Heterogeneous Solid-Liquid Interfacial Premelting and its Applications

in Brownian Motion of Liquid Inclusions, Wetting/Spreading

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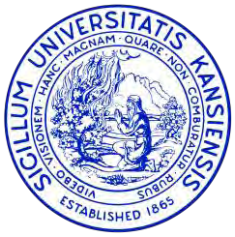
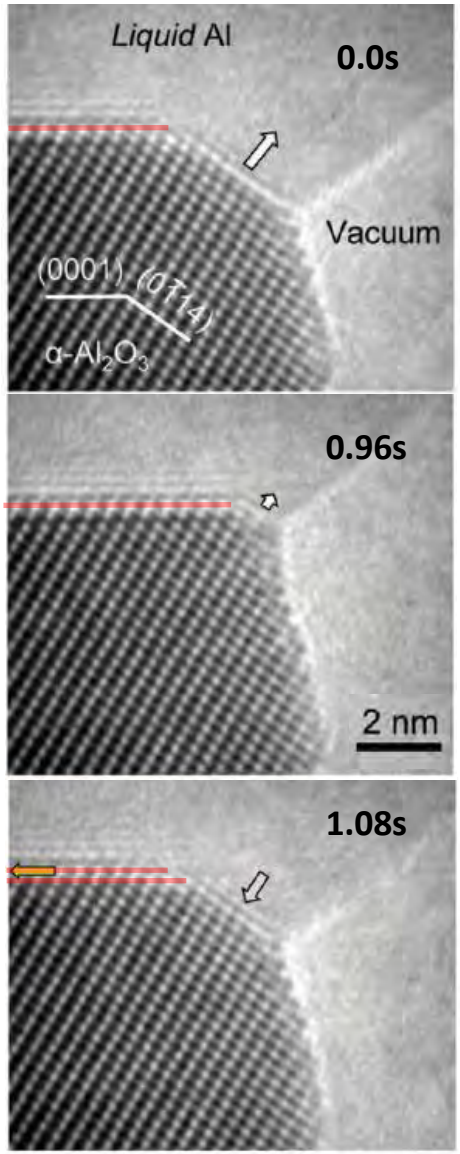


Heterogeneous Solid-Liquid Interfaces (SLIs)

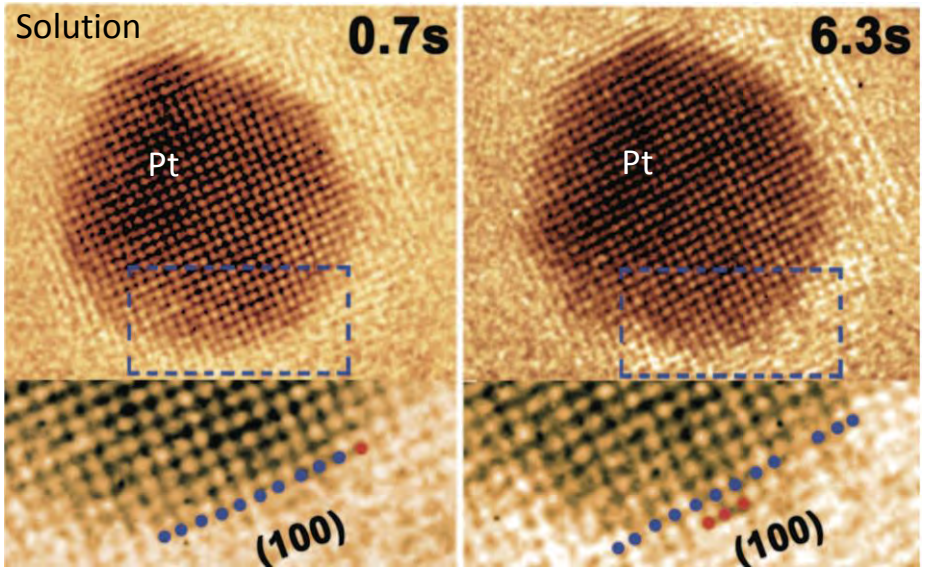
Wetting

Nucleation



VLS Nanowire Growth

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



Crystal Growth from Solution

H.-G. Liao *et al.*,*Science* (2014)

Grain Refiner in Casting

P. Schumacher *et al.*, *Mat. Sci. Tech.* (1998)

Various Structural Types of Heterogeneous SLIs

Outstanding Issues Remain Incompletely Understood

Due to size mismatch, alloying, anisotropy, *T:*

- Layer ordering of interfacial liquid.
- Lateral short range ordering of interfacial liquid.
- Prefreezing (lateral long range ordering) of interfacial liquid.
- Roughening (disordering) of interfacial solid.
- Premelting (disordering) of interfacial solid.

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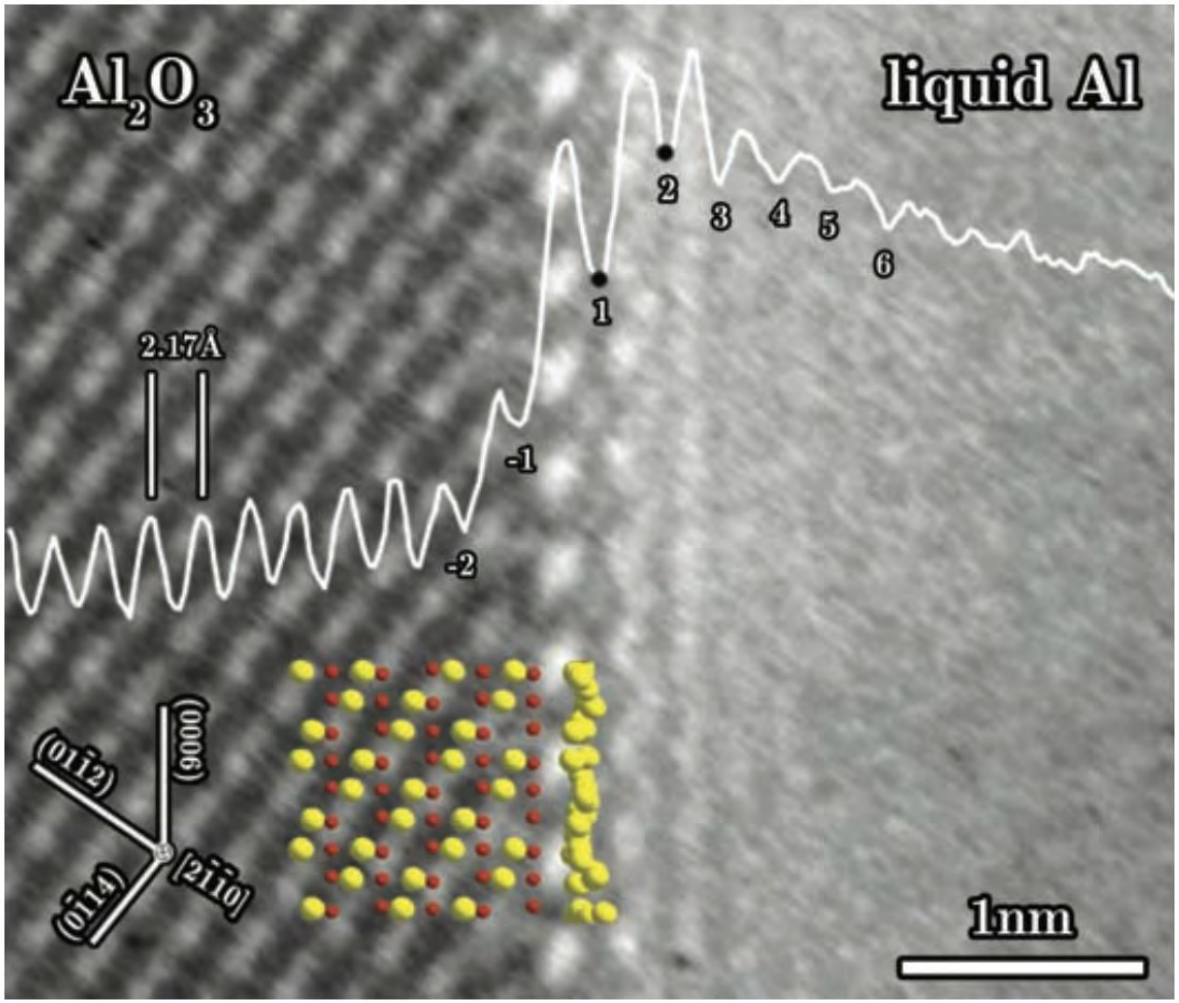

TEM observation of VSL interface, Layer ordering of liquid Al

S.-H. Oh *et al.*, *Science* (2005)

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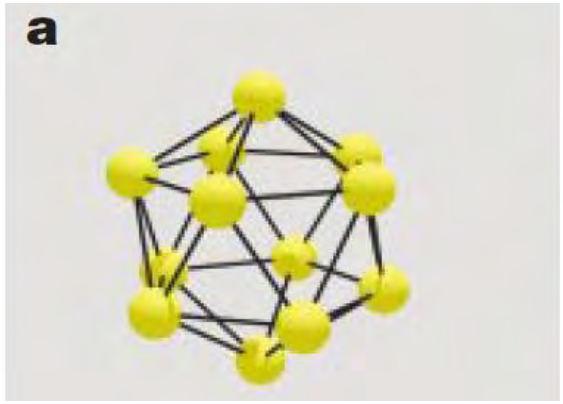

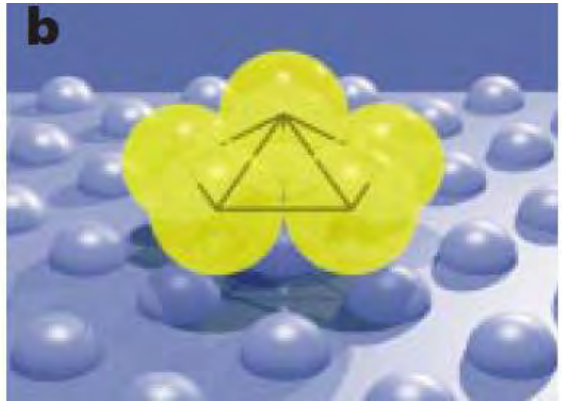

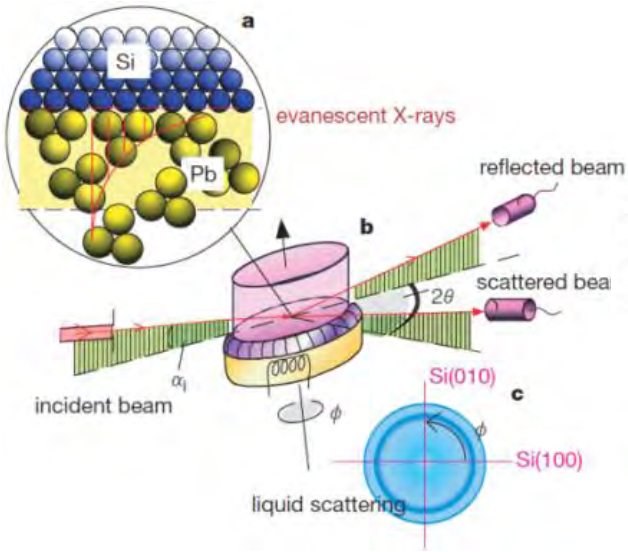

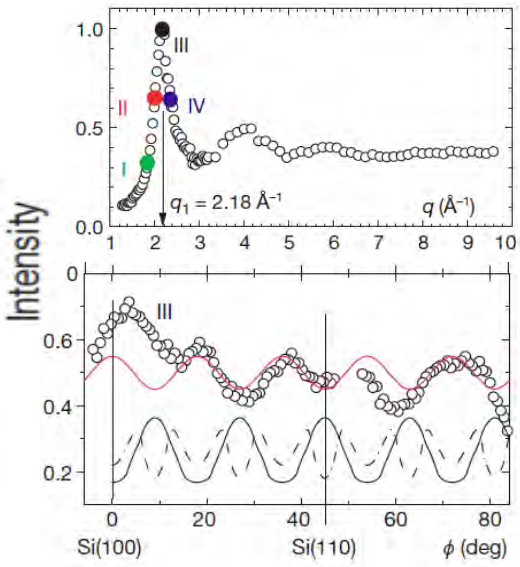

In-plane X-ray, liquid Pb in contact with Si(100), five-fold lateral ordering

H. Reichert *et al.*, *Nature* (2000)

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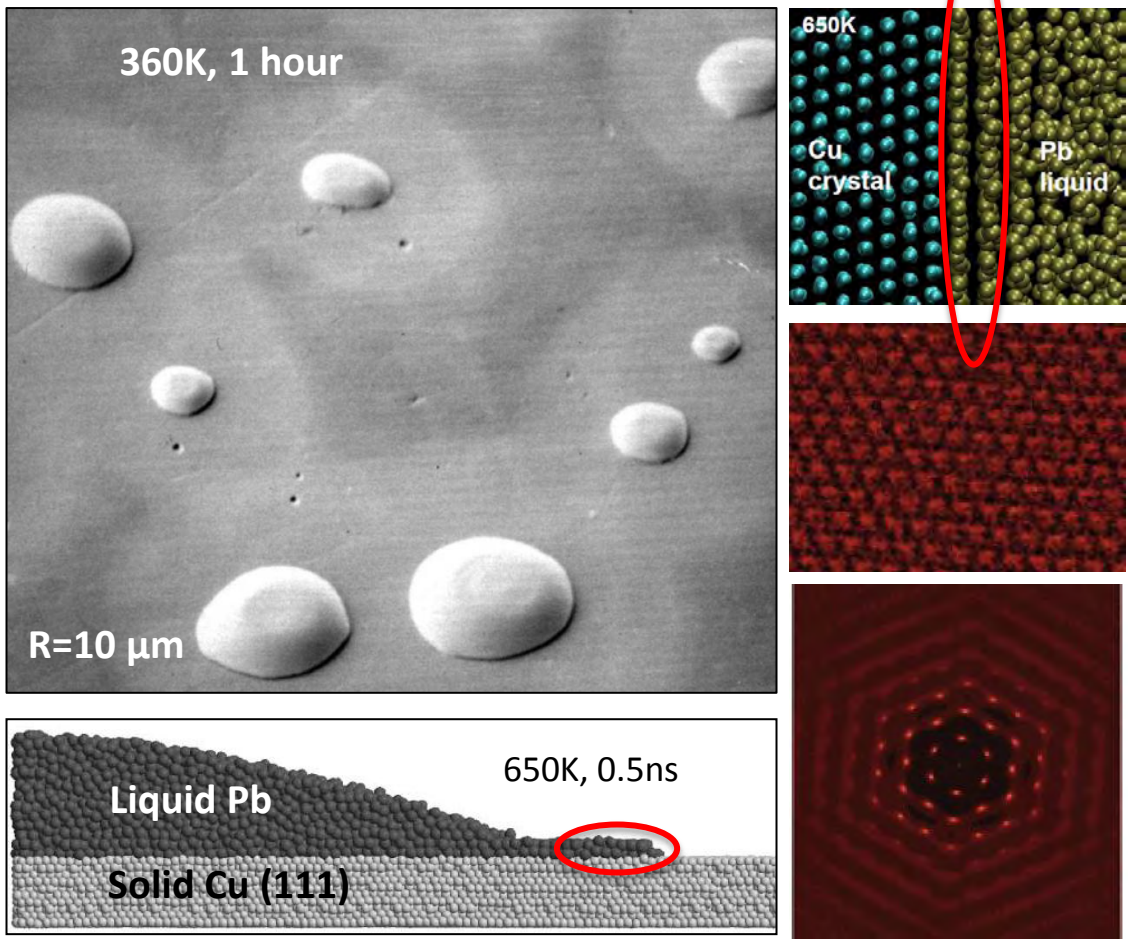

Spreading of Pb(l) on Cu surfaces with rapid precursor film

Moon *et al.*, *Surf. Sci.* (2001)
E. B. Webb *et al.*, *Phy. Rev. Lett.* (2003)
J. P. Palafox-Hernandez *et al.*, *Acta Mat.* (2010)

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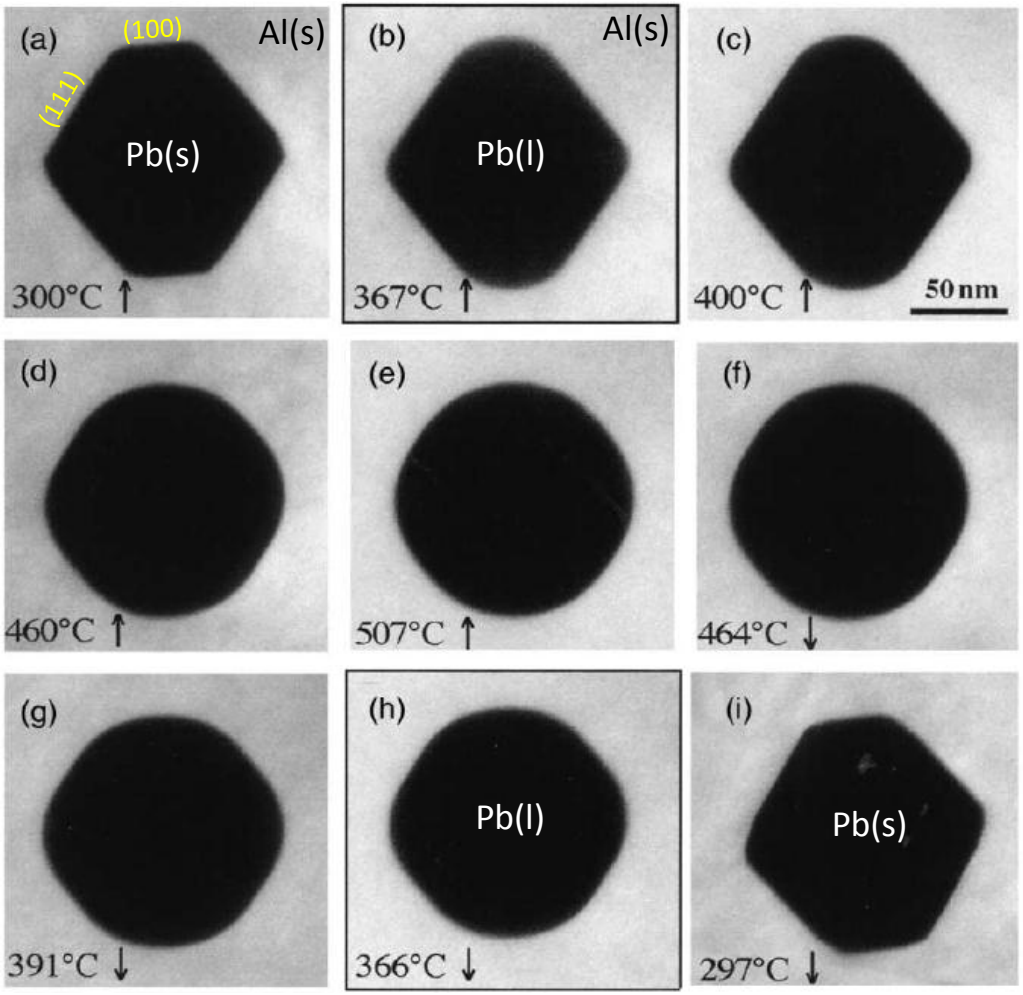

TEM observation Pb inclusion in solid Al

Rounding in (100), (110) and (111), T_r=823K, 2% anisotropy.

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

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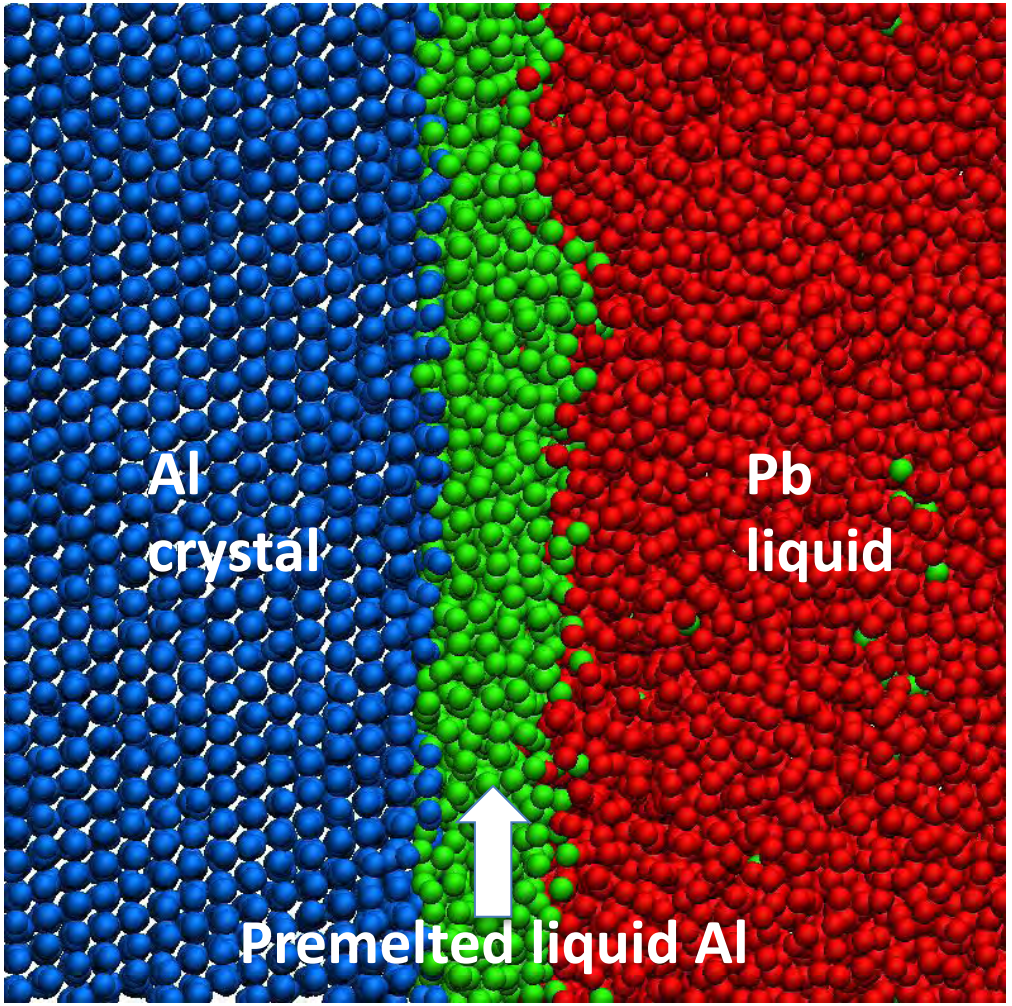
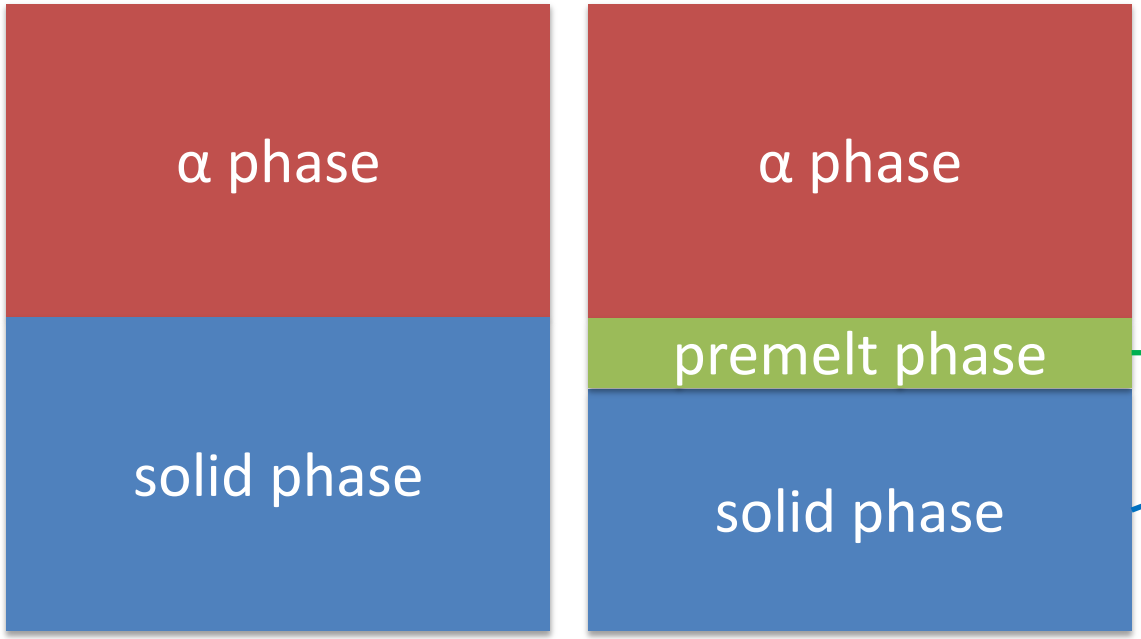


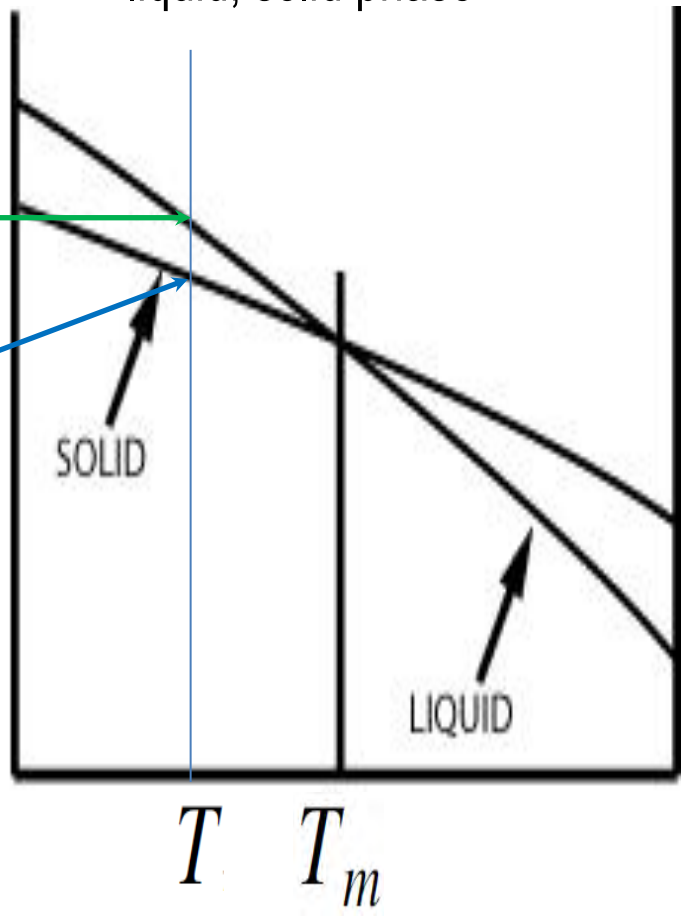
MD simulation predict the existence of premelting at SLI.

Y. Yang *et al.*, *Phy. Rev. Lett.* (2013)

Interfacial Premelting Transitions



- α phase could be vapor, liquid, solid phase



$$\Delta\gamma = \gamma_{s\alpha} - [\gamma_{sl} + \gamma_{l\alpha}] > 0$$

If the undercooling is not too great, it is thermodynamically favorable to form a thin film of metastable liquid because the increase in bulk free energy is more than compensated for by a lowering of the total interfacial free energy.

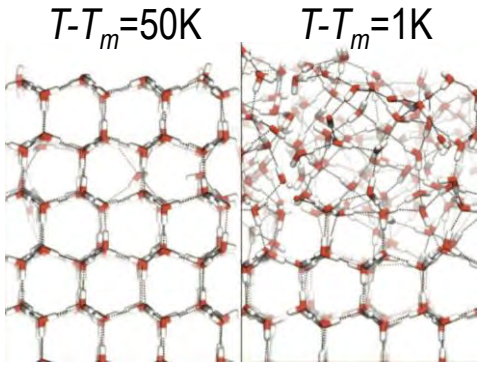
Interfacial Premelting Transitions

α phase

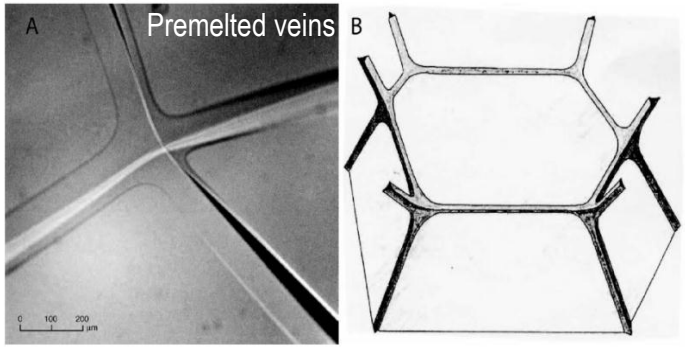
premelt phase

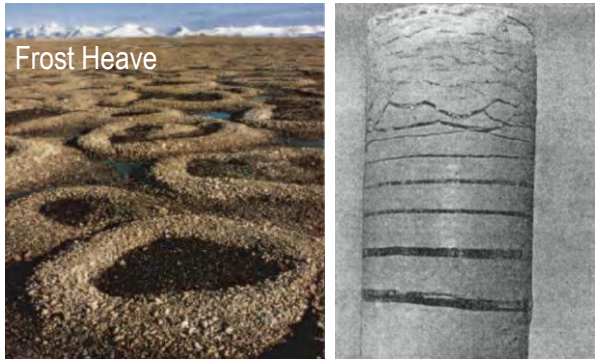
solid phase

"Why Is Ice Slippery?", *Phys. Today* (2005)



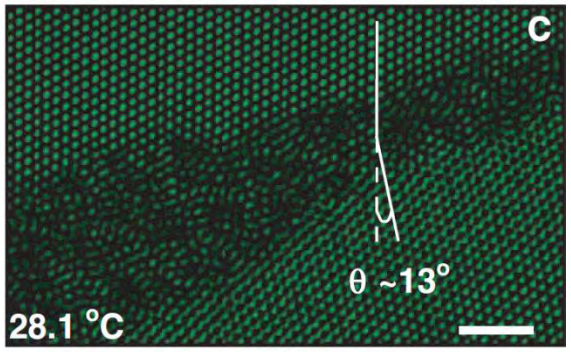
D. Limmer and D. Chandler, *J. Chem. Phys.* (2014)



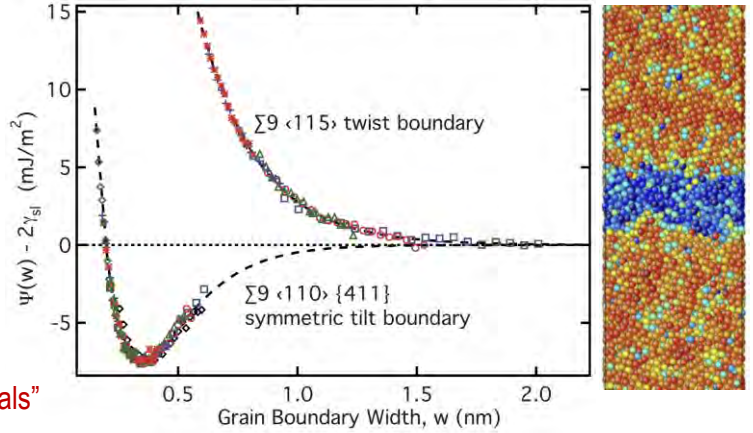


"The physics of premelted ice and its geophysical consequences", *Rev. Mod. Phys.*, 78, 3, (2006)

- α is vapor. Surface melting.
- α is solid. Grain-boundary premelting.
- Numerous continuum modeling studies, atomistic simulations and experimental studies on these two types of premelting.
- Few studies on case that α is liquid.

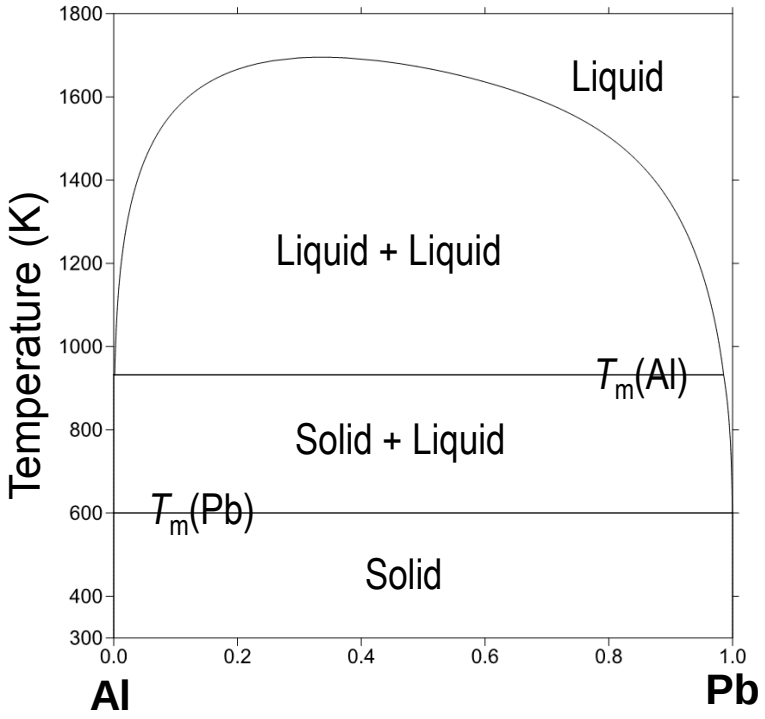


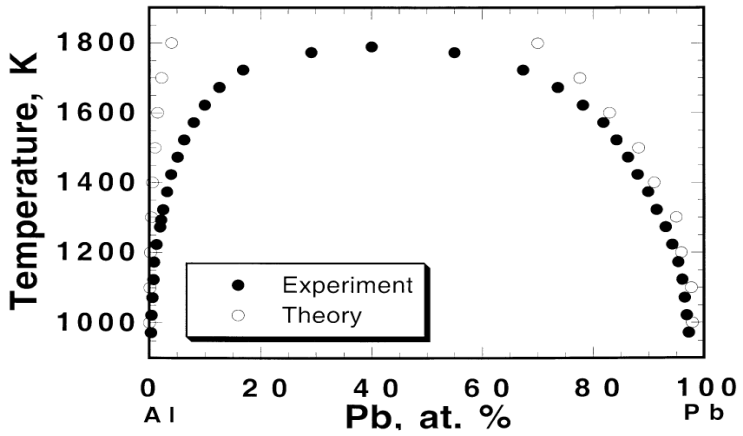
"Premelting at Defects Within Bulk Colloidal Crystals" *Science*, 309, 19, 1207, (2005)



S. J. Fensin *et al.*, *Phys. Rev. E* (2010)

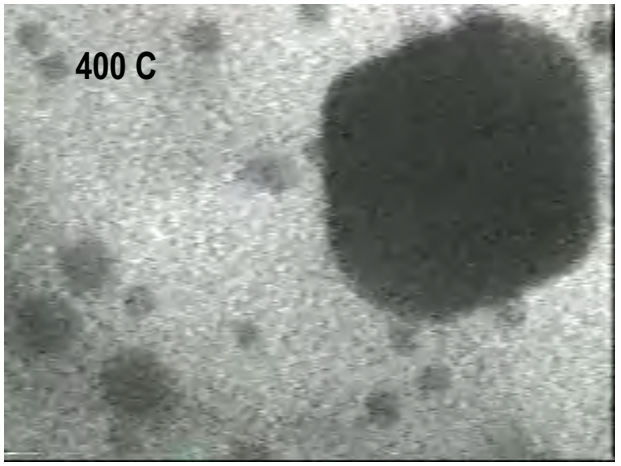
Premelting at Heterogeneous Al-Pb Solid-Liquid Interfaces



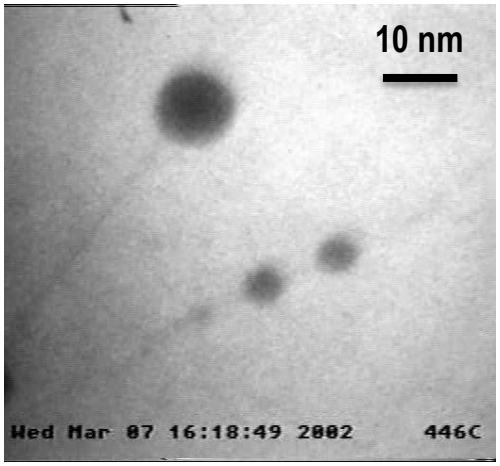


A. Landa *et al., Acta Mat.* (2000)

- Ideal model alloy for the study of chemically heterogeneous solid-liquid interfaces
- Simple monotectic, broad liquid-liquid miscibility gap, negligible solubility of Pb in the Al solid phase
- Widely separated T_m
- Zoo of interesting phenomena observed from experiment



TEM, Brownian motion of Pb inclusion in Al



Collective motion along dislocation line

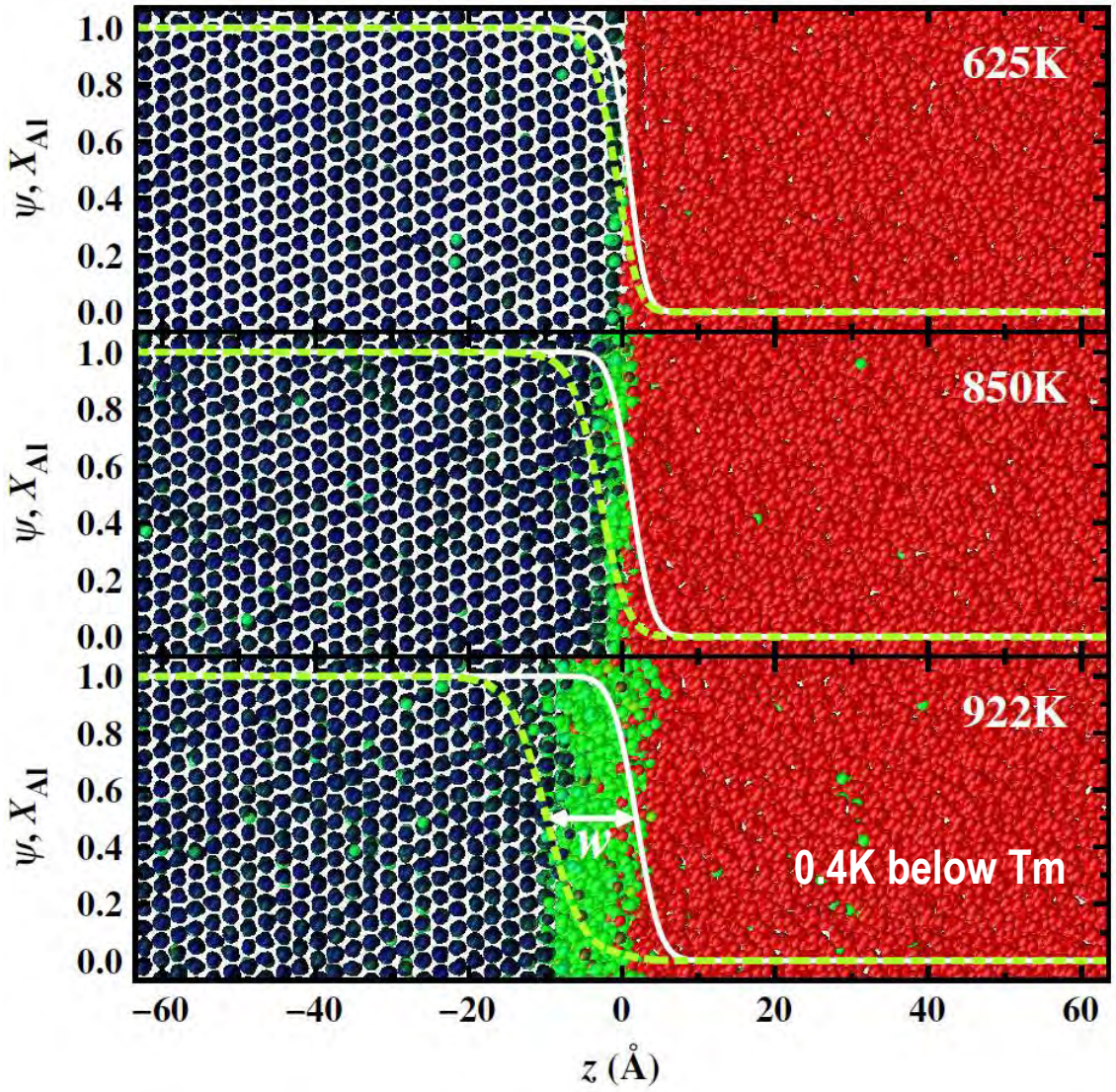
E. Johnson *et al., J. Mater. Sci.* (2005), and Privately provided by Uli Dahmen.

Molecular dynamics simulation

- LAMMPS (Sandia National Labs)
- EAM potential by Landa *et al.*
- *NVT,* Nosé-Hoover thermostat
- Equilibrium SLIs between the melting points of Al and Pb (from 625K to 922K)

	MD	Exp.
T_m(Al):	922.4K (649C)	932K (659C)
T_m(Pb)	615K (342C)	600K (327C)

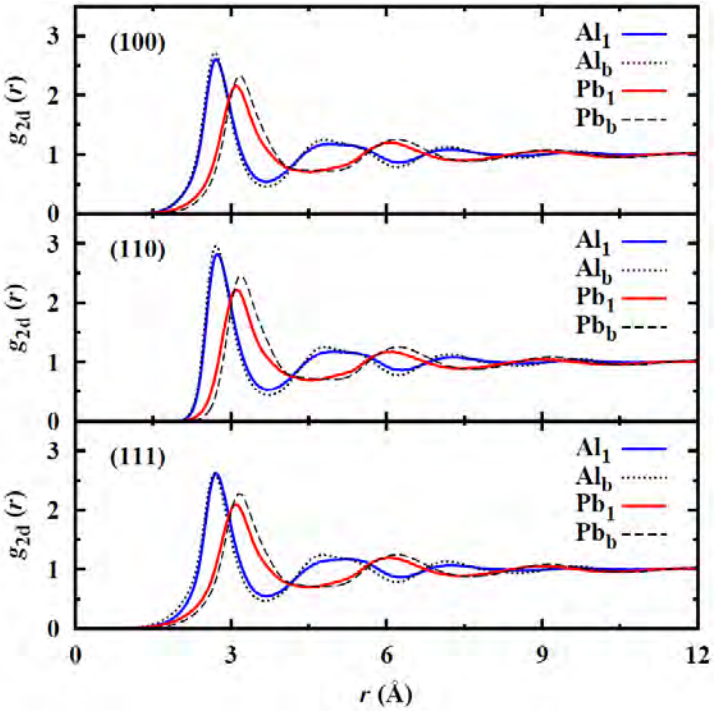
Premelting at Heterogeneous Al-Pb Solid-Liquid Interfaces



- Snapshot, three *T* for (111)
- Gibbs Dividing Surface
- Red for Pb, order parameter color
- OP interfacial profiles

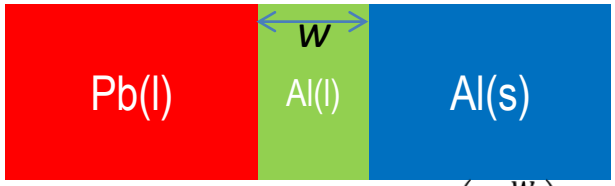
$$\psi(z) = \frac{\langle \psi_z \rangle}{V_z} \quad X_{\mathrm{Al}}(z) = \frac{\rho_{\mathrm{Al}}(z)}{\rho(z)}$$

- Determining premelting width



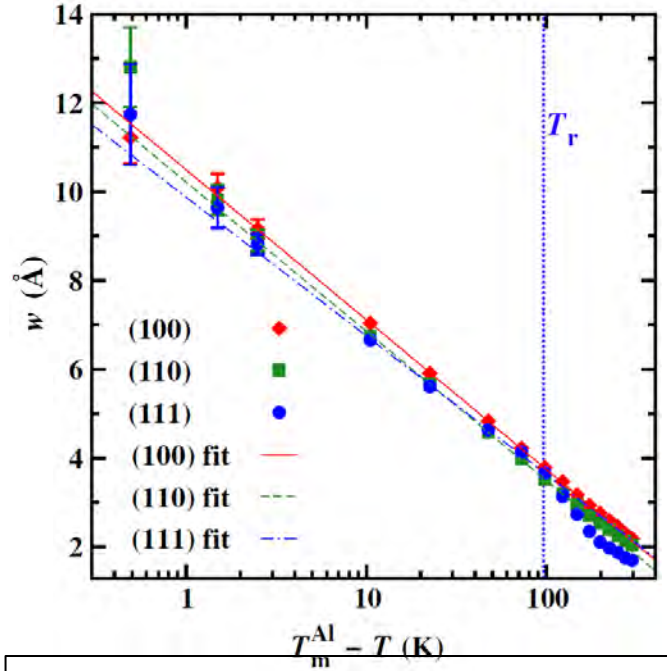
2D lateral structure analysis for 922K

Premelting at Heterogeneous Al-Pb Solid-Liquid Interfaces



$$\gamma_{SL} = \gamma_{sl-AlAl} + \gamma_{ll-AlPb} + \Delta\gamma \exp\left(-\frac{w}{w0}\right) + \rho w \Delta\mu$$

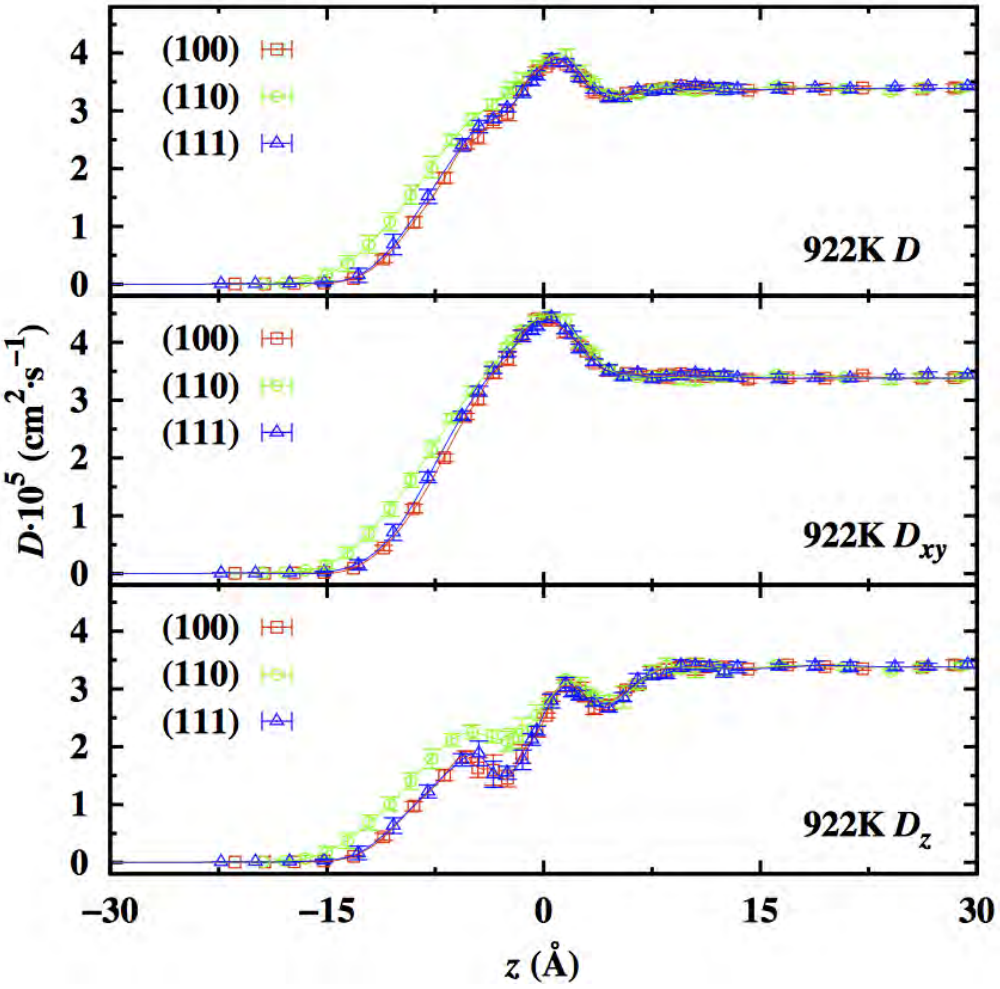
$$w = w_0 \ln T_0 - w_0 \ln(T_m - T)$$



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

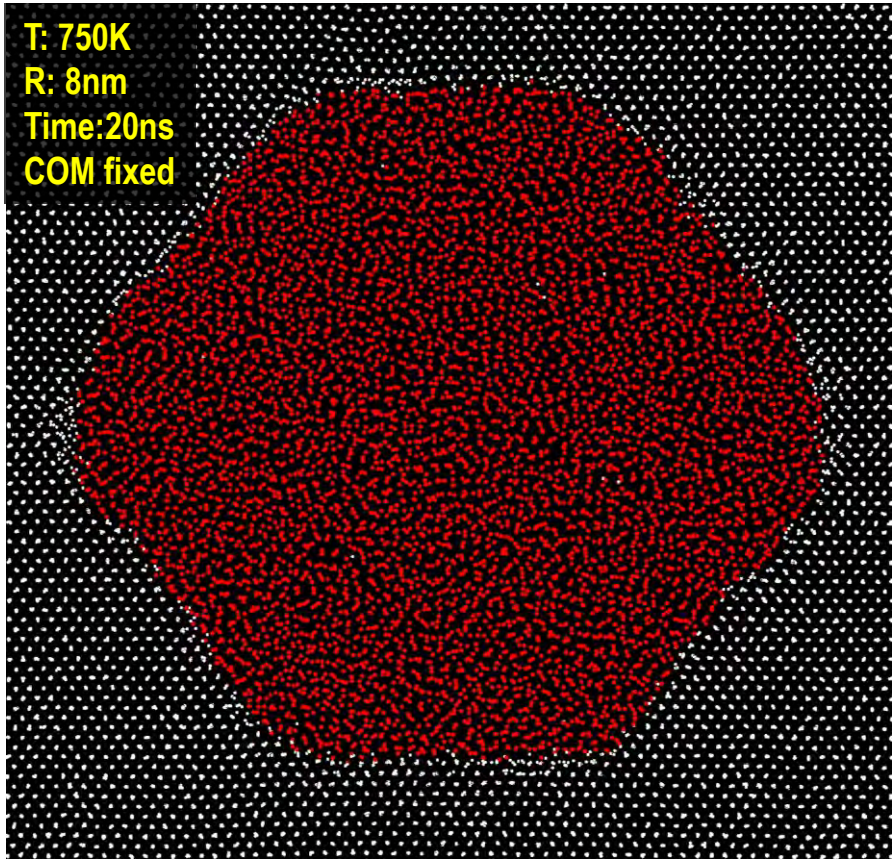
The third category of premelting in nature.

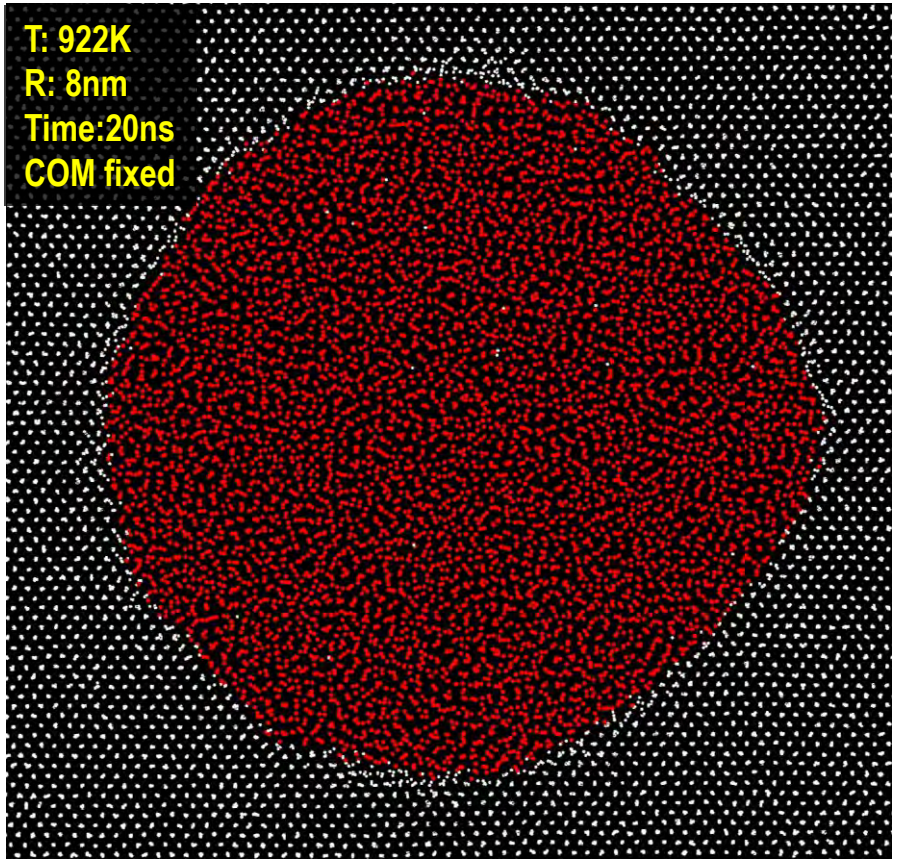
- Isotropic, (100) (110) (111)
- Satisfy condition that the melt phase of the solid and the liquid phase are mutually immiscible
- Interfacial transport channel, $D_{xy} > D_z$
- Email contact with other groups



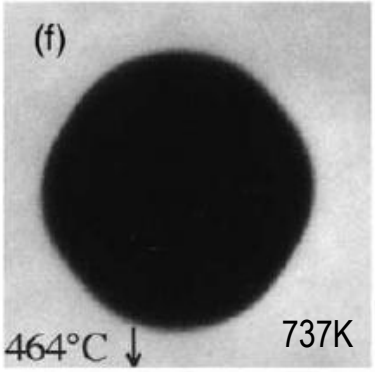
Kikuchi and Cahn, *Phys. Rev. B* (1980)
Lipowsky, *Phys. Rev. Lett.* (1982)
Broughton and Gilmer, *J Chem. Phys.* (1987)

Liquid Pb Inclusion Embedded in Al Matrix



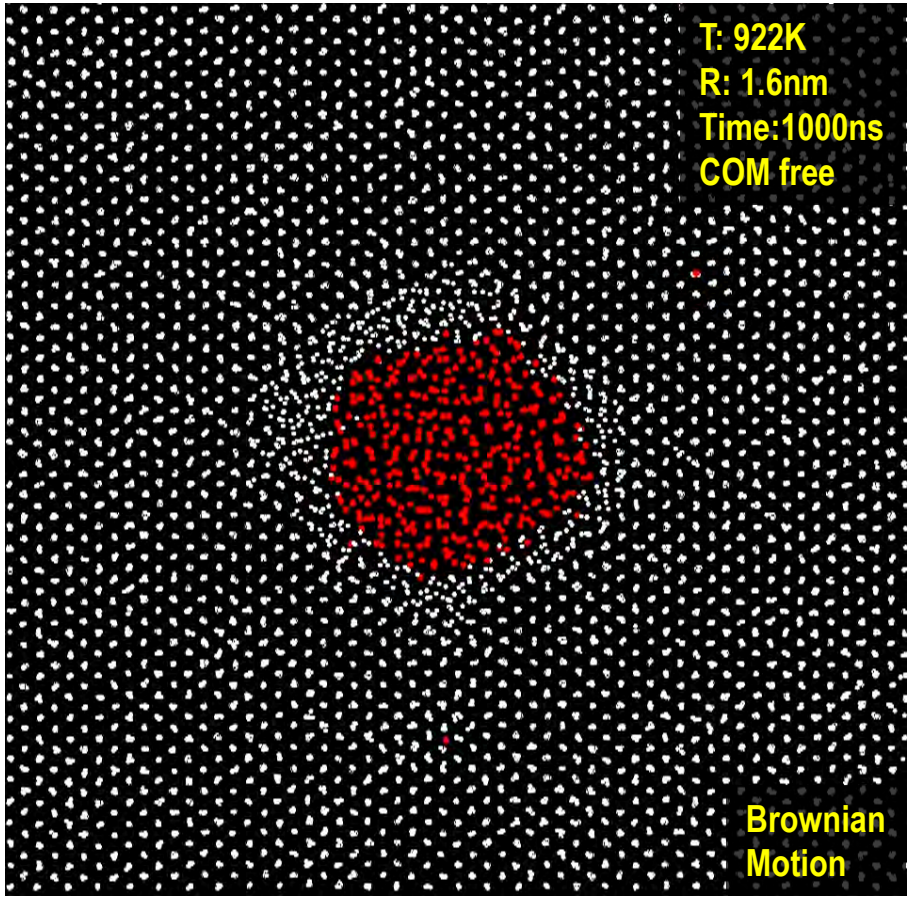


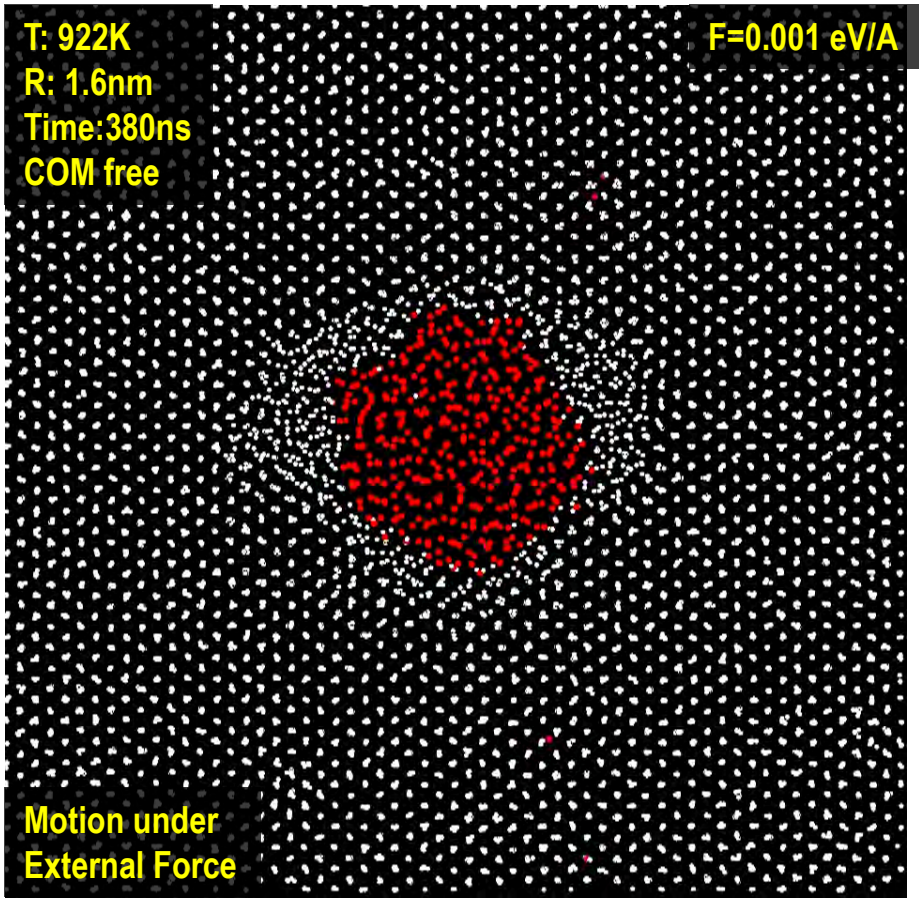
Runs for 20ns to reach equilibrium shape, agrees perfectly with TEM observation.

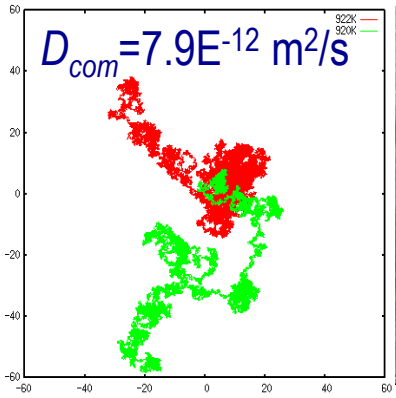


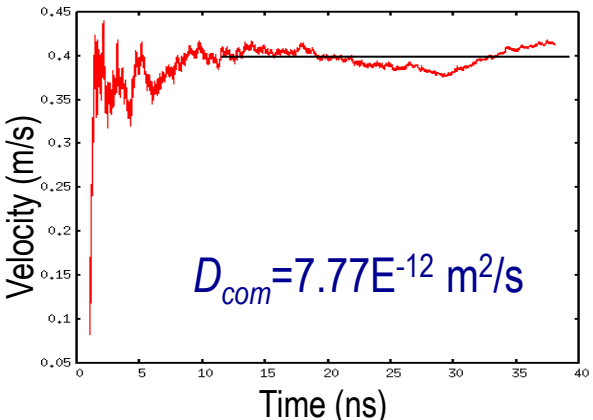
Spherical Pb droplet surrounded with a highly dynamical premelted liquid Al film.
Not observed in experiment

Liquid Pb Inclusion Embedded in Al Matrix



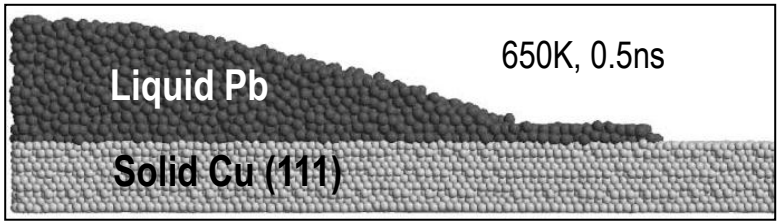


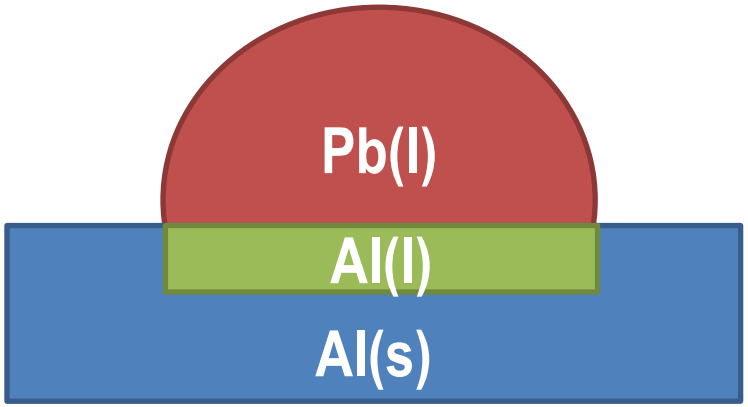




Diffusion coefficient of the inclusion is about 1000 times smaller than the atomic self diffusion constant (Al or Pb).

Spreading/Wetting of Pb Droplet on Al (111) Surface





It would be of great interest to study wetting/spreading of a Pb droplet on Al surface at temperatures that solid-liquid interfacial premelting happens.

- Will there be a complete wetting and spreading?
- What is the spreading dynamics?
- If partial wetting, are there four phases existing in the equilibrium droplet/substrate system? (Pb(l)—Al(s)—Al(l)—Vapor). Are there multiple contact angles?

Theoretical model of main droplet spreading

$$\frac{\partial T\{r(t);\dot{r}(t)\}}{\partial \dot{r}(t)} = \frac{\partial F\{r(t)\}}{\partial r(t)}$$

- Standard approach to the dynamics of mechanical dissipative systems.

Dissipation function $T\{r(t);\dot{r}(t)\} = {}^{T}\Sigma_{l} + {}^{T}\Sigma_{w}$

$${}^{T}\Sigma_{l} \sim \zeta_0 \dot{r}(t)^2 \quad \zeta_0 \equiv \Delta n k_B T / K\lambda$$ (Surface lattice sites)

$${}^{T}\Sigma_{w} \sim \eta \phi(\theta(t)) r(t) \dot{r}(t)^2 \ln[r(t)/a]$$ (Viscosity)

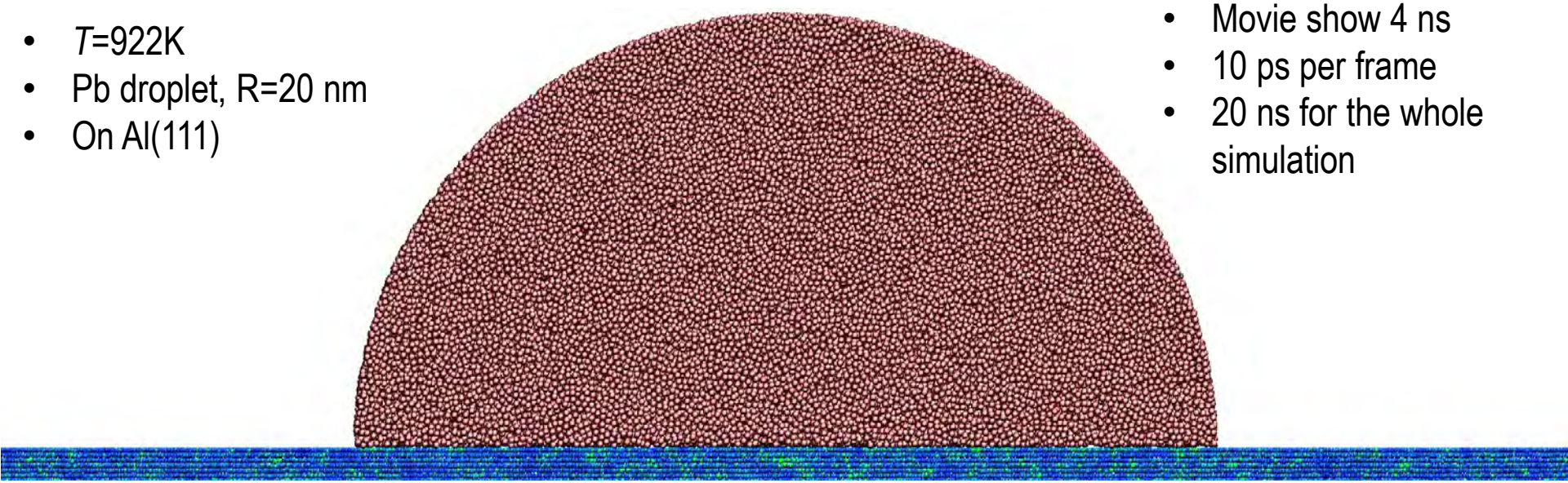
$$r(t) \sim (R_0)^{4/5} \left(\frac{t}{\zeta_0}\right)^{1/5}$$ **Kinetic model assuming** $\eta = 0$

$$r(t) \sim (R_0)^{6/7} \left(\frac{t}{\eta}\right)^{1/7}$$ **Hydrodynamic model Assuming** $\zeta_0 = 0$

E. B. Webb *et al.*, *Phys. Rev. E* 70, 011606 (2004)
M. J. de Ruijter *et al.*, *Langmuir*, 15, 2209 (1999)
P. G. de Gennes, *Rev. Mod. Phys.*, 57, 827 (1985)

Spreading of Pb Droplet on Al (111) Surface

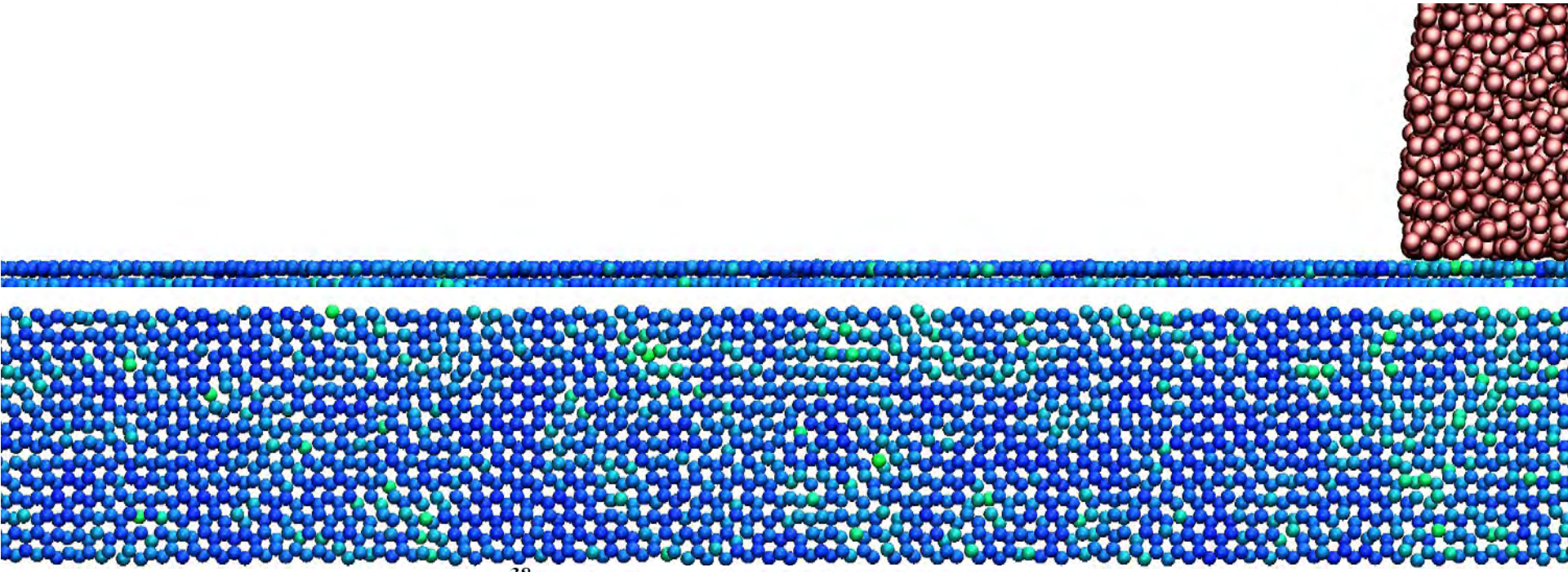
- *T*=922K
- Pb droplet, R=20 nm
- On Al(111)



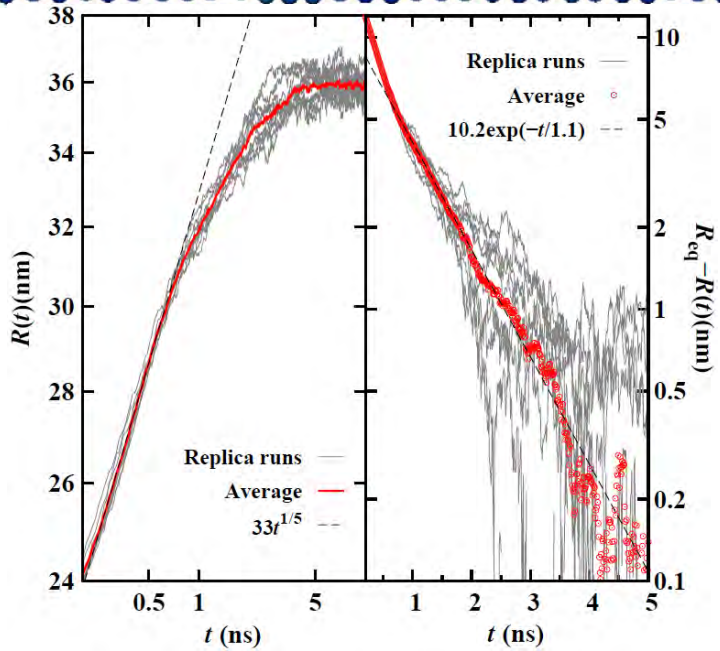
- Movie show 4 ns
- 10 ps per frame
- 20 ns for the whole simulation

- Partial spreading and wetting.
- The development of premelting layer observed.
- After 4 ns of spreading, the system reached equilibrium.

Spreading of Pb Droplet on Al (111) Surface



- Spreading coupled with SLI premelting.
- A continuously 2D melting of Al into metasable liquid phase induced by the spreading droplet.



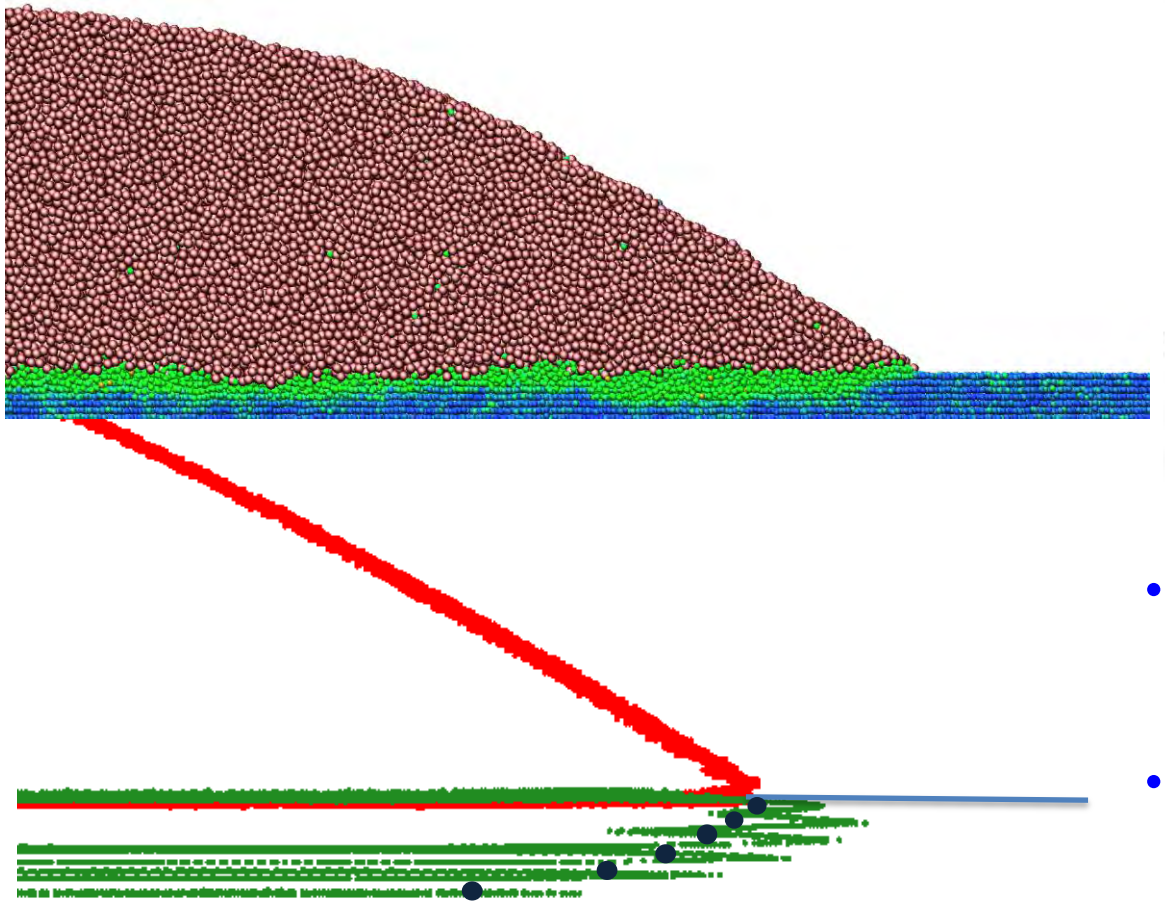
$$r(t) \sim (R_0)^{4/5}(\frac{t}{\zeta_0})^{1/5}$$

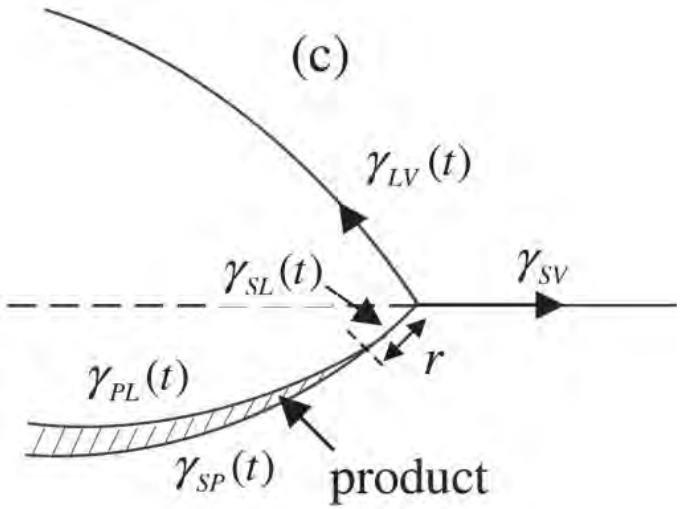
Spreading with SLI premelting perfectly follows kinetic scaling law.

$$\zeta_0 \equiv \Delta n k_B T / K\lambda$$

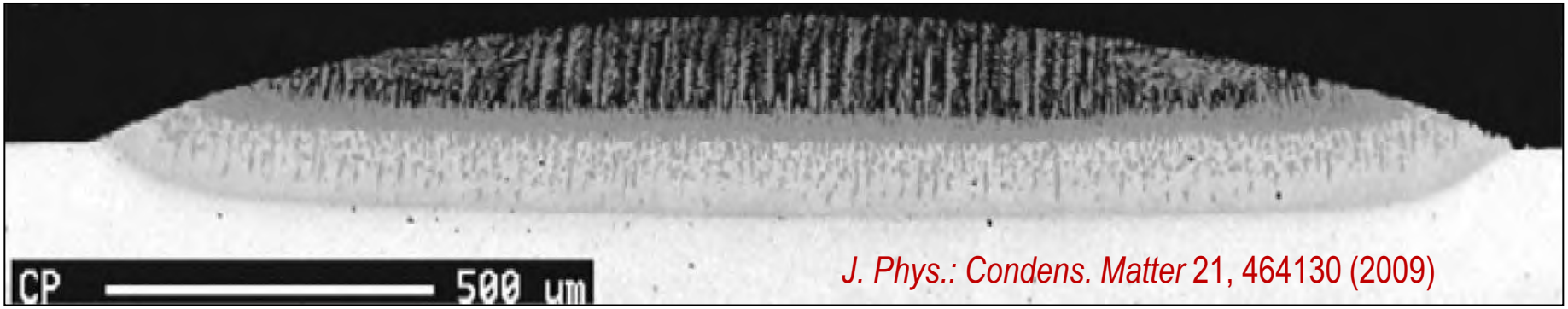
(Surface lattice sites)

Wetting of Pb Droplet on Al (111) Surface





- Force balance is similar to the case of reactive wetting. eg. pure Sn wetting on pure Au
- Difference, AuSn compound layer---Premelting layer(non-reactive wetting)



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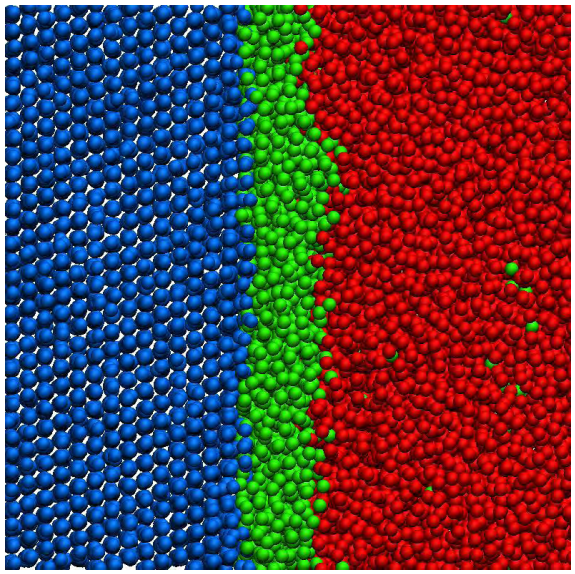
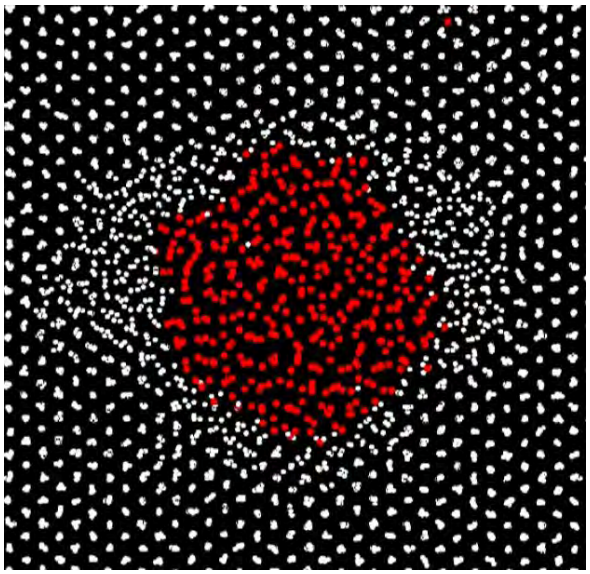
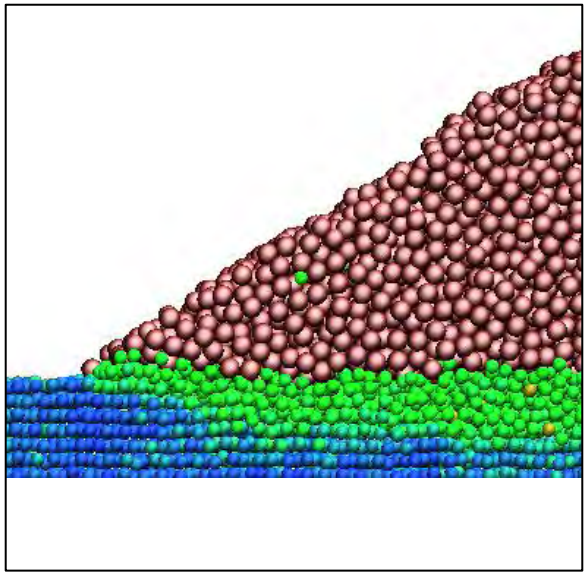
Summary

1. MD simulation predicted premelting transition in heterogeneous solid-liquid Al-Pb interface.
2. MD study of Pb liquid inclusion in Al matrix and spreading/wetting behaviour with premelting transition.
   - rapid Brownian motion due to the interfacial mass transport.
   - premelting-spreading coupling.
   - four phase balance at equilibrium wetting system.

3. Methodology could be extented to more interfacial systems, eg. He bubble.

Thank You for Your Time and Attention !
Have a Wonderful Day !

Yang Research Group @ ECNU