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# On derivation of thermodynamically consistent boundary conditions for Korteweg type fluids

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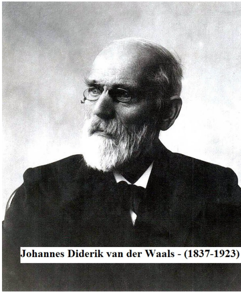
# Korteweg type fluids

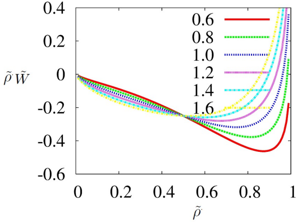
- Allow to model phase co-existence and phase change phenomena (liquid-vapor)
- Allow to incorporate surface tension effects into bulk equations of motion (e.g. Navier Stokes eq.)
- Diffuse interface type model ($\times$ sharp interface) - i.e. interface between phases is a bulk region of finite thickness (in reality typically $\sim 10\text{Å}$)
- Order parameter $=$ density - no extra equation for order parameter (as e.g. in Cahn-Hilliard eq.)

- Simplest Korteweg type model: van der Waals bulk free energy + interface penalization by non-local $|\nabla \rho|$ term

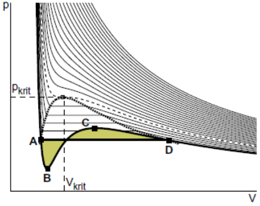
$$\mathcal{F} = \int_\Omega \rho \left( W(\rho, \vartheta) + \frac{\sigma}{2\rho} |\nabla \rho|^2 \right) \, dx$$

$$W(\rho, \vartheta) = -a\rho + R\vartheta \log\left(\frac{\rho}{b-\rho}\right) - c\vartheta \log\left(\frac{\vartheta}{\vartheta_0}\right) - d\vartheta + e$$




- van der Waals eqution of state:

$$p = \rho^2 \frac{\partial W}{\partial \rho} = R\vartheta\rho \frac{b}{b-\rho}$$




from Brand (96)

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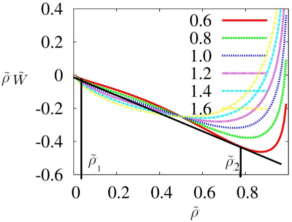


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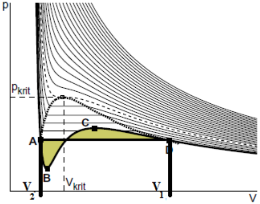



from Brand (96)

# Navier-Stokes-Korteweg system

- Coupling of surface tension effects with flow
- Additional stress - Korteweg stress tensor **K**

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0$$

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) = -\nabla p + \operatorname{div} \mathsf{T} + \operatorname{div} \mathsf{K} + \rho \mathbf{f}$$

- Constitutive relations:

$$p = \rho^2 \frac{\partial W}{\partial \rho} = R\vartheta\rho \frac{b}{b-\rho}$$

$$\mathsf{T} = \lambda \operatorname{div} \mathbf{v} \mathbf{I} + 2\mu \boldsymbol{D}(\mathbf{v})$$

$$\mathsf{K} = \sigma \left( \rho \Delta \rho + \frac{1}{2} |\nabla \rho|^2 \right) \mathbf{I} - \sigma \nabla \rho \otimes \nabla \rho$$

# Korteweg type fluids

- First thermodynamic derivation - Dunn&Serrin (1983) - rational thermodynamics
- We employ thermodynamic model in the bulk by Heida&Málek (2010)
- Starting point - extension of this model (free parameter $\alpha \in \langle 0, 1 \rangle$)

$$\text{Heat flux:} \quad \mathbf{q} = \kappa \nabla \left( \frac{1}{\vartheta} \right) + \alpha \rho^2 \frac{\partial \hat{\varepsilon}}{\partial \nabla \rho} \operatorname{div} \mathbf{v}$$

$$\text{Entropy flux:} \quad {}^{\eta}\Phi_\Omega = \frac{1}{\vartheta} \left( \kappa \nabla \left( \frac{1}{\vartheta} \right) - (1 - \alpha) \rho^2 \frac{\partial \hat{\varepsilon}}{\partial \nabla \rho} \operatorname{div} \mathbf{v} \right)$$

- $\alpha = 1$ - Dunn&Serrin (1983) (interstitial working contribution in $\mathbf{q}$) and classical entropy flux

# Integral balance, single continuum - general form

- Additive quantity $\Psi$

$$\boldsymbol{\Psi} = \int_{\Omega^+ \cup \Omega^-} \Psi_\Omega \, dx + \int_\Gamma \Psi_\Gamma \, dS$$

- Flux ${}^\Psi\mathcal{F}$

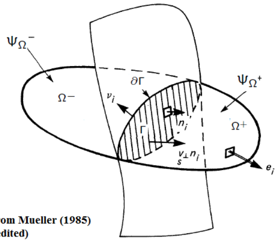
$${}^\Psi\mathcal{F} = \int_{S^+ \cup S^-} {}^\Psi\Phi_\Omega \cdot \mathbf{n} \, dS + \int_{\partial\Gamma} {}^\Psi\Phi_\Gamma \cdot \boldsymbol{\nu} \, dl$$

- Production ${}^\Psi\mathcal{P}$

$${}^\Psi\mathcal{P} = \int_{\Omega^+ \cup \Omega^-} {}^\Psi\Pi_\Omega \, dx + \int_\Gamma {}^\Psi\Pi_\Gamma \, dS$$

- Supply ${}^\Psi\mathcal{S}$

$${}^\Psi\mathcal{S} = \int_{\Omega^+ \cup \Omega^-} {}^\Psi\Sigma_\Omega \, dx + \int_\Gamma {}^\Psi\Sigma_\Gamma \, dS$$




from Mueller (1985)
(edited)

# Integral balance, single continuum - generic form

- Integral form

$$\frac{d}{dt}\boldsymbol{\Psi} = -{}^{\Psi}\mathcal{F} + {}^{\Psi}\mathcal{P} + {}^{\Psi}\mathcal{S}$$

- Generalized Reynolds' transport theorem + Gauss theorem + diff. geometry $\rightarrow$ local form

$$\frac{\partial \Psi_\Omega}{\partial t} + \mathrm{div}({}^{\Psi}\Phi_\Omega + \Psi_\Omega \mathbf{v}) - {}^{\Psi}\Pi - {}^{\Psi}\Sigma = 0 \qquad \text{in } \Omega^+ \cup \Omega^-$$

$$\frac{\partial \Psi_\Gamma}{\partial t} + \mathrm{div}_\Gamma({}^{\Psi}\Phi_\Gamma + \Psi_\Gamma \mathbf{v}_\Gamma) \underbrace{-2K_m \Psi_\Gamma \mathbf{v}_\Gamma^\perp}_{\text{geom. curvature effect}} - {}^{\Psi}\Pi_\Gamma - {}^{\Psi}\Sigma_\Gamma$$

$$= \underbrace{-\left[{}^{\Psi}\Phi_\Omega + \Psi_\Omega(\mathbf{v} - \mathbf{v}_\Gamma^\perp)\mathbf{n}_\Gamma\right]_-^+ \cdot \mathbf{n}_\Gamma}_{\text{coupling with bulk}} \qquad \text{at } \Gamma$$

# Local form of balance laws - bulk

- Mass balance

$$\frac{\partial \varrho}{\partial t} + \operatorname{div}(\varrho \mathbf{v}) = 0$$

- Momentum balance

$$\frac{\partial (\varrho \mathbf{v})}{\partial t} + \operatorname{div}(\varrho \mathbf{v} \otimes \mathbf{v}) = \operatorname{div} \mathsf{T} + \varrho \mathbf{f}$$

- Energy balance

$$\frac{\partial}{\partial t}\left(\varrho(e + \frac{1}{2}|\mathbf{v}|^2)\right) + \operatorname{div}\left(\varrho(e + \frac{1}{2}|\mathbf{v}|^2)\mathbf{v}\right) = \operatorname{div}(\mathsf{T}\mathbf{v} - \mathbf{q}) + \varrho(\mathbf{b} \cdot \mathbf{v} + q)$$

- Entropy balance

$$\frac{\partial (\varrho \eta)}{\partial t} + \operatorname{div}(\varrho \eta \mathbf{v}) + \operatorname{div} \mathbf{\Phi} = \xi$$

# Local form of balance laws - interface

- Mass balance

$$\frac{\partial \varrho_\Gamma}{\partial t} + \mathrm{div}_\Gamma(\varrho_\Gamma \mathbf{v}_\Gamma) - 2K_m \varrho_\Gamma \mathbf{v}_\Gamma^\perp = -[\varrho(\mathbf{v} - \mathbf{v}_\Gamma)]_-^+ \cdot \mathbf{n}_\Gamma$$

- Momentum balance

$$\frac{\partial(\varrho_\Gamma \mathbf{v}_\Gamma)}{\partial t} + \mathrm{div}_\Gamma(\varrho_\Gamma \mathbf{v}_\Gamma \otimes \mathbf{v}_\Gamma) - 2K_m \varrho_\Gamma \mathbf{v}_\Gamma - \mathrm{div}_\Gamma \mathbf{T}_\Gamma - \varrho_\Gamma \mathbf{f}_\Gamma$$
$$= \left[\varrho \mathbf{v} \otimes (\mathbf{v} - \mathbf{v}_\Gamma^\perp \mathbf{n}_\Gamma) - \mathbf{T}\right]_-^+ \cdot \mathbf{n}_\Gamma$$

- Energy balance

$$\frac{\partial}{\partial t}\left(\varrho_\Gamma(e_\Gamma + \frac{1}{2}|\mathbf{v}_\Gamma|^2)\right) + \mathrm{div}_\Gamma\left(\varrho_\Gamma(e_\Gamma + \frac{1}{2}|\mathbf{v}_\Gamma|^2)\mathbf{v}_\Gamma\right) - 2K_m \varrho_\Gamma(e_\Gamma + \frac{1}{2}|\mathbf{v}_\Gamma|^2)\mathbf{v}_\Gamma^\perp$$
$$- \mathrm{div}_\Gamma(\mathbf{T}_\Gamma \mathbf{v}_\Gamma - \mathbf{q}_\Gamma) - \varrho_\Gamma(\mathbf{b}_\Gamma \cdot \mathbf{v}_\Gamma + q_\Gamma) = -\left[\varrho(e + \frac{1}{2}|\mathbf{v}|^2)(\mathbf{v} - \mathbf{v}_\Gamma) - \mathbf{T}\mathbf{v} + \mathbf{q}\right]_-^+ \cdot \mathbf{n}_\Gamma$$

- Entropy balance

$$\frac{\partial(\varrho_\Gamma \eta_\Gamma)}{\partial t} + \mathrm{div}(\varrho_\Gamma \eta_\Gamma \mathbf{v}_\Gamma) - 2K_m \varrho_\Gamma \eta_\Gamma \mathbf{v}_\Gamma^\perp - \mathrm{div}_\Gamma \mathbf{\Phi}_\Gamma + \left[\mathbf{\Phi} + \varrho\eta(\mathbf{v} - \mathbf{v}_\Gamma^\perp \mathbf{n}_\Gamma)\right]_-^+ \cdot \mathbf{n}_\Gamma = \xi_\Gamma$$

# Local form of balance laws - interface

- Mass balance

$$\frac{\partial \varrho_\Gamma}{\partial t} + \mathrm{div}_\Gamma(\varrho_\Gamma \mathbf{v}_\Gamma) - 2K_m \varrho_\Gamma \mathbf{v}_\Gamma^\perp = -[\varrho(\mathbf{v} - \mathbf{v}_\Gamma)]_-^+ \cdot \mathbf{n}_\Gamma$$

- Momentum balance

$$\varrho_\Gamma \frac{d_\Gamma \mathbf{v}_\Gamma}{dt} - \mathrm{div}_\Gamma \mathbf{T}_\Gamma - \varrho_\Gamma \mathbf{f}_\Gamma = \left[\varrho(\mathbf{v} - \mathbf{v}_\Gamma) \otimes (\mathbf{v} - \mathbf{v}_\Gamma^\perp \mathbf{n}_\Gamma) - \mathbf{T}\right]_-^+ \cdot \mathbf{n}_\Gamma$$

- Internal energy balance

$$\frac{\partial}{\partial t}(\varrho_\Gamma e_\Gamma) + \mathrm{div}_\Gamma(\varrho_\Gamma e_\Gamma \mathbf{v}_\Gamma) - 2K_m \varrho_\Gamma e_\Gamma \mathbf{v}_\Gamma^\perp - \mathrm{div}_\Gamma \mathbf{q}_\Gamma - \varrho_\Gamma q_\Gamma$$
$$- \left(\mathbf{T}_\Gamma : \nabla_\Gamma \mathbf{v}_\Gamma + \left[\frac{\varrho}{2}(\mathbf{v}_\Gamma - \mathbf{v})^2 (\mathbf{v} - \mathbf{v}_\Gamma^\perp \mathbf{n}_\Gamma) - \mathbf{T}(\mathbf{v}_\Gamma - \mathbf{v})\right]_-^+ \cdot \mathbf{n}_\Gamma\right)$$
$$= - \left[\varrho e(\mathbf{v} - \mathbf{v}_\Gamma^\perp \mathbf{n}_\Gamma) + \mathbf{q}\right]_-^+ \cdot \mathbf{n}_\Gamma$$

- Entropy balance

$$\frac{\partial(\varrho_\Gamma \eta_\Gamma)}{\partial t} + \mathrm{div}(\varrho_\Gamma \eta_\Gamma \mathbf{v}_\Gamma) - 2K_m \varrho_\Gamma \eta_\Gamma \mathbf{v}_\Gamma^\perp - \mathrm{div}_\Gamma \mathbf{\Phi}_\Gamma + \left[\mathbf{\Phi} + \varrho\eta(\mathbf{v} - \mathbf{v}_\Gamma^\perp \mathbf{n}_\Gamma)\right]_-^+ \cdot \mathbf{n}_\Gamma = \xi_\Gamma$$

# Local form of balance laws - interface

- Key observation: Boundaries are just special interfaces
- Second law: $\xi \geq 0$, $\xi_\Gamma \geq 0$
- Constitutive procedure:
  1. Assumption on thermodynamic potential in its natural variables
  2. Identification of the bulk and surface entropy flux
  3. Identification of the bulk and surface entropy production terms
  4. Constitutive ansatz or "maximization of the rate of entropy production"-derivation which ensures the fulfillment of the second law

# Example - boundary conditions for Korteweg type fluids

- 3 models of different complexity

$$\tilde{\varepsilon}_\Gamma = \tilde{\varepsilon}_\Gamma(\tilde{\eta}_\Gamma, \rho) \ , \qquad \tilde{\varepsilon}_\Gamma = \tilde{\varepsilon}_\Gamma(\tilde{\eta}_\Gamma) \ , \qquad \tilde{\varepsilon}_\Gamma \equiv 0, \ \tilde{\eta}_\Gamma \equiv 0$$

- Boundary considered as a static membrane, non-penetrating

$$\mathbf{v}^+ = \mathbf{0} \qquad \mathbf{v}_\Gamma = \mathbf{0} \qquad \mathbf{v}^- \cdot \mathrm{n}_\Gamma = 0$$

- Surface momentum balance

$$-\operatorname{div}_\Gamma \mathbf{T}_\Gamma = [\mathbf{T}] \cdot \mathrm{n}_\Gamma$$

- Membrane model - only constant surface tension constitutes the surface stress tensor:

$$\operatorname{div}_\Gamma \mathbf{T}_\Gamma = 2K_m \sigma \mathrm{n}_\Gamma \Rightarrow ([\mathbf{T}] \cdot \mathrm{n}_\Gamma)_\tau = 0,$$

- Friction:

$$\left[\mathbf{T}^{\mathrm{T}} \mathbf{v}\right] \cdot \mathrm{n}_\Gamma \quad = \quad (\mathbf{T}\mathrm{n}_\Gamma)_\tau \cdot [\mathbf{v}_\tau] = -(\mathbf{T}\mathrm{n}_\Gamma)_\tau \cdot \mathbf{v}_\tau^- \, .$$

# Example - boundary conditions for Korteweg type fluids

- Heat flux from the bulk

$$\mathbf{q}^{-} = \kappa \nabla \left( \frac{1}{\vartheta} \right) + \alpha (\rho^{-})^2 \frac{\partial \hat{\varepsilon}^{-}}{\partial \nabla \rho^{-}} \operatorname{div} \mathbf{v}^{-}$$

- Entropy flux from the bulk

$${}^{\eta}\Phi_{\Omega} = \frac{1}{\vartheta} \left( \kappa \nabla \left( \frac{1}{\vartheta} \right) - (1-\alpha)(\rho^{-})^2 \frac{\partial \hat{\varepsilon}^{-}}{\partial \nabla \rho^{-}} \operatorname{div} \mathbf{v}^{-} \right)$$

- Identity

$$\operatorname{div} \mathbf{v}^{-} = \frac{\partial \mathbf{v}_n^{-}}{\partial \mathrm{n}_{\Gamma}} + 2K_m \mathbf{v}^{-} \cdot \mathrm{n}_{\Gamma} + \operatorname{div}_{\Gamma} \mathbf{v}_{\tau}^{-} = \frac{\partial \mathbf{v}_{\mathrm{n}}^{-}}{\partial \mathrm{n}_{\Gamma}} + \operatorname{div}_{\Gamma} \mathbf{v}_{\tau}^{-}$$

- Surface energy balance
- Surface entropy balance

# Example - boundary conditions for Korteweg type fluids

- Identification of surface entropy supply

$$ {}^{\eta}\Sigma_{\Gamma} = \frac{\rho_{\Gamma} r_{\Gamma}}{\vartheta_{\Gamma}}, $$

- Identification of surface entropy flux
- Identification of surface entropy production as a product of thermodynamic fluxes and affinities

$$ {}^{\eta}\Pi_{\Gamma} = \sum_{\alpha} \mathcal{J}_{\alpha} \mathcal{X}_{\alpha} $$

- Linear Irreversible Thermodynamics closure relations - positive definiteness of entropy production

# Boundary conditions for Korteweg type fluids - general form

- Heat transfer along $\Gamma$

$$\mathbf{q}_\Gamma = c_1 \nabla_\Gamma \left( \frac{1}{\vartheta_\Gamma} \right) + c_2 \mathbf{v}_\tau^-$$

- Generalized slip

$$(\mathbf{T} \mathrm{n}_\Gamma)_\tau = c_3 \mathbf{v}_\tau^- + c_4 \nabla_\Gamma \left( \frac{1}{\vartheta_\Gamma} \right) + c_5 (\nabla \rho^-)_\tau$$

- Kapitza resistance ("temperature slip")

$$\kappa \frac{\partial}{\partial \mathrm{n}_\Gamma} \left( \frac{1}{\vartheta} \right)^- = c_6 \left( \frac{1}{\vartheta_\Gamma} - \frac{1}{\vartheta^-} \right)$$

- Dynamic contact angle

$$\frac{\partial \rho^-}{\partial \mathrm{n}_\Gamma} = c_7 + c_8 \frac{\partial \mathbf{v}_n^-}{\partial \mathrm{n}_\Gamma} + c_9 \,\mathrm{div}\, \mathbf{v}^-$$

# Dynamic contact angle - numerical experiments

- Dimensionless formulation according to Gomez et al. (2010)

$$\frac{\partial \tilde{\rho}}{\partial \tilde{t}} + \tilde{\mathrm{div}}(\tilde{\rho}\tilde{\mathbf{v}}) = 0$$

$$\frac{\partial (\tilde{\rho}\tilde{\mathbf{v}})}{\partial \tilde{t}} + \tilde{\mathrm{div}}\left(\tilde{\rho}\tilde{\mathbf{v}} \otimes \tilde{\mathbf{v}} - \tilde{p}\mathbf{I}\right) = \frac{1}{\mathrm{Re}} \tilde{\mathrm{div}} \tilde{\mathbf{T}}^{v} - \mathrm{Ca}^2 \tilde{\rho} \tilde{\nabla}(\tilde{\Delta}\tilde{\rho}) + \tilde{\rho}\tilde{\mathbf{f}}$$

- Constitutive relations:

$$\tilde{p} = \frac{8}{27} \frac{\tilde{\vartheta}\tilde{\rho}}{1 - \tilde{\rho}} - \tilde{\rho}^2$$

$$\tilde{\mathbf{T}}^{v} = -\frac{1}{3} \tilde{\mathrm{div}} \tilde{\mathbf{v}} \mathbf{I} + \left(\tilde{\nabla}\tilde{\mathbf{v}} + \tilde{\nabla}^T \tilde{\mathbf{v}}\right)$$

- Dimensionless parameters:

$$\mathrm{Ca} = \frac{\sqrt{\sigma/a}}{L_0} = \frac{h}{L_0} \qquad \mathrm{Re} = \frac{L_0 b \sqrt{ab}}{\mu} = \alpha \mathrm{Ca}^{-1}$$

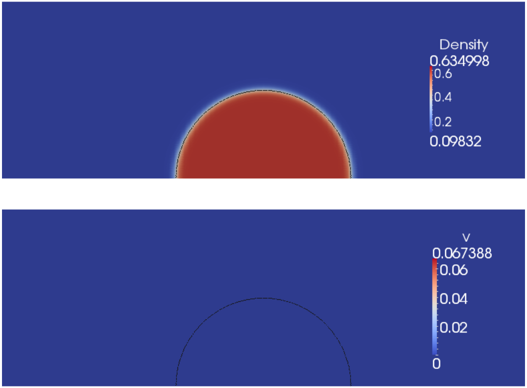
# Dynamic contact angle - numerical experiments

- Isothermal compressible Navier-Stokes-Korteweg system
- Implementation: FEM package FEniCS (www.fenics.com)
- Non-conservative form of the K. tensor: $\operatorname{div} \mathbf{K} = \sigma \rho \nabla \Delta \rho$
- SUPG stabilization of mass transport eq.
- $P_1(P)$-$P_2(\rho, \Delta\rho, \mathbf{v})$ space discretization
- Backward-Euler time-discretization
- Domain $\Omega = (0,3) \times (0,1)$, $100 \times 100 \times 4$
- free-slip $+$ no-slip b.c.

# Numerical experiments

- Static contact angle - no gravity, $\vartheta = 0.85\vartheta^{crit}$

$$\frac{\partial \rho}{\partial \mathrm{n}_\Gamma} = -\cos\gamma |\nabla \rho| \sim -\cos\gamma \frac{(\rho-\rho_{min})(\rho_{max}-\rho)}{4} \frac{\rho_{max}-\rho_{min}}{\delta}$$



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# Numerical experiments

- Static contact angle + gravity, $\vartheta = 0.85\vartheta^{crit}$

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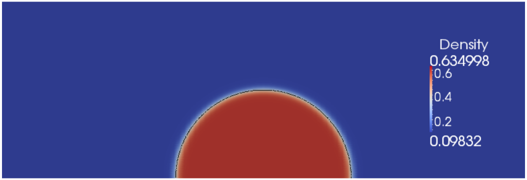


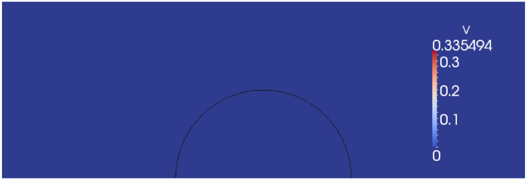

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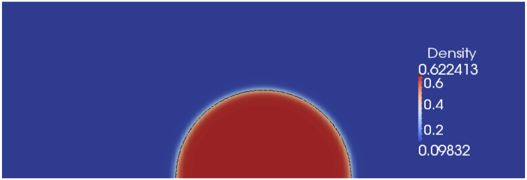


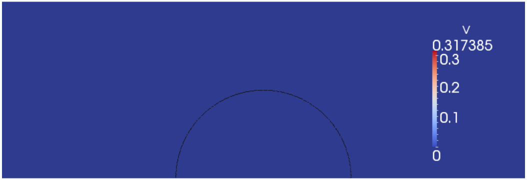

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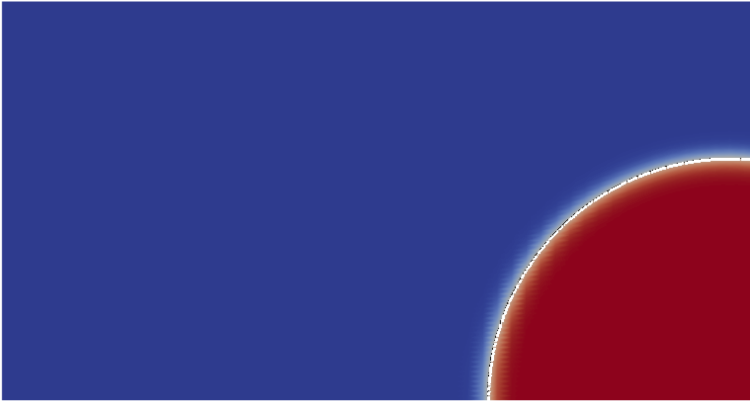
# Numerical experiments

- Comparison - dynamic (white contour) v.s. static (black contour) contact angle + gravity, $\vartheta = 0.85\vartheta^{crit}$



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- Comparison - dynamic (white contour) v.s. static (black contour) contact angle + gravity, $\vartheta = 0.85\vartheta^{crit}$

# Conclusion

- We presented a self-consistent thermodynamic framework for the treatment of boundary conditions
- For Korteweg fluid model the general class of b.c. represents a generalization of Xu et al. (2012)
- A particular interesting result is the class of dynamic contact angle conditions
- Preliminary numerical experiments indicate possible interesting dynamical effects

Thank you for your attention!