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Migration of substructures in complex fluids

Paolo Maria Mariano

Dipartimento di Ingegneria Strutturale e Geotecnica, Università di Roma ‘La Sapienza’,
via Eudossiana 18, I-00184 Roma, Italy

E-mail: paolo.mariano@uniroma1.it

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Abstract

Migration of substructures in complex fluids at meso-, micro- and nano-level is described in the hydrodynamic range. We show that the primary mechanism ruling this kind of transport leading to clustering and self-organization of microstructures is the competition between substructural actions from place to place. We make use of abstract morphological descriptors so that our treatment is independent of the specific features of each special material substructure.

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1. Introduction

Complex fluids are characterized by a prominent influence of their substructure at meso-, micro- and nano-level on the behaviour of macroscopic flows. Examples of such an influence, exerted by means of substructural interactions, are topological transitions in vortex structures [1].

Complexity in fluids appears in different aspects. We can list some cases. (1) Populations of stick molecules embedded in a melt characterize nematic liquid crystals; in the smectic phase they are organized in superposed layers, each of which with translational order (far from the defect core), an order broken across layers. (2) Two-phase flows admitting phase changes display diffuse interfaces. (3) Polymeric fluids are constituted by long flexible molecules smeared in a ground simple fluid. Such molecules may also be arranged as stars or may be polarizable (as in polyelectrolyte polymers). (4) Polarization can also be recognized in ferrofluids. (5) Additives appear as families of particles smeared in a fluid. They interact with the underlying liquid and also, possibly, with one another, depending on their density, so that they render the fluid complex.

In all these cases, when one tries to represent the morphology of a complex fluid to describe flows, e.g. at kinematical level, one realizes that the standard format in which just a position in space is assigned to each material element (which is thus ‘collapsed’ in its centre of mass) is insufficient. In fact, in complex fluids each material element is not morphologically equivalent to an indistinct sphere. It is a system (roughly speaking a ‘box’ with at least one family of substructures, say, molecules embedded in a melt as in the case of liquid crystals),

so that appropriate morphological descriptors need to be introduced as order parameters. To this end, elements of the projective plane are used to represent nematic order in liquid crystals [2, 3]; a scalar is added in the smectic phase to account for the thickness of layers [4, 5]; second-order tensors may describe local independent deformations of flexible molecules in polymeric fluids [6, 7]; polarization in ferrofluids is represented by vectors [8]; more complicated tensor structures may help in modelling the behaviour of superfluid helium [9].

Morphological descriptors enter in the constitutive structure of the energy to account for energetic changes associated with substructural events. Also, the gradient of the morphological descriptors is involved when weakly non-local effects (due, e.g., to the presence of diffused interfaces or branching of substructures) are present. Typical expressions of the energy are of Ginzburg–Landau type. The derivatives of the energy with respect to the morphological descriptor and its gradient represent respectively self-interactions ‘within’ each material element and ‘contact’ interactions (of gradient type) between neighbouring material elements. At each place they satisfy an appropriate local balance (Capriz balance).

Moreover, individuals or groups that belong to families of substructures pertaining to each material element may migrate from place to place and coherent structures may appear along flows as a consequence of clustering and self-organization. A typical example is the segregation of phases in two-phase flows where coarsening is ruled by the Cahn–Hilliard equation [10]. Other coherent structures appear in polymer fluids where the cooperation of families of polymeric chains generates drag reduction in turbulent flows [11]. A similar phenomenon accrues in fluids with bubbles or with small particles dispersed finely.

Here we show that the primary mechanism ruling the migration of substructures is the competition between substructural interactions from place to place. Such a mechanism is *universal* in the sense that it is independent of (i) the specific geometric features of each substructure and (ii) the constitutive structure of the fluid. Actually, such a result points out that migration of substructures may occur even in perfect fluids: in certain sense, the inhomogeneity of the energy distribution, induced by substructural events, generates energy gradients that ‘drive’ the walk of substructures from place to place. Viscosity is *not crucial* in describing the migration mechanism although viscous effects may have a prominent role in driving substructures, and vice versa; phenomena of migration may be cast in hydrodynamic equations at macroscopic level as ‘apparent’ viscosity. When present, in fact, viscosity contributes additionally to the migration of substructures. A paradigmatic example is the case of polymeric fluids where the friction between the polymeric macromolecules and the ground liquid play a prominent role in the migration of the macromolecules themselves.

In the argument we propose below, a key role is played by a mechanical dissipation inequality. Its use is justified by the following circumstance: a *configurational entropy* can be related to morphological changes in families of substructures and, when substructures migrate, such changes tend to increase it.

If μ denotes the chemical potential, we may write the configurational entropy flux \mathbf{h} related to substructural migration as $h^i = -\mu A^{ij}(\text{grad } \mu)_j$. The second-order tensor \mathbf{A} (of components A^{ij}) denotes mobility of material substructures. We disregard here heat flux (although it could be accounted for easily).

The main technical result here is the derivation of an evolution equation for the time rate of the local *numerosity*¹ of substructures involving substructural interactions.

¹ By the term *numerosity* we indicate the ‘number’ of substructures per unit volume, by presuming that the volume chosen as representative unitary cell can be significantly defined in each special case. For example, in liquid crystals, the numerosity is the density of stick molecules with end-to-tail symmetry in a unit volume of the fluid. In other words, the unit volume is the representative volume element (the material element) the characteristic geometric and constitutive features of which we attribute to a generic point.

We proceed without considering any specific substructure. We assign to each material element a *coarse grained morphological descriptor* ν of its substructure. To develop calculations we do not need to specify the nature of ν . We require only that it be an element of a finite-dimensional paracompact manifold \mathcal{M} without boundary. In this way we follow the general format of multifield theories for complex materials [9, 12, 13]. In fact, the mechanics associated with maps between manifolds constitute a unifying framework for models of condensed matter physics, at least in the hydrodynamic range.

The results summarized below are on one hand a unifying framework for describing migration of substructures in the classes of complex fluids we know and, on the other hand, a tool to analyse possible exotic situations in potentially new complex fluids that industrial requirements may drive to produce.

In the case of two-phase fluids, ν reduces to a scalar quantity (coincident with the mass density of one phase) and the associated energy is double well with the addition of a quadratic part in $\text{grad } \nu$: the evolution equation we derive here reduces to the Cahn–Hilliard one or the generalization of it derived in [14]. Equations describing transport of polymer chains (ν becomes a second-order symmetric tensor) can also be recovered as special cases.

The issue discussed here is rather subtle because the program to analyse migration of substructures forces us to change a basic point of the abstract format of multifield theories describing complex bodies at a continuum level. In fact, in multifield theories each material element is considered as a *system* (in a certain sense a sort of minute machinery) but it is not foreseen that parts of it migrate from element to element (see [9, 13]). In contrast, here the material element is intended as a *container* of at least one family of substructures; then the morphological descriptor has (perhaps remotely) a statistical nature. In the presence of migration, an *evolution equation* for the numerosity of a given family is then necessary besides the balances of standard and substructural interactions. By indicating with $n = \tilde{n}(\nu)$ the numerosity of substructures of the type ν at a given point and assuming for the free energy ψ of the fluid a constitutive structure of the type $\psi = \tilde{\psi}(\iota, \nu, \text{grad } \nu)$, with ι being the specific volume, in the absence of substructural kinetic energy and external fields acting directly on the substructure, such an evolution equation reads

$$\dot{n} = -\text{div} \left(\mathbf{A} \text{grad} \left(\frac{1}{\|D_\nu n\|_{T_\nu^* \mathcal{M}}^2} \langle (\text{div}(\partial_{\text{grad } \nu} \psi) - \partial_\nu \psi), D_\nu n \rangle_{T_\nu^* \mathcal{M}} \right) \right), \quad (1)$$

where \mathbf{A} is the mobility as above, $(\text{div}(\partial_{\text{grad } \nu} \psi) - \partial_\nu \psi) \in T_\nu^* \mathcal{M}$ and $\langle \cdot, \cdot \rangle_{T_\nu^* \mathcal{M}}$ is a scalar product over $T_\nu^* \mathcal{M}$ with $\|\cdot\|_{T_\nu^* \mathcal{M}}$ being the associated norm. Generalizations of this equation are discussed below. They include external fields acting directly on the substructure (as, e.g., electric fields on polarizable fluids), possible inertia effects pertaining to the substructure itself and effects of bulk and substructural viscosity.

In summary, the characteristic features of the approach presented here are as follows.

- (i) We use general descriptors of the morphology of substructures to render the result independent of any particular geometric feature that may be prominent in special cases.
- (ii) Since such descriptors are elements of an abstract manifold, in general, we cannot postulate *a priori* an integral balance of substructural interactions as can be done in the scalar case (see [14]) or when the manifold coincides with a linear space (see discussions in [16]).
- (iii) We assume the validity of an equation of continuity for the numerosity of a population of substructures pertaining to each material element and relate the flux of substructures to the configurational entropy flux (which is generated, to a wide extent, by the *loss of information about substructural states* due to the migration of substructures).

The analyses below show how substructural interactions influence the time rate of the numerosity of substructures².

2. Morphological descriptors in the kinematics of complex flows

The fluid occupies a regular³ region \mathcal{B} of the three-dimensional Euclidean point space \mathcal{E}^3 . A spatial (Riemannian) metric \mathbf{g} is pertinent to \mathcal{B} and depends smoothly on places so that we have a field $\mathcal{B} \ni \mathbf{x} \xrightarrow{\mathbf{g}} \mathbf{g} = \tilde{\mathbf{g}}(\mathbf{x}) \in \text{Sym}^+(T_{\mathbf{x}}\mathcal{B}, T_{\mathbf{x}}^*\mathcal{B})$. The determinant of \mathbf{g} is indicated by ι and represents the specific volume of the fluid. As usual in continuum mechanics, each material element is ‘collapsed’ in a point $\mathbf{x} \in \mathcal{B}$. However, the assignment of the sole place to each material element (as usual in the standard hydrodynamics picture of simple flows) is not sufficient to get information about the substructural morphology of complex fluids. We furnish such information at a coarse grained level by means of a *descriptor* ν of the morphology of (say) the characteristic macromolecule or the population of macromolecules at \mathbf{x} . We do not specify the nature of ν to assure generality to our result. Examples of concrete physical cases are presented later.

To develop subsequent calculations, we require only that ν be an element of a manifold \mathcal{M} that we assume to be finite dimensional, paracompact and without boundary. We then have a sufficiently smooth map $\tilde{\nu}$, namely

$$\mathcal{B} \ni \mathbf{x} \xrightarrow{\tilde{\nu}} \nu = \tilde{\nu}(\mathbf{x}) \in \mathcal{M}, \quad (2)$$

that assigns to each \mathbf{x} the pertinent morphological descriptor ν of the geometrical features of the substructure *inside* the material element at \mathbf{x} .

For any *motion* developing along a time interval $[0, \bar{t}]$ where (2) changes as $\mathcal{B} \times [0, \bar{t}] \ni (\mathbf{x}, t) \xrightarrow{\tilde{\nu}} \nu = \tilde{\nu}(\mathbf{x}, t) \in \mathcal{M}$, we write

$$\mathcal{B} \times [0, \bar{t}] \ni (\mathbf{x}, t) \xrightarrow{\tilde{\mathbf{v}}} \mathbf{v} = \tilde{\mathbf{v}}(\mathbf{x}, t) \in T_{\mathbf{x}}\mathcal{B} \quad (3)$$

for the standard velocity field and

$$\mathcal{B} \times [0, \bar{t}] \ni (\mathbf{x}, t) \xrightarrow{\tilde{\nu}} \nu = \tilde{\nu}(\mathbf{x}, t) \in T_{\nu}\mathcal{M} \quad (4)$$

for the rate field of the morphological descriptor ν .

When we want to account for migration of substructures, we need to add another information: the *numerosity* n of substructures with a certain morphology ν *within* each material element. We then have a sufficiently smooth map \tilde{n} such that

$$\mathcal{B} \times [0, \bar{t}] \ni (\mathbf{x}, t) \xrightarrow{\tilde{n}} n = \tilde{n}(\nu) = \tilde{n}(\tilde{\nu}(\mathbf{x}, t)) \in \mathbb{R}^+. \quad (5)$$

² *Notations.* Some standard notations are summarized here. Let \mathbf{A} and \mathbf{B} be tensors of the type (p, q) of components, e.g. $A_{j_1 \dots j_q}^{i_1 \dots i_p}$ and $B_{j_1 \dots j_q}^{i_1 \dots i_p}$. We denote with $\mathbf{A} \cdot \mathbf{B}$ the standard scalar product given by $A_{j_1 \dots j_q}^{i_1 \dots i_p} B_{j_1 \dots j_q}^{i_1 \dots i_p}$. In particular, if \mathbf{A} and \mathbf{B} are second-order tensors, we denote with \mathbf{AB} the product which contracts only one index and bears a second-order tensor; for example, we have $(\mathbf{AB})_{ij} = A_{ik} B_j^k$. If \mathbf{A} is a tensor of the type (p, q) , with $p, q > 0$, and \mathbf{B} is another tensor of the type (r, s) , with $r, s > 0$ and $r < p, s < q$, or $(r = p, s < q)$ or $(r < p, s = q)$, we indicate with \mathbf{AB} (with some slight abuse of notation with respect to the product between second-order tensors) the product which contracts all the indices of \mathbf{B} ; in particular, if $p = 0$ or $q = 0$ we consider valid the notation when $r = 0$ and $s = 0$ respectively. Given two vectors \mathbf{a} and \mathbf{b} , $\mathbf{a} \otimes \mathbf{b}$ denotes their tensor product. In particular, if \mathbf{A} and \mathbf{B} are second-order tensors we have $\mathbf{AB} \cdot (\mathbf{a} \otimes \mathbf{b}) = \mathbf{A}^T \mathbf{a} \cdot \mathbf{Bb}$. For any region \mathfrak{b} of the space, $\partial \mathfrak{b}$ represents its boundary. For a couple of spaces A and B , $\text{Hom}(A, B)$ is the space of linear transformations from A to B . Latin indices i, j, k, \dots will indicate coordinate over a regular region \mathcal{B} of the three-dimensional Euclidean point space \mathcal{E}^3 while Greek indices α, \dots will denote coordinates in an appropriate atlas of an abstract manifold \mathcal{M} . Moreover, $T_{\nu}\mathcal{M}$ is the tangent space to \mathcal{M} at $\nu \in \mathcal{M}$ while $T_{\nu}^*\mathcal{M}$ is the relevant cotangent space at ν .

³ Here regularity is intended in the sense of D-regions [17].

Here, the point of view is as follows. *Within* each material element we imagine at least one family of substructures. The order parameter describes the morphology of each member of a given family and $n = \tilde{n}(\nu)$ indicates how many individuals of the type ν are present. Actually, one would be pushed to think of the morphological descriptor ν as an *averaged* value over a population of substructures. This point of view is natural when \mathcal{M} coincides with or is embedded (isometrically) in a linear space. In contrast, by considering \mathcal{M} as an abstract manifold, the average of ν over a population of substructures could not make sense (see remark 4). A way to avoid such a difficulty is the one followed here where we consider separately each morphological descriptor ν and the numerosity of substructures within each material element.

3. Standard and substructural interactions

Substructures may interact with each other so that relevant interactions should be accounted for, represented appropriately and balanced. To focus ideas about substructural interactions, the reader may think of dense or semi-dense polymer solutions when polymeric chains meet and possibly ‘join’.

Roughly speaking, for general viscous complex flows, balance equations of standard and substructural interactions result from generalizations of Navier–Stokes and Ginzburg–Landau equations; they are, in fact, spatial representations of Cauchy and Capriz balances respectively. There are various manners to derive and justify such balances of macroscopic and substructural interactions. For the purpose of our developments, it is helpful to follow a way in which the issues of representation of interactions and their balance are separated from those arising out from the need to justify constitutive structures⁴. Such a point of view assures widest generality to the interpretation of the results about migration. In fact, the abstract classification of interactions and their balance is pertinent to a set of ‘classes’ of bodies, while the specification of the functional dependence of such interactions on state variables implies directly the selection of a specific class of bodies.

Representation of interactions and their constitutive structures are mixed in variational approaches where Lagrangian or Hamiltonian densities are involved. To allow comparisons and to clarify the point of view followed here, we recall briefly one of the possible variational approaches to the mechanics of complex flows. For the sake of simplicity we focus attention here on the simple case of *perfect compressible complex fluids* where in addition to the standard law of conservation of mass, namely

$$\partial_t \rho + \operatorname{div}(\rho \mathbf{v}) = 0 \quad (6)$$

with ρ being the mass density, a variational principle of the type

$$\delta \int_{B \times [0, \bar{t}]} \mathcal{L} d^3 \mathbf{x} \wedge dt = \delta \int_{B \times [0, \bar{t}]} \tilde{\mathcal{L}}(\mathbf{x}, \mathbf{v}, t, \nu, v, \operatorname{grad} \nu) d^3 \mathbf{x} \wedge dt = 0 \quad (7)$$

is involved. In (7), $\tilde{\mathcal{L}}(\cdot)$ is a sufficiently smooth function such that

$$\mathcal{L} = \frac{1}{2} \rho \|\mathbf{v}\|^2 + \chi(\nu, v) - e(t, \nu, \operatorname{grad} \nu) - U(\mathbf{x}, \nu). \quad (8)$$

In (8), $U(\cdot)$ is the potential of external interactions: it is the sum $U_1(\mathbf{x}) + U_2(\nu)$ of the standard gravitational potential $U_1(\mathbf{x})$ and the potential of external direct actions on the substructure $U_2(\nu)$ (for example, in the case of polarizable fluids $U_2(\nu)$ accounts for the action of external electric fields). Moreover, $e(\cdot)$ is the internal potential of matter fields while, when kinetic energy $k(\nu, v)$ can be attributed to the substructure, $\chi(\cdot, \cdot)$ is the kinetic co-energy,

⁴ Such an approach is classical in continuum mechanics (see, for instance, the treatises [9, 18, 19]).

i.e. a C^1 scalar function with such a Legendre transform $\sup_{v \in T_\nu \mathcal{M}} (\partial_v \chi(\nu, v) \cdot v - \chi(\nu, v))$ with respect to v that the ‘sup’ is attained at a unique point in the domain of $\chi(\nu, \cdot)$ in $T_\nu \mathcal{M}$ at each ν and coincides with the substructural kinetic energy, namely $k(\nu, v) = \partial_v \chi(\nu, v) \cdot v - \chi(\nu, v)$. The product $\partial_v \chi(\nu, v) \cdot v$ is associated with the natural pairing between $T_\nu^* \mathcal{M}$ and $T_\nu \mathcal{M}$.

As regards the variations involved, we consider first a one-parameter family of smooth automorphisms $s \mapsto \mathbf{f}_s \in \text{Aut}(\mathcal{B} \times [0, \bar{t}])$ which leaves invariant the time scale $[0, \bar{t}]$ and is also smooth with respect to the parameter s . We indicate by $\mathbf{u} = \tilde{\mathbf{u}}(\mathbf{x}, t)$ the derivative $\frac{d}{ds} \mathbf{f}_s|_{s=0}(\mathbf{x}, t)$ and assume that

$$\tilde{\mathbf{u}}(\mathbf{x}, t)|_{\partial \mathcal{B}} = 0, \quad \forall t \in [0, \bar{t}], \quad (9)$$

$$\tilde{\mathbf{u}}(\mathbf{x}, 0) = \tilde{\mathbf{u}}(\mathbf{x}, \bar{t}) = 0, \quad \forall \mathbf{x} \in \mathcal{B}. \quad (10)$$

We then select $\delta \mathbf{x} = \mathbf{u}$, $\delta v = \dot{u}$ (where the dot means total time derivative) and also

$$\delta t = t \operatorname{div} \mathbf{u}. \quad (11)$$

For the variation of the morphological descriptor we choose a smooth field

$$\mathcal{B} \times [0, \bar{t}] \ni (\mathbf{x}, t) \xrightarrow{\tilde{\mathbf{w}}} \mathbf{w} = \tilde{\mathbf{w}}(\mathbf{x}, t) \in T_\nu \mathcal{M} \quad (12)$$

such that

$$\tilde{\mathbf{w}}(\mathbf{x}, t)|_{\partial \mathcal{B}} = 0, \quad \forall t \in [0, \bar{t}], \quad (13)$$

$$\tilde{\mathbf{w}}(\mathbf{x}, 0) = \tilde{\mathbf{w}}(\mathbf{x}, \bar{t}) = 0, \quad \forall \mathbf{x} \in \mathcal{B}. \quad (14)$$

Then, we select $\delta \nu = \mathbf{w}$ and

$$\delta \operatorname{grad} \nu = \operatorname{grad} \mathbf{w} + (\operatorname{grad} \nu) \operatorname{grad} \mathbf{u}, \quad (15)$$

or, more clearly in components,

$$(\delta \operatorname{grad} \nu)_i^\alpha = (\operatorname{grad} \mathbf{w})_i^\alpha + (\operatorname{grad} \nu)_j^\alpha (\operatorname{grad} \mathbf{u})_i^j. \quad (16)$$

With these premises, appropriate Euler–Lagrange equations for the variational principle (7) are then given by

$$\mathbf{b} + \operatorname{div} \mathbf{T} = \rho \dot{\mathbf{v}}, \quad (17)$$

where $\dot{\mathbf{v}} = \partial_t \mathbf{v} + (\mathbf{v} \cdot \operatorname{grad}) \mathbf{v}$, and

$$\beta - \mathbf{z} + \operatorname{div} \mathcal{S} = \frac{d}{dt} \partial_v \chi(\nu, v) - \partial_\nu \chi(\nu, v). \quad (18)$$

Equations (17) and (18) are the balances of standard and substructural interactions respectively. Commonly, I call (18) *Capriz balance* (see [12]).

Notations used in (17) and (18) are

$$b_i = (\partial_{\mathbf{x}} U(\mathbf{x}, \nu))_i, \quad (19a)$$

$$T_i^j = (t \partial_t e) \delta_i^j - (\operatorname{grad} \nu)_i^{*\alpha} (\partial_{\operatorname{grad} \nu} e)_\alpha^j, \quad (19b)$$

with δ_i^j being the components of \mathbf{I} , the unit second-order tensor, $(\operatorname{grad} \nu)^* \in \operatorname{Hom}(T_\nu^* \mathcal{M}, T_{\mathbf{x}}^* \mathcal{B})$ the adjoint of $\operatorname{grad} \nu$ and

$$\beta_\alpha = (\partial_\nu U(\mathbf{x}, \nu))_\alpha, \quad (20a)$$

$$z_\alpha = (\partial_\nu e)_\alpha, \quad (20b)$$

$$\mathcal{S}_\alpha^j = (\partial_{\operatorname{grad} \nu} e)_\alpha^j. \quad (20c)$$

Remark 1. The term $(\text{grad } \nu)^* \partial_{\text{grad } \nu} e$ in (19b) rules the possible transfer of energy between macroscopic and substructural scales, a transfer that may induce topological transitions in the structure of flows. To recognize this kind of effect, let us indicate with ω the vorticity, namely $\omega = \text{curl } \mathbf{v}$, and evaluate the curl of (17) by taking into account (19b). We get (see also [1])

$$\frac{d\omega}{dt} = (\omega \cdot \text{grad})\mathbf{v} + \text{grad } \iota \times \text{div } \mathbf{T} - \iota \text{curl}(\text{div } \mathbf{T}^E), \tag{21}$$

where we have used the notation $\mathbf{T}^E = (\text{grad } \nu)^* \partial_{\text{grad } \nu} e$. In the incompressible limit, (21) reduces to

$$\frac{d\omega}{dt} = (\omega \cdot \text{grad})\mathbf{v} - \iota \text{curl}(\text{div } \mathbf{T}^E). \tag{22}$$

The term $\text{curl}(\text{div } \mathbf{T}^E)$ measures the direct influence of material substructures on the alteration of vortex structures. For *two-dimensional flows* of incompressible perfect complex fluids, in fact, the equation for the transport of vorticity becomes

$$\frac{d\omega}{dt} = -\iota \text{curl}(\text{div } \mathbf{T}^E) \tag{23}$$

so that, in contrast to simple incompressible perfect fluids, ω is in general *not* conserved unless (i) there exists a scalar field $\mathcal{B} \ni \mathbf{x} \mapsto \pi(\mathbf{x})$ such that $\text{grad } \pi = \text{div } \mathbf{T}^E$ or (ii) there exists a second-order tensor-valued field $\mathcal{B} \ni \mathbf{x} \mapsto \mathbf{A}(\mathbf{x}) \in \mathbb{R}^3 \otimes \mathbb{R}^3$ such that $\text{curl}(\mathbf{T}^E)^T = (\text{curl } \mathbf{A})^T$. This situation is a typical circumstance of topological transition in vortex structures generated by the influence of material substructures. Of course the possibility of these topological transitions in complex fluids is independent of the geometrical shape and the constitutive nature of specific substructures. The independence is pointed out by the abstract way in which one obtains the result.

3.1. The general case

Let us forget perfect fluids and follow a procedure that allows us to obtain balance equations able to account for viscous effects.

We call *part* any subset \mathfrak{b} of \mathcal{B} which has the same regularity properties of \mathcal{B} itself. We indicate by $\mathfrak{P}(\mathcal{B})$ the set of parts of \mathcal{B} and by $\text{Vel}_c(\mathcal{B})$ the set of pairs of sufficiently smooth fields of the type (3) and (4), namely $\tilde{\mathbf{v}}$ and \tilde{v} , with compact support in \mathcal{B} .

For us the *power* is a map $P : \mathfrak{P}(\mathcal{B}) \times \text{Vel}_c(\mathcal{B}) \rightarrow \mathbb{R}$ such that $P(\cdot, \mathbf{v}, v)$ is *additive* and both $P(\mathfrak{b}, \cdot, v)$ and $P(\mathfrak{b}, \mathbf{v}, \cdot)$ are *linear*. For any part \mathfrak{b} we are interested in representing the power of *external* interactions over \mathfrak{b} , a power that we indicate by $\mathcal{P}_{\mathfrak{b}}^{\text{ext}}(\mathbf{v}, v)$ for any fixed \mathfrak{b} (considered as a control volume). Such interactions are of *bulk* and *contact* nature, the latter exerted across the boundary $\partial \mathfrak{b}$ of \mathfrak{b} ; the outward unit normal to such a boundary is indicated by \mathbf{n} . Under the suggestions of the treatment leading to (17)–(20), we claim the existence of vector and tensor fields (we omit the dependence on time for notational convenience)

$$\mathcal{B} \ni \mathbf{x} \mapsto \tilde{\mathbf{b}} = \tilde{\mathbf{b}}(\mathbf{x}) \in T_{\mathbf{x}}^* \mathcal{B} \cong \mathbb{R}^3, \tag{24}$$

$$\mathcal{B} \ni \mathbf{x} \mapsto \tilde{\mathbf{T}} = \tilde{\mathbf{T}}(\mathbf{x}) \in \text{Hom}(T_{\mathbf{x}}^* \mathcal{B}, T_{\mathbf{x}}^* \mathcal{B}) \cong \mathbb{R}^3 \otimes \mathbb{R}^3, \tag{25}$$

$$\mathcal{B} \ni \mathbf{x} \mapsto \tilde{\beta} = \tilde{\beta}(\mathbf{x}) \in T_{\nu}^* \mathcal{M}, \tag{26}$$

$$\mathcal{B} \ni \mathbf{x} \mapsto \tilde{\mathcal{S}} = \tilde{\mathcal{S}}(\mathbf{x}) \in \text{Hom}(T_{\mathbf{x}}^* \mathcal{B}, T_{\nu}^* \mathcal{M}), \tag{27}$$

such that

$$P(\mathfrak{b}, \mathbf{v}, v) = \mathcal{P}_{\mathfrak{b}}^{\text{ext}}(\mathbf{v}, v) = \int_{\mathfrak{b}} (\tilde{\mathbf{b}} \cdot \mathbf{v} + \tilde{\beta} \cdot v) d^3 \mathbf{x} + \int_{\partial \mathfrak{b}} (\mathbf{T} \mathbf{n} \cdot \mathbf{v} + \mathcal{S} \mathbf{n} \cdot v) d\mathcal{H}^2, \tag{28}$$

where $d\mathcal{H}^2$ is the two-dimensional Hausdorff measure over ∂b . Substructural interactions are measured by means of volume ($\bar{\beta}$) and surface ($S\mathbf{n}$) densities as in the case of standard interactions. $\bar{\beta}$ may account for both possible substructural inertia effects and interactions due, for example, to electromagnetic fields acting on the substructure. As usual the standard bulk forces $\bar{\mathbf{b}}$ are assumed to be the sum of non-inertial and inertial parts. S is called *microstress*. Roughly speaking, $S\mathbf{n}$ is a ‘generalized traction’; the product $S\mathbf{n} \cdot \mathbf{v}$ measures the local power exchanged between two adjacent parts at \mathbf{x} through a surface of normal \mathbf{n} , as a consequence of the change of the substructure at the same point. \mathbf{T} is the standard Cauchy stress tensor⁵.

We now impose $SO(3)$ invariance for $\mathcal{P}_b^{\text{ext}}(\mathbf{v}, \nu)$ which corresponds to invariance with respect to changes in *classical* observers.

In the common usage of classical mechanics, an observer is a ‘representation’ of the ambient space and the time scale. Here, a more enlarged notion is needed. For us, an *observer* is a representation of all geometrical environments necessary to describe the morphology of a body and its motion (thus the time scale). When morphological descriptors are involved, as in the abstract format of multifield theories describing the mechanics of complex bodies, the notion of observer includes the representation of the manifold \mathcal{M} of substructural shapes (see also [16]). General changes in observers involve the action of the group of automorphisms on the ambient space (here the three-dimensional Euclidean point space \mathcal{E}^3) and the action of an arbitrary Lie group G over \mathcal{M} (see discussions in [24]). When we restrict our attention to the observers that we call *classical*, the time parametrized family of automorphisms acting on the ambient space is the one of isometries so that, as usual, if \mathbf{v}^* is the value of the velocity \mathbf{v} after such a change ruled by $SO(3)$, we get

$$\mathbf{v}^* = \mathbf{v} + \mathbf{c}(t) + \dot{\mathbf{q}}(t) \times (\mathbf{x} - \mathbf{x}_0), \quad (29)$$

where $\mathbf{c}(t)$ is the translational velocity, constant in space, \mathbf{x}_0 is a point chosen arbitrarily and $\dot{\mathbf{q}} \times \in \mathfrak{so}(3)$ at each t . Moreover, still for such changes in observers, we consider that the same copy of $SO(3)$ acts also over \mathcal{M} and we indicate with \mathbf{v}^* the rate \mathbf{v} measured after the change in observer, so that we get

$$\mathbf{v}^* = \mathbf{v} + \mathcal{A}\dot{\mathbf{q}}, \quad (30)$$

where, at each $\nu \in \mathcal{M}$, $\mathcal{A}(\nu) \in \text{Hom}(\mathbb{R}^3, T_\nu\mathcal{M})$ and is represented by a matrix with three columns and a number of lines equal to $\dim \mathcal{M}$; in particular, if $\nu_{\mathbf{q}}$ denotes the value of ν after the right action of $SO(3)$ over \mathcal{M} , we have $\mathcal{A} = \left. \frac{d\nu_{\mathbf{q}}}{d\mathbf{q}} \right|_{\mathbf{q}=\mathbf{0}}$ where \mathbf{q} is connected with $\mathbf{Q} \in SO(3)$ by the exponential map, so that $\mathbf{Q} = \exp(-\mathbf{e}\mathbf{q})$ with \mathbf{e} being Ricci’s permutation index.

⁵ The proof of the existence of \mathbf{T} (without resorting to constitutive issues and energy as in Lagrangian–Hamiltonian approach) is standard and can be obtained invoking directly balance of tensions over special parts of \mathcal{B} even in very weak conditions (see general results in [20]). Moreover, when substructures are not considered and $\text{Vel}_c(\mathcal{B})$ contains just standard velocity fields $\bar{\mathbf{v}}(\cdot)$, the addition of appropriate analytical conditions satisfied by the power (besides the additivity over parts and the linearity with respect to rates) allows one to get its representation in terms of \mathbf{T} by using techniques of geometric measure theory (see [21]). The proof of the existence of S (in the sense used for \mathbf{T}) is a rather subtle issue. In fact, the standard *direct* technique used for \mathbf{T} cannot be utilized, unless \mathcal{M} is embedded in a linear space. The field $\mathbf{x} \mapsto (S\mathbf{n})(\mathbf{x}) = S(\mathbf{x})\mathbf{n}(\mathbf{x})$ takes values on $T^*\mathcal{M} = \bigcup_{\nu \in \mathcal{M}} T_\nu^*\mathcal{M}$ which does not coincide with a linear space although each $T_\nu^*\mathcal{M}$ is a linear space. As a consequence, averages of $S\mathbf{n}$ over special polyhedral subregions (the ones necessary to get \mathbf{T}) do not make sense. A proof of the existence of S is available with the additional assumption that \mathcal{M} is embedded in a linear space [22]. However, even if we consider the isometric embedding of \mathcal{M} in a linear space (an embedding preferable from a physical point of view because it preserves the quadratic part of the substructural kinetic energy), the embedding is not unique and its choice becomes strict matter of modelling. A proof based on analytical restrictions on $P(\mathbf{b}, \mathbf{v}, \nu)$ and techniques of geometric measure theory is not yet available even if I am personally optimistic about its future availability. Perhaps techniques proposed by Segev (see, e.g., [23]) could constitute another way to solve the problem without resorting to embeddings.

As a basic *axiom* we require that $\mathcal{P}_b^{\text{ext}}$ be invariant under changes in observers ruled by the action of $SO(3)$, for any b , i.e.

$$\mathcal{P}_b^{\text{ext}}(\mathbf{v}^*, \mathbf{v}^*) = \mathcal{P}_b^{\text{ext}}(\mathbf{v}, \mathbf{v}), \tag{31}$$

for any choice of $\mathbf{c}(t)$, $\dot{\mathbf{q}}(t)$ and b .

By using (29) and (30), thanks to the arbitrariness of \mathbf{c} and $\dot{\mathbf{q}}$, we obtain the *standard integral balance of forces*

$$\int_b \bar{\mathbf{b}} d^3\mathbf{x} + \int_{\partial b} \mathbf{Tn} d\mathcal{H}^2 = 0, \tag{32}$$

and a *generalized integral balance of moments*

$$\int_b ((\mathbf{x} - \mathbf{x}_0) \times \bar{\mathbf{b}} + \mathcal{A}^* \bar{\beta}) d^3\mathbf{x} + \int_{\partial b} ((\mathbf{x} - \mathbf{x}_0) \times \mathbf{Tn} + \mathcal{A}^* \mathcal{S}\mathbf{n}) d\mathcal{H}^2 = 0, \tag{33}$$

with $\mathcal{A}^*(\nu) \in \text{Hom}(T_\nu^* \mathcal{M}, \mathbb{R}^3)$. From (32), the common pointwise balance of forces

$$\bar{\mathbf{b}} + \text{div } \mathbf{T} = \mathbf{0} \quad \text{in } \mathcal{B} \tag{34}$$

follows thanks to the arbitrariness of b , while, from (33), we get

$$\mathcal{A}^*(\bar{\beta} + \text{div } \mathcal{S}) = \mathbf{e}\mathbf{T} - (\text{grad } \mathcal{A}^*)\mathcal{S}. \tag{35}$$

with \mathbf{e} being Ricci's alternator. This last condition implies that the co-vector $\mathbf{e}\mathbf{T} - (\text{grad } \mathcal{A}^*)\mathcal{S}$ with components $e_{ijk} T^{kj} - (\text{grad } \mathcal{A}^*)_{ij}^\alpha \mathcal{S}_\alpha^j$ belongs to the range of the linear operator \mathcal{A}^* at each ν . Two pieces of information can be then obtained from (35): (i) there exists an element of the cotangent space of \mathcal{M} at ν , say \mathbf{z} , such that

$$\mathcal{A}^* \mathbf{z} = \mathbf{e}\mathbf{T} - (\text{grad } \mathcal{A}^*)\mathcal{S}, \tag{36}$$

and (ii) \mathbf{z} is just equal to the co-vector $\bar{\beta} + \text{div } \mathcal{S}$, namely⁶

$$\bar{\beta} - \mathbf{z} + \text{div } \mathcal{S} = \mathbf{0} \quad \text{in } \mathcal{B}. \tag{37}$$

As regards inertial components, they are included in the bulk interactions $\bar{\mathbf{b}}$ and $\bar{\beta}$ that coincide respectively with $\mathbf{b} + \mathbf{b}^{\text{in}}$ and $\beta + \beta^{\text{in}}$, where \mathbf{b} and β are non-inertial (objective) components, as in (17), (18), and \mathbf{b}^{in} and β^{in} their inertial counterparts. The identification of \mathbf{b}^{in} and β^{in} follows by imposing that their power is equal to the opposite of the rate of the kinetic energy for any part b chosen *fixed* in time, namely

$$\frac{d}{dt} \int_b \left(\frac{1}{2} \rho \|\mathbf{v}\|^2 + k(\nu, \mathbf{v}) \right) d^3\mathbf{x} + \int_b (\mathbf{b}^{\text{in}} \cdot \mathbf{v} + \beta^{\text{in}} \cdot \mathbf{v}) d^3\mathbf{x} = 0. \tag{38}$$

The time derivative in (38) and the identification of analogous terms imply $\mathbf{b}^{\text{in}} = -\rho \dot{\mathbf{v}}$ and the need of the existence of such a function $\chi(\nu, \mathbf{v})$ with the properties described in previous section that $\beta^{\text{in}} = -\frac{d}{dt} \partial_\nu \chi(\nu, \mathbf{v}) + \partial_\nu \chi(\nu, \mathbf{v})$. Substructural inertia is often negligible unless the substructure oscillates at very high frequencies.

Remark 2. By means of the integral balance (38), β^{in} is determined unless a powerless term. A case in which such a kind of term becomes important is the one of spin fluids

⁶ For the procedure used here to derive balance equations, the case of scalar-order parameters appears pathological because \mathcal{A} vanishes. Actually, one could make use of spherical second-order tensors as an intermediate step; by obtaining (37) first, one then may reduce straight away to the scalar case.

(or hyperfluids) in which ν is selected to be a vector ζ constrained to have unit length. Such a constraint implies that the inertia is just of rotational nature. By assuming equal to 1 possible constitutive constants, let us select $\beta^{\text{in}} = -\zeta \times \dot{\zeta}$ which is evidently powerless. In addition, if the fluid is incompressible and the free energy $\psi(\zeta, \text{grad } \zeta)$ is chosen to be of the form $\frac{1}{2} \|\text{grad } \zeta\|^2$, with unitary constitutive constants even in this case, the balance of substructural interactions becomes

$$\dot{\zeta} = -\zeta \times \Delta \zeta, \quad (39)$$

which coincides with the Landau–Lifshitz–Gilbert equation when only gyromagnetic effects are accounted for (see also [25]).

Remark 3. In the Hamiltonian setting, one may show that (34) and (37) satisfy not only $SO(3)$ invariance but also complete covariance associated with general changes in observers ruled by the action of the group of automorphisms and a generic Lie group over the ambient space and \mathcal{M} respectively. The covariance of (34) is a classical result (see [26]) while the covariance of (37) is shown in [24, 27]. Additionally, in [24] the covariance of the surface balances of actions due to the interaction between diffuse interfaces and sharp discontinuities endowed with surface energy is also obtained.

Remark 4. In the general setting sketched here, we *cannot* postulate *a priori* an integral version of (37) by assuming it as a *primitive* balance of substructural interactions, unless we presume—even tacitly—that \mathcal{M} is (isometrically) embedded in a linear space, select a special embedding and includes it in the model as a ‘constitutive’ element—in fact, since \mathcal{M} is finite dimensional, the embedding exists always but it is not unique. The basic reason has been underlined in footnote 4 but we recall it here adding details. Actually, if one considered naively the integral version of (37), one would have an integral over some arbitrary part \mathfrak{b} of the difference of $\tilde{\beta} - \mathbf{z}$ and an integral over the boundary $\partial \mathfrak{b}$ of $S\mathbf{n}$. However, the field $\mathbf{x} \mapsto \tilde{\beta}(\mathbf{x}) - \mathbf{z}(\mathbf{x})$ takes values on the cotangent bundle of \mathcal{M} , namely $T^*\mathcal{M} = \bigcup_{\nu \in \mathcal{M}} T_\nu^*\mathcal{M}$, which does not coincide with a linear space though each ‘component’ $T_\nu^*\mathcal{M}$ of it is a linear space. The same remark holds for $\mathbf{x} \mapsto (S\mathbf{n})(\mathbf{x})$ as underlined in footnote 4. Consequently, the possible integrals involving $\tilde{\beta} - \mathbf{z}$ and $S\mathbf{n}$ would not be defined. In fact, we know from elementary calculus that, although the *domain of integration* of integrals as indicated above could be even a manifold, the *integrand* must take values in a linear space in order for the integral to be defined. This is the reason that would push us to embed \mathcal{M} in a linear space if we would like to postulate *a priori* an integral balance of substructural interactions.

4. Migration of substructures

4.1. A continuity equation for the numerosity

When migration of substructures comes into play, local variations of numerosity of substructural individuals must be accounted for. Here we assume (i) to treat complex fluids isolated with respect to the exchange of mass with the external environment and (ii) that phenomena of coalescence or nucleation of substructures are absent. In other words, we consider substructural elements as distinct individuals. Under these assumptions, for any part \mathfrak{b} , the numerosity satisfies an integral balance of the type

$$\frac{d}{dt} \int_{\mathfrak{b}} n \, d^3\mathbf{x} + \int_{\partial \mathfrak{b}} \boldsymbol{\omega} \cdot \mathbf{n} \, d\mathcal{H}^2 = 0, \quad (40)$$

where ω is the flux vector of substructures across $\partial\mathfrak{b}$ and vanishes at the boundary $\partial\mathcal{B}$. If we choose \mathfrak{b} as a control volume fixed in time, its arbitrariness implies

$$\dot{n} + \operatorname{div} \omega = 0, \quad (41)$$

where⁷ $\dot{n}(\nu(\mathbf{x}, t)) = D_\nu n \cdot (\partial_t \nu + (\operatorname{grad} \nu) \mathbf{v})$, the product being associated with the natural pairing between $T_\nu \mathcal{M}$ and $T_\nu^* \mathcal{M}$.

In writing formally the local continuity equation for the numerosity, we assume implicitly a certain regularity for $\tilde{n}(\cdot)$. However, physical circumstances imposing irregularity to $\tilde{n}(\cdot)$ might require that (41) be considered in a distributional sense.

Remark 5. Two prominent situations may occur. (i) There are many families of substructures and ν is associated with elements of only one of them. (ii) There is just one family of substructures. In case (i) the migration can develop in a way in which molecules of the family associated with ν move and are substituted by molecules of other families so that mass is locally conserved and one should consider (6) separately from (41). In case (ii) we have a sort of two-component fluid (the ground liquid and the embedded (macro-)molecules) and (41) coincides with the conservation of mass of one component when multiplied by the (constant) mass $\bar{\rho}$ of the single macromolecule. In this way, the flux ω is strictly a mass flux $\bar{\rho}\bar{\omega}$.

4.2. The role of substructural interactions in the evolution of numerosity

For the sake of simplicity we restrict our treatment to isothermal processes and consider an isothermal version of the second law prescribing that for any part \mathfrak{b} chosen as above and for any choice of the rates involved

$$\frac{d}{dt} \int_{\mathfrak{b}} \psi \, d^3\mathbf{x} - \int_{\partial\mathfrak{b}} \mathbf{h} \cdot \mathbf{n} \, d\mathcal{H}^2 - \mathcal{P}_{\mathfrak{b}}^{\text{ext}}(\mathbf{v}, \mathbf{v}) \leq 0, \quad (42)$$

where ψ denotes the Helmholtz free energy and \mathbf{h} is the flux of entropy due to the ‘loss of information’ about substructural morphology induced by the migration of substructures. When one uses a coarse-grained description of substructures, one loses information about substructural shapes (see in the case of polymer configurations the results of Ferrari and Lebowitz [28]). Migration increases such a loss of information hence the associated entropy that we call here configurational just to recall the connection with local changes in substructural shapes (see also [28, 29]). We represent such an effect of increment of entropy due to a loss of information (in isothermal conditions) as due to the flux \mathbf{h} at a gross level and assume that \mathbf{h} is linked with the flux of numerosity by means of the chemical potential μ as in the standard case of mass transport, namely

$$\mathbf{h} = \mu \omega. \quad (43)$$

By selecting \mathfrak{b} fixed in time as a control volume and arbitrary, the time derivative in (42), Gauss theorem and (41) allows us to get from (42) a local dissipation inequality⁸:

$$\dot{\psi} + \mu \dot{n} - \omega \cdot \operatorname{grad} \mu - (\mathbf{T} \cdot \operatorname{grad} \mathbf{v} + \mathcal{S} \cdot \operatorname{grad} \mathbf{v} + \mathbf{z} \cdot \mathbf{v}) \leq 0. \quad (44)$$

At thermodynamical equilibrium we presume (tentatively) that Cauchy stress \mathbf{T} , microstress \mathcal{S} and self-force \mathbf{z} admit the constitutive structures

⁷ $D_\nu n$ indicates the derivative of n with respect to ν .

⁸ We recall that the validity of local balances of standard and substructural interactions implies

$$\mathcal{P}_{\mathfrak{b}}^{\text{ext}}(\mathbf{v}, \mathbf{v}) = \mathcal{P}_{\mathfrak{b}}^{\text{int}} \equiv \int_{\mathfrak{b}} (\mathbf{T} \cdot \operatorname{grad} \mathbf{v} + \mathcal{S} \cdot \operatorname{grad} \mathbf{v} + \mathbf{z} \cdot \mathbf{v}) \, d^3\mathbf{x},$$

where $\mathcal{P}_{\mathfrak{b}}^{\text{int}}$ is called internal power.

$$\mathbf{T} = \tilde{\mathbf{T}}(\iota, \nu, \text{grad } \nu, \mu, \text{grad } \mu), \quad (45)$$

$$\mathbf{z} = \tilde{\mathbf{z}}(\iota, \nu, \text{grad } \nu, \mu, \text{grad } \mu), \quad (46a)$$

$$S = \tilde{S}(\iota, \nu, \text{grad } \nu, \mu, \text{grad } \mu), \quad (46b)$$

and that also ψ and ω have the form

$$\psi = \tilde{\psi}(\iota, \nu, \text{grad } \nu, \mu, \text{grad } \mu), \quad \omega = \tilde{\omega}(\iota, \nu, \text{grad } \nu, \mu, \text{grad } \mu) \quad (47)$$

The time derivative in (44) implies

$$\begin{aligned} & (\iota \partial_t \psi \mathbf{I} - \mathbf{T} - (\text{grad } \nu)^* (\partial_{\text{grad } \nu} \psi)) \cdot \text{grad } \mathbf{v} + (\partial_\nu \psi - \mathbf{z} + \mu D_\nu n) \cdot \nu \\ & + \partial_\mu \psi \dot{\mu} + \partial_{\text{grad } \mu} \psi \cdot \overline{\text{grad } \mu} + (\partial_{\text{grad } \nu} \psi - S) \cdot \text{grad } \nu - \omega \cdot \text{grad } \mu \leq 0 \end{aligned} \quad (48)$$

where we have used

$$i = \iota \text{div } \mathbf{v} = \iota \mathbf{I} \cdot \text{grad } \mathbf{v}, \quad (49)$$

a relation coming from Euler formula (see (11)), and

$$\overline{\text{grad } \nu} = \text{grad } \nu + (\text{grad } \nu) \text{grad } \mathbf{v}. \quad (50)$$

Once a state $(\iota, \nu, \text{grad } \nu, \mu, \text{grad } \mu)$ has been selected, we may choose *arbitrarily* $\text{grad } \mathbf{v}$, ν , $\text{grad } \nu$, $\dot{\mu}$ and $\overline{\text{grad } \mu}$ so that we get

$$\partial_\mu \psi = 0, \quad \partial_{\text{grad } \mu} \psi = 0, \quad (51)$$

since (42) is assumed to hold for any choice of the velocity fields. Such a result prescribes that ψ *cannot* depend on the chemical potential and its gradient together with \mathbf{T} and S which must satisfy the restrictions

$$\mathbf{T} = \iota \partial_t \psi \mathbf{I} - (\text{grad } \nu)^* (\partial_{\text{grad } \nu} \psi), \quad S = \partial_{\text{grad } \nu} \psi. \quad (52)$$

Moreover, \mathbf{z} *cannot* depend on $\text{grad } \mu$ but *may* depend on μ and we get

$$\mathbf{z} - \mu D_\nu n = \partial_\nu \psi. \quad (53)$$

In addition we find that $\omega \cdot \text{grad } \mu \geq 0$, i.e. the flux of substructures goes along the gradient of chemical potential, so that ω must be of the form

$$\omega = \mathbf{A} \text{grad } \mu \quad (54)$$

($\omega^j = A^{ij} (\text{grad } \mu)_j$ in components), with \mathbf{A} the *mobility*, such a positive definite second-order tensor that $\mathbf{A} = \tilde{\mathbf{A}}(\iota, \nu, \text{grad } \nu, \mu)$. Circumstances may suggest that \mathbf{A} be coincident with a spherical tensor $a \mathbf{I}$, with a being an appropriate constant.

Although the formal expression of ω in (54) is coincident with the one used in standard mass transport, we have here a basic difference because we obtain that in general the mobility is influenced by the shape of the substructure and its spatial inhomogeneity due for example to the branching of substructures.

So far we have used the mechanical dissipation inequality as a criterion of selection of physically admissible constitutive equations, by following a classical point of view [30]. Of course, another possible use of the second law is as a criterion of stability, but it is not needed here.

From (53) we get

$$\mu = \frac{1}{\|D_\nu n\|_{T_\nu^* \mathcal{M}}^2} \langle (\mathbf{z} - \partial_\nu \psi), D_\nu n \rangle_{T_\nu^* \mathcal{M}}, \quad (55)$$

where $\langle \cdot, \cdot \rangle_{T_\nu^* \mathcal{M}}$ is a scalar product defined in each $T_\nu^* \mathcal{M}$ and $\|\cdot\|_{T_\nu^* \mathcal{M}}$ being the associated norm. By inserting (37), (55) and (54) in (41), we obtain the evolution equation for the numerosity:

$$\dot{n} = -\operatorname{div} \left(\mathbf{A} \operatorname{grad} \left(\frac{1}{\|D_\nu n\|_{T_\nu^* \mathcal{M}}^2} \langle (\bar{\beta} + \operatorname{div} \mathcal{S} - \partial_\nu \psi), D_\nu n \rangle_{T_\nu^* \mathcal{M}} \right) \right), \quad (56)$$

which is the natural extension of (1) when external fields and possible substructural inertia effects are accounted for.

The structure of equation (56) suggests the physical interpretation anticipated in the introduction: the basic mechanism ruling migration of substructures is (or, more prudently, seems to be) the competition of substructural interactions from place to place.

In particular, the gradient of the projection of substructural interactions along the derivative of the numerosity with respect to ν , namely $D_\nu n$ is an essential ingredient. We may regard the map $\mathcal{M} \ni \nu \xrightarrow{\tilde{n}} n = \tilde{n}(\nu) \in \mathbb{R}^+$ through the level sets it induces over \mathcal{M} , so that $D_\nu n$ can be considered a normal to the boundary of these sets and $\langle (\bar{\beta} + \operatorname{div} \mathcal{S} - \rho \partial_\nu \psi), D_\nu n \rangle_{T_\nu^* \mathcal{M}}$ is then the associated flux of substructural actions across the same boundary, conjugated with the migration of substructures.

Equation (56) renders more perspicuous and completes the preliminary results in [31].

Remark 6. In the absence of migration and for purely reversible processes, when ψ coincides with the potential e used in (8), the constitutive restrictions (52) and (53) coincide with (19b), (20b) and (20c). Moreover, in this case Capriz balance reduces to Ginzburg–Landau equation for appropriate choices of the explicit structures of the energy (see [16]).

4.3. The simplest substructural viscosity

Far from thermodynamical equilibrium, rates come into play in constitutive equations and account for internal friction. More generally, they measure the removal from thermodynamical equilibrium. However, the second law (even in its mechanical form (42)) excludes their presence in the list of entries of ψ . We would have, in fact, terms multiplied by accelerations without any counterparts in terms of measures of interactions, so that the assumed validity of (42) for any choice of rates would imply that these terms vanish. For example, if one selected $\psi = \tilde{\psi}(\iota, \nu, \operatorname{grad} \nu, \nu)$, then in (48) one would add only a term of the type $\partial_\nu \psi \cdot \dot{\nu}$. However, the arbitrariness of the choice of $\dot{\nu}$ would imply $\partial_\nu \psi = 0$, i.e. ψ cannot depend on ν . By taking into account this type of restriction, a reasonable way to proceed is to imagine that the measures of interactions can be divided *additively* into thermodynamic *equilibrium* (*eq*) and *non-equilibrium* (*ne*) parts, the former determined by $\psi = \tilde{\psi}(\iota, \nu, \operatorname{grad} \nu)$ and the latter strictly dissipative.

The simplest case occurs when only substructural viscosity is present within each material element so that in (46) only (46b) changes as

$$\mathbf{z} = \mathbf{z}^{\text{eq}} + \mathbf{z}^{\text{ne}} = \tilde{\mathbf{z}}^{\text{eq}}(\iota, \nu, \operatorname{grad} \nu, \mu) + \tilde{\mathbf{z}}^{\text{ne}}(\iota, \nu, \operatorname{grad} \nu, \mu, \nu), \quad (57)$$

and \mathbf{z}^{eq} satisfies (53), while \mathbf{z}^{ne} is strictly dissipative in the sense that $\mathbf{z}^{\text{ne}} \cdot \nu \geq 0$ for any choice of ν . Such an assumption implies (as a special case)

$$\mathbf{z}^{\text{ne}} = \tilde{l}_z(\iota, \nu, \operatorname{grad} \nu, \mu) \nu^{\flat} := l_z \nu^{\flat}, \quad (58)$$

with $\tilde{l}_z(\cdot)$ being a positive scalar function⁹ and ν^{\flat} being the 1-form associated with ν .

Consequently, (56) becomes

$$\dot{n} = -\operatorname{div} \left(\mathbf{A} \operatorname{grad} \left(\frac{1}{\|D_\nu n\|_{T_\nu^* \mathcal{M}}^2} \langle (\bar{\beta} + \operatorname{div} \mathcal{S} - \partial_\nu \psi - l_z v^b), D_\nu n \rangle_{T_\nu^* \mathcal{M}} \right) \right). \quad (59)$$

4.4. Macroscopic and gradient substructural viscosity

Besides the simplest case of substructural viscosity described above, more complicated situations arise when macroscopic and substructural viscosity are present and cooperate with each other to drive material substructures. In this case, thermodynamic non-equilibrium parts of \mathbf{T} and \mathcal{S} occur so that we have $\mathbf{T} = \mathbf{T}^{\text{eq}} + \mathbf{T}^{\text{ne}}$ and $\mathcal{S} = \mathcal{S}^{\text{eq}} + \mathcal{S}^{\text{ne}}$, with the equilibrium parts depending also on $\operatorname{grad} \mathbf{v}$, v , $\operatorname{grad} v$. A procedure analogous to the one used above would get more complicated expressions involving $\operatorname{grad} \mathbf{v}$ and $\operatorname{grad} v$. However, it is important to note that, although standard viscosity and gradient substructural viscosity may enhance or obstruct the migration of substructures, the basic mechanism producing such a kind of transport is the one illustrated by (56), and may accrue even in perfect complex fluids. Additional viscosity alters just the landscape, but the *source* mechanism is the one induced by substructural interactions. This is the key physical significance of the developments presented here.

Remark 7. In the absence of substructural viscosity but in the presence of macroscopic viscosity, the balance of standard forces (34) reduces to a generalized form of Navier–Stokes equations.

5. Special cases of physical interest

The unified description of migration of substructures proposed here can be applied to a wide class of cases with physical concreteness. Some of them are summarized in the present section. In addition, the proposed framework can be considered as a tool to describe even some possible exotic physical circumstances that are beyond the cases listed here.

5.1. Two-phase fluids: Cahn–Hilliard equation

In the case of two-phase fluids in which phase transformations are allowed, ν can be selected as the mass fraction ν of one of the two components, so that (41) coincides with the continuity equation for the mass density of arbitrarily one of the two components. In other words, $\tilde{n}(\nu) = \tilde{n}(\nu) = \nu$. We restrict further our attention to the circumstance in which the following assumptions apply.

- (i) The fluid is incompressible (possibly at rest).

⁹ Actually, when one inserts in (48) the decomposition $\mathbf{z}^{\text{eq}} + \mathbf{z}^{\text{ne}}$ by presuming that only \mathbf{z}^{eq} can be associated with the free energy, after the reasoning leading to (52) and (53), the local form of the mechanical dissipation inequality (48) reduces to

$$\mathbf{z}^{\text{ne}} \cdot v + \omega \cdot \operatorname{grad} \mu \geq 0.$$

Thanks to the arbitrariness of v and $\operatorname{grad} \mu$, an appropriate solution of the previous inequality would be

$$\mathbf{z}^{\text{ne}} = \mathfrak{A}_z v + \mathfrak{A}'_z \operatorname{grad} \mu, \quad \omega = A \operatorname{grad} \mu + \mathfrak{A}' v,$$

with $\mathfrak{A}_z \in \operatorname{Hom}(T_\nu \mathcal{M}, T_\nu^* \mathcal{M})$, $\mathfrak{A}'_z \in \operatorname{Hom}(\mathbb{R}^3, T_\nu^* \mathcal{M})$, $\mathfrak{A} \in \operatorname{Hom}(T_\nu \mathcal{M}, \mathbb{R}^3)$, and, as in (54), $\mathbf{A} \in \mathbb{R}^3 \otimes \mathbb{R}^3$. One obtains the case in (58) when \mathfrak{A}'_z and \mathfrak{A}' vanish while \mathfrak{A}_z is equal to $l_z \mathbf{g}_\mathcal{M}$, with $\mathbf{g}_\mathcal{M}$ the metric over \mathcal{M} so that $v^b = \mathbf{g}_\mathcal{M} v$. Note that the previous inequality does not imply that each addendum be semi-definite positive—only the sum must be greater than or equal to zero, as a consequence of the second law. In this sense, if we consider \mathbf{z}^{ne} strictly dissipative, the inequality $\mathbf{z}^{\text{ne}} \cdot v \geq 0$ is additional to the second law and is a sort of anholonomic constraint.

- (ii) $\bar{\beta} = 0$, i.e. direct bulk actions over the phases (different from the gravitational field) are absent.
- (iii) $\psi = \tilde{\psi}(v, \text{grad } v) = g(v) + \frac{1}{2}b|\text{grad } v|^2$, with $g(\cdot)$ being a two-well energy accounting for spinodal decomposition and b a constant.
- (iv) \mathbf{A} reduces to a constant $a > 0$.

In this case, the evolution equation (56) reduces to the Cahn–Hilliard equation

$$\dot{v} = a\Delta[g'(v) - b\Delta v], \quad (60)$$

with $g'(v) = \frac{dg}{dv}(v)$.

The treatment discussed here reduces in this case to the one presented by Gurtin in [14]. Actually, just in reading that lucid paper I realized that the question could have a general aspect so that I tried to develop the description of the possible migration of rather arbitrary substructures in complex fluids.

It is worth noting that the Cahn–Hilliard equation can be derived (in a certain sense alternatively) in a pure thermodynamical setting by exploiting the second law and Liu’s method of constraints, as proposed by Ván [15].

5.2. Nematic liquid crystals

In the case of nematics, ν is an element of the unit sphere with the identification of antipodes [2, 3] (in other words ν is a direction \mathbf{n} because nematic stick molecules do not have distinct head and tail so that \mathcal{M} is identified with the projective plane P^2). In this case, we (i) consider the ground fluid incompressible and (ii) assume for ψ the simplest expression of Frank’s potential, namely $\frac{1}{2}\gamma(\text{grad } \mathbf{n} \cdot \text{grad } \mathbf{n})$ with γ being a constant. Leaving $\tilde{n}(\cdot)$ without an explicit expression, considering $\bar{\beta} = 0$ and \mathbf{A} as a constant a , we get

$$\dot{\mathbf{n}} = -a\Delta \left(\frac{1}{\|D_{\mathbf{n}}\mathbf{n}\|_{T_{\mathbf{n}}^*P^2}^2} \langle \gamma \Delta \mathbf{n}, D_{\mathbf{n}}\mathbf{n} \rangle_{T_{\mathbf{n}}^*P^2} \right). \quad (61)$$

5.3. Sketch of further special cases

To develop further applications of the general framework presented above to concrete cases, basic ingredients are the choices of a morphological descriptor ν (hence of the structure of \mathcal{M}) and of an explicit expression of the free energy in each situation envisaged. We list below some examples.

- (a) *Polymeric fluids.* ν coincides with a second-order tensor $\mathbf{R} = \mathbf{r} \otimes \mathbf{r}$, where \mathbf{r} is a stretchable end-to-end vector describing the generic polymer chain (see [6, 11] for specific expressions of the energy). In polymer stars one should add a scalar order parameter to account for the radius of gyration of each star-shaped molecule.
- (b) *Polyelectrolyte polymers.* Two morphological descriptors are involved: the above-mentioned second-order symmetric tensor \mathbf{R} and a vector \mathbf{p} belonging to a ball $\mathfrak{B}_{|\mathbf{p}|_{\max}}$ in \mathbb{R}^3 and representing the local polarization of polymer chains; the radius of the ball is $|\mathbf{p}|_{\max}$, the saturation value of the polarization. In this case, the application of an external electric field induces local substructural interactions that may enhance or obstruct the possible migration of polymeric molecules.
- (c) *Liquid crystals in the smectic-A phase.* In such a phase, liquid crystals exhibit a layered structure, each layer containing stick molecules that tend to be aligned orthogonally to the layer interface. If we aim to describe the possible migration of stick molecules across layers, we should consider a scalar function $w(\mathbf{x}, t, \tau\lambda)$ parametrizing layers (with λ a

length scale and τ running in a set of integers) in addition to the vector-order parameter \mathbf{n} describing nematic order. In particular, far from the defect core we have $\mathbf{n} = \frac{\text{grad } w}{|\text{grad } w|}$. In this case, a reasonable form of the energy is given by

$$\phi = \tilde{\phi}(t, w, \text{grad } w) = \tilde{\phi}(t) + \frac{1}{2}\gamma_1(|\text{grad } w| - 1)^2 + \frac{1}{2}\gamma_2(\text{div } \mathbf{n})^2, \quad (62)$$

with γ_1 and γ_2 being material constants. The term $(|\text{grad } w| - 1)^2$ accounts for the compression of layers, while $(\text{div } \mathbf{n})^2$ describes the nematic phase and is the first addendum of the three-constant Frank's potential. In these conditions and in the absence of viscosity, the evolution equation becomes

$$\dot{\mathbf{n}} = -\text{div} \left(\mathbf{A} \text{grad} \left(\frac{1}{|D_w n|^2} (\text{div } \partial_{\text{grad } w} \phi - \partial_w \phi) D_w n \right) \right). \quad (63)$$

- (d) The hydrodynamics of *granular materials* may be described in the multifield setting by using both scalar [32] and tensor [33] morphological descriptors. The results about migration of substructures might be applied in this setting to analyse segregation in granular media, a problem for which essential results have obtained in [34] by using a kinetic approach.

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References

- [1] Mariano P M 2003 *J. Phys. A: Math. Gen.* **36** 9961–72
- [2] Ericksen J L 1991 *Arch. Rat. Mech. Anal.* **113** 97–120
- [3] de Gennes P G and Prost J 1993 *The Physics of Liquid Crystals* (Oxford: Clarendon)
- [4] Capriz G 1995 *Meccanica* **30** 621–7
- [5] Weinan E 1997 *Arch. Rat. Mech. Anal.* **137** 159–75
- [6] Edwards S F 1983 *Proc. R. Soc. A* **385** 267–88
- [7] Remmelgas J and Leal L G 2000 *J. Non-Newton. Fluid Mech.* **89** 231–49
- [8] Odenbach S (ed) 2003 *Ferrofluids Lecture Notes in Physics* (Berlin: Springer)
- [9] Capriz G 1989 *Continua with Microstructure* (Berlin: Springer)
- [10] van Saarloos W 2003 *Phys. Rep.* **386** 29–222
- [11] De Angelis E, Casciola C M, L'vov V S, Piva R and Procaccia I 2003 *Phys. Rev. E* **67** 056312
- [12] Capriz G 1995 *Arch. Rat. Mech. Anal.* **90** 43–56
- [13] Mariano P M 2002 *Adv. Appl. Mech.* **38** 1–93
- [14] Gurtin M E 1996 *Physica D* **92** 178–92
- [15] Ván P 2001 *Phys. Lett. A* **190** 88–92
- [16] Mariano P M 2006 *Elements of Multifield Theories for Complex Bodies* (Boston, MA: Birkhäuser) at press
- [17] Del Piero G 2003 *J. Elast.* **70** 175–95
- [18] Truesdell C A and Noll W 2004 *The Non-linear Field Theories of Mechanics* 3rd edn (Berlin: Springer)
- [19] Šilhavý M 1997 *The Mechanics and Thermodynamics of Continuous Media* (Berlin: Springer)
- [20] Šilhavý M 1991 *Arch. Rat. Mech. Anal.* **116** 223–55
- [21] Musesti A 2004 *Boll. U. M. I.* **7-B** 305–18
- [22] Capriz G and Virga E G 1990 *Arch. Rat. Mech. Anal.* **109** 323–42
- [23] Segev R 2004 in *Advances in Multifield Theories for Continua with Substructure* ed G Capriz and P M Mariano (Boston, MA: Birkhauser)
- [24] de Fabritiis C and Mariano P M 2005 *J. Geom. Phys.* **54** 301–23
- [25] Mariano P M and Stazi F L 2006 *Arch. Comput. Methods Eng.* at press
- [26] Marsden J E and Hughes T R J 1994 *Mathematical Foundations of Elasticity* (New York: Dover)
- [27] Capriz G and Mariano P M 2003 *J. Elast.* **72** 57–70
- [28] Ferrari P L and Lebowitz J L 2003 *J. Phys. A: Math. Gen.* **36** 5719–30

-
- [29] Mariano P M 1997 *Z. Angew. Math. Phys.* **48** 1002–11
 - [30] Coleman B D and Noll W 1963 *Arch. Rat. Mech. Anal.* **13** 167–78
 - [31] Mariano P M and Augusti G 1998 *J. Physique IV* **8** 223–30
 - [32] Goodman M A and Cowin S C 1972 *Arch. Rat. Mech. Anal.* **44** 249–66
 - [33] Capriz G 2003 *Rend. Sem. Mat. Univ. Padova* **110** 179–98
 - [34] Trujillo L and Herrmann H J 2003 *Physica A* **330** 519–42