Fluid mixtures and applications to biological systems

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Abstract We apply the free energy principle to fluid systems, where the components react with each other. As example we treat the predator-prey system and cyclic reactions. We deal with the polymerization of actin filaments and with the general diffusion limit.

1 Introduction

We consider a mixture of fluids with applications as they widely occur in biology, biophysics and biochemistry. It is assumed that for each fluid a conservation law for the momentum is satisfied. This is true for a mixture of particle systems, where the attraction force for molecules of the same kind is stronger that the attraction between different species of the mixture. For example, this is the case for liquid-solid mixtures, see Rajagopal [10, 3.3 Basic Equations].

In section 3 we consider mass and momentum balances for each component of the mixture, each component having it's own velocity with interaction terms between the different momentum equations. See the system (1).

Constitutive equations will be derived with the help of the entropy principle in the version of I. Müller [9]. That book also contains a treatment of mixtures, but his theory of mixtures of fluids is restricted to the non-viscous case [9, Chap. 6 $(6.18)_2$]. We insert also viscous terms in the momentum equations.

We consider the isothermal case. In this case the entropy principle becomes the free energy inequality. We show how this leads to restrictions on the constitutive equations and end up with an equivalent system (17), which is the basis for further studies.

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We deal with several special topics, among them free energies depending on gradients (section 6), the system for total density and fractional densities (section 9), a contribution to quasistatic problems (section 8), which is followed by a consideration of a diffusive limit (section 10). Beside this we give some particular examples from biology (sections 5 and 7) as the Lotka-Volterra system and the polymerization of actin filaments. There is a full theory for chemical systems, but a theory for general biological problems goes beyond this and is new. The reason is that the non-negativity for each reaction is a too strong assumption for the non-negativity of the free energy production. In this paper we cannot give a full theory for all cases so this is reserved to considerations in a future paper.

Wir möchten uns an dieser Stelle bei der DFG bedanken, die in den Sonderforschungsbereichen SBF123 "Stochastische Mathematische Modelle", SFB72 "Approximation und Mathematische Optimierung", SFB256 "Nichtlineare Partielle Differentialgleichungen" und SFB611 "Singuläre Phänomene und Skalierung in mathematischen Modellen" für eine ausgezeichnete Umgebung für Mathematiker gesorgt hat. Dies hat uns das systematische Forschen auf dem Gebiet der Partiellen Differentialgleichungen erst ermöglicht.

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2 Fluid mixtures

We consider a mixture of compressible fluids, where ρ_α is the mass density and v_α the velocity of the α-th constituent. The balance laws for mass and momentum for each fluid component α are [1]

$$\begin{aligned}&\partial_t\rho_\alpha + \operatorname{div}(\rho_\alpha v_\alpha) = \tau_\alpha\,,\\ &\partial_t(\rho_\alpha v_\alpha) + \operatorname{div}(\rho_\alpha v_\alpha\otimes v_\alpha + \Pi_\alpha) = g_\alpha + \tau_\alpha v_\alpha + \mathbf{f}_\alpha\,.\end{aligned} \tag{1}$$

This holds for each α. Here τ_α are reaction terms, $\mathbf{f}_\alpha$ are possible external forces and g_α are interaction forces. The matrix Π_α is the pressure tensor containing as part the negative stress tensor, as we will see later in statement 10.

Besides these balance laws we have constitutive relations for τ_α, Π_α, and g_α, which couple the equations. These conditions are subject to restrictions coming from the principle of objectivity (see the remark 7 below). So the mass production τ_α is an objective scalar, the pressure tensor Π_α an objective tensor, $\mathbf{f}_\alpha$ transform like an external force and the coupling term g_α is an objective vector.

1 Constitutive equations. Using the notation

$$\rho = (\rho_\beta)_\beta\,,\quad v = (v_\beta)_\beta\,, \tag{2}$$

[1] Note: In the second equation the divergence acts on the second index of tensors.

we assume constitutive relations for

$$\tau_\alpha, g_\alpha, \Pi_\alpha,$$

in general depending on $(\rho, v, \nabla\rho, \mathrm{D}v)$. We do not specify $\mathbf{f}_\alpha$.

In a single fluid it often happens that dependencies on the velocity drop out by objectivity. For mixtures the situation is quite different, since differences $v_{\alpha_1} - v_{\alpha_2}$ of two velocities are objectives vectors (see [10, 4. Constitutive Equations]). Therefore we define in accordance with [7, Chap. XI §2]

2 Barycentric velocity. A mean density and a mean velocity is defined by

$$\bar\rho := \sum_\alpha \rho_\alpha, \quad \bar v := \tfrac{1}{\bar\rho}\sum_\alpha \rho_\alpha v_\alpha$$

where α runs from 1 to N, the number of components. We define the relative velocities by

$$u_\alpha := v_\alpha - \bar v, \tag{3}$$

and it follows that these are objective vectors (see remark 7).

3 Lemma. Obviously

$$\sum_\alpha \rho_\alpha u_\alpha = 0. \tag{4}$$

As a consequence

$$\mathrm{D}\bar v = \sum_\alpha \tfrac{\rho_\alpha}{\bar\rho}\mathrm{D}v_\alpha + \sum_\alpha \tfrac{1}{\bar\rho} u_\alpha \otimes \nabla\rho_\alpha, \tag{5}$$

Proof. Equation (4) is a direct consequence of the definition of $\bar v$. Computing the derivative of (4) one obtains

$$\begin{aligned} 0 &= \mathrm{D}\Big(\sum_\alpha \rho_\alpha u_\alpha\Big) = \sum_\alpha u_\alpha \otimes \nabla\rho_\alpha + \sum_\alpha \rho_\alpha \mathrm{D}u_\alpha \\ &= \sum_\alpha u_\alpha \otimes \nabla\rho_\alpha + \sum_\alpha \rho_\alpha \mathrm{D}v_\alpha - \bar\rho\mathrm{D}\bar v \end{aligned}$$

by using that $u_\alpha = v_\alpha - \bar v$. □

Here we consider materials, where all velocities v_α are independent variables. Likewise $\bar v$ and the u_α, obviously with the constraint (4), are independent variables. Summing up the equations (1) and using (4) we obtain, that these mean quantities satisfy the total mass and total momentum balance equations

$$\begin{aligned} \partial_t\bar\rho + \operatorname{div}(\bar\rho\,\bar v) &= \sum_\alpha \tau_\alpha, \\ \partial_t(\bar\rho\bar v) + \operatorname{div}\Big(\bar\rho\,\bar v\otimes\bar v + \sum_\alpha \rho_\alpha u_\alpha\otimes u_\alpha + \sum_\alpha \Pi_\alpha\Big) &= \sum_\alpha (g_\alpha + \tau_\alpha v_\alpha + \mathbf{f}_\alpha). \end{aligned} \tag{6}$$

We now interpret the quantities in these common equations.

4 Collective quantities. It follows that (6) is equivalent to

$$\begin{aligned} \partial_t\bar\rho + \operatorname{div}(\bar\rho\,\bar v) &= \bar\tau, \\ \partial_t(\bar\rho\bar v) + \operatorname{div}\Big(\bar\rho\,\bar v\otimes\bar v + \bar\Pi\Big) &= \bar g + \bar\tau\bar v + \bar{\mathbf{f}}, \end{aligned} \tag{7}$$

if the production of the total mass $\bar{\rho}$ is

$$\bar{\tau} := \sum_\alpha \tau_\alpha$$

and if the pressure tensor $\bar{\Pi}$ for the total fluid is

$$\bar{\Pi} := \sum_\alpha \rho_\alpha u_\alpha \otimes u_\alpha + \sum_\alpha \Pi_\alpha \,.$$

We assume that $\bar{\Pi}$ is a symmetric objective tensor (the tensors Π_α do not need to be symmetric). Moreover, the momentum production terms are given by

$$\bar{g} := \sum_\alpha (\tau_\alpha u_\alpha + g_\alpha) \,, \quad \bar{\mathbf{f}} := \sum_\alpha \mathbf{f}_\alpha \,.$$

For a closed system one assumes that $\bar{\tau}$ and $\bar{g}$ vanish (see statement 11). To include other systems we will proceed with arbitrary values of $\bar{\tau}$ and $\bar{g}$, although then one would insist to extend the system to a closed one, or to say on which closed system the model relies.

For further considerations it is important how the total kinetic free energy is defined. The sum of the kinetic energy of each fluid

$$f_{kin} := \sum_\alpha \tfrac{\rho_\alpha}{2} |v_\alpha|^2 = \tfrac{\bar{\rho}}{2} |\bar{v}|^2 + \sum_\alpha \tfrac{\rho_\alpha}{2} |u_\alpha|^2 \tag{8}$$

is a basis for it, and a single kinetic energy satisfies the following evolution equation.

5 Proposition. For each α it follows from the equations in (1) that the following identity

$$\begin{aligned} &\partial_t \Big(\frac{\rho_\alpha}{2} |v_\alpha|^2 \Big) + \operatorname{div} \Big(\frac{\rho_\alpha}{2} |v_\alpha|^2 v_\alpha + \Pi_\alpha^T v_\alpha \Big) \\ &= \mathrm{D} v_\alpha \bullet \Pi_\alpha + v_\alpha \bullet (g_\alpha + \mathbf{f}_\alpha) + \frac{\tau_\alpha}{2} |v_\alpha|^2 \end{aligned}$$

is satisfied.

Proof. (This is standard.) For each index α and any linear first order differential operator $L = \beta_0 \partial_t + \sum_i \beta_i \partial_i$ we compute

$$L(\frac{\rho_\alpha}{2} |v_\alpha|^2) = \frac{|v_\alpha|^2}{2} L\rho_\alpha + \rho_\alpha v_\alpha \bullet L v_\alpha = -\frac{|v_\alpha|^2}{2} L\rho_\alpha + v_\alpha \bullet L(\rho_\alpha v_\alpha) \,,$$

and for $L = \partial_t + v_\alpha \bullet \nabla$ we write the differential equations (1) as

$$\begin{aligned} L\rho_\alpha &= -\rho_\alpha \operatorname{div} v_\alpha + \tau_\alpha \,, \\ L(\rho_\alpha v_\alpha) &= -\rho_\alpha (\operatorname{div} v_\alpha) v_\alpha - \operatorname{div} \Pi_\alpha + (g_\alpha + \tau_\alpha v_\alpha + \mathbf{f}_\alpha) \end{aligned}$$

and obtain

$$
\begin{aligned}
&L\Big(\frac{\rho_\alpha |v_\alpha|^2}{2}\Big) = -\frac{|v_\alpha|^2}{2} L\rho_\alpha + v_\alpha \bullet L(\rho_\alpha v_\alpha) \\
&= \Big(\frac{|v_\alpha|^2}{2} - v_\alpha \bullet v_\alpha\Big)\rho_\alpha \operatorname{div} v_\alpha - \frac{|v_\alpha|^2}{2}\tau_\alpha - v_\alpha \bullet \operatorname{div} \Pi_\alpha + v_\alpha \bullet (g_\alpha + \tau_\alpha v_\alpha + \mathbf{f}_\alpha) \\
&= -\frac{|v_\alpha|^2}{2}\rho_\alpha \operatorname{div} v_\alpha - \operatorname{div}({\Pi_\alpha}^{\mathrm{T}} v_\alpha) + \mathrm{D}v_\alpha \bullet \Pi_\alpha + v_\alpha \bullet (g_\alpha + \mathbf{f}_\alpha) + \frac{|v_\alpha|^2}{2}\tau_\alpha \,.
\end{aligned}
$$

This gives the result

$$
\begin{aligned}
&\partial_t\Big(\frac{\rho_\alpha}{2}|v_\alpha|^2\Big) + \operatorname{div}\Big(\frac{\rho_\alpha}{2}|v_\alpha|^2 v_\alpha + \Pi_\alpha^T v_\alpha\Big) \\
&= L\Big(\frac{\rho_\alpha}{2}|v_\alpha|^2\Big) + \frac{|v_\alpha|^2}{2}\rho_\alpha \operatorname{div} v_\alpha + \operatorname{div}(\Pi_\alpha^T v_\alpha) \\
&= \mathrm{D}v_\alpha \bullet \Pi_\alpha + v_\alpha \bullet (g_\alpha + \mathbf{f}_\alpha) + \tau_\alpha \frac{|v_\alpha|^2}{2} \,.
\end{aligned}
$$

□

The equations have to be supplemented by the entropy principle, which in the here considered isothermal case is equivalent to the free energy inequality. This requires a definition of the (total) free energy, which as a part consists of the kinetic free energy f^{kin}.

6 Free energy principle. The postulate is that there exist a (total) free energy f^{tot} and a free energy flux φ^{tot}, such that for all solutions (ρ, v) of the mixture problem the inequality

$$
\partial_t f^{tot} + \operatorname{div} \varphi^{tot} - g^{tot} \le 0 \tag{9}
$$

holds, and $(f^{tot}, \varphi^{tot}, g^{tot})$ satisfy certain constitutive relations. Among this

$$
f^{tot} := \textstyle\sum_\alpha \frac{\rho_\alpha}{2}|v_\alpha|^2 + f = f^{kin} + f \,, \tag{10}
$$

where the internal free energy f is an objective scalar. The constitutive assumption on f is a consequence of the materials considered here (see (11) and (23)), in any case it will depend on ρ. For the flux we assume

$$
\varphi^{tot} := \textstyle\sum_\alpha \frac{\rho_\alpha}{2}|v_\alpha|^2 v_\alpha + f\bar{v} + \sum_\alpha \Pi_\alpha^T v_\alpha + \varphi \,,
$$

where φ is an objective vector, which has to be determined later. The term g^{tot} has in accordance with objectivity the form

$$
g^{tot} = \frac{\bar{\tau}}{2}|\bar{v}|^2 + \bar{g} \bullet \bar{v} + \textstyle\sum_\alpha v_\alpha \bullet \mathbf{f}_\alpha \,.
$$

This contains the usual external force terms $\mathbf{f}_\alpha$, but also terms containing the external quantities $\bar{\tau}$ and $\bar{g}$.

It is important to say, that the inequality (9) implies that

$$
h := \partial_t f^{tot} + \operatorname{div} \varphi^{tot} - g^{tot}
$$

has to be an objective scalar (see [1, Lemma 10.3]). That is the reason, why a term g^{tot} is necessary. The free energy f^{tot} transforms in the same way as f^{kin} does. This determines the transformation formula for the flux φ^{tot}, which has an unknown term φ and which turns out to be an objective vector. It can be written as

$$\varphi^{tot} = f^{tot}\bar{v} + \Big(\sum_\alpha \tfrac{\rho_\alpha}{2}|v_\alpha|^2 u_\alpha + \sum_\alpha \Pi_\alpha^T v_\alpha\Big) + \varphi\,.$$

7 Remark on objectivity. The objectivity of the system itself can be found in [1, Chapter 8]. In [1] an arbitrary observer transformation is given by a map Y,

$$\begin{bmatrix} t \\ x \end{bmatrix} = Y\Big(\begin{bmatrix} t^* \\ x^* \end{bmatrix}\Big) = \begin{bmatrix} t^* + a \\ X(t^*,x^*) \end{bmatrix}, \quad X(t^*,x^*) = Q(t^*)x^* + b(t^*)\,,$$

where the quantities with respect to the new observer are indicated by a star. Then besides well known transformations of terms in the α-system (1), in particular, the following is true. The velocity transforms like

$$v_\alpha \circ Y = \dot{X} + Q v_\alpha^*\,,$$

the force of the α-system transforms like

$$\mathbf{f}_\alpha \circ Y = \rho_\alpha^*(\ddot{X} + 2\dot{Q}v_\alpha^*) + Q\mathbf{f}_\alpha^*\,,$$

and the force for the global system (6) transforms like

$$\bar{\mathbf{f}} \circ Y = \bar{\rho}^*(\ddot{X} + 2\dot{Q}\bar{v}^*) + Q\bar{\mathbf{f}}^*\,,$$

which is consistent with the definition of the collective $\bar{\mathbf{f}}$. The objectivity about the terms in (9), which assumes (7), can be found in [1, Chapter 10]. As mentioned above, the term g^{tot} has to contain the not objective scalar terms

$$\frac{\bar{\tau}}{2}|\bar{v}|^2 + (\bar{g} + \bar{\mathbf{f}})\bullet\bar{v}\,,$$

and it can be shown that the term $\sum_\alpha u_\alpha \bullet \mathbf{f}_\alpha$ is an objective scalar. (It is not clear, where an objective scalar should be placed, in g^{tot} or h, one has to perform the entropy inequality to clarify this.)

The free energy inequality reduces to the following inequality for the internal free energy.

8 Proposition. For the free energy production h one computes

$$\begin{aligned} 0 \geq h = {} & \partial_t f + \operatorname{div}(f\bar{v} + \varphi) \\ & + \sum_\alpha \Big(\mathrm{D}v_\alpha \bullet \Pi_\alpha + u_\alpha \bullet g_\alpha + \tfrac{\tau_\alpha}{2}|u_\alpha|^2\Big) \end{aligned}$$

for every solution of system (1).

Proof. Summing up in Proposition 5 one obtains

$$\partial_t f^{kin} + \operatorname{div}\Big(\sum_\alpha\big(\tfrac{\rho_\alpha}{2}|v_\alpha|^2 v_\alpha + \Pi_\alpha^T v_\alpha\big)\Big)$$
$$= \sum_\alpha \Big(\mathrm{D}v_\alpha \bullet \Pi_\alpha + v_\alpha \bullet (g_\alpha + \mathbf{f}_\alpha) + \tfrac{\tau_\alpha}{2}|v_\alpha|^2\Big)\,.$$

Inserting this in the definition of h gives

$$\begin{aligned} h &= \partial_t f^{tot} + \operatorname{div}\varphi^{tot} - g^{tot} \\ &= \partial_t (f^{kin} + f) + \operatorname{div}\Big(\sum_\alpha \Big(\tfrac{\rho_\alpha}{2}|v_\alpha|^2 v_\alpha + \Pi_\alpha^T v_\alpha\Big) + f\bar{v} + \varphi\Big) - g^{tot} \\ &= \partial_t f + \operatorname{div}(f\bar{v} + \varphi) - g^{tot} \\ &\quad + \sum_\alpha \Big(\mathrm{D}v_\alpha \bullet \Pi_\alpha + v_\alpha \bullet (g_\alpha + \mathbf{f}_\alpha) + \tfrac{\tau_\alpha}{2}|v_\alpha|^2\Big)\,. \end{aligned}$$

Since

$$\begin{aligned} &\sum_\alpha \Big(v_\alpha \bullet (g_\alpha + \mathbf{f}_\alpha) + \tfrac{\tau_\alpha}{2}|v_\alpha|^2\Big) \\ &= \sum_\alpha \Big((u_\alpha + \bar{v})\bullet g_\alpha + \tfrac{\tau_\alpha}{2}|u_\alpha + \bar{v}|^2\Big) + \sum_\alpha v_\alpha \bullet \mathbf{f}_\alpha \\ &= \sum_\alpha \Big(u_\alpha \bullet g_\alpha + \tfrac{\tau_\alpha}{2}|u_\alpha|^2\Big) + R\,, \end{aligned}$$

where

$$\begin{aligned} R &= \sum_\alpha \Big(\bar{v}\bullet g_\alpha + \tfrac{\tau_\alpha}{2}(2u_\alpha \bullet \bar{v} + |\bar{v}|^2)\Big) + \sum_\alpha v_\alpha \bullet \mathbf{f}_\alpha \\ &= \bar{v}\bullet \sum_\alpha \Big(g_\alpha + \tau_\alpha u_\alpha\Big) + |\bar{v}|^2 \sum_\alpha \tfrac{\tau_\alpha}{2} + \sum_\alpha v_\alpha \bullet \mathbf{f}_\alpha \\ &= \bar{v}\bullet\bar{g} + |\bar{v}|^2 \frac{\bar{\tau}}{2} + \sum_\alpha v_\alpha \bullet \mathbf{f}_\alpha = g^{tot}\,, \end{aligned}$$

the assertion follows. □

It is the aim to determine the consequences of the free energy principle. For this it is now essential, what constitutive properties f and φ have.

3 Exploiting the free energy inequality

In this section we make use of the assumption, that the free energy f depends on all the densities ρ_α, and with this assumption we go into the free energy inequality 8.

9 Proposition. If the free energy is given by

$$f \equiv f(\rho)\,, \tag{11}$$

then we obtain for the free energy production

$$h = \operatorname{div}\varphi + \sum_\alpha f'_{\rho_\alpha}\tau_\alpha + \sum_\alpha u_\alpha \bullet \Big(g_\alpha + \tfrac{\tau_\alpha}{2}u_\alpha + \big(\tfrac{f}{\bar\rho} - f'_{\rho_\alpha}\big)\nabla\rho_\alpha\Big)$$
$$+ \sum_\alpha \mathrm{D}v_\alpha \bullet \Big(\Pi_\alpha + \rho_\alpha\big(\tfrac{f}{\bar\rho} - f'_{\rho_\alpha}\big)\mathrm{Id}\Big)\,.$$

Thus the production term is written in the independent gradient terms $\mathrm{D}v_\alpha$ and $\nabla\rho_\alpha$.

Proof. Since $f = f((\rho_\alpha)_\alpha)$ we compute, by making use of the mass conservations,

$$\begin{aligned}
&\partial_t f + \operatorname{div}(f\bar v) = (\partial_t + \bar v\bullet\nabla)f + f\operatorname{div}\bar v\\
&= \textstyle\sum_\alpha f'_{\rho_\alpha}\cdot\Big(\partial_t\rho_\alpha + \bar v\bullet\nabla\rho_\alpha\Big) + f\operatorname{div}\bar v\\
&= \textstyle\sum_\alpha f'_{\rho_\alpha}\cdot\Big(\tau_\alpha - \operatorname{div}(\rho_\alpha v_\alpha) + \bar v\bullet\nabla\rho_\alpha\Big) + f\operatorname{div}\bar v\\
&= \textstyle\sum_\alpha f'_{\rho_\alpha}\tau_\alpha - \sum_\alpha f'_{\rho_\alpha}u_\alpha\bullet\nabla\rho_\alpha - \sum_\alpha \rho_\alpha f'_{\rho_\alpha}\operatorname{div}v_\alpha + f\operatorname{div}\bar v\,.
\end{aligned}$$

We plug this into the expression for h and obtain

$$\begin{aligned}
h = {}&\operatorname{div}\varphi + \textstyle\sum_\alpha f'_{\rho_\alpha}\tau_\alpha - \sum_\alpha f'_{\rho_\alpha}u_\alpha\bullet\nabla\rho_\alpha\\
&- \textstyle\sum_\alpha \rho_\alpha f'_{\rho_\alpha}\operatorname{div}v_\alpha + f\operatorname{div}\bar v\\
&+ \textstyle\sum_\alpha \mathrm{D}v_\alpha\bullet\Pi_\alpha + \sum_\alpha u_\alpha\bullet g_\alpha + \sum_\alpha \tfrac{\tau_\alpha}{2}|u_\alpha|^2\,.
\end{aligned}$$

Now we use (5) to derive

$$\operatorname{div}\bar v = \textstyle\sum_\alpha \tfrac{\rho_\alpha}{\bar\rho}\operatorname{div}v_\alpha + \sum_\alpha \tfrac{1}{\bar\rho}u_\alpha\bullet\nabla\rho_\alpha\,,$$

which gives

$$\begin{aligned}
&-\textstyle\sum_\alpha \rho_\alpha f'_{\rho_\alpha}\operatorname{div}v_\alpha + f\operatorname{div}\bar v\\
&= \textstyle\sum_\alpha\big(\tfrac{\rho_\alpha f}{\bar\rho} - \rho_\alpha f'_{\rho_\alpha}\big)\operatorname{div}v_\alpha + \sum_\alpha \tfrac{f}{\bar\rho}u_\alpha\bullet\nabla\rho_\alpha\,.
\end{aligned}$$

Therefore we obtain for the energy production

$$\begin{aligned}
h = {}&\operatorname{div}\varphi + \textstyle\sum_\alpha f'_{\rho_\alpha}\tau_\alpha - \sum_\alpha f'_{\rho_\alpha}u_\alpha\bullet\nabla\rho_\alpha\\
&+ \textstyle\sum_\alpha u_\alpha\bullet g_\alpha + \sum_\alpha\tfrac{\tau_\alpha}{2}|u_\alpha|^2 + \sum_\alpha\tfrac{f}{\bar\rho}u_\alpha\bullet\nabla\rho_\alpha\\
&+ \textstyle\sum_\alpha \mathrm{D}v_\alpha\bullet\Big(\Pi_\alpha + \big(\tfrac{\rho_\alpha f}{\bar\rho} - \rho_\alpha f'_{\rho_\alpha}\big)\mathrm{Id}\Big)\\
= {}&\operatorname{div}\varphi + \textstyle\sum_\alpha f'_{\rho_\alpha}\tau_\alpha\\
&+ \textstyle\sum_\alpha u_\alpha\bullet\Big(g_\alpha + \tfrac{\tau_\alpha}{2}u_\alpha + \big(\tfrac{f}{\bar\rho} - f'_{\rho_\alpha}\big)\nabla\rho_\alpha\Big)\\
&+ \textstyle\sum_\alpha \mathrm{D}v_\alpha\bullet\Big(\Pi_\alpha + \rho_\alpha\big(\tfrac{f}{\bar\rho} - f'_{\rho_\alpha}\big)\mathrm{Id}\Big)\,.
\end{aligned}$$

□

We define the specific free energy and the specific pressures by

$$f^{sp} = \frac{f}{\bar\rho}\,,\quad p^{sp}_\alpha = \frac{p_\alpha}{\rho_\alpha}\,, \tag{12}$$

where the specific pressure p^{sp}_α is defined with respect to the density ρ_α. Then we obtain the following theorem as a consequence.

10 Theorem. Let $f \equiv f(\rho)$ and

$$p^{sp}_\alpha := f_{\prime\rho_\alpha} - \tfrac{f}{\bar\rho}\,, \quad \mu_\alpha := f_{\prime\rho_\alpha}\,. \tag{13}$$

If in addition to assumption (11) we suppose $\varphi = 0$ and

$$\begin{aligned} \Pi_\alpha &= p_\alpha \mathrm{Id} - S_\alpha\,, \quad p_\alpha = \rho_\alpha p^{sp}_\alpha\,, \\ g_\alpha &= p^{sp}_\alpha \nabla\rho_\alpha - \frac{\tau_\alpha}{2} u_\alpha + g^{fr}_\alpha - \rho_\alpha g^{sp}\,, \end{aligned} \tag{14}$$

where the objective quantities S_α, τ_α, g^{fr}_α, and g^{sp} are arbitrary constitutive functions, then for solutions of (1) the free energy production h reads

$$0 \geq h = -\textstyle\sum_\alpha \mathrm{D}v_\alpha \bullet S_\alpha + \sum_\alpha \tau_\alpha \mu_\alpha + \sum_\alpha g^{fr}_\alpha \bullet u_\alpha\,. \tag{15}$$

We also have the identity

$$f_{\prime\rho_\alpha} - \frac{f}{\bar\rho} = \bar\rho \left(\frac{f}{\bar\rho}\right)_{\prime\rho_\alpha} = \bar\rho \cdot f^{sp}_{\prime\rho_\alpha}$$

and therefore

$$p^{sp}_\alpha = \bar\rho \cdot f^{sp}_{\prime\rho_\alpha}\,. \tag{16}$$

The friction terms g^{fr}_α are those terms of the interactive force, which contribute to the free energy production. The vector field g^{sp}, which is independent of α, is due to the constraint (4) and contributes to the external term $\bar g$ and to the differential equations, see the statements 12 and 13.

Proof. This follows immediately from statement 9, where one has to take into account the constraint (4) for the relative velocities u_α. □

11 Remark (External quantities). Define

$$\bar g^{fr} := \textstyle\sum_\alpha g^{fr}_\alpha\,.$$

Then

$$\begin{aligned} \bar\tau &= \textstyle\sum_\alpha \tau_\alpha\,, \\ \bar g &= \textstyle\sum_\alpha \frac{\tau_\alpha}{2} u_\alpha + \bar\rho(\nabla f^{sp} - g^{sp}) + \bar g^{fr}\,. \end{aligned}$$

Note: The external terms $\bar\tau$ and $\bar g$ vanish for a completely closed model as mentioned in section 2, see statement 13 below.

Proof. From (14) we obtain

$$g_\alpha + \tau_\alpha u_\alpha = \frac{\tau_\alpha}{2} u_\alpha + p^{sp}_\alpha \nabla\rho_\alpha + g^{fr}_\alpha - \rho_\alpha g^{sp}\,,$$

hence

$$\bar{g} = \sum_\alpha \tfrac{\tau_\alpha}{2} u_\alpha + \sum_\alpha (p_\alpha^{sp} \nabla \rho_\alpha - \rho_\alpha g^{sp}) + \bar{g}^{fr}$$

and from (16)

$$\sum_\alpha (p_\alpha^{sp} \nabla \rho_\alpha - \rho_\alpha g^{sp}) = \sum_\alpha \bar{\rho} f^{sp}_{,\rho_\alpha} \nabla \rho_\alpha - \big(\sum_\alpha \rho_\alpha\big) g^{sp} = \bar{\rho}(\nabla f^{sp} - g^{sp})\,.$$

□

We summarize:

12 Conclusion. Under the assumptions of Theorem 10, the mixture system (1) is equivalent to

$$\begin{aligned}
&\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha v_\alpha) = \tau_\alpha\,,\\
&\rho_\alpha\big(\partial_t v_\alpha + (v_\alpha \bullet \nabla) v_\alpha\big)\\
&\quad = \operatorname{div} S_\alpha - \rho_\alpha(\nabla p_\alpha^{sp} + g^{sp}) - \frac{\tau_\alpha}{2} u_\alpha + g_\alpha^{fr} + \mathbf{f}_\alpha
\end{aligned} \tag{17}$$

for all α. The free energy inequality (15) is satisfied.

Proof. With the assumptions in 10 the momentum law in (1) becomes

$$\begin{aligned}
&\partial_t(\rho_\alpha v_\alpha) + \operatorname{div}(\rho_\alpha v_\alpha \otimes v_\alpha + p_\alpha \mathrm{Id} - S_\alpha)\\
&= \tau_\alpha v_\alpha + g_\alpha + \mathbf{f}_\alpha\\
&= \tau_\alpha \frac{\bar{v} + v_\alpha}{2} + p_\alpha^{sp} \nabla \rho_\alpha - \rho_\alpha g^{sp} + g_\alpha^{fr} + \mathbf{f}_\alpha\,,
\end{aligned}$$

or if we use the mass equation in (1)

$$\begin{aligned}
&\rho_\alpha\big(\partial_t v_\alpha + (v_\alpha \bullet \nabla) v_\alpha\big) + \operatorname{div}(p_\alpha \mathrm{Id} - S_\alpha)\\
&= g_\alpha + \mathbf{f}_\alpha\\
&= -\frac{\tau_\alpha}{2} u_\alpha + p_\alpha^{sp} \nabla \rho_\alpha - \rho_\alpha g^{sp} + g_\alpha^{fr} + \mathbf{f}_\alpha\,,
\end{aligned}$$

or equivalently

$$\begin{aligned}
&\rho_\alpha\big(\partial_t v_\alpha + (v_\alpha \bullet \nabla) v_\alpha\big)\\
&= \operatorname{div} S_\alpha - \nabla p_\alpha + g_\alpha + \mathbf{f}_\alpha\\
&= \operatorname{div} S_\alpha + p_\alpha^{sp} \nabla \rho_\alpha - \nabla p_\alpha - \rho_\alpha g^{sp} - \frac{\tau_\alpha}{2} u_\alpha + g_\alpha^{fr} + \mathbf{f}_\alpha\\
&= \operatorname{div} S_\alpha - \rho_\alpha(\nabla p_\alpha^{sp} + g^{sp}) - \frac{\tau_\alpha}{2} u_\alpha + g_\alpha^{fr} + \mathbf{f}_\alpha\,.
\end{aligned}$$

Here we have used the fact that

$$\nabla p_\alpha = \nabla(\rho_\alpha p_\alpha^{sp}) = \rho_\alpha \nabla p_\alpha^{sp} + p_\alpha^{sp} \nabla \rho_\alpha\,.$$

□

The additional term g^{sp} can be chosen so, that $\bar{g} = 0$.

13 Consequence. It is $\bar{g} = 0$, if we choose g^{sp} as

$$g^{sp} := \frac{1}{2\bar{\rho}} \sum_\alpha \tau_\alpha u_\alpha + \nabla f^{sp} + \tfrac{1}{\bar{\rho}} \bar{g}^{fr} .$$

This follows immediately from the representation in 11. With this assumption we obtain the following theorem.

14 Theorem. Under the assumptions of theorem 10 and if g^{sp} is chosen as in 13, the system (1) is equivalent to

$$\begin{aligned} &\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha v_\alpha) = \tau_\alpha , \\ &\rho_\alpha \big(\partial_t v_\alpha + (v_\alpha \bullet \nabla) v_\alpha\big) \\ &\qquad = \operatorname{div} S_\alpha - \rho_\alpha \nabla \mu_\alpha - \big(\frac{1}{2} + \frac{\rho_\alpha}{2\bar{\rho}}\big) \tau_\alpha u_\alpha + g_\alpha^{fr} - \frac{\rho_\alpha}{\bar{\rho}} \bar{g}^{fr} + \mathbf{f}_\alpha \end{aligned}$$

for all α. Here $\mu_\alpha := f'_{\rho_\alpha}$ are the chemical potentials.

If one chooses the g_α^{fr} with $\bar{g}^{fr} = 0$, the $\bar{g}^{fr}$ term in the momentum equation vanishes.

Proof. It is $p_\alpha^{sp} + f^{sp} = f'_{\rho_\alpha} = \mu_\alpha$. With this the assertion follows from the previous statement 12. □

The easiest way to verify that the free energy inequality (15) is satisfied is to assume that all three components of the free energy production have a sign. (We remark, that in [2, §4] a different splitting is used.) This is the case in the following

15 Lemma. Denote $\mu = (\mu_\alpha)_\alpha$ and $u := (u_\alpha)_\alpha$. If

$$\begin{aligned} &S_\alpha \equiv S_\alpha(\rho, (\mathrm{D}v)^S) := \sum_\beta \big(a_{\alpha\beta} (\mathrm{D}v_\beta)^S + b_{\alpha\beta} \cdot \operatorname{div}(v_\beta) \cdot \mathrm{Id}\big) , \\ &\tau_\alpha \equiv \tau_\alpha(\rho, \mu) , \quad g_\alpha^{fr} \equiv g_\alpha^{fr}(\rho, u) , \end{aligned}$$

with

$$\begin{aligned} &a_{\alpha\beta} \equiv a_{\alpha\beta}(\rho),\ b_{\alpha\beta} \equiv b_{\alpha\beta}(\rho) \text{ positiv semidefinite in } (\alpha, \beta), \\ &\textstyle\sum_\beta \mu_\beta \tau_\beta(\rho, \mu) \le 0 , \quad \sum_\beta u_\beta \bullet g_\beta^{fr}(\rho, u) \le 0 , \end{aligned}$$

then the free energy inequality (15) is satisfied.

4 Remark on pressure

If we change in the equations (1)

$$\Pi_\alpha = \Pi_\alpha^{new} + \omega_\alpha \mathrm{Id} , \quad g_\alpha = g_\alpha^{new} + \nabla \omega_\alpha , \tag{18}$$

the differential equations stay the same, since $\operatorname{div}(\omega_\alpha \mathrm{Id}) = \nabla\omega_\alpha$. This would only transfer a part of the pressure to the right side of the equations. Exactly this happens, if one chooses in the proof of the free energy inequality a nonzero term

$$\varphi = \textstyle\sum_\alpha \widetilde{\omega}_\alpha u_\alpha$$

(compare [9, $(6.52)_4$]). If we define

$$\bar{\omega} = \textstyle\sum_\alpha \widetilde{\omega}_\alpha$$

then, using the representation (5),

$$\begin{aligned}\operatorname{div}\varphi &= u_\alpha \bullet \nabla\widetilde{\omega}_\alpha + \mathrm{D}u_\alpha \bullet (\widetilde{\omega}_\alpha \mathrm{Id})\\ &= u_\alpha \bullet (\nabla\widetilde{\omega}_\alpha - \frac{\bar{\omega}}{\bar{\rho}}\nabla\rho_\alpha) + \mathrm{D}v_\alpha \bullet ((\widetilde{\omega}_\alpha - \frac{\bar{\omega}}{\bar{\rho}}\rho_\alpha)\mathrm{Id})\\ &= u_\alpha \bullet \nabla\omega_\alpha + \mathrm{D}v_\alpha \bullet (\omega_\alpha \mathrm{Id}) \quad \text{ if } \omega_\alpha = \widetilde{\omega}_\alpha - \frac{\bar{\omega}}{\bar{\rho}}\rho_\alpha\,,\end{aligned}$$

since (4) holds. If we would use this in the computation of section 3 we would get the new terms in (18). We remark, that then

$$\varphi = \textstyle\sum_\alpha \omega_\alpha u_\alpha \text{ with } \sum_\alpha \omega_\alpha = 0\,.$$

5 Examples

We describe three examples, the first is a gradient flow, for which the τ_α are proportional to μ_α, the second is the predator-prey system, for which the τ_α are partially orthogonal to μ_α, and the last one is a cyclic reaction with an intermediate state of τ_α. In all cases the sum of the τ_α values are 0 and the free energy inequality (see 15)

$$\textstyle\sum_\alpha \tau_\alpha \mu_\alpha \le 0 \quad \text{where} \quad \mu_\alpha = f'_{\rho_\alpha}(\rho) \tag{19}$$

is satisfied. Besides this we assume, for simplicity, that the relative velocities u_α are all 0, and that the fluid as a whole is incompressible or, is a rigid body. Then the mass equations reduce to

$$\dot{\rho}_\alpha = \tau_\alpha\,,$$

where $\dot{\psi} = \partial_t\psi + \bar{v}\bullet\nabla\psi$ for functions ψ. The following considerations generalize to the general case of system (1).

16 Gradient flow. For given free energy function f consider the gradient flow system

$$\dot{\rho}_\alpha = -\lambda\mu_\alpha\,,$$

where $\lambda \equiv \lambda(\rho) > 0$. Then inequality (19) is satisfied. In this case the sum of the reaction terms does not need to be zero.

In the literature you will find a system consisting of the second and third equation below, the classical Lotka-Volterra system. We refer to [8, Chap. 6] and [Wikipedia: Lotka-Volterra equation].

17 Lotka-Volterra system. For the predator-prey model we let $x > 0$ be the number of prey and $y > 0$ the number of predator and consider the system

$$\begin{aligned} \dot{b} &= -\lambda x\,, \\ \dot{x} &= x \cdot (\alpha - \beta y)\,, \\ \dot{y} &= -y \cdot (\gamma - \delta x)\,, \\ \dot{z} &= \eta x y\,, \\ \dot{d} &= \kappa y\,. \end{aligned}$$

The additional variables are a quantity b proportional to birth of prey, d proportional to death of predator, and z proportional to interactions between predator and prey. This system satisfies the inequality (19), which reduces to

$$\varepsilon\lambda x + \zeta\kappa y + \xi\eta x y \geq 0\,,$$

if the free energy is given by

$$f \equiv \widetilde{f}(b,x,y,z,d) = -\gamma \log x - \alpha \log y + \delta x + \beta y + \varepsilon b - \zeta d - \xi z\,,$$

which is a convex function for constants $\gamma > 0$ and $\alpha > 0$. The inequality (19) holds, if in addition the constants ε, ζ, η, λ, κ and ξ satisfy $\varepsilon\lambda > 0$, $\zeta\kappa > 0$, and $\xi\eta > 0$. The remaining quantities β and δ are positive because of biological reasons.

The variables transform into (bio)mass densities by $\rho_b = b m_b$, $\rho_x = x m_x$, $\rho_y = y m_y$, $\rho_d = d m_d$, $\rho_z = z m_z$ with positive mass constants satisfying

$$\begin{aligned} \lambda = \frac{\alpha m_x}{m_b}\,, \quad \kappa = \frac{\gamma m_y}{m_d}\,, \\ \eta = \frac{\beta m_x - \delta m_y}{m_z}\,, \end{aligned} \tag{20}$$

which implies that the sum of the mass production terms are 0. The parameter η is positive if and only if biomass is lost during transfer from prey to predator.

Proof. It is $f = -\log K + \varepsilon b - \zeta d - \xi z$ with

$$K \equiv K(x,y) = \frac{x^\gamma y^\alpha}{\mathrm{e}^{-\delta x}\mathrm{e}^{-\beta y}}$$

and one computes for solutions of the system that $\dot{K} = 0$, that is, this convex part of f is constant for solutions, and moreover, we see that solutions rotate around the equilibrium

$$x = \frac{\gamma}{\delta}\,, \quad y = \frac{\alpha}{\beta}\,.$$

This is the basis for the entire result: For the mass densities the system is

$$\begin{aligned}
\dot\rho_b &= \tau_b = m_b\tau'_b\,, \quad \tau'_b := -\lambda x\,,\\
\dot\rho_x &= \tau_x = m_x\tau'_x\,, \quad \tau'_x = x\cdot(\alpha-\beta y)\,,\\
\dot\rho_y &= \tau_y = m_y\tau'_y\,, \quad \tau'_y = -y\cdot(\gamma-\delta x)\,,\\
\dot\rho_z &= \tau_z = m_z\tau'_z\,, \quad \tau'_z := \eta xy\,,\\
\dot\rho_d &= \tau_d = m_d\tau'_d\,, \quad \tau'_d := \kappa y\,,
\end{aligned}$$

and, using the identities (20), that is

$$\beta m_x = \delta m_y + \eta m_z\,, \quad \lambda m_b = \alpha m_x\,, \quad \kappa m_d = \gamma m_y\,, \tag{21}$$

we obtain

$$\begin{aligned}
&\tau_b = -\mathbf{r}_b\,, \quad \mathbf{r}_b := \lambda m_b x\,,\\
&\tau_x = \mathbf{r}_b - \mathbf{r}_{xy}\,, \quad \mathbf{r}_{xy} := cxy\,, \quad c := \beta m_x\,,\\
&\tau_y = -\mathbf{r}_d + (1-\omega)\mathbf{r}_{xy}\,, \quad \omega := \frac{\eta m_z}{c}\,,\\
&\tau_z = \omega\mathbf{r}_{xy}\,, \quad \big(\omega c = \eta m_z, (1-\omega)c = \delta m_y\big)\\
&\tau_d = \mathbf{r}_d\,, \quad \mathbf{r}_d := \kappa m_d y\,,
\end{aligned}$$

hence $\bar\tau = 0$. Then one easily computes

$$\begin{aligned}
&\tau'_x \widetilde{f}_{\prime x} + \tau'_y \widetilde{f}_{\prime y} = -\frac{1}{K}(\tau'_x K_{\prime x} + \tau'_y K_{\prime y})\\
&= -\frac{1}{K}(\dot x K_{\prime x} + \dot y K_{\prime y}) = -\frac{1}{K}\dot K = 0\,,
\end{aligned}$$

and therefore

$$\begin{aligned}
&\textstyle\sum_\beta \tau_\beta \mu_\beta = \tau'_b \widetilde{f}_{\prime b} + \tau'_x \widetilde{f}_{\prime x} + \tau'_y \widetilde{f}_{\prime y} + \tau'_z \widetilde{f}_{\prime z} + \tau'_d \widetilde{f}_{\prime d}\\
&= \tau'_b \widetilde{f}_{\prime b} + \tau'_z \widetilde{f}_{\prime z} + \tau'_d \widetilde{f}_{\prime d} = -\varepsilon\lambda x - \zeta\kappa y - \xi\eta xy \le 0\,.
\end{aligned}$$

□

As a last example we consider cyclic reactions, which are important cases and often the basis for biological processes.

18 Cyclic processes.

$$\begin{aligned}
&\dot\rho_\alpha = \tau_\alpha \text{ for } \alpha = 1,\dots,N\,,\\
&\tau_\alpha := \eta_{\alpha+1}\rho_{\alpha+1} - \eta_\alpha\rho_\alpha\,,
\end{aligned} \tag{22}$$

with cyclic repetition, $\rho_{N+1} := \rho_1$, $\eta_{N+1} := \eta_1$. Here η_α are positive constants. This system satisfies the inequality (19), if

$$f \equiv f(\rho) = f_0(\bar\rho) + b(\bar\rho)\textstyle\sum_\alpha \eta_\alpha\rho_\alpha^2$$

with positive functions $b(\bar\rho) > 0$.

The stationary solutions are values $\rho^0 = \{\rho^0_\alpha\,;\ \alpha\}$ with

$$\eta_{\alpha+1}\rho^0_{\alpha+1} = \eta_\alpha\rho^0_\alpha =: \eta^0\,.$$

This $\rho^0 \in \mathbb{R}^N$ is a unique point, if the value of $\bar\rho^0$ is considered to be given. For general solutions ρ is rotating around the stationary line and converging to a value ρ^0, what can be seen from the free energy. We mention that the sum in the free energy can be written as

$$\sum_\alpha \eta_\alpha\rho_\alpha^2 = \sum_\alpha \eta_\alpha(\rho_\alpha-\rho^0_\alpha)^2 + 2\eta^0\bar\rho - \sum_\alpha \eta_\alpha(\rho^0_\alpha)^2\,.$$

Moreover, we again obtain overall mass conservation, that is $\bar\tau = 0$.

Proof. If $f = f(\bar\rho,\rho)$, the derivative with respect to $\bar\rho$ has no effect, since the total mass production is zero. Therefore is is enough to consider a free energy

$$f = f(\rho) = \frac{1}{2}\sum_\alpha b_\alpha\rho_\alpha^2\,,$$

so that

$$\mu_\alpha = f\prime_{\rho_\alpha}(\rho) = b_\alpha\rho_\alpha\,.$$

Then, with $b_\alpha = \eta_\alpha\widetilde{b}_\alpha$ and assuming $\widetilde{b}_\alpha > 0$,

$$\begin{aligned}\sum_\alpha \tau_\alpha\mu_\alpha &= \sum_\alpha(\eta_{\alpha+1}\rho_{\alpha+1}-\eta_\alpha\rho_\alpha)b_\alpha\rho_\alpha\\ &= \sum_\alpha\left(\widetilde{b}_\alpha(\eta_{\alpha+1}\rho_{\alpha+1})(\eta_\alpha\rho_\alpha) - \widetilde{b}_\alpha(\eta_\alpha\rho_\alpha)^2\right)\\ &= \sum_\alpha\left(\sqrt{\tfrac{\widetilde{b}_\alpha}{\widetilde{b}_{\alpha+1}}}\cdot\xi_{\alpha+1}\xi_\alpha - \xi_\alpha^2\right),\end{aligned}$$

where $\xi_\alpha := \eta_\alpha\rho_\alpha\sqrt{\widetilde{b}_\alpha}$. Letting

$$c_\alpha := \sqrt{\frac{\widetilde{b}_\alpha}{\widetilde{b}_{\alpha+1}}}$$

and using $\xi_\alpha\xi_{\alpha+1} \le \frac{1}{2}(\xi_\alpha^2+\xi_{\alpha+1}^2)$, this is

$$\begin{aligned}&= \sum_\alpha\left(c_\alpha\xi_{\alpha+1}\xi_\alpha - \xi_\alpha^2\right) \le \sum_\alpha\left(\tfrac{c_\alpha}{2}\xi_{\alpha+1}^2 + \tfrac{c_\alpha}{2}\xi_\alpha^2 - \xi_\alpha^2\right)\\ &= \sum_\alpha\left(\tfrac{c_{\alpha-1}}{2} + \tfrac{c_\alpha}{2} - 1\right)\xi_\alpha^2 = 0 \text{ if } c_\alpha = 1\,,\end{aligned}$$

that is

$$b = \widetilde{b}_\alpha = \widetilde{b}_{\alpha+1} > 0 \text{ for all } \alpha,$$

or $b_\alpha = \eta_\alpha b$. □

6 Handling gradient terms

It is often necessary, to consider a gradient dependence of the free energy. For a biological application see for example [6]. In general we consider f to depend on all densities ρ_α and density derivatives $\nabla\rho_\alpha$, that is

$$f \equiv f(\rho, \nabla\rho)\,. \tag{23}$$

In particular situations f usually depends only on the gradient of one species or on the gradient of a fraction. Both are special cases of (23). In analogy to section 3 we state a version of 10, but now with the following chemical potentials

$$\mu_\alpha := \frac{\delta f}{\delta\rho_\alpha} = f'_{\rho_\alpha} - \operatorname{div}\left(f'_{\nabla\rho_\alpha}\right), \tag{24}$$

and the following generalization of the specific pressures

$$\begin{aligned} P_\alpha^{sp} &:= \Big(\frac{\delta f}{\delta\rho_\alpha} - \frac{f}{\bar\rho}\Big)\mathrm{Id} + \textstyle\sum_\beta \frac{1}{\bar\rho}\nabla\rho_\beta \otimes f'_{\nabla\rho_\beta} \\ &= \bar\rho\,\frac{\delta f^{sp}}{\delta\rho_\alpha}\mathrm{Id} + \textstyle\sum_\beta \nabla\rho_\beta \otimes f'^{sp}_{\nabla\rho_\beta} \end{aligned} \tag{25}$$

with $f = \bar\rho f^{sp}$ as usual. (If f does not depend on the gradients, the matrix P_α^{sp} will reduce to $p_\alpha^{sp}\mathrm{Id}$.) With these definitions the following holds

19 Proposition. If the free energy is given by (23) then we obtain for the free energy production

$$\begin{aligned} h = {} & \operatorname{div}\Big(\varphi + \textstyle\sum_\alpha \dot\rho_\alpha f'_{\nabla\rho_\alpha}\Big) \\ & + \textstyle\sum_\alpha \tau_\alpha\mu_\alpha + \sum_\alpha u_\alpha \bullet \Big(g_\alpha + \frac{\tau_\alpha}{2}u_\alpha - P_\alpha^{sp}\nabla\rho_\alpha\Big) \\ & + \textstyle\sum_\alpha \mathrm{D}v_\alpha \bullet \Big(\Pi_\alpha - \rho_\alpha P_\alpha^{sp}\Big)\,. \end{aligned}$$

Proof. The proof follows the one of 9, but now we have to use the identity

$$(\dot{\partial_j\rho_\alpha}) = (\partial_t + \bar v \bullet \nabla)\partial_j\rho_\alpha = \partial_j\dot\rho_\alpha - (\partial_j\bar v)\bullet\nabla\rho_\alpha\,,$$

hence for $z \in \mathbb{R}^n$

$$(\dot{\nabla\rho_\alpha})\bullet z = (\nabla\dot\rho_\alpha)\bullet z - \mathrm{D}\bar v \bullet (\nabla\rho_\alpha \otimes z)\,. \tag{26}$$

We therefore compute

$$\begin{aligned} & \partial_t f + \operatorname{div}(f\bar v) = \dot f + f\operatorname{div}\bar v \\ & = \textstyle\sum_\alpha f'_{\rho_\alpha}\dot\rho_\alpha + \sum_\alpha f'_{\nabla\rho_\alpha}\bullet(\dot{\nabla\rho_\alpha}) + f\operatorname{div}\bar v \\ & = \textstyle\sum_\alpha (f'_{\rho_\alpha}\dot\rho_\alpha + f'_{\nabla\rho_\alpha}\bullet\nabla\dot\rho_\alpha) + \mathrm{D}\bar v \bullet \Big(f\mathrm{Id} - \sum_\alpha \nabla\rho_\alpha \otimes f'_{\nabla\rho_\alpha}\Big) \\ & = \operatorname{div}\Big(\textstyle\sum_\alpha \dot\rho_\alpha f'_{\nabla\rho_\alpha}\Big) + \sum_\alpha \frac{\delta f}{\delta\rho_\alpha}\cdot\dot\rho_\alpha + \mathrm{D}\bar v \bullet \Big(f\mathrm{Id} - \sum_\alpha \nabla\rho_\alpha \otimes f'_{\nabla\rho_\alpha}\Big) \end{aligned}$$

and

$$\begin{aligned}\textstyle\sum_\alpha \frac{\delta f}{\delta\rho_\alpha}\cdot\dot\rho_\alpha &= \textstyle\sum_\alpha \mu_\alpha\cdot\Big(\tau_\alpha - \operatorname{div}(\rho_\alpha v_\alpha) + \bar v\bullet\nabla\rho_\alpha\Big)\\ &= \textstyle\sum_\alpha \mu_\alpha\tau_\alpha - \sum_\alpha \mu_\alpha u_\alpha\bullet\nabla\rho_\alpha - \sum_\alpha \mathrm{D}v_\alpha\bullet(\rho_\alpha\mu_\alpha\mathrm{Id})\,.\end{aligned}$$

We plug this into the expression for h in 8 and obtain

$$\begin{aligned}0\ge h &= \partial_t f + \operatorname{div}(f\bar v+\varphi)\\ &\quad+\textstyle\sum_\alpha\Big(\mathrm{D}v_\alpha\bullet\Pi_\alpha + u_\alpha\bullet g_\alpha + \frac{\tau_\alpha}{2}|u_\alpha|^2\Big)\\ &= \operatorname{div}\Big(\varphi+\textstyle\sum_\alpha\dot\rho_\alpha f_{\prime\nabla\rho_\alpha}\Big) + \textstyle\sum_\alpha\mu_\alpha\tau_\alpha\\ &\quad+\textstyle\sum_\alpha u_\alpha\bullet g_\alpha + \sum_\alpha\frac{\tau_\alpha}{2}|u_\alpha|^2 + R\end{aligned}$$

with

$$\begin{aligned}R &= -\textstyle\sum_\alpha\mu_\alpha u_\alpha\bullet\nabla\rho_\alpha + \mathrm{D}\bar v\bullet\Big(f\mathrm{Id} - \sum_\alpha\nabla\rho_\alpha\otimes f_{\prime\nabla\rho_\alpha}\Big)\\ &\quad+\textstyle\sum_\alpha \mathrm{D}v_\alpha\bullet(\Pi_\alpha - \rho_\alpha\mu_\alpha\mathrm{Id})\,.\end{aligned}$$

Using formula (5) for $\mathrm{D}\bar v$ this equation for R becomes

$$\begin{aligned}R &= \textstyle\sum_\alpha(u_\alpha\otimes\nabla\rho_\alpha)\bullet\Big(-\mu_\alpha\mathrm{Id} + \frac{1}{\bar\rho}\Big(f\mathrm{Id} - \sum_\beta\nabla\rho_\beta\otimes f_{\prime\nabla\rho_\beta}\Big)\Big)\\ &\quad+\textstyle\sum_\alpha\mathrm{D}v_\alpha\bullet\Big(\Pi_\alpha - \rho_\alpha\mu_\alpha\mathrm{Id} + \frac{\rho_\alpha}{\bar\rho}\Big(f\mathrm{Id} - \sum_\beta\nabla\rho_\beta\otimes f_{\prime\nabla\rho_\beta}\Big)\Big)\\ &= \textstyle\sum_\alpha(u_\alpha\otimes\nabla\rho_\alpha)\bullet P_\alpha^{sp} + \sum_\alpha\mathrm{D}v_\alpha\bullet(\Pi_\alpha - \rho_\alpha P_\alpha^{sp})\,,\end{aligned}$$

and $(u_\alpha\otimes\nabla\rho_\alpha)\bullet P_\alpha^{sp} = u_\alpha\bullet(P_\alpha^{sp}\nabla\rho_\alpha)$. □

Then we obtain the following version of 10 as a consequence.

20 Theorem. Let

$$f\equiv f(\rho,\nabla\rho)\,,\quad \varphi := -\textstyle\sum_\alpha\dot\rho_\alpha f_{\prime\nabla\rho_\alpha}\,. \tag{27}$$

Suppose that

$$\begin{aligned}\Pi_\alpha &= P_\alpha\mathrm{Id} - S_\alpha\,,\quad P_\alpha = \rho_\alpha P_\alpha^{sp}\,,\\ g_\alpha &= P_\alpha^{sp}\nabla\rho_\alpha - \frac{\tau_\alpha}{2}u_\alpha + g_\alpha^{fr} - \rho_\alpha g^{sp}\,,\end{aligned} \tag{28}$$

then for solutions of (1) the free energy production h reads

$$0\ge h = -\textstyle\sum_\alpha\mathrm{D}v_\alpha\bullet S_\alpha + \sum_\alpha\tau_\alpha\mu_\alpha + \sum_\alpha g_\alpha^{fr}\bullet u_\alpha\,. \tag{29}$$

The result is the same as in section 3, where only the scalar p_α is replaced by the matrix P_α. It follows directly from 19, where now in the free energy inequality the new chemical potentials μ_α from (24) are used. We remark that also now the term $P_\alpha^{sp}\nabla\rho_\alpha$ in the momentum equation cancels since

$$\operatorname{div}(\rho_\alpha P_\alpha^{sp}) = P_\alpha^{sp}\nabla\rho_\alpha + \rho_\alpha\operatorname{div}P_\alpha^{sp}\,.$$

We summarize:

21 Conclusion. Under the above assumptions the mixture system (1) is

$$\begin{aligned}
&\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha v_\alpha) = \tau_\alpha \,, \\
&\rho_\alpha \big(\partial_t v_\alpha + (v_\alpha \bullet \nabla) v_\alpha\big) \\
&\qquad = \operatorname{div} S_\alpha - \rho_\alpha (\operatorname{div} P_\alpha^{sp} + g^{sp}) - \frac{\tau_\alpha}{2} u_\alpha + g_\alpha^{fr} + \mathbf{f}_\alpha
\end{aligned}$$

for all α. The free energy inequality (29) is satisfied.

Again a statement like 14 holds, if in the momentum equation one considers the term $\rho_\alpha(\operatorname{div} P_\alpha^{sp} + \nabla f^{sp})$.

We now go back to the standard case p_α^{sp}.

7 Polymerization of actin filaments

We consider a four component system, a reactive polymer-solvent mixture. The mass densities are ρ_m for actin monomers, ρ_a for polymerized actin filaments, ρ_c for cross-linked actin filaments, and the mass density ρ_s for the solvent. We consider the following conservation laws

$$\begin{aligned}
&\partial_t \rho_c + \operatorname{div}(\rho_c v_c) = \tau_c := -\mathbf{r}_c \,, \\
&\partial_t \rho_a + \operatorname{div}(\rho_a v_a) = \tau_a := \mathbf{r}_c - \mathbf{r}_a \,, \\
&\partial_t \rho_m + \operatorname{div}(\rho_m v_m) = \tau_m := \mathbf{r}_a \,, \\
&\partial_t \rho_s + \operatorname{div}(\rho_s v_s) = \tau_s := 0 \,.
\end{aligned} \tag{30}$$

Here the reactions are given by

$$\begin{aligned}
&\mathbf{r}_a = \lambda_a(\rho)\big(\eta_a \rho_a - \nu \rho_m\big) \,, \\
&\mathbf{r}_c = \lambda_c(\rho)\Big(\eta_c \rho_c - \chi \frac{\rho_a^2}{K^2 + \rho_a^2}\Big) \,,
\end{aligned} \tag{31}$$

where η_a, η_c, χ, ν, and K are assumed to be positive and constant, and λ_a and λ_c are positive functions. Obviously the sum of the mass productions

$$\bar{\tau} = \textstyle\sum_{\alpha=m,a,c,s} \tau_\alpha = 0 \,.$$

The following theorem shows the existence of a free energy. We emphasize, that there might by a different free energy also satisfying the free energy inequality. It is important for the dynamics of the system which free energy one chooses.

22 Theorem. With $\rho = (\rho_m, \rho_a, \rho_c, \rho_s)$ a possible free energy is defined by

$$f(\rho) = \frac{\eta_c}{2} \rho_c^2 + \chi \psi_{K_m}(\rho_m) + \chi \psi_{K_a}(\rho_a) + f_s(\rho_s) \,,$$

where $\nu K_m = \eta_0 K_a$ and

$$\psi_K(z) = z - K \arctan\left(\frac{z}{K}\right) \text{ for } z \in \mathbb{R}\,.$$

The function f_s is an arbitrary (convex) function. Then

$$\textstyle\sum_\beta \tau_\beta \mu_\beta \leq 0\,.$$

Therefore this part of the free energy inequality is satisfied (compare 15).

Proof. It is

$$\psi_K'(z) = 1 - \frac{1}{1+(\frac{z}{K})^2} = \frac{z^2}{K^2+z^2}\,,$$

therefore we obtain

$$\begin{aligned} \mu_c &= \eta_c \rho_c\,, \\ \mu_a &= \chi \frac{\rho_a^2}{K_a^2+\rho_a^2} \\ \mu_m &= \chi \frac{\rho_m^2}{K_m^2+\rho_m^2} = \chi \frac{\left(\frac{\nu}{\eta_a}\rho_m\right)^2}{K_a^2+\left(\frac{\nu}{\eta_a}\rho_m\right)^2}\,. \end{aligned} \tag{32}$$

We therefore compute

$$\begin{aligned} &\textstyle\sum_{\beta=c,a,m,s} \tau_\beta \mu_\beta = \tau_c \mu_c + \tau_a \mu_a + \tau_m \mu_m \\ &= -\mathbf{r}_c \mu_c + (\mathbf{r}_c - \mathbf{r}_a)\mu_a + \mathbf{r}_a \mu_m = \mathbf{r}_c \cdot (\mu_a - \mu_c) + \mathbf{r}_a \cdot (\mu_m - \mu_a)\,, \end{aligned}$$

and obtain

$$\begin{aligned} &-\mathbf{r}_c \cdot (\mu_a - \mu_c) \\ &= \lambda_c(\rho) \cdot \left(\eta_c \rho_c - \chi \frac{\rho_a^2}{K^2+\rho_a^2}\right)^2 \geq 0\,, \\ &-\mathbf{r}_a \cdot (\mu_m - \mu_a) \\ &= \lambda_a(\rho)\eta_a \chi \cdot \left(\frac{\nu}{\eta_a}\rho_m - \rho_a\right)\left(\frac{\left(\frac{\nu}{\eta_a}\rho_m\right)^2}{K_a^2+\left(\frac{\nu}{\eta_a}\rho_m\right)^2} - \frac{\rho_a^2}{K_a^2+\rho_a^2}\right) \geq 0\,. \end{aligned}$$

This shows the result. □

One can also define a different free energy by applying a given monotone function to the definitions of the chemical potentials in (32). There is another point to be mentioned. The proof above shows that each reaction, $\mathbf{r}_c$ and $\mathbf{r}_a$, give a nonpositive contribution to the free energy production as it is common in chemical processes. But this is in contrast to the proof of 17 and 18, indicating that the situation in biological processes generally is more complex.

8 The quasistatic Problem

The momentum equation of the α-component contains the term Π_α under the divergence and the term g_α on the right side. By (14) these two terms have the representation

$$\begin{aligned} \Pi_\alpha &= \rho_\alpha p_\alpha^{sp}\mathrm{Id} - S_\alpha\,, \\ g_\alpha &= p_\alpha^{sp}\nabla\rho_\alpha - \rho_\alpha g^{sp} - \frac{\tau_\alpha}{2}u_\alpha + g_\alpha^{fr}\,. \end{aligned} \tag{33}$$

It has been shown in the previous sections that system (1) is equivalent to

$$\begin{aligned} &\partial_t\rho_\alpha + \mathrm{div}\,(\rho_\alpha v_\alpha) = \tau_\alpha\,, \\ &\rho_\alpha(\partial_t v_\alpha + (v_\alpha\bullet\nabla)v_\alpha) = \mathrm{div}\,S_\alpha \\ &\qquad -\rho_\alpha(\nabla p_\alpha^{sp} + g^{sp}) - \frac{\tau_\alpha}{2}u_\alpha + g_\alpha^{fr} + \mathbf{f}_\alpha\,. \end{aligned} \tag{34}$$

We suppose that the terms on the right side of these equations have the property in 15 which is the free energy inequality

$$0 \geq h = -\textstyle\sum_\alpha \mathrm{D}v_\alpha\bullet S_\alpha + \sum_\alpha \tau_\alpha\mu_\alpha + \sum_\alpha g_\alpha^{fr}\bullet u_\alpha\,.$$

In biological systems one often has the situation that some of the terms in the differential equation have large coefficients compared to the others, for example

- the stress tensor and the pressure and the friction.
- the pressure and the friction (see section 10).
- the pressure and the friction and the external force (for example in a rotating cylinder).

In the first case, for example as $\varepsilon \searrow 0$,

$$\varepsilon\cdot S_{\varepsilon\alpha} \to S_\alpha\,, \quad \varepsilon\cdot f_\varepsilon \to f\,, \quad \varepsilon\cdot g_{\varepsilon\alpha}^{fr} \to g_\alpha^{fr}\,,$$

then it follows also that $\varepsilon\cdot p_{\varepsilon\alpha} \to p_\alpha$ (from (13)) and $\varepsilon\cdot g_\varepsilon^{sp} \to g^{sp}$ (at least for closed systems), whereas the other coefficients stay bounded and have a limit. The solutions $(\rho_\varepsilon, v_\varepsilon)$ of the ε-problem satisfying the system (1)

$$\begin{aligned} &\partial_t\rho_{\varepsilon\alpha} + \mathrm{div}\,(\rho_{\varepsilon\alpha}v_{\varepsilon\alpha}) = \tau_{\varepsilon\alpha}\,, \\ &\partial_t(\rho_{\varepsilon\alpha}v_{\varepsilon\alpha}) + \mathrm{div}\,(\rho_{\varepsilon\alpha}v_{\varepsilon\alpha}\otimes v_{\varepsilon\alpha} + \Pi_{\varepsilon\alpha}) \\ &\qquad = g_{\varepsilon\alpha} + \tau_{\varepsilon\alpha}v_{\varepsilon\alpha} + \mathbf{f}_{\varepsilon\alpha} \end{aligned}$$

converge in the limit $(\rho_\varepsilon, v_\varepsilon) \to (\rho, v)$ and satisfy a reduced problem

$$\begin{aligned} &\partial_t\rho_\alpha + \mathrm{div}\,(\rho_\alpha v_\alpha) = \tau_\alpha\,, \\ &\mathrm{div}\,\Pi_\alpha = g_\alpha \end{aligned} \tag{35}$$

for all α. Alternatively, the equivalent system in 12 for $(\rho_\varepsilon, v_\varepsilon)$ leads to the reduced problem for the limit (ρ, v)

$$\begin{aligned} &\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha v_\alpha) = \tau_\alpha\,, \\ &0 = \operatorname{div} S_\alpha - \rho_\alpha(\nabla p^{sp}_\alpha + g^{sp}) + g^{fr}_\alpha\,. \end{aligned} \tag{36}$$

One also has in the limit

$$\bar{g} = \bar{\rho}(\nabla f^{sp} - g^{sp}) + \bar{g}^{fr} \tag{37}$$

In addition one has to consider the limit in the free energy inequality. From the inequality

$$0 \geq \varepsilon h_\varepsilon = -\sum_\alpha \mathrm{D}v_{\varepsilon\alpha} \bullet (\varepsilon S_{\varepsilon\alpha}) + \sum_\alpha \tau_{\varepsilon\alpha}(\varepsilon\mu_{\varepsilon\alpha}) + \sum_\alpha (\varepsilon g^{fr}_{\varepsilon\alpha}) \bullet u_{\varepsilon\alpha}$$

one obtains, that the limit $\varepsilon h_\varepsilon \to h^{red}$ exists with

$$0 \geq h^{red} = -\sum_\alpha \mathrm{D}v_\alpha \bullet S_\alpha + \sum_\alpha \tau_\alpha \mu_\alpha + \sum_\alpha g^{fr}_\alpha \bullet u_\alpha\,. \tag{38}$$

In this connection we refer to [4] where a limit entropy inequality is considered.

In [5] the second author treats a functional, whose first variation with respect to v are the quasistatic momentum equations.

23 The quasistatic functional. Consider a function $J = J(\rho, v, \nabla\rho, \mathrm{D}v)$ which satisfies

$$\frac{\delta J}{\delta v_\alpha} = \operatorname{div} \Pi_\alpha - g_\alpha\,, \tag{39}$$

where $\frac{\delta J}{\delta v_\alpha} := J_{\prime v_\alpha} - \operatorname{div} J_{\prime \mathrm{D}v_\alpha}$, which requires some assumptions on Π_α and g_α. Concerning the dependence on $(\mathrm{D}v)^{\mathrm{S}}$, the free energy inequality in the form of 15 is equivalent to the convexity of J in $(\mathrm{D}v)^{\mathrm{S}}$.

9 Fractional densities

Often in mixture models one is confronted with the fractional densities

$$\theta_\alpha := \frac{\rho_\alpha}{\bar\rho} = \frac{\rho_\alpha}{\rho_1 + \cdots + \rho_N} . \tag{40}$$

Then instead of the variables $(\rho_\alpha)_\alpha$ one can use as new variables $(\bar\rho, (\theta_\alpha)_\alpha)$, where one has the side condition

$$\textstyle\sum_\alpha \theta_\alpha = 1 . \tag{41}$$

For the mass equations it holds that

24 Lemma. The N mass equations in (1) are equivalent to

$$\begin{aligned}
&\partial_t \bar\rho + \operatorname{div}(\bar\rho\,\bar v) = \bar\tau ,\\
&\bar\rho\,\dot\theta_\alpha + \operatorname{div}(\bar\rho\,\theta_\alpha u_\alpha) = \tau_\alpha - \theta_\alpha \bar\tau \text{ for all } \alpha,
\end{aligned}$$

where $\dot\psi := \partial_t \psi + \bar v \bullet \nabla \psi$ for any function ψ. These again are N independent equations, the sum of the α-equations is 0.

Proof. One obtains the new equations, if one subtracts from the old one θ_α times the equation for the sum. Thus

$$\begin{aligned}
&\tau_\alpha - \theta_\alpha \bar\tau\\
&= \partial_t \rho_\alpha - \theta_\alpha \partial_t \bar\rho + \operatorname{div}(\rho_\alpha v_\alpha) - \theta_\alpha \operatorname{div}(\bar\rho\,\bar v)\\
&= \partial_t(\bar\rho\,\theta_\alpha) - \theta_\alpha \partial_t \bar\rho + \operatorname{div}(\bar\rho\,\theta_\alpha (v_\alpha - \bar v)) + \bar\rho\,\bar v \bullet \nabla \theta_\alpha\\
&= \bar\rho\,\partial_t \theta_\alpha + \operatorname{div}(\bar\rho\,\theta_\alpha u_\alpha) + \bar\rho\,\bar v \bullet \nabla \theta_\alpha .
\end{aligned}$$

Because of (41) and (4) the sum of these equations is equal to zero. □

One could use the same procedure for the momentum equations. We will do this here for the quasistatic case, that is, for system $\operatorname{div} \Pi_\alpha = g_\alpha$ in (35). We obtain

25 Theorem. In the quasistatic regime the equations (35) are equivalent to the equations in 24 and

$$\begin{aligned}
&\operatorname{div} \bar\Pi = \bar g ,\\
&\operatorname{div}(\Pi_\alpha - \theta_\alpha \bar\Pi) = g_\alpha - \theta_\alpha \bar g - \bar\Pi \nabla \theta_\alpha \text{ for all } \alpha.
\end{aligned}$$

Here the equations (43) and (44) are satisfied, and it holds that

$$\begin{aligned}
\Pi_\alpha &= \rho_\alpha p_\alpha^{sp} \mathrm{Id} - S_\alpha ,\\
g_\alpha &= p_\alpha^{sp} \nabla \rho_\alpha - \rho_\alpha g^{sp} + g_\alpha^{fr} .
\end{aligned}$$

A different equivalent version is

$$\begin{aligned}
&\operatorname{div}\bar{S} = \nabla\bar{p} - \bar{\rho}\left(\nabla f^{sp} - g^{sp}\right) - \bar{g}^{fr}\,,\\
&\operatorname{div}(S_\alpha - \theta_\alpha\bar{S}) = \bar{\rho}\,\theta_\alpha\left(\nabla\mu_\alpha - \textstyle\sum_\beta \theta_\beta\nabla\mu_\beta\right) - (g_\alpha^{fr} - \theta_\alpha\bar{g}^{fr}) - \bar{S}\nabla\theta_\alpha
\end{aligned} \tag{42}$$

for all α. The sum of the α-equations is zero.

Here we mention, that the following identity for the entire pressure

$$\bar{\rho}\textstyle\sum_\beta \theta_\beta\nabla\mu_\beta = \nabla\bar{p}$$

holds, if f is a function of ρ alone.

Proof. The procedure for the momentum equation says

$$g_\alpha - \theta_\alpha\bar{g} = \operatorname{div}\mathit{\Pi}_\alpha - \theta_\alpha\operatorname{div}\bar{\mathit{\Pi}}\,,$$

where now

$$\bar{\mathit{\Pi}} = \textstyle\sum_\alpha \mathit{\Pi}_\alpha\,, \quad \bar{g} = \textstyle\sum_\alpha g_\alpha\,. \tag{43}$$

With this

$$\operatorname{div}\mathit{\Pi}_\alpha - \theta_\alpha\operatorname{div}\bar{\mathit{\Pi}} = \operatorname{div}(\mathit{\Pi}_\alpha - \theta_\alpha\bar{\mathit{\Pi}}) + \bar{\mathit{\Pi}}\nabla\theta_\alpha\,.$$

Hence the equation becomes

$$\operatorname{div}(\mathit{\Pi}_\alpha - \theta_\alpha\bar{\mathit{\Pi}}) = g_\alpha - \theta_\alpha\bar{g} - \bar{\mathit{\Pi}}\nabla\theta_\alpha\,.$$

Since $\bar{\mathit{\Pi}} = \bar{p}\mathrm{Id} - \bar{S}$ and

$$\bar{g} = \bar{\rho}(\nabla f^{sp} - g^{sp}) + \bar{g}^{fr}\,, \quad \bar{p} = \textstyle\sum_\alpha \rho_\alpha p_\alpha^{sp}\,, \tag{44}$$

we can write this equation also as

$$\begin{aligned}
&-\operatorname{div}(S_\alpha - \theta_\alpha\bar{S})\\
&= g_\alpha - \theta_\alpha\bar{g} + \bar{S}\nabla\theta_\alpha - \operatorname{div}(\rho_\alpha p_\alpha^{sp}\mathrm{Id}) + \theta_\alpha\operatorname{div}(\bar{p}\mathrm{Id})\\
&= \ p_\alpha^{sp}\nabla\rho_\alpha - \rho_\alpha\bar{g}^{sp} + g_\alpha^{fr}\\
&\quad -\theta_\alpha\textstyle\sum_\beta p_\beta^{sp}\nabla\rho_\beta + \bar{\rho}\,\theta_\alpha g^{sp} - \theta_\alpha\bar{g}^{fr}\\
&\quad -\nabla(\rho_\alpha p_\alpha^{sp}) + \theta_\alpha\nabla\bar{p} + \bar{S}\nabla\theta_\alpha\\
&= -\rho_\alpha\nabla p_\alpha^{sp} + \theta_\alpha\textstyle\sum_\beta \rho_\beta\nabla p_\beta^{sp} + g_\alpha^{fr} - \theta_\alpha\bar{g}^{fr} + \bar{S}\nabla\theta_\alpha\\
&= -\bar{\rho}\,\theta_\alpha\left(\nabla p_\alpha^{sp} - \textstyle\sum_\beta \theta_\beta\nabla p_\beta^{sp}\right) + g_\alpha^{fr} - \theta_\alpha\bar{g}^{fr} + \bar{S}\nabla\theta_\alpha\,.
\end{aligned}$$

Since $p_\alpha^{sp} = \mu_\alpha - f^{sp}$ we can replace

$$\nabla p_\alpha^{sp} - \textstyle\sum_\beta \theta_\beta\nabla p_\beta^{sp} = \nabla\mu_\alpha - \textstyle\sum_\beta \theta_\beta\nabla\mu_\beta\,.$$

The equation $\operatorname{div}\bar{\mathit{\Pi}} = \bar{g}$ becomes $0 = \operatorname{div}\bar{S} + \bar{g} - \nabla\bar{p}$ and in the quasistatic case $\bar{g}$ is given by (37). □

10 Diffusion limit

Usual biochemical and cell-biological situations are characterized by a relatively low Reynolds number and relatively high friction, so that the quasi-steady-state hypothesis can be assumed (see section 8). Then the corresponding force balance equations yield a generalized system of Darcy type equations, see (49). To derive this we assume the following form of friction forces

$$g_\alpha^{fr} = -\sum_\beta \gamma_{\alpha\beta} u_\beta \,, \quad \gamma_{\alpha\beta} \equiv \gamma_{\alpha\beta}(\rho)\,, \tag{45}$$

where the $\gamma_{\alpha\beta}$ are called friction coefficients. Also the free energy f is relatively high, and we assume that there is no mass exchange, that is $\tau_\alpha = 0$, and no viscosity, that is $S_\alpha = 0$. Then the system (36) with g^{sp} as in statement 13 is equivalent to

$$\begin{aligned} &\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \bar{v} + \rho_\alpha u_\alpha) = 0\,, \\ &\rho_\alpha \nabla \mu_\alpha = g_\alpha^{fr} - \frac{\rho_\alpha}{\bar{\rho}} \bar{g}^{sp} \end{aligned} \tag{46}$$

for all α. The free energy inequality (38) reduces to

$$0 \geq h^{red} = \sum_\alpha g_\alpha^{fr} \bullet u_\alpha = -\sum_{\alpha\beta} \gamma_{\alpha\beta} u_\beta \bullet u_\alpha \,, \tag{47}$$

and this is satisfied, if $\left(\gamma_{\alpha\beta}\right)_{\alpha\beta}$ is positive semidefinite. If

$$\sum_{\alpha\beta} \gamma_{\alpha\beta} u_\beta = 0\,, \tag{48}$$

that is, $\bar{g}^{fr} = 0$, the system (46) is

$$\begin{aligned} &\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \bar{v} + \rho_\alpha u_\alpha) = 0\,, \\ &-\rho_\alpha \nabla \mu_\alpha = \sum_\beta \gamma_{\alpha\beta} u_\beta \,. \end{aligned} \tag{49}$$

These equations are of Darcy's type. Eventually this can be used to compute the relative velocities u_α explicitly, so that by substitution into the mass equations one obtains a system of diffusion equations. This procedure can be used to derive from the general system (1) a single momentum equation for $\bar{v}$ and diffusion equations for the α-components containing the velocity, see (49). The equation (48) is satisfied for the following

26 Example. Choose the following form of friction forces

$$g_\alpha^{fr} = -\widetilde{\gamma} \rho_\alpha u_\alpha - \sum_{\beta \neq \alpha} \widetilde{\gamma}_{\alpha\beta} \rho_\alpha \rho_\beta (u_\alpha - u_\beta) \tag{50}$$

with a nonnegative friction coefficient $\widetilde{\gamma}$ and nonnegative drag coefficients $\widetilde{\gamma}_{\alpha\beta}$ being symmetric in α and β. Then g_α^{fr} has the properties (47) and (48).

Proof. The property (47) follows from

$$\sum_\alpha g_\alpha^{fr} \bullet u_\alpha = -\widetilde{\gamma} \sum_\alpha \rho_\alpha |u_\alpha|^2 - \tfrac{1}{2} \sum_{\beta \neq \alpha} \widetilde{\gamma}_{\alpha\beta} \rho_\alpha \rho_\beta |u_\alpha - u_\beta|^2 .$$

□

For example, such friction forces could appear for a mixture of polymers in a solvent.

11 Polymer mixtures including gradients

Consider general mixtures of polymers being of a similar type but attaining different configuration states. In [2] we have treated a biophysical two-component system of lipid monolayers in lung alveoli. They can consist of ordered lipid clusters, but the lipids can also be in a diffusive unordered phase. In such a model the free energy would typically be a function of the volume fractions of the mixture components, see section 9, and on the partial gradients

$$\nabla \theta_\alpha = \nabla \left(\frac{\rho_\alpha}{\bar{\rho}} \right) = \sum_\beta (\rho_\beta \nabla \rho_\alpha - \rho_\alpha \nabla \rho_\beta)$$

For more details compare [11, Section 3]. Then the free energy is of the general type as in (23), namely

$$f \equiv f(\rho, \nabla \rho) = \widetilde{f}(\bar{\rho}, \theta, \nabla \theta) .$$

Using section 6 for this free energy, we derive the balance equations in 21 and in the quasistatic case the system (42). However in [2] this free energy was considered in a one momentum system. Section 10 leads to a connection of these two approaches.

12 Conclusion

We have considered a mixture of fluids in the isothermal case, for which we successfully developed a theory based on the free energy inequality. Also a theory with gradients has been presented, but its comparison with various biological problems, see [6], have still to be studied. In principle the dependence of the free energy on other quantities are possible.

The theory has been applied to several biological problems, and it turns out that the complexity of biological systems goes beyond the well-known methods for chemical reactions. In biological problems the free energy inequality comprises several reaction terms as the example of Lotka-Volterra system shows (there $\dot{K} = 0$ and K contains two reaction terms).

The diffusion limit in section 10 has opened a possibility to approximate the system by diffusion equations plus a single momentum equation. We hope to come back to this point in a forthcoming paper, where the single momentum approximation for general solutions of system (1) will be studied.

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