

Statistical Mechanics of Coarse-Graining

Pep Español

Departamento de Física Fundamental, UNED, Apartado 60141, 28080 Madrid, Spain

1 Introduction

Complex fluids are fluids which despite their continuum appearance at macroscopic scales present structure at mesoscopic scales. Suspended particles or macromolecules, bubbles, droplets, vesicles, micelles, and lamellae are examples of such structures. Many fluids of technological importance, such as lubricants, paints, surfactant-aided oil recovery fluids, liquid crystals, plastics, shampoos, etc., are complex fluids. What makes these fluids “complex” is the conspicuous coupling between the mesoscopic structures of the fluids with their flow properties. Such highly non-linear coupling defies analytical approaches and it is usually necessary to resort to computer simulations in order to have a better understanding of the physical behaviour of these systems. Of course, there is a great interest from an economic perspective to simulate complex fluid systems of industrial and technological importance. A simulation allows one to gain insight in the processing of materials and propose new directions for design without expensive and time consuming experimentation in a laboratory. However, computer equipment is also a limited resource and there is need for developing simulation models that allow to capture the essential features of the materials with the minimum of computational units and computer time.

The process of representing a system with fewer degrees of freedom than those actually present in the system is called coarse-graining. By coarse-graining, one eliminates the “uninteresting” fast variables and keeps the coarse-grained variables with time scales much larger than typical molecular scales. Therefore, by coarse-graining we not only gain in terms of a reduction of computational units, but also on the possibility of exploring a much larger time span. In the field of complex fluids, coarse-grained models are usually constructed with a judicious balance of physical intuition, simplicity, and respect of symmetries. The validity of such coarse grained models is inferred a posteriori, by confronting its predictions with experiments. However, molecular specificity is usually lost in these phenomenological approaches. Only by appealing to a microscopic foundation of coarse-graining one can expect to relate a coarse grained model with the underlying molecular system. Of course, several question may spring to the mind: Is there a general method for coarse-graining? Is it always possible to coarse-grain a system? How to ensure thermodynamic consistency in a coarse-grained model? We will try to answer these questions later in this chapter, but for the time being we simply state that a microscopic basis for coarse-graining exists. Actually, the general program for coarse-graining was put on a rigorous basis in middle of last century by people like Kirkwood [1], Green [2], Zwanzig [3], Mori [4], and many, many others. In particular,

starting from the microscopic equations governing atomic variables, projection operator techniques allowed to derive the equations of motion of the coarse-grained variables that evolve in distinctly slow time scales from the rest of variables in the system [5]. It is our belief that, despite of its “too formal” appearance, a clear understanding of the theory behind coarse-graining is necessary for anyone willing to simulate the behaviour of complex fluids.

This chapter is structured as follows. Sections 2 and 3 introduce the general concepts of the theory and illustrate them for the case of a colloidal suspension, respectively. The mathematical details of the theory are given in Sect. 4, where the projection operator derivation of the Fokker–Planck equation is presented [3,5]. We return to colloidal suspensions in Sect. 5, where we show how the different objects of the Fokker–Planck equation can be explicitly computed in principle, giving the microscopic expressions for them. In Sect. 6 we present a general strategy for computing the objects in the Fokker–Planck equation by running a molecular dynamics of the system and highlight a basic problem concerning the high dimensionality of the coarse state space. Nevertheless, the coarse-graining theory still provides for a large number of restrictions that help in the modelling of the objects in the Fokker–Planck equation. We review these restrictions in Sect. 7 for the case in which the dynamical invariants of the system can be expressed in terms of the coarse-grained variables. In this case, a powerful thermodynamically consistent structure called GENERIC emerges [6]. In Sect. 8 we illustrate how to use the GENERIC formalism to design discrete models for complex fluids. As particular examples, the Smoothed Particle Hydrodynamics and Dissipative Particle Dynamics models will be presented. Finally, we will suggest how these particle models can be enriched by using additional internal variables in order to simulate viscoelastic fluids, transport of pollutants, and chemically reacting mixtures.

2 The Theory of Coarse-Graining in a Nutshell

In this section we first enumerate the fundamental concepts on which the theory of coarse graining is based on. In the next section these concepts will be illustrated in a specific example of a complex fluid, a colloidal suspension. The mathematical aspects of the theory are deferred to Sect. 4.

A given system of many degrees of freedom, such as a complex fluid, may be described at different levels of description. Each level of description is characterized by a set of relevant variables that specify the state of the system at that level. The word “level” suggests a hierarchical structure and, in fact, the levels of description for a given system order themselves in terms of the amount of information captured by the relevant variables. Less detailed levels (coarser levels) have a smaller number of variables and capture less information. For each level of description there is a dynamic equation for the relevant variables. The evolution of the relevant variables occurs with a time scale characteristic of the level of description. A coarse grained level is valid for describing phenomena that occur at time scales equal or larger than the typical time scale of the level. It cannot reproduce the behaviour at shorter time scales. In any system, among all the possible levels of description two of them are particularly important because they lay at the extremes of the hierarchy. They are the microscopic and macroscopic lev-

els. The microscopic level has the position and momenta of all the atoms of the system as set of relevant variables, the dynamic equations are Hamilton's equations, and the time scale is a typical collision or vibration time. The macroscopic level is the level of Thermodynamics where the relevant variables are the dynamical invariants of the system (mass, momentum, energy). At the macroscopic level, there is no equation of motion, because the relevant variables are constant in time and the time scale is infinite. Any other level of description is in between these two levels and could be named as a mesoscopic level. It is apparent that a given system may have many mesoscopic levels, each one of different detail. The connection between these levels of description is made through a coarse graining procedure in which some degrees of freedom are eliminated from the description. It may happen that there exists a clear separation of the time scales of the relevant variables and the time scales of the eliminated degrees of freedom. When this fortunate case occurs, the coarse-grained level of description has evolution equations for the relevant variables that are Markovian, that is, the future state of the system is determined by the present, but not past, values of the relevant variables. This is fortunate because, from a mathematical point of view, non-Markovian dynamic equations are integro-differential equations which are much more difficult to treat than the usual differential equations that result from a Markovian description. The loss of information that occurs when going from one level of description to a more coarser one is reflected on a stochastic description of coarse-grained levels. The idea is that even if the description is Markovian, the knowledge of the coarse state of the system at a given time is not sufficient to predict the future coarse state with certainty. This is because many microscopic states are compatible with the initial coarse state. The uncertainty in the actual initial microscopic state amounts to an uncertainty to the final coarse state. These uncertainties are ultimately responsible for the need of a statistical description based on the probability distribution function for the relevant variables. The dynamic equation is therefore an equation for the probability distribution function and has, under the Markovian approximation, the form of a Fokker-Planck equation (FPE). When the evolution equation is of the Fokker-Planck type, the eliminated degrees of freedom show up in a systematic dissipative effect on the relevant variables and also in the form of thermal fluctuations. Fluctuations and dissipation have the same essential origin, the elimination of degrees of freedom. They are related through the fluctuation-dissipation theorem.

The main objective of the theory of coarse-graining is to derive the FPE that governs the probability distribution of the coarse-grained variables. This was achieved in a landmark paper by Green [2], and the FPE was subsequently re-derived by using a projection operator technique by Zwanzig [3]. In this way, explicit molecular expressions for the coefficients appearing in the FPE were obtained in terms of the microscopic dynamics. The technique can be generalized for jumping not only from the microscopic level to a mesoscopic level but also from any mesoscopic level to any other more coarse-grained mesoscopic level [7].

The FPE can only be obtained under the assumption of clear separation of time scales between the selected variables and the rest of variables of the system. In particular, the coarse-grained variables should be slow. But, how do we know if such separation of time scale exists? The sad answer is that we do not have any a priori way to

know in advance the time scales of evolution of our selected relevant variables. A large degree of physical intuition is required in order to select a proper set of relevant variables. If the theory does not predict correctly the results of experiments or simulations, we should think what other variables might evolve in the time scale of the description and include them also as relevant variables with the hope that we new capture all the slow dynamics of the system.

Before closing this introductory section, it is worth to compare the coarse-graining strategy based on projection operators with the older and venerable approach of kinetic theory [8]. Kinetic theory is also a theory of coarse graining in which the reduction of information is achieved by considering the probability distribution functions of small subsets of particles. Starting from the Liouville equation, one constructs a hierarchy of equations (the BBGKY hierarchy) for the probability distribution functions at a given time in which the equation for a given n -particle distribution depends on higher particle distributions. Therefore, the equation for the lowest distribution, although being a differential equation involving only the present time, is not closed. This is in contrast with the projection operator approach in which one obtains a closed equation for the distribution function, which, however, involves past times. Of course, one has to be as careful in truncating the kinetic hierarchy in order to obtain a closed equation as in approximating the memory equation in the projection operator approach in order to have a memoryless equation.

3 Example: A Colloidal Suspension

In this section we will illustrate the fundamental concepts of the theory by studying several different levels of description that are used to describe colloidal suspensions. A colloidal suspension is made of a collection of small solid objects (like spherical latex particles) of the size of, say, a micron suspended in a fluid such as, for example, water. A roadmap of this section is shown in Fig. 1.

3.1 Microscopic Level: Classical Mechanics

At the most microscopic level, we can model a colloidal suspension by assuming that the solid suspended objects are spherical and we need only 6 degrees of freedom for describing the state of the object, the position \mathbf{Q}_i and the momentum \mathbf{P}_i of its center of mass. For irregular objects we would need also to consider orientation, angular velocities, etc. The fluid in which these solid colloidal particles are suspended will be described at the most microscopic level by the positions \mathbf{q}_i and momenta \mathbf{p}_i of the centers of mass of the molecules constituting the fluid. Again, we assume spherical molecules for simplicity. The microscopic state will be denoted by $z = \{\mathbf{q}_i, \mathbf{p}_i, \mathbf{Q}_i, \mathbf{P}_i\}$. The evolution of the microstate is governed by Hamilton's equations,

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\partial H(z)}{\partial \mathbf{p}_i}, & \dot{\mathbf{Q}}_i &= \frac{\partial H(z)}{\partial \mathbf{P}_i}, \\ \dot{\mathbf{p}}_i &= -\frac{\partial H(z)}{\partial \mathbf{q}_i}, & \dot{\mathbf{P}}_i &= -\frac{\partial H(z)}{\partial \mathbf{Q}_i}, \end{aligned} \quad (1)$$

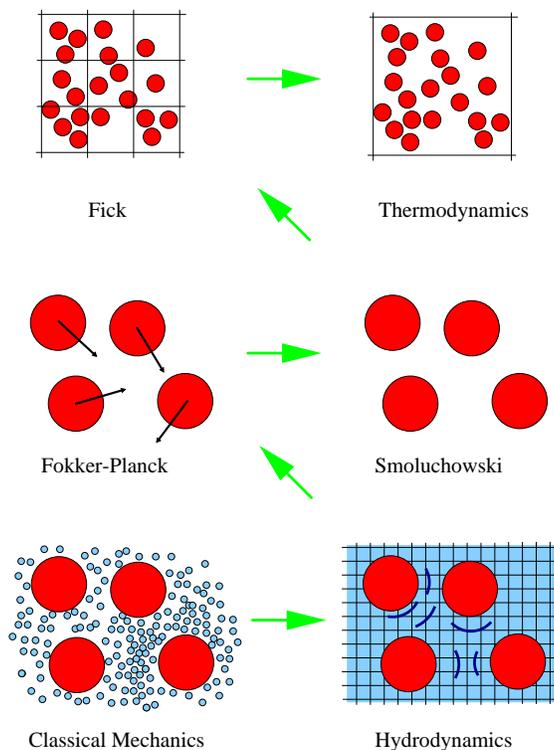


Fig. 1. Different levels of description in a colloidal suspension. Arrows denote the direction of coarse graining from the Classical Mechanics level at the lower left hand corner to Thermodynamics level at the top right hand corner

where the Hamiltonian is given by

$$H(z) = \sum_i \left(\frac{p_i^2}{2m_i} + \frac{P_i^2}{2M_i} \right) + \frac{1}{2} \sum_{ij} (V_{ij}^{SS}(q) + V_{ij}^{SC}(q, Q) + V_{ij}^{CC}(Q)). \quad (2)$$

Here, m_i is the mass of a solvent molecule, M_i the mass of a colloidal particle, and V^{SS} , V^{SC} , V^{CC} are the potentials of the forces between solvent molecules, solvent and colloidal particles, and colloidal particles, respectively.

In principle, the differential equations (1) can be solved numerically with a computer. The technique is known as molecular dynamics and allows us to keep track of all the microscopic dynamics of the system [9]. The smallest typical time scale is a collision time in the range of picoseconds and, consistently, we will need to use a time step for the numerical solution which is much smaller than this time scale. However, if the mass of the colloidal particles is much larger than the mass of the solvent particles, as it occurs in reality, the evolution of the colloidal particles will be very slow in comparison with the evolution of the solvent molecules. If we are interested in the motion of the colloidal particles, then we would need an enormous number of time steps (and,

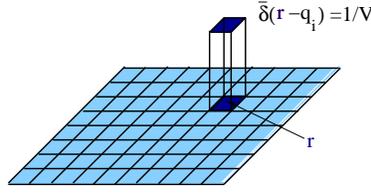


Fig. 2. Coarse-grained delta function $\bar{\delta}(\mathbf{r} - \mathbf{q}_i)$ takes the value $1/V$, V being the volume of the cell, if \mathbf{q}_i is within the cell labeled with r , and zero otherwise. The “point” r actually represents a portion of space

therefore, of computer time) to observe an appreciable motion of the colloidal particles. To study these large time scales in a colloidal suspension, molecular dynamics is absolutely impracticable.

3.2 Mesoscopic Level 1: Hydrodynamics

If we look at the motion of the solvent molecules, we will see that they collide with each other resulting in a rapid motion. However, if we look “from a distant point” to the multitude of molecules, a collective motion will be appreciated in which molecules in a region of space move coherently (overwhelming the small erratic motions due to collision). It will be possible to appreciate slowly evolving waves, vortices and other sort of collective motion. The variables that capture these collective motions are the hydrodynamic variables. These variables are the mass density field $\rho_{\mathbf{r}}(z)$, the momentum density field $\mathbf{g}_{\mathbf{r}}(z)$, and the energy density field $e_{\mathbf{r}}(z)$, defined by

$$\begin{aligned}\rho_{\mathbf{r}}(z) &= \sum_i m \bar{\delta}(\mathbf{r} - \mathbf{q}_i), \\ \mathbf{g}_{\mathbf{r}}(z) &= \sum_i \mathbf{p}_i \bar{\delta}(\mathbf{r} - \mathbf{q}_i), \\ e_{\mathbf{r}}(z) &= \sum_i e_i \bar{\delta}(\mathbf{r} - \mathbf{q}_i),\end{aligned}\tag{3}$$

where $\bar{\delta}(\mathbf{r} - \mathbf{q}_i)$ is a coarse-grained delta function (a function with a support over a finite small region and normalized to unity, see Fig. 2). In the above equations, e_i is the energy of particle i (the sum of its kinetic energy plus half the potential energy due to the interaction with its neighbours). It may appear as a contradiction to coarse-grain through a set of field variables (which have, in principle an infinite number of degrees of freedom). However, we should note that the above fields involving the coarse-grained delta functions are “smooth” fields (which have a small number of Fourier components with large wavelengths). Implicit in the definition of the hydrodynamic variables in (3) there is a partition of physical space in little cells that contain many solvent molecules. The hydrodynamic variables tell us about how many particles have a given average velocity and energy in a certain region of space, rather than providing the exact location and velocity of each solvent molecule. The reduction of information in passing from

solvent atoms to smooth hydrodynamic fields is then apparent. Therefore, at a coarse-grained level we can describe the colloidal suspension by the set of hydrodynamic fields and the position and momenta of the colloidal particles.

The equations that govern the hydrodynamic variables are the well-known hydrodynamic equations [10]. They include the microscopic details of the solvent (what particular molecules constitute the solvent) through the pressure and temperature equations of state, and through the particular values of the transport coefficients (shear and bulk viscosities, and thermal conductivity). The time scales of the hydrodynamic variables depend on the length scale being considered. Typically, perturbations with large wavelengths evolve slowly. In a colloidal suspension these length scales are either the radius of the particles or the typical distance between colloidal particles. Roughly speaking, there is a hydrodynamic time scale for mass evolution which is a sound traversal time, a time scale for momentum evolution given by a viscous time, and a time scale for energy transport, given by a thermal diffusion time. The hydrodynamic equations for the solvent fields are coupled with the Newton's equation for the colloidal particles through boundary conditions, whereas the forces on the colloidal particles are given through the integral of the stress tensor of the fluid over the surface of the colloidal particle. We observe that the motion of a given colloidal particle depends on the motion of the rest through the coupling with the hydrodynamic fields of the solvent. These solvent mediated interactions between colloidal particles are known as hydrodynamic interactions.

As a result of the coarse-graining of the solvent, the hydrodynamic variables are subject to fluctuations. Physically, these fluctuations came from the fact that solvent molecules can enter and go out of the little cells that are used to define the hydrodynamic variables. Mathematically, the fluctuations are described as stochastic contributions to the stress tensor and heat flux in the Navier–Stokes equations, as proposed by Landau and Lifshitz in their theory of fluctuating hydrodynamics [11]. A very remarkable property of these fluctuations is that their variance is proportional to the transport coefficients of the solvent, this is, to the shear and bulk viscosities and to the thermal conductivity. This is the fluctuation-dissipation theorem for this level of description. The hydrodynamic fluctuations are transmitted to the colloidal particles through the boundary conditions on the surface of the particles and are ultimately responsible for the Brownian motion of the particles [12]. In the highly dilute limit (that is, for an isolated colloidal particle) and for neutral buoyant particles (with density equal to the solvent density) it is possible to compute explicitly the velocity autocorrelation of the colloidal particle [13], which exhibits the famous long-time tail, an algebraic decay as $t^{-3/2}$ [14]. The physical origin of this slow algebraic decay is that, due to a spontaneous fluctuation, the colloidal particle pushes the fluid in front of it. The push generates a vortex centered on the particle that, in turn, pushes the particle from its rear, thus maintaining the initial state of motion of the particle. These long-time tails have been observed experimentally for colloidal systems [15].

There is a large number of simulation techniques for the hydrodynamic level of description. In general, any Navier–Stokes solver for the solvent that allows to describe thermal fluctuations and Molecular Dynamics for the colloidal particles will do. Lattice Boltzmann [16] or Dissipative Particle Dynamics [17] have been used for this purpose. The Malevanets–Kapral method can also be used in this problem [18].

3.3 Mesoscopic Level 2: Fokker–Planck

We have already noted that if the colloidal particles are massive their motion will be slow. In that case, we could expect that the propagation of the hydrodynamic interactions is very fast, instantaneous, compared with the time scale of variation of the colloidal position and momenta. If this is the case, we can eliminate the solvent hydrodynamic variables from the description. The state of the system at this mesoscopic level of description is given by $x = \{\mathbf{Q}_i, \mathbf{P}_i\}$. The FPE that corresponds to the mesoscopic level 2 is given by [19]

$$\begin{aligned} \frac{\partial}{\partial t} P(x, t) = & - \sum_i \left[\mathbf{V}_i \cdot \frac{\partial}{\partial \mathbf{Q}_i} + \mathbf{F}_i^{\text{CC}} \cdot \frac{\partial}{\partial \mathbf{P}_i} \right] P(x, t) \\ & + k_B T \sum_{ij} \frac{\partial}{\partial \mathbf{P}_i} \cdot \zeta_{ij}(Q) \cdot \left[\frac{\partial}{\partial \mathbf{P}_j} + \frac{\mathbf{P}_j}{M_j k_B T} \right] P(x, t). \end{aligned} \quad (4)$$

Here, $\mathbf{V}_i = \mathbf{P}_i/M_i$, \mathbf{F}_i^{CC} is the effective force due to the rest of colloidal particles exerted on particle i and $\zeta_{ij}(Q)$ is a friction tensor which depends on the position of the colloidal particles. The physical picture behind (4) can be best appreciated in the mathematically equivalent stochastic differential equations (SDE)

$$d\mathbf{Q}_i = \mathbf{V}_i dt \quad \text{and} \quad d\mathbf{P}_i = \mathbf{F}_i^{\text{CC}} dt - \sum_j \zeta_{ij}(Q) \cdot \mathbf{V}_j dt + d\tilde{\mathbf{F}}_i.$$

We observe that the particles evolve according to their velocities and that they are subjected to forces due to the other colloidal particles that depend on their positions, \mathbf{F}_i^{CC} , and velocities, $-\zeta_{ij}(Q) \cdot \mathbf{V}_j$. Note that if a colloidal particle j is moving, it will exert forces on the colloidal particle i . These forces are the result of the hydrodynamic interactions that are captured at this level of description through the friction tensor $\zeta_{ij}(Q)$. Finally, the particles are also subject to stochastic forces $d\tilde{\mathbf{F}}_i$ that are mathematically described in terms of Wiener processes. The variance of these forces is given by the Fluctuation-Dissipation theorem which, at this level of description, takes the form $d\tilde{\mathbf{F}}_i d\tilde{\mathbf{F}}_j = 2k_B T \zeta_{ij}(Q) dt$.

If the colloidal particles are very far from each other, as it happens when the suspension is dilute, we may expect that the mutual influence among colloidal particles is negligible and that the friction tensor is diagonal, this is $\zeta_{ij} = \delta_{ij} \mathbf{1} \zeta$, where ζ is called the friction coefficient. In this case, the SDE equivalent to the FPE (4) decouple into a set of independent equations, called Langevin equations. The Langevin equations for a dilute suspension predict that the velocity autocorrelation function of a colloidal particle decays exponentially. As we have seen, this is at variance with experiments that show a clear long-time tail for neutrally buoyant particles. The reason for this discrepancy between theory and experiments for neutrally buoyant particles can only be attributed to the fact that the time scales of evolution of the colloidal variables $\mathbf{Q}_i, \mathbf{P}_i$ are not neatly separated from the time scales of hydrodynamic variables. We have here one example of the hazards of selecting a too low number of variables. Even though $\mathbf{Q}_i, \mathbf{P}_i$ look as a reasonable set of relevant variables, they are not. If we are interested in the time scale in which the momentum of the particles evolves, we have to include, necessarily, the

hydrodynamic modes as a part of the description. This time scale is typically 10^{-6} s. It turns out, however, that the density ratio between the colloidal particle density and the solvent density governs the separation of time scales between colloidal momenta and hydrodynamic variables [12]. For colloidal suspensions of particles which are much denser than the solvent, these time scales are well-separated and the Fokker–Planck level of description is a good level of description. Finally, we note that the numerical solution of the SDE (5) is called Brownian Dynamics [9,20].

3.4 Mesoscopic Level 3: Smoluchowski

Even though the coarse-grained variables $\mathbf{Q}_i, \mathbf{P}_i$ are not a good set of coarse variables for neutrally buoyant suspensions, it turns out that the \mathbf{Q}_i alone do actually define a proper level of description. The reason is that the time scale of evolution of the positions of the colloidal particles is much longer than the time scale of evolution of the momentum and hydrodynamic modes. The typical time scale of evolution of the position variables for a colloidal suspension is 10^{-3} s. Therefore, by using \mathbf{Q}_i alone, we will be able to describe correctly the phenomena that occur in time scales above 10^{-3} s.

The FPE that now governs the probability density $P(\mathbf{Q}, t)$ is called the Smoluchowski equation. It has the form [19]

$$\frac{\partial}{\partial t} P(\mathbf{Q}, t) = - \sum_i \frac{\partial}{\partial \mathbf{Q}_i} \cdot \left[\mathbf{D}_{ij} \cdot \frac{\mathbf{F}_j^{\text{CC}}}{k_B T} P(\mathbf{Q}, t) \right] + \sum_{ij} \frac{\partial}{\partial \mathbf{Q}_i} \mathbf{D}_{ij} \frac{\partial}{\partial \mathbf{Q}_j} P(\mathbf{Q}, t), \quad (5)$$

where D_{ij} is called the diffusion tensor, and it captures the mutual influence between colloidal particles due to the elimination of the solvent and momentum variables. The mathematically equivalent set of SDE corresponding to (5) is

$$d\mathbf{Q}_i = \sum_j \mathbf{D}_{ij}(Q) \mathbf{F}_i^{\text{CC}}(Q) dt + k_B T \sum_j \frac{\partial}{\partial Q_j} \mathbf{D}_{ij}(Q) dt + d\tilde{\mathbf{Q}}_i,$$

and the Fluctuation-Dissipation theorem at this level of description takes the form $d\tilde{\mathbf{Q}}_i d\tilde{\mathbf{Q}}_j = 2k_B \mathbf{D}_{ij}(Q) dt$. Again, for dilute suspensions $\mathbf{D}_{ij} = \delta_{ij} D$, where D is the self-diffusion coefficient of the colloidal particles.

3.5 Mesoscopic Level 4: Fick

Further coarse graining can be performed if we are interested not in the actual positions \mathbf{Q}_i of the colloidal particles but on the number of colloidal particles that are in a region of the space located around \mathbf{r} . This amounts to the introduction of the number of colloidal particles per unit volume and to the use of a concentration field $c(\mathbf{r})$ as the variables x describing the state of the system. The concentration variable contains a much reduced amount of information because it tells us how many particles are in a region, but not which one is exactly where. We expect that the concentration field evolves in a time scale much larger than the time scale of evolution of the positions of the colloidal particles because in order to have an appreciable change in the number of

particles in a given sufficiently large region, these particles must move (diffuse) for a long time in order to traverse this region.

Due to the field character of the concentration variable, we have now a probability functional $P[c(\mathbf{r}), t]$ which will obey a functional FPE. The mathematically equivalent SDE takes the form of a continuity equation

$$\partial_t c = -\nabla \mathbf{J} \quad \text{with} \quad \mathbf{J} = -\frac{c}{\zeta} \nabla \mu + \tilde{\mathbf{J}}, \quad (6)$$

where the mass flux \mathbf{J} has a systematic contribution proportional to the chemical potential of the colloidal particles plus a stochastic part $\tilde{\mathbf{J}}$ with a variance proportional to the transport coefficient c/ζ . For the sake of simplicity, we have assumed that the suspension is dilute, in such a way that hydrodynamic interactions can be neglected. Otherwise, one obtains non-local in space equations [7]. When the suspension is dilute, we may use the ideal gas expression for the chemical potential $\mu = k_B T \ln c$ that leads to the usual diffusion equation $\partial_t c = D \nabla^2 c - \nabla \tilde{\mathbf{J}}$ where $D = k_B T / \zeta$ is the Einstein expression for the diffusion coefficient. Equation (6) can be easily simulated by discretizing the resulting stochastic diffusion equation with finite differences or any other discretization technique for stochastic partial differential equations [21].

3.6 Macroscopic Level: Thermodynamics

Finally, we might be interested in very long time scales in which the system has arrived at equilibrium. In this case, the only relevant variables are the dynamical invariants, i.e., those coarse-grained variables that are independent of time due to particular symmetries of the microscopic Hamiltonian, like total energy, or those coarse-grained variables like mass and volume, that are constant parameters in the Hamiltonian. Note that the volume of the container of the colloidal suspension can be understood as a parameter of a confining potential in the Hamiltonian. Obviously, there is no equation of motion for this level of description because we are interested in the long time, equilibrium state of the system.

In summary, in this section we have illustrated several different levels of description that can be defined for the study of a colloidal suspension. The general theme is that every level captures less information than its predecessor and allows one to describe time scales at and above the typical time scale of evolution of the coarse-grained variables.

The levels of description presented above for a colloidal suspension do not exhaust the possibilities and they have been selected as providing a pedagogical presentation of the main ideas involved in coarse-graining. Of course, other levels of intermediate complexity can and must be formulated depending on the physical situation that one wants to describe. For example, one can define a level of description where the relevant variables are the hydrodynamic solvent variables plus the concentration field for the colloidal particles. This purely hydrodynamic level of description is particularly useful for the description of transport of dilute pollutants by fluid flows. In this case, the equations are the hydrodynamic equations (that contain the effect of the dilute suspension through an osmotic pressure term) plus an advection-diffusion equation for the concentration field. If the colloidal suspension is more concentrated and anisotropic effects due to flow start to play a role, then it is necessary to enrich the level of description by

including a vectorial or tensorial quantity representing the degree of local anisotropy in the system [22].

4 The Mathematics of the Theory of Coarse-Graining

In the previous section we have presented the evolution equations for the relevant variables of a colloidal suspension at different levels of description without explaining the origin of these equations. These evolution equations are Fokker–Planck equations or its equivalent stochastic differential equations. Actually, the objective of a theory for coarse-graining is to provide for the particular form of the different objects that appear in the FPE corresponding to a particular level of description. More precisely, one would like to relate the drift and diffusion terms of the FPE with molecular details or with the drift and diffusion of a more detailed mesoscopic level. In this section, we will present a method based on a projection operator that allows one to derive the FPE at a given level of description from the Liouville equation that governs the microscopic level. In this procedure, one obtains explicit expressions for the objects that appear in the FPE. It is also possible to relate different mesoscopic levels, obtaining expressions for the coefficients of the FPE at a mesoscopic level in terms of the dynamics at a more detailed but still mesoscopic level [7]. However, and for the sake of simplicity, we will consider here only the coarse graining from the most detailed, microscopic level.

Apparently, there are many different projection operators [5] and one can be bewildered about which one is “the correct one”. Here we select the Zwanzig projection because: (1) it leads to non-linear dynamic equations describing arbitrarily far from equilibrium situations (the Mori projection leads to linear equations valid near equilibrium and it is a particular case of the Zwanzig projection) (2) it allows to obtain the FPE which captures all the statistics of the stochastic process. Projection onto relevant variables instead of onto distribution of relevant variables leads to an incomplete description of the stochastic process [23], and (3) it is time-independent, which is much simpler to handle than time-dependent projections [5].

The scope of this chapter has some restrictions. In particular, we will consider only isolated systems. We will assume also that at the most microscopic level the system can be well described by classical mechanics or, to be more specific, by Hamilton’s equations. No reference to quantum mechanics will be made. Another crucial assumption is that the Hamiltonian dynamics of the system has a well-defined equilibrium state that is reached by the system as the time proceeds. The assumption of isolated system implies that we will look at the relaxational dynamics of the system towards its equilibrium state. This might seem a strong restriction from an experimental point of view. Experiments often deal with situations in which a system is subject to the action of “external influences”, usually through the boundary of the system. Nevertheless, the theory for isolated systems already provides the basic model equations to which boundary conditions can be applied in a latter stage.

4.1 The Microscopic Level

All the complex fluid systems we are interested in can be described with classical mechanics. For this reason, we stop at reviewing the basic concepts of classical mechanics

for a Hamiltonian system. Let us denote the microstate of the system by $z = \{\mathbf{q}_i, \mathbf{p}_i\}$. The set of all z constitutes the phase space Γ of the system. Hamilton's equations are

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\partial H(z)}{\partial \mathbf{p}_i}, \\ \dot{\mathbf{p}}_i &= -\frac{\partial H(z)}{\partial \mathbf{q}_i},\end{aligned}\quad \dot{z} = L_0 \frac{\partial H(z)}{\partial z}, \quad (7)$$

where the right hand side is a condensed way of writing Hamilton's equations, with the matrix L_0 having a block diagonal matrix form with the blocks given by

$$\begin{pmatrix} 0 & \mathbf{1} \\ -\mathbf{1} & 0 \end{pmatrix}. \quad (8)$$

Note that Hamilton's equations are first order differential equations that require the knowledge of an initial condition. Given an initial microstate z_0 , the solution of Hamilton's equations can be denoted by $z(z_0, t) = T_t z_0$, where we have introduced formally the time evolution operator T_t . This operator satisfies $T_0 = \mathbf{1}$ and $T_t T_{t'} = T_{t+t'}$. In addition, the coordinate transformation $z \rightarrow T_t z$ has unit Jacobian for all t (this is the theorem of the integral invariants of Poincaré [24]).

4.2 Liouville Theorem

Even though the evolution of $z(t)$ is deterministic, it is usually difficult to know with precision the initial state z_0 of the system. All what we know is the probability distribution function of the initial state $\rho_0(z)$. The probability distribution function at a subsequent time is denoted by $\rho_t(z)$ and it obeys the Liouville equation which we derive here for completeness. Let M be a region of not vanishing measure of Γ and $T_t M$ the region resulting from the evolution of each point of M according to Hamilton's equations. It is obvious that the probability that the system is in the region M at $t = 0$ is identical to the probability of being at $T_t M$ at $t = t$. For this reason,

$$\int_M \rho(z, 0) dz = \int_{T_t M} \rho(z, t) dz. \quad (9)$$

By performing the change of variables $z' = T_{-t} z$ (with unit Jacobian) the integral in the left hand side becomes

$$\int_{T_t M} \rho(z, t) dz = \int_M \rho(T_t z, t) dz. \quad (10)$$

This is true for any region M and, therefore, the integrand of the right hand side of (9) and the left hand side of (10) should be equal, i.e.

$$\rho(z, 0) = \rho(T_t z, t), \quad (11)$$

or, by a simple change of variables,

$$\rho(z, t) = \rho(T_{-t} z, 0). \quad (12)$$

By taking the time derivative on both sides of (11) we obtain the Liouville theorem,

$$\frac{d}{dt}\rho(T_t z, t) = \frac{d}{dt}\rho(z, 0) = 0. \quad (13)$$

Further application of the chain rule leads to the Liouville equation for the probability density in phase space,

$$\frac{\partial}{\partial t}\rho(z, t) = -iL\rho(z, t), \quad (14)$$

where the Liouville operator is defined by

$$iL \equiv \sum_i \left(\frac{\partial H}{\partial \mathbf{p}_i} \frac{\partial}{\partial \mathbf{q}_i} - \frac{\partial H}{\partial \mathbf{q}_i} \frac{\partial}{\partial \mathbf{p}_i} \right) = \frac{\partial H}{\partial z} L_0 \frac{\partial}{\partial z}. \quad (15)$$

This operator satisfies

$$\int dz \rho^{\text{eq}}(z) A(z) iL B(z) = - \int dz \rho^{\text{eq}}(z) B(z) iL A(z), \quad (16)$$

for arbitrary functions $A(z), B(z)$.

4.3 Equilibrium at the Microscopic Level

Let us consider now the final state predicted by the Liouville equation. A basic mathematical question that has not been solved in its full generality is under which conditions the Liouville equation (14), which is a first order partial differential equation, leads to a stationary solution with $\partial_t \rho(z, t) = 0$. That this is not generally the case can be seen by considering a delta like initial distribution $\rho(z, 0) = \delta(z - z_0)$, where we know exactly the initial state z_0 . In this case, we know that the solution is given by $\rho(z, t) = \delta(T_t z_0 - z)$, this is, the distribution function remains peaked at the solution of Hamilton's equations. There is no broadening of the distribution function and the system does not reach a stationary state. However, if the dynamics generated by the Hamiltonian is highly unstable (i.e. chaotic), we may expect that any non-delta initial distribution will evolve with a sort of broadening. To be more specific, if the dynamics of the system is of the mixing type, then the system reaches an effective stationary state [25]. We will assume, without rigorous proof, that the most general stationary distribution function of (14) is a function of the dynamical invariants of the system. A dynamical invariant $I(z)$ is a dynamical function that does not change in time, this is,

$$\frac{d}{dt}I(z(t)) = 0.$$

The Hamiltonian $H(z)$ is a dynamical invariant (and we say that energy is conserved). As it is well-known, if the Hamiltonian is translationally and rotationally invariant, the total momentum and angular momentum are also dynamical invariants. The number of particles of the system and the parameters of the Hamiltonian (the mass of the particles, the range of potential, etc.) are also trivial dynamical invariants.

Any distribution function $\rho(z)$ which is a function $g(I(z))$ will be, therefore, a stationary solution of the Liouville equation and, as stated, we will assume that any stationary solution is of this type. This stationary distribution is called the equilibrium ensemble $\rho^{\text{eq}}(z)$. Therefore,

$$\lim_{t \rightarrow \infty} \rho(z, t) = \rho^{\text{eq}}(z) = g(I(z)). \quad (17)$$

Let us investigate the meaning of the function $g(I)$ by considering the probability distribution $P^{\text{eq}}(I)$ of dynamical invariants at equilibrium. By definition,

$$P^{\text{eq}}(I) = \int dz \rho^{\text{eq}}(z) \delta(I(z) - I) = \int dz g(I(z)) \delta(I(z) - I) = g(I) \Omega^{\text{eq}}(I), \quad (18)$$

where we have introduced the measure $\Omega^{\text{eq}}(I)$ of the region of phase space compatible with a given set of dynamical invariants

$$\Omega^{\text{eq}}(I) = \int dz \delta(I(z) - I). \quad (19)$$

Equation (18) allows to identify $g(I)$ and (17) becomes

$$\rho^{\text{eq}}(z) = \frac{P^{\text{eq}}(I(z))}{\Omega^{\text{eq}}(I(z))}. \quad (20)$$

Therefore, the equilibrium ensemble is fully determined by the probability distribution of dynamical invariants at equilibrium. It is obvious that the distribution of dynamical invariants at any time is itself invariant (use $\rho(z, t)$ instead of $\rho^{\text{eq}}(z)$ in (18), take the time derivative and use the Liouville equation). This means that the equilibrium ensemble is fully determined once the initial distribution of dynamical invariants is known at the initial time. As a particular example of (20), let us assume that at the initial time we know with absolute precision the values of the invariants I_0 . In this case, the equilibrium probability density (20) becomes the microcanonical ensemble

$$\rho^{\text{mic}}(z) = \frac{\delta(I(z) - I_0)}{\Omega^{\text{eq}}(I_0)}. \quad (21)$$

4.4 The Mesoscopic Level

At a given mesoscopic level, the state of the system is described by certain set of dynamical functions $X(z)$ which may take numerical values x . These functions are actually the coarse-grained variables or relevant variables that define the level of description. For the case of a colloidal suspension, the above functions can be the hydrodynamic fields, or the positions and momenta of the colloidal particles, or the concentration field, depending on the level of description selected. The coarse grained variables evolve in time due to the implicit evolution of z . Actually, we can compute the time derivative of $X(T_t z_0)$ through the chain rule

$$\frac{d}{dt} X(T_t z_0) = (iLX)(T_t z_0). \quad (22)$$

A formal solution of this equation is

$$X(T_t z_0) = (\exp\{iLt\}X)(z_0), \quad (23)$$

where the exponential operator is defined formally through the Taylor series

$$\exp\{iLt\} \equiv 1 + iLt + \frac{1}{2!}(iLt)^2 + \frac{1}{3!}(iLt)^3 + \dots \quad (24)$$

When $X(z) = z$, we see that the evolution operator has the form $T_t = \exp\{iLt\}$.

We discuss now the essential source of stochasticity that appears in any coarse-graining process. Let us assume that we know the initial numerical values of the coarse grained variables x_0 with precision and consider two different microstates z_0, z'_0 that are both compatible with x_0 , this is, $X(z_0) = X(z'_0) = x_0$. As the initial microstates evolve, the functions $X(T_t z_0), X(T_t z'_0)$ will take different numerical values in general, i.e. $X(T_t z_0) \neq X(T_t z'_0)$. Therefore, even if we know with certainty the actual initial state x_0 different outcomes are possible for the value of the coarse-grained variables at later times, just because there is no control over the actual microscopic state that produces the given macroscopic initial state x_0 . In order to describe our ignorance about the values of the coarse-grained variables at later times, we will use a distribution function $P(x, t)$. Of course, the distribution function at the mesoscopic level is related to the distribution function at the microscopic level through

$$P(x, t) = \int \delta(X(z) - x)\rho(z, t)dz. \quad (25)$$

Note that (25) is the general way of relating the probability distribution of a function $X(z)$ of a stochastic variable with the probability distribution of the stochastic variable z itself. By using the solution (12) and a change of variables we can rewrite (25) also as

$$P(x, t) = \int \delta(X(T_t z) - x)\rho(z, 0)dz, \quad (26)$$

where it is made apparent that all the stochasticity at a mesoscopic level of description comes essentially from our ignorance about the initial microscopic state, represented by the distribution function $\rho(z, 0)$.

A basic question that arises now is, what is the actual functional form of $\rho(z, 0)$? As mentioned, in principle we cannot measure the initial microscopic state z_0 exactly. If we are going to describe a system at a given coarse-grained level, we must assume that we have access to the measurement of the coarse-grained variables $X(z)$. In general, all the information we have about our system at the initial time is a particular distribution $P(x, 0)$, which is the outcome of a repeated set of measurements of the functions $X(z)$ with numerical outcomes x over the system prepared in an identical manner at the initial time. Therefore, we have to determine the distribution function $\rho_0(z)$ with the sole information that it should provide precisely the distribution $P(x, 0)$, according to (25), this is

$$P(x, 0) = \int dz \delta(X(z) - x)\rho_0(z). \quad (27)$$

However, there are many different $\rho_0(z)$ that can produce the same $P(x, 0)$. Which is the correct one? Perhaps there is no answer to this question, but there is an answer to the best selection. According to information theory [26], the least biased distribution which is compatible with the restriction (27) is the one that maximizes the entropy functional

$$S[\rho_0] \equiv -k_B \int_{\Gamma} \rho_0(z) \ln \frac{\rho_0(z)}{\rho^{\text{eq}}(z)} dz. \quad (28)$$

We encounter here a problem of Lagrange multipliers. By introducing the multipliers $\lambda(x)$ for the continuum set of restrictions (27) (one for each x), we maximize the functional $I[\rho_0] = S[\rho_0] + \int dx \lambda(x) P(x, 0) + \mu \int dx P(x, 0)$, where the μ Lagrange multiplier stands for the normalization to unity restriction of $\rho_0(z)$. The Lagrange multipliers are obtained by substituting the maximum value into the restriction (27). The following final result is obtained [27]

$$\rho_0(z) = \frac{P(X(z), 0)}{\Omega(X(z))}, \quad (29)$$

where $\Omega(x)$ is given by

$$\Omega(x) = \int dz \delta(X(z) - x) \rho^{\text{eq}}(z). \quad (30)$$

$\Omega(x)$ can be interpreted as a measure of the region of phase space which is compatible with the state x . Note also that $\Omega(x)$ must be the equilibrium distribution function at the coarse-grained level of description, because (30) is just the way in which the probability at the coarse-grained level relates with the microscopic probability.

4.5 Exact Equation for $P(x, t)$

In (25) we observe that the evolution of $\rho(z, t)$ according to the Liouville equation induces an evolution of $P(x, t)$. Of course, we would like to have a closed dynamical equation for $P(x, t)$ that makes no reference to the underlying dynamics given by $\rho(z, t)$. This closed equation can be obtained with the help of a projection operator technique. Following Zwanzig [3], we introduce a projection operator \mathcal{P} that applies to any function $F(z)$ of phase space Γ

$$\mathcal{P}F(z) = \langle F \rangle^{X(z)}, \quad (31)$$

where we have introduced the constrained average $\langle F \rangle^x$ by

$$\langle F \rangle^x = \frac{1}{\Omega(x)} \int dz \rho^{\text{eq}}(z) \delta(X(z) - x) F(z), \quad (32)$$

Note that the effect of the operator \mathcal{P} on an arbitrary function of phase space is to transform it into a function of the relevant variables $X(z)$. The operator \mathcal{P} satisfies the projection property $\mathcal{P}^2 = \mathcal{P}$. We introduce also the complementary projection operator $\mathcal{Q} = 1 - \mathcal{P}$ which satisfies $\mathcal{P}\mathcal{Q} = 0$ and $\mathcal{Q}^2 = \mathcal{Q}$. The operators \mathcal{P}, \mathcal{Q} satisfy

$$\int dz \rho^{\text{eq}}(z) A(z) \mathcal{P}B(z) = \int dz \rho^{\text{eq}}(z) B(z) \mathcal{P}A(z), \quad (33)$$

for arbitrary functions $A(z), B(z)$. It is convenient to introduce the following notation

$$\Psi_x(z) = \delta(X(z) - x), \quad (34)$$

and consider the Dirac's delta function as an ordinary phase function with a continuum index x . According to the formal solution (23) this phase function will evolve according to

$$\Psi_x(T_t z) = \exp\{iLt\}\Psi_x(z), \quad (35)$$

and, therefore,

$$\partial_t \Psi_x(T_t z) = \exp\{iLt\}iL\Psi_x(z). \quad (36)$$

Now we introduce a mathematical identity between operators

$$\exp\{iLt\} = \exp[iLt]\mathcal{P} + \int_0^t dt' \exp[iLt']\mathcal{P}iL\mathcal{Q} \exp[iL\mathcal{Q}(t-t')] + \mathcal{Q} \exp[iL\mathcal{Q}t]. \quad (37)$$

This identity can be proved by taking the time derivative on both sides. If two operators have the same derivative and coincide at $t = 0$ then they are the same operator. We now apply this identity (37) to the left hand side of (36). After some algebra, which uses the explicit form of the operators \mathcal{P}, \mathcal{Q} , the properties (16), (33), and the chain rule in the form

$$iL\Psi_x(z) = iLX_i \frac{\partial}{\partial x_i} \Psi_x(z),$$

where summation over repeated indices is implied, one obtains,

$$\begin{aligned} \partial_t \Psi_x(T_t z) &= -\frac{\partial}{\partial x_i} \cdot v_i(x) \Psi_x(T_t z) \\ &+ \int_0^t dt' \int dx' \Omega(x') \frac{\partial}{\partial x_i} \cdot D_{ij}(x, x', t-t') \cdot \frac{\partial}{\partial x'_j} \frac{\Psi_{x'}(T_{t'} z)}{\Omega(x')} \\ &+ \mathcal{Q} \exp\{iL\mathcal{Q}t\} \mathcal{Q}iL\Psi_x(T_t z). \end{aligned} \quad (38)$$

We have defined the drift $v_i(x)$ and the diffusion tensor $D_{ij}(x, x', t)$ through

$$\begin{aligned} v_i(x) &= \langle iLX_i \rangle^x, \\ D_{ij}(x, x', t) &= \langle (iLX_j - \langle iLX_j \rangle^{x'}) \exp\{iL\mathcal{Q}t\} \Psi_x(iLX_i - \langle iLX_i \rangle^x) \rangle^{x'}. \end{aligned} \quad (39)$$

If we multiply (38) by $\rho(z, 0)$, integrate over z , and use (26), we obtain a final exact and closed equation for $P(x, t)$

$$\begin{aligned} \partial_t P(x, t) &= -\frac{\partial}{\partial x_i} \cdot v_i(x) P(x, t) \\ &+ \int_0^t dt' \int dx' \Omega(x') \frac{\partial}{\partial x_i} \cdot D_{ij}(x, x', t-t') \cdot \frac{\partial}{\partial x'_j} \frac{P(x', t')}{\Omega(x')}, \end{aligned} \quad (40)$$

where we have used that the initial ensemble (29) is a function of $X(z)$ and, therefore,

$$\int dz \rho(z, 0) \mathcal{Q} \exp\{iL\mathcal{Q}t\} \mathcal{Q}iL\Psi_x(T_t z) = 0,$$

where $\mathcal{Q} = 1 - \mathcal{P}$ and (33) have been used along with the property $\mathcal{Q}f(A) = 0$.

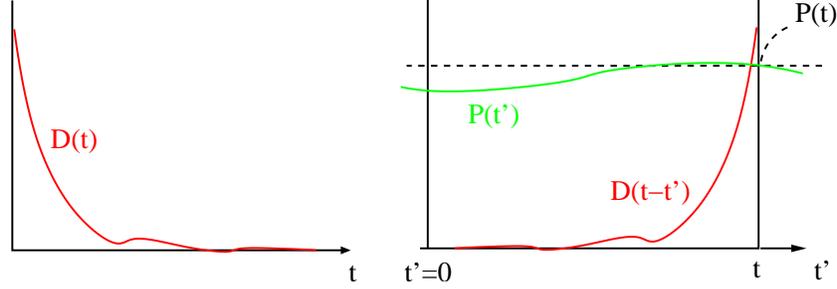


Fig. 3. The Markovian approximation

4.6 The Fokker–Planck Equation

Equation (40) is an exact and rigorous closed equation governing the distribution function $P(x, t)$. No approximations have been made and, essentially, it is another way of rewriting the Liouville equation. In principle, it is as difficult to solve as the original Liouville equation. However, as it happens often in Physics, just by rewriting the same thing in a different form, it is possible to perform suitable approximations that allow for an advance in the understanding of the problem. In the case of (40), the approximation is called the Markovian approximation and transforms the integro-differential equation into a simple Fokker–Planck equation.

The Markovian assumption is one about separation of time scales between the time scale of evolution of the phase function $X(z)$ and the rest of variables of the system. If this separation of time scales exists then, in the time scale in which the tensor $D_{ij}(x, x', t-t')$ decays, the probability $P(x, t')$ has not changed appreciably. Schematically, we write the memory term in (40) as

$$\int_0^t dt' D(t-t') P(t') \approx P(t) \int_0^\infty D(t') dt'. \quad (41)$$

This approximation is depicted in Fig. 3. We have extended in (41) the upper limit of integration to infinity, due to the fast decay of $D(t)$. Note that the tensor $D_{ij}(x, x', t-t')$ is a quantity of order $(iLX)^2$, i.e. second order in the time derivatives of the relevant variables. The time scale of evolution of $P(x, t)$ is the same as the time scale of the variables $X(z)$. The approximation (41) amounts, therefore, to neglect third order time derivatives of the relevant variables in front of second order terms. We, therefore, consistently perform a formal expansion of the tensor $D_{ij}(x, x', t-t')$ in (39) in terms of iLX and keep only second order terms. Then,

$$\exp\{iLQt\} \Psi_x Q iLX = \Psi_x \exp\{iLQt\} Q iLX + \mathcal{O}(iLX)^2. \quad (42)$$

Therefore, up to terms of order $\mathcal{O}(iLX^3)$ we have

$$D_{ij}(x, x', t) = \delta(x - x') \langle (iLX_j - \langle iLX_j \rangle^x) \exp\{iLQt\} (iLX_i - \langle iLX_i \rangle^x) \rangle^x, \quad (43)$$

and the tensor becomes diagonal in x, x' . By substitution of the approximate form (43) into the exact equation (40) and using (41) we obtain

$$\partial_t P(x, t) = -\frac{\partial}{\partial x_i} \cdot v_i(x) P(x, t) + \frac{\partial}{\partial x_i} \cdot \Omega(x) D_{ij}(x) \cdot \frac{\partial}{\partial x_j} \frac{P(x, t)}{\Omega(x)}, \quad (44)$$

where we have defined the diffusion tensor

$$D_{ij}(x) = \int_0^\infty dt' \langle (iLX_j - \langle iLX_j \rangle^x) \exp\{iLQt'\} (iLX_i - \langle iLX_i \rangle^x) \rangle^x, \quad (45)$$

and we summarize for completeness the rest of quantities appearing in (44)

$$\begin{aligned} v_i(x) &= \langle iLX_i \rangle^x, \\ \langle \dots \rangle^x &= \frac{1}{\Omega(x)} \int dz \rho^{\text{eq}}(z) \delta(X(z) - x) \dots, \\ \Omega(x) &= \int dz \rho^{\text{eq}}(z) \delta(X(z) - x). \end{aligned} \quad (46)$$

Equation (44) is the desired Fokker–Planck equation for the dynamics at the mesoscopic coarse-grained level of description. This equation is one of the cornerstones of non-equilibrium statistical mechanics and was obtained by Zwanzig in 1961 [3] following the path pioneered by Green in [2]. In this equation, all the objects $v_i(x)$, $D_{ij}(x, t)$ and $\Omega(x)$ have a definite microscopic definition. In particular, (45) is a general form of the well-known Green–Kubo formulae that relates the transport coefficients $D_{ij}(x)$ with a time integral of a correlation function of microscopic variables. The FPE (44) is valid whenever there is a clear separation of time scales such that the Markovian approximation is valid. Clearly, the FPE will describe correctly the evolution of $P(x, t)$ only for times which are larger than the typical time scales of decay of the correlation involved in $D_{ij}(x)$. We cannot investigate with this equation shorter time scales. For this short time scales, the transport coefficients start to depend on time.

As a final remark, we can check that, despite the approximations taken to derive the FPE (44), $\Omega(x)$ is still the equilibrium solution. By substituting $\Omega(x)$ into (44) we have that $\Omega(x)$ will be a stationary solution of the FPE (44) if and only if

$$\sum_i \frac{\partial}{\partial x_i} v_i(x) \Omega(x) = 0. \quad (47)$$

By using the definition (39), the constrained average (32), and the chain rule we have

$$\frac{\partial}{\partial x_i} v_i(x) \Omega(x) = \int dz \rho^{\text{eq}}(z) \frac{\partial}{\partial x_i} \Psi_x(z) iLX_i(z) = - \int dz \rho^{\text{eq}}(z) iL\Psi_x(z) = 0, \quad (48)$$

where we have used (16) and $iL\rho^{\text{eq}} = 0$.

5 Example: Smoluchowski Level

We illustrate now how the general formalism developed in the previous section can be applied to the case of a colloidal suspension in order to derive the FPE at the Smoluchowski level discussed in Sect. 3.4. The idea is simply to translate to our system the

different objects defined in (45), (46) that appear in the FPE (44). The microscopic Hamiltonian is given in (2). The equilibrium ensemble is given by, for example, the canonical ensemble

$$\rho^{\text{eq}}(z) = \frac{1}{Z} \exp\{-\beta H(z)\},$$

where $\beta = (k_B T)^{-1}$ is proportional to the inverse of the temperature T . The relevant variables $X(z) = x$ at the Smoluchowski level are the positions of the colloidal particles \mathbf{Q}_i which take numerical values $\bar{\mathbf{Q}}_i$. The equilibrium solution $\Omega(x)$ of the FPE in (46) is given by

$$\begin{aligned} \Omega(\bar{Q}) &= \int dz \rho^{\text{eq}}(z) \prod_i \delta(\mathbf{Q}_i - \bar{\mathbf{Q}}_i) \\ &\propto \exp\{-\beta V^{\text{CC}}(\bar{Q})\} \int dq \exp\{-\beta (V^{\text{CS}}(\bar{Q}, q) + V^{\text{SS}}(q))\} \\ &\equiv \exp\{-\beta \bar{V}^{\text{eff}}(\bar{Q})\}, \end{aligned} \quad (49)$$

where $\int dq$ is a condensed notation for the integral over solvent positions. We have introduced the effective potential as

$$\bar{V}^{\text{eff}}(\bar{Q}) = V^{\text{CC}}(\bar{Q}) - k_B T \ln \int dq \exp\{-\beta (V^{\text{CS}}(\bar{Q}, q) + V^{\text{SS}}(q))\}. \quad (50)$$

The effective potential has a contribution $V^{\text{CC}}(\bar{Q})$ coming from the direct interaction potential and an additional contribution that represents the effect of the static and equilibrium averaged solvent mediated interaction between colloidal particles.

After performing the integrals over the Dirac delta functions, the constrained average in (46) now takes the form

$$\langle \dots \rangle_{\bar{Q}} = \frac{1}{\Omega(\bar{Q})} \int dq \rho^{\text{eq}}(q, \bar{Q}) \dots$$

Note that this constrained average is simply an equilibrium average over the solvent degrees of freedom, in which the colloidal particles are assumed to be fixed at the values \bar{Q} . It is, therefore, an equilibrium ensemble average in which the colloidal particles act as external static force fields.

Because the time derivatives iLX are simply P_i/M_i , the drift term $v(x) = \langle iLX \rangle^x$ defined in (46) is now the constrained equilibrium average of the momentum of the colloidal particles, which is zero by isotropy of the equilibrium ensemble. The diffusion tensor (45) becomes

$$\mathbf{D}_{ij}(\bar{Q}) = \int_0^\infty dt' \langle \mathbf{V}_j \exp\{iLQ t'\} \mathbf{V}_i \rangle_{\bar{Q}}.$$

The final FPE (44) takes now the form

$$\partial_t P(Q, t) = \frac{\partial}{\partial \mathbf{Q}_i} \left[\beta \mathbf{D}_{ij}(Q) \frac{\partial \bar{V}^{\text{eff}}(Q)}{\partial \mathbf{Q}_j} \right] P(Q, t) + \frac{\partial}{\partial \mathbf{Q}_i} \mathbf{D}_{ij}(Q) \cdot \frac{\partial}{\partial \mathbf{Q}_j} P(Q, t),$$

which, has been presented already in (5).

In this example, we observe how the general Fokker–Planck description can be applied to a specific level of description of a given system. The essential benefits of this approach are that it is very simple to get the structure of the coarse-grained equation. Also, we obtain explicit microscopic expressions for all the objects in the FPE. In particular, the diffusion tensor which describes the mutual, solvent-mediated influence of the colloidal particles is given in terms of the auto and cross-correlations of the velocities of the colloidal particles, where the averages are taken over the solvent degrees of freedom which are distributed according to an equilibrium ensemble in the presence of the external fields due to the static colloidal particles.

6 How to Compute the Objects in the FPE from a MD Simulation?

The FPE (44) governs the full dynamics at a coarse-grained level of description. In the equation there appear three objects, the drift $v_i(x)$, the diffusion tensor $D_{ij}(x)$ and the equilibrium distribution function $\Omega(x)$ which are defined in terms of the microscopic dynamics of the system. It would be very useful to have a definite way to compute these objects through a numerical solution of the microscopic equations, that is, through a molecular dynamics (MD) simulation. In the previous example of the colloidal system at the Smoluchowski level, one could run a molecular dynamics simulation in which the colloidal particles are at fixed positions and compute the velocity correlation functions in order to extract the corresponding diffusion tensors. Note that this is perhaps the only way of using a molecular dynamics in order to study a colloidal suspension. In this example, it has been possible to deal with the Dirac delta functions over the relevant variables that appear in the constrained averages (46) because the relevant variables are very simple functions of the microscopic state. In a general case, it is not possible to perform explicitly the integral over the Dirac delta functions appearing in the definitions (45), (46) and it is necessary to devise a new method for dealing with the constrained averages. In this section, we briefly sketch a general route to compute the quantities that appear in the general FPE and highlight the problems that usually appear.

First, we have to compute $\Omega(x)$ which is the equilibrium distribution function of our state variables. One route for getting this distribution function is to simply bin the x state space and get an histogram of occurrences of the different values of $x = X(z)$ as the microscopic state z evolves in our equilibrium MD simulation. However, we will need also to compute constrained averages in the drift and diffusion tensors, and the presence of a Dirac delta function complicates such computation enormously. For this reason, it is convenient to find another route for the calculations which is not microcanonical but canonical, in the following sense. Consider the following partition function $Z(\lambda)$ defined as

$$Z(\lambda) = \int dz \rho^{\text{eq}}(z) \exp\{-\lambda X(z)\} = \langle \exp\{-\lambda X\} \rangle^{\text{eq}}. \quad (51)$$

This quantity can be understood as the normalization factor of an equilibrium ensemble in which there is a coupling between external fields λ and the relevant variables. Strictly speaking, it is the equilibrium average of the phase function $\exp\{-\lambda X(z)\}$, which is

very easy to compute during a MD run. Note that, in principle, a single run allows to compute $Z(\lambda)$ for all λ simultaneously. By introducing the following identity

$$1 = \int dx \delta(X(z) - x), \quad (52)$$

within the integral sign of (51) we can relate $Z(\lambda)$ with $\Omega(x)$

$$Z(\lambda) = \int dx \Omega(x) \exp\{-\lambda x\}.$$

In most applications, we will have that the argument of the integral is highly peaked at a particular maximum value x^* and, by the usual steepest descent argument, we can approximate

$$Z(\lambda) \approx \Omega(x^*) \exp\{-\lambda x^*\}, \quad (53)$$

where the maximum occurs at x^* , which is the solution of

$$\frac{\partial \ln \Omega(x^*)}{\partial x} = \lambda. \quad (54)$$

By taking the derivatives with respect to λ in (53) and using (54) we have the expression conjugate to (54)

$$-\frac{\partial \ln Z(\lambda)}{\partial \lambda} = x^*.$$

This partial derivative can be easily computed from MD, because from (51),

$$-\frac{\partial \ln Z(\lambda)}{\partial \lambda} = \frac{\langle X \exp\{-\lambda X\} \rangle^{\text{eq}}}{\langle \exp\{-\lambda X\} \rangle^{\text{eq}}}.$$

In this way, we get the functional relation $x^*(\lambda)$ that can be inverted to give $\lambda(x)$ ¹ and, from (53) one can recover the equilibrium distribution function in the form

$$\Omega(x) \approx Z(\lambda(x)) \exp\{\lambda(x)x\}.$$

Note that although this is a quite involved route to get $\Omega(x)$, now we can compute the constrained averages as “canonical” averages which are defined as

$$\langle \dots \rangle^\lambda = \int dz \rho^{\text{eq}}(z) \exp\{-\lambda X(z)\} \dots \quad (55)$$

The idea, of course, is to introduce again (52) and resort to the sharpness of the function involved to approximate the constrained average with the canonical one, this is,

$$\langle \dots \rangle^x \approx \langle \dots \rangle^{\lambda(x)},$$

¹ Note that $\partial x^*/\partial \lambda = \langle \delta x \delta x \rangle^{\text{eq}}$ which, being a second moment of a distribution, is a positive definite quantity. This is the main hypothesis of the inverse function theorem [28] that ensures that the function $x(\lambda)$ can be inverted.

where the functional relation $\lambda(x)$ has already been obtained. In this way, the constrained average involved in the definition of $v_i(x)$ is now easily computed from an equilibrium MD simulation.

The term that remains to be computed is the diffusion tensor, which is given by a correlation function. Note, however, that the evolution operator that appears in the definition of the diffusion tensor corresponds to the projected dynamics, i.e. $\exp\{iLQ\}$, instead of being the actual dynamics $\exp\{iL\}$ that is reproduced in a MD simulation. The question thus arises about whether we can approximate the projected dynamics by the real one. This can be done, actually, because under the approximation where we have neglected terms of order $(iLX)^3$, both dynamics coincide. Note that $\exp\{iLQ\} = \exp\{iLt\} + \mathcal{O}(iLX)$, as can be seen from the Taylor series (24). However, this apparently innocent approximation has terrible consequences. To appreciate them, let us write the diffusion tensor (45) with the approximation $\exp\{iLQ\} \approx \exp\{iLt\}$ in the form

$$D_{ij}(x) = \lim_{\tau \rightarrow \infty} \int_0^\tau dt' \langle (iLX_j - \langle iLX_j \rangle^x) \exp\{iLt'\} (iLX_i - \langle iLX_i \rangle^x) \rangle^x, \quad (56)$$

that leads to

$$D_{ij}(x) = \lim_{\tau \rightarrow \infty} [\langle iLX_j X_i(\tau) \rangle^x - \langle iLX_i \rangle^x \langle X_i(\tau) \rangle^x], \quad (57)$$

where we have used that $iLX_i = \dot{X}_i$ and we have performed the time integral explicitly. If we take $\tau \rightarrow \infty$ in this expression, we note that

$$\lim_{\tau \rightarrow \infty} \langle iLX_j X_i(\tau) \rangle^x = \langle iLX_i \rangle^x \langle X_i(\tau) \rangle^x, \quad (58)$$

because as time proceeds, any two dynamical variables become uncorrelated and statistically independent. We arrive, therefore at the very surprising result that the diffusion tensor is zero! This is known as the plateau problem and has its origin in the uncontrollable step of approximating the projected dynamics $\exp\{iLQ\}$ with the actual dynamics $\exp\{iLt\}$. The solution of this problem is to not take the limit $\tau \rightarrow \infty$. Due to the clear separation of time scales, by choosing τ large enough for the correlation to have decayed sufficiently, but short in the time scale of the relevant variables, the diffusion tensor takes a constant value that does not depend appreciably on the actual value of τ . For a clear discussion of the plateau problem for the simple case of Brownian motion see [29].

In this section, we have presented a general strategy for the microscopic calculation of the different objects of the FPE from equilibrium molecular dynamics simulations. Of course, in practice there is a big problem in pursuing the above program due to the fact that the state vector x may belong to a highly dimensional space. It is very difficult to deal with multidimensional functions like $\Omega(x)$, for example. Think, for example, on the level of description of hydrodynamics where, in principle, we have several variables (mass, momentum, and energy) for every little cell in which we have divided the space occupied by our fluid. Fortunately enough, for the case of hydrodynamic variables one can focus on one cell only by resorting to the local equilibrium assumption. In this case one can reduce the problem to two variables (mass and energy densities) because

the momentum variables can be easily eliminated with a Galilean transformation. In this way, the usual Green–Kubo formulae for transport coefficients can be obtained [5]. Other systems and levels of description usually lead to multivariate problems that are in general difficult, if not impossible, to handle. Even in cases where the local equilibrium assumption can be taken, if the hydrodynamic description requires further structural variables of tensorial nature, we readily obtain a difficult multivariate problem [30]. In part due to this reason, there have been not so many actual explicit implementations of the program of coarse-graining from molecular dynamics.

The alternative route is that of modeling, that is, to assume particular functional forms for the diffusion tensors, drift terms and equilibrium probability function, inspired from a good knowledge of the physical processes at hand, and check that the resulting predictions agree with experiments. Of course, one would like to use as much information as possible from the microscopic derivation in order to formulate models with the minimum of arbitrariness. In the next section, we will present the GENERIC structure for which a large number of restriction on the possible form of the objects appearing in the FPE exist. These restrictions help enormously in the task of formulating new models for complex fluids [6,31].

7 GENERIC Structure of the Fokker–Planck Equation

In this section, we study those levels of description that satisfy a very strong property: the microscopic dynamical invariants $I(z)$ of the system can be expressed as functions of the relevant variables $X(z)$ of this level of description, this is

$$I(z) = \mathcal{I}(X(z)), \quad (59)$$

where $\mathcal{I}(x)$ is a suitable function. When our level of description has this property a very powerful structure, named GENERIC, emerges [32]. As a particular case of (59), the Hamiltonian must be expressible in terms of the relevant variables, this is

$$H(z) = E(X(z)). \quad (60)$$

Therefore, in order to have a GENERIC structure, our level of description must allow to define an energy function $E(x)$ that coincides with the actual value of the energy of the system. Note that not every level of description can have the GENERIC structure. Even when the relevant variables are slow and well time separated, if the total energy cannot be written as a function of the relevant variables, there will be no GENERIC structure. For example, in the colloidal suspension discussed in Sect. 5, the state at the Smoluchowski level is described by the set of coordinates \mathbf{Q}_i of the colloidal particles. The energy of the whole system contains a contribution that comes from the solvent degrees of freedom that cannot be expressed in terms of the colloidal variables alone. Therefore, this level of description has no GENERIC structure.

In order to appreciate the beauty of the GENERIC structure we have first to exploit the consequences of (59) on the FPE (44). We first consider which form takes the average $\langle \dots \rangle^x$ when (59) holds. For this reason, we first note that the equilibrium ensemble

$\rho^{\text{eq}}(z)$ is a function of dynamical invariants (see (20)) and, therefore,

$$\Omega(x) = \int dz \rho^{\text{eq}}(z) \delta(X(z) - x) = \frac{P^{\text{eq}}(\mathcal{I}(x))}{\Omega^{\text{eq}}(\mathcal{I}(x))} \overline{\Omega}(x), \quad (61)$$

where we have introduced

$$\overline{\Omega}(x) = \int dz \delta(X(z) - x). \quad (62)$$

As a result,

$$\langle \dots \rangle^x = \frac{1}{\Omega(x)} \int dz \rho^{\text{eq}}(z) \delta(X(z) - x) \dots = \frac{1}{\overline{\Omega}(x)} \int dz \delta(X(z) - x) \dots, \quad (63)$$

and we see that the constrained average does not depend on the equilibrium ensemble.

Note that we can write the equilibrium distribution function $\Omega(x)$ in the form

$$P^{\text{eq}}(x) = \Omega(x) = \frac{P^{\text{eq}}(\mathcal{I}(x))}{\Omega^{\text{eq}}(\mathcal{I}(x))} \exp\{S(x)/k_{\text{B}}\}, \quad (64)$$

where the entropy is defined by

$$S(x) = k_{\text{B}} \ln \overline{\Omega}(x). \quad (65)$$

It is apparent that the concept of entropy as defined in (65) is level dependent. It makes no sense to speak about “the” entropy of a system. Different levels of description of the same system have different entropies which depend on different sets of variables.

Equation (64) has the form of the so-called Einstein equilibrium distribution in the presence of dynamical invariants [25]. Note that if we know with precision the initial values \mathcal{I}_0 of the dynamical invariants, we have

$$P^{\text{eq}}(x) = \frac{\delta(\mathcal{I}(x) - \mathcal{I}_0)}{\Omega^{\text{eq}}(\mathcal{I}_0)} \exp\{S(x)/k_{\text{B}}\}. \quad (66)$$

An alternative to (65) is to define the entropy as $S(x) = k_{\text{B}} \ln \Omega(x)$. However, this definition of the entropy makes problematic the treatment of situations like the one represented in (66) where we have Dirac delta functions describing exact knowledge about the dynamical invariants.

Let us continue with the consequences of (59). We may algebraically manipulate the reversible term $v_i(x) = \langle iLX_i \rangle^x$ as follows,

$$iLX_i = \frac{\partial X_i}{\partial z} iLz = \frac{\partial X_i}{\partial z} L_0 \frac{\partial H}{\partial z} = \frac{\partial X_i}{\partial z} L_0 \frac{\partial X_j}{\partial z} \frac{\partial E}{\partial x_j}(X(z)). \quad (67)$$

By using this result into the definition of the constrained average (32) we obtain

$$v_i(x) = \langle iLX_i \rangle^x = L_{ij}(x) \frac{\partial E}{\partial x_j}(x), \quad (68)$$

where the reversible operator L_{ij} is defined by

$$L_{ij}(x) = \left\langle \frac{\partial X_i}{\partial z} \cdot L_0 \cdot \frac{\partial X_j}{\partial z} \right\rangle^x. \quad (69)$$

Here, the microscopic reversible operator L_0 is the block diagonal matrix introduced in (8).

For convenience, we introduce a dissipative matrix M as $M_{ij} = D_{ij}/k_B$. By using (67) and (68) in the definition (45) we easily arrive at the following degeneracy property of M

$$M \cdot \frac{\partial \mathcal{I}}{\partial x} = 0. \quad (70)$$

By collecting (64), (65), (68) and (70) we can finally write the FPE (44) in the GENERIC form

$$\partial_t P(x, t) = -\frac{\partial}{\partial x} \left[L(x) \frac{\partial E}{\partial x} + M(x) \frac{\partial S}{\partial x} \right] P(x, t) + k_B \frac{\partial}{\partial x} M^S(x) \frac{\partial}{\partial x} P(x, t). \quad (71)$$

Note that only the symmetric part M^S of M appears in the last term involving the second derivatives. For reasons that will become clear later the term $L \frac{\partial E}{\partial x}$ is named the reversible part of the dynamics, and $M(x) \frac{\partial S}{\partial x}$ the irreversible or dissipative part of the dynamics. The last term proportional to k_B is a fluctuation term that describes the broadening of the distribution function.

7.1 Properties of L and M

The first property of the matrix L is its antisymmetry, which derives from the definition in (69) and the fact that the matrix L_0 is antisymmetric. On the other hand, the matrix $M_{ij}^S = \frac{1}{2} [M_{ij} + M_{ji}]$ is, by definition, symmetric. By using (45) we can write M_{ij}^S in the form

$$\begin{aligned} M_{ij}^S &= \frac{1}{2k_B} \int_0^\infty dt' \langle (iLX_j - \langle iLX_j \rangle^x) \exp\{iLQt'\} (iLX_i - \langle iLX_i \rangle^x) \rangle^x \\ &\quad + \frac{1}{2k_B} \int_0^\infty dt' \langle (iLX_i - \langle iLX_i \rangle^x) \exp\{iLQt'\} (iLX_j - \langle iLX_j \rangle^x) \rangle^x. \end{aligned} \quad (72)$$

The second term in the right hand side of (72) can be arranged by using the properties (16) and (33) of L and Q , which are inherited by $\exp\{iLQt'\}$ in the form

$$\langle A \exp\{iLQt'\} B \rangle^x = \langle B \exp\{-iLt'Q\} A \rangle^x.$$

In this way, (72) becomes

$$M_{ij}^S = \frac{1}{2k_B} \int_{-\infty}^\infty dt' \langle (iLX_j - \langle iLX_j \rangle^x) \exp\{iLQt'\} (iLX_i - \langle iLX_i \rangle^x) \rangle^x. \quad (73)$$

It is possible to show that M^S is semi definite positive. If we double contract M^S with an arbitrary vector a we obtain

$$\sum_{ij} a_i M_{ij}^S a_j = \frac{1}{2k_B} \int_{-\infty}^\infty \langle (A \exp\{iLQt\} A)^x \rangle dt, \quad (74)$$

where $A = \sum_i (iLX_i - \langle iLX_i \rangle^x) a_i$. Equation (74) is the time integral of an autocorrelation function. By recalling the Wiener-Knichine theorem that states that the Fourier transform of a stationary autocorrelation function is positive [10], we conclude that this double contraction is positive or, in other words, that M^S is a positive matrix. That M^S is not positive definite but semidefinite follows from (70) which shows that there are non-null eigenvectors with null eigenvalue.

A property similar to (70) but now for the matrix L takes the following form

$$\begin{aligned} \frac{\partial E}{\partial x} \cdot L \cdot \frac{\partial \mathcal{I}}{\partial x} &= \frac{1}{\Omega(x)} \frac{\partial E}{\partial x_i} \int dz \rho^{\text{eq}}(z) \Psi_x(z) \frac{\partial X_i}{\partial z} \cdot L_0 \cdot \frac{\partial X_j}{\partial z} \frac{\partial \mathcal{I}}{\partial x_j} \\ &= \frac{1}{\Omega(x)} \int dz \rho^{\text{eq}}(z) \Psi_x(z) \frac{\partial H}{\partial z} L_0 \frac{\partial \mathcal{I}}{\partial z} \\ &= \frac{1}{\Omega(x)} \int dz \rho^{\text{eq}}(z) \Psi_x(z) iLI = 0. \end{aligned} \quad (75)$$

Another important property of the matrix L is obtained from (47) which becomes,

$$\frac{\partial}{\partial x_i} \left[L_{ij} \frac{\partial E}{\partial x_j} + M_{ij}^A \frac{\partial E}{\partial x_j} \right] \Omega(x) = 0, \quad (76)$$

where $M_{ij}^A = (M_{ij} - M_{ji})/2$ is the antisymmetric part of M . Further use of the chain rule, the (anti)-symmetries of L_{ij} , M_{ij}^A and the definition (65) leads to

$$\frac{\partial E}{\partial x_i} L_{ij} \frac{\partial S}{\partial x_j} = k_B \left[\frac{\partial L_{ij}}{\partial x_j} \frac{\partial E}{\partial x_i} + \frac{\partial M_{ij}^A}{\partial x_i} \frac{\partial S}{\partial x_j} \right]. \quad (77)$$

This seems to be a complicated differential equation to be satisfied by the different objects appearing in the FPE (71). The interest of this equation (77) is that it tells us that the left hand side is of order k_B . As we will see in Sect. 7.3, terms of this order can be neglected whenever fluctuations effects are small.

Further properties for the blocks E, S, L, M can be derived by resorting to the time reversibility of the microscopic dynamics [5], which lead to generalized Onsager reciprocity relations. Also, it is possible to study how the symmetries of the microscopic dynamics reflect on symmetries of the blocks E, S, L, M [33].

7.2 GENERIC Stochastic Differential Equation

The Fokker-Planck equation governs the probability distribution function $P(x, t)$ of a stochastic variable x and, therefore, characterizes the dynamics of these variables. Another, mathematically equivalent, way of describing the dynamics of the stochastic variables is through a stochastic differential equation (SDE) [34]. The SDE associated to the FPE (44) is, within the Ito interpretation

$$dx = \left[L(x) \frac{\partial E}{\partial x} + M(x) \frac{\partial S}{\partial x} + k_B \nabla M^S(x) \right] dt + d\tilde{x}, \quad (78)$$

where $d\tilde{x}$ is a linear combination of independent increments of the Wiener process of the form

$$d\tilde{x}_i = \sum_j B_{ij}(x) dW_j(t), \quad (79)$$

where the (generally non-square) matrix $B(x)$ satisfies

$$B(x)B^T(x) = 2k_B M^S(x). \quad (80)$$

The term $k_B \nabla M(x)$ in (78) is a consequence of both, the particular form in which the matrix M appears in the FPE (44), that is, in between the two partial derivatives in the last term, and the use of the Ito interpretation of the SDE.

By recalling that the independent increments of the Wiener process have a variance proportional to dt , we can write (79) and (80) in the form

$$d\tilde{x}(t)d\tilde{x}^T(t) = 2k_B M^S(x(t))dt, \quad (81)$$

which is a formal and compact statement of the Fluctuation-Dissipation theorem. This theorem, which is nothing else than the rule for obtaining the SDE from the FPE, states that the amplitude of the fluctuations is related to the matrix of transport coefficients M^S . Following a common practice in some stochastic physics literature, we can introduce the white noise terms $\zeta(t)$ as the time derivative of the random terms $d\tilde{x}$, although, strictly speaking, the Wiener process is not differentiable [34]. The white noise terms have zero mean and the variance is given by (81) in the form

$$\langle \zeta(t)\zeta(t') \rangle = 2k_B M(x)\delta(t-t'). \quad (82)$$

It is very tempting to make the identification

$$\zeta(t) \leftrightarrow \exp\{iLQt\} [iLX_i - \langle iLX_i \rangle^x], \quad (83)$$

because, then, we can relate the Fluctuation-Dissipation (81) theorem with the Green-Kubo formula (45). Even though this identification is certainly not rigorous, it shows that the rapidly varying functions that appear in the microscopic derivation, are modeled at the mesoscopic level as white noise, the prime example of a rapidly varying function. The identification (83) is useful in practice because, in general, it is simple to compute the time derivatives of the relevant variables, and this provides for the structure of the random terms. In turn, by having a raw understanding of the structure of the noise, one can, through the Fluctuation-Dissipation theorem (81) obtain the structure of the matrix M .

As an example, consider the following scalar product $\zeta \cdot \frac{\partial E}{\partial x}$. According to the identification (83) and by using (67) we easily arrive at the conclusion that this scalar product is zero. In terms of the properly defined noise terms $d\tilde{x}$ we have

$$d\tilde{x} \cdot \frac{\partial E}{\partial x} = 0. \quad (84)$$

In geometrical terms this expression has a lot of sense. It tells us that the stochastic kicks $d\tilde{x}$ in (78) are perpendicular to the gradient of the energy, which is a vector that

is normal to the surface of constant energy. Therefore, these kicks are tangential to the energy shell, and the noise lets the state at constant energy. In other words, the noise conserves energy. This can be explicitly shown by computing the stochastic differential of the energy function $E(x)$. According to Ito calculus, one has

$$dE(t) = \frac{\partial E}{\partial x} \cdot dx + \frac{1}{2} \frac{\partial^2 E}{\partial x \partial x} : dx dx. \quad (85)$$

Note the usual occurrence of higher order terms, which is a consequence of the peculiarities of Ito calculus. By substitution of the SDE (78) in (85), and use of (81) we arrive at

$$dE(t) = \frac{\partial}{\partial x} \left[M(x) \frac{\partial E}{\partial x} \right] = 0,$$

as can be seen from the form of M in (81) and the property (84). A similar orthogonality condition holds for the rest of dynamical invariants, this is,

$$d\tilde{x} \cdot \frac{\partial \mathcal{I}}{\partial x} = 0.$$

7.3 The Size of the Fluctuations and the Deterministic equations

The size of the thermal fluctuations is formally controlled by the Boltzmann constant k_B , which has dimensions of entropy and which is small compared with macroscopic entropies [35]. In practical situations, what controls the effect of thermal fluctuations is a dimensionless ratio k_B/S_0 where S_0 is a characteristic entropy that scales with the size of the system. With this understanding, we can take the formal limit $k_B \rightarrow 0$ in the FPE (under the assumption that all the objects E, S, L, M do not depend on k_B). This amounts to neglect the last diffusive term that contains second derivatives with respect to the state variables. The resulting equation, which has only first order derivatives, describes deterministic motion, in much the same way as the Liouville equation does. This is even more clear at the level of the SDE (78) which, in the limit $k_B \rightarrow 0$, becomes an ordinary differential equation (note that $d\tilde{x}$ scales like $k_B^{1/2}$)

$$\dot{x} = L(x) \frac{\partial E}{\partial x} + M(x) \frac{\partial S}{\partial x}. \quad (86)$$

At the same time, in the limit $k_B \rightarrow 0$ we have from (77) the following degeneracy

$$L(x) \frac{\partial S}{\partial x} = 0, \quad (87)$$

which, together with the degeneracy (70) for the case of the energy, i.e.

$$M(x) \frac{\partial E}{\partial x} = 0, \quad (88)$$

gave the name to the GENERIC structure, which is an acronym for General Equation for Non-Equilibrium Reversible Irreversible Coupling [6]. Actually, (87),(88) are a particular way of expressing the First and Second Laws of Thermodynamics [36]. For example, one can compute the time derivative of the energy function, with the result

$$\dot{E}(x) = \frac{\partial E}{\partial x} \cdot \dot{x} = 0,$$

as a consequence of the antisymmetry of L and (87). On the other hand,

$$\dot{S}(x) = \frac{\partial S}{\partial x} \cdot \dot{x} = \frac{\partial S}{\partial x} M^S(x) \frac{\partial S}{\partial x} \geq 0, \quad (89)$$

where, again, the antisymmetry of L and M^A have been used, and the inequality stands because M^S is positive semidefinite. Note that the term $L \frac{\partial E}{\partial x}$ does not contribute to the production of entropy, which comes entirely from $M \frac{\partial S}{\partial x}$. It is for this reason and for their transformation properties under time reversibility that these terms receive their names (reversible and irreversible or dissipative terms, respectively).

The reversible dynamics $\dot{x} = L(x) \partial E / \partial x$ induces a Poisson bracket structure. For example, by using the chain rule, we have for an arbitrary function $F(x)$ that

$$\dot{F}(x) = \frac{\partial F}{\partial x} L(x) \frac{\partial E}{\partial x} \equiv \{F, E\}, \quad (90)$$

where the last equality defines the bracket. An important property of a Poisson bracket is the Jacobi identity $\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0$, that implies the time invariance of the Poisson bracket structure, i.e.

$$\frac{d}{dt} \{F, G\} = \{\dot{F}, G\} + \{F, \dot{G}\}. \quad (91)$$

The Jacobi identity has not yet been derived from the microscopic definition of the matrix L in (69), but it is a generally valid property that restricts the possible forms of the L matrix [37].

It should be remarked that the Second Law is a macroscopic law. If thermal fluctuations are important, the entropy function may be a decreasing function of time due to random fluctuations. Nevertheless, there is a strong result, which applies to any Fokker–Planck equation that states that the entropy functional

$$S[P(x, t)] = -k_B \int dx P(x, t) \ln \frac{P(x, t)}{P^{\text{eq}}(x)}, \quad (92)$$

is a non-decreasing function of time. This result is known as the H-theorem [34]. Note that in the limit $k_B \rightarrow 0$, the distribution function $P(x, t)$ is very peaked and the numerical value of the entropy functional coincides with that of the entropy function $S(x)$ evaluated at the most probable value of $P(x, t)$, thus recovering the Second Law in the form (89).

A final word is in order about the definition of the entropy in (65). Note that $\Omega(x)$ is a probability distribution, and under a change of variables $x \rightarrow y$ it transforms as

$$\Omega'(y) = \int dx \delta(Y(x) - y) \Omega(x) = \Omega(X(y)) \det \left| \frac{\partial X(y)}{\partial(y)} \right|,$$

where the last term is the Jacobian of the transformation. This implies that the entropy as defined in (65) does not transform as a scalar in a change of variables, but rather as

$$S'(y) = S(X(y)) + k_B \ln \det \left| \frac{\partial X(y)}{\partial(y)} \right|.$$

The last term is of order k_B , which is small in front of the overall entropy, for physically sensible changes of variables. This means that the entropy can be assumed to transform as a scalar whenever fluctuations can be neglected. An alternative is to define the entropy in terms of a privileged set of variables x^{ref} , in such a way that in an arbitrary set of variables, the entropy is defined as [33]

$$S'(y) = S(X(y)) - k_B \ln \det \left| \frac{\partial X^{\text{ref}}(y)}{\partial(y)} \right|.$$

In this way, the entropy always transforms as a scalar under change of variables. However, there is no a priori criteria for knowing what set of variables are to be taken as privileged. As mentioned, this is not a serious problem when fluctuations are small.

8 Fluid Particle Models for Simulating Complex Fluids

Computer simulation of a fluid requires the formulation of discrete models for describing its hydrodynamic behaviour. As we have discussed in Sect. 3.2 not only a discrete representation is necessary but it may even be more adequate from a conceptual point of view. Understood as the result of a coarse-graining procedure, the continuum hydrodynamic equations emerge only as an approximation, valid when the variation of the discrete quantities defined in each little cell is small from cell to cell. This approximation is very useful because it allows one to introduce the concept of spatial derivative and to obtain analytical solutions for particularly simple problems. Yet, from a computational point of view we are interested in discrete models. The question, of course, is whether it is possible to apply the coarse-graining strategy delineated in the previous sections for the derivation of discrete models for hydrodynamics. To our knowledge this has not been done yet, although attempts in that direction have been taken [38]. What has been successfully accomplished is the derivation of the continuum hydrodynamic equations starting from the microscopic dynamics of the system, see, for example, [5], or more recently [39] for a simple fluid and [40] for a fluid mixture.

We briefly sketch how one could derive the discrete hydrodynamic equations following the strategy of the previous sections. As in any coarse-graining procedure, we have to first define the relevant variables as functions of the microscopic degrees of freedom. In the case of discrete hydrodynamics of a simple fluid, these variables are the extensive variables corresponding to the densities (3)

$$\begin{aligned} M_\mu(z) &= m \sum_i \chi_\mu(\mathbf{q}_i), \\ \mathbf{P}_\mu(z) &= \sum_i \mathbf{p}_i \chi_\mu(\mathbf{q}_i), \\ E_\mu(z) &= \sum_i \left[\frac{m}{2} (\mathbf{v}_i - \mathbf{V}_\mu)^2 + \phi_i \right] \chi_\mu(\mathbf{q}_i), \end{aligned} \quad (93)$$

where $\mathbf{v}_i = \mathbf{p}_i/m$, $\mathbf{V}_\mu = \mathbf{P}_\mu/M_\mu$, and ϕ_i is half the potential energy of interaction between molecule i and the rest of molecules. Here $\chi_\mu(\mathbf{r})$ is the characteristic function of the cell μ , that takes the value 1 if \mathbf{r} belongs to this cell and zero otherwise. Therefore,

M_μ is the total mass of the molecules that are in cell μ , \mathbf{P}_μ its total momentum and E_μ its total internal energy. One recognizes the coarse-grained delta function in these equations as $\bar{\delta}(\mathbf{r}_\mu - \mathbf{r}) = \chi_\mu(\mathbf{r})/\mathcal{V}_\mu$, where \mathcal{V}_μ is the volume of the cell labeled μ . Note that the total Hamiltonian can actually be written in terms of the above variables because we have the partition of unity property for the characteristic function

$$\sum_{\mu} \chi_{\mu}(\mathbf{r}) = 1,$$

that reflects that the little cells are non-overlapping and cover the whole physical space. In this way,

$$H(z) = \sum_{\mu} \frac{\mathbf{P}_{\mu}^2(z)}{2M_{\mu}(z)} + E_{\mu}(z). \quad (94)$$

The total momentum $\mathbf{P}(z) = \sum_i \mathbf{p}_i$ can also be written in terms of the relevant variables because $\mathbf{P}(z) = \sum_{\mu} \mathbf{P}_{\mu}(z)$. Because the dynamical invariants can be written in terms of the relevant variables, we will have the GENERIC structure, with the energy function given by

$$E(x) = \sum_{\mu} \frac{\mathbf{P}_{\mu}^2}{2M_{\mu}} + E_{\mu}.$$

Next, we have to compute the equilibrium distribution function $\Omega(x)$ at this level of description. That is, we need to compute the probability density that a fluid at equilibrium has a particular realization of the mass, momentum and internal energy in each of the little cells in which the space has been divided. We have computed explicitly this distribution function in [41], which turns out to have the form

$$P^{\text{eq}}(M, P, E) = \frac{1}{\Omega_0} \delta(E(x) - E_0) \delta(\mathbf{P}(x) - \mathbf{P}_0) \exp \left\{ \frac{1}{k_B} \sum_{\mu} S(M_{\mu}, E_{\mu}, \mathcal{V}_{\mu}) \right\}. \quad (95)$$

Here E_0 is the total energy of the system and \mathbf{P}_0 is the total momentum that can be set to zero without loss of generality. The function $S(M, E, \mathcal{V})$ is the usual thermodynamic entropy of a system with mass M , energy E , and volume \mathcal{V} . Implicit in the derivation of (95) is the assumption that the cells in which the physical space is divided are sufficiently large to be in the thermodynamic limit for the entropy of the cell $S(M_{\mu}, E_{\mu}, \mathcal{V}_{\mu})$ to be a well-defined first order function. We have also neglected the interaction energy between neighbour cells in front of the energy content of each cell (this assumption must be revised when surface tension effects need to be included [41]). Equation (95) has the form of the Einstein distribution function (64), and we can identify the entropy at our level of description as

$$S(x) = \sum_{\mu} S(M_{\mu}, E_{\mu}, \mathcal{V}_{\mu}). \quad (96)$$

Note that the entropy $S(x)$ that appears in the left hand side of (96), is a conceptually different quantity from the entropy appearing in the right hand side. In particular, they are functions of a different number of variables.

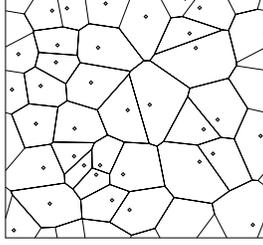


Fig. 4. The Voronoi tessellation for a randomly distributed set of points in a periodic box

The next step would be to compute the time derivative iLX of the relevant variables needed in the two other quantities appearing in the FPE $v(x), D(x)$, or, in the GENERIC framework $L(x), M(x)$. Once iLX is computed we need to perform the constrained averages in $v(x), D(x)$. These averages can be computed by following essentially the same approximations involved in the calculation of $P^{\text{eq}}(x)$ in (95).

For reasons of space we do not dwell further into this microscopic derivation of the discrete hydrodynamic equations. Instead, we follow a very different route for the formulation of the equations governing the dynamics of the discrete hydrodynamic variables [42]. First, note that we can write the relevant variables (93) in the following form

$$\begin{aligned} M_\mu(z) &= \int d\mathbf{r} \chi_\mu(\mathbf{r}) \rho_{\mathbf{r}}(z), \\ \mathbf{P}_\mu(z) &= \int d\mathbf{r} \chi_\mu(\mathbf{r}) \mathbf{g}_{\mathbf{r}}(z), \\ E_\mu(z) &= \int d\mathbf{r} \chi_\mu(\mathbf{r}) \epsilon_{\mathbf{r}}(z), \end{aligned} \quad (97)$$

where we have used (3). Therefore, the discrete, extensive variables (93) are just the space integral over each cell of the continuum densities (3). As we know that the continuum variables obey the continuum hydrodynamic equations, we can simply integrate the continuum equations over every little cell with the hope of obtaining a closed set of equations for the extensive variables (93). This is, actually, the well-known technique of finite volumes used to discretize the continuum equations [43]. In [42] and inspired by the work in [38], we have proposed a finite volume discretization of the Navier–Stokes continuum equations. The particularity of our approach lays in the fact that the partition of physical space is done with the help of a Voronoi tessellation that follows the flow field and thermodynamic consistency. The Voronoi tessellation is a way of partitioning the physical space by associating to a set of points named cell centers the region of space that is closer to each center. The result is a cellular structure like the one in Fig. 4. One of the basic requirements of our discrete model formulation is that the model must have the GENERIC structure, thus ensuring a fulfillment of the First and Second Laws of Thermodynamics in an exact way. Of course, the continuum equations do satisfy these laws, and therefore, in the continuum limit any sensible discretization of the continuum equations will also respect them, up to certain errors related to the way in which we have performed the discretization. Our approach produces a model in which these

essential laws are satisfied exactly. The physical picture is that the cells are understood as real portions of the material rather than the mathematical nodes where the continuum equations are discretized. In a way, we are pouring physics into the numerics.

The model has been tested in its basic aspects, showing that it reproduces the desired hydrodynamic and thermodynamic behaviour [42,44] in two space dimensions. However, the implementation of the Voronoi tessellation in three dimensions is rather involved and one has to rely on geometrical libraries where this implementation is done efficiently [45]. For this reason, we have devised a model that, although still based on the idea of fluid particles that represent physical portions of material, does not require the use of the Voronoi tessellation.

8.1 Soft Fluid Particles

We would like to illustrate in this section how the GENERIC structure can help in order to formulate new discrete models for the simulation of complex fluids. As a start we will construct step by step a model of fluid particles for the simulation of a simple Newtonian fluid. As a reference we have the continuum hydrodynamic equations [10]

$$\begin{aligned}\frac{d\rho}{dt} &= -\rho\nabla\cdot\mathbf{v}, \\ \rho\frac{d\mathbf{v}}{dt} &= -\nabla P + \eta\nabla^2\mathbf{v} + \frac{\eta}{3}\nabla\nabla\cdot\mathbf{v}, \\ \rho\frac{de}{dt} &= -P\nabla\cdot\mathbf{v} + 2\eta\overline{\nabla\mathbf{v}} : \overline{\nabla\mathbf{v}} + \kappa\nabla^2T.\end{aligned}\quad (98)$$

These equations are written in Lagrangian form by introducing the well-known substantial derivative $\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla$. The pressure P and temperature T are functions of the mass density ρ and the specific internal energy e (internal energy per unit mass) through the equilibrium equations of state. The transport coefficients are the shear viscosity η and the thermal conductivity κ (we assume for simplicity a zero bulk viscosity). Our aim is to present a discrete model that captures the essential physics described by the continuum equations (98).

The discrete elements of the model are the fluid particles, a concept that is actually used in order to motivate the continuum equations (98) [11]. We understand a fluid particle as a small moving thermodynamic subsystem of the whole system characterized by its position \mathbf{r}_i , velocity \mathbf{v}_i , volume \mathcal{V}_i , mass m_i , internal energy E_i , entropy S_i , temperature T_i , and pressure P_i . Not all these variables are independent. We choose as independent variables that fully characterize the state of the system the set $x = \{\mathbf{r}_i, \mathbf{v}_i, E_i\}$. In this model we will assume for simplicity that the mass of the fluid particles is constant and equal for all particles $m_i = m$. The dependent variables are the volume \mathcal{V}_i , that we will assume completely determined by the relative positions between fluid particles, and the entropy $S_i = S(\mathcal{V}_i, E_i, m)$, which is a function of the extensive variables of the fluid particles given by the equilibrium entropy. The pressure and temperature are given by the thermodynamic relationships

$$\frac{1}{T_i} = \frac{\partial S_i}{\partial E_i} \quad \text{and} \quad -\frac{P_i}{T_i} = \frac{\partial S_i}{\partial \mathcal{V}_i}.$$

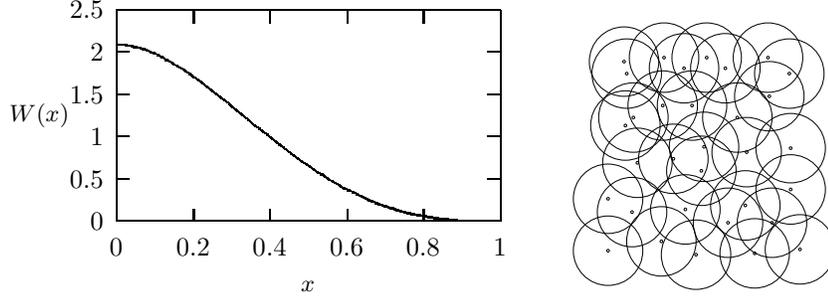


Fig. 5. The weight function $W(r/h) = \frac{105}{16\pi h^3} \left(1 + 3\frac{r}{h}\right) \left(1 - \frac{r}{h}\right)^3$, known as the Lucy function, and a pictorial view of a set of soft fluid particles, to be compared with the Voronoi tessellation in Fig. 4

At this point we must specify how we assign a volume to each fluid particle. For the case of the Voronoi tessellation, there is an obvious way of giving a volume to the fluid particle, precisely the volume of the corresponding cell. If we do not want to use the Voronoi tessellation due to its difficult implementation, we must find an alternative way. Basically, we would like to assign a small volume to those particles that have many neighbours, because then the physical volume will be shared by these neighbours. One way to achieve this is by introducing a density d_i associated to each fluid particle as

$$d_i = \sum_j W(r_{ij}), \quad (99)$$

where $W(r)$ is a weight function of finite support h and normalized to unity $\int dr W(r) = 1$ of the kind plotted in Fig. 5. The volume of particle i is defined as $\mathcal{V}_i = d_i^{-1}$. Note that when the particle i has many close neighbours, the sum in (99) is large, and, therefore, its volume will be correspondingly small.

The energy and entropy of the model are given by (94) and (96) which we write as

$$E(x) = \sum_i \left(\frac{m}{2} \mathbf{v}_i^2 + E_i \right) \quad \text{and} \quad S(x) = \sum_i S(E_i, \mathcal{V}_i).$$

Its derivatives with respect to the state variables are

$$\frac{\partial E}{\partial x} = \begin{pmatrix} \frac{\partial E}{\partial \mathbf{r}_i} \\ \frac{\partial E}{\partial \mathbf{v}_i} \\ \frac{\partial E}{\partial E_i} \end{pmatrix} = \begin{pmatrix} 0 \\ m\mathbf{v}_i \\ 1 \end{pmatrix}, \quad \frac{\partial S}{\partial x} = \begin{pmatrix} \frac{\partial S}{\partial \mathbf{r}_i} \\ \frac{\partial S}{\partial \mathbf{v}_i} \\ \frac{\partial S}{\partial E_i} \end{pmatrix} = \begin{pmatrix} \sum_j \frac{P_j}{T_j} \frac{\partial \mathcal{V}_i}{\partial \mathbf{r}_i} \\ 0 \\ \frac{1}{T_j} \end{pmatrix}. \quad (100)$$

We now construct the reversible part of the dynamics $\dot{x}|_{\text{rev}} = L(x)\nabla E(x)$ by defining the antisymmetric matrix L

$$\begin{pmatrix} \dot{\mathbf{r}}_i \\ \dot{\mathbf{v}}_i \\ \dot{E}_i \end{pmatrix} = \sum_j \begin{pmatrix} \mathbf{0} & \frac{\delta_{ij}}{m} \mathbf{1} & 0 \\ -\frac{\delta_{ij}}{m} \mathbf{1} & \mathbf{\Lambda}_{ij} & \mathbf{\Omega}_{ij} \\ 0 & -\mathbf{\Omega}_{ji} & \Delta_{ij} \end{pmatrix} \begin{pmatrix} 0 \\ m\mathbf{v}_j \\ 1 \end{pmatrix}. \quad (101)$$

The first row is postulated by our desire of having the reasonable equation $\dot{\mathbf{r}}_i = \mathbf{v}_i$. The first column is then fixed by antisymmetry. The matrix $\mathbf{\Lambda}_{ij}$ should satisfy the antisymmetry $\mathbf{\Lambda}_{ij} = -\mathbf{\Lambda}_{ji}^T$ and the scalar should satisfy $\Delta_{ij} = -\Delta_{ji}$ in order to have L antisymmetric. Next, we make use of the degeneracy condition $0 = L(x)\nabla S(x)$ as it appears in (87)

$$\begin{pmatrix} \mathbf{0} \\ \mathbf{0} \\ 0 \end{pmatrix} = \sum_j \begin{pmatrix} \mathbf{0} & \frac{\delta_{ij}}{m} \mathbf{1} & 0 \\ -\frac{\delta_{ij}}{m} \mathbf{1} & \mathbf{\Lambda}_{ij} & \mathbf{\Omega}_{ij} \\ 0 & -\mathbf{\Omega}_{ji} & \Delta_{ij} \end{pmatrix} \begin{pmatrix} \sum_k \frac{P_k}{T_k} \frac{\partial \mathcal{V}_k}{\partial \mathbf{r}_j} \\ 0 \\ \frac{1}{T_j} \end{pmatrix}. \quad (102)$$

We obtain, therefore, the conditions

$$\sum_j \left[-\frac{P_j}{mT_j} \frac{\partial \mathcal{V}_j}{\partial \mathbf{r}_i} + \mathbf{\Omega}_{ij} \frac{1}{T_j} \right] = 0 \quad \text{and} \quad \sum_j \Delta_{ij} \frac{1}{T_j} = 0. \quad (103)$$

Apparently, the simplest way of satisfying these conditions is by assuming

$$\mathbf{\Omega}_{ij} = \frac{P_j}{m} \frac{\partial \mathcal{V}_j}{\partial \mathbf{r}_i}, \quad \text{and} \quad \Delta_{ij} = 0. \quad (104)$$

Although we do not have any restriction for $\mathbf{\Lambda}_{ij}$, we will assume for simplicity that $\mathbf{\Lambda}_{ij} = 0$. In this way, the final reversible equations are

$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{v}_i, \\ m\dot{\mathbf{v}}_i &= \sum_j \frac{\partial \mathcal{V}_j}{\partial \mathbf{r}_i} P_j, \\ \dot{E}_i &= -P_i \sum_j \frac{\partial \mathcal{V}_i}{\partial \mathbf{r}_j} \mathbf{v}_j = -P_i \dot{\mathcal{V}}_i. \end{aligned} \quad (105)$$

The last equation makes a lot of sense if we think on the First Law expressed as $dE = -Pd\mathcal{V} + TdS + \mu dM$. In a reversible dynamics where $dS = 0$, the changes in internal energy are due only to changes in the volume (we assumed that the fluid particles have constant mass, so $dM = 0$). Note that this interpretation would break down if $\Delta_{ij} \neq 0$,

so the last equation in (104) was a sensible requirement. We can use now the definition of the volume in terms of the density (99) in order to compute

$$\frac{\partial \mathcal{V}_j}{\partial \mathbf{r}_i} = -\frac{1}{d_j^2} \left[\delta_{ij} \sum_k W'(r_{ik}) \mathbf{e}_{ik} + W'(r_{ij}) \mathbf{e}_{ij} \right]. \quad (106)$$

Substitution of (106) into (105) leads to

$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{v}_i, \\ m \dot{\mathbf{v}}_i &= - \sum_j W'(r_{ij}) \left[\frac{P_i}{d_i^2} + \frac{P_j}{d_j^2} \right] \mathbf{e}_{ij}, \\ \dot{E}_i &= \frac{P_i}{d_i^2} \sum_j W'(r_{ij}) \mathbf{e}_{ij} \cdot \mathbf{v}_{ij}. \end{aligned} \quad (107)$$

At this point, we would like to compare these equations with the reversible part of the continuum equations (98) (obtained by setting η, κ to zero). First, let us introduce the discrete counterpart of the mass density, $\rho_i = m d_i$, and of the internal energy per unit mass $e_i = E_i/m$. If we take the time derivative of ρ_i with the help of $\dot{\mathbf{r}}_i = \mathbf{v}_i$ we obtain

$$\dot{\rho}_i = m \sum_j W'(r_{ij}) \mathbf{e}_{ij} \cdot \mathbf{v}_{ij}, \quad (108)$$

which, after comparison with the continuity equation in (98), suggest that a discrete version of the divergence of the velocity field is given by

$$(\nabla \cdot \mathbf{v})_i = -\frac{1}{d_i} \sum_j W'(r_{ij}) \mathbf{e}_{ij} \cdot \mathbf{v}_{ij}.$$

We can now compute $\rho_i \dot{e}_i = d_i \dot{E}_i$ which, after use of \dot{E}_i in (107), is given by

$$\rho_i \dot{e}_i = \frac{P_i}{d_i} \sum_j W'(r_{ij}) \mathbf{e}_{ij} \cdot \mathbf{v}_{ij} = -P_i (\nabla \cdot \mathbf{v})_i.$$

This shows that we have made a good choice by selecting $\Lambda_{ij} = 0$ and $\Delta_{ij} = 0$, because the resulting equations (107) are, term by term, very close in form to the continuum equations. We can actually understand (107) as a particularly nice discretization of the reversible part of the continuum equations (98) that conserve exactly mass, momentum, energy, and entropy.

We have now to consider the irreversible part of the dynamics. The route that we will follow consists on formulating first the stochastic noise terms $d\tilde{x} = (d\tilde{\mathbf{r}}_i, d\tilde{\mathbf{v}}_i, d\tilde{E}_i)$. As we have already noticed, we have some restrictions on the possible form of these noise, in particular (84). The basic benefit of formulating the noises is that we can construct in a straightforward manner the matrix $M(x)$ through the Fluctuation-Dissipation theorem (81), which, by construction, ensures that $M(x)$ will be symmetric and positive semi-definite. The first requirement about the noise terms is that $d\tilde{\mathbf{r}}_i = 0$. The basic reason

is that we want to retain the equation $\dot{\mathbf{r}}_i = \mathbf{v}_i$. If $d\tilde{\mathbf{r}}_i \neq 0$ we would obtain additional terms in this equation. The next requirement is (84) which, after using (100), takes the form

$$\sum_i m\mathbf{v}_i \cdot d\tilde{\mathbf{v}}_i + d\tilde{E}_i = 0. \quad (109)$$

Physically, this equation states that the momentum and energy noises are not independent, because the power dissipated by the momentum forces must be canceled by (a term in) the energy noise in order to conserve total energy. We have to specify now the explicit forms of $m d\tilde{\mathbf{v}}_i$, $d\tilde{E}_i$, that is, how they are expressed in terms of independent increments of the Wiener process. As a rule of thumb to follow when formulating stochastic noises, we may say that every noise term reflects an elementary transport process. For example, we expect that the stochastic change of the momentum of a fluid particle is due to a random interchange of momentum between neighbouring particles, i.e. $m d\tilde{\mathbf{v}}_i = \sum_j d\mathbf{P}_{ij}$. The elementary momentum interchange $d\mathbf{P}_{ij}$ is a stochastic vector. We can construct many different stochastic vectors in terms of the Wiener process. For reasons that will become clear later, we assume

$$m d\tilde{\mathbf{v}}_i = \sum_j A_{ij} d\mathbf{W}_{ij} \cdot \mathbf{e}_{ij}, \quad (110)$$

where $d\mathbf{W}_{ij} = d\mathbf{W}_{ji}$ is a matrix of Wiener processes and \mathbf{e}_{ij} is the unit vector pointing from particle j to particle i . We postulate $A_{ij} = A_{ji}$ in such a way that $\sum_i m d\tilde{\mathbf{v}}_i = 0$ and, therefore, momentum will be exactly conserved not only by the stochastic terms but also for the full dissipative terms. Concerning the elementary process involved in the energy transport, we assume it is of the form $C_{ij} dV_{ij}$ where the Wiener process $dV_{ij} = -dV_{ji}$ and $C_{ij} = C_{ji}$. In this way, in every stochastic elementary process, a small amount of energy $C_{ij} dV_{ij}$ is transferred from particle j to i (and particle j loses this energy, as it appears from the symmetry properties assumed for C_{ij} and dV_{ij}). Therefore, we will assume that the stochastic energy term has the form

$$d\tilde{E}_i = \sum_j C_{ij} dV_{ij} - \frac{1}{2} \sum_j A_{ij} d\mathbf{W}_{ij} : \mathbf{e}_{ij} \mathbf{v}_{ij}. \quad (111)$$

The last term is included in such a way that (109) is exactly satisfied and represents the stochastic energy transfer that occurs as a consequence of the stochastic transfer of momentum among the fluid particles. Of course, we still have to specify the stochastic properties of the Wiener processes $d\mathbf{W}_{ij}$, dV_{ij} according to its symmetry properties. They are

$$\begin{aligned} d\mathbf{W}_{ii'}^{\alpha\alpha'} d\mathbf{W}_{jj'}^{\beta\beta'} &= [\delta_{ij} \delta_{i'j'} + \delta_{ij'} \delta_{i'j}] \delta^{\alpha\beta} \delta^{\alpha'\beta'} dt, \\ dV_{ii'} dV_{jj'} &= [\delta_{ij} \delta_{i'j'} - \delta_{ij'} \delta_{i'j}] dt, \\ d\mathbf{W}_{ii'}^{\alpha\alpha'} dV_{ii'} &= 0. \end{aligned} \quad (112)$$

Superscripts denote tensorial components. These properties imply the following properties of the stochastic terms (110) and (111)

$$\begin{aligned}
 m^2 \frac{d\tilde{\mathbf{v}}_i^\alpha d\tilde{\mathbf{v}}_j^\beta}{dt} &= \delta_{ij} \left[\sum_k \frac{A_{ik}^2}{2} \left(\delta^{\alpha\beta} + \mathbf{e}_{ik}^\alpha \mathbf{e}_{ik}^\beta \right) \right] - \frac{A_{ij}^2}{2} \left(\delta^{\alpha\beta} + \mathbf{e}_{ij}^\alpha \mathbf{e}_{ij}^\beta \right), \\
 -m \frac{d\tilde{\mathbf{v}}_i^\alpha d\tilde{E}_j}{dt} &= \delta_{ij} \left[\sum_k \frac{A_{ik}^2}{2} \left(\frac{\mathbf{v}_{ik}^\alpha}{2} + \mathbf{e}_{ik} \cdot \frac{\mathbf{v}_{ik}}{2} \mathbf{e}_{ik}^\alpha \right) \right] + \frac{A_{ij}^2}{2} \left(\frac{\mathbf{v}_{ij}^\alpha}{2} + \mathbf{e}_{ij} \cdot \frac{\mathbf{v}_{ij}}{2} \mathbf{e}_{ij}^\alpha \right), \\
 -m \frac{d\tilde{E}_i d\tilde{\mathbf{v}}_j^\alpha}{dt} &= \delta_{ij} \left[\sum_k \frac{A_{ik}^2}{2} \left(\frac{\mathbf{v}_{ik}^\alpha}{2} + \mathbf{e}_{ik} \cdot \frac{\mathbf{v}_{ik}}{2} \mathbf{e}_{ik}^\alpha \right) \right] - \frac{A_{ij}^2}{2} \left(\frac{\mathbf{v}_{ij}^\alpha}{2} + \mathbf{e}_{ij} \cdot \frac{\mathbf{v}_{ij}}{2} \mathbf{e}_{ij}^\alpha \right), \\
 \frac{d\tilde{E}_i d\tilde{E}_j}{dt} &= \delta_{ij} \left[\sum_k \frac{A_{ik}^2}{2} \left(\left(\frac{\mathbf{v}_{ik}}{2} \right)^2 + \left(\mathbf{e}_{ik} \cdot \frac{\mathbf{v}_{ik}}{2} \right)^2 \right) \right] \\
 &\quad + \frac{A_{ij}^2}{2} \left(\left(\frac{\mathbf{v}_{ij}}{2} \right)^2 + \left(\mathbf{e}_{ij} \cdot \frac{\mathbf{v}_{ij}}{2} \right)^2 \right) + \delta_{ij} \sum_k C_{ik}^2 - C_{ij}^2. \tag{113}
 \end{aligned}$$

Equations (101) and (113) provide all the elements to formulate the deterministic equations $\dot{x} = L(x)\nabla E(x) + M(x)\nabla S(x)$, i.e.,

$$\begin{aligned}
 \begin{pmatrix} \dot{\mathbf{r}}_i \\ \dot{\mathbf{v}}_i \\ \dot{E}_i \end{pmatrix} &= \sum_j \begin{pmatrix} \mathbf{0} & \frac{\delta_{ij}}{m} \mathbf{1} & 0 \\ -\frac{\delta_{ij}}{m} \mathbf{1} & \mathbf{0} & -\frac{P_j}{m} \frac{\partial \mathcal{V}_j}{\partial \mathbf{r}_i} \\ 0 & \frac{P_j}{m} \frac{\partial \mathcal{V}_j}{\partial \mathbf{r}_j} & 0 \end{pmatrix} \begin{pmatrix} 0 \\ m\mathbf{v}_j \\ 1 \end{pmatrix} \\
 &\quad + \sum_j \begin{pmatrix} 0 & \mathbf{0} & 0 \\ \mathbf{0} & \frac{d\tilde{\mathbf{v}}_i d\tilde{\mathbf{v}}_j^T}{2k_B dt} & \frac{d\tilde{\mathbf{v}}_i d\tilde{E}_j}{2k_B dt} \\ 0 & \frac{d\tilde{E}_i d\tilde{\mathbf{v}}_j^T}{2k_B dt} & \frac{d\tilde{E}_i d\tilde{E}_j}{2k_B dt} \end{pmatrix} \begin{pmatrix} -\sum_k \frac{P_k}{T_k} \frac{\partial \mathcal{V}_k}{\partial \mathbf{r}_j} \\ 0 \\ \frac{1}{T_j} \end{pmatrix}, \tag{114}
 \end{aligned}$$

which, by using (113) lead to the following set of equations

$$\begin{aligned}
 \dot{\mathbf{r}}_i &= \mathbf{v}_i, \\
 m\dot{\mathbf{v}}_i &= -\sum_j W'(r_{ij}) \left[\frac{P_i}{d_i^2} + \frac{P_j}{d_j^2} \right] \mathbf{e}_{ij} - \sum_j a_{ij} (\mathbf{v}_{ij} + \mathbf{e}_{ij} \cdot \mathbf{v}_{ij} \mathbf{e}_{ij}), \\
 \dot{E}_i &= P_i \sum_j W'(r_{ij}) \mathbf{e}_{ij} \cdot \mathbf{v}_{ij} + \frac{1}{2} \sum_j a_{ij} (\mathbf{v}_{ij}^2 + (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2) - \sum_j c_{ij} (T_i - T_j), \tag{115}
 \end{aligned}$$

where we have introduced

$$a_{ij} = \frac{A_{ij}^2}{8k_B} \left(\frac{1}{T_i} + \frac{1}{T_j} \right) \quad \text{and} \quad c_{ij} = \frac{C_{ij}^2}{2k_B T_i T_j}.$$

Equations (115) are our final set of dynamical equation for the model of soft fluid particles. Everything is known in these equations except the factors a_{ij} and c_{ij} and we have to propose reasonable expressions for these objects. In principle, these factors govern the overall amplitude of the dissipation and, therefore, they govern the dissipative transport of momentum and energy. By comparing the structure of (115) with the continuum equations (98) we observe a nice correspondence between each term in both sets of equations. We expect that a_{ij} will be related to the viscosity and c_{ij} to the thermal conductivity, and these terms will correspond to a sort of discrete version of second spatial derivatives. In order to make the connection even more explicit, consider the following integral version of the matrix of second derivatives of an arbitrary function $A(\mathbf{r})$,

$$\nabla\nabla A(\mathbf{r}_i) = \int d\mathbf{r}' [A(\mathbf{r}') - A(\mathbf{r}_i)] \frac{W'(|\mathbf{r}' - \mathbf{r}_i|)}{|\mathbf{r}' - \mathbf{r}_i|} \left[\mathbf{1} - 5 \frac{(\mathbf{r}' - \mathbf{r}_i)(\mathbf{r}' - \mathbf{r}_i)}{(\mathbf{r}' - \mathbf{r}_i)^2} \right] + \mathcal{O}(\nabla^4 A h^2). \quad (116)$$

This equation is demonstrated by Taylor expanding $A(\mathbf{r}')$ around \mathbf{r}_i and making use of the isotropy and normalization to unity of the weight function $W(r)$. The integral $\int d\mathbf{r}$ can be further approximated with a discrete sum $\sum_i d_i^{-1}$ over the fluid particles in such a way that

$$\nabla\nabla A(\mathbf{r}_i) = \sum_j \frac{1}{d_j} [A_j - A_i] \frac{W'_{ij}}{r_{ij}} [\mathbf{1} - 5\mathbf{e}_{ij}\mathbf{e}_{ij}] + \mathcal{O}(\nabla^4 A h^2). \quad (117)$$

In this way, we can approximate the second spatial derivatives of a function in terms of the value of the function in the neighbourhood. If we look at the second derivative terms that appear in (98) we can obtain the following discrete versions for them,

$$\begin{aligned} \eta \left[(\nabla^2 \mathbf{v})_i + \frac{1}{3} (\nabla \nabla \cdot \mathbf{v})_i \right] &\approx \frac{5\eta}{3} d_i \sum_j \omega_{ij} [\mathbf{v}_{ij} + \mathbf{e}_{ij}\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}], \\ \kappa (\nabla^2 T)_i &\approx 2\kappa d_i \sum_j \omega_{ij} T_{ij}, \end{aligned} \quad (118)$$

where ω_{ij} is a geometrical object that depends only on the positions of the particles,

$$\omega_{ij} = \omega_{ji} = -\frac{W'_{ij}}{r_{ij} d_i d_j} \geq 0.$$

By comparing (118) with the dissipative terms in (115) we may postulate

$$a_{ij} = \frac{5\eta}{3} \omega_{ij} \quad \text{and} \quad c_{ij} = 2\kappa \omega_{ij}. \quad (119)$$

In this way, we can understand the discrete model (115) with (119) as a discretization of the continuum equations (98). According to the approximation (117) the simulation of (115) will produce results that are compatible with a given viscosity η and thermal conductivity κ .

Equations (115) conserve mass, momentum, energy and have a positive production of entropy. Arbitrary equations of state can be introduced through the specific functional

form of the entropy function and we have, therefore, full thermodynamic consistency. The physical meaning of every term in these equations is also very transparent: The particles move following the flow field and they exert forces to its neighbouring particles of two kinds. First, a reversible force due to the average pressure of the interacting particles, which is directed to the line joining the particles. Second, a dissipative force that tries to reduce the velocity differences between neighbouring particles, and with an overall amplitude given by the viscosity of the fluid. Because these forces try to stop the particles, the kinetic energy which is dissipated must be transformed into internal energy, a fact that is described by the term quadratic in the velocity in the energy equation. In the energy equation there is a term due to the reversible work done by the pressure forces, and another dissipative term that tries to reduce the temperature differences between neighbouring particles, describing the phenomenon of heat conductivity.

Of course, (115) are deterministic equations. In order to construct the stochastic differential equations, we have to compute the term $k_B \nabla M$ appearing in (78) and add the stochastic forces $d\tilde{x}$. The resulting final SDE are

$$\begin{aligned}
 d\mathbf{r}_i &= \mathbf{v}_i dt, \\
 m d\mathbf{v}_i &= -\sum_j W'(r_{ij}) \left[\frac{P_i}{d_i^2} + \frac{P_j}{d_j^2} \right] \mathbf{e}_{ij} dt - \frac{5\eta}{3} \sum_j (1-d_{ij}) \omega_{ij} (\mathbf{v}_{ij} + \mathbf{e}_{ij} \cdot \mathbf{v}_{ij} \mathbf{e}_{ij}) dt + m d\tilde{\mathbf{v}}_i, \\
 dE_i &= P_i \sum_j W'(r_{ij}) \mathbf{e}_{ij} \cdot \mathbf{v}_{ij} dt \\
 &\quad + \frac{5\eta}{6} \sum_j \left[1-d_{ij} - \frac{T_j}{T_i+T_j} \frac{k_B}{C_i} \right] \omega_{ij} (\mathbf{v}_{ij}^2 + (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2) - 2\kappa \sum_j \omega_{ij} (T_i - T_j) \\
 &\quad - \frac{20k_B}{3m} \sum_j \frac{T_i T_j}{T_i + T_j} \omega_{ij} dt - 2\kappa \frac{k_B}{C_i} \sum_j \omega_{ij} T_j dt + d\tilde{E}_i, \tag{120}
 \end{aligned}$$

where we have introduced the dimensionless quantity

$$d_{ij} = \frac{T_i T_j}{(T_i + T_j)^2} \left[\frac{k_B}{C_i} + \frac{k_B}{C_j} \right], \tag{121}$$

where C_i is the heat capacity at constant volume of particle i . which is an extensive quantity. Therefore, for large fluid particles the dimensionless ratio k_B/C_i is very small. Note that in the limit $k_B \rightarrow 0$, one recovers the deterministic equations (115). We have here an explicit example of what has been discussed in Sect. 7.3 about the size of thermal fluctuations. In this case, the importance of thermal fluctuations is dictated by the physical size of the fluid particles.

Equations (115) with (119) are just a version of Smoothed Particle Hydrodynamics (SPH). SPH is a well-known technique used to discretize continuum equations with the aid of suitable weight functions [46]. In that respect, (120) represent a generalization of SPH that include thermal fluctuations in a thermodynamically consistent way. This generalization will be necessary when the fluid particles are very small. As the size of the fluid particles is dictated essentially by the need of resolving with sufficient accuracy the length scales of the problem, the fluctuating SPH equations (120) will be required

in microhydrodynamic problems as those appearing in microfluidic devices or in the simulation of the solvent in colloidal suspensions.

There are many different implementations of the SPH idea and every group seems to have its favourite [46]. The particular discretization (116) is new. Other formulations of the stochastic forces are possible and they lead to different structural forms for the irreversible part of the dynamics which, still, can be considered as discretizations of second derivative terms [42]. In particular, it is possible to introduce a stochastic stress tensor and heat flux associated to each fluid particle, and formulate discrete divergences of these quantities for the corresponding stochastic terms in the momentum and energy equations [48]. This procedure is closely related to the Landau and Lifshitz method of introducing thermal fluctuation in continuum hydrodynamics. The basic reason for the formulation of the discrete model for hydrodynamics in the form (120) is to obtain a set of discrete equations that involve dissipative forces that depend on the velocity differences between neighbouring fluid particles. This was also the motivation to write the stochastic force in terms of a matrix of Wiener processes in the form (110). In this way, one can derive a model that is closely related to the Dissipative Particle Dynamics (DPD) model.

The DPD model was introduced as a promising mesoscopic technique that would allow to simulate complex fluids efficiently [47]. For a couple of recent reviews of the method see [49,50]. The model is characterized by a set of point particles with positions \mathbf{r}_i and velocities \mathbf{v}_i variables (generalizations of the model with an internal energy variable were presented later in [51,52]). The postulated DPD equations have the form

$$\begin{aligned} d\mathbf{r}_i &= \mathbf{v}_i dt, \\ m d\mathbf{v}_i &= - \sum_j W_{ij} \mathbf{e}_{ij} dt - \gamma \sum_j W_{ij} \mathbf{e}_{ij} \cdot \mathbf{v}_{ij} \mathbf{e}_{ij} dt + m d\tilde{\mathbf{v}}_i, \end{aligned} \quad (122)$$

where $W_{ij} = W(r_{ij})$ is a bell-shaped function, γ is a friction coefficient, and $d\tilde{\mathbf{v}}_i$ is a random term with a form similar to (110) where the matrix $d\mathbf{W}_{ij}$ is replaced by a single scalar dW_{ij} . The similitude of the DPD model and the SPH model is apparent.

We definitely prefer the SPH model over the DPD model as originally formulated. First of all, there are no restrictions in the DPD model about the form of the function $W(r)$ that determines the range of interaction between particles. The fluid particles have no physical size and the scale of the DPD particles is undetermined. There is no direct connection between the friction coefficient γ and the viscosity of the solvent and one has to resort to kinetic theory for such a connection [53]. The model is purely isothermal, as a consequence of the missing internal energy of the fluid particles, and energy is not conserved. The thermodynamic behaviour of the system is dictated by the form of $W(r)$, and cannot be varied (it produces a pressure that scales quadratically with the density [54]). Although attempts have been taken to introduce arbitrary equations of state [55], they are still isothermal. None of these problems appear in the stochastic SPH equations (78). The particles have definite sizes that fix the relevance of thermal fluctuations and the actual scale being simulated. The transport properties of the fluid

being simulated are input of the model, arbitrary equations of state can be introduced, and non-isothermal situations can be studied.

8.2 Complex Fluids

In the previous sections we have discussed two discrete fluid particle models for the simulation of the Navier–Stokes equations. These models can be understood as suitable discretizations of the continuum equations, with the bonus of having thermodynamic consistency even at the discrete level. Of course, one is interested in the simulation of complex fluids, which may even not have a known constitutive equation. There are two possible strategies for the simulation of complex fluids. The first one has been used by the DPD community in order to study complex fluid systems like colloids, polymers, mixtures, amphiphilic systems, membranes, etc. The basic strategy has been to complexify the simple fluid particle model by introducing further conservative interactions between dissipative particles. By connecting fluid particles with springs one has a model for macromolecules, by moving the particles within a sphere like a rigid solid one can model solid spherical colloidal particles, by having two types of particles which repel in different ways one gets a binary mixture that can phase separate, etc. [49,50].

The second one is the introduction of additional internal variables characterizing the microstructural state of the fluid particles. These variables are coupled to the conventional hydrodynamic variables. The coupling renders the behaviour of the fluid non-Newtonian and complex. For example, polymer melts are characterized by additional conformation tensors, colloidal suspensions can be described by further concentration fields, mixtures are characterized by several density fields (one for each chemical specie), emulsions are described with the amount and orientation of interface, etc. All these continuum models rely on the hypothesis of local equilibrium and, therefore, the fluid particles are regarded as thermodynamic subsystems. The physical picture emerging from these fluid particles is that they represent large portions of the fluid and therefore, the scale of these fluid particles is supramolecular. This allows one to study time scales larger than those described with a DPD model with additional conservative interactions. The price, of course, is the need for a deep understanding of the physics at this more coarse-grained level, which appears in the form of entropy and energy functionals depending on internal variables, and kinematic and dissipative matrices $L(x)$, $M(x)$ describing the complex coupling of the internal microstructure and flow.

In order to model polymer solutions, for example, we have developed a thermodynamically consistent model of fluid particles inspired by a previous model introduced by Ten Bosch [56]. In this fluid particle model the dissipative particles include as additional variables the number N of polymer molecules within the fluid particle and an elongation vector \mathbf{Q} representing the average elongation of polymer molecules within the fluid particle. A graphical view of the fluid particle for polymer solutions is given in Fig. 6

The formulation of the equations of motion for the hydrodynamic and elastic variables in this model is very much simplified by the GENERIC structure of the dynamic equations and requires very simple assumptions about the underlying motion of the polymer molecules [57]. The model allows for the interchange of polymer molecules among fluid particles, leading to advection-diffusion behaviour. Also, the elastic state

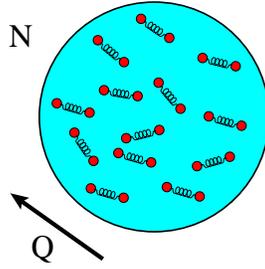


Fig. 6. A fluid particle containing N polymer molecules (dumbbells) with a typical orientation \mathbf{Q} . These two further variables, N and \mathbf{Q} characterize, along with $\mathbf{r}_i, \mathbf{v}_i, \mathcal{V}_i, S_i$, the state of the fluid particle, and their dynamics is specified from simple physical grounds: fluid particles exchange dumbbells due to chemical potential differences and the vector \mathbf{Q} changes due to the underlying Brownian motion of the dumbbells and the extensional state of the fluid particle

of the fluid particle produces forces on the fluid particles leading to a viscoelastic behaviour for the model.

Another example where the strategy of internal variables is successful is in the simulation of chemically reacting mixtures. Chemically reacting mixtures are not easily implemented with the usual approach taken by DPD in order to model mixtures. In DPD, mixtures are represented by red and blue particles. It is not trivial to specify a chemical reaction in which, for example, two red particles react with a blue particle to form a green particle. In this case, it is better to start from the well established continuum equations for chemical reactions [11,58]. The resulting discrete model consists on fluid particles that have as additional variable the fraction of component red and blue inside the fluid particle. There are diffusion terms that change this fraction depending on the difference between chemical potentials of neighbouring particles, and there are simple reaction terms, that can be expressed in measurable reaction rates [59].

9 Summary

In this chapter we have reviewed the theory of coarse graining, a well-established subject since the early 50's of last century under the name of non-equilibrium statistical mechanics. Under the basic assumption that the coarse-grained variables are slow, it is possible to obtain a Fokker–Planck equation that governs the full dynamics at the coarse-grained level. All the objects appearing in the FPE have a well-defined molecular interpretation and, in principle, it is straightforward to compute these objects from molecular dynamics simulations. In practice, however, this task is extremely difficult due to the high dimensionality of the coarse state space. One is condemned to model. However, the microscopic derivation provides a large number of restrictions on the possible forms of the objects in the FPE. This is particularly true for the case of GENERIC, a thermodynamically consistent structure that emerges as a particular case when the dynamical invariants can be expressed as functions of the coarse variables.

One of the focuses of this chapter is the formulation of fluid particle models for complex fluids. Rather than sticking to coarse-graining from the microscopic dynamics,

it proves sufficient to construct models according to the GENERIC framework. In this way, we have shown how a fully thermodynamically consistent model of fluid particles can be devised in the spirit of the DPD model, but without any of its conceptual flaws. The resulting model belongs to the family of Smoothed Particle Hydrodynamics models with thermal fluctuations included consistently. Finally, we emphasize the usefulness of the GENERIC framework when devising new discrete models for complex fluids, which can be constructed by including additional structural variables describing the inner microstructure of the fluid and its coupling to hydrodynamic flow.

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