arXiv:cond-mat/9904312v1 [cond-mat.soft] 22 Apr 1999

To appear in: *Zeitschrift für angewandte Mathematik und Physik*

Microforces and the Theory of Solute Transport

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Abstract

A generalized continuum framework for the theory of solute transport in fluids is proposed and systematically developed. This framework rests on the introduction of a generic force balance for the solute, a balance distinct from the macroscopic momentum balance associated with the mixture. Special forms of such a force balance have been proposed and used going back at least as far as Nernst's 1888 theory of diffusion. Under certain circumstances, this force balance yields a Fickian constitutive relation for the diffusive solute flux, and, in conjunction with the solute mass balance, provides a generalized Smoluchowski equation for the mass fraction. Our format furnishes a systematic procedure for generalizing convection-diffusion models of solute transport, allowing for constitutive nonlinearities, external forces acting on the diffusing constituents, and coupling between convection and diffusion.

1 Introduction

The transport of a solute in an incompressible fluid mixture of *density* ϱ is commonly modeled by the convection-diffusion equation[1]

$$\dot{c} = div\,\big(D(c)\,grad\,c\big), \tag{1.1}$$

with c the *solute mass fraction* and $D \geq 0$ the mass fraction-dependent *diffusivity*. This equation is often derived (see, for example, Landau & Lifshitz [1], de Groot & Mazur [2], and Cussler [3]) by adjoining to the solute mass balance

$$\varrho\dot{c} = -div\,\boldsymbol{\jmath}, \tag{1.2}$$

a constitutive relation

$$\boldsymbol{\jmath} = -\varrho D(c)\,grad\,c \tag{1.3}$$

of the sort proposed by Fick [4] for the *diffusive solute flux* $\boldsymbol{\jmath}$.

Here, we propose and systematically develop an alternative approach to solute transport. Our approach is based on the viewpoint that to each independent kinematic process there should correspond a system of power-conjugate forces subject to a distinct force

[1] Here, the operations of material and spatial time-differentiation are denoted with a superposed dot and a superposed grave accent, respectively; thus, for instance, $\dot{c} = \grave{c} + \boldsymbol{v}\cdot grad\,c$, with $\boldsymbol{v}$ being the *mixture velocity*.

balance.[2] Specifically, in the context of solute transport, *we identify mixture convection and solute diffusion as independent kinematic processes*: mixture convection is a macroscopic phenomenon described kinematically by the convective mixture velocity $\boldsymbol{v}$, whereas solute diffusion is a microscopic phenomenon described kinematically at a continuum level by the diffusive solute flux $\boldsymbol{\jmath}$, an object that measures the motion of solute particles relative to the macroscopic motion of the mixture comprised of solute and solvent. Further, to account for power expenditures associated with the diffusive motion of atoms, we introduce at a continuum level a system of forces conjugate to the diffusive solute flux $\boldsymbol{\jmath}$. Since they are associated with the microscopic processes governing the diffusion of the solute, we use the expression "microforce" to identify these forces. Additionally, we require that these microforces be consistent with a *solute microforce balance*. This balance is a postulate ancillary to the conventional momentum balance, which involves the forces that act power conjugate to the convective mixture velocity $\boldsymbol{v}$. Importantly, we do not assume that the diffusive solute flux $\boldsymbol{\jmath}$ is determined by a constitutive relation—Fickian or otherwise. Rather, *we treat $\boldsymbol{\jmath}$ as an independent kinematic variable whose evolution is governed by the microforce balance*.

There is ample historical precedence for basing solute transport on additional, independent force balances. Nernst [16], following upon van't Hoff's [17] analogy between the *osmotic pressure* ϖ of the molecules of a sufficiently dilute solute and the pressure of an ideal gas, viewed diffusion as driven by osmotic pressure gradients and developed a theory of diffusion based on a balance of forces acting on the solute molecules. Nernst proposed such force balances to account for the influences of osmotic, viscous, electrostatic, gravitational, centrifugal, and magnetic forces. For example, for electrolyte solutions, Nernst assumed separate force balances for the positive and negative ions. Subsequently Planck [18] also exploited these ideas in his work on electrolyte solutions. Further, in developing his theory of Brownian motion, Einstein [19, 20, 21] employed force balances on the Brownian particles. Neglecting the inertia of the diffusing solute, we may write Nernst's solute force balance as

$$\boldsymbol{h} + \boldsymbol{\ell} = \frac{1}{n}\, \mathrm{grad}\, \varpi = \frac{M}{\varrho c}\, \mathrm{grad}\, \varpi, \tag{1.4}$$

wherein $\boldsymbol{h}$ is the *hydrodynamic drag force* acting on the solute particles during motion through the solvent, $\boldsymbol{\ell}$ represents the *external forces* acting on the solute particles, M is the *molecular weight* of the solute, and n is the number density—so that the right-hand side of (1.4) can be interpreted as the *osmotic force* per solute particle. Typically the hydrodynamic drag force is taken to be linear in the solute velocity relative to the mixture, whereby

$$\boldsymbol{h} = -\zeta \boldsymbol{\jmath}, \tag{1.5}$$

with ζ a non-negative coefficient called the *frictional resistance* and ζ^{-1} called the *mobility*.[3] For an ideal solution, the *osmotic pressure* ϖ is linear in the number density n, that is

$$\varpi = k_{\mathrm{B}} \theta n = \frac{\varrho k_{\mathrm{B}} \theta c}{M}, \tag{1.6}$$

[2] A foundation for this viewpoint can be devised using the *principle of virtual power*, see, for example, Germain [5], Antman & Osborn [6], Maugin [7], and Frémond [8]. We follow here an alternative, but essentially equivalent, approach taken by Ericksen [9], Goodman & Cowin [10], Capriz & Podio-Guidugli [11], Capriz [12], Fried & Gurtin [13], Fried [14], and Gurtin [15].

[3] Since we take the solute flux $\boldsymbol{\jmath}$ as a generalized velocity, our definitions of frictional resistance and mobility differ from the usual ones by a factor of ϱc.

with k_{B} being *Boltzmann's constant* and θ being the *absolute temperature*. Thus, in an isothermal, constant density mixture,

$$grad\, \varpi = k_{\mathrm{B}}\theta\, grad\, n = \frac{\varrho k_{\mathrm{B}}\theta}{M} grad\, c, \tag{1.7}$$

which, in conjunction with (1.4) leads to the flux

$$\boldsymbol{\jmath} = -\frac{k_{\mathrm{B}}\theta}{c\zeta}\, grad\, c + \frac{\boldsymbol{\ell}}{\zeta}. \tag{1.8}$$

Hence, provided that external forces are absent, the balance (1.4) and constitutive relations (1.5) and (1.7) yield an expression similar to the Fickian constitutive equation (1.3) with the classical relation (see Nernst [16, Page 615])

$$D = \frac{k_{\mathrm{B}}\theta}{\varrho c\zeta}, \tag{1.9}$$

between diffusivity and frictional resistance (or mobility).

There is, however, disagreement over the form and interpretation of the solute force balance. For example, Einstein [22, § 4] asserted that the osmotic pressure is a "virtual" force, so that it cannot be treated as a force acting on the individual molecules.[4] In fact, Einstein [20], in his original treatment of Brownian motion, proposed instead a fictitious force $\boldsymbol{k}$ that acted on the individual particles but that balanced the osmotic pressure gradient:

$$\boldsymbol{k} = \frac{M}{\varrho c}\, grad\, \varpi. \tag{1.10}$$

Einstein [20] then took the solute force balance as

$$\boldsymbol{h} + \boldsymbol{l} = \boldsymbol{k} \tag{1.11}$$

and thereby claimed (see Einstein [22]) to have resolved the apparent difficulty of having a virtual force act on the individual particles.

Additionally, Debye [23, Page 106] asserted that osmotic forces are not "true" mechanical forces, so that the solute force balance should be instead

$$\boldsymbol{h} + \boldsymbol{\ell} = \boldsymbol{0}. \tag{1.12}$$

In this alternative point of view, the flux $\boldsymbol{\jmath}$ is decomposed as a sum

$$\boldsymbol{\jmath} = \boldsymbol{\jmath}_D + \boldsymbol{\jmath}_F \tag{1.13}$$

involving a purely diffusive part $\boldsymbol{\jmath}_D$ (usually called the "ordinary diffusion") and a part $\boldsymbol{\jmath}_F$ due to external forces (usually called the "forced diffusion"). Commonly, Fick's first law is invoked for the ordinary diffusive flux, so that

$$\boldsymbol{\jmath}_D = -D grad\, c, \tag{1.14}$$

and the flux due to the external forces is assumed to have the form

$$\boldsymbol{\jmath}_F = \frac{\boldsymbol{\ell}}{\zeta}, \tag{1.15}$$

[4]The exact meaning of this statement is unclear to the authors.

which follows from (1.5) and (1.12). Combining (1.15) with the balance (1.2) leads to the *generalized convection-diffusion equation*

$$\dot{c} = div\,\big(D grad\, c - \frac{\boldsymbol{\ell}}{\varrho\zeta}\big), \tag{1.16}$$

typically referred to as a Smoluchowski [24] equation. The diffusivity D can be determined by considering the special case where the external forces are given by a potential, viz.,

$$\boldsymbol{\ell} = -\,grad\, V, \tag{1.17}$$

and requiring the steady-state solution to correspond to that of a Boltzmann [25] distribution, so that

$$c = c_0 \exp\big(\frac{-V}{k_{\rm B}\theta}\big). \tag{1.18}$$

This yields the relation (1.9), which is usually enforced even when (1.18) no longer holds.

This latter format was used by Debye [26, 27] in his theory of rotary diffusion in dielectrics to include the effect of the external electric field on the diffusing dipoles. It is still commonly used to obtain extensions of the Fickian constitutive relation to include, for instance, the effects of external electric fields on electrolytes. Additionally it is used to model the interaction of diffusion and external fields on dilute suspensions (see, for example, Giesekus [28] and, more recently, Doi & Edwards [29]). However, Bird, Armstrong, & Hassager [30] based their approach to polymeric suspensions on a force balance such as (1.4) that explicitly includes a contribution attributed to the Brownian forces on the polymer molecule (see, for example, [30, Equation 13.2-1]).

Interestingly, in the case of linear constitutive relations, the approaches described above lead to the same resulting equations—namely (1.16) and (1.9). However, the assumptions involved are rather different. In particular, it is not clear how to generalize either approach to allow for constitutive nonlinearities. For example, in (1.13) the ordinary diffusive flux $\boldsymbol{\jmath}_D$ is determined by a constitutive relation, whereas the forced diffusive part $\boldsymbol{\jmath}_F$ is determined by a balance law—a procedure highly atypical for a continuum theory. Furthermore, the validity of (1.9), derived from an assumed steady-state solution, is not clear in unsteady situations.

In our opinion, these issues can be resolved by a more general treatment of the notion of forces in a binary mixture. Consequently, in the following, we develop a theoretical framework for diffusion based on a *generic* microforce balance without a priori assumptions on the nature of the microforces or of steady-state concentration profiles. Furthermore, we allow for constitutive nonlinearities and external fields. We follow the procedure of modern thermodynamics, wherein consistency with the second law restricts the form of the constitutive relations. Our proposed format provides a systematic procedure for the generalization of convection-diffusion equation models for solute transport. In particular, it leads to a force balance that explicitly includes the diffusive or Brownian forces acting on the solute. Only in special cases, such as linear constitutive relations, can this force balance be expressed in the oft used form (1.12) with the corresponding decomposition (1.13) of the flux proposed by Debye.

For clarity, we restrict our attention to purely mechanical processes in a binary mixture of solute and solvent, ignoring thermal and other effects. In this context, the first and second laws of thermodynamics are replaced by a *free-energy imbalance* that accounts for power expenditures associated not only with mixture convection but also with solute diffusion. That diffusion does, indeed, lead to the expenditure of power was clearly

recognized and utilized by van't Hoff [17] as an experimental means of measuring the osmotic pressure. First, we consider simple diffusion without mixture convection. This special case allows us to develop the theory without the complications of coupling with the macroscopic mixture motion. We then treat both convection and diffusion.

2 Simple theory accounting only for diffusion

We consider a binary mixture of solute and solvent that occupies a fixed region $\mathcal{R}$ of three-dimensional space. In the present context, where we ignore the macroscopic motion of the mixture, the mixture density is constant. Without loss of generality, we take that constant to be unity.

2.1 Basic laws

The simple theory is based upon the following basic laws:

- solute mass balance;
- solute microforce balance;
- mixture free-energy imbalance.

We formulate these laws in global form for an arbitrary subregion $\mathcal{P}$ of $\mathcal{R}$. The outward unit-normal field on the boundary $\partial\mathcal{P}$ of $\mathcal{P}$ is denoted by $\boldsymbol{\nu}$.

2.1.1 Solute mass balance

We introduce fields[5]

$$\begin{array}{ll} c & \textit{solute mass fraction,} \\ \boldsymbol{\jmath} & \textit{diffusive solute flux,} \\ m & \textit{external solute supply,} \end{array}$$

in which case the integrals

$$\int_{\mathcal{P}} c\,dv, \qquad \int_{\partial\mathcal{P}} \boldsymbol{\jmath}\cdot\boldsymbol{\nu}\,da, \qquad \text{and} \qquad \int_{\mathcal{P}} m\,dv \tag{2.1}$$

represent, respectively, the solute mass in $\mathcal{P}$, the solute mass added to $\mathcal{P}$, per unit time, by diffusion across $\partial\mathcal{P}$, and the solute mass added to $\mathcal{P}$, per unit time, by external agencies.

Solute mass balance is the postulate that, for each subregion $\mathcal{P}$ of $\mathcal{R}$ and each instant,

$$\overline{\int_{\mathcal{P}} c\,dv} = -\int_{\partial\mathcal{P}} \boldsymbol{\jmath}\cdot\boldsymbol{\nu}\,da + \int_{\mathcal{P}} m\,dv. \tag{2.2}$$

Equivalently, since $\mathcal{P}$ is arbitrary, we may enforce solute mass balance via the local field equation

$$\grave{c} = -div\,\boldsymbol{\jmath} + m. \tag{2.3}$$

[5]Since the mixture density is assumed to be unity, there is no distinction between solute mass and solute mass fraction, or between solute mass flux and solute mass fraction flux.

2.1.2 Solute microforce balance

Associated with the evolution of the diffusive solute flux $\boldsymbol{\jmath}$, we introduce a system of power-conjugate *microforces*, consisting of

$$\begin{aligned} \boldsymbol{\Pi} &\quad \textit{solute microstress tensor}, \\ \boldsymbol{h} &\quad \textit{internal solute body microforce}, \\ \boldsymbol{\ell} &\quad \textit{external solute body microforce}, \end{aligned}$$

in which case the integrals

$$\int\limits_{\mathcal{P}} \boldsymbol{\Pi}\boldsymbol{\nu}\, da, \qquad \int\limits_{\mathcal{P}} \boldsymbol{h}\, dv, \qquad \text{and} \qquad \int\limits_{\mathcal{P}} \boldsymbol{\ell}\, dv \tag{2.4}$$

represent, respectively, the solute microforces exerted on the region $\mathcal{P}$ by the solute microtraction distributed over $\partial\mathcal{P}$, by agencies within $\mathcal{P}$, and by agencies external to $\mathcal{P}$, respectively. In the present mixture context, internal forces arise from the action of the solvent on the solute, or from solute-solute interactions. External forces are those arising from sources remote from the mixture, such as those arising from applied electromagnetic or gravitational fields. The microstress tensor $\boldsymbol{\Pi}$ allows for surface tractions that are not parallel to the surface normal. We assume that the inertia associated with solute diffusion is negligible and, hence, impose a *solute microforce balance*, which is the postulate that, for each subregion $\mathcal{P}$ of $\mathcal{R}$ and each instant, the resultant microforce acting on $\mathcal{P}$ must vanish:

$$\int\limits_{\partial\mathcal{P}} \boldsymbol{\Pi}\boldsymbol{\nu}\, da + \int\limits_{\mathcal{P}} (\boldsymbol{h} + \boldsymbol{\ell})\, dv = \boldsymbol{0}. \tag{2.5}$$

Equivalently, since $\mathcal{P}$ is arbitrary, we may enforce solute microforce balance via the local field equation

$$div\, \boldsymbol{\Pi} + \boldsymbol{h} + \boldsymbol{\ell} = \boldsymbol{0}. \tag{2.6}$$

A comparison to the Nernst force balance (1.4) suggests an interpretation of the quantity $\boldsymbol{\Pi}$ as a generalized stress tensor that allows for the possibility of tangential osmotic forces on a semipermeable membrane. At this point, we impose no constitutive assumptions concerning the microforces. In particular, we allow for the possibility that $\boldsymbol{\Pi}$ vanish identically, which would correspond to the alternative balance (1.12) proposed by Debye.

2.1.3 Free-energy imbalance

In this purely mechanical theory, the first and second laws of thermodynamics are replaced by a *free-energy imbalance*. To formulate this imbalance, we introduce fields

$$\begin{aligned} \psi &\quad \textit{mixture free-energy density}, \\ \mu &\quad \textit{solute diffusion potential}, \end{aligned}$$

in which case that the integrals

$$\int\limits_{\mathcal{P}} \psi\, dv \qquad \text{and} \qquad \int\limits_{\mathcal{P}} \mu m\, dv \tag{2.7}$$

represent, respectively, the free-energy in $\mathcal{P}$ and the rate at which free-energy is added to $\mathcal{P}$ by the external supply of solute to $\mathcal{P}$.

Further, the integrals

$$\int_{\partial\mathcal{P}} \boldsymbol{\Pi}\boldsymbol{\nu}\cdot\boldsymbol{\jmath}\, da \qquad \text{and} \qquad \int_{\mathcal{P}} \boldsymbol{\ell}\cdot\boldsymbol{\jmath}\, dv \tag{2.8}$$

provide an accounting of the power expended on $\mathcal{P}$ by the solute microtraction distributed over $\partial\mathcal{P}$ and by the agencies acting external to that region. These expressions represent the power expended by the diffusion of the solute particles.

Consistent with our assumption that solute inertia is negligible, we neglect the kinetic energy of solute diffusion. *Free-energy imbalance* is, then, the postulate that, for each subregion $\mathcal{P}$ of $\mathcal{R}$ and each instant:

$$\overset{\cdot}{\int_{\mathcal{P}}} \psi\, dv \;\leq\; \int_{\partial\mathcal{P}} \boldsymbol{\Pi}\boldsymbol{\nu}\cdot\boldsymbol{\jmath}\, da + \int_{\mathcal{P}} (\boldsymbol{\ell}\cdot\boldsymbol{\jmath} + \mu m)\, dv. \tag{2.9}$$

Equivalently, since $\mathcal{P}$ is arbitrary, we may enforce free-energy imbalance via the local field inequality

$$-\dot{\psi} + \mu\dot{c} - \boldsymbol{h}\cdot\boldsymbol{\jmath} + (\boldsymbol{\Pi} + \mu\boldsymbol{1})\cdot grad\,\boldsymbol{\jmath} \geq 0. \tag{2.10}$$

2.2 Constitutive equations

The preceding balance laws do not form a determinate system of equations. We now develop constitutive equations that will provide closure relations. We assume that the free-energy density ψ, the solute diffusion potential μ, the solute microstress tensor $\boldsymbol{\Pi}$, and the internal solute body microforce $\boldsymbol{h}$ are determined constitutively as functions of the solute mass fraction c and the diffusive solute flux $\boldsymbol{\jmath}$, so that

$$(\psi,\, \mu,\, \boldsymbol{\Pi},\, \boldsymbol{h}) = \big(\hat{\psi}(c,\boldsymbol{\jmath}),\, \hat{\mu}(c,\boldsymbol{\jmath}),\, \hat{\boldsymbol{\Pi}}(c,\boldsymbol{\jmath}),\, \hat{\boldsymbol{h}}(c,\boldsymbol{\jmath})\big). \tag{2.11}$$

We emphasize that, in contrast to the standard approach to the theory of mass diffusion, the diffusive flux $\boldsymbol{\jmath}$ is not given by a constitutive relation.

Inserting the constitutive relations (2.11) into the local free-energy imbalance (2.10), we arrive at the functional inequality

$$\big(\frac{\partial\hat{\psi}}{\partial c}(c,\boldsymbol{\jmath}) - \hat{\mu}(c,\boldsymbol{\jmath})\big)\dot{c} + \frac{\partial\hat{\psi}}{\partial\boldsymbol{\jmath}}(c,\boldsymbol{\jmath})\cdot\dot{\boldsymbol{\jmath}} + \hat{\boldsymbol{h}}(c,\boldsymbol{\jmath})\cdot\boldsymbol{\jmath} - \big(\hat{\boldsymbol{\Pi}}(c,\boldsymbol{\jmath}) + \hat{\mu}(c,\boldsymbol{\jmath})\boldsymbol{1}\big)\cdot grad\,\boldsymbol{\jmath} \leq 0, \tag{2.12}$$

and, following the procedure founded by Coleman & Noll [31] in their incorporation of the second law into continuum thermomechanics, conclude that:

(i) the constitutive response functions $\hat{\psi}$, $\hat{\mu}$, and $\hat{\boldsymbol{\Pi}}$ delivering the free-energy density ψ, the diffusion potential μ, and the stress $\boldsymbol{\Pi}$ must be independent of the diffusive mass flux $\boldsymbol{\jmath}$, with[6]

$$\psi = \hat{\psi}(c), \qquad \mu = \hat{\psi}'(c), \qquad \text{and} \qquad \boldsymbol{\Pi} = -\hat{\psi}'(c)\boldsymbol{1}; \tag{2.13}$$

(ii) the constitutive response function $\hat{\boldsymbol{h}}$ for the internal solute body microforce $\boldsymbol{h}$ must be consistent with the *residual inequality*

$$\hat{\boldsymbol{h}}(c,\boldsymbol{\jmath})\cdot\boldsymbol{\jmath} \leq 0. \tag{2.14}$$

[6]Here, a prime indicates with respect to the argument of a function depending on a scalar field. It is noteworthy that the solute microstress reduces to an isotropic tensor because we do not include the gradient $grad\,\boldsymbol{\jmath}$ of the diffusive solute flux $\boldsymbol{\jmath}$ in the list of independent constitutive variables.

Granted smoothness of the response function $\hat{\boldsymbol{h}}$, a result appearing in Gurtin & Voorhees [32] yields the general solution

$$\hat{\boldsymbol{h}}(c,\boldsymbol{\jmath}) = -\boldsymbol{Z}(c,\boldsymbol{\jmath})\boldsymbol{\jmath} \tag{2.15}$$

of (2.14), where the symmetric *generalized frictional resistance tensor* $\boldsymbol{Z}$ must obey

$$\boldsymbol{\jmath}\cdot\boldsymbol{Z}(c,\boldsymbol{\jmath})\boldsymbol{\jmath} \geq 0. \tag{2.16}$$

Objectivity further requires that under the transformation

$$c \mapsto c, \qquad \boldsymbol{\jmath} \mapsto \boldsymbol{Q}\boldsymbol{\jmath}, \tag{2.17}$$

with $\boldsymbol{Q}$ an arbitrary rotation, the quantities ψ, μ, $\boldsymbol{\Pi}$, $\boldsymbol{h}$, and $\boldsymbol{\ell}$ transform as

$$\psi \mapsto \psi, \qquad \mu \mapsto \mu, \qquad \boldsymbol{\Pi} \mapsto \boldsymbol{Q}\boldsymbol{\Pi}\boldsymbol{Q}^{\top}, \qquad \boldsymbol{h} \mapsto \boldsymbol{Q}\boldsymbol{h}, \qquad \boldsymbol{\ell} \mapsto \boldsymbol{Q}\boldsymbol{\ell}, \tag{2.18}$$

which, in particular, implies that

$$\boldsymbol{Z}(c,\boldsymbol{\jmath}) = \zeta(c,\jmath)\boldsymbol{1}, \qquad \jmath = |\boldsymbol{\jmath}|, \tag{2.19}$$

where the *scalar frictional resistance* ζ must obey

$$\zeta(c,\jmath) \geq 0 \tag{2.20}$$

for all $(c,\jmath)$. Combining (2.15) and (2.19), we see that

$$\boldsymbol{h} = -\zeta(c,\jmath)\boldsymbol{\jmath}, \tag{2.21}$$

so that the internal solute body microforce $\boldsymbol{h}$ must be collinear with the diffusive solute flux $\boldsymbol{\jmath}$.

The foregoing results show that the behavior of a medium of the sort considered here is completely determined by the provision of two constitutive response functions: (i) $\hat{\psi}$ determining the mixture free-energy density as a function of the solute mass fraction c; and, (ii) the scalar frictional resistance ζ, which determines the internal solute body microforce $\boldsymbol{h}$ and, in general, may depend on both the solute mass fraction c and the magnitude $\jmath$ of the diffusive solute flux $\boldsymbol{\jmath}$.

The governing equations that arise on substituting the foregoing thermodynamically consistent constitutive equations in the local field equations (2.3) and (2.6) expressing solute mass balance and solute microforce balance are

$$\left.\begin{aligned} \dot{c} + \mathrm{div}\,\boldsymbol{\jmath} &= m, \\ \zeta(c,\jmath)\boldsymbol{\jmath} + \mathrm{grad}\,\big(\hat{\psi}'(c)\big) &= \boldsymbol{\ell}. \end{aligned}\right\} \tag{2.22}$$

Provided that ζ is nonvanishing, $(2.22)_2$ yields an expression

$$\boldsymbol{\jmath} = -\frac{\hat{\psi}''(c)}{\zeta(c,\jmath)}\,\mathrm{grad}\,c + \frac{\boldsymbol{\ell}}{\zeta(c,\jmath)}, \tag{2.23}$$

for the diffusive solute flux $\boldsymbol{\jmath}$. This leads, in conjunction with $(2.22)_1$, to the *generalized Smoluchowski equation*

$$\dot{c} = \mathrm{div}\,\Big(\frac{\hat{\psi}''(c)}{\zeta(c,\jmath)}\,\mathrm{grad}\,c - \frac{\boldsymbol{\ell}}{\zeta(c,\jmath)}\Big). \tag{2.24}$$

Note that, when the frictional resistance ζ depends on $\jmath$, the evolution equation (2.24) *does not* decouple from the microforce balance $(2.22)_2$. In this case, the flux $\boldsymbol{\jmath}$ does not separate into distinct ordinary and forced diffusive contributions. Comparing (2.23) with the conventional relation (1.3), we obtain a generalized expression

$$D(c,\jmath) = \frac{\hat{\psi}''(c)}{\zeta(c,\jmath)} \tag{2.25}$$

for the diffusivity, which is not predicated on a particular steady-state solution and, moreover, is not restricted to the linear regime. Hence, within our framework, the Fickian constitutive relation (1.3) can be interpreted as an expression of the solute microforce balance, granted that the internal body microforce is linear in the diffusive solute flux and that the external solute body microforce vanishes. In the special case governed by (1.17), the steady-state solution is

$$\mu = \hat{\psi}'(c) = -V + \text{constant}, \tag{2.26}$$

which need not correspond to the Boltzmann distribution (1.18).

Our results for the microforce balance are consistent with the Nernst balance (1.4). In fact, a comparison of (1.4) to $(2.22)_2$ shows that they are identical in form if

$$\varpi'(c) = \frac{c}{M}\hat{\psi}''(c) = \frac{c}{M}\hat{\mu}'(c). \tag{2.27}$$

Thus, (2.13) shows that the osmotic traction acts only normal to a semipermeable membrane and is determined by the mixture free-energy density. Note that $(2.22)_2$ is consistent with the Debye (1.12) balance only when the frictional resistance ζ is independent of the flux $\boldsymbol{\jmath}$.

2.3 Special case: diffusion of non-interacting spheres

We now specialize the preceding results to the case of diffusing, non-interacting spherical particles, which corresponds to the dilute Brownian spheres originally treated by Einstein [19]. Our framework requires only the specification of constitutive relations for the mixture free-energy density and the frictional resistance. We stipulate that ψ be determined by a response function $\hat{\psi}$ of the form

$$\hat{\psi}(c) = k_{\mathrm{B}}\theta c \log c, \tag{2.28}$$

which corresponds to an *ideal mixture* in the sense that it consists (to within an arbitrary additive constant) only of a classical *entropic* contribution, a contribution that drives diffusion. This choice does not encompass particle-particle interactions. Insertion of (2.28) into (2.27) leads to

$$\varpi(c) = \frac{k_{\mathrm{B}}\theta c}{M}. \tag{2.29}$$

Further, we require that the response function $\hat{\boldsymbol{h}}$ be linear in the diffusive solute flux $\boldsymbol{\jmath}$ with the specific form

$$\boldsymbol{h} = \hat{\boldsymbol{h}}(c,\boldsymbol{\jmath}) = -\zeta(c)\boldsymbol{\jmath}, \qquad \text{with} \qquad \zeta(c) = \frac{6\pi\eta_s r}{c}, \tag{2.30}$$

so that the internal body microforce is consistent with Stokes' [33] law for the drag on a rigid spherical particle slowly translating in an incompressible Newtonian fluid. Here,

η_s is the shear viscosity of the pure fluid solvent and r is the particle radius. Finally, we suppose that the external body microforce is generated by the gradient of a potential according to (1.17).

Granted these assumptions, we may use (2.23) to obtain

$$\boldsymbol{\jmath} = -\frac{k_{\mathrm{B}}\theta}{6\pi\eta_s r}\,\mathrm{grad}\,c - \frac{c}{6\pi\eta_s r}\,\mathrm{grad}\,V, \tag{2.31}$$

which, when inserted into the mass balance $(2.22)_2$ yields the generalized diffusion equation

$$\dot{c} = D\,\mathrm{div}\left(\mathrm{grad}\,c + \frac{c}{k_{\mathrm{B}}\theta}\,\mathrm{grad}\,V\right), \tag{2.32}$$

with the diffusivity D having the explicit form

$$D = \frac{k_{\mathrm{B}}\theta}{6\pi\eta_s r} \tag{2.33}$$

consistent with the diffusivity expression originally derived by Einstein [19] for Brownian spheres. Thus, the contribution of ψ in (2.31) leads to a classical, linear second-order diffusion term that tends to randomize concentrations, which justifies our description of it as *entropic*. Additionally the steady-state mass fraction has the classical Boltzmann form (1.18).

Importantly, our derivation of (2.32) and (2.33) relies neither on a Fickian constitutive relation for the diffusive mass flux nor on an assumed form for the mass fraction distribution in equilibrium. Rather, the relation (2.33) is a *consequence* of the thermodynamic theory and the specialized ideal constitutive expressions (2.28) and (2.30).

3 Theory accounting for both mass diffusion and convection

We now account for motion of the mixture as described by a convective velocity $\boldsymbol{v}$. Further, we allow the region $\mathcal{R}$ of three-dimensional space occupied by the mixture to evolve with time.

3.1 Basic laws

The theory is based upon the following laws:

- mixture mass balance;
- solute mass balance;
- mixture momentum balance;
- moment of mixture-momentum balance;
- solute microforce balance;
- mixture free-energy imbalance.

As in our treatment of the theory without mixture convection, we formulate the basic laws in global form for an arbitrary *material* subregion $\mathcal{P}$ of $\mathcal{R}$.

3.1.1 Mixture mass balance

We now allow for convection and variations in the mixture mass density, so that we introduce fields

$$\begin{aligned} &\varrho && \textit{mixture mass density},\\ &\boldsymbol{v} && \textit{mixture velocity}. \end{aligned}$$

Mixture mass balance is the postulate that, for each material subregion $\mathcal{P}$ of $\mathcal{R}$ and each instant,

$$\overset{\cdot}{\int_{\mathcal{P}}} \varrho \, dv = 0. \tag{3.1}$$

Equivalently, since $\mathcal{P}$ is arbitrary, we may enforce mixture mass balance via the local field equation

$$\dot{\varrho} + \varrho \, div \, \boldsymbol{v} = 0. \tag{3.2}$$

3.1.2 Solute mass balance

With mixture convection taken into account, the global statement of solute mass balance for a material subregion $\mathcal{P}$ of $\mathcal{R}$ has the form (2.2) considered in the absence of convection, provided that c is replaced by ϱc. Thus, bearing in mind the mixture mass balance (3.2), the local equivalent of solute mass balance now reads

$$\varrho \dot{c} = -div \, \boldsymbol{\jmath} + m. \tag{3.3}$$

3.1.3 Solute microforce balance

With mixture convection taken into account, the global and local statements, (2.5) and (2.6), of solute microforce balance remain unchanged from those introduced earlier.

3.1.4 Mixture momentum balance and moment of mixture-momentum balance

Associated with the convective mixture velocity, we introduce fields

$$\begin{aligned} &\boldsymbol{T} && \textit{mixture stress},\\ &\boldsymbol{b} && \textit{external mixture body force density}, \end{aligned}$$

in which case the integrals

$$\int_{\mathcal{P}} \boldsymbol{T}\boldsymbol{\nu} \, da \qquad \text{and} \qquad \int_{\mathcal{P}} \boldsymbol{b} \, dv \tag{3.4}$$

represent the mixture forces exerted on the region $\mathcal{P}$ by the mixture traction distributed over $\partial\mathcal{P}$, by agencies within $\mathcal{P}$, and by agencies external to $\mathcal{P}$, respectively.

In addition to the mixture mass balance (3.2), the solute mass balance (3.3), and the solute microforce balance (2.6), we enforce balances of mixture momentum and momentum of mixture momentum.

Mixture momentum balance is the postulate that, for each material subregion $\mathcal{P}$ of $\mathcal{R}$ and each instant, the time-rate at which the convective momentum within $\mathcal{P}$ changes be equal to the resultant of the convective forces acting on $\mathcal{P}$:

$$\overset{\grave{}}{\int_{\mathcal{P}} \varrho \boldsymbol{v} \, dv} = \int_{\partial\mathcal{P}} \boldsymbol{T}\boldsymbol{\nu} \, da + \int_{\mathcal{P}} \boldsymbol{b} \, dv. \tag{3.5}$$

Further, *moment of mixture momentum balance* is the postulate that, for each material subregion $\mathcal{P}$ of $\mathcal{R}$ and each instant, the time-rate at which the moment of the convective momentum within $\mathcal{P}$ changes be equal to the resultant of the convective torques acting on $\mathcal{P}$:

$$\overset{\grave{}}{\int_{\mathcal{P}} \boldsymbol{x}\wedge\varrho \boldsymbol{v} \, dv} = \int_{\partial\mathcal{P}} \boldsymbol{x}\wedge\boldsymbol{T}\boldsymbol{\nu} \, da + \int_{\mathcal{P}} \boldsymbol{x}\wedge\boldsymbol{b} \, dv. \tag{3.6}$$

Equivalent to these balances, we have the local field equations

$$\varrho\dot{\boldsymbol{v}} = div\, \boldsymbol{T} + \boldsymbol{b} \qquad \text{and} \qquad \boldsymbol{T} = \boldsymbol{T}^{\top}. \tag{3.7}$$

3.1.5 Free-energy imbalance

Our previous statement of free-energy imbalance must be modified to account for variations in the mixture mass density, the kinetic energy of the mixture, and the power expended by the mixture stress and external mixture body force. Specifically, we now require that for each material subregion $\mathcal{P}$ of $\mathcal{R}$ and each instant:

$$\overset{\grave{}}{\int_{\mathcal{P}} \varrho(\psi + \tfrac{1}{2}|\boldsymbol{v}|^2) \, dv} \;\leq\; \int_{\partial\mathcal{P}} \big(\boldsymbol{\Pi}^{\top}\boldsymbol{\jmath} + \boldsymbol{T}^{\top}\boldsymbol{v}\big)\cdot\boldsymbol{\nu} \, da + \int_{\mathcal{P}} (\boldsymbol{\ell}\cdot\boldsymbol{\jmath} + \mu m + \boldsymbol{b}\cdot\boldsymbol{v}) \, dv. \tag{3.8}$$

Equivalently, since $\mathcal{P}$ is arbitrary, we may enforce mixture energy imbalance via the local inequality

$$-\varrho\dot{\psi} + \varrho\mu\dot{c} - \boldsymbol{h}\cdot\boldsymbol{\jmath} + \boldsymbol{T}\cdot\boldsymbol{D} + (\boldsymbol{\Pi} + \mu\boldsymbol{1})\cdot grad\, \boldsymbol{\jmath} \geq 0, \tag{3.9}$$

with

$$\boldsymbol{D} = \tfrac{1}{2}(grad\, \boldsymbol{v} + (grad\, \boldsymbol{v})^{\top}) \tag{3.10}$$

the symmetric *strain-rate*.

3.2 Constitutive equations

We consider the cases of compressible and incompressible mixtures separately.

3.2.1 Compressible mixture

To the lists of dependent and independent constitutive variables we add the convective stress $\boldsymbol{T}$ and the mixture density ϱ and strain-rate $\boldsymbol{D}$, respectively, so that

$$(\psi,\, \mu,\, \boldsymbol{\Pi},\, \boldsymbol{h},\, \boldsymbol{T}) = \big(\hat{\psi}(z),\, \hat{\mu}(z),\, \hat{\boldsymbol{\Pi}}(z),\, \hat{\boldsymbol{h}}(z),\, \hat{\boldsymbol{T}}(z)\big), \tag{3.11}$$

where, for brevity, we have introduced

$$z = (\varrho, c, \boldsymbol{\jmath}, \boldsymbol{D}). \tag{3.12}$$

Inserting the constitutive relations (3.11) into the local energy imbalance (3.9), we arrive at the functional inequality

$$\varrho\big(\frac{\partial\hat{\psi}}{\partial c}(z)-\hat{\mu}(z)\big)\dot{c}+\varrho\frac{\partial\hat{\psi}}{\partial \boldsymbol{\jmath}}(z)\cdot\dot{\boldsymbol{\jmath}}+\varrho\frac{\partial\hat{\psi}}{\partial \boldsymbol{D}}(z)\cdot\dot{\boldsymbol{D}}+\hat{\boldsymbol{h}}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\cdot\boldsymbol{\jmath}$$
$$-\big(\hat{\boldsymbol{T}}(z)-\varrho^2\frac{\partial\hat{\psi}}{\partial\varrho}(z)\boldsymbol{1}\big)\cdot\boldsymbol{D}-\big(\hat{\boldsymbol{\Pi}}(z)+\hat{\mu}(z)\boldsymbol{1}\big)\cdot grad\,\boldsymbol{\jmath}\leq 0. \quad (3.13)$$

Hence, proceding as in the our treatment of the theory without mixture convection, we find that:

(*i*) the constitutive response functions $\hat{\psi}$, $\hat{\mu}$, and $\hat{\boldsymbol{\Pi}}$ delivering the mixture energy density ψ, the mixture diffusion potential μ, and the solute microstress $\boldsymbol{\Pi}$ must be independent of $\boldsymbol{\jmath}$, with

$$\psi=\hat{\psi}(\varrho,c),\qquad \mu=\frac{\partial}{\partial c}\hat{\psi}(\varrho,c),\qquad \text{and}\qquad \boldsymbol{\Pi}=-\hat{\mu}(\varrho,c)\boldsymbol{1}\,; \quad (3.14)$$

(*ii*) the constitutive response function $\hat{\boldsymbol{h}}$ for the internal solute body force density $\boldsymbol{h}$ and the mixture stress $\boldsymbol{T}$ must be consistent with the *residual inequality*

$$\hat{\boldsymbol{h}}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\cdot\boldsymbol{\jmath}-\boldsymbol{T}_{\rm vis}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\cdot\boldsymbol{D}\leq 0, \quad (3.15)$$

in which

$$\hat{\boldsymbol{T}}_{\rm vis}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})=\varrho^2\frac{\partial}{\partial\varrho}\hat{\psi}(\varrho,c)\boldsymbol{1}+\boldsymbol{T} \quad (3.16)$$

determines the dissipative contribution $\boldsymbol{T}_{\rm vis}$ to the mixture stress.

Further, granted smoothness of the response functions $\hat{\boldsymbol{h}}$ and $\hat{\boldsymbol{T}}_{\rm vis}$, the previously employed result of Gurtin & Voorhees [32] yields a general solution

$$\left.\begin{aligned}\boldsymbol{h}&=-\boldsymbol{Z}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{\jmath}-\boldsymbol{Y}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{D},\\ \boldsymbol{T}_{\rm vis}&=\quad\boldsymbol{U}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{\jmath}+\boldsymbol{V}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{D},\end{aligned}\right\} \quad (3.17)$$

of (3.15), where $\boldsymbol{Z}$, $\boldsymbol{Y}$, $\boldsymbol{U}$, and $\boldsymbol{V}$ are isotropic due to objectivity and must obey

$$\boldsymbol{\jmath}\cdot\boldsymbol{Z}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{\jmath}+\boldsymbol{\jmath}\cdot\boldsymbol{Y}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{D}+\boldsymbol{D}\cdot\boldsymbol{U}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{\jmath}+\boldsymbol{D}\cdot\boldsymbol{V}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{D}\geq 0 \quad (3.18)$$

for all $(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})$. Despite their objectivity, these coefficients need not reduce to scalars.

In this case, the full system of governing equations is

$$\left.\begin{aligned}\dot{\varrho}&=-\varrho\,div\,\boldsymbol{v},\\ \varrho\dot{c}&=-div\,\boldsymbol{\jmath}+m,\\ \varrho\dot{\boldsymbol{v}}&=-grad\,\big(\varrho^2\frac{\partial\hat{\psi}}{\partial\varrho}(\varrho,c)\big)+div\,\big(\boldsymbol{U}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{\jmath}+\boldsymbol{V}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{D}\big)+\boldsymbol{b},\\ \boldsymbol{Z}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{\jmath}&=-grad\,\big(\frac{\partial\hat{\psi}}{\partial c}(\varrho,c)\big)-\boldsymbol{Y}(\varrho,c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{D}+\boldsymbol{\ell},\end{aligned}\right\} \quad (3.19)$$

These equations are susbstantially more complicated than those for the case of simple diffusion without convection. However, if we require that $\hat{\boldsymbol{h}}$ and $\hat{\boldsymbol{T}}_{\rm vis}$ be linear functions of $(\boldsymbol{\jmath}, \boldsymbol{D})$, the general result (3.17) specializes to yield

$$\left.\begin{aligned} \boldsymbol{h} &= -\zeta(\varrho, c)\boldsymbol{\jmath}, \\ \boldsymbol{T}_{\rm vis} &= 2\eta_1(\varrho, c)\boldsymbol{D} + \eta_2(\varrho, c)(tr\,\boldsymbol{D})\boldsymbol{1}, \end{aligned}\right\} \tag{3.20}$$

with

$$\zeta(\varrho, c) \geq 0, \qquad \eta_1(\varrho, c) \geq 0, \qquad \text{and} \qquad 2\eta_1(\varrho, c) + 3\eta_2(\varrho, c) \geq 0 \tag{3.21}$$

for all (ϱ, c). In this case, the full system of governing equations has the form

$$\left.\begin{aligned} \dot{\varrho} &= -\varrho\, div\, \boldsymbol{v}, \\ \varrho\dot{c} &= -div\, \boldsymbol{\jmath} + m, \\ \varrho\dot{\boldsymbol{v}} &= -grad\, \big(\varrho^2 \frac{\partial \hat{\psi}}{\partial \varrho}(\varrho, c)\big) + div\, \big(2\eta_1(\varrho, c)\boldsymbol{D}\big) + grad\, \big(\eta_2(\varrho, c) div\, \boldsymbol{v}\big) + \boldsymbol{b}, \\ \zeta(\varrho, c)\boldsymbol{\jmath} &= -grad\, \big(\frac{\partial \hat{\psi}}{\partial c}(\varrho, c)\big) + \boldsymbol{\ell}, \end{aligned}\right\} \tag{3.22}$$

which constitutes a system of coupled equations for the fields $(\varrho, c, \boldsymbol{v}, \boldsymbol{\jmath})$.

3.2.2 Incompressible mixture

If the convective mixture velocity obeys

$$div\, \boldsymbol{v} = tr\, \boldsymbol{D} = 0, \tag{3.23}$$

so that the motion of the mixture is *isochoric*, we may without loss of generality assume that $\varrho = 1$ and consequently delete the mixture density from the list of independent constitutive variables. For convenience, we introduce the fields

$$\begin{aligned} p \quad & \textit{mixture pressure}, \\ \boldsymbol{S} \quad & \textit{mixture extra stress}, \end{aligned}$$

defined by the decomposition

$$\boldsymbol{T} = -p\boldsymbol{1} + \boldsymbol{S}, \qquad p = -\tfrac{1}{3} tr\, \boldsymbol{T}, \qquad tr\, \boldsymbol{S} = 0, \tag{3.24}$$

of the mixture stress into a constitutively indeterminate *pressure* p that reacts to the constraint (3.23) and a traceless but constitutively determinate *extra stress* $\boldsymbol{S}$.

We then assume that

$$(\psi, \mu, \boldsymbol{\Pi}, \boldsymbol{h}, \boldsymbol{S}) = \big(\hat{\psi}(z), \hat{\mu}(z), \hat{\boldsymbol{\Pi}}(z), \hat{\boldsymbol{h}}(z), \hat{\boldsymbol{S}}(z)\big), \tag{3.25}$$

with

$$z = (c, \boldsymbol{\jmath}, \boldsymbol{D}), \tag{3.26}$$

and, requiring that these relations satisfy the energy imbalance (3.9) in all processes, find that the constitutive response functions $\hat{\psi}$, $\hat{\mu}$, and $\hat{\boldsymbol{\Pi}}$ delivering the mixture energy

density ψ, the solute diffusion potential μ, and the solute microstress $\boldsymbol{\Pi}$ must, as in (2.13), be independent of the diffusive mass flux $\boldsymbol{\jmath}$ and the strain-rate $\boldsymbol{D}$, so that

$$\psi = \hat{\psi}(c), \qquad \mu = \hat{\psi}'(c), \qquad \text{and} \qquad \boldsymbol{\Pi} = -\hat{\psi}'(c)\,\boldsymbol{1}\,. \tag{3.27}$$

Further, granted that the constitutive response functions $\hat{\boldsymbol{h}}$ and $\hat{\boldsymbol{S}}$ for the internal solute body microforce $\boldsymbol{h}$ and the traceless component $\boldsymbol{S}$ of the mixture stress are smooth functions of $(c, \boldsymbol{\jmath}, \boldsymbol{D})$, we find that

$$\left.\begin{aligned} \boldsymbol{h} &= -\boldsymbol{Z}(c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{\jmath} - \boldsymbol{Y}(c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{D}, \\ \boldsymbol{S} &= \quad \boldsymbol{U}(c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{\jmath} + \boldsymbol{V}(c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{D}, \end{aligned}\right\} \tag{3.28}$$

where $\boldsymbol{Z}$, $\boldsymbol{Y}$, $\boldsymbol{U}$, and $\boldsymbol{V}$ must obey

$$\boldsymbol{\jmath}\cdot\boldsymbol{Z}(c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{\jmath} + \boldsymbol{\jmath}\cdot\boldsymbol{Y}(c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{D} + \boldsymbol{D}\cdot\boldsymbol{U}(c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{\jmath} + \boldsymbol{D}\cdot\boldsymbol{V}(c,\boldsymbol{\jmath},\boldsymbol{D})\boldsymbol{D} \geq 0 \tag{3.29}$$

for all $(c, \boldsymbol{\jmath}, \boldsymbol{D})$.

If, as in the compressible case considered above, we require that $\hat{\boldsymbol{h}}$ and $\hat{\boldsymbol{S}}$ be linear functions of $(\boldsymbol{\jmath}, \boldsymbol{D})$, the general result (3.28) reduces to

$$\left.\begin{aligned} \boldsymbol{h} &= -\zeta(c)\boldsymbol{\jmath}, \\ \boldsymbol{S} &= 2\eta_1(c)\boldsymbol{D}, \end{aligned}\right\} \tag{3.30}$$

with

$$\zeta(c) \geq 0 \qquad \text{and} \qquad \eta_1(c) \geq 0 \tag{3.31}$$

for all c. In this case, the full system of governing equations is:

$$\left.\begin{aligned} 0 &= \mathit{div}\,\boldsymbol{v}, \\ \dot{c} &= -\mathit{div}\,\boldsymbol{\jmath} + m, \\ \dot{\boldsymbol{v}} &= -\mathit{grad}\,p + \mathit{div}\left(2\eta_1(c)\boldsymbol{D}\right) + \boldsymbol{b}, \\ \zeta(c)\boldsymbol{\jmath} &= -\mathit{grad}\left(\hat{\psi}'(c)\right) + \boldsymbol{\ell}, \end{aligned}\right\} \tag{3.32}$$

which constitutes a system of coupled equations for the fields $(p, c, \boldsymbol{v}, \boldsymbol{\jmath})$.

4 Discussion

Our theory is based upon the interpretation of the diffusive flux as a generalized velocity and the introduction of corresponding power-conjugate forces, which we call microforces, into an otherwise conventional continuum-mechanical description. A systematic, thermodynamically consistent derivation generates a final system of governing equations—(2.22) when convection is ignored, and (3.22) or (3.32) when convection is taken into account—that constitutes a generalization of common convection-diffusion equations, a generalization that accounts for constitutive nonlinearities and external forces acting on the diffusing constituents.

In the absence of mixture convection, we find that the constitutive response of the material is determined by the provision of two scalar functions, one for the energy density and the other for the frictional resistance. This result generalizes naturally to account for dissipation associated with the convective motion of the mixture. Importantly, we arrive at our theory without introducing a constitutive relation such as (1.3) for the diffusive flux.

Additionally, our proposed format also leads to a generalization, (2.25), of the classical relation between diffusion coefficient and frictional resistance. We find that the classical form for the relation (1.9) holds when the free-energy density is given by the special constitutive relation (2.28).

A distinction between the final governing equations of our theory and those arising from more standard derivations of diffusion equations is that, in our approach, a vector-valued microforce balance provides a generalization between diffusive solute flux and gradient of the solute diffusion potential. Furthermore, consistent with Nernst's treatment of osmotic forces, the gradient of solute diffusion potential emerges naturally as the diffusive force in this balance. This result for the diffusive driving force is consistent with Batchelor's [34] "thermodynamic force" on particles in suspension. Typically, however, this diffusive force is not formally included in force balances, but, rather, a diffusive flux is added *ad hoc* to the total flux. We point out that Bird, Armstrong & Hassager [30] include such a diffusive force in their force balance for polymer suspensions.

Acknowledgements

This work was partially supported by the U. S. Department of Energy and the EPSRC (UK).

References

[1] L. D. Landau & E. M. Lifshitz, *Fluid Mechanics*, Pergamon Press, London, 1959.

[2] S. R. de Groot & P. Mazur, *Non-Equilibrium Thermodynamics*, Dover, New York, 1983.

[3] E. L. Cussler, *Diffusion, Mass Transfer in Fluid Systems*, Cambridge University Press, Cambridge, 1984.

[4] A. Fick, Über Diffusion, *Poggendorffs Annalen* **94** (1855), 59–86.

[5] P. Germain, Sur l'application de la méthode des puissances virtuelles en mécanique des milieux continus, *Comptes Rendus de l'Académie des Sciences, série A* **274** (1973), 1051–1055.

[6] S. S. Antman & J. E. Osborn, The principle of virtual work and integral laws of motion, *Archive for Rational Mechanics and Analysis* **69** (1979), 231–262.

[7] G. A. Maugin, The principle of virtual power in continuum mechanics—application to coupled fields, *Acta Mechanica* **35** (1980), 1–70.

[8] M. Frémond, Endommagement et principe des puissances virtuelles, *Comptes Rendus de l'Académie des Sciences, série II* **317** (1993), 857–863.

[9] J. L. Ericksen, Conservation laws for liquid crystals, *Transactions of the Society of Rheology* **5** (1961), 23–34.

[10] M. A. Goodman & S. C. Cowin, A continuum theory for granular materials, *Archive for Rational Mechanics and Analysis* **44** (1972), 249–266.

[11] G. Capriz & P. Podio-Guidugli, Structured continua from a Lagrangian point of view, *Annali di Matematica Pura ed Applicata* **135** (1983), 1–25.

[12] G. Capriz, *Continua with Microstructure*, Springer-Verlag, New York, 1989.

[13] E. Fried & M. E. Gurtin, Dynamic solid-solid transitions with phase characterized by an order parameter, *Physica D* **68** (1993), 326–343.

[14] E. Fried, Continua described by a microstructural field, *Zeitschrift für angewandte Mathematik und Physik* **47** (1996), 168–175.

[15] M. E. Gurtin, Generalized Ginzburg-Landau and Cahn-Hilliard equations based on a microforce balance, *Physica D* **92** (1996), 178–192.

[16] W. Nernst, Zur Kinetik der in Lösung befindlichen Körper: I. Theorie der Diffusion, *Zeitschrift für physikalische Chemie* **2** (1888), 613–637.

[17] J. H. van't Hoff, Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen, *Zeitschrift für physikalische Chemie* **1** (1887), 481–508.

[18] M. Planck, Ueber die Erregung von Electricität und Wärme in Electrolyten, *Annalen der Physik und Chemie* (*Neue Folge*) **39** (1890), 161–186.

[19] A. Einstein, Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen, *Annalen der Physik* **17** (1905), 549–560.

[20] A. Einstein, Zur Theorie der Brownschen Bewegung, *Annalen der Physik* **19** (1906), 371–381.

[21] A. Einstein, Elementare Theorie der Brownschen Bewegung, *Zeitschrift für Elektrochemie* **14** (1908), 235–239.

[22] A. Einstein, Eine neue Bestimmung der Moleküldimensionen, *Annalen der Physik* **19** (1906), 289–306.

[23] A. Prock & G. McConkey, *Topics in Chemical Physics: Based on the Harvard Lectures of Peter J. W. Debye*, Elsevier, Amsterdam, 1962.

[24] M. von Smoluchowski, Über Brownsche Molekularbewegung unter Einwirkung äußerer Kräfte und deren Zusammenhang mit der verallgemeinerten Diffusionsgleichung, *Annalen der Physik* **48** (1915), 1103–1112.

[25] L. Boltzmann, Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen. *Sitzungsberichte der Akademie der Wissenschaften, Wien* **66** (1872), 275–370.

[26] P. Debije, Zur Theorie der anomalen Dispersion im Gebiete der langwelligen elektrischen Strahlung, *Berichte der deutschen physikalischen Gesellschaft* **15** (1913), 777–793.

[27] P. Debye, *Polar Molecules*, Chemical Catalog Company, New York, 1929.

[28] H. Giesekus, Die rheologische Zustandsgleichung, *Rheologica Acta* **1** (1958), 2–20.

[29] M. Doi & S. F. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press, Oxford, 1986.

[30] R. B. Bird, R. C. Armstrong & O. Hassager, *The Dynamics of Polymeric Liquids*, Volume 2, Wiley, New York, 1977.

[31] B. D. Coleman & W. Noll, The thermodynamics of elastic materials with heat conduction and viscosity, *Archive for Rational Mechanics and Analysis* **13** (1963), 167–178.

[32] M. E. Gurtin & P. W. Voorhees, The continuum mechanics of coherent two-phase elastic solids with mass transport, *Proceedings of the Royal Society of London A* **444** (1993), 323–343.

[33] G. G. Stokes, On the effect of internal friction of fluids on the motion of pendulums, *Transactions of the Cambridge Philosophical Society* **9** (1851), 8–106 = *Mathematical and Physical Papers*, Volume 3, Cambridge University Press, Cambridge, 1901.

[34] G. K. Batchelor, Brownian diffusion of particles with hydrodynamic interaction, *Journal of Fluid Mechanics* **74** (1976), 1–29.