Atomistic simulations of chemically heterogeneous metal interfaces

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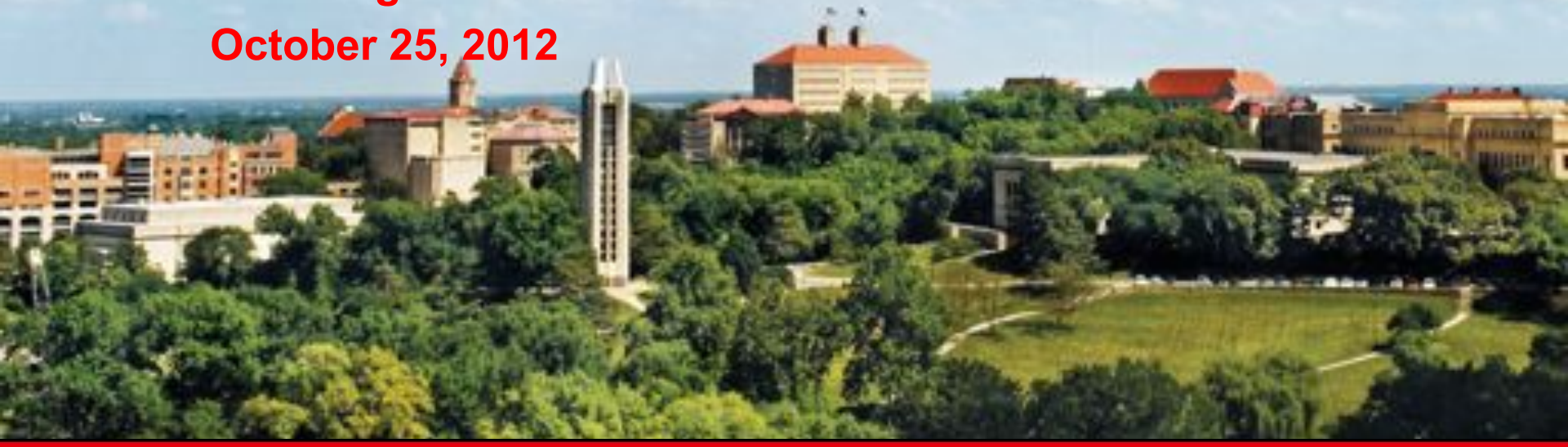
IPAM Workshop on Atomistic and Mesoscale Modeling of Material Defects

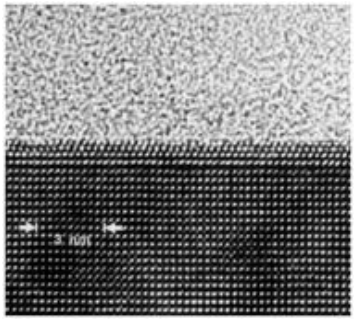
October 25, 2012



Why Study Chemically Heterogeneous Solid-Liquid Interfaces?

Wetting

http://en.wikipedia.org/wiki/Wetting



Grain Refiners in Casting

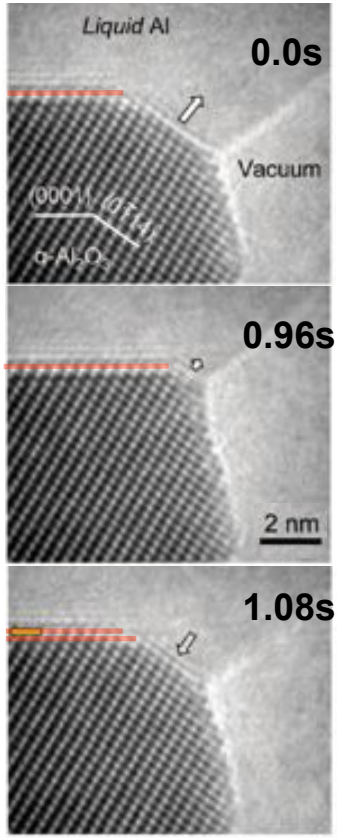
P. Schumacher & L Greer, in *Light Metals,* W. Hale, ed. (TMS, 1996).

Heterogeneous Nucleation

http://wiki.fisski.com/index.php/Heterogeneous_nucleation

Colloidal Stability

http://www.crc.dk/flab/colloida.htm



Vapor-Solid-Liquid Nanowire Growth

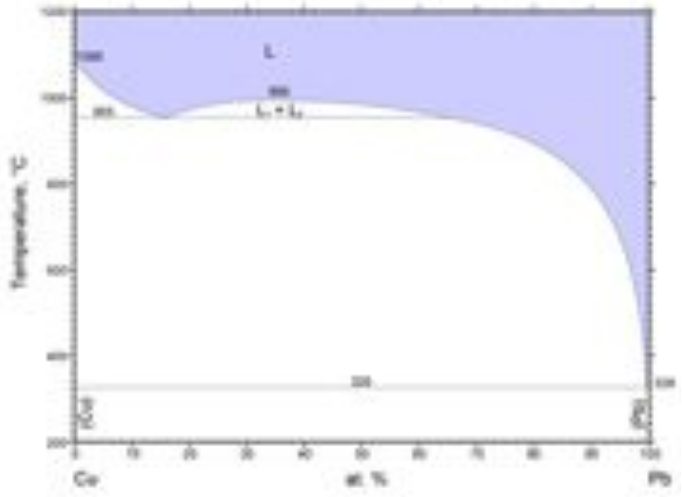
S.-H. Oh *et. al*, *Science* (2010)

National Science Foundation
WHERE DISCOVERIES BEGIN

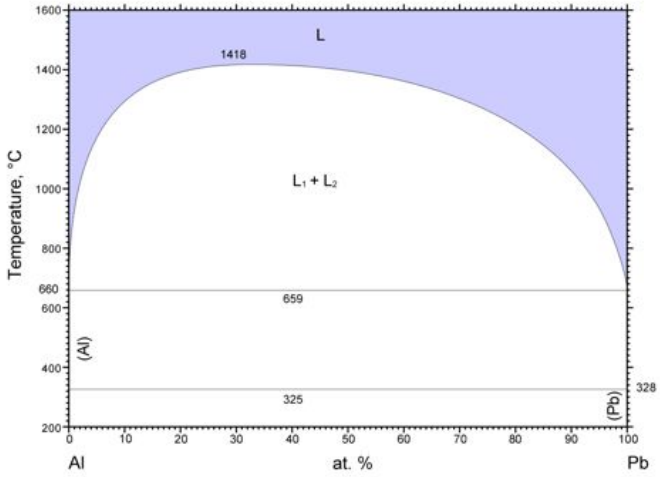
Part I: Chemically Heterogeneous Metal Interfaces

- Focus on Solid-Liquid Interfaces Between Liquid Pb and Solid Cu or Al
- Features
  - Large Temperature Range for Solid-Liquid Equilibria
  - Large Range of Size Mismatch: $a_{Pb} / a_{Al} = 1.22$, $a_{Pb} / a_{Cu} = 1.37$
- Current Study
  - Simulation Studies of Structure, Roughening, and Dynamics
  - Comparison with Electron Microscopy Observations for Al/Pb & Droplet spreading MD for Cu/Pb

Cu-Pb



Al-Pb



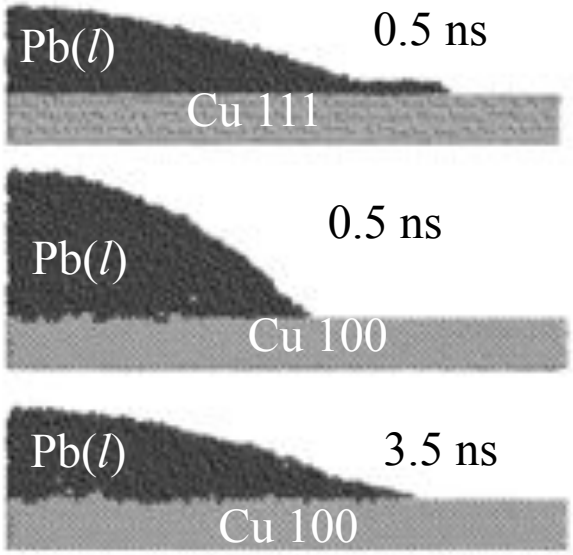
http://www1.asminternational.org/asmenterprise/APD/default.aspx

MD Simulation Details

- **Molecular dynamics simulations of liquid Pb in contact with solid Al or Cu**
  - Simulations for (100), (110) and (111) orientations
  - Runs for up to a few 100s of ns to investigate interface structure and diffusion and to equilibrate composition profiles
  - Use of LAMMPS code: http://lammps.sandia.gov/
- **Embedded-atom-method interatomic potentials**
  - Al-Pb: *A. Landa, P. Wynblatt, D. J. Siegel, J. B. Adams, O. N. Mryasov and X.-Y. Liu, Acta mater. 48, 1753 (2000)*
  - Cu-Pb: *J. J. Hoyt, J. W. Garvin, E. B. Webb III, M. Asta, Model. Simul. Mater. Sci. Eng. 11, 287299 (2003)*
  - Potentials reproduce large positive heat of mixing in liquid state, Pb melting temperature and qualitative features of phase diagram
  - Available at NIST potentials repository: http://www.ctcms.nist.gov/potentials/

Solid Cu/liquid Pb interface

Motivation: Earlier simulations on spreading of Pb droplets on Al



E. B. Webb III, *et al,* PRL **91**, 236102 (2003)

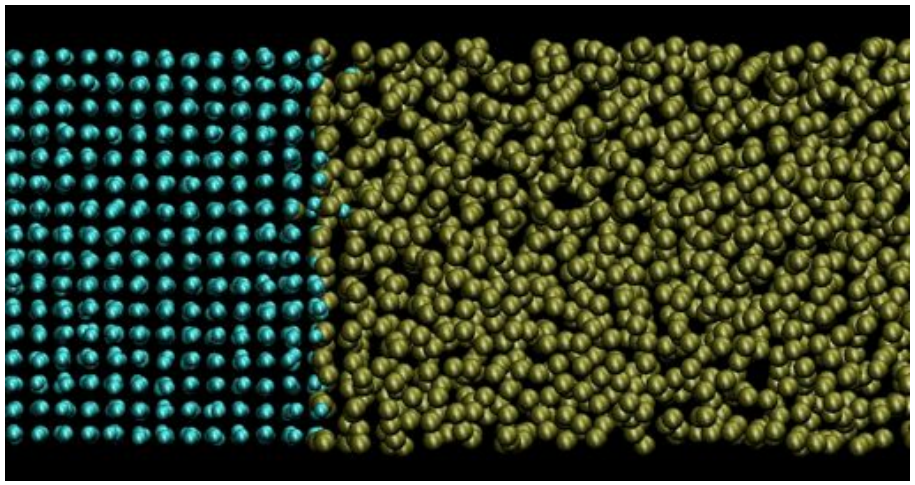
Large anisotropy in droplet spreading kinetics.

with
Mark Asta (UC Berkeley, Mat. Sci & Eng.)

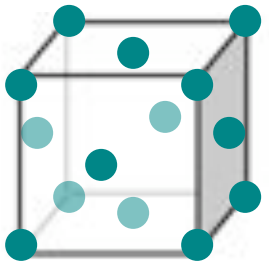
Pablo Palofox-Hernandez (KU, now at Deakin Univ. Geelong, VIC, Australia)

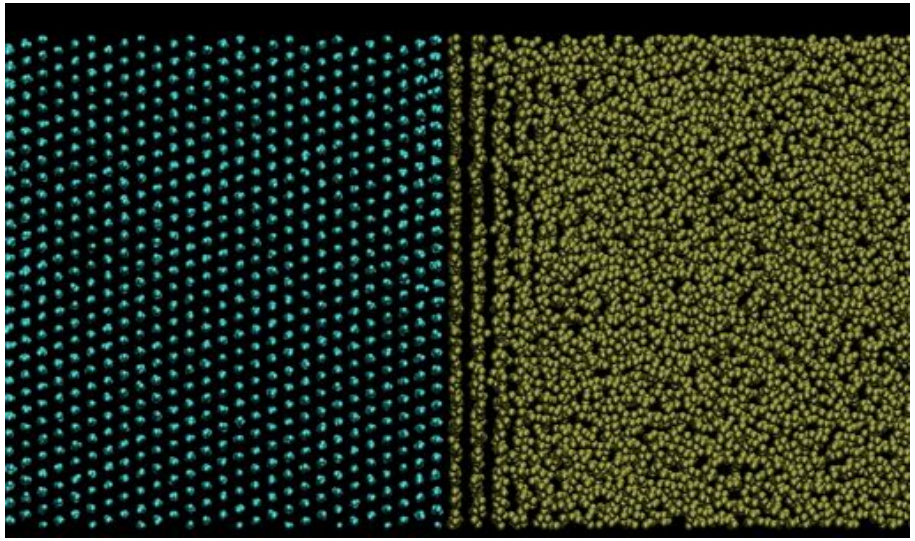
Solid Cu/liquid Pb interface

625K

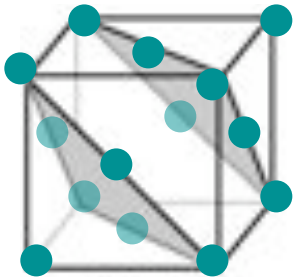


(100) Cu/Pb





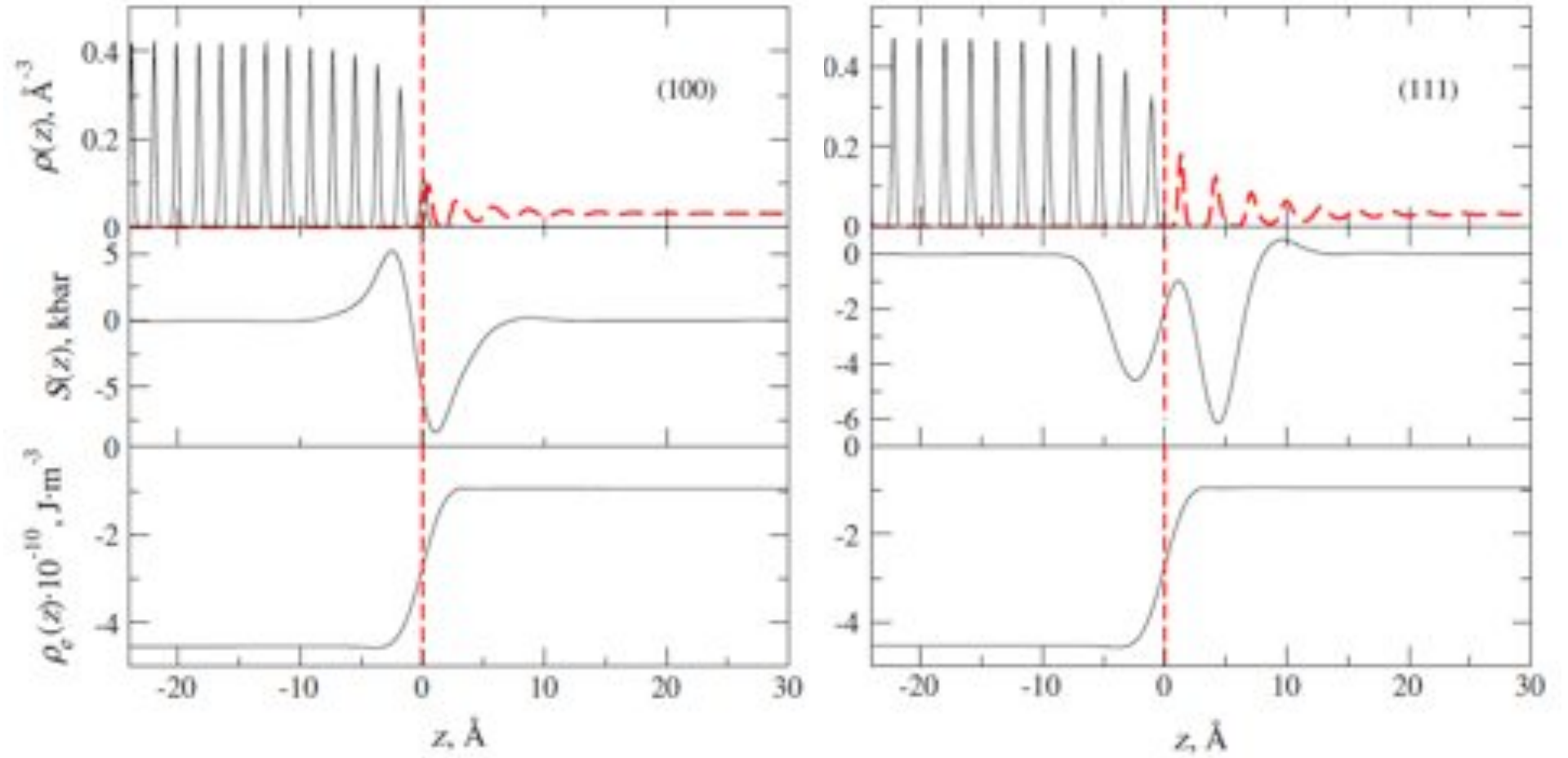
(111) Cu/Pb



Note “prefreezing” layer!

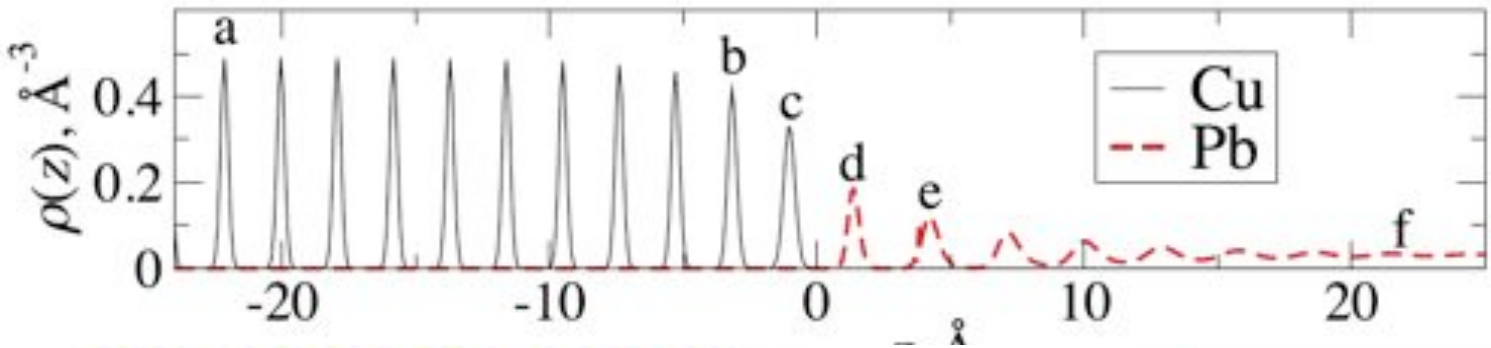
Solid Cu/liquid Pb interface

Density and Stress Profiles at T = 625 K



Solid Cu/liquid Pb interface

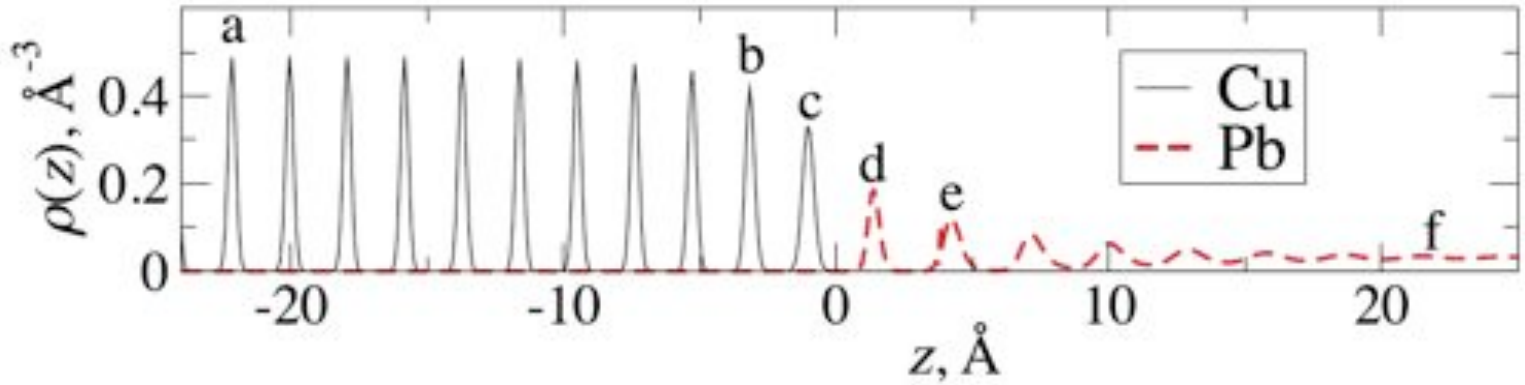
In-Plane Structure for (111) Interface at T = 625 K



b

Solid Cu/liquid Pb interface

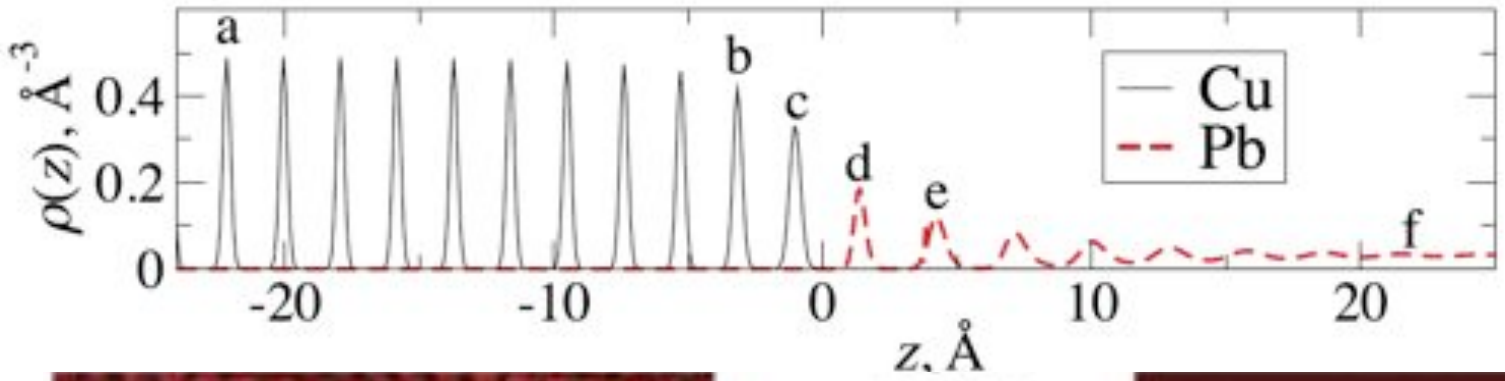
In-Plane Structure for (111) Interface at T = 625 K



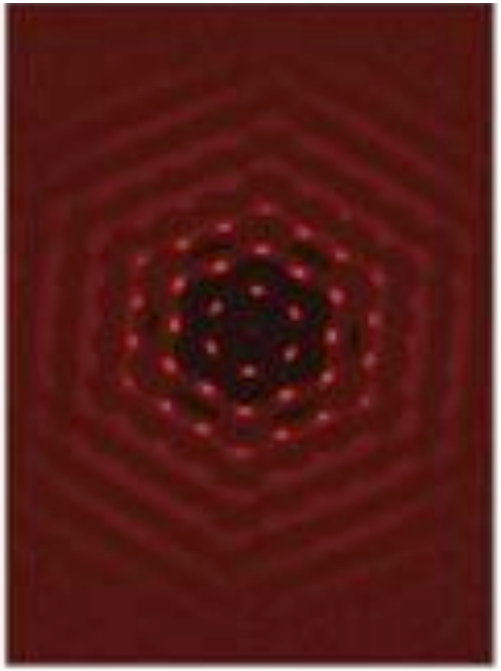
C

Solid Cu/liquid Pb interface

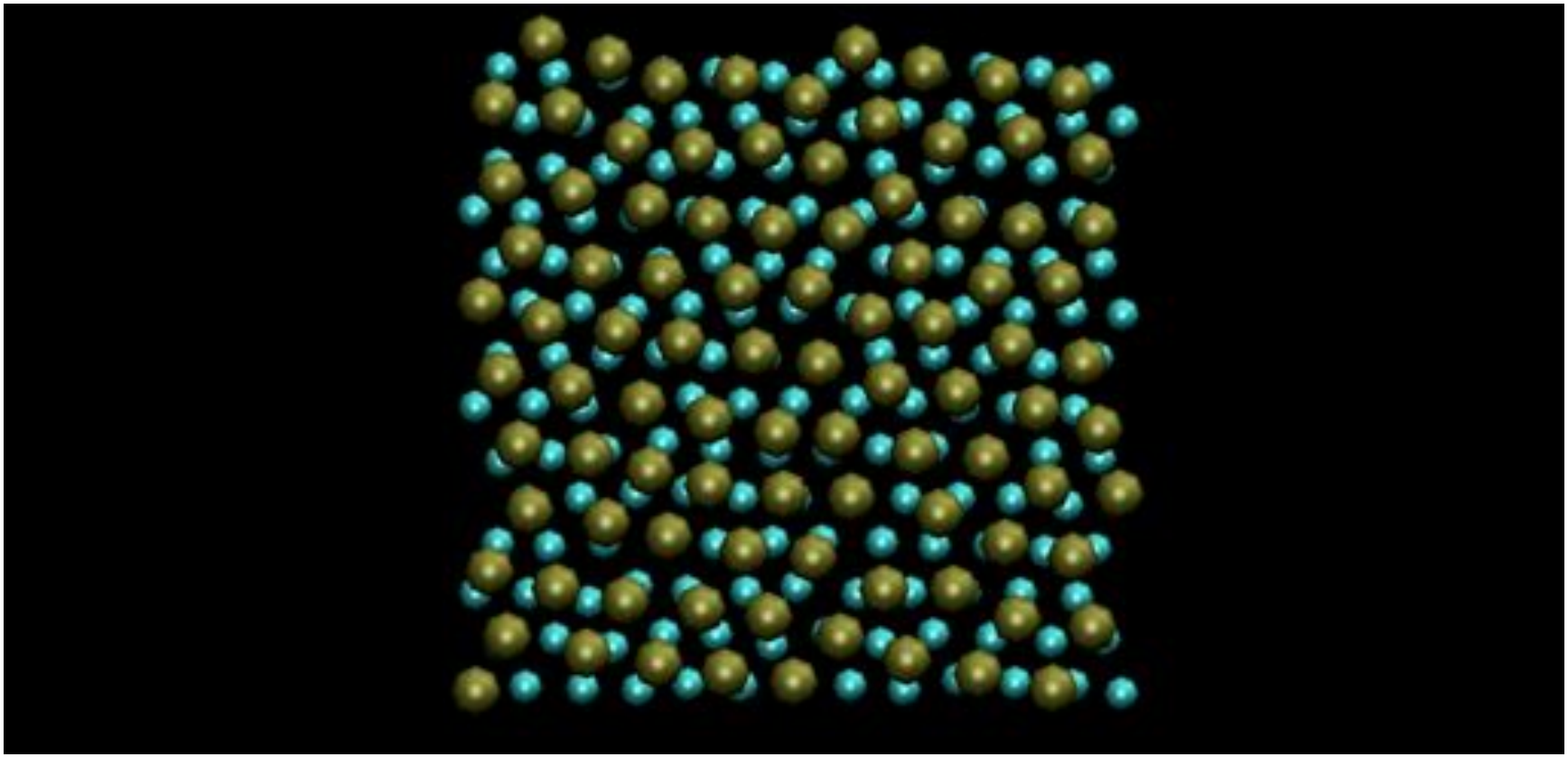
In-Plane Structure for (111) Interface at T = 625 K



d

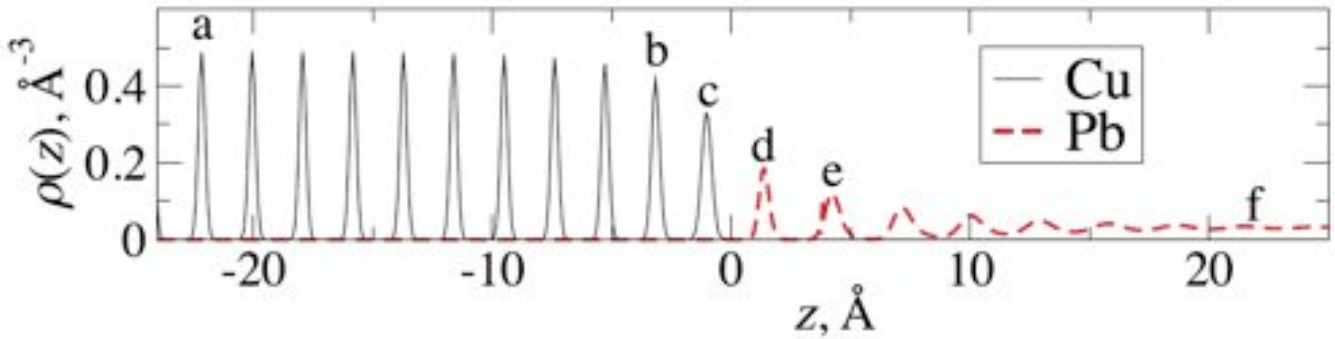


First prefreezing layer Cu-Pb (111)



Solid Cu / Liquid Pb Interface

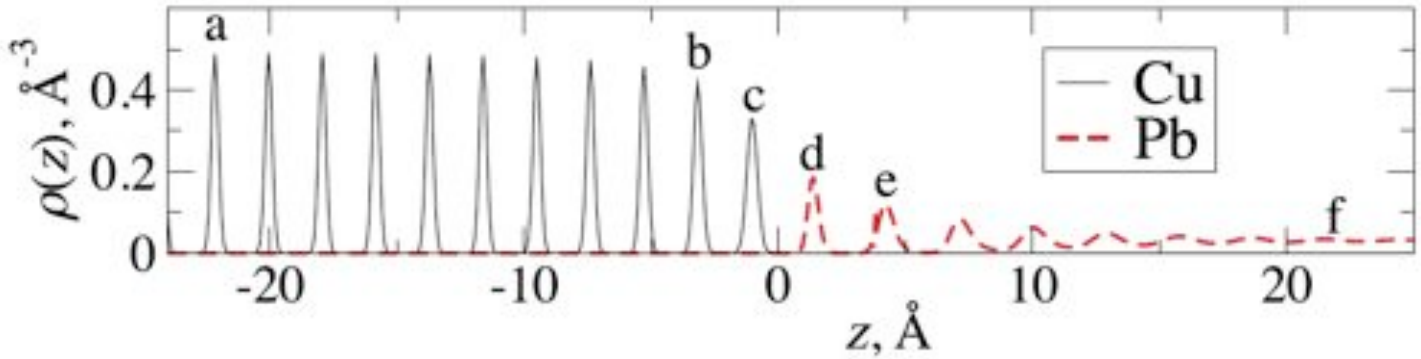
In-Plane Structure for (111) Interface at T = 625 K



e

Solid Cu / Liquid Pb Interface

In-Plane Structure for (111) Interface at T = 625 K



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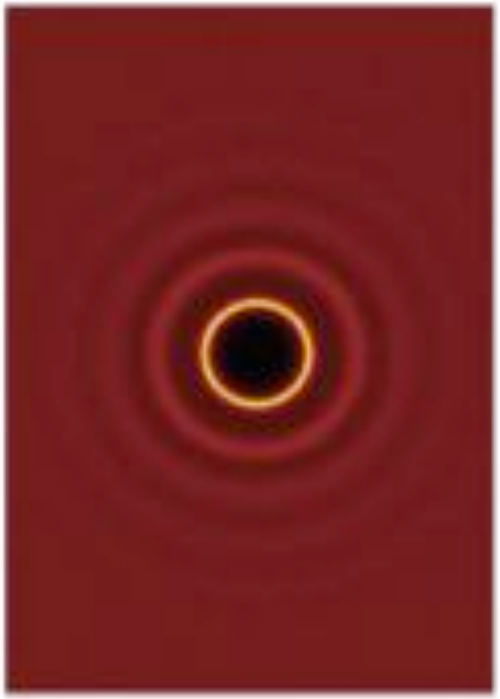
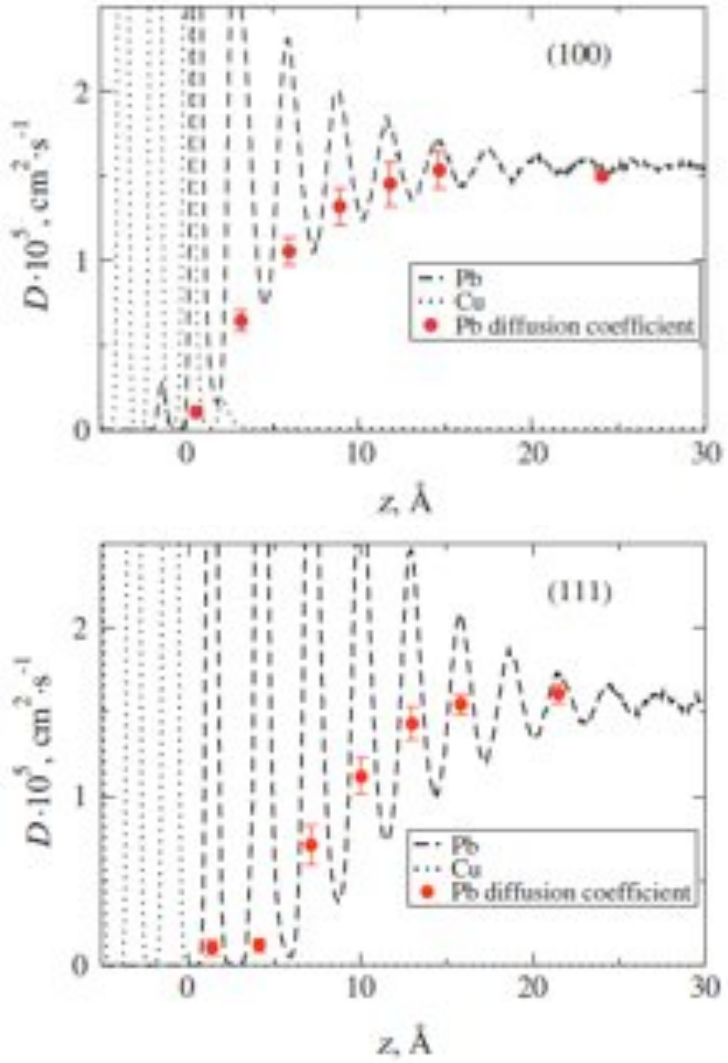
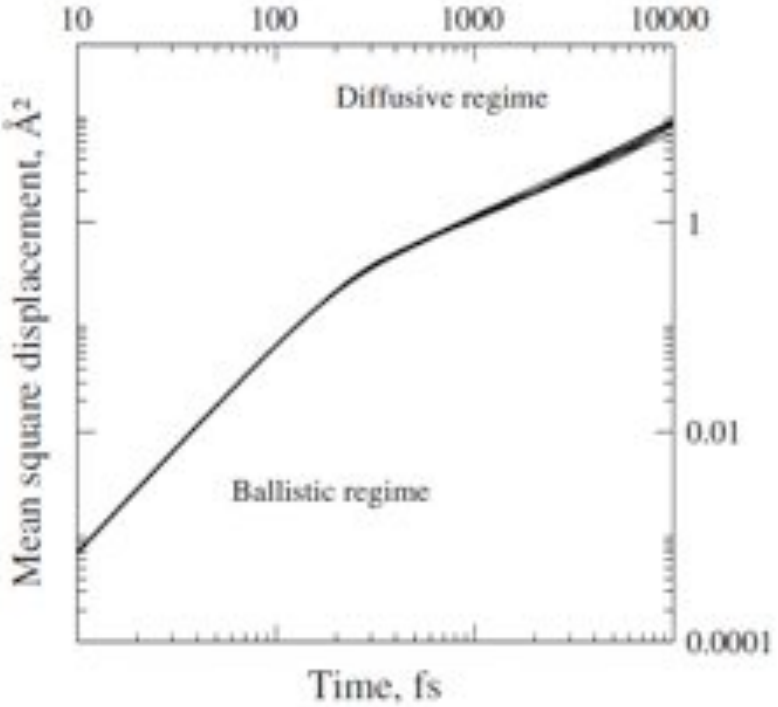


Solid Cu / Liquid Pb Interface

Diffusion Profile at T = 650 K

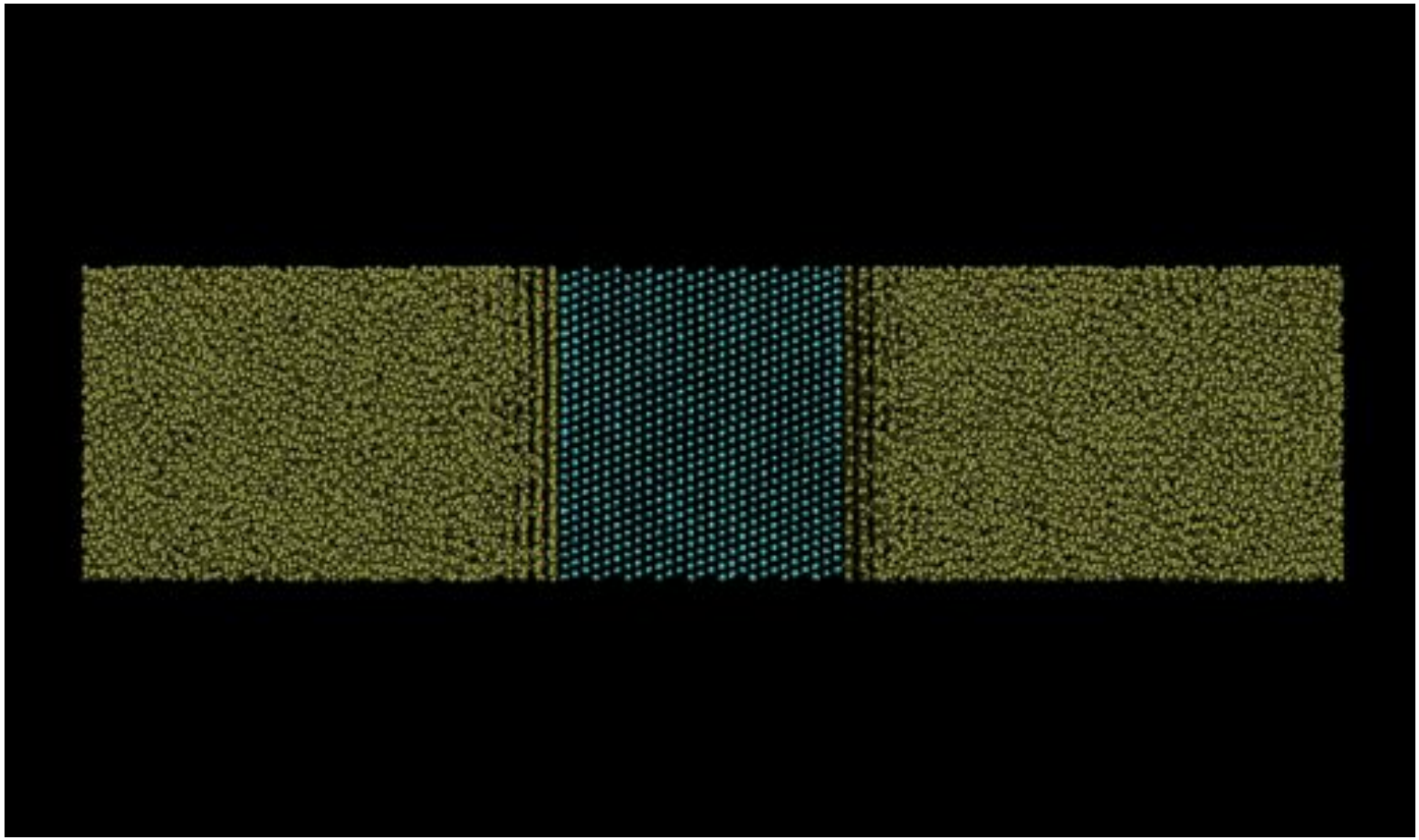




Solid Cu / liquid Pb interface

Effect of Prefreezing layer on heterogeneous nucleation (111)

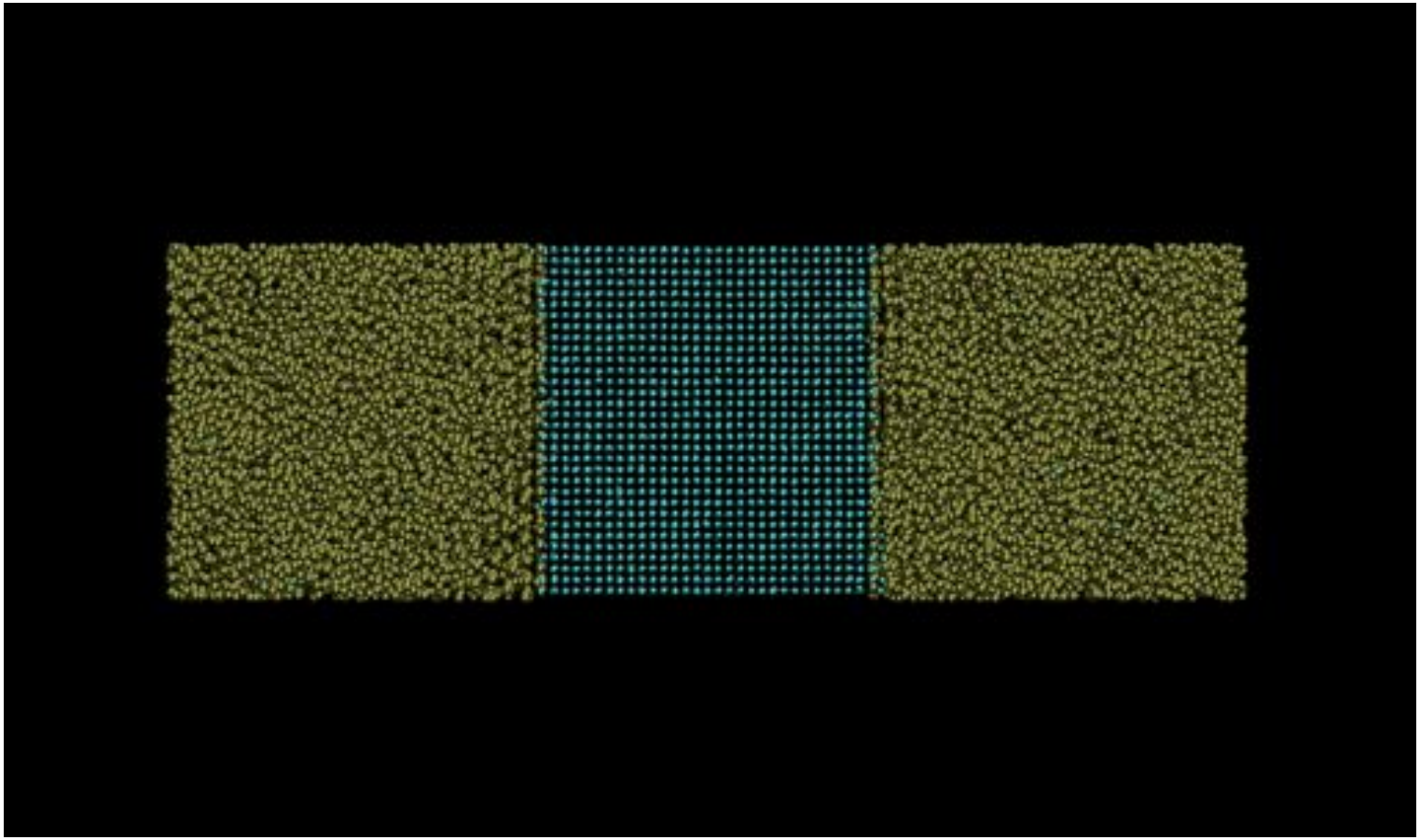
$T = 592$ K



Solid Cu/liquid Pb interface

Effect of Prefreezing layer on heterogeneous nucleation (100)

$T = 450$ K

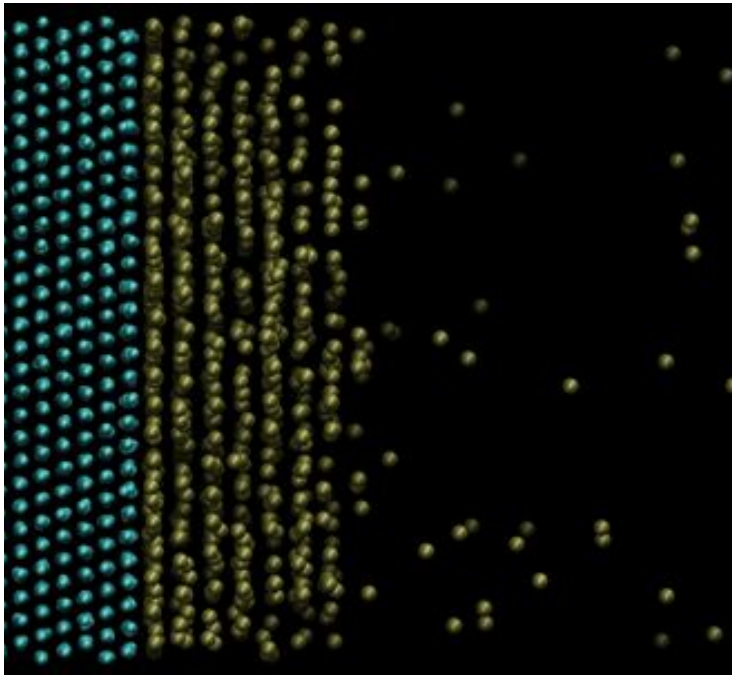


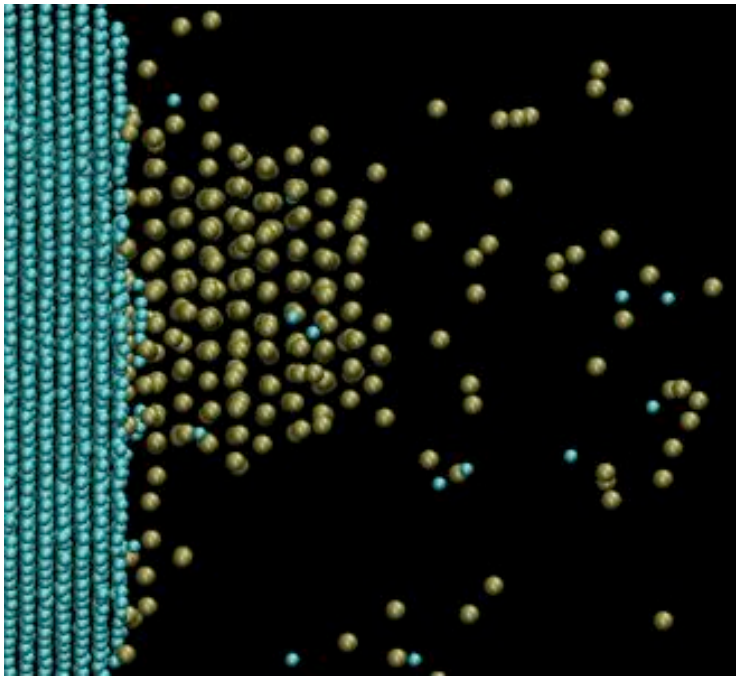
Solid Cu/liquid Pb interface

Effect of Prefreezing layer on heterogeneous nucleation (100)

layer-wise nucleation

(111) 592 K

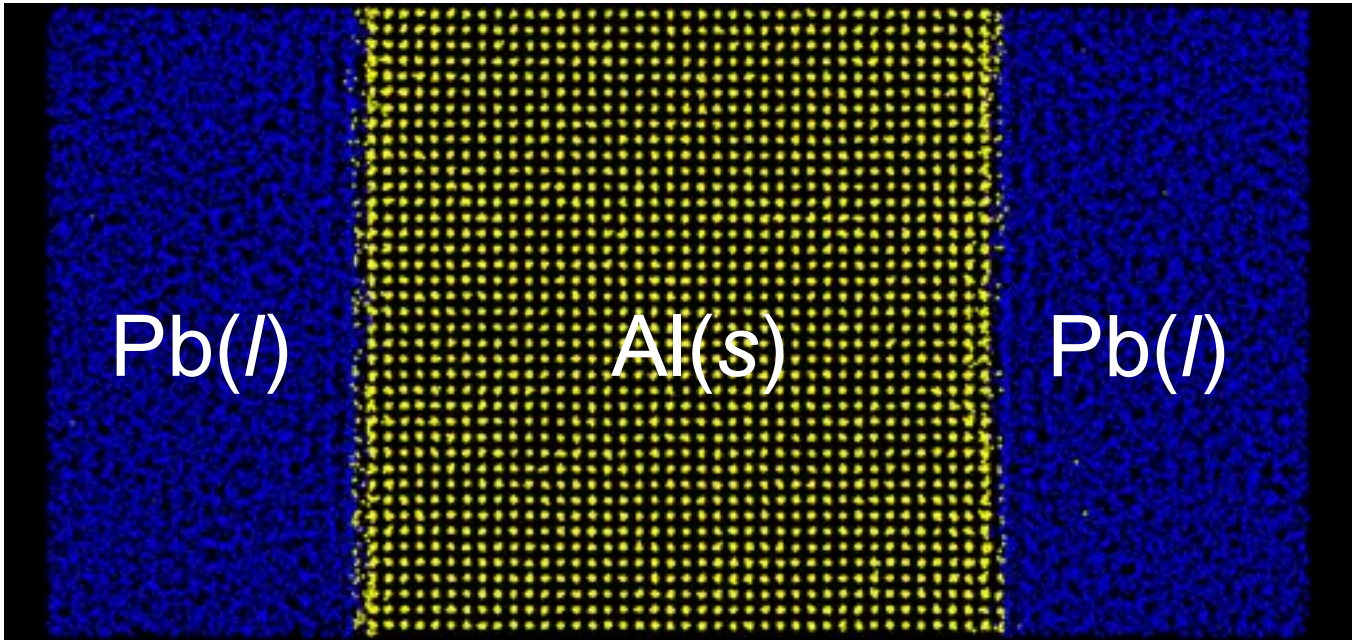




(100) 450 K

nucleation by
"Partial wetting"

Solid Al/liquid Pb interface



Collaborators:

- Yang Yang (KU)

- Mark Asta (UC Berkeley, Mat. Sci. & Eng.

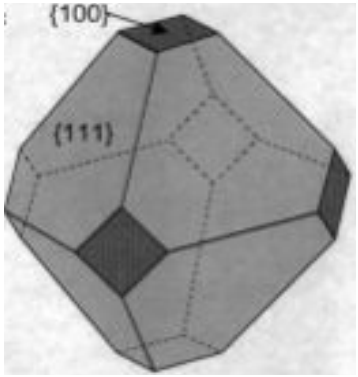
Solid Al/liquid Pb interface

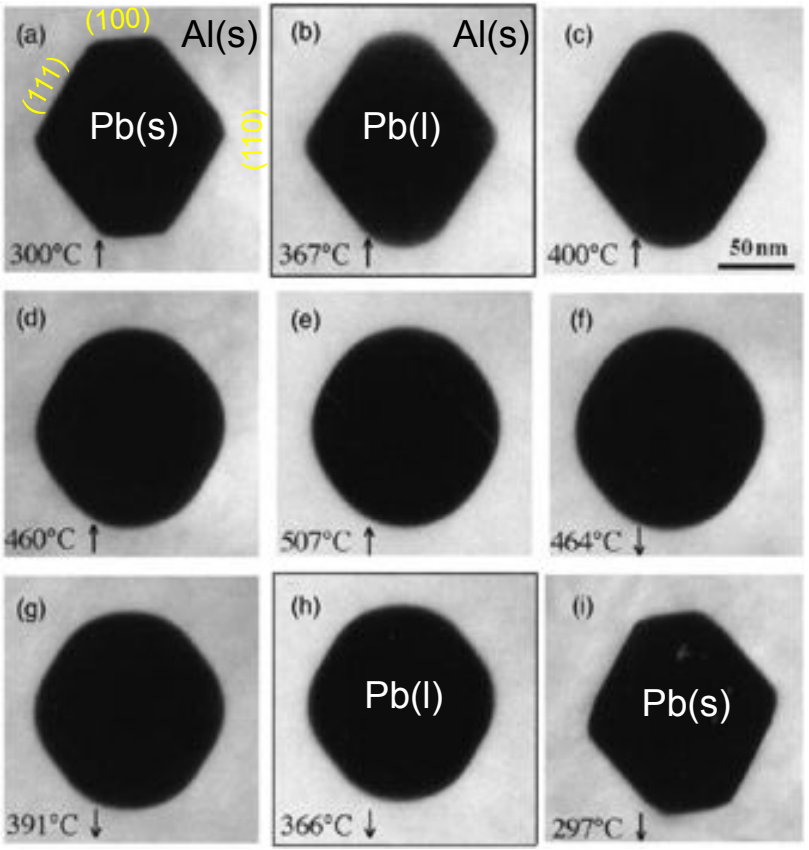
Motivation: Dahmen group TEM experiments on Pb inclusions in Al matrix.

$T < T_m(Pb)$: (100), (110), (111) faceted

$T_m(Pb) < T < 823\ K$: (111) faceted, others rough

$T > 823\ K$: all faces rough (~2% anisotropy)



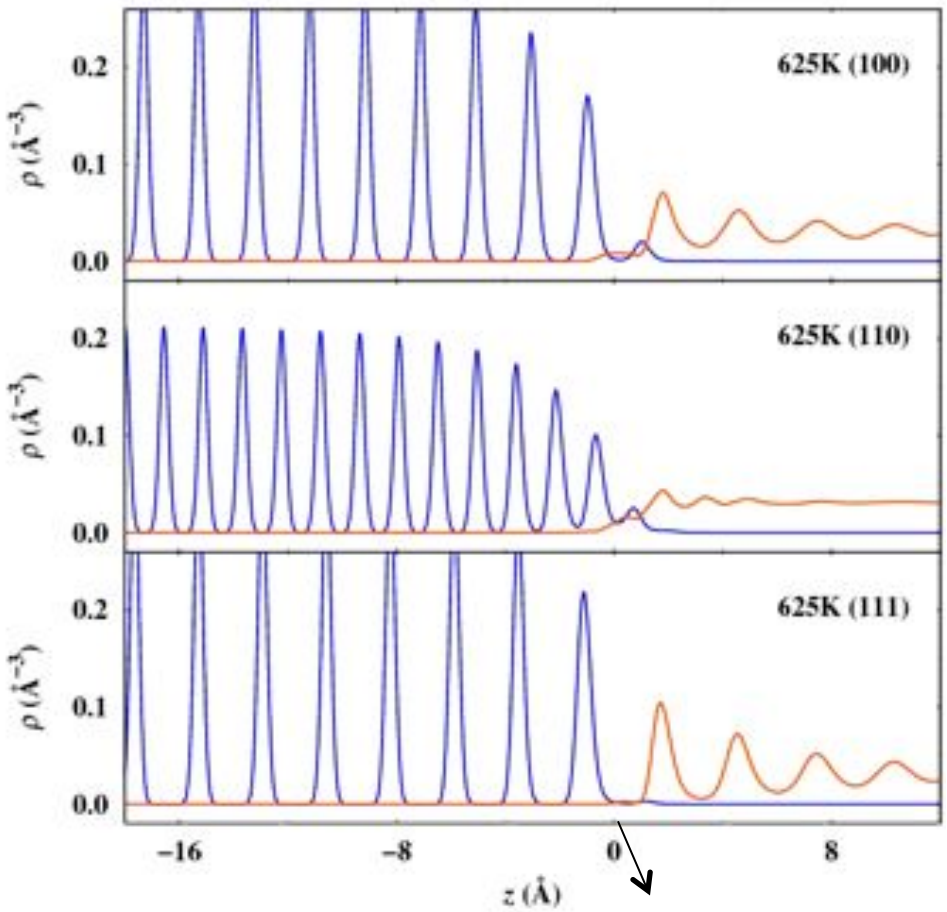


H. Gabrisch *et. al*, *Acta Mat.* (2001)

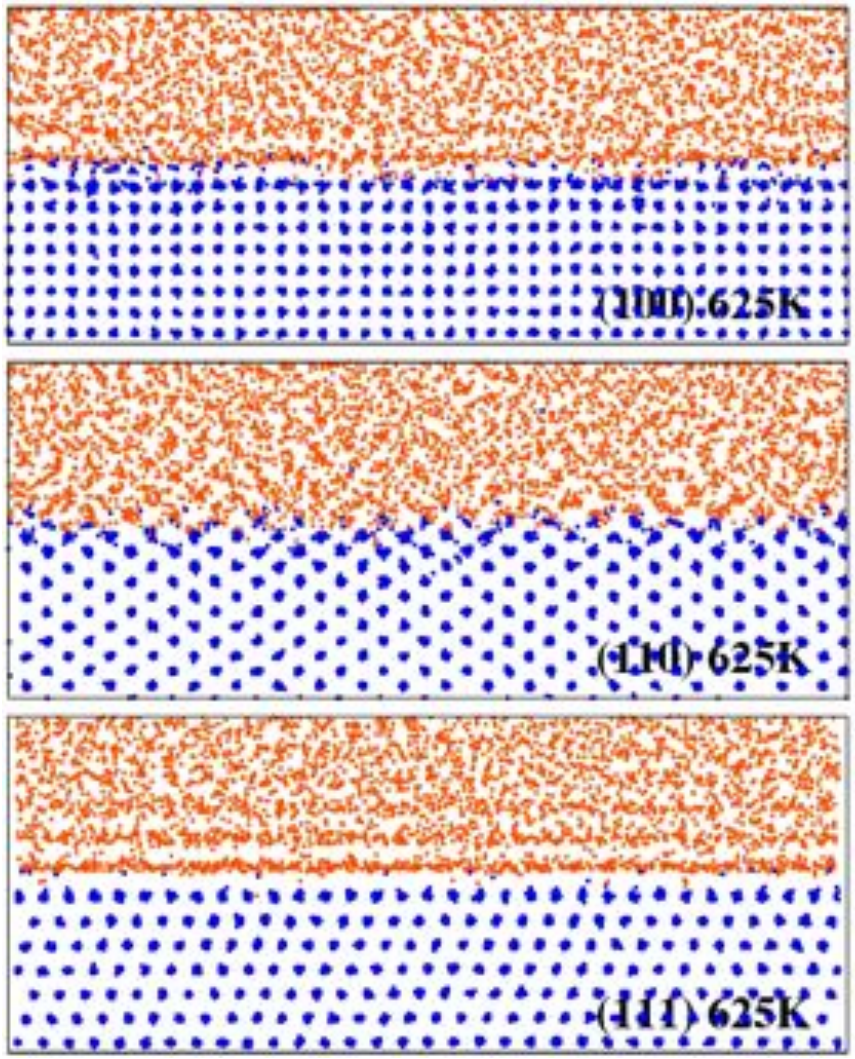
T_m(Pb): 600 K (327ºC)

Planar Solid Al/liquid Pb interfaces

Snapshots and Density Profiles

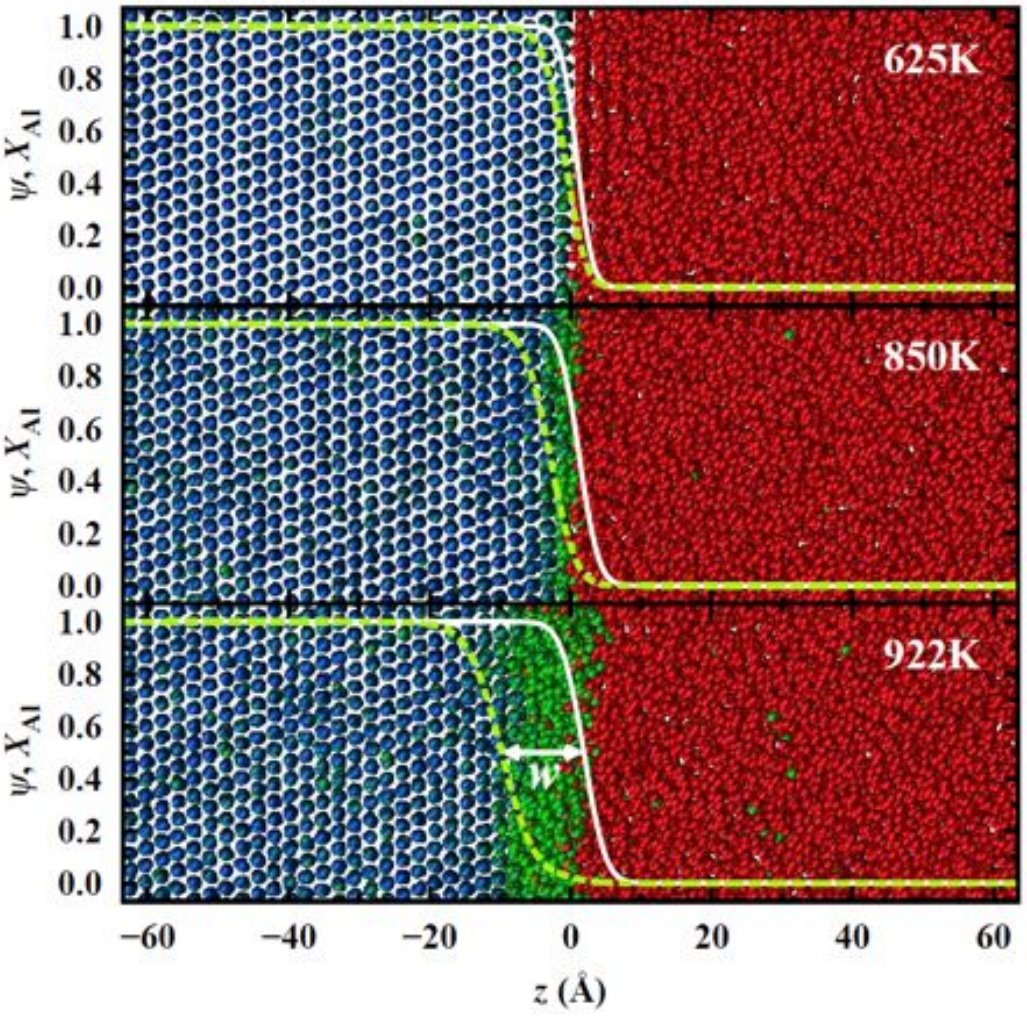


Gibbs Dividing Surface



Planar Solid Al/liquid Pb interfaces

Disordering of Interfacial Al



Coarse-grained profiles of structural order parameter (green line) and Al concentration (white line)

Atoms colored coded on the structural order parameter

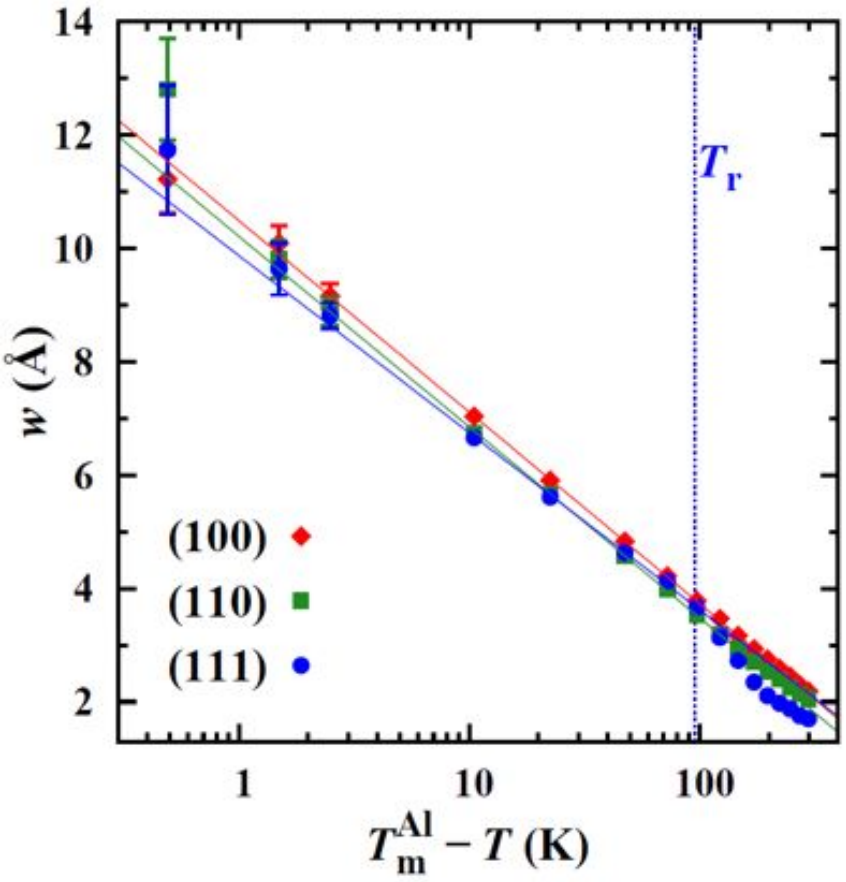
$$\psi(i) = \left| \frac{1}{6Z} \sum_{j=1}^{Z} \sum_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r}_j) \right|^2$$

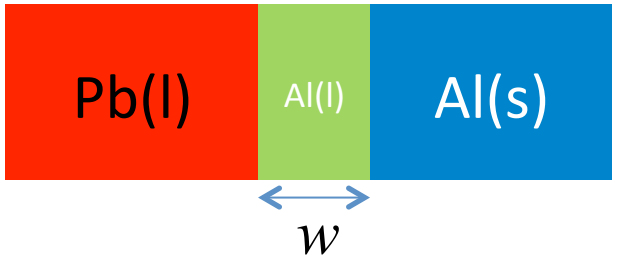
J. R. Morris, *PRB* (2002)

Blue atoms: solid Al
Green atoms: liquid Al
Red atoms: liquid Pb

Planar Solid Al/liquid Pb interfaces

Premelting Transitions in Three Orientations





$$\gamma_{sl} = \gamma_{sl}^{AlPb} + \gamma_{ll}^{AlPb} + \Delta\gamma \exp(-w/w_0) + \rho w \Delta\mu$$

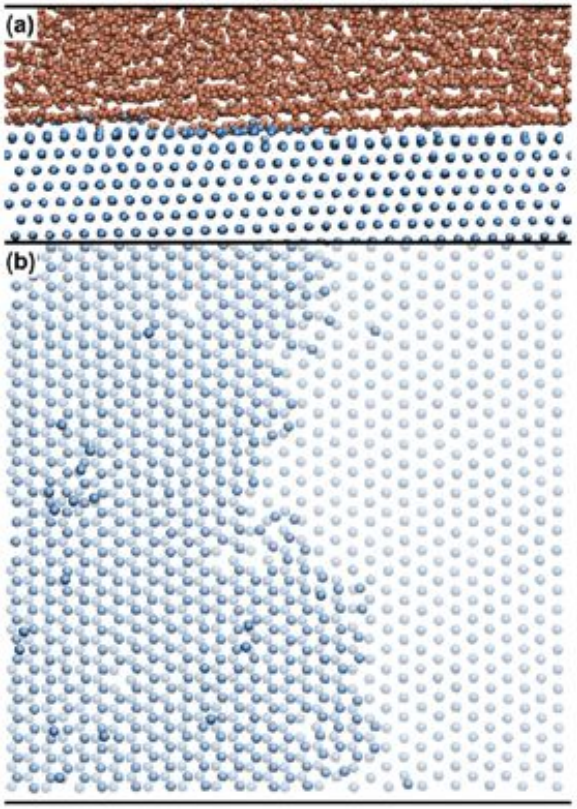
$$w = w_0 \ln T_0 - w_0 ln(T_m - T)$$

Kikuchi and Cahn, *PRB* (1980)
R. Lipowsky, *PRL* (1982)
Broughton and Gilmer, *JCP* (1987)

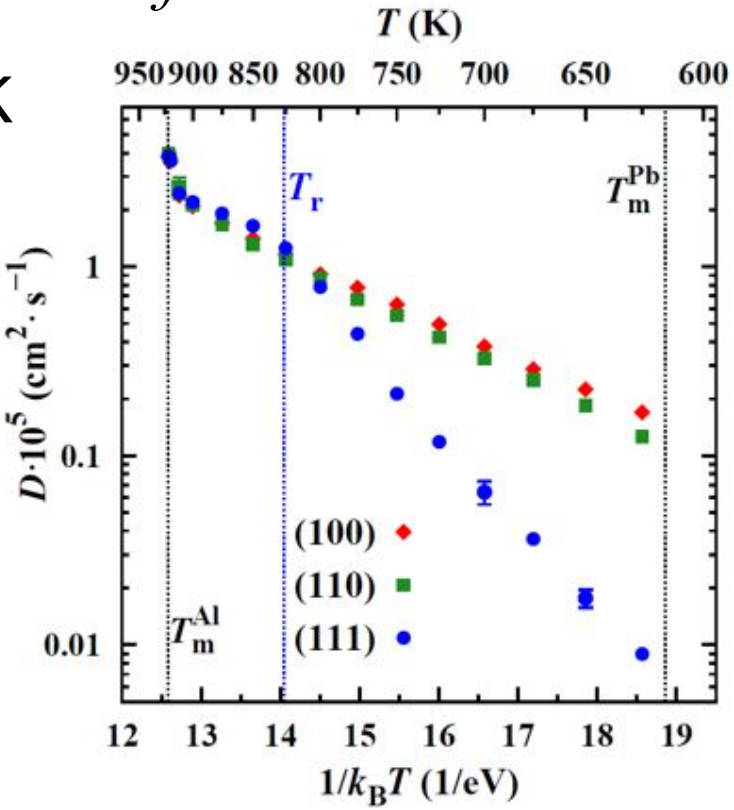
Logarithmic dependence of *w* with respect to undercooling, supporting the existence of solid-liquid premelting transition.

Planar Solid Al / Liquid Pb Interfaces

Roughening Transition in (111) Interface



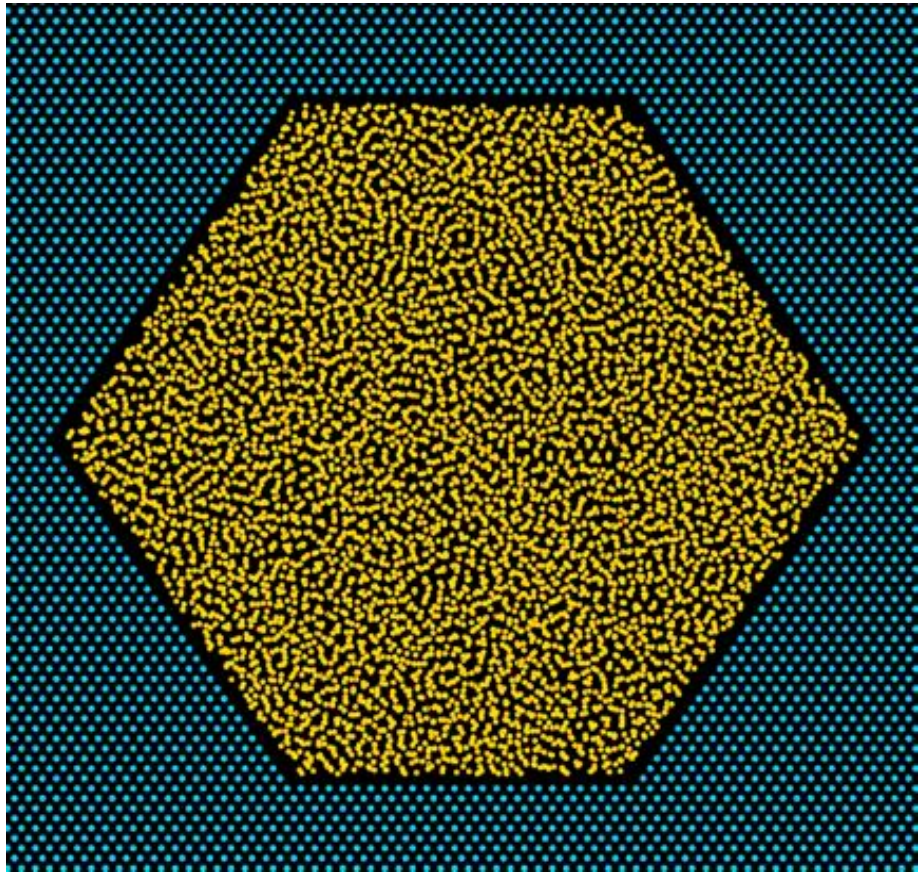
T = 625K



Current study found Tr = 825K, agrees with TEM experiment. Supports validity of interatomic potential.

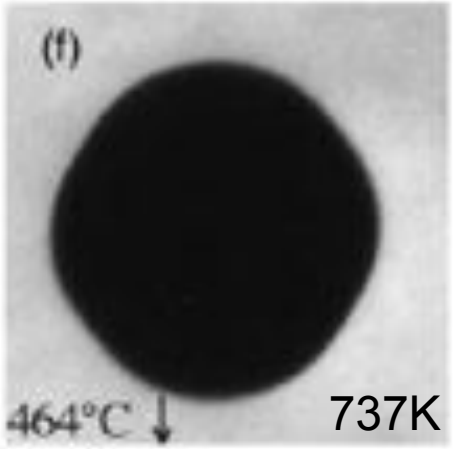
Liquid Pb Nanoparticle in Solid Al

Low temperature with (111) facets



T = 750 K

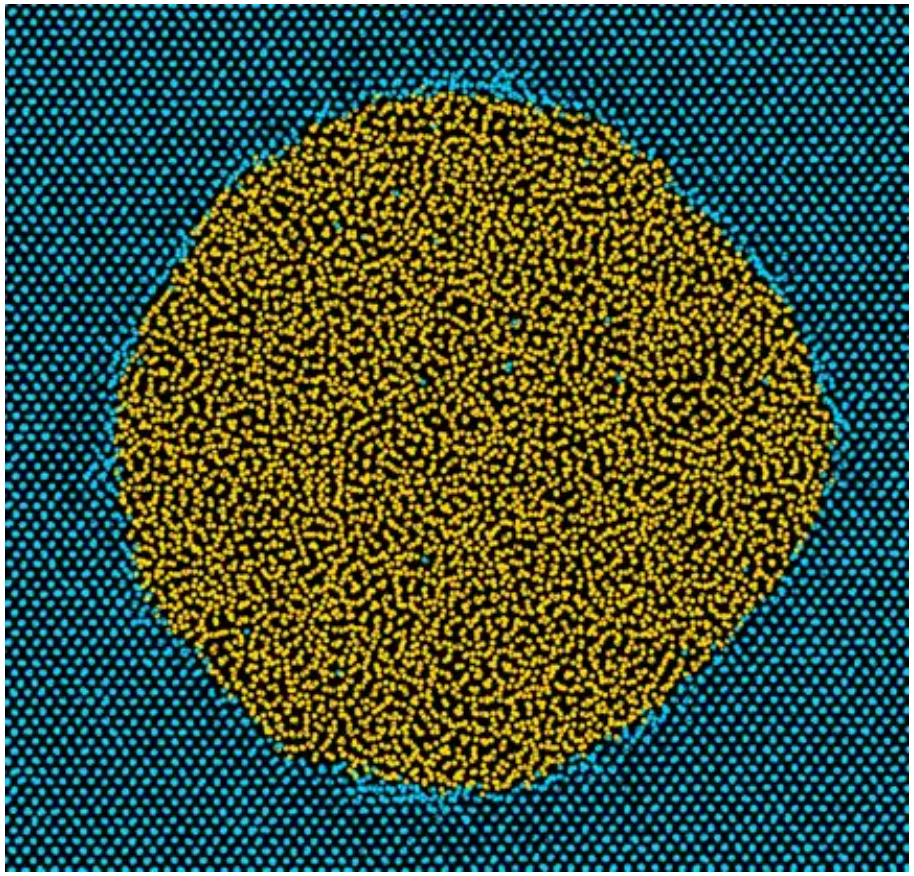
r = 8 nm



Runs for 20ns to reach equilibrium shape, agrees well with TEM observation.

Liquid Pb Nanoparticle in Solid Al

Temperature above roughening transition



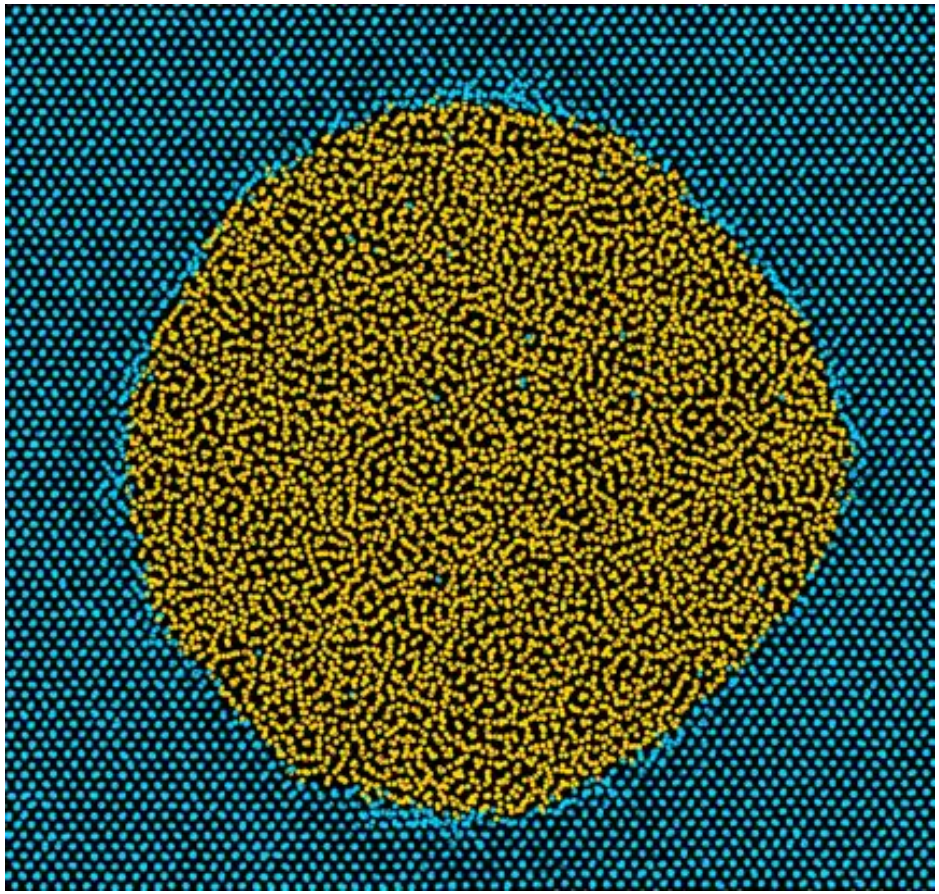
T = 850 K

Complete rounding in all orientations

(111) now rough

Liquid Pb Nanoparticle in Solid Al

Temperature above premelting transition



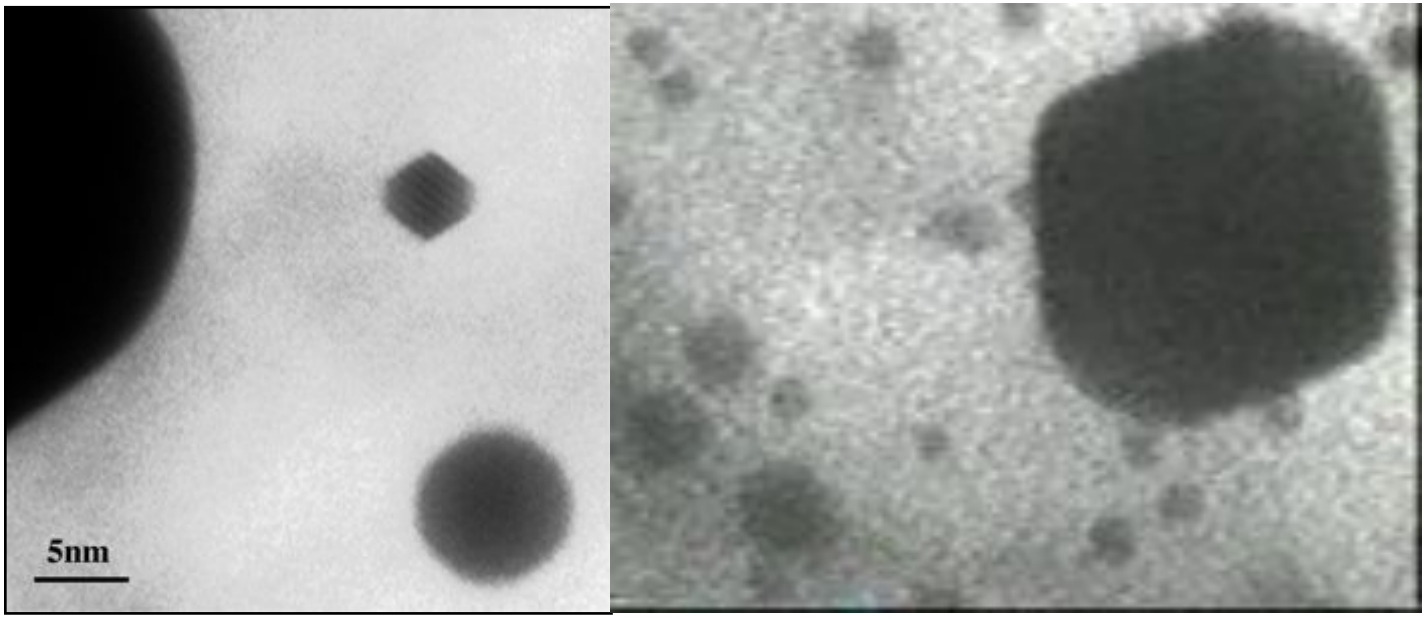
T = 922 K

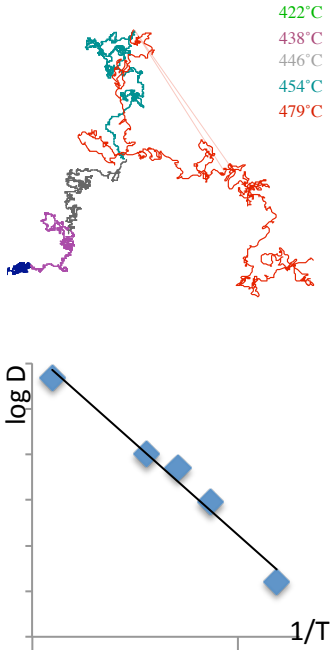
Spherical Pb droplet encased in highly dynamic premelted liquid Al shell

This temperature regime was not examined in experiment

Brownian Motion of Liquid Pb Inclusions

In-situ TEM observation at T=693 K (Dahmen group, LBNL)



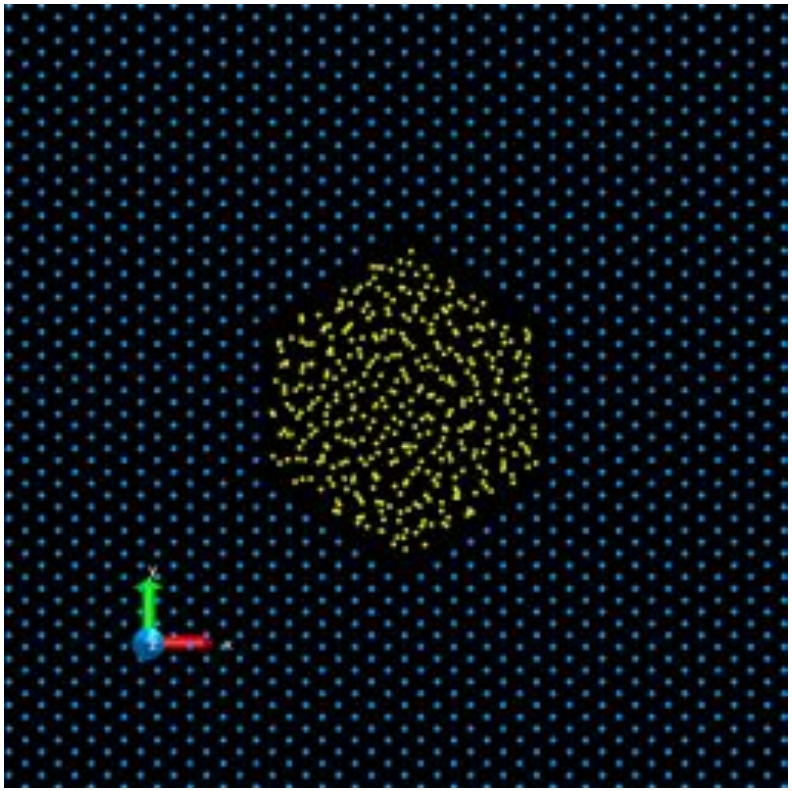


- Large particles are liquid and immobile.
- Small particles are solid and immobile.
- Medium particles are liquid and move.

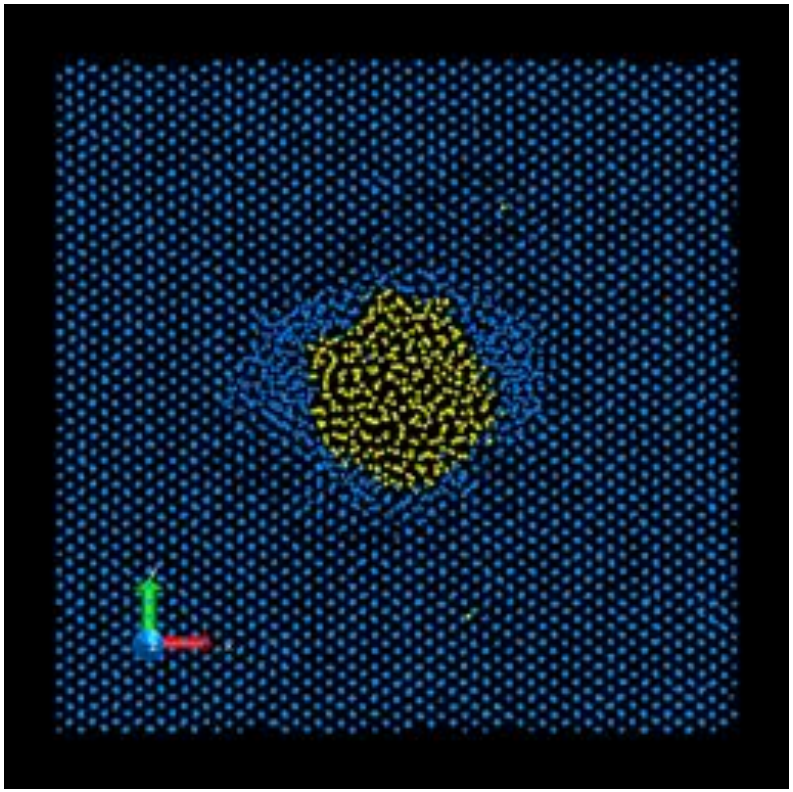
Activation energy of particle diffusion
Q=2.5 eV
R=11.5 nm

Brownian Motion of Liquid Pb Inclusions

Simulations



Random walk at premelted Al/Pb interface (922 K)



Forced motion at premelted Al/Pb interface (922 K): add force of 1 meV/nm/Pb atom.

Part II: Curvature dependence of γ_{sl}

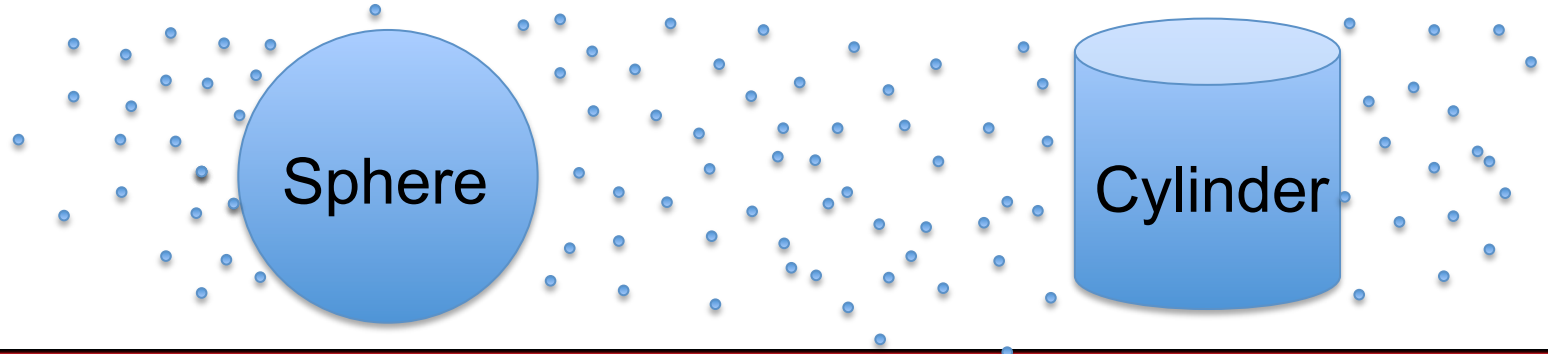
Interfacial free energy between a static surface and a fluid. Important for understanding

- Wetting
- Stability of colloids in solution

Problem: how does the interfacial free energy depend upon the curvature of the wall.

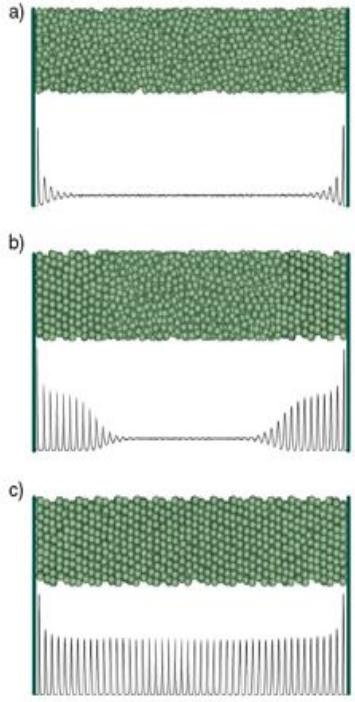
with
Dr. Ruslan Davidchack
Dept. of Mathematics
University of Leicester, UK

Model: hard-sphere fluid at hard wall: two geometries



The planar hard-sphere/hard-wall interface

- 1992, Courtmanche and Van Swol [PRL 69, 2078 (1992)] report "wetting layer" of (111) crystal at a HS wall/fluid interface below the freezing density.
- 2004, M. Dijkstra, [PRL 93, 108303 (2004)] reports more conclusive evidence in simulations of hard spheres in a slit-pore geometry with L_z ranging from 21.8σ to 86.9σ.

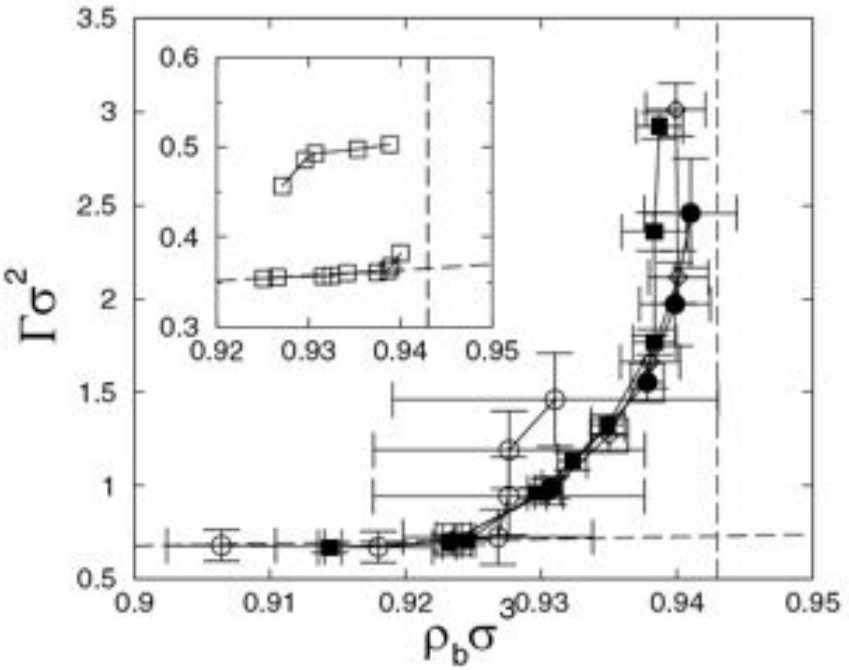


Absorption at wall (G):

• independent of system size

•diverges near freezing density

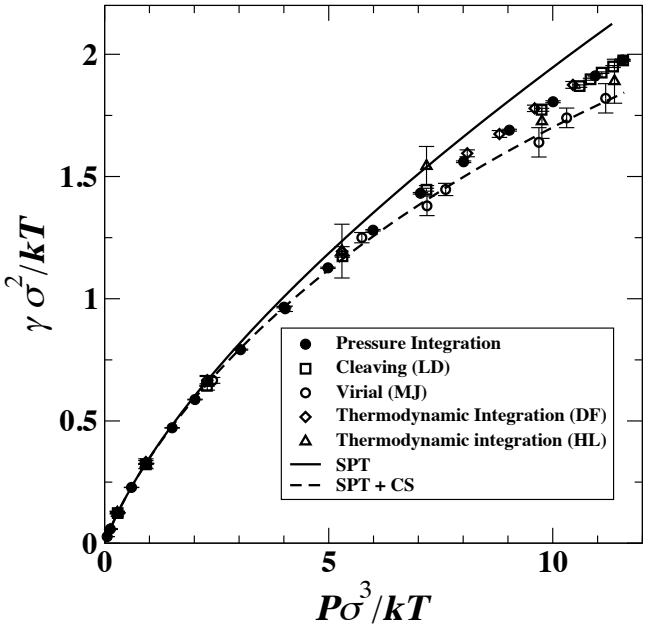
Can this be predicted thermodynamically?

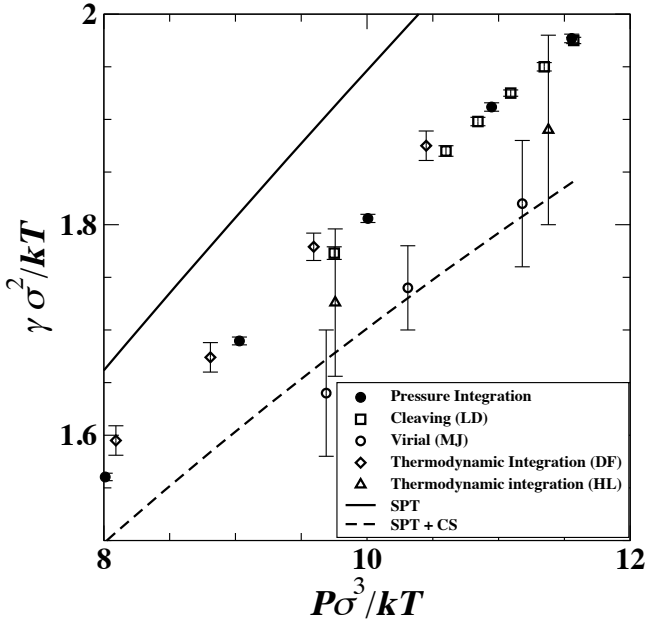


The planar hard-sphere/hard-wall interface

Free energies from Gibbs-Cahn Integration[1]

$$\gamma = \int_0^P v(P)dP \quad v(P) = \int_0^\infty [1 - \rho(z;P)/\rho]d\rho$$





At freezing ($\rho\sigma^3 = 0.939$)

$$\gamma_{\rm wf} = 1.974(2)kT\sigma^{-2}$$

$$\gamma_{\rm wc}^{111} = 1.410(2)kT\sigma^{-2}$$

$$\gamma_{\rm cl} = 0.542(2)kT\sigma^{-2}$$

$$\gamma_{\rm wc}^{111} + \gamma_{\rm cl} < \gamma_{\rm wf}$$

Driving force for prefreezing!

Laird & Davidchack, *J. Chem. Phys* **132**, 204101 (2010); J. Phys. Chem. C, **111,** 15952 (2007)

Curved Walls: Hadwiger's Theorem[1]

A motion invariant, continuous and additive valuation Ω, defined on a surface S, can be written as a linear combination of four measures of S

$$\Omega[S] = -pV + \gamma_0 A + hH + \kappa K$$

where V = volume, A = surface area, H and K are the integrated mean and Gaussian curvatures, respectively. Here, we view Ω as a free energy of a surface solvated in a fluid.[2]

A curvature-dependent interfacial free energy can be defined

$$\gamma[S] = \gamma_0 + h\bar{H} + \kappa\bar{K}$$

where the average mean and Gaussian curvatures are defined as

$$\bar{H} = \frac{H}{A} = \frac{1}{2A}\int_S \left(\frac{1}{R_1} + \frac{1}{R_2}\right) dS \text{ and } \bar{K} = \frac{K}{A} = \frac{1}{A}\int_S \left(\frac{1}{R_1 R_2}\right) dS$$

[1]H. Hadwiger, *Vorlesungen über Inhalt, Oberfläche und Isoperimetrie* (Springer, Berlin, Germany, 1957)
[2]P.M. König, R. Roth and M. Mecke, PRL, 160601 (2004).

Spherical and Cylindrical Walls

Hadwiger's theorem (Morphometric Thermodynamics) gives

Sphere: $\gamma_s = \gamma_0 + 2h/R_s + \kappa/R_s^2$

Cylinder: $\gamma_c = \gamma_0 + h/R_c$

h and *κ* are independent of wall shape!

Theoretical results

- Scaled Particle Theory (1961) (for sphere)

$$\gamma^*_{\mathrm{SPT}}(\eta) = \frac{3\eta(2+\eta)}{2\pi(1-\eta)^2} + \frac{3\eta}{2\pi(1-\eta)}\frac{1}{R} + \frac{\ln(1-\eta)}{4\pi}\frac{1}{R^2}$$

Reiss, Frisch, Helfand & Lebowitz, JCP **32**,119 (1960); Henderson, JCP, **116,** 5039 (2002).

- Density Functional Theory (FMT, White Bear)

$$\Omega[\rho(r)] = F[\rho(r)] + \int dr[V(r) - \mu]\rho(r)$$

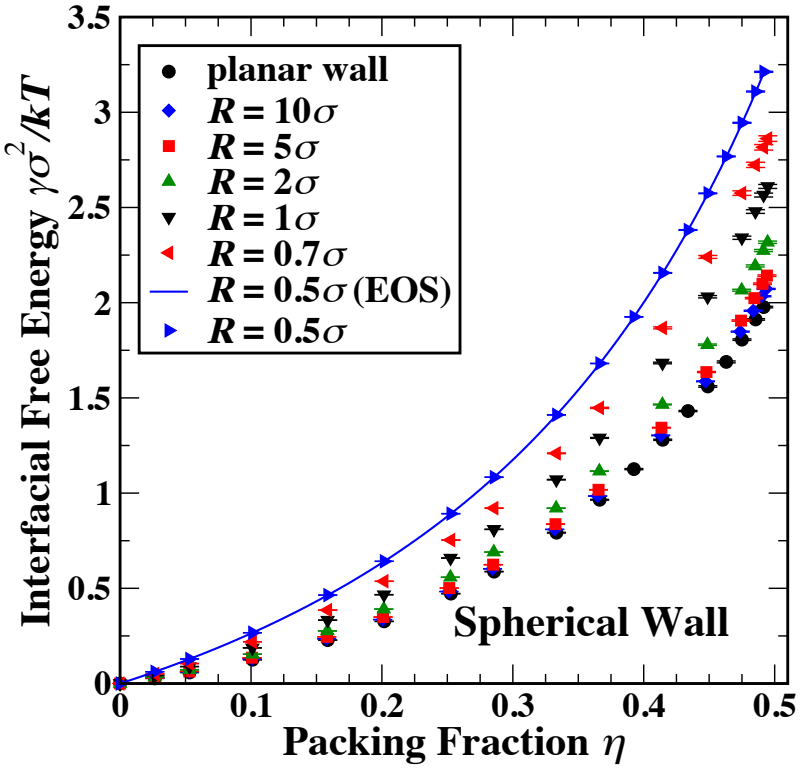
Bryk, Roth, Mecke & Dietrich, PRE **68**,031602 (2003).

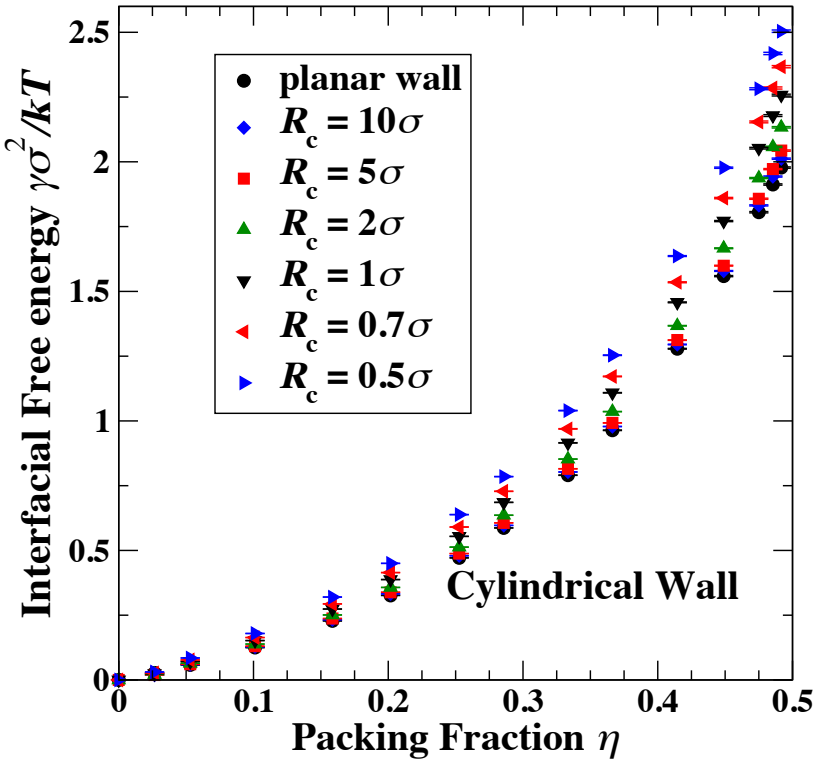
Results for hard-sphere fluid at curved walls

$$\gamma(\eta) = \int_0^{P(\eta)} v_{\rm ex}(P;R)\, dP \qquad v_{\rm ex} = \frac{1}{R^i}\int r^i[1-\rho(r)/\rho_0]dr$$

Sphere: $i = 2$
Cylinder: $i = 1$

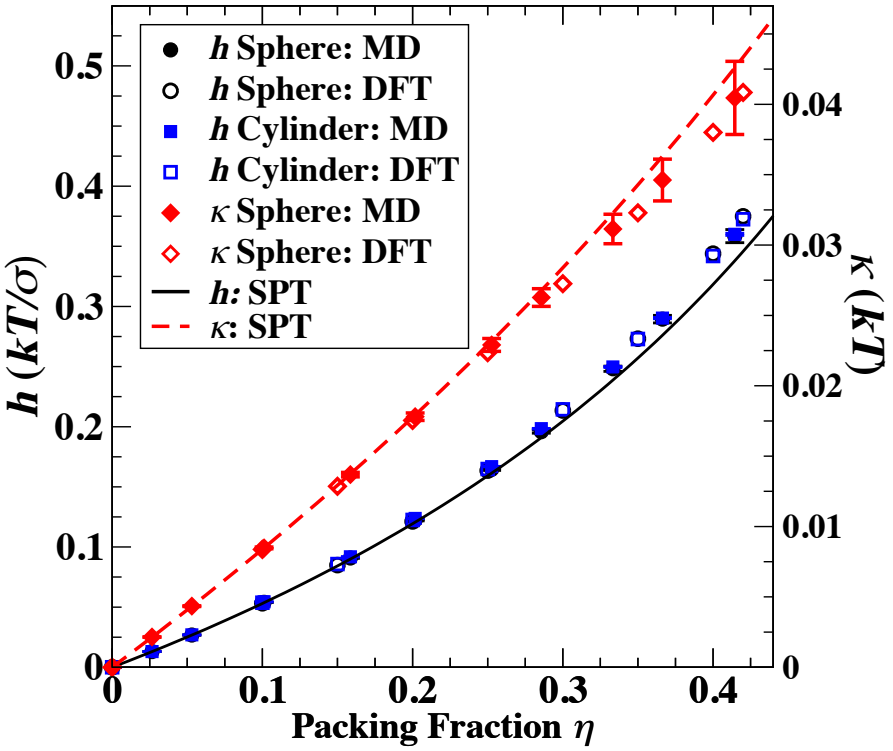
Packing Fraction $\eta = \pi\rho\sigma^3/6$

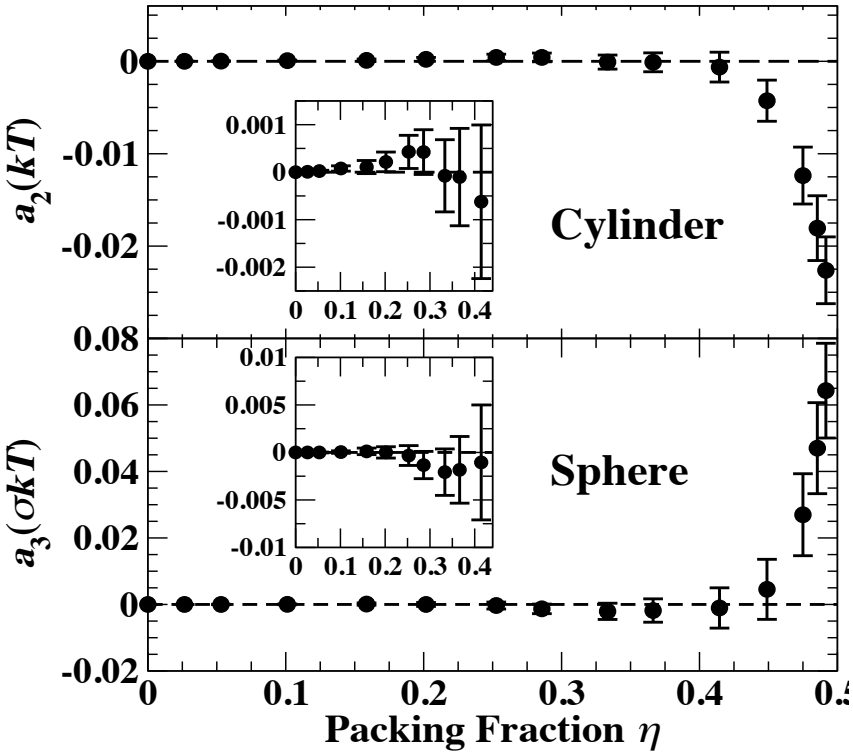




Laird & Davidchack, submitted

Results for hard-sphere fluid at curved walls





Hadwiger's theorem holds for packing fractions to 0.42, but breaks down at higher densities.

The Laird Group