Materials Sciences Division, Lawrence Berkeley Nat. Laboratory
Regents' Program Review, Napa, August 2006

High Temperature Capillarity

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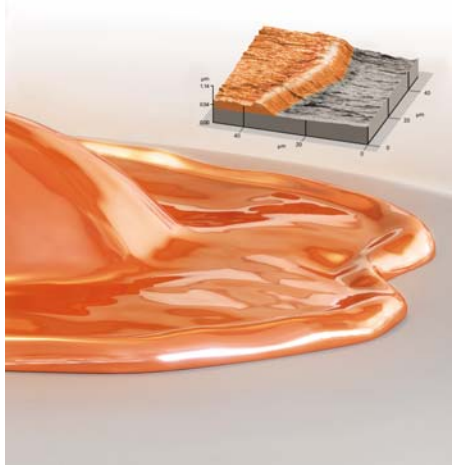

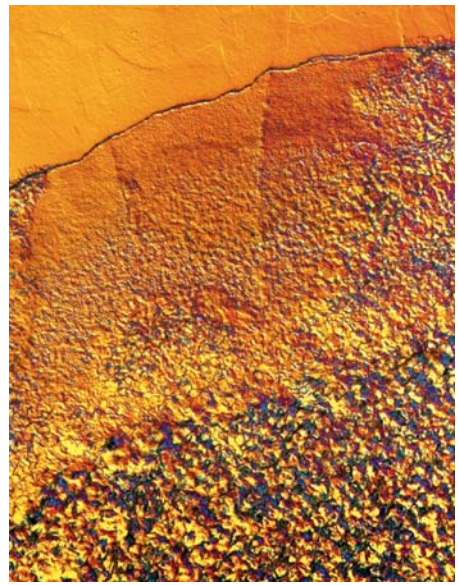

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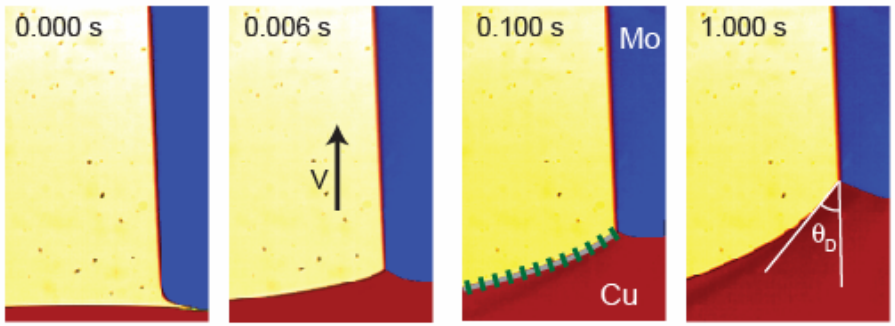
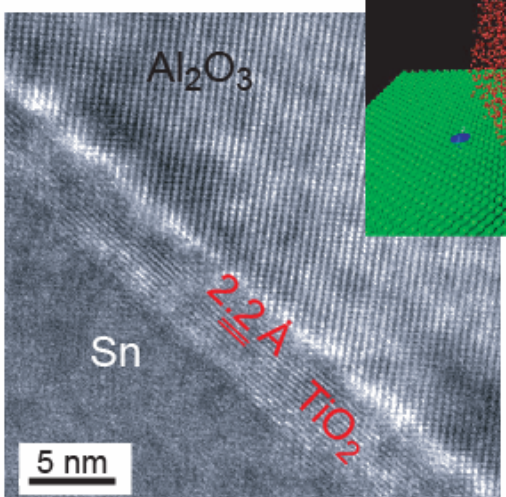
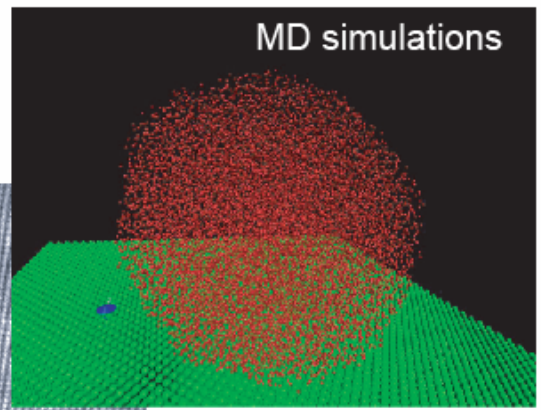
The Challenge

Develop an experimental set-up to record flow and spreading under controlled conditions: High-speed photography & image analysis



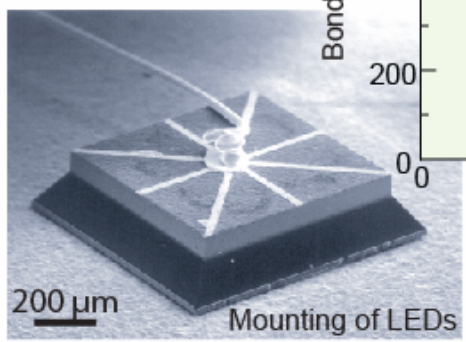
Characterization & modeling

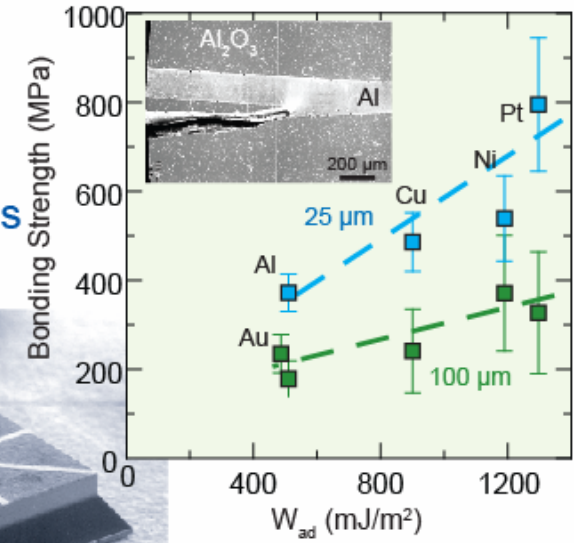


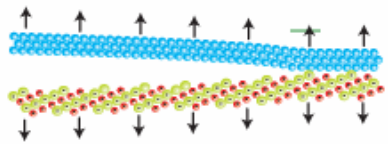


Interface formation & performance

Joining
Composites
Oxide scales
Stability of thin films & heterostructures







- Metal-oxide interfaces:
  Adhesion, atomic transport, segregation
- High-temperature flow & spreading of molten metals and oxides

Link macroscopic measurements to phenomena occurring at the microscopic and atomic levels

Metal/Oxide Interfaces-Adhesion

Fundamental role of oxygen activity: adsorption

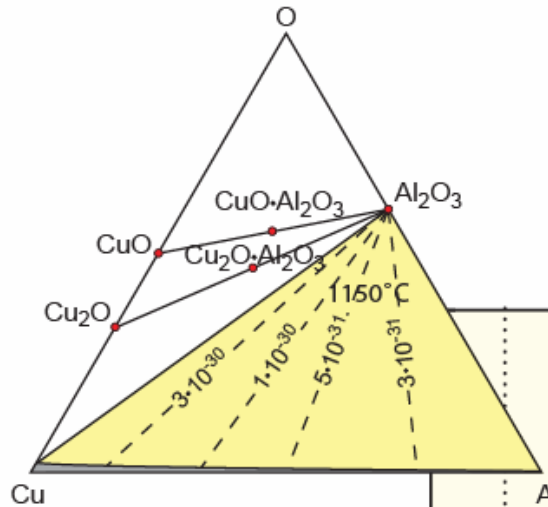
Role of image and dispersion forces plus chemical bonding

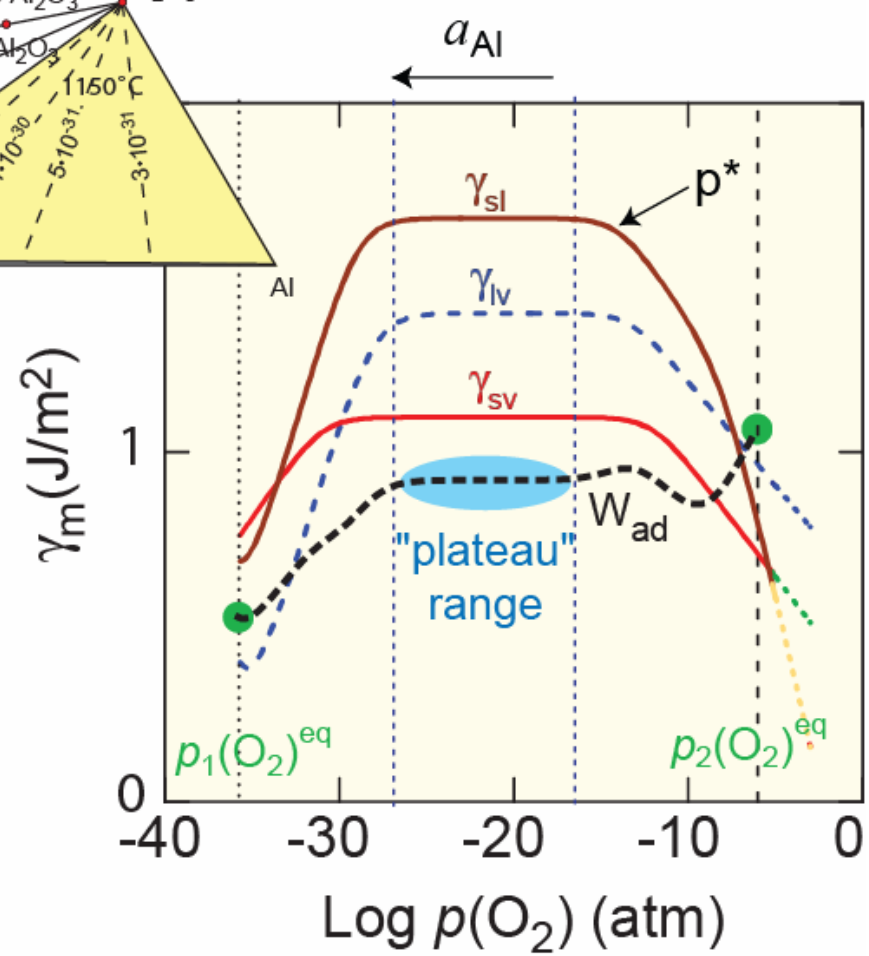
$$p(\mathrm{O}_2)^{\mathrm{eq}} \propto e^{\frac{\Delta G_R}{kT}}$$

$$p^* \propto e^{\frac{\Delta G_R + \Delta G_{ad}}{kT}}$$

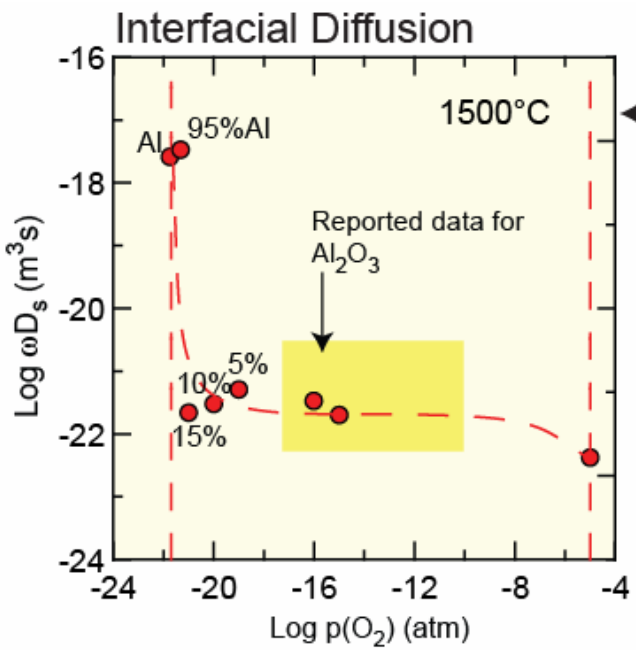
$$\frac{p(\mathrm{O}_2)^{\mathrm{eq}}}{p^*} \propto e^{-\frac{\Delta G_{ad}}{kT}}$$

$$\Gamma = -kT \frac{d\gamma}{d \ln a_i}$$

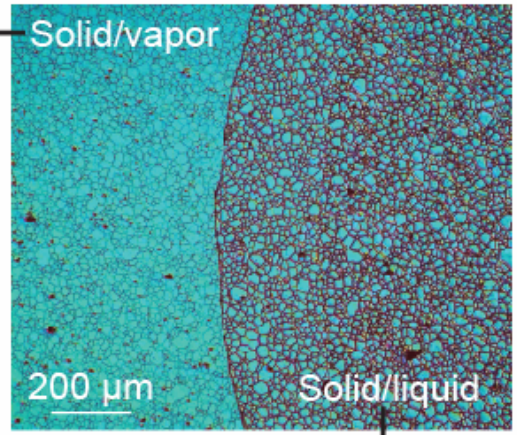


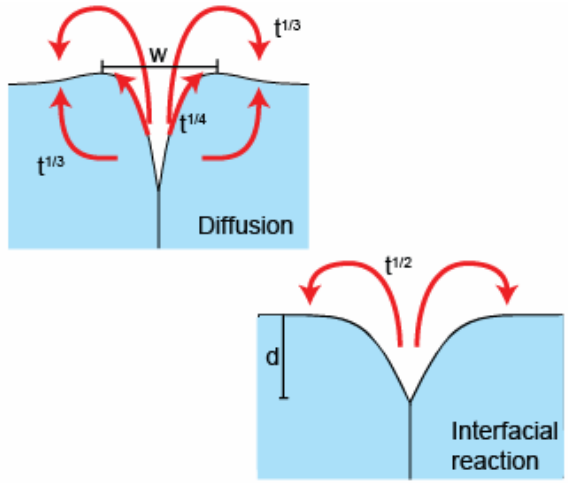


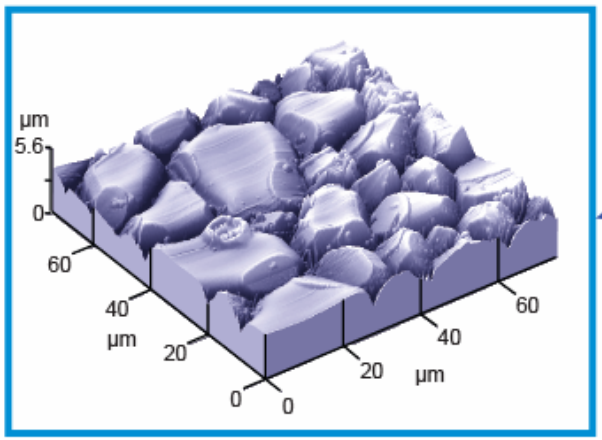
Metal/Oxide Interfaces-Atomic Transport

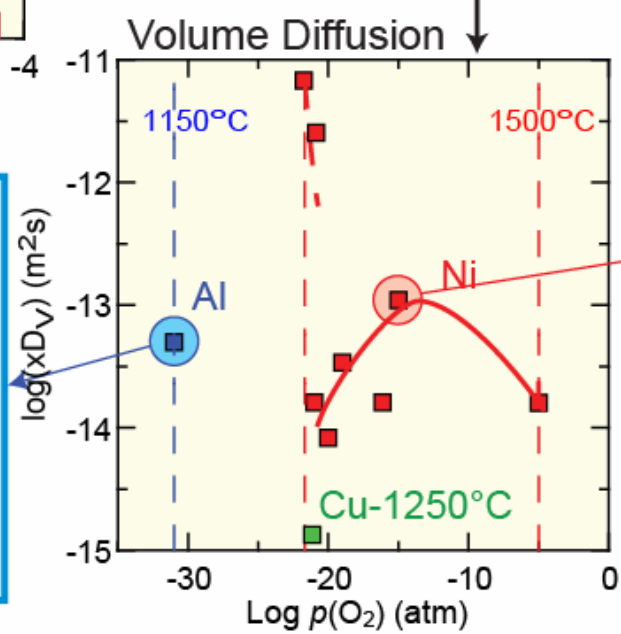


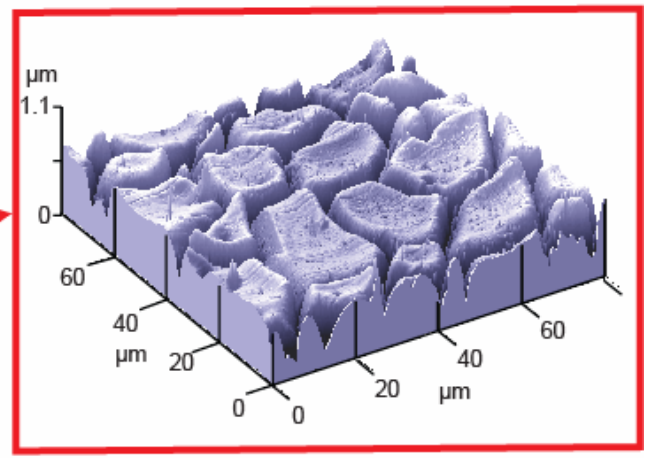
Ni/Al_2O_3











Saiz et al., *Adv. Mater.*, 2000
Gremillard, Saiz, Radmilovic & Tomsia, *in press*

Spreading at High Temperature

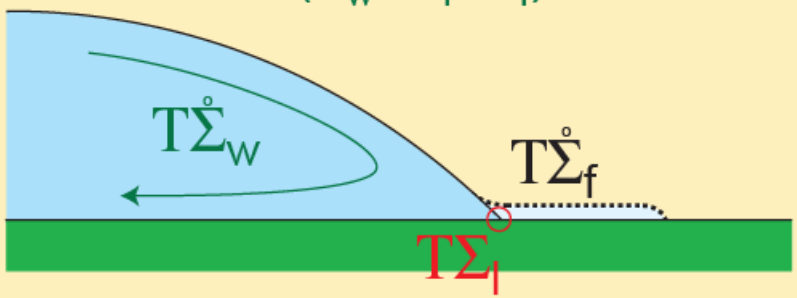
Non-reactive systems

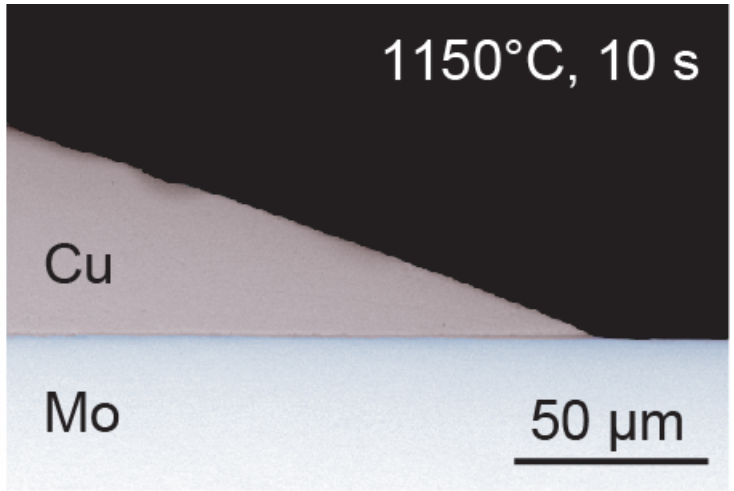
Driving forces:

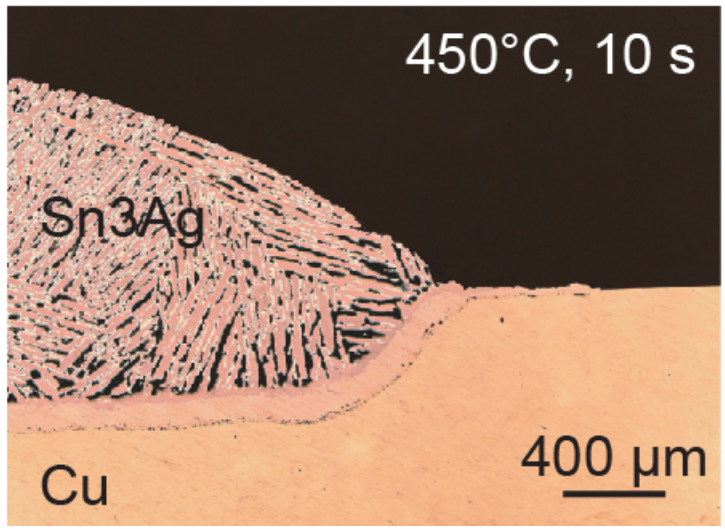
$\gamma_{sv}-\gamma_{sl}-\gamma_{lv}\cos\theta_D$

Dissipation

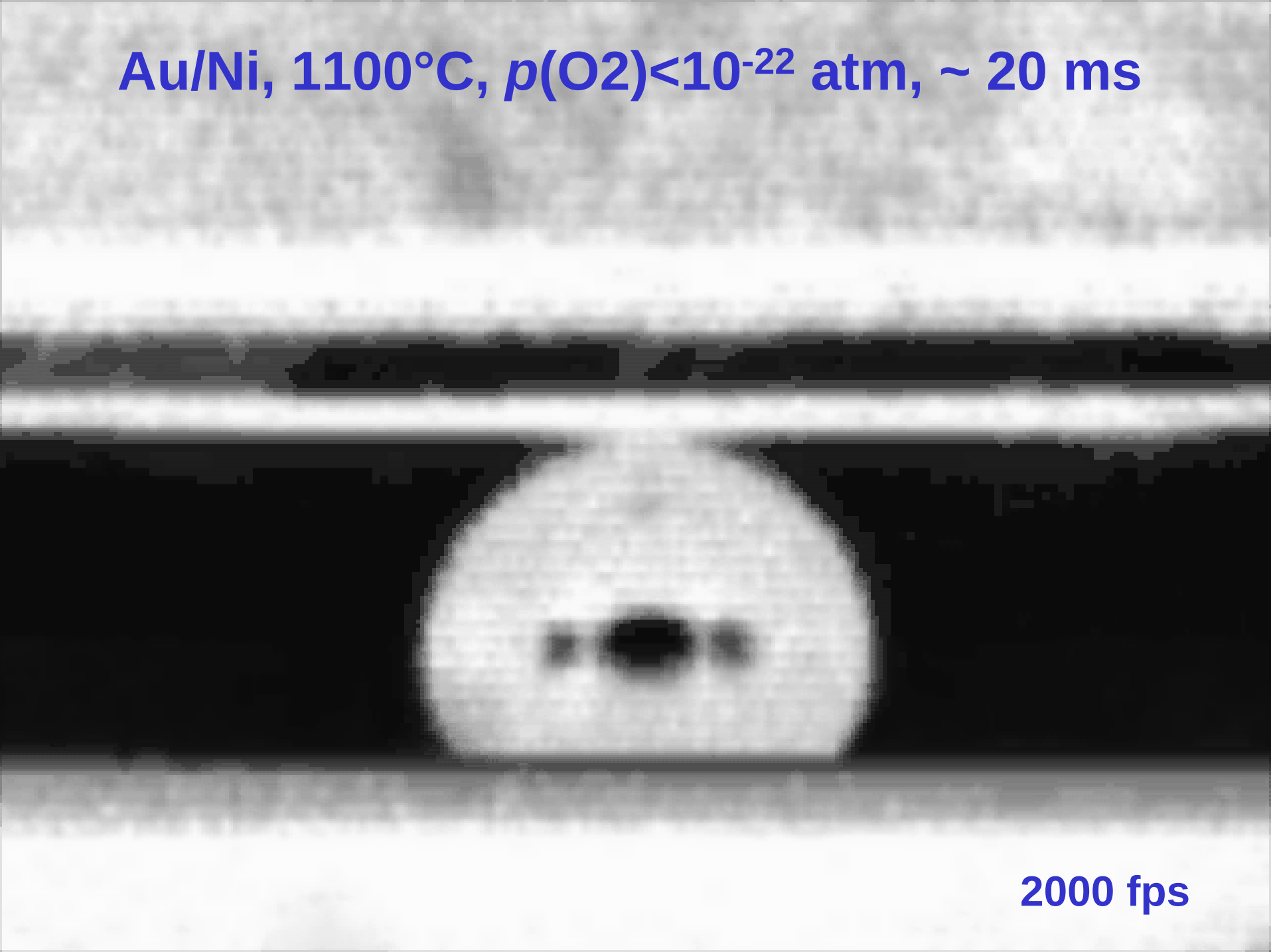
$T(\mathring{\Sigma}_w+\mathring{\Sigma}_f+\mathring{\Sigma}_l)$



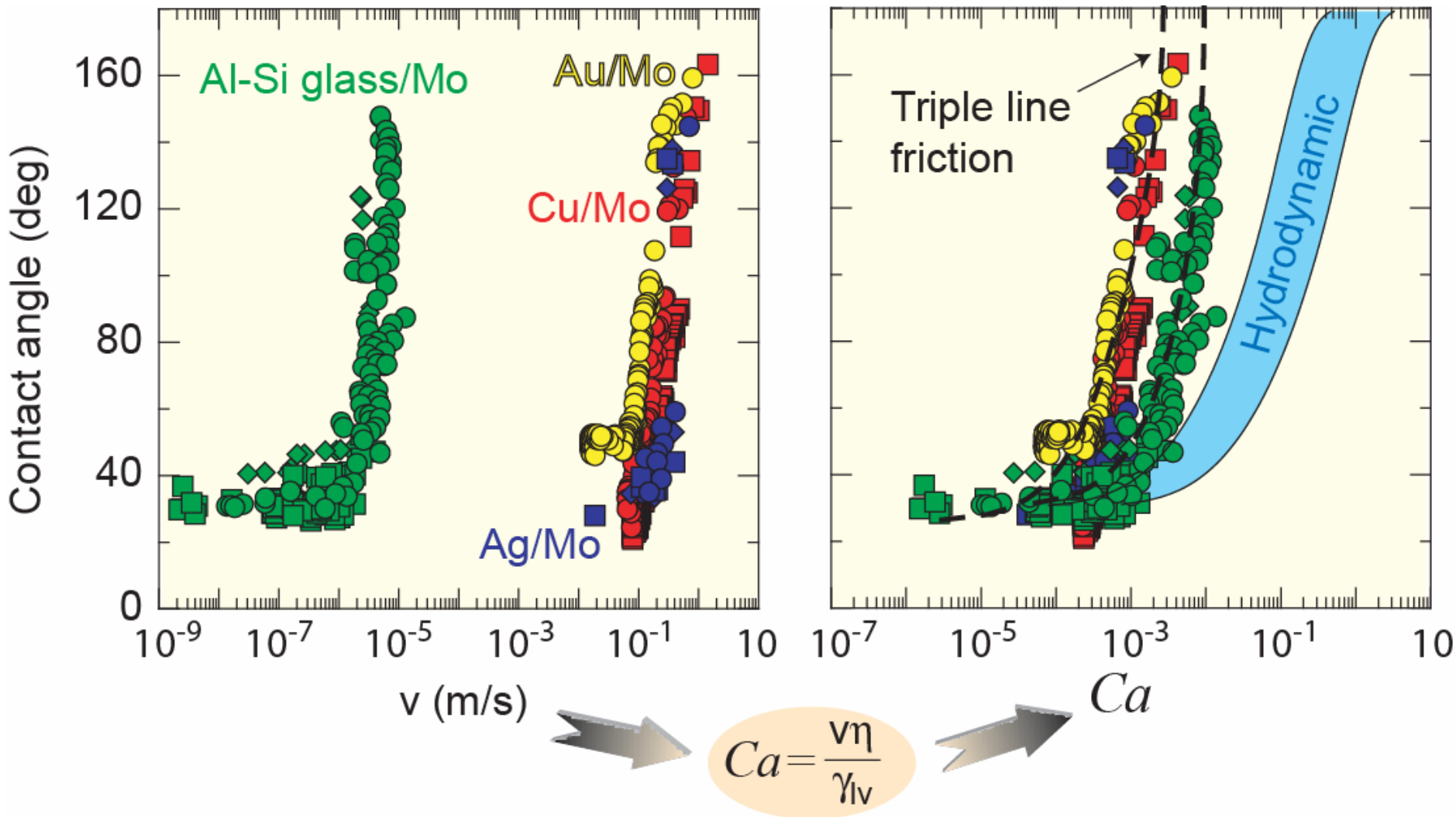




Au/Ni, 1100°C, $p(O_2)<10^{-22}$ atm, ~ 20 ms



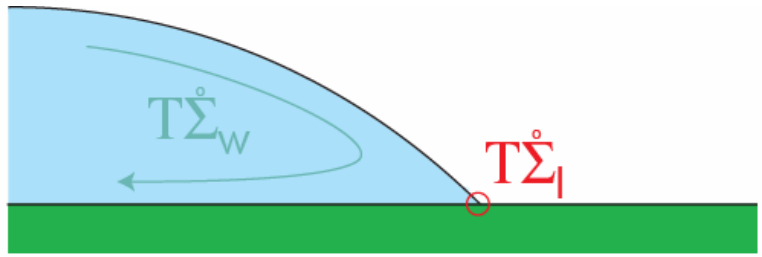
Non-reactive Spreading

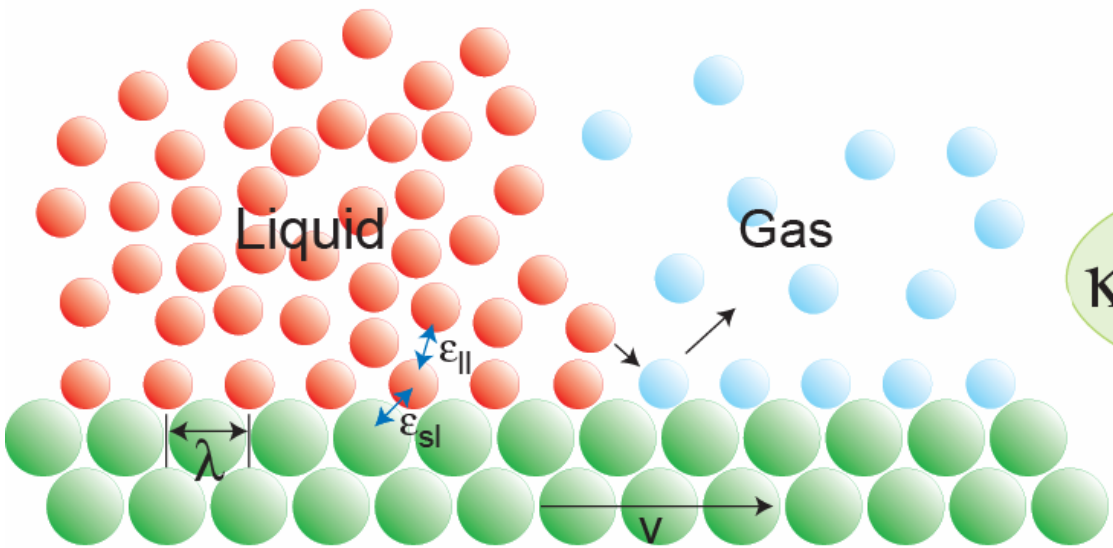


Saiz & Tomsia, *Nature Materials*, 2004; Rauch et al., *Z. Metall.*, 2005; Lopez-Esteban et al., *Langmuir*, 2005

Molecular-kinetics Models

Reaction-rate approach
Triple-line friction

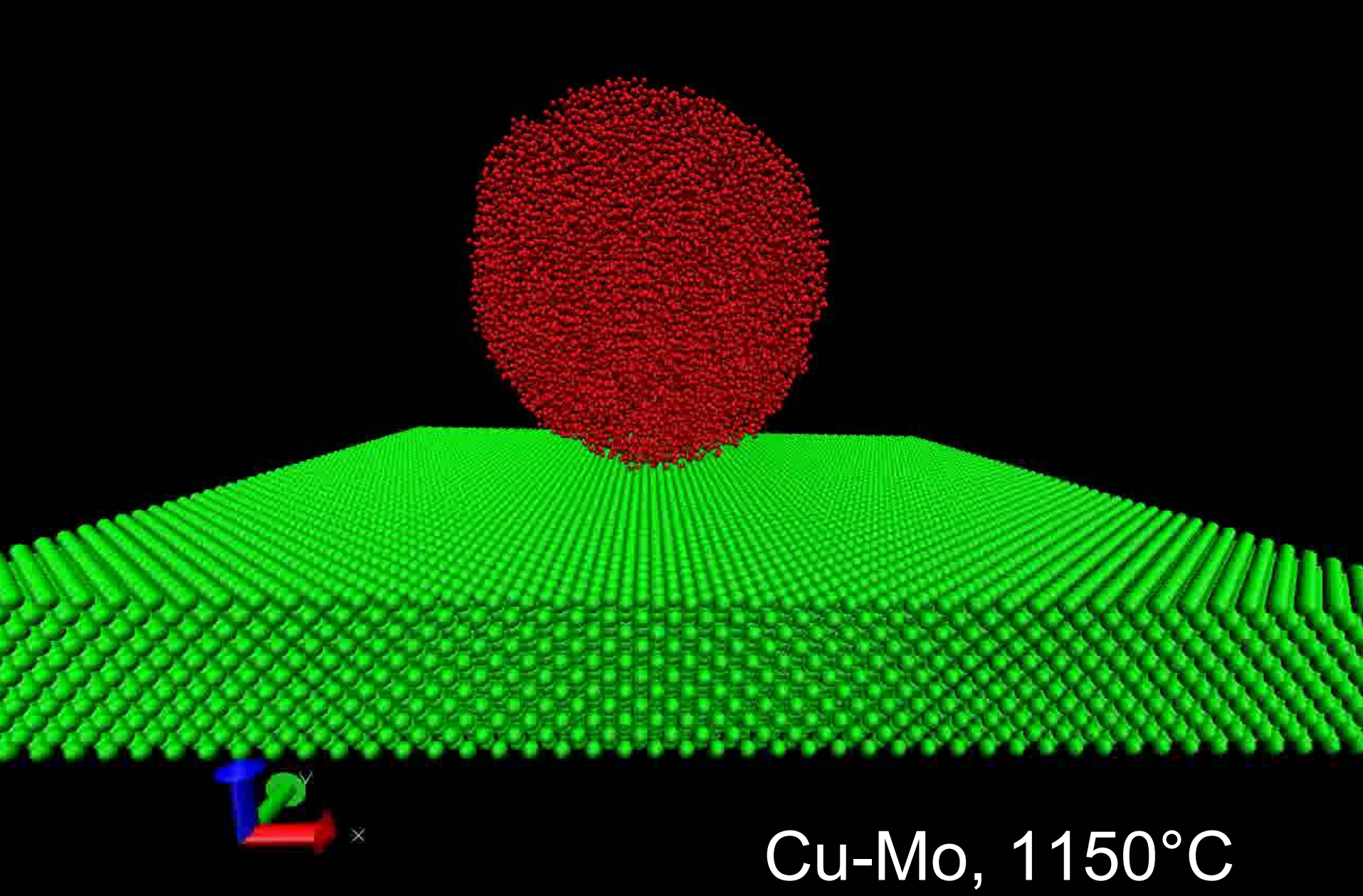




$$\kappa_w^0 = \frac{kT}{h} e^{-\frac{\Delta G_w}{NkT}}$$

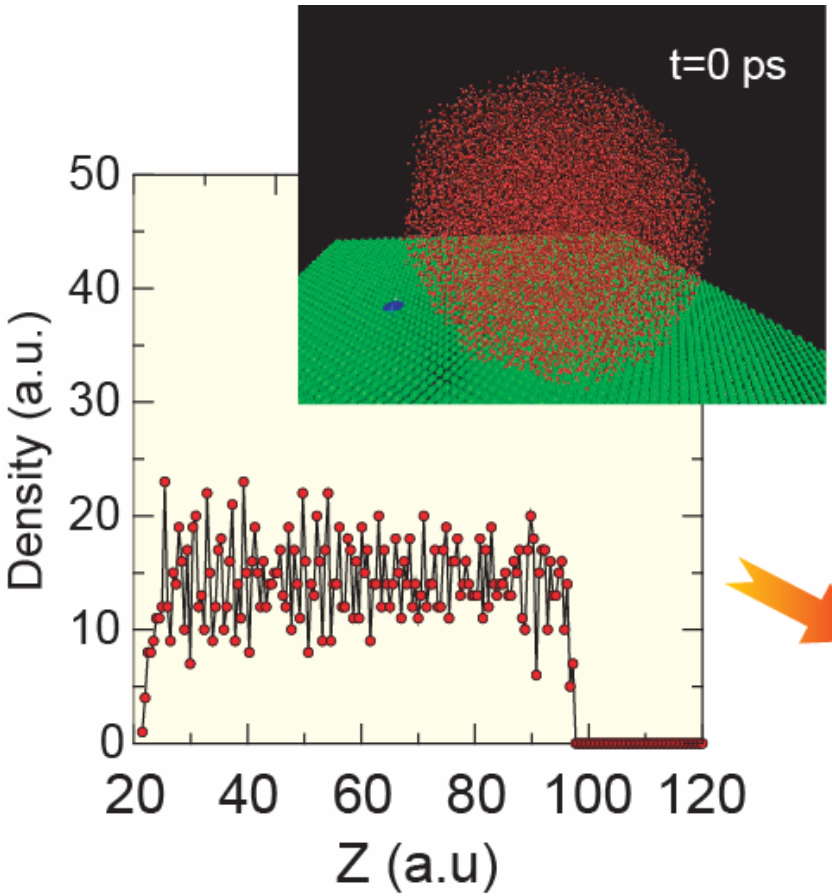
$$\Delta G_w = \Delta G_{sl} + \Delta G_{ll}$$

$$v = 2\lambda\kappa_w^0 \left[\sinh\left(\frac{\lambda^2 \gamma_{lv}}{2kT} \left(\cos\left(\theta_{1D}^0\right) - \cos\left(\theta_D\right) \right) \right) \right]$$



Cu-Mo, 1150°C

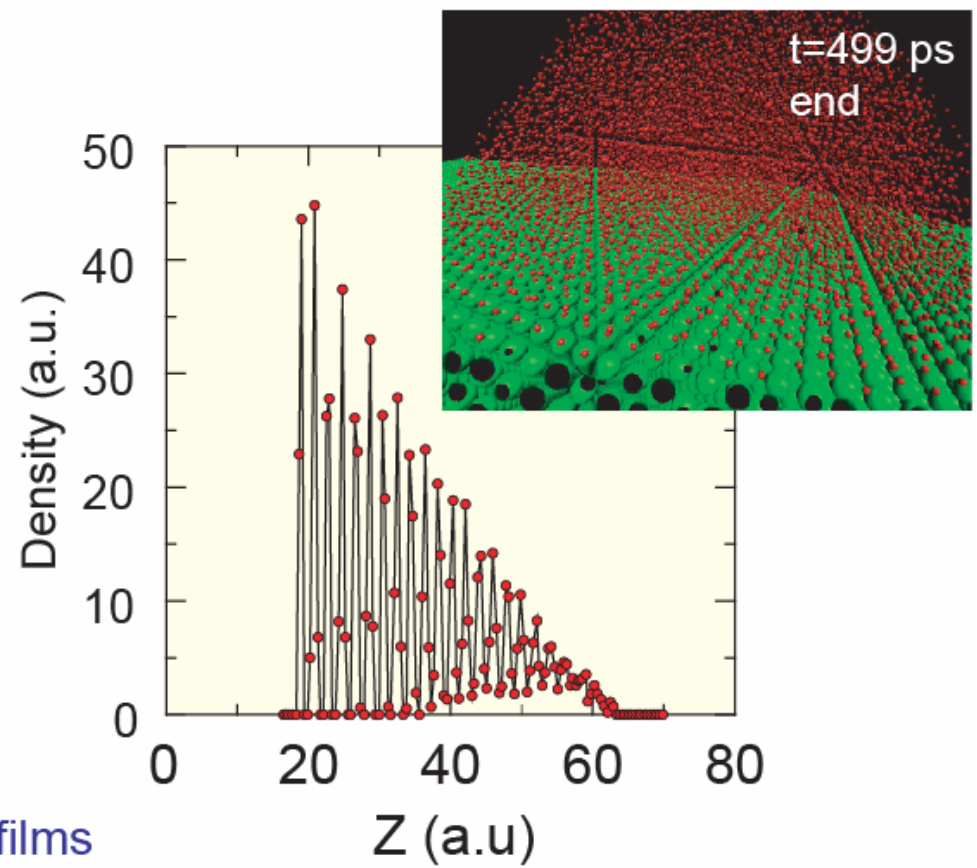
MD Simulations



Cu/Mo

Interfacial ordering of liquid atoms

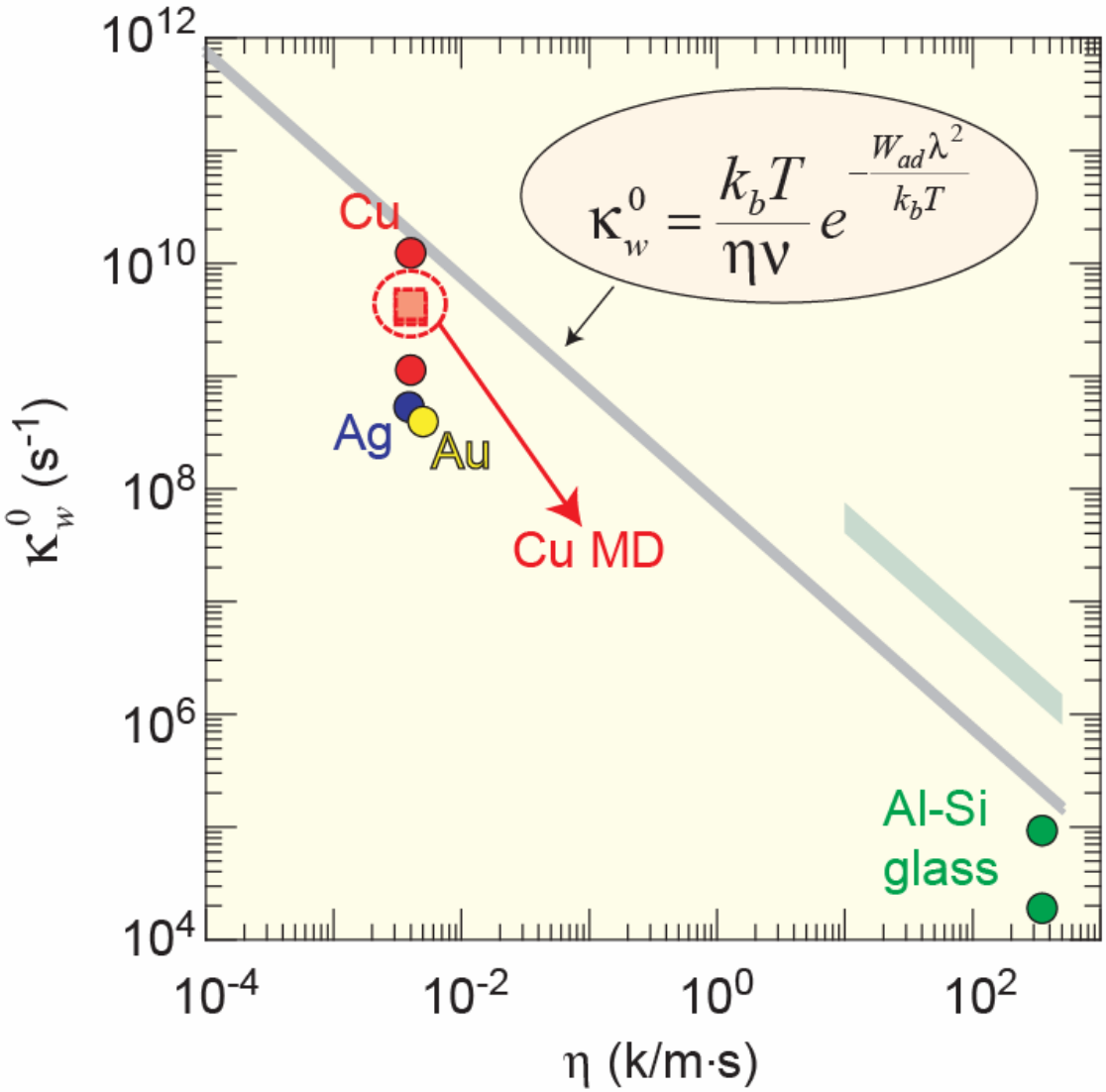
Liquid Cu layers separated ~2.51 Å



Calculate frequencies
- From spreading data
- Directly

Density profiles, adsorption, precursor films

Physical Implications



$$\eta = \frac{h}{V} e^{\frac{\Delta G_\eta}{NkT}}$$

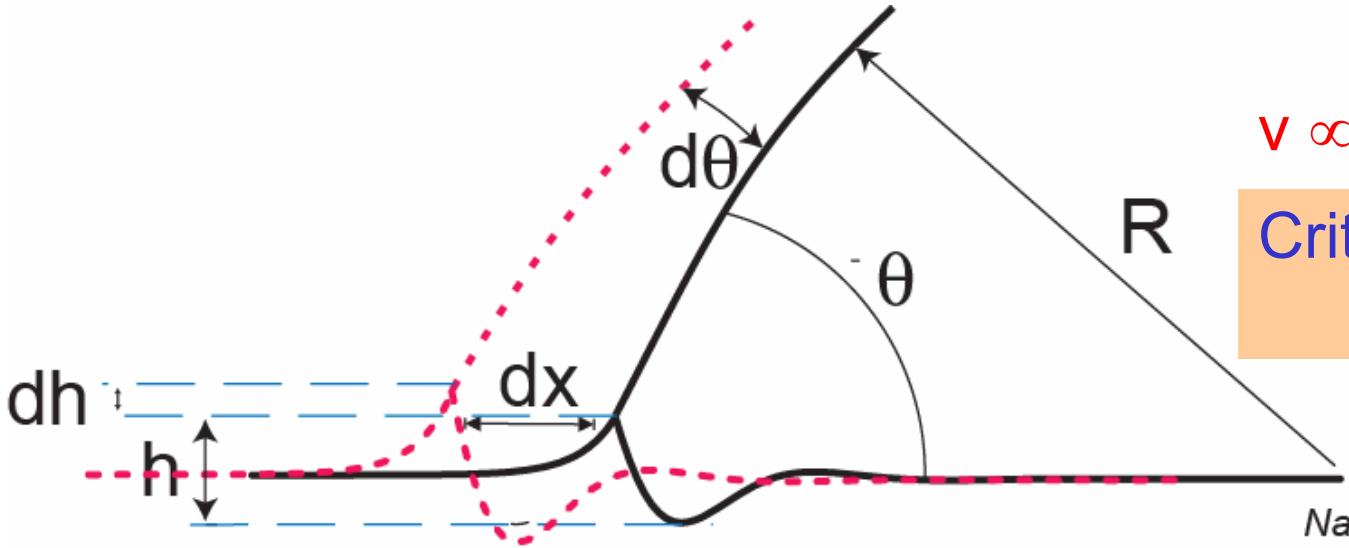
W_{ad}

$$\kappa_w^0 = \frac{kT}{h} e^{-\frac{\Delta G_{sl} + \Delta G_{ll}}{NkT}}$$

Liquid metals:
$\Delta G_w \approx \Delta G_{sl} \approx$ 80-140 kJ/mol
Activation energy for surface diffusion

Molten Oxides:
$\Delta G_w \approx \Delta G_{ll} \approx$230–300 kJ/mol
Activation free energy for viscous flow (ΔG_η)

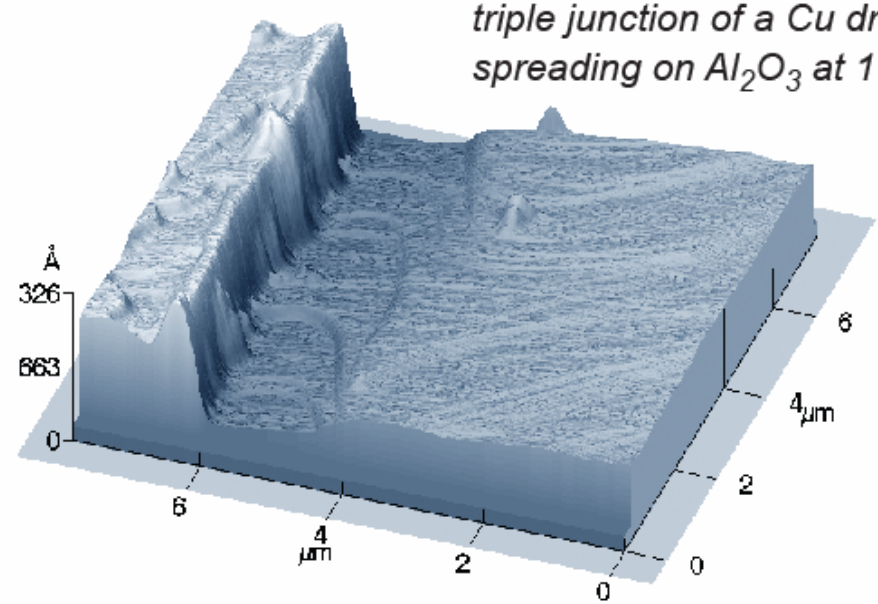
Triple Line Ridges



$v \propto D/h^3$

Critical velocity:
$v_{cr} \sim 6D/a$

Nanosized ridge formed at the triple junction of a Cu drop spreading on Al_2O_3 at 1150°C



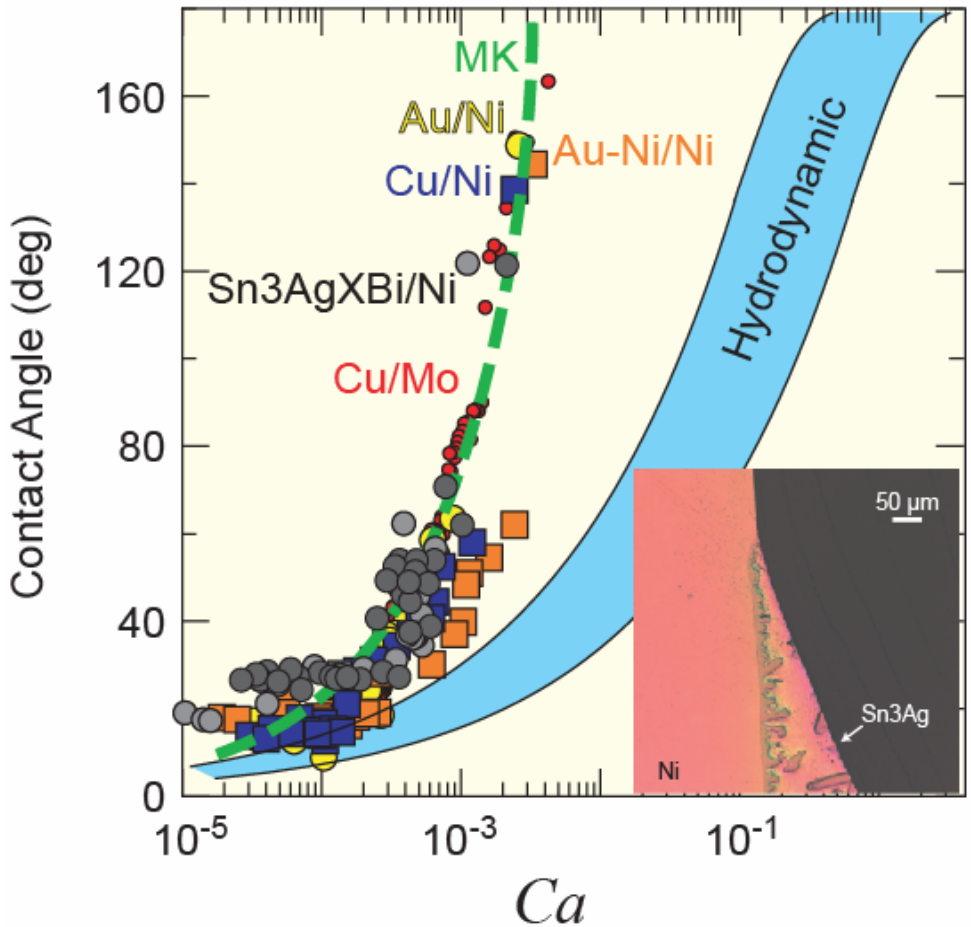
Microscopic 2-D equilibrium

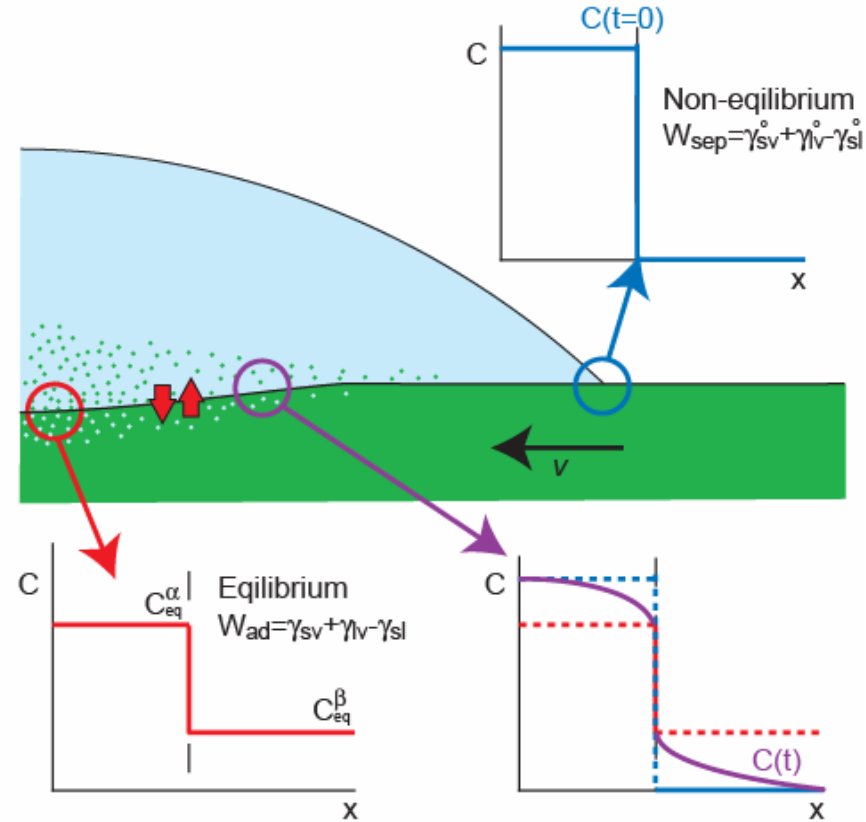
$h/R << 1 \Rightarrow \theta \rightarrow \theta_{1D}$

$v_{\parallel} = dx/dt \qquad v_{\perp} = dh/dt$

Lopez-Esteban et al., *Langmuir*, 2005
Saiz & Tomsia, *Curr. Op. Sol. St. Mat. Sci.*, 2006
Gremillard, Saiz, Radmilovic & Tomsia, *in press*

Reactive Systems





Reactive lead-free solders & miscible systems
Similar kinetics → similar frequencies

Saiz et al., *Acta Mater.*, 2003
Saiz & Tomsia, *Nature Materials*, 2004
Saiz & Tomsia, *Curr. Op. Sol. St. Mat. Sci.*, 2006

Collaborations

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