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Mixtures with continuous diversity: general theory and application to polymer solutions

S.H. Faria

Institut für Mechanik, Technische Universität Darmstadt, Darmstadt, 64289, Germany

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This work concerns a generalization of the classical theory of mixtures appropriate for multicomponent media made up of an infinite number of constituents with continuously varying properties. Such a concept affords a valuable starting point for the description of many thermodynamic systems found in physical, geological, chemical and biological sciences. The main matter of this study lies in an extension of the entropy principle of continuum thermodynamics to the higher-dimensional spaces which characterize such kind of multicomponent media. To illustrate the potential of the theory, it is applied to the analysis of induced anisotropy in rigid rodlike polymer solutions, in different concentration regimes. Among other interesting inferences of the constitutive theory, it is shown that the microstructure evolution is governed by a hyperbolic equation, which after suppression of inertial effects reduces to a non-linear evolution equation of the Fokker-Planck type. Finally, an analogy between the results derived by this continuum approach and those usually obtained from molecular theories is established, by particularizing the predictions for ideal solutions.

1 Introduction

Presently, it seems rather natural to regard any common chemical mixture as composed of a discrete number of chemically distinct species. Some hundred years ago, however, this fact was far from trivial even for the most prominent alchemists, and particularly doubtful for those who did not believe in the atomistic nature of the matter, as conceived by Democritus more than two thousand years ago. Indeed, since then there was an arduous way to explain, formally, why every substance should present particular physical and chemical properties [1].

Of course, the modern theory of mixtures [2]–[28] was mostly developed under this scheme, with the identification of the constituents being usually performed through a discrete set of labels or indices. Nevertheless, it must be observed that the fundamentals of this theory are in fact based on a much wider realm than that of usual chemical mixtures. This enabled scientists to apply such concepts to many other multicomponent environments, from granular media [22]–[24], [26]–[28] and bubbly liquids [23] to composite materials [20, 23] and (after a suitable change of terminology) also population dynamics [29]–[33].

Ironically, in some of the examples above, the discrete identification of species seems to be a simplified picture of the macroscopic reality. It is basically about such less conventional applications of the mixtures theory that this work is concerned.

An apology is needed to the language employed in this communication. In order to exploit the generality of the theme, words like *mixture*, *species*, *constituents* and *diversity* will be often utilized in their broadest

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Dedicated to Prof. Kolumban Hutter on the occasion of his 60th birthday.

sense, instead restricted to their specific meanings in chemistry, physics or biology. In particular, I ask permission to introduce here the neologism *mixture with continuous diversity*, in order to generically refer to a multicomponent medium made up of a continuous set of mutually interacting components (i.e., constituents whose distinctive properties vary smoothly from one to another).

To illustrate this concept, consider the example of a dry granular medium composed of (roughly) spherical solid particles of the same material but with different sizes. Experience shows that the mechanical response of this medium is strongly dependent on the grain size distribution [34]–[37], in such a way that one can expect distinct material behavior, depending on the dimensions of the grains. In other words, the granular medium can be viewed as a mixture of solid particles, of which the different species are classified according to their grain sizes (e.g. diameters). While the gross features of such a medium can be qualitatively understood with the usual mixture theory, by using some discrete classification of the granular species (for example, a 2-component mixture of large and small grains, as considered by Savage & Lun [38]), a general theory should take into account the whole grain size distribution, in order to afford *quantitative* predictions. This is particularly true if one intends to describe, quantitatively, complex size effects like grain size segregation, or the (more or less) gradual degradation of large grains to smaller ones by erosional phenomena like abrasion and fragmentation [39]. However, a modern thermodynamic theory, founded on an appropriate entropy principle capable of dealing with the whole continuous spectrum of grain diameters, is lacking.

Actually, it is not difficult to construct an heuristic procedure to extend the fundamental concepts of some well-known discrete description, in order to obtain a continuous version of it. In fact, such an idea was already used at the end of the 19th century by Volterra [40] (see also the note of Whittaker [41]) to construct a mathematical theory for what he named "functions depending on other functions", nowadays simply called *functionals*, due to Hadamard [42, 43]. More closely related to the framework of multicomponent media, Prager [44] remarked that the translational diffusion phenomenon in an isotropic suspension of rodlike solid particles resembles well diffusive processes in a mixture of species with different diffusion coefficients. On the other hand, the similarity between a gas of non-spherical molecules and a mixture with continuous diversity was demonstrated by Curtiss [45]. Later, Condiff & Brenner [46] took advantage of this analogy to construct a phenomenological theory of fluids composed of orientable particles, using some classical results of the irreversible thermodynamic theory of mixtures.

The aim of this article is actually twofold. First, a general theory of mixtures with continuous diversity is presented, including the formulation of an entropy principle adequate for such multicomponent media. Thereafter, a practical application of the theory is illustrated by considering a simple constitutive model for the study of microstructure evolution in suspensions of rigid rodlike polymers (evidently, the general results remain valid also for homogeneous suspensions of axially symmetric slender rigid-bodies). These topics are organized in the text as follows. The next three sections are concerned with the formulation of the thermodynamic theory already cited. Section 2 draws a sketchy survey of the classical theory of mixtures, emphasizing the generality of mass balance and entropy inequality. The results presented there form the basis for the heuristic derivation of the equations of a mixture with continuous diversity, presented in Sects. 3 and 4. After that, the remainder of the work deals with the use of this extended concept of mixture in the microstructural dynamics of polymeric suspensions in different concentration regimes. The fundamentals of the theory are presented in Sect. 5, while the appropriate forms of the balance equations of energy and momenta are discussed in Sect. 6; Section 7 deals with the generalities of the constitutive theory, while an exploitation of the entropy inequality by means of the method of Lagrange multipliers of Liu [47] is performed in Sects. 8 and 9; finally, an evolution equation for the suspension microstructure is derived in Sect. 10, being applied for dilute as well as non-dilute polymer suspensions. Conclusions of the whole analysis are discussed in Sect. 11.

Cartesian tensor notation with the usual summation convention is adopted for capital as well as lowercase Latin indices. By contrast, *repeated (dummy) Greek indices should not be summed*, except when explicitly indicated. Lowercase Latin indices refer always to components of some tensorial field in the usual three-dimensional Euclidian space. On the other hand, capital Latin indices serve to denote the components of a tensorial field in arbitrary finite-dimensional Cartesian spaces. Parentheses denote symmetrization of all Latin indices while square brackets and angular parentheses indicate antisymmetrization and traceless symmetrization, respectively. Finally, all thermodynamic fields are assumed continuously differentiable functions of their arguments.

2 Short survey of the classical mixture theory

Following the assertion of Truesdell [24], the continuum theory of mixtures will be regarded here so as to describe the phenomena of diffusion, dissociation, combination, transformation and interaction of the constituents in the broader sense.

Mathematically, a mixture is defined as a superposition of N continuous bodies $\mathscr{B}^\alpha$ $(\alpha = 1, 2, \ldots, N)$, all able to occupy simultaneously the same region of space. Consequently, in order to refer to any particle of some constituent of this continuum, at a given time t, it is necessary to identify not only the current position x_i of the respective particle, but also its *constituent label* α. Accordingly, the mass density of the component α at the position x_i and time t is given by $\varrho^\alpha(x_i, t)$, while the mass density of the mixture $\varrho(x_i, t)$ and the concentration, or mass fraction, of the constituent $f^\alpha(x_i, t)$ are respectively defined by

$$\varrho = \sum_{\alpha=1}^{N} \varrho^\alpha \qquad \text{and} \qquad f^\alpha = \frac{\varrho^\alpha}{\varrho}. \tag{2.1}$$

The balances of mass of the constituents are expressed by the set of equations

$$\frac{\partial \varrho^\alpha}{\partial t} + \frac{\partial \varrho^\alpha v_i^\alpha}{\partial x_i} = \varGamma^\alpha, \qquad (\alpha = 1, 2, \ldots, N) \tag{2.2}$$

where v_i^α is the constituent velocity (relative to some frame of reference) and $\varGamma^\alpha$ is the production density of mass of the α^{th} species. In most cases of interest, the conservation of mass implies the condition

$$\sum_{\alpha=1}^{N} \varGamma^\alpha = 0. \tag{2.3}$$

Hence, as a consequence of (2.1)–(2.3) and the third *metaphysical principle* of Truesdell[1] [24], there follows the continuity equation for the mixture in its usual form

$$\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_i}{\partial x_i} = 0, \tag{2.4}$$

with $v_i(x_n, t)$ denoting the barycentric velocity of the mixture

$$v_i = \sum_{\alpha=1}^{N} \frac{\varrho^\alpha}{\varrho} v_i^\alpha = \sum_{\alpha=1}^{N} f^\alpha v_i^\alpha. \tag{2.5}$$

When local conservation of mass cannot be asserted (e.g. in non-local continua [48, 49]) and exchanges of mass with the outside world are allowed (i.e., open systems [30]), then (2.3) does not hold and the mass balances (2.2) and (2.4) take the general forms

$$\frac{\partial \varrho^\alpha}{\partial t} + \frac{\partial \varrho^\alpha v_i^\alpha}{\partial x_i} = \varGamma^\alpha + m^\alpha, \qquad (\alpha = 1, 2, \ldots, N) \tag{2.6}$$

and

$$\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_i}{\partial x_i} = \sum_{\alpha=1}^{N} \left(\varGamma^\alpha + m^\alpha\right), \tag{2.7}$$

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[1] In resume, the three metaphysical principles of Truesdell state that: 1) all properties of the mixture are mathematical consequences of the constituent properties; 2) so as to describe the motion of a constituent, one can imagine it isolated from the rest of the mixture, provided the actions of the other constituents upon it are allowed; 3) the motion of the mixture is governed by the same equations as a single medium.

where m^α denotes the mass supply density of the component α, and the right-hand side of (2.7) defines the net mass production of the mixture. Note that (2.6) and (2.7) are quite general, involving all mass changes in non-relativistic continua (relativistic counterparts of (2.2) and (2.4) can be found in [17, 50, 51]).

Balance equations of momenta and energy will not be presented explicitly here for two reasons. The first is brevity: they play no role in the formulation of the entropy principle at all. The second is generality: in fact there are no general forms of these equations capable to encompass at the same time all possible applications. To illustrate this last assertion, it is sufficient to mention a few examples of media where these balance equations take distinct forms:

- porous and granular media [22]–[24], [26]–[28],
- mixtures with multiple temperatures [11, 13, 19, 21, 24, 27, 28],
- non-local mixtures [14],
- electromagnetic multicomponent media [6],
- composite materials [20, 23],
- mixtures of continua with microstructure, like polar media and liquid crystals, as well as emulsions and bubbly liquids [12, 16, 23].

In any case, however, the balances of momenta and energy of the α^{th} constituent of the mixture must be compatible with the *general balance equation* [5, 25]

$$\frac{\partial \Psi^\alpha}{\partial t} + \frac{\partial}{\partial x_i}\left(\Psi^\alpha v_i^\alpha + \Phi_i^\alpha\right) = \Xi^\alpha + \Sigma^\alpha \qquad (\alpha = 1, 2, \ldots, N) \tag{2.8}$$

where Ψ^α is the density of some additive quantity, Φ_i^α is its non-convective flux, Ξ^α its production density and Σ^α an external supply.

The entropy density of the mixture is also governed by a balance equation of the type (2.8). Its most general form reads (see [5, 10, 18, 24, 25, 52])

$$\frac{\partial \varrho\eta}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho\eta v_i + \phi_i\right) = \varrho\varsigma + \varrho s\,. \tag{2.9}$$

In the expression above, η denotes the specific entropy of the mixture, ϕ_i its flux, ς the specific entropy production and s the specific entropy supply. Moreover, as a consequence of the second law of thermodynamics, the inequality

$$\varsigma \geq 0 \tag{2.10}$$

must hold for all *thermodynamic processes*, defined as the solutions of the system of field equations derived from (2.6) and (2.8). The generality of (2.9) (subjected to (2.10)) is also quite remarkable. It embraces actually almost all entropy inequalities found in the literature of non-relativistic continua, with only very scarce exceptions [7, 14, 28, 48, 49].

Finally, the general balance equation (2.8) can be rewritten in a compact notation (cf. [50]) which will be very useful in the next sections. Consider first the 4-dimensional *(standard) Newtonian space-time* $\mathscr{E} \times \mathbb{R}$ of the classical mechanics [53], formed by the product space (Cartesian product) of a 3-dimensional Euclidean space $\mathscr{E} = \mathbb{R}^3$ and the reals $\mathbb{R}$. A point y_A $(A = 1, 2, 3, 4)$ in this hyperspace is called an *event* and consists of the position coordinates x_i and the time t, respectively. Accordingly, introduce the 4-dimensional vector

$$\Psi_A^\alpha = \left(\Psi^\alpha v_i^\alpha + \Phi_i^\alpha,\, \Psi^\alpha\right), \qquad (\alpha = 1, 2, \ldots, N) \tag{2.11}$$

and rewrite (2.8) in a compact way as

$$\frac{\partial \Psi_A^\alpha}{\partial y_A} = \Xi^\alpha + \Sigma^\alpha, \qquad (\alpha = 1, 2, \ldots, N) \tag{2.12}$$

which states that the divergence of Ψ^α in space-time is balanced by its production and supply, defined before.

The compact formulation discussed in the last paragraph evidences that spatial and temporal variables can be treated at the same footing, as coordinates of an event. In addition, the assumption of form invariance of the balance equation (2.12) will serve as starting point for the heuristic generalizations to be presented in the next two sections.

3 Mixtures with continuous diversity

Suppose that the label α is no longer related to a finite-enumerating set of integer numbers, but defined in a closed interval $[\alpha_{\min}, \alpha_{\max}] = \mathscr{A} \subset \mathbb{R}$, which will be called the *species assemblage*. The extrema $\alpha_{\min}$ and $\alpha_{\max}$ are so defined as the assemblage $\mathscr{A}$ to be *complete*, i.e., it accounts for all possible species in the medium. At first sight, the adoption of this new picture brings no dramatic changes in the description of the medium. For instance, whatever the particular meaning given for α, the reference to any particle of the continuum, at a given time t, continues to be defined by the current position x_i of this particle and its constituent label α.

However, α is now continuous. In other words, this means that $\alpha \in \mathscr{A}$ acquired the status of a new variable, in addition to x_i and t, whence the Newtonian space-time $\mathscr{E} \times \mathbb{R}$, introduced at the end of the last section, must be replaced by the *space-time-assemblage* $\mathscr{E} \times \mathbb{R} \times \mathscr{A}$. Without loss of generality, it will be assumed that α is chosen in such a way that the space-time-assemblage is a Cartesian hyperspace. A point of it will be called a *sorted event*, being denoted by $z_B = (x_i, t, \alpha)$, with $B = 1, 2, \ldots, 5$.

Regarding this 5-dimensional space structure, the derivation of balance equations appropriate for a mixture with continuous diversity is reduced to a simple heuristic generalization of the results presented in the last section. Effectively, if $\Psi^*(x_i, t, \alpha)$ denotes the density of some arbitrary additive quantity in this hyperspace[2], then one can introduce the 5-dimensional vector

$$\Psi^*_B = \left(\Psi^* v^*_i + \Phi^*_i\,,\ \Psi^*\,,\ \Psi^* u^* + \Upsilon^*\right), \tag{3.13}$$

and obtain a general balance equation similar in form to (2.12), but in the space-time-assemblage:

$$\frac{\partial \Psi^*_B}{\partial z_B} = \Xi^* + \Sigma^*. \tag{3.14}$$

As might be expected, by using (3.13) and the definition of sorted event, Eq. (3.14) can be rewritten as (cf. (2.8))

$$\frac{\partial \Psi^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\Psi^* v^*_i + \Phi^*_i\right) + \frac{\partial}{\partial \alpha}\left(\Psi^* u^* + \Upsilon^*\right) = \Xi^* + \Sigma^*. \tag{3.15}$$

In (3.13)–(3.15), the fields $v^*_i(x_j, t, \alpha)$, $\Phi^*_i(x_j, t, \alpha)$, $\Xi^*(x_i, t, \alpha)$ and $\Sigma^*(x_i, t, \alpha)$ have basically the same meaning as their standard counterparts v^α_i, Φ^α_i, Ξ^α and Σ^α, presented in the last section. Moreover, in order to account for fluxes in the direction of the species axis (i.e., the α-direction) two new scalar fields were introduced, viz. the *interspecies flux* $\Upsilon^*(x_i, t, \alpha)$ and the *transition rate* $u^*(x_i, t, \alpha)$. Notice that the completeness assumed for the species assemblage can be written as

$$\int\limits_{\mathscr{A}} \frac{\partial(\Psi^* u^*)}{\partial \alpha}\, d\alpha = \int\limits_{\mathscr{A}} \frac{\partial \Upsilon^*}{\partial \alpha}\, d\alpha = 0, \tag{3.16}$$

which simply reflects the fact that there are no species defined outside $\mathscr{A}$.

To clarify the meaning of the field of transition rate, consider first the example of a non-reacting mixture whose mass is conserved. In this case one obtains for the balance of mass the identifications

$$\Psi^* = \varrho^* \qquad \text{and} \qquad \Phi^*_i = \Upsilon^* = \Xi^* = \Sigma^* = 0 \tag{3.17}$$

which allow the derivation of the following balance equation of mass for the α^{th} constituent

$$\frac{\partial \varrho^*}{\partial t} + \frac{\partial \varrho^* v^*_i}{\partial x_i} + \frac{\partial \varrho^* u^*}{\partial \alpha} = 0, \tag{3.18}$$

where $\varrho^*(x_i, t, \alpha)$ denotes the mass density of the constituent α.

Equation (3.18) is the simplest non-trivial generalization of the continuity equation (2.4) for a mixture with continuous diversity. It asserts that, besides the usual mass changes due to transport phenomena, the

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[2] In order to distinguish the thermodynamic fields of the components from those of the mixture, from now on a superscribed asterisk will serve to indicate that the respective quantity is a function of x_i, t and α.

density of constituent α can vary in time also through species transitions. In fact, by considering a unit volume in a medium at rest ($v_i^* = 0$), it is easy to conclude that the quantity u^* determines the rate at which the amount of mass ϱ^* performs a continuous transition from constituent α to some other species, by altering its distinguishing properties. Note that the nature of such a transition is not restricted to any particular type of transformation, mutation, degradation or regeneration of the constituent properties. Nevertheless, it must be continuous. In other words, it must occur between *familiar* species.

The concept of *familiarity* is the key to characterize a medium as a mixture with continuous diversity. It is a direct consequence of the existence of a metric in the interval $\mathscr{A}$, and is in fact the counterpart of the notion of closeness in Euclidian space. Transitions between familiar species are very peculiar processes in mixtures with continuous diversity, and they occur frequently, even when chemical reactions are absent. For example, in the gas with non-spherical molecules considered by Curtiss [45], a transition of this kind would be given simply by a slight reorientation of the particles. The rate at which such continuous changes occur is just described by the transition rate u^*.

In some situations, the mass balance of the α^{th} component of the mixture can assume more complicated forms, when compared with the simple example considered above. For the general case of an open and reacting medium, the following identifications are necessary

$$\Psi^* = \varrho^*, \qquad \Phi_i^* = \Upsilon^* = 0, \qquad \Xi^* = \Gamma^* \qquad \text{and} \qquad \Sigma^* = m^*, \tag{3.19}$$

which lead to the balance equation

$$\frac{\partial \varrho^*}{\partial t} + \frac{\partial \varrho^* v_i^*}{\partial x_i} + \frac{\partial \varrho^* u^*}{\partial \alpha} = \Gamma^* + m^*, \tag{3.20}$$

where Γ^* and m^* have the same meaning as their classical counterparts Γ^α and m^α.

For any case, however, the relations

$$\int_{\mathscr{A}} \varrho^* \, d\alpha = \varrho, \qquad f^* = \frac{\varrho^*}{\varrho} \qquad \text{and} \qquad \int_{\mathscr{A}} f^* v_i^* \, d\alpha = v_i, \tag{3.21}$$

remain valid (cf. (2.1), (2.5)), with $\varrho(x_i, t)$ and $v_i(x_j, t)$ denoting (again) the mass density and the barycentric velocity of the mixture, respectively, while $f^*(x_i, t, \alpha)$ expresses the mass fraction of constituent α. From (3.16) and (3.21) follows, by integration of (3.20) over all species, the usual mass balance of the mixture

$$\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_i}{\partial x_i} = \int_{\mathscr{A}} \left(\Gamma^* + m^*\right) \, d\alpha, \tag{3.22}$$

and therefore, the third metaphysical principle (see last section) is again fulfilled. Moreover, for a closed system whose mass is locally conserved, the additional conditions

$$m^* = 0, \qquad \int_{\mathscr{A}} \Gamma^* \, d\alpha = 0 \tag{3.23}$$

hold, and (3.22) reduces to the common continuity equation (2.4).

As discussed in the last section, balance equations of momenta and energy will not be considered at this stage. Besides the reasons presented above, one more argument arises in the case of mixtures with continuous diversity: different forms of such balance equations can occur, depending on the physical meaning specified for the variable α. Of course, these equations must have the same general form, namely Eq. (3.15).

Before proceeding with thermodynamics, some remarks are appropriate here. For simplicity, throughout this communication only one temperature field, the temperature of the mixture, will be considered. Accordingly, the main objective of the thermodynamic theory, viz., the prediction of the mixture behavior once the external agents are specified, reduces to the determination of the constituent fields of density, velocity and transition rate, as well as the temperature of the mixture (if no further fields are specified). Clearly, balance equations of mass, momenta and energy do not suffice for the determination of these fields, because they contain also additional fluxes and production terms which depend on the particularities of the medium. Hence, one must introduce supplementary hypotheses, in order to relate these additional quantities to the basic fields of the theory, through the so called *constitutive relations*. Nonetheless, these relations cannot be arbitrary. They must satisfy some fundamental physical axioms, among them the entropy principle.

The results presented up to now provide a solid background for the formulation of an entropy principle appropriate for mixtures with continuous diversity. Actually, no modification of the classical version of this principle is necessary for the mixture as a whole, the relations (2.9) and (2.10) still being valid. Nevertheless, in contrast to the usual theory of mixtures, an entropy inequality in the form (2.10) is somewhat unworthy for a constitutive theory in the space-time-assemblage. In fact, the standard method of exploitation of the entropy principle by the use of Lagrange multipliers, as proposed by Liu [47], is no longer applicable in such a situation. The reason is that the algebraic equivalence on which the whole method is founded cannot be justified, in this case, by customary arguments.

The admissibility of the method of Lagrange multipliers became a very desirable feature for any thermodynamic theory of continua. In fact, the use of Lagrange multipliers makes the exploitation of the entropy principle not only a systematic and straightforward procedure, but also equivalent to the maximization of entropy in non-equilibrium, as proved by Dreyer [54]. Therefore, in order to confer such a pleasant feature to the theory developed here, one has two alternatives: the first could be the derivation of a new version of the method of Lagrange multipliers, by introducing multiplier-functions in integral form; the second would require a reformulation of the entropy principle in space-time-assemblage, which should be compatible (at least for the most common cases) with the conventional form of the Lagrange multiplier method. In this work I will deal with the second option, the first one being left for the mathematicians.

In order to present the entropy principle appropriate for mixtures with continuous diversity, it is sufficient to rephrase (with only some slight modifications) the axiomatic formulation of Müller [25]. It will be stated here in three parts:

Postulate [Entropy principle]

1. *There exists for each component of the mixture an additive scalar quantity, the entropy of constituent α.*
2. *The specific entropy, the entropy fluxes and the specific entropy production of each component of the mixture are given by constitutive equations.*
3. *The entropy production of the mixture is non-negative for all thermodynamic processes.*

From the first axiom follows, with the help of (3.14) (or equivalently of (3.15)), the entropy balance equation in the form

$$\frac{\partial \varrho^* \eta^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\varrho^* \eta^* v_i^* + \phi_i^*\right) + \frac{\partial}{\partial \alpha}\left(\varrho^* \eta^* u^* + \varphi^*\right) = \varrho^* \varsigma^* + \varrho^* s^*, \tag{3.24}$$

where η^* is the specific entropy of the α^{th} constituent, ϕ_i^* and φ^* its fluxes, ς^* its specific production and s^* its external supply. According to the second axiom, all these fields (but the last, which is defined by external conditions) are given by constitutive functions. Note also that the additivity of the densities of entropy, entropy production and entropy supply immediately imply the following relations between constituent and mixture fields (cf. Eq. (2.9))

$$\int_{\mathscr{A}} \varrho^* \eta^* \, d\alpha = \varrho\eta, \qquad \int_{\mathscr{A}} \varrho^* \varsigma^* \, d\alpha = \varrho\varsigma \qquad \text{and} \qquad \int_{\mathscr{A}} \varrho^* s^* \, d\alpha = \varrho s. \tag{3.25}$$

Hence, in order to derive the entropy balance equation of the mixture (2.9) using Eqs. (3.24) and (3.25), one more definition is necessary, viz.,

$$\varrho\eta v_i + \phi_i = \int_{\mathscr{A}} \left(\phi_i^* + \varrho^* \eta^* v_i^*\right) \, d\alpha. \tag{3.26}$$

Finally, the last axiom guarantees the validity (again) of the inequality (2.10), i.e.,

$$\varsigma = \int_{\mathscr{A}} f^* \varsigma^* \, d\alpha \geq 0. \tag{3.27}$$

Observe that the production ς^* can also assume negative values, caused by the influence of the other components present in the mixture. One can exclude for a while such intricate influences by considering the limiting case when all constituents are absent but one, i.e., a one-component continuum. In such a simple situation, the specific entropy production of the pure constituent would be given simply by

$$\varsigma^{*\mathrm{p}} \geq 0, \tag{3.28}$$

as obviously should be for a single medium.

Consequently, returning to the general case, one can define for every component of the mixture, a deviation measure of the constituent entropy production from its expected behavior in a single medium by

$$\delta^* = \varsigma^* - \varsigma^{*\mathrm{p}}, \tag{3.29}$$

which will be called the entropy production deviation due to constituent interactions, or for short, *entropy production deviation*.

Once ς^* is a constitutive function (due to the second axiom of the entropy principle), so it is $\varsigma^{*\mathrm{p}}$. Accordingly, from (3.29) there follows that the deviation function $\delta^*(x_i, t, \alpha)$ must also be a constitutive quantity. These results, combined with the inequality (3.28), complete the proof of

Theorem [Entropy production deviation]
There exists a function $\delta^* : \mathscr{E} \times \mathbb{R} \times \mathscr{A} \to \mathbb{R}$*, defined through (3.29), which is given by a constitutive equation and such that the inequality*

$$\varsigma^* \geq \delta^* \tag{3.30}$$

holds for all thermodynamic processes.

This theorem is the most prominent result of the theory, and enables the entropy principle to be expressed in the space-time-assemblage. In simple words, it guarantees the existence of the deviation function $\delta^*(x_i, t, \alpha)$ and asserts that it is a constitutive quantity whose value is upper-bounded by the constituent entropy production for all thermodynamic processes.

4 Extension for the case of multi-labelled species

The generalization of the mixture theory presented in the last section is still not able to deal with many of the common mixtures with continuous diversity found in nature. In fact, the identification of a particular species requires in many situations the specification of more than one distinctive property. A simple example is the gas with non-spherical molecules considered by Curtiss [45], where any species is identified by two parameters, related to the azimuthal and the polar orientation angles, respectively. Therefore, following the motto "once you start with generalizations, it is hard to stop", a trivial extension of the theory, valid for the case of multi-labelled species, will now be derived.

Consider first that every component of the mixture is identified with a set of continuous labels α_I ($I = 1, 2, \ldots, M$), each one defined in a particular closed interval $\mathscr{A}_I \subset \mathbb{R}$. Hence, the space-time-assemblage assumes the multi-dimensional form $\mathscr{E} \times \mathbb{R} \times \mathscr{M}$, where $\mathscr{M} = \mathscr{A}_1 \times \mathscr{A}_2 \times \cdots \times \mathscr{A}_M$. A sorted event in such a hyperspace is given by $z_{C'} = (x_i, t, \alpha_I)$, with $C' = 1, \ldots, (M+4)$, and one can introduce, in a similar way as before, a $(M+4)$-dimensional vector of the form

$$\Psi^*_{C'} = \left(\Psi^* v^*_i + \Phi^*_i \, , \; \Psi^* \, , \; \Psi^* u^*_I + \Upsilon^*_I\right) . \tag{4.31}$$

Accordingly, the general balance equation appropriate for the case of multi-labelled species remains essentially identic in form to (3.14), with a simple substitution of y_B by $z_{C'}$. Consequently, with the help of (3.14), (4.31) and the definition of sorted event, such a balance equation can be rewritten as (cf. (3.15))

$$\frac{\partial \Psi^*}{\partial t} + \frac{\partial}{\partial x_i}\left(\Psi^* v^*_i + \Phi^*_i\right) + \frac{\partial}{\partial \alpha_I}\left(\Psi^* u^*_I + \Upsilon^*_I\right) = \Xi^* + \Sigma^*, \tag{4.32}$$

with the evident summation convention of the dummy indices $i = 1, 2, 3$ and $I = 1, 2, \ldots, M$.

All the essential assumptions considered in the last section remaining valid, it is straightforward to derive the extended version of the theory, by trivial replacement of α, u^* and $\mathscr{A}$ in Eqs. (3.16)–(3.30) respectively by α_I, u_I^* and $\mathscr{M}$. For instance, the mass balance equation (3.20) and the expressions $(3.21)_1$ and $(3.21)_3$ are rewritten in this case as

$$\frac{\partial \varrho^*}{\partial t} + \frac{\partial \varrho^* v_i^*}{\partial x_i} + \frac{\partial \varrho^* u_I^*}{\partial \alpha_I} = \Gamma^* + m^*, \tag{4.33}$$

$$\int_{\mathscr{M}} \varrho^* \, d^M\alpha = \varrho, \qquad \text{and} \qquad \int_{\mathscr{M}} f^* v_i^* \, d^M\alpha = v_i, \tag{4.34}$$

where the following notation was adopted:

$$\int_{\mathscr{M}} (\ \ ) \, d^M\alpha = \int_{\mathscr{A}_1} \int_{\mathscr{A}_2} \cdots \int_{\mathscr{A}_M} (\ \ ) \, d\alpha_M \ldots d\alpha_2 d\alpha_1 .$$

Furthermore, the completeness assumption (3.16) takes the form

$$\int_{\mathscr{M}} \frac{\partial (\Psi^* u_I^*)}{\partial \alpha_I} \, d^M\alpha = \int_{\mathscr{M}} \frac{\partial \Upsilon_J^*}{\partial \alpha_J} \, d^M\alpha = 0. \tag{4.35}$$

From the considerations above, the vectorial character achieved by the label α_I, the interspecies flux Υ_I^* and the transition rate u_I^* becomes now clear. As remarked by Condiff & Brenner [46], this vectorial character is a fundamental feature in the study of anisotropic media.

Finally, keeping in mind also that, in such a generalized case, all thermodynamic fields are defined in the hyperspace $\mathscr{E} \times \mathbb{R} \times \mathscr{M}$, no further modification of the entropy principle and production deviation theorem, as presented in the last section, is necessary. Therefore, the extension of the theory is complete[3]. In the next sections, the application of these concepts will be illustrated through the study of the induced anisotropy in polymeric suspensions.

5 Configuration and mass changes in solutions of rodlike polymers

When rigid rodlike polymer molecules are suspended in a carrier liquid (like some polypeptides in suitable helicogenic solvents [55, 56]), complex microstructures can be induced by flow, affecting the material response of the fluid in several ways. For instance, stream-induced anisotropy can be optically measured by flow birefringence [57]–[59] and dynamic light scattering [56, 60, 61]. In fact, the instantaneous configuration of these polymeric suspensions is determined not only by the position of fluid particles, but in addition also by the orientational distribution of the identical rodlike molecules which constitute its microstructure.

Motivated by this microstructural picture, Kirkwood and co-workers [62]–[64] studied in a series of papers (within the frames of statistical rheology) the flow of dilute suspensions of rodlike macromolecules, basing on early works of Jeffery [65], Burgers [66] and Kuhn & Kuhn [67]. These were followed, among others, by the works of Prager [68], Kotaka [69], Doi & Edwards [70] and Dahler and co-workers [71, 72] by extending the range of the theory to the semidilute regime. An extensive survey of the literature on molecular theories of polymeric fluids can be found in the treatises of Ferry [55], Bird et al. [73], Doi & Edwards [74], Larson [75] and Beris & Edwards [76]. In addition, the research on dilute and semidilute suspensions of slender rigid-bodies was reviewed by Brenner [77] and Petrie [78]. (Worthy of note is also the series of papers of Hinch & Leal [79]–[82]). Common to all microscopic approaches cited above is the adoption of an *orientational distribution function* to describe the microstructure configuration of the fluid.

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[3] Of course, an "hybrid" version of the theory could also be obtained by mixing continuous and discrete distinctive properties. Nonetheless, once such derivation is straightforward from the results presented here, I will omit it for brevity. (After all, it is included by simply using the measure theoretic concept of integration over $\mathscr{M}$).

On the other hand, the analogy between a microstructured medium and a multicomponent mixture was mainly evidenced by Prager [44] and Curtiss [45]. The first author observed that, in dealing with translational diffusion of suspended rod-shaped particles, a group of randomly oriented rods should behave fairly like a mixture of species with different diffusion coefficients. Curtiss went further and, after deriving a kinetic theory for a gas of rigid non-spherical molecules, he showed that many of the resulting relations were similar to expressions for a mixture made up of an infinite number of components of continuously varying properties. Condiff & Brenner [46] later also emphasized this equivalence, designating it a “dichotomy of representation”. They made use of some fundamentals of irreversible thermodynamics of mixtures to derive a phenomenological theory of suspensions of orientable particles.

Curiously, not much attention was devoted to this theme from that time on, despite the drastic progress achieved in continuum thermodynamics of mixtures. In fact, in the frames of phenomenological approaches there always prevailed the description of microstructural dynamics by means of tensorial measures associated to observable anisotropic phenomena of optical and thermomechanical character. Such a type of description has a long tradition in continuum theories, dating back to the turn of the 20th century and being associated with the names of Duhem [83] and the Cosserat brothers [84]. The cited tensorial measures were at the beginning one or several unitary vectors called directors [5], [85]–[87] (in the classical case, a rigid triad of them [83]), but later more elaborate descriptions using structure tensors (also called order, alignment or conformation tensors) became avaliable [88]–[90].

Whilst the connection between the orientational distribution function of statistical physics and the tensorial measures of phenomenological approaches was already known in the domain of molecular theories for a long time (through the moments of the distribution function), a concept somewhat equivalent to the orientational distribution function was formally introduced in continuum thermodynamics in a much slower pace. In some sense, it could be traced back to Condiff & Brenner [46]. Actually, the essential idea proposed by these authors lies on a well-known concept of statistical rheology and kinetic theory, namely the consideration of a 6-dimensional hyperspace, which is nothing else than the product of the Newtonian space-time $\mathscr{E} \times \mathbb{R}$ and the 2-dimensional *orientation space*, defined by the surface of the unitary sphere $\mathscr{S}^2$. At any instant of time t, a particle of the medium is identified in $\mathscr{E} \times \mathbb{R} \times \mathscr{S}^2$ by a composition of coordinates, related to the independent Cartesian components of the position vector x_i and the (normalized) orientation vector n_j, radial to the spherical surface of $\mathscr{S}^2$. Contrary to the directors of the Cosserat continua, the orientation vector has no direct relation to any directional property of the medium; in other words, it is not attached to any material particle. Consequently, one can regard the reference to n_j in $\mathscr{S}^2$ as the orientational counterpart to the spatial (Eulerian) description in the usual physical space $\mathscr{E}$.

From the considerations above, the correspondence between the 6-dimensional description of the microstructure and the theory of mixtures with continuous diversity presented in the foregoing sections becomes clear. For instance, one may define for any monodisperse and homogeneous suspension[4] of rigid rodlike polymers the *partial mass density* $\varrho^*(x_i, t, n_j)$[5], which represents the mass density, at position x_i and time t, of the “constituent” with orientation n_j. In accordance with $(4.34)_1$, the mass density of the “mixture” is given by

$$\varrho(x_i, t) = \oint_{\mathscr{S}^2} \varrho^*(x_k, t, n_j)\, d^2 n, \tag{5.36}$$

integration being performed over the whole spherical surface of $\mathscr{S}^2$.

In the absence of chemical reactions and mass supplies, there follows from (4.33) the partial mass balance

$$\frac{\partial \varrho^*}{\partial t} + \frac{\partial \varrho^* v_i^*}{\partial x_i} + \partial_i \left(\varrho^* u_i^*\right) = 0, \tag{5.37}$$

where

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[4] For inhomogeneous suspensions one should necessarily distinguish between the fields of mass density and polymer concentration; on the other hand, polydispersity would imply on an additional dimension to the space-time-assemblage, related to the length distribution of the polymer chains. Such features, although tractable, will not be considered in this simple version of the theory.

[5] As a matter of fact, the orientation vector has only two independent components, since it is normalized. For simplicity, however, the notation n_j will be maintained, together with the constraint $n_k n_k = 1$.

$$\partial_i = \frac{\partial}{\partial n_i} - n_i n_j \frac{\partial}{\partial n_j} \tag{5.38}$$

denotes the *orientational gradient operator* (sometimes also written as $\epsilon_{ijk} n_j \, \partial / \partial n_k$, see, e.g., [46]). Its peculiar form results from the explicit consideration of the normalization condition[6] $n_k n_k = 1$. A further consequence of this normalization is the identity $n_i u_i^* = 0$, which allows one to rewrite the transition rate as

$$u_i^* = \epsilon_{ijk} s_j^* n_k = S_{ik}^* n_k . \tag{5.39}$$

In the definition above, $s_i^*(x_j, t, n_k)$ denotes the *partial spin* (i.e., the partial field of microstructural angular velocity), while $S_{ik}^* = \epsilon_{kij} s_j^*$ represents its respective skew-symmetric tensor. It should be observed that (5.39) does not specify the component of partial spin parallel to n_i. Insofar as needle-like polymer molecules are considered, it seems natural to assume that these molecules will tend to rotate about their long-axis with the fluid in which they are embedded, that is,

$$s_i^* n_i = \frac{1}{2} n_i \, \epsilon_{ijk} \frac{\partial v_k}{\partial x_j} . \tag{5.40}$$

The adoption of (5.39) and (5.40) allows a simple statistical interpretation of s_i^* as the angular velocity average of the suspended molecules instantaneously located in x_i and oriented in the n_i direction.

Finally, by introducing the *co-transitional time derivative*

$$\grave{\mathfrak{A}}^* = \frac{\partial \mathfrak{A}^*}{\partial t} + v_i^* \frac{\partial \mathfrak{A}^*}{\partial x_i} + u_k^* \, \partial_k \mathfrak{A}^* , \tag{5.41}$$

where $\mathfrak{A}^*$ denotes some arbitrary tensor field, Eq. (5.37) can be rewritten as

$$\grave{\varrho}^* + \varrho^* \frac{\partial v_i^*}{\partial x_i} + \varrho^* \partial_k u_k^* = 0. \tag{5.42}$$

As expected, with the help of (5.36), (A.4)$_1$ and revoking the usual definition of barycentric velocity of the "mixture", namely (cf. (4.34)$_2$)

$$v_i(x_j, t) = \oint_{\mathscr{S}^2} f^*(x_k, t, n_l) v_i^*(x_p, t, n_q) \, d^2 n , \tag{5.43}$$

one can retrieve the usual equation of continuity (2.4), after integration of (5.37) over the whole orientation space $\mathscr{S}^2$.

6 Balance equations of energy and momenta

Isotropic suspensions of rigid polymers can be generally reckoned as macromolecular liquids with complex microstructures, whose thermodynamics is well described by the conservation laws for polar fluids [91]–[93]. In the light of the approach presented here, this means that the balance equations of momenta and energy appropriate for the "mixture" as a whole are

$$\varrho \dot{v}_i - \frac{\partial t_{ij}}{\partial x_j} = \varrho g_i , \tag{6.44}$$

$$\varrho \left[\epsilon_{ijk} x_j \dot{v}_k + \left(I_{ij} s_j \right)^{\dot{}} \right] - \frac{\partial}{\partial x_l} \left(\epsilon_{ijk} x_j t_{kl} + m_{il} \right) = \varrho \left(\epsilon_{ijk} x_j g_k + c_i \right) , \tag{6.45}$$

$$\varrho \left[\dot{e} + v_k \dot{v}_k + \tfrac{1}{2} \left(s_i I_{ij} s_j \right)^{\dot{}} \right] + \frac{\partial}{\partial x_j} \left(q_j - t_{ij} v_i - m_{ij} s_i \right) = \varrho \left(r + g_i v_i + c_i s_i \right) , \tag{6.46}$$

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[6] Indeed, with reference to a polar coordinate system, the components of ∂_i can be readily obtained from the components of the usual gradient operator by simply discarding the radial term and assuming the normalization condition for the radius vector [46, 76].

where

$$\dot{\mathfrak{A}} = \frac{\partial \mathfrak{A}}{\partial t} + \upsilon_j \frac{\partial \mathfrak{A}}{\partial x_j} \qquad (6.47)$$

expresses the usual material time derivative of an arbitrary quantity $\mathfrak{A}$, while e, q_i, s_i, t_{ij} and m_{ij} denote the "mixture" fields of specific internal energy, heat flux, spin, Cauchy stress and Voigt couple-stress, respectively. Moreover, r, g_i and c_i are the extrinsic supplies per unit mass of internal energy (radiation), linear momentum (body force) and angular momentum (body couple). Finally, the tensor field $I_{ij}(x_k, t)$ represents the moment of inertia of the microstructure.

Equations in the form (6.44)–(6.46) were first obtained from statistical considerations in the celebrated memoir of Grad [94]. Later, this was followed by a number of different derivations and constitutive theories [91, 92], [95]–[98]. A comprehensive formulation of these equations in the framework of continuum thermodynamics, together with an historical synopsis of the subject, can be found in the review of Cowin [91].

Assuming the cogency of the metaphysical principles of Truesdell (see Sect. 2), balance equations for partial momenta and energy (i.e., for the "constituents of the mixture") can be easily obtained from the results (3.14), (4.31), (4.32), (6.44)–(6.46) derived above. First, (2.4), (3.14), (4.31), (4.32), (5.43), (6.44) and (6.47) immediately suggest the identifications

$$\Psi^* = \varrho^* \upsilon_i^*, \qquad \Phi_i^* = t_{ij}^*, \qquad \Upsilon_i^* = \tau_{ij}^*, \qquad \Xi^* = \varrho^* \kappa_i^* \qquad \Sigma^* = \varrho^* g_i^*, \qquad (6.48)$$

where t_{ij}^* is the partial Cauchy stress and g_i^* the the partial field of extrinsic body force per unit mass. Relations (3.14), (4.31), (4.32), (5.41) and (6.48) lead thence to the general form of the balance equation of partial linear momentum

$$\varrho^* \grave{\upsilon}_i^* - \frac{\partial t_{ij}^*}{\partial x_j} - \partial_j \tau_{ij}^* = \varrho^* \left(\kappa_i^* + g_i^*\right), \qquad (6.49)$$

with τ_{ij}^* and κ_i^* playing the roles of an *interspecies stress (flux of linear momentum)* and a *specific interaction force*, respectively.

Notice that, by construction, any given interspecies flux Υ_i^* must be tangential to the spherical surface of $\mathscr{S}^2$, i.e.

$$\Upsilon_i^* n_i = 0, \qquad (6.50)$$

since every species is assumed to be completely determined by the direction of the orientation vector n_i. Due to (6.50), the completeness condition (4.35) is automatically satisfied, as proved in the Appendix A. Furthermore, there follows from $(6.48)_3$ and (6.50) that $\tau_{ij}^* n_j = 0$.

Accordingly, repeating the foregoing procedure, one can introduce the partial fields of Voigt couple-stress m_{ij}^* and extrinsic body couple per unit mass c_i^*, obtaining with the help of (3.14), (4.31), (4.32), (5.41), (6.45) and (6.49) the general form of the balance equation of partial angular momentum

$$\begin{aligned} &\varrho^* \left[\epsilon_{ijk} x_j \grave{\upsilon}_k^* + \left(I_{ij}^* s_j^*\right)^{\grave{}}\right] - \frac{\partial}{\partial x_l}\left(\epsilon_{ijk} x_j t_{kl}^* + m_{il}^*\right) - \\ &- \partial_l \left(\epsilon_{ijk} x_j \tau_{kl}^* + \varpi_{il}^*\right) = \varrho^* \left[\epsilon_{ijk} x_j \left(g_k^* + \kappa_k^*\right) + c_i^* + \nu_i^*\right], \end{aligned} \qquad (6.51)$$

where ϖ_{ij}^* and ν_i^* denote the *interspecies couple-stress* and the *specific interaction couple*, respectively. In accordance with (5.40), the slenderness of the suspended macromolecules imply that the rotational inertia about their long-axis can be neglected, and consequently, the moment of inertia I_{ij}^* can be explicitly given by

$$I_{ij}^* = R^2 \left(\delta_{ij} - n_i n_j\right), \qquad (6.52)$$

where R^2 is a material constant related to the radius of gyration of a typical polymer molecule. Again, from (6.50), $\varpi_{ij}^* n_j = 0$.

Finally, the time rate of the sum of internal and kinetic energies is assumed to be balanced, as usual, by heat supplies and the power of the forces and couples occurring in the balance of momenta. Therefore, using the same arguments presented above, there follows from (3.14), (4.31), (4.32), (5.41), (6.46), (6.49) and (6.51) the general form of the balance equation of partial energy

$$\begin{aligned}\varrho^* \left[\grave{e}^* + v_k^* \grave{v}_k^* + \tfrac{1}{2}\left(s_i^* I_{ij}^* s_j^*\right)^{\grave{}}\right] + \frac{\partial}{\partial x_j}\left(q_j^* - t_{ij}^* v_i^* - m_{ij}^* s_i^*\right) + \\ + \partial_j \left(\xi_j^* - \tau_{ij}^* v_i^* - \varpi_{ij}^* s_i^*\right) = \varrho^* \left[\left(\kappa_i^* + g_i^*\right) v_i^* + \left(\nu_i^* + c_i^*\right) s_i^* + \varepsilon^* + r^*\right],\end{aligned} \tag{6.53}$$

with e^*, q_i^* and r^* denoting the partial fields of specific internal energy, heat flux and extrinsic radiation per unit mass, respectively, while ξ_i^* and ε^* define the *interspecies heat flux* and the *specific interaction energy supply*. Once again, due to (6.50), $\xi_i^* n_i = 0$.

Relationships between partial and respective “mixture” fields are furnished by the third metaphysical principle (see Sect. 2), through the procedure outlined by Truesdell [4]. Effectively, after integration of (6.49), (6.51) and (6.53) over the whole orientation space $\mathscr{S}^2$ (with the aid of (5.36)–(5.41), (5.43), (6.50) and (A.4)) and further confrontation of the results with (6.44)–(6.46), one can straightforwardly derive

$$g_i = \oint\limits_{\mathscr{S}^2} f^* g_i^* \, d^2n, \qquad \oint\limits_{\mathscr{S}^2} f^* \kappa_i^* \, d^2n = 0, \qquad t_{ij} = \oint\limits_{\mathscr{S}^2} \left(t_{ij}^* - \varrho^* C_i^* C_j^*\right) d^2n, \tag{6.54}$$

$$I_{ij} s_j = \oint\limits_{\mathscr{S}^2} f^* I_{ij}^* s_j^* \, d^2n, \qquad I_{ij} = \oint\limits_{\mathscr{S}^2} f^* I_{ij}^* \, d^2n, \qquad c_i = \oint\limits_{\mathscr{S}^2} f^* c_i^* \, d^2n, \tag{6.55}$$

$$\oint\limits_{\mathscr{S}^2} f^* \nu_i^* \, d^2n = 0, \qquad m_{ij} = \oint\limits_{\mathscr{S}^2} \left(m_{ij}^* - \varrho^* N_i^* C_j^*\right) d^2n, \tag{6.56}$$

$$e = \oint\limits_{\mathscr{S}^2} f^* \left(e^* + \frac{C^{*2}}{2} + \frac{N_i^* \Sigma_i^*}{2}\right) d^2n, \qquad (\text{with } C^{*2} = C_k^* C_k^*) \tag{6.57}$$

$$q_j = \oint\limits_{\mathscr{S}^2} \left[q_j^* + \varrho^* \left(e^* + \frac{C^{*2}}{2} + \frac{N_i^* \Sigma_i^*}{2}\right) C_j^* - t_{ij}^* C_i^* - m_{ij}^* \Sigma_i^*\right] d^2n, \tag{6.58}$$

$$r = \oint\limits_{\mathscr{S}^2} f^* \left(r^* + g_i^* C_i^* + c_i^* \Sigma_i^*\right) d^2n, \tag{6.59}$$

$$\oint\limits_{\mathscr{S}^2} f^* \left(\varepsilon^* + \kappa_i^* C_i^* + \nu_i^* \Sigma_i^*\right) d^2n = 0, \tag{6.60}$$

where $C_i^* = v_i^* - v_i$ and $\Sigma_i^* = s_i^* - s_i$ are the diffusion velocities of translation and angular motion, while $N_i^* = I_{ij}^* s_j^* - I_{ij} s_j$.

Moreover, by subtracting (6.49) from (6.51) and likewise (6.49) and (6.51) from (6.53), there remain the balance equations of partial spin and internal energy, respectively

$$\varrho^* \left(I_{ij}^* s_j^*\right)^{\grave{}} - \frac{\partial m_{ij}^*}{\partial x_j} - \partial_j \varpi_{ij}^* + \epsilon_{ijk} t_{jk}^* = \varrho^* \left(c_i^* + \nu_i^*\right), \tag{6.61}$$

and

$$\begin{aligned}\varrho^* \grave{e}^* + \frac{\partial q_j^*}{\partial x_j} - t_{ij}^* \frac{\partial v_i^*}{\partial x_j} - m_{ij}^* \frac{\partial s_i^*}{\partial x_j} + \partial_j \xi_j^* - \tau_{ij}^* \partial_j v_i^* - \\ - \varpi_{ij}^* \partial_j s_i^* - \epsilon_{ijk} s_i^* t_{jk}^* = \varrho^* \left(\varepsilon^* + r^*\right).\end{aligned} \tag{6.62}$$

Expressions similar to (5.42) and (6.49)–(6.62) were already derived by Condiff & Brenner [46] and later (statistically) by Blenk et al. [99], however with some slight differences. In the first work cited, the kinetic energy of spin and the power sources due to couple-stresses were subsumed in “generalized” expressions for the internal energy and heat flux, respectively. In the work of Blenk et al., which was concerned with thermotropic liquid crystals, interaction terms were ignored as well as the rotation of the rodlike molecules about their long-axes.

Finally, from (3.24)–(3.26), (5.41), (5.42) and the preceding arguments, immediately follows the entropy balance equation

$$\varrho^* \grave{\eta}^* + \frac{\partial \phi_i^*}{\partial x_i} + \partial_i \varphi_i^* = \varrho^* \varsigma^* + \varrho^* s^* , \tag{6.63}$$

where

$$\int_{\mathscr{S}^2} \varrho^* \eta^* \, d^2 n = \varrho \eta , \qquad \int_{\mathscr{S}^2} \varrho^* \varsigma^* \, d^2 n = \varrho \varsigma , \qquad \int_{\mathscr{S}^2} \varrho^* s^* \, d^2 n = \varrho s , \tag{6.64}$$

and

$$\varrho \eta v_i + \phi_i = \int_{\mathscr{S}^2} \left(\phi_i^* + \varrho^* \eta^* v_i^* \right) \, d^2 n . \tag{6.65}$$

Again, due to (6.50), $\varphi_i^* n_i = 0$ holds.

The results (5.42), (6.49), (6.61), (6.62) and (6.63) constitute the fundamental equations of the present theory.

7 Constitutive relations

A thermodynamic process in an homogeneous and monodisperse solution of rigid rodlike polymers will be characterized by the fields of

$$\begin{array}{ll} \varrho^*(x_i, t, n_j) & \text{partial mass density,} \\ v_i^*(x_j, t, n_k) & \text{partial velocity,} \\ s_i^*(x_j, t, n_k) & \text{partial spin,} \\ T(x_i, t) & \text{absolute temperature.} \end{array} \tag{7.66}$$

It is immediate to recognize that, at this stage, (5.42), (6.49), (6.61) and (6.62) cannot serve as a closed system for the basic fields (7.66), since these equations still contain many other unknown quantities. As commented in Sect. 3, to close the system one has to consider these additional quantities as material functions, that are related to the basic fields through constitutive relations. Such relations are furthermore constrained by the entropy principle, as expressed by (3.30) and (6.63), as well as the axiom of frame indifference. Thus, by considering a first order gradient theory, one can employ the rule of equipresence [100] to propose the following isotropic constitutive functional form

$$\begin{aligned} &\left\{ t_{ij}^*, \tau_{ij}^*, \kappa_i^*, m_{ij}^*, \varpi_{ij}^*, \nu_i^*, e^*, q_i^*, \xi_i^*, \varepsilon^*, \eta^*, \phi_i^*, \varphi_i^*, \delta^* \right\} = \\ &\qquad = \mathsf{F} \left(x_k, n_l, t; \varrho^\circ, T, v_m^\circ, S_{no}^\circ, \frac{\partial \varrho^\circ}{\partial x_p}, \frac{\partial T}{\partial x_q}, D_{rs}^\circ, W_{tu}^\circ, \frac{\partial s_v^\circ}{\partial x_w} \right) , \end{aligned} \tag{7.67}$$

where Ψ° denotes the set of values of the quantity Ψ^* in all points of the orientation space, i.e., $\Psi^\circ = \{\Psi^*(x_i, t, p_j) : p_j \in \mathscr{S}^2\}$, and

$$D_{ij}^* = \frac{\partial v_{(i}^*}{\partial x_{j)}} = \frac{1}{2} \left(\frac{\partial v_i^*}{\partial x_j} + \frac{\partial v_j^*}{\partial x_i} \right) , \qquad W_{ij}^* = \frac{\partial v_{[i}^*}{\partial x_{j]}} = \frac{1}{2} \left(\frac{\partial v_i^*}{\partial x_j} - \frac{\partial v_j^*}{\partial x_i} \right) \tag{7.68}$$

denote the partial tensor fields of strain-rate and vorticity, respectively.

Of course, the functional (7.67) is quite general and too difficult to handle. Searching for a rather more modest description, I will impose the following simplifying assumptions:

1. Invariance of material response with respect to inversions of the orientation vector n_i (i.e., fore-aft symmetry: rodlike molecules oriented anti-parallel to each other are assumed to be indistinguishable);
2. Exclusion of the functional dependence on gradients of density, provided that the elastic energy effects characteristic of the liquid crystalline phases are beyond the scope of the present isotropic theory;
3. Linearization of (7.67) with respect to partial spin and all gradients of the basic fields;
4. Neglect of infinitesimal memory effects associated with the history of the entire microstructure configuration by switching $S^{\circ}_{ij} \to S^{*}_{ij}$ on the set of constitutive variables;
5. Exclusion of the functional dependence on gradients of the spin, by assuming that S^{*}_{ij} is of the order of W^{*}_{ij} and, consequently, that $\partial s^{*}_{i}/\partial x_j$ is proportional to second order gradients;
6. Elision of translational diffusion effects by setting $\upsilon^{\circ}_{i} = \upsilon^{*}_{i} = \upsilon_i(x_j, t)$, in order to concentrate attention on the microstructure evolution driven by rotational diffusion phenomena.

The first two assumptions make clear that highly concentrated and optically active polymeric solutions are excluded from the present constitutive theory. Besides that, the last restrictions are conspicuously stronger than the first ones.

Additionally, the constitutive dependence on the instantaneous microstructure configuration (given by ϱ°) will be approximated in a coarse, but effective manner, through the splitting of it in two independent variables. These are namely the partial mass density ϱ^{*} of the "constituent" and its complementary *structure parameter* β^{*}, this last a non-dimensional quantity which drafts the current microstructure configuration with reference to the orientation n_i. Generically, it can be defined by

$$\beta^{*}\left(x_i, t, n_j\right) = \oint_{\mathscr{S}^2} \mathsf{B}\left(f^{*}_{(p)}, p_m, f^{*}, n_q\right) d^2 p, \tag{7.69}$$

with the functional B obeying the condition (which ensures that β^{*} is independent of ϱ^{*})

$$\mathsf{B}\left(f^{*}_{(p)}, p_m, f^{*}, n_q\right)\Big|_{p_i = n_i} = 0, \tag{7.70}$$

where $f^{*}\left(x_i, t, n_j\right)$ is (again) the mass fraction defined in (3.21), while $f^{*}_{(p)} = f^{*}\left(x_k, t, p_l\right)$. The definite form of the functional B depends on the character of the relevant microstructure interactions, usually modelled from microscopic considerations. An explicit expression for the functional B will not be necessary in the constitutive theory developed here (an illustrative expression for B, associated with the so-called *entanglement interactions*, can be found in the specializations discussed in Sect. 10).

After the simplifications above, (7.67) reads

$$\left\{t^{*}_{ij}, \tau^{*}_{ij}, \kappa^{*}_{i}, m^{*}_{ij}, \varpi^{*}_{ij}, \nu^{*}_{i}, e^{*}, q^{*}_{i}, \xi^{*}_{i}, \varepsilon^{*}, \eta^{*}, \phi^{*}_{i}, \varphi^{*}_{i}, \delta^{*}\right\} = \\ = \mathsf{G}\left(x_k, n_l, t; \varrho^{*}, T, \beta^{*}, \upsilon_m, S^{*}_{no}, \frac{\partial T}{\partial x_q}, D_{rs}, W_{tu}\right). \tag{7.71}$$

Further restrictions upon the constitutive functional (7.71) are imposed by the *principle of frame indifference* [100]. It rests upon the invariance (objectivity) of the constitutive functions with respect to non-inertial frame changes, which are given by the *Euclidean transformation*

$$\tilde{x}_i = O_{ij} x_j + b_i, \qquad \tilde{t} = t + \chi, \qquad \tilde{n}_i = O_{ij} n_j, \tag{7.72}$$

where $(\tilde{x}_i, \tilde{t}, \tilde{n}_j)$ and (x_i, t, n_j) denote position, time and orientation in two different frames of reference, with χ representing an arbitrary time shift, while $b_i(t)$ and $O_{ij}(t)$ denote arbitrary time-dependent vector- and orthogonal tensor-valued functions, respectively.

By using standard arguments, it is straightforward to derive from (7.72) the transformation rules

$$\tilde{\upsilon}_i = \dot{O}_{ij} x_j + O_{ij} \upsilon_j + \dot{b}_i, \qquad \tilde{D}_{ij} = O_{ik} O_{jl} D_{kl}, \tag{7.73}$$

$$\tilde{W}_{ij} = O_{ik} O_{jl} W_{kl} + \varOmega_{ij}, \qquad \tilde{S}^{*}_{ij} = O_{ik} O_{jl} S^{*}_{kl} + \varOmega_{ij}, \tag{7.74}$$

$$\tilde{T} = T\,, \qquad \frac{\partial \tilde{T}}{\partial \tilde{x}_i} = O_{ik}\frac{\partial T}{\partial x_k}\,, \qquad \tilde{\varrho}^* = \varrho^*\,, \qquad \tilde{\beta}^* = \beta^*\,, \tag{7.75}$$

$$\tilde{t}^*_{ij} = O_{ik}O_{jl}t^*_{kl}\,, \qquad \tilde{\tau}^*_{ij} = O_{ik}O_{jl}\tau^*_{kl}\,, \qquad \tilde{\kappa}^*_i = O_{ij}\kappa^*_j\,, \tag{7.76}$$

$$\tilde{m}^*_{ij} = sO_{ik}O_{jl}m^*_{kl}\,, \qquad \tilde{\varpi}^*_{ij} = sO_{ik}O_{jl}\varpi^*_{kl}\,, \qquad \tilde{\nu}^*_i = sO_{ij}\nu^*_j\,, \tag{7.77}$$

$$\tilde{e}^* = e^*\,, \qquad \tilde{q}^*_i = O_{ij}q^*_j\,, \qquad \tilde{\xi}^*_i = O_{ij}\xi^*_j\,, \qquad \tilde{\varepsilon}^* = \varepsilon^*\,, \tag{7.78}$$

$$\tilde{\eta}^* = \eta^*\,, \qquad \tilde{\phi}^*_i = O_{ij}\phi^*_j\,, \qquad \tilde{\varphi}^*_i = O_{ij}\varphi^*_j\,, \qquad \tilde{\delta}^* = \delta^*\,, \tag{7.79}$$

where $\varOmega_{ij} = \dot{O}_{ik}O_{jk}$, and $s = \text{sign}\left[\det\left(O_{ij}\right)\right]$, with $s = -1$ for improper transformations (inversions of frame), otherwise $s = 1$. Moreover, it should be recalled that

$$\delta_{ij} = O_{ik}O_{jk} = O_{ik}O_{jl}\delta_{kl} \qquad \text{and} \qquad \epsilon_{ijk} = sO_{il}O_{jm}O_{kn}\epsilon_{lmn}\,. \tag{7.80}$$

Therefore, exploiting the frame-indifference principle in the usual manner, one can easily conclude that the constitutive functions (7.71) cannot depend explicitly on x_i, t, v_i, S^*_{ij} and W_{ij}, implying a reformulation of the constitutive functional (7.71) to

$$\begin{aligned}\left\{t^*_{ij}, \tau^*_{ij}, \kappa^*_i, m^*_{ij}, \varpi^*_{ij}, \nu^*_i, e^*, q^*_i, \xi^*_i, \varepsilon^*, \eta^*, \phi^*_i, \varphi^*_i, \delta^*\right\} = &\\ = \mathsf{J}\left(n_l, \varrho^*, T, \beta^*, H^*_{mn}, \frac{\partial T}{\partial x_q}, D_{rs}\right)&,\end{aligned} \tag{7.81}$$

where H^*_{ij} is the partial field of the *relative spin tensor*, defined by

$$H^*_{ij}(x_l, t, n_k) = S^*_{ij} - W_{ij}\,. \tag{7.82}$$

It should be remarked that, due to (5.40) and $(7.68)_2$, $\epsilon_{ijk}n_iH^*_{jk} = 0$.

Explicit forms for the constitutive functions defined in (7.81) are summarized in the Appendix B. At this point, however, it may suffice to express explicitly only the constitutive dependence on the linearized variables D_{ij}, H^*_{ij} and $\partial T/\partial x_i$, viz.,

$$e^* = e^{*(1)} + e^{*I}_{ij}D_{ij}\,, \qquad \eta^* = \eta^{*(1)} + \eta^{*I}_{ij}D_{ij}\,, \qquad \varepsilon^* = \varepsilon^{*(1)} + \varepsilon^{*I}_{ij}D_{ij}\,, \tag{7.83}$$

$$q^*_i = q^{*I}_{ij}\frac{\partial T}{\partial x_j}\,, \qquad \phi^*_i = \phi^{*I}_{ij}\frac{\partial T}{\partial x_j}\,, \qquad \kappa^*_i = \kappa^{*I}_{ij}\frac{\partial T}{\partial x_j}\,, \tag{7.84}$$

$$\nu^*_i = \nu^{*(1)}\epsilon_{ijk}H^*_{jk} + \nu^{*(2)}\epsilon_{ijk}n_jD_{<kl>}n_l\,, \tag{7.85}$$

$$\varphi^*_i = \varphi^{*(1)}(n_in_j - \delta_{ij})D_{<jk>}n_k - \varphi^{*(2)}H^*_{ij}n_j\,, \tag{7.86}$$

$$\xi^*_i = \xi^{*(1)}(n_in_j - \delta_{ij})D_{<jk>}n_k - \xi^{*(2)}H^*_{ij}n_j\,, \qquad m^*_{ij} = m^{*I}_{ijk}\frac{\partial T}{\partial x_k}\,, \tag{7.87}$$

$$\tau^*_{ij} = \tau^{*I}_{ijk}\frac{\partial T}{\partial x_k}\,, \qquad \varpi^*_{ij} = \varpi^*\epsilon_{ijk}n_k + \varpi^{*(1)}n_i\epsilon_{jkl}H^*_{kl} + \varpi^{*I}_{ijkl}D_{kl}\,, \tag{7.88}$$

$$\begin{aligned}t^*_{ij} = -\left(p^* + p^{*I}_{kl}D_{kl}\right)\delta_{ij} + \sigma^*n_{<i}n_{j>} + \sigma^{*I}_{<ij>kl}D_{kl} + \sigma^{*II}_{<ij>kl}H^*_{kl} - &\\ - 2t^{*(1)}n_{[i}D_{<j]k>}n_k - 2t^{*(2)}n_{[i}H^*_{j]k}n_k - t^{*(3)}H^*_{ij}&,\end{aligned} \tag{7.89}$$

where the fore-aft symmetry of the molecules and the transformation properties (7.73)–(7.80) were already considered. Furthermore, in the representations above, all scalar transport coefficients are functions only of ϱ^*, T and β^*, while the tensorial ones present an additional dependence on the orientation n_i.

Finally, it should be remarked that no representation was proposed for δ^*. In fact, a linearization assumption for the entropy production deviation usually seems to be physically inconsistent. The reason is that this function is related by (3.29) to entropy production terms, which must be non-linear quantities even though the constitutive relations are assumed linear. The information enclosed in the non-linear part of δ^* could be called with no shame "the price of ignorance". Indeed, it is related to very complex microstructural interactions in non-dilute solutions, which are expected to be hardly described (when feasible) even by ingenious molecular models. As will be shown in the next sections, however, this price is actually not so high. The most important features of the material behavior can be derived without any reference to the non-linearity of δ^*, while for some simple cases the entropy production deviation can be readily neglected by plain physical arguments.

8 Exploitation of the entropy inequality

Insertion of (6.63) into (3.30) leads to the entropy inequality

$$\varrho^* \grave{\eta}^* + \frac{\partial \phi_i^*}{\partial x_i} + \partial_i \varphi_i^* - \varrho^* \delta^* - \varrho^* s^* \geq 0, \tag{8.90}$$

which must hold, according to the entropy principle and the production deviation theorem (see Sect. 3), for all thermodynamic processes.

To exploit the restrictions imposed by this inequality, I will employ the method of Lagrange multipliers proposed by Liu [47], which asserts that, for the case at hand, the following inequality should be valid for arbitrary values of the basic fields (7.66) (cf. (5.39), (5.40), (5.42), (6.49), (6.52), (6.61) and (6.62))

$$\begin{aligned} &\varrho^* \grave{\eta}^* + \frac{\partial \phi_i^*}{\partial x_i} + \partial_i \varphi_i^* - \varrho^* \delta^* - \Lambda^{*\varrho} \left(\grave{\varrho}^* + \varrho^* \frac{\partial v_i}{\partial x_i} + \varrho^* \partial_i S_{ij}^* n_j \right) - \\ &- \Lambda_i^{*v} \left(\varrho^* \dot{v}_i - \frac{\partial t_{ij}^*}{\partial x_j} - \partial_j \tau_{ij}^* - \varrho^* \kappa_i^* \right) - \Lambda_i^{*s} \left(\varrho^* I_{ij}^* \grave{s}_j^* - \varrho^* \frac{R^2}{2} S_{ij}^* n_j n_k \epsilon_{klm} \frac{\partial v_m}{\partial x_l} - \right. \\ &\left. - \frac{\partial m_{il}^*}{\partial x_l} - \partial_j \varpi_{ij}^* + \epsilon_{ijk} t_{jk}^* - \varrho^* \nu_i^* \right) - \Lambda^{*e} \left(\varrho^* \grave{e}^* + \frac{\partial q_j^*}{\partial x_j} - t_{ij}^* \frac{\partial v_i}{\partial x_j} - \right. \\ &\left. - m_{ij}^* \frac{\partial s_i^*}{\partial x_j} + \partial_j \xi_j^* - \varpi_{ij}^* \partial_j s_i^* - \epsilon_{ijk} s_i^* t_{jk}^* - \varrho^* \varepsilon^* \right) \geq 0. \end{aligned} \tag{8.91}$$

Without loss of generality, the balance equations were written here free of external supplies. As usual, it is assumed that the undetermined multipliers $\Lambda^{*\varrho}$, Λ_i^{*v}, Λ_i^{*s} and Λ^{*e} are functions of the same constitutive variables listed in (7.81).

By performing the derivatives presented in (8.91), one obtains an inequality which is explicitly linear in the quantities

$$\frac{\partial v_i}{\partial t}, \frac{\partial s_i^*}{\partial t}, \frac{\partial \varrho^*}{\partial t}, \frac{\partial \beta^*}{\partial t}, \frac{\partial T}{\partial t}, \frac{\partial D_{ij}}{\partial t}, \frac{\partial s_i^*}{\partial x_j}, \frac{\partial \varrho^*}{\partial x_i}, \frac{\partial \beta^*}{\partial x_i}, \frac{\partial^2 T}{\partial x_i \partial x_j}, \partial_i \varrho^*, \partial_i \beta^*, \partial_i H_{jk}^*.$$

Since the basic fields (7.66) are now arbitrary, so are the above derivatives, and in order to preserve the inequality (8.91) the coefficients of these derivatives must vanish. Consequently,

$$\Lambda_i^{*v} = 0, \qquad \Lambda_i^{*s} = \Lambda^{*s} n_i, \qquad m_{ij}^* = 0, \tag{8.92}$$

$$\frac{\partial \eta^*}{\partial \varrho^*} - \Lambda^{*e} \frac{\partial e^*}{\partial \varrho^*} = \frac{\Lambda^{*\varrho}}{\varrho^*}, \qquad \frac{\partial \eta^*}{\partial \beta^*} - \Lambda^{*e} \frac{\partial e^*}{\partial \beta^*} = 0, \tag{8.93}$$

$$\frac{\partial \eta^*}{\partial T} - \Lambda^{*e}\frac{\partial e^*}{\partial T} = 0, \qquad \frac{\partial \eta^*}{\partial D_{ij}} - \Lambda^{*e}\frac{\partial e^*}{\partial D_{ij}} = 0, \tag{8.94}$$

$$\frac{\partial \phi_i^*}{\partial \varrho^*} - \Lambda^{*e}\frac{\partial q_i^*}{\partial \varrho^*} = 0, \qquad \frac{\partial \phi_i^*}{\partial \beta^*} - \Lambda^{*e}\frac{\partial q_i^*}{\partial \beta^*} = 0, \tag{8.95}$$

$$\frac{\partial \phi_{(i}^*}{\partial T_{,j)}} - \Lambda^{*e}\frac{\partial q_{(i}^*}{\partial T_{,j)}} = 0, \qquad \frac{\partial \varphi_i^*}{\partial \varrho^*} - \Lambda^{*e}\frac{\partial \xi_i^*}{\partial \varrho^*} + \Lambda^{*s} n_j \frac{\partial \varpi_{ji}^*}{\partial \varrho^*} = 0, \tag{8.96}$$

$$\frac{\partial \varphi_i^*}{\partial \beta^*} - \Lambda^{*e}\frac{\partial \xi_i^*}{\partial \beta^*} + \Lambda^{*s} n_j \frac{\partial \varpi_{ji}^*}{\partial \beta^*} = 0, \tag{8.97}$$

$$\frac{\partial \varphi_i^*}{\partial H_{jk}^*} - \Lambda^{*e}\frac{\partial \xi_i^*}{\partial H_{jk}^*} + \Lambda^{*s} n_l \frac{\partial \varpi_{li}^*}{\partial H_{jk}^*} - \varrho^* \Lambda^{*\varrho} \delta_{i[j} n_{k]} = \frac{\Lambda^{*e}}{2} \epsilon_{jkl} \varpi_{li}^*, \tag{8.98}$$

where the abbreviation $T_{,i} = \partial T / \partial x_i$ was introduced. The remainder of the inequality (8.91) reads

$$\left(\frac{\partial \phi_i^*}{\partial T} - \Lambda^{*e}\frac{\partial q_i^*}{\partial T} \right) \frac{\partial T}{\partial x_i} - \varrho^* \Lambda^{*\varrho} D_{kk} + \Lambda^{*e} \left(t_{(ij)}^* D_{ij} - t_{[ij]}^* H_{ij}^* + \varrho^* \varepsilon^* \right) - \varrho^* \delta^* + \\ + \varrho^* \left(\hat{\partial}_i \eta^* - \Lambda^{*e} \hat{\partial}_i e^* \right) S_{ij}^* n_j + \hat{\partial}_i \varphi_i^* - \Lambda^{*e} \hat{\partial}_i \xi_i^* + \Lambda^{*s} n_i \, \hat{\partial}_j \varpi_{ij}^* \geq 0, \tag{8.99}$$

with $\hat{\partial}_i \mathfrak{Q}^* = (\partial_i \mathfrak{Q}^*)_{\varrho^*, \beta^*, H_{pq}^*}$ for any given constitutive quantity $\mathfrak{Q}^*$.

From (7.84) and $(8.96)_1$ immediately follows

$$\phi_{(ij)}^{*I} - \Lambda^{*e} q_{(ij)}^{*I} = 0. \tag{8.100}$$

However, according to (B.2), the general representation of the tensor q_{ij}^{*I} reads

$$q_{ij}^{*I} = -q^{*(1)} n_{<i} n_{j>} - \lambda^* \delta_{ij}, \tag{8.101}$$

where the thermal conductivities $q^{*(1)}$ and λ^* are functions of ϱ^*, β^* and T (a similar representation holds also for ϕ_{ij}^{*I}). Hence, $\phi_{[ij]}^{*I} = q_{[ij]}^{*I} = 0$ and

$$\phi_i^* = \Lambda^{*e} q_i^*, \tag{8.102}$$

with $\Lambda^{*e} = \Lambda^{*e}(\varrho^*, \beta^*, T)$.

Condition $(8.95)_1$, combined with (8.101) and (8.102), implies then

$$\lambda^* \frac{\partial \Lambda^{*e}}{\partial \varrho^*} = 0. \tag{8.103}$$

Therefore, excluding the unrealistic solution $\lambda^* = 0$, expression (8.103) constrains Λ^{*e} to $\Lambda^{*e}(\beta^*, T)$. Accomplishing the same procedure with $(8.95)_2$, one finally obtains

$$\Lambda^{*e} = \Lambda^e = \Lambda^e(T). \tag{8.104}$$

On the other hand, $(8.93)_2$ and $(8.94)_2$ combined with (8.104) read

$$\frac{\partial(\eta^* - \Lambda^e e^*)}{\partial \beta^*} = \frac{\partial(\eta^* - \Lambda^e e^*)}{\partial D_{ij}} = 0, \tag{8.105}$$

and hence, from $(8.94)_1$ and (8.105) ensues the condition

$$\frac{\partial(\eta^* - \Lambda^e e^*)}{\partial T} = -e^* \frac{\partial \Lambda^e}{\partial T}. \tag{8.106}$$

Refusing the possibility that Λ^e be a mere constant, (8.106) implies

$$e^* = e^*(\varrho^*, T), \qquad \eta^* = \eta^*(\varrho^*, T). \tag{8.107}$$

The final step towards the determination of Λ^e arises from the following arguments. First, recall that for the whole "mixture", which is assumed to be a customary polar fluid, there holds the Gibbs equation in its usual form [92, 98], and thereby also the well-known result

$$\frac{\partial(\varrho e)}{\partial T} = T\frac{\partial(\varrho\eta)}{\partial T}. \tag{8.108}$$

On the other hand, relations (6.57) and $(6.64)_1$ immediately allow one to express (8.108) in the integral form

$$\oint_{\mathscr{S}^2} \frac{\partial(\varrho^* e^*)}{\partial T}\, d^2n = T\oint_{\mathscr{S}^2} \frac{\partial(\varrho^*\eta^*)}{\partial T}\, d^2n. \tag{8.109}$$

Therefore, after multiplication of $(8.94)_1$ by ϱ^* and integration over all orientations, with further subtraction of the result from (8.109), one finally obtains

$$\Lambda^e(T) = \frac{1}{T}, \tag{8.110}$$

provided that $\partial e/\partial T \not= 0$.

Through the introduction of the *partial Helmholtz free energy*

$$\psi^* = e^* - T\eta^*, \tag{8.111}$$

one achieves to ascertain from $(8.93)_1$ one more undetermined multiplier, viz.

$$\Lambda^{*\varrho}(\varrho^*, T) = -\frac{\varrho^*}{T}\frac{\partial\psi^*}{\partial\varrho^*}. \tag{8.112}$$

On the other hand, with the help of (7.86)–(7.88), (8.98), (8.110) and (8.112), it is straightforward to infer that the derivative $\partial\varpi^*_{li}/\partial H^*_{jk}$ must vanish, independently of the value of Λ^{*s}, in order to satisfy (8.98) for arbitrary values of H^*_{ij}. Consequently, the left hand side of (8.98) becomes a function only of ϱ^*, β^*, T and n_i, implying that

$$\varpi^*_{ij} = \varpi^*\epsilon_{ijk}n_k, \tag{8.113}$$

with $\varpi^* = \varpi^*(\varrho^*, \beta^*, T)$. By inserting (8.110) and (8.113) into $(8.96)_2$ and (8.97) there results

$$\frac{\partial\iota^*_i}{\partial\varrho^*} = \frac{\partial\iota^*_i}{\partial\beta^*} = 0, \tag{8.114}$$

where $\iota^*_i = \varphi^*_i - \xi^*_i/T$. Hence, by considering (7.86) and $(7.87)_1$ there results the representation

$$\iota^*_i = \iota^{(1)}(n_i n_j - \delta_{ij})D_{<jk>}n_k - \iota^{(2)}H^*_{ij}n_j, \tag{8.115}$$

where both coefficients $\iota^{(1)}$ and $\iota^{(2)}$ are functions only of the temperature. Finally, (8.98) and (8.112)–(8.115) lead to

$$\varpi^*(\varrho^*, T) = \varrho^{*2}\frac{\partial\psi^*}{\partial\varrho^*} - T\iota^{(2)}. \tag{8.116}$$

This exhausts the consequences of the conditions (8.92)–(8.98). Notice that Λ^{*s} remains undetermined. This is in fact a natural consequence of the constraint (5.40).

9 Analysis of equilibrium

The *thermodynamic equilibrium* will be defined here as the state of maximum entropy attained by the medium when it moves in a rigid-body motion, with an uniform temperature field and in absence of internal interactions, i.e.

$$D_{ij}\big|_E = H^*_{ij}\big|_E = \left.\frac{\partial T}{\partial x_i}\right|_E = \delta^*\big|_E = \kappa^*_i\big|_E = \nu^*_i\big|_E = \varepsilon^*\big|_E = 0, \tag{9.117}$$

where $|_E$ denotes the equilibrium value of the respective quantity.

An immediate consequence of (9.117) is

$$\varepsilon^{*I} = 0, \qquad \text{and thence,} \qquad \varepsilon^* = \varepsilon^{*(1)} D_{kk} + \varepsilon^{*(2)} D_{<ij>} n_i n_j \,. \tag{9.118}$$

Moreover, from (9.118) and the results obtained in the last section, the inequality (8.99) reduces to

$$\begin{aligned}\varsigma^{*\mathrm{P}} = {} & \left[3T\iota^{(1)} + \sigma^* + \varrho^* \left(\varepsilon^{*(2)} - T\delta^{*(2)}\right)\right] D_{<ij>} n_i n_j + \\ & + \left[\varrho^{*2}\frac{\partial\psi^*}{\partial\varrho^*} - p^* + \varrho^*\left(\varepsilon^{*(1)} - T\delta^{*(1)}\right)\right] D_{kk} - \frac{q^{*I}_{ij}}{T}\frac{\partial T}{\partial x_j}\frac{\partial T}{\partial x_i} + \\ & + \sigma^{*I}_{<ij>kl} D_{kl} D_{<ij>} + \sigma^{*II}_{<ij>kl} H^*_{kl} D_{<ij>} - p^{*I}_{kl} D_{kl} D_{ii} + \\ & + 2t^{*(1)} n_i H^*_{ij} D_{jk} n_k + 2t^{*(2)} n_i H^*_{ij} H^*_{jk} n_k + t^{*(3)} H^*_{ij} H^*_{ij} - \varrho^* T \delta^{*NL} \geq 0,\end{aligned} \tag{9.119}$$

where the deviation δ^* was decomposed in linear and non-linear parts, viz.,

$$\delta^* = \delta^{*(1)} D_{kk} + \delta^{*(2)} D_{<ij>} n_i n_j + \delta^{*NL}, \tag{9.120}$$

with $\delta^{*(1)}$ and $\delta^{*(2)}$ being functions only of ϱ^*, β^* and T, while δ^{*NL} is non-linear in D_{ij}, H^*_{ij} and $\partial T/\partial x_i$. Of course, $\delta^{*NL}\big|_E = 0$ due to (9.117), and the requirement of fore-aft symmetry was already taken into account in (9.118) and (9.120).

An important consequence of the definition of equilibrium stated above is that the inequality (9.119) achieves its minimum value, namely zero, at this state. In other words,

$$\varsigma^{*\mathrm{P}}\big|_E \left(n_l, \varrho^*, T, \beta^*, H^*_{mn}, T_{,q}, D_{rs}\right) = \varsigma^{*\mathrm{P}}\left(n_l, \varrho^*, T, \beta^*, 0, 0, 0\right) = 0. \tag{9.121}$$

Necessary conditions for the occurrence of this minimum follow from the theory of extrema:

$$\left.\frac{\partial\varsigma^{*\mathrm{P}}}{\partial T_{,i}}\right|_E = 0, \qquad \left.\frac{\partial\varsigma^{*\mathrm{P}}}{\partial H^*_{ij}}\right|_E = 0, \qquad \left.\frac{\partial\varsigma^{*\mathrm{P}}}{\partial D_{ij}}\right|_E = 0, \tag{9.122}$$

and also the Hessian matrix

$$\left.\frac{\partial^2\varsigma^{*\mathrm{P}}}{\partial\mathscr{X}_A\partial\mathscr{X}_B}\right|_E \qquad \text{is positive semi-definite,} \tag{9.123}$$

where $\mathscr{X}_A = \{T_{,i}, H^*_{jk}, D_{pq}\}$ and $A = 1, 2, 3, \ldots, 12$. While $(9.122)_{1,2}$ are automatically satisfied, $(9.122)_3$ implies the relations

$$p^* = \varrho^{*2}\frac{\partial\psi^*}{\partial\varrho^*} + \varrho^*\left(\varepsilon^{*(1)} - T\delta^{*(1)}\right), \tag{9.124}$$

$$\sigma^* = -3T\iota^{(1)} - \varrho^*\left(\varepsilon^{*(2)} - T\delta^{*(2)}\right). \tag{9.125}$$

The first of them has a particular significance. Indeed, recalling that $C^*_i\big|_E = 0$, one immediately concludes from $(6.54)_3$ that

$$p = \oint_{\mathscr{S}^2} p^* \, d^2 n, \tag{9.126}$$

with $p(x_i, t)$ denoting the usual thermodynamic pressure. In addition, Eq. (6.60) together with (7.85) and (9.118) lead to

$$\oint_{\mathscr{S}^2} \varrho^* \varepsilon^{*(1)} \, d^2 n = 0. \tag{9.127}$$

On the other hand, from (3.27), (3.30) and (9.120) follows

$$\oint_{\mathscr{S}^2} \varrho^* \delta^{*(1)} \, d^2 n = 0. \tag{9.128}$$

The reason for this last result is that the entropy production of the whole ”mixture”, as given by (3.27), must be a positive semi-definite quadratic form in the (linearized) dissipative variables D_{ij}, H_{ij} and $\partial T / \partial x_i$. A non-vanishing value for the integral (9.128) could thus violate the inequality (3.27), especially for small deviations from equilibrium. Finally, rephrasing the arguments of the last section, once the whole ”mixture” is assumed to be a usual polar fluid, for which the Gibbs equation in its customary form applies, there holds the well-known relation

$$p = \varrho^2 \frac{\partial \psi}{\partial \varrho}, \tag{9.129}$$

where (due to (6.57), $(6.64)_1$ and (8.111))

$$\psi(x_i, t) = \oint_{\mathscr{S}^2} f^* \psi^* \, d^2 n, \tag{9.130}$$

is the Helmholtz free energy of the ”mixture”. Notice that the kinetic part of (6.57) was not taken into account in (9.130) since it is non-linear in S^*_{ij}, and therefore, negligible. Gathering the results (9.126)–(9.130) together, one obtains the identity

$$\varrho^2 \frac{\partial \psi}{\partial \varrho} = \oint_{\mathscr{S}^2} \varrho^{*2} \frac{\partial \psi^*}{\partial \varrho^*} \, d^2 n, \tag{9.131}$$

which imposes additional restrictions on the form of ψ^*. In particular, (9.131) suggests the introduction of another useful quantity, namely the *chemical potential* $\mu^*(x_i, t, n_j)$, defined by

$$\mu^* = \frac{\partial(\varrho^* \psi^*)}{\partial \varrho^*}, \qquad \text{with} \qquad p + \varrho\psi = \oint_{\mathscr{S}^2} \varrho^* \mu^* \, d^2 n, \tag{9.132}$$

the last result being inferred from (9.130) and (9.131). Finally, from (8.116), (9.124) and (9.132) one derives the identities

$$\varrho^* \left(\mu^* - \psi^*\right) = p^* - \varrho^* \left(\varepsilon^{*(1)} - T\delta^{*(1)}\right) = \varpi^* + T\iota^{(2)}. \tag{9.133}$$

The residual inequality then reads

$$\begin{aligned} \varsigma^{*\mathrm{p}} = {} & \sigma^{*I}_{<ij>kl} D_{kl} D_{<ij>} + \sigma^{*II}_{<ij>kl} H^*_{kl} D_{<ij>} - p^{*I}_{kl} D_{kl} D_{ii} + 2t^{*(1)} n_i H^*_{ij} D_{jk} n_k + \\ & + 2t^{*(2)} n_i H^*_{ij} H^*_{jk} n_k + t^{*(3)} H^*_{ij} H^*_{ij} - \frac{q^{*I}_{ij}}{T} \frac{\partial T}{\partial x_j} \frac{\partial T}{\partial x_i} - \varrho^* T \delta^{*NL} \geq 0. \end{aligned} \tag{9.134}$$

Due to the presence of δ^{*NL}, no further results can be extracted from (9.134) via (9.123). As commented before, this is the price to be paid by the inclusion of the deviation function δ^* in the theory. The analysis of the consequences of (9.123) on (9.134) will be therefore postponed to the particular cases considered in the next section.

10 On the microstructure evolution

The results $(8.92)_3$ and (8.113) suffice to rewrite the balance equation of partial spin (6.61) as

$$2t^*_{[ij]}n_j - \varrho^*\epsilon_{ijk}n_j\nu^*_k = \partial_i\varpi^* + \varrho^*\partial_i U^* - \varrho^*\epsilon_{ijk}n_j\left(I^*_{kl}s^*_l\right)^{\grave{}}, \tag{10.135}$$

where the extrinsic couple c^*_i was related to an external potential $U^*(x_i, t, n_j)$ through the relation $\epsilon_{ijk}n_jc^*_k = \partial_i U^*$. Accordingly, recalling (7.85), (7.89), (9.132), (9.133) and (10.135), one can straightforwardly obtain the transition rate

$$u^*_i = S^*_{ij}n_j = h^*_i - \frac{\mathscr{D}^{*(\mu)}}{\varrho^*}\left[\partial_i\left(\mu^* + U^*\right) - \epsilon_{ijk}n_j\left(I^*_{kl}s^*_l\right)^{\grave{}}\right], \tag{10.136}$$

where

$$h^*_i = W_{ij}n_j + B^*\left(D_{ij}n_j - n_jD_{jk}n_kn_i\right), \tag{10.137}$$

and

$$\mathscr{D}^{*(\mu)} = \frac{1}{2}\left(\frac{\nu^{*(1)}}{\varrho^*} + \frac{t^{*(3)} - t^{*(2)}}{\varrho^{*2}}\right)^{-1}, \qquad B^* = \mathscr{D}^{*(\mu)}\left(\frac{\nu^{*(2)}}{\varrho^*} + 2\frac{t^{*(1)}}{\varrho^{*2}}\right). \tag{10.138}$$

Moreover, the usual requirement of stability of the isotropic orientational distribution of the suspended molecules at equilibrium implies that $\mathscr{D}^{*(\mu)} \geq 0$.

Finally, the insertion of (10.136) into (5.42) leads, with the help of (9.132), to the *microstructure evolution equation*

$$\frac{\partial\varrho^*}{\partial t} = \partial_i\left(\mathscr{D}^{*(\varrho)}\partial_i\varrho^* + \mathscr{D}^{*(\mu)}\partial_i U^*\right) - \partial_i\left(\varrho^*h^*_i\right) - \frac{\partial}{\partial x_i}\left(\varrho^*\upsilon_i\right) - \partial_i\left[\mathscr{D}^{*(\mu)}\epsilon_{ijk}n_j\left(I^*_{kl}s^*_l\right)^{\grave{}}\right], \tag{10.139}$$

which is, apart from the last term on the right-hand side, an equation of the Fokker-Planck type for the partial density [101], h^*_i and υ_i playing the role of drift vectors, while the Fickian diffusion coefficient $\mathscr{D}^{*(\varrho)}$ is given by

$$\mathscr{D}^{*(\varrho)} = \mathscr{D}^{*(\mu)}\frac{\partial^2\left(\varrho^*\psi^*\right)}{\partial^2\varrho^*}. \tag{10.140}$$

The similarity between (10.136) and the contemporary generalizations of the empirical law of Fick, as found in the literature on diffusion [2, 10, 18, 24, 25], is striking. In particular, the inertial contribution in the last term on the right hand side of (10.136) is precisely responsible for the hyperbolic features of the evolution equation (10.139), which avoid a rotatory equivalent to the so-called "diffusion paradox" of the classical theory of mixtures, according to which small disturbances in concentration can propagate with infinite speed. By keeping this last term in (10.139), no rotatory diffusion paradox arises. Of course, this small inertial correction manifests itself only in the high-frequency range, tending to be unperceivable in the large time-scales of common rheological processes.

It should be remarked that (10.139) is also valid in the case of non-uniform and time-dependent thermodynamic fields. In fact, it is a continuum generalization of the usual evolution equations utilized in the framework of statistical rheology and molecular theory for dilute and semidilute solutions, as will become clear below. To facilitate the comparison with prior works, the common restriction to incompressible flows will be assumed from now on.

a) (Pseudo) non-ideal solutions According to the literature on chemical thermodynamics [102]–[104], the chemical potential μ^α of the α^{th} constituent of a mixture can be generally expressed by the formula

$$\mu^\alpha = K^\alpha T \ln\left(f^\alpha \gamma^\alpha\right) + \mu_0, \qquad K^\alpha = \frac{N_\mathrm{A} k_\mathrm{B}}{M^\alpha}, \tag{10.141}$$

where k_B is the Boltzmann constant, N_A the Avogadro number, M^α the molecular weight of the respective constituent, while f^α expresses its mass fraction, defined in (2.1). In addition, $\mu_0(\varrho, T)$ is a function only of the mixture variables and $\gamma^\alpha(\varrho^\beta, T)$ denotes the so-called *activity coefficient*. If γ^α is just a unit constant, then the behavior of the respective component is said *ideal*, otherwise it is called *non-ideal*. In most common cases, a non-unitary activity coefficient is ultimately related to microscopic interactions among the constituents of the mixture in such a manner that usually only dilute solutions can manifest ideal behavior.

Accepting that the notions just introduced remain valid for the case at hand, the definition (10.141) can be rewritten as

$$\mu^* = KT \ln\left(f^* \gamma^*\right) + \mu_0, \qquad K = \frac{N_\mathrm{A} k_\mathrm{B}}{M}, \tag{10.142}$$

with μ^*, f^*, γ^* and μ_0 having the same meaning of their standard counterparts presented above, while M is related to the molecular weight of the polymer in solution.

Therefore, after neglect of inertial effects by setting $R \to 0$ in (6.52), there follows from $(3.21)_2$, (9.132), (10.139), (10.140) and (10.142) the evolution equation

$$\frac{\partial f^*}{\partial t} = \partial_i \left(\mathscr{D}^{*(\varrho)} \partial_i f^* + \frac{f^* \mathscr{D}^*}{KT} \partial_i U^* \right) - \partial_i \left(f^* h_i^* \right) - \frac{\partial}{\partial x_i} \left(f^* v_i \right), \tag{10.143}$$

where

$$\mathscr{D}^{*(\varrho)} = \mathscr{D}^* \left(1 + \frac{\varrho^*}{\gamma^*} \frac{\partial \gamma^*}{\partial \varrho^*} \right), \qquad \mathscr{D}^* = \mathscr{D}^{*(\mu)} \frac{KT}{\varrho^*}. \tag{10.144}$$

Additionally, according to statistical theories [70, 72, 74], the diffusion coefficient $\mathscr{D}^*$ can be defined through

$$\mathscr{D}^* = \beta^{*-2} \mathscr{D}, \tag{10.145}$$

where $\mathscr{D}(\varrho, T)$ is the diffusion coefficient for an isotropic distribution of rods, while the structure parameter β^* is given explicitly by (cf. (7.69) and (7.70))

$$\beta^* \left(x_i, t, n_j \right) = \frac{4}{\pi} \oint_{\mathscr{S}^2} f^* \left(x_r, t, p_s \right) \sqrt{\epsilon_{ijk} \epsilon_{ipq} n_j n_p p_k p_q} \, d^2 p, \tag{10.146}$$

an expression derived from considerations about the topological interactions (*entanglements*) of the rodlike molecules.

Worthy of note is the fact that, due to (8.107), (8.111) and (9.132), the activity coefficient γ^* does not depend on the structure parameter β^*, i.e., it is insensitive to microstructural changes which maintain ϱ^* and T constant. On the other hand, the activity coefficient in semidilute suspensions of rigid rods should be fundamentally related to hydrodynamic as well as entanglement interactions, which hinder the rotatory Brownian motion of the polymer molecules in solution [70, 71]. Once these interactions necessarily depend on the microstructure configuration, it becomes evident that an independence of the activity coefficient on β^* can only occur if γ^* remains always very close to unity (consequently inferring an ideal behavior), except eventually for strongly aligned nematic configurations (e.g., promoted by an intense external field). In other words, a *pseudo non-ideal behavior* of the solution, induced by strong alignment, is allowed. A simple interpretation of this conjecture is afforded by the “mixture” representation: due to the large number of species and the relatively high dilution of the solution, the concentration of each “constituent” tends to remain low sufficient to uphold ideal behavior. Nonetheless, supposing that one of the “constituents” of the suspension achieves an overwhelming concentration, it can eventually exhibit some sensible deviation from ideality, manifested for instance in an abnormal increase of the diffusion coefficient. Notwithstanding, as discussed by Doi & Edwards [70, 74], the experimental corroboration of this hypothesis (e.g., through measurements of birefringence relaxation from the highly ordered state) is hindered by various factors, like chain flexibility, dipole-dipole interactions and other effects.

b) Ideal solutions In ideal solutions, interactions among the suspended molecules are negligible and the activity coefficient, introduced in (10.142), reduces simply to unity. Evidently, dilute solutions are classical examples of them. Moreover, the absence of microstructural interactions implicates a number of suitable simplifications on the whole theory, since

$$\delta^* = \kappa_i^* = \nu_i^* = \varepsilon^* = 0 \tag{10.147}$$

become valid. Concisely, some of the most important consequences are the reduction of the expressions (9.124), (9.133), (10.138) and (10.144) to

$$p^* = \varrho^{*2} \frac{\partial \psi^*}{\partial \varrho^*} = \varpi^* + T\iota^{(2)} = \varrho^* \left(\mu^* - \psi^*\right) \tag{10.148}$$

and

$$\mathscr{D}^{*(\varrho)} = \mathscr{D}^{*(\mu)} \frac{KT}{\varrho^*} = \frac{\varrho^* KT}{\zeta^*} = \mathscr{D}_0^*, \qquad \zeta^* = 2\left(t^{*(3)} - t^{*(2)}\right). \tag{10.149}$$

The residual inequality (9.134) can now be exploited in the usual manner to get information about the positiveness of some transport coefficients, like the shear viscosity and heat conductivity, in different orientations. In particular, one can find that $\zeta^* \geq 0$. Moreover, according to an old result of Jeffery [65] (see also [77, 105]), the relation

$$B^* = B = \frac{r^2 - 1}{r^2 + 1} \tag{10.150}$$

holds for (semi-)dilute suspensions of non-interacting rigid prolate ellipsoids of aspect ratio $r > 1$, with B being called the *shape factor*.

Hence, restricting attention only to incompressible flows with spatially-independent fields of partial density and negligible inertial effects of the microstructure, one can derive from $(3.21)_2$, (9.132), (10.139), (10.140), (10.142), (10.148), (10.149) and (10.150) the evolution equation

$$\frac{\partial f^*}{\partial t} = \partial_i \left(\mathscr{D}_0^* \partial_i f^* + \frac{f^* \mathscr{D}_0^*}{KT} \partial_i U^* \right) - \partial_i \left(f^* h_i^* \right), \tag{10.151}$$

which resembles well the kinetic equation adopted by Doi & Edwards [70] and Dahler et al. [72] for the dynamics of semidilute suspensions of rigid rodlike polymers, provided that the diffusion coefficient $\mathscr{D}_0^*$ is (again) given by

$$\mathscr{D}_0^* = \beta^{*-2} \mathscr{D}_0, \qquad \mathscr{D}_0 = \mathscr{D}_0(\varrho, T), \tag{10.152}$$

with β^* defined as in (10.146).

A further simplification of (10.149) can also be obtained by assuming

$$\zeta^* = f^* \zeta, \qquad \zeta = \zeta(\varrho, T), \tag{10.153}$$

which seems to be reasonable in the dilute regime. This assumption allows one to rewrite (10.151) as

$$\frac{\partial f^*}{\partial t} = \mathscr{D}_0 \, \partial_i \left(\partial_i f^* + \frac{f^*}{KT} \partial_i U^* \right) - \partial_i \left(f^* h_i^* \right), \tag{10.154}$$

which is readily recognized as the Smoluchowski equation proposed by Kirkwood and co-workers [62]–[64] for the rheology of dilute suspensions of rigid rodlike polymers, with the diffusion coefficient obeying the Stokes-Einstein relation

$$\mathscr{D}_0 = \frac{\varrho KT}{\zeta}. \tag{10.155}$$

11 Conclusion

Dry granular media (discussed in Sect. 1) and suspensions of slender rigid-bodies (studied in Sects. 5–10) are only two examples of thermodynamic systems for which the concept of mixture with continuous diversity can be fruitful.

For instance, the constitutive theory for suspensions of rigid rod-shaped macromolecules presented in this work was capable not only to reproduce the main results for the microstructural evolution of polymeric solutions usually derived by statistical methods, but also to predict possible effects due to rotatory inertia of the molecules and deviations from ideal behavior in a thermodynamically consistent manner. Evidently, still more realistic descriptions should also account for translational diffusion processes, inhomogeneities in concentration and polydispersity, which were for simplicity excluded in this first approach (although the technique to account for them was sketched along the text).

Natural extensions of the constitutive theory presented in Sects. 7–9 include, of course, liquid crystalline media and polycrystals. The thermodynamic description of such materials does not involve major conceptual difficulties, though a much more complex and exhaustive analysis, due to the account of elastic effects and long-range interactions. With respect to polycrystals, a particular virtue of the theory of mixtures with continuous diversity is that it yields an inherent framework for the study of recrystallization phenomena, by simply accounting for the mass production Γ^* (cf. (3.20)) in a similar way as done in usual theories of chemically reacting mixtures.

As a concluding remark (concerning multidisciplinary applications), while the classical theory of mixtures furnishes very prolific results in the population dynamics of a discrete number of interacting species [31]–[33], the fundamentals of the theory of mixtures with continuous diversity seems to be of great value in studies of biodiversity dynamics, particularly in tropical environments. For instance, Stork [106] reported 2800 species of arthropod collected from only ten trees belonging to five species in a rain forest of Borneo. Such a kind of data, which seem to be customary (see, e.g, [107, 108]), has led biologists to estimate about 27 million arthropod species living in the tropics today. This huge variety of species is a clear evidence of how effective the use of the formalism of mixtures with continuous diversity could be to study also the biodiversity dynamics in tropical rain forests.

Appendices

A Some consequences of the Stokes theorem

Intending to prove the compatibility between the completeness assumption (4.35) and the condition (6.50), one starts with the usual expression of the Stokes theorem on an unit spherical surface for an arbitrary (smooth) vector field $\mathfrak{A}_i^* = \mathfrak{A}_i^*(x_j, t, n_k)$, viz.,

$$\oint\limits_{\mathscr{S}^2} \epsilon_{ijk} n_i \frac{\partial \mathfrak{A}_k^*}{\partial n_j} \, d^2 n = 0. \tag{A.1}$$

Evidently, $\mathfrak{A}_i^*$ can be decomposed in orthogonal and parallel parts to n_i as

$$\mathfrak{A}_i^* = \epsilon_{ijk} n_j \mathfrak{B}_k^* + \mathfrak{C}^* n_i \,, \tag{A.2}$$

where $\mathfrak{B}_i^*$ and $\mathfrak{C}^*$ denote two arbitrary fields. With the help of (5.38), the insertion of (A.2) into (A.1) leads straightforward to

$$\oint\limits_{\mathscr{S}^2} \left(\partial_i \mathfrak{B}_i^* - 2 n_i \mathfrak{B}_i^* \right) \, d^2 n = 0. \tag{A.3}$$

Consequently, provided that (5.39) and (6.50) hold, (A.3) implies that

$$\oint\limits_{\mathscr{S}^2} \partial_i \left(\Psi^* u_i^* \right) \, d^2 n = \oint\limits_{\mathscr{S}^2} \partial_i \Upsilon_i^* \, d^2 n = 0, \tag{A.4}$$

which is just the proper form of the completeness assumption (4.35) in the orientation space $\mathscr{S}^2$.

Actually, (A.3) is a particularization of an useful identity which can be easily derived as follows. First, consider the generalization of the Stokes theorem (A.1) for an arbitrary (smooth) tensor field $\mathfrak{A}^*_{ijk\ldots lm} = \mathfrak{A}^*_{ijk\ldots lm}(x_p, t, n_q)$, viz.,

$$\oint_{\mathscr{S}^2} \epsilon_{ijk} n_i \frac{\partial \mathfrak{A}^*_{klm\ldots np}}{\partial n_j} \, d^2n = 0. \tag{A.5}$$

A generic decomposition, equivalent to (A.2), is not helpful in this case, due to the complexity of the resulting expression. Therefore, to simplify the calculations, one can restrict attention only to a particular class of tensors, given by

$$\mathfrak{A}^*_{klm\ldots np} = \mathfrak{B}^*_{lm\ldots n} \epsilon_{krp} n_r \,, \tag{A.6}$$

where $\mathfrak{B}^*_{lm\ldots n}$ is still an arbitrary tensor (of lower order). Further, inserting (A.6) into (A.5), there follows from (5.38)

$$\oint_{\mathscr{S}^2} \epsilon_{ijk} \epsilon_{krp} n_i \partial_j (\mathfrak{B}^*_{lm\ldots n} n_r) \, d^2n = 0, \tag{A.7}$$

which can be easily rewritten as

$$\oint_{\mathscr{S}^2} \left(\partial_i \mathfrak{B}^*_{jk\ldots l} - 2 n_i \mathfrak{B}^*_{jk\ldots l} \right) \, d^2n = 0. \tag{A.8}$$

This identity, named by Condiff & Brenner [46] the "specialized Green's theorem on a spherical surface", is essential in many calculations involving integrals of orientational gradients.

B Representations of constitutive functions

All polynomial representations presented below are derived from the representation theorems for isotropic functions found in the literature [109]–[111]. They are classified according to the transformation and invariance properties of their respective constitutive quantities (defined in Sect. 7). The tensor field $\mathfrak{Q}^*_{ij\ldots pq}$ denotes a generic constitutive quantity and its dependence on x_i and t is omitted here for brevity.

a) $\{e^*, \eta^*, \varepsilon^*\}$ Absolute scalar, $\mathfrak{Q}^*(n_i) = \mathfrak{Q}^*(-n_i)$:

$$\mathfrak{Q}^* = \mathfrak{Q}^{*(1)} + \mathfrak{Q}^{*(2)} D_{kk} + \mathfrak{Q}^{*(3)} n_i D_{ij} n_j \tag{B.1}$$

b) $\{q^*_i, \phi^*_i, \kappa^*_i\}$ Absolute vector, $\mathfrak{Q}^*_i(n_j) = \mathfrak{Q}^*_i(-n_j)$:

$$\mathfrak{Q}^*_i = \mathfrak{Q}^{*(1)} \frac{\partial T}{\partial x_i} + \mathfrak{Q}^{*(2)} n_i \frac{\partial T}{\partial x_j} n_j \tag{B.2}$$

c) $\{\nu^*_i\}$ Axial vector, $\mathfrak{Q}^*_i(n_j) = \mathfrak{Q}^*_i(-n_j)$:

$$\mathfrak{Q}^*_i = \mathfrak{Q}^{*(1)} \epsilon_{ijk} H^*_{jk} + \mathfrak{Q}^{*(2)} \epsilon_{ijk} n_j D_{<kl>} n_l \tag{B.3}$$

d) $\{\xi^*_i, \varphi^*_i\}$ Absolute vector, $\mathfrak{Q}^*_i n_i = 0$, $\mathfrak{Q}^*_i(n_j) = -\mathfrak{Q}^*_i(-n_j)$:

$$\mathfrak{Q}^*_i = \mathfrak{Q}^{*(1)} (n_i n_j - \delta_{ij}) D_{<jk>} n_k + \mathfrak{Q}^{*(2)} H^*_{ij} n_j \tag{B.4}$$

e) $\left\{t^*_{ij}\right\}$ Absolute tensor, $\mathfrak{Q}^*_{ij}(n_k) = \mathfrak{Q}^*_{ij}(-n_k)$:

$$\begin{aligned}\mathfrak{Q}^*_{ij} = &\left(\mathfrak{Q}^{*(1)} + \mathfrak{Q}^{*(2)}D_{kk} + \mathfrak{Q}^{*(3)}n_k D_{<kl>} n_l\right)\delta_{ij} + \mathfrak{Q}^{*(4)}D_{<ij>} + \\ &+\mathfrak{Q}^{*(5)}H^*_{ij} + \left(\mathfrak{Q}^{*(6)} + \mathfrak{Q}^{*(7)}D_{kk} + \mathfrak{Q}^{*(8)}n_k D_{<kl>} n_l\right) n_{<i} n_{j>} + \\ &+\left(\mathfrak{Q}^{*(9)} + \mathfrak{Q}^{*(10)}\right) n_i D_{<jk>} n_k + \left(\mathfrak{Q}^{*(9)} - \mathfrak{Q}^{*(10)}\right) n_j D_{<ik>} n_k + \\ &+\left(\mathfrak{Q}^{*(11)} + \mathfrak{Q}^{*(12)}\right) n_i H^*_{jk} n_k + \left(\mathfrak{Q}^{*(11)} - \mathfrak{Q}^{*(12)}\right) n_j H^*_{ik} n_k\end{aligned} \tag{B.5}$$

f) $\left\{m^*_{ij}\right\}$ Axial tensor, $\mathfrak{Q}^*_{ij}(n_k) = \mathfrak{Q}^*_{ij}(-n_k)$:

$$\mathfrak{Q}^*_{ij} = \mathfrak{Q}^{*(1)}\epsilon_{ijk}\frac{\partial T}{\partial x_k} + \mathfrak{Q}^{*(2)}\epsilon_{ijk}\frac{\partial T}{\partial x_l} n_l n_k + \mathfrak{Q}^{*(3)} n_{(i}\epsilon_{j)kl} n_k \frac{\partial T}{\partial x_l} \tag{B.6}$$

g) $\left\{\tau^*_{ij}\right\}$ Absolute tensor, $\mathfrak{Q}^*_{ij} n_j = 0$, $\mathfrak{Q}^*_{ij}(n_k) = -\mathfrak{Q}^*_{ij}(-n_k)$:

$$\mathfrak{Q}^*_{ij} = \mathfrak{Q}^{*(1)}\left(n_i n_j - \delta_{ij}\right)\frac{\partial T}{\partial x_k} n_k + \mathfrak{Q}^{*(2)}\frac{\partial T}{\partial x_k} n_{[i}\delta_{k]j} \tag{B.7}$$

h) $\left\{\varpi^*_{ij}\right\}$ Axial tensor, $\mathfrak{Q}^*_{ij} n_j = 0$, $\mathfrak{Q}^*_{ij}(n_k) = -\mathfrak{Q}^*_{ij}(-n_k)$:

$$\begin{aligned}\mathfrak{Q}^*_{ij} = &\left(\mathfrak{Q}^{*(1)} + \mathfrak{Q}^{*(2)}D_{kk} + \mathfrak{Q}^{*(3)}n_k D_{<kl>} n_l\right)\epsilon_{ijk} n_k + \\ &+\mathfrak{Q}^{*(4)} n_i \epsilon_{jkl} H^*_{kl} + \frac{1}{2}\left(\mathfrak{Q}^{*(5)} - \mathfrak{Q}^{*(6)}\right)\epsilon_{ijk} D_{<kl>} n_l + \\ &+\mathfrak{Q}^{*(5)} D_{k<i}\epsilon_{j>kl} n_l + \mathfrak{Q}^{*(6)} n_k n_{<i}\epsilon_{j>kl} D_{lp} n_p\end{aligned} \tag{B.8}$$

C List of symbols

For rapid reference, some notations and symbols frequently used in the text are listed below. The reader is assumed to be familiar with the usual notations of set theory and tensor calculus.

$\mathbb{R}$	Real numbers.
$\mathscr{E} = \mathbb{R}^3$	(3-dimensional) Euclidean space.
$\mathscr{A} = [\alpha_{\min}, \alpha_{\max}] \subset \mathbb{R}$	Species assemblage (unidimensional).
$\mathscr{M} = \mathscr{A}_1 \times \mathscr{A}_2 \times \cdots \times \mathscr{A}_M$	M-dimensional species assemblage.
$\mathscr{E} \times \mathbb{R}$	Standard Newtonian space-time of the classical mechanics.
$\mathscr{E} \times \mathbb{R} \times \mathscr{M}$	Space-time-assemblage.
$\mathscr{S}^2$	2-dimensional orientation space (unitary spherical surface embedded in $\mathbb{R}^3$).
$\upsilon^\alpha_i(x_j, t)$, $\upsilon^*_i(x_j, t, \alpha_J)$	Translational velocity of the constituent, for a usual mixture and a mixture with continuous diversity, respectively.
$\Psi^\alpha(x_i, t)$, $\Psi^*(x_i, t, \alpha_I)$	Density of some arbitrary additive quantity of the constituent, for a usual mixture and a mixture with continuous diversity, respectively.
$\Phi^\alpha_i(x_j, t)$, $\Phi^*_i(x_j, t, \alpha_J)$	Non-convective fluxes of the quantities $\Psi^\alpha(x_i, t)$ and $\Psi^*(x_i, t, \alpha_I)$, respectively.
$\Xi^\alpha(x_i, t)$, $\Xi^*(x_i, t, \alpha_I)$	Production densities of the quantities $\Psi^\alpha(x_i, t)$ and $\Psi^*(x_i, t, \alpha_I)$, respectively.
$\Sigma^\alpha(x_i, t)$, $\Sigma^*(x_i, t, \alpha_I)$	External supply densities of the quantities $\Psi^\alpha(x_i, t)$ and $\Psi^*(x_i, t, \alpha_I)$, respectively.
$\Upsilon^*_I(x_j, t, \alpha_J)$ $(I = 1, 2, \ldots, M)$	(M-dimensional) interspecies flux of the quantity $\Psi^*(x_j, t, \alpha_J)$.
$u^*_I(x_j, t, \alpha_J)$ $(I = 1, 2, \ldots, M)$	(M-dimensional) transition rate.
$\partial_i = \dfrac{\partial}{\partial n_i} - n_i n_j \dfrac{\partial}{\partial n_j}$	Orientational gradient operator (5.38).
$\grave{\mathfrak{A}}^* = \dfrac{\partial \mathfrak{A}^*}{\partial t} + \upsilon^*_i \dfrac{\partial \mathfrak{A}^*}{\partial x_i} + u^*_k \partial_k \mathfrak{A}^*$	Co-transitional time derivative (5.41) of the arbitrary tensor field $\mathfrak{A}^*$.
$\dot{\mathfrak{A}} = \dfrac{\partial \mathfrak{A}}{\partial t} + \upsilon_j \dfrac{\partial \mathfrak{A}}{\partial x_j}$	Material time derivative (6.47) of the arbitrary tensor field $\mathfrak{A}$.

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References

1. Asimov I (1979) A short history of chemistry. Westport: Greenwood
2. Eckart C (1940) The thermodynamics of irreversible processes II: fluid mixtures. Phys. Rev. 58: 269–275
3. Prigogine I (1945) Modération et transformations irréversibles des systèmes ouverts. Bull. Cl. Sci., Acad. R. Belg. 31: 600–606
4. Truesdell C (1957) Sulle basi della termomeccanica. Rend. Fis. Acc. Lincei Series VIII 22: 33–38, 158–166
5. Truesdell C, Toupin R (1960) The classical field theories. In: Flügge S (Ed.) Handbuch der Physik, III/3, pp. 226–793. Berlin: Springer
6. Kelly PD (1964) A reacting continuum. Int. J. Engng. Sci. 2: 129–153
7. Eringen AC, Ingram JD (1965) A continuum theory of chemically reacting media I. Int. J. Engng. Sci. 3: 197–212
8. Green AE, Naghdi PM (1965) A dynamical theory of interacting continua. Int. J. Engng. Sci. 3: 231–241
9. Bowen RM (1967) Toward a thermodynamics and mechanics of mixtures. Arch. Rat. Mech. Anal. 24: 370–403
10. Müller I (1968) A thermodynamic theory of mixtures of fluids. Arch. Rat. Mech. Anal. 28: 1–39
11. Dunwoody NT, Müller I (1968) A thermodynamic theory of two chemically reacting ideal gases with different temperatures. Arch. Rat. Mech. Anal. 29: 344–369
12. Allen SJ, Kline KA (1969) A theory of mixtures with microstructure. J. Appl. Math. Phys. (ZAMP) 20: 145–155
13. Bowen RM, Garcia DJ (1970) On the thermodynamics of mixtures with several temperatures. Int. J. Engng. Sci. 8: 68–83
14. Green AE, Laws N (1971) Global properties of mixtures. Arch. Rat. Mech. Anal. 43: 45–61
15. Gurtin ME (1971) On the thermodynamics of chemically reacting fluid mixtures. Arch. Rat. Mech. Anal. 43: 198–212
16. Twiss RJ, Eringen AC (1971) Theory of mixtures for Micromorphic materials – I: balance laws. Int. J. Engng. Sci. 9: 1019–1044
17. Hutter K, Müller I (1975) On mixtures of relativistic fluids. Helv. Phys. Acta 48: 675–698
18. Müller I (1975) Thermodynamics of mixtures of fluids. J. Mécanique 14: 267–303
19. Bowen RM (1976) Theory of mixtures. In: Eringen AC (Ed.) Continuum physics, III, pp. 1–127. New York: Academic Press
20. Pop JJ, Bowen RM (1978) A theory of mixtures with a long range spatial interaction. Acta Mechanica 29: 21–34
21. Sampaio R, Williams WO (1979) Thermodynamics of diffusing mixtures. J. Mécanique 18: 19–45
22. Nunziato JW, Walsh EK (1980) On ideal multiphase mixtures with chemical reactions and diffusion. Arch. Rat. Mech. Anal. 73: 285–311
23. Bedford A, Drumheller DS (1983) Theories of immiscible and structured mixtures. Int. J. Engng. Sci. 21: 863–960
24. Truesdell C (1984) Rational thermodynamics, 2nd Edn. New York: Springer
25. Müller I (1985) Thermodynamics. London: Pitman
26. Svendsen B, Hutter K (1995) On the thermodynamics of a mixture of isotropic materials with constraints. Int. J. Engng. Sci. 33: 2021–2054
27. Wilmański K (1998) Thermomechanics of continua. Berlin: Springer
28. Drew DA, Passman SL (1999) Theory of multicomponent fluids. New York: Springer
29. Turing AM (1952) The chemical basis of morphogenesis. Phil. Trans. Roy. Soc. London B 237: 37–72
30. Nicolis G, Prigogine I (1977) Self-organization in nonequilibrium systems. New York: Wiley
31. Okubo A (1980) Diffusion and ecological problems: mathematical models. Berlin: Springer
32. Murray JD (1993) Mathematical biology, 2nd Edn. Berlin: Springer
33. Müller I (2001) Integration and segregation in a population – a thermodynamicists's view. To appear in: Straughan B, Greve R, Ehrentraut H, Wang Y (Eds.) Continuum mechanics and applications in geophysics and the environment. Heidelberg: Springer
34. Hutter K, Rajagopal KR (1994) On flows of granular materials. Continuum Mech. Thermodyn. 6: 81–139
35. Gray JMNT, Hutter K (1997) Pattern formation in granular avalanches. Continuum Mech. Thermodyn. 9: 341–345
36. Gray JMNT, Tai YC (1998) Particle size segregation, granular shocks and stratification patterns. In: Herrmann HJ, Hovi J-P, Luding S (Eds.) Physics of dry granular media (NATO science series: E), pp. 697–702. Dordrecht: Kluwer
37. Hutter K (1999) Order and disorder in granular materials. In: Hutter K, Wilmański K (Eds.) Kinetic and continuum theories of granular and porous media (CISM courses and lectures series), pp. 1–65. Wien: Springer
38. Savage SB, Lun CKK (1988) Particle size segregation in inclined chute flow of dry cohesionless granular solids. J. Fluid Mech. 189: 311–335
39. Kirchner NP, Hutter K (2001) Thermodynamic modelling of granular continua exhibiting quasi-static frictional behavior with abrasion. To appear in: Capriz G, Ghionna G, Giovine G (Eds.) Mathematical models of granular and porous materials (modelling and simulation in science, engineering and technology series). Basel: Birkhäuser
40. Volterra V (1887) Sopra le funzioni che dipendono da altre funzioni. R. Acc. Lincei Rend. 3: 97–105, 141–146, 153–158
41. Whittaker ET (1941) Vito Volterra. Obituary Notices of Fellows of the Roy. Soc. London 3: 619–729
42. Hadamard J (1903) Sur les opérations fonctionnelles. C. R. Acad. Sci. (Paris) 136: 351–354
43. Hadamard J (1910) Leçons sur le calcul des variations. Paris: Hermann
44. Prager S (1955) Interaction of rotational and translational diffusion. J. Chem. Phys. 23: 2404–2407
45. Curtiss CF (1956) Kinetic theory of nonspherical molecules. J. Chem. Phys. 24: 225–241
46. Condiff DW, Brenner H (1969) Transport mechanics in systems of orientable particles. Phys. Fluids 12: 539–551
47. Liu I-S (1972) Method of Lagrange multipliers for exploitation of the entropy principle. Arch. Rat. Mech. Anal. 46: 131–148

48. Eringen AC (1972) On nonlocal fluid mechanics. Int. J. Engng. Sci. 10: 561–575
49. Edelen DGB (1976) Nonlocal field theories. In: Eringen AC (Ed.) Continuum physics, IV, pp. 75–204. New York: Academic Press
50. Müller I, Ruggeri T (1998) Rational extended thermodynamics, 2nd Edn. New York: Springer
51. Kremer GM, Müller I (1998) Thermal conductivity and dynamic pressure in extended thermodynamics of chemically reacting mixture of gases. Ann. Inst. H. Poincaré (Phys. Theor.) 69: 309–334
52. Müller I (1967) On the entropy inequality. Arch. Rat. Mech. Anal. 26: 118–141
53. Marsden JE, Hughes TJR (1983) Mathematical foundations of elasticity. Englewood Cliffs: Prentice-Hall
54. Dreyer W (1987) Maximisation of the entropy in non-equilibrium. J. Phys. A: Math. Gen. 20: 6505–6517
55. Ferry JD (1970) Viscoelastic properties of polymers, 2nd Edn. New York: Wiley
56. Zero KM, Pecora R (1982) Rotational and translational diffusion in semidilute solutions of rigid-rod macromolecules. Macromolecules 15: 87–93
57. Peterlin A, Stuart HA (1939) Zur Theorie der Strömungsdoppelbrechung von Kolloiden und großen Molekülen in Lösung. Z. Phys. 112: 1–19
58. Peterlin A, Stuart HA (1939) Über die Bestimmung der Größe und Form, sowie der elektrischen, optischen und magnetischen Anisotropie von submikroskopischen Teilchen mit Hilfe der künstlichen Doppelbrechung und der inneren Reibung. Z. Phys. 112: 129–147
59. Odell JA, Keller A, Atkins EDT (1985) Diffusion and orientability of rigid-rodlike molecules in solution. Macromolecules 18: 1443–1453
60. Berne BJ, Pecora R (1976) Dynamic light scattering. New York: Wiley
61. Lehner D, Lindner H, Glatter O (2000) Determination of the translational and rotational diffusion coefficients of rodlike particles using depolarized dynamic light scattering. Langmuir 16: 1689–1695
62. Riseman J, Kirkwood JG (1950) The intrinsic viscosity, translational and rotatory diffusion constants of rod-like macromolecules in solution. J. Chem. Phys. 18: 512–516
63. Kirkwood JG, Auer PL (1951) The visco-elastic properties of solutions of rod-like macromolecules. J. Chem. Phys. 19: 281–283
64. Kirkwood JG, Plock RJ (1956) Non-Newtonian viscoelastic properties of rod-like macromolecules in solution. J. Chem. Phys. 24: 665–669
65. Jeffery GB (1922) The motion of ellipsoidal particles immersed in a viscous fluid. Proc. Roy. Soc. London A 102: 161–179
66. Burgers JM (1938) On the motion of small particles of elongated form suspended in a viscous liquid. In: Second report on viscosity and plasticity, Ch. III, Kon. Ned. Akad. Wet. (Erste Sectie) 16: 113–184
67. Kuhn W, Kuhn H (1945) Die Abhängigkeit der Viskosität vom Strömungsgefälle bei hochverdünnten Suspensionen und Lösungen. Helv. Chim. Acta 28: 97–127
68. Prager S (1957) Stress-strain relations in a suspension of dumbbells. Trans. Soc. Rheol. 1: 53–62
69. Kotaka T (1959) Note on the normal stress effect in the solution of rodlike molecules. J. Chem. Phys. 30: 1566–1567
70. Doi M, Edwards SF (1978) Dynamics of rod-like macromolecules in in concentrated solution. J. Chem. Soc., Faraday Trans. II 74: 560–570, 918–932
71. Fesciyan S, Dahler JS (1982) Screened hydrodynamic interactions in a semidilute solution of rodlike macromolecules. Macromolecules 15: 517–520
72. Dahler JS, Fesciyan S, Xystris N (1983) Rheological properties of a semidilute solution of rodlike macromolecules II: transient flows. Macromolecules 16: 1673–1677
73. Bird RB, Hassager O, Armstrong RC, Curtiss CF (1977) Dynamics of polymeric liquids, I and II. New York: Wiley
74. Doi M, Edwards SF (1986) The theory of polymer dynamics. Oxford: Oxford University Press
75. Larson RG (1988) Constitutive equations for polymer melts and solutions. Boston: Butterworths
76. Beris AN, Edwards BJ (1994) Thermodynamics of flowing systems with internal structure. Oxford: Oxford University Press
77. Brenner H (1974) Rheology of a dilute suspension of axisymmetric Brownian particles. Int. J. Multiphase Flow 1: 195–341
78. Petrie CJS (1999) The rheology of fibre suspensions. J. Non-Newton. Fluid Mech. 87: 369–402
79. Leal LG, Hinch EJ (1971) The effect of weak Brownian rotations on particles in shear flow. J. Fluid Mech. 46: 685–703
80. Leal LG, Hinch EJ (1973) Theoretical studies of a suspension of rigid particles affected by Brownian couples. Rheol. Acta 12: 127–132
81. Hinch EJ, Leal LG (1972) The effect of Brownian motion on the rheological properties of a suspension of non-spherical particles J. Fluid Mech. 52: 683–712
82. Hinch EJ, Leal LG (1973) Time-dependent shear flows of a suspension of particles with weak Brownian rotations. J. Fluid Mech. 57: 753–767
83. Duhem P (1893) Le potentiel thermodynamique et la pression hydrostatique. Ann. Sci. École Norm. Sup. 10: 187–230
84. Cosserat E, Cosserat F (1909) Théorie des corps déformables. Paris: Hermann
85. Ericksen JL (1960) Anisotropic fluids. Arch. Rational Mech. Anal. 4: 231–237
86. Green AE, Naghdi PM, Rivlin RS (1965) Directors and multipolar displacements in continuum mechanics. Int. J. Engng. Sci. 2: 611–620
87. Leslie FM (1992) Continuum theory of nematic liquid crystals. Continuum Mech. Thermodyn. 4: 167–175
88. Hand GL (1962) A theory of anisotropic fluids. J. Fluid Mech. 13: 33–47
89. Maugin GA, Drouot R (1983) Internal variables and the thermodynamics of macromolecule solutions. Int. J. Engng. Sci. 21: 705–724
90. MacMillan EH (1989) Slow flows of anisotropic fluids. J. Rheol. 33: 1071–1105
91. Cowin SC (1974) The theory of polar fluids. Adv. Appl. Mech. 14: 279–347
92. Leslie FM (1979) On the thermodynamics of polar fluids. Arch. Rational Mech. Anal. 70: 189–202
93. Eringen AC (2000) A unified continuum theory for electrodynamics of polymeric liquid crystals. Int. J. Engng. Sci. 38: 959–987

94. Grad H (1952) Statistical mechanics, thermodynamics and fluid dynamics of systems. Commun. Pure Appl. Math. 5: 455–494
95. Condiff DW, Dahler JS (1964) Fluid mechanical aspects of antisymmetric stress. Phys. Fluids 7: 842–854
96. Eringen AC, Kafadar CB (1976) Polar field theories. In: Eringen AC (Ed.) Continuum physics, IV, pp. 1–73. New York: Academic Press
97. Gaio DC, Kremer GM (1991) Kinetic theory for polyatomic dense gases of rough spherical molecules. J. Non-Eq. Thermodyn. 16: 357–379
98. Faria SH, Kremer GM (1997) Some aspects in the thermodynamic theory of polar fluids. ARI 50: 105–109; Corrigendum ibid. (1998) 51: 103
99. Blenk S, Ehrentraut H, Muschik W (1991) Statistical foundation of macroscopic balances for liquid crystals in alignment tensor formulation. Physica A 174: 119–138
100. Truesdell C, Noll W (1965) The nonlinear field theories of mechanics. In: Flügge S (Ed.) Handbuch der Physik, III/3. Berlin: Springer
101. Risken H (1996) The Fokker-Planck equation, 2nd Edn. Berlin: Springer
102. Denbigh K (1959) Prinzipien des chemischen Gleichgewichts. Translated by HJ Oel and W Jost. Darmstadt: Steinkopff
103. Lewis GN, Randall M (1961) Thermodynamics, 2nd Edn. Revised by KS Pitzer and L Brewer. New York: McGraw-Hill
104. Sage BH (1965) Thermodynamics of multicomponent systems. New York: Reinhold
105. Peterlin A (1938) Über die Viskosität von verdünnten Lösungen und Suspensionen in Abhängigkeit von der Teilchenform. Z. Phys. 111: 232–263
106. Stork NE (1988) Insect diversity: facts, fiction and speculation. Biol. J. Linnean Soc. 35: 321–337
107. May RM (1990) How many species? Phil. Trans. Roy. Soc. London B 330: 293–304
108. Rosenzweig ML (1996) Species diversity in space and time. Cambridge: Cambridge University Press
109. Wang C-C (1970) A new representation theorem for isotropic functions. Arch. Rational Mech. Anal. 36: 166–197, 198–223; Corrigendum ibid. (1971) 43: 392–395
110. Smith GF (1971) On isotropic functions of symmetric tensors, skew-symmetric tensors and vectors. Int. J. Engng. Sci. 9: 899–916
111. Spencer AJM (1971) Theory of invariants. In: Eringen AC (Ed.) Continuum physics, I, pp. 239–353. New York: Academic Press