High Temperature Capillarity in Metal Systems: Insights from Atomic Modeling

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Outline

• Introduction: High temperature wetting and spreading
  • liquid metals on metals (also oxides/ceramics)
  • reactive wetting models / experiments

• Enhanced reactive wetting in a brazing geometry
  • Cu(l) entering pore in Ni
  • model for rate of substrate dissolution
  • connecting free energy of dissolution to spreading kinetics

• Conclusions and outlook
Wetting & Spreading

• Classical applications
  – Joining
  – Adhesion
  – Encapsulants
  – Lubrication

• Modern applications
  – Photolithography
  – Microcontact printing
  – Microfluidics
High Temperature Capillarity

- Welding, brazing, and soldering used for centuries to join metals and metals and oxides (ceramics)
  - construction, auto manufacturing, (micro)electronics, jewelry

- Braze/Solder melts at lower T than materials to be joined

- Reactions between the liquid braze/solder and the solid materials result in strong mechanical bonding (also hermeticity)

- Despite centuries of application, underlying phenomena still unclear (empirical engineering)
Modeling Wetting in Metal Systems

• Classical atomistic simulations
  • Molecular Dynamics - real space, real time atomic trajectories
  • Monte Carlo - equilibrium properties (phase diagrams)

• Realistic interatomic potentials for metals (EAM)

• We’re examining liquid Cu infiltrating a pore in Ni

\[
E_i = F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} \Phi_{ij}(R_{ij})
\]

\[
\rho_i = \sum_{j \neq i} \rho_j^a(R_{ij})
\]
• Model system has well characterized thermodynamic properties
Brazing Simulation

T = 1750K

Solid Ni (100)  Liquid Cu

d = 11 nm

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• Substrate dissolution observed during infiltration - how does this effect wetting kinetics?

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What is the flow profile for liquid infiltration into a pore?

Milner, 1958: Poiseuille flow ...

\[ v_x(y) = \frac{P}{2\eta l} \left( \frac{d^2}{4} - y^2 \right) \]

Assume No Dissolution
Laminar Flow Velocity Profile

\[ v_x(y) = \frac{P}{2\eta l} \left( \frac{d^2}{4} - y^2 \right) \]

\[ P_{\text{model}} = 750 \text{ bar} \]

\[ P_{\text{sim}} = 835 \text{ bar} \]

- Flow profile agrees with capillarity based model
• How fast does liquid metal penetrate a pore?

Milner, 1958:

\[ l^2 = \frac{P d^2}{6\eta} \quad t = \frac{d\gamma_L \cos\theta}{3\eta} \]

\( l \) = pressure
\( l^2 \) = liquid surface tension
\( \eta \) = viscosity
\( d \) = depth
\( \gamma_L \) = liquid surface tension
\( \theta \) = contact angle
Computing the Contact Angle

• Regardless of dissolution, we assume the solid/liquid interface remains flat near the contact line.

• Compute the position of the front as a function of y (shown by black points below in figs on left); fit either linear (near contact line) or circular (entire front) in figs on right.

\[ T = 1750 \, \text{K} \] Dissolutive System

In this geometry, two methods give similar results (not so for sessile drops!)

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Contact Angle with Time

- $T = 1750 \text{ K}$
- ND : $\theta \approx 58^\circ$
- D : $\theta \approx 45^\circ$

- $T = 1500 \text{ K}$
- ND : $\theta \approx 64^\circ$
- D : $\theta \approx 62^\circ$

$\gamma = 738 \text{ mJ/m}^2 (T=1500 \text{ K})$
$\gamma = 698 \text{ mJ/m}^2 (T=1750 \text{ K})$
$\eta = 2.8 \text{ cP} (T=1500 \text{ K})$
$\eta = 2.2 \text{ cP} (T=1750 \text{ K})$
Infiltration Rate

\[ l^2 = \frac{d\gamma_L \cos \theta}{3\eta} t \]

(a) and (b): \( T = 1500 \, K \)

Fits
\[ l^2 = 44 \, \text{Å/ps} \, t \, (ND) \]
\[ l^2 = 47 \, \text{Å/ps} \, t \, (D) \]

Theory
\[ l^2 = 42 \, \text{Å/ps} \, t \, (ND) \]
\[ l^2 = 45 \, \text{Å/ps} \, t \, (D) \]

(c) and (d): \( T = 1750 \, K \)

Fits
\[ l^2 = 62 \, \text{Å/ps} \, t \, (ND) \]
\[ l^2 = 125 \, \text{Å/ps} \, t \, (D) \]

Theory
\[ l^2 = 60 \, \text{Å/ps} \, t \, (ND) \]
\[ l^2 = 80 \, \text{Å/ps} \, t \, (D) \]
Infiltration Rate

\[ l^2 = \frac{d \left( \gamma_L \cos \theta + Q_{\text{diss}} \right)}{3 \eta} t \]

- \( Q_{\text{diss}} \) is an energy related to dissolution

- For \( T = 1750 \) K dissolutive case, \( Q_{\text{diss}} \sim 0.24 \text{ J/m}^2 \) (compared to \( \gamma_L \cos \theta = 0.49 \text{ J/m}^2 \))

- Energy of dissolution plays significant role in determining wetting kinetics at sufficiently high \( T \)
Model for Influence of Dissolution
Model for Dissolution Rate

Proposal: Velocity of dissolving interface is given by:

\[ V = V_o(T)[1 - \exp(-\Delta\mu / kT)] \]

Chemical potential of base metal atom in the solid minus that in the liquid

This relationship has been established for the solidification rate as a function of undercooling in pure metals.
Dissolution Driving Force

Free energy

$\Delta \mu$

Liquid

Solid

Pure liquid represents the case of infinite driving force, $V=V_0$

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Dissolution for Varying Liquid Composition

Compositions studied, $T=1750$ K

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Dissolution Simulations

- Extract rate from early t slope

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Dissolution Rate

![Graph showing the relationship between dissolution rate and a function involving $1 - \exp(-\Delta \mu / kT)$](image-url)

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Test for Arrhenius Behavior of $V_0$

$E_a = 2.9 \text{ eV}$
(close to value for self-diffusion in Ni)
• Arrhenius behavior of \( V_0 \) explains significant effect of dissolution whereas the effect was negligible at \( T = 1500 \) K

• \( E_a = 2.9 \) eV means \( Q_{\text{diss}} \) at \( T = 1500 \) K should be roughly 1/20 of the value at \( T = 1750 \) K

• For \( T = 1750 \) K dissolutive case, \( Q_{\text{diss}} \sim 0.24 \) J/m\(^2\) (compared to \( \gamma_L \cos \theta = 0.49 \) J/m\(^2\))

• For \( T = 1500 \) K dissolutive case, \( Q_{\text{diss}} \sim 0.01 \) J/m\(^2\) (compared to \( \gamma_L \cos \theta = 0.35 \) J/m\(^2\))
Conclusions

• Infiltration rate of liquid Cu through a channel obeys \( l^2 \sim t \) law; kinetics enhanced due to dissolution of base metal at \( T = 1750 \) K

• Dissolution rate of base metal obeys:

\[
V = V_o(T)[1 - \exp(-\Delta \mu / kT)]
\]

• \( V_0 \) exhibits Arrhenius behavior; at high enough dissolution rate, \( Q_{diss} \) increases driving force for infiltration

• Dissolution is a reaction for which the ‘reaction volume’ can increase significantly with increasing reaction rate AND this happens on a time scale comparable to the time for liquid to advance across surface