{L}$  is exactly (6) and the transformed  $\mathbf{B}$  is exactly (5). The transformed equations have an extra forcing term due to the non-constant Jacobian,

$$\begin{aligned} \partial_t \rho &= -\nabla \cdot (\rho \mathbf{v}) \\ \rho (\partial_t \mathbf{v}) &= -\rho \mathbf{v} \cdot \nabla \mathbf{v} - \nabla \left( P + \frac{k_B T}{\Delta V} \ln \rho \right) + \nabla \cdot (\boldsymbol{\eta} \nabla \mathbf{v}) + \nabla \cdot [(2k_B T \boldsymbol{\eta}) \mathbf{W}(t)], \end{aligned} \quad (11)$$

which can be interpreted as a modification of the thermodynamic pressure. Conversely, if we assumed that the “natural” variable is  $\mathbf{v}$ , then the momentum equation (9) would have an extra forcing term.

Note, however, that this term can be seen to be of the order of  $N_p^{-1}$ , where  $N_p = \rho \Delta V / m$  is the number of particles in a representative (coarse-graining) volume. For an ideal gas  $\nabla P = (k_B T / m) \nabla \rho$  while the new term gives  $N_p^{-1} (k_B T / m) \nabla \rho$ , which is of  $O(N_p^{-1})$ . Note that the free-energy functional is usually only known to this order anyway. For example, for an ideal gas, the equilibrium distribution of  $N_p$  should be a Poisson distribution, whereas the free-energy functional usually written already makes a Gaussian approximation. If we define  $\epsilon(\rho)$  based on the knowledge that the distribution of  $N_p$  when  $g = 0$  is Poisson, and analytically extend  $N_p! \equiv \Gamma(N_p + 1)$  to non-integers,

$$\exp \left[ -\frac{\tilde{\epsilon}(\rho)}{k_B T} \right] \sim \frac{\bar{N}_p^{N_p} \exp(-\bar{N}_p)}{\Gamma(N_p + 1)},$$

then the forcing term in the momentum equation would obtain a leading order correction

$$\rho \nabla \tilde{\epsilon}' = \nabla \tilde{P}, \text{ where } \tilde{P} = P - \frac{k_B T}{2\Delta V} \ln \rho,$$

which is of the same order as the correction in (11). This suggests that omitting the Jacobian terms will lead to a somewhat modified equilibrium distribution, but the correction is a “finite-coarse-graining” effect and thus expected to be small.

## 1.2 Fluid Mixtures

It is useful in applications to include at least one additional “advected” scalar field  $c(\mathbf{r}, t)$ , which we will call concentration but which can more appropriately be thought of as an order parameter. For example,  $c = \rho_1 / \rho$  could be the mass fraction in a two-component fluid, then it is more appropriate to use  $\rho_1$  as a variable. As was discussed above, the choice of variables is an important and nontrivial issue, especially when writing the free energy functional. Here we assume that the functional derivatives of the free energy with respect to the hydrodynamic variables are not affected by the order parameter.

Using the coarse-grained variables  $\mathbf{x}(t) = (\rho(\mathbf{r}, t), \mathbf{g}(\mathbf{r}, t), c(\mathbf{r}, t))$ , the reversible part of the dynamics is generated by [see (2.60) in [4], and also [5]],

$$\mathbf{L} = \begin{bmatrix} 0 & -\frac{\partial}{\partial \mathbf{r}} \cdot \rho & 0 \\ -\rho \frac{\partial}{\partial \mathbf{r}} & \mathbf{L}_g & (\nabla c) \\ 0 & -(\nabla c) & 0 \end{bmatrix},$$

Note that the reversible dynamics now includes a body force  $\mathbf{F} = \mu \nabla c$  in the concentration equation. For a mixture of dynamically identical species the difference in chemical potential between the species is  $\mu = 0$  and the concentration does not affect the hydrodynamic variables.

### 1.2.1 Order Parameter is Conserved

If the order parameter  $c$  is conserved, then we denote

$$\frac{\partial H}{\partial c} = \mu(\rho, c) \quad (12)$$

as the chemical potential of the mixture, where  $H$  is the coarse-grained free energy functional. The dissipative dynamics that ensures strict local decrease in the free energy (more precisely, positive entropy production) is

$$\mathbf{B} = \begin{bmatrix} 0 & 0 \\ \mathbf{B}_v & 0 \\ 0 & \frac{\partial}{\partial \mathbf{r}} \cdot \tilde{\chi}^{1/2} \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ \mathbf{B}_v & 0 \\ 0 & \mathbf{B}_c \end{bmatrix},$$

giving the familiar advection-diffusion equation for concentration,

$$\partial_t c + \mathbf{v} \cdot \nabla c = \nabla \cdot (\tilde{\chi} \nabla \mu) + \nabla \cdot \left[ (2k_B T \tilde{\chi})^{1/2} \tilde{\mathbf{W}} \right],$$

where  $\tilde{\mathbf{W}}$  is a stochastic white-noise flux associated with order parameter fluctuations. Assuming that  $\mu$  depends only on  $c$ , we get

$$\tilde{\chi} \nabla \mu = \left( \tilde{\chi} \frac{\partial \mu}{\partial c} \right) \nabla c = \chi \nabla c, \quad (13)$$

relating the usual diffusion coefficient  $\chi = \tilde{\chi} (\partial \mu / \partial c)$  to the coefficient that determines the covariance of the stochastic flux.

### 1.2.2 Order Parameter is a Scalar

If the conserved quantity is  $\rho c$  (that is,  $c$  is a ratio of densities), then the appropriate definition of the chemical potential is [It does not look like there is a consistent unit of  $\mu$ ]

$$\frac{\partial H}{\partial c} = \mu \rho, \quad (14)$$

and the dissipative generator is

$$\mathbf{B}_c = \rho^{-1} \frac{\partial}{\partial \mathbf{r}} \cdot \tilde{\chi}^{1/2},$$

leading to the relation  $\chi = \rho^{-1} \tilde{\chi} (\partial \mu / \partial c)$  and the concentration equation [7]

$$\rho (\partial_t c + \mathbf{v} \cdot \nabla c) = \nabla \cdot (\rho \chi \nabla c) + \nabla \cdot \left[ \left( \frac{2k_B T \chi \rho}{(\partial \mu / \partial c)} \right)^{1/2} \tilde{\mathbf{W}} \right].$$

### 1.2.3 Isothermal Multicomponent Mixtures

When there are more than two fluid components, using the concentrations  $c_i = \rho_i/\rho$  becomes cumbersome and it is better to use the conserved partial densities  $\rho_i$  as variables [3]. For the two component fluid, we can start from the equations above and convert to the new variables to see what the appropriate form of the equations is. We should, however, keep in mind that a good approximation to the free energy functional requires selecting “natural” variables and in some cases the appropriate choice may be  $\rho_1$  and  $\rho_2$  and not  $\rho$  and  $c$ . This is the case, for example, for a mixture of two non-interacting colored random walkers (each color representing a species). Because the transformation from densities to concentrations is nonlinear, the Jacobian is not constant and needs to be taken into account.

We consider an isothermal mixture of  $n$  species and choose as our variables  $\mathbf{x} = (\boldsymbol{\rho}, \mathbf{v})$  where  $\boldsymbol{\rho} = \{\rho_1, \dots, \rho_n\}$ . Denoting the chemical potential of species  $i$  with  $\mu_i$  [Donev: *Not sure about how consistent this is with stat mech books...*], we have

$$\frac{\partial H}{\partial \rho_i} = \frac{v^2}{2} + \mu_i, \text{ and } \frac{\partial H}{\partial \mathbf{v}} = \rho \mathbf{v},$$

where the total density is  $\rho = \sum_{i=1}^n \rho_i$ , the generator of the fluctuating hydrodynamic equations can be written as

$$\mathbf{N} = \begin{bmatrix} \frac{\partial}{\partial \mathbf{r}} \cdot \boldsymbol{\Lambda} \frac{\partial}{\partial \mathbf{r}} & \left\{ -\frac{\partial}{\partial \mathbf{r}} \cdot \frac{\rho_i}{\rho} \right\} \\ \left\{ -\frac{\rho_i}{\rho} \frac{\partial}{\partial \mathbf{r}} \right\} & \boldsymbol{\omega} \rho^{-1} \end{bmatrix},$$

where the notation  $\left\{ -\frac{\partial}{\partial \mathbf{r}} \cdot \frac{\rho_i}{\rho} \right\}$  denotes a column vector of differential operators, one per species. Here  $\boldsymbol{\Lambda}$  is a symmetric positive-semidefinite matrix of diffusion coefficients whose rows and columns sum to zero, giving a total of  $n(n-1)/2$  independent diffusion coefficients.

That this choice gives the usual velocity equation can be seen from the Gibbs-Duhem relation for an isothermal system [Donev: *Also not sure this is right*],

$$\sum_{i=1}^n \rho_i \nabla \mu_i = \nabla P. \tag{15}$$

For the individual species, using the fact that the rows of  $\boldsymbol{\Lambda}$  add to zero we see that there is no contribution from  $\nabla(v^2)$ , and so we get the advection-diffusion equation

$$\partial_t \rho = \frac{\partial}{\partial \mathbf{r}} \cdot \{ -\rho \mathbf{v} + \boldsymbol{\Lambda} \cdot (\nabla \boldsymbol{\mu}) \}.$$

By adding these equations together and noting that the columns of  $\boldsymbol{\Lambda}$  add to zero we get the expected density equation without any diffusive terms.

### 1.2.4 Thermo-Diffusion in Multicomponent Mixtures

For mixtures there is an additional complication due to the coupling between concentration and temperature due to the Soret/Dufour effect, especially when there are more than two species. We therefore consider a mixture of  $n$  species and include the internal energy density  $\epsilon(\mathbf{r}, t)$  as a variable,  $\mathbf{x} = (\boldsymbol{\rho}, \mathbf{g}, \epsilon)$ , where  $\boldsymbol{\rho} = \{\rho_1, \dots, \rho_n\}$ . In numerical implementations the total energy  $e = \epsilon + g^2/(2\rho)$  would be used to ensure strict energy conservation, but this does not change the form of the equations except for the advective terms. An isothermal description is not appropriate when energy is included and one should use the two-generator GENERIC equation (??). Here we

focus on the dissipative part of the dynamics, i.e., diffusion and thermo-diffusion, responsible for a non-decreasing entropy.

Since the momentum does not enter in the dissipative part, we focus on the variable  $\mathbf{x} = (\boldsymbol{\rho}, \epsilon)$  for the remainder of this section. For ideal fluid mixtures, we define the chemical potential via [3]

$$\frac{\partial S}{\partial \rho_i} = -\frac{\mu_i}{T},$$

and for the energy we have the usual thermodynamic relation

$$\frac{\partial S}{\partial \epsilon} = \frac{1}{T}, \text{ so that } \frac{\partial}{\partial \mathbf{r}} \left( \frac{\partial S}{\partial \epsilon} \right) = -\frac{1}{T^2} \frac{\partial T}{\partial \mathbf{r}}.$$

It is possible to relate the gradient of the chemical potentials to concentrations as in (13) [7] but for more than two components this obscures the form of the equations and it is better to work with chemical potentials directly.

The dissipative part of the dynamics is given by

$$\mathbf{M} = - \left[ \begin{array}{cc} \frac{\partial}{\partial \mathbf{r}} \cdot \boldsymbol{\Lambda} \frac{\partial}{\partial \mathbf{r}} & \frac{\partial}{\partial \mathbf{r}} \cdot (\boldsymbol{\Lambda} \boldsymbol{\lambda}) \frac{\partial}{\partial \mathbf{r}} \\ \frac{\partial}{\partial \mathbf{r}} \cdot (\boldsymbol{\lambda}^T \boldsymbol{\Lambda}) \frac{\partial}{\partial \mathbf{r}} & \frac{\partial}{\partial \mathbf{r}} \cdot (\boldsymbol{\lambda}^T \boldsymbol{\Lambda} \boldsymbol{\lambda}) \frac{\partial}{\partial \mathbf{r}} \end{array} \right],$$

where we omit dots for the matrix-vector products to simplify the notation and  $\boldsymbol{\Lambda}$  was introduced in the previous section. Here  $\boldsymbol{\lambda}$  is vector of  $n$  thermo-diffusion coefficients, but because the product  $\boldsymbol{\Lambda} \cdot \boldsymbol{\lambda}$  is not affected by adding a constant to  $\boldsymbol{\lambda}$ , there are only  $n - 1$  thermo-diffusion coefficients (for two species the familiar Soret coefficient is proportional to  $\lambda_1 - \lambda_2$ ). The above  $\mathbf{M}$  leads to the contribution to the dynamics due to diffusion

$$\begin{aligned} (\partial_t \boldsymbol{\rho})_{\text{diff}} &= \frac{\partial}{\partial \mathbf{r}} \cdot \left\{ \boldsymbol{\Lambda} \left[ \frac{\partial}{\partial \mathbf{r}} \left( \frac{\boldsymbol{\mu}}{T} \right) + \frac{\boldsymbol{\lambda}}{T^2} \frac{\partial T}{\partial \mathbf{r}} \right] \right\} \\ (\partial_t \epsilon)_{\text{diff}} &= \frac{\partial}{\partial \mathbf{r}} \cdot \left\{ \boldsymbol{\lambda}^T \boldsymbol{\Lambda} \left[ \frac{\partial}{\partial \mathbf{r}} \left( \frac{\boldsymbol{\mu}}{T} \right) + \frac{\boldsymbol{\lambda}}{T^2} \frac{\partial T}{\partial \mathbf{r}} \right] \right\}. \end{aligned}$$

In order to obtain  $\mathbf{B}$ , we need to factorize  $\mathbf{M}$ . This can be done explicitly, assuming that we have first performed a Cholesky decomposition

$$\boldsymbol{\Lambda} = \boldsymbol{\chi} \boldsymbol{\chi}^T,$$

where  $\boldsymbol{\chi}$  is an  $n \times (n - 1)$  lower-triangular matrix whose columns sum to zero [containing the  $n(n - 1)/2$  “diffusion coefficients”, which need not be positive]. The special properties of  $\boldsymbol{\Lambda}$  ensure that one of its eigenvalues is zero and such a decomposition exists [*Donev: One hopes that the formulae for gas mixtures from kinetic theory ensure all but one zero eigenvalues are positive but this should be checked numerically if nothing else.*]. It is not hard to show that we can factorize

$$\mathbf{M} = - \left[ \begin{array}{cc} \left\{ \frac{\partial}{\partial \mathbf{r}} \cdot \right\} & 0 \\ 0 & \frac{\partial}{\partial \mathbf{r}} \cdot \end{array} \right] \cdot \mathbf{C} \cdot \mathbf{C}^T \cdot \left[ \begin{array}{cc} \left\{ \frac{\partial}{\partial \mathbf{r}} \right\} & 0 \\ 0 & \frac{\partial}{\partial \mathbf{r}} \end{array} \right] = \mathbf{B} \mathbf{B}^*,$$

where the notation  $\left\{ \frac{\partial}{\partial \mathbf{r}} \cdot \right\}$  denotes a diagonal matrix of  $n$  divergence operators, and

$$\mathbf{C} = \left[ \begin{array}{c} \boldsymbol{\chi} \\ \boldsymbol{\lambda}^T \boldsymbol{\chi} \end{array} \right].$$

The above gives us the desired form of the stochastic forcing terms as a divergence of stochastic fluxes,

$$\mathbf{B} \cdot \mathbf{W} = \left[ \begin{array}{c} \frac{\partial}{\partial \mathbf{r}} \cdot (\boldsymbol{\chi} \mathbf{W}) \\ \frac{\partial}{\partial \mathbf{r}} \cdot (\boldsymbol{\lambda}^T \boldsymbol{\chi} \mathbf{W}) \end{array} \right],$$

where  $\mathbf{W}$  is a vector of  $(n - 1)$  white-noise processes (stochastic diffusion fluxes). The property that the columns of  $\boldsymbol{\chi}$  add up to zero ensures that there is no stochastic flux in the equation for the total density  $\rho = \sum_{i=1}^n \rho_i$ . The above construction shows that the Soret coefficients do not enter in the covariance of the stochastic fluxes, instead, they give the coefficients with which the stochastic diffusive fluxes are weighted in the energy equation, just like the deterministic fluxes (as expected, a physical system should not be able to separate the influence of the fluctuations from the mean).

## 2 Particle-Fluid Coupling

The basic problem we consider is coupling a fluctuating fluid solver with immersed particles that have some mass (inertia). Ultimately the goal is to develop accurate methods for modeling the Brownian motion of the immersed structures, driven by the thermal velocity fluctuations. Ideally, we would like the equations to take the form (??), thus ensuring the coupled particle-fluid system that have the right statistical mechanics (notably fluctuation-dissipation balance). One could try to derive the coarse-grained equations from a more detailed model in which the coarse-grained variables are chosen to be the position of the immersed particle and the hydrodynamic fields of the fluid. Here we simply write equations that include a *postulated no-slip constraint*, which states that the velocity of the immersed particle matches the local velocity of the fluid. There will appear operators in our formulation which should have some relation to the microscopic dynamics, but here they are simply taken for granted.

### 2.1 No-Slip Constraint

Let us just consider one particle of physical mass  $m$  and radius  $a$  immersed in an *isothermal* fluid at temperature  $T$ . The position of the particle is  $\mathbf{q}(t)$  and its *apparent velocity*  $\mathbf{u} = \dot{\mathbf{q}}$ , and the velocity field for the fluid is  $\mathbf{v}(\mathbf{r}, t)$ . The coupling between the fluid and the particle is captured by the requirement (here a postulate, though of course one can justify it in various ways) that the particle follow the local velocity of the fluid. In the deterministic setting, the terminology “point particle” is often used and the particle is thought of as a Lagrangian marker,  $\mathbf{u} = \mathbf{v}(\mathbf{q}(t), t)$ . This “point particle” picture is not only hard to implement numerically, but is also not appropriate in the stochastic setting. Namely, in fluctuating hydrodynamics the fluid velocity is a distribution and cannot be evaluated pointwise, therefore, to give a well-defined meaning to the concept of advection by a local velocity spatial averaging over a region of size  $a$  must be used. Then the diffusion coefficient is inversely proportional to the size of the particle, as it should based on Einstein’s relation. Here we consider the fluid to cover the whole domain instead of being excluded by the particle, to avoid complications in implementing the resulting model numerically. It should however be easy to extend the model to account for the repulsion between the Brownian particle and the fluid particles.

Given these considerations, we postulate a *no-slip condition* of the form

$$\mathbf{u} = \dot{\mathbf{q}} = \mathbf{J} \mathbf{v}, \tag{16}$$

which simply states that the particle and the local fluid move together. Here the *local averaging operator*  $\mathbf{J}(\mathbf{q})$  averages a (scalar, vector, or tensor) field inside the particle to approximate the field



at the position of the particle,

$$\mathbf{J}\mathbf{v} = \int \delta_a(\|\mathbf{q} - \mathbf{r}\|) \mathbf{v}(\mathbf{r}, t) d\mathbf{r}, \quad (17)$$

where  $\delta_a(r)$  is a smooth kernel with compact support of size  $a$  that integrates to unity,

$$\int \delta_a(\mathbf{r}) d\mathbf{r} = \int (4\pi r^2) \delta_a(r) dr = 1. \quad (18)$$

The reverse *local spreading operator*  $\mathbf{S}(\mathbf{q})$  takes a (scalar, vector or tensor) value at the position of the particle and returns a smooth density field,

$$\mathbf{S}\mathbf{u} = \delta_a(\|\mathbf{q} - \mathbf{r}\|) \mathbf{u}. \quad (19)$$

The two operators are *adjoint*,  $\mathbf{S} = \mathbf{J}^*$ , i.e., the natural dot products in the particle (Lagrangian) and fluid (Eulerian) domains are related via

$$(\mathbf{J}\mathbf{v}) \cdot \mathbf{u} = \int \mathbf{v} \cdot (\mathbf{S}\mathbf{u}) d\mathbf{r} = \int \delta_a(\|\mathbf{q} - \mathbf{r}\|) (\mathbf{v} \cdot \mathbf{u}) d\mathbf{r}. \quad (20)$$

Note that  $\mathbf{J}$  is dimensionless, but  $\mathbf{S}$  has dimensions of inverse volume. In particular, we can identify the volume of the particle  $\Delta V$  with the volume under the kernel,

$$\Delta V = (\mathbf{J}\mathbf{S})^{-1} = \left[ \int \delta_a^2(\mathbf{r}) d\mathbf{r} \right]^{-1}. \quad (21)$$

### 2.1.1 Some Generalizations

The kernel in the definition of the fluid-particle coupling operators does not need to be isotropic, that is, only a function of distance. More generally, we can consider a tensor kernel  $\boldsymbol{\delta}_a(\mathbf{q} - \mathbf{r})$ , and define

$$\begin{aligned} \mathbf{J}\mathbf{v} &= \int \boldsymbol{\delta}_a(\mathbf{q} - \mathbf{r}) \cdot \mathbf{v}(\mathbf{r}, t) d\mathbf{r}, \\ \mathbf{S}\mathbf{u} &= \boldsymbol{\delta}_a(\mathbf{q} - \mathbf{r}) \cdot \mathbf{u}. \end{aligned}$$

A Mori-Zwanzig calculation by Pep Espanol suggested the form

$$\boldsymbol{\delta}_a(\mathbf{r}) = \beta^{-1} K_a(r) \left[ 1 + \alpha \frac{\mathbf{r}\mathbf{r}^T}{r^2} \right],$$

where  $\alpha$  is some parameter ( $B/A$  in his notes), while

$$\beta = \int K_a(r) \left[ 1 + \alpha \frac{\mathbf{r}\mathbf{r}^T}{r^2} \right] d\mathbf{r} = \left( 1 + \frac{2}{3}\alpha \right) \mathbf{I}$$

is a normalization prefactor. Here  $K_a(r)$  is a normalized kernel similar to  $\delta_a(r)$  in (18), and for a rigid-like sphere it is expected that

$$K(r) \approx (4\pi a^2)^{-1} \delta(r - a)$$

is localized on the surface of the particle. The adjoint condition (20) still holds. In discretizations, one may use a kernel that is not spherically symmetric but rather has cubic symmetry, such as the diagonal tensor

$$[\boldsymbol{\delta}_a(\mathbf{r})]_{ij} = \delta_a(q_i - r_i) \delta_{ij}.$$

## 2.2 Postulated Equations

The equations of motion are *postulated* to be

$$\rho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -\nabla \cdot \boldsymbol{\sigma} - \mathbf{S}\boldsymbol{\lambda} \quad (22)$$

$$m_e \dot{\mathbf{u}} = \mathbf{F} + \boldsymbol{\lambda} \quad (23)$$

$$\text{s.t. } \mathbf{u} = \mathbf{J}\mathbf{v}, \quad (24)$$

where the fluid-particle force  $\boldsymbol{\lambda}$  is a Lagrange multiplier that enforces the no-slip constraint (24). Here the fluid stress tensor

$$\boldsymbol{\sigma} = -P\mathbf{I} + \eta\nabla\mathbf{v}$$

and the density is assumed to follow the usual continuity equation. In particular, if the Brownian particle were not present,  $\boldsymbol{\lambda} = \mathbf{0}$ , the fluid would obey the fluctuating Navier-Stokes equations (1). The equations (23,22) obey certain physical requirements, notably, momentum is conserved. Furthermore, in the case of a neutrally-boyant particle,  $m_e = 0$ ,  $\boldsymbol{\lambda} = -\mathbf{F}$  and the fluid follows the usual fluctuating Navier-Stokes equation under the influence of an external force  $\mathbf{S}\mathbf{F}$ , as in the stochastic immersed-boundary method [8, 9].

We can in fact easily eliminate  $\boldsymbol{\lambda}$  from the equations of motion by simply adding them, and also eliminate  $\mathbf{u}$  by using the no-slip constraint, to get the effective equation of motion,

$$\rho_{\text{eff}} \partial_t \mathbf{v} = -\rho \mathbf{v} \cdot \nabla \mathbf{v} - \nabla \cdot \boldsymbol{\sigma} + \mathbf{S}\mathbf{F} - m_e \mathbf{S} \left( \mathbf{u} \cdot \frac{\partial \mathbf{J}}{\partial \mathbf{q}} \right) \mathbf{v}. \quad (25)$$

This equation shows that the excess mass of the particle is distributed back onto the fluid to give a fluid equation where the scalar density field is replaced by an the effective density *matrix*

$$\boldsymbol{\rho}_{\text{eff}} = \rho \mathbf{I} + m_e \mathbf{S}\mathbf{J}, \quad (26)$$

which is positive-definite if the effective mass of the particle  $m = m_e + \rho \Delta V > 0$ .

## 2.3 Fluctuations

The coarse-grained variables are  $\mathbf{x}(t) = (\rho(\mathbf{r}, t), \mathbf{v}(\mathbf{r}, t), \mathbf{q}(t))$ , and we postulate a coarse-grained free energy of the form

$$H(\mathbf{x}) = U(\mathbf{q}) + m_e \frac{u^2}{2} + \int \left[ \rho \frac{v^2}{2} + \epsilon(\rho) \right] d\mathbf{r}, \quad (27)$$

where  $\epsilon(\rho)$  is the internal energy of the fluid (at constant temperature), and  $U$  is an applied external potential, with associated force

$$\mathbf{F}(\mathbf{q}) = -\frac{\partial U}{\partial \mathbf{q}}.$$

The way to justify this choice by first including the *true* velocity  $\mathbf{w}$  of the Brownian particle as a variable, and then split it into a slow “apparent” velocity and a fast “fluctuating” velocity,

$$\mathbf{w} = \mathbf{J}\mathbf{v} + \Delta\mathbf{u} = \mathbf{u} + \Delta\mathbf{u}.$$

We can then convert from the variables  $\mathbf{y} = (\rho, \mathbf{v}, \mathbf{q}, \mathbf{w})$  to the variables  $\tilde{\mathbf{y}} = (\rho, \mathbf{v}, \mathbf{q}, \Delta\mathbf{u})$ , and also convert the natural coarse-grained free energy

$$H(\mathbf{y}) = U(\mathbf{q}) + m_e \frac{w^2}{2} + \int \left[ \rho \frac{v^2}{2} + \epsilon(\rho) \right] d\mathbf{r}$$

using the fact that the Jacobian of the transformation is unity (see Section ??),

$$\tilde{H}(\tilde{\mathbf{y}}) = \tilde{H}(\mathbf{x}, \Delta\mathbf{u}) = H(\mathbf{x}) + m_e (\Delta\mathbf{u})^2 + m_e (\mathbf{u} \cdot \Delta\mathbf{u}).$$

If we then assume that  $\Delta\mathbf{u}$  is a fast variable that is uncorrelated with  $\mathbf{u}$ , we can average over the equilibrium distribution keeping  $\mathbf{x}$  fixed, and obtain the coarse-grained free energy (27) in the reduced set of variables,

$$H(\mathbf{x}) = -k_B T \ln \left\langle \exp \left[ -\frac{\tilde{H}(\mathbf{x}, \Delta\mathbf{u})}{k_B T} \right] \right\rangle_{\mathbf{x}}.$$

### 2.3.1 Langevin Equations

In order to avoid having to deal with constrained dynamics, we can eliminate the particle velocity from the Hamiltonian,

$$m_e \frac{u^2}{2} = m_e \frac{\mathbf{u} \cdot \mathbf{u}}{2} = m_e \frac{(\mathbf{J}\mathbf{v}) \cdot \mathbf{u}}{2} = \frac{m_e}{2} \int \mathbf{v} \cdot (\mathbf{S}\mathbf{u}) d\mathbf{r} = \frac{m_e}{2} \int \mathbf{v}^T (\mathbf{S}\mathbf{J}) \mathbf{v} d\mathbf{r}$$

by using the adjoint condition (20), leading to the effective Hamiltonian

$$H(\mathbf{x}) = U(\mathbf{q}) + \int \frac{\mathbf{v}^T \boldsymbol{\rho}_{\text{eff}} \mathbf{v}}{2} d\mathbf{r} + \int \epsilon(\rho) d\mathbf{r}. \quad (28)$$

The (functional or partial) derivatives (thermodynamic driving forces) are

$$\frac{\partial H}{\partial \rho} = \frac{v^2}{2} + \frac{d\epsilon}{d\rho} \quad \text{and} \quad \frac{\partial H}{\partial \mathbf{v}} = \boldsymbol{\rho}_{\text{eff}} \mathbf{v} \quad \text{and} \quad (29)$$

$$\frac{\partial H}{\partial \mathbf{q}} = -\mathbf{F}(\mathbf{q}) + \mathbf{v} \cdot \left( \mathbf{S} \frac{\partial \mathbf{J}}{\partial \mathbf{q}} \right) \mathbf{v} = -\mathbf{F}(\mathbf{q}) + \left( \mathbf{u} \cdot \frac{\partial \mathbf{J}}{\partial \mathbf{q}} \right) \mathbf{v}, \quad (30)$$

We can now generalize the generators given in Section (1.1) to include the additional degrees of freedom  $\mathbf{q}$ . We can write the conservative part of the dynamics as

$$\mathbf{L} = \begin{bmatrix} 0 & -\frac{\partial}{\partial \mathbf{r}} \cdot (\boldsymbol{\rho}_{\text{eff}}^{-1}) & \mathbf{0} \\ -(\boldsymbol{\rho}_{\text{eff}}^{-1} \rho) \frac{\partial}{\partial \mathbf{r}} & (\boldsymbol{\rho}_{\text{eff}}^{-1} \rho) \boldsymbol{\omega} \boldsymbol{\rho}_{\text{eff}}^{-1} & -\boldsymbol{\rho}_{\text{eff}}^{-1} \mathbf{S} \\ \mathbf{0} & \mathbf{J} \boldsymbol{\rho}_{\text{eff}}^{-1} & \mathbf{0} \end{bmatrix}. \quad (31)$$

In general there may survive some dissipative/fluctuating contributions from eliminating  $\Delta\mathbf{u}$  (the particle velocity fluctuations around the mean flow) as a degree of freedom, but here we assume that the dissipative dynamics consists only of viscous dissipation,

$$\mathbf{B} = \begin{bmatrix} 0 \\ \boldsymbol{\rho}_{\text{eff}}^{-1} \boldsymbol{\nabla} \cdot \boldsymbol{\eta}^{1/2} \\ 0 \end{bmatrix}.$$

It is not hard to see by the special way we placed  $\boldsymbol{\rho}_{\text{eff}}^{-1}$  in the generators that the equation of motion

$$\partial_t \mathbf{x} = (\mathbf{L} - \mathbf{B}\mathbf{B}^*) \cdot \frac{\partial H}{\partial \mathbf{x}} + (2k_B T)^{1/2} \mathbf{B} \cdot \mathbf{W}(t)$$

is exactly our postulated (25).

The remaining term that needs to be added to the right hand side of (25) to ensure fluctuation-dissipation balance is the term

$$(k_B T) \frac{\partial}{\partial \mathbf{x}} \cdot (\mathbf{L} - \mathbf{B}\mathbf{B}^*)^* = - (k_B T) \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{L}.$$

This term is not zero for velocity, since the second entry in the third column/row of  $\mathbf{L}$  depends on  $\mathbf{q}$ . For the simpler case  $m_e = 0$ ,  $\rho_{\text{eff}} = \rho \mathbf{I}$ , the extra forcing term needed in the fluid equation due to phase-space compressibility of the dynamics can be written in the form

$$- (k_B T) \left( \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{L} \right)_v = \rho^{-1} \nabla \mathbf{S} (k_B T).$$

This is consistent with a contribution  $\mathbf{S} (k_B T)$  being added to the pressure due to the thermal motion of the particle around the mean flow. For the case of a neutrally-buoyant particle Atzberger obtained this term through a careful reduction of the stochastic dynamics with a Stokes coupling [9]. For the case of non-zero  $m_e$  there is additional dependence on  $\mathbf{q}$  due to  $\rho_{\text{eff}}$ , and the calculation of  $\frac{\partial}{\partial \mathbf{q}} \cdot (\rho_{\text{eff}}^{-1} \mathbf{S})$  is somewhat more involved...*My preliminary calculation indicates that the term  $\rho_{\text{eff}}^{-1} \nabla \mathbf{S} (k_B T)$  is needed in this case, but I need to repeat more carefully. Physically it makes sense since this term comes because of the Kirkwood stress*

$$\left\langle m_e (\Delta \mathbf{u}) (\Delta \mathbf{u})^T \right\rangle_{\mathbf{x}} = (k_B T) \mathbf{I},$$

which is independent of  $m_e$ . So the corrected fluid equation seems to be

$$\rho_{\text{eff}} \partial_t \mathbf{v} = -\rho \mathbf{v} \cdot \nabla \mathbf{v} - \nabla \cdot \boldsymbol{\sigma} + \nabla \mathbf{S} (k_B T) + \mathbf{S} \mathbf{F} - m_e \mathbf{S} \left( \mathbf{u} \cdot \frac{\partial \mathbf{J}}{\partial \mathbf{q}} \right) \mathbf{v}.$$

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