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Cross-coupling effects for viscoelastic interfaces in the presence of E-Fields

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1. Maxwell's equations and charge conservation

We can consider systems where flowing matter is formed by charges species, hence causing and experiencing electromagnetic fields. Specifically, we are able to define the charge per unit mass of species α

$$z_\alpha = n_\alpha \frac{\tilde{F}}{\tilde{M}_\alpha} \tag{1}$$

where $\tilde{F}$ is the Faraday constant, and n_α is the elementary integer charge of species α.

The balance equation for the electric charge (2) derives from the continuity equation for species mass density and can be written as

$$\frac{\partial \rho_{el}}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{i} = -\boldsymbol{\nabla} \cdot (\rho_{el} \boldsymbol{v} + \boldsymbol{j}_{el}) \qquad \text{where} \qquad \sum_{\alpha=1}^{k} \tilde{M}_\alpha z_\alpha \tilde{\nu}_\alpha = 0 \tag{2}$$

where the electric charge conservation is guaranteed even for chemically reacting systems. The total electric charge density ρ_{el} and the total electric current flux $\boldsymbol{i}$ are given, respectively, by

$$\rho_{el} = \sum_{\alpha=1}^{k} z_\alpha \rho_\alpha \qquad\qquad \boldsymbol{i} = \sum_{\alpha=1}^{k} z_\alpha \rho_\alpha \boldsymbol{v}_\alpha \tag{3}$$

or, alternatively by

$$\boldsymbol{i} = \rho_{el} \boldsymbol{v} + \boldsymbol{j}_{el} \qquad \text{with} \qquad \boldsymbol{j}_{el} = \sum_{\alpha=1}^{k} z_\alpha \boldsymbol{j}_\alpha \tag{4}$$

where $\boldsymbol{j}_{el}$ is the flux relative to the mass-average velocity.

The total electric charge density ρ_{el} and the current density $\boldsymbol{i}$ are related to both electric $\boldsymbol{E}$ and magnetic $\boldsymbol{H}$ fields via the so-called *Maxwell's equations*. If we consider a polarizable and magnetizable medium, it is useful to express the Maxwell's equations in Lorentz-Heaviside units [1], as follows

$$\begin{aligned} \boldsymbol{\nabla} \times \boldsymbol{E} &= -\frac{1}{c} \frac{\partial}{\partial t} \boldsymbol{B} & \boldsymbol{\nabla} \cdot \boldsymbol{D} &= \rho_{el} \\ \boldsymbol{\nabla} \times \boldsymbol{H} &= \frac{1}{c} \frac{\partial}{\partial t} \boldsymbol{D} + \frac{\boldsymbol{i}}{c} & \boldsymbol{\nabla} \cdot \boldsymbol{B} &= 0 \end{aligned} \tag{5}$$

where $\boldsymbol{D}$ is the electric displacement field and $\boldsymbol{B}$ is the magnetic displacement field.

On the dividing surface, these equations give

$$\begin{aligned} \boldsymbol{\nabla} \times \boldsymbol{E}^s + \boldsymbol{n} \times \left(\boldsymbol{E}^{II} - \boldsymbol{E}^{I}\right) &= -\frac{1}{c} \frac{\partial}{\partial t} \boldsymbol{B}^s + \frac{1}{c} v_\perp^s \left(\boldsymbol{B}^{II} - \boldsymbol{B}^{I}\right) & \boldsymbol{\nabla} \cdot \boldsymbol{D}^s + \left(D_\perp^{II} - D_\perp^{I}\right) &= \rho_{el}^s \\ \boldsymbol{\nabla} \times \boldsymbol{H}^s + \boldsymbol{n} \times \left(\boldsymbol{H}^{II} - \boldsymbol{H}^{I}\right) &= \frac{1}{c} \frac{\partial}{\partial t} \boldsymbol{D}^s - \frac{1}{c} v_\perp^s \left(\boldsymbol{D}^{II} - \boldsymbol{D}^{I}\right) + \frac{1}{c} \boldsymbol{i}^s & \boldsymbol{\nabla} \cdot \boldsymbol{B}^s + \left(B_\perp^{II} - B_\perp^{I}\right) &= 0 \end{aligned} \tag{6}$$

Charge conservation on the interface is given by

$$\frac{\partial}{\partial t} q^s + \frac{1}{c} \boldsymbol{\nabla} \cdot \boldsymbol{i}^s + \boldsymbol{n} \cdot \left[\boldsymbol{i}^{II} - \boldsymbol{i}^{I} - \boldsymbol{v}^s \left(\rho_{el}^{II} - \rho_{el}^{I}\right)\right] = 0 \tag{7}$$

together with the interfacial electric current

$$i_\perp^s - v_\perp^s \rho_{el}^s = 0 \tag{8}$$

and the transversality conditions

$$\begin{aligned} \boldsymbol{n}\times\boldsymbol{E}^s-\frac{1}{c}v_\perp^s\boldsymbol{B}^s=\boldsymbol{0} \qquad & \qquad \boldsymbol{n}\cdot\boldsymbol{D}^s=0 \\ \boldsymbol{n}\times\boldsymbol{H}^s+\frac{1}{c}v_\perp^s\boldsymbol{D}^s=\boldsymbol{0} \qquad & \qquad \boldsymbol{n}\cdot\boldsymbol{B}^s=0 \end{aligned} \tag{9}$$

As to simplify future expressions, we can introduce the electromagnetic fields measured by an observer moving with *barycentric* velocity $\boldsymbol{v}$ in the nonrelativistic approximation. As proposed by Albano et al. [1],

$$\begin{aligned} \boldsymbol{E}^*=\boldsymbol{E}+\frac{\boldsymbol{v}}{c}\times\boldsymbol{B} \qquad & \qquad \boldsymbol{H}^*=\boldsymbol{H}-\frac{\boldsymbol{v}}{c}\times\boldsymbol{D} \qquad & \qquad \boldsymbol{i}^*=\boldsymbol{i}-\boldsymbol{v}\rho_{el} \\ \boldsymbol{D}^*=\boldsymbol{D}+\frac{\boldsymbol{v}}{c}\times\boldsymbol{H} \qquad & \qquad \boldsymbol{B}^*=\boldsymbol{B}-\frac{\boldsymbol{v}}{c}\times\boldsymbol{E} \qquad & \qquad \rho_{el}^*=\rho_{el} \end{aligned} \tag{10}$$

These relations are perfectly valid in the bulk regions; on the dividing interface, we will have the same expressions with $\boldsymbol{v}=\boldsymbol{v}^s$. By applying the relation (8) and the transversality conditions (9), we get the useful result for a dividing interface "at rest" ($\boldsymbol{v}^s=0$)

$$\boldsymbol{n}\times\boldsymbol{E}^{s*}=\boldsymbol{n}\cdot\boldsymbol{D}^{s*}=\boldsymbol{n}\times\boldsymbol{H}^{s*}=\boldsymbol{n}\cdot\boldsymbol{B}^{s*}=\boldsymbol{n}\cdot\boldsymbol{i}^{s*}=0 \tag{11}$$

In a polarizable and magnetizable material, we can define fundamental quantities such as the polarization $\boldsymbol{P}$ and the magnetization $\boldsymbol{M}$. Recalling the expressions for $\boldsymbol{P}$ and $\boldsymbol{M}$ from theory [1], we write

$$\boldsymbol{P}\equiv\boldsymbol{D}-\boldsymbol{E} \qquad \text{and} \qquad \boldsymbol{M}\equiv\boldsymbol{B}-\boldsymbol{H} \tag{12}$$

similarly to (10), we obtain the barycenter-related (or surface-related if $\boldsymbol{v}=\boldsymbol{v}^s$) relations

$$\boldsymbol{P}^*=\boldsymbol{P}-\frac{\boldsymbol{v}}{c}\times\boldsymbol{M} \qquad \text{and} \qquad \boldsymbol{M}^*=\boldsymbol{M}+\frac{\boldsymbol{v}}{c}\times\boldsymbol{P} \tag{13}$$

with the relative transversality conditions

$$\boldsymbol{P}_\parallel^{s*}=\boldsymbol{D}_\parallel^{s*} \qquad \boldsymbol{M}_\parallel^{s*}=\boldsymbol{B}_\parallel^{s*} \qquad P_\perp^{s*}=-E_\perp^{s*} \qquad M_\perp^{s*}=-H_\perp^{s*} \tag{14}$$

If we refer to previous works [5, 16], we can recall the definition in Lorentz-Heaviside units of the bulk-phase electromagnetic energy density per unit volume g^i

$$g^i\equiv\frac{1}{2}\left|\boldsymbol{E}^i\right|^2+\frac{1}{2}\left|\boldsymbol{B}^i\right|^2-\boldsymbol{M}^i\cdot\boldsymbol{B}^i-\frac{\boldsymbol{v}^i}{c}\cdot\left(\boldsymbol{E}^i\times\boldsymbol{M}^i\right) \qquad \text{with} \qquad i=I,II \tag{15}$$

and the interfacial electromagnetic energy density per unit of surface area g^s

$$g^s\equiv\bar{\boldsymbol{D}}\cdot\boldsymbol{E}^{s*}+\bar{\boldsymbol{B}}\cdot\boldsymbol{H}^{s*}-\frac{\boldsymbol{v}^s}{c}\cdot\left(\bar{\boldsymbol{H}}\times\boldsymbol{E}^s+\boldsymbol{H}^s\times\bar{\boldsymbol{E}}\right) \tag{16}$$

The quantity $\frac{1}{c}\left(\boldsymbol{E}^i\times\boldsymbol{M}^i\right)$ represents the momentum density of the electromagnetic field and the superscript "$\bar{}$" indicates a quantity averaged over the different bulk phases.

Finally, combining Maxwell's equations (5) we can derive the fundamental Poynting's theorem for the bulk

$$\boldsymbol{E}\cdot\frac{\partial}{\partial t}\boldsymbol{D}+\boldsymbol{H}\cdot\frac{\partial}{\partial t}\boldsymbol{B}=-\boldsymbol{\nabla}\cdot c\left(\boldsymbol{E}\times\boldsymbol{H}\right)-\boldsymbol{i}\cdot\boldsymbol{E} \tag{17}$$

From (17) it has been obtained [7] the evolution equation for the bulk total energy density (i.e. kinetic energy and electromagnetic energy) for a polarizable system (with $i=I,II$ the two bulk phases)

$$\begin{aligned} &\frac{\partial}{\partial t}\left\{\frac{1}{2}\rho^i\left|\boldsymbol{v}^i\right|^2+\frac{1}{2}\left|\boldsymbol{E}^i\right|^2+\frac{1}{2}\left|\boldsymbol{B}^i\right|^2-\boldsymbol{M}^{i*}\cdot\boldsymbol{B}^i-\frac{\boldsymbol{v}^i}{c}\cdot\left(\boldsymbol{E}^{i*}\times\boldsymbol{M}^i\right)\right\} \qquad \text{with} \qquad i=I,II \\ &\quad=\frac{\partial}{\partial t}\left\{\frac{1}{2}\rho^i\left|\boldsymbol{v}^i\right|^2+g^i\right\} \\ &\quad=-\boldsymbol{\nabla}\cdot\left\{\frac{1}{2}\rho^i\left|\boldsymbol{v}^i\right|^2\boldsymbol{v}^i+\boldsymbol{\pi}^i\cdot\boldsymbol{v}^i-\left(\boldsymbol{P}^{i*}\cdot\boldsymbol{E}^i+\boldsymbol{M}^{i*}\cdot\boldsymbol{B}^i\right)\boldsymbol{v}^i+c\left(\boldsymbol{E}^i\times\boldsymbol{H}^i\right)\right\} \\ &\qquad+\boldsymbol{\pi}^i:\boldsymbol{\nabla}_\parallel\boldsymbol{v}^i-\boldsymbol{i}^i\cdot\boldsymbol{E}^{i*}-\rho^i\boldsymbol{E}^{i*}\cdot\frac{d\boldsymbol{p}^{i*}}{dt}-\rho^i\boldsymbol{B}^{i*}\cdot\frac{d\boldsymbol{m}^{i*}}{dt} \end{aligned} \tag{18}$$

In the same way as in (17) and in (18), we now report [1] the Poynting's theorem for the interface (19)

$$\begin{aligned}\bar{\boldsymbol{E}}\cdot\frac{\partial}{\partial t}\boldsymbol{D}^s+\bar{\boldsymbol{H}}\cdot\frac{\partial}{\partial t}\boldsymbol{B}^s+\boldsymbol{E}^s\cdot\left(\frac{\partial}{\partial t}\bar{\boldsymbol{D}}\right)+\boldsymbol{H}^s\cdot\left(\frac{\partial}{\partial t}\bar{\boldsymbol{B}}\right)&\\ =-c\left[\boldsymbol{\nabla}\cdot\left(\bar{\boldsymbol{E}}\times\boldsymbol{H}^s+\boldsymbol{E}^s\times\bar{\boldsymbol{H}}\right)\right]+c\,\boldsymbol{n}\cdot\left(\boldsymbol{H}^{II}\times\boldsymbol{E}^{II}-\boldsymbol{H}^I\times\boldsymbol{E}^I\right)&\\ +v_\perp^s\left[\bar{\boldsymbol{E}}\cdot\left(\boldsymbol{D}^{II}-\boldsymbol{D}^I\right)+\bar{\boldsymbol{H}}\cdot\left(\boldsymbol{B}^{II}-\boldsymbol{B}^I\right)\right]-\boldsymbol{i}^s\cdot\bar{\boldsymbol{E}}-\bar{\boldsymbol{i}}\cdot\boldsymbol{E}^s&\end{aligned}\tag{19}$$

and the evolution equation for the total energy density for a polarizable interface (20)

$$\begin{aligned}&\frac{\partial}{\partial t}\left\{\frac{1}{2}\,\rho^s\left|\boldsymbol{v}^s\right|^2+\bar{\boldsymbol{D}}\cdot\boldsymbol{E}^{s*}+\bar{\boldsymbol{B}}\cdot\boldsymbol{H}^{s*}-\frac{\boldsymbol{v}^s}{c}\cdot\left(\bar{\boldsymbol{H}}\times\boldsymbol{E}^s+\boldsymbol{H}^s\times\bar{\boldsymbol{E}}\right)\right\}=\frac{\partial}{\partial t}\left\{\frac{1}{2}\rho^s\left|\boldsymbol{v}^s\right|^2+g^s\right\}\\
=\;&-\boldsymbol{i}^{s*}\cdot\bar{\boldsymbol{E}}^*-\bar{\boldsymbol{i}}^*\cdot\boldsymbol{E}^{s*}+\boldsymbol{\pi}^s:\left(\boldsymbol{\nabla}\boldsymbol{v}^s\right)^T\\
&-\left\{\boldsymbol{\nabla}\cdot\left[\frac{1}{2}\rho^s\left|\boldsymbol{v}^s\right|^2\boldsymbol{v}^s+\boldsymbol{\pi}^s\cdot\boldsymbol{v}^s-\boldsymbol{v}^s\left(\bar{\boldsymbol{D}}^*\cdot\boldsymbol{P}_\perp^s+\bar{\boldsymbol{E}}^*\cdot\boldsymbol{P}_\parallel^s+\bar{\boldsymbol{B}}^*\cdot\boldsymbol{M}_\perp^s+\bar{\boldsymbol{H}}^*\cdot\boldsymbol{M}_\parallel^s\right)\right.\right.\\
&\qquad\left.\left.+c\left(\bar{\boldsymbol{E}}\times\boldsymbol{H}^s+\boldsymbol{E}^s\times\bar{\boldsymbol{H}}\right)\right]\right\}-\boldsymbol{n}\cdot\left(\boldsymbol{\pi}^{II}-\boldsymbol{\pi}^I\right)\cdot\boldsymbol{v}^s\\
&-\bar{\boldsymbol{D}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{P}_\perp^{s*}-\bar{\boldsymbol{E}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{P}_\parallel^{s*}\\
&-\bar{\boldsymbol{B}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{M}_\perp^{s*}-\bar{\boldsymbol{H}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{M}_\parallel^{s*}\\
&-\frac{1}{c}\bar{\boldsymbol{M}}\cdot\left[\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\left(\boldsymbol{v}_\perp^s\times\boldsymbol{P}^s\right)\right]+\frac{1}{c}\bar{\boldsymbol{P}}\cdot\left[\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\left(\boldsymbol{v}_\perp^s\times\boldsymbol{M}^s\right)\right]+c\,\boldsymbol{n}\cdot\left(\boldsymbol{H}^{II}\times\boldsymbol{E}^{II}-\boldsymbol{H}^I\times\boldsymbol{E}^I\right)\\
&+v_\perp^s\left[\frac{1}{2}\left|\boldsymbol{E}^{II}\right|^2-\frac{1}{2}\left|\boldsymbol{E}^I\right|^2+\frac{1}{2}\left|\boldsymbol{B}^{II}\right|^2-\frac{1}{2}\left|\boldsymbol{B}^I\right|^2+\boldsymbol{P}^{II}\cdot\boldsymbol{E}^{II}-\boldsymbol{P}^I\cdot\boldsymbol{E}^I\right]\\
&+\frac{1}{c}\boldsymbol{v}^s\left[\left(v_\perp^{II}-v_\perp^s\right)\left(\boldsymbol{P}^{II}\times\boldsymbol{B}^{II}+\boldsymbol{E}^{II}\times\boldsymbol{M}^{II}\right)-\left(v_\perp^I-v_\perp^s\right)\left(\boldsymbol{P}^I\times\boldsymbol{B}^I+\boldsymbol{E}^I\times\boldsymbol{M}^I\right)\right]\\
&-\frac{1}{2}\left[\rho^{II}\left(v_\perp^{II}-v_\perp^s\right)\left(\left|\boldsymbol{v}^{II}\right|^2-\left|\boldsymbol{v}^{II}-\boldsymbol{v}^s\right|^2\right)-\rho^I\left(v_\perp^I-v_\perp^s\right)\left(\left|\boldsymbol{v}^I\right|^2-\left|\boldsymbol{v}^I-\boldsymbol{v}^s\right|^2\right)\right]\end{aligned}\tag{20}$$

2. Derivation of σ^s in the presence of electromagnetic fields

2.1 Balance equations

Here we derive the interfacial entropy production rate σ^s for a polarizable multicomponent system in the presence of electromagnetic fields. In our case, we make the assumption of local equilibrium in both the bulk phases as well as for the interface. This means

$$\begin{aligned} s^i &= s^i\left(u^i, \rho^i, N^i_\alpha, \boldsymbol{p}^{i*}, \boldsymbol{m}^{i*}\right) \qquad \text{in the bulk regions with } i = I, II \\ s^s &= s^s\left(u^s, \rho^s, N^s_\alpha, \boldsymbol{p}^{s*}, \boldsymbol{m}^{s*}\right) \qquad \text{at the interface} \end{aligned} \tag{21}$$

where the polarization $\boldsymbol{p}$ and the magnetization $\boldsymbol{m}$ are expressed per unit volume (for the bulk) and per unit area (for the interface).

Firstly, we recall Gibbs' thermodynamic fundamental form for a one-component system in the absence of electromagnetic fields:

$$dU = TdS - pdV + \mu dN + \gamma dA \tag{22}$$

which can be extended for an entire system at equilibrium in the form of the Euler (23) and the Gibbs-Duhem (24) equations :

$$U = TS - pV + \mu N + \gamma A \tag{23}$$

$$SdT - Vdp + Nd\mu + Ad\gamma = 0 \tag{24}$$

For each of the two equilibrium bulk phases (I and II) we then have

$$\begin{aligned} U^i &= TS^i - pV^i + \mu N^i \qquad \text{for} \qquad i = I, II \\ S^i dT &- V^i dp + N^i d\mu = 0 \end{aligned} \tag{25}$$

By defining the interfacial quantities $N^s = N - N^1 - N^2$, $U^s = U - U^1 - U^2$ and $S^s = S - S^1 - S^2$ (with $V = V^1 + V^2$) [16], we can re-write expressions (23) and (24) for interfacial systems in global equilibrium:

$$u^s = Ts^s + \gamma + \hat{\mu}\rho^s \tag{26}$$

$$s^s d^s T + d^s\gamma + \rho^s d^s\hat{\mu} = 0 \tag{27}$$

From now on, we will identify d^s as $\dfrac{d^s}{dt}$, which can be seen as an "interface total time derivative". Note that in (26) and (27) the purely intensive quantities T, $\hat{\mu}$ and γ are now closely related to the ambiguous gauge-variant excess densities u^s, s^s and ρ^s. As for other physical systems, according to the Gibbs phase rule, one independent physical variable is lost because of the coexistence of two phases.

We can now extend (26) and (27) for a polarizable and magnetizable system in the presence of an electromagnetic field.

$$u^s = Ts^s + \gamma + \hat{\mu}\rho^s + \left(\bar{\boldsymbol{E}}^*_\parallel\right)_{eq} \cdot \boldsymbol{p}^{s*}_\parallel + \left(\bar{D}^*_\perp\right)_{eq} p^{s*}_\perp + \left(\bar{\boldsymbol{H}}^*_\parallel\right)_{eq} \cdot \boldsymbol{m}^{s*}_\parallel + \left(\bar{B}^*_\perp\right)_{eq} m^{s*}_\perp \tag{28}$$

$$s^s d^s T + d^s\gamma + \rho^s d^s\hat{\mu} + \boldsymbol{p}^{s*}_\parallel \cdot d^s\left(\bar{\boldsymbol{E}}^*_\parallel\right)_{eq} + p^{s*}_\perp\, d^s\left(\bar{D}^*_\perp\right)_{eq} + \boldsymbol{m}^{s*}_\parallel \cdot d^s\left(\bar{\boldsymbol{H}}^*_\parallel\right)_{eq} + m^{s*}_\perp\, d^s\left(\bar{B}^*_\perp\right)_{eq} = 0 \tag{29}$$

Rewriting (28), (29) for a multi-component systems, given $\hat{\mu}_k = \hat{\mu}_k\left(T, \hat{\mu}_1, ..., \hat{\mu}_{k-1}\right)$ and $\gamma = \gamma\left(T, \hat{\mu}_1, ..., \hat{\mu}_{k-1}\right)$

$$u^s = Ts^s + \gamma + \sum_{\alpha=1}^{k-1}\hat{\mu}_\alpha\rho^s_\alpha + \hat{\mu}_k\rho^s_k + \left(\bar{\boldsymbol{E}}^*_\parallel\right)_{eq} \cdot \boldsymbol{p}^{s*}_\parallel + \left(\bar{D}^*_\perp\right)_{eq} p^{s*}_\perp + \left(\bar{\boldsymbol{H}}^*_\parallel\right)_{eq} \cdot \boldsymbol{m}^{s*}_\parallel + \left(\bar{B}^*_\perp\right)_{eq} m^{s*}_\perp \tag{30}$$

$$s^s d^s T + d^s\gamma + \sum_{\alpha=1}^{k-1} \rho_\alpha^s d^s \hat{\mu}_\alpha + \rho_k^s d^s \hat{\mu}_k + \boldsymbol{p}_\parallel^{s*} \cdot d^s \left(\bar{\boldsymbol{E}}_\parallel^*\right)_{eq} + p_\perp^{s*}\, d^s \left(\bar{D}_\perp^*\right)_{eq} + \boldsymbol{m}_\parallel^{s*} \cdot d^s \left(\bar{\boldsymbol{H}}_\parallel^*\right)_{eq} + m_\perp^{s*}\, d^s \left(\bar{B}_\perp^*\right)_{eq} = 0 \tag{31}$$

We can now obtain the expression for the total interfacial energy density e^s. To accomplish this, we simply add to (30) the kinetic energy density term $\frac{1}{2}\left|\boldsymbol{v}^s\right|^2$ to account for interface movements, i.e. $e^s = u^s + \frac{1}{2}\left|\boldsymbol{v}^s\right|^2$.

$$e^s = T^s s^s + \gamma + \sum_{\alpha=1}^{k} \left(\hat{\mu}_\alpha^s + \frac{1}{2}\left|\boldsymbol{v}^s\right|^2\right) \rho_\alpha^s + \left(\bar{\boldsymbol{E}}_\parallel^*\right)_{eq} \cdot \boldsymbol{p}_\parallel^{s*} + \left(\bar{D}_\perp^*\right)_{eq} p_\perp^{s*} + \left(\bar{\boldsymbol{H}}_\parallel^*\right)_{eq} \cdot \boldsymbol{m}_\parallel^{s*} + \left(\bar{B}_\perp^*\right)_{eq} m_\perp^{s*} \tag{32}$$

By differentiating the Euler equation (32) and using the Gibbs-Duhem equation (31), we get the expression

$$\begin{aligned} \frac{d^s}{dt} e^s = T^s \frac{d^s}{dt} s^s + \sum_{\alpha=1}^{k} \left(\hat{\mu}_\alpha^s - \frac{1}{2}\left|\boldsymbol{v}^s\right|^2\right) \frac{d^s}{dt} \rho_\alpha^s + \boldsymbol{v}^s \cdot \frac{d^s}{dt} \left(\rho^s \boldsymbol{v}^s\right) \\ + \left(\bar{\boldsymbol{E}}_\parallel^*\right)_{eq} \cdot \frac{d^s}{dt} \boldsymbol{p}_\parallel^{s*} + \left(\bar{D}_\perp^*\right)_{eq} \frac{d^s}{dt} p_\perp^{s*} + \left(\bar{\boldsymbol{H}}_\parallel^*\right)_{eq} \cdot \frac{d^s}{dt} \boldsymbol{m}_\parallel^{s*} + \left(\bar{B}_\perp^*\right)_{eq} \frac{d^s}{dt} m_\perp^{s*} \end{aligned} \tag{33}$$

where $\boldsymbol{v}^s \cdot \boldsymbol{v}^s d\rho_\alpha^s + \rho_\alpha^s \boldsymbol{v}^s \cdot d\boldsymbol{v}^s = \boldsymbol{v}^s \cdot d\left(\rho_\alpha^s \boldsymbol{v}^s\right)$; the third term in (33) is associated with the kinetic energy.

Let us call a the density of a generic conserved quantity and a^s its ambiguous excess density. For an inhomogeneous (i.e. non planar) moving interface, the interface normal velocity v_{na}^s may be affected by the transport processes occurring within the very same interface. If we consider as a reference the interface defined by the gauge $a^s = 0$, we can write the generalized expression

$$v_{na}^s \left(a^{II} - a^I\right) = \boldsymbol{n} \cdot \left(\boldsymbol{v}^{II} a^{II} + \boldsymbol{j}_a^{II} - \boldsymbol{v}^I a^I - \boldsymbol{j}_a^{II}\right) - \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{j}_a^s + \mathcal{F} \tag{34}$$

where $\boldsymbol{j}_a^s$ is the interface analog of the bulk conductive fluxes $\boldsymbol{j}_a^I$ and $\boldsymbol{j}_a^{II}$, and the symbol $\mathcal{F}$ represents the electromagnetic source term.

In addition, we report the jump momentum balance,

$$-\left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1} \boldsymbol{n} \cdot \left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right)\left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right) = \boldsymbol{n} \cdot \left(\boldsymbol{\pi}^{II} - \boldsymbol{\pi}^I\right) - \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{\pi}^s \tag{35}$$

together with other jump relations [16] (36) and (37),

$$\rho^I \left(\boldsymbol{v}^I - \boldsymbol{v}^s\right) = \left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1} \left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right) \tag{36}$$

$$\rho^{II} \left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right) = \left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1} \left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right) \tag{37}$$

Let us now assume the gauge $\rho^s = 0$, we can then recall from previous works [16] the time evolution (i.e. rate of change) equation for a generic extensive interfacial density b^s

$$\frac{\partial^s b^s}{\partial t} = \left(v_{n\rho}^s - v_n^s\right)\left(b^{II} - b^I\right) - \boldsymbol{\nabla}_\parallel \cdot \left(\boldsymbol{v}_{def}^s b^s\right) - b^s \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{v}_{tr}^s \tag{38}$$

In the equation above (see (38)), the "interface partial time derivative" has been introduced; for a surface moving with velocity $\boldsymbol{v}^s$, it can be formally expressed as

$$\boldsymbol{v}^s = \boldsymbol{v}_{\text{translational}}^s + \boldsymbol{v}_{\text{deformational}}^s \qquad \Rightarrow \qquad \frac{\partial^s}{\partial t} = \frac{\partial}{\partial t} + \boldsymbol{v}_{\text{tr}}^s \cdot \boldsymbol{\nabla} \tag{39}$$

By combining expressions (34), (38) and the evolution equation for the total energy density in a polarizable interface (see (20)), we derive the evolution equation for the excess total energy density e^s in the gauge $\rho^s = 0$

$$\begin{aligned}
\frac{\partial^s e^s}{\partial t} &= -\boldsymbol{\nabla}_{\parallel} \cdot \left(\boldsymbol{v}^s_{def} e^s + \boldsymbol{j}^s_q + \boldsymbol{\pi}^s \cdot \boldsymbol{v}^s \right) - e^s \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}^s_{tr} \\
&+ \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s \right) e^{II} + \boldsymbol{j}^{II}_q + \boldsymbol{\pi}^{II} \cdot \boldsymbol{v}^{II} - \left(\boldsymbol{v}^I - \boldsymbol{v}^s \right) e^I - \boldsymbol{j}^I_q - \boldsymbol{\pi}^I \cdot \boldsymbol{v}^I \right] \\
&+ \boldsymbol{\nabla}_{\parallel} \left\{ \boldsymbol{p}^{s*}_{\parallel} \cdot \left[\bar{\boldsymbol{E}}^*_{\parallel} - \left(\bar{\boldsymbol{E}}^*_{\parallel} \right)_{eq} \right] + p^{s*}_{\perp} \left[\bar{D}^*_{\perp} - \left(\bar{D}^*_{\perp} \right)_{eq} \right] + \boldsymbol{m}^{s*}_{\parallel} \cdot \left[\bar{\boldsymbol{H}}^*_{\parallel} - \left(\bar{\boldsymbol{H}}^*_{\parallel} \right)_{eq} \right] + m^{s*}_{\perp} \left[\bar{B}^*_{\perp} - \left(\bar{B}^*_{\perp} \right)_{eq} \right] \right\} \\
&+ \boldsymbol{i}^{s*} \cdot \bar{\boldsymbol{E}}^* + \bar{\boldsymbol{i}}^* \cdot \boldsymbol{E}^{s*} \\
&+ \bar{\boldsymbol{D}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s \right) \boldsymbol{p}^{s*}_{\perp} + \bar{\boldsymbol{E}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s \right) \boldsymbol{p}^{s*}_{\parallel} \\
&+ \bar{\boldsymbol{B}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s \right) \boldsymbol{m}^{s*}_{\perp} + \bar{\boldsymbol{H}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s \right) \boldsymbol{m}^{s*}_{\parallel} \\
&+ \frac{1}{c} \bar{\boldsymbol{m}} \cdot \left[\boldsymbol{\nabla} \cdot \boldsymbol{v}^s \left(\boldsymbol{v}^s_{\perp} \times \boldsymbol{p}^s \right) \right] - \frac{1}{c} \bar{\boldsymbol{p}} \cdot \left[\boldsymbol{\nabla} \cdot \boldsymbol{v}^s \left(\boldsymbol{v}^s_{\perp} \times \boldsymbol{m}^s \right) \right] \\
&+ \boldsymbol{n} \cdot \boldsymbol{v}^s_{\perp} \left[\frac{1}{2} \left| \boldsymbol{E}^{II} \right|^2 - \frac{1}{2} \left| \boldsymbol{E}^I \right|^2 + \frac{1}{2} \left| \boldsymbol{B}^{II} \right|^2 - \frac{1}{2} \left| \boldsymbol{B}^I \right|^2 + \boldsymbol{p}^{II} \cdot \boldsymbol{E}^{II} - \boldsymbol{p}^I \cdot \boldsymbol{E}^I \right] \\
&+ \boldsymbol{v}^s \left\{ \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s \right) \left(\boldsymbol{p}^{II} \times \boldsymbol{B}^{II} + \boldsymbol{E}^{II} \times \boldsymbol{m}^{II} \right) - \left(\boldsymbol{v}^I - \boldsymbol{v}^s \right) \left(\boldsymbol{p}^I \times \boldsymbol{B}^I + \boldsymbol{E}^I \times \boldsymbol{m}^I \right) \right] \right\}
\end{aligned} \tag{40}$$

We set $e^s = u^s + \frac{1}{2} \left(\boldsymbol{v}^s \cdot \boldsymbol{v}^s \right)$ in (40), and recognize in (40) the definition of the Lorentz-Heaviside bulk-phase electromagnetic energy density per unit volume g^i as defined in (15). Then, we can start to derive the evolution equation for the excess internal energy density u^s

$$\begin{aligned}
\frac{\partial^s u^s}{\partial t} &= -\boldsymbol{\nabla}_{\parallel} \cdot \left(\boldsymbol{v}^s_{def} u^s + \boldsymbol{j}^s_q \right) - u^s \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}^s_{tr} - \boldsymbol{\pi}^s : \boldsymbol{\nabla}_{\parallel} \boldsymbol{v}^s - \boldsymbol{v}^s \cdot \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{\pi}^s \\
&+ \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s \right) \left(u^{II} + \frac{1}{2} \rho^{II} \boldsymbol{v}^{II} \cdot \boldsymbol{v}^{II} + \boldsymbol{v}^s \left\{ \boldsymbol{p}^{II} \times \boldsymbol{B}^{II} + \boldsymbol{E}^{II} \times \boldsymbol{m}^{II} \right\} \right) - g^{II} \boldsymbol{v}^s + \boldsymbol{\pi}^{II} \cdot \boldsymbol{v}^{II} + \boldsymbol{j}^{II}_q \right. \\
&\qquad \left. - \left(\boldsymbol{v}^I - \boldsymbol{v}^s \right) \left(u^I + \frac{1}{2} \rho^I \boldsymbol{v}^I \cdot \boldsymbol{v}^I + \boldsymbol{v}^s \left\{ \boldsymbol{p}^I \times \boldsymbol{B}^I + \boldsymbol{E}^I \times \boldsymbol{m}^I \right\} \right) + g^I \boldsymbol{v}^s - \boldsymbol{\pi}^I \cdot \boldsymbol{v}^I - \boldsymbol{j}^I_q \right] \\
&+ \boldsymbol{i}^{s*} \cdot \bar{\boldsymbol{E}}^* + \bar{\boldsymbol{i}}^* \cdot \boldsymbol{E}^{s*} \\
&+ \bar{\boldsymbol{D}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s \right) \boldsymbol{p}^{s*}_{\perp} + \bar{\boldsymbol{E}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s \right) \boldsymbol{p}^{s*}_{\parallel} \\
&+ \bar{\boldsymbol{B}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s \right) \boldsymbol{m}^{s*}_{\perp} + \bar{\boldsymbol{H}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s \right) \boldsymbol{m}^{s*}_{\parallel} \\
&+ \frac{1}{c} \bar{\boldsymbol{m}} \cdot \left[\boldsymbol{\nabla} \cdot \boldsymbol{v}^s \left(\boldsymbol{v}^s_{\perp} \times \boldsymbol{p}^s \right) \right] - \frac{1}{c} \bar{\boldsymbol{p}} \cdot \left[\boldsymbol{\nabla} \cdot \boldsymbol{v}^s \left(\boldsymbol{v}^s_{\perp} \times \boldsymbol{m}^s \right) \right]
\end{aligned} \tag{41}$$

Multiplication of (35) by $\boldsymbol{v}^s\cdot$ and substitution for the last term in the first line of (41) gives the following

$$\begin{aligned}
\frac{\partial^s u^s}{\partial t} &= -\boldsymbol{\nabla}_{\parallel}\cdot\left(\boldsymbol{v}^s_{def}u^s+\boldsymbol{j}^s_q\right)-u^s\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{v}^s_{tr}-\boldsymbol{\pi}^s:\boldsymbol{\nabla}_{\parallel}\boldsymbol{v}^s\\
&+\boldsymbol{n}\cdot\Big\{\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)\left[u^{II}+\frac{1}{2}\rho^{II}\boldsymbol{v}^{II}\cdot\boldsymbol{v}^{II}-\rho^{II}\boldsymbol{v}^{II}\cdot\boldsymbol{v}^s+\boldsymbol{v}^s\cdot\left(\boldsymbol{p}^{II}\times\boldsymbol{B}^{II}+\boldsymbol{E}^{II}\times\boldsymbol{m}^{II}\right)\right]-g^{II}\boldsymbol{v}^s\\
&\qquad-\left(\boldsymbol{v}^{I}-\boldsymbol{v}^s\right)\left[u^{I}+\frac{1}{2}\rho^{I}\boldsymbol{v}^{I}\cdot\boldsymbol{v}^{I}-\rho^{I}\boldsymbol{v}^{I}\cdot\boldsymbol{v}^s+\boldsymbol{v}^s\cdot\left(\boldsymbol{p}^{I}\times\boldsymbol{B}^{I}+\boldsymbol{E}^{I}\times\boldsymbol{m}^{I}\right)\right]+g^{I}\boldsymbol{v}^s\\
&\qquad+\boldsymbol{\pi}^{II}\cdot\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)+\boldsymbol{j}^{II}_q-\boldsymbol{\pi}^{I}\cdot\left(\boldsymbol{v}^{I}-\boldsymbol{v}^s\right)-\boldsymbol{j}^{I}_q\Big\}\\
&+\boldsymbol{i}^{s*}\cdot\bar{\boldsymbol{E}}^*+\bar{\boldsymbol{i}}^*\cdot\boldsymbol{E}^{s*}\\
&+\bar{\boldsymbol{D}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{p}^{s*}_{\perp}+\bar{\boldsymbol{E}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{p}^{s*}_{\parallel}\\
&+\bar{\boldsymbol{B}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{m}^{s*}_{\perp}+\bar{\boldsymbol{H}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{m}^{s*}_{\parallel}\\
&+\frac{1}{c}\bar{\boldsymbol{m}}\cdot\left[\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\left(\boldsymbol{v}^s_{\perp}\times\boldsymbol{p}^s\right)\right]-\frac{1}{c}\bar{\boldsymbol{p}}\cdot\left[\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\left(\boldsymbol{v}^s_{\perp}\times\boldsymbol{m}^s\right)\right]
\end{aligned}\tag{42}$$

recalling the bulk pressure tensor $\boldsymbol{\pi}=p\boldsymbol{\delta}+\boldsymbol{\tau}$ and the thermodynamic volume-normalized relation $h=u+p$, we can re-write

$$\begin{aligned}
\frac{\partial^s u^s}{\partial t} &= -\boldsymbol{\nabla}_{\parallel}\cdot\left(\boldsymbol{v}^s_{def}u^s+\boldsymbol{j}^s_q\right)-u^s\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{v}^s_{tr}-\boldsymbol{\pi}^s:\boldsymbol{\nabla}_{\parallel}\boldsymbol{v}^s\\
&+\boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)h^{II}+\boldsymbol{j}^{II}_q-\left(\boldsymbol{v}^{I}-\boldsymbol{v}^s\right)h^{I}-\boldsymbol{j}^{I}_q+\boldsymbol{\tau}^{II}\cdot\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)-\boldsymbol{\tau}^{I}\cdot\left(\boldsymbol{v}^{I}-\boldsymbol{v}^s\right)\right]\\
&+\rho^I\left(\boldsymbol{v}^I-\boldsymbol{v}^s\right)\cdot\boldsymbol{n}\left[\frac{1}{2}\left(\boldsymbol{v}^{II}\cdot\boldsymbol{v}^{II}-\boldsymbol{v}^{I}\cdot\boldsymbol{v}^{I}\right)-\boldsymbol{v}^s\cdot\left(\boldsymbol{v}^{II}-\boldsymbol{v}^{I}\right)\right]-v^s_{\perp}\left(g^{II}-g^{I}\right)\\
&+\rho^I\left(\boldsymbol{v}^I-\boldsymbol{v}^s\right)\cdot\boldsymbol{n}\left[\boldsymbol{v}^s\cdot\left(\boldsymbol{p}^{II}\times\boldsymbol{B}^{II}-\boldsymbol{p}^{I}\times\boldsymbol{B}^{I}+\boldsymbol{E}^{II}\times\boldsymbol{m}^{II}-\boldsymbol{E}^{I}\times\boldsymbol{m}^{I}\right)\right]\\
&+\boldsymbol{i}^{s*}\cdot\bar{\boldsymbol{E}}^*+\bar{\boldsymbol{i}}^*\cdot\boldsymbol{E}^{s*}\\
&+\bar{\boldsymbol{D}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{p}^{s*}_{\perp}+\bar{\boldsymbol{E}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{p}^{s*}_{\parallel}\\
&+\bar{\boldsymbol{B}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{m}^{s*}_{\perp}+\bar{\boldsymbol{H}}^*\cdot\left(\frac{\partial}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\right)\boldsymbol{m}^{s*}_{\parallel}\\
&+\frac{1}{c}\bar{\boldsymbol{m}}\cdot\left[\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\left(\boldsymbol{v}^s_{\perp}\times\boldsymbol{p}^s\right)\right]-\frac{1}{c}\bar{\boldsymbol{p}}\cdot\left[\boldsymbol{\nabla}\cdot\boldsymbol{v}^s\left(\boldsymbol{v}^s_{\perp}\times\boldsymbol{m}^s\right)\right]
\end{aligned}\tag{43}$$

where we have used the jump balance for mass at the dividing interface.

$$\boldsymbol{n}\cdot\left(\boldsymbol{v}^I-\boldsymbol{v}^s\right)\rho^I=\boldsymbol{n}\cdot\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)\rho^{II}\tag{44}$$

By using (36), (37) and (35), we obtain the final evolution equation for the excess internal energy density u^s

$$\begin{aligned}
\frac{\partial^s u^s}{\partial t} &= -\boldsymbol{\nabla}_\parallel \cdot \left(\boldsymbol{v}^s_{def} u^s + \boldsymbol{j}^s_q\right) - u^s \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{v}^s_{tr} - \boldsymbol{\pi}^s : \boldsymbol{\nabla}_\parallel \boldsymbol{v}^s \\
&+ \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right) h^{II} + \boldsymbol{j}^{II}_q - \left(\boldsymbol{v}^I - \boldsymbol{v}^s\right) h^I - \boldsymbol{j}^I_q\right] - v^s_\perp \left(g^{II} - g^I\right) \\
&+ \left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1} \times \left\{\left[\frac{1}{2}\frac{\rho^I + \rho^{II}}{\rho^I - \rho^{II}}\left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right)^2 + \boldsymbol{n} \cdot \left(\frac{\boldsymbol{\tau}^{II}}{\rho^{II}} - \frac{\boldsymbol{\tau}^I}{\rho^I}\right) \cdot \boldsymbol{n}\right] \boldsymbol{n} \cdot \left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right)\right. \\
&\qquad \left. + \boldsymbol{n} \cdot \left(\frac{\boldsymbol{\tau}^{II}}{\rho^{II}} - \frac{\boldsymbol{\tau}^I}{\rho^I}\right) \cdot \left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right)_\parallel\right\} \\
&+ \left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1} \boldsymbol{n} \cdot \left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right) \left[\boldsymbol{v}^s \cdot \left(\boldsymbol{p}^{II} \times \boldsymbol{B}^{II} - \boldsymbol{p}^I \times \boldsymbol{B}^I + \boldsymbol{E}^{II} \times \boldsymbol{m}^{II} - \boldsymbol{E}^I \times \boldsymbol{m}^I\right)\right] \\
&+ \boldsymbol{i}^{s*} \cdot \bar{\boldsymbol{E}}^* + \bar{\boldsymbol{i}}^* \cdot \boldsymbol{E}^{s*} \\
&+ \bar{\boldsymbol{D}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s\right) \boldsymbol{p}^{s*}_\perp + \bar{\boldsymbol{E}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s\right) \boldsymbol{p}^{s*}_\parallel \\
&+ \bar{\boldsymbol{B}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s\right) \boldsymbol{m}^{s*}_\perp + \bar{\boldsymbol{H}}^* \cdot \left(\frac{\partial}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{v}^s\right) \boldsymbol{m}^{s*}_\parallel \\
&+ \frac{1}{c}\bar{\boldsymbol{m}} \cdot \left[\boldsymbol{\nabla} \cdot \boldsymbol{v}^s \left(\boldsymbol{v}^s_\perp \times \boldsymbol{p}^s\right)\right] - \frac{1}{c}\bar{\boldsymbol{p}} \cdot \left[\boldsymbol{\nabla} \cdot \boldsymbol{v}^s \left(\boldsymbol{v}^s_\perp \times \boldsymbol{m}^s\right)\right]
\end{aligned} \tag{45}$$

where the velocity difference between bulk phases was decomposed into normal and tangential components as

$$\boldsymbol{v}^{II} - \boldsymbol{v}^I = \left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right)_\parallel + \boldsymbol{n}\boldsymbol{n} \cdot \left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right) \tag{46}$$

Combining expressions (34) and (38), we obtain for $b = s$ the evolution equation for the excess entropy density e^s in the gauge $\rho^s = 0$

$$\frac{\partial^s s^s}{\partial t} = -\boldsymbol{\nabla}_\parallel \cdot \left(\boldsymbol{v}^s_{def} s^s + \boldsymbol{j}^s_s\right) - s^s \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{v}^s_{tr} + \sigma^s + \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right) s^{II} + \boldsymbol{j}^{II}_s - \left(\boldsymbol{v}^I - \boldsymbol{v}^s\right) s^I - \boldsymbol{j}^I_s\right] \tag{47}$$

and the excess species mass density

$$\frac{\partial^s \rho^s_\alpha}{\partial t} = -\boldsymbol{\nabla}_\parallel \cdot \left(\boldsymbol{v}^s_{def} \rho^s_\alpha + \boldsymbol{j}^s_\alpha\right) - \rho^s_\alpha \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{v}^s_{tr} + \nu^s_\alpha \Gamma^s + \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right) \rho^{II}_\alpha + \boldsymbol{j}^{II}_\alpha - \left(\boldsymbol{v}^I - \boldsymbol{v}^s\right) \rho^I_\alpha - \boldsymbol{j}^{II}_\alpha\right] \tag{48}$$

where $\Gamma^s = \dfrac{1}{A}\dfrac{d\xi^s}{dt}$ is the mass rate of reaction per unit area, and ν^s_α is related to the stoichiometric coefficient of species α.

2.2 Derivation of the interfacial entropy production rate $\boldsymbol{\sigma}^s$

For a multi-component system, expression (33) in the gauge $\rho^s = 0$ becomes

$$\frac{\partial^s e^s}{\partial t} = T^s \frac{\partial^s s^s}{\partial t} + \sum_{\alpha=1}^{k} \left(\hat{\mu}^s_\alpha - \frac{1}{2}\left|\boldsymbol{v}^s\right|^2\right) \frac{\partial^s \rho^s_\alpha}{\partial t} + \left(\bar{\boldsymbol{E}}^*_\parallel\right)_{eq} \cdot \frac{d^s}{dt}\boldsymbol{p}^{s*}_\parallel + \left(\bar{D}^*_\perp\right)_{eq} \frac{d^s}{dt} p^{s*}_\perp + \left(\bar{\boldsymbol{H}}^*_\parallel\right)_{eq} \cdot \frac{d^s}{dt}\boldsymbol{m}^{s*}_\parallel + \left(\bar{B}^*_\perp\right)_{eq} \frac{d^s}{dt} m^{s*}_\perp \tag{49}$$

Recalling the generalized irreversible contribution to the diffusive entropy flux $\boldsymbol{j}_s$

$$\boldsymbol{j}_s = \frac{1}{T}\left(\boldsymbol{j}_q - \sum_{\alpha=1}^{k} \hat{\mu}_\alpha \boldsymbol{j}_\alpha\right) \tag{50}$$

and its equivalent for the diffusive entropy flux within the surface $\boldsymbol{j}^s_s$

$$\boldsymbol{j}^s_s = \frac{1}{T^s}\left(\boldsymbol{j}^s_q - \sum_{\alpha=1}^{k} \hat{\mu}^s_\alpha \boldsymbol{j}^s_\alpha\right) \tag{51}$$

Substituting the expressions (40), (47) and (48) into (49), together with the definitions (50) and (51), we get

$$
\begin{aligned}
&-\boldsymbol{\nabla}_{\|}\cdot\left(\boldsymbol{v}^s_{def}e^s+\boldsymbol{j}^s_q+\boldsymbol{\pi}^s\cdot\boldsymbol{v}^s\right)-e^s\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}^s_{tr}\\
&\quad+\boldsymbol{\nabla}_{\|}\left\{\boldsymbol{p}^{s*}_{\|}\cdot\left[\bar{\boldsymbol{E}}^*_{\|}-\left(\bar{\boldsymbol{E}}^*_{\|}\right)_{eq}\right]+p^{s*}_{\perp}\left[\bar{D}^*_{\perp}-\left(\bar{D}^*_{\perp}\right)_{eq}\right]+\boldsymbol{m}^{s*}_{\|}\cdot\left[\bar{\boldsymbol{H}}^*_{\|}-\left(\bar{\boldsymbol{H}}^*_{\|}\right)_{eq}\right]+m^{s*}_{\perp}\left[\bar{B}^*_{\perp}-\left(\bar{B}^*_{\perp}\right)_{eq}\right]\right\}\\
&\quad+\boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)e^{II}+\boldsymbol{j}^{II}_q+\boldsymbol{\pi}^{II}\cdot\boldsymbol{v}^{II}-\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)e^I-\boldsymbol{j}^I_q-\boldsymbol{\pi}^I\cdot\boldsymbol{v}^I\right]\\
=\;& T^s\left\{-\boldsymbol{\nabla}_{\|}\cdot\left[\boldsymbol{v}^s_{def}s^s+\frac{1}{T^s}\left(\boldsymbol{j}^s_q-\sum_{\alpha=1}^{k}\hat{\mu}^s_{\alpha}\boldsymbol{j}^s_{\alpha}\right)\right]-s^s\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}^s_{tr}+\sigma^s\right.\\
&\quad+\boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)\left(s^{II}+\frac{1}{T^{II}}\left\{\frac{1}{2}\left|\boldsymbol{E}^{II}\right|^2+\frac{1}{2}\left|\boldsymbol{B}^{II}\right|^2+\boldsymbol{p}^{II*}\cdot\left[\boldsymbol{E}^{II*}-\left(\boldsymbol{E}^{II*}\right)_{eq}\right]\right\}\right)\right.\\
&\qquad-\left(\boldsymbol{v}^I-\boldsymbol{v}^s\right)\left(s^I+\frac{1}{T^I}\left\{\frac{1}{2}\left|\boldsymbol{E}^I\right|^2+\frac{1}{2}\left|\boldsymbol{B}^I\right|^2+\boldsymbol{p}^{I*}\cdot\left[\boldsymbol{E}^{I*}-\left(\boldsymbol{E}^{I*}\right)_{eq}\right]\right\}\right)\\
&\qquad\left.\left.+\frac{1}{T^{II}}\left(\boldsymbol{j}^{II}_q-\sum_{\alpha=1}^{k}\hat{\mu}^{II}_{\alpha}\boldsymbol{j}^{II}_{\alpha}\right)-\frac{1}{T^I}\left(\boldsymbol{j}^I_q-\sum_{\alpha=1}^{k}\hat{\mu}^I_{\alpha}\boldsymbol{j}^I_{\alpha}\right)\right]\right\}\\
&+\sum_{\alpha=1}^{k}\left(\hat{\mu}^s_{\alpha}-\frac{1}{2}\left|\boldsymbol{v}^s\right|^2\right)\left\{-\boldsymbol{\nabla}_{\|}\cdot\left(\boldsymbol{v}^s_{def}\rho^s_{\alpha}+\boldsymbol{j}^s_{\alpha}\right)-\rho^s_{\alpha}\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}^s_{tr}+\nu^s_{\alpha}\Gamma^s\right.\\
&\qquad\left.+\boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)\rho^{II}_{\alpha}+\boldsymbol{j}^{II}_{\alpha}-\left(\boldsymbol{v}^I-\boldsymbol{v}^s\right)\rho^I_{\alpha}-\boldsymbol{j}^I_{\alpha}\right]\right\}\\
&-\frac{1}{2}\left[\boldsymbol{i}^{s*}_{\|}\cdot\left(\boldsymbol{E}^{I*}_{\|}+\boldsymbol{E}^{II*}_{\|}\right)+\left(i^{I*}_{\perp}+i^{II*}_{\perp}\right)E^{s*}_{\perp}\right]\\
&-\frac{1}{2}\left\{\left[\left(\boldsymbol{E}^{I*}_{\|}+\boldsymbol{E}^{II*}_{\|}\right)-\left(\boldsymbol{E}^{I*}_{\|}+\boldsymbol{E}^{II*}_{\|}\right)_{eq}\right]\cdot\frac{d^s}{dt}\boldsymbol{p}^{s*}_{\|}-\left[\left(D^{I*}_{\perp}+D^{II*}_{\perp}\right)-\left(D^{I*}_{\perp}+D^{II*}_{\perp}\right)_{eq}\right]\frac{d^s}{dt}p^{s*}_{\perp}\right.\\
&\quad\left.-\left[\left(\boldsymbol{H}^{I*}_{\|}+\boldsymbol{H}^{II*}_{\|}\right)-\left(\boldsymbol{H}^{I*}_{\|}+\boldsymbol{H}^{II*}_{\|}\right)_{eq}\right]\cdot\frac{d^s}{dt}\boldsymbol{m}^{s*}_{\|}-\left[\left(B^{I*}_{\perp}+B^{II*}_{\perp}\right)-\left(B^{I*}_{\perp}+B^{II*}_{\perp}\right)_{eq}\right]\frac{d^s}{dt}m^{s*}_{\perp}\right\}
\end{aligned}
\tag{52}
$$

We can define the following averages of the bulk fields at the dividing interface

$$
\begin{aligned}
\bar{\boldsymbol{E}}^*_{\|}&=\frac{1}{2}\left(\boldsymbol{E}^{I*}_{\|}+\boldsymbol{E}^{II*}_{\|}\right) & \bar{D}^*_{\perp}&=\frac{1}{2}\left(D^{I*}_{\perp}+D^{II*}_{\perp}\right) & \bar{i}^*_{\perp}&=\frac{1}{2}\left(i^{I*}_{\perp}+i^{II*}_{\perp}\right)\\
\bar{\boldsymbol{H}}^*_{\|}&=\frac{1}{2}\left(\boldsymbol{H}^{I*}_{\|}+\boldsymbol{H}^{II*}_{\|}\right) & \bar{B}^*_{\perp}&=\frac{1}{2}\left(B^{I*}_{\perp}+B^{II*}_{\perp}\right)
\end{aligned}
\tag{53}
$$

We add and subtract the terms $\boldsymbol{m}^{i*} \cdot \left[\boldsymbol{B}^{i*} - \left(\boldsymbol{B}^{i*}\right)_{eq}\right]$ in line five and six of (52), and we also substitute the expressions (53) in the last three lines of (52); we obtain

$$
\begin{aligned}
&-\boldsymbol{\nabla}_{\parallel} \cdot \left(\boldsymbol{v}^s_{def} e^s + \boldsymbol{j}^s_q + \boldsymbol{\pi}^s \cdot \boldsymbol{v}^s\right) - e^s \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}^s_{tr} \\
&\quad + \boldsymbol{\nabla}_{\parallel} \left\{ \boldsymbol{p}^{s*}_{\parallel} \cdot \left[\bar{\boldsymbol{E}}^*_{\parallel} - \left(\bar{\boldsymbol{E}}^*_{\parallel}\right)_{eq}\right] + p^{s*}_{\perp} \left[\bar{D}^*_{\perp} - \left(\bar{D}^*_{\perp}\right)_{eq}\right] + \boldsymbol{m}^{s*}_{\parallel} \cdot \left[\bar{\boldsymbol{H}}^*_{\parallel} - \left(\bar{\boldsymbol{H}}^*_{\parallel}\right)_{eq}\right] + m^{s*}_{\perp} \left[\bar{B}^*_{\perp} - \left(\bar{B}^*_{\perp}\right)_{eq}\right] \right\} \\
&\quad + \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right) e^{II} + \boldsymbol{j}^{II}_q + \boldsymbol{\pi}^{II} \cdot \boldsymbol{v}^{II} - \left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right) e^I - \boldsymbol{j}^I_q - \boldsymbol{\pi}^I \cdot \boldsymbol{v}^I\right] \\
= \;& T^s \left\{ -\boldsymbol{\nabla}_{\parallel} \cdot \left[\boldsymbol{v}^s_{def} s^s + \frac{1}{T^s} \left(\boldsymbol{j}^s_q - \sum_{\alpha=1}^{k} \hat{\mu}^s_\alpha \boldsymbol{j}^s_\alpha \right) \right] - s^s \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}^s_{tr} + \sigma^s \right. \\
&\quad + \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right) \left(s^{II} + \frac{1}{T^{II}} \left\{ \frac{1}{2} \left|\boldsymbol{E}^{II}\right|^2 + \frac{1}{2} \left|\boldsymbol{B}^{II}\right|^2 - \boldsymbol{m}^{II*} \cdot \left[\boldsymbol{B}^{II*} - \left(\boldsymbol{B}^{II*}\right)_{eq}\right] \right\} \right.\right. \\
&\qquad\qquad \left.\left. + \frac{1}{T^{II}} \left\{ \boldsymbol{p}^{II*} \cdot \left[\boldsymbol{E}^{II*} - \left(\boldsymbol{E}^{II*}\right)_{eq}\right] + \boldsymbol{m}^{II*} \cdot \left[\boldsymbol{B}^{II*} + \left(\boldsymbol{B}^{II*}\right)_{eq}\right] \right\} \right) \\
&\qquad - \left(\boldsymbol{v}^I - \boldsymbol{v}^s\right) \left(s^I + \frac{1}{T^I} \left\{ \frac{1}{2} \left|\boldsymbol{E}^I\right|^2 + \frac{1}{2} \left|\boldsymbol{B}^I\right|^2 - \boldsymbol{m}^{I*} \cdot \left[\boldsymbol{B}^{I*} - \left(\boldsymbol{B}^{I*}\right)_{eq}\right] \right\} \right. \\
&\qquad\qquad \left. + \frac{1}{T^I} \left\{ \boldsymbol{p}^{I*} \cdot \left[\boldsymbol{E}^{I*} - \left(\boldsymbol{E}^{I*}\right)_{eq}\right] + \boldsymbol{m}^{I*} \cdot \left[\boldsymbol{B}^{I*} + \left(\boldsymbol{B}^{I*}\right)_{eq}\right] \right\} \right) \\
&\qquad + \frac{1}{T^{II}} \left(\boldsymbol{j}^{II}_q - \sum_{\alpha=1}^{k} \hat{\mu}^{II}_\alpha \boldsymbol{j}^{II}_\alpha \right) - \frac{1}{T^I} \left(\boldsymbol{j}^I_q - \sum_{\alpha=1}^{k} \hat{\mu}^I_\alpha \boldsymbol{j}^I_\alpha \right) \Big] \Big\} \\
&\quad + \sum_{\alpha=1}^{k} \left(\hat{\mu}^s_\alpha - \frac{1}{2} \left|\boldsymbol{v}^s\right|^2 \right) \left\{ -\boldsymbol{\nabla}_{\parallel} \cdot \left(\boldsymbol{v}^s_{def} \rho^s_\alpha + \boldsymbol{j}^s_\alpha\right) - \rho^s_\alpha \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}^s_{tr} + \nu^s_\alpha \Gamma^s \right. \\
&\qquad\qquad \left. + \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right) \rho^{II}_\alpha + \boldsymbol{j}^{II}_\alpha - \left(\boldsymbol{v}^I - \boldsymbol{v}^s\right) \rho^I_\alpha - \boldsymbol{j}^I_\alpha\right] \right\} \\
&\quad - \left(\boldsymbol{i}^{s*}_{\parallel} \cdot \bar{\boldsymbol{E}}^*_{\parallel} + \bar{i}^*_{\perp} E^{s*}_{\perp} \right) \\
&\quad - \left\{ \left[\bar{\boldsymbol{E}}^*_{\parallel} - \left(\bar{\boldsymbol{E}}^*_{\parallel}\right)_{eq}\right] \cdot \frac{d^s}{dt} \boldsymbol{p}^{s*}_{\parallel} + \left[\bar{D}^*_{\perp} - \left(\bar{D}^*_{\perp}\right)_{eq}\right] \frac{d^s}{dt} p^{s*}_{\perp} \right. \\
&\qquad \left. + \left[\bar{\boldsymbol{H}}^*_{\parallel} - \left(\bar{\boldsymbol{H}}^*_{\parallel}\right)_{eq}\right] \cdot \frac{d^s}{dt} \boldsymbol{m}^{s*}_{\parallel} + \left[\bar{B}^*_{\perp} - \left(\bar{B}^*_{\perp}\right)_{eq}\right] \frac{d^s}{dt} m^{s*}_{\perp} \right\}
\end{aligned}
\tag{54}
$$

In our gauge $\rho^s = 0$, we can neglect the term for the momentum density of the electromagnetic field $\frac{1}{c}\left(\boldsymbol{E}^i \times \boldsymbol{M}^i\right)$. We then notice that the expressions in curly brackets in lines 5 and 7 represent the Lorentz-Heaviside bulk-phase electromagnetic energy densities per unit volume g^i for the two phases I and II (see

expression (15)). Therefore we can re-write (54) as

$$
\begin{aligned}
&-\boldsymbol{\nabla}_{\|}\cdot\left(\boldsymbol{v}_{def}^{s}e^{s}+\boldsymbol{j}_{q}^{s}+\boldsymbol{\pi}^{s}\cdot\boldsymbol{v}^{s}\right)-e^{s}\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}_{tr}^{s}\\
&\quad+\boldsymbol{\nabla}_{\|}\left\{\boldsymbol{p}_{\|}^{s*}\cdot\left[\bar{\boldsymbol{E}}_{\|}^{*}-\left(\bar{\boldsymbol{E}}_{\|}^{*}\right)_{eq}\right]+p_{\perp}^{s*}\left[\bar{D}_{\perp}^{*}-\left(\bar{D}_{\perp}^{*}\right)_{eq}\right]+\boldsymbol{m}_{\|}^{s*}\cdot\left[\bar{\boldsymbol{H}}_{\|}^{*}-\left(\bar{\boldsymbol{H}}_{\|}^{*}\right)_{eq}\right]+m_{\perp}^{s*}\left[\bar{B}_{\perp}^{*}-\left(\bar{B}_{\perp}^{*}\right)_{eq}\right]\right\}\\
&\quad+\boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^{II}-\boldsymbol{v}^{s}\right)e^{II}+\boldsymbol{j}_{q}^{II}+\boldsymbol{\pi}^{II}\cdot\boldsymbol{v}^{II}-\left(\boldsymbol{v}^{II}-\boldsymbol{v}^{s}\right)e^{I}-\boldsymbol{j}_{q}^{I}-\boldsymbol{\pi}^{I}\cdot\boldsymbol{v}^{I}\right]\\
=\;& T^{s}\left\{-\boldsymbol{\nabla}_{\|}\cdot\left[\boldsymbol{v}_{def}^{s}s^{s}+\frac{1}{T^{s}}\left(\boldsymbol{j}_{q}^{s}-\sum_{\alpha=1}^{k}\hat{\mu}_{\alpha}^{s}\boldsymbol{j}_{\alpha}^{s}\right)\right]-s^{s}\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}_{tr}^{s}+\sigma^{s}\right.\\
&\quad+\boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^{II}-\boldsymbol{v}^{s}\right)\left(s^{II}+\frac{1}{T^{II}}g^{II}+\frac{1}{T^{II}}\left\{\boldsymbol{p}^{II*}\cdot\left[\boldsymbol{E}^{II*}-\left(\boldsymbol{E}^{II*}\right)_{eq}\right]+\boldsymbol{m}^{II*}\cdot\left[\boldsymbol{B}^{II*}+\left(\boldsymbol{B}^{II*}\right)_{eq}\right]\right\}\right)\right.\\
&\qquad-\left(\boldsymbol{v}^{I}-\boldsymbol{v}^{s}\right)\left(s^{I}+\frac{1}{T^{I}}g^{I}+\frac{1}{T^{I}}\left\{\boldsymbol{p}^{I*}\cdot\left[\boldsymbol{E}^{I*}-\left(\boldsymbol{E}^{I*}\right)_{eq}\right]+\boldsymbol{m}^{I*}\cdot\left[\boldsymbol{B}^{I*}+\left(\boldsymbol{B}^{I*}\right)_{eq}\right]\right\}\right)\\
&\qquad\left.\left.+\frac{1}{T^{II}}\left(\boldsymbol{j}_{q}^{II}-\sum_{\alpha=1}^{k}\hat{\mu}_{\alpha}^{II}\boldsymbol{j}_{\alpha}^{II}\right)-\frac{1}{T^{I}}\left(\boldsymbol{j}_{q}^{I}-\sum_{\alpha=1}^{k}\hat{\mu}_{\alpha}^{I}\boldsymbol{j}_{\alpha}^{I}\right)\right]\right\}\\
&+\sum_{\alpha=1}^{k}\left(\hat{\mu}_{\alpha}^{s}-\frac{1}{2}\left|\boldsymbol{v}^{s}\right|^{2}\right)\left\{-\boldsymbol{\nabla}_{\|}\cdot\left(\boldsymbol{v}_{def}^{s}\rho_{\alpha}^{s}+\boldsymbol{j}_{\alpha}^{s}\right)-\rho_{\alpha}^{s}\boldsymbol{\nabla}_{\|}\cdot\boldsymbol{v}_{tr}^{s}+\nu_{\alpha}^{s}\Gamma^{s}\right.\\
&\qquad\left.+\boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^{II}-\boldsymbol{v}^{s}\right)\rho_{\alpha}^{II}+\boldsymbol{j}_{\alpha}^{II}-\left(\boldsymbol{v}^{I}-\boldsymbol{v}^{s}\right)\rho_{\alpha}^{I}-\boldsymbol{j}_{\alpha}^{I}\right]\right\}\\
&-\left(\boldsymbol{i}_{\|}^{s*}\cdot\bar{\boldsymbol{E}}_{\|}^{*}+\bar{i}_{\perp}^{*}E_{\perp}^{s*}\right)\\
&-\left\{\left[\bar{\boldsymbol{E}}_{\|}^{*}-\left(\bar{\boldsymbol{E}}_{\|}^{*}\right)_{eq}\right]\cdot\frac{d^{s}}{dt}\boldsymbol{p}_{\|}^{s*}+\left[\bar{D}_{\perp}^{*}-\left(\bar{D}_{\perp}^{*}\right)_{eq}\right]\frac{d^{s}}{dt}p_{\perp}^{s*}\right.\\
&\quad\left.+\left[\bar{\boldsymbol{H}}_{\|}^{*}-\left(\bar{\boldsymbol{H}}_{\|}^{*}\right)_{eq}\right]\cdot\frac{d^{s}}{dt}\boldsymbol{m}_{\|}^{s*}+\left[\bar{B}_{\perp}^{*}-\left(\bar{B}_{\perp}^{*}\right)_{eq}\right]\frac{d^{s}}{dt}m_{\perp}^{s*}\right\}
\end{aligned}
\tag{55}
$$

We use the following definitions of the modified chemical potentials at the dividing interface [1]:

$$
\begin{aligned}
\tilde{\mu}_{\alpha}^{i}&\equiv\hat{\mu}_{\alpha}^{i}-\boldsymbol{p}^{i*}\cdot\left[\boldsymbol{E}^{i*}-\left(\boldsymbol{E}^{i*}\right)_{eq}\right]-\boldsymbol{m}^{i*}\cdot\left[\boldsymbol{B}^{i*}-\left(\boldsymbol{B}^{i*}\right)_{eq}\right]-\frac{1}{2}\left|\boldsymbol{v}^{i}\right|^{2}\qquad\text{with}\qquad i=I,II\\
\tilde{\mu}_{\alpha}^{s}&\equiv\hat{\mu}_{\alpha}^{s}-\boldsymbol{p}_{\|}^{s*}\cdot\left[\bar{\boldsymbol{E}}_{\|}^{*}-\left(\bar{\boldsymbol{E}}_{\|}^{*}\right)_{eq}\right]-p_{\perp}^{s*}\left[\bar{D}_{\perp}^{*}-\left(\bar{D}_{\perp}^{*}\right)_{eq}\right]\\
&\qquad-\boldsymbol{m}_{\|}^{s*}\cdot\left[\bar{\boldsymbol{H}}_{\|}^{*}-\left(\bar{\boldsymbol{H}}_{\|}^{*}\right)_{eq}\right]-m_{\perp}^{s*}\left[\bar{B}_{\perp}^{*}-\left(\bar{B}_{\perp}^{*}\right)_{eq}\right]-\frac{1}{2}\left|\boldsymbol{v}^{s}\right|^{2}
\end{aligned}
\tag{56}
$$

Solving expression (55) for σ^s and substituting (56), we obtain

$$
\begin{aligned}
T^s\sigma^s = &-\boldsymbol{\nabla}_\parallel\cdot\left(\boldsymbol{v}^s_{def}e^s\right)+T^s\boldsymbol{\nabla}_\parallel\cdot\left(\boldsymbol{v}^s_{def}s^s\right)+\sum_{\alpha=1}^{k}\hat{\mu}^s_\alpha\boldsymbol{\nabla}_\parallel\cdot\left(\boldsymbol{v}^s_{def}\rho^s_\alpha\right)\\
&+T^s\boldsymbol{j}^s_q\cdot\boldsymbol{\nabla}_\parallel\frac{1}{T^s}-T^s\sum_{\alpha=1}^{k}\boldsymbol{j}^s_\alpha\cdot\boldsymbol{\nabla}_\parallel\frac{\hat{\mu}^s_\alpha}{T^s}-\sum_{\alpha=1}^{k}\nu^s_\alpha\hat{\mu}^s_\alpha\Gamma^s\\
&-\boldsymbol{v}^s\cdot\left(\boldsymbol{\nabla}_\parallel\cdot\boldsymbol{\pi}^s\right)-\boldsymbol{\pi}^s:\boldsymbol{\nabla}_\parallel\boldsymbol{v}^s-\left(e^s-T^ss^s-\sum_{\alpha=1}^{k}\hat{\mu}^s_\alpha\rho^s_\alpha\right)\boldsymbol{\nabla}_\parallel\cdot\boldsymbol{v}^s_{tr}\\
&+\boldsymbol{n}\cdot\left\{\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)\left(e^{II}-T^ss^{II}-\sum_{\alpha=1}^{k}\hat{\mu}^s_\alpha\rho^{II}_\alpha\right)-\left(\boldsymbol{v}^{I}-\boldsymbol{v}^s\right)\left(e^{I}-T^ss^{I}-\sum_{\alpha=1}^{k}\hat{\mu}^s_\alpha\rho^{I}_\alpha\right)\right\}\\
&+T^s\boldsymbol{n}\cdot\boldsymbol{j}^{II}_q\left(\frac{1}{T^s}-\frac{1}{T^{II}}\right)-T^s\boldsymbol{n}\cdot\boldsymbol{j}^{I}_q\left(\frac{1}{T^s}-\frac{1}{T^{I}}\right)\\
&-T^s\sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\boldsymbol{j}^{II}_\alpha\left(\frac{\tilde{\mu}^s_\alpha}{T^s}-\frac{\tilde{\mu}^{II}_\alpha}{T^{II}}\right)+T^s\sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\boldsymbol{j}^{I}_\alpha\left(\frac{\tilde{\mu}^s_\alpha}{T^s}-\frac{\tilde{\mu}^{I}_\alpha}{T^{I}}\right)\\
&+\boldsymbol{n}\cdot\left[\boldsymbol{\pi}^{II}\cdot\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)-\boldsymbol{\pi}^{I}\cdot\left(\boldsymbol{v}^{I}-\boldsymbol{v}^s\right)\right]+\boldsymbol{n}\cdot\left(\boldsymbol{\pi}^{II}-\boldsymbol{\pi}^{I}\right)\cdot\boldsymbol{v}^s\\
&+\left(\boldsymbol{i}^{s*}_\parallel\cdot\bar{\boldsymbol{E}}^*_\parallel+\bar{i}^*_\perp E^{s*}_\perp\right)\\
&+\left\{\left[\bar{\boldsymbol{E}}^*_\parallel-\left(\bar{\boldsymbol{E}}^*_\parallel\right)_{eq}\right]\cdot\frac{d^s}{dt}\boldsymbol{p}^{s*}_\parallel+\left[\bar{D}^*_\perp-\left(\bar{D}^*_\perp\right)_{eq}\right]\frac{d^s}{dt}p^{s*}_\perp\right.\\
&\quad\left.+\left[\bar{\boldsymbol{H}}^*_\parallel-\left(\bar{\boldsymbol{H}}^*_\parallel\right)_{eq}\right]\cdot\frac{d^s}{dt}\boldsymbol{m}^{s*}_\parallel+\left[\bar{B}^*_\perp-\left(\bar{B}^*_\perp\right)_{eq}\right]\frac{d^s}{dt}m^{s*}_\perp\right\}
\end{aligned}
\tag{57}
$$

Let us now recall the surface pressure tensor decomposition $\boldsymbol{\pi}^s=-\gamma\boldsymbol{\delta}_\parallel+\boldsymbol{\tau}^s$, together with the Euler equation (30) and the fundamental thermodynamic form (33); let us also express energy and entropy densities in terms of bulk intensive variables.

Finally, we decompose the bulk pressure tensor $\boldsymbol{\pi}$ as $\boldsymbol{\pi}=p\boldsymbol{\delta}+\boldsymbol{\tau}$ and we recall the general expression for the conservation of the bulk energy density

$$
e+p-Ts-\sum_{\alpha=1}^{k}\hat{\mu}_\alpha\rho_\alpha=\frac{1}{2}\rho\boldsymbol{v}^2 \tag{58}
$$

We ultimately expand the expression (57)

$$
\begin{aligned}
\sigma^s = & \boldsymbol{j}_q^s \cdot \boldsymbol{\nabla}_\parallel \frac{1}{T^s} - \frac{1}{T^s}\boldsymbol{\tau}^s : \boldsymbol{\nabla}_\parallel \boldsymbol{v}^s - \sum_{\alpha=1}^{k} \boldsymbol{j}_\alpha^s \cdot \boldsymbol{\nabla}_\parallel \frac{\hat{\mu}_\alpha^s}{T^s} - \frac{1}{T^s}\sum_{\alpha=1}^{k} \nu_\alpha^s \hat{\mu}_\alpha^s \Gamma^s \\
& + \frac{1}{T^s}\left\{ \boldsymbol{n} \cdot \left[\rho^{II}\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right)\frac{1}{2}\boldsymbol{v}^{II\,2} - \rho^I\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\frac{1}{2}\boldsymbol{v}^{I\,2}\right] + \boldsymbol{n} \cdot \left[\boldsymbol{\tau}^{II} \cdot \left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right) - \boldsymbol{\tau}^I \cdot \left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\right]\right\} \\
& + \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right)\left(T^{II}s^{II} + g^{II}\right) + \boldsymbol{j}_q^{II}\right]\left(\frac{1}{T^s} - \frac{1}{T^{II}}\right) - \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\left(T^I s^I + g^I\right) + \boldsymbol{j}_q^I\right]\left(\frac{1}{T^s} - \frac{1}{T^I}\right) \\
& - \sum_{\alpha=1}^{k} \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right)\rho_\alpha^{II}\left(\frac{\hat{\mu}_\alpha^s}{T^s} - \frac{\hat{\mu}_\alpha^{II}}{T^s}\right) + \boldsymbol{j}_\alpha^{II}\left(\frac{\hat{\mu}_\alpha^s}{T^s} - \frac{\hat{\mu}_\alpha^{II}}{T^{II}}\right)\right] \\
& + \sum_{\alpha=1}^{k} \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\rho_\alpha^{I}\left(\frac{\hat{\mu}_\alpha^s}{T^s} - \frac{\hat{\mu}_\alpha^{I}}{T^s}\right) + \boldsymbol{j}_\alpha^{I}\left(\frac{\hat{\mu}_\alpha^s}{T^s} - \frac{\hat{\mu}_\alpha^{I}}{T^I}\right)\right] \\
& + \frac{1}{T^s}\left[\boldsymbol{n} \cdot \left(\boldsymbol{\pi}^{II} - \boldsymbol{\pi}^I\right) \cdot \boldsymbol{v}^s - \boldsymbol{v}^s \cdot \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{\pi}^s\right] \\
& + \frac{1}{T^s}\left(\boldsymbol{i}_\parallel^{s*} \cdot \bar{\boldsymbol{E}}_\parallel^* + \bar{i}_\perp^* E_\perp^{s*}\right) \\
& + \frac{1}{T^s}\left\{\left[\bar{\boldsymbol{E}}_\parallel^* - \left(\bar{\boldsymbol{E}}_\parallel^*\right)_{eq}\right] \cdot \frac{d^s}{dt}\boldsymbol{p}_\parallel^{s*} + \left[\bar{D}_\perp^* - \left(\bar{D}_\perp^*\right)_{eq}\right]\frac{d^s}{dt}p_\perp^{s*}\right. \\
& \qquad \left. + \left[\bar{\boldsymbol{H}}_\parallel^* - \left(\bar{\boldsymbol{H}}_\parallel^*\right)_{eq}\right] \cdot \frac{d^s}{dt}\boldsymbol{m}_\parallel^{s*} + \left[\bar{B}_\perp^* - \left(\bar{B}_\perp^*\right)_{eq}\right]\frac{d^s}{dt}m_\perp^{s*}\right\}
\end{aligned}
\tag{59}
$$

It is known the basic thermodynamic relation

$$
Ts = h - g - \sum_{\alpha=1}^{k} \hat{\mu}_\alpha \rho_\alpha \tag{60}
$$

Using the expressions (35), (36), (37) and (60) and decomposing the velocity difference into normal and tangential components, we can re-write Equation (59)

$$
\begin{aligned}
\sigma^s = & \boldsymbol{j}_q^s \cdot \boldsymbol{\nabla}_\parallel \frac{1}{T^s} - \frac{1}{T^s}\boldsymbol{\tau}^s : \boldsymbol{\nabla}_\parallel \boldsymbol{v}^s - \sum_{\alpha=1}^{k} \boldsymbol{j}_\alpha^s \cdot \boldsymbol{\nabla}_\parallel \frac{\hat{\mu}_\alpha^s}{T^s} - \frac{1}{T^s}\sum_{\alpha=1}^{k} \nu_\alpha^s \hat{\mu}_\alpha^s \Gamma^s \\
& + \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right)\left(h^{II} - g^{II}\right) + \boldsymbol{j}_q^{II}\right]\left(\frac{1}{T^s} - \frac{1}{T^{II}}\right) - \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\left(h^I - g^I\right) + \boldsymbol{j}_q^I\right]\left(\frac{1}{T^s} - \frac{1}{T^I}\right) \\
& + \frac{1}{T^s}\left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1}\left\{\frac{1}{2}\frac{\rho^I + \rho^{II}}{\rho^I - \rho^{II}}\left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right)^2 + \boldsymbol{n} \cdot \left(\frac{\boldsymbol{\tau}^{II}}{\rho^{II}} - \frac{\boldsymbol{\tau}^I}{\rho^I}\right) \cdot \boldsymbol{n}\right\}\boldsymbol{n} \cdot \left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right) \\
& + \frac{1}{T^s}\left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1}\boldsymbol{n} \cdot \left(\frac{\boldsymbol{\tau}^{II}}{\rho^{II}} - \frac{\boldsymbol{\tau}^I}{\rho^I}\right) \cdot \left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right)_\parallel \\
& - \sum_{\alpha=1}^{k} \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right)\rho_\alpha^{II} + \boldsymbol{j}_\alpha^{II}\right]\left(\frac{\tilde{\mu}_\alpha^s}{T^s} - \frac{\tilde{\mu}_\alpha^{II}}{T^{II}}\right) + \sum_{\alpha=1}^{k} \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\rho_\alpha^I + \boldsymbol{j}_\alpha^I\right]\left(\frac{\tilde{\mu}_\alpha^s}{T^s} - \frac{\tilde{\mu}_\alpha^I}{T^I}\right) \\
& + \frac{1}{T^s}\left(\boldsymbol{i}_\parallel^{s*} \cdot \bar{\boldsymbol{E}}_\parallel^* + \bar{i}_\perp^* E_\perp^{s*}\right) \\
& + \frac{1}{T^s}\left\{\left[\bar{\boldsymbol{E}}_\parallel^* - \left(\bar{\boldsymbol{E}}_\parallel^*\right)_{eq}\right] \cdot \frac{d^s}{dt}\boldsymbol{p}_\parallel^{s*} + \left[\bar{D}_\perp^* - \left(\bar{D}_\perp^*\right)_{eq}\right]\frac{d^s}{dt}p_\perp^{s*}\right. \\
& \qquad \left. + \left[\bar{\boldsymbol{H}}_\parallel^* - \left(\bar{\boldsymbol{H}}_\parallel^*\right)_{eq}\right] \cdot \frac{d^s}{dt}\boldsymbol{m}_\parallel^{s*} + \left[\bar{B}_\perp^* - \left(\bar{B}_\perp^*\right)_{eq}\right]\frac{d^s}{dt}m_\perp^{s*}\right\}
\end{aligned}
\tag{61}
$$

As done by other authors [16], the following *flat-average* chemical potentials are introduced

$$\tilde{\mu}^I = \frac{1}{k}\sum_{\alpha=1}^{k}\tilde{\mu}^I_\alpha \qquad \tilde{\mu}^{II} = \frac{1}{k}\sum_{\alpha=1}^{k}\tilde{\mu}^{II}_\alpha \qquad \tilde{\mu}^s = \frac{1}{k}\sum_{\alpha=1}^{k}\tilde{\mu}^s_\alpha \tag{62}$$

together with the expression for the momentum density

$$k\boldsymbol{m} = \left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\rho^I = \left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right)\rho^{II} \tag{63}$$

Substituting equations (62) and (63) into (61), we ultimately get

$$\begin{aligned}
\sigma^s = {} & \boldsymbol{j}^s_q \cdot \boldsymbol{\nabla}_\parallel \frac{1}{T^s} - \frac{1}{T^s}\boldsymbol{\tau}^s : \boldsymbol{\nabla}_\parallel \boldsymbol{v}^s - \sum_{\alpha=1}^{k}\boldsymbol{j}^s_\alpha \cdot \boldsymbol{\nabla}_\parallel \frac{\hat{\mu}^s_\alpha - \hat{\mu}^s}{T^s} - \frac{1}{T^s}\sum_{\alpha=1}^{k}\nu^s_\alpha \hat{\mu}^s_\alpha \Gamma^s \\
& + \boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right)\left(h^{II} - g^{II}\right) + \boldsymbol{j}^{II}_q\right]\left(\frac{1}{T^s} - \frac{1}{T^{II}}\right) - \boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\left(h^I - g^I\right) + \boldsymbol{j}^I_q\right]\left(\frac{1}{T^s} - \frac{1}{T^I}\right) \\
& + \frac{1}{T^s}\left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1}\left\{T^s\left(\frac{\tilde{\mu}^{II}}{T^{II}} - \frac{\tilde{\mu}^I}{T^I}\right) + \frac{1}{2}\frac{\rho^I + \rho^{II}}{\rho^I - \rho^{II}}\left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right)^2 + \boldsymbol{n}\cdot\left(\frac{\boldsymbol{\tau}^{II}}{\rho^{II}} - \frac{\boldsymbol{\tau}^I}{\rho^I}\right)\cdot\boldsymbol{n}\right\}\boldsymbol{n}\cdot\left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right) \\
& + \frac{1}{T^s}\left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1}\boldsymbol{n}\cdot\left(\frac{\boldsymbol{\tau}^{II}}{\rho^{II}} - \frac{\boldsymbol{\tau}^I}{\rho^I}\right)\cdot\left(\boldsymbol{v}^{II} - \boldsymbol{v}^I\right)_\parallel \\
& - \sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right)\rho^{II}_\alpha - \boldsymbol{m} + \boldsymbol{j}^{II}_\alpha\right]\left(\frac{\tilde{\mu}^s_\alpha - \tilde{\mu}^s}{T^s} - \frac{\tilde{\mu}^{II}_\alpha - \tilde{\mu}^{II}}{T^{II}}\right) \\
& + \sum_{\alpha=1}^{k}\boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\rho^I_\alpha - \boldsymbol{m} + \boldsymbol{j}^I_\alpha\right]\left(\frac{\tilde{\mu}^s_\alpha - \tilde{\mu}^s}{T^s} - \frac{\tilde{\mu}^I_\alpha - \tilde{\mu}^I}{T^I}\right) \\
& + \frac{1}{T^s}\left(\boldsymbol{i}^{s*}_\parallel \cdot \bar{\boldsymbol{E}}^*_\parallel + \bar{i}^*_\perp E^{s*}_\perp\right) \\
& + \frac{1}{T^s}\left\{\left[\bar{\boldsymbol{E}}^*_\parallel - \left(\bar{\boldsymbol{E}}^*_\parallel\right)_{eq}\right]\cdot\frac{d^s}{dt}\boldsymbol{p}^{s*}_\parallel + \left[\bar{D}^*_\perp - \left(\bar{D}^*_\perp\right)_{eq}\right]\frac{d^s}{dt}p^{s*}_\perp\right. \\
& \qquad \left. + \left[\bar{\boldsymbol{H}}^*_\parallel - \left(\bar{\boldsymbol{H}}^*_\parallel\right)_{eq}\right]\cdot\frac{d^s}{dt}\boldsymbol{m}^{s*}_\parallel + \left[\bar{B}^*_\perp - \left(\bar{B}^*_\perp\right)_{eq}\right]\frac{d^s}{dt}m^{s*}_\perp\right\}
\end{aligned} \tag{64}$$

The expression (64) is the FINAL form of the entropy production rate for a polarizable chemically-active multicomponent system in the presence of electromagnetic fields.

It is important to note that the entropy production rate depends only on gauge-invariant surface properties and on the definition of the externally applied electromagnetic field.

3. Examples of Cross Effects via Force-Flux coupling at the interface

3.1 Heat and Mass transfer coupling

For simplicity, let us consider a non-isothermal two-component system with cross effects between the diffusive fluxes of mass and energy within an interface. We assume there are NO externally applied electromagnetic fields and there are NO chemical reactions occurring within the system.

We can rewrite the first line in equation (64) for the entropy production rate σ^s as:

$$\sigma^s = \boldsymbol{j}_q^s \cdot \boldsymbol{\nabla}_\parallel \frac{1}{T^s} - \boldsymbol{j}_1^s \cdot \boldsymbol{\nabla}_\parallel \frac{\hat{\mu}_1^s - \hat{\mu}^s}{T^s} - \boldsymbol{j}_2^s \cdot \boldsymbol{\nabla}_\parallel \frac{\hat{\mu}_2^s - \hat{\mu}^s}{T^s} \tag{65}$$

If we sum the momenta of each species in a generic k-component system, we have:

$$\begin{aligned} \sum_{\alpha=1}^{k} \boldsymbol{v}_\alpha \rho_\alpha &= \rho \sum_{\alpha=1}^{k} \boldsymbol{v}_\alpha w_\alpha \\ &= \sum_{\alpha=1}^{k} \boldsymbol{v}_\alpha \rho_\alpha + \sum_{\alpha=1}^{k} \boldsymbol{j}_\alpha = \boldsymbol{v}\rho + \sum_{\alpha=1}^{k} \boldsymbol{j}_\alpha \end{aligned} \tag{66}$$

where w_α is the mass fraction of species α. In a 2-component system this implies that:

$$\sum_{\alpha=1}^{k} \boldsymbol{j}_\alpha = 0 \quad \Longrightarrow \boldsymbol{j}_1 = -\boldsymbol{j}_2 \tag{67}$$

From Equation (67) we can rewrite (65) as

$$\sigma_s = \boldsymbol{j}_q^s \cdot \boldsymbol{\nabla}_\parallel \frac{1}{T^s} - \boldsymbol{j}_1^s \cdot \boldsymbol{\nabla}_\parallel \frac{\hat{\mu}_2^s - \hat{\mu}_1^s}{T^s} \tag{68}$$

We need to guarantee the non-negativity of the entropy production for the terms on the right-hand side of Equation (68)

$$\boldsymbol{j}_q^s = L_{qq}^s \cdot \boldsymbol{\nabla}_\parallel \frac{1}{T^s} - L_{1q}^s \cdot \boldsymbol{\nabla}_\parallel \frac{\hat{\mu}_2^s - \hat{\mu}_1^s}{T^s} \tag{69}$$

$$\boldsymbol{j}_1^s = L_{q1}^s \cdot \boldsymbol{\nabla}_\parallel \frac{1}{T^s} - L_{11}^s \cdot \boldsymbol{\nabla}_\parallel \frac{\hat{\mu}_2^s - \hat{\mu}_1^s}{T^s} \tag{70}$$

where $L_{q1}^s = L_{1q}^s$, L_{qq}^s and L_{11}^s are phenomenological transport coefficients defining a phenomenological symmetric matrix. We know from mass conservation that $\rho^s = \rho_1^s + \rho_2^s = 0$, so we can write

$$d\left(\frac{\hat{\mu}_2^s - \hat{\mu}_1^s}{T^s}\right) = \frac{1}{T_s} d\left(\hat{\mu}_2^s - \hat{\mu}_1^s\right) - \frac{\hat{\mu}_2^s - \hat{\mu}_1^s}{{T^s}^2} dT^s = \frac{1}{T_s \rho_1^s}\left(s^s dT^s + d\gamma\right) - \frac{\hat{\mu}_2^s - \hat{\mu}_1^s}{{T^s}^2} dT^s \tag{71}$$

Recalling the thermodynamic definition of the interfacial tension $\gamma = \gamma\left(T^s, \hat{\mu}_1^s\right)$, we can expand

$$d\gamma = \left(\frac{\partial \gamma}{\partial T_1^s}\right)_{\hat{\mu}_1^s} dT^s + \left(\frac{\partial \gamma}{\partial \hat{\mu}_1^s}\right)_{T_1^s} d\hat{\mu}_1^s \tag{72}$$

Recalling the thermodynamic gauge-invariant expressions ($\rho_k^s = 0$) for the surface excess entropy density s^s and the surface excess species mass density ρ_α^s

$$d\gamma = -s^s dT^s + \rho_1^s \left(\frac{\partial \hat{\mu}_2^s}{\partial T^s}\right)_{\hat{\mu}_1^s} dT^s - \rho_1^s \left[1 - \left(\frac{\partial \hat{\mu}_2^s}{\partial \hat{\mu}_1^s}\right)_{T^s}\right] d\hat{\mu}_1^s \tag{73}$$

Substituting Equation (73) into Equation (71) we obtain the expression

$$d\left(\frac{\hat{\mu}_2^s - \hat{\mu}_1^s}{T^s}\right) = -\frac{1}{T^{s2}}\left[\hat{\mu}_2^s - \hat{\mu}_1^s - T^s\left(\frac{\partial \hat{\mu}_2^s}{\partial T^s}\right)_{\hat{\mu}_1^s}\right] dT^s - \frac{1}{T^s}\left[1 - \left(\frac{\partial \hat{\mu}_2^s}{\partial \hat{\mu}_1^s}\right)_{T^s}\right] d\hat{\mu}_1^s \tag{74}$$

Substituting (74) into (70) we get

$$\begin{aligned}\boldsymbol{\jmath}_1^s &= -\frac{1}{T^{s2}}\left\{L_{qq}^s + L_{11}^s\left[\hat{\mu}_2^s - \hat{\mu}_1^s - T^s\left(\frac{\partial \hat{\mu}_2^s}{\partial T^s}\right)_{\hat{\mu}_1^s}\right]\right\}\boldsymbol{\nabla}_\parallel T^s - \frac{L_{11}^s}{T^s}\left[1 - \left(\frac{\partial \hat{\mu}_2^s}{\partial \hat{\mu}_1^s}\right)_{T^s}\right]\boldsymbol{\nabla}_\parallel \hat{\mu}_1^s \\ &= -\rho_1^s \frac{D_{q1}^s}{T^s}\boldsymbol{\nabla}_\parallel T^s - D_{12}^s \boldsymbol{\nabla}_\parallel \hat{\mu}_1^s\end{aligned} \tag{75}$$

where we defined D_{12}^s, i.e. the surface diffusivity of species 1 relative to species 2, and D_{q1}^s, i.e. the surface thermal diffusion coefficient of species 1, as

$$D_{12}^s = \frac{L_{11}^s}{T^s}\left[1 - \left(\frac{\partial \hat{\mu}_2^s}{\partial \hat{\mu}_1^s}\right)_{T^s}\right]\left(\frac{\partial \hat{\mu}_1^s}{\partial \rho_1^s}\right)_{T^s} \tag{76}$$

$$D_{q1}^s = \frac{L_{qq}^s + L_{11}^s\left[\hat{\mu}_2^s - \hat{\mu}_1^s - T^s\left(\frac{\partial \hat{\mu}_2^s}{\partial T^s}\right)_{\hat{\mu}_1^s}\right]}{\rho_1^s T^s} \tag{77}$$

We can repeat the same process for the interfacial diffusive energy flux $\boldsymbol{\jmath}_q^s$:

$$\boldsymbol{\jmath}_q^s = -\frac{L_{qq}^s}{T^{s2}}\boldsymbol{\nabla}_\parallel T^s - \frac{L_{q1}^s}{T^{s2}}\left[\hat{\mu}_2^s - \hat{\mu}_1^s - T^s\left(\frac{\partial \hat{\mu}_2^s}{\partial T^s}\right)_{\hat{\mu}_1^s}\right]\boldsymbol{\nabla}_\parallel T^s - \frac{L_{q1}^s}{T^s}\left[1 - \left(\frac{\partial \hat{\mu}_2^s}{\partial \hat{\mu}_1^s}\right)_{T^s}\right]\left(\frac{\partial \hat{\mu}_1^s}{\partial \rho_1^s}\right)_{T^s}\boldsymbol{\nabla}_\parallel \rho_1^s \tag{78}$$

Having defined both $\boldsymbol{\jmath}_q^s$ and $\boldsymbol{\jmath}_1^s$, we are finally able to derive the expression for the interfacial modified diffusive energy flux $\boldsymbol{\jmath}_q^{s\prime}$:

$$\begin{aligned}\boldsymbol{\jmath}_q^{s\prime} &= \boldsymbol{\jmath}_q^s - \left[\hat{\mu}_1^s - \hat{\mu}_2^s - T^s\left(\frac{\partial \hat{\mu}_2^s}{\partial T^s}\right)_{\hat{\mu}_1^s}\right]\boldsymbol{\jmath}_1^s \\ &= -\frac{1}{T^{s2}}\left\{L_{qq}^s + 2L_{q1}^s\left[\hat{\mu}_2^s - \hat{\mu}_1^s - T^s\left(\frac{\partial \hat{\mu}_2^s}{\partial T^s}\right)_{\hat{\mu}_1^s}\right] + L_{11}^s\left[\hat{\mu}_2^s - \hat{\mu}_1^s - T^s\left(\frac{\partial \hat{\mu}_2^s}{\partial T^s}\right)_{\hat{\mu}_1^s}\right]^2\right\}\boldsymbol{\nabla}_\parallel T^s \\ &\quad - \frac{1}{T^s}\left\{L_{q1}^s + 2L_{11}^s\left[\hat{\mu}_2^s - \hat{\mu}_1^s - T^s\left(\frac{\partial \hat{\mu}_2^s}{\partial T^s}\right)_{\hat{\mu}_1^s}\right]\right\}\left[1 - \left(\frac{\partial \hat{\mu}_2^s}{\partial \hat{\mu}_1^s}\right)_{T^s}\right]\left(\frac{\partial \hat{\mu}_1^s}{\partial \rho_1^s}\right)_{T^s}\boldsymbol{\nabla}_\parallel \rho_1^s \\ &= -\lambda^{s\prime}\boldsymbol{\nabla}_\parallel T^s - \rho_1^s\left[1 - \left(\frac{\partial \hat{\mu}_2^s}{\partial \hat{\mu}_1^s}\right)_{T^s}\right]\left(\frac{\partial \hat{\mu}_1^s}{\partial \rho_1^s}\right)_{T^s} D_{q1}^s \boldsymbol{\nabla}_\parallel \rho_1^s\end{aligned} \tag{79}$$

where we can define $\lambda^{s\prime}$, i.e. the interfacial modified thermal conductivity, as

$$\lambda^{s\prime} = \frac{L_{qq}^s + 2L_{q1}^s\left[\hat{\mu}_2^s - \hat{\mu}_1^s - T^s\left(\frac{\partial \hat{\mu}_2^s}{\partial T^s}\right)_{\hat{\mu}_1^s}\right] + L_{11}^s\left[\hat{\mu}_2^s - \hat{\mu}_1^s - T^s\left(\frac{\partial \hat{\mu}_2^s}{\partial T^s}\right)_{\hat{\mu}_1^s}\right]^2}{T^{s2}} \tag{80}$$

3.2 Mass transfer and Chemical Reactions coupling

Active transport is the transport of mass from regions at low concentration to regions at high concentration [16]; this phenomenon is made possible by a coupling of diffusive mass transport and chemical reactions. In

this section, we will examine an example of simplified active transport which can well model many processes occurring within biological cells [6, 12].

We assume there are NO externally applied electromagnetic fields and we NEGLECT both mechanical and thermal effects, i.e. $T^I = T^s = T^{II} = T$.

Let us consider the rate of entropy production σ^s at an interface where chemical reactions (with a surface reaction affinity $\mathcal{A}^s = \sum_{\alpha=1}^{k} \tilde{\nu}_\alpha^s \tilde{\mu}_\alpha^s$), and mass transfer can occur. Re-writing (64) we get

$$\begin{aligned} T\sigma^s = &\sum_{\alpha=1}^{k} \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\rho_\alpha^I - \boldsymbol{m} + \boldsymbol{j}_\alpha^I\right]\left[\left(\hat{\mu}_\alpha^s - \hat{\mu}^s\right) - \left(\hat{\mu}_\alpha^I - \hat{\mu}^I\right)\right] - \tilde{\Gamma}^s\mathcal{A}^s \\ &- \sum_{\alpha=1}^{k} \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right)\rho_\alpha^{II} - \boldsymbol{m} + \boldsymbol{j}_\alpha^{II}\right]\left[\left(\hat{\mu}_\alpha^s - \hat{\mu}^s\right) - \left(\hat{\mu}_\alpha^{II} - \hat{\mu}^{II}\right)\right] \end{aligned} \tag{81}$$

It can be noticed in (81) that coupling between species mass transfer and chemical reactions is possible as expression (81) only displays scalar force-flux pairs.

Limiting for simplicity our analysis to passive interfaces, we can now consider a steady-state system and assume that the interface between bulk phases is uniform. In this way, excess species mass densities are position and time-independent, thus allowing us to use the jump balances for species mass densities

$$\boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\rho_\alpha^I + \boldsymbol{j}_\alpha^I\right] = \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^{II} - \boldsymbol{v}^s\right)\rho_\alpha^{II} + \boldsymbol{j}_\alpha^{II}\right] - \boldsymbol{\nabla}_\parallel \cdot \boldsymbol{j}_\alpha^s + \nu_\alpha^s \Gamma^s \tag{82}$$

We can then rewrite (81) as

$$T\sigma^s = \sum_{\alpha=1}^{k} \boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\rho_\alpha^I - \boldsymbol{m} + \boldsymbol{j}_\alpha^I\right]\left[\left(\hat{\mu}_\alpha^{II} - \hat{\mu}^{II}\right) - \left(\hat{\mu}_\alpha^I - \hat{\mu}^I\right)\right] - \tilde{\Gamma}^s \sum_{\alpha=1}^{k} \tilde{\nu}_\alpha^s \tilde{\mu}_\alpha^{II} \tag{83}$$

which states that species mass transfer occurs directly between the bulk phases, and where the surface chemical potentials have disappeared. We can further assume that the interface is perfectly equilibrated with the bulk solution phase on the "incoming" side, i.e. $\hat{\mu}_\alpha^{II} = \tilde{\mu}_\alpha^s$. We can therefore express the reaction term in Equation (83) as $-\tilde{\Gamma}^s\tilde{\mathcal{A}}^s$. As proposed in previous works [16] for the bulk case, we have to ensure nonnegativity of the entropy production for the two force-flux pairs in (83); to achieve this, we can write

$$\tilde{\Gamma}^s = -L_{\mathcal{A}\mathcal{A}}\mathcal{A}^s - \sum_{\beta=1}^{k} L_{\mathcal{A}\beta}\left(\hat{\mu}_\beta^I - \hat{\mu}_\beta^{II}\right) \tag{84}$$

$$\boldsymbol{n} \cdot \left[\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\rho_\alpha^I - \boldsymbol{m} + \boldsymbol{j}_\alpha^I\right] = -L_{\alpha\mathcal{A}}\mathcal{A}^s - \sum_{\beta=1}^{k} L_{\alpha\beta}\left(\hat{\mu}_\beta^I - \hat{\mu}_\beta^{II}\right) \tag{85}$$

where

$$L_{\alpha\beta} = \begin{bmatrix} L_{11} & L_{1k} & \dots \\ \vdots & \ddots & \\ L_{k1} & & L_{kk} \end{bmatrix} \qquad L_{\alpha\mathcal{A}} = \begin{bmatrix} L_{1\mathcal{A}} \\ \vdots \\ L_{k\mathcal{A}} \end{bmatrix} \qquad L_{\mathcal{A}\beta} = \begin{bmatrix} L_{\mathcal{A}1} & \dots & L_{\mathcal{A}k} \end{bmatrix} \tag{86}$$

Similarly to what already described in previous analysis [16], the terms $L_{\alpha,\beta}$ with $\alpha, \beta = 1, 2, ...k$ define a *(k-1)*-rank matrix of phenomenological coefficients under the constraints $\sum_{\alpha=1}^{k} L_{\alpha\beta} = \sum_{\alpha=1}^{k} L_{\beta\alpha} = 0$, while $L_{\alpha\mathcal{A}}$ and $L_{\mathcal{A}\beta}$ represent a column and a row vector, respectively, with $L_{\mathcal{A}\mathcal{A}}$ as the diagonal element and the property $\sum_{\alpha=1}^{k} L_{\alpha\mathcal{A}} = \sum_{\beta=1}^{k} L_{\mathcal{A}\beta} = 0$.

We now assume to consider a dilute, multicomponent system with species 1 as the only actively transported solute and species k as the solvent; specifically, this implies that [16]

$$L_{11} = -L_{1k} = -L_{k1} = L_{kk} \qquad \text{and} \qquad L_{1\mathcal{A}} = -L_{k\mathcal{A}} = -L_{\mathcal{A}k} = L_{\mathcal{A}1} \qquad \text{and} \qquad L_{\mathcal{A}\mathcal{A}} \tag{87}$$

are the only non-vanishing phenomenological coefficients. Thus we can rewrite expressions (84) and (85)

$$\tilde{\Gamma}^s = -L_{\mathcal{A}\mathcal{A}}\mathcal{A}^s - L_{\mathcal{A}1}\Delta\hat{\mu} \tag{88}$$

$$\boldsymbol{n}\cdot\left[\left(\boldsymbol{v}^I - \boldsymbol{v}^s\right)\rho_\alpha^I - \boldsymbol{m} + \boldsymbol{j}_\alpha^I\right] = -L_{1\mathcal{A}}\mathcal{A}^s - L_{11}\Delta\hat{\mu} \tag{89}$$

where $\Delta\hat{\mu} = \hat{\mu}_1^I - \hat{\mu}_1^{II} - \left(\hat{\mu}_k^I - \hat{\mu}_k^{II}\right)$ which becomes $\Delta\hat{\mu} = \hat{\mu}_1^I - \hat{\mu}_1^{II}$ at equilibrium.

Finally, we may assume that the interface is at rest and the diffusive flux of species 1 is perfectly compensated by the diffusive solvent flux, i.e. $\boldsymbol{v}^I = \boldsymbol{v}^s = \boldsymbol{m} = \boldsymbol{0}$. In addition, we can recall the molar quantities

$$N_1^I = \frac{1}{\tilde{M}_1}\boldsymbol{n}\cdot\boldsymbol{j}_1^I \qquad \text{and} \qquad \Delta\hat{\mu}_1 = \frac{1}{\tilde{M}_1}\Delta\tilde{\mu}_1 = \frac{1}{\tilde{M}_1}\left(\tilde{\mu}_1^I - \tilde{\mu}_1^{II}\right) \tag{90}$$

In such a way, expressions (88) and (89) can be rewritten as

$$\tilde{\Gamma}^s = -L_{\mathcal{A}\mathcal{A}}\mathcal{A}^s - \frac{L_{\mathcal{A}1}}{\tilde{M}_1}\Delta\tilde{\mu}_1 \tag{91}$$

$$N_1^I = -\frac{L_{1\mathcal{A}}}{\tilde{M}_1}\mathcal{A}^s - \frac{L_{11}}{\tilde{M}_1^2}\Delta\tilde{\mu}_1 \tag{92}$$

By construction, both forms are consistent with a nonnegative rate of entropy production. As firstly proposed by Öttinger and Venerus [16], we can compute the transport process efficiency η defined as

$$\eta = -\frac{N_1^I\Delta\tilde{\mu}_1}{\tilde{\Gamma}\mathcal{A}^s} \tag{93}$$

which can be rearranged, according to (91) and (92), as

$$\eta = \frac{(q - Z)\,Z}{1 - qZ} \tag{94}$$

where

$$q = \frac{L_{\mathcal{A}1}}{\sqrt{L_{\mathcal{A}\mathcal{A}}L_{11}}} \qquad Z = -\sqrt{\frac{L_{11}}{L_{\mathcal{A}\mathcal{A}}\tilde{M}_1^2}}\frac{\Delta\tilde{\mu}_1}{\mathcal{A}^s} \tag{95}$$

We can easily spot in Equation (95) the transport coupling coefficient $q \leq 1$, which determines the strength of the cross effect, and the factor Z (where $Z < q$) relating the entropy generated from the species mass transport and the entropy resulting from chemical reactions.

3.3 Electrocoalescence: theory and examples

Electrocoalescence is a process by which an electric field is applied across a suspension of (usually) conducting fluid droplets dispersed in an insulating liquid in order to force the droplets to merge together [15]. The process has found applications in a number of technologies in which conducting water droplets are dispersed in insulating oils, such as lab-on-a-chip manufacturing [17], various biomedical diagnostic assays and water-in-crude-oil desalting operations in the oil refining industry [8].

Specifically, electrocoalescence is driven by the polarization of charge in conducting droplets, which is induced by an externally applied field and which generates electric dipoles out of the droplets. When such polarized droplets are oriented along the direction of the field, their induced dipoles create large attractive electrical stresses which drive coalescence. Finally, it is worth recalling another important phenomenon which can be described with electrocoalescence theory: the drainage of emulsion thin films stimulated by the application of an external electric field. As can be seen in figure 1, the drainage of liquid thin films in water (or air) can be approximated as the coalescence of 2 water drops (or air bubbles) whose radii are much greater than their

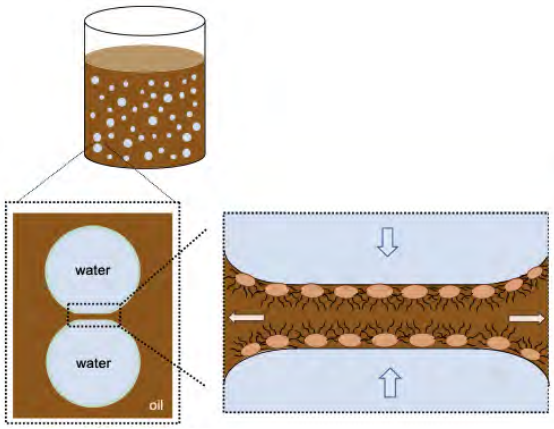


Figure 1: Drainage of liquid thin films can be approximated as the coalescence of 2 drops [2].

center-to-center separation. In this case, the additional presence of surface active agents (e.g. de-emulsifiers) has to be considered, since it greatly affects the behavior of the under-drainage thin film.

Of course, cross-coupling effects between mechanical and electrical stresses at the interfaces play a major role in both electrocoalescence and drainage phenomena. We start assuming there are NO externally applied magnetic fields, there are NO chemical reactions occurring and thermal effects can be neglected, i.e. $T^I = T^s = T^{II} = T$.

3.3.1 Interactions between droplets

Let us consider a single spherical drop A (of radius a) of conducting liquid and let us use subscripts d and m for *drop* and *medium* domains, respectively. If a uniform electric field E_0 is applied, the influence of the drop can be approximated by a dipolar moment p located at the sphere center. Outside the droplet, the electric potential V is simply given by:

$$V(r,\theta) = \frac{p\ cos\theta}{4\pi\epsilon_m r^2} - E_0 r cos\theta \tag{96}$$

where we have used spherical coordinates and defined $\epsilon_m = \epsilon_0\epsilon_r$ as the permittivity of the insulating liquid (e.g. oil) outside the droplet. By expressing the boundary conditions at the water/oil interface, we obtain the expression for p, V

$$p = 4\pi\epsilon_m E_0 a^3 \tag{97}$$

$$V(r,\theta) = E_0 r cos\theta \left(\frac{a^3}{r^3} - 1\right) \tag{98}$$

and the field components E_r (i.e. radial) and E_θ (i.e. angular)

$$\begin{aligned} E_r(r,\theta) &= E_0 cos\theta \left(1 + 2\frac{a^3}{r^3}\right) \\ E_\theta(r,\theta) &= E_0 sin\theta \left(\frac{a^3}{r^3} - 1\right) \end{aligned} \tag{99}$$

Let us now analyze the case of two drops A and B of radius a and b (with $b < a$ as initial reference), respectively. Calling s the center-to-center separation between the drops, where $s = a + b + d$ and d is the drops' surfaces separation in the undeformed state, the interaction force can be calculated as $\boldsymbol{F} = -\nabla U$ where U is the potential energy of the p_A-field-induced dipolar moment p_B on B:

$$p_B = \alpha_B E_0 = 4\pi\epsilon_m b^3 E_0 \tag{100}$$

Recalling equations (99) and (100), the force exerted on drop B by drop A will be (in spherical coordinates) equal to:

$$F_r = -12\pi\epsilon_m b^3 {E_0}^2 \frac{a^3}{s^4}\left(3cos^2\theta - 1\right)\frac{\epsilon_d - \epsilon_m}{\epsilon_d + 2\epsilon_d}\frac{R-1}{R+2} \qquad \text{where} \qquad s = a + b + d \tag{101}$$

and

$$F_\theta = -12\pi\epsilon_m b^3 {E_0}^2 \frac{a^3}{s^4} sin(2\theta)\frac{\epsilon_d - \epsilon_m}{\epsilon_d + 2\epsilon_d}\frac{R-1}{R+2} \tag{102}$$

Note that both expressions (101) and (102) display the end-term

$$\frac{\epsilon_d - \epsilon_m}{\epsilon_d + 2\epsilon_d}\frac{R-1}{R+2} \tag{103}$$

which is a correction used to describe the so called "leaky-dielectric" systems [14]. In these systems, the droplets' dielectric properties are comparable to those of the dividing dielectric thin-film; in other words, as the droplets are weakly conducting and bring zero net charge, if an external electric field is applied the free charge accumulated on the droplets' interface modifies the local field.

Formulas derived in (101) and (102) are valid for spherical droplets at large center-to-center distances. However, in the study of thin-films drainage by electrocoalescence, these assumptions are no longer valid. As suggested by previous work [3], when the distance d ($d = s - a - b$) between spheres becomes lower than b (i.e. the smallest possible radius), the surface charge distributions on the spheres are heavily altered. Hence, corrective coefficients ξ and ψ have to be introduced; they will take into account eventual asymmetries of the two drops and can be expressed [14] as complicated higher-order series mainly depending on the ratio d/b:

$$\begin{aligned}
\xi &= 1 + \frac{a^3 s^5}{\left(s^2 - b^2\right)^4} + \frac{b^3 s^5}{\left(s^2 - a^2\right)^4} + \frac{3a^3 b^3\left(3s^2 - a^2 - b^2\right)}{\left(s^2 - a^2 - b^2\right)^4} \\
\psi &= 1 + \frac{a^3 s^3}{2\left(s^2 - b^2\right)^3} + \frac{b^3 s^3}{2\left(s^2 - a^2\right)^3} + \frac{3a^3 b^3}{\left(s^2 - a^2 - b^2\right)^3}
\end{aligned} \tag{104}$$

The corrected expression of equations (101) and (102) will then be

$$F_r = -12\pi\epsilon_m b^3 {E_0}^2 \frac{a^3}{s^4}\left(3\xi cos^2\theta - 1\right)\frac{\epsilon_d - \epsilon_m}{\epsilon_d + 2\epsilon_d}\frac{R-1}{R+2} \tag{105}$$

and

$$F_\theta = -12\pi\epsilon_m b^3 {E_0}^2 \frac{a^3}{s^4}\psi sin(2\theta)\frac{\epsilon_d - \epsilon_m}{\epsilon_d + 2\epsilon_d}\frac{R-1}{R+2} \tag{106}$$

As expected for a large center-to-center separation between the drops, i.e. $d/b >> 1$, the corrective coefficients in (104) tend to unity and the effective dipolar approximations above are recovered. On the other side, there exists a rather significant torque which tends to align two very close drops in the direction of the applied field.

Let us now assume our system to be identified by two drops of equal radius a aligned in the direction of the applied electric field (i.e. $\theta = 0$ and $s = 2a + d$). Equations (105) and (106) reduce to

$$\begin{aligned}
F_r &= -12\pi\epsilon_m {E_0}^2 \frac{a^6}{s^4}\left(3\xi - 1\right)\frac{\epsilon_d - \epsilon_m}{\epsilon_d + 2\epsilon_d}\frac{R-1}{R+2} \qquad \text{where} \qquad s = 2a + d \\
F_\theta &= 0
\end{aligned} \tag{107}$$

where

$$\begin{aligned}
\xi &= 1 + \frac{2a^3\left(2a + d\right)^5}{\left[\left(2a + d\right)^2 - a^2\right]^4} + \frac{3a^6[3\left(2a + d\right)^2 - 2a^2]}{\left[\left(2a + d\right)^2 - 2a^2\right]^4} = 1 + \frac{2a^3\left(2a + d\right)^5}{\left(3a^2 + 4ad + d^2\right)^4} + \frac{3a^6\left(10a^2 + 12ad + 3d^2\right)}{\left(2a^2 + 4ad + d^2\right)^4} \\
\psi &= 1 + \frac{a^3\left(2a + d\right)^3}{\left[\left(2a + d\right)^2 - a^2\right]^3} + \frac{3a^6}{\left[\left(2a + d\right)^2 - 2a^2\right]^3} = 1 + \frac{a^3\left(2a + d\right)^3}{\left(3a^2 + 4ad + d^2\right)^3} + \frac{3a^6}{\left(2a^2 + 4ad + d^2\right)^3}
\end{aligned} \tag{108}$$

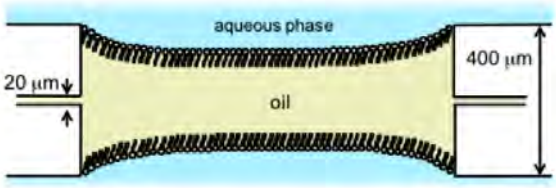


Figure 2: Example of system comprising of two droplets of saline water divided by a thin oil film [2].

We consider electrocoalescence in the scope of thin-film drainage phenomena; it is oftentimes experimental practice to analyze NOT-"leaky dielectric" systems. As shown in figure 2, studied systems usually comprise of two droplets of saline aqueous solution divided by a thin oil film. The aqueous phase can be considered a perfectly conducting medium (i.e. high ϵ_d and high conductivity σ_d), while the hydrocarbon phase can be seen as a perfectly dielectric film (i.e. low ϵ_m and low conductivity σ_m).
A practical example is offered in the work by Alexandra Alicke in Prof. Jan Vermant's group at ETH Zürich; values of ϵ and σ for each of the substance that have been used is reported in Table 1:

	Phase	Dielectric constant ϵ	Conducticity σ $(^{mS}/_{cm})$
Aqueous solution (d)	0.5M NaCl in Mili-Q water	77.7	9.2
Hydrophobic core (m)	Hexadecane	2.1	0.03

Table 1: Parameters values for the model

As will be discussed later, it is possible to add surfactants (e.g. 1 wt% *Span80* nonionic surfactant) in the hydrophobic phase to tune the thin-film drainage behavior.
If we consider a system similar to that presented in Table 1, the following approximations can be made:

$$\epsilon_d \gg \epsilon_m \qquad \text{and} \qquad \sigma_m \gg \sigma_d \qquad \Rightarrow \qquad \epsilon_d - \epsilon_m \approx \epsilon_d \qquad \text{and} \qquad R = \frac{\sigma_m}{\sigma_d} \approx 0 \tag{109}$$

Hence, the end-term in (103) can be eliminated and expressions in (107) reduce to

$$\begin{aligned} F_r &= -12\pi\epsilon_m {E_0}^2 \frac{a^6}{s^4}\left(3\xi - 1\right) \\ F_\theta &= 0 \end{aligned} \tag{110}$$

3.3.2 Time of contact of 2 drops

Correctly estimating the time of contact of two initially-divided droplets under electrocoalescence represents a key issue in the study of foams and emulsions. Together with the external electric field, other major forces influence droplets' motion in the liquid medium, and their assessment is traditionally not trivial. For example, as suggested by previous research [14], a major drag resistive force acting on the drops (usually at a large separation) must be taken into account.
This force can be expressed via the Hadamard-Rybczynski [9] equation as

$$F_{Drag} = 4\pi\mu_m a v k \tag{111}$$

where μ_m is the viscosity of the low-dielectric medium, $v = \dfrac{ds}{dt}$ is the velocity of drop approach and k a viscosity parameter defined as

$$k = \frac{3\lambda + 2}{2\left(\lambda + 1\right)} \qquad \text{with} \qquad \lambda = \frac{\mu_d}{\mu_m} \tag{112}$$

Under the assumption of mutual induction of dipoles between the drops, the bipolar electrostatic force of attraction between uniform size drops aligned in the direction of an applied electric field will be given by (110).
To estimate the time of contact (t) of two drops from their initial surface-surface separation d_0, we combine equations (110) and (111) as to get a force balance resulting in

$$\begin{aligned} &F_{Bipolar} = 2F_r = -2 \cdot 12\pi\epsilon_m {E_0}^2 \frac{a^6}{s^4}\left(3\xi - 1\right) = F_{Drag} = 4\pi\mu_m a v k \\ &F_\theta = 0 \end{aligned} \tag{113}$$

rearranging

$$v\left(\mu_m a k\right) = -6\epsilon_m {E_0}^2 \frac{a^6}{s^4}\left(3\xi - 1\right); \qquad \frac{ds}{dt} = -\frac{6\epsilon_m E_0^2}{\mu_m k}\frac{a^5}{\left(2a+d\right)^4}\left(3\xi - 1\right) \tag{114}$$

We can assume that the drops' radii remain constant in time (a=const.)

$$\text{if} \qquad \frac{ds}{dt} = \frac{d(2a+d)}{dt} = \dot{d}(t) \qquad \Rightarrow \qquad \dot{d}(t) = -\frac{6\epsilon_m E_0^2}{\mu_m k}\frac{a^5}{\left(2a+d\right)^4}\left(3\xi - 1\right) \tag{115}$$

Recalling the expression for $\xi(d)$ and imposing the boundary conditions

$$\begin{aligned} d\left(t=0\right) &= d_0 \qquad \text{initial state} \\ d\left(\bar{t}\right) &= 0 \qquad \text{when contact occurs} \end{aligned} \tag{116}$$

we can solve the differential equation in (115):

$$\int_0^{\bar{t}} \mathrm{d}t = -\int_{d_0}^{0} \frac{\mu_m k}{6\epsilon_m E_0^2}\frac{\left(2a+d\right)^4}{a^5}\frac{1}{\left(3\xi(d)-1\right)}\mathrm{d}d \tag{117}$$

Integration of the right-hand side term of (117) is neither trivial nor straightforward, so further assumptions are necessary.

- Firstly, we explore the case of droplets at large center-to-center separation:

$$d \gg a \qquad \Rightarrow \qquad \xi \approx 1 \qquad \Rightarrow \qquad \dot{d}(t) = -\frac{12\epsilon_m E_0^2}{\mu_m k}\frac{a^5}{\left(2a+d\right)^4} \tag{118}$$

$$\bar{t}_{\text{Large}} = \frac{8}{15}\frac{\mu_m k}{\epsilon_m E_0^2}\left[\left(\frac{d_0}{2a}+1\right)^5 - 1\right] \tag{119}$$

- Secondly,the particular case of the drainage of an hydrophobic thin film in water will be explored. We assume our film to be FULLY PLANAR on both sides, i.e. drops' radii tend to infinity ($a \to +\infty$). We can then adjust the corrective factor ξ for extremely thin films:

$$\begin{aligned} \lim_{a\to+\infty}\xi(a) &= \lim_{a\to+\infty} 1 + \frac{2a^3\left(2a+d\right)^5}{\left(3a^2+4ad+d^2\right)^4} + \frac{3a^6\left(10a^2+12ad+3d^2\right)}{\left(2a^2+4ad+d^2\right)^4} \\ &\sim 1 + \frac{64a^8}{81a^8} + \frac{30a^8}{16a^8} = \frac{2375}{648} \approx 3.67 \end{aligned} \tag{120}$$

hence

$$\dot{d}(t) = -\frac{60\epsilon_m E_0^2}{\mu_m k}\frac{a^5}{\left(2a+d\right)^4} \tag{121}$$

and

$$\bar{t}_{\text{Planar Film}} = \frac{8}{75}\frac{\mu_m k}{\epsilon_m E_0^2}\left[\left(\frac{d_0}{2a}+1\right)^5 - 1\right] \tag{122}$$

In general, we can notice that the electrostatic interaction is proportional to $1/s^4$, while Stokes drag is independent of s for bulk drag and is proportional to $1/s$ in the lubrication limit. Thus, as the two drops get closer (or alternatively as the liquid film drainage proceeds) the electrical force heavily dominates the drag.

3.3.3 Thin films drainage

3.3.3.1 Cross-coupling effects, bilayers and the role of surface active agents

As suggested at the beginning of this discussion, cross-coupling effects between mechanical and electrical stresses at the interfaces play a major role electrocoalescence-driven drainage phenomena. In order to analyze such effects, we have to make the following assumptions:

- NO externally applied magnetic fields → we can use laws of electrostatics;
- NO chemical reactions occurring;
- thermal effects can be neglected → $T^I = T^s = T^{II} = T$;
- a fully planar film → uniform electric field across the film;
- the liquid inside the film is incompressible ($\boldsymbol{\nabla \cdot v}$) and we ignore fluid inertia during the drainage → low Reynolds number;
- we have a perfectly dielectric film (i.e. hexadecane) in a perfectly conducting medium (i.e. water with high salt concentration).
- we neglect gravity effect to account for small drops size and small difference in density of the droplet-medium pair.

As already suggested [13], the propagation time of electromagnetic waves is traditionally very fast compared to the time scales characteristic of the electrohydrodynamics motions and thus, for times longer than the average charge relaxation time, any free charge experiences a confinement to the interfacial region. This phenomenon combined with the absence of an applied magnetic field in the system implies that the electric field in the two fluid phases is irrotational

$$\boldsymbol{\nabla} \times \boldsymbol{E} = \boldsymbol{0} \qquad \text{or} \qquad \boldsymbol{E} = -\boldsymbol{\nabla}\phi \tag{123}$$

and so according to the Gauss' law of electrostatics

$$\boldsymbol{\nabla} \cdot \boldsymbol{E} = 0 \qquad \text{or} \qquad \nabla^2\phi = 0 \tag{124}$$

We identify the drops liquid phase as I and the thin-film hydrophobic phase as II; in addition, let the two droplet-medium interfaces be called Λ_I and Λ_{II}, respectively. The boundary conditions at the fluid-fluid interface Λ_I and Λ_{II} in the most most general case are:

$$\begin{aligned} &\boldsymbol{n} \cdot \boldsymbol{E}^I = R\boldsymbol{n} \cdot \boldsymbol{E}^{II} && \text{continuity of current} \\ &\boldsymbol{t} \cdot \boldsymbol{E}^I = \boldsymbol{t} \cdot \boldsymbol{E}^{II} && \text{continuity of tangential electric field} \\ &\boldsymbol{E}^{II} \to \boldsymbol{E}_0 && \text{as} \quad |\boldsymbol{x}| \to +\infty \end{aligned} \tag{125}$$

The last condition indicates that far away from the drop, electric field is given by the external applied electric field $\boldsymbol{E}_0$. Note that the $\boldsymbol{n}$ and $\boldsymbol{t}$ are the outward unit normal and tangent vectors at the interface and $\boldsymbol{x}$ is the position vector.

The discontinuity in electric properties (e.g. refractive index, dielectric constants) at the drop-thin fluid interface causes a jump in the Maxwell stress tensor $\boldsymbol{T}_E$:

$$\boldsymbol{T}_E^i = \epsilon_0 \epsilon_i \left(\boldsymbol{EE} - \frac{1}{2} E^2 \boldsymbol{\delta} \right) \qquad \text{where} \qquad i = I, II \tag{126}$$

the corresponding fluid-fluid interface electric stress jump being:

$$\boldsymbol{n} \cdot \left(\boldsymbol{T}_E^{II} - \boldsymbol{T}_E^I \right) = \frac{1}{2} \epsilon_0 \epsilon_I \left[{E_\perp^I}^2 \left(1 - \frac{1}{R^2} \frac{\epsilon_{II}}{\epsilon_I} \right) - {E_\parallel^I}^2 \left(1 - \frac{\epsilon_{II}}{\epsilon_I} \right) \right] \boldsymbol{n} + \epsilon_0 \epsilon_I E_\parallel^I E_\perp^I \left(1 - \frac{1}{R} \frac{\epsilon_{II}}{\epsilon_I} \right) \boldsymbol{t} \tag{127}$$

where we identify $E_\perp = \boldsymbol{n} \cdot \boldsymbol{E}^I$ and $E_\parallel = \boldsymbol{t} \cdot \boldsymbol{E}^I$ as the normal and tangential components of the electric field evaluated just inside the drop surface. Of course, if no flow fields are applied, the Maxwell stresses are sufficient to induce drops and fluid motion. In particular, we can notice that for a perfect dielectric medium (here the hydrophobic thin film) we can approximate [14]:

$$R \to \frac{\epsilon_{II}}{\epsilon_I} \qquad \Rightarrow \qquad \boldsymbol{n} \cdot \left(\boldsymbol{T}_E^{II} - \boldsymbol{T}_E^I \right)_{\text{Perfect}} = \frac{1}{2} \epsilon_0 \epsilon_I \left({E_\perp^I}^2 + \frac{\epsilon_{II}}{\epsilon_I} {E_\parallel^I}^2 \right) \left(1 - \frac{\epsilon_I}{\epsilon_{II}} \right) \boldsymbol{n} \tag{128}$$

Note that for a perfect dielectric, the interfacial stress jump is purely normal to the interface.

Given the jump relation above, we now have to determine the relationship between electrical stresses and the mechanical stresses in the fluid so as to make cross-coupling effects in this system evident.
As assumed at the beginning of the paragraph, absence of inertia and gravity as well as fluid incompressibility force the system to exist at low Reynolds numbers. For a non-compressible Newtonian fluid, the momentum balance equation can be simplified to give the Navier-Stokes equation:

$$\rho \left(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} \boldsymbol{v} \right) = \eta \nabla^2 \boldsymbol{v} - \boldsymbol{\nabla} P \tag{129}$$

where P is the modified pressure, which here coincides with the standard pressure p.
The balance equation for momentum is known

$$\frac{\partial \boldsymbol{m}}{\partial t} = -\boldsymbol{\nabla} \cdot (\boldsymbol{vm} + \boldsymbol{\pi}) + \rho \boldsymbol{g} \qquad \xrightarrow{\text{NO Gravity}} \qquad \frac{\partial \boldsymbol{m}}{\partial t} = -\boldsymbol{\nabla} \cdot (\boldsymbol{vm} + \boldsymbol{\pi}) \tag{130}$$

where $\boldsymbol{vm}$ is the tensorial momentum flux (i.e. momentum transport by flow) and $\boldsymbol{\pi}$ is the second-rank hydrodynamic pressure-stress tensor. In other words, $\boldsymbol{\pi}$ represents the momentum flux associated with intermolecular interactions inside the fluid. Recalling the definition of material derivative and momentum $\boldsymbol{m} = \rho \boldsymbol{v}$, we re-write (130) as

$$\rho \frac{D\boldsymbol{v}}{Dt} = -\boldsymbol{\nabla} \cdot \boldsymbol{\pi} \tag{131}$$

We can notice that the terms on the left-hand side of both equations (129) and (131) are identical, thus allowing us to combine the two expressions

$$-\boldsymbol{\nabla} \cdot \boldsymbol{\pi} = \eta \nabla^2 \boldsymbol{v} - \boldsymbol{\nabla} p \tag{132}$$

Note that the "minus" sign on the left-hand side of equation (132) is coherent with our initial assumption on the orientation of the surface element unit vector. Let us now decompose the pressure tensor $\boldsymbol{\pi}$ as to discriminate the contribution coming from normal stresses p and viscous stresses $\boldsymbol{\tau}$:

$$\boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau} = p\boldsymbol{\delta} - \eta \left[\boldsymbol{\nabla} \boldsymbol{v} + (\boldsymbol{\nabla} \boldsymbol{v})^T - \frac{2}{3} (\boldsymbol{\nabla} \cdot \boldsymbol{v}) \boldsymbol{\delta} \right] - \eta_d (\boldsymbol{\nabla} \cdot \boldsymbol{v}) \boldsymbol{\delta} \tag{133}$$

where the nonnegative transport coefficient η_d is known as the dilatational or bulk viscosity leading to an additional contribution to viscous stresses. Under the assumption of fluid incompressibility ($\boldsymbol{\nabla} \cdot \boldsymbol{v}$), expression (133) becomes:

$$\boldsymbol{\pi} = p\boldsymbol{\delta} - \eta \left[\boldsymbol{\nabla} \boldsymbol{v} + (\boldsymbol{\nabla} \boldsymbol{v})^T \right] \tag{134}$$

Combining the previous relations, we are now able to write the balance equation at the interface for the stresses:

$$\boldsymbol{n}\cdot\left(\boldsymbol{\pi}^{II}-\boldsymbol{\pi}^{I}\right)+\boldsymbol{n}\cdot\left(\boldsymbol{T}_E^{II}-\boldsymbol{T}_E^{I}\right)=\gamma\kappa\boldsymbol{n}\qquad\text{with}\qquad\kappa=\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{n}=[(\boldsymbol{\delta}-\boldsymbol{nn})\cdot\boldsymbol{\nabla}]\cdot\boldsymbol{n}\tag{135}$$

where κ is the mean curvature of the interface and $\boldsymbol{\nabla}_{\parallel}\equiv(\boldsymbol{\delta}-\boldsymbol{nn})\cdot\boldsymbol{\nabla}$ is the surface gradient operator. It is clear that at the interface the jump in the total stress, i.e. electric plus viscous, is balanced by the interfacial tension γ.

It is possible to make the following observations:

- Fundamental equation (135) clearly shows that electrocoalescence is heavily dependent on the value of the interfacial tension γ. The presence of **surface active agents**, such as (de-)emulsifiers, can thus facilitate or penalize the coalescence process;
- It is possible to stimulate electrocoalescence of two drops by increasing the jump in both mechanical $(\boldsymbol{\pi}^{II}-\boldsymbol{\pi}^{I})$ and electrical $(\boldsymbol{T}_E^{II}-\boldsymbol{T}_E^{I})$ stresses. For the electrical stresses jump, according to equation (128), it is sufficient to increase the normal $E_{\perp}$ or tangential $E_{\parallel}$ component of the electric field in the drops or in the thin film. To accomplish this the externally applied electric field E_0 have to be increased. In other words, the **higher** the modulus of the **external electric field**, the **easier** will be to have coalescence (or film drainage);
- In case of drainage a **perfectly planar** thin film of infinite extension (i.e. $\kappa=0$), then the **electrocoalescence process is independent of the surface tension**.

  $$\kappa=0\qquad\Rightarrow\qquad\boldsymbol{n}\cdot\left(\boldsymbol{\pi}^{II}-\boldsymbol{\pi}^{I}\right)+\boldsymbol{n}\cdot\left(\boldsymbol{T}_E^{II}-\boldsymbol{T}_E^{I}\right)=0\tag{136}$$

  Hence, adding surface active agents with the purpose only to increase or decrease γ will not alter the final outcome nor increase the overall process. Of course, the added substances may also alter the mechanical stress jump at the interface as a collateral effect; in this case, modifications of the system dynamics are expected.
- **Bilayers** represent a particular scenario in the scope of thin-film drainage. Here, electrocoalescence of the two aqueous phases (i.e. the droplets) is prevented only by a double layer of surface active species, traditionally amphiphilic molecules. As we assumed that the phase in the film core is hydrophobic while the outer one is water-based, the double layer will display the hydrophilic "heads" in contact with water and the (conventionally polymeric) hydrophobic long chains on the inside (see figure 3). We can then assume that the thickness of the hydrophobic film (i.e. phase II) is approximately equal to double the length of an entire amphiphilic molecule (heads+tails). As also shown in figure 3, we can compute:

  $$\mathcal{P}=\frac{\mathcal{V}}{a_0 l_c}\tag{137}$$

  where $\mathcal{P}$ is the packing factor, $\mathcal{V}$ is the hydrodynamic volume of the hydrophobic part and a_0 is the area of the circular projection of an head-group on its hydrophobic chain. Let us compute the attraction forces between the two aqueous phases if an in-between bilayer is present; we consider the formula for the dipolar forces in the case of a perfectly planar film

  $$d\approx 2\left(l_c+\chi\right)=2\left(\frac{\mathcal{V}}{a_0\mathcal{P}}+\chi\right)\qquad\Rightarrow\qquad F_r=-\frac{15}{2}\pi\epsilon_{II}{E_0}^2\frac{a^6}{\left(a+\chi+\frac{\mathcal{V}}{a_0\mathcal{P}}\right)^4}\qquad F_\theta=0\tag{138}$$

  where χ is the average length of the hydrophilic head at the interface.

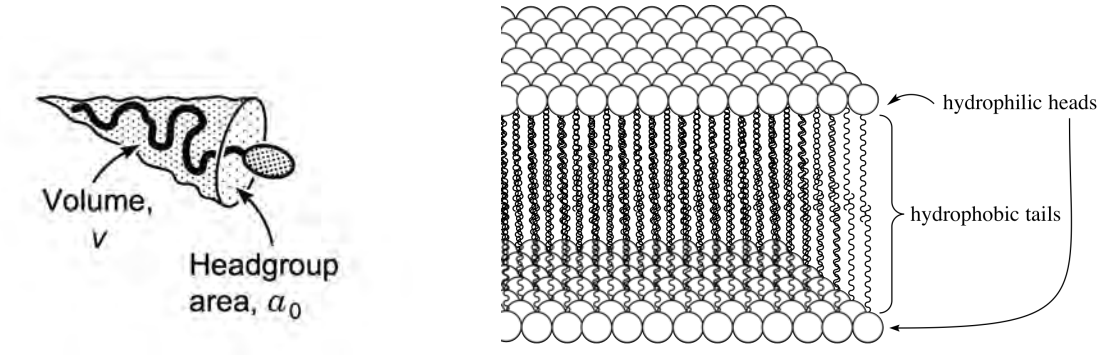


Figure 3: Structural parameters of an amphiphilic molecule (on the left) [11] and typical structure of a planar bilayer (on the right) [10].

- It is possible to connect the discontinuity of the electrical stresses at the droplets-film interface with properties of both bulk phase and of our gauge-identified dividing interface. Recalling equation (35)

$$\boldsymbol{n}\cdot\left(\boldsymbol{\pi}^{II}-\boldsymbol{\pi}^{I}\right)=\left(\frac{1}{\rho^{II}}-\frac{1}{\rho^{I}}\right)^{-1}\boldsymbol{n}\cdot\left(\boldsymbol{v}^{II}-\boldsymbol{v}^{I}\right)\left(\boldsymbol{v}^{II}-\boldsymbol{v}^{I}\right)-\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{\pi}^{s} \tag{139}$$

we can substitute it into (135)

$$\left(\frac{1}{\rho^{II}}-\frac{1}{\rho^{I}}\right)^{-1}\boldsymbol{n}\cdot\left(\boldsymbol{v}^{II}-\boldsymbol{v}^{I}\right)\left(\boldsymbol{v}^{II}-\boldsymbol{v}^{I}\right)+\boldsymbol{n}\cdot\left(\boldsymbol{T}_{E}^{II}-\boldsymbol{T}_{E}^{I}\right)=\gamma\kappa\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{nn}+\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{\pi}^{s} \tag{140}$$

then substitute (128)

$$\begin{aligned}\left(\frac{1}{\rho^{II}}-\frac{1}{\rho^{I}}\right)^{-1}\boldsymbol{n}\cdot\left(\boldsymbol{v}^{II}-\boldsymbol{v}^{I}\right)\left(\boldsymbol{v}^{II}-\boldsymbol{v}^{I}\right)+\frac{1}{2}\epsilon_0\epsilon_I\left(E_{\perp}^{I\,2}+\frac{\epsilon_{II}}{\epsilon_I}E_{\parallel}^{I\,2}\right)\left(1-\frac{\epsilon_I}{\epsilon_{II}}\right)\boldsymbol{n}=\\ =\gamma\kappa\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{nn}+\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{\pi}^{s}\end{aligned} \tag{141}$$

As can be seen in the expression above, it is possible to describe interfacial phenomena during electrocoalescence by knowing just the properties of the two bulk phases.
Moreover, if we substituted equation (133) into (135), we could relate the jump in electrical stresses to the rheological properties of both droplets and hydrophobic dividing film.

3.3.3.2 Entropy production rate

As clearly displayed in (141), there is a strong coupling between mechanical and electrical properties at the interface. We now try to study the entropy production term σ in the specific case of planar thin-film drainage. We start recalling expression (110) of the interaction forces in a non leaky dielectric system (i.e. perfectly conducting aqueous phase in contact with a perfectly dielectric hydrophobic phase)

$$\begin{aligned}F_r&=-12\pi\epsilon_{II}{E_0}^2\frac{a^6}{s^4}\left(3\xi-1\right)\\ F_\theta&=0\end{aligned} \tag{142}$$

We know from (120) that $\xi\approx 3.67$ for a fully planar film. We then substitute

$$\begin{aligned}F_r&=-120\pi\epsilon_{II}{E_0}^2\frac{a^6}{s^4}\\ F_\theta&=0\end{aligned} \tag{143}$$

The expression for the jump in Maxwell's stress tensor has already been derived in (128); however, expressions for the normal ($E_\perp$) and tangential ($E_\parallel$) components of the electric field at the interface are still missing.In our analysis, we will look only at one droplet-film interfacial system, as the other one is perfectly identical. First, we report [4] the expression for the dimensionless electric fields external and internal to a single isolated spherical conducting drop

$$\begin{aligned} \boldsymbol{E}_{in}(\boldsymbol{r}) &= \boldsymbol{E}_0 + \frac{R-1}{R+2}\left(\frac{3\boldsymbol{E}_0\cdot\boldsymbol{r}\boldsymbol{r}}{r^5} - \frac{\boldsymbol{E}_0}{r^3}\right) \qquad \text{inside} \\ \boldsymbol{E}_{out}(\boldsymbol{r}) &= \frac{3}{R+2}\boldsymbol{E}_0 \qquad\qquad\qquad\qquad\quad \text{outside (uniform field)} \end{aligned} \tag{144}$$

where $\boldsymbol{r}$ is the position vector measured from the drop center.
The tangential component of the electric field is continuous at the interface, while the normal component undergoes a jump whenever the drop and suspending fluid have different electrical properties. This said, we can now combine equations (143) and (144), together with the governing conditions (125)

$$\boldsymbol{E}_0(\boldsymbol{x}) + \frac{R-1}{4\pi R}\int_{\Lambda_i}\frac{\boldsymbol{x}-\boldsymbol{y}}{|\boldsymbol{x}-\boldsymbol{y}|^3}E_\perp(\boldsymbol{y})d\Lambda_y = \begin{cases} \boldsymbol{E}^i(\boldsymbol{x}) & \boldsymbol{x} \in \text{ bulk of } i = I, II \\ \frac{1}{2}\left[\boldsymbol{E}^I(\boldsymbol{x}) + \boldsymbol{E}^{II}(\boldsymbol{x})\right] & \boldsymbol{x_s} \in \bar{\Lambda} \text{ with surface } \bar{\Lambda} = \Lambda_1 + \Lambda_2 \end{cases} \tag{145}$$

where $\boldsymbol{E}_0$ is the external electric field and $\boldsymbol{x}_s$ is the position vector for a generic point on the interface. We can now solve the second-kind integral equation in (145) by computing the inner product of (145) and $\boldsymbol{n}(\boldsymbol{x}_s)$ along the interface; the result is the expression for the normal component of the electric field $E_\perp$ along the interface

$$E_\perp^{II}(\boldsymbol{x}_s) = \frac{2}{1+R}\boldsymbol{n}(\boldsymbol{x}_s)\cdot\boldsymbol{E}_0(\boldsymbol{x}_s) + \frac{1-R}{2\pi(1+R)}\boldsymbol{n}(\boldsymbol{x}_s)\cdot\sum_{i=1}^{2}\int_{\Lambda_i}\frac{\boldsymbol{x}_s-\boldsymbol{y}}{|\boldsymbol{x}_s-\boldsymbol{y}|^3}E_\perp^i(\boldsymbol{y})\ \mathrm{d}\Lambda_y(\boldsymbol{x}) \tag{146}$$

The equation above determines the distribution of $E_\perp(\boldsymbol{x}_s)$ inside the hydrophobic thin film (i.e. phase II). Of course, the modulus of the electric field depends on the conductivity ratio R and the shape of the drops Λ_i; indeed, the complete planarity of the interface that we experience in the film drainage case is embedded here in the surface term Λ_i. Using the boundary condition (125), we can easily compute the interfacial normal component of E inside the droplet (i.e. phase I):

$$E_\perp^I(\boldsymbol{x}_s) = RE_\perp^{II}(\boldsymbol{x}_s) = \frac{2R}{1+R}\boldsymbol{n}(\boldsymbol{x}_s)\cdot\boldsymbol{E}_0(\boldsymbol{x}_s) + \frac{R(1-R)}{2\pi(1+R)}\boldsymbol{n}(\boldsymbol{x}_s)\cdot\sum_{i=1}^{2}\int_{\Lambda_i}\frac{\boldsymbol{x}_s-\boldsymbol{y}}{|\boldsymbol{x}_s-\boldsymbol{y}|^3}E_\perp^i(\boldsymbol{y})\ \mathrm{d}\Lambda_y(\boldsymbol{x}) \tag{147}$$

Note that the tangential component of the electric field $E_\parallel^i = \boldsymbol{t}\cdot\boldsymbol{E}^i$ can be analogously computed by integration of (145). Since we are in an electrostatic system and the normal electric field $E_\perp$ is known, we can apply equation (123) to calculate the electric potential ϕ^{II} across the hydrophobic thin-film

$$\phi^{II}(\boldsymbol{x}_0) = \phi_0(\boldsymbol{x}_0) - \frac{1-R}{4\pi}\sum_{i=1}^{2}\int_{\Lambda_i}\frac{E_\perp^i}{|\boldsymbol{x}_0-\boldsymbol{y}|}\ \mathrm{d}\Lambda_y(\boldsymbol{x}) \tag{148}$$

where ϕ_0 is the externally-applied electric potential.

It is important to notice that the closer the two water-oil interfaces get during the drainage (i.e. as the hydrophobic film gets thinner), the greater is the **locally-enhanced electric transport** at the interface. During real experiments, of course the non-zero mean curvature of the interface κ and the applied potential ϕ_0 exert a major influence on the electrocoalescence phenomenon.
In Prof. Jan Vermant's group at ETH Zürich it was also proved that the rupture of a stable film can be achieved by applying increasing DC electric fields up to a certain threshold value; when this value is reached, the enhanced electric forces greatly exceed the interfacial tension, and the thin film breaks. As to measure the thickness h of a film (of surface area A) up to its rupture, capacitance (C) measurements were performed and the modulus of the locally-enhanced electric field $|\boldsymbol{E}_{\text{Enhanced}}|$ was derived using the following relations:

$$|\boldsymbol{E}_{\text{Enhanced}}| \approx \frac{\Delta\phi}{h} \qquad \text{where} \qquad h = \frac{1}{\epsilon_0\epsilon_r}\frac{1}{A} \tag{149}$$

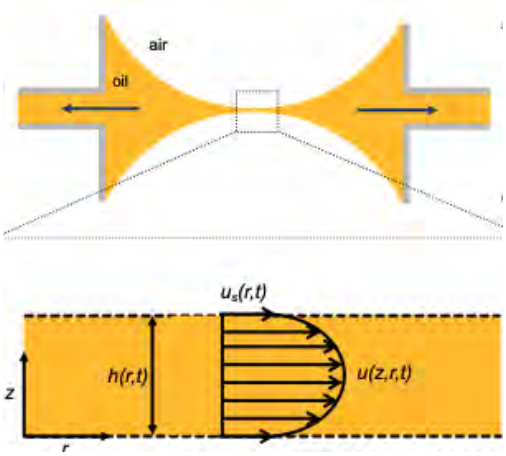


Figure 4: Oil in the hydrophobic film core is removed via pumping from multiple directions [2].

FINALLY, let us now analyze the entropy production rate σ in the case of the drainage of a thin film. All assumptions made at the beginning of the section are still valid. Moreover, we can further assume

- the droplet-film interface to be FULLY PLANAR and NON-DEFORMABLE;
- there are only 2 components in the system (aqueous solution and oil)
- the system comprises of two phases, one perfectly hydrophilic and the other perfectly hydrophobic
  $\Rightarrow$ NO mass transfer occurs within the interface.
  The absence of mass transfer can be experimentally achieved by removing the liquid from the hydrophobic film core via pumping from multiple directions (see figure 4 for reference).

We can know recall equation (59), which can be simplified according to the assumptions above:

$$\begin{aligned}\sigma^s_{\text{1st interf}} = &\frac{1}{T^s}\left\{\boldsymbol{n}\cdot\left[\rho^{II}\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)\frac{1}{2}\boldsymbol{v}^{II\,2}-\rho^{I}\left(\boldsymbol{v}^{I}-\boldsymbol{v}^s\right)\frac{1}{2}\boldsymbol{v}^{I\,2}\right]+\boldsymbol{n}\cdot\left[\boldsymbol{\tau}^{II}\cdot\left(\boldsymbol{v}^{II}-\boldsymbol{v}^s\right)-\boldsymbol{\tau}^{I}\cdot\left(\boldsymbol{v}^{I}-\boldsymbol{v}^s\right)\right]\right\}\\ &+\frac{1}{T^s}\left[\boldsymbol{n}\cdot\left(\boldsymbol{\pi}^{II}-\boldsymbol{\pi}^{I}\right)\cdot\boldsymbol{v}^s-\boldsymbol{v}^s\cdot\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{\pi}^s\right]\\ &+\frac{1}{T^s}\left(\boldsymbol{i}^{s*}_{\parallel}\cdot\bar{\boldsymbol{E}}^{*}_{\parallel}+\bar{i}^{*}_{\perp}E^{s*}_{\perp}\right)\\ &+\frac{1}{T^s}\left\{\left[\bar{\boldsymbol{E}}^{*}_{\parallel}-\left(\bar{\boldsymbol{E}}^{*}_{\parallel}\right)_{eq}\right]\cdot\frac{d^s}{dt}\boldsymbol{p}^{s*}_{\parallel}+\left[\bar{D}^{*}_{\perp}-\left(\bar{D}^{*}_{\perp}\right)_{eq}\right]\frac{d^s}{dt}p^{s*}_{\perp}\right\}\end{aligned} \tag{150}$$

In the absence of mass transport across the interface, we know from the jump balance of mass that

$$\boldsymbol{v}^I\cdot\boldsymbol{n}=\boldsymbol{v}^s\cdot\boldsymbol{n}=\boldsymbol{v}^{II}\cdot\boldsymbol{n} \tag{151}$$

in the absence of a magnetic field, we know from the Poynting's theorem for the interface (19) that

$$\bar{\boldsymbol{E}}^{*}\cdot\frac{\partial}{\partial t}\boldsymbol{D}^{s*}+\boldsymbol{E}^{s*}\cdot\left(\frac{\partial}{\partial t}\bar{\boldsymbol{D}}^{*}\right)=v^s_{\perp}\bar{\boldsymbol{E}}^{*}\cdot\left(\boldsymbol{D}^{II}-\boldsymbol{D}^{I}\right)-\boldsymbol{i}^{s*}\cdot\bar{\boldsymbol{E}}^{*}-\bar{\boldsymbol{i}}^{*}\cdot\boldsymbol{E}^{s*} \tag{152}$$

from the definition of $\boldsymbol{D}^*$:

$$\boldsymbol{D}^{*}\equiv\boldsymbol{P}^{*}+\boldsymbol{E}^{*}=\epsilon_0\epsilon_r\boldsymbol{E}^{*}\qquad\xrightarrow[\text{Electrostatics}]{}\qquad\frac{\partial\boldsymbol{E}^{*}}{\partial t}=0\quad\Rightarrow\quad\frac{\partial\boldsymbol{D}^{*}}{\partial t}=0 \tag{153}$$

from expression (153), equation (152) further simplifies into

$$\boldsymbol{i}^{s*} \cdot \bar{\boldsymbol{E}}^{*} + \bar{\boldsymbol{i}}^{*} \cdot \boldsymbol{E}^{s*} = v_{\perp}^{s} \bar{\boldsymbol{E}}^{*} \cdot \left(\boldsymbol{D}^{II} - \boldsymbol{D}^{I} \right) \tag{154}$$

substituting (154) into (150)

$$\begin{aligned} \sigma^{s}_{\text{1st interface}} = & \frac{1}{T^{s}} \left[\boldsymbol{n} \cdot \left(\boldsymbol{\pi}^{II} - \boldsymbol{\pi}^{I} \right) \cdot \boldsymbol{v}^{s} - \boldsymbol{v}^{s} \cdot \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{\pi}^{s} \right] \\ & + \frac{1}{T^{s}} v_{\perp}^{s} \bar{\boldsymbol{E}}^{*} \cdot \left(\boldsymbol{D}^{II} - \boldsymbol{D}^{I} \right) \\ & + \frac{1}{T^{s}} \left\{ \left[\bar{\boldsymbol{E}}_{\parallel}^{*} - \left(\bar{\boldsymbol{E}}_{\parallel}^{*} \right)_{eq} \right] \cdot \frac{d^{s}}{dt} \boldsymbol{p}_{\parallel}^{s*} + \left[\bar{D}_{\perp}^{*} - \left(\bar{D}_{\perp}^{*} \right)_{eq} \right] \frac{d^{s}}{dt} p_{\perp}^{s*} \right\} \end{aligned} \tag{155}$$

Recalling equation (135)

$$\begin{aligned} \sigma^{s}_{\text{1st interface}} = & \frac{1}{T^{s}} \left[\gamma \kappa \boldsymbol{n} \cdot \boldsymbol{v}^{s} - \boldsymbol{v}^{s} \cdot \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{\pi}^{s} \right] \\ & + \frac{1}{T^{s}} \boldsymbol{v}^{s} \left[\bar{\boldsymbol{E}}^{*} \cdot \left(\boldsymbol{D}^{II} - \boldsymbol{D}^{I} \right) - \left(\boldsymbol{T}_{E}^{II} - \boldsymbol{T}_{E}^{I} \right) \right] \cdot \boldsymbol{n} \\ & + \frac{1}{T^{s}} \left\{ \left[\bar{\boldsymbol{E}}_{\parallel}^{*} - \left(\bar{\boldsymbol{E}}_{\parallel}^{*} \right)_{eq} \right] \cdot \frac{d^{s}}{dt} \boldsymbol{p}_{\parallel}^{s*} + \left[\bar{D}_{\perp}^{*} - \left(\bar{D}_{\perp}^{*} \right)_{eq} \right] \frac{d^{s}}{dt} p_{\perp}^{s*} \right\} \end{aligned} \tag{156}$$

As already done in the previous paragraphs, we can decompose the surface pressure tensor $\boldsymbol{\pi}^{s} = -\gamma \boldsymbol{\delta}_{\parallel} + \boldsymbol{\tau}^{s}$; recalling the definition of mean curvature $\kappa = \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{n}$ we obtain

$$\begin{aligned} \sigma^{s}_{\text{1st interface}} = & \frac{1}{T^{s}} \boldsymbol{v}^{s} \cdot \left[\gamma \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{n}\boldsymbol{n} - \boldsymbol{\nabla}_{\parallel} \cdot \left(-\gamma \boldsymbol{\delta}_{\parallel} + \boldsymbol{\tau}^{s} \right) \right] \\ & + \frac{1}{T^{s}} \boldsymbol{v}^{s} \left[\bar{\boldsymbol{E}}^{*} \cdot \left(\boldsymbol{D}^{II} - \boldsymbol{D}^{I} \right) - \left(\boldsymbol{T}_{E}^{II} - \boldsymbol{T}_{E}^{I} \right) \right] \cdot \boldsymbol{n} \\ & + \frac{1}{T^{s}} \left\{ \left[\bar{\boldsymbol{E}}_{\parallel}^{*} - \left(\bar{\boldsymbol{E}}_{\parallel}^{*} \right)_{eq} \right] \cdot \frac{d^{s}}{dt} \boldsymbol{p}_{\parallel}^{s*} + \left[\bar{D}_{\perp}^{*} - \left(\bar{D}_{\perp}^{*} \right)_{eq} \right] \frac{d^{s}}{dt} p_{\perp}^{s*} \right\} \end{aligned} \tag{157}$$

Note that $\boldsymbol{\delta}_{\parallel}$ is the surface or tangential projector tensor defined as $\boldsymbol{\delta}_{\parallel} = \boldsymbol{\delta} - \boldsymbol{n}\boldsymbol{n}$. Substituting $\boldsymbol{\delta}_{\parallel}$ with is definition

$$\begin{aligned} \sigma^{s}_{\text{1st interface}} = & \frac{1}{T^{s}} \boldsymbol{v}^{s} \cdot \left[\gamma \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{n}\boldsymbol{n} + \gamma \boldsymbol{\nabla}_{\parallel} \cdot \left(\boldsymbol{\delta} - \boldsymbol{n}\boldsymbol{n} \right) - \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{\tau}^{s} \right] \\ & + \frac{1}{T^{s}} \boldsymbol{v}^{s} \left[\bar{\boldsymbol{E}}^{*} \cdot \left(\boldsymbol{D}^{II} - \boldsymbol{D}^{I} \right) - \left(\boldsymbol{T}_{E}^{II} - \boldsymbol{T}_{E}^{I} \right) \right] \cdot \boldsymbol{n} \\ & + \frac{1}{T^{s}} \left\{ \left[\bar{\boldsymbol{E}}_{\parallel}^{*} - \left(\bar{\boldsymbol{E}}_{\parallel}^{*} \right)_{eq} \right] \cdot \frac{d^{s}}{dt} \boldsymbol{p}_{\parallel}^{s*} + \left[\bar{D}_{\perp}^{*} - \left(\bar{D}_{\perp}^{*} \right)_{eq} \right] \frac{d^{s}}{dt} p_{\perp}^{s*} \right\} \end{aligned} \tag{158}$$

Finally, we are now able to write the FINAL form of the interfacial entropy production rate σ for one of the two interfaces in the scope of thin films drainage.

$$\begin{aligned} \sigma^{s}_{\text{1st interface}} = & \frac{1}{T^{s}} \boldsymbol{v}^{s} \cdot \boldsymbol{\nabla}_{\parallel} \cdot \left(\gamma \boldsymbol{\delta} - \boldsymbol{\tau}^{s} \right) \\ & + \frac{1}{T^{s}} \boldsymbol{v}^{s} \left[\bar{\boldsymbol{E}}^{*} \cdot \left(\boldsymbol{D}^{II} - \boldsymbol{D}^{I} \right) - \left(\boldsymbol{T}_{E}^{II} - \boldsymbol{T}_{E}^{I} \right) \right] \cdot \boldsymbol{n} \\ & + \frac{1}{T^{s}} \left\{ \left[\bar{\boldsymbol{E}}_{\parallel}^{*} - \left(\bar{\boldsymbol{E}}_{\parallel}^{*} \right)_{eq} \right] \cdot \frac{d^{s}}{dt} \boldsymbol{p}_{\parallel}^{s*} + \left[\bar{D}_{\perp}^{*} - \left(\bar{D}_{\perp}^{*} \right)_{eq} \right] \frac{d^{s}}{dt} p_{\perp}^{s*} \right\} \end{aligned} \tag{159}$$

with

$$\boldsymbol{n} \cdot \left(\boldsymbol{T}_{E}^{II} - \boldsymbol{T}_{E}^{I} \right) = \frac{1}{2} \epsilon_{0} \epsilon_{I} \left({E_{\perp}^{I}}^{2} + \frac{\epsilon_{II}}{\epsilon_{I}} {E_{\parallel}^{I}}^{2} \right) \left(1 - \frac{\epsilon_{I}}{\epsilon_{II}} \right) \boldsymbol{n} \tag{160}$$

where $E_{\perp}^{I}$ and $E_{\parallel}^{I}$ are those previously derived in (147).
However, the real entropy generation rate must reflect the presence in the system of two identical interface

(i.e. top and bottom water-oil interfaces). To correct for this, it is sufficient to multiply by a factor 2 the entropy production rate for a single interface.

$$\sigma^s_{\text{Total}} = 2\,\sigma^s_{\text{1st interface}} \tag{161}$$

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