PDE's for polymer phase separation

Irena Pawłow

Systems Research Institute, Polish Academy of Sciences,

Institute of Mathematics and Cryptology,
Cybernetics Faculty, Military University of Technology, Warsaw

I. Provide a theoretical background for the *degenerate singular polymer model:*

  ▷ Flory-Huggins-de Gennes free energy
  ▷ Cahn-Hilliard-de Gennes model

- G. Schimperna, I.P., *A Cahn-Hilliard equation with singular diffusion*, submitted 2012

  ▷ the existence and uniqueness proof in the talk by G. Schimperna

II. Present the nonisothermal version of the Cahn-Hilliard-de Gennes model. Discuss relations to the conserved Penrose-Fife model.

- H.W. Alt, I.P., *On the entropy principle of phase transition models with a conserved order parameter*, Adv. Math. Sci. Appl. **6** (1996), 291–376.

  ▷ rigorous derivation of general "thermodynamically consistent" phase field models of a conserved type
  ▷ discussion of polymer free energy models

- H.W. Alt, I.P, *The Cahn-Hilliard equation for a polymer mixture*, SFB 256 Universität Bonn, unpublished notes (1996)

  ▷ methods by C.M. Elliott and H. Garcke (1996), and C.M. Elliott and S. Luckhaus (1991)

The 4th and 6th order Cahn-Hilliard type problems with nonlinear diffusion

- G. Schimperna, I.P., *On a class of Cahn-Hilliard models with nonlinear diffusion*, submitted 2011

$$\text{Free energy}: \quad \mathcal{F} = F(u) - \frac{\lambda}{2}u^2 + \frac{a(u)}{2}|\nabla u|^2 + \frac{\delta}{2}|\Delta u|^2, \quad \lambda \geq 0, \quad \delta \geq 0$$

$$F(u) = (1-u)\log(1-u) + (1+u)\log(1+u), \quad u \in [-1,1]$$

$$a(u) \text{ positive, nonlinear, } \mathbf{bounded}$$

  ▷ Existence and uniqueness of weak solutions

Examples of 4th order:

- face-centered cubic crystal model, E.A. Lass et. al. (2006)
  $a(u) = a_0 + a_1 u + a_2 u^2$, $a_0 > 0$, $a_1, a_2 \in \mathbb{R}$ depending on the level of approximation of the nearest neighbor interactions
- de Gennes (1980) polymer model with singular $a(u) = \frac{1}{(1-u)(1+u)}$

- oil-water-surfactant mixture model (three phases: microemulsion, almost pure oil and almost pure water), G. Gompper et al. (1992)

$$F(u) = (u+1)^2(u^2+h_0)(u-1)^2, \ \ a(u) = g_0+g_2u^2, \ \ g_2 > 0, \ \ h_0, g_0 \in \mathbb{R}, \ \ \delta > 0$$

- phase field crystal (PFC) atomistic model of crystal growth, K.R. Elder et al. (2004)

$$F(u) \ - \ \text{polynomial}, \quad a = \text{const} < 0, \quad \delta > 0$$

▷ Existence and uniqueness of global strong solutions

- I.P., W. Zając zkowski, *A sixth order Cahn-Hilliard type equation arising in oil-water-surfactant mixtures*, Comm. Pure Appl. Anal. (2011).
- I.P., W. Zając zkowski, *The global solvability of a sixth order Cahn-Hilliard type equation via the Bäcklund transformation*, submitted 2012.

$$\mathcal{F} = F(u) + \frac{a(u)}{2}|\nabla u|^2 + \frac{\delta}{2}|\Delta u|^2, \quad \delta > 0$$

$$F(u) = \sum_{i=0}^{2k} a_i u^i, \quad a_{2k} > 0, \quad k \geq 1, \quad a(u) = \sum_{i=0}^{2l} b_i u^i, \quad b_{2l} > 0, \quad l \geq 1$$

"Simplified" version of polymer model with constant mobility $M \equiv 1$

$$(P) \quad \begin{cases} u_t - \Delta w = 0 & \text{in } \Omega \times (0,T) \\[2mm] w = -a(u)\Delta u - \dfrac{a'(u)}{2}|\nabla u|^2 + f(u) - \lambda u + \varepsilon u_t & \\[2mm] u|_{t=0} = u_0 & \text{in } \Omega \\[2mm] \partial_n u = \partial_n w = 0 & \text{on } \Gamma \times (0,T) \end{cases}$$

$\Omega \subset \mathbb{R}^3$ bounded with a smooth boundary Γ

$u \in [-1,1]$ – order parameter, w – chemical potential

$\mathcal{F} = F(u) - \frac{\lambda}{2}u^2 + \frac{a(u)}{2}|\nabla u|^2$ – free energy

$F(u) = (1-u)\log(1-u) + (1+u)\log(1+u)$ – logarithmic volumetric part

$f(u) = F'(u) = \log \frac{1+u}{1-u}$

$a(u) = \frac{2}{(1-u)(1+u)} = f'(u)$

$\lambda,\ \varepsilon$ (viscosity) – nonnegative parameters

Assume
$$E_0 := \int_\Omega \left(F(u_0) - \frac{\lambda}{2} u_0^2 + \frac{a(u_0)}{2} |\nabla u_0|^2 \right) < +\infty,$$

$$m := \frac{1}{|\Omega|} \int_\Omega u_0 \in (-1,1); \quad \Omega \text{ is convex}$$

Then for any $T > 0$ problem (P) admits at least a weak or "energy" solution (u, w) such that
$u \in H^1(0,T;V') \cap L^\infty(0,T,V) \cap L^\infty((0,T) \times \Omega), \quad \varepsilon u \in H^1(0,T;H),$
$F(u) \in L^\infty(0,T;L^1(\Omega)), \quad v = f(u) \in L^2(0,T;V),$
$\nabla v \in L^p((0,T) \times \Omega)$ *for some $p > 2$,* $w \in L^2(0,T;V)$
$(H := L^2(\Omega),\ V := H^1(\Omega),\ V \subset H \subset V'),$
satisfying a.e. in $(0,T)$ the equations

$$u_t + Aw = 0 \qquad\qquad\qquad\qquad \text{in } V'$$

$$w = -\Delta v + v + \frac{u}{2}|\nabla v|^2 - \lambda u + \varepsilon u_t, \quad \text{a.e. in } \Omega$$

$$v = f(u) \qquad\qquad\qquad\qquad\qquad \text{a.e. in } \Omega$$

$$\partial_n v = 0 \qquad\qquad\qquad\qquad\qquad \text{a.e. on } \Gamma$$

together with the initial condition $u|_{t=0} = u_0$.

Moreover, for any $\tau > 0$, (u, w) is a "classical" solution over (τ, T) with the regularity

$$u \in W^{1,\infty}(\tau, T; V') \cap H^1(\tau, T; V) \cap L^\infty(\tau, T; H^2(\Omega)), \quad \varepsilon u \in W^{1,\infty}(\tau, T; H)$$
$$w \in L^\infty(\tau, T; V) \cap L^2(\tau, T; H^3(\Omega)), \quad \varepsilon w \in L^\infty(\tau, T; H^2(\Omega)),$$

satisfying a.e. in (τ, T), the equations

$$u_t - \Delta w = 0 \qquad\qquad\qquad\qquad \text{a.e. in } \Omega$$

$$w = -a(u)\Delta u - \frac{a'(u)}{2}|\nabla u|^2 + f(u) - \lambda u + \varepsilon u_t \quad \text{a.e. in } \Omega$$

$$\partial_n u = \partial_n w = 0 \qquad\qquad\qquad\qquad \text{a.e. on } \Gamma,$$

and for all $(t, x) \in [\tau, T] \times \bar{\Omega}$ satisfies the separation property

$$-1 + \epsilon \leq u(t, x) \leq 1 - \epsilon \quad \text{with} \quad \epsilon^{-1} = Q(E_0, \tau^{-1})$$

where Q is a nonnegative, monotone increasing function of its arguments.

polymer-polymer, polymer-solvent, polymer-polymer-solvent

- Scientific and practical importance

  ▷ Structure formation is easy to follow experimentally because of long diffusion times

  ▷ There are many practical materials applications due to the special morphology which can be design e.g., by means of temperature control

- Extensive physical and numerical literature:

  Flory (1953), Debye (1959), de Gennes (1971, 1980), McMaster (1975), Vrij and Esker (1975), Nose (1976), Pincus (1981), Binder (1983), Brochard et al. (1983), Nesterov and Lipatov (1984), Mitlin et al. (1985, 1990), Nauman et al. (1988)

$$m_1\omega_1 + m_2\omega_2 = V \qquad\qquad m_i - \text{number of molecules } i$$

$$\omega_i - \text{volume of } i\text{-th molecule,} \quad V - \text{total volume}$$

$$c_1\omega_1 + c_2\omega_2 = 1 \qquad\qquad c_i - \text{density of molecules } i$$

$$\varphi_i = \frac{c_i\omega_i}{c_1\omega_1 + c_2\omega_2} = c_i\omega_i \qquad - \text{volume fraction of molecules } i$$

$$\varphi_1 + \varphi_2 = 1 \quad - \text{incompressibility condition}$$

$$\varphi \equiv \varphi_1 \in [0, 1] - \text{order parameter} \quad (u := 2\varphi - 1 \in [-1, 1])$$

N_i – number of segments in i-th molecule (chain length)

σ_i – the size of segments in i-th molecule (lattice constant)

R_{g_i} – the mean radius of gyration of i-th molecule

$\theta > 0$ – absolute temperature

$k_B = 1$ – Boltzmann's constant

f – free energy

e – internal energy

η – entropy

It is assumed that in each polymer molecule the average density of segments, $\zeta_i(r)$, at a distance r from the center of gravity of the molecule is given by a Gaussian distribution

$$\zeta_i(r) = \frac{N_i}{(a_i\sqrt{\Pi})^3} \exp(-r^2/a_i^2)$$

where $a_i > 0$ is a measure of the dimension of the molecule.
The mean radius of gyration, R_{g_i}, is *the root of the mean square distance from the center of the molecule*

$$R_{g_i}^2 = \int r^2 \zeta_i(r) dV / \int \zeta_i(r) dV$$

where the integral is taken over the volume of the whole system;

$$\text{in 3D}: \quad R_{g_i}^2 = \frac{3}{2}a_i^2 = \frac{1}{6}N_i\sigma_i^2$$

$$f_{\text{FHdG}}(\varphi, \nabla\varphi, \theta) = \underbrace{f_0(\varphi, \theta)}_{\text{volumetric (Flory}-\text{Huggins)}} + \underbrace{\frac{1}{2}\varkappa(\varphi, \theta)|\nabla\varphi|^2}_{\text{gradient (de Gennes)}}$$

$$f_0(\varphi, \theta) = \theta \underbrace{\left[\frac{\varphi}{N_1}\log\varphi + \frac{1-\varphi}{N_2}\log(1-\varphi)\right]}_{-\text{ configurational entropy}} + \underbrace{\chi\varphi(1-\varphi)}_{\text{energy of interaction}}$$

$$\chi = \underset{\substack{\uparrow \\ \text{energetic}}}{\chi_e} + \underset{\substack{\uparrow \\ \text{entropic}}}{\theta\chi_\eta} \qquad \text{Flory-Huggins interaction parameter}$$

Standard case: $\chi_e > 0$, $\chi_\eta \geq 0$ constants

In particular, if $N_1 = N_2 = N$, $\chi = \chi_e > 0$ then $\exists\, \chi_{\text{crit}} = \frac{2\theta}{N}$ such that:

for $\chi < \chi_{\text{crit}}$ f_0 strictly convex

for $\chi > \chi_{\text{crit}}$ f_0 has double-well form

$$\varkappa(\varphi, \theta) = \underset{\underset{\text{energetic}}{\uparrow}}{\varkappa_e} + \underset{\underset{\text{entropic (de Gennes 1971)}}{\uparrow}}{\theta \varkappa_\eta(\varphi)}$$

$\varkappa_e$ – interactions between different molecules

$\varkappa_\eta$ – connectivity of segments

- de Gennes (1971) – random phase approximation method
- Debye (1959), Vrij and Esker (1975), and others – analytical derivations

$$\varkappa_e = \frac{1}{3}(R_{g_1}^2 + R_{g_2}^2)\chi_e$$

$$\varkappa_\eta(\varphi) = \frac{1}{3}(R_{g_1}^2 + R_{g_2}^2)\chi_\eta + \underbrace{\frac{1}{3}\left[\frac{R_{g_1}^2}{N_1\varphi} + \frac{R_{g_2}^2}{N_2(1-\varphi)}\right]}_{=\frac{1}{18}\left[\frac{\sigma_1^2}{\varphi} + \frac{\sigma_2^2}{1-\varphi}\right]}$$

According to de Gennes: $\varkappa_e \ll \varkappa_\eta(\varphi)$, thus can be neglected

Extension of the Flory-Huggins formula for the entropy of mixing

$$-\frac{S - S_0}{k_B} = \int [c_1 \log \varphi_1 + c_2 \log \varphi_2] dV$$

into inhomogeneous case by the following local modification accounting for the connectivity of segments within polymer molecule

$$n_i = N_i c_i + \frac{1}{6} R_{g_i}^2 N_i \Delta c_i,$$

where n_i is the segment density. Using this, we get the modified expression describing the entropy of mixing of nonuniform systems

$$-\frac{S - S_0}{k_B} = \int \left[\frac{n_1}{N_1} \log \varphi_1 + \frac{n_2}{N_2} \log \varphi_2 \right] dV$$

$$-\frac{1}{6} \int [R_{g_1}^2 \Delta c_1 \log \varphi_1 + R_{g_2}^2 \Delta c_2 \log \varphi_2] dV$$

Expressing both integrals in terms of molecule volume fractions

$$\left(n_i = N_i \frac{\varphi_i}{\omega_i}, \quad c_i = \frac{\varphi_i}{\omega_i} \right)$$

$$-\frac{S - S_0}{k_B} = \int \left[\frac{\varphi_1}{\omega_1} \log \varphi_1 + \frac{\varphi_2}{\omega_2} \log \varphi_2 \right] dV$$

$$-\frac{1}{6} \int \left[\frac{R_{g1}^2}{\omega_1} \Delta \varphi_1 \log \varphi_1 + \frac{R_{g2}^2}{\omega_2} \Delta \varphi_2 \log \varphi_2 \right] dV$$

Integrating by parts the second integral and using B.C. $\quad \boldsymbol{n} \cdot \nabla \varphi_i = 0 \quad$ at the boundary of the volume, we arrive at the singular expression for the entropy of mixing

$$-\frac{S - S_0}{k_B} = \int \left[\frac{\varphi_1}{\omega_1} \log \varphi_1 + \frac{\varphi_2}{\omega_2} \log \varphi_2 \right] dV$$

$$+\frac{1}{6} \int \left[\frac{R_{g1}^2}{\omega_1} \frac{1}{\varphi_1} + \frac{R_{g2}^2}{\omega_2} \frac{1}{\varphi_2} \right] |\nabla \varphi|^2 dV$$

- Extends the Cahn-Hilliard theory to $FHdG$ free energy
  Let $\bar{\theta} = \text{const} < \theta_{\text{crit}}, \quad f_{\text{FHdG}}(\varphi, \nabla\varphi, \bar{\theta}) = f_0(\varphi, \bar{\theta}) + \frac{1}{2}\varkappa(\varphi, \bar{\theta})|\nabla\varphi|^2$
  $$\underset{\text{SINGULARITY}}{\uparrow}$$

$$(\text{CHdG}) \quad \begin{cases} \varphi_t + \nabla \cdot \boldsymbol{j}^d = 0 & \text{mass balance} \\[2mm] -\boldsymbol{j}^d = \dfrac{\Lambda(\varphi)}{\bar{\theta}}\nabla\mu & \text{mass flux} \\[2mm] \mu = \dfrac{\delta f_{\text{FHdG}}}{\delta\varphi} = f_{0,\varphi} - \dfrac{1}{2}\varkappa_{,\varphi}|\nabla\varphi|^2 - \varkappa\Delta\varphi \end{cases}$$

$\mu = \mu_1 - \mu_2$ – exchange chemical potential, $\Lambda(\varphi)$ – Onsager coefficient

▷ de Gennes (1980), Binder (1983) et al., incompressibility $\Rightarrow$

$$\Lambda(\varphi) = \frac{\Lambda_1\Lambda_2}{\Lambda_1 + \Lambda_2} = M_0\varphi(1 - \varphi) \leftarrow \text{DEGENERATION}$$

where $\Lambda_i = M_0\varphi_i$, $M_0 > 0$ – Onsager coefficient for the i-th component ($\varphi \equiv \varphi_1, \quad \varphi_1 + \varphi_2 = 1$).

System (CHdG) satisfies the free energy inequality with multipliers

$$f_t + \nabla \cdot \underbrace{[\mu \boldsymbol{j}^d - \varphi_t f_{,\nabla \varphi}]}_{\boldsymbol{\Phi}} - \Lambda_\varphi (\varphi_t + \nabla \cdot \boldsymbol{j}^d) - \Lambda_\mu (-\mu + f_{,\varphi} - \nabla \cdot f_{,\nabla \varphi})$$

$$= \nabla \mu \cdot \boldsymbol{j}^d = -\frac{\Lambda(\varphi)}{\bar{\theta}} |\nabla \mu|^2 =: -\Sigma \leq 0 \quad \forall\, fields\ \varphi, \mu$$

where:

$$f \equiv f_{FHdG}(\varphi, \nabla \varphi, \theta)$$
$$\Lambda_\varphi = \mu, \quad \Lambda_\mu = \varphi_t \quad - multipliers$$
$$\boldsymbol{\Phi} \quad - free\ energy\ flux, \quad \Sigma \quad - dissipation$$

Remark:

$$-\boldsymbol{j}^d = \frac{\Lambda(\varphi)}{\bar{\theta}} \nabla \mu \quad \Leftrightarrow \quad -\boldsymbol{j}^d = \mathcal{D}_{,\nabla \mu} \equiv \frac{\partial \mathcal{D}}{\partial \nabla \mu}$$

where

$$\mathcal{D} = \frac{1}{2} \frac{\Lambda(\varphi)}{\bar{\theta}} |\nabla \mu|^2$$

is the dissipation potential.

Sufficiently smooth solutions of system (CHdG) satisfy the free energy inequality

$$f_t + \nabla \cdot [\mu \boldsymbol{j}^d - \varphi_t f_{,\nabla\varphi}] = -\frac{\Lambda(\varphi)}{\bar{\theta}}|\nabla\mu|^2 = -\Sigma \leq 0.$$

Integrating the above over Ω and assuming "variational" B.C. which ensure that

$$\boldsymbol{n} \cdot (\mu \boldsymbol{j}^d - \varphi_t f_{,\nabla\varphi}) = 0 \quad \text{on} \ \ \Gamma,$$

it follows that f is the Lyapunov functional

$$\frac{d}{dt}\int_\Omega f(\varphi, \nabla\varphi, \bar{\theta})dx \leq 0.$$

Assume given:

- Free energy $f = f(\varphi, \nabla\varphi, \theta)$ strictly concave with respect to θ

- Dissipation potential $\mathcal{D} = \mathcal{D}(X; \omega) \geq 0$,
  where:

$$X := (\nabla\frac{\mu}{\theta}, \nabla\frac{1}{\theta}, \varphi_t) \ - \text{thermodynamic forces}$$

$$\omega := (\varphi, \nabla\varphi, \nabla^2\varphi, \theta, \frac{\mu}{\theta}) - \text{state variables}$$

$$\frac{\mu}{\theta} \ - \text{rescaled chemical potential}$$

$$\frac{1}{\theta} \ - \text{inverse temperature}$$

$\mathcal{D}$ is nonnegative, convex in X and such that $\mathcal{D}(0; \omega) = 0$

- Basic thermodynamic relations

$$f = e - \theta\eta, \quad \eta = -f_{,\theta}, \quad c = e_{,\theta} = -\theta f_{,\theta\theta}$$

where:

e − internal energy, $\quad \eta$ − entropy, $\quad c$ − specific heat

- $$f(\varphi, \nabla\varphi, \theta) = \underbrace{f_*(\theta)}_{\text{thermal}} + \underbrace{f_{\text{FHdG}}(\varphi, \nabla\varphi, \theta)}_{\text{Flory−Huggins−de Gennes}}$$

   ▷ Ex.:   (1) $f_*(\theta) = -c_v\theta \log \dfrac{\theta}{\theta_1} + c_v\theta + \bar{c}, \quad c_v, \theta_1, \bar{c} > 0$

$$\Rightarrow c = -\theta f_*''(\theta) = c_v \quad -\text{specific heat}$$

        (2) $f_*(\theta) = -\dfrac{1}{2}c_v\theta^2 \Rightarrow c = -\theta f_*''(\theta) = c_v\theta$

- $$\mathcal{D}(X;\omega) = \frac{1}{2}\underbrace{M(\varphi,\theta)}_{\text{mobility}}\left|\nabla\frac{\mu}{\theta}\right|^2 + \frac{1}{2}\underbrace{k(\varphi,\theta)}_{\text{heat conductivity}}\left|\nabla\frac{1}{\theta}\right|^2 + \frac{1}{2}\underbrace{\beta(\varphi,\theta)}_{\text{viscosity}}\varphi_t^2$$

  "close to equilibrium" standard form

   ▷ Ex.: $M = M_0\varphi(1-\varphi), \quad M_0 > 0, \quad k = k_0\theta^2, \ k_0 > 0,$

                                                (Fourier law)

$$\beta = \frac{\beta_0}{\theta} + \beta_1, \ \ \beta_0, \beta_1 \geq 0$$

Assume the standard form of $f_*(\theta)$ in Ex.(1) $\Rightarrow c = c_v > 0$.
By the thermodynamic relations:

- Internal energy

$$e(\varphi, \nabla\varphi, \theta) = c_v\theta + \chi_e\varphi(1-\varphi) + \frac{1}{2}\varkappa_e|\nabla\varphi|^2, \quad c_v, \chi_e, \varkappa_e > 0$$

- Entropy

$$\eta(\varphi, \nabla\varphi, \theta) = c_v\log\frac{\theta}{\theta_1} - \left[\frac{\varphi}{N_1}\log\varphi + \frac{1-\varphi}{N_2}\log(1-\varphi)\right] - \chi_\eta\varphi(1-\varphi)$$
$$- \frac{1}{2}\varkappa_\eta(\varphi)|\nabla\varphi|^2,$$

where:

$$c_v > 0, \quad \chi_\eta \geq 0, \quad \varkappa_\eta(\varphi) = \frac{1}{3}(R_{g_1}^2 + R_{g_2}^2)\chi_\eta + \frac{1}{18}\left(\frac{\sigma_1^2}{\varphi} + \frac{\sigma_2^2}{1-\varphi}\right).$$

Note: In polymer model both e and η include gradient term.
In Penrose-Fife model only η has gradient term with constant coefficient
$\varkappa_\eta$, and e is purely volumetric i.e., $\varkappa_e = 0$.

- A question of particular interest in phase field modelling is whether to modify the energy or the entropy equation by *"extra" terms, see e.g., M. Fabrizio, C. Giorgi, and A. Morro (2006).*

- A freedom in arbitrary choice of a nonstationary parts of energy and entropy fluxes has been discovered by rigorous analytical considerations of the entropy principle in *H.W. Alt, I.P. (1996).*

- Following the above ideas, we apply a method based on the exploitation of the *Müller-Liu entropy inequality with multipliers* combined with the *dual approach* which consists in using energy or entropy in place of temperature as an independent thermal variable.

- To solve the resulting dissipation inequality we apply *Edelen's decomposition theorem* [Arch. Ration. Mech. Analysis **51** (1973)] which asserts the existence of a dissipation potential and the splitting of the solution to the dissipation inequality into a dissipative and a nondissipative part.

- Another approaches: *E. Fried and M.E. Gurtin theory (1993)* based on microforce balance, and *M. Frémond theory (2002)* based on microscopic motions.

$$(PFS) \quad \begin{cases} \varphi_t + \nabla \cdot \boldsymbol{j}^d = 0 \\[2mm] \dfrac{\mu}{\theta} = \dfrac{\delta(f/\theta)}{\delta\varphi} + \boldsymbol{h}^e \cdot \nabla\dfrac{1}{\theta} + a^d \\[2mm] e_t + \nabla \cdot (\underbrace{\boldsymbol{q}^d - \varphi_t \boldsymbol{h}^e}_{\boldsymbol{q}}) = g \end{cases}$$

where:

$\dfrac{f}{\theta}$ – rescaled free energy (Massieu function)

e – internal energy,

$\boldsymbol{q}$ – energy flux, g – external heat source

$\boldsymbol{h}^e = \boldsymbol{h}^e(X; \omega)$ – extra nondissipative vector field, not restricted by the entropy principle

$\boldsymbol{j}^d$, $\boldsymbol{q}^d$, a^d – dissipative quantities defined through $\mathcal{D}$ by

$$-\boldsymbol{j}^d = \mathcal{D}_{,\nabla(\mu/\theta)}, \quad \boldsymbol{q}^d = \mathcal{D}_{,\nabla(1/\theta)}, \quad a^d = \mathcal{D}_{,\varphi_t}.$$

Let us set $h^e := e_{,\nabla\varphi}$ "extra" vector field. Then (PFS) becomes

(1)
$$
\begin{cases}
\varphi_t + \nabla \cdot \boldsymbol{j}^d = 0, & -\boldsymbol{j}^d = M(\varphi,\theta)\nabla\frac{\mu}{\theta} \\[2mm]
\dfrac{\mu}{\theta} = \dfrac{\delta(f/\theta)}{\delta\varphi} + \underbrace{e_{,\nabla\varphi} \cdot \nabla\frac{1}{\theta}}_{\text{extra term}} + a^d, & a^d = \beta(\varphi,\theta)\varphi_t \\[2mm]
e_t + \nabla \cdot (\boldsymbol{q}^d \underbrace{-\varphi_t e_{,\nabla\varphi}}_{\text{extra energy flux}}) = g, & \boldsymbol{q}^d = k(\varphi,\theta)\nabla\frac{1}{\theta}
\end{cases}
$$

satisfied in $\Omega \times (0,T)$, together with the initial conditions

(2)
$$
\varphi|_{t=0} = \varphi_0, \quad \theta|_{t=0} = \theta_0 \quad \text{in } \Omega,
$$

and appropriate boundary conditions, e.g.,

(3)
$$
\boldsymbol{n} \cdot e_{,\nabla\varphi} = \boldsymbol{n} \cdot \eta_{,\nabla\varphi} = 0, \quad \boldsymbol{n} \cdot \boldsymbol{j}^d = 0, \quad \boldsymbol{n} \cdot \boldsymbol{q}^d = 0 \quad \text{on } \Gamma \times (0,T).
$$

Such B. C. ensure the total mass and energy conservation and the Lyapunov property of the system.

Let us consider system (1)–(3). Then

(i) the rescaled chemical potential equation $(1)_2$ admits the forms

$$\frac{\mu}{\theta} = \frac{\delta(f/\theta)}{\delta\varphi} + e_{,\nabla\varphi} \cdot \nabla\frac{1}{\theta} + a^d$$

$$= \frac{1}{\theta}\frac{\delta f}{\delta\varphi} - \frac{1}{\theta}\eta_{,\nabla\varphi} \cdot \nabla\theta + a^d$$

$$= \frac{1}{\theta}\left(\frac{\delta e}{\delta\varphi} - \theta\frac{\delta\eta}{\delta\varphi}\right) + a^d$$

(ii) the energy equation $(1)_3$ admits the form

$$c\theta_t + \nabla \cdot \boldsymbol{q}^d + \varphi_t\frac{\delta e}{\delta\varphi} = g$$

where
$c = -\theta f_{,\theta\theta} = c_v$ (for Ex. (1)).

Assume symmetrical polymer mixture, i.e.,

$$N_1 = N_2 = N, \quad \sigma_1 = \sigma_2 = \sigma, \quad R_{g_1}^2 = R_{g_2}^2 = R_g^2 = \frac{1}{6} N \sigma^2.$$

Then for the polymer free energy and dissipation potentials given above system (1)–(3) takes the form

$$
\begin{cases}
\varphi_t - \nabla \cdot \left[M_0 \varphi (1 - \varphi) \nabla \frac{\mu}{\theta} \right] = 0 \\[2mm]
\frac{\mu}{\theta} = \frac{1}{N} \log \frac{\varphi}{1 - \varphi} + \left(\frac{\chi_e}{\theta} + \chi_\eta \right) (1 - 2\varphi) + \frac{R_g^2}{6N} \frac{1 - 2\varphi}{[\varphi(1 - \varphi)]^2} |\nabla \varphi|^2 \\[2mm]
\qquad - \left[\frac{\varkappa_e}{\theta} + \frac{2R_g^2}{3} \chi_\eta + \frac{R_g^2}{3N} \frac{1}{\varphi(1 - \varphi)} \right] \Delta \varphi + \left(\frac{\beta_0}{\theta} + \beta_1 \right) \varphi_t, \\[2mm]
c_v \theta_t - k_0 \Delta \theta + [\chi_e (1 - 2\varphi) - \varkappa_e \Delta \varphi] \varphi_t = g,
\end{cases}
$$

satisfied in $\Omega \times (0, T)$, with the initial and boundary conditions

$$\varphi|_{t=0} = \varphi_0, \quad \theta|_{t=0} = \theta_0 \qquad\qquad \text{in } \Omega,$$

$$\boldsymbol{n} \cdot \nabla \varphi = 0, \quad \boldsymbol{n} \cdot \nabla \frac{\mu}{\theta} = 0, \quad \boldsymbol{n} \cdot \nabla \theta = 0 \qquad \text{on } \Gamma \times (0, T).$$

Recall that $M_0, \chi_e, \varkappa_e, k_0, c_v > 0$ and $\chi_\eta, \beta_0, \beta_1 \geq 0$.

- $f(\varphi, \nabla\varphi, \theta) = \underbrace{f_*(\theta)}_{\text{thermal Ex.(1)}} + \underbrace{f_0(\varphi, \theta)}_{\text{volumetric}} + \underbrace{\frac{1}{2}\theta\varkappa_\eta|\nabla\varphi|^2}_{\substack{\text{gradient energy} \\ \text{of "entropic" type}}}, \quad \varkappa_\eta = \text{const} > 0$

$f_0(\varphi, \theta) = \theta f_1(\varphi) + f_2(\varphi)$

$e(\varphi, \nabla\varphi, \theta) = c_v\theta + f_2(\varphi)$ – purely volumetric, i.e., $e_{,\nabla\varphi} = 0$

$\eta(\varphi, \nabla\varphi, \theta) = c_v \log\theta - f_1(\varphi) - \frac{1}{2}\varkappa_\eta|\nabla\varphi|^2$

- $\mathcal{D} = \frac{1}{2}M(\varphi, \theta)\left|\nabla\frac{\mu}{\theta}\right|^2 + \frac{1}{2}k(\varphi, \theta)\left|\nabla\frac{1}{\theta}\right|^2$

In the "entropic" case: $e_{,\nabla\varphi} = 0 \Leftrightarrow f_{,\nabla\varphi} = -\theta\eta_{,\nabla\varphi}$, system (1) (with $a^d \equiv 0$) coincides with the **Penrose-Fife model**

$$(PF) \qquad \begin{cases} \varphi_t - \nabla\cdot\left(M\nabla\frac{\mu}{\theta}\right) = 0 \\[2mm] \dfrac{\mu}{\theta} = f_1'(\varphi) + \dfrac{f_2'(\varphi)}{\theta} - \varkappa_\eta\Delta\varphi \\[2mm] c_v\theta_t + f_2'(\varphi)\varphi_t + \nabla\cdot\left(k\nabla\frac{1}{\theta}\right) = g. \end{cases}$$

Thus, in the case the term $\frac{1}{2}\varkappa_e|\nabla\varphi|^2$ is neglected, the nonisothermal polymer model takes the form of the *Penrose-Fife model of degenerate singular type*.

Theorem: *System (1)–(3) satisfies the entropy inequality with multipliers*

$$\eta_t + \nabla \cdot \underbrace{\left[-\frac{\mu}{\theta} j^d + \frac{1}{\theta} q^d - \varphi_t \eta_{,\nabla\varphi} \right]}_{\Psi} - \Lambda_\varphi (\varphi_t + \nabla \cdot j)$$

$$- \Lambda_{\bar{\mu}} \left[-\frac{\mu}{\theta} + \frac{f_{,\varphi}}{\theta} - \nabla \cdot (f_{,\nabla\varphi}/\theta) + e_{,\nabla\varphi} \cdot \nabla(1/\theta) + a^d \right]$$

$$- \Lambda_e [e_t + \nabla \cdot (q^d - \varphi_t e_{,\nabla\varphi})]$$

$$= -\nabla(\mu/\theta) \cdot j^d + \nabla(1/\theta) \cdot q^d + \varphi_t a^d$$

$$= \nabla(\mu/\theta) \cdot \mathcal{D}_{,\nabla(\mu/\theta)} + \nabla(1/\theta) \cdot \mathcal{D}_{,\nabla(1/\theta)} + \varphi_t \mathcal{D}_{,\varphi,t} =: \Sigma \geq 0$$

$$\forall \ \text{fields} \ \varphi, \frac{\mu}{\theta} \ \text{and} \ \theta,$$

where:

$\Lambda_\varphi = -\frac{\mu}{\theta}, \quad \Lambda_{\bar{\mu}} = -\varphi_t, \quad \Lambda_e = \frac{1}{\theta}$ *– multipliers*

Ψ *– entropy flux*

Σ *– dissipation (entropy production)*

Corollary 1 *Sufficiently regular solutions to system (1)–(3) satisfy the entropy equation and inequality*

$$\eta_t + \nabla \cdot \mathbf{\Psi} = \Sigma + \frac{g}{\theta} \geq \frac{g}{\theta}$$

with the entropy flux $\mathbf{\Psi}$ and the dissipation $\Sigma \geq 0$ as above.
Note:

$$\mathbf{q} = \underbrace{\mathbf{q}^d}_{\substack{\uparrow \\ \text{dissipative}}} \underbrace{-\varphi_t e_{,\nabla\varphi}}_{\text{nondissipative}} \,, \quad \mathbf{\Psi} = \underbrace{-\frac{\mu}{\theta}\mathbf{j}^d + \frac{1}{\theta}\mathbf{q}^d}_{\text{dissipative}} \underbrace{-\varphi_t \eta_{,\nabla\varphi}}_{\text{nondissipative}}$$

- Extra nondissipative terms are linked by the thermodynamic relation

$$e_{,\nabla\varphi} - \theta\eta_{,\nabla\varphi} = f_{,\nabla\varphi}.$$

Corollary 2. *Sufficiently regular solutions to system (1)–(3) satisfy the so-called availability identity and the inequality*

$$(4) \qquad (e - \alpha\eta)_t + \nabla \cdot \left[\underbrace{(q^d - \varphi_t e_{,\nabla\varphi})}_{q} - \alpha \underbrace{\left(-\frac{\mu}{\theta} j^d + \frac{1}{\theta} q^d - \varphi_t \eta_{,\nabla\varphi} \right)}_{\Psi} \right]$$

$$= -\alpha\Sigma + \left(1 - \frac{\alpha}{\theta} \right) g \leq \left(1 - \frac{\alpha}{\theta} \right) g$$

where $\alpha > 0$ is an arbitrary constant, and $\Sigma \geq 0$ the dissipation as above.

Corollary 3. (Integral forms)
Integrating the local mass balance $(1)_1$ over Ω, and assuming

$$(5) \qquad\qquad n \cdot j^d = 0 \quad \text{on} \ \ \Gamma \quad \text{(mass isolation)}$$

$\Rightarrow$ • *total mass conservation*

$$\frac{d}{dt} \int_\Omega \varphi dx = 0$$

Integrating the local energy balance $(1)_3$ *over* Ω*, and assuming*

$$(6) \qquad g = 0, \quad \boldsymbol{n} \cdot (\boldsymbol{q}^d - \varphi_t e_{,\nabla\varphi}) = 0 \quad \text{on } \Gamma$$

$\Rightarrow$ ● *total energy conservation*

$$\frac{d}{dt} \int_\Omega e\, dx = 0$$

Integrating the local availability identity (4) over Ω*, and assuming in addition to (6) that*

$$\boldsymbol{n} \cdot \left(-\frac{\mu}{\theta} \boldsymbol{j}^d + \frac{1}{\theta} \boldsymbol{q}^d - \varphi_t \eta_{,\nabla\varphi} \right) = 0 \quad \text{on } \Gamma$$

$\Rightarrow$ ● *total availability identity*

$$\frac{d}{dt} \int_\Omega (e - \alpha\eta)\, dx + \alpha \int_\Omega \Sigma\, dx = 0, \quad \alpha > 0, \quad \Sigma \geq 0$$

$\Rightarrow$ ● *the Lyapunov property*

$$\frac{d}{dt} \int_\Omega (e - \alpha\eta)\, dx \leq 0$$

$$\frac{d}{dt} \int_\Omega \left\{ c_v \theta + \chi_e \varphi(1 - \varphi) + \frac{1}{2} \varkappa_e |\nabla \varphi|^2 \right.$$

$$+ \alpha \left[- c_v \log \frac{\theta}{\theta_1} + \frac{1}{N} (\varphi \log \varphi + (1 - \varphi) \log(1 - \varphi)) \right.$$

$$\left. \left. + \chi_\eta \varphi(1 - \varphi) + \frac{\sigma^2}{36\varphi(1 - \varphi)} |\nabla \varphi|^2 \right] \right\} dx$$

$$+ \alpha \int_\Omega \left[M(\varphi, \theta) \left| \nabla \frac{\mu}{\theta} \right|^2 + k(\varphi, \theta) \left| \nabla \frac{1}{\theta} \right|^2 + \beta(\varphi, \theta) \varphi_t^2 \right] dx = 0$$

where
c_v, k, χ_e, $\varkappa_e$, $\alpha > 0$, and χ_η, M, $\beta \geq 0$

- **First step.** Consider system of balance equations

$$\varphi_t + \nabla \cdot \boldsymbol{j} = 0$$

$$e_t + \nabla \cdot \boldsymbol{q} = g$$

with constitutive equations

$$\boldsymbol{j} = \hat{\boldsymbol{j}}(Y_e), \quad \boldsymbol{q} = \hat{\boldsymbol{q}}(Y_e),$$

$$Y_e := \{\underbrace{\varphi, \boldsymbol{D}\varphi, \ldots, \boldsymbol{D}^K \varphi}_{\text{long range interactions}}, \underbrace{\boldsymbol{D}e, \ldots, \boldsymbol{D}^L e}_{\text{thermal effects}}, \underset{\substack{\text{material} \\ \text{viscosity}}}{\varphi_t}\}, \quad K \geq 2, \quad L \geq 1.$$

- **Second step.** Postulate the *Müller-Liu entropy inequality with multipliers*: There exists the entropy $\tilde{\eta} = \hat{\tilde{\eta}}(Y_e)$, the entropy flux $\boldsymbol{\Psi} = \boldsymbol{\Psi}(Y_e)$ and the multipliers $\lambda_\varphi = \hat{\lambda}_\varphi(Y_e)$, $\lambda_e = \hat{\lambda}_e(Y_e)$ such that the inequality

$$\tilde{\eta}_t + \nabla \cdot \boldsymbol{\Psi} - \lambda_\varphi(\varphi_t + \nabla \cdot \boldsymbol{j}) - \lambda_e(e_t + \nabla \cdot \boldsymbol{q}) \geq 0$$

is satisfied for all fields φ and e.

Postulate two structural assumptions:

(A1) $\tilde{\eta}_{,e}(Y_e) > 0 \quad \forall\, Y_e$ (nondegeneracy condition)

(A2) $\boldsymbol{\Psi}^0 = \lambda_\varphi^0 \boldsymbol{j}^0 + \lambda_e^0 \boldsymbol{q}^0$, where $\boldsymbol{\Psi}^0 := \boldsymbol{\Psi}|_{\varphi_t=0}$, etc.

Next, making no assumptions on the multipliers we exploit the above inequality by using appropriately arranged algebraic operations. As a result we conclude a collection of algebraic restrictions on the constitutive equations.

● **Third step.** We presuppose that the multipliers λ_φ and λ_e are additional independent variables. Then, regarding algebraic restrictions obtained in the previous step, we deduce an extended system of equations including in addition to balance laws the relations for the multipliers.
The extended system $(PF)_e$ takes the form:

(i)   The unknowns are fields φ, e, λ_φ and $\lambda_e > 0$;

(ii)   A thermodynamic potential is the entropy $\tilde{\eta} = \tilde{\eta}(\varphi, \boldsymbol{D}\varphi, e)$ satisfying the nondegeneracy condition $\tilde{\eta}_{,e}(\varphi, \boldsymbol{D}\varphi, e) > 0 \quad \forall\, (\varphi, \boldsymbol{D}\varphi, e)$

(iii)   The fields φ, e, λ_φ and λ_e satisfy the equations

$(PF)_e$
$$
\begin{cases}
\varphi_t + \nabla \cdot \boldsymbol{j} = 0 \\[2mm]
-\lambda_\varphi = -\dfrac{\delta \tilde{\eta}}{\delta \varphi} + a \\[2mm]
e_t + \nabla \cdot \boldsymbol{q} = g \\[2mm]
\lambda_e = \tilde{\eta}_{,e} > 0
\end{cases}
$$

where the quantities $\boldsymbol{j} = \hat{\boldsymbol{j}}(\mathscr{Z}_e)$, $\boldsymbol{q} = \hat{\boldsymbol{q}}(\mathscr{Z}_e)$ and $a = \hat{a}(\mathscr{Z}_e)$ are subject to the *residual dissipation inequality*

$$
\boldsymbol{D}\lambda_\varphi \cdot \boldsymbol{j} + \boldsymbol{D}\lambda_e \cdot \boldsymbol{q} + \varphi_t a \geq 0
$$

to be satisfied for all variables
$\mathscr{Z}_e := \{\varphi, \boldsymbol{D}\varphi, D^2\varphi, e, \boldsymbol{D}e, \lambda_\varphi, \boldsymbol{D}\lambda_\varphi, \lambda_e, \boldsymbol{D}\lambda_e, \varphi_t\}$, or equivalently for all fields φ, e, λ_φ and λ_e.

- We express problem $(PF)_e$ in terms of the inverse temperature $\vartheta = 1/\theta > 0$ as an independent thermal variable and the rescaled free energy

$$\phi = \hat{\phi}(\varphi, \boldsymbol{D}\varphi, \vartheta) := \vartheta \hat{f}\left(\varphi, \boldsymbol{D}\varphi, \frac{1}{\vartheta}\right)$$

  as a thermodynamic potential.
- To apply the duality relations we assume the *thermal stability condition* i.e., strict positivity of the specific heat coefficient, which implies that

$$\hat{\tilde{\eta}}(\varphi, \boldsymbol{D}\varphi, e) \ \textit{is strictly concave as a function of } e.$$

Moreover, $\hat{\tilde{\eta}}_{,e}(\varphi, \boldsymbol{D}\varphi, e) > 0 \quad \forall$ arguments $(\varphi, \boldsymbol{D}\varphi, e)$.
Under such assumption we have the *duality relations*

$(DR)_e$
$$\begin{cases} \hat{\tilde{\eta}}(\varphi, \boldsymbol{D}\varphi, e) + \hat{\phi}(\varphi, \nabla\varphi, \vartheta) = \vartheta e \\ \hat{\tilde{\eta}}_{,e}(\varphi, D\varphi, e) = \vartheta \end{cases}$$

Hence,
$\lambda_e = \tilde{\eta}_e = \vartheta,$ i.e., energy multiplier is identified with $\vartheta = \frac{1}{\theta}.$

- The strict concavity of $\hat{\tilde{\eta}}(\varphi, \boldsymbol{D}\varphi, e)$ w.r. to e is equivalent to the strict concavity of $\hat{\phi}(\varphi, \boldsymbol{D}\varphi, \vartheta)$ w.r. to $\vartheta > 0$.
- The duality relations $(DR)_e$ are equivalent to

$$(DR)_\vartheta \qquad \begin{cases} \hat{\phi}(\varphi, \boldsymbol{D}\varphi, \vartheta) + \hat{\tilde{\eta}}(\varphi, \boldsymbol{D}\varphi, \vartheta) = \vartheta e \\[2mm] e = \hat{e}(\varphi, \boldsymbol{D}\varphi, \vartheta) = \hat{\phi}_{,\vartheta}(\varphi, \boldsymbol{D}\varphi, \vartheta) \end{cases}$$

with

$$\hat{\tilde{\eta}}(\varphi, \boldsymbol{D}\varphi, \vartheta) = \hat{\tilde{\eta}}(\varphi, \boldsymbol{D}\varphi, \hat{e}(\varphi, \boldsymbol{D}\varphi, \vartheta))$$

- Moreover, it holds

$$-\hat{\tilde{\eta}}_{,\varphi}(\varphi, \boldsymbol{D}\varphi, e) = \hat{\phi}_{,\varphi}(\varphi, \boldsymbol{D}\varphi, \vartheta)$$

$$-\tilde{\eta}_{,\boldsymbol{D}\varphi}(\varphi, \boldsymbol{D}\varphi, e) = \hat{\phi}_{,\boldsymbol{D}\varphi}(\varphi, \boldsymbol{D}\varphi, \vartheta)$$

$$-\frac{\delta\hat{\tilde{\eta}}}{\delta\varphi}(\varphi, \boldsymbol{D}\varphi, \boldsymbol{D}^2\varphi, e, \boldsymbol{D}e) = \frac{\delta\hat{\phi}}{\delta\varphi}(\varphi, \boldsymbol{D}\varphi, \boldsymbol{D}^2\varphi, \vartheta, \boldsymbol{D}\vartheta)$$

- We identity $-\lambda_\varphi$ with a rescaled demical potential

$$-\lambda_\varphi \equiv \bar{\mu} := \vartheta\mu$$

Formulation with $\hat{\phi}(\varphi, \boldsymbol{D}\varphi, \vartheta)$ as a thermodynamic potential

$(PF)_\vartheta$

$$\begin{cases} \varphi_t + \nabla \cdot \boldsymbol{j} = 0 \\[2mm] \bar{\mu} = \dfrac{\delta\phi}{\delta\varphi} + a \\[2mm] e_t + \nabla \cdot \boldsymbol{q} = g \end{cases}$$

where

$$e = \hat{e}(\varphi, \boldsymbol{D}\varphi, \vartheta) = \hat{\phi}_{,\vartheta}(\varphi, \boldsymbol{D}\varphi, \vartheta)$$

$$\hat{\phi}(\varphi, \boldsymbol{D}\varphi, \vartheta) + \hat{\eta}(\varphi, \boldsymbol{D}\varphi, \vartheta) = \vartheta\hat{e}(\varphi, \boldsymbol{D}\varphi, \vartheta)$$

The quantities j, q and a are subject to the *residual dissipation inequality*

$$-D\bar{\mu} \cdot \boldsymbol{j} + \boldsymbol{D}\vartheta \cdot \boldsymbol{q} + \varphi_t a \geq 0$$

$\forall$ fields φ, $\bar{\mu}$ and $\vartheta > 0$.

Let $X \in E^N$, $\omega \in E^P$, and let $J(X;\omega)\colon E^N \times E^P \to E^N$ be a mapping of class C^1 in X and C^0 in ω.

There exists a scalar-valued function $\mathcal{D}(X;\omega)$ that is unique to within an added function of ω, and a unique vector-valued function $U(X;\omega)$ such that

$$J(X;\omega) = \nabla_X \mathcal{D}(X;\omega) + U(X;\omega),$$

$$X \cdot U(X;\omega) = 0, \quad U(0;\omega) = 0.$$

The mappings $\mathcal{D}(X;\omega)$ and $U(X;\omega)$ are given by

$$\mathcal{D}(X;\omega) = \int_0^1 X \cdot J(\tau X;\omega)d\tau,$$

$$U_i(X;\omega) = \int_0^1 \tau X_j \left\{ \frac{\partial J_i(\tau X;\omega)}{\partial(\tau X_j)} - \frac{\partial J_j(\tau X;\omega)}{\partial(\tau X_i)} \right\} d\tau.$$

Moreover, if $J(X;\omega)$ is of class C^2 in X, then $\mathcal{D}(X;\omega)$ is of class C^2 in X, and the symmetry relations

$$\nabla_X \wedge (J(X;\omega) - U(X;\omega)) = 0,$$

where "$\wedge$" denotes the exterior product operation, are satisfied identically on $E^N \times E^P$.

We have

$$\Sigma := -\nabla\frac{\mu}{\theta} \cdot \boldsymbol{j} + \nabla\frac{1}{\theta} \cdot \boldsymbol{q} + \varphi_t a \geq 0 \Leftrightarrow \Sigma = \boldsymbol{X} \cdot \boldsymbol{J}(\boldsymbol{X};\boldsymbol{\omega}) \geq 0 \,\forall\, (\boldsymbol{X};\boldsymbol{\omega})$$

$$\boldsymbol{X} := \left(\nabla\frac{\mu}{\theta}, \nabla\frac{1}{\theta}, \varphi_t\right) \quad \text{thermodynamic forces}$$

$$\boldsymbol{J}(X;\boldsymbol{\omega}) = (-\boldsymbol{j}, \boldsymbol{q}, a) \quad \text{thermodynamic fluxes}$$

Assume

$$\boldsymbol{j} = \boldsymbol{j}^d, \quad \boldsymbol{q} = \boldsymbol{q}^d \underbrace{-\varphi_t \boldsymbol{h}^e}_{\text{nondissipative}}, \quad a = a^d + \underbrace{\boldsymbol{h}^e \cdot \nabla\frac{1}{\theta}}_{\text{nondissipative}}$$

Then

$$\Sigma = \left[-\nabla\frac{\mu}{\theta} \cdot \boldsymbol{j}^d + \nabla\frac{1}{\theta} \cdot \boldsymbol{q}^d + \varphi_t a^d\right] + \left[\nabla\frac{1}{\theta} \cdot (-\varphi_t \boldsymbol{h}^e) + \varphi_t\left(\boldsymbol{h}^e \cdot \nabla\frac{1}{\theta}\right)\right]$$

$$= \boldsymbol{X} \cdot [\boldsymbol{J}^d(\boldsymbol{X};\boldsymbol{\omega}) + \boldsymbol{U}(\boldsymbol{X};\boldsymbol{\omega})] = \boldsymbol{X} \cdot \boldsymbol{J}^d(\boldsymbol{X};\boldsymbol{\omega}),$$

where $\boldsymbol{J}^d(\boldsymbol{X};\boldsymbol{\omega}) = (-\boldsymbol{j}^d, \boldsymbol{q}^d, a^d),$ $\boldsymbol{U}(\boldsymbol{X};\boldsymbol{\omega}) = \left(0, -\varphi_t \boldsymbol{h}^e, \boldsymbol{h}^e \cdot \nabla\frac{1}{\theta}\right).$