Dynamic Van der Waals Theory

A diffuse interface model for **two-phase hydrodynamics** involving **the liquid-gas transition** in non-uniform temperature [A. Onuki, PRL (2005) & PRE (2007)]

Hydrodynamic equations
for liquid-gas flows in the bulk region
[well developed]
+
Boundary conditions at fluid-solid interface
[J. Chem. Phys. (2010) and ongoing]

Helmholtz free energy density:

$$f(n,T) = nk_B T\left[\ln\left(\lambda_{\text{th}}^3 n\right) - 1 - \ln\left(1 - v_0 n\right)\right] - \varepsilon v_0 n^2$$

Internal energy density, entropy per molecule, and pressure

$$e(n,T) = 3nk_B T/2 - \varepsilon v_0 n^2$$

$$s(n,T) = -k_B \ln\left[\lambda_{\text{th}}^3 n / \left(1 - v_0 n\right)\right] + 5k_B/2$$

$$p(n,T) = nk_B T/\left(1 - v_0 n\right) - \varepsilon v_0 n^2$$

Gradient contributions to the internal energy density and entropy density

$$\hat{e} = e + \frac{K(n)}{2}\left|\nabla n\right|^2 \qquad \hat{S} = ns(n,e) - \frac{C(n)}{2}\left|\nabla n\right|^2$$

Free energy minimization leads to the equilibrium structure of a diffuse liquid-gas interface. *van der Waals*

Elasticity in one-component liquid-gas systems, manifested through a reversible stress tensor $-\overleftrightarrow{\mathbf{\Pi}}$, which is anisotropic.

Balance equations for particle number, momentum, and energy

$$\frac{\partial n}{\partial t}+\nabla\cdot(n\mathbf{v})=0$$ — the continuity equation

$$\frac{\partial}{\partial t}(\rho\mathbf{v})+\nabla\cdot(\rho\mathbf{v}\mathbf{v})=\nabla\cdot\overleftrightarrow{\mathbf{M}}$$ — the momentum equation

$\overleftrightarrow{\mathbf{M}}\equiv-\overleftrightarrow{\mathbf{\Pi}}+\overleftrightarrow{\boldsymbol{\sigma}}$ is the total stress tensor.

reversible | irreversible (viscous)

$$\frac{\partial\hat{e}}{\partial t}+\nabla\cdot(\hat{e}\mathbf{v})=-\overleftrightarrow{\mathbf{\Pi}}:\nabla\mathbf{v}+\overleftrightarrow{\boldsymbol{\sigma}}:\nabla\mathbf{v}-\nabla\cdot\mathbf{q}$$ for the internal energy density

Use of standard thermodynamic relations

$$\frac{\partial\hat{S}}{\partial t}+\nabla\cdot\left(\hat{S}\mathbf{v}\right)=-\nabla\cdot\hat{\mathbf{J}}_f^S+\frac{1}{T}\overleftrightarrow{\boldsymbol{\sigma}}:\nabla\mathbf{v}-\frac{1}{T^2}\mathbf{q}\cdot\nabla T+\frac{1}{T}\left(-\overleftrightarrow{\mathbf{\Pi}}+\hat{p}\overleftrightarrow{\mathbf{I}}+M\nabla n\nabla n\right):\nabla\mathbf{v}$$

— *the balance equation for the density of entropy*

$$\hat{\mathbf{J}}_f^S\equiv\left[M\nabla n\left(\partial n/\partial t+\mathbf{v}\cdot\nabla n\right)+\mathbf{q}\right]/T$$ — *the total entropy flux*

The rate of entropy production in the bulk region

$$\sigma = \frac{1}{T}\overleftrightarrow{\boldsymbol{\sigma}} : \nabla \mathbf{v} - \frac{1}{T^2}\mathbf{q}\cdot\nabla T + \frac{1}{T}\left(-\overleftrightarrow{\boldsymbol{\Pi}} + \hat{p}\overleftrightarrow{\mathbf{I}} + M\nabla n\nabla n\right) : \nabla \mathbf{v}$$

The density inhomogeneity does not contribute to entropy production.

$$\boxed{-\overleftrightarrow{\boldsymbol{\Pi}} = -M\nabla n\nabla n - \hat{p}\overleftrightarrow{\mathbf{I}}}$$ — the reversible stress

$$\hat{p} = p - \frac{M}{2}|\nabla n|^2 + \frac{nM_n}{2}|\nabla n|^2 - Tn\nabla n\cdot\nabla\frac{M}{T} - Mn\nabla^2 n$$ and $$M(n,T) = K(n) + C(n)T$$

The positive definiteness of $\sigma = \frac{1}{T}\overleftrightarrow{\boldsymbol{\sigma}} : \nabla \mathbf{v} - \frac{1}{T^2}\mathbf{q}\cdot\nabla T$

can be ensured by the constitutive relations

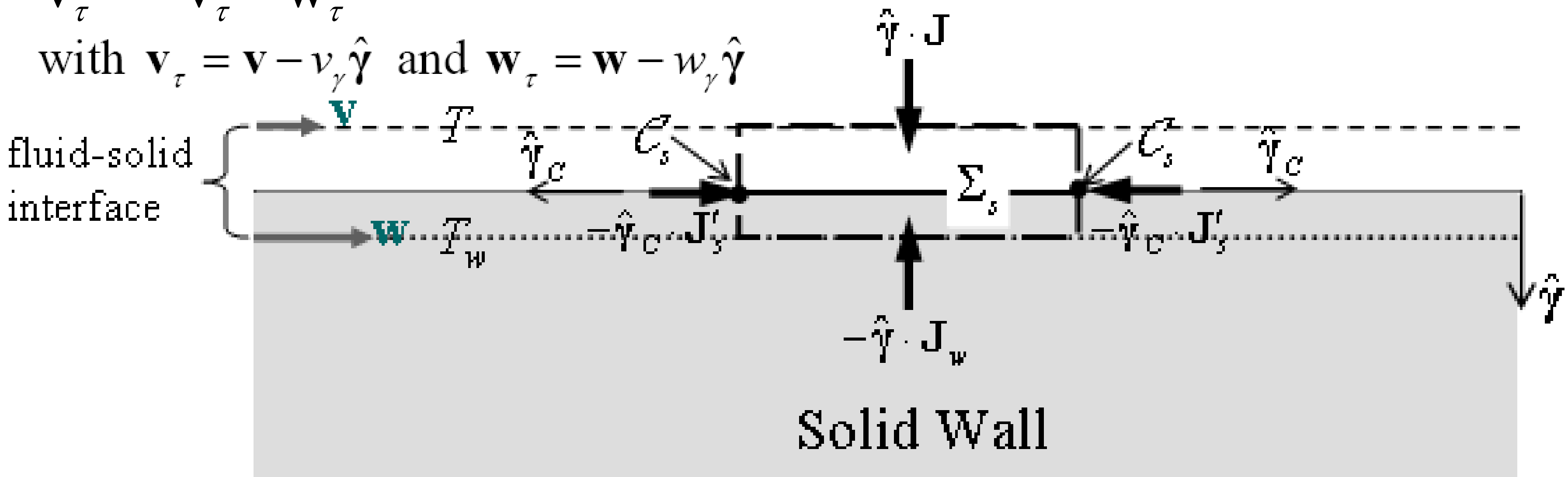
$$\overleftrightarrow{\boldsymbol{\sigma}} = \eta\left(\nabla\mathbf{v} + \nabla\mathbf{v}^T\right) + (\zeta - 2\eta/3)\overleftrightarrow{\mathbf{I}}\nabla\cdot\mathbf{v}$$ — viscous stress

$$\mathbf{q} = -\lambda\nabla T$$ — heat flux

$$v_\gamma = w_\gamma$$

$$\mathbf{v}_\tau^{slip} = \mathbf{v}_\tau - \mathbf{w}_\tau$$

with $\mathbf{v}_\tau = \mathbf{v} - v_\gamma \hat{\boldsymbol{\gamma}}$ and $\mathbf{w}_\tau = \mathbf{w} - w_\gamma \hat{\boldsymbol{\gamma}}$



A schematic illustration of the fluxes into the surface region Σ_s bounded by the closed curve $\mathcal{C}_s$

- No adsorption at the fluid-solid interface.
- The area densities of surface energy and surface entropy are flunctions of *n*, the boundary value of fluid density.
- Surface stress tensor and surface heat flux are present, but no surface viscosity.

The general boundary (jump) condition in differential form
(a special case of the extended Kotchine's theorem)

$$\frac{\partial \phi_s'}{\partial t} + \nabla_\tau \cdot \left(\phi_s' \mathbf{v}_\tau\right) = -\nabla_\tau \cdot \mathbf{J}_s' + \left[\!\left[\hat{\boldsymbol{\gamma}} \cdot \mathbf{J} \right]\!\right] + \pi_s' \quad \text{with} \quad \left[\!\left[\hat{\boldsymbol{\gamma}} \cdot \mathbf{J} \right]\!\right] \equiv \hat{\boldsymbol{\gamma}} \cdot \left(\mathbf{J} - \mathbf{J}_w\right)$$

Here the prime denotes the surface quantities whose dimensions are different from the corresponding bulk quantities.

Surface entropy and surface energy

$$S_s = \int dA\, \sigma_s'(n) \qquad E_s = \int dA\, e_s'(n)$$

Helmholtz free energy per unit area $f_s'(n,T) = e_s'(n) - T\sigma_s'(n)$

A Gibbs-type equation $d\sigma_s' = \frac{1}{T} de_s' - \frac{1}{T}\left(\frac{\partial f_s'}{\partial n}\right)_T dn$

$\gamma_{fs} = f_s'$ — the fluid-solid interfacial tension

Surface stress tensor is tangential and symmetric: $\overleftrightarrow{\mathbf{M}}_s' \equiv \gamma_{fs} \overleftrightarrow{\boldsymbol{\tau}} = f_s' \overleftrightarrow{\boldsymbol{\tau}}$

$$\overleftrightarrow{\boldsymbol{\tau}} \equiv \overleftrightarrow{\mathbf{I}} - \hat{\boldsymbol{\gamma}}\hat{\boldsymbol{\gamma}}$$

Balance equations at the fluid-solid interface

Force balance $\nabla_\tau f_s' - \hat{\boldsymbol{\gamma}} \cdot \overleftrightarrow{\mathbf{M}} + \mathbf{F} = 0$ $\begin{cases} \nabla_\tau f_s' - \hat{\boldsymbol{\gamma}} \cdot \overleftrightarrow{\mathbf{M}} \cdot \overleftrightarrow{\boldsymbol{\tau}} + \mathbf{F}_\tau = 0 \\ -\hat{\boldsymbol{\gamma}} \cdot \overleftrightarrow{\mathbf{M}} \cdot \hat{\boldsymbol{\gamma}} + F_\gamma = 0 \end{cases}$

Three forces by the interface, fluid, and wall

Energy balance

$$\frac{\partial e_s'}{\partial t} + \nabla_\tau \cdot (e_s' \mathbf{v}_\tau) = \nabla_\tau \cdot (f_s' \mathbf{v}_\tau) - \nabla_\tau \cdot \mathbf{q}_s' + [\![\hat{\boldsymbol{\gamma}} \cdot \mathbf{q}]\!] - \hat{\boldsymbol{\gamma}} \cdot \overleftrightarrow{\mathbf{M}} \cdot \mathbf{v}_\tau^{slip} - \mathbf{w}_\tau \cdot \nabla_\tau f_s'$$

$\mathbf{v}_\tau^{slip} = \mathbf{v}_\tau - \mathbf{w}_\tau$ — tangential slip velocity

First law of thermodynamics applied at the fluid-solid interface

Entropy balance from

$$\frac{\partial \sigma_s'}{\partial t} = \frac{1}{T}\frac{\partial e_s'}{\partial t} - \frac{1}{T}\left(\frac{\partial f_s'}{\partial n}\right)_T \frac{\partial n}{\partial t}$$

Entropy balance

$$\frac{\partial \sigma_s'}{\partial t} + \nabla_\tau \cdot (\sigma_s' \mathbf{v}_\tau) = -\nabla_\tau \cdot \left(\frac{\mathbf{q}_s'}{T} \right) + \left(\hat{\boldsymbol{\gamma}} \cdot \hat{\mathbf{J}}^S - \hat{\boldsymbol{\gamma}} \cdot \hat{\mathbf{J}}_w^S \right) + \sigma_{surf}$$

$$\hat{\boldsymbol{\gamma}} \cdot \hat{\mathbf{J}}^S \equiv \left(\hat{\boldsymbol{\gamma}} \cdot \mathbf{q} + M\dot{n}\nabla_\gamma n \right) / T \qquad -\hat{\boldsymbol{\gamma}} \cdot \hat{\mathbf{J}}_w^S \equiv -\hat{\boldsymbol{\gamma}} \cdot \mathbf{q}_w / T_w$$

— entropy fluxes

$$\sigma_{surf} \equiv \mathbf{q}_s' \cdot \nabla_\tau \frac{1}{T} - \left(\frac{1}{T} - \frac{1}{T_w} \right) \hat{\boldsymbol{\gamma}} \cdot \mathbf{q}_w - \frac{1}{T} \mathbf{F}_\tau \cdot \mathbf{v}_\tau^{slip} - \frac{1}{T} L\dot{n}$$

— entropy production

$$L = M\nabla_\gamma n + \left(\partial f_s' / \partial n \right)_T$$

is equal to zero in equilibrium.

Interfacial constitutive relations

$$\mathbf{q}_s' = -\lambda_s' \nabla_\tau T - \chi \mathbf{F}_\tau \qquad \kappa \hat{\boldsymbol{\gamma}} \cdot \mathbf{q}_w = -\left(\frac{1}{T} - \frac{1}{T_w} \right)$$

$$\beta \mathbf{v}_\tau^{slip} = -\beta \frac{\chi}{T} \nabla_\tau T - \mathbf{F}_\tau \qquad \alpha \dot{n} = -L$$

Balance equations
(conservation laws)

Constitutive relations

} Hydrodynamic equations

From the bulk region to the interface

Balance equations

Constitutive relations

} Hydrodynamic boundary conditions

A continuum hydrodynamic model formed by differential equations and boundary conditions.

Hydrodynamic Boundary Conditions

Density relaxation $$\alpha\left(\frac{\partial n}{\partial t}+\mathbf{v}_\tau\cdot\nabla_\tau n\right)=-M\nabla_\gamma n-\left(\frac{\partial f_s'}{\partial n}\right)_T$$

Impermeability $\hat{\boldsymbol{\gamma}}\cdot\mathbf{v}=\hat{\boldsymbol{\gamma}}\cdot\mathbf{w}=0$

Velocity slip $$\beta\mathbf{v}_\tau^{slip}=-\eta\nabla_\gamma\mathbf{v}_\tau+\left[M\nabla_\gamma n+\left(\frac{\partial f_s'}{\partial n}\right)_T\right]\nabla_\tau n-\left(\sigma_s'+\beta\frac{\chi}{T}\right)\nabla_\tau T$$

Temperature slip $$\kappa\lambda_w\nabla_\gamma T_w=\frac{1}{T}-\frac{1}{T_w}$$

Heat fluxes

$$-\lambda\nabla_\gamma T+\lambda_w\nabla_\gamma T_w=\frac{\partial e_s'}{\partial t}+\nabla_\tau\cdot\left(T\sigma_s'\mathbf{v}_\tau\right)+\mathbf{v}_\tau\cdot\nabla_\tau f_s'$$
$$-\nabla_\tau\cdot\left(\lambda_s'\nabla_\tau T\right)-\frac{1}{\beta}\mathbf{F}_\tau\cdot\mathbf{F}_\tau-\nabla_\tau\cdot\left(\chi\mathbf{F}_\tau\right)-\frac{\chi}{T}\mathbf{F}_\tau\cdot\nabla_\tau T$$

$$\mathbf{F}_\tau=\eta\nabla_\gamma\mathbf{v}_\tau-M\nabla_\gamma n\nabla_\tau n-\nabla_\tau f_s'$$ $$\nabla_\tau f_s'=-\sigma_s'\nabla_\tau T+\left(\partial f_s'/\partial n\right)_T\nabla_\tau n$$

A limiting case Xu and Qian, J. Chem. Phys. **133**, 204704 (2010)

No cross coupling: $\chi \to 0$

Constant temperatures at the fluid-solid interface: $T = T_w = \text{const.}$

$\kappa \to 0$ and fast relaxation toward thermal equilibrium in the solid

Density relaxation

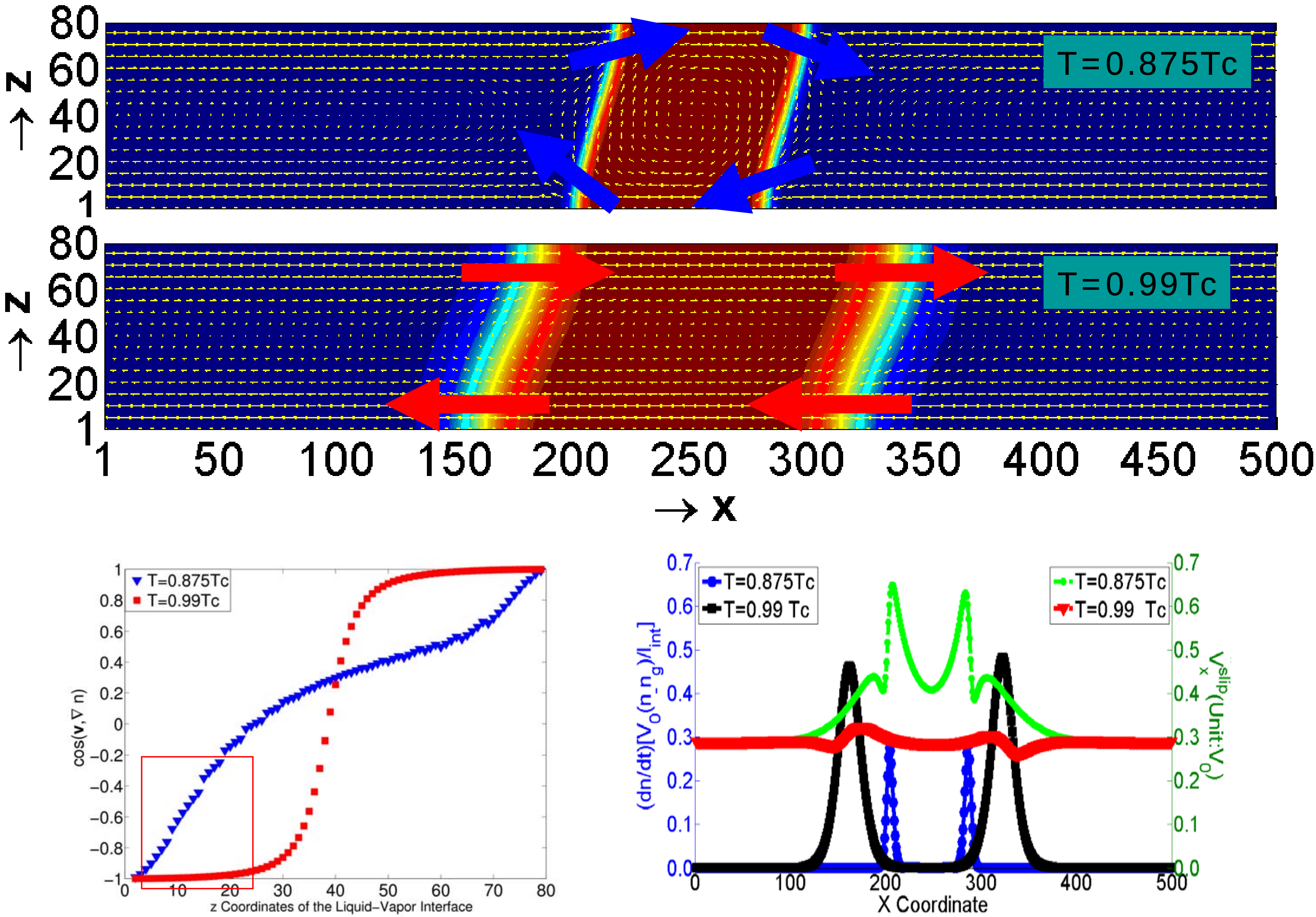
$$\alpha\left(\frac{\partial n}{\partial t} + \mathbf{v}_\tau \cdot \nabla_\tau n\right) = -M\nabla_\gamma n - \left(\frac{\partial f_s'}{\partial n}\right)_T$$

Impermeability $\hat{\boldsymbol{\gamma}} \cdot \mathbf{v} = \hat{\boldsymbol{\gamma}} \cdot \mathbf{w} = 0$

Velocity slip

$$\beta \mathbf{v}_\tau^{slip} = -\eta \nabla_\gamma \mathbf{v}_\tau + \left[M\nabla_\gamma n + \left(\frac{\partial f_s'}{\partial n}\right)_T\right]\nabla_\tau n$$

Dirichlet temperature condition $T = T_w = \text{const}$



T=0.875Tc
T=0.99Tc
→ z
→ x
1
50
100
150
200
250
300
350
400
450
500
80
60
40
20
1
T=0.875Tc
T=0.99Tc
cos(v,∇ n)
z Coordinates of the Liquid−Vapor Interface
T=0.875Tc
T=0.99 Tc
T=0.875Tc
T=0.99 Tc
(dn/dt)[V0(n_l-n_g)/l_int]
V_x^slip(Unit:V0)
X Coordinate