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Systematic derivation of hydrodynamic equations for viscoelastic phase separation

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Abstract

We present a detailed derivation of a simple hydrodynamic two-fluid model, which aims at the description of the phase separation of non-entangled polymer solutions, where viscoelastic effects play a role. It is directly based upon the coarse-graining of a well-defined molecular model, such that all degrees of freedom have a clear and unambiguous molecular interpretation. The considerations are based upon a free-energy functional, and the dynamics is split into a conservative and a dissipative part, where the latter satisfies the Onsager relations and the second law of thermodynamics. The model is therefore fully consistent with both equilibrium and non-equilibrium thermodynamics. The derivation proceeds in two steps: firstly, we derive an extended model comprising two scalar and four vector fields, such that inertial dynamics of the macromolecules and of the relative motion of the two fluids is taken into account. In the second step, we eliminate these inertial contributions and, as a replacement, introduce phenomenological dissipative terms, which can be modeled easily by taking into account the principles of non-equilibrium thermodynamics. The final simplified model comprises the momentum conservation equation, which includes both interfacial and elastic stresses, a convection–diffusion equation where interfacial and elastic contributions occur as well, and a suitably convected relaxation equation for the end-to-end vector field. In contrast to the traditional two-scale description that is used to derive rheological equations of motion, we here treat the hydrodynamic and the macromolecular degrees of freedom on the same basis. Nevertheless, the resulting model is fairly similar, though not fully identical, to models that have been discussed previously. Notably, we find a rheological constitutive equation that differs from the standard Oldroyd-B model. Within the framework of kinetic theory, this difference may be traced back to a different underlying statistical-mechanical ensemble that is used for averaging the stress. To what extent the model is able to reproduce

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the full phenomenology of viscoelastic phase separation is presently an open question, which shall be investigated in the future.

Keywords: viscoelastic phase separation, two-fluid model, GENERIC, Poisson brackets, coarse-graining, rheology

1. Introduction

1.1. General background

The kinetics of first-order phase transitions is a fascinating subject of non-equilibrium thermodynamics, which has found considerable interest in the last decades [1]. Simple situations are meanwhile well understood in terms of ‘model A’, ‘model B’, ‘model H’, etc [2, 3]. We are here interested in a generalization of ‘model H’, where the order parameter is conserved and is, beyond diffusion, convectively coupled to hydrodynamic flow, while acting back on that flow via bulk and interfacial stresses. The prototypical physical system that is described by these equations is an unmixing binary fluid.

The situation becomes much more involved if one of the unmixing species is macromolecular, such that the time scale of molecular relaxation becomes comparable to that of domain coarsening. The interplay of the intramolecular degrees of freedom with the macroscopic unmixing results in a plethora of interesting and non-trivial phenomena, which were first discovered by Tanaka [4], given the name ‘viscoelastic phase separation’, and then extensively studied by him and his collaborators [5–14]; reference [10] provides a review. The crucial aspect seems to be *dynamical asymmetry*, meaning that the structural relaxation of one component is much slower than that of the other one. Indeed, a very recent numerical investigation by Tateno and Tanaka [14] reveals the phenomenon for a phase-separating colloidal dispersion. For macromolecular systems this implies that they do not necessarily have to be entangled. On the other hand, though, non-entangled systems tend to exhibit only small to moderate dynamic asymmetry, such that they show the typical phenomena of viscoelastic phase separation only to a small (or even unobservable) degree. At any rate, the reader should be aware that, for the purposes of the present paper, we mean by the term ‘viscoelastic phase separation’ not necessarily the set of characteristic observations described in e.g. reference [10], but rather simply phase separation in a system where coupling to viscoelasticity plays a role.

The attempts to describe the phenomena theoretically by suitably combining ‘model H’ with viscoelastic models such as the upper convected Maxwell model, or Oldroyd-B [15, 16] are nearly as old as their experimental investigation. Such models, which we will call here ‘viscoelastic model H’ (VEMH) systems, have been considered in nearly all of the papers cited above [4, 6–12] as well as in references [17, 18], mainly building on older work by Doi and Onuki [19] and Milner [20]. While these studies have undoubtedly advanced our understanding significantly, we nevertheless believe that

not all problems have fully been solved already. For this reason, we wish to contribute to the field by developing our own VEMH, and this is the main purpose of the present paper. As in most of the existing models, we will base our reasoning on a so-called ‘two-fluid model’, where each of the components is assigned its own velocity flow field. The central guiding principle is that the formulation should permit a direct comparison with microscopic or mesoscopic computer simulations, where the polymer conformations as well as the polymer and solvent velocities appear explicitly. In other words, it should be possible to ‘measure’ each and every dynamical variable that appears in the theory.

Before we embark on the details of the derivation, we first want to explain why we believe that a new and fresh look at the problem may be helpful. We therefore first outline the problems that, in our opinion, still affect the existing literature. On the one hand, we believe that the existing VEMHs are in some aspects a bit unsatisfactory in terms of their physical interpretation, and we will explain these aspects in subsection 1.2. On the other hand, we believe that the existing standard methods to derive rheological constitutive equations have a very subtle conceptual problem, and we will try to elucidate this in subsection 1.3. Our work attempts to address both types of difficulty. We therefore present not only a new set of VEMH equations, which turns out to be fairly simple, and quite similar to existing sets, but also a somewhat unconventional method of derivation, which, to the best of our knowledge, has not yet been applied to the VEMH problem, and which may turn out to be useful even beyond the VEMH context, i.e. for rheology in general. The general ‘philosophy’ of our strategy will therefore be outlined in subsection 1.4. Subsection 1.5 will then provide an overview over the remainder of the paper.

1.2. Physical problems of existing VEMHs

In reference [18], which, to our knowledge, is the most recent existing VEMH model, Zhou *et al* start from a predecessor model, due to Tanaka and coworkers [11] and criticize it as violating the second law. They then modify the set of equations in such a way that they are strictly and provenly dissipative. In the typical isothermal setting of theories of phase separation, this means that the associated free energy functional decreases monotonously with time. This is of course a big advantage, and a property that a physically sound model should certainly satisfy. However, another condition for soundness is that all terms in the equations should have clear and well-defined molecular counterparts, and that all contributions in the free energy should scale properly, as they are known from mechanics, thermodynamics, and polymer physics. We believe that the model

of reference [18] fails in that respect. The functional features a putative ‘bulk stress’ and a putative ‘shear stress’, where the ‘shear stress’ enters *linearly* but the ‘bulk stress’ *quadratically*. As stresses are essentially the same objects, regardless of whether they refer to volume or to shear deformation, the powers should rather be identical. Furthermore, it is not clear how these objects are related to the conformations of the macromolecules. From polymer physics, i.e., more precisely, the concept of entropic elasticity, it is known that, for small deformations and in the absence of excluded-volume interactions and entanglements, the elastic energy should scale quadratically with the molecular extension, or linearly with the conformation tensor, which is the tensor product of the molecule’s end-to-end vector with itself.

An even more subtle problem occurs in the model by Taniguchi and Onuki [17]. Here the elastic energy is based upon a tensor \mathbf{W} , whose meaning is explained in the paper by Milner [20] as a *strain*. The idea is to start from a set of phantom Gaussian chains, originally in equilibrium, which is being subjected to an affine deformation that may be parameterized by \mathbf{W} . The partition function before and after the deformation may be calculated, which in turn permits the calculation of the free energy as function of \mathbf{W} . The harmonic approximation to this expression is the elastic free energy appearing in reference [17]. The problem about this is that \mathbf{W} is *not an observable*, meaning that its value cannot be straightforwardly inferred from the configurations of polymer chains in, say, a molecular dynamics (MD) simulation. For a solid, this would be possible, since in this case undeformed reference positions of all the atoms are known, such that the strain can be measured by comparing the actual atom positions with the reference positions. In the present situation, however, we have a fluid, such that a reference configuration simply does not exist. We speculate that it might perhaps be possible to assign a well-defined thermodynamic meaning to \mathbf{W} in analogy to, say, a chemical potential, and to construct advanced sampling schemes to estimate its value; however, at present this must be viewed as a completely unsolved problem. For the purposes of the present paper, we can therefore conclude that the formulation in terms of \mathbf{W} is not very suitable for a direct comparison with microscopic or mesoscopic simulations.

Finally, the work by Elafif *et al* [21] only discusses the overall structure of the theory but does not specify an explicit form of the elastic energy.

1.3. Rheological modelling

As far as we know, there exist two major streams of research in the goal to construct rheological models or constitutive equations for complex fluids. These are nicely separated in terms of the two volumes of the monograph by Bird *et al* [15, 16]. On the one hand there is the ‘phenomenological paradigm’ (volume 1). Here one starts from known conservation laws and symmetry principles, which turn out to significantly restrict the form of the equation of motion for the stress. Nevertheless, a significant freedom remains, and this is used to postulate simple assumptions (like linear relaxation) or to

reproduce experiments. Here one either deliberately refrains from attempting a molecular interpretation, or invokes molecular kinetic theory, which is however the subject of volume 2. Interestingly, such ambiguities, which result in a certain freedom of choice, occur not only in the construction of rheological constitutive equations but also in the definition of two-fluid models [22]. In both cases, the ambiguity occurs only on the purely phenomenological level, while it is removed as soon as a well-defined molecular picture is invoked. For rheology, this is known from kinetic theory [16], while for the two-fluid model case the same will become apparent in the course of this paper.

The kinetic-theory approach to rheology (volume 2) may be called the ‘distribution function paradigm’. Here one considers the Brownian dynamics of model chains (e.g. harmonic or FENE dumbbells, Gaussian chains, etc) in an external flow, within the framework of a Fokker–Planck equation (FPE), whose solution is a time-dependent distribution function in conformation space. This function may then be used for defining time-dependent thermal averages of observables like the conformation tensor or the virial. The resulting expression of the stress is then fed into the momentum equation, while the FPE results in relaxation equations for observables (e.g. the conformation tensor components) that are needed to obtain a closed set. By construction, the method does provide a clear molecular interpretation.

The conceptual problem that we see in that approach lies in the fact that the statistical-mechanical averages are done without any *constraint*. To elucidate what we mean by this point, let us, for a moment, go back to the simple hydrodynamics of a monatomic fluid, and its root in statistical mechanics. The idea is that we may consider a small volume element that, despite its smallness, contains a large number of particles such that we may reasonably treat it in terms of statistical physics. Furthermore, hydrodynamics assumes that, within the volume element, all variables are in *local equilibrium*, *except* the hydrodynamic variables like the mass (or particle number), the total energy, and the total momentum. These latter variables may therefore be viewed as *constraints that define the appropriate thermodynamic ensemble* for the local volume element. Now, if we introduce, say, the chain conformation tensor as an additional variable into the hydrodynamic description, then, in our opinion, this variable should occur as a corresponding additional constraint in the definition of the thermodynamic ensemble. However, here one should watch out that only *independent* variables are used as constraints. In other words: the stress should not be calculated as a full average over all chain conformations, but rather as a restricted average over the constrained ensemble. In this context, note that in standard statistical physics one typically ignores this problem by relying on the equivalence of constrained and non-constrained ensembles. However, this equivalence holds only in the asymptotic limit of infinite system size, with error terms which scale linearly with the inverse number of the involved degrees of freedom. To extend this notion down to the scale of a single macromolecule seems somewhat problematic, and we believe that this is more than a

petty formality. Indeed, the different ensembles do result in different equations of motion on the macroscale. In more explicit terms, this difference is worked out in appendix C. As one sees there, the difference boils down, for a Hookean dumbbell, to the difference between *mechanical* and *thermal* equilibrium, which is substantial for a strongly fluctuating soft-matter system like a polymer solution. We believe that a consistent way to treat the effects of fluctuations is *not* by doing an unconstrained average (as in the derivation of the standard Oldroyd-B model) but rather by augmenting *all* macroscopic equations with Langevin noise. As we will see below, the equations of motion that result from the constrained average (see appendix C) are *identical* to those that are derived in the present paper, using a completely different approach—but different from the standard Oldroyd-B model. In the present paper, we ignore Langevin noise in the macroscopic equations and defer that aspect to future work.

1.4. Basic ‘philosophy’ of our model

The route that we take is somewhat different from the usual rheological literature, and it may be called a ‘coarse-graining paradigm’. Its spirit is similar (although technically simpler) to analogous developments in the theory of liquid crystals [23]. We start from a microscopic model and then define microscopic expressions for various fields. To give an example for illustration: for a monatomic fluid of particles located at positions \mathbf{r}_i , the expression for the particle number density at position \mathbf{r} would be $\sum_i \delta(\mathbf{r} - \mathbf{r}_i)$. We then subject that system to coarse-graining and derive corresponding field-theoretic equations of motion. This is (roughly spoken—for details see below) done by (i) mapping the microscopic Hamiltonian onto the corresponding field-theoretic one; (ii) doing an analogous mapping from a microscopic dissipation rate to a field-theoretic one; (iii) postulating a dissipative Hamiltonian system; (iv) finding the Hamiltonian part of the dynamics via the Poisson brackets of the fields, which in turn are found via reference to the microscopic counterparts; and (v) reading off the dissipative part of the dynamics directly from the dissipation rate. After that, several fields are identified as fast variables and therefore eliminated adiabatically, where unknown terms are replaced by phenomenological dissipative terms. At the end, we arrive at a model that looks similar to the existing VEMH equations, but differs in various subtle aspects.

We believe that this is a quite powerful approach and has potential beyond the immediate application to the VEMH problem. The Poisson bracket formalism has proven extremely fruitful in hydrodynamics [24–30]; readers not familiar with that formalism are advised to briefly consult [appendices A and B](#). Due to the construction via a dissipative Hamiltonian system, whose equation of motion can be found as a by-product of the GENERIC formalism [31–34], we automatically make sure that the second law is satisfied. Fully in line with the arguments put forward in reference [18], we consider this as very important both from the point of view of fundamental physical consistency, but also from the point of view of mathematical analysis and derivation of stable and convergent numerical algorithms [35, 36].

The hydrodynamic model that we construct in the first step (before the adiabatic elimination of the fast variables) comprises two scalar and four vector fields, which are chosen in order to be able to take full advantage of Hamiltonian dynamics and the Poisson bracket formalism. The fields are (i) the mass densities of the two components (solvent and polymer), (ii) the two associated momentum densities (note we study a two-fluid model), (iii) a vector field of molecular end-to-end vectors, and (iv) an associated momentum density. The fast variables that we eliminate in the second step are the relative velocity, the internal molecular momentum, plus the fluctuations of the total density (and the associated longitudinal modes).

The elastic Hamiltonian is quadratic, but not in terms of the conformation tensor but rather the end-to-end vector, which we use as the elementary field to describe the internal relaxation of the macromolecules. The equation of motion for the end-to-end vector can, in the final stage, be transformed to an equation for the conformation tensor. Except for constant prefactors, the stress tensor is just the product of the conformation tensor and the polymer density (which makes perfect sense, since there should be no elastic stress in spatial regions where there is no polymer). All in all, our new model has the big advantage that (i) all degrees of freedom have a well-defined molecular meaning, and (ii) its derivation has a solid foundation in Hamiltonian dynamics and non-equilibrium thermodynamics. As a limitation, the reader should however notice that entanglements are not considered by the present model.

Phenomenological closures are imposed only in the second step, where the fast variables are removed, while in the first step (the derivation of the six-field hydrodynamics) no such closure occurs. This is possible since our microscopic model is significantly simplified, compared to a truly atomistic system. In essence, it is our computer model for polymer–solvent systems [37–39], in which bead-spring polymer chains are simulated by MD, while the solvent is represented by an ideal-gas type hydrodynamic background, simulated by lattice Boltzmann (LB). The coupling between MD and LB is of a purely dissipative nature, facilitated by assigning a Stokes friction coefficient to the beads. Starting from there, we simplify the model even further by replacing the polymer chains by phantom Hookean dumbbells with non-bonded interactions being replaced by a Van der Waals mean field model (see below). This model is so simple that the construction of the six-field hydrodynamics can be done exactly, except, of course, for the inevitable approximations that come from the field-theoretic ‘smoothing’ of the microscopic fields.

1.5. Outline of the remainder of the paper

Section 2 defines the microscopic model and, from there, the fields and the field-theoretic Hamiltonian. Section 3 discusses the basic equation of motion of isothermal dissipative Hamiltonian systems, which is then used to derive the reversible (section 4) and the irreversible (section 5) parts of the six-field hydrodynamics, which is summarized in section 6. In section 7 we transform to new variables (total density and density

contrast, barycentric velocity and relative velocity). This is the basis for the application of various approximations and simplifications (outlined in section 8), which, in essence, boil down to adiabatic elimination of fast variables. Section 9 then provides a detailed analysis of the resulting VEMH system, showing that it is compatible with the second law and the Onsager symmetry relations. It is also in this section where the phenomenological terms are specified; again the second law is here the essential guiding principle. Section 10 sketches the polymer version of Van der Waals theory, upon which the bulk part of the Hamiltonian is based, and section 11 provides a few concluding remarks. Appendices A and B are meant as background material, where the Poisson bracket formalism, and its application to derive the standard Euler equations, are outlined. Finally, appendix C further elucidates the difference between constrained and unconstrained averages in the derivation of rheological equations.

At this point, let us emphasize that the present paper is concerned with the derivation of rheological equations of motion, and *not* with the question if (or to what extent) the resulting model is able to reproduce the existing experimental observations that are known for viscoelastic phase separation. In our opinion, this question can only be answered by detailed computer simulations, which are however beyond the scope of the present investigation.

2. Model

2.1. Solvent

The dynamics of the solvent degrees of freedom is always (i.e. both on the microscopic level and on the fully field-theoretic level) represented by the isothermal Navier–Stokes equations

$$\partial_t \rho^{(s)} + \nabla \cdot \mathbf{j}^{(s)} = 0, \quad (1)$$

$$\partial_t \mathbf{j}_\alpha^{(s)} + \partial_\beta \left(\rho^{(s)} v_\alpha^{(s)} v_\beta^{(s)} \right) = -\partial_\alpha p^{(s)} + \eta_{\alpha\beta\gamma\delta} \partial_\beta \partial_\gamma v_\delta^{(s)} + f_\alpha. \quad (2)$$

Here, the upper index ‘(s)’ refers to the solvent, such that $\rho^{(s)}$ is the solvent mass density etc.... The symbol ∂_t denotes the time derivative $\partial/\partial t$, and similarly ∂_α the spatial derivative $\partial/\partial r_\alpha$. Greek subscripts are Cartesian indexes for which we assume the Einstein summation convention. $\mathbf{j}^{(s)}$ is the solvent momentum density, related to the solvent velocity flow field $\mathbf{v}^{(s)}$ via $\mathbf{j}^{(s)} = \rho^{(s)} \mathbf{v}^{(s)}$. $p^{(s)}$ is the solvent partial pressure, for which the LB model prescribes the equation of state of an ideal gas, $p^{(s)} = \rho^{(s)} c_s^2$, where c_s is the speed of sound of the LB fluid. $\eta_{\alpha\beta\gamma\delta}$ is the fourth-rank viscosity tensor, which for an isotropic Newtonian fluid (like our LB fluid) reads

$$\eta_{\alpha\beta\gamma\delta} = \left(\eta_V - \frac{2}{3} \eta_s \right) \delta_{\alpha\beta} \delta_{\gamma\delta} + \eta_s (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) \quad (3)$$

with bulk viscosity η_V and shear viscosity η_s . Finally, \mathbf{f} is a dissipative force density, which comes from the coupling to the polymer component. If the latter is being described in terms of Stokes beads, as on the microscopic level, \mathbf{f} can be written

down explicitly. On the fully field-theoretic level, the corresponding expression must be constructed with care; section 5 will outline how to do that.

In a shorthand notation, we may write equation (2) as

$$\partial \mathbf{j}^{(s)} + \nabla \cdot (\rho^{(s)} \mathbf{v}^{(s)} \mathbf{v}^{(s)}) = -\nabla p^{(s)} + \boldsymbol{\eta} : \nabla \nabla \mathbf{v}^{(s)} + \mathbf{f}. \quad (4)$$

The Hamiltonian of the solvent is

$$H^{(s)} = \int d^3 \mathbf{r} \left(\frac{(\mathbf{j}^{(s)})^2}{2\rho^{(s)}} + f^{(s)} \right), \quad (5)$$

where $f^{(s)}$ is the free energy density of the solvent; note that in our isothermal setting we need to interpret the Hamiltonian as the Helmholtz free energy. The pressure is derived from the free energy via

$$p^{(s)} = (\rho^{(s)})^2 \frac{\partial}{\partial \rho^{(s)}} \left(\frac{f^{(s)}}{\rho^{(s)}} \right), \quad (6)$$

$$\nabla p^{(s)} = \rho^{(s)} \nabla \left(\frac{\partial f^{(s)}}{\partial \rho^{(s)}} \right). \quad (7)$$

2.2. Polymer component: microscopic description

Each polymer chain is represented by a Hookean dumbbell. The center-of-mass coordinate of dumbbell number i is denoted by $\mathbf{r}_i^{(d)}$, and the two beads are located at the positions $\mathbf{r}_i^{(d)} \pm \mathbf{q}_i/2$, such that \mathbf{q}_i is the connector vector of the two beads. If we assign a mass m to each bead, then the total mass is $m^{(d)} = 2m$ and the reduced mass $m^{(r)} = m/2$. We denote $\Gamma = m^{(r)}/m^{(d)}$, which takes the value $\Gamma = 1/4$ for our model; however, we would like to keep Γ as a parameter that may perhaps be adjusted. Momenta associated with the dumbbell are $\mathbf{p}_i^{(d)} = m^{(d)} \dot{\mathbf{r}}_i^{(d)}$ for the center-of-mass motion and $\mathbf{p}_i^{(r)} = m^{(r)} \dot{\mathbf{q}}_i = \Gamma m^{(d)} \dot{\mathbf{q}}_i$ for the relative motion. Furthermore, the spring constant of the dumbbells is denoted by k . The Hamiltonian of the dumbbell system is thus given by

$$\hat{H}^{(d)} = \sum_i \left(\frac{(\mathbf{p}_i^{(d)})^2}{2m^{(d)}} + \Gamma^{-1} \frac{(\mathbf{p}_i^{(r)})^2}{2m^{(d)}} + \frac{k}{2} \mathbf{q}_i^2 \right) + U_{\text{nb}} \left(\{\mathbf{r}_i^{(d)}\}, \{\mathbf{q}_i\} \right), \quad (8)$$

where U_{nb} is the non-bonded interaction potential, which we do not need to specify in detail. As a typical example of what we mean by this, the reader may assume a pairwise bead–bead interaction that acts in the same way for all pairs of beads. The associated potential is then characterized by a strong repulsive core at short interparticle distances, and an attractive tail at larger distances. We may then assume that the strength of the attractive part parameterizes the solvent quality, such that the polymer component falls out of solution as soon as the attraction exceeds a critical value.

It is clear that such a model is a simple caricature of a real polymer solution, and that it certainly is unable to describe

entanglements. Nevertheless, it is the standard starting point of many theoretical developments of rheology [16].

Since the interaction between solvent and dumbbell system is purely dissipative, the total Hamiltonian is just the sum of the individual Hamiltonians

$$\hat{H} = H^{(s)} + \hat{H}^{(d)}. \quad (9)$$

2.3. Polymer component: microscopic expressions for fields

We can now construct microscopic expressions for various fields associated with the dumbbell degrees of freedom. These are: (i) the dumbbell mass density

$$\rho^{(d)}(\mathbf{r}) = m^{(d)} \sum_i \delta(\mathbf{r} - \mathbf{r}_i^{(d)}), \quad (10)$$

(ii) the dumbbell momentum density

$$\mathbf{j}^{(d)}(\mathbf{r}) = \sum_i \mathbf{p}_i^{(d)} \delta(\mathbf{r} - \mathbf{r}_i^{(d)}), \quad (11)$$

and analogous vector fields for the polymer extension, i.e. (iii) the elastic force density

$$\mathbf{k}^{(r)}(\mathbf{r}) = k \sum_i \mathbf{q}_i \delta(\mathbf{r} - \mathbf{r}_i^{(d)}), \quad (12)$$

and (iv) the relative momentum density

$$\mathbf{j}^{(r)}(\mathbf{r}) = \sum_i \mathbf{p}_i^{(r)} \delta(\mathbf{r} - \mathbf{r}_i^{(d)}). \quad (13)$$

2.4. Polymer component: field-theoretic description

After coarse-graining ('smoothing'), these fields are replaced by continuous functions, and we will consider these smoothed fields, together with $\rho^{(s)}$ and $\mathbf{j}^{(s)}$, as the independent degrees of freedom of the continuum theory that we wish to construct. We thus assume that the orientation and stretching of the polymer chains in the flow can be reasonably described by a smooth vector field $\mathbf{k}^{(r)}(\mathbf{r})$, and the internal motions by a corresponding smooth vector field $\mathbf{j}^{(r)}(\mathbf{r})$. Now, it is clear that on the microscopic level the physics does not change if we replace \mathbf{q}_i by $-\mathbf{q}_i$ (we call this a 'flip'), which also means $\dot{\mathbf{q}}_i \rightarrow -\dot{\mathbf{q}}_i$ and $\mathbf{p}_i^{(r)} \rightarrow -\mathbf{p}_i^{(r)}$. Therefore, on the field-theoretic level, the physics should not change under the analogous flip transformation $\mathbf{k}^{(r)}(\mathbf{r}) \rightarrow -\mathbf{k}^{(r)}(\mathbf{r})$ and $\mathbf{j}^{(r)}(\mathbf{r}) \rightarrow -\mathbf{j}^{(r)}(\mathbf{r})$. This, in turn, means that the model should be 'flip covariant', meaning that, within a given equation of motion, all occurring terms must have the same transformation behavior under flip—they must all be even, or they must all be odd. As can be easily checked throughout the derivation that we will present below, this is indeed the case, step by step. It does *not* imply, though, that only even terms are permitted. To illustrate that point, just consider Newton's equation of motion, where both the force and the acceleration have the same transformation behavior under reflection—but both are odd, not even.

The intuitive picture that we associate with the assumption of a *smooth* vector field $\mathbf{k}^{(r)}(\mathbf{r})$ is this: we arbitrarily pick one

particular dumbbell, and then arbitrarily pick one of its two possible orientations. This defines the connector vector for that particular dumbbell. Now we go to another dumbbell in the immediate vicinity of the first one, and again pick its orientation. We are now no longer free to pick it arbitrarily, but rather must choose it in such a way that its alignment with the already assigned orientation is as good as possible. This is dictated by the requirement that the coarse-grained vector field is supposed to be *smooth*. In this way, we scan the whole system and assign one well-defined orientation after the other. In some cases, frustration might occur, but we assume that such cases are rare. The resulting connector vectors enter the definition of the field $\mathbf{k}^{(r)}(\mathbf{r})$. We believe that, with this picture in mind, the assumption of a smooth vector field is quite reasonable.

At this point, one might ask if it would not be more advisable to rather assign a conformation tensor to each molecule (this is even under flip), and then subject these quantities to coarse-graining, such that one obtains a smooth conformation tensor field. This would obviously eliminate the difficulties mentioned above. However, upon considering this idea in more detail, we found ourselves unable to construct suitable canonical momenta, and a Hamiltonian theory based upon them, without running into severe algebraic difficulties, of which we do not know if they can be resolved or not. The main problem is that the components of the conformation tensor are not all independent; rather the very construction of the tensor implies that it has only three independent parameters. A similar difficulty also appears in the Fokker–Planck description, see appendix C. We therefore found it much easier to rather base our considerations on vector fields.

The transition from the microscopic model to the field theory then consists of replacing the dumbbell Hamiltonian by an analogous field-theoretic expression:

$$H^{(d)} = \int d^3\mathbf{r} \left[\frac{(\mathbf{j}^{(d)})^2}{2\rho^{(d)}} + \Gamma^{-1} \frac{(\mathbf{j}^{(r)})^2}{2\rho^{(d)}} + \frac{m^{(d)}}{k} \frac{(\mathbf{k}^{(r)})^2}{2\rho^{(d)}} + f^{(d)} + \frac{\kappa}{2} (\nabla\rho^{(d)})^2 \right]. \quad (14)$$

Here the first two terms describe the kinetic energy of the center-of-mass motion and the relative motion, respectively, while the third term describes the elastic (or spring) energy. The fourth and fifth term are the replacement for the non-bonded interaction U_{nb} , where $f^{(d)}$ is the bulk part of the configurational free energy density. The last term is meant to penalize the occurrence of interfaces; the parameter κ is called 'interfacial stiffness'. Such terms always occur in the field-theoretic description of phase separation (both statics and dynamics) [2] and there is a well-defined statistical-mechanical procedure to derive them. For a simple approach the reader is referred to reference [40], while a more advanced machinery is found in reference [41]. For the bulk free energy density we will assume that $f^{(d)} = f^{(d)}(\rho^{(d)})$ and that $f^{(d)}$ can be constructed from a Van der Waals model, which is the simplest well-known model for a fluid that undergoes a gas–liquid transition. This choice is inspired by the fact that the solvent is

just an ideal gas (i.e. thermodynamically inert), such that the decomposition between polymer and solvent may be viewed (from the point of view of thermodynamics, not hydrodynamics) as just a gas–liquid transition of the polymer component. The structure of the theory is completely independent of the precise form of $f^{(d)}$; therefore one may as well assume a different function for $f^{(d)}$ (possibly even an empirical function derived from simulation results).

After this ‘smoothing operation’, we can then define further fields: (i) the dumbbell velocity flow field

$$\mathbf{v}^{(d)}(\mathbf{r}) = \frac{\mathbf{j}^{(d)}(\mathbf{r})}{\rho^{(d)}(\mathbf{r})} = \frac{\delta H}{\delta \mathbf{j}^{(d)}(\mathbf{r})} \quad (15)$$

(here $\delta \dots / \delta \dots$ denotes the functional derivative), (ii) the ‘relative flow field’

$$\mathbf{v}^{(r)}(\mathbf{r}) = \Gamma^{-1} \frac{\mathbf{j}^{(r)}(\mathbf{r})}{\rho^{(d)}(\mathbf{r})} = \frac{\delta H}{\delta \mathbf{j}^{(r)}(\mathbf{r})}, \quad (16)$$

and (iii) the ‘extension field’

$$\mathbf{q}(\mathbf{r}) = \frac{m^{(d)} \mathbf{k}^{(r)}(\mathbf{r})}{k \rho^{(d)}(\mathbf{r})} = \frac{\delta H}{\delta \mathbf{k}^{(r)}(\mathbf{r})}. \quad (17)$$

We also note

$$\begin{aligned} \frac{\delta H}{\delta \rho^{(d)}} &= \frac{\partial f^{(d)}}{\partial \rho^{(d)}} - \kappa \nabla^2 \rho^{(d)} \\ &- \frac{1}{2} \left[(\mathbf{v}^{(d)})^2 + \Gamma (\mathbf{v}^{(r)})^2 + \frac{k}{m^{(d)}} \mathbf{q}^2 \right]. \end{aligned} \quad (18)$$

3. General equation of motion

In the present paper, we will be concerned with equations of motion for a set of fields $\Phi_i = \Phi_i(\mathbf{r}, t)$ in three-dimensional space, of the form

$$\partial_t \Phi_i = \mathcal{L}_i - \mathcal{M}_i. \quad (19)$$

We will assume a domain with periodic boundary conditions, such that integrations by parts will never involve surface terms. The symbols $\mathcal{L}_i = \mathcal{L}_i(\{\Phi_k\}, \mathbf{r}) = \mathcal{L}_i(\mathbf{r})$, $\mathcal{M}_i = \mathcal{M}_i(\{\Phi_k\}, \mathbf{r}) = \mathcal{M}_i(\mathbf{r})$ denote fields that depend on the field degrees of freedom and describe the dynamics. The functional $H = H(\{\Phi_k\})$ is of central importance, and we will call it the Hamiltonian of the system. Since we study the system in the isothermal ensemble, it may also be called the (Helmholtz) free energy functional. We require that the dynamics is dissipative, i.e. that $dH/dt \leq 0$. The fields \mathcal{L}_i and \mathcal{M}_i have been introduced to denote the conservative (\mathcal{L}_i) and the dissipative (\mathcal{M}_i) parts of the dynamics. Obviously,

$$\frac{dH}{dt} = \sum_i \int d^3\mathbf{r} (\mathcal{L}_i(\mathbf{r}) - \mathcal{M}_i(\mathbf{r})) \frac{\delta H}{\delta \Phi_i(\mathbf{r})}. \quad (20)$$

Furthermore, we require

$$\sum_i \int d^3\mathbf{r} \mathcal{L}_i(\mathbf{r}) \frac{\delta H}{\delta \Phi_i(\mathbf{r})} = 0, \quad (21)$$

$$\sum_i \int d^3\mathbf{r} \mathcal{M}_i(\mathbf{r}) \frac{\delta H}{\delta \Phi_i(\mathbf{r})} \geq 0. \quad (22)$$

We will always require that the dissipative terms can be described in terms of linear Onsager theory, where the dissipative responses \mathcal{M}_i are proportional to the driving forces $\delta H / \delta \Phi_j$:

$$\mathcal{M}_i(\mathbf{r}) = \sum_j \int d^3\mathbf{r}' M_{ij}(\mathbf{r}, \mathbf{r}') \frac{\delta H}{\delta \Phi_j(\mathbf{r}')}, \quad (23)$$

where the elements M_{ij} form a matrix that is symmetric with respect to the simultaneous exchanges $i \leftrightarrow j$, $\mathbf{r} \leftrightarrow \mathbf{r}'$; this expresses the Onsager reciprocity relations. Furthermore, the second law requires that the matrix is positive-semidefinite. The total dissipation rate therefore takes the form

$$\frac{dH}{dt} = - \sum_{ij} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\delta H}{\delta \Phi_i(\mathbf{r})} M_{ij}(\mathbf{r}, \mathbf{r}') \frac{\delta H}{\delta \Phi_j(\mathbf{r}')} \leq 0. \quad (24)$$

If in addition the conservative part of the dynamics has a Hamiltonian structure, then we have a dissipative Hamiltonian system. In this case, the Poisson brackets $\{\Phi_i(\mathbf{r}), \Phi_j(\mathbf{r}')\}$ form a closed system (i.e. they can be expressed in terms of the fields Φ_i , with no reference to additional ‘hidden’ degrees of freedom), and we have

$$\mathcal{L}_i(\mathbf{r}) = \sum_j \int d^3\mathbf{r}' \{\Phi_i(\mathbf{r}), \Phi_j(\mathbf{r}')\} \frac{\delta H}{\delta \Phi_j(\mathbf{r}')}. \quad (25)$$

For more details on the Poisson bracket formalism, see [appendices A and B](#). The conservative nature of this dynamics is then a direct consequence of the antisymmetry of the Poisson brackets. It should be noted that equation (19) with the specific forms equations (23) and (25) can be derived from the GENERIC formalism [31–34].

We will use these general considerations in two ways. In the first part of the paper, where we consider the six-field hydrodynamics, we will be able to construct, by reference to the underlying microscopic model, the Poisson brackets, the functional derivatives of the Hamiltonian, and the dissipation rate dH/dt . The latter can be written in a form that matches equation (24), which will enable us to read off the matrix elements M_{ij} . In the second part, i.e. the VEMH where the fast degrees of freedom have been eliminated, we know \mathcal{L}_i (and we can explicitly show that this is indeed conservative), but we know \mathcal{M}_i only up to unknown phenomenological terms. We can then find expressions for these terms by assuming a simple but consistent model, where the matrix is diagonal and positive-definite.

4. Equations of motion I: Hamiltonian part

We first focus on the Hamiltonian part of the dynamics. We note that on the Hamiltonian level our model implies that the polymer system and the solvent system are completely decoupled, and may therefore be treated separately. For the solvent system, the conservative part of the dynamics is given by

the Euler equations. These are known to be Hamiltonian, and this can be shown straightforwardly by means of the Poisson bracket formalism, see appendix B.

We therefore need to execute the same methodology for the dumbbell system. The functional derivatives of the Hamiltonian have already been evaluated in section 2; therefore the next step is to calculate the Poisson brackets by insertion of the microscopic expressions, plus reference to the Poisson brackets of coordinates and momenta, as they are known from classical mechanics. The evaluation is somewhat tedious but straightforward and yields

$$\left\{ \rho^{(d)}(\mathbf{r}), j_{\beta}^{(d)}(\mathbf{r}') \right\} = -\rho^{(d)}(\mathbf{r}') \partial_{\beta} \delta(\mathbf{r} - \mathbf{r}'), \quad (26)$$

$$\left\{ k_{\alpha}^{(r)}(\mathbf{r}), j_{\beta}^{(d)}(\mathbf{r}') \right\} = -k_{\alpha}^{(r)}(\mathbf{r}') \partial_{\beta} \delta(\mathbf{r} - \mathbf{r}'), \quad (27)$$

$$\left\{ j_{\alpha}^{(r)}(\mathbf{r}), j_{\beta}^{(d)}(\mathbf{r}') \right\} = -j_{\alpha}^{(r)}(\mathbf{r}') \partial_{\beta} \delta(\mathbf{r} - \mathbf{r}'), \quad (28)$$

$$\left\{ j_{\alpha}^{(d)}(\mathbf{r}), j_{\beta}^{(d)}(\mathbf{r}') \right\} = j_{\beta}^{(d)}(\mathbf{r}') \partial_{\alpha} \delta(\mathbf{r} - \mathbf{r}') - j_{\alpha}^{(d)}(\mathbf{r}') \partial_{\beta} \delta(\mathbf{r} - \mathbf{r}'), \quad (29)$$

$$\left\{ k_{\alpha}^{(r)}(\mathbf{r}), j_{\beta}^{(r)}(\mathbf{r}') \right\} = \delta_{\alpha\beta} \frac{k}{m^{(d)}} \rho^{(d)}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'). \quad (30)$$

The remaining Poisson brackets that have not been listed simply vanish.

We then insert the Poisson brackets, plus the functional derivatives of the Hamiltonian with respect to the fields, into the general equation of motion. After some algebra (quite a few terms cancel) we arrive at the following set.

For the dumbbell density and the dumbbell momentum density, we recover the standard Euler equations (cf also appendix B), augmented by the interfacial force term:

$$\partial_t \rho^{(d)} + \nabla \cdot \mathbf{j}^{(d)} = 0, \quad (31)$$

$$\partial_t j_{\alpha}^{(d)} + \partial_{\beta} \left(\rho^{(d)} v_{\alpha}^{(d)} v_{\beta}^{(d)} \right) = -\partial_{\alpha} p^{(d)} + \kappa \rho^{(d)} \partial_{\alpha} \nabla^2 \rho^{(d)}, \quad (32)$$

where $p^{(d)}$ is the dumbbell partial pressure, defined as

$$p^{(d)} = (\rho^{(d)})^2 \frac{\partial}{\partial \rho^{(d)}} \left(\frac{f^{(d)}}{\rho^{(d)}} \right). \quad (33)$$

It should be noted that the interfacial force term does conserve the total momentum, i.e. its spatial integral is zero, as can be shown by integration-by-parts.

The equation of motion for the force density is found to be

$$\partial_t k_{\alpha}^{(r)} + \partial_{\beta} \left(k_{\alpha}^{(r)} v_{\beta}^{(d)} \right) = \frac{k}{m^{(r)}} j_{\alpha}^{(r)}; \quad (34)$$

this takes a somewhat more intuitive form after transforming to the corresponding equation for the extension field, which reads, by taking into account the mass conservation equation for $\rho^{(d)}$,

$$\partial_t q_{\alpha} + v_{\beta}^{(d)} \partial_{\beta} q_{\alpha} = v_{\alpha}^{(r)}; \quad (35)$$

note that the left-hand side is just the convective derivative of q_{α} .

Finally, we find for the relative momentum density

$$\partial_t j_{\alpha}^{(r)} + \partial_{\beta} \left(j_{\alpha}^{(r)} v_{\beta}^{(d)} \right) = -k_{\alpha}^{(r)}. \quad (36)$$

Again transforming to the corresponding velocity field, we find

$$m^{(r)} \left(\partial_t v_{\alpha}^{(r)} + v_{\beta}^{(d)} \partial_{\beta} v_{\alpha}^{(r)} \right) = -k q_{\alpha}, \quad (37)$$

which is essentially Newton's equation of motion for the oscillator, taking into account convection with $v^{(d)}$.

In summary, we thus find a set of equations which has not only been derived with a well-founded formalism, but is also intuitively quite plausible.

5. Equations of motion II: dissipative part

To take into account dissipation, and in particular the dissipative coupling of the dumbbell system to the background solvent fluid, we first need to consider the dumbbell number i in the solvent flow field $v^{(s)}$. The two beads are located at the positions $\mathbf{r}_i^{(d)} \pm \mathbf{q}_i/2$, which means that the relevant terms for the coupling are proportional to the difference between bead velocity $\dot{\mathbf{r}}_i^{(d)} \pm \dot{\mathbf{q}}_i/2$ and the flow velocity at the position of the bead, $v^{(s)}(\mathbf{r}_i^{(d)} \pm \mathbf{q}_i/2)$. Ignoring the (Hamiltonian) part that comes from the spring force, we may thus write down the equations of motion for the two beads:

$$m \frac{d}{dt} \left(\dot{\mathbf{r}}_i^{(d)} + \dot{\mathbf{q}}_i/2 \right) = -\zeta \mathbf{u}_i^{(1)}, \quad (38)$$

$$m \frac{d}{dt} \left(\dot{\mathbf{r}}_i^{(d)} - \dot{\mathbf{q}}_i/2 \right) = -\zeta \mathbf{u}_i^{(2)}; \quad (39)$$

here m denotes the bead mass and ζ is the friction coefficient, whose value controls the strength of the coupling, while

$$\mathbf{u}_i^{(1)} = \dot{\mathbf{r}}_i^{(d)} + \dot{\mathbf{q}}_i/2 - v^{(s)}(\mathbf{r}_i^{(d)} + \mathbf{q}_i/2), \quad (40)$$

$$\mathbf{u}_i^{(2)} = \dot{\mathbf{r}}_i^{(d)} - \dot{\mathbf{q}}_i/2 - v^{(s)}(\mathbf{r}_i^{(d)} - \mathbf{q}_i/2). \quad (41)$$

Introducing

$$\begin{aligned} \mathbf{u}_i^{(0)} &= (\mathbf{u}_i^{(1)} + \mathbf{u}_i^{(2)})/2 \\ &= \dot{\mathbf{r}}_i^{(d)} - \left[v^{(s)}(\mathbf{r}_i^{(d)} + \mathbf{q}_i/2) + v^{(s)}(\mathbf{r}_i^{(d)} - \mathbf{q}_i/2) \right]/2, \end{aligned} \quad (42)$$

$$\begin{aligned} \Delta \mathbf{u}_i &= \mathbf{u}_i^{(1)} - \mathbf{u}_i^{(2)} \\ &= \dot{\mathbf{q}}_i - \left[v^{(s)}(\mathbf{r}_i^{(d)} + \mathbf{q}_i/2) - v^{(s)}(\mathbf{r}_i^{(d)} - \mathbf{q}_i/2) \right], \end{aligned} \quad (43)$$

and a relaxation time τ associated with the coupling, $\tau = m/\zeta$, we may rewrite the equations as

$$\tau \frac{d}{dt} \dot{\mathbf{r}}_i^{(d)} = -\mathbf{u}_i^{(0)}, \quad (44)$$

$$\tau \frac{d}{dt} \dot{\mathbf{q}}_i = -\Delta \mathbf{u}_i. \quad (45)$$

Scaling the equations with the masses $m^{(d)}$ and $m^{(r)}$, respectively, we find

$$\tau \frac{d}{dt} \mathbf{p}_i^{(d)} = -m^{(d)} \mathbf{u}_i^{(0)}, \quad (46)$$

$$\tau \frac{d}{dt} \mathbf{p}_i^{(r)} = -\Gamma m^{(d)} \Delta \mathbf{u}_i. \quad (47)$$

We now expand $\mathbf{v}^{(s)}$ by a Taylor series with respect to \mathbf{q}_i . This can be formalized by introducing the operators

$$\Omega_+(\mathbf{q}) = 1 + \frac{1}{2} q_\alpha q_\beta \partial_\alpha \partial_\beta + \dots, \quad (48)$$

$$\Omega_-(\mathbf{q}) = q_\alpha \partial_\alpha + \frac{1}{24} q_\alpha q_\beta q_\gamma \partial_\alpha \partial_\beta \partial_\gamma + \dots, \quad (49)$$

which allows us to write

$$\mathbf{u}_i^{(0)} = \dot{\mathbf{r}}_i^{(d)} - \Omega_+(\mathbf{q}_i) \mathbf{v}^{(s)}(\mathbf{r})|_{\mathbf{r}=\mathbf{r}_i^{(d)}}, \quad (50)$$

$$\Delta \mathbf{u}_i = \dot{\mathbf{q}}_i - \Omega_-(\mathbf{q}_i) \mathbf{v}^{(s)}(\mathbf{r})|_{\mathbf{r}=\mathbf{r}_i^{(d)}}. \quad (51)$$

We can now calculate the rate at which the microscopic dumbbell Hamiltonian changes, again taking into account only the dissipative part of the dynamics:

$$\frac{d}{dt} \widehat{H}^{(d)} = \sum_i \left[\dot{\mathbf{r}}_i^{(d)} \cdot \dot{\mathbf{p}}_i^{(d)} + \dot{\mathbf{q}}_i \cdot \dot{\mathbf{p}}_i^{(r)} \right], \quad (52)$$

i.e.

$$\tau \frac{d}{dt} \widehat{H}^{(d)} = -m^{(d)} \sum_i \left[\dot{\mathbf{r}}_i^{(d)} \cdot \mathbf{u}_i^{(0)} + \Gamma \dot{\mathbf{q}}_i \cdot \Delta \mathbf{u}_i \right]. \quad (53)$$

Let us now consider the solvent. Again we ignore the Hamiltonian part of the dynamics. We also ignore the contribution by viscous dissipation ($\propto \eta_{\alpha\beta\gamma\delta}$), because this can be considered separately from the dissipative coupling to the dumbbells—it is known that the viscous term is dissipative, conserves the momentum, and just yields a well-known additive contribution to the overall dissipation rate. We thus obtain

$$\partial_i \rho^{(s)} = 0, \quad (54)$$

$$\partial_j \mathbf{j}^{(s)} = \mathbf{f}, \quad (55)$$

with

$$\mathbf{f}(\mathbf{r}) = \sum_i \left[\delta(\mathbf{r} - \mathbf{r}_i^{(d)} - \mathbf{q}_i/2) \mathbf{F}_i^{(1)} + \delta(\mathbf{r} - \mathbf{r}_i^{(d)} + \mathbf{q}_i/2) \mathbf{F}_i^{(2)} \right], \quad (56)$$

$$\mathbf{F}_i^{(1)} = \zeta \mathbf{u}_i^{(1)}, \quad (57)$$

$$\mathbf{F}_i^{(2)} = \zeta \mathbf{u}_i^{(2)}. \quad (58)$$

The rate of change of the solvent Hamiltonian, coming from the dissipative coupling, is then calculated to be

$$\begin{aligned} \frac{d}{dt} H^{(s)} = \sum_i & \left[\mathbf{v}^{(s)}(\mathbf{r}_i^{(d)} + \mathbf{q}_i/2) \cdot \mathbf{F}_i^{(1)} \right. \\ & \left. + \mathbf{v}^{(s)}(\mathbf{r}_i^{(d)} - \mathbf{q}_i/2) \cdot \mathbf{F}_i^{(2)} \right], \end{aligned} \quad (59)$$

or

$$\begin{aligned} \tau \frac{d}{dt} H^{(s)} = m \sum_i & \left[\mathbf{v}^{(s)}(\mathbf{r}_i^{(d)} + \mathbf{q}_i/2) \cdot \mathbf{u}_i^{(1)} \right. \\ & \left. + \mathbf{v}^{(s)}(\mathbf{r}_i^{(d)} - \mathbf{q}_i/2) \cdot \mathbf{u}_i^{(2)} \right]. \end{aligned} \quad (60)$$

In terms of $\mathbf{u}_i^{(0)}$ and $\Delta \mathbf{u}_i$, this is rewritten as

$$\begin{aligned} \tau \frac{d}{dt} H^{(s)} = m \sum_i & \left[2\mathbf{u}_i^{(0)} \cdot \Omega_+(\mathbf{q}_i) \mathbf{v}^{(s)}(\mathbf{r})|_{\mathbf{r}=\mathbf{r}_i^{(d)}} \right. \\ & \left. + \frac{1}{2} \Delta \mathbf{u}_i \cdot \Omega_-(\mathbf{q}_i) \mathbf{v}^{(s)}(\mathbf{r})|_{\mathbf{r}=\mathbf{r}_i^{(d)}} \right], \end{aligned} \quad (61)$$

or, taking into account $2m = m^{(d)}$, $\Gamma = 1/4$,

$$\begin{aligned} \tau \frac{d}{dt} H^{(s)} = m^{(d)} \sum_i & \left[\mathbf{u}_i^{(0)} \cdot \Omega_+(\mathbf{q}_i) \mathbf{v}^{(s)}(\mathbf{r})|_{\mathbf{r}=\mathbf{r}_i^{(d)}} \right. \\ & \left. + \Gamma \Delta \mathbf{u}_i \cdot \Omega_-(\mathbf{q}_i) \mathbf{v}^{(s)}(\mathbf{r})|_{\mathbf{r}=\mathbf{r}_i^{(d)}} \right]. \end{aligned} \quad (62)$$

Combining equations (53) and (62), we find for the total dissipation rate that comes from the dumbbell–solvent coupling in the microscopic model:

$$\tau \frac{d}{dt} \left(\widehat{H}^{(d)} + H^{(s)} \right) = -m^{(d)} \sum_i \left[\left(\mathbf{u}_i^{(0)} \right)^2 + \Gamma (\Delta \mathbf{u}_i)^2 \right], \quad (63)$$

showing that the coupling is strictly compatible with the second law.

On the field-theoretic level, we postulate the analogous expression

$$\begin{aligned} \tau \frac{d}{dt} (H^{(d)} + H^{(s)}) \\ = - \int d^3 \mathbf{r} \rho^{(d)}(\mathbf{r}) \left[\left(\mathbf{u}^{(0)}(\mathbf{r}) \right)^2 + \Gamma (\Delta \mathbf{u}(\mathbf{r}))^2 \right] \end{aligned} \quad (64)$$

with the field analogues of equations (50) and (51),

$$\mathbf{u}^{(0)}(\mathbf{r}) = \mathbf{v}^{(d)}(\mathbf{r}) - \Omega_+(\mathbf{q}(\mathbf{r})) \mathbf{v}^{(s)}(\mathbf{r}), \quad (65)$$

$$\Delta \mathbf{u}(\mathbf{r}) = \mathbf{v}^{(r)}(\mathbf{r}) - \Omega_-(\mathbf{q}(\mathbf{r})) \mathbf{v}^{(s)}(\mathbf{r}). \quad (66)$$

Decomposing the dissipation rate into the various contributions, we find

$$\begin{aligned} - \tau \frac{d}{dt} (H^{(d)} + H^{(s)}) \\ = \int d^3 \mathbf{r} \rho^{(d)} (\Omega_+ \mathbf{v}^{(s)})^2 + \Gamma \int d^3 \mathbf{r} \rho^{(d)} (\Omega_- \mathbf{v}^{(s)})^2 \end{aligned}$$

$$\begin{aligned}
& + \int d^3\mathbf{r} \rho^{(d)} (\mathbf{v}^{(d)})^2 + \Gamma \int d^3\mathbf{r} \rho^{(d)} (\mathbf{v}^{(r)})^2 \\
& - 2 \int d^3\mathbf{r} \rho^{(d)} \mathbf{v}^{(d)} \cdot \Omega_+ \mathbf{v}^{(s)} \\
& - 2\Gamma \int d^3\mathbf{r} \rho^{(d)} \mathbf{v}^{(r)} \cdot \Omega_- \mathbf{v}^{(s)}. \tag{67}
\end{aligned}$$

At this point, we introduce the adjoint operators

$$\Omega_+^\dagger = 1 + \frac{1}{8} \partial_\alpha \partial_\beta q_\alpha q_\beta + \dots, \tag{68}$$

$$\Omega_-^\dagger = -\partial_\alpha q_\alpha - \frac{1}{24} \partial_\alpha \partial_\beta \partial_\gamma q_\alpha q_\beta q_\gamma - \dots; \tag{69}$$

this allows us to write

$$\begin{aligned}
& - \tau \frac{d}{dt} (H^{(d)} + H^{(s)}) \\
& = \int d^3\mathbf{r} \mathbf{v}^{(s)} \cdot \left[\Omega_+^\dagger \rho^{(d)} \Omega_+ + \Gamma \Omega_-^\dagger \rho^{(d)} \Omega_- \right] \mathbf{v}^{(s)} \\
& - \int d^3\mathbf{r} \mathbf{v}^{(s)} \cdot \Omega_+^\dagger \rho^{(d)} \mathbf{v}^{(d)} - \Gamma \int d^3\mathbf{r} \mathbf{v}^{(s)} \cdot \Omega_-^\dagger \rho^{(d)} \mathbf{v}^{(r)} \\
& + \int d^3\mathbf{r} \mathbf{v}^{(d)} \cdot \rho^{(d)} \mathbf{v}^{(d)} - \int d^3\mathbf{r} \mathbf{v}^{(d)} \cdot \rho^{(d)} \Omega_+ \mathbf{v}^{(s)} \\
& + \Gamma \int d^3\mathbf{r} \mathbf{v}^{(r)} \cdot \rho^{(d)} \mathbf{v}^{(r)} - \Gamma \int d^3\mathbf{r} \mathbf{v}^{(r)} \cdot \rho^{(d)} \Omega_- \mathbf{v}^{(s)}. \tag{70}
\end{aligned}$$

Recalling $\mathbf{v}^{(s)} = \delta H / \delta \mathbf{j}^{(s)}$, $\mathbf{v}^{(d)} = \delta H / \delta \mathbf{j}^{(d)}$, and $\mathbf{v}^{(r)} = \delta H / \delta \mathbf{j}^{(r)}$, one sees (cf equation (24)) that this is precisely the form that is required by the general formalism. This, in turn, allows us to directly read off the continuum equations of motion (again, we emphasize that we here ignore the Hamiltonian contribution and the viscous part $\propto \eta_{\alpha\beta\gamma\delta}$):

$$\partial_t \rho^{(s)} = 0, \tag{71}$$

$$\partial_t \rho^{(d)} = 0, \tag{72}$$

$$\partial_t \mathbf{k}^{(r)} = 0, \tag{73}$$

$$\begin{aligned}
\tau \partial_t \mathbf{j}^{(s)} &= \Omega_+^\dagger \rho^{(d)} [\mathbf{v}^{(d)} - \Omega_+ \mathbf{v}^{(s)}] \\
&+ \Gamma \Omega_-^\dagger \rho^{(d)} [\mathbf{v}^{(r)} - \Omega_- \mathbf{v}^{(s)}], \tag{74}
\end{aligned}$$

$$\tau \partial_t \mathbf{j}^{(d)} = -\rho^{(d)} [\mathbf{v}^{(d)} - \Omega_+ \mathbf{v}^{(s)}], \tag{75}$$

$$\tau \partial_t \mathbf{j}^{(r)} = -\Gamma \rho^{(d)} [\mathbf{v}^{(r)} - \Omega_- \mathbf{v}^{(s)}]. \tag{76}$$

One can show that these equations are compatible with momentum conservation. To this end, we note that Gauss' theorem implies

$$\int d^3\mathbf{r} \Omega_+^\dagger (\dots) = \int d^3\mathbf{r} 1 (\dots), \tag{77}$$

$$\int d^3\mathbf{r} \Omega_-^\dagger (\dots) = 0. \tag{78}$$

Therefore

$$\begin{aligned}
& \tau \frac{d}{dt} \int d^3\mathbf{r} \mathbf{j}^{(s)} \\
& = \int d^3\mathbf{r} \rho^{(d)} \mathbf{v}^{(d)} - \int d^3\mathbf{r} \rho^{(d)} \Omega_+ \mathbf{v}^{(s)}, \tag{79}
\end{aligned}$$

$$\begin{aligned}
& \tau \frac{d}{dt} \int d^3\mathbf{r} \mathbf{j}^{(d)} \\
& = - \int d^3\mathbf{r} \rho^{(d)} \mathbf{v}^{(d)} + \int d^3\mathbf{r} \rho^{(d)} \Omega_+ \mathbf{v}^{(s)}, \tag{80}
\end{aligned}$$

$$\tau \frac{d}{dt} \int d^3\mathbf{r} (\mathbf{j}^{(s)} + \mathbf{j}^{(d)}) = 0; \tag{81}$$

the last equation obviously implies conservation of the total momentum—note that the relative motion of the beads with respect to each other does not contribute to the overall momentum balance.

6. Final set of equations

Let us summarize what we have achieved so far. We started from an extremely simple microscopic dumbbell model for viscoelastic phase separation. We then defined a set of fields (two scalar fields, four vector fields) which can be explicitly constructed from the microscopic configurations in real and momentum space. The microscopic dynamics then allowed us to evaluate the Poisson brackets of the fields; from there it turned out that the field-theoretic set of variables is closed, meaning that the Poisson brackets do not generate additional variables. We then applied four important approximations and assumptions, which allowed us to go from the microscopic model to field theory. These are: (i) replacement of the non-bonded interactions with a Van der Waals free energy, augmented with an interfacial stiffness term; (ii) replacement of the particle Hamiltonian with the corresponding field-theoretic expression; (iii) a similar replacement for the dissipation rate, and (iv) the assumption that the molecular conformations may be represented by a smooth vector field. *No further assumptions or approximations were made.* The formalism of dissipative Hamiltonian systems then made it possible to construct the field-theoretic equations of motion in a somewhat tedious but straightforward fashion. We thus arrive at a set of equations which are fully compatible with non-equilibrium thermodynamics, conserve the momentum, and have a well-defined transformation behavior under flip (which is easily checked by inspection). In total, the resulting equations read:

$$\partial_t \rho^{(s)} + \nabla \cdot \mathbf{j}^{(s)} = 0, \tag{82}$$

$$\partial_t \rho^{(d)} + \nabla \cdot \mathbf{j}^{(d)} = 0, \tag{83}$$

$$\partial_t \mathbf{k}^{(r)} + \nabla \cdot (\mathbf{k}^{(r)} \mathbf{v}^{(d)}) = \frac{k}{m^{(r)}} \mathbf{j}^{(r)}, \tag{84}$$

$$\begin{aligned}
& \partial_t \mathbf{j}^{(s)} + \nabla \cdot (\mathbf{j}^{(s)} \mathbf{v}^{(s)}) \\
& = -\nabla p^{(s)} + \boldsymbol{\eta} : \nabla \nabla \mathbf{v}^{(s)} + \frac{1}{\tau} \Omega_+^\dagger \rho^{(d)} [\mathbf{v}^{(d)} - \Omega_+ \mathbf{v}^{(s)}]
\end{aligned}$$

$$+ \frac{\Gamma}{\tau} \Omega_-^\dagger \rho^{(d)} [\mathbf{v}^{(r)} - \Omega_- \mathbf{v}^{(s)}], \quad (85)$$

$$\begin{aligned} \partial_t \mathbf{j}^{(d)} + \nabla \cdot (\mathbf{j}^{(d)} \mathbf{v}^{(d)}) \\ = -\nabla p^{(d)} + \kappa \rho^{(d)} \nabla \nabla^2 \rho^{(d)} - \frac{1}{\tau} \rho^{(d)} [\mathbf{v}^{(d)} - \Omega_+ \mathbf{v}^{(s)}], \end{aligned} \quad (86)$$

$$\begin{aligned} \partial_t \mathbf{j}^{(r)} + \nabla \cdot (\mathbf{j}^{(r)} \mathbf{v}^{(d)}) \\ = -\mathbf{k}^{(r)} - \frac{\Gamma}{\tau} \rho^{(d)} [\mathbf{v}^{(r)} - \Omega_- \mathbf{v}^{(s)}]. \end{aligned} \quad (87)$$

By making use of the mass conservation equations, we can transform these equations for ‘extensive’ fields ($\mathbf{k}^{(r)}$, $\mathbf{j}^{(s)}$, $\mathbf{j}^{(d)}$, $\mathbf{j}^{(r)}$) to equivalent equations for the corresponding ‘intensive’ fields (\mathbf{q} , $\mathbf{v}^{(s)}$, $\mathbf{v}^{(d)}$, $\mathbf{v}^{(r)}$). Here it is useful to introduce the convective derivatives

$$D_t^{(s)} = \partial_t + \mathbf{v}^{(s)} \cdot \nabla, \quad (88)$$

$$D_t^{(d)} = \partial_t + \mathbf{v}^{(d)} \cdot \nabla. \quad (89)$$

Straightforward transformation yields

$$D_t^{(s)} \rho^{(s)} + \rho^{(s)} \nabla \cdot \mathbf{v}^{(s)} = 0, \quad (90)$$

$$D_t^{(d)} \rho^{(d)} + \rho^{(d)} \nabla \cdot \mathbf{v}^{(d)} = 0, \quad (91)$$

$$D_t^{(d)} \mathbf{q} = \mathbf{v}^{(r)}, \quad (92)$$

$$\begin{aligned} \rho^{(s)} D_t^{(s)} \mathbf{v}^{(s)} &= -\nabla p^{(s)} + \eta \nabla \nabla \mathbf{v}^{(s)} \\ &+ \frac{1}{\tau} \Omega_+^\dagger \rho^{(d)} [\mathbf{v}^{(d)} - \Omega_+ \mathbf{v}^{(s)}] \\ &+ \frac{\Gamma}{\tau} \Omega_-^\dagger \rho^{(d)} [\mathbf{v}^{(r)} - \Omega_- \mathbf{v}^{(s)}], \end{aligned} \quad (93)$$

$$\begin{aligned} \rho^{(d)} D_t^{(d)} \mathbf{v}^{(d)} &= -\nabla p^{(d)} + \kappa \rho^{(d)} \nabla \nabla^2 \rho^{(d)} \\ &- \frac{1}{\tau} \rho^{(d)} [\mathbf{v}^{(d)} - \Omega_+ \mathbf{v}^{(s)}], \end{aligned} \quad (94)$$

$$D_t^{(d)} \mathbf{v}^{(r)} = -\frac{k}{m^{(r)}} \mathbf{q} - \frac{1}{\tau} [\mathbf{v}^{(r)} - \Omega_- \mathbf{v}^{(s)}]. \quad (95)$$

It should be noted that for the case $\mathbf{q} = 0$, $\mathbf{v}^{(r)} = 0$ (which implies $\Omega_+ = 1$, $\Omega_- = 0$) we recover a simple non-viscoelastic two-fluid model:

$$D_t^{(s)} \rho^{(s)} + \rho^{(s)} \nabla \cdot \mathbf{v}^{(s)} = 0, \quad (96)$$

$$D_t^{(d)} \rho^{(d)} + \rho^{(d)} \nabla \cdot \mathbf{v}^{(d)} = 0, \quad (97)$$

$$\begin{aligned} \rho^{(s)} D_t^{(s)} \mathbf{v}^{(s)} &= -\nabla p^{(s)} + \eta \nabla \nabla \mathbf{v}^{(s)} \\ &+ \frac{1}{\tau} \rho^{(d)} [\mathbf{v}^{(d)} - \mathbf{v}^{(s)}], \end{aligned} \quad (98)$$

$$\begin{aligned} \rho^{(d)} D_t^{(d)} \mathbf{v}^{(d)} &= -\nabla p^{(d)} + \kappa \rho^{(d)} \nabla \nabla^2 \rho^{(d)} \\ &- \frac{1}{\tau} \rho^{(d)} [\mathbf{v}^{(d)} - \mathbf{v}^{(s)}]. \end{aligned} \quad (99)$$

7. Transformation to new variables

It is instructive to transform the equations to a new set of variables that is adapted to the kinematics of the two-body problem. We start by defining the total mass density

$$\rho = \rho^{(d)} + \rho^{(s)} \quad (100)$$

and the reduced mass density

$$\rho^{(\text{red})} = \rho^{-1} \rho^{(d)} \rho^{(s)}. \quad (101)$$

In velocity space, we introduce the mass-averaged velocity

$$\mathbf{V} = \rho^{-1} (\rho^{(d)} \mathbf{v}^{(d)} + \rho^{(s)} \mathbf{v}^{(s)}) \quad (102)$$

and the relative velocity

$$\mathbf{w} = \mathbf{v}^{(d)} - \mathbf{v}^{(s)}. \quad (103)$$

The inverse transformation is given by

$$\mathbf{v}^{(d)} = \mathbf{V} + \frac{\rho^{(\text{red})}}{\rho^{(d)}} \mathbf{w}, \quad (104)$$

$$\mathbf{v}^{(s)} = \mathbf{V} - \frac{\rho^{(\text{red})}}{\rho^{(s)}} \mathbf{w}. \quad (105)$$

Furthermore, we define a new convective derivative via

$$D_t = \partial_t + \mathbf{V} \cdot \nabla, \quad (106)$$

such that

$$D_t^{(d)} = D_t + \frac{\rho^{(\text{red})}}{\rho^{(d)}} \mathbf{w} \cdot \nabla, \quad (107)$$

$$D_t^{(s)} = D_t - \frac{\rho^{(\text{red})}}{\rho^{(s)}} \mathbf{w} \cdot \nabla. \quad (108)$$

The mass conservation equations for $\rho^{(d)}$ and $\rho^{(s)}$ are thus written as

$$D_t \rho^{(d)} + \rho^{(d)} \nabla \cdot \mathbf{V} + \nabla \cdot (\rho^{(\text{red})} \mathbf{w}) = 0, \quad (109)$$

$$D_t \rho^{(s)} + \rho^{(s)} \nabla \cdot \mathbf{V} - \nabla \cdot (\rho^{(\text{red})} \mathbf{w}) = 0. \quad (110)$$

For the total mass density this implies the simple relation

$$D_t \rho + \rho \nabla \cdot \mathbf{V} = 0. \quad (111)$$

Apart from ρ , we need yet another combination of $\rho^{(d)}$ and $\rho^{(s)}$ to describe the dynamics of the density contrast. $\rho^{(\text{red})}$ is not suitable for that purpose, due to its invariance with respect to the exchange $\rho^{(d)} \leftrightarrow \rho^{(s)}$. We therefore take the normalized density difference

$$c = \rho^{-1} (\rho^{(d)} - \rho^{(s)}). \quad (112)$$

This implies

$$\rho^{(d)} = \frac{\rho}{2} (1 + c), \quad (113)$$

$$\rho^{(s)} = \frac{\rho}{2} (1 - c), \quad (114)$$

$$\rho^{(\text{red})} = \frac{\rho}{4} (1 - c^2), \quad (115)$$

$$\mathbf{v}^{(\text{d})} = \mathbf{V} + \frac{1}{2}(1 - c)\mathbf{w}, \quad (116)$$

$$\mathbf{v}^{(\text{s})} = \mathbf{V} - \frac{1}{2}(1 + c)\mathbf{w}, \quad (117)$$

$$D_t^{(\text{d})} = D_t + \frac{1}{2}(1 - c)\mathbf{w} \cdot \nabla, \quad (118)$$

$$D_t^{(\text{s})} = D_t - \frac{1}{2}(1 + c)\mathbf{w} \cdot \nabla. \quad (119)$$

From the equations of motion for $\rho^{(\text{d})}$ and $\rho^{(\text{s})}$ we can find the equations of motion for c and $\rho^{(\text{red})}$:

$$\rho D_t c = -2 \nabla \cdot (\rho^{(\text{red})} \mathbf{w}), \quad (120)$$

$$1 \partial_t \rho^{(\text{red})} + \nabla \cdot (\rho^{(\text{red})} \mathbf{V}) = c \nabla \cdot (\rho^{(\text{red})} \mathbf{w}). \quad (121)$$

We now turn to the velocity equations. We already have derived the dynamics for $\mathbf{v}^{(\text{d})}$ and $\mathbf{v}^{(\text{s})}$, which we abbreviate as

$$\rho^{(\text{d})} D_t^{(\text{d})} \mathbf{v}^{(\text{d})} = \mathbf{f}^{(\text{d})}, \quad (122)$$

$$\rho^{(\text{s})} D_t^{(\text{s})} \mathbf{v}^{(\text{s})} = \mathbf{f}^{(\text{s})}. \quad (123)$$

This information, together with the equations of motion for the densities, is sufficient to construct the equations of motion for \mathbf{V} and \mathbf{w} . After some lengthy algebra we finally find

$$\rho D_t \mathbf{V} + \nabla \cdot (\rho^{(\text{red})} \mathbf{w} \mathbf{w}) = \mathbf{f}^{(\text{d})} + \mathbf{f}^{(\text{s})}, \quad (124)$$

$$\begin{aligned} D_t \mathbf{w} + \mathbf{w} \cdot \nabla \mathbf{V} - c \mathbf{w} \cdot \nabla \mathbf{w} - \frac{1}{2} \mathbf{w} \mathbf{w} \cdot \nabla c \\ = \frac{1}{\rho^{(\text{d})}} \mathbf{f}^{(\text{d})} - \frac{1}{\rho^{(\text{s})}} \mathbf{f}^{(\text{s})}. \end{aligned} \quad (125)$$

The equations for \mathbf{q} and $\mathbf{v}^{(\text{r})}$ may also be transformed; however, we believe this does not provide lots of insight. For this reason, we do not mention the explicit expressions here.

8. Approximations

We now subject the derived equations of motion to a number of approximations, and by this try to find guidelines to construct a simplified field-theoretic model.

(a) *Overdamped harmonic oscillator.* We assume that inertial effects for the motion of \mathbf{q} are negligible. This is a standard assumption in the theory of polymer dynamics, e.g. the Rouse model (see, e.g., reference [42]). This means that in equation (95) we set $D_t^{(\text{d})} \mathbf{v}^{(\text{r})} = 0$. This yields

$$\frac{1}{\tau} [\mathbf{v}^{(\text{r})} - \Omega_- \mathbf{v}^{(\text{s})}] = -\frac{k}{m^{(\text{r})}} \mathbf{q} \quad (126)$$

and

$$\mathbf{v}^{(\text{r})} = \Omega_- \mathbf{v}^{(\text{s})} - \frac{k\tau}{m^{(\text{r})}} \mathbf{q} = \Omega_- \mathbf{v}^{(\text{s})} - \frac{1}{\tau_q} \mathbf{q}; \quad (127)$$

here we have introduced the relaxation time $\tau_q = m^{(\text{r})}/(k\tau)$, which may be viewed as the configurational relaxation time of the polymer chains. We may thus write $k/m^{(\text{r})} = 1/(\tau\tau_q)$; note that we should view τ as a rather small time and τ_q as a large time such that the product $\tau\tau_q$ is of order unity.

In the other equations, we thus eliminate $\mathbf{v}^{(\text{r})}$. On the one hand, we obtain a first-order equation of motion for \mathbf{q} :

$$D_t^{(\text{d})} \mathbf{q} = \Omega_- \mathbf{v}^{(\text{s})} - \frac{1}{\tau_q} \mathbf{q}, \quad (128)$$

while on the other hand the force expression for the solvent is simplified:

$$\begin{aligned} \mathbf{f}^{(\text{s})} = & -\nabla p^{(\text{s})} + \boldsymbol{\eta} : \nabla \nabla \mathbf{v}^{(\text{s})} \\ & + \frac{1}{\tau} \Omega_+^\dagger \rho^{(\text{d})} [\mathbf{v}^{(\text{d})} - \Omega_+ \mathbf{v}^{(\text{s})}] - \frac{\Gamma}{\tau\tau_q} \Omega_-^\dagger \rho^{(\text{d})} \mathbf{q}. \end{aligned} \quad (129)$$

(b) *Lowest-order viscoelastic coupling.* The operators Ω_+ and Ω_- represent the Taylor expansion of the flow field on the scale of the extension of the macromolecules. It is reasonable to assume that the flow field does not vary extremely strongly on that scale, such that a low-order Taylor expansion should be sufficient. We here assume that actually an expansion up to linear order is good enough, which means that we set $\Omega_- = \mathbf{q} \cdot \nabla$ and $\Omega_+ = 1$. This simplifies the force expressions significantly:

$$\begin{aligned} \mathbf{f}^{(\text{s})} = & -\nabla p^{(\text{s})} + \boldsymbol{\eta} : \nabla \nabla \mathbf{v}^{(\text{s})} \\ & + \frac{1}{\tau} \rho^{(\text{d})} \mathbf{w} + \frac{\Gamma}{\tau\tau_q} \nabla \cdot (\rho^{(\text{d})} \mathbf{q} \mathbf{q}), \end{aligned} \quad (130)$$

$$\mathbf{f}^{(\text{d})} = -\nabla p^{(\text{d})} + \kappa \rho^{(\text{d})} \nabla \nabla^2 \rho^{(\text{d})} - \frac{1}{\tau} \rho^{(\text{d})} \mathbf{w}, \quad (131)$$

which means ($p = p^{(\text{s})} + p^{(\text{d})}$ denotes the total pressure)

$$\begin{aligned} \mathbf{f}^{(\text{d})} + \mathbf{f}^{(\text{s})} = & -\nabla p + \boldsymbol{\eta} : \nabla \nabla \mathbf{v}^{(\text{s})} \\ & + \kappa \rho^{(\text{d})} \nabla \nabla^2 \rho^{(\text{d})} + \frac{\Gamma}{\tau\tau_q} \nabla \cdot (\rho^{(\text{d})} \mathbf{q} \mathbf{q}), \end{aligned} \quad (132)$$

$$\begin{aligned} \frac{1}{\rho^{(\text{d})}} \mathbf{f}^{(\text{d})} - \frac{1}{\rho^{(\text{s})}} \mathbf{f}^{(\text{s})} = & -\frac{\nabla p^{(\text{d})}}{\rho^{(\text{d})}} + \frac{\nabla p^{(\text{s})}}{\rho^{(\text{s})}} \\ & - \frac{\boldsymbol{\eta}}{\rho^{(\text{s})}} : \nabla \nabla \mathbf{v}^{(\text{s})} + \kappa \nabla \nabla^2 \rho^{(\text{d})} \\ & - \frac{1}{\tau} \frac{2}{1-c} \mathbf{w} - \frac{\Gamma}{\tau\tau_q} \frac{1}{\rho^{(\text{s})}} \nabla \cdot (\rho^{(\text{d})} \mathbf{q} \mathbf{q}). \end{aligned} \quad (133)$$

The equation of motion for \mathbf{q} gets simplified further:

$$D_t^{(\text{d})} \mathbf{q} = \mathbf{q} \cdot \nabla \mathbf{v}^{(\text{s})} - \frac{1}{\tau_q} \mathbf{q}. \quad (134)$$

- (c) *Incompressibility*. We assume that the total mass density is spatially and temporally constant. The conservation equation for the total mass then simplifies to

$$\nabla \cdot \mathbf{V} = 0. \quad (135)$$

The pressure is therefore no longer derived from an equation of state, but rather acts as a Lagrange multiplier to enforce the incompressibility constraint.

- (d) *Small \mathbf{w}* . The relative velocity \mathbf{w} is a non-hydrodynamic variable, which is therefore expected to relax fairly rapidly. Therefore it is expected to never deviate very much from its value at local thermal equilibrium, which is zero. Let us therefore inspect the so-far derived dynamics for terms linear or quadratic in \mathbf{w} . For this purpose, we replace $\mathbf{w} \rightarrow \varepsilon \mathbf{w}$, where ε is a scalar expansion parameter. This allows us to sort the expressions in terms of powers of ε .

Firstly, we have the conservation of total mass,

$$\nabla \cdot \mathbf{V} = 0, \quad (136)$$

and, secondly, the conservation of the composition, which we represent by the dynamics for $\rho^{(d)}$:

$$D_t \rho^{(d)} = O(\varepsilon). \quad (137)$$

Thirdly, we have the overdamped dynamics for \mathbf{q} :

$$D_t \mathbf{q} = \mathbf{q} \cdot \nabla \mathbf{V} - \frac{1}{\tau_q} \mathbf{q} + O(\varepsilon). \quad (138)$$

In the fourth place, we need to consider the momentum balance

$$\begin{aligned} \rho D_t \mathbf{V} &= -\nabla p + \boldsymbol{\eta} : \nabla \nabla \mathbf{V} + \kappa \rho^{(d)} \nabla \nabla^2 \rho^{(d)} \\ &\quad + \frac{\Gamma}{\tau \tau_q} \nabla \cdot (\rho^{(d)} \mathbf{q} \mathbf{q}) + O(\varepsilon) \\ &= -\nabla p + \eta_s \nabla^2 \mathbf{V} + \kappa \rho^{(d)} \nabla \nabla^2 \rho^{(d)} \\ &\quad + \frac{\Gamma}{\tau \tau_q} \nabla \cdot (\rho^{(d)} \mathbf{q} \mathbf{q}) + O(\varepsilon). \end{aligned} \quad (139)$$

And finally we need to consider the equation of motion for \mathbf{w} (cf equation (125)), which we do not write down explicitly here.

- (e) *Overdamped dynamics for \mathbf{w}* . It is assumed that \mathbf{w} is a fast variable and that it may therefore be adiabatically eliminated for time scales significantly larger than τ , similar to the adiabatic elimination of $\mathbf{v}^{(l)}$ at the beginning of this section. To do this systematically is however a daunting task, and probably (if possible and successful) only of limited value, since the resulting set is probably not fully consistent with non-equilibrium thermodynamics. We therefore take a simpler approach and rather replace the terms $O(\varepsilon)$ with unknown phenomenological terms which need to be chosen in order to ensure consistency with non-equilibrium thermodynamics.

Based upon this philosophy, we thus obtain a set of dynamic equations for the three fields $\rho^{(d)}$, \mathbf{V} , and \mathbf{q} . They read:

$$\nabla \cdot \mathbf{V} = 0, \quad (140)$$

$$D_t \rho^{(d)} = -\nabla \cdot \mathbf{j}^{(int)}, \quad (141)$$

$$\begin{aligned} \rho D_t \mathbf{V} &= -\nabla p + \eta_s \nabla^2 \mathbf{V} + \kappa \rho^{(d)} \nabla \nabla^2 \rho^{(d)} \\ &\quad + \frac{\Gamma}{\tau \tau_q} \nabla \cdot (\rho^{(d)} \mathbf{q} \mathbf{q}) + \nabla \cdot \boldsymbol{\sigma}, \end{aligned} \quad (142)$$

$$D_t \mathbf{q} = \mathbf{q} \cdot \nabla \mathbf{V} - \frac{1}{\tau_q} \mathbf{q} + \mathbf{Q}. \quad (143)$$

Here we have introduced three phenomenological terms: (i) the interdiffusion current $\mathbf{j}^{(int)}$, (ii) a stress tensor $\boldsymbol{\sigma}$, and (iii) the vector \mathbf{Q} , which describes the influence of \mathbf{w} on the dynamics of \mathbf{q} . Note that divergence operators have been introduced in order to keep the conservation laws for the dumbbell mass and the overall momentum.

We have thus gone from a set for two scalar fields and four vector fields to a simplified set that involves only one scalar field and two vector fields as the system's state variables, plus the pressure that acts as a Lagrange multiplier for incompressibility. The arguments presented in this section should not be viewed as rigorous but rather as heuristic. It should be noted that the term $\nabla \cdot (\rho^{(d)} \mathbf{q} \mathbf{q})$ is symmetric under time reversal and hence conservative. The prefactor has been written in terms of two relaxation times; however, physically this should be viewed as the square of an oscillation frequency.

9. Simplified model

It is natural to ask to what extent Poisson brackets might be helpful in deriving equations (140)–(143). To answer this question, let us consider a compressible system (we do not wish to deal with the mathematical complications that arise from an incompressibility constraint), where the dynamical variables are the fields ρ , $\rho^{(d)}$, $\mathbf{j} = \rho \mathbf{V}$ and \mathbf{q} with Hamiltonian

$$H = \int d^3 \mathbf{r} \left[\frac{\mathbf{j}^2}{2\rho} + f + \frac{\kappa}{2} (\nabla \rho^{(d)})^2 + \frac{k}{2} \frac{\rho^{(d)}}{m^{(d)}} \mathbf{q}^2 \right]; \quad (144)$$

here f is the free energy density depending on both ρ and $\rho^{(d)}$.

For the non-vanishing Poisson brackets we find

$$\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r}')\} = -\rho(\mathbf{r}') \nabla \delta(\mathbf{r} - \mathbf{r}'), \quad (145)$$

$$\{\rho^{(d)}(\mathbf{r}), \mathbf{j}(\mathbf{r}')\} = -\rho^{(d)}(\mathbf{r}') \nabla \delta(\mathbf{r} - \mathbf{r}'), \quad (146)$$

$$\begin{aligned} \{q_\alpha(\mathbf{r}), j_\beta(\mathbf{r}')\} \\ = \left[\frac{\rho^{(d)}(\mathbf{r}')}{\rho^{(d)}(\mathbf{r})} q_\alpha(\mathbf{r}) - q_\alpha(\mathbf{r}') \right] \partial_\beta \delta(\mathbf{r} - \mathbf{r}'), \end{aligned} \quad (147)$$

$$\begin{aligned} \{j_\alpha(\mathbf{r}), j_\beta(\mathbf{r}')\} \\ = j_\beta(\mathbf{r}) \partial'_\alpha \delta(\mathbf{r}' - \mathbf{r}) - j_\alpha(\mathbf{r}') \partial_\beta \delta(\mathbf{r} - \mathbf{r}'), \end{aligned} \quad (148)$$

while the functional derivatives of the Hamiltonian are

$$\frac{\delta H}{\delta \mathbf{j}} = \mathbf{V}, \quad (149)$$

$$\frac{\delta H}{\delta \rho} = -\frac{1}{2} \mathbf{V}^2 + \frac{\partial f}{\partial \rho}, \quad (150)$$

$$\frac{\delta H}{\delta \rho^{(d)}} = \frac{\partial f}{\partial \rho^{(d)}} - \kappa \nabla^2 \rho^{(d)} + \frac{k}{2m^{(d)}} \mathbf{q}^2, \quad (151)$$

$$\frac{\delta H}{\delta \mathbf{q}} = k \frac{\rho^{(d)}}{m^{(d)}} \mathbf{q}. \quad (152)$$

We can now insert these results to calculate the conservative equations of motion, *as they are produced by the Poisson bracket formalism*. After some lengthy but straightforward algebra we find

$$\partial_t \rho = -\nabla \cdot (\rho \mathbf{V}), \quad (153)$$

$$\partial_t \rho^{(d)} = -\nabla \cdot (\rho^{(d)} \mathbf{V}), \quad (154)$$

$$D_t q_\alpha = q_\alpha \frac{1}{\rho^{(d)}} \mathbf{V} \cdot \nabla \rho^{(d)}, \quad (155)$$

$$\begin{aligned} \partial_t j_\alpha &= -\partial_\beta (j_\alpha V_\beta) - \partial_\alpha p + \kappa \rho^{(d)} \nabla^2 \rho^{(d)} \\ &\quad - \frac{k}{m^{(d)}} \mathbf{q}^2 \partial_\alpha \rho^{(d)}, \end{aligned} \quad (156)$$

here the pressure involves contributions from both $\partial f/\partial \rho$ and $\partial f/\partial \rho^{(d)}$. Comparing this with the set of equations that we heuristically derived in the previous section, we see that (i) the equation of motion for \mathbf{q} couples to the flow field in a significantly different fashion, and that (ii) the elastic force term in the momentum equation looks different, and *does not conserve the momentum*. Such an equation is however simply unsuitable for hydrodynamics. We therefore conclude that for the simplified (or reduced) set of equations of motion *we have to abandon the Poisson bracket formalism*. In other words: it is impossible to eliminate the undesired velocities adiabatically, and at the same time maintain the Hamiltonian structure of the theory. Given the fact that momentum variables play a decisive role in Hamiltonian dynamics, and the fact that we have removed them, this result is hardly surprising. It is perhaps possible to do the development within some Hamiltonian formalism with constraints, but this is beyond the scope of the present paper.

We therefore go back to equations (140)–(143), which we consider as a reasonable starting point for further developments. The Hamiltonian

$$\begin{aligned} H &= \int d^3 \mathbf{r} \left[\frac{\rho}{2} \mathbf{V}^2 + f + \frac{\kappa}{2} (\nabla \rho^{(d)})^2 + \frac{k}{2} \frac{\rho^{(d)}}{m^{(d)}} \mathbf{q}^2 \right] \\ &= \int d^3 \mathbf{r} \left[\frac{\rho}{2} \mathbf{V}^2 + f + \frac{\kappa}{2} (\nabla \rho^{(d)})^2 \right. \\ &\quad \left. + \frac{1}{2} \frac{\Gamma}{\tau \tau_q} \rho^{(d)} \mathbf{q}^2 \right] \end{aligned} \quad (157)$$

must be viewed as a functional of \mathbf{V} , \mathbf{q} and $\rho^{(d)}$; its derivatives are

$$\frac{\delta H}{\delta \mathbf{V}} = \rho \mathbf{V}, \quad (158)$$

$$\frac{\delta H}{\delta \rho^{(d)}} = \frac{\partial f}{\partial \rho^{(d)}} - \kappa \nabla^2 \rho^{(d)} + \frac{1}{2} \frac{\Gamma}{\tau \tau_q} \mathbf{q}^2, \quad (159)$$

$$\frac{\delta H}{\delta \mathbf{q}} = \frac{\Gamma}{\tau \tau_q} \rho^{(d)} \mathbf{q}. \quad (160)$$

We now consider a reduced version of the dynamic equations equations (140)–(143), where we discard the phenomenological terms $\mathbf{j}^{(\text{int})}$, $\boldsymbol{\sigma}$ and \mathbf{Q} , as well as the viscous dissipation and the dissipative relaxation of \mathbf{q} ($\propto 1/\tau_q$):

$$\nabla \cdot \mathbf{V} = 0, \quad (161)$$

$$D_t \rho^{(d)} = 0, \quad (162)$$

$$\begin{aligned} \rho D_t \mathbf{V} &= -\nabla p + \kappa \rho^{(d)} \nabla \nabla^2 \rho^{(d)} \\ &\quad + \frac{\Gamma}{\tau \tau_q} \nabla \cdot (\rho^{(d)} \mathbf{q} \mathbf{q}) \end{aligned} \quad (163)$$

$$D_t \mathbf{q} = \mathbf{q} \cdot \nabla \mathbf{V}. \quad (164)$$

In what follows, we wish to demonstrate that this system is conservative, i.e. is characterized by $dH/dt = 0$.

We first notice that for any field ϕ the relation

$$\int d^3 \mathbf{r} \phi \mathbf{V} \cdot \nabla \phi = 0 \quad (165)$$

holds, as can be seen from integration by parts and incompressibility. As a consequence, we have

$$\int d^3 \mathbf{r} \phi D_t \phi = \int d^3 \mathbf{r} \phi \partial_t \phi. \quad (166)$$

From equation (159) we conclude

$$\partial_\alpha \left(\frac{\delta H}{\delta \rho^{(d)}} \right) = \partial_\alpha \frac{\partial f}{\partial \rho^{(d)}} - \kappa \partial_\alpha \nabla^2 \rho^{(d)} + \frac{\Gamma}{\tau \tau_q} q_\beta \partial_\alpha q_\beta, \quad (167)$$

$$\rho^{(d)} \partial_\alpha \left(\frac{\delta H}{\delta \rho^{(d)}} \right) = \partial_\alpha p^{(d)} - \kappa \rho^{(d)} \partial_\alpha \nabla^2 \rho^{(d)} + \frac{\delta H}{\delta q_\beta} \partial_\alpha q_\beta. \quad (168)$$

We may use this to eliminate the interface term in the momentum equation:

$$\begin{aligned} \rho D_t V_\alpha &= -\partial_\alpha p + \partial_\alpha p^{(d)} \\ &\quad - \rho^{(d)} \partial_\alpha \left(\frac{\delta H}{\delta \rho^{(d)}} \right) + \frac{\delta H}{\delta q_\beta} \partial_\alpha q_\beta + \partial_\beta \left(\frac{\delta H}{\delta q_\beta} q_\alpha \right). \end{aligned} \quad (169)$$

We now multiply this equation with V_α and integrate over space. On the left-hand side, this yields, making use of equation (166),

$$\begin{aligned} \int d^3\mathbf{r} V_\alpha \rho D_t V_\alpha &= \int d^3\mathbf{r} \rho V_\alpha \partial_t V_\alpha \\ &= \int d^3\mathbf{r} \frac{\delta H}{\delta \mathbf{V}} \cdot \partial_t \mathbf{V}. \end{aligned} \quad (170)$$

On the right-hand side, we employ a few integrations by parts and incompressibility, and also insert the other equations of motion. In particular, we obtain the term

$$\begin{aligned} - \int d^3\mathbf{r} V_\alpha \rho^{(d)} \partial_\alpha \left(\frac{\delta H}{\delta \rho^{(d)}} \right) \\ = \int d^3\mathbf{r} \frac{\delta H}{\delta \rho^{(d)}} V_\alpha \partial_\alpha \rho^{(d)} = \int d^3\mathbf{r} \frac{\delta H}{\delta \rho^{(d)}} (D_t - \partial_t) \rho^{(d)} \\ = - \int d^3\mathbf{r} \frac{\delta H}{\delta \rho^{(d)}} \partial_t \rho^{(d)} \end{aligned} \quad (171)$$

as well as

$$\begin{aligned} \int d^3\mathbf{r} V_\alpha \frac{\delta H}{\delta q_\beta} \partial_\alpha q_\beta &= \int d^3\mathbf{r} \frac{\delta H}{\delta q_\beta} (D_t - \partial_t) q_\beta \\ &= - \int d^3\mathbf{r} \frac{\delta H}{\delta \mathbf{q}} \cdot \partial_t \mathbf{q} + \int d^3\mathbf{r} \frac{\delta H}{\delta q_\beta} q_\alpha \partial_\alpha V_\beta \\ &= - \int d^3\mathbf{r} \frac{\delta H}{\delta \mathbf{q}} \cdot \partial_t \mathbf{q} - \int d^3\mathbf{r} V_\beta \partial_\alpha \left(\frac{\delta H}{\delta q_\beta} q_\alpha \right) \end{aligned} \quad (172)$$

and

$$\begin{aligned} \int d^3\mathbf{r} V_\alpha \partial_\beta \left(\frac{\delta H}{\delta q_\beta} q_\alpha \right) \\ = \int d^3\mathbf{r} V_\alpha \partial_\beta \left(\frac{\delta H}{\delta q_\alpha} q_\beta \right) = \int d^3\mathbf{r} V_\beta \partial_\alpha \left(\frac{\delta H}{\delta q_\beta} q_\alpha \right). \end{aligned} \quad (173)$$

This yields

$$\int d^3\mathbf{r} \left[\frac{\delta H}{\delta \mathbf{V}} \cdot \partial_t \mathbf{V} + \frac{\delta H}{\delta \rho^{(d)}} \partial_t \rho^{(d)} + \frac{\delta H}{\delta \mathbf{q}} \cdot \partial_t \mathbf{q} \right] = 0. \quad (174)$$

The left-hand side of this equation amounts to dH/dt .

It is therefore clear that the additional terms $\mathbf{j}^{(\text{int})}$, $\boldsymbol{\sigma}$, and \mathbf{Q} , should be of *dissipative* nature. For the dissipative part of the dynamics we thus have

$$\nabla \cdot \mathbf{V} = 0, \quad (175)$$

$$\partial_t \rho^{(d)} = -\nabla \cdot \mathbf{j}^{(\text{int})}, \quad (176)$$

$$\rho \partial_t \mathbf{V} = \eta_s \nabla^2 \mathbf{V} + \nabla \cdot \boldsymbol{\sigma}, \quad (177)$$

$$\partial_t \mathbf{q} = -\frac{1}{\tau_q} \mathbf{q} + \mathbf{Q}. \quad (178)$$

For the various contributions to the dissipation rate we obtain

$$\begin{aligned} \int d^3\mathbf{r} \frac{\delta H}{\delta V_\alpha} \partial_t V_\alpha &= \int d^3\mathbf{r} V_\alpha \rho \partial_t V_\alpha \\ &= \eta_s \int d^3\mathbf{r} V_\alpha \partial_\beta \partial_\beta V_\alpha + \int d^3\mathbf{r} V_\alpha \partial_\beta \sigma_{\alpha\beta} \\ &= -\eta_s \int d^3\mathbf{r} (\partial_\beta V_\alpha)^2 - \int d^3\mathbf{r} \sigma_{\alpha\beta} \partial_\beta V_\alpha, \end{aligned} \quad (179)$$

$$\begin{aligned} \int d^3\mathbf{r} \frac{\delta H}{\delta \mathbf{q}} \cdot \partial_t \mathbf{q} \\ = \frac{\Gamma}{\tau \tau_q} \int d^3\mathbf{r} \rho^{(d)} \mathbf{q} \cdot \left[-\frac{1}{\tau_q} \mathbf{q} + \mathbf{Q} \right] \\ = -\frac{\Gamma}{\tau \tau_q^2} \int d^3\mathbf{r} \rho^{(d)} \mathbf{q}^2 + \frac{\Gamma}{\tau \tau_q} \int d^3\mathbf{r} \rho^{(d)} \mathbf{q} \cdot \mathbf{Q}, \end{aligned} \quad (180)$$

$$\begin{aligned} \int d^3\mathbf{r} \frac{\delta H}{\delta \rho^{(d)}} \partial_t \rho^{(d)} &= - \int d^3\mathbf{r} \frac{\delta H}{\delta \rho^{(d)}} \nabla \cdot \mathbf{j}^{(\text{int})} \\ &= \int d^3\mathbf{r} \mathbf{j}^{(\text{int})} \cdot \nabla \left(\frac{\delta H}{\delta \rho^{(d)}} \right). \end{aligned} \quad (181)$$

In what follows, we will assume a simple model for the dissipative terms. We will assume that $\boldsymbol{\sigma}$ and \mathbf{Q} vanish (or that their effect can be absorbed in a re-definition of η_s and τ_q), and that

$$\mathbf{j}^{(\text{int})} = -M(\rho^{(d)}) \nabla \left(\frac{\delta H}{\delta \rho^{(d)}} \right), \quad (182)$$

where the function $M(\rho^{(d)}) \geq 0$ is essentially the Onsager coefficient for interdiffusion. It is then obvious that the relation $dH/dt \leq 0$ strictly holds. It should also be noted that, in terms of the general formalism of section 3, we have a matrix of dissipative terms that is diagonal and therefore obviously symmetric. In other words, the model assumes the absence of dissipative cross-couplings. Whether such cross-terms are permitted at all by symmetry, and, if yes, what form they may have, is an open question that we do not wish to investigate here. In any case, when introducing such terms one needs to take care that the symmetry and the positive-definiteness of the matrix is strictly maintained. An important observation is that the interdiffusion current is driven by a bulk term, an interface term, and an elastic term. This last driving force, which has apparently first been noted by Doi and Onuki [19], appears here as a straightforward consequence of the second law.

In summary, we have obtained the set of equations of motion

$$\nabla \cdot \mathbf{V} = 0, \quad (183)$$

$$D_t \rho^{(d)} = \nabla \cdot \left[M(\rho^{(d)}) \nabla \left(\frac{\delta H}{\delta \rho^{(d)}} \right) \right], \quad (184)$$

$$\begin{aligned} \rho D_t \mathbf{V} &= -\nabla p + \eta_s \nabla^2 \mathbf{V} + \kappa \rho^{(d)} \nabla \nabla^2 \rho^{(d)} \\ &\quad + \frac{\Gamma}{\tau \tau_q} \nabla \cdot (\rho^{(d)} \mathbf{q} \mathbf{q}), \end{aligned} \quad (185)$$

$$D_t \mathbf{q} = \mathbf{q} \cdot \nabla V - \frac{1}{\tau_q} \mathbf{q}. \quad (186)$$

In principle, this concludes our derivation. To make contact with the standard rheological literature, we transform the equations from the vector field \mathbf{q} to the conformation tensor field $\mathbf{C} = \mathbf{q}\mathbf{q}$, which is strictly invariant under flip $\mathbf{q} \rightarrow -\mathbf{q}$. In the momentum equation and in the convection–diffusion equation for $\rho^{(d)}$, this is a simple insertion (note $\mathbf{q}^2 = \text{tr } \mathbf{C}$). The equation of motion for \mathbf{q} is easily transformed to

$$D_t C_{\alpha\beta} - C_{\alpha\gamma} \partial_\gamma V_\beta - C_{\beta\gamma} \partial_\gamma V_\alpha = -\frac{2}{\tau_q} C_{\alpha\beta}. \quad (187)$$

It should be noted that the left-hand side is nothing but the so-called ‘upper convected derivative’ known in the rheological literature. Furthermore, it should be noted that the equation of motion of the standard Oldroyd-B model *differs* from equation (187); it rather reads

$$\begin{aligned} D_t C_{\alpha\beta} - C_{\alpha\gamma} \partial_\gamma V_\beta - C_{\beta\gamma} \partial_\gamma V_\alpha \\ = -\frac{2}{\tau_q} \left[C_{\alpha\beta} - \frac{k_B T}{k} \delta_{\alpha\beta} \right], \end{aligned} \quad (188)$$

where $k_B T$ denotes the thermal energy. The difference can be traced back to the ensemble problems already mentioned in the Introduction; in explicit terms this is worked out in appendix C.

10. Van der Waals model

We have so far not yet specified what free energy we use for $f^{(d)}(\rho^{(d)})$. Since the solvent in our model is just a structureless ideal gas whose main purpose is to transport momentum, we may view the phase separation, from the point of view of thermodynamics, as just a gas–liquid transition of the polymer component. The standard mean field model for the gas–liquid transition is however the Van der Waals model. The purpose of the present section is therefore to briefly elucidate how the model should be modified in order to take into account the loss of translational entropy due to chain connectivity.

10.1. Monatomic ideal gas

Let us first start with the well-known case of a monatomic fluid. For a single point particle in a volume V , the canonical partition function at temperature T is

$$z_{\text{id}}(V, T) = \frac{V}{\Lambda^3}, \quad (189)$$

where Λ is the thermal de Broglie wavelength, which just acts as a normalization factor to make sure z_{id} is dimensionless. For N indistinguishable non-interacting particles the partition function then is

$$\mathcal{Z}_c(N, V, T) = \frac{z_{\text{id}}^N}{N!}. \quad (190)$$

With Stirling’s approximation, the corresponding Helmholtz free energy of the ideal gas is

$$\beta F_{\text{id}}(N, V, T) = -\ln \mathcal{Z}_c = -N \ln \left(\frac{V}{\Lambda^3} \right) + N \ln N - N. \quad (191)$$

Here $\beta = 1/(k_B T)$, where k_B is Boltzmann’s constant. The resulting pressure is the well-known expression

$$\beta p_{\text{id}} = -\beta \frac{\partial F_{\text{id}}}{\partial V} = \frac{N}{V}. \quad (192)$$

10.2. Monatomic Van der Waals fluid

The Van der Waals mean field approximation assumes that the multi-particle partition function may be factorized into the product of effective single-particle partition functions,

$$\mathcal{Z}_c(N, V, T) = \frac{z_{\text{eff}}^N}{N!}, \quad (193)$$

where the model assumes that the effects of short-range molecular repulsion and medium-range attraction may be taken into account by (i) an effective atomic volume b , such that only the volume $V - Nb$ is available for each particle, and (ii) an effective attraction energy per atom U ($U > 0$). Therefore we get

$$z_{\text{eff}} = \frac{1}{\Lambda^3} (V - Nb) \exp(\beta U). \quad (194)$$

Within the mean field picture, U should be proportional to the probability to find another particle in the vicinity of a test particle, or, in other words, proportional to the density N/V . We therefore write

$$U = a \frac{N}{V} \quad (195)$$

with a parameter $a > 0$, such that

$$z_{\text{eff}} = z_{\text{id}} \left(1 - \frac{Nb}{V} \right) \exp \left(\beta a \frac{N}{V} \right). \quad (196)$$

This results in the Helmholtz free energy

$$\begin{aligned} \beta F &= -N \ln z_{\text{eff}} + N \ln N - N \\ &= \beta F_{\text{id}} - N \ln \left(1 - \frac{Nb}{V} \right) - \beta a \frac{N^2}{V}, \end{aligned} \quad (197)$$

and in turn in the pressure

$$\beta p = -\beta \frac{\partial F}{\partial V} = \frac{N}{V - Nb} - \beta a \left(\frac{N}{V} \right)^2. \quad (198)$$

10.3. Polymeric Van der Waals fluid

We now assume that the system comprises N polymer chains, each of which is in turn composed of M monomers. We therefore have to deal with two densities, (i) the number of chains per unit volume, N/V , and (ii) the number of monomers per unit volume, MN/V .

The polymer analog of the single free particle is the single free random walk, where all interactions are turned off, except the bonded interactions that keep the monomers together. The partition function of that walk is therefore

$$z_{\text{id}}(V, T) = \frac{V}{\Lambda^3} z_{\text{conf}}, \quad (199)$$

where the factor z_{conf} takes into account the entropy that is associated with the different conformations of the walk. We do not attempt to write down an explicit expression for z_{conf} but only note that (i) it depends exponentially on M , and (ii) it is independent of both N and V . This latter independence means that the precise form does not matter for the further development.

In analogy to the previous subsection, we may then write down the single-walk effective partition function for a polymeric Van der Waals system:

$$z_{\text{eff}} = z_{\text{id}} \left(1 - \frac{NMb}{V} \right) \exp \left(\beta a \frac{NM}{V} M \right); \quad (200)$$

here we have replaced the density N/V by the monomer density NM/V , which is logical when taking into account the physical origin of the corresponding terms. The last factor of M in the Boltzmann factor takes into account that for the statistical weight of the whole walk we have to add up all the attractions which the monomers of the walk experience.

Therefore we obtain for the Helmholtz free energy

$$\begin{aligned} \beta F &= -N \ln z_{\text{eff}} + N \ln N - N \\ &= \beta F_{\text{id}} - N \ln \left(1 - \frac{NMb}{V} \right) - \beta a \frac{N^2 M^2}{V}. \end{aligned} \quad (201)$$

For calculating the equation of state, we only need to take into account that the ideal-gas pressure of the system of walks is given by

$$\beta p_{\text{id}} = \frac{N}{V}, \quad (202)$$

and hence the pressure is given by

$$\beta p = -\beta \frac{\partial F}{\partial V} = \frac{N}{V - NMb} - \beta a \left(\frac{NM}{V} \right)^2. \quad (203)$$

11. Conclusions

This paper has presented a somewhat unconventional approach to the derivation of rheological equations for polymer solutions, which we nevertheless consider as quite useful. Instead of the usual two-scale description, i.e. hydrodynamics on the macroscopic scale coupled to a FPE with unconstrained averaging on the macromolecular scale, we here treat the hydrodynamic degrees of freedom and the macromolecular ones on the same basis. The procedure consists of (i) the definition of a sufficiently simple molecular system, (ii) the definition of a set of fields which can be expressed in terms of the molecular quantities, and which is chosen sufficiently large to facilitate a consistent description of the conservative dynamics by a

Hamiltonian (Poisson bracket) formalism, (iii) the direct construction of the corresponding dynamic equations within the framework of a dissipative Hamiltonian system, (iv) simplification via adiabatic elimination of fast variables, and (v) postulating phenomenological expressions for the unknown terms, such that the second law is automatically built into the description. This approach is in spirit somewhat similar to analogous developments in the theory of liquid crystals [23]. As discussed in section 2.4, we believe that it is physically justified to describe the polymer conformations in terms of a vector field of end-to-end vectors. Compared to the rheology, the ‘model H’ aspects are fairly straightforward to take into account.

From our model (phantom Hookean dumbbells which interact with the solvent via Stokes friction, and with each other via a Van der Waals background) we find a set of relatively simple equations with a straightforward coupling of the conformation tensor to both the momentum conservation equation and to the interdiffusion, while the dynamics of the conformation tensor itself is, except for convection described by the upper convected derivative, just a simple relaxation towards zero. We believe that a nonzero average conformation tensor should be described by coupling the whole system consistently to Langevin noise. This extension of the model is however left for future work.

Furthermore, it is far from clear if the model has sufficient physical content to reproduce the rich phenomenology that is observed experimentally for viscoelastic phase separation. This question can only be answered by detailed simulations, and the scan of wide ranges of parameters, which is also deferred to future work. In this context, we would like to emphasize that the parameter $\Gamma/(\tau\tau_q)$ may be viewed as a parameter which controls the strength of the viscoelastic coupling: if we set that parameter to zero, we recover the standard model H. Conversely, for large values of the parameter one should expect a strong coupling to the macromolecular internal degree of freedom, and therefore at least some viscoelastic effects on the phase separation dynamics.

Additional directions for future research are: (i) rigorous mathematical analysis of the derived model with respect to existence, weak–strong uniqueness and stability; (ii) numerical approximation and extensive benchmarking; (iii) generalization to non-Hookean force laws such as, e.g. the FENE potential [43]; and (iv) a more detailed description of polymer conformations by higher-order Rouse modes [42]. It is our strong belief that our new approach may have an important impact to new developments of consistent and physically well-founded rheological models.

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Data availability statement

No new data were created or analysed in this study.

Appendix A. Poisson brackets I: general formalism

For the convenience of the reader, we quickly review here the Poisson bracket formalism of Hamiltonian dynamics. We start with a set of generalized coordinates $\{q_i\}$ and the corresponding canonically conjugate momenta $\{p_i\}$, which together form the phase space. The Hamiltonian $H = H(\{q_i\}, \{p_i\})$ is assumed to not explicitly depend on time, and the basic Hamiltonian equations of motion are given by

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad (\text{A.1})$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}. \quad (\text{A.2})$$

We now consider observables f, g, h, \dots , i.e. functions on the phase space, where again we assume the absence of explicit time dependence. The Poisson bracket between f and g is then defined via

$$\{f, g\} = \sum_i \left(\frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \right). \quad (\text{A.3})$$

We note that $\{f, g\}$ is bilinear and antisymmetric. Furthermore, we note the elementary brackets

$$\{q_i, p_j\} = \delta_{ij} \quad (\text{A.4})$$

and the product rule

$$\{f, gh\} = \{f, g\}h + g\{f, h\}. \quad (\text{A.5})$$

The equation of motion of f then reads, as a direct consequence of the basic Hamiltonian equations of motion,

$$\dot{f} = \{f, H\}. \quad (\text{A.6})$$

We now assume that there is some new set of variables $\{x_i\}$, in terms of which the Hamiltonian H can be conveniently written, $H = H(\{x_i\})$. Importantly, we do *not* assume that these variables form pairs of canonically conjugate variables. The equation of motion for f then reads

$$\dot{f} = \sum_j \{f, x_j\} \frac{\partial H}{\partial x_j}. \quad (\text{A.7})$$

In particular,

$$\dot{x}_i = \sum_j \{x_i, x_j\} \frac{\partial H}{\partial x_j}. \quad (\text{A.8})$$

If we now assume that, in terms of Poisson brackets, the new variables form a closed set, i.e. that $\{x_i, x_j\}$ may be expressed again in terms of the x_i , then we get a closed system of equations where no reference to the original canonical variables needs to be made. This is particularly useful if the x_i form a small set of collective variables.

The generalization to field theory is obvious. We assume that the Hamiltonian H is a functional of a set of fields $\Phi_i(\mathbf{r})$, $H = H(\{\Phi_i\})$, and we again assume that the fields form a closed set in terms of Poisson brackets. Then the field-theoretic equations of motion are written as

$$\dot{\Phi}_i(\mathbf{r}) = \sum_j \int d^3\mathbf{r}' \{\Phi_i(\mathbf{r}), \Phi_j(\mathbf{r}')\} \frac{\delta H}{\delta \Phi_j(\mathbf{r}')}, \quad (\text{A.9})$$

where $\delta H/\delta \Phi$ denotes the functional derivative. For hydrodynamic theories, where the continuum formulation is intended to be a simplified and coarse-grained description of an underlying particle system, it is useful to write the fields in terms of the microscopic coordinates and momenta, and use these representations to evaluate the Poisson brackets.

Appendix B. Poisson brackets II: Euler equations

Let us try to elucidate that strategy via the simple example of the Euler equations of hydrodynamics. Starting point are the fields mass density

$$\rho(\mathbf{r}) = m \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (\text{B.1})$$

(we assume we have a system of particles with mass m located at positions \mathbf{r}_i), and momentum density

$$\mathbf{j}(\mathbf{r}) = \sum_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (\text{B.2})$$

with particle momenta \mathbf{p}_i . We do not consider an energy or entropy field since we are interested in isothermal hydrodynamics, such that the conserved Hamiltonian should be interpreted as the Helmholtz free energy of the system. One immediately finds, for any observable φ ,

$$\{\delta(\mathbf{r} - \mathbf{r}_i), \varphi\} = -\frac{\partial \varphi}{\partial \mathbf{p}_i} \cdot \nabla \delta(\mathbf{r} - \mathbf{r}_i) \quad (\text{B.3})$$

and thus

$$\{\rho(\mathbf{r}), \rho(\mathbf{r}')\} = 0, \quad (\text{B.4})$$

$$\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r}')\} = -\rho(\mathbf{r}') \nabla \delta(\mathbf{r} - \mathbf{r}'), \quad (\text{B.5})$$

$$\{j_\alpha(\mathbf{r}), j_\beta(\mathbf{r}')\} = j_\beta(\mathbf{r}) \partial'_\alpha \delta(\mathbf{r}' - \mathbf{r}) - j_\alpha(\mathbf{r}') \partial_\beta \delta(\mathbf{r} - \mathbf{r}'), \quad (\text{B.6})$$

where Greek letters denote Cartesian indexes (with Einstein summation convention implied), and $\partial_\alpha \equiv \partial/\partial r_\alpha$.

The transition from the particle picture to field theory is done by replacing ρ and \mathbf{j} by ‘smeared’ continuous fields. Here it is useful to define

$$\mathbf{v}(\mathbf{r}) = \frac{\mathbf{j}(\mathbf{r})}{\rho(\mathbf{r})}. \quad (\text{B.7})$$

We then postulate a field-theoretic Hamiltonian via

$$H[\rho, \mathbf{j}] = \int d^3\mathbf{r} \left[\frac{\mathbf{j}^2}{2\rho} + f(\rho) \right], \quad (\text{B.8})$$

where f is the free energy density. The derivatives are given by

$$\frac{\delta H}{\delta \rho} = -\frac{1}{2}v^2 + \frac{\partial f}{\partial \rho}, \quad (\text{B.9})$$

$$\frac{\delta H}{\delta \mathbf{j}} = \mathbf{v}. \quad (\text{B.10})$$

Inserting these results into the field-theoretic Hamiltonian equations of motion, we find, after a few lines of straightforward algebra

$$\partial_t \rho + \nabla \cdot \mathbf{j} = 0, \quad (\text{B.11})$$

$$\partial_t j_\alpha + \partial_\beta (\rho v_\alpha v_\beta) = -\rho \partial_\alpha \left(\frac{\partial f}{\partial \rho} \right); \quad (\text{B.12})$$

the first equation obviously is the mass conservation equation.

According to the first law, we have for the free energy per mass

$$d \left(\frac{f}{\rho} \right) = -s dT - p d \left(\frac{1}{\rho} \right), \quad (\text{B.13})$$

where s is the entropy per mass, T the temperature, and p the pressure. In an isothermal situation, $dT = 0$, and

$$\frac{\partial}{\partial \rho} \left(\frac{f}{\rho} \right) = \frac{p}{\rho^2} \quad (\text{B.14})$$

or

$$p = \rho^2 \frac{\partial}{\partial \rho} \left(\frac{f}{\rho} \right) = \rho \frac{\partial f}{\partial \rho} - f, \quad (\text{B.15})$$

which implies

$$\partial_\alpha p = \rho \partial_\alpha \left(\frac{\partial f}{\partial \rho} \right). \quad (\text{B.16})$$

The momentum equation therefore reads

$$\partial_t j_\alpha + \partial_\beta (\rho v_\alpha v_\beta) = -\partial_\alpha p, \quad (\text{B.17})$$

which is the well-known Euler equation.

Appendix C. Ensemble problems in meso–macro coupling

The present appendix attempts to elucidate in some more detail what we mean with our remarks about ‘ensemble problems’ in the main text. We hope that formulating these considerations in a general and abstract language helps to clarify our point.

We assume that the macroscopic domain can be divided into small cells, such that the mesoscale description for a particular cell comprises a set of dynamic variables ξ_i , $i = 1, \dots, n$. We may e.g. assume that the ξ_i describe the conformational degrees of freedom of a polymer chain, or similar. Importantly, we assume that the ξ_i only describe *internal* degrees of freedom of the macromolecules (such as first or higher-order Rouse modes), while the center-of-mass coordinates of the molecules are *not* included in the set.

Furthermore, we assume, in accord with the development outlined in the monograph by Bird *et al* [16], that the ξ_i are subject to a (known) Fokker–Planck dynamics, which describes

the time evolution of the probability density $P(\{\xi_i\}, t)$. The ingredients of this description are the (symmetric and positive-semidefinite) diffusion tensor $D_{ij} = D_{ij}(\{\xi_k\})$, the mesoscopic free energy $H_{\text{meso}}(\{\xi_i\})$, the thermal energy $k_B T$ (or $\beta = 1/(k_B T)$), and an additional non-equilibrium driving force F_j that is inferred from the macroscale—for example, we may think of the effects of a local shear flow. The Fokker–Planck equation (FPE) is then written as

$$\begin{aligned} \partial_t P &= \sum_{ij} \frac{\partial}{\partial \xi_i} D_{ij} \left(\frac{\partial}{\partial \xi_j} + \beta \frac{\partial H_{\text{meso}}}{\partial \xi_j} - \beta F_j \right) P \\ &=: \mathcal{L}_{\text{FP}} P, \end{aligned} \quad (\text{C.1})$$

which defines the Fokker–Planck operator \mathcal{L}_{FP} . In the absence of external driving ($F_j = 0$), the Boltzmann distribution $P \propto \exp(-\beta H_{\text{meso}})$ is an obvious stationary solution.

The meso–macro coupling is then facilitated by a set of observables $A_i(\{\xi_j\})$, $i = 1, \dots, m$, which are taken as additional dynamic variables in the macroscopic equations of motion. ‘Additional’ here means ‘in addition to the standard hydrodynamic variables’ like mass and momentum. As the A_i appear at the macro-level, they should be considered as slow variables, i.e. ideally have a significantly slower dynamics than the remaining mesoscopic degrees of freedom.

For each of the A_i , an additional equation of motion on the macro-level is needed. The most reasonable dynamics that we may assume for the A_i on the macroscale is the time evolution of the *thermal averages*

$$A_i^{(\text{mac})} := \langle A_i \rangle = \int d^n \xi A_i P, \quad (\text{C.2})$$

which can be evaluated either by analytical solution of the FPE (if feasible) or by numerical simulation. Introducing $\mathcal{L}_{\text{FP}}^\dagger$, the adjoint Fokker–Planck operator, we may write

$$\begin{aligned} \partial_t \langle A_i \rangle &= \int d^n \xi A_i \mathcal{L}_{\text{FP}} P = \int d^n \xi \left[\mathcal{L}_{\text{FP}}^\dagger A_i \right] P \\ &= \left\langle \mathcal{L}_{\text{FP}}^\dagger A_i \right\rangle, \end{aligned} \quad (\text{C.3})$$

which provides an analytical form for the equation of motion if the solution of the FPE, plus the subsequent averaging, may be calculated analytically. However, the conceptual framework does not depend on the analytical solvability at all, since the averages may always be sampled by numerical simulation.

The thus-derived equations of motion for the $\langle A_i \rangle$ may then be used as additional equations on the macroscale, however with the following ‘recipe’, which takes into account that the center-of-mass coordinates have been omitted, such that convection effects have to be put in ‘by hand’: (i) the expression $\partial_t \langle A_i \rangle$ must be replaced by $D_t A_i^{(\text{mac})}$, where $D_t = \partial_t + \mathbf{V} \cdot \nabla$ is the convective derivative and \mathbf{V} denotes the macroscopic flow field. (ii) If the mesoscale description implies the evaluation of some property of the flow field (e.g. its value, or its derivatives) at a molecular center-of-mass coordinate, the corresponding evaluation on the macroscale must be done at the position \mathbf{r} , which denotes the position of the meso-cell in the macro-domain.

As a second step, we need to consider the important back-coupling of the mesoscale degrees of freedom to the macroscopic hydrodynamics. This means that an additional viscoelastic stress needs to appear in the momentum conservation equation.

The key element is here the Kramers (or virial) expression for the stress tensor components $\Pi_{\alpha\beta}$, which allows us to evaluate a momentary (and local) stress from a given mesoscopic configuration. For the time being, we do not give the explicit formula here but just write this as a function $\tilde{\Pi}_{\alpha\beta}(\{\xi_i\})$. The ξ_i , however, do not appear in the macroscopic description—here we rather consider the dynamics of $A_i^{(\text{mac})}$. Therefore another function $\bar{\Pi}_{\alpha\beta}(\{A_i^{(\text{mac})}\})$ is needed. The important question is hence: how should $\bar{\Pi}_{\alpha\beta}(\{A_i^{(\text{mac})}\})$ be constructed from $\tilde{\Pi}_{\alpha\beta}(\{\xi_i\})$?

To tackle this question, the approach put forward in the textbook by Bird *et al* [16] starts from a straightforward observation: just as the time-dependent averages $\langle A_i \rangle$, we may also evaluate

$$\langle \tilde{\Pi}_{\alpha\beta} \rangle = \int d^n \xi \tilde{\Pi}_{\alpha\beta} P, \quad (\text{C.4})$$

again, either by analytic solution of the FPE, or by numerical simulation.

From there, the textbook proceeds as follows: first, it is observed that, for suitably chosen observables A_i , equations (C.2) and (C.4) happen to result in a relation that expresses $\langle \tilde{\Pi}_{\alpha\beta} \rangle$ as a function of the $\langle A_i \rangle$:

$$\langle \tilde{\Pi}_{\alpha\beta} \rangle = \Sigma_{\alpha\beta}(\{\langle A_i \rangle\}). \quad (\text{C.5})$$

As a matter of fact, the approach *chooses* the variables A_i in such a way such that the construction of such a relation becomes possible—or, more precisely, essentially trivial, as the A_i are (except for trivial transformations) just chosen as the components $\tilde{\Pi}_{\alpha\beta}(\{\xi_i\})$. If one then assumes that this relation can be directly transferred to the macroscale, i.e. that one should use $\bar{\Pi}_{\alpha\beta}(\{A_i^{(\text{mac})}\}) = \Sigma_{\alpha\beta}(\{A_i^{(\text{mac})}\})$, the coupling is established and the problem ‘solved’.

However, there are two aspects of the procedure which are, in our opinion, somewhat unsatisfactory: firstly, the choice of the A_i is not primarily driven by the notion of ‘slowness’, but rather by the technical need to obtain a stress. Fortunately, however, for polymeric fluids the stresses *are* slow variables, such that this argument does not count very much. The second argument, though, is much more severe: the averaging procedure of equation (C.4) completely disregards the *ensemble-defining* property of the A_i . As the A_i are assumed to be ‘slow’, the averaging should only be done by integrating out the remaining ‘fast’ (or ‘non- A ’) degrees of freedom. Formally this means that, after having established the macroscopic dynamics of the A_i (the functions $A_i^{(\text{mac})}(t)$), one should evaluate the average of any observable X via the prescription

$$\begin{aligned} [X](t) &= \frac{\int d^n \xi P \left[\prod_{j=1}^m \delta(A_j(\{\xi_i\}) - A_j^{(\text{mac})}(t)) \right] X(\{\xi_i\})}{\int d^n \xi P \left[\prod_{j=1}^m \delta(A_j(\{\xi_i\}) - A_j^{(\text{mac})}(t)) \right]}, \end{aligned} \quad (\text{C.6})$$

in analogy to the microcanonical ensemble. We have deliberately introduced a new notation for this average, to distinguish it from $\langle \dots \rangle$, which does not have any constraining delta functions. Obviously,

$$[A_i](t) = A_i^{(\text{mac})}(t) = \langle A_i \rangle(t), \quad (\text{C.7})$$

while such an identity of averages does in general *not* hold for other observables. In particular, this must typically be expected for $X = \tilde{\Pi}_{\alpha\beta}$.

This, in turn, means that the averaging procedure according to equation (C.6) will produce a stress that *differs* from the stress that results from the simple average according to equation (C.4). It is clear that equation (C.6) results in a prescription for the macroscopic stress that reads

$$\bar{\Pi}_{\alpha\beta}(\{A_i^{(\text{mac})}\}) = \left[\tilde{\Pi}_{\alpha\beta} \right], \quad (\text{C.8})$$

which *differs* from the prescription of reference [16],

$$\bar{\Pi}_{\alpha\beta}(\{A_i^{(\text{mac})}\}) = \langle \tilde{\Pi}_{\alpha\beta} \rangle. \quad (\text{C.9})$$

We strongly believe that the constrained average $[\dots]$ is more consistent with the general principles of statistical physics than the simple average $\langle \dots \rangle$. One obvious advantage is that the thus-constructed stress depends on the set of macroscopic observables $A_i^{(\text{mac})}$ by *construction*, *regardless* of how these variables are chosen.

Now, equation (C.7) tells us that the problem would not occur if the A_i were permitted to be chosen to be simply the components of the stress tensor (or the conformation tensor, which is essentially the same object). *This is however not the case*. The components are not independent from each other, and therefore treating each component as an independent constraint would result in an overconstrained system. In general, we need $m \leq n$ to avoid such an overconstrained situation.

This is seen particularly easily for a simple dumbbell, which has, beyond the (disregarded) center-of-mass coordinates, just three degrees of freedom ($n = 3$), which we can parameterize in terms of the connector vector \mathbf{q} . The Kramers expression for the stress tensor is therefore

$$\tilde{\Pi}_{\alpha\beta}(\mathbf{q}) = -k \frac{\rho^{(d)}}{m^{(d)}} q_\alpha q_\beta = -k \frac{\rho^{(d)}}{m^{(d)}} C_{\alpha\beta}; \quad (\text{C.10})$$

here k , $\rho^{(d)}$, $m^{(d)}$, and $C_{\alpha\beta}$ have the same meaning as in the main text. The kinetic part $\propto \delta_{\alpha\beta}$ has been ignored, since it can, for an incompressible system, be absorbed in a re-definition of the

overall pressure. In terms of the parameterization introduced in the main text, we may also write this as

$$\tilde{\Pi}_{\alpha\beta}(\mathbf{q}) = -\frac{\Gamma}{\tau\tau_q}\rho^{(d)}q_\alpha q_\beta = -\frac{\Gamma}{\tau\tau_q}\rho^{(d)}C_{\alpha\beta}. \quad (\text{C.11})$$

Obviously, there are only three independent components of the stress tensor (or the conformation tensor). Therefore, we should pick $\{A_i\} = \{q_\alpha\}$ and *not* $\{A_i\} = \{C_{\alpha\beta}\}$. As a result of this choice ($m = n$), equation (C.6) reduces, in this special case, to a fairly trivial result:

$$\begin{aligned} [X](t) &= \frac{\int d^3\mathbf{q} P(\mathbf{q}) \delta(\mathbf{q} - \mathbf{q}^{(\text{mac})}) X(\mathbf{q})}{\int d^3\mathbf{q} P(\mathbf{q}) \delta(\mathbf{q} - \mathbf{q}^{(\text{mac})})} \\ &= \frac{P(\mathbf{q}^{(\text{mac})}) X(\mathbf{q}^{(\text{mac})})}{P(\mathbf{q}^{(\text{mac})})} = X(\mathbf{q}^{(\text{mac})}). \end{aligned} \quad (\text{C.12})$$

Therefore, we propose in the present work to use

$$\begin{aligned} \bar{\Pi}_{\alpha\beta} &= -\frac{\Gamma}{\tau\tau_q}\rho^{(d)}q_\alpha^{(\text{mac})}q_\beta^{(\text{mac})} \\ &= -\frac{\Gamma}{\tau\tau_q}\rho^{(d)}\langle q_\alpha \rangle \langle q_\beta \rangle \end{aligned} \quad (\text{C.13})$$

instead of

$$\bar{\Pi}_{\alpha\beta} = -\frac{\Gamma}{\tau\tau_q}\rho^{(d)}C_{\alpha\beta}^{(\text{mac})} = -\frac{\Gamma}{\tau\tau_q}\rho^{(d)}\langle q_\alpha q_\beta \rangle, \quad (\text{C.14})$$

which would be the prescription of reference [16]. The fact that these expressions differ significantly is a hallmark of the strong thermal fluctuations in polymer systems.

This does *not* imply that we propose to simply disregard thermal fluctuations. We rather believe that they should be taken into account not by a thermal average along the lines of equation (C.14), but rather by explicit Langevin noise on the macroscopic level.

Let us work out what these considerations imply for the simple case of a Hookean dumbbell in a flow field. Again we assume a frictional coupling of the beads to the flow field, with a friction constant ζ , and assume that second and higher-order derivatives of the flow field may be neglected, just as in the main text. The Fokker–Planck operator for the overdamped Brownian motion of the dumbbell can then be constructed easily:

$$\begin{aligned} \mathcal{L}_{\text{FP}} &= -\frac{\partial}{\partial \mathbf{q}} \cdot \left(-\frac{2k}{\zeta} \mathbf{q} + \mathbf{q} \cdot \nabla \mathbf{V} \right) \\ &\quad + \frac{2k_B T}{\zeta} \frac{\partial^2}{\partial \mathbf{q}^2}; \end{aligned} \quad (\text{C.15})$$

here $\nabla \mathbf{V}$ is the gradient of the velocity field at the position of the dumbbell's center of mass. In terms of the parameterization of the main text we may write this as

$$\begin{aligned} \mathcal{L}_{\text{FP}} &= -\frac{\partial}{\partial \mathbf{q}} \cdot \left(-\frac{1}{\tau_q} \mathbf{q} + \mathbf{q} \cdot \nabla \mathbf{V} \right) \\ &\quad + \frac{k_B T}{k\tau_q} \frac{\partial^2}{\partial \mathbf{q}^2}. \end{aligned} \quad (\text{C.16})$$

The adjoint operator is then found as

$$\mathcal{L}_{\text{FP}}^\dagger = \left(-\frac{1}{\tau_q} \mathbf{q} + \mathbf{q} \cdot \nabla \mathbf{V} \right) \cdot \frac{\partial}{\partial \mathbf{q}} + \frac{k_B T}{k\tau_q} \frac{\partial^2}{\partial \mathbf{q}^2}, \quad (\text{C.17})$$

from which we evaluate

$$\mathcal{L}_{\text{FP}}^\dagger \mathbf{q} = -\frac{1}{\tau_q} \mathbf{q} + \mathbf{q} \cdot \nabla \mathbf{V} \quad (\text{C.18})$$

and

$$\begin{aligned} \mathcal{L}_{\text{FP}}^\dagger q_\alpha q_\beta &= q_\alpha q_\gamma \partial_\gamma V_\beta + q_\beta q_\gamma \partial_\gamma V_\alpha - \frac{2}{\tau_q} q_\alpha q_\beta + \frac{2k_B T}{k\tau_q} \delta_{\alpha\beta}, \end{aligned} \quad (\text{C.19})$$

which in turn implies

$$\partial_t \langle \mathbf{q} \rangle = \left\langle \mathcal{L}_{\text{FP}}^\dagger \mathbf{q} \right\rangle = -\frac{1}{\tau_q} \langle \mathbf{q} \rangle + \langle \mathbf{q} \rangle \cdot \nabla \mathbf{V} \quad (\text{C.20})$$

and

$$\begin{aligned} \partial_t \langle q_\alpha q_\beta \rangle &= \left\langle \mathcal{L}_{\text{FP}}^\dagger q_\alpha q_\beta \right\rangle \\ &= \langle q_\alpha q_\gamma \rangle \partial_\gamma V_\beta + \langle q_\beta q_\gamma \rangle \partial_\gamma V_\alpha - \frac{2}{\tau_q} \langle q_\alpha q_\beta \rangle \\ &\quad + \frac{2k_B T}{k\tau_q} \delta_{\alpha\beta}. \end{aligned} \quad (\text{C.21})$$

From equation (C.20) we find

$$\begin{aligned} \partial_t (\langle q_\alpha \rangle \langle q_\beta \rangle) &= \langle q_\alpha \rangle \langle q_\gamma \rangle \partial_\gamma V_\beta + \langle q_\beta \rangle \langle q_\gamma \rangle \partial_\gamma V_\alpha - \frac{2}{\tau_q} \langle q_\alpha \rangle \langle q_\beta \rangle. \end{aligned} \quad (\text{C.22})$$

After replacing the partial time derivative with the convective derivative, we see that this is precisely the equation of motion for the conformation tensor that has been derived in the main text. In other words, the present paper proposes to define the macroscopic conformation tensor as $\langle q_\alpha \rangle \langle q_\beta \rangle$. Conversely, reference [16] (or, in other words, the standard Oldroyd-B model) proposes to use $\langle q_\alpha q_\beta \rangle$, whose equation of motion differs from the one proposed here by the term $[(2k_B T)/(k\tau_q)]\delta_{\alpha\beta}$. The fact that the difference is proportional to the thermal energy $k_B T$ makes it obvious that the difference lies in the different treatment of thermal fluctuations.

In equilibrium, where $\partial_t(\dots) = 0$, $\mathbf{V} = 0$, we have $\langle q_\alpha \rangle \langle q_\beta \rangle = 0$, while $\langle q_\alpha q_\beta \rangle = [(k_B T)/k]\delta_{\alpha\beta}$ in accord with the equipartition theorem. We may therefore say that the prescription of the present paper implies a relaxation towards *mechanical* equilibrium, while the prescription of reference [16] implies relaxation towards *thermal* equilibrium.

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