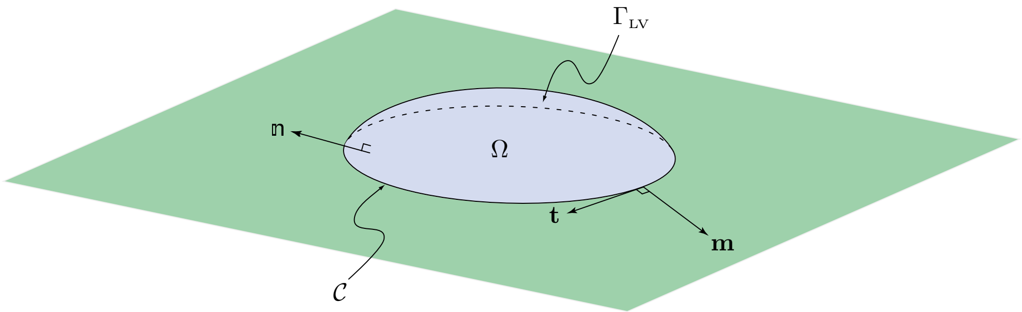
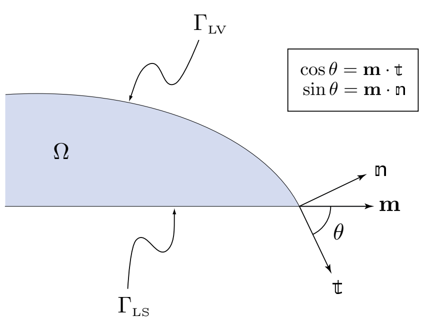
Dynamical equations for the contact line of an evaporating sessile drop

Eliot Fried
Department of Mechanical Engineering
McGill University

Background

- Many developing and advanced technologies rely on processes involving evaporating sessile drops.





- Basic modes:
  - Constant contact radius.
  - Constant contact angle.
  - Mixed or stick-slip.
- For sufficiently small drops, the time scales of evaporation and contact line motion become comparable.
- Due to the absence of a reliable theory and the challenges of making measurements at small length and time scales, a complete understanding of the mechanisms governing the various modes is not yet available.

Questions

1. What are the evolution equations for the contact line of an evaporating sessile drop?
2. Are dissipative mechanisms important and, if so, under what circumstances is coupling between those mechanisms significant?

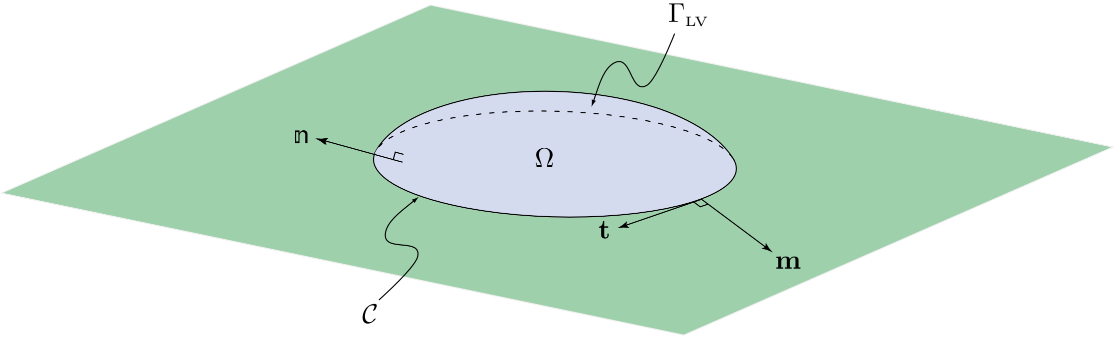
Theory for the liquid-vapor interface alone:

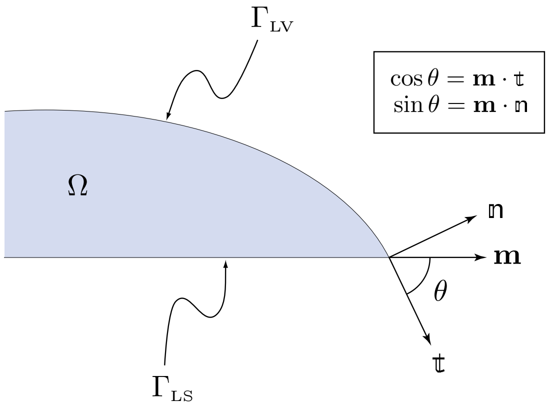
- E. Fried, A.Q. Shen & M.E. Gurtin, Theory for solvent, momentum, and energy transfer between a surfactant solution and a vapor atmosphere, *Phys. Rev. E* **73** (2006), 061601.
- D.M. Anderson, P. Cermelli, E. Fried, M.E. Gurtin & G.B. McFadden, General dynamical sharp-interface conditions for phase transformations in viscous heat-conducting fluids, *J. Fluid Mech.* **501** (2007), 323–370.

Outline

- Variational description of the equilibrium of a sessile drop
- Discussion and interpretation of the variational results
- The Young–Dupré equation
- Questions concerning the variational conditions at the contact line
- Mechanical balances at the contact line
- Configurational forces
- Dynamical equations for the contact line
- Take-home points

Variational description of the equilibrium of a sessile drop





- ϱ . . . liquid density
- ψ . . . specific Helmholtz free-energy of liquid (relative to vapor)
- φ . . . specific gravitational potential-energy ($\text{grad}\,\varphi = -\mathbf{g}$)
- $\psi_{\rm LV}$ . . . Helmholtz free-energy density of liquid-vapor interface
- $\psi_{\rm LS}$ . . . Helmholtz free-energy density of liquid-solid interface
- $\psi_{\rm SV}$ . . . Helmholtz free-energy density of solid-vapor interface
- $\psi_{\mathcal{C}}$ . . . Helmholtz free-energy density of contact line

Assumptions

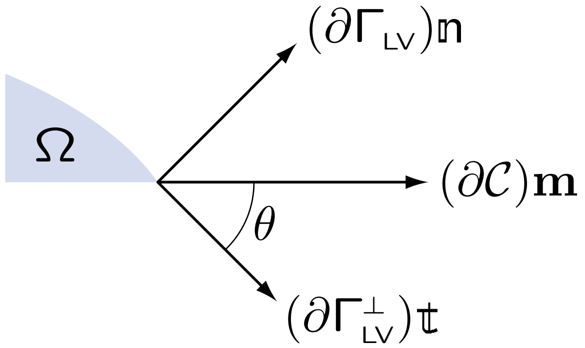
- The substrate is rigid, impermeable, and chemically inert with respect to both the liquid and the vapor.
- The liquid and vapor are in thermodynamic equilibrium.
- ψ is constant, as are ψ_{LV}, ψ_{LS}, and ψ_{SV}, and $\psi_{\mathcal{C}}$.

Net potential energy

$$\boxed{\mathcal{E} = \int_{\Omega} \varrho(\psi + \varphi)\,\mathsf{d}v + \int_{\Gamma_{\mathsf{LV}}} \psi_{\mathsf{LV}}\,\mathsf{d}a + \int_{\Gamma_{\mathsf{LS}}} (\psi_{\mathsf{LS}} - \psi_{\mathsf{SV}})\,\mathsf{d}a + \int_{\mathcal{C}} \psi_{\mathcal{C}}\,\mathsf{d}s}$$

Variations

- $\delta\mathbf{x}$ satisfying $\mathsf{div}\,(\delta\mathbf{x}) = 0$
- $\delta\Gamma_{\mathsf{LV}}$
- $\delta m_{\mathsf{LV}} = \varrho(\mathbb{n}\cdot\delta\mathbf{x} - \delta\Gamma_{\mathsf{LV}})$
- $\delta\mathcal{C}$
- $\delta\Gamma^{\perp}_{\mathsf{LV}} = \cos\theta\,\delta\mathcal{C}$



Variational description of equilibrium

To ensure satisfaction of the constraint $\operatorname{div}(\delta\mathbf{x}) = 0$, introduce a multiplier field p (ultimately the pressure of the liquid relative to that of the vapor). Then, the system is in equilibrium only if

$$\boxed{\delta\mathcal{E} - \int_\Omega p \operatorname{div}(\delta\mathbf{x})\, \mathrm{d}v = 0}$$

or, equivalently, only if

$$\begin{aligned} 0 = \int\limits_\Omega (\operatorname{grad} p - \varrho\mathbf{g})\cdot\delta\mathbf{x}\, \mathrm{d}v \\ - \int\limits_{\Gamma_{\mathsf{LV}}} (p + \psi_{\mathsf{LV}} K_{\mathsf{LV}})\delta\Gamma_{\mathsf{LV}}\, \mathrm{d}a - \int\limits_{\Gamma_{\mathsf{LV}}} \Big(\psi + \frac{p}{\varrho} + \varphi\Big)\delta m_{\mathsf{LV}}\, \mathrm{d}a \\ - \int\limits_{\mathcal{C}} (\psi_{\mathsf{LV}} \cos\theta + \psi_{\mathsf{LS}} - \psi_{\mathsf{SV}} - \psi_{\mathcal{C}}\kappa_{\mathcal{C}})\delta\mathcal{C}\, \mathrm{d}s, \end{aligned}$$

where $K_{\mathsf{LV}} = -\operatorname{div}_{\mathsf{LV}}\mathbb{n}$ is twice the mean curvature of Γ_{LV} and $\kappa_{\mathcal{C}}$ is the curvature of $\mathcal{C}$.

Necessary conditions for equilibrium

Since $\delta\mathbf{x}$ can be varied arbitrarily subject to the constraint div$\,(\delta\mathbf{x}) = 0$ on Ω:

$$\boxed{\text{grad}\, p = \varrho\mathbf{g} \qquad \text{on } \Omega}$$

Since $\delta\Gamma_{\text{LV}}$ and δm_{LV} can be varied arbitrarily and independently on Γ_{LV}:

$$\boxed{p + \psi_{\text{LV}} K_{\text{LV}} = 0 \qquad \text{and} \qquad \psi + \frac{p}{\varrho} + \varphi = 0 \qquad \text{on } \Gamma_{\text{LV}}}$$

Since $\delta\mathcal{C}$ can be varied arbitrarily on $\mathcal{C}$:

$$\boxed{\psi_{\text{LV}} \cos\theta + \psi_{\text{LS}} - \psi_{\text{SV}} + \psi_{\mathcal{C}}\kappa_{\mathcal{C}} = 0 \qquad \text{on } \mathcal{C}}$$

Discussion and interpretation of the necessary conditions

- The relations

$$\boxed{\text{grad}\, p = \varrho \mathbf{g} \qquad \text{and} \qquad p + \psi_{\mathsf{LV}} K_{\mathsf{LV}} = 0}$$

  express force balance in bulk and on the liquid-vapor interface, respectively. The latter is the Young–Laplace equation.

- For a single-component system in a gravitational field, the specific Gibbs free-energy $\psi + p/\varrho + \varphi$ is the driving force, measured per unit mass, per unit area, for evaporation-condensation. The relation

$$\boxed{\psi + \frac{p}{\varrho} + \varphi = 0}$$

  expresses the requirement that, in equilibrium, that driving force must vanish. (Ward & Sasges (1999) discuss the experimental significance of the gravitational contribution.)

- Eliminating p between the relations for the liquid-vapor interface yields a combined balance

$$\boxed{\varrho(\psi + \varphi) = \psi_{\mathsf{LV}} K_{\mathsf{LV}}}$$

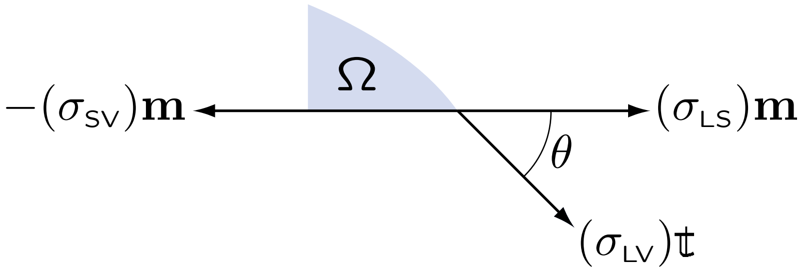
that can be imposed in place of the balance $\psi + p/\varrho + \varphi = 0$. This combined balance is reminiscent of the Gibbs–Thomson condition arising in models of solidification.

- When $\psi_{\mathcal{C}}$ is negligible, the relation

$$\boxed{\psi_{\mathsf{LV}} \cos\theta + \psi_{\mathsf{LS}} - \psi_{\mathsf{SV}} - \psi_{\mathcal{C}} \kappa_{\mathcal{C}} = 0}$$

reduces to an equation first derived by Gibbs (1878). Boruvka & Newmann (1977) provide a substantially broader generalization that allows the substrate to be deformable and accounts for dependence of the various interfacial free-energy densities on suitable strain measures.

The Young equation



$$\boxed{\sigma_{\mathsf{LV}} \cos\theta + \sigma_{\mathsf{LS}} - \sigma_{\mathsf{SV}} = 0}$$

Questions

- How, if at all, are the variational condition and the Young equation related?
- How can a contribution from line tension (or line energy) be incorporated in the Young equation?
- What are the forms of the vertical and tangential components of the vectorial force balance that encompasses the Young equation?

Controversy surrounding these and other related questions is ongoing. See:

- R. Finn, Contact angle in capillarity, *Phys. Fluids* **18** (2006), 047102.
- I. Lunati, Young's law and the effects of interfacial energy on the pressure at the solid-fluid interface, *Phys. Fluids* **19** (2007), 118105.
- R. Finn, Comments related to my paper "The contact angle in capillarity", *Phys. Fluids* **20** (2008), 107104.
- Y.D. Shikhmurzaev, On Young's (1805) equation and Finn's (2006) 'counterexample', *Phys. Lett. A* **372** (2008), 704–707.

Mechanical balances at the contact line

Suppose that:

- The liquid-vapor, liquid-solid, and solid-vapor interfaces Γ_{LV}, Γ_{LS}, and Γ_{SV} are endowed with (symmetric and tangential) Cauchy stresses $\mathbb{T}_{\mathsf{LV}}$, $\mathbb{T}_{\mathsf{LS}}$, and $\mathbb{T}_{\mathsf{SV}}$.
- The contact line $\mathcal{C}$ is endowed with Cauchy line stress $\boldsymbol{\tau}_{\mathcal{C}}$ and a line force $r_{\mathcal{C}}\mathbf{e}$, where $\mathbf{e}$ denotes the upward unit normal on the substrate.
- The interfaces and the contact line are not sufficiently massy to warrant the inclusion of interfacial or contact-line inertia.

The linear- and angular-momentum balances for a segment $\mathcal{L}$ of $\mathcal{C}$ are then given by

$$\int_{\mathcal{L}}(\mathbb{T}_{\mathsf{LS}}-\mathbb{T}_{\mathsf{SV}})\mathbf{m}\,\mathrm{d}s-\int_{\mathcal{L}}\mathbb{T}_{\mathsf{LV}}\mathbb{t}\,\mathrm{d}s+\boldsymbol{\tau}_{\mathcal{C}}\Big|_{\partial\mathcal{L}}+\int_{\mathcal{L}}r_{\mathcal{C}}\mathbf{e}\,\mathrm{d}s=\mathbf{0}$$

and

$$\int_{\mathcal{L}} (\mathbf{x}-\mathbf{o}) \times (\mathbb{T}_{\mathsf{LS}} - \mathbb{T}_{\mathsf{SV}})\mathbf{m}\,\mathrm{d}s - \int\limits_{\mathcal{L}} (\mathbf{x}-\mathbf{o}) \times \mathbb{T}_{\mathsf{LV}}\mathbb{t}\,\mathrm{d}s \\ + (\mathbf{x}-\mathbf{o}) \times \boldsymbol{\tau}_{\mathcal{C}}\Big|_{\partial\mathcal{L}} + \int_{\mathcal{L}} (\mathbf{x}-\mathbf{o}) \times r_{\mathcal{C}}\mathbf{e}\,\mathrm{d}s = \mathbf{0}.$$

- Since $\mathcal{L}$ is arbitrary, these balances localize to

$$\boxed{(\mathbb{T}_{\mathsf{LS}} - \mathbb{T}_{\mathsf{SV}})\mathbf{m} - \mathbb{T}_{\mathsf{LV}}\mathbb{t} + \frac{\partial \boldsymbol{\tau}_{\mathcal{C}}}{\partial s} + r_{\mathcal{C}}\mathbf{e} = \mathbf{0},}$$

where s denotes arclength along $\mathcal{C}$, and

$$\mathbf{t} \otimes \boldsymbol{\tau}_{\mathcal{C}} = \boldsymbol{\tau}_{\mathcal{C}} \otimes \mathbf{t}.$$

- The latter balances implies that $\boldsymbol{\tau}_{\mathcal{C}}$ is tangential to $\mathcal{C}$:

$$\boxed{\boldsymbol{\tau}_{\mathcal{C}} = \tau_{\mathcal{C}}\mathbf{t}.}$$

- Anderson, Cermelli, Fried, Gurtin & McFadden establish the representation

$$\boxed{\mathbb{T}_{\mathsf{LV}} = \psi_{\mathsf{LV}}(\mathbf{1} - \mathbb{n} \otimes \mathbb{n}) - \mathbb{S}_{\mathsf{LV}}}$$

  for the Cauchy stress on the liquid-vapor interface, where $\mathbb{S}_{\mathsf{LV}} = \mathbb{S}_{\mathsf{LV}}^{\top}$ is a viscous extra stress.

- For a rigid substrate, the results of Anderson, Cermelli, Fried, Gurtin & McFadden can be adapted to yield

$$\boxed{\mathbb{T}_{\mathsf{LS}} - \mathbb{T}_{\mathsf{SV}} = (\psi_{\mathsf{LS}} - \psi_{\mathsf{SV}})(\mathbf{1} - \mathbf{e} \otimes \mathbf{e}).}$$

- The force $r_{\mathcal{C}}\mathbf{e}$ is a reaction, to the constraint of substrate rigidity, that is determined by the vertical component of the linear-momentum balance for $\mathcal{C}$ by

$$\boxed{r_{\mathcal{C}} = \psi_{\mathsf{LV}} \sin\theta - \mathbf{e} \cdot \mathbb{S}_{\mathsf{LV}}\mathbb{t}.}$$

- In view of the Frenet relation $\partial\mathbf{t}/\partial s = \kappa_{\mathcal{C}}\mathbf{m}$, the linear-momentum balance for $\mathcal{C}$ has normal and tangential components

$$\boxed{\psi_{\mathsf{LV}}\cos\theta - \mathbf{m}\cdot\mathbb{S}_{\mathsf{LV}}\mathbb{t} + \psi_{\mathsf{LS}} - \psi_{\mathsf{SV}} + \tau_{\mathcal{C}}\kappa_{\mathcal{C}} = 0}$$

  and

$$\mathbf{t}\cdot\mathbb{S}_{\mathsf{LV}}\mathbb{t} = \frac{\partial\tau_{\mathcal{C}}}{\partial s}.$$

- The first of the above equations does not coincide with the variational condition

$$\boxed{\psi_{\mathsf{LV}}\cos\theta + \psi_{\mathsf{LS}} - \psi_{\mathsf{SV}} + \psi_{\mathcal{C}}\kappa_{\mathcal{C}} = 0}$$

  unless $\mathbf{m}\cdot\mathbb{S}_{\mathsf{LV}}\mathbb{t} = 0$ and $\tau_{\mathcal{C}} = \psi_{\mathcal{C}}$.

- If $\psi_{\mathcal{C}} = \tau_{\mathcal{C}} = 0$, then the variational condition and the Young equation coincide.

Observations

This approach resolves:

- Issues concerning balances normal to the substrate and tangential to the contact line.
- The connection between the interfacial tensions and the interfacial energies: $\sigma_{\mathsf{LV}} = \psi_{\mathsf{LV}} + \mathrm{tr}\,\$_{\mathsf{LV}}$

Additional questions

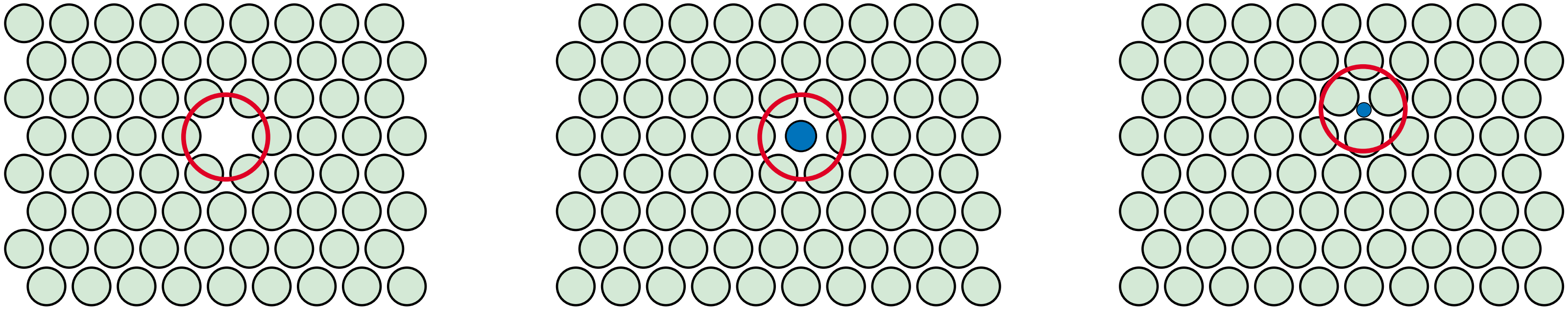
- Why does the variational approach yield two equilibrium conditions on the liquid-vapor interface but only a single condition at the contact line?
- Does $\tau_{\mathcal{C}} = \psi_{\mathcal{C}}$ in equilibrium?
- Does a single balance suffice away from equilibrium?

Digression: Configurational forces

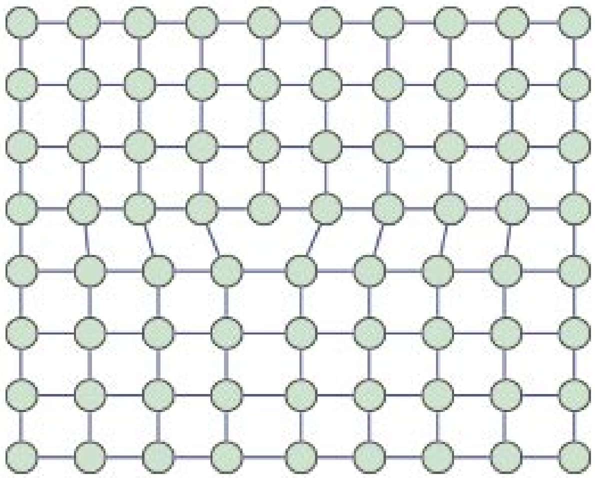
Sixty years ago, solid state physicists and materials scientists began to promote the view that the forces governing the arangement of defects in crystalline solids are distinct from the Newtonian forces that are classically associated with the motion of atoms. These nonstandard forces are nowadays called configurational.

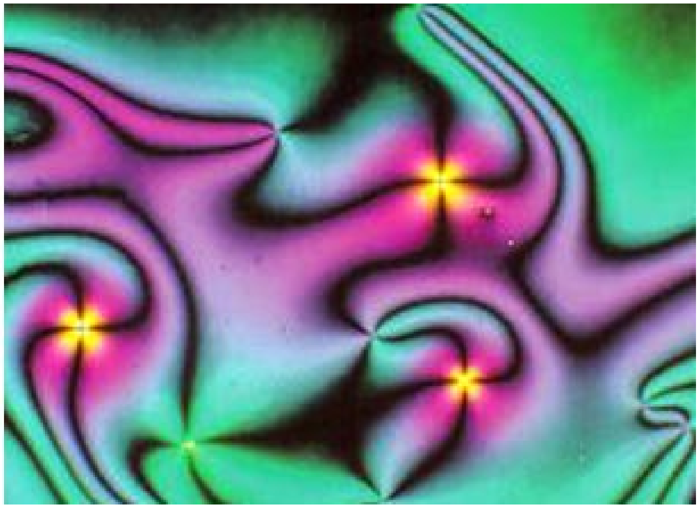
- M.O. Peach & J.S. Koehler, The forces exerted on dislocations and the stress fields produced by them, *Phys. Rev.* **80** (1950), 436–439.
- J.D. Eshelby, The force on an elastic singularity, *Phil. Trans. R. Soc. A* **244** (1951), 87–112.
- C. Herring, Surface tension as a motivation for sintering, in *The Physics of Powder Metallurgy* (W.E. Kingston, ed.), McGraw-Hill, New York, 1951.
- W.W. Mullins, Two-dimensional motion of idealized grain boundaries, *J. Appl. Phys.* **27** (1956), 900–904.

- Configurational forces act over *nonmaterial* entities, such as:
  - Vacancies, substitutional impurities, interstitial impurities

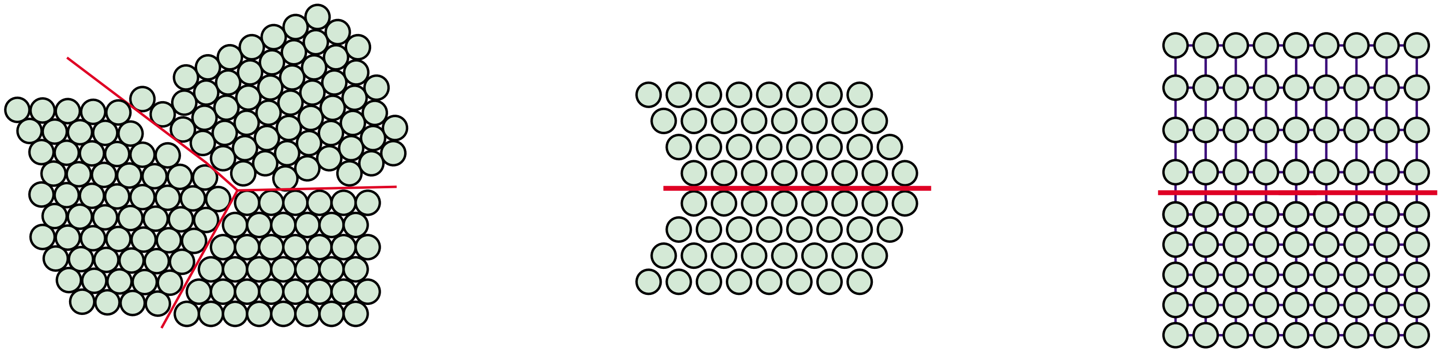


  - Dislocations, disclinations

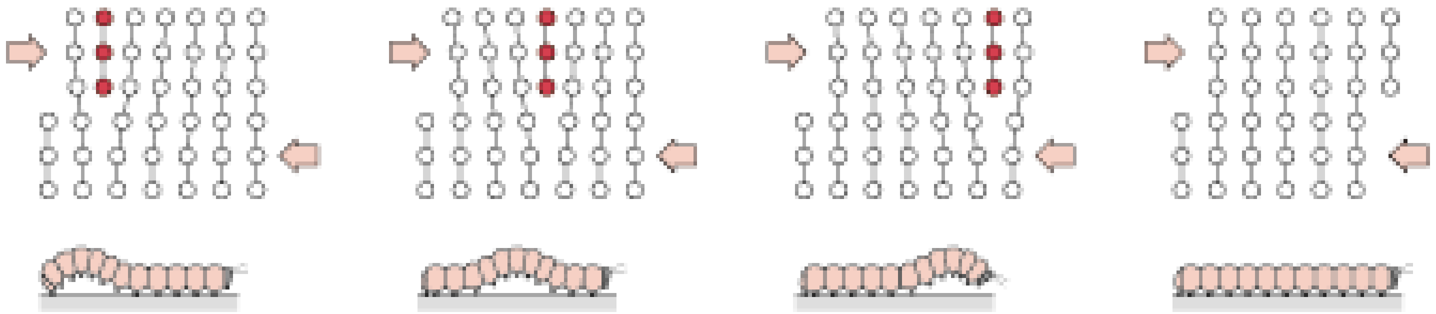




- Grain boundaries, twin boundaries, phase interfaces



- Defects move relative to the underlying material



and, thus, involve kinematical descriptors and power-conjugate pairings that are distinct from those associated with the motion of the material.

How are configurational forces characterized?

- The early workers relied exclusively on variational arguments.
- This approach persisted until nearly two decages ago at which point Gurtin began developing an approach designed to describe dynamical processes involving dissipation.
- Gurtin's program involves:
    - Introducing configurational forces as primitive quantities subject to a balance distinct from those governing standard Newtonian forces.
    - Accounting properly for all power expenditures and using the second law of thermodynamics to obtain constitutive restrictions on configurational forces.
- The program has been applied successfully to develop theories for various classes of phase transformations, including most recently evaporation-condensation processes in fluids—where viscous dissipation is of prominent importance.

Treatment of the contact line

For a segment $\mathcal{L}$ of $\mathcal{C}$, the configurational momentum balance is imposed in the form

$$\int_{\mathcal{L}}(\mathbb{C}_{\mathsf{LS}} - \mathbb{C}_{\mathsf{SV}})\mathbf{m}\,\mathrm{d}s - \int_{\mathcal{L}}\mathbb{C}_{\mathsf{LV}}\mathbb{t}\,\mathrm{d}s + \mathbf{c}_{\mathcal{C}}\Big|_{\partial\mathcal{L}} + \int_{\mathcal{L}}\mathbf{f}_{\mathcal{C}}\,\mathrm{d}s = \mathbf{0},$$

where:

- $\mathbb{C}_{\mathsf{LV}}$, $\mathbb{C}_{\mathsf{LS}}$, and $\mathbb{C}_{\mathsf{SV}}$ are interfacial configurational stresses analogous to the interfacial Cauchy stresses $\mathbb{T}_{\mathsf{LV}}$, $\mathbb{T}_{\mathsf{LS}}$, and $\mathbb{T}_{\mathsf{SV}}$. However, they needn't be symmetric.
- $\mathbf{c}_{\mathcal{C}}$ is a configurational line tension analogous to $\boldsymbol{\tau}_{\mathcal{C}}$. However, it needn't be tangential.
- $\mathbf{f}_{\mathcal{C}}$ is an internal configurational line force.

The configurational balance should be compared with the mechanical balance

$$\int_{\mathcal{L}}(\mathbb{T}_{\mathsf{LS}} - \mathbb{T}_{\mathsf{SV}})\mathbf{m}\,\mathrm{d}s - \int_{\mathcal{L}}\mathbb{T}_{\mathsf{LV}}\mathbb{t}\,\mathrm{d}s + \boldsymbol{\tau}_{\mathcal{C}}\Big|_{\partial\mathcal{L}} + \int_{\mathcal{L}}r_{\mathcal{C}}\mathbf{e}\,\mathrm{d}s = \mathbf{0}.$$

The final, intrinsic form of the free-energy inequality for a segment $\mathcal{L}$ of $\mathcal{C}$ is

$$\begin{aligned}\frac{d}{dt}\int_{\mathcal{L}}\psi_{\mathcal{C}}\,\mathsf{d}s \leq -\int_{\mathcal{L}} f_{\mathcal{C}}V_{\mathcal{C}}^{\mathsf{mig}}\,\mathsf{d}s + \int_{\mathcal{L}}\tau_{\mathcal{C}}\mathbf{m}\cdot\frac{\partial\mathbf{u}}{\partial s}\,\mathsf{d}s \\ + \int_{\mathcal{L}}\xi_{\mathcal{C}}\frac{\partial V_{\mathcal{C}}^{\mathsf{mig}}}{\partial s}\,\mathsf{d}s - \int_{\mathcal{L}}\psi_{\mathcal{C}}\kappa_{\mathcal{C}}V_{\mathcal{C}}^{\mathsf{mig}}\,\mathsf{d}s + \psi_{\mathcal{C}}V_{\mathcal{C}}^{\mathsf{mig}}\big|_{\partial\mathcal{L}},\end{aligned}$$

where:

- $V_{\mathcal{C}}^{\mathsf{mig}}$ is the component of the velocity of $\mathcal{C}$ in the direction of $\mathbf{m}$ relative to the component $\mathbf{u}\cdot\mathbf{m}$ of the fluid velocity $\mathbf{u}$ at $\mathcal{C}$ in the direction of $\mathbf{m}$.

- $\xi_{\mathcal{C}} = \mathbf{c}_{\mathcal{C}}\cdot\mathbf{m}$ is the normal component of the configurational line stress $\mathbf{c}_{\mathcal{C}}$ (which is analogous to the Cauchy line stress $\boldsymbol{\tau}_{\mathcal{C}}$).

- $f_{\mathcal{C}} = \mathbf{f}_{\mathcal{C}}\cdot\mathbf{m}$ is the normal component of the internal configurational force $\mathbf{f}_{\mathcal{C}}$.

General contact line equations

Normal component of the linear-momentum balance:

$$\boxed{\psi_{\mathsf{LV}}\cos\theta + \mathbf{m}\cdot\mathbb{S}_{\mathsf{LV}}\mathbb{t} + \psi_{\mathsf{LS}} - \psi_{\mathsf{SV}} - \tau_{\mathcal{C}}\kappa_{\mathcal{C}} = 0}$$

Tangential component of the linear-momentum balance:

$$\boxed{\mathbf{t}\cdot\mathbb{S}_{\mathsf{LV}}\mathbb{t} + \frac{\partial\tau_{\mathcal{C}}}{\partial s} = 0}$$

Normal component of the configurational-momentum balance:

$$\boxed{\begin{aligned}&\psi_{\mathsf{LV}}\cos\theta + \psi_{\mathsf{LS}} - \psi_{\mathsf{SV}} - \psi_{\mathcal{C}}\kappa_{\mathcal{C}} + \frac{\partial\psi_{\mathcal{C}}}{\partial s}\cos\theta\\ &\qquad\qquad\qquad - \xi_{\mathcal{C}}\kappa_{\mathcal{C}}\cos\theta + \frac{\partial\xi_{\mathcal{C}}}{\partial s} + \mathbb{c}_{\mathsf{LV}}\cdot\mathbb{t} = f_{\mathcal{C}}\end{aligned}}$$

Thermodynamic restrictions

Granted that $\psi_{\mathcal{C}}$ is constant, $\tau_{\mathcal{C}}$, $\xi_{\mathcal{C}}$, and $f_{\mathcal{C}}$ are restricted by a dissipation inequality,

$$\boxed{(\psi_{\mathcal{C}} - \tau_{\mathcal{C}})\mathbf{t} \cdot \frac{\partial \mathbf{u}}{\partial s} + f_{\mathcal{C}} V_{\mathcal{C}}^{\mathsf{rel}} - \xi_{\mathcal{C}} \frac{\partial V_{\mathcal{C}}^{\mathsf{rel}}}{\partial s} \le 0,}$$

that expresses the second law of thermodynamics and suggests that, at very least,

- $\psi_{\mathcal{C}} - \tau_{\mathcal{C}}$ should be given constitutively by a function depending upon $\mathbf{t} \cdot (\partial \mathbf{u}/\partial s)$,
- $f_{\mathcal{C}}$ should be given constitutively by a function depending upon $V_{\mathcal{C}}^{\mathsf{rel}}$, and
- $\xi_{\mathcal{C}}$ should be given constitutively by a function depending upon $\partial V_{\mathcal{C}}^{\mathsf{rel}}/\partial s$.

Allowing for linear, coupled dissipative mechanisms yields

$$\begin{aligned}
\psi_{\mathcal{C}} - \tau_{\mathcal{C}} &= -\gamma_{11}\mathbf{t}\cdot\frac{\partial \mathbf{u}}{\partial s} - \gamma_{12}V_{\mathcal{C}}^{\mathsf{rel}} - \gamma_{13}\frac{\partial V_{\mathcal{C}}^{\mathsf{rel}}}{\partial s}, \\
f_{\mathcal{C}} &= -\gamma_{21}\mathbf{t}\cdot\frac{\partial \mathbf{u}}{\partial s} - \gamma_{22}V_{\mathcal{C}}^{\mathsf{rel}} - \gamma_{23}\frac{\partial V_{\mathcal{C}}^{\mathsf{rel}}}{\partial s}, \\
-\xi_{\mathcal{C}} &= -\gamma_{31}\mathbf{t}\cdot\frac{\partial \mathbf{u}}{\partial s} - \gamma_{23}V_{\mathcal{C}}^{\mathsf{rel}} - \gamma_{33}\frac{\partial V_{\mathcal{C}}^{\mathsf{rel}}}{\partial s},
\end{aligned}$$

where the matrix

$$\begin{pmatrix} \gamma_{11} & \gamma_{12} & \gamma_{13} \\ \gamma_{12} & \gamma_{22} & \gamma_{23} \\ \gamma_{12} & \gamma_{23} & \gamma_{33} \end{pmatrix}$$

of contact-line viscosities is positive semidefinite.

Questions

1. Are dissipative mechanisms important and, if so, is coupling between those mechanisms significant?
2. Can we design experiments to accurately measure the contact-line viscosities? Contact-line rheometry???

Other questions for contact lines

- Why does the variational approach yield two equilibrium conditions on the liquid-vapor interface but only a single condition at the contact line?
- Does $\tau_{\mathcal{C}} = \psi_{\mathcal{C}}$ in equilibrium?
- Does a single balance suffice away from equilibrium?

Answers

- In equilibrium, unless the interface and contact line are massy, there is no analog of the driving force $\psi + p/\varrho + \varphi$ and the normal components of the linear- and configurational-momentum balances for $\mathcal{C}$ coalesce.
- In general, $\tau_{\mathcal{C}} = \psi_{\mathcal{C}} + \sigma_{\mathcal{C}}$, where $\sigma_{\mathcal{C}}$ is dissipative.
- Away from equilibrium, the normal component of the configurational-momentum balance on the contact line is not redundant. It governs the kinetics of contact line motion.

Connection with previous contact line conditions

- When dissipative effects are neglected, the balances for the contact line $\mathcal{C}$ reduce to a single balance

$$\boxed{\psi_{\mathsf{LV}}\cos\theta + \psi_{\mathsf{LS}} - \psi_{\mathsf{SV}} - \psi_{\mathcal{C}}\kappa_{\mathcal{C}} + \frac{\partial\psi_{\mathcal{C}}}{\partial s}\cos\theta = 0.}$$

This equation was derived by Boruvka & Newmann (1977) using variational means. More recently, it was rediscovered by Swain & Lipowsky (1998) and Schimmele, Napiórkowski & Dietrich (2007).

- In a very early attempt to explain observed hysteretic behavior of a contact line, Adam & Jessop (1925) used

$$\boxed{\psi_{\mathsf{LV}}\cos\theta + \psi_{\mathsf{LS}} - \psi_{\mathsf{SV}} = f,}$$

with f depending on the contact line velocity but not necessarily in a way that would ensure satisfaction of the second law of thermodynamics.

Take-home points

- Away from equilibrium,
  - the Young equation is replaced by an equation expressing linear-momentum balance, and
  - the configurational-momentum balance yields an additional, independent equation for the kinetics of contact line motion.
- At equilibrium,
  - the additional, independent equation for the contact line is satisfied trivially, and
  - the variational condition for the contact line and the Young equation coincide.
- Configurational forces arise and are important not only to lattice defects, but also to phase transformations in fluids.
- Analysis of the full system of equations for an evaporating drop is in progress. Experiments are also being designed.
- Questions regarding the role/importance of dissipative mechanisms at contact lines remain unaddressed. . .