

# INCORPORATING SHEAR INTO STOCHASTIC EULERIAN LAGRANGIAN METHODS FOR RHEOLOGICAL STUDIES OF COMPLEX FLUIDS AND SOFT MATERIALS

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**Abstract.** We develop computational methods that incorporate shear into fluctuating hydrodynamics methods. We are motivated by the rheological responses of complex fluids and soft materials. Our approach is based on continuum stochastic hydrodynamic equations that are subject to shear boundary conditions on the unit periodic cell in a manner similar to the Lees-Edwards conditions of molecular dynamics. Our methods take into account consistently the microstructure elastic mechanics, fluid-structure hydrodynamic coupling, and thermal fluctuations. For practical simulations, we develop numerical methods for efficient stochastic field generation that handle the sheared generalized periodic boundary conditions. We show that our numerical methods are consistent with fluctuation dissipation balance and near-equilibrium statistical mechanics. As a demonstration in practice, we present several prototype rheological response studies. These include (i) shear thinning of a polymeric fluid, (ii) complex moduli for the oscillatory responses of a polymerized lipid vesicle, and (iii) aging under shear of a gel-like material.

**Key words.** Statistical Mechanics, Complex Fluids, Soft Materials, Stochastic Eulerian Lagrangian Methods, SELM, Stochastic Immersed Boundary Methods, SIB, Fluctuating Hydrodynamics, Fluid-Structure Coupling, Polymeric Fluid, FENE, Vesicles, Gels.

Related Software: <https://github.com/atzberg/mango-selm>.

Additional Information: <http://atzberger.org/>.

**1. Introduction.** In the study of complex fluids and soft materials an important aim is to understand how macroscopic properties emerge from microstructure order and kinetics. Examples include liquid crystals, colloidal suspensions, gels, lipids, and emulsions [40, 31, 47, 28, 20, 17, 48]. The microstructures of these materials often have interactions on energy scales comparable to thermal energy resulting in phases dependent on the balance between enthalpic and entropic effects [36, 20, 12]. For biological materials, such as the cell membrane or cytoskeleton, microstructures may in addition exert their own active forces [2]. The individual and collective dynamics of the microstructures often span a wide range of length scales and time scales [28, 36]. To obtain insights, simplified models are often developed which are tailored to specific mechanistic questions about material responses. To perform simulations of dynamic responses requires tractable numerical methods that can account for microstructure mechanics, hydrodynamics, and the roles played by thermal fluctuations [18, 38, 43].

We present an approach based on the Stochastic Eulerian Lagrangian Method (SELM) [5]. In SELM the microstructure mechanics and solvent dynamics is formulated at the level of continuum mechanics. The fluid-structure interactions are treated on an approximate level avoiding the need for computations of the surface traction stresses or coupling tensors. The SELM approach is closely related to the Stochastic Immersed Boundary Method [7, 46], Force Coupling Method [41], Stokesian-Brownian Dynamics [13, 9], Arbitrary Eulerian-Lagrangian Method [14], Fluctuating Hydrodynamics Methods of [19, 55, 8, 21], and others [16, 56, 26, 30, 45, 22]. The SELM formulation can be used to study results in different limiting physical regimes either incorporating or neglecting various types of coupling and inertial effects [5, 53]. In this work, we extend SELM for rheological studies in the following ways: (i) we formulate generalized periodic boundary conditions for the fluctuating hydrodynamic equations that account for shear deformations, (ii) we develop numerical dis-

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cretizations for the fluid equations based on a moving reference frame to handle the shear deformation and boundary conditions, and (iii) we develop efficient computational methods for stochastic field generation methods to account for thermal fluctuations. We also perform analysis of the time-dependent numerical discretizations to study the statistical mechanics of the numerical methods.

The SELM framework is presented in Section 2. To extend SELM to incorporate shear, we introduce generalized periodic boundary conditions in Section 3. We develop stochastic numerical methods for the fluctuating hydrodynamic equations in Section 4. To demonstrate how the methods work in practice, we present results for a few example applications in Section 6. We present results for the shear thinning of a polymeric fluid in Section 6.1. We investigate the complex moduli for the oscillatory responses of a polymerized lipid vesicle in Section 6.2. We study the aging of the shear viscosity of a gel-like material in Section 6.3. Overall, we expect the presented approaches to be useful in adopting fluctuating hydrodynamics descriptions to investigate diverse models and phenomena arising in studies of complex fluids and soft materials.

**2. Stochastic Eulerian Lagrangian Method.** We describe the microstructure and solvent dynamics using the Stochastic Eulerian Lagrangian Method (SELM) [5]. This has the fluid-structure equations

$$(2.1) \quad \rho \frac{d\mathbf{u}}{dt} = \mu \Delta \mathbf{u} - \nabla p + \Lambda[-\nabla_{\mathbf{X}} \Phi(\mathbf{X})] + (\nabla_{\mathbf{X}} \cdot \Lambda) k_B T + \mathbf{g}_{\text{thm}}$$

$$(2.2) \quad \nabla \cdot \mathbf{u} = 0$$

$$(2.3) \quad \frac{d\mathbf{X}}{dt} = \Gamma \mathbf{u}$$

$$(2.4) \quad \langle \mathbf{g}_{\text{thm}}(s) \mathbf{g}_{\text{thm}}^T(t) \rangle = -(2k_B T) \mu \Delta \delta(t - s).$$

The  $\mathbf{u}$  denotes the fluid velocity and  $\mathbf{X}$  the microstructure configurations. The potential energy of the microstructures is given by  $\Phi[\mathbf{X}]$ . It is assumed throughout that to a good approximation the solvent fluid can be treated as incompressible with Newtonian stresses [1, 11]. The  $\mathbf{u}$  denotes the fluid velocity,  $\rho$  denotes the uniform fluid density,  $\mu$  the dynamic fluid viscosity, and  $p$  the fluid pressure. To account for thermal fluctuations, we introduce a stochastic driving field  $\mathbf{g}_{\text{thm}}$  which is assumed to be a Gaussian process with mean zero and  $\delta$ -correlation in time. The notation  $\mathbf{a}(s) \mathbf{b}^T(t)$  should be interpreted as the tensor product of  $\mathbf{a}$  and  $\mathbf{b}$ . The transpose notation is used to be consistent with the discrete setting and the outer-product between column vectors.

The fluid and microstructure degrees of freedom are coupled through the linear operators  $\Gamma$ ,  $\Lambda$ , see Figure 2.1. The operators themselves are assumed to have dependence only on the configuration degrees of freedom and time  $\Gamma = \Gamma[\mathbf{X}, t]$ ,  $\Lambda = \Lambda[\mathbf{X}, t]$ . To ensure the coupling is non-dissipative and conserves energy, the following adjoint condition is imposed [5, 46]

$$(2.5) \quad \int_{\mathcal{S}} (\Gamma \mathbf{u})(\mathbf{s}) \cdot \mathbf{v}(\mathbf{s}) d\mathbf{s} = \int_{\Omega} \mathbf{u}(\mathbf{x}) \cdot (\Lambda \mathbf{v})(\mathbf{x}) d\mathbf{x}.$$

This is required to hold for any  $\mathbf{u}$  and  $\mathbf{v}$ . The adjoint condition ensures the fluid-structure coupling is not a source of energy dissipation and provides a model having properties similar to imposing a no-slip boundary condition on the microstructures. This condition is also important to the fluctuation-dissipation balance in the system and simplifies the formulation by ensuring there is no need for additional stochastic driving fields to compensate for losses in the fluid-structure coupling. The  $\mathcal{S}$  and  $\Omega$  denote the spaces used to parameterize respectively the microstructure configurations and the fluid. We denote adjoints in the sense of equation 2.5 by  $\Lambda = \Gamma^\dagger$  and  $\Gamma = \Lambda^\dagger$ . A specific form for the coupling operators will be given in Section 4.3.

We remark that SELM can also accommodate active forces exerted on the microstructures which would appear in the fluid equations in the same place as  $-\nabla \Phi$  term. An important constraint given the periodic unit cell used in simulations is that the total momentum must

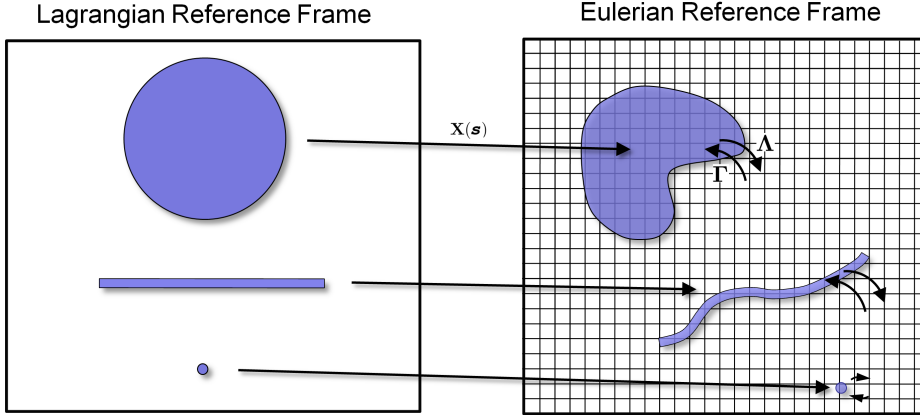


FIG. 2.1. The description of the fluid-structure system utilizes both Eulerian and Lagrangian reference frames. The structure mechanics are often most naturally described using a Lagrangian reference frame. The fluid mechanics are often most naturally described using an Eulerian reference frame. The mapping  $\mathbf{X}(\mathbf{s})$  relates the Lagrangian reference frame to the Eulerian reference frame. The operator  $\Gamma$  prescribes how structures are to be coupled to the fluid. The operator  $\Lambda$  prescribes how the fluid is to be coupled to the structures. A variety of fluid-structure interactions can be represented in this way. This includes rigid and deformable bodies, membrane structures, polymeric structures, or point particles.

be conserved. This is assumed when solving the fluid equations to determine the degenerate constant mode of the fluid (usually one assumes the total momentum is zero). If this is not the case, then artefacts in which there is a global back-flow of the fluid can arise in simulations to compensate for the unbalanced forces acting on the system. Provided the active forces are introduced in a balanced manner the fluid-structure formulation and numerical methods we present can be used.

It should be mentioned that when interpreting the fluctuating hydrodynamic equations the thermal fluctuations cause significant irregularity in the fluid velocity field  $\mathbf{u}$ . In fact, the  $\mathbf{u}$  is not defined in a point-wise sense as a classical function but only in the sense of a generalized function (distribution) [39]. As a consequence, some care must be taken in the treatment of the material derivative  $d\mathbf{u}/dt = \partial\mathbf{u}/\partial t + \mathbf{u} \cdot \nabla\mathbf{u}$ , see [5, 21]. The convective term involves a product of distributions and is not mathematically well-defined. The convective term arises from deriving a local statement of the conservation of momentum as a differential equation in the Eulerian frame of reference. The issue has to do with the tacit assumption in continuum mechanics that deformations of the material body are smooth which does not hold in this stochastic setting. A number of ways to handle this issue can be considered. One is to introduce a regularisation length-scale to smooth the velocity field motivated on physical grounds by the fact that the hydrodynamic description is not expected to hold below sufficiently small length-scales since the continuum hypothesis breaks down as we approach the mean-free path of the fluid molecules. Provided this regularisation preserves the skew-symmetry of the convective term, it would not contribute to dissipation of energy and would not change significantly the stochastic driving fields and numerical methods we present. From our dimension analysis of the fluctuating hydrodynamics equations, it would seem that the time derivative term plays the more dominant role given the rapid oscillations introduced by the thermal fluctuations, see discussion in [5, 53]. However, such comparisons can be subtle since the time-derivative by itself is also not a well-defined term and requires an interpretation to be given to the SPDEs, such as Ito stochastic calculus [44]. To avoid these technical issues, we consider here only models that use the time-dependent Stokes equations with the linearized material derivative  $d\mathbf{u}/dt = \partial\mathbf{u}/\partial t$ .

**3. Extension of SELM for Investigations of Shear Responses.** To introduce shear we generalize the usual periodic boundary conditions. We are motivated by the approach introduced by Lees-Edwards for molecular dynamics methods [37, 23, 24]. In this work, the material is modeled by periodically repeating the unit cell of a molecular model. To simulate the material undergoing a shear deformation at a given rate, the periodic images are treated as shifting in time relative to the unit cell. This has the effect of modifying both the location of periodic images of molecules and their assigned velocities. This approach has some advantages over methods which enforce a strict affine-like deformation everywhere within the material body [25, 57, 32]. For the Lees-Edwards approach, the shear is imposed only at the boundaries allowing within the unit cell for the molecular interactions to determine the shear response, see Figure 3.1.

Motivated by this approach, we develop a corresponding methodology for the SELM approach. By considering the effect of shifting periodic images of the unit cell, we introduce the generalized periodic boundary conditions for the fluid velocity

$$(3.1) \quad \mathbf{u}(x, y, L, t) = \mathbf{u}(x - vt, y, 0, t) + v\mathbf{e}_x.$$

To simplify the presentation, we only consider the case where a shear is imposed in the z-direction giving shear induced velocities in the x-direction. The other cases follow similarly. In our notation, the  $L$  is the side length of the periodic cell in the z-direction,  $v = L\dot{\gamma}$  is the velocity of the top face of the unit cell relative to the bottom face,  $\dot{\gamma}$  denotes the rate of shear deformation, and  $\mathbf{e}_j$  is the standard unit vector in the  $j^{\text{th}}$  direction. The interactions between microstructures of the system can be readily handled in the same manner as in the molecular dynamics simulation. This is done by shifting the location of any microstructure of a periodic image involved in an interaction, see Figure 3.1.

In practice, these boundary conditions present significant challenges for the numerical discretization of the fluid equations. The conditions introduce both a jump discontinuity at periodic boundaries and a shift. For uniform discretizations typically used for the unit cell, this results in significant misalignments of the nodes at the domain boundaries and a degradation in accuracy, see Figure 3.1. When incorporating stochastic driving fields to account for thermal fluctuations these issues are further compounded.

To address these issues, we reformulate the momentum equations in terms of a reference frame that is more naturally suited to the deformation of the material. This is achieved by letting  $\mathbf{w}(\mathbf{q}, t) = \mathbf{u}(\phi(\mathbf{q}, t), t)$ , where  $\mathbf{q} = (q_1, q_2, q_3)$  parameterizes the deformed unit cell. The map from the moving coordinate frame to the fixed Eulerian coordinate frame is denoted by  $\mathbf{x} = \phi(\mathbf{q})$  and given by  $\phi(\mathbf{q}, t) = (q_1 + q_3\dot{\gamma}t, q_2, q_3)$ . The SELM equations 2.1–2.4 in this reference frame are given by

$$(3.2) \quad \rho \frac{d\mathbf{w}^{(d)}}{dt} = \mu \tilde{\nabla}^2 \mathbf{w} - \nabla p + \Lambda [-\nabla_{\mathbf{x}} \Phi] + (\nabla_{\mathbf{x}} \cdot \Lambda) k_B T + \mathbf{J} + \mathbf{G}_{\text{thm}}$$

$$(3.3) \quad \nabla \cdot \mathbf{w} = \mathbf{e}_z^T \nabla \mathbf{w} \mathbf{e}_x \dot{\gamma} t + \mathbf{K}$$

$$(3.4) \quad \frac{d\mathbf{X}}{dt} = \Gamma \mathbf{w}$$

$$(3.5) \quad \langle \mathbf{G}_{\text{thm}}(s) \mathbf{G}_{\text{thm}}^T(t) \rangle = -(2k_B T) \mu \tilde{\nabla}^2 \delta(t - s).$$

The Laplacian of the velocity field under the change of variable is given by

$$(3.6) \quad [\tilde{\nabla}^2 \mathbf{w}]^{(d)} = [\mathbf{e}_d - \delta_{d,3} \dot{\gamma} t \mathbf{e}_x]^T \nabla^2 \mathbf{w}^{(d)} [\mathbf{e}_d - \delta_{d,3} \dot{\gamma} t \mathbf{e}_x].$$

In this reference frame the misalignment arising from the shear boundary conditions is removed. The boundary conditions for the reformulation become formally periodic boundary conditions

$$(3.7) \quad \mathbf{w}(q_1, q_2, L, t) = \mathbf{w}(q_1, q_2, 0, t).$$

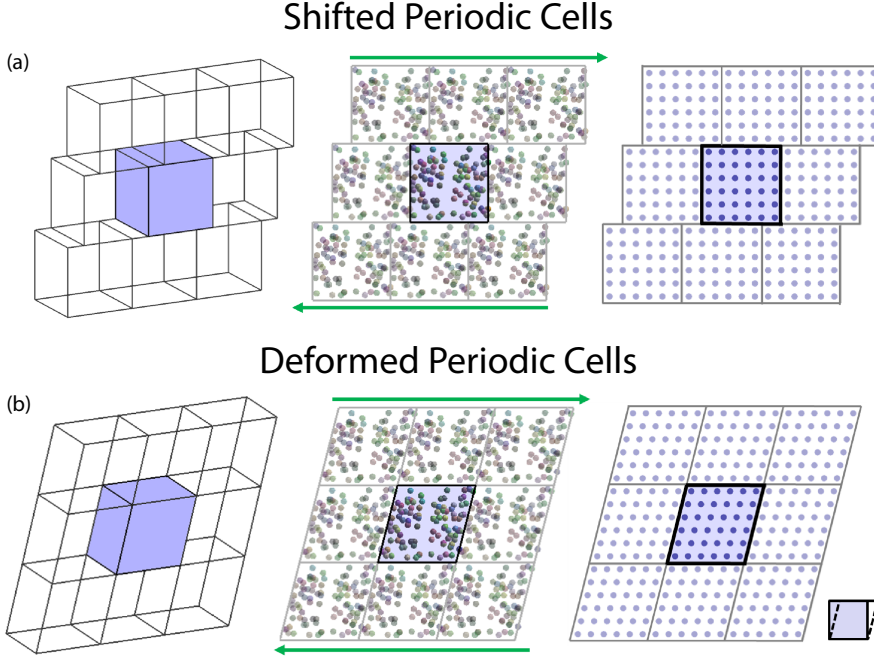


FIG. 3.1. Lees-Edwards Boundary Conditions and Discretization Mesh. The boundary conditions can be thought of in two equivalent ways. The first is to consider shear induced by shifting the periodic images of the unit cell by a shift relative to the unit cell, see panel (a). If the unit cell is discretized directly using a standard uniform mesh this presents challenges since the mesh sites become misaligned at boundaries between the unit cell and the periodic images. The second is to use the periodic symmetry which allows for the shifted images to be equivalently expressed in terms of a periodic tiling of a deformed unit cell, see panel (b). By discretizing the momentum equations in a moving coordinate frame, a discretization mesh is obtained which aligns with the periodic images. In this case, the unit cell and mesh change over time from a cube to a sheared parallelepiped. The periodicity further introduces a symmetry by which a unit cell distorted by the shift  $\frac{1}{2}L$  is equivalent to the distortion by shift  $-\frac{1}{2}L$ . Using this symmetry we always keep in the numerical calculations the unit cell deformation within the range  $[-\frac{1}{2}L, \frac{1}{2}L]$ .

The jump discontinuities arising from the boundary condition 3.1 still remain but in the reformulation are now taken into account by introducing the terms  $\mathbf{J}, \mathbf{K}$ . The term  $\mathbf{G}_{\text{thm}}$  denotes the stochastic driving field accounting for thermal fluctuations in the moving frame of reference.

The  $\mathbf{q} = (q_1, q_2, q_3)$  parameterizes the deformed unit cell,  $\delta_{k,\ell}$  denotes the Kronecker  $\delta$ -function,  $\dot{\gamma}$  denotes the rate of the shear deformation, and  $\mathbf{e}_i$  the standard basis vector in the  $i^{\text{th}}$  direction with  $i \in \{x, y, z\}$ . In the notation the parenthesized superscript denotes a vector component. We also use the notational conventions

$$(3.8) \quad [\nabla \mathbf{w}]_j^{(d)} = \frac{\partial \mathbf{w}^{(d)}}{\partial q_j}, \quad [\nabla^2 \mathbf{w}]_{i,j}^{(d)} = \frac{\partial^2 \mathbf{w}^{(d)}}{\partial q_i \partial q_j}.$$

**4. Computational Methodology.** To use this approach in practice requires the development of numerical methods to approximate the stochastic differential equations. A variety of methods could be used, such as Finite Difference Methods, Spectral Methods, or

Finite Element Methods [29, 52, 51]. We present here discretizations based on Finite Difference Methods. A challenge for discretizations is that the solutions to stochastic equations are irregular and approximation errors may disrupt the statistical mechanics structure of the system. To obtain physically relevant results, we shall design our numerical methods by developing a finite dimensional dynamical system that approximates the continuum mechanics while adhering to principles from statistical mechanics. To introduce the stochastic driving fields in our numerical methods, we develop discretizations that take into account the difference between the dissipative properties of the continuum operators and the discrete operators so that our methods satisfy fluctuation-dissipation balance [7, 53, 19, 30, 56]. These conditions in the absence of shear are closely related to the requirement that the Gibbs-Boltzmann ensemble be invariant with detailed-balance [7, 53]. To perform simulations in practice we also develop efficient methods for generating the stochastic driving fields with the required covariance structure.

The stochastic differential equations of SELM can also exhibit dynamics over a significant range of time-scales resulting in numerical stiffness [7, 53]. To facilitate the development of efficient numerical methods, we consider two distinct physical regimes. In the first we explicitly resolve the fluctuations and relaxation of the hydrodynamics. We refer to this as the Fluctuating Hydrodynamics Regime. In the second we treat the solvent fluid as having relaxed to a quasi-steady-state with respect the instantaneous configuration of the microstructures. We refer to this as the Overdamped Regime.

#### 4.1. Numerical Methods for the Fluctuating Hydrodynamics Regime.

**4.1.1. Semi-discretization.** To approximate the stochastic differential equations and to discretize the stochastic driving fields, we first consider a semi-discretization of the equations 3.2–3.5. This is given by

$$(4.1) \quad \rho \frac{d\mathbf{w}}{dt} = L(t)\mathbf{w} + \lambda + \Lambda[-\nabla_{\mathbf{x}}\Phi] + (\nabla_{\mathbf{x}} \cdot \Lambda) k_B T + \mathbf{J} + \mathbf{h}_{\text{thm}}$$

$$(4.2) \quad S(t) \cdot \mathbf{w} = \mathbf{K}$$

$$(4.3) \quad \frac{d\mathbf{X}}{dt} = \Gamma \mathbf{w}.$$

We use for the discretized operators

$$(4.4) \quad S(t) \cdot \mathbf{w} = D \cdot \mathbf{w} + \mathbf{e}_z^T G \mathbf{w} \mathbf{e}_x \dot{\gamma} t$$

$$(4.5) \quad L(t)\mathbf{w} = \mu [\mathbf{e}_d - \delta_{d,3} \dot{\gamma} t \mathbf{e}_x]^T A \mathbf{w} [\mathbf{e}_d - \delta_{d,3} \dot{\gamma} t \mathbf{e}_x]$$

where

$$(4.6) \quad D \cdot \mathbf{w} = \sum_{d=1}^3 \frac{\mathbf{w}^{(d)}(\mathbf{q} + \mathbf{e}_d) - \mathbf{w}^{(d)}(\mathbf{q} - \mathbf{e}_d)}{2\Delta x}$$

$$(4.7) \quad [G\mathbf{w}]_{ij} = \frac{\mathbf{w}^{(i)}(\mathbf{q} + \mathbf{e}_j) - \mathbf{w}^{(i)}(\mathbf{q} - \mathbf{e}_j)}{2\Delta x}$$

and

$$(4.8) \quad [A\mathbf{w}]_{ii} = \frac{\mathbf{w}^{(i)}(\mathbf{q} + \mathbf{e}_i) - 2\mathbf{w}^{(i)}(\mathbf{q}) + \mathbf{w}^{(i)}(\mathbf{q} - \mathbf{e}_i)}{\Delta x^2}$$

$$(4.9) \quad [A\mathbf{w}]_{ij} = \frac{\mathbf{w}^{(d)}(\mathbf{q} + \mathbf{e}_i + \mathbf{e}_j) - \mathbf{w}^{(d)}(\mathbf{q} - \mathbf{e}_i + \mathbf{e}_j)}{4\Delta x^2} - \frac{\mathbf{w}^{(d)}(\mathbf{q} + \mathbf{e}_i - \mathbf{e}_j) - \mathbf{w}^{(d)}(\mathbf{q} - \mathbf{e}_i - \mathbf{e}_j)}{4\Delta x^2}, \quad i \neq j.$$

For the semi-discretized system we consider the energy

$$(4.10) \quad E[\mathbf{w}, \mathbf{X}] = \frac{\rho}{2} \sum_{\mathbf{q}} |\mathbf{w}(\mathbf{q})|^2 \Delta x_{\mathbf{q}}^3 + \Phi[\mathbf{X}].$$

The first term is the total kinetic energy of the system. The second term is the potential energy of the microstructures.

For the discretized equations and energy, the  $\mathbf{w}$  denotes the velocity field of the fluid on a uniform periodic lattice in the coordinates  $\mathbf{q}$  with  $\mathbf{w} \in \mathbb{R}^{3N}$ . The  $N$  denotes the number of lattice sites. The  $\mathbf{X}$  denotes a finite number of microstructure degrees of freedom with  $\mathbf{X} \in \mathbb{R}^M$ . As a consequence of the coordinate frame moving with the deformation of the unit cell, the discretized operators now have a direct dependence on time. The  $\lambda$  denotes a Lagrange multiplier used to impose the incompressibility condition 4.2 and will be discussed in more detail below.

To obtain the source terms  $\mathbf{J}$ ,  $\mathbf{K}$  for the discretized equations, we use the discretization stencils of the operators given in equations 4.1– 4.2. When the stencil weights are applied at the boundaries of the unit cell, the values at lattice sites crossing the boundary would use the modified image value  $\mathbf{w}_m \pm \dot{\gamma}L$  under the boundary conditions 3.1. The use in the stencils of this modified lattice site value can be avoided by separating the contributions coming from the jump part of the boundary condition from the usual lattice site value of a periodic image. These contributions are given by the stencil weights multiplied by  $\pm\dot{\gamma}L$  for any term crossing the boundary. When these are collected over all boundary mesh sites and terms on the right-hand side involving  $\mathbf{w}$ , we obtain the source terms  $\mathbf{J}$ ,  $\mathbf{K}$ .

The incompressibility constraint for the solvent fluid is approximated in practice using the projection of a vector  $\mathbf{v}^*$  to the sub-space  $\{\mathbf{v} \in \mathbb{R}^{3N} \mid S(t) \cdot \mathbf{v} = 0\}$ . We denote this projection operation by

$$(4.11) \quad \mathbf{v} = \varphi(t)\mathbf{v}^*.$$

The discretized incompressibility constraint is imposed by using the Lagrange multiplier

$$(4.12) \quad \lambda = -(\mathcal{I} - \varphi(t)) [L(t)\mathbf{w} + \Lambda[-\nabla_{\mathbf{x}}\Phi] + (\nabla_{\mathbf{x}} \cdot \Lambda) k_B T + \mathbf{J} + \mathbf{h}_{\text{thm}}].$$

We remark that the incompressibility constraint is imposed exactly provided that  $\mathbf{K}$  is independent of time. In practice,  $\mathbf{K}$  is expected to have some dependence on time so that this approach results in an approximation in imposing the incompressibility constraint 4.2.

An important feature of the discretization for the SELM equations and incompressibility constraint is that the resulting operators are cyclic. This allows for Fast Fourier Transforms (FFTs) to be used in evaluating the action of the operators and in computing inverses. As a consequence, the projection operator can be computed efficiently with only  $O(N \log(N))$  computational steps.

To obtain appropriate behaviors for the thermal fluctuations, it is important to develop stochastic driving fields which are tailored to the specific semi-discretization used. Another important issue is to develop methods for efficient generation of the stochastic fields. Once these issues are resolved, which is the subject of the next few sections, the semi-discretized equations can be integrated in time using traditional methods for stochastic differential equations, such as the Euler-Maruyama Method or a Stochastic Runge-Kutta Method [34]. More sophisticated integrators in time can also be developed to cope with possible sources of stiffness [7].

**4.1.2. Thermal Fluctuations.** To account for thermal fluctuations, we introduce into the discretized equations a stochastic driving field. Given the highly irregular nature of the stochastic driving fields in the undiscretized equations 2.1– 2.4, formulating appropriate terms for the discretized equations must be done carefully. To obtain results consistent with statistical mechanics, we consider the relationship between the choice of stochastic driving field and the equilibrium fluctuations expected for the system. To simplify the discussion, we initially consider only the case when  $\Phi = 0$  and neglect the  $\mathbf{X}$  degrees of freedom. We then discuss how the results obtained apply to the more general case.

The statistical mechanics of the system requires equilibrium fluctuations which follow the Gibbs-Boltzmann distribution

$$(4.13) \quad \Psi(\mathbf{w}, \mathbf{X}) = \frac{1}{Z} \exp[-E[\mathbf{w}, \mathbf{X}]/k_B T].$$

The  $Z$  is the normalization constant ensuring the probability integrates to one. The  $k_B$  is Boltzmann's constant and  $T$  is the temperature [49]. By considering the energy associated with the discretized system given in equation 4.10, we see that fluctuations of  $\mathbf{w}$  are Gaussian under the Gibbs-Boltzmann distribution. This specific form of the energy along with the incompressibility constraint requires equilibrium fluctuations that have mean zero and covariance given by

$$(4.14) \quad C = \langle \mathbf{w}\mathbf{w}^T \rangle = \frac{2}{3} \frac{k_B T}{\rho \Delta x^3} \mathcal{I}.$$

The factor of  $2/3$  arises from the incompressibility constraint. The stochastic driving field  $\mathbf{h}_{\text{thm}}$  introduced into the discretized equations is assumed to be a Gaussian process with mean zero and  $\delta$ -correlation in time [27, 44]. Such processes can be expressed formally as

$$(4.15) \quad \mathbf{h}_{\text{thm}} = Q(t) \frac{d\mathbf{B}(t)}{dt}.$$

The  $Q(t)$  denotes a linear operator and  $\mathbf{B}(t)$  denotes a standard Brownian motion on  $\mathbb{R}^{3N}$ , see [44]. The covariance of this process is given by

$$(4.16) \quad G(s, t) = \langle \mathbf{h}_{\text{thm}}(s) \mathbf{h}_{\text{thm}}(t)^T \rangle = Q(s)Q(t)^T \delta(t - s).$$

The discretized equations are linear in  $\mathbf{w}$ . As a consequence, the covariance of the equilibrium fluctuations and the covariance of the stochastic driving field are related by

$$(4.17) \quad G(s, t) = -2\wp(t)L(t)C\delta(t - s).$$

This relation can be interpreted as a variant of the fluctuation-dissipation principle. We establish this relationship for systems having time dependent dissipative operators in Appendix A.

This gives the the stochastic driving field  $\mathbf{h}_{\text{thm}}$  tailored to the moving coordinate frame and the semi-discretized equations 4.1–4.3. By considering the Fokker-Planck equations of the discretized system  $(\mathbf{w}, \mathbf{X})$ , this choice can be shown to yield stochastic dynamics which have the Gibbs-Boltzmann distribution invariant, see [5]. This shows the stochastic dynamics exhibit fluctuations consistent with equilibrium statistical mechanics. It should be mentioned, evaluating the appropriateness of this choice for the stochastic driving field also can be investigated by considering other properties, such as the dynamic structure factor of the stochastic dynamics that could be used to make comparisons with the undiscretized equations or with physical systems [21, 42]. Another important issue arising in practice is to develop computational methods for the efficient generation of the stochastic driving field. This is the subject of the next section.

**4.1.3. Generation of Stochastic Driving Fields.** To account for thermal fluctuations, we must generate each time step the Gaussian stochastic field with the covariance structure given by equation 4.17. In general, generating a Gaussian variate  $\mathbf{h}$  with a prescribed covariance  $G$  is computationally expensive. A common approach is to generate standard normal variates  $\boldsymbol{\xi}$  having covariance  $\langle \boldsymbol{\xi}\boldsymbol{\xi}^T \rangle = I$ . To obtain a correlated Gaussian a Cholesky factorization is often used to obtain  $QQ^T = G$  and the Gaussian is generated using  $\mathbf{h} = Q\boldsymbol{\xi}$ . For  $\mathbf{h} \in \mathbb{R}^N$ , the Cholesky factorization has a cost of  $O(N^3)$  computational steps and the generation of each variate through the matrix-vector multiplication has a cost of  $O(N^2)$  computational steps. For the discretized equations  $N$  will typically be rather large making this approach prohibitive.

To generate the stochastic driving field more efficiently, we make use of specific properties of the discretization and FFTs. These properties include that  $\mathbf{w}$  is periodic in the moving coordinate frame and that the discretized operators  $L(t)$ ,  $C$ , and  $\wp(t)$  are block diagonalizable in the Fourier basis (with blocks of small size). By working with the diagonalized form of each of the operators  $L(t)$ ,  $C$ , and  $\wp(t)$ , a square-root  $Q(t)$  of the operator  $G(t)$  can be found in Fourier space. Given the sparse structure of  $Q(t)$  in the Fourier space, the stochastic fields are generated using FFTs in  $O(N \log(N))$  computational steps.



**4.2. Numerical Methods for the Overdamped Regime.** For many physical systems of interest, there are significant differences in the time scales associated with the hydrodynamic relaxation of the solvent fluid and the time scales associated with the diffusion of the microstructures an appreciable distance. For the fluctuating hydrodynamics regime this can result in significant stiffness in the stochastic differential equations.

For investigations of complex fluids and soft materials in which the relaxation of the hydrodynamics is not of primary interest, it is useful to introduce a reduced description removing this source of stiffness. In the limit of fluid dynamics which rapidly equilibrate given the instantaneous configuration of the microstructures we have the reduced equations,

$$(4.18) \quad \frac{d\mathbf{X}}{dt} = H_{\text{SELM}}[-\nabla_{\mathbf{X}}\Phi(\mathbf{X})] + (\nabla_{\mathbf{X}} \cdot H_{\text{SELM}})k_B T + \mathbf{h}_{\text{thm}}$$

$$(4.19) \quad H_{\text{SELM}} = \Gamma(-\wp L)^{-1}\Lambda$$

$$(4.20) \quad \langle \mathbf{h}_{\text{thm}}(s) \mathbf{h}_{\text{thm}}^T(t) \rangle = (2k_B T) H_{\text{SELM}} \delta(t - s).$$

The  $\wp$  denotes a projection operator imposing constraints, such as incompressibility. The adjoint property  $\Lambda = \Gamma^\dagger$  and symmetry of  $\wp L$  yields an operator  $H_{\text{SELM}}$  which is symmetric. The semi-discretization of these equations is obtained by using the discretized operators given in equations 4.4– 4.5. The thermal fluctuations are determined by the principle of detailed-balance and the requirement that the Gibbs-Boltzmann distribution be invariant under the stochastic dynamics, see [5, 53]. The semi-discretized equations can be integrated in time using standard methods for stochastic differential equations [34].

We remark that when using the Immersed Boundary Method to coupled the fluid and structures the hydrodynamic coupling tensor closely resembles the Rotne-Prager-Yamakawa tensor [5]. We remark that while  $H_{\text{SELM}}$  accounts well for the far-field hydrodynamics, additional near-field corrections could also be added readily to the hydrodynamic coupling, such as terms to account for lubrication effects as is done in such methods as Stokesian-Brownian dynamics [13]. However, for polymers and other soft microstructures the near-field interactions are less clear than at larger length-scales and ideally should be determined from more detailed molecular models and considerations. We also remark that the far-field hydrodynamic interactions pose the most computational challenge since they couple long-range the microstructures in a nearly all-to-all manner while the near-field interactions are local and can be handled for a small cluster around each microstructure at much less computational expense. Since these terms can be treated additively throughout, the methods we shall present for the long-range hydrodynamics can be extended readily to incorporate near-field interactions. The central challenge for such methods in practice is the long-range hydrodynamics and the efficient generation of the stochastic driving field  $\mathbf{h}_{\text{thm}}$  with the required covariance structure given by equation 4.20.

**4.2.1. Generation of Stochastic Driving Fields.** To use this description in practice requires efficient methods for generating the stochastic driving field with the covariance given in equation 4.20. For this purpose we express the covariance of the stochastic driving field as

$$(4.21) \quad G = (2k_B T) H_{\text{SELM}} = (2k_B T) \left( \Gamma \wp (-L)^{-1} \wp^T \Gamma^T \right).$$

This makes use of  $\Lambda = \Gamma^T$  and properties of the specific discretized operators  $L$  and  $\wp$ . In particular, commutativity  $\wp L = L \wp$  and the projection operator properties  $\wp^2 = \wp$ ,  $\wp = \wp^T$ . Let  $U$  be a factor so that  $U U^T = -L^{-1}$ . Using this factor we can express the covariance as

$$(4.22) \quad G = \left( \sqrt{2k_B T} \Gamma \wp U \right) \left( \sqrt{2k_B T} \Gamma \wp U \right)^T.$$

From this expression a matrix square-root of  $G$  is readily obtained,  $Q = \sqrt{2k_B T} \Gamma \wp U$ .

We remark this is different than the Cholesky factor obtained for  $G$  which is required to be lower triangular [54, 50]. Obtaining such a factor by Cholesky factorization would

cost  $O(M^3)$ , where  $M$  is the number of structure degrees of freedom. For the current discretization considered, the operators  $L$  and  $\wp$  are block diagonalizable in Fourier space (with small blocks). This has the consequence that the action of the operators  $U$  and  $\wp$  can be computed using FFTs with a cost of  $O(N \log(N))$ . The  $N$  is the number of lattice sites used to discretize  $L$ . The stochastic driving field is computed from  $\mathbf{h} = Q\xi$ . This allows for the stochastic driving field to be generated in  $O(N \log(N) + M)$  computational steps, assuming the action  $\Gamma$  can be compute in  $O(M)$  steps. This is in contrast to using the often non-sparse matrix arising from Cholesky factorization which generates the stochastic field with a cost of  $O(M^2)$ . Other methods based on splittings or multigrid can also be utilized to efficiently generate stochastic fields with this required covariance structure or for discretizations on multilevel adaptive meshes, see [5, 3].

### 4.3. Operators for Coupling the Microstructures and Solvent Fluid.

Many different operators could be used to couple the microstructure and solvent dynamics [5]. We will take an approach similar to the Stochastic Immersed Boundary Method [7, 46] and use the following specific form for the operators that couple the microstructures and solvent fluid

$$(4.23) \quad [\Gamma \mathbf{u}](\mathbf{s}) = \int_{\Omega} \eta(\mathbf{y} - \mathbf{X}(\mathbf{s})) \mathbf{u}(\mathbf{y}) d\mathbf{y}$$

$$(4.24) \quad [\Lambda \mathbf{F}](\mathbf{y}) = \int_{\mathcal{S}} \mathbf{F}(\mathbf{s}) \eta(\mathbf{y} - \mathbf{X}(\mathbf{s})) d\mathbf{s}.$$

The  $\mathbf{F}$  denotes the force acting on the microstructures, which is typically given by  $\mathbf{F} = -\nabla_{\mathbf{x}}\Phi$ . The kernel function  $\eta$  is used to smooth the irregular velocity field and determines an effective hydrodynamic radius for the microstructures, see [5, 7] and Appendix B. It can be shown these operators satisfy the adjoint condition given by equation 2.5. This pair of operators has been successfully used in the past and extensive validation studies have been conducted to characterize how these operators represent hydrodynamic coupling [7, 4, 6, 5, 35, 15].

To couple the semi-discretized description of the solvent fluid and microstructures we use the discretized operators

$$(4.25) \quad [\Gamma \mathbf{u}]^{[j]} = \sum_{\mathbf{m}} \eta(\mathbf{y}_{\mathbf{m}} - \mathbf{X}^{[j]}) \mathbf{u}_{\mathbf{m}} \Delta y_{\mathbf{m}}^d$$

$$(4.26) \quad [\Lambda \mathbf{F}]_{\mathbf{m}} = \sum_{j=1}^M \mathbf{F}^{[j]}(\mathbf{X}) \eta(\mathbf{y}_{\mathbf{m}} - \mathbf{X}^{[j]}).$$

It can be shown these operators satisfy an adjoint condition analogous to equation 2.5 for the semi-discretized equations 4.1–4.3. More general discretized operators can also be used, see [5].

**5. Estimating Macroscopic Stresses.** An important issue in the study of complex fluids and soft materials is to relate microscopic features of the material to macroscopic properties. For this purpose, we develop estimators for an effective macroscopic stress tensor for the material. The stress tensor is estimated from the forces acting on the microstructures in a manner similar to that used in the Irving-Kirkwood-Kramer formulas [33, 20, 11, 12]. The contributions from the solvent fluid are assumed to be Newtonian throughout.

The stress tensor is estimated by considering cut-planes which divide the unit cell. A component of the stress tensor is estimated by considering the forces exerted by the material which lies above the cut-plane on the material which lies below the cut-plane. The totality of these forces is then divided by the area of the cut-plane. We average these estimates over all possible cut-planes having a given normal to avoid sensitive dependence on the microstructure configuration, the  $n$ -body interactions, and the cut-plane location, see Figure 5.1.

To estimate the stress tensor, it is convenient to consider separately each of the different types of  $n$ -body interactions which occur between the microstructures, such as two-body

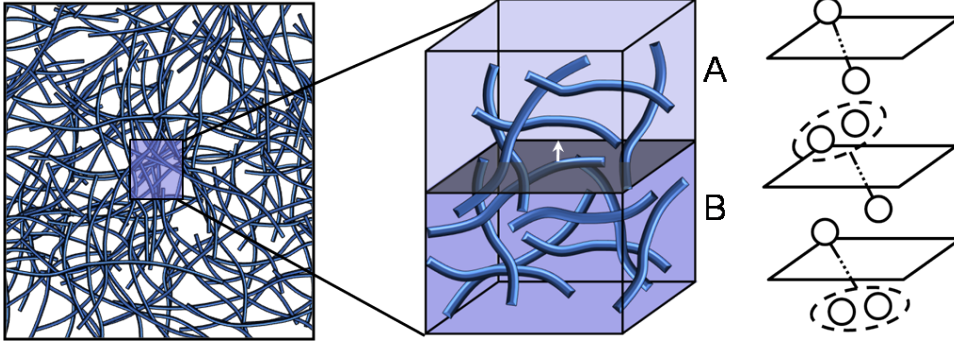


FIG. 5.1. *Estimating Macroscopic Stresses.* The components of the stress tensor are estimated from microscopic interactions by considering cut-planes through the sample. The cut-plane divides the sample into two bodies labeled A and B, shown in the middle. The effective stress is given by the forces exerted by the material of body A on material of body B divided by the cut-plane area. For  $n$ -body interactions, contributions to the stress can arise in different ways. On the far right is shown for a given cut-plane the cases when two-body and three-body interactions make a contribution to the stress.

bonding interactions or three-body bond-angle interactions. To estimate the contributions to the components of the stress tensor arising from a particular  $n$ -body interaction, we use

$$(5.1) \quad \sigma_{\ell,z}^{(n)} = \frac{1}{L} \left\langle \int_a^b \Theta_{\ell,z}^{(n)}(\zeta) d\zeta \right\rangle.$$

The  $L = b - a$  is the length of the unit-cell domain in the  $z$ -direction and  $\langle \cdot \rangle$  denotes averaging over the ensemble. The  $\Theta_{\ell,z}^{(n)}$  denotes the effective stress arising from the  $n$ -body interactions associated with a given stress plane and is defined by

$$(5.2) \quad \Theta_{\ell,z}^{(n)}(\zeta) = \frac{1}{A} \sum_{\mathbf{q} \in \mathcal{Q}_n} \sum_{k=1}^{n-1} \sum_{j=1}^k \mathbf{f}_{\mathbf{q},j}^{(\ell)} \prod_{j=1}^k \mathcal{H}(\zeta - \mathbf{x}_{q_j}^{(z)}) \prod_{j=k+1}^n \mathcal{H}(\mathbf{x}_{q_j}^{(z)} - \zeta).$$

The  $\mathcal{Q}_n$  is the set of  $n$ -tuple indices  $\mathbf{q} = (q_1, \dots, q_n)$  describing the  $n$ -body interactions of the system,  $\mathbf{f}_{\mathbf{q},j}$  denotes the force acting on the  $j^{\text{th}}$  particle of the interaction, and  $\mathbf{x}_{q_j}$  denotes the  $j^{\text{th}}$  particle involved in the interaction. As a matter of convention in the indexing  $\mathbf{q}$ , we require that  $i \leq j$  implies  $\mathbf{x}_{q_i}^{(z)} \leq \mathbf{x}_{q_j}^{(z)}$ . This expression corresponds to a sum over all the forces exerted by particles of the material above the cross-section at  $\zeta = z$  on the particles of the material below. Each term of the summation over  $k = 1, \dots, n - 1$  corresponds to a specific number of particles of the  $n$ -body interaction lying below the cross-section at  $\zeta = z$ , see Figure 5.1.

This expression for estimating the stress tensor can be simplified by using the following identity

$$(5.3) \quad \int_a^b \prod_{j=1}^k \mathcal{H}(\zeta - \mathbf{x}_{q_j}^{(z)}) \cdot \prod_{j=k+1}^n \mathcal{H}(\mathbf{x}_{q_j}^{(z)} - \zeta) d\zeta = \mathbf{x}_{q_{k+1}}^{*(z)} - \mathbf{x}_{q_k}^{*(z)}$$

where

$$(5.4) \quad \mathbf{x}_{q_j}^{*(z)} = \begin{cases} b, & \text{if } \mathbf{x}_{q_j}^{(z)} \geq b \\ \mathbf{x}_{q_j}^{(z)}, & \text{if } a \leq \mathbf{x}_{q_j}^{(z)} \leq b \\ a, & \text{if } \mathbf{x}_{q_j}^{(z)} \leq a. \end{cases}$$

By integrating equation 5.2 and using the identity given in equation 5.3, we obtain

$$(5.5) \quad \int_a^b \Theta_{\ell,z}^{(n)}(\zeta) d\zeta = \frac{1}{A} \sum_{\mathbf{q} \in \mathcal{Q}_n} \sum_{k=1}^{n-1} \sum_{j=1}^k \mathbf{f}_{\mathbf{q},j}^{(\ell)} \cdot (\mathbf{x}_{q_{k+1}}^{*(z)} - \mathbf{x}_{q_k}^{*(z)}).$$

This can be further simplified by switching the order of summation of  $j$  and  $k$  and using the telescoping property of the summation over  $k$ . This gives the following estimate for the  $n$ -body contributions to the stress tensor

$$(5.6) \quad \sigma_{\ell,z}^{(n)} = \frac{1}{AL} \sum_{\mathbf{q} \in \mathcal{Q}_n} \sum_{j=1}^{n-1} \left\langle \mathbf{f}_{\mathbf{q},j}^{(\ell)} \cdot \left( \mathbf{x}_{q_n}^{*,(z)} - \mathbf{x}_{q_j}^{*,(z)} \right) \right\rangle.$$

This is obtained by using equation 5.1 and equation 5.5.

To obtain the effective macroscopic stress tensor we sum over all  $n$ -body contributions to obtain

$$(5.7) \quad \sigma_{\ell,z} = \sum_n \sigma_{\ell,z}^{(n)}.$$

This effective macroscopic stress tensor will be used to link the microscopic simulations to macroscopic material properties.

**6. Applications.** To demonstrate how the computational methods can be used to study the rheological behaviors of complex fluids and soft materials, we present a few specific applications. We investigate the shear thinning of a polymeric fluid in Section 6.1. We study the complex moduli for the oscillatory responses of a polymerized lipid vesicle in Section 6.2. We study the aging of the shear viscosity of a gel-like material in Section 6.3.

**6.1. Application I: Shearing Thinning of a Polymeric Fluid.** As a demonstration of the proposed computational methodology we consider a fluid with microstructures consisting of elastic polymers. The polymers are modeled as elastic dimers which have the FENE potential energy [12]

$$(6.1) \quad \phi(r) = \frac{1}{2} K r_0^2 \log \left( 1 - \left( \frac{r}{r_0} \right)^2 \right).$$

The  $K$  denotes the polymer stiffness,  $r$  denotes the length of extension of the dimer, and  $r_0$  denotes the maximum permitted extension length. The configuration of a dimer will be represented using two degrees of freedom  $\mathbf{X}_k^{(1)}$ ,  $\mathbf{X}_k^{(2)}$  with the potential energy  $\Phi(\mathbf{X}) = \sum_k \phi(|\mathbf{X}_k^{(2)} - \mathbf{X}_k^{(1)}|)$ . The  $\mathbf{X}$  denotes the composite vector over all dimers.

To study the rheology of the polymeric fluid, we consider the shear viscosity  $\eta_p$  and the first normal stress coefficient  $\Psi_1$ . These are defined as [11, 12]

$$(6.2) \quad \eta_p = \sigma_p^{(s,v)} / \dot{\gamma}$$

$$(6.3) \quad \Psi_1 = (\sigma_p^{(s,s)} - \sigma_p^{(v,v)}) / \dot{\gamma}^2.$$

The  $\dot{\gamma}$  is the rate of shear. In the notation, the superscript  $(s, v)$  indicates the tensor component with the index  $s$  corresponding to the direction of the shear gradient and the index  $v$  corresponding to the direction of the velocity induced by the shear. The contributions of the solvent fluid to the shear viscosity and normal stresses can be considered separately [12]. The solvent fluid is assumed to be Newtonian throughout so we only report the contributions arising from the elastic dimers.

From the simulations, we find there is a strong dependence on the rate of shear in the manifested shear viscosity and normal stress of the polymeric fluid, see Figure 6.1. This can be understood by considering the interplay between the thermal fluctuations and the shear stresses acting on the dimers. Since the dimers only resist stretching, they exert forces only in the direction of the dimer orientation. As a consequence, contributions are made to the shear viscosity only when the dimer orientation has a non-negligible component in the  $z$ -direction, see equation 6.2.

The thermal fluctuations and shear stresses play opposing roles with respect to the  $z$ -component. The thermal fluctuations act to randomize the dimer orientation generating on

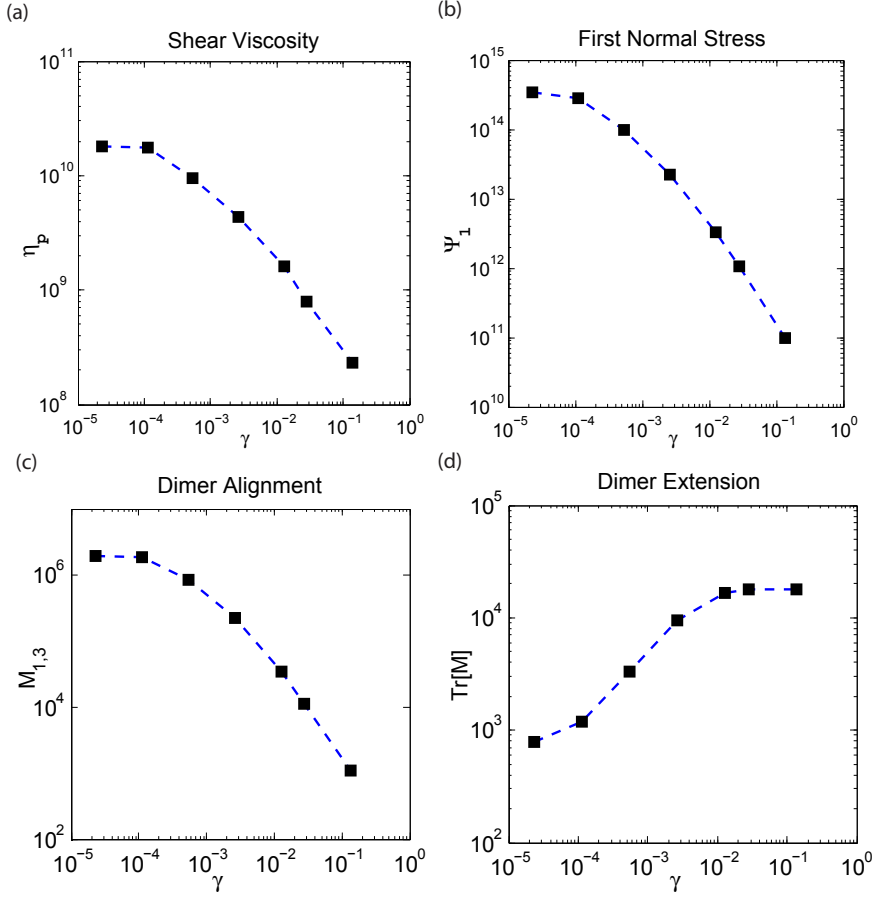


FIG. 6.1. *Polymeric Fluid Shear Response : Simulation Results.* (a–b) The shear viscosity and first normal stresses of the polymeric fluid in response to shear at the rate  $\dot{\gamma}$ . To quantitate the alignment and extension of the polymers, the orientation matrix is considered given by  $M = \langle \mathbf{z}\mathbf{z}^T \rangle$ , with  $\mathbf{z} = \mathbf{X}^{(2)} - \mathbf{X}^{(1)}$ . (c) The component  $M_{1,3}$  gives a measure of the alignment of the polymers with the direction of shear. (d) The trace of  $M$  gives a measure of the extension of the polymers.

average a non-negligible z-component while the shear stresses act to align the dimers with the direction of shear and suppress the z-component. As the shear rate increases, this results in an increase in the shear stresses and an increase in the degree of alignment of the dimers. This results in a decrease in the shear viscosity. This can be quantitated in the simulations by considering for the dimers the orientation tensor  $M = \langle \mathbf{z}\mathbf{z}^T \rangle$ , where  $\mathbf{z} = \mathbf{X}^{(2)} - \mathbf{X}^{(1)}$ , see Figure 6.1. This highlights the important roles that thermal fluctuations can play in material properties. For this polymeric fluid, if thermal fluctuations were neglected, there would be no contributions to the shear viscosity by the dimers since they would all eventually align with the direction of shear.

The observed decrease of the shear viscosity with an increase in the shear rate is a common phenomena observed for many complex fluids [12]. This behavior is referred to as “shear-thinning“, see [12]. These simulations give a proof-of-principle for how such phenomena can be studied for complex fluids using the presented computational methodology. For the simulation parameters used in our simulations see Tables 6.1 and Table 6.2.

Parameter	Description
$N$	Number of mesh points in each direction.
$\Delta x$	Mesh spacing.
$L$	Domain size in each direction.
$T$	Temperature.
$k_B$	Boltzmann's constant.
$\mu$	Dynamic viscosity of the solvent fluid.
$\rho$	Mass density of the solvent fluid.
$K$	Bond stiffness.
$r_0$	Maximum permissible bond extension.
$\gamma_s$	Stokesian drag of a particle.
$\dot{\gamma}^0$	Shear rate amplitude.
$\gamma^0$	Strain rate amplitude.
$a$	Effective radius of particle estimated via Stokes drag.

TABLE 6.1

*Description of the parameters used in simulations of the polymeric fluid.*

Parameter	Value
$N$	36
$\Delta x$	11.25 nm
$L$	405 nm
$T$	300 K
$k_B$	$8.3145 \times 10^3 \text{ nm}^2 \cdot \text{amu} \cdot \text{ns}^{-2} \cdot \text{K}^{-1}$
$\mu$	$6.0221 \times 10^5 \text{ amu} \cdot \text{cm}^{-1} \cdot \text{ns}^{-1}$
$\rho$	$6.0221 \times 10^2 \text{ amu} \cdot \text{nm}^{-3}$
$K$	$8.9796 \times 10^3 \text{ amu} \cdot \text{ns}^{-2}$
$r_0$	200 nm
$\gamma_s$	$1.7027 \times 10^8 \text{ amu} \cdot \text{ns}^{-1}$
$a$	15 nm

TABLE 6.2

*Values of the parameters used in simulations of the polymeric fluid.*

**6.2. Application II: Complex Moduli for Oscillatory Responses of Polymerized Lipid Vesicles.** As a further demonstration of the computational methods, we investigate the material properties of a fluid containing polymerized lipid vesicles. We discuss how the methods can be used to study responses to an oscillatory shear applied over a wide range of frequencies.

To account for the mechanics of a polymerized lipid vesicle, we discretize the spherical surface using a triangular mesh. The mechanics is modeled by the following interactions between the control points of the mesh

$$(6.4) \quad \phi_1(r, \ell) = \frac{1}{2} K_1 (r - \ell)^2$$

$$(6.5) \quad \phi_2(\boldsymbol{\tau}_1, \boldsymbol{\tau}_2) = \frac{1}{2} K_1 |\boldsymbol{\tau}_1 - \boldsymbol{\tau}_2|^2.$$

The  $r$  denotes the displacement between two control points,  $\ell$  denotes a preferred distance between control points, and  $\boldsymbol{\tau}$  denotes a normalized displacement vector (tangent vector) between two control points. The  $\phi_1$  energy accounts for the stretching of a bond between two control points beyond its preferred extension. The  $\phi_2$  energy accounts for bending of the surface locally by penalizing the misalignment of tangent vectors. The total energy for

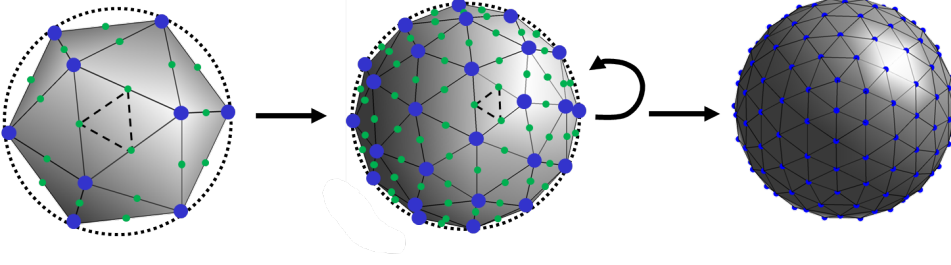


FIG. 6.2. *Vesicle Mesh Construction using a Recursive Refinement Method.* The triangulated mesh for a spherical vesicle is constructed by starting with the vertices and faces of a regular icosahedron, shown on the left. The edges of the icosahedron are bisected and connected to divide each triangular face into four smaller triangular faces. The vertices located at the bisection points are projected radially outward to the surface of the sphere, shown in the middle. This refinement procedure is repeated recursively until a mesh of sufficient resolution is obtained. The mesh obtained after two levels of recursive refinement is shown on the far right.

a given configuration of the vesicle is given by

$$(6.6) \quad \Phi[\mathbf{X}] = E_1[\mathbf{X}] + E_2[\mathbf{X}]$$

$$(6.7) \quad E_1[\mathbf{X}] = \sum_{(i,j) \in \mathcal{Q}_1} \phi_1(r_{ij}, \ell_{ij})$$

$$(6.8) \quad E_2[\mathbf{X}] = \sum_{(i,j,k) \in \mathcal{Q}_2} \phi_2(\boldsymbol{\tau}_{ij}, \boldsymbol{\tau}_{jk}).$$

The  $\mathbf{X}$  denotes the composite vector of control points. The  $j^{\text{th}}$  control point is denoted by  $\mathbf{X}^{[j]}$ . The  $\mathcal{Q}_1$  and  $\mathcal{Q}_2$  are index sets defined by the topology of the triangulated mesh.

The first energy term  $E_1$  accounts for stretching of the vesicle surface and is computed by summing over all local two body interactions  $\mathcal{Q}_1$  defined by the topology of the triangulated mesh. For the distance  $r_{ij} = |\mathbf{X}^{[i]} - \mathbf{X}^{[j]}|$  between the two points having index  $i$  and  $j$ , the energy  $E_1$  penalizes deviations from the preferred distance  $\ell_{ij}$ . The preferred distances  $\ell_{ij}$  are defined by the geometry of a spherical reference configuration for the vesicle. To ensure the two body interactions are represented by a unique index in  $\mathcal{Q}_1$  we adopt the convention that  $i < j$ .

The second energy term  $E_2$  accounts for curvature of the vesicle surface and is computed by summing over all local three body interactions  $\mathcal{Q}_2$  defined by the topology of the triangulated mesh. The energy penalizes the misalignment of the tangent vectors  $\boldsymbol{\tau}_{ij} = (\mathbf{X}^{[i]} - \mathbf{X}^{[j]})/r_{ij}$  and  $\boldsymbol{\tau}_{jk} = (\mathbf{X}^{[j]} - \mathbf{X}^{[k]})/r_{jk}$ . In the set of indices in  $\mathcal{Q}_2$  it is assumed that the point with index  $j$  is always adjacent to both  $i$  and  $k$ . To ensure the three body interactions are represented by a unique index in  $\mathcal{Q}_2$  we adopt the convention that  $i < k$ .

To obtain a triangulated mesh which captures the shape of a vesicle having a spherical geometry we start with an icosahedron which is circumscribed by a sphere of a given radius. We use the faces of the icosahedron as an initial triangulated mesh. To obtain a mesh which better approximates the sphere we bisect the three edges of each triangular face to obtain four sub-triangles. The newly introduced vertices are projected radially outward to the surface of the sphere. The process is then repeated recursively to obtain further refinements of the mesh. This yields a high quality mesh for spherical geometries. We use a vesicle represented by a mesh obtained using two levels of recursive refinement. The recursive generation procedure and the mesh used to represent a vesicle is shown in Figure 6.2.

We investigate the response of the vesicle to oscillatory shear stresses applied with time-varying rate  $\dot{\gamma} = \dot{\gamma}^0 \cos(\omega t)$ . We consider a dilute regime in which it is sufficient to study a single polymerized vesicle subject to the oscillatory shear. The effective stress tensor

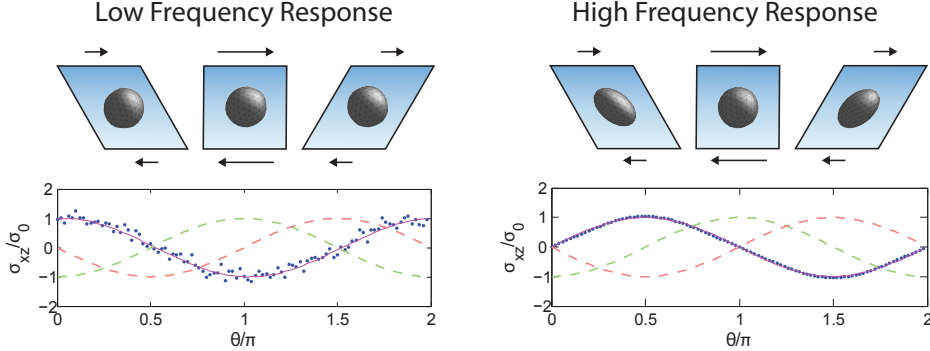


FIG. 6.3. *Polymerized Vesicle subject to Oscillatory Shear.* (left) At low frequencies the distortion of the vesicle shape is rather small and masked by the thermal fluctuations. When averaging over many cycles, the vesicle stress follows closely in phase with the applied shear stress plotted in green. (right) At high frequencies the distortion of the vesicle shape is significant and the vesicle stress follows closely the strain plotted in red. The particular low frequency responses shown are for  $\omega = 3.9294 \times 10^{-3} \text{ ns}^{-1}$ ,  $\dot{\gamma} = 1.9647 \times 10^{-3} \text{ ns}^{-1}$ ,  $\sigma_0 = 3.7114 \times 10^8 \text{ amu} \cdot \text{nm}^{-1} \cdot \text{ns}^{-2}$ . The particular high frequency responses shown are for  $\omega = 1.2426 \times 10^2 \text{ ns}^{-1}$ ,  $\dot{\gamma} = 6.2129 \times 10^1 \text{ ns}^{-1}$ ,  $\sigma_0 = 4.6314 \times 10^{10} \text{ amu} \cdot \text{nm}^{-1} \cdot \text{ns}^{-2}$ . The vesicle configurations for each frequency is shown for  $\theta = 1.6\pi, 0.0\pi$  and  $0.4\pi$  respectively left to right.

associated with the vesicle suspension at a given time  $\sigma(t)$  is estimated using the approach discussed in Section 5.

As a measure of the material response, we consider the dynamic complex modulus  $G(\omega) = G'(\omega) + iG''(\omega)$ , whose components are defined from measurements of the stress as the least-squares fit of the periodic stress component  $\sigma_{xz}(t)$  by the function  $g(t) = G'(\omega)\gamma^0 \cos(\omega t) + G''(\omega)\gamma^0 \sin(\omega t)$ . This offers one characterization of the response of the material to oscillating applied shear stresses and strains as the frequency  $\omega$  is varied. The  $G'$  is referred to as the Elastic Storage Modulus and  $G''$  is referred to as the Viscous Loss Modulus. These dynamic moduli are motivated by considering the linear response of the stress components  $\sigma_{xz}(t)$  to applied stresses and strains. For many materials linearity holds to a good approximation over a wide range of frequencies provided the amplitudes of the applied stresses and strains are not too large [47].

To estimate the dynamic complex modulus in practice, the least-squares fit is performed for  $\sigma_{xz}(t)$  over the entire stochastic trajectory of a simulation (after some transient period). Throughout our discussion we refer to  $\theta = \omega t$  as the phase of the periodic response. In our simulations, the maximum strain over each period was chosen to always be half the periodic unit cell in the x-direction, corresponding to a strain amplitude of  $\gamma^0 = \frac{1}{2}$ . This was achieved by adjusting the shear rate amplitude for each frequency using the expression  $\dot{\gamma}^0 = \gamma^0 \omega$ .

We performed simulations subjecting the vesicle to shear over a wide range of frequencies. At low frequency the distortion of the vesicle shape was found to be small and masked by thermal fluctuations when averaged over hundreds of periods. At low frequency the vesicle stresses appear to have sufficient time to equilibrate to the applied shear stresses. This is manifested in  $\sigma_{xz}(t)$ , which is seen to track very closely the applied stress, see Figure 6.3. At high frequencies, the vesicle shape was found to become visibly distorted and the vesicle stresses did not appear to have sufficient time to equilibrate to the applied shear stresses. These distortions can be seen in the configurations for phase  $\theta = 1.6, 0.4$ . The  $\sigma_{xz}$  is seen to be out of phase with the applied stresses but in phase with respect to the applied strain, see Figure 6.3.

These responses can be quantitated by considering the dynamic moduli. From the simulations, it is seen for the low frequency responses that the vesicle stress follows closely



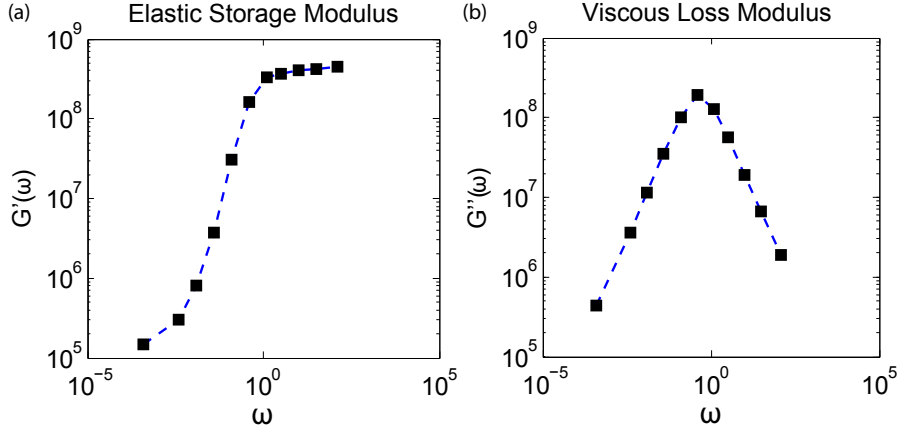


FIG. 6.4. *Vesicle Frequency Response : Dynamic Moduli.* The Elastic Storage Modulus  $G'(\omega)$  is shown in panel (a) and the Viscous Loss Modulus  $G''(\omega)$  is shown in panel (b).

the applied stress. It is also found that the Viscous Loss Modulus is significantly larger than the Elastic Storage Modulus. For the high frequency response, it was found that the Elastic Storage Modulus increases and is eventually much larger than the Viscous Loss Modulus. It was also found that the Viscous Loss Modulus exhibited a non-monotonic behavior at intermediate frequencies, see Figure 6.4. A description of the parameters and specific values used in the simulations can be found in Table 6.3 and Table 6.4.

Parameter	Description
$N$	Number of mesh points in each direction.
$\Delta x$	Mesh spacing.
$L$	Domain size in each direction.
$T$	Temperature.
$k_B$	Boltzmann's constant.
$\mu$	Dynamic viscosity of the solvent fluid.
$\rho$	Mass density of the solvent fluid.
$K_1$	Vesicle bond stiffness.
$K_2$	Vesicle bending stiffness.
$D$	Vesicle diameter.
$\omega$	Frequency of oscillating shearing motion.
$\theta$	Phase of the oscillatory motion, $\theta = \omega t$ .
$\dot{\gamma}$	Shear rate.
$\dot{\gamma}^0$	Shear rate amplitude.
$\gamma$	Strain rate.
$\gamma^0$	Strain rate amplitude.

TABLE 6.3

*Description of the parameters used in simulations of the polymerized vesicle.*

Parameter	Value
$N$	27
$\Delta x$	7.5 nm
$L$	$2.025 \times 10^2$ nm
$T$	300 K
$k_B$	$8.3145 \times 10^3$ nm <sup>2</sup> · amu · ns <sup>-2</sup> · K <sup>-1</sup>
$\mu$	$6.0221 \times 10^5$ amu · cm <sup>-1</sup> · ns <sup>-1</sup>
$\rho$	$6.0221 \times 10^2$ amu · nm <sup>-3</sup>
$K_1$	$2.2449 \times 10^7$ amu · ns <sup>-2</sup>
$K_2$	$8.9796 \times 10^7$
$D$	50 nm

TABLE 6.4

*Fixed values of the parameters used in simulations of the polymerized vesicle.*

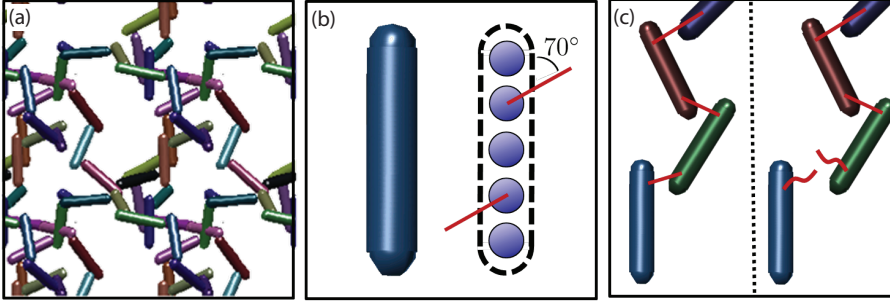


FIG. 6.5. *Microstructure of the Gel-like Material. (a) The microstructure of the gel is comprised of polymeric chains which bind together. (b) The polymeric chains are each comprised of five control points and each have specialized binding sites at the second and fourth control point. (c) The inter-polymer bonds have a preferred extension and angle. When an inter-polymer bond is strained beyond 50% of its preferred rest length, the bond breaks irreversibly.*

**6.3. Application III: Aging of the Shear Viscosity of a Gel-like Material.** As a further demonstration of how the computational methods can be used, we investigate the aging of a gel-like material subject to shear. The methods are used to study how the shear viscosity changes over time as the gel is subjected to shear at a constant rate.

The gel-like material is modeled as a collection of polymer chains which are able to bond together at two specialized sites along the chain, see Figure 6.5. The energy associated with the mechanics of the individual polymer chains and the bonds which they form are given by

$$(6.9) \quad \phi_1(r) = \frac{1}{2}K_1(r - r_{0,1})^2$$

$$(6.10) \quad \phi_2(\boldsymbol{\tau}_1, \boldsymbol{\tau}_2) = \frac{1}{2}K_2|\boldsymbol{\tau}_1 - \boldsymbol{\tau}_2|^2$$

$$(6.11) \quad \phi_3(r) = \sigma^2 K_3 \exp\left[-\frac{(r - r_{0,3})^2}{2\sigma^2}\right]$$

$$(6.12) \quad \phi_4(\theta) = -K_4 \cos(\theta - \theta_{0,4}).$$

The  $r$  is the separation distance between two control points,  $\theta$  is the bond angle between three control points, and  $\boldsymbol{\tau}$  is a tangent vector along the polymer chain, see Figure 6.5.

The  $\phi_1$  energy accounts for stretching of a bond within a polymer chain from its preferred extension  $r_{0,1}$ . The  $\phi_2$  energy accounts for bending of the polymer chain locally. To account for interactions at the specialized binding sites of the polymers the potentials  $\phi_3$  and  $\phi_4$  are introduced. The potential  $\phi_3$  gives the energy of the bond between the two polymer chains and penalizes deviation from the preferred bond extension  $r_{0,3}$ . The exponential of  $\phi_3$  is introduced so that the resistance in the bond behaves initially like a harmonic bond but decays rapidly to zero when the bond is stretched beyond the length  $\sigma$ . The potential  $\phi_4$  gives the energy for the preferred bond angle when two of the polymer chains are bound together.

The total energy of the system is given by

$$(6.13) \quad \Phi[\mathbf{X}] = E_1[\mathbf{X}] + E_2[\mathbf{X}] + E_3[\mathbf{X}] + E_4[\mathbf{X}]$$

$$(6.14) \quad E_1[\mathbf{X}] = \sum_{(i,j) \in \mathcal{Q}_1} \phi_1(r_{ij}), \quad E_2[\mathbf{X}] = \sum_{(i,j,k) \in \mathcal{Q}_2} \phi_2(\boldsymbol{\tau}_{ij}, \boldsymbol{\tau}_{jk})$$

$$(6.15) \quad E_3[\mathbf{X}] = \sum_{(i,j) \in \mathcal{Q}_3} \phi_3(r_{ij}), \quad E_4[\mathbf{X}] = \sum_{(i,j,k) \in \mathcal{Q}_4} \phi_4(\theta_{ijk}).$$

The sets  $\mathcal{Q}_k$  define the interactions according to the structure of the individual polymer chains and the topology of the gel network. When bonds are stretched beyond the critical

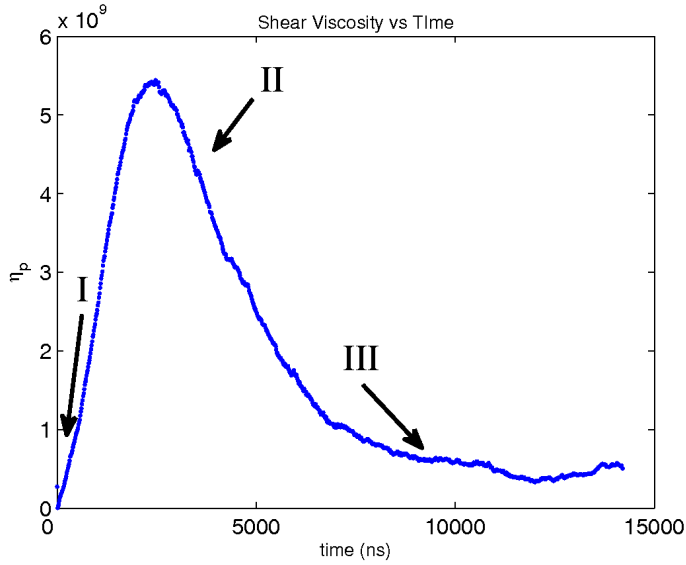


FIG. 6.6. *Aging of the Shear Viscosity Over Time.* The aging of the shear viscosity exhibits roughly three stages, labeled by I, II, III. In the first stage, the gel-network maintains its integrity. Contributions to the shear viscosity arise from stretching of the inter-polymer and intra-polymer bonds. In the second stage, the inter-polymer bonds of the gel-network break. The polymers are then free to align with the direction of shear which results in relaxation of the intra-polymer bonds to their preferred rest-length. In the third stage, the contributions to the shear viscosity arise from thermal fluctuations that drive transient misalignments of the polymers with the direction of shear. These stages are each discussed in more detail in Section 6.3.

length  $3\sigma$  they are broken irreversibly, which results in the sets  $\mathcal{Q}_3$  and  $\mathcal{Q}_4$  being time dependent.

To study the rheological response of the gel-like material the system is subjected to shear at a constant rate. To obtain an effective macroscopic stress  $\sigma_p$  for the system, we use the approach from Section 5. To characterize the rheology of the gel, we consider the shear viscosity defined by

$$(6.16) \quad \eta_p = \sigma_p^{(s,v)} / \dot{\gamma}.$$

The  $\dot{\gamma}$  is the rate of the applied shear. In the notation, the superscript  $(s, v)$  indicates the tensor component with the index  $s$  corresponding to the direction of shear and the index  $v$  corresponding to the direction of shear induced velocity. The contributions of the solvent fluid to the shear viscosity are assumed to be Newtonian and can be considered separately [12].

To investigate how the shear viscosity of the gel behaves over time, multiple simulations were performed starting from an undisturbed configuration of the gel network. A shear was then applied to the unit cell boundary to induce a shear deformation of the network. The shear deformation over time resulted in the breakage of bonds of the gel network. To investigate how the macroscopic material properties depend on the reorganization of the polymer chains, we considered the shear viscosity over time.

From the simulations, an interesting behavior was found. The material initially exhibited an increased shear viscosity before eventually settling down to a steady-state value. It was found that the responses of the gel-like material to shear can be roughly divided into three stages. In the first, there is an initial increase of the shear viscosity which can be attributed to the stretching of the inter-chain bonds between the polymer chains and the intra-chain bonds within each polymer chain. This occurs as the gel as a whole is strained for a relatively short

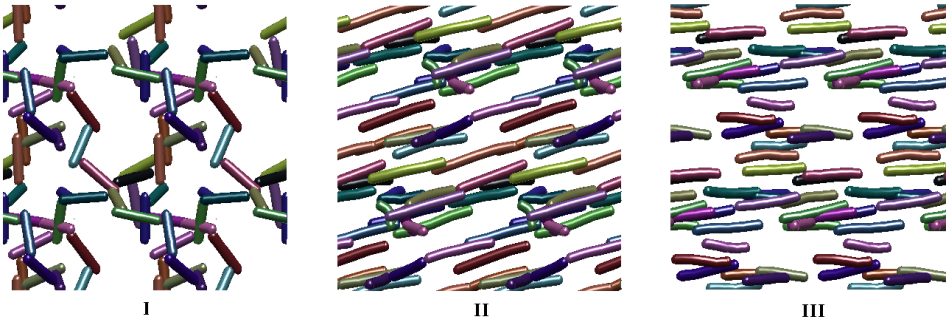


FIG. 6.7. *Microstructure Configurations for the Gel-like Material.* Configurations of the microstructure are shown as the gel ages for each of the three stages discussed in Section 6.3. The times shown in these figures from left to right are  $t = 0$  ns,  $t = 2844$  ns,  $t = 7111$  ns.

period. The bonds between the polymer chains are observed to break with the remaining contributions to the stress arising from the shear stresses of the fluid which stretch the polymer chains. The shear viscosity in this stage and the microstructure of the gel are shown in the regions labeled by I in Figure 6.6 and Figure 6.7.

In the second stage, the individual polymer chains are seen to rotate and to start aligning with the direction of the shear. As a result of the intra-chain restoring forces the strain of the individual polymer chains is also seen to relax. The increased alignment and reduction of strain of the polymer chains yields an overall decrease in the forces transmitted in the direction of the shear gradient. Consequently, the shear viscosity begins to decrease, see the regions labeled by II in Figure 6.6 and Figure 6.7.

In the third, and last stage, the chains eventually settle into a statistical steady-state in which the thermal fluctuations drive the chains to misalign transiently with the direction of shear. These misaligned excursions by the polymer chains result on average in non-negligible forces transmitted in the direction of the shear gradient. As a consequence, the shear viscosity has a non-zero steady-state value. This is shown in the regions labeled by III in Figure 6.6 and Figure 6.7. Similar aging phenomenon is seen for many different types of soft materials and complex fluids and is often referred to as “thixotropy”, see [10, 12, 20]. For the specific physical parameters used in these simulations see Table 6.5 and 6.6.

The modeling approach presented here, along with the computational methods, allow for other types of phenomena to be studied. This includes looking at the case in which the bonds between the polymer chains are able to reform. An interesting investigation in this case would be to study the kinetics and organization of the gel network when subject to both bond breaking and bond formation when the shear is greatly decreased or arrested for periods of time.

The computational methods also provide a straight-forward means to incorporate active forces operating on the filaments of the gel network. This could be useful in the study of biological materials, such as actin where motor proteins act like active cross-linkers to slide filaments past one another [18, 38, 43]. These effects could readily be taken into account in such simulations.

Parameter	Description
$N$	Number of mesh points in each direction.
$\Delta x$	Mesh spacing.
$\Delta t$	Time step.
$L$	Domain size in each direction.
$T$	Temperature.
$k_B$	Boltzmann's constant.
$\mu$	Dynamic viscosity of the solvent fluid.
$\rho$	Mass density of the solvent fluid.
$\dot{\gamma}$	Shear rate.
$N_p$	Number of polymer chains.
$N_s$	Number of control points per polymer chain.
$r_p$	Polymer effective cylindrical radius.
$K_1$	Stiffness of the bonds of the polymer chain.
$r_{0,1}$	Rest length of the bonds of the polymer chain.
$K_2$	Bending stiffness of the polymer chain.
$K_3$	Stiffness of the bonds at a polymer binding site.
$r_{0,3}$	Rest length of the bond at a polymer binding site.
$K_4$	Bending stiffness of the bond at a polymer binding site.
$\theta_{0,4}$	Preferred angle of a bond at a polymer binding site.

TABLE 6.5

*Description of the parameters used in simulations of the gel-like material.*

Parameter	Value
$N$	72
$\Delta x$	11.25 nm
$\Delta t$	1.4222 ns
$L$	810 nm
$T$	300 K
$k_B$	$8.3145 \times 10^3 \text{ nm}^2 \cdot \text{amu} \cdot \text{ns}^{-2} \cdot \text{K}^{-1}$
$\mu$	$6.0221 \times 10^5 \text{ amu} \cdot \text{cm}^{-1} \cdot \text{ns}^{-1}$
$\rho$	$6.0221 \times 10^2 \text{ amu} \cdot \text{nm}^{-3}$
$\dot{\gamma}$	$1.2 \times 10^{-3} \text{ ns}^{-1}$
$N_p$	110
$N_s$	5
$r_p$	15 nm
$K_1$	$2.9932 \times 10^5 \text{ amu} \cdot \text{ns}^{-2}$
$r_{0,1}$	30 nm
$K_2$	$2.9932 \times 10^8$
$K_3$	$2.9932 \times 10^5 \text{ amu} \cdot \text{ns}^{-2}$
$r_{0,3}$	30 nm
$K_4$	$2.9932 \times 10^8$
$\theta_{0,4}$	$70^\circ$

TABLE 6.6

*Fixed values of the parameters used in simulations of the gel-like material.*

**7. Conclusions.** We have presented an approach for incorporating shear into fluctuating hydrodynamics methods for studies of the rheological responses of complex fluids and soft materials. We have shown how generalized periodic boundary conditions and stochastic numerical methods can be formulated to handle shear. We have shown that formulating the momentum conservation equations in a moving frame of reference that tracks the distortion of the unit cell provides a number of advantages. We have furthermore presented some analysis of the time-dependent discretization methods to show how stochastic driving fields can be introduced to satisfy a fluctuation-dissipation balance despite truncation errors. As can be seen from the example applications presented, the introduced methods provide a number of ways to simulate phenomena relevant to rheological responses. We expect the presented approaches to be useful in adopting fluctuating hydrodynamics descriptions to investigate models and phenomena relevant in studies of complex fluids and soft materials.

**8. Software.** A related simulation package for the discussed methods can be found at <https://github.com/atzberg/mango-selm>. This includes an interface to readily setup models and perform simulation studies. Additional tutorials, videos, and other information can be found at <http://atzberger.org/>.

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**Appendix A. A Fluctuation-Dissipation Principle for Time-Dependent Operators.** Consider the stochastic process given by

$$(A.1) \quad d\mathbf{z}_t = L(t)\mathbf{z}_t dt + Q(t)d\mathbf{B}_t$$

$$(A.2) \quad G(t) = QQ^T.$$

We now establish the following fluctuation-dissipation relation

$$(A.3) \quad G(t) = -L(t)\bar{C} - \bar{C}^T L(t)^T.$$

This relates the covariance  $G(t)$  of the stochastic driving field to a time-dependent dissipative operator  $L(t)$  and a time-independent equilibrium covariance  $\bar{C}$ . We show that this relation allows for  $G(t)$  to be chosen to ensure that the stochastic dynamics exhibits at statistical steady-state equilibrium fluctuations with the specified covariance  $\bar{C}$ .

Let the covariance at time  $t$  be denoted by

$$(A.4) \quad C(t) = \langle \mathbf{u}(t)\mathbf{u}(t)^T \rangle.$$

By Ito’s Lemma the second moment satisfies

$$(A.5) \quad dC(t) = \left( L(t)C(t) + C(t)^T L(t)^T + G(t) \right) dt.$$

It will be convenient to express this equation by considering all of the individual entries of the matrix  $C(t)$  collected into a single column vector denoted by  $\mathbf{c}_t$ . Similarly, for covariance

matrix  $G(t)$  we denote the column vector of entries by  $\mathbf{g}_t$  and for  $\bar{C}$  by  $\bar{\mathbf{c}}$ . Since the products  $L(t)C(t)$  and  $C(t)^T L(t)^T$  are both linear operations in the entries of the matrix  $C(t)$  we can express this in terms of multiplication by of a matrix  $A(t)$  acting on  $\mathbf{c}_t$ .

This notation allows for equation A.5 to be expressed equivalently as

$$(A.6) \quad d\mathbf{c}_t = (A(t)\mathbf{c}_t + \mathbf{g}_t) dt.$$

The equation A.5 can be solved formally by the method of integrating factors to obtain

$$(A.7) \quad \mathbf{c}_t = e^{\Xi(0,t)} \mathbf{c}_0 + \int_0^t e^{\Xi(s,t)} \mathbf{g}_s ds$$

where  $\Xi(s, t) = \int_s^t A(r) dr$ .

The fluctuation-dissipation relation given by equation A.3 is equivalent to choosing

$$(A.8) \quad \mathbf{g}_s = -A(s)\bar{\mathbf{c}}.$$

For this choice, a useful identity is

$$(A.9) \quad e^{\Xi(s,t)} \mathbf{g}_s = \frac{\partial}{\partial s} e^{\Xi(s,t)} \bar{\mathbf{c}}.$$

Substitution into equation A.7 gives

$$(A.10) \quad \mathbf{c}_t = e^{\Xi(0,t)} \mathbf{c}_0 + \left( e^{\Xi(t,t)} - e^{\Xi(0,t)} \right) \bar{\mathbf{c}}.$$

Now, if  $L(t)$  is negative definite uniformly in time,  $\mathbf{v}^T L(t) \mathbf{v} < \alpha_0 < 0$ , then  $A(t)$  is also uniformly negative definite. This implies that

$$(A.11) \quad \lim_{t \rightarrow \infty} e^{\Xi(0,t)} = 0.$$

Taking the limit of both sides of equation A.10 and using equation A.11 yields

$$(A.12) \quad \lim_{t \rightarrow \infty} \mathbf{c}_t = \bar{\mathbf{c}}.$$

This shows that the stochastic driving field with covariance given by equation A.3 yields equilibrium fluctuations with covariance  $\bar{C}$ . This extends the fluctuation-dissipation relation to the case of time-dependent operators.

**Appendix B. Coupling Kernel : Peskin  $\delta_a$ -Function .** We utilize a similar kernel function to the one which was used in the Immersed Boundary Method to represent structures [7, 46]. This is given by

$$(B.1) \quad \phi(r) = \begin{cases} 0 & , \text{ if } r \leq -2 \\ \frac{1}{8} (5 + 2r - \sqrt{-7 - 12r - 4r^2}) & , \text{ if } -2 \leq r \leq -1 \\ \frac{1}{8} (3 + 2r + \sqrt{1 - 4r - 4r^2}) & , \text{ if } -1 \leq r \leq 0 \\ \frac{1}{8} (3 - 2r + \sqrt{1 + 4r - 4r^2}) & , \text{ if } 0 \leq r \leq 1 \\ \frac{1}{8} (5 - 2r - \sqrt{-7 + 12r - 4r^2}) & , \text{ if } 1 \leq r \leq 2 \\ 0 & , \text{ if } 2 \leq r. \end{cases}$$

For three dimensional systems the function  $\delta_a$  is given by

$$(B.2) \quad \delta_a(\mathbf{r}) = \frac{1}{a^3} \phi\left(\frac{\mathbf{r}^{(1)}}{a}\right) \phi\left(\frac{\mathbf{r}^{(2)}}{a}\right) \phi\left(\frac{\mathbf{r}^{(3)}}{a}\right),$$

where the superscript indicates the index of the vector component. To maintain good numerical properties, the particles are restricted to sizes  $a = n\Delta x$ , where  $n$  is a positive integer. For a derivation and a detailed discussion of the properties of this kernel function, see [46, 7, 15].

### Appendix C. Table.

Parameter	Description
$N_A$	Avogadro's number.
amu	Atomic mass unit.
nm	Nanometer.
ns	Nanosecond.
$k_B$	Boltzmann's Constant.
$T$	Temperature.
$\eta$	Dynamic viscosity of water.
$\gamma_s = 6\pi\eta R$	Stokes' drag of a spherical particle.

Parameter	Value
$N_A$	$6.02214199 \times 10^{23}$ .
amu	$1/10^3 N_A$ kg.
nm	$10^{-9}$ m.
ns	$10^{-9}$ s.
$k_B$	$8.31447 \times 10^3$ amu nm <sup>2</sup> /ns <sup>2</sup> K.
$T$	300K.
$\eta$	6.02214199 amu/cm ns.