

Dynamics of complex interfaces. I. Rheology, morphology, and diffusion

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In this paper, we investigate, on two levels of description, the isothermal coupling: (i) between rheology and morphology in immiscible blends (A/B) and (ii) among rheology, morphology, and diffusion in mixtures consisting of an immiscible blend (A/B) and one simple fluid, s . The interface separating the phases A and B is described, on the kinetic level by an area density distribution function and on the mesoscopic level by a scalar and a traceless symmetric second order tensor. The nonlinear formulations are derived using the general equation for nonequilibrium reversible and irreversible coupling formalism which ensures the consistency of dynamics with thermodynamics. In addition to the non-Fickian character of mass transport, the coupled three-dimensional governing equations explicitly show the effects of the external flow and diffusion on the size and shape of the interface. New expressions for the stress tensor emerge naturally in the models including the contributions of the diffusion fluxes and the isotropic (Laplace) and anisotropic deformations of the interface. Asymptotic solutions of the governing equations also show that the transport coefficients (diffusivity, etc.) are explicitly dependent on the interfacial tension and on the velocity gradient of the applied flow. The latter dependence renders the process of mass transfer highly anisotropic even in the absence of internal stresses created by the deformation of the interface. The diffusion-free models of Doi–Ohta and Lee–Park are recovered as particular cases. © 2003 American Institute of Physics. [DOI: 10.1063/1.1571052]

I. INTRODUCTION

Individual components of most multiphase mixtures, such as polymeric blends, are immiscible, and this generally manifests itself by the presence of a complex interface whose morphology plays an important role in the properties of the blend. The time-dependent and equilibrium sizes and shapes of the interface are determined by the competition among many factors, the most important of which are identified to be the applied flow, viscoelasticity, and the interfacial tension. Conversely, the dynamics of the blend is also observed to be influenced by the presence of the interface and its deformation.

If, in addition, the immiscible blend also contains low-molecular weight substances such as solvents or surface active agents, its morphology may also undergo additional changes due to the contribution of the diffusion fluxes of these inclusions and their physicochemical nature. In this

case, suitable descriptions of a nonequilibrium behavior of immiscible blends containing other substances, such as solvents, possibly miscible with their components, should consider not only the effects of the coupling between rheology and the deformation of the interfacial morphology but also their relationship with mass transport.

In *diffusion-free* immiscible polymeric blends (A/B), the morphology–rheology coupling has been the subject of many theoretical as well as experimental investigations.^{1–16} Under an applied flow, the interface undergoes deformations/distortions that generally lead to complex morphologies and patterns (Fig. 1) resulting from simultaneous and complex processes such as coalescence and break-up. Previous developments^{3–11} show that the behavior of the interface contributes to the dynamics of the whole multiphase system by the addition of an excess stress attributed to the shape anisotropy. One popular approach involves the mesoscopic model⁴ derived for dynamics of interfaces. The interface is characterized by two structural variables, a scalar associated with the area density, and a second-order tensor associated with the anisotropic changes of the shape. These variables

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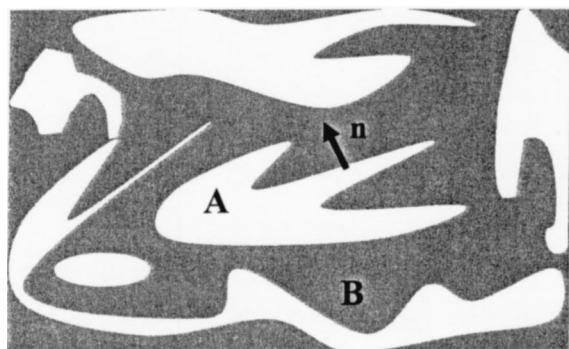


FIG. 1. Blend of two immiscible fluids A and B with a complex interface.

can be defined either over the whole interfacial area of the blend⁴ or over the surface of a single droplet,¹⁶ if coalescence and break-up processes are discarded. Several improvements of this model for incompressible fluids for both constrained^{5–10} or unconstrained¹⁶ volumes have been suggested and comparisons with experimental measurements determined the range of validity of its predictions.^{10–16} While most previous derivations for incompressible blends arrive at similar terms for the reversible part of the governing equations for the area and shape densities, some discrepancies still appear in the irreversible portion (dissipation). Moreover, the expression for the stress tensor for compressible blends is still considered to be incomplete (e.g., the Laplace term is absent) and thus the time evolution equations describing the dynamics of the blend and the flow behavior are inaccurate. One goal of this paper is to clarify some of these points for compressible immiscible blends. We then derive a thermodynamically compatible model on a kinetic level and use it as a starting point to achieve a mesoscopic description. Several earlier models such as those of Doi and Ohta,⁴ Lee and Park,⁵ Grmela *et al.*,^{6,7} Lacroix *et al.*¹⁰ are recovered as particular cases.

In *interface-free* miscible polymer solutions, the coupling between rheology and diffusion has led to interesting and unexpected observations such as phase separation, migration across streamlines,^{17–19} etc. In these studies, the polymeric chains and the solvent molecules are regarded as thermodynamically miscible in all proportions and hence interfacial quantities are irrelevant (Fig. 2). Due to the large amount of both experimental and theoretical^{17–35} studies de-

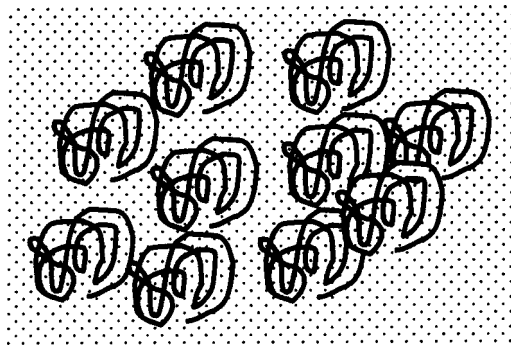


FIG. 2. Polymer solution consisting of a solvent (dots) and polymeric chains.

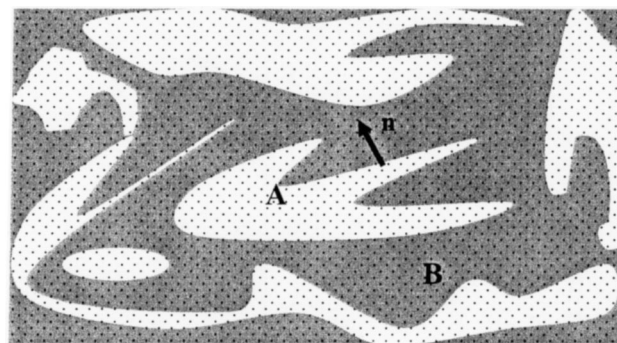


FIG. 3. Mixture of a simple fluid (dots) and a blend of two immiscible fluids with a complex interface.

voted to these effects, their origin seems to be well understood. Most of the reported observations can be reproduced if the deformation of the polymer internal structure is taken into account. Qualitatively, mass transfer deviates from the predictions of Fick's laws and these deviations are observed to be more noticeable when the diffusion characteristic time scale is comparable to, or smaller than, the relaxation characteristic time scale of the internal structure. The breakthrough in modeling, for expressing explicitly and rigorously this mutual interdependence in the governing equations, is mainly attributed to the so-called two-fluid model.³⁶ As a result, the expression of the diffusion mass flux is extended by explicitly including the internal stresses. Although there are many studies dealing with miscible solvent/polymer mixtures, few investigations have considered features of rheology and morphology with mass transport in multiphase immiscible blends containing simple substances. A more fundamental understanding of such processes would be beneficial since they are omnipresent in many biological and industrial systems. For instance, in lungs, surfactants reduce the air–liquid interfacial tension and thus minimize the risk of a probable obstruction of pulmonary airways that occurs during respiratory distress syndrome (RDS).³⁷ Another interesting case involves the behavior of gas bubbles rising freely in non-Newtonian polymeric solutions. Measurements show some unexpected behavior such as the occurrence of a discontinuity in their rise velocity at a certain critical volume.³⁸ In addition to the goal of addressing the rheology–morphology coupling described earlier, we address the relationships among rheology, morphology and mass transport in mixtures consisting of an immiscible blend (A/B) and a simple fluid, *s* (e.g., solvent) (Fig. 3). Here, we also provide two levels of description to study the relationship amongst these three phenomena.

In summary, the goal of this paper is twofold. First, we investigate the effects of the coupling between rheology and morphology in compressible immiscible blends (A/B) that do not contain other substances (e.g., solvent). Second, we generalize this study to examine how such a coupling is affected by mass transport in the case of mixtures of an immiscible blend (A/B) containing a simple fluid, *s*. Our aim is to provide a family of compatible models suitable for discussing such couplings on both kinetic and mesoscopic levels of description. To develop these models, we use the general equa-

tion for the nonequilibrium reversible and irreversible couplings (GENERIC) (Ref. 39) that guarantees the consistency of dynamics with thermodynamics. The obtained governing equations are parameterized by the internal free energy and the kinetic coefficients which express all the individual features of the system under consideration.

This paper is organized as follows: A brief description of the GENERIC method is given in Sec. II. In Sec. III, we derive new models on two levels of description for discussing the relationship between rheology and morphology in compressible immiscible fluids (A/B). We first formulate the model on a kinetic level of description, and then use it to derive, directly and rigorously, the model on the mesoscopic level. We discuss in detail two well-known models retrieved as particular cases.^{4,5} In Sec. IV, we extend this study to address the coupling among rheology, morphology, and diffusion in multiphase mixtures of an immiscible blend (A/B) and a simple fluid, *s* (e.g., solvent). The main outcome is that the size and shape of the interface are modified by both the applied flow and diffusion. In turn, the diffusion process becomes influenced by the presence of the interface.

II. THE GENERIC FORMALISM

The GENERIC (Ref. 39) method has been introduced to describe the behavior of nonequilibrium systems while ensuring the consistency of their dynamics with thermodynamics. This Hamiltonian method extended to dissipative systems has been developed and evolved during the last two decades due to the contributions of many groups. These efforts started with the pioneering works of Grmela,⁴⁰ followed by the dissipation bracket method of Beris and Edwards⁴¹ to reach a final structure known in the literature as GENERIC developed by Grmela and Öttinger.

In these two papers, we shall assume that the system under consideration is kept at a constant temperature denoted by *T*. If *X* represents the set of the independent state variables used for a complete description of the system under consideration, then GENERIC can be written in the following condensed form:⁴²

$$\frac{\partial X}{\partial t} = L \frac{\partial \Phi}{\partial X} - \frac{\partial \Psi}{\delta(\delta\Phi/\delta X)}, \quad (1)$$

where *t* denotes time. Equation (1) involves two potentials Φ and Ψ . The first, $\Phi = E - TS$, is the Helmholtz free energy, where *E* and *S* are the total energy and entropy potentials of the system expressed in the space of the state variables. The second, Ψ , is the dissipation potential expressed in the space of the conjugate variables $\delta\Phi/\delta X$. *L* is the Poisson operator. The first term on the right-hand side of Eq. (1) accounts for the reversible kinematics, whereas the second represents the irreversible kinematics or dissipation. Since the temperature is constant in this analysis, Eq. (1) is in fact a particular case of a more general and rich structure introduced in (Ref. 39).

A bracket can be defined from the bivector operator *L* as $\{A, B\} = \langle \delta A/\delta X, L(\delta B/\delta X) \rangle$, where $\langle \cdot, \cdot \rangle$ is the inner product and *A* and *B* are smooth real valued functionals of *X*. This

bracket is called a Poisson bracket if (i) $\{A, B\} = -\{B, A\}$ ($L = -L^T$, i.e., *L* is antisymmetric, the superscript *T* stands for the transpose operator), (ii) the Jacobi identity $\{\{B, C\}, A\} + \{\{A, B\}, C\} + \{\{C, A\}, B\} = 0$ holds. The latter identity expressing the time invariance of the reversible structure may help to single out physically admissible closure approximations.⁴³

The dissipation potential Ψ satisfies the following properties: (i) $\Psi|_{\text{equilibrium}} = 0$, (ii) Ψ reaches its minimum at equilibrium, (iii) Ψ is convex. In view of the properties listed above, Eq. (1) implies the dissipation inequality $d\Phi/dt \leq 0$.

A GENERIC derivation of a new set of coupled time evolution equations consists in an adequate choice of the state variables, a determination of their reversible (Poisson operator *L*) and irreversible (dissipation potential Ψ) kinematics and finally a specification of the Helmholtz free energy Φ . These four steps are followed in the forthcoming sections; first for the rheology and morphology relationship and second for the rheology–morphology–diffusion coupling in compressible immiscible fluids.

III. RHEOLOGY AND MORPHOLOGY IN COMPRESSIBLE IMMISCIBLE BLENDS: A TWO-LEVEL DESCRIPTION

In this section, we investigate the relationship between rheology and morphology changes on two levels of description. The system under consideration is a blend consisting of two compressible immiscible fluids A and B. The presence of the interface makes the fluid behave as a complex fluid even though the latter is composed of simple Newtonian fluids. It is well known that, in most complex fluids, deviations from the Newtonian behavior are due to the contribution of the inherent internal structure. Here, the internal structure is regarded to mainly stem from the morphology of the interface.

We consider the case where the two phases have equal velocities. This approximation holds far from critical points, or in case of high interfacial friction between the components of the blend.^{44,45} The blend is regarded as a pseudo-one-component fluid embedding an interface.^{4–16} The first step in the GENERIC algorithm requires an adequate choice of the independent state variables. The usual state variables used to describe a fluid under consideration are the fields of the classical fluid mechanics (hydrodynamics), i.e., a scalar mass density $\rho(\mathbf{r})$ and a linear momentum density vector $\mathbf{u}(\mathbf{r})$, where \mathbf{r} is the position vector. However, the presence of the interface necessitates additional state variables to account for its contribution. To gain a better physical insight for the dynamics of this immiscible blend, we provide a description on two levels; a kinetic level and an averaged level. On the kinetic level (to be denoted by *f*-level), the interface is described by an area density distribution function $f(\mathbf{r}, \mathbf{n}, t)$, \mathbf{n} is the outward unit vector normal to the interface and *t* stands for time (*f* can also be seen as a distribution function for the orientation of the vector \mathbf{n}). On the mesoscopic level [to be denoted by (*Q*, *q*)-level], other averaged variables can be defined as moments of the kinetic function f^4 : the zeroth moment, a scalar

$$Q = \int d^2n f(\mathbf{r}, \mathbf{n}, t), \tag{2}$$

denoting the interfacial area density, and the traceless second moment, a second order tensor

$$\mathbf{q} = \int d^2n (\mathbf{nn} - \frac{1}{3}\mathbf{I}) f(\mathbf{r}, \mathbf{n}, t), \tag{3}$$

denoting, interfacial orientation tensor density. \mathbf{I} is the unit second order tensor, \mathbf{nn} is the dyadic tensor, and d^2n is the differential solid angle. A combination of Eqs. (2) and (3) gives

$$\overline{\mathbf{nn}} = \int d^2n f(\mathbf{n}, \mathbf{r}, t) \mathbf{nn} = \mathbf{q} + \frac{1}{3}Q\mathbf{I}. \tag{4}$$

The two state variables Q and \mathbf{q} constitute the basis state variables for the mesoscopic averaged approach introduced by Doi and Ohta,⁴ and adopted later by many groups.⁵⁻¹⁶ It has been derived originally⁴ for describing the dynamics of incompressible immiscible fluids at the (Q, \mathbf{q}) -level. Here, we first provide, for compressible fluids, a “kinetic” description on the f -level and derive from it a description on the (Q, \mathbf{q}) -level. This extension to compressible fluids becomes ineluctable when diffusion is involved in dynamical processes since mass transport is in most cases accompanied by volume changes due to swelling or shrinkage of the system undergoing diffusion.

Summing up: in this multistage formulation, the fluid is described either by the state variables ρ, \mathbf{u} , and f on the kinetic f -level or alternatively by ρ, \mathbf{u}, Q , and \mathbf{q} on the averaged (Q, \mathbf{q}) -level. In the following, we shall derive the reversible and irreversible kinematics embodied respectively by the Poisson bracket and by the dissipative potential and provide the governing equations on both levels of description.

The reversible kinematics is expressed through the Poisson bracket. For notation convenience, we write the Poisson bracket as a sum of two contributions: the first results from the fields of classical fluid mechanics (to be abbreviated here by cfm): $\rho(\mathbf{r})$ and $\mathbf{u}(\mathbf{r})$, and the second arises from the interface fields: f or $Q(\mathbf{r})$ and $\mathbf{q}(\mathbf{r})$,

$$\{A, B\} = \{A, B\}^{(cfm)} + \{A, B\}^{(Interface)}. \tag{5}$$

The irreversible kinematics is generated by dissipation which stems from two contributions. The first is due to the effective shear and bulk viscosities of the whole fluid as a response to the velocity gradient of the applied external flow, $\mathbf{v} = \mathbf{u}/\rho$. The second arises from the relaxation of the interface due to its surface tension which reduces the size of the interfacial area and tends to render the shape isotropic. The dissipation potential can therefore be written as a sum of two parts,

$$\Psi = \Psi^{(cfm)} + \Psi^{(Interface)}. \tag{6}$$

We shall first determine the reversible $\{A, B\}^{(cfm)}$ and irreversible $\Psi^{(cfm)}$ kinematics of the contribution of the classical fluid mechanics variables ρ and \mathbf{u} . The task of deriving the same quantities on the two levels of description for the interface is postponed to the next two subsections.

The first bracket in Eq. (5) has the following classical form:⁴⁶

$$\begin{aligned} \{A, B\}^{(cfm)} = & \int d^3r \rho \left[\left(\frac{\delta B}{\delta u_\alpha} \right) \partial_\alpha \left(\frac{\delta A}{\delta \rho} \right) - \left(\frac{\delta A}{\delta u_\alpha} \right) \partial_\alpha \left(\frac{\delta B}{\delta \rho} \right) \right] \\ & + u_\gamma \left[\left(\frac{\delta B}{\delta u_\alpha} \right) \partial_\alpha \left(\frac{\delta A}{\delta u_\gamma} \right) - \left(\frac{\delta A}{\delta u_\alpha} \right) \partial_\alpha \left(\frac{\delta B}{\delta u_\gamma} \right) \right], \end{aligned} \tag{7}$$

where A and B are arbitrary regular real valued functionals.

The dissipation potential, on the other hand, can be written as

$$\begin{aligned} \Psi^{(cfm)} = & \int d^3r \left(\partial_\beta \left(\frac{\delta \Phi}{\delta u_\alpha} \right) + \partial_\alpha \left(\frac{\delta \Phi}{\delta u_\beta} \right) \right) \frac{\eta}{4} \left(\partial_\beta \left(\frac{\delta \Phi}{\delta u_\alpha} \right) \right. \\ & \left. + \partial_\alpha \left(\frac{\delta \Phi}{\delta u_\beta} \right) \right) + \int d^3r \partial_\beta \left(\frac{\delta \Phi}{\delta u_\alpha} \right) \frac{1}{2} \\ & \times \left(\eta_d - \frac{2}{3} \eta \right) \partial_\beta \left(\frac{\delta \Phi}{\delta u_\alpha} \right), \end{aligned} \tag{8}$$

where η and η_d are, respectively, the effective shear and dilational viscosities of the blend. In Eqs. (7) and (8), we have used the following notations: $\partial_\alpha \equiv \partial/\partial r_\alpha$, $\alpha \in \{1, 2, 3\}$ and $\delta A/\delta \mathbf{u}$ to represent the Volterra functional derivative of A with respect to \mathbf{u} (idem for ρ , etc.).⁴¹ For repeated indices, the summation convention is understood.

In Sec. III A, we shall derive the Poisson bracket $\{A, B\}^{(Interface)}$, the dissipation potential $\Psi^{(Interface)}$ for the interface and the governing equations on the f -level of description. This f -level of description will be used, in Sec. III B as a starting point to derive a family of models on the (Q, \mathbf{q}) -level.

A. Kinetic level of description: f -level

1. Poisson bracket

The complex fluid on the f -level of description is characterized by the set of the independent state variables,

$$X = (\rho, \mathbf{u}, f). \tag{9}$$

The reversible part of the time evolution equation for the interface variable f can be written under the following form:

$$\left. \frac{\delta f}{\delta t} \right|_{\text{reversible}} = - \frac{\partial}{\partial r_\alpha} (\dot{r}_\alpha f) - \frac{\partial}{\partial n_\alpha} (\dot{n}_\alpha f) + Rf. \tag{10}$$

\mathbf{n} is the outward unit vector normal to the interface and $\dot{\mathbf{n}}$ refers to its time derivative whose expression is given by^{2,4}

$$\dot{n}_\alpha = -\kappa_{\beta\alpha} n_\beta + \kappa_{\beta\gamma} n_\beta n_\gamma n_\alpha, \tag{11}$$

where $\kappa_{\alpha\beta} = \partial v_\alpha/\partial r_\beta$ is the macroscopic velocity gradient. The third term on the right-hand side of Eq. (10) is attributed

to the changes of the surface by the flow, with a certain rate, R , having the following form:^{2,4}

$$R = \kappa_{\alpha\alpha} - \kappa_{\beta\alpha} n_{\beta} n_{\alpha}. \quad (12)$$

Inserting expressions (11) and (12) into Eq. (10), we obtain

$$\begin{aligned} \left. \frac{\partial f}{\partial t} \right|_{\text{reversible}} &= -v_{\alpha} \frac{\partial f}{\partial r_{\alpha}} + \frac{\partial}{\partial n_{\alpha}} (n_{\beta} f \kappa_{\beta\alpha}) \\ &\quad - \frac{\partial}{\partial n_{\alpha}} (n_{\beta} n_{\gamma} n_{\alpha} f \kappa_{\beta\gamma}) - \kappa_{\beta\alpha} n_{\beta} n_{\alpha} f. \end{aligned} \quad (13)$$

Using Eq. (13), we construct the Poisson bracket for the interface variable, f , as follows:

$$\begin{aligned} \{A, B\}^{\text{Interface}} &= \int d^3r \int d^2n f(\mathbf{r}, \mathbf{n}, t) \left[\partial_{\alpha} \left(\left(\frac{\delta A}{\delta f} \right) \left(\frac{\delta B}{\delta u_{\alpha}} \right) \right) - \partial_{\alpha} \left(\left(\frac{\delta B}{\delta f} \right) \left(\frac{\delta A}{\delta u_{\alpha}} \right) \right) \right] - \int d^3r \int d^2n n_{\beta} f(\mathbf{r}, \mathbf{n}, t) \\ &\quad \times \left[\frac{\partial}{\partial n_{\alpha}} \left(\frac{\partial A}{\partial f} \right) \partial_{\alpha} \left(\frac{\delta B}{\delta u_{\beta}} \right) - \frac{\partial}{\partial n_{\alpha}} \left(\frac{\delta B}{\delta f} \right) \partial_{\alpha} \left(\frac{\delta A}{\delta u_{\beta}} \right) \right] + \int d^3r \int d^2n n_{\beta} n_{\gamma} n_{\alpha} f(\mathbf{r}, \mathbf{n}, t) \left[\frac{\partial}{\partial n_{\alpha}} \left(\frac{\delta A}{\delta f} \right) \partial_{\gamma} \left(\frac{\delta B}{\delta u_{\beta}} \right) \right. \\ &\quad \left. - \frac{\partial}{\partial n_{\alpha}} \left(\frac{\delta B}{\delta f} \right) \partial_{\gamma} \left(\frac{\delta A}{\delta u_{\beta}} \right) \right] - \int d^3r \int d^2n n_{\alpha} n_{\beta} f(\mathbf{r}, \mathbf{n}, t) \left[\left(\frac{\delta A}{\delta f} \right) \partial_{\beta} \left(\frac{\delta B}{\delta u_{\alpha}} \right) - \left(\frac{\delta B}{\delta f} \right) \partial_{\beta} \left(\frac{\delta A}{\delta u_{\alpha}} \right) \right]. \end{aligned} \quad (14)$$

While the first term in each integral, contributes to the advection of the distribution function f by the flow, its symmetric counterpart contributes to the total stress tensor arising in the momentum governing equation (force balance).

2. Dissipation potential

The dissipation potential for the interface is chosen to be a quadratic functional of the conjugate variable, $\delta\Phi/\delta f$, of f ,

$$\Psi^{\text{(Interface)}} = \int d^3r \int d^2n \left(\frac{\lambda_f}{2} \right) (f(\mathbf{n}, \mathbf{r}) - f^*(\mathbf{n}, \mathbf{r})) \left(\frac{\delta\Phi}{\delta f} \right)^2, \quad (15)$$

where λ_f is a positive phenomenological parameter related to the rate of relaxation of f , and f^* refers to a final state reached after cessation of the applied flow. If \mathbf{F} designates the deformation gradient tensor and f_0 is a reference (e.g., initial) distribution function, then following Ref. 4,

$$f^*(\mathbf{n}, \mathbf{r}) = f_0 \frac{(\det \mathbf{F})^2}{|\mathbf{F}^+ \cdot \mathbf{n}|^4}.$$

We have singled out the form for this potential to express that dissipation arises mainly from a simple relaxation of the interface area density function. The relaxation may arise from collisions and interaction phenomena that lead to coalescence and break up processes. In case of coalescence, the parameter λ_f can be related to the frequency of collisions between the drops and the probability of their coalescence.⁴⁷ A more general description may arise by defining a dissipation potential similar to a Boltzmann-type collision expression. Here, we limit the investigation to the simplest expression similar to the collision factor proposed by Bhatnagar–Gross–Krook.⁴⁸ We will show that with this simple choice for the dissipation potential, we are capable of developing a more general formulation on the (Q, \mathbf{q}) -level (mesoscopic level) from which some previously derived models are recovered as particular cases,^{4,5} provided that appropriate expressions for the interfacial free energy are used.

Therefore the contribution of the relaxation to the governing equation for the state variable f is

$$\begin{aligned} \left. \frac{\partial f}{\partial t} \right|_{\text{relaxation}} &= - \frac{\delta\Psi}{\delta(\delta\Phi/\delta f)} \\ &= -\lambda_f (f(\mathbf{r}, \mathbf{n}) - f^*(\mathbf{r}, \mathbf{n})) \left(\frac{\delta\Phi}{\delta f} \right). \end{aligned} \quad (16)$$

Note that the quantity, $\lambda_f(\delta\Phi/\delta f)$, has a dimension of inverse of time.

3. Free energy

We first limit ourselves to a partial specification for the free energy. The total free energy density always involves a kinetic and internal energy terms, i.e.,

$$\tilde{\varphi} = \left(\frac{\mathbf{u}^2}{2\rho} \right) + \varphi(\rho, f), \quad (17)$$

where $\tilde{\varphi}$ denotes the Helmholtz free energy density, i.e., $\Phi = \int d^3r \tilde{\varphi}$ and φ stands for the internal free energy density that is independent of the linear momentum $\mathbf{u} = \rho \mathbf{v}$.

4. Governing equations

Substituting into Eq. (1) the contributions of the reversible kinematics embodied by Eqs. (7) and (14), the irreversible kinematics given by Eq. (8) or (15) and the partial specification for the free energy (17), we arrive at the governing equations for the set $X = (\rho, \mathbf{u}, f)$,

$$\frac{\partial \rho}{\partial t} = -\partial_\alpha(\rho v_\alpha), \quad (18)$$

$$\frac{\partial u_\alpha}{\partial t} = -\partial_\beta(u_\alpha v_\beta) - \partial_\alpha p - \partial_\beta \sigma_{\beta\alpha}, \quad (19)$$

$$\begin{aligned} \frac{\partial f}{\partial t} = & -v_\alpha \partial_\alpha f + \frac{\partial}{\partial n_\alpha}(n_\beta f \kappa_{\beta\alpha}) - \frac{\partial}{\partial n_\alpha}(n_\beta n_\gamma n_\alpha f \kappa_{\beta\gamma}) \\ & - n_\alpha n_\beta f \kappa_{\alpha\beta} - \lambda_f (f - f^*) \left(\frac{\delta \varphi}{\delta f} \right). \end{aligned} \quad (20)$$

The first equation, (18), is the well-known continuity equation (mass conservation). The second equation, (19), represents the momentum conservation equation. This equation involves the quantities: the hydrodynamic pressure given by

$$p = -\varphi + \rho \frac{\partial \varphi}{\partial \rho} + \int d^2 n f(\mathbf{n}, \mathbf{r}) \left(\frac{\delta \varphi}{\delta f} \right) \quad (21)$$

and the stress tensor

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(\text{cfm})} + \sigma_{\alpha\beta}^{(\text{Interface})}, \quad (22)$$

where the first term on the right-hand side has the following classical form:⁴⁹

$$\sigma_{\alpha\beta}^{(\text{cfm})} = -\eta \dot{\gamma}_{\alpha\beta} - \left(\eta_d - \frac{2}{3} \eta \right) \kappa_{\gamma\gamma} \delta_{\alpha\beta}. \quad (23)$$

The parameters η and η_d have been defined earlier as the effective shear and dilational viscosities respectively and the symbol $\delta_{\alpha\beta}$ stands for the Kronecker delta. We recall that $\kappa_{\alpha\beta} = \partial v_\alpha / \partial r_\beta$ and $\dot{\gamma}_{\alpha\beta} = \kappa_{\alpha\beta} + \kappa_{\beta\alpha}$ represent, respectively, the gradient of the overall velocity and the symmetric deformation-rate tensor.⁴⁹ The contribution of the interface to the extra stress tensor, given by the second term on the right-hand side in Eq. (22), is expressed as

$$\begin{aligned} \sigma_{\alpha\beta}^{(\text{Interface})} = & \int d^2 n f(\mathbf{n}, \mathbf{r}) \left[n_\beta \frac{\partial}{\partial n_\alpha} \left(\frac{\delta \varphi}{\delta f} \right) - n_\alpha n_\beta n_\gamma \frac{\partial}{\partial n_\gamma} \left(\frac{\delta \varphi}{\delta f} \right) \right. \\ & \left. + n_\alpha n_\beta \left(\frac{\delta \varphi}{\delta f} \right) - \delta_{\alpha\beta} \left(\frac{\delta \varphi}{\delta f} \right) \right]. \end{aligned} \quad (24)$$

The last equation, (20) represents the time evolution kinetic equation for the distribution function f . The dissipation process is chosen, here, to be of a relaxation type but yet

involving the conjugate variable of f and thus the internal free energy density, φ . The latter can be specified depending on the physical insight we have of the problem under investigation. One of the simplest choices is

$$\varphi(\rho, f) = \Gamma \int d^2 n f(\mathbf{n}, \mathbf{r}), \quad (25)$$

where the parameter, Γ , refers to the interfacial tension. Therefore, the irreversible part of Eq. (20) becomes

$$\left. \frac{\partial f}{\partial t} \right|_{\text{relaxation}} = -\lambda_f \Gamma (f - f^*), \quad (26)$$

and the expression for the stress tensor simplifies to

$$\sigma_{\alpha\beta}^{(\text{Interface})} = \Gamma \int d^2 n f(\mathbf{n}, \mathbf{r}, t) [n_\alpha n_\beta - \delta_{\alpha\beta}], \quad (27)$$

with a deviatoric part, $\Sigma = \sigma^{(\text{Interface})} - \frac{1}{3} \text{Tr}(\sigma^{(\text{Interface})}) \mathbf{I} = \Gamma \mathbf{q}$, corresponding exactly to the expression derived in previous investigations.^{1,3}

B. Mesoscopic approach: (Q, \mathbf{q})-level

Here, we investigate the same problem (rheology–morphology coupling) on the mesoscopic averaged (Q, \mathbf{q})-level by using as a starting point the setting that we have already provided on the f -level (previous subsection). While the necessary derivation on the f -level ensures a more physical understanding regarding the interface and its dynamics, the details provided may be overwhelming and sometimes not easily handled. This issue is removed on the (Q, \mathbf{q})-level, where the predictions and consequences of the model become directly comparable to experimental data. We then derive a family of compatible models on the (Q, \mathbf{q})-level by following the same GENERIC procedure.

1. Poisson bracket

The complex fluid is now characterized by the set of the independent state variables,

$$X = (\rho, \mathbf{u}, \mathbf{q}, Q). \quad (28)$$

To arrive at the Poisson bracket on the (Q, \mathbf{q})-level, we start from the Poisson bracket, Eq. (14), derived on the f -level of description, and use the following chain rule:

$$\frac{\delta}{\delta f} = n_i n_j \left(\left(\delta_{i\alpha} \delta_{j\beta} - \frac{1}{3} \delta_{ij} \delta_{\alpha\beta} \right) \frac{\delta}{\delta q_{\alpha\beta}} + \delta_{ij} \frac{\delta}{\delta Q} \right). \quad (29)$$

By substituting Eq. (29) into Eq. (14), we obtain

$$\begin{aligned} \{A, B\}^{\text{Interface}} = & \int d^3 r \left[q_{\alpha\beta} \partial_\gamma \left(\frac{\delta A}{\delta q_{\alpha\beta}} \frac{\delta B}{\delta u_\gamma} \right) - q_{\alpha\gamma} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_\beta \left(\frac{\delta B}{\delta u_\gamma} \right) - q_{\beta\gamma} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_\alpha \left(\frac{\delta B}{\delta u_\gamma} \right) + \frac{q_{\alpha\beta} q_{\theta\nu}}{Q} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_\nu \left(\frac{\delta B}{\delta u_\theta} \right) \right. \\ & - \frac{Q}{3} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \left(\partial_\beta \left(\frac{\delta B}{\delta u_\alpha} \right) + \partial_\alpha \left(\frac{\delta B}{\delta u_\beta} \right) \right) + \frac{1}{3} \left(q_{\alpha\beta} + \frac{2Q}{3} \delta_{\alpha\beta} \right) \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_\gamma \left(\frac{\delta B}{\delta u_\gamma} \right) + \frac{2}{3} \delta_{\alpha\beta} q_{\theta\nu} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_\nu \left(\frac{\delta B}{\delta u_\theta} \right) \\ & \left. - \left(q_{\alpha\beta} + \frac{Q}{3} \delta_{\alpha\beta} \right) \left(\frac{\delta A}{\delta Q} \right) \partial_\alpha \left(\frac{\delta B}{\delta u_\beta} \right) + Q \partial_\gamma \left(\frac{\delta A}{\delta Q} \frac{\delta B}{\delta u_\gamma} \right) - A \leftrightarrow B \right]. \end{aligned} \quad (30)$$

The notation, $A \leftrightarrow B$ (used in this bracket will be used for the sake of simplicity in the rest of this paper) stands for the same quantities but with A and B interchanged. To arrive at this final form in Eq. (30), we have also used the fact that $\mathbf{nn} = \int d^2n f(\mathbf{n}, \mathbf{r}, t) \mathbf{nn} = \mathbf{q} + \frac{1}{3} Q \mathbf{I}$. Moreover, a fourth order moment \mathbf{nnnn} arises while transforming the bracket from the f -level to the (Q, \mathbf{q}) -level, forcing us to use the quadratic closure approximation put forward in Ref. 4 and proved to be physically admissible,⁴³

$$\overline{n_i n_j n_\alpha n_\beta} = \frac{1}{Q} \overline{n_i n_j} \overline{n_\alpha n_\beta} = \frac{q_{ij} q_{\alpha\beta}}{Q} + \frac{1}{3} \delta_{ij} q_{\alpha\beta} + \frac{1}{3} \delta_{\alpha\beta} q_{ij} + \frac{Q}{9} \delta_{ij} \delta_{\alpha\beta}. \quad (31)$$

A slightly different Poisson bracket has been derived in Refs. 6 and 7 for incompressible fluids by noting that the tensor $Q(\mathbf{q} + \mathbf{I}Q/3)$ transforms covariantly under the flow. Our formulation has the advantage of starting from a kinetic level of description and of providing an extension to compressible fluids. The Poisson brackets given in Refs. 6 and 7 are recovered as particular cases of Eq. (30) if incompressibility is assumed ($\nabla \cdot \mathbf{v} = 0$).

We should emphasize that all the results that will be obtained in this paper are intimately dependent on the chosen closure approximation (31). A more general Poisson bracket is given in the Appendix, where the fourth-order moment has been kept in its original form. In that case any other (more accurate) closure^{8,43} can be used to close the set of governing equations. Thus the outcome, or more precisely the reversible part, will be of a different structure.

2. Dissipation potential

The dissipation potential is constructed in the same manner as the Poisson bracket. We insert the chain rule (29) into the dissipation potential (15) suggested on the f -level. The result is straightforward and is given by

$$\Psi^{(\text{Interface})} = \int d^3r \left[\left(\frac{\delta\Phi}{\delta q_{ij}} \right) \frac{\lambda_{\alpha\beta ij}^q}{2} \left(\frac{\delta\Phi}{\delta q_{\alpha\beta}} \right) + \left(\frac{\delta\Phi}{\delta Q} \right) \frac{\lambda^Q}{2} \left(\frac{\delta\Phi}{\delta Q} \right) + \left(\frac{\delta\Phi}{\delta q_{ij}} \right) \lambda_{ij}^{qQ} \left(\frac{\delta\Phi}{\delta Q} \right) \right], \quad (32)$$

where the parameters arising in Eq. (32) have the following explicit form:

$$\lambda_{\alpha\beta ij}^q = \int d^2n (f(\mathbf{n}, \mathbf{r}) - f^*(\mathbf{n}, \mathbf{r})) \lambda_f [n_i n_j n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta} n_i n_j - \frac{1}{3} \delta_{ij} n_\alpha n_\beta + \frac{1}{9} \delta_{ij} \delta_{\alpha\beta}], \quad (33)$$

$$\lambda^Q = \int d^2n (f(\mathbf{n}, \mathbf{r}) - f^*(\mathbf{n}, \mathbf{r})) \lambda_f, \quad (34)$$

$$\lambda_{ij}^{qQ} = \int d^2n (f(\mathbf{n}, \mathbf{r}) - f^*(\mathbf{n}, \mathbf{r})) \lambda_f [n_i n_j - \frac{1}{3} \delta_{ij}]. \quad (35)$$

Note that these parameters are functions of one parameter, λ_f , related to the rate of relaxation of the distribution

function f . The first, Eq. (33), denotes the rate of relaxation of the shape of the interface and the second, Eq. (34), refers to the rate of relaxation of the size (coalescence). The last one, Eq. (35), refers to a coupling tensorial coefficient which relates the relaxation processes of the size and the shape (break-up). These parameters, in addition to be positive semi-definite, possess the following symmetry properties: $\lambda_{\alpha\beta ij}^q = \lambda_{ij\alpha\beta}^q = \lambda_{\alpha\beta ji}^q = \lambda_{\beta\alpha ij}^q$ for the first and $\lambda_{\alpha\beta}^{qQ} = \lambda_{\beta\alpha}^{qQ}$ for the third.

The irreversible parts of the time evolution equations for Q and \mathbf{q} are given as

$$\left. \frac{\partial Q}{\partial t} \right|_{\text{relaxation}} = - \frac{\delta\Psi}{\delta(\delta\Phi/\delta Q)} = - \lambda^Q \left(\frac{\delta\Phi}{\delta Q} \right) - \lambda_{ij}^{qQ} \left(\frac{\delta\Phi}{\delta q_{ij}} \right), \quad (36)$$

$$\left. \frac{\partial q_{ij}}{\partial t} \right|_{\text{relaxation}} = - \frac{\delta\Psi}{\delta(\delta\Phi/\delta q_{ij})} = - \lambda_{ij}^{qQ} \left(\frac{\delta\Phi}{\delta Q} \right) - \lambda_{ij\alpha\beta}^q \left(\frac{\delta\Phi}{\delta q_{\alpha\beta}} \right). \quad (37)$$

The first term on the right-hand side of Eq. (36) accounts for coalescence and the second represents break-up processes. The relaxation of the shape is expressed by the two terms on the right-hand side of Eq. (37). The physical meaning associated with these terms will become clearer when discussing the Doi–Ohta and Lee–Park special cases.

3. Free energy

The free energy density defined by $\Phi = \int d^3r \tilde{\varphi}$, can be written as

$$\tilde{\varphi} = \left(\frac{\mathbf{u}^2}{2\rho} \right) + \varphi(\rho, Q, \mathbf{q}). \quad (38)$$

The quantity φ is still left unspecified at this point, but we shall suggest, in the next subsection, some expressions accounting for the contribution of the interface.

4. Governing equations

The governing equations on the (Q, \mathbf{q}) -level are

$$\frac{\partial \rho}{\partial t} = - \partial_\alpha (\rho v_\alpha), \quad (39)$$

$$\frac{\partial u_\alpha}{\partial t} = - \partial_\beta (u_\alpha v_\beta) - \partial_\alpha p - \partial_\beta \sigma_{\beta\alpha}, \quad (40)$$

$$\begin{aligned} \frac{\partial Q}{\partial t} = & - v_\alpha \partial_\alpha Q - q_{\alpha\gamma} \kappa_{\gamma\alpha} - \frac{Q}{3} \kappa_{\alpha\alpha} \\ & - \lambda^Q \left(\frac{\partial\varphi}{\partial Q} \right) - \lambda_{\alpha\beta}^{qQ} \left(\frac{\partial\varphi}{\partial q_{\alpha\beta}} \right), \end{aligned} \quad (41)$$

$$\begin{aligned} \frac{\partial q_{\alpha\beta}}{\partial t} = & -v_{\theta} \partial_{\theta} q_{\alpha\beta} - q_{\alpha\gamma} \kappa_{\gamma\beta} - q_{\beta\gamma} \kappa_{\gamma\alpha} + \frac{q_{\alpha\beta} q_{\theta\nu}}{Q} \kappa_{\theta\nu} \\ & - \frac{Q}{3} \dot{\gamma}_{\alpha\beta} + \frac{1}{3} \left(q_{\alpha\beta} + \frac{2Q}{3} \delta_{\alpha\beta} \right) \kappa_{\theta\theta} \\ & + \frac{2}{3} \delta_{\alpha\beta} q_{\theta\nu} \kappa_{\theta\nu} - \lambda_{\alpha\beta}^q \left(\frac{\partial \varphi}{\partial Q} \right) - \lambda_{ij\alpha\beta}^q \left(\frac{\partial \varphi}{\partial q_{ij}} \right). \end{aligned} \quad (42)$$

Here, the momentum balance equation, (40), will depend on the constitutive equations which are expressed now in terms of the state variables, Q and \mathbf{q} . The hydrodynamic pressure p is given by

$$p = -\varphi + \rho \frac{\partial \varphi}{\partial \rho} + Q \frac{\partial \varphi}{\partial Q} + q_{\alpha\beta} \frac{\partial \varphi}{\partial q_{\alpha\beta}}, \quad (43)$$

and the contribution of the interface to the extra stress tensor, $\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(\text{cfm})} + \sigma_{\alpha\beta}^{(\text{Interface})}$ reads as

$$\begin{aligned} \sigma_{\alpha\beta}^{(\text{Interface})} = & 2q_{\alpha\gamma} \left(\frac{\partial \varphi}{\partial q_{\gamma\beta}} \right) + q_{\alpha\beta} \left(\frac{\partial \varphi}{\partial Q} \right) + \frac{2Q}{3} \left(\frac{\partial \varphi}{\partial q_{\alpha\beta}} \right) \\ & - \frac{q_{\alpha\beta} q_{\gamma\nu}}{Q} \left(\frac{\partial \varphi}{\partial q_{\gamma\nu}} \right) - \frac{2}{3} \delta_{\alpha\beta} \left(Q \left(\frac{\partial \varphi}{\partial Q} \right) \right. \\ & \left. + 2q_{\nu\theta} \left(\frac{\partial \varphi}{\partial q_{\nu\theta}} \right) \right) - \frac{2}{3} \delta_{ij} \left(q_{\alpha\beta} + \frac{1}{3} Q \delta_{\alpha\beta} \right) \left(\frac{\partial \varphi}{\partial q_{ij}} \right). \end{aligned} \quad (44)$$

The hydrodynamics part, $\sigma^{(\text{cfm})}$, remains unchanged with respect to its expression given by Eq. (23). While, the first four terms in Eq. (44) are similar to those derived in Refs. 6 and 10, the last four terms are new. The fifth term, $\frac{2}{3} Q (\partial \varphi / \partial Q)$, is the well known Laplace contribution ($\partial \varphi / \partial Q = \Gamma$ is the interfacial tension), which is now extended by a nonequilibrium contribution, $\frac{4}{3} q_{\nu\theta} (\partial \varphi / \partial q_{\nu\theta})$, stemming from the anisotropy of the interface. Note that, if the blend consists of a matrix (major phase) and a dispersed phase (minor) composed of spherical droplets with radius R and a volume fraction ϕ , one recovers Laplace's equation, $\Delta p = (2\Gamma/R)\phi$ (where $Q = 3\phi/R$ and $\mathbf{q} = \mathbf{0}$ due to isotropy). We emphasize that expressions (43) and (44) arise naturally in the governing equations from the Poisson bracket and no ad hoc assumptions are required. Using the transformation Eq. (29), one can verify that these expressions are consistent with their kinetic counterparts given by Eq. (21) and (24).

Equations (41) and (42) are the governing equations for the interface on the mesoscopic (Q, q)-level. The fact that we have started the derivation from a kinetic level of description allows us to derive a more general formulation on the averaged level. Indeed, we recover as particular cases most of the earlier derivations.^{4-7,10} Their reversible part is recovered by putting $\nabla \cdot \mathbf{v} = 0$ (incompressibility constraint). In addition, the irreversible terms in our approach also derived rigorously from a kinetic level, show new interesting consequences. The relaxation is not only produced by direct processes but also by cross coupling terms. By choosing adequately the expression of the internal free energy, many relaxation processes become thus available depending on the physical problem

under consideration. As an illustration, we shall discuss two well-known specific cases, namely the Doi–Ohta⁴ and Lee–Park⁵ formulations.

5. Special cases

If $\lambda_f = \lambda_f^0$ is assumed to be a constant independent of \mathbf{n} , then Eqs. (33)–(35) become

$$\begin{aligned} \lambda_{\alpha\beta ij}^q = & \lambda_f^0 \int d^2 n (f - f^*) [n_i n_j n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta} n_i n_j \\ & - \frac{1}{3} \delta_{ij} n_\alpha n_\beta + \frac{1}{9} \delta_{ij} \delta_{\alpha\beta}] \\ = & \lambda_f^0 \left(\frac{q_{ij} q_{\alpha\beta}}{Q} - \frac{q_{ij}^* q_{\alpha\beta}^*}{Q^*} \right), \end{aligned} \quad (45)$$

$$\lambda^Q = \lambda_f^0 \int d^2 n (f - f^*) = \lambda_f^0 (Q - Q^*), \quad (46)$$

$$\lambda_{\alpha\beta}^{qQ} = \lambda_f^0 \int d^2 n (f - f^*) [n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta}] = \lambda_f^0 (q_{\alpha\beta} - q_{\alpha\beta}^*), \quad (47)$$

where expressions (2)–(4) and (31) have been used. Notice that Eq. (45) involves a fourth moment and if the quadratic closure (31) is not used, Eq. (45) will result in a different expression. The quantities Q^* and \mathbf{q}^* denote the values for the size and shape of the interface given, respectively, by

$$Q^* = \int d^2 n f_0 \frac{(\det \mathbf{F})^2}{|\mathbf{F}^+ \cdot \mathbf{n}|^4}$$

and

$$q_{\alpha\beta}^* = \int d^2 n f_0 \frac{(\det \mathbf{F})^2}{|\mathbf{F}^+ \cdot \mathbf{n}|^4} \left(n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta} \right).$$

a. Doi–Ohta model: To recover the Doi–Ohta model,⁴ we put $Q^* = 0$ (complete phase separation) and $\mathbf{q}^* = \mathbf{0}$ and choose the internal free energy density as

$$\varphi(\rho, Q, \mathbf{q}) = \Gamma Q, \quad (48)$$

where Γ is the interfacial tension. Therefore, Eqs. (36) and (37) simplify as

$$\left. \frac{\partial Q}{\partial t} \right|_{\text{relaxation}} = -\lambda^Q \left(\frac{\partial \varphi}{\partial Q} \right) = -\lambda_f^0 \Gamma Q, \quad (49)$$

$$\left. \frac{\partial q_{\alpha\beta}}{\partial t} \right|_{\text{relaxation}} = -\lambda_{\alpha\beta}^{qQ} \left(\frac{\partial \varphi}{\partial q_{\alpha\beta}} \right) = -\lambda_f^0 \Gamma q_{\alpha\beta}. \quad (50)$$

If the system does not possess a length scale, dimensional analysis yields⁴

$$\lambda_f^0 = r_1 \left(\frac{Q}{\eta} \right), \quad (51)$$

where r_1 is a positive parameter. This choice leads to a complete phase separation, since $Q^* = 0$. We notice that on the (Q, \mathbf{q})-level, contrary to the original Doi–Ohta model, only one positive parameter, r_1 is involved. This is in agreement with the comparison with other simulation data carried out in Ref. 9. It is also interesting to note that from Eq. (50), the

relaxation of the shape is produced uniquely by the relaxation of the size through the coupling tensorial parameter, $\lambda^q Q$. This assumes that the relaxation of the shape, occurring very slowly ($\lambda^q \equiv 0$), is indirectly but completely controlled by the relaxation of the size.

Furthermore, the contribution of the interface to the stress tensor becomes

$$\sigma_{\alpha\beta}^{(\text{Interface})} = \Gamma q_{\alpha\beta} - \frac{2}{3} \delta_{\alpha\beta} \Gamma Q. \quad (52)$$

The second term on the right-hand side is Laplace's contribution to the stress tensor. This term is missing in the derivation of Doi and Ohta.

b. Lee and Park model: Here, we also put $Q^* = 0$ (complete phase separation) and $q^* = 0$ (isotropy) and write the internal free energy under a form including the anisotropic changes of the interface,

$$\varphi(\rho, Q, \mathbf{q}) = \Gamma Q + \frac{1}{2} \alpha \mathbf{q} : \mathbf{q}. \quad (53)$$

The second term on the right-hand side has been suggested⁷ to account for nonequilibrium contributions of the variable \mathbf{q} . α is a parameter accounting for the anisotropy of the interface. Therefore, Eqs. (36) and (37) reduce to

$$\left. \frac{\partial Q}{\partial t} \right|_{\text{relaxation}} = -\lambda_f^0 (\Gamma Q + \alpha q_{\alpha\beta} q_{\alpha\beta}), \quad (54)$$

$$\left. \frac{\partial q_{\alpha\beta}}{\partial t} \right|_{\text{relaxation}} = -\lambda_f^0 \left(\Gamma q_{\alpha\beta} + \alpha \frac{q_{ij} q_{\alpha\beta}}{Q} q_{ij} \right). \quad (55)$$

We recover rigorously the ad hoc equations put forward in Ref. 5, provided the free energy has the form of Eq. (53). Their physical⁵ intuitive choice for the relaxation processes is justified by the possible occurrence of coalescence [the first term on the right-hand side of Eq. (54)] and break-up of the droplets [second term on the right-hand side of Eq. (54)] under the flow conditions. Via our formulation, a more physical understanding for the relaxation processes is available. The relaxation of the size is described directly as well as indirectly through the first and second terms on the right-hand side of Eq. (36), respectively. The same is true for the relaxation of the shape. Moreover, we can now more easily distinguish between the direct and indirect processes (produced by the coupling) that are involved in the relaxation.

The interfacial contribution to the stress tensor becomes

$$\sigma_{\alpha\beta}^{(\text{Interface})} = \Gamma q_{\alpha\beta} + \alpha \left(2q_{\alpha\gamma} q_{\gamma\beta} - \frac{q_{\gamma\nu} q_{\gamma\nu}}{Q} q_{\alpha\beta} - \frac{2}{3} Q q_{\alpha\beta} \right) - \frac{2}{3} \delta_{\alpha\beta} (\Gamma Q + 2\alpha q_{\gamma\nu} q_{\gamma\nu}).$$

In this nonequilibrium description, the Laplace term is modified by the contribution of the anisotropy, $\frac{4}{3} \alpha q_{\gamma\nu} q_{\gamma\nu}$. Only the first term on the right-hand side of the above expression is present in the Lee and Park model.

We point out that the relaxation processes on the (Q, \mathbf{q}) -level, which consider the relaxation of the size, shape and also their coupling, are obtained from a kinetic formulation suggested in this work. We have reproduced these two models by assuming that $\lambda_f = \lambda_f^0$ is constant and by applying the quadratic closure (31). If this is not the case, as may be

expected in more complex situations, then the formulation provided by Eqs. (33)–(44) is well suited and offers a more general description.

IV. RHEOLOGY, MORPHOLOGY, AND DIFFUSION IN MIXTURES OF AN IMMISCIBLE BLEND (A/B) AND A SIMPLE FLUID *s*: A TWO-LEVEL DESCRIPTION

A. Problem statement

In Sec. III, we have discussed the coupling occurring between the flow dynamics and the deformation of the interface in an immiscible blend $b \equiv (A/B)$ that does not contain other substances such as solvents. In this section, we extend this investigation, by adding a simple fluid, *s* to the immiscible blend *b* (see Fig. 3). That is, we address the dynamic behavior of mixtures, $\{b + s\}$ consisting of an immiscible blend *b* (e.g., polymeric blend) and one simple fluid, *s* (e.g., a solvent) miscible with the blend components A and B. As discussed earlier, the fluids A and B are assumed to retain their immiscibility (no interpenetration between A and B) in the presence of the simple fluid. The blend *b* is regarded as a pseudo-one-component fluid in which an interface is embedded^{4–16} (see Sec. III). The only diffusion process that occurs in this multiphase mixture is the one resulting from the transport of the simple fluid in both phases A and B. The molecules of the simple fluid are assumed to have equal velocities in A and B. This reduces the number of independent state variables and thus the number of the governing equations. The whole mixture, $\{b + s\}$ can be considered as consisting of two fluids:³⁶ i.e., the pseudo-one-component immiscible blend *b* with an apparent mass density ρ_b and a momentum density $\mathbf{u}_b = \rho_b \mathbf{v}_b$ and the simple fluid, *s* with an apparent mass density ρ_s and a momentum density $\mathbf{u}_s = \rho_s \mathbf{v}_s$. Since, the fluid, *s* and the blend, *b* are miscible they can be regarded as two interpenetrating media.³⁶ As discussed earlier, we choose to describe the interface by its area density distribution function $f(\mathbf{r}, \mathbf{n}, t)$ or by its moments: the scalar $Q(\mathbf{r}, t)$ and the second-order tensor $\mathbf{q}(\mathbf{r}, t)$.

For rheological studies, it is preferable to use global and relative variables of the whole mixture. Consequently, we use the following one-to-one transformation,^{33,50,51}

$$\begin{aligned} \rho &= \rho_s + \rho_b, \\ \mathbf{u} &= \mathbf{u}_s + \mathbf{u}_b, \\ c &= \frac{\rho_s}{\rho_s + \rho_b}, \\ \mathbf{J} &= \frac{\rho_b}{\rho_s + \rho_b} \mathbf{u}_s - \frac{\rho_s}{\rho_s + \rho_b} \mathbf{u}_b, \end{aligned} \quad (56)$$

where $\rho(\mathbf{r})$ is the total mass density, $\mathbf{u}(\mathbf{r})$ is the total momentum vector, $c(\mathbf{r})$ is the mass fraction of the simple fluid concentration, and $\mathbf{J}(\mathbf{r})$ is its relative momentum density vector. The latter coincides exactly with the mass flux density relative to the local mass-average velocity.⁵¹ The whole

mixture is now characterized by the set of the state variables,

$$X = (\rho, \mathbf{u}, c, \mathbf{J}, f) \quad (57)$$

if f is used to describe the complex interface, or alternatively by

$$X = (\rho, \mathbf{u}, c, \mathbf{J}, Q, \mathbf{q}) \quad (58)$$

if Q and \mathbf{q} are used instead.

$$\begin{aligned} \{A, B\}^{(\text{diffusion})} = & \int d^3r \left[J_\gamma \partial_\alpha \left(\frac{\partial A}{\partial J_\gamma} \right) \left(\frac{\partial B}{\partial u_\alpha} \right) + J_\gamma \partial_\alpha \left(\frac{\delta A}{\delta u_\gamma} \right) \left(\frac{\delta B}{\delta J_\alpha} \right) - \partial_\alpha (c) \left(\frac{\delta A}{\delta c} \right) \left(\frac{\delta B}{\delta u_\alpha} \right) - J_\gamma \partial_\alpha \left(c \frac{\delta A}{\delta J_\gamma} \right) \left(\frac{\delta B}{\delta J_\alpha} \right) \right. \\ & \left. + (1-c)(cu_\gamma + J_\gamma) \partial_\alpha \left(\frac{\delta A}{\delta J_\gamma} \right) \left(\frac{\delta B}{\delta J_\alpha} \right) + \rho c(1-c) \partial_\alpha \left(\frac{1}{\rho} \frac{\delta A}{\delta c} \right) \frac{\delta B}{\delta J_\alpha} - \rho c(1-c) \partial_\alpha \left(\frac{u_\gamma}{\rho} \frac{\delta A}{\delta J_\gamma} \right) \frac{\delta B}{\delta J_\alpha} - A \leftrightarrow B \right]. \end{aligned} \quad (60)$$

We shall derive the last bracket in Eq. (59) accounting for the interface on two levels of description [f and (Q, \mathbf{q}) levels] in Secs. IV B and IV C.

2. Dissipation potential

In addition to the dissipation phenomena stemming from the relaxation of the interface (attributed mainly to its interfacial tension), and from the viscosity of the fluids (as a response to the velocity gradient of the external flow), there is also a contribution due to diffusion. Therefore, the dissipation potential can be written as

$$\Psi = \Psi^{(\text{cfm})} + \Psi^{(\text{Interface})} + \Psi^{(\text{diffusion})}. \quad (61)$$

The first term on the right-hand side is similar to Eq. (8), and the second term is given by^{33,51}

$$\Psi^{(\text{diffusion})} = \int d^3r \left(\frac{\delta \Phi}{\delta \mathbf{J}} \right)^T \frac{\rho c(1-c) \Lambda_J}{2} \left(\frac{\delta \Phi}{\delta \mathbf{J}} \right), \quad (62)$$

where T is the transpose operator. The phenomenological parameter, Λ_J is the inverse of the relaxation time. In view of the properties of the dissipation potential, Ψ , Λ_J must be a positive parameter. In the vicinity of equilibrium, we can express this coefficient as a function of the Bearman microscopic friction coefficient,⁵² ξ_{sb}^* , i.e.,

$$\Lambda_J = \frac{\rho N_A^2}{M_s M_b} \xi_{sb}^*,$$

where N_A is Avogadro's number and M_j denotes the molecular weight of component j . As we focus on interfaces with infinite friction coefficient between the two phases A and B ($\xi_{AB}^* \rightarrow \infty$), we express the solvent/blend friction coefficient as

$$\frac{1}{\xi_{sb}^*} = \left(\frac{\phi_A^* \gamma_A}{\xi_{sA}^*} + \frac{(1-\phi_A^*) \gamma_B}{\xi_{sB}^*} \right) / (\gamma_A \phi_A^* + \gamma_B (1-\phi_A^*)),$$

as a function of the friction coefficients, ξ_{sA}^* and ξ_{sB}^* of the systems s/A and s/B , respectively. $\phi_A^* = V_A / (V_A + V_B)$ is

1. Poisson bracket

The Poisson bracket for the whole mixture is now given by

$$\{A, B\} = \{A, B\}^{(\text{cfm})} + \{A, B\}^{(\text{diffusion})} + \{A, B\}^{(\text{Interface})}. \quad (59)$$

The first term remains unchanged with respect to Eq. (7). The bracket expressing the contribution of diffusion to the reversible dynamics is given as in³³

the volume fraction of phase A in the blend $b \equiv A/B$, and γ_i refers to the material density of the component i ($i \equiv A$ or B).

The specification of the dissipation potential, $\Psi^{(\text{Interface})}$, accounting for the interface contribution is provided in Secs. IV B and IV C.

3. Free energy

Using the one-on-one transformation (56), and assuming that the kinetic energy for the mixture can be written as a sum of the kinetic energy expressions for the blend and for the simple fluid, ($(\mathbf{u}_s^2/2\rho_s) + (\mathbf{u}_b^2/2\rho_b)$), we arrive at the following expression:⁵¹

$$\tilde{\varphi} = \left(\frac{\mathbf{u}^2}{2\rho} + \frac{\mathbf{J}^2}{2\rho c(1-c)} \right) + \varphi, \quad (63)$$

where the first term on the right-hand side represents the global kinetic energy and the second term stands for the relative kinetic energy. The quantity φ , still left unspecified, denotes the internal free energy density that is independent of \mathbf{u} and \mathbf{J} . That is, $\varphi = \varphi(\rho, c, f)$ or $\varphi = \varphi(\rho, c, Q, \mathbf{q})$ if Eq. (57) or Eq. (58) are used, respectively, as the sets for the independent variables. This functional can be written as a sum of two contributions: a Flory–Huggins⁵³ expression for mixing and an additional term describing the interface contribution,

$$\varphi = \varphi^{\text{mixing}}(c) + \varphi^{\text{Interface}}(\rho, c, Q, \mathbf{q}), \quad (64)$$

if Eq. (58) is used as the set of state variables.

So far, we have partially specified the Poisson brackets and the dissipation potentials for classical fluid mechanics (cfm) and diffusion. What remains to be done is to determine the same quantities for the interface on both the f and (Q, \mathbf{q}) levels of description and derive the corresponding equations governing the time evolution for the whole mixture $\{s+b\}$.

B. Model on the f -level of description

Here we determine the remaining quantities: $\{A, B\}^{(Interface)}$, $\Psi^{(Interface)}$, and the corresponding governing equations on the f -level.

$$\begin{aligned} \{A, B\}^{(Interface)} = & \{A, B\}^{(1.14)} - \int d^3r \int d^2n f(\mathbf{r}, \mathbf{n}, t) \left[\partial_\alpha \left(c \left(\frac{\partial A}{\partial f} \right) \left(\frac{\delta B}{\delta J_\alpha} \right) \right) - \partial_\alpha \left(c \left(\frac{\delta B}{\delta f} \right) \left(\frac{\delta A}{\delta J_\alpha} \right) \right) \right] \\ & + \int d^3r \int d^2n \left(\mathbf{n}_\beta f(\mathbf{r}, \mathbf{n}, t) \left[\frac{\partial}{\partial n_\alpha} \left(\frac{\partial A}{\partial f} \right) \partial_\alpha \left(c \frac{\partial B}{\delta J_\beta} \right) - \frac{\partial}{\partial n_\alpha} \left(\frac{\delta B}{\delta f} \right) \partial_\alpha \left(c \frac{\partial A}{\delta J_\beta} \right) \right] \right) \\ & - \int d^3r \int d^2n \left(n_\beta n_\gamma n_\alpha f(\mathbf{r}, \mathbf{n}, t) \left[\frac{\partial}{\partial n_\alpha} \left(\frac{\delta A}{\delta f} \right) \partial_\gamma \left(c \frac{\partial B}{\delta J_\beta} \right) - \frac{\partial}{\partial n_\alpha} \left(\frac{\delta B}{\delta f} \right) \partial_\gamma \left(c \frac{\delta A}{\delta J_\beta} \right) \right] \right) \\ & + \int d^3r \int d^2n \left(n_\alpha n_\beta f(\mathbf{r}, \mathbf{n}, t) \left[\left(\frac{\delta A}{\delta f} \right) \partial_\beta \left(c \frac{\delta B}{\delta J_\alpha} \right) - \left(\frac{\delta B}{\delta f} \right) \partial_\beta \left(c \frac{\delta A}{\delta J_\alpha} \right) \right] \right), \end{aligned} \tag{65}$$

where the first bracket on the right-hand side in Eq. (65) is the Poisson bracket given by Eq. (14).

2. Dissipation potential

We assume, as previously that dissipation is generated by a simple relaxation. In this way, we ignore any intrinsic diffusion process between the phases A and B of the immiscible blend $b \equiv A/B$. Therefore,

$$\begin{aligned} \Psi^{(Interface)} = & \int d^3r \int d^2n \left(\frac{\Lambda_f(c)}{2} \right) (f(\mathbf{n}, \mathbf{r}, t) - f_{eq}(c)) \\ & \times \left(\frac{\delta \Phi}{\delta f} \right)^2, \end{aligned} \tag{66}$$

where Λ_f , concentration dependent, is a positive parameter related to the relaxation rate of the interface. f_{eq} is the area distribution function density at equilibrium. The presence of the simple fluid in the blend may determine the amount of the interfacial area, which leads to an equilibrium value. Contrary to the diffusion-free problem, the system may now have a characteristic length scale and thus an intrinsic time scale.

3. Governing equations

Using Eqs. (63), (65), and (66), we arrive at the governing equations for the state variables $(\rho, \mathbf{u}, c, \mathbf{J}, f)$,

$$\frac{\partial \rho}{\partial t} = -\partial_\alpha (\rho v_\alpha), \tag{67}$$

$$\frac{\partial u_\alpha}{\partial t} = -\partial_\beta (u_\alpha v_\beta) - \partial_\alpha p - \partial_\beta \sigma_{\beta\alpha}, \tag{68}$$

$$\rho \frac{\partial c}{\partial t} = -\rho v_\alpha \partial_\alpha c - \partial_\alpha J_\alpha, \tag{69}$$

1. Poisson bracket

Now, in addition to the changes brought about by the external flow, the Poisson bracket for the interface contains the contribution of the mass transfer. We express it as

$$\begin{aligned} \frac{\delta J_\alpha}{\delta t} = & -\partial_\gamma (J_\alpha v_\gamma) - J_\gamma \kappa_{\alpha\gamma} - (1-c) \partial_\beta \left(\frac{J_\alpha J_\beta}{\rho c (1-c)} \right) \\ & + \partial_\beta \left(\frac{J_\alpha J_\beta}{\rho c (1-c)} \right) - \rho c (1-c) \partial_\alpha \left(\frac{1}{\rho} \frac{\partial \varphi}{\partial c} \right) \\ & + c \int d^2n f(\mathbf{n}, \mathbf{r}, t) \partial_\alpha \left(\frac{\partial \varphi}{\partial f} \right) \\ & + c \partial_\gamma \sigma_{\alpha\gamma}^{(Interface)} - \Lambda_f J_\alpha, \end{aligned} \tag{70}$$

$$\begin{aligned} \frac{\delta f}{\delta t} = & -\left(v_\alpha - \frac{J_\alpha}{\rho(1-c)} \right) \partial_\alpha f + \frac{\partial}{\partial n_\alpha} (n_\beta f (\kappa_{\beta\alpha} - d_{\beta\alpha})) \\ & - \frac{\partial}{\partial n_\alpha} (n_\beta n_\gamma n_\alpha (\kappa_{\beta\gamma} - d_{\beta\gamma}) f) \\ & - n_\alpha n_\beta (\kappa_{\alpha\beta} - d_{\alpha\beta}) f - \Lambda_f(c) (f - f_{eq}(c)) \left(\frac{\partial \varphi}{\partial f} \right). \end{aligned} \tag{71}$$

We now deal with five nonlinear coupled time evolution equations describing the flow dynamics of the mixture $\{b+s\}$, the diffusion process of the simple fluid, and the deformation of the interface produced by the applied flow and diffusion. While the hydrodynamic pressure p has the same expression as in Eq. (21), the stress tensor, σ , now becomes

$$\sigma = \sigma^{(cfm)} + \sigma^{(Interface)} + \sigma^{(diffusion)}. \tag{72}$$

The first term, $\sigma^{(cfm)}$ is given by Eq. (23). The second term, $\sigma^{(Interface)}$, is given by Eq. (24) except that the free energy density must now consider the effects of mass transport of the simple fluid into the blend A/B. This will generally lead to a different expression attributed to the dependence of the state equations of the model (e.g., interfacial tension) on the penetrant mass fraction. The last term representing the direct effect of diffusion on the dynamics has the following form:

$$\sigma^{(\text{diffusion})} = \mathbf{J} \left(\frac{\partial \bar{\varphi}}{\partial \mathbf{J}} \right) = \frac{\mathbf{J} \mathbf{J}}{\rho c (1-c)}. \quad (73)$$

The third equation refers to the continuity equation for the simple fluid, and the fourth represents the time evolution equation for the diffusion mass flux. In addition to the effect of the flow on diffusion through the velocity gradient $\kappa_{\alpha\beta} = \partial v_\alpha / \partial r_\beta$, the diffusion mass flux equation explicitly contains the chemical potential of the simple fluid also representing the osmotic pressure of the blend, $b \equiv A/B$ (the fifth and sixth terms on the right-hand side). Note also that the diffusion is explicitly influenced by the interfacial stresses (seventh term) created by the deformation of the interface.

The last equation (71) provides the time evolution of the changes that occur at the interface. Both flow and diffusion directly affect the distribution function density f . In addition to the gradient of the applied velocity, $\kappa_{\alpha\beta} = \partial v_\alpha / \partial r_\beta$, a new gradient,

$$d_{\alpha\beta} = \frac{\partial}{\partial r_\beta} \left(\frac{J_\alpha}{\rho(1-c)} \right), \quad (74)$$

involving the diffusion mass flux enters Eq. (71). We point out that this term arises in the governing equation naturally

$$\begin{aligned} \{A,B\}^{(\text{Interface})} = \{A,B\}^{(1,30)} + \int d^3r \left[-q_{\alpha\beta} \partial_\gamma \left(c \frac{\partial A}{\partial q_{\alpha\beta}} \frac{\delta B}{\delta J_\gamma} \right) + q_{\alpha\gamma} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_\beta \left(c \frac{\delta B}{\delta J_\gamma} \right) + q_{\beta\gamma} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_\alpha \left(c \frac{\delta B}{\delta J_\gamma} \right) \right. \\ \left. - \frac{q_{\alpha\beta} q_{\theta\nu}}{Q} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_\nu \left(c \frac{\delta B}{\delta J_\theta} \right) - \frac{1}{3} \left(q_{\alpha\beta} + \frac{2Q}{3} \delta_{\alpha\beta} \right) \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_{gg} \left(c \frac{\delta B}{\delta J_\gamma} \right) - \frac{2}{3} \delta_{\alpha\beta} q_{\theta\nu} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_\nu \left(c \frac{\delta B}{\delta J_\theta} \right) \right. \\ \left. + \frac{Q}{3} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \left[\partial_\beta \left(c \frac{\delta B}{\delta J_\alpha} \right) + \partial_\alpha \left(c \frac{\delta B}{\delta J_\beta} \right) \right] - Q \partial_\gamma \left(c \frac{\delta A}{\delta Q} \frac{\delta B}{\delta J_\gamma} \right) + \left(q_{\alpha\beta} + \frac{Q}{3} \delta_{\alpha\beta} \right) \left(\frac{\partial A}{\partial Q} \right) \partial_\alpha \left(c \frac{\delta B}{\delta J_\beta} \right) - A \leftrightarrow B \right], \end{aligned} \quad (75)$$

where the first bracket on the right-hand side is given by Eq. (30).

2. Dissipation potential

On the other hand, the calculated dissipation potential has the same form as in Eq. (32), except that the kinetic phenomenological parameters have now different meanings due to their intimate dependence on the parameter Λ_f introduced on the f -level. Therefore,

$$\begin{aligned} \Psi^{(\text{Interface})} = \int d^3r \left[\left(\frac{\delta \Phi}{\delta q_{ij}} \right) \frac{\Lambda_{\alpha\beta ij}^q(c)}{2} \left(\frac{\delta \Phi}{\delta q_{\alpha\beta}} \right) \right. \\ \left. + \left(\frac{\delta \Phi}{\delta q_{ij}} \right) \Lambda_{ij}^{qQ}(c) \left(\frac{\delta \Phi}{\delta Q} \right) \right. \\ \left. + \left(\frac{\delta \Phi}{\delta Q} \right) \frac{\Lambda^Q(c)}{2} \left(\frac{\delta \Phi}{\delta Q} \right) \right]. \end{aligned} \quad (76)$$

The phenomenological parameters Λ^q , Λ^Q , and Λ^{qQ} satisfying the symmetry and positive semidefiniteness properties are expressed by Eqs. (33)–(35) but with λ_f replaced by Λ_f ,

from the reversible kinematics (i.e., Poisson bracket) without any ad hoc assumption. The emergence of this gradient indicates clearly the direct and explicit influence of mass transport on the interface dynamics.

C. (Q, \mathbf{q})-level of description

As discussed in Sec. III, we have shown the usefulness of deriving the governing equations on the (Q, \mathbf{q})-level for investigating the relationship between flow and morphology changes. Here we intend to similarly examine the relationship among the flow, the morphology deformation and diffusion on the mesoscopic level. What remains is to determine are the interfacial quantities: $\{A,B\}^{(\text{Interface})}$, $\Psi^{(\text{Interface})}$, and the corresponding governing equations on the (Q, \mathbf{q})-level.

1. Poisson bracket

The Poisson bracket on this level can be obtained either from the Poisson bracket derived on the f -level and using the chain rule (29) or via the Poisson bracket (30) using the one-to-one transformation (56). The result is given as

Q^* by $Q_{\text{eq}}(c)$, and \mathbf{q}^* by $\mathbf{q}_{\text{eq}}(c)$. Diffusion introduces a characteristic length scale identified here by $1/Q_{\text{eq}}$ which gives a characteristic time scale for the system as

$$\tau = (\Gamma \Lambda_f)^{-1} = \eta / \Gamma Q_{\text{eq}}. \quad (77)$$

3. Governing equations

Using Eqs. (63), (76), and (77), and following the same procedure as before, we obtain the following governing equations for the set of state variables $(\rho, \mathbf{u}, c, \mathbf{J}, Q, \mathbf{q})$:

$$\frac{\partial \rho}{\partial t} = -\partial_\alpha (\rho v_\alpha), \quad (78)$$

$$\frac{\partial u_\alpha}{\partial t} = -\partial_\beta (u_\alpha v_\beta) - \partial_\alpha p - \partial_\beta \sigma_{\beta\alpha}, \quad (79)$$

$$\rho \frac{\partial c}{\partial t} = -\rho v_\alpha \partial_\alpha c - \partial_\alpha J_\alpha, \quad (80)$$

$$\begin{aligned} \frac{\partial J_\alpha}{\partial t} = & -\partial_\gamma(J_\alpha v_\gamma) - J_\gamma \kappa_{\alpha\gamma} - (1-c)\partial_\beta\left(\frac{J_\alpha J_\beta}{\rho c(1-c)}\right) \\ & + \partial_\beta\left(\frac{J_\alpha J_\beta}{\rho(1-c)}\right) - \rho c(1-c)\partial_\alpha\left(\frac{1}{\rho}\frac{\partial\varphi}{\partial c}\right) \\ & + cQ\partial_\alpha\left(\frac{\partial\varphi}{\partial Q}\right) + cq_{\beta\gamma}\partial_\alpha\left(\frac{\partial\varphi}{\partial q_{\beta\gamma}}\right) + c\partial_\gamma\sigma_{\alpha\gamma}^{(\text{Interface})} \\ & - \Lambda_J J_\alpha, \end{aligned} \tag{81}$$

$$\begin{aligned} \frac{\partial Q}{\partial t} = & -\left(v_\alpha - \frac{J_\alpha}{\rho(1-c)}\right)\partial_\alpha Q - q_{\alpha\gamma}(\kappa_{\gamma\alpha} - d_{\gamma\alpha}) \\ & - \frac{Q}{3}(\kappa_{\alpha\alpha} - d_{\alpha\alpha}) - \Lambda^Q(c)\left(\frac{\partial\varphi}{\partial Q}\right) - \Lambda_{\alpha\beta}^{qQ}(c) \\ & \times \left(\frac{\partial\varphi}{\partial q_{\alpha\beta}}\right), \end{aligned} \tag{82}$$

$$\begin{aligned} \frac{\partial q_{\alpha\beta}}{\partial t} = & -\left(v_\gamma - \frac{J_\gamma}{\rho(1-c)}\right)\partial_\gamma q_{\alpha\beta} - q_{\alpha\gamma}(\kappa_{\gamma\beta} - d_{\gamma\beta}) \\ & - q_{\beta\gamma}(\kappa_{\gamma\alpha} - d_{\gamma\alpha}) + \frac{q_{\alpha\beta}q_{\theta\gamma}}{Q}(\kappa_{\theta\gamma} - d_{\theta\gamma}) \\ & - \frac{Q}{3}(\dot{\gamma}_{\alpha\beta} - (d_{\alpha\beta} + d_{\beta\alpha})) + \frac{1}{3}\left(q_{\alpha\beta} + \frac{2Q}{3}\delta_{\alpha\beta}\right) \\ & \times (\kappa_{\gamma\gamma} - d_{\gamma\gamma}) + \frac{2}{3}\delta_{\alpha\beta}q_{\theta\gamma}(\kappa_{\theta\gamma} - \delta_{\theta\gamma}) - \Lambda_{\alpha\beta}^{qQ}(c) \\ & \times \left(\frac{\partial\varphi}{\partial Q}\right) - \Lambda_{\alpha\beta ij}^q(c)\left(\frac{\partial\varphi}{\partial q_{ij}}\right). \end{aligned} \tag{83}$$

On this mesoscopic level, six coupled governing equations are necessary to describe the flow behavior, the diffusion of the simple fluid as well as the deformation of the size and shape of the interface. Here, the constitutive equations are now expressed in terms of the Q and \mathbf{q} variables. Here the hydrodynamic pressure p is as in Eq. (43) and the stress tensor, $\boldsymbol{\sigma}$, is given by

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^{(\text{cfm})} + \boldsymbol{\sigma}^{(\text{Interface})} + \boldsymbol{\sigma}^{(\text{diffusion})}, \tag{84}$$

where $\boldsymbol{\sigma}^{(\text{cfm})}$ is given by Eq. (23), $\boldsymbol{\sigma}^{(\text{Interface})}$ by Eq. (44), and $\boldsymbol{\sigma}^{(\text{diffusion})}$ by Eq. (73).

As already established on the f -level of description, diffusion is strongly affected by the presence of the interface as well as by the applied flow. This is shown in the governing equation of the diffusion mass flux of the simple fluid, where the stresses created by the deformation of the interface contribute to mass transport. In turn, the gradient $d_{\alpha\beta} = \partial_\beta(J_\alpha/\rho(1-c))$, entering the governing Eqs. (82) and (83) for the interface variables Q and \mathbf{q} demonstrates that mass transport causes significant changes in both the size and shape. Such interrelationships among dynamics, diffusion and morphology become more transparent in the next subsection discussing asymptotic solutions.

4. Asymptotic solutions

In this section, we look for some particular cases where some state variables become dependent. In this reduction, we show that the model provided on the (Q, \mathbf{q}) -level encompasses the well-known Fickian diffusion and also new extended formulations where the changes of both the size and shape of the interface contribute to the mass flux.

When the relaxation characteristic time scale, $(\Lambda_J)^{-1}$, is smaller than the diffusion characteristic time scale, \mathbf{J} equilibrates faster and we can assume that $d\mathbf{J}/dt \approx 0$. Moreover, we assume that the quadratic terms appearing in the mass flux governing Eq. (81) are small enough to be relevant to the process of diffusion.

In the following, we shall discuss two particular cases: the first corresponding to a weak coupling between the flow and diffusion and the second to a general case where such a coupling may become strong. In the latter case, we will demonstrate that the transport coefficients are directly modified by the applied flow.

5. Weak coupling with the flow $\kappa_{\alpha\beta} \ll \Lambda_J$

Here, in addition to the above assumptions, we ignore the effect of the gradient of the applied flow $\kappa_{\alpha\beta} = \partial v_\alpha/\partial r_\beta$ assumed to be small compared with the friction coefficient Λ_J . Thereby, the governing Eq. (81) for the diffusion mass flux \mathbf{J} reduces to the following expression:

$$\begin{aligned} \Lambda_J J_\alpha = & -\rho c(1-c)\partial_\alpha\left(\frac{1}{\rho}\frac{\partial\varphi}{\partial c}\right) + cQ\partial_\alpha\left(\frac{\partial\varphi}{\partial Q}\right) \\ & + cq_{\beta\gamma}\partial_\alpha\left(\frac{\partial\varphi}{\partial q_{\beta\gamma}}\right) + c\partial_\beta\sigma_{\alpha\beta}^{(\text{Interface})}. \end{aligned} \tag{85}$$

Reformulating this equation, we arrive at the diffusion mass flux,

$$J_\alpha = -\rho D\partial_\alpha c - \rho H\partial_\alpha Q - \rho G_{\beta\gamma}\partial_\alpha q_{\beta\gamma} + R\partial_\beta\sigma_{\alpha\beta}^{(\text{Interface})}, \tag{86}$$

where the interface stress tensor, $\boldsymbol{\sigma}^{(\text{Interface})}$, is given by Eq. (44). The transport coefficients D , K , \mathbf{G} , and E arising in Eq. (86) have the following explicit form:

$$D = \frac{c}{\Lambda_J}\left(\frac{\partial\mu}{\partial c}\right), \tag{87}$$

$$H = \frac{c}{\Lambda_J}\left(\frac{\partial\mu}{\partial Q}\right), \tag{88}$$

$$G_{\beta\gamma} = \frac{c}{\Lambda_J}\left(\frac{\partial\mu}{\partial q_{\beta\gamma}}\right), \tag{89}$$

$$R = \frac{c}{\Lambda_J}, \tag{90}$$

where

$$\rho(\mu - \mu^0) = \varphi + (1-c)\left(\frac{\partial\varphi}{\partial c}\right) - Q\left(\frac{\partial\varphi}{\partial Q}\right) - q_{\alpha\beta}\left(\frac{\partial\varphi}{\partial q_{\alpha\beta}}\right) \tag{91}$$

is the chemical potential per unit mass of the simple fluid, μ^0 is a reference value at the pure state. In view of the definition suggested for the internal free energy density Eq. (64), we note that the chemical potential can be written as

$$\mu = \mu^{\text{mixing}} + \mu^{\text{Interface}}, \tag{92}$$

where

$$\rho(\mu - \mu^0)^{\text{mixing}} = \varphi^{\text{mixing}} + (1 - c) \left(\frac{\partial \varphi^{\text{mixing}}}{\partial c} \right), \tag{93}$$

$$\begin{aligned} \rho(\mu - \mu^0)^{\text{Interface}} = & \varphi^{\text{Interface}} + (1 - c) \left(\frac{\partial \varphi^{\text{Interface}}}{\partial c} \right) \\ & - Q \left(\frac{\partial \varphi^{\text{Interface}}}{\partial Q} \right) - q_{\alpha\beta} \left(\frac{\partial \varphi^{\text{Interface}}}{\partial q_{\alpha\beta}} \right). \end{aligned} \tag{94}$$

Substituting these expressions into Eqs. (87)–(89), we obtain

$$D = D^{\text{mixing}} + D^{\text{Interface}}, \tag{95}$$

$$H = H^{\text{Interface}}, \tag{96}$$

$$G = G^{\text{Interface}}. \tag{97}$$

D refers to a cooperative diffusion coefficient, involving mixing and interface contributions. The mass transport of the simple fluid, s may be different in phases A and B. This is due to the different attractive/repulsive forces arising between the simple fluid molecules with the two phases. In our model, the governing equations as well as the transport coefficients (e.g., diffusion coefficient) are parameterized by the free energy density which explicitly involves the Flory–Huggins interaction parameters⁵³ accounting for such interactions (steric, van der Waals,...). The interaction parameter of the simple fluid/blend mixture can be expressed as a function of the interaction parameters of the solvent with each component A and B, i.e., $\chi_{sb} = \phi_A^* \chi_{sA} + (1 - \phi_A^*) \chi_{sB}$, where $\phi_A^* = V_A / (V_A + V_B)$ is the volume fraction of phase A in the blend $b \equiv A/B$. This is justified by the fact that here, we focus on the simplified case where the phases A and B have equal velocities, and that the molecules of the simple fluid also move with a same velocity in both phases A and B. The mixture, $\{s + b\}$ is regarded as consisting of two fluids: a pseudo-one-component fluid, b and a simple fluid, s . In this case, the mixing part of the free energy can be written approximately as

$$\begin{aligned} \varphi^{\text{(Flory-Huggins)}} \cong & \frac{RT}{V_s} \left(\phi_s \ln \phi_s + \frac{(1 - \phi_s)}{x_n} \ln(1 - \phi_s) \right. \\ & \left. + \chi_{sb} \phi_s (1 - \phi_s) \right), \end{aligned}$$

where V_s is the molar volume of the simple fluid, R is the gas constant, T is the temperature, x_n is an average chain monomer number for the blend, and $\phi_s = V_s / (V_s + V_b)$ is the volume fraction of the simple fluid in the mixture $\{s + b\}$. Note that the volume fraction of component i is related to its mass fraction c_i by $\rho c_i = \gamma_i \phi_i$, where ρ is the mass density of the whole mixture, $\gamma_i = m_i / V_i$ is the material density of component i (m , mass; V , volume). The equilibrium state is attained when the chemical potential of the simple fluid in its pure state equals its value in the blend b , i.e., $\mu = \mu^0$. The latter equation provides an average value for the equilibrium concentration of the penetrant in the blend, which is expressed in terms of the properties of phases A and B, since the mass fraction of the blend reads as

$$c_b = \frac{(1 - \phi_s)}{\rho} (\gamma_A \phi_A^* + \gamma_B (1 - \phi_A^*)).$$

The combination of Eqs. (86) and (63) generates a quantity to be denoted here by $\Phi^{(JJ)}$ that does not involve the kinetic and internal energy terms. Therefore,

$$\begin{aligned} \Phi^{(JJ)} = & \int d^3r \left(\frac{\mathbf{J}^2}{2\rho c(1-c)} \right) \\ = & \int d^3r \left(\frac{1}{2c(1-c)} \right) [\rho D^2 |\nabla c|^2 + \rho H^2 |\nabla Q|^2 \\ & + \rho G_{ij} G_{kl} \nabla q_{ij} \nabla q_{kl} + R^2 |\nabla \cdot \boldsymbol{\sigma}|^2 + 2\rho DH \nabla c \cdot \nabla Q \\ & + 2\rho DG_{ij} \nabla c \cdot \nabla q_{ij} + 2\rho HG_{ij} \nabla Q \cdot \nabla q_{ij} \\ & - 2R(D \nabla c + G_{ij} \nabla q_{ij} + H \nabla Q) \cdot \nabla \cdot \boldsymbol{\sigma}]. \end{aligned} \tag{98}$$

Equation (98) indicates that fluctuations may occur in the concentration as well as in the size and shape of the interface. The first term on the right-hand side ($\propto |\nabla c|^2$) is well-known from irreversible thermodynamic considerations,⁵⁴ while the other terms are new. Performing the same calculations for the diffusion stresses (73), we arrive at

$$\begin{aligned} \sigma_{\alpha\beta}^{\text{diffusion}} = & \frac{1}{\rho c(1-c)} [\rho^2 D^2 \partial_{\alpha c} \partial_{\beta c} + \rho^2 H^2 \partial_{\alpha Q} \partial_{\beta Q} + \rho^2 G_{ij} G_{kl} \partial_{\alpha q_{ij}} \partial_{\beta q_{kl}} + R^2 \partial_i \sigma_{ai}^{\text{Interface}} \partial_j \sigma_{j\beta}^{\text{Interface}} + \rho^2 DH (\partial_{\alpha c} \partial_{\beta Q} \\ & + \partial_{\beta c} \partial_{\alpha Q}) + \rho^2 DG_{lm} (\partial_{\alpha c} \partial_{\beta q_{lm}} + \partial_{\beta c} \partial_{\alpha q_{lm}}) + \rho^2 HG_{lm} (\partial_{\alpha Q} \partial_{\beta q_{lm}} + \partial_{\alpha Q} \partial_{\beta q_{lm}}) - \rho RD (\partial_{\alpha c} \partial_{\beta \gamma} \sigma_{\gamma\beta} \\ & + \partial_{\beta c} \partial_{\gamma} \sigma_{\gamma\alpha}) - \rho RH (\partial_{\alpha Q} \partial_{\gamma} \sigma_{\gamma\beta} + \partial_{\beta Q} \partial_{\gamma} \sigma_{\gamma\alpha}) - \rho RG_{ij} (\partial_{\alpha q_{ij}} \partial_{\gamma} \sigma_{\gamma\beta} + \partial_{\beta q_{ij}} \partial_{\gamma} \sigma_{\gamma\alpha})]. \end{aligned} \tag{99}$$

Fluctuations in the concentration and in the size and shape of the interface create additional stresses that may affect the flow dynamics. Such phenomena have in fact been observed in some sheared polymer solutions,^{17–19} and it would be interesting to establish whether similar behavior occur in immiscible solutions under an applied flow.

To summarize, the governing equations are

$$\rho \frac{\partial c}{\partial t} = -\rho v_\alpha \partial_\alpha c + \partial_\alpha (\rho D \partial_\alpha c + \rho H \partial_\alpha Q + \rho G_{\beta\theta} \partial_\alpha q_{\beta\theta} - R \partial_\beta \sigma_{\alpha\beta}^{\text{Interface}}), \quad (100)$$

where the momentum balance is given by Eq. (79), the pressure is given by Eq. (43), the stress tensor is given by Eq. (84), the mass flux is given by Eq. (86), and the governing equations for (Q, \mathbf{q}) are given by Eqs. (82) and (83), respectively.

6. Coupling with the flow

In this section, we keep the influence of the gradient of the applied velocity which is assumed to be of the same magnitude (or larger) than the friction coefficient, Λ_J . Equation (81) now reduces to

$$\Lambda_J J_\alpha = -\rho c(1-c) \partial_\alpha \left(\frac{1}{\rho} \frac{\partial \varphi}{\partial c} \right) + c Q \partial_\alpha \left(\frac{\partial \varphi}{\partial Q} \right) + c q_{\beta\gamma} \partial_\alpha \left(\frac{\partial \varphi}{\partial q_{\beta\gamma}} \right) + c \partial_\beta \sigma_{\alpha\beta}^{\text{Interface}} - J_\gamma \kappa_{\alpha\gamma} - J_\alpha \kappa_{\beta\beta}. \quad (101)$$

The last two terms on the right-hand side are the two additional terms that were ignored in Eq. (85). Rearranging Eq. (101), we arrive at the following form for the diffusion mass flux:

$$J_\alpha = -\rho D_{\alpha\gamma}^* \partial_\gamma c - \rho H_{\alpha\gamma}^* \partial_\gamma Q - \rho G_{\beta\theta\alpha\gamma}^* \partial_\gamma q_{\beta\theta} + R_{\alpha\gamma}^* \partial_\beta \sigma_{\gamma\beta}^{\text{Interface}}, \quad (102)$$

where now the transport coefficients are

$$D_{\alpha\gamma}^* = \frac{D}{\left(1 + \frac{\kappa_{\beta\beta}}{\Lambda_J}\right) \delta_{\alpha\gamma} + \frac{\kappa_{\alpha\gamma}}{\Lambda_J}}, \quad (103)$$

$$H_{\alpha\gamma}^* = \frac{K}{\left(1 + \frac{\kappa_{\beta\beta}}{\Lambda_J}\right) \delta_{\alpha\gamma} + \frac{\kappa_{\alpha\gamma}}{\Lambda_J}}, \quad (104)$$

$$G_{\alpha\gamma\epsilon\theta}^* = \frac{G_{\epsilon\theta}}{\left(1 + \frac{\kappa_{\beta\beta}}{\Lambda_J}\right) \delta_{\alpha\gamma} + \frac{\kappa_{\alpha\gamma}}{\Lambda_J}}, \quad (105)$$

$$R_{\alpha\gamma}^* = \frac{E}{\left(1 + \frac{\kappa_{\beta\beta}}{\Lambda_J}\right) \delta_{\alpha\gamma} + \frac{\kappa_{\alpha\gamma}}{\Lambda_J}}. \quad (106)$$

In the presence of the flow, the transport coefficients transform into higher order tensors. The flow affects the process of diffusion which becomes therefore highly anisotropic. These off-diagonal terms in the transport coefficients may generate new fluxes that cannot be observed in the absence of the flow.

The governing equations are now

$$\rho \frac{\partial c}{\partial t} = -\rho v_\alpha \partial_\alpha c + \partial_\alpha (\rho D_{\alpha\gamma}^* \partial_\gamma c + \rho H_{\alpha\gamma}^* \partial_\gamma Q + \rho G_{\beta\theta\alpha\gamma}^* \partial_\gamma q_{\beta\theta} - R_{\alpha\gamma}^* \partial_\beta \sigma_{\gamma\beta}^{\text{Interface}}), \quad (107)$$

where the momentum balance is given by Eq. (79), the pressure is given by Eq. (43), the stress tensor is given by Eq. (84), the mass flux is given by Eq. (102) with Eqs. (103)–(106), and the governing equations for (Q, \mathbf{q}) are given, respectively, by Eqs. (82) and (83).

V. CONCLUSION

We have addressed, in the framework of GENERIC, a systematic study on two levels of description on the relationship (i) between rheology and morphology in a compressible immiscible blend A/B embedding an interface and (ii) among rheology, morphology, and diffusion in a compressible mixture of one immiscible blend (A/B) and one simple fluid, s . We first provide a kinetic description, (denoted by the f -level) and then use it as a starting point to derive an averaged mesoscopic approach, (Q, \mathbf{q}) -level. The use of the GENERIC formalism guarantees the consistency of the dynamical models with thermodynamics.

In the former investigation, the compressible immiscible blend A/B is characterized by its mass density, its momentum density vector, and structural variables characterizing the interface. The latter are chosen to be either the area density distribution function $f(\mathbf{n}, \mathbf{r})$ or its moments, the scalar area density $Q(\mathbf{r})$ and the shape density $\mathbf{q}(\mathbf{r})$. New expressions for the extra stress tensor on both levels of description are obtained and include in addition to the Laplace contribution, the anisotropic deformation of the interface. This shows that the flow dynamics depend explicitly on the interface structural changes. By expressing the dissipation for the variable f as a simple relaxation, we develop richer and more general expressions for the relaxation phenomena occurring on the averaged (Q, \mathbf{q}) -level. We emphasize that the latter formulation is derived rigorously and completely from the f -level of description. As a result, we were able to distinguish between the direct and indirect relaxation processes involved in the dissipation of the size and shape of the interface. Many previous models are recovered as particular cases.

In the latter investigation (rheology, morphology, and diffusion), the state variables of the whole mixture, $\{b \equiv A/B + s\}$, are the mass density $\rho(\mathbf{r})$, the overall momentum density $\mathbf{u}(\mathbf{r})$, the mass fraction $c(\mathbf{r})$ of the simple fluid and its diffusion mass flux vector $\mathbf{J}(\mathbf{r})$ and the structural variables accounting for the interface state variables f or Q and \mathbf{q} . We show that the presence of the solvent in the immiscible blend b directly affects the flow dynamics and the morphology of the interface. A new gradient of the diffusion mass flux of the simple fluid,

$$d_{\alpha\beta} = \frac{\partial}{\partial r_\beta} \left(\frac{J_\alpha}{\rho(1-c)} \right)$$

emerges naturally in the governing equations of the interface. Mass transport becomes non-Fickian due to the dynamic changes occurring in the interface. For the particular case where the inertia of the diffusion mass flux becomes irrelevant, we have found that the transport coefficients become

explicitly dependent on the surface tension of the interface $\Gamma(c)$ and also on the velocity gradient of the applied flow $\kappa_{\alpha\beta} = \partial v_\alpha / \partial r_\beta$.

These studies can be regarded as an interesting framework for discussing other problems involving couplings among diffusion, morphology and rheology in blends of two viscoelastic fluids and multicomponent mixtures. We should point out that we here examine only processes that are far from critical points. In the vicinity of criticality, the thickness of the interface and the interfacial tension become also controlled by molecular diffusion between the two phases A and B. This plays a determinant role for the dynamics of the interface.⁵⁵

In Paper II, we investigate the particular situation where the mixture is not subjected to any external flow and forces.

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APPENDIX: POISSON BRACKET WITHOUT THE DECOUPLING APPROXIMATION

The Poisson bracket without any closure approximation has the following form:

$$\begin{aligned} \{A, B\}^{\text{Interface}} = & \int d^3r \left[q_{\alpha\beta} \partial_\gamma \left(\frac{\delta A}{\delta q_{\alpha\beta}} \frac{\delta B}{\delta u_\gamma} \right) - q_{\alpha\gamma} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_\beta \left(\frac{\delta B}{\delta u_\gamma} \right) - q_{\beta\gamma} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \partial_\alpha \left(\frac{\delta B}{\delta u_\gamma} \right) - \frac{Q}{3} \left(\frac{\delta A}{\delta q_{\alpha\beta}} \right) \left(\partial_\beta \left(\frac{\delta B}{\delta u_\alpha} \right) \right. \right. \\ & \left. \left. + \partial_\alpha \left(\frac{\delta B}{\delta u_\beta} \right) \right) - \left(q_{\alpha\beta} + \frac{Q}{3} \delta_{\alpha\beta} \right) \left(\frac{\delta A}{\delta Q} \right) \partial_\alpha \left(\frac{\delta B}{\delta u_\beta} \right) + \frac{1}{3} \delta_{ij} \left(q_{\alpha\beta} + \frac{Q}{3} \delta_{\alpha\beta} \right) \left(\frac{\delta A}{\delta q_{ij}} \right) \partial_\alpha \left(\frac{\delta B}{\delta u_\beta} \right) + Q \partial_\gamma \left(\frac{\delta A}{\delta Q} \frac{\delta B}{\delta u_\gamma} \right) \right. \\ & \left. + \overline{n_k n_l n_j n_i} \left(\frac{\delta A}{\delta q_{ij}} \right) \partial_l \left(\frac{\delta B}{\delta u_k} \right) - A \leftrightarrow B \right], \end{aligned}$$

which involves the fourth-order moment $\overline{\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{n}} = \int d^2n \mathbf{n}\mathbf{n}\mathbf{n}\mathbf{n} f(\mathbf{n}, \mathbf{r}, t)$.

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