Modeling of solidification in nano-scale Molecular dynamics for alloying process

Erwan Deriaz Erwan.Deriaz@ippt.gov.pl

ZMiFP - Warsaw - March 26th 2008

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- Alloy solidification
- Lennard Jones model of atomic interaction
- Molecular Dynamics
- 2 Experiments on alloys
 - Alloys facility
 - Experimental conditions
 - Lennard Jones approximation of liquid metals

- ccf spot rates
- Diffusion
- Strain-stress response

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Structures in alloys

The various structures present in alloys are:

- the macro-structure (~10 µm) gives configuration of the constituents of alloys → dendrite growth
- different crystal configuration for each constituents
- the temperature of solidification T_f solidification can be quite complex (solidus-liquidus)

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Alloy macro-structure

www.copper.org

copper alloy



0.5 mm

Cu 80%, Pb 8%, Sn 10%, Zn 0.5%, Ni 1%, S 0.5%



 $25 \ \mu m$

Cu 35.8%, Al 10.2%, Fe 4.0%



50 μ m

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Examples of alloy macro-structures

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Crystal structure

cst-www.nrl.navy.mil/lattice



Examples of crystals

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Examples of alloys

Most common alloys

- bronze (Cu + Sn)
- steel (Fe + C)
- aluminum alloys (Al + Cu, Si, Mg, Zn, Ti, B, Sb, Na, Sr, Fe)

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Properties of alloy composition

The rate of the constituents and the conditions of solidification have an impact on:

- mechanical properties (elasticity, solidity)
- electrostatic/electric properties
- temperature of fusion
- resistance to corrosion
- behavior under manufacturing processes (cutting, molding)

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Aluminum alloys

Pure aluminum:

- it forms a cubic centered face crystal,
- it forms a thin impermeable layer at its surface.
- it is a ductile, light material

Possibilities of alloying aluminum are:

- + Mg → improves mechanical properties, most used alloying element for Al.
- + Cu \rightarrow improves mechanical properties, repulsive to aquatic life.
- + Si \rightarrow for complex molds
- + Sb or Na or Sr → used in Al-Si alloys, modifies the eutectic growth, not to be mixed!

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Lennard-Jones potential



One-to-one interaction model with the potential:

$$V(r) = \varepsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right)$$

Two different potentials:

- a pair potential to account for the repulsion resulting from Pauli's exclusion principle,
- and the local electronic density accounting for cohesion.

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Lennard-Jones potential



minimum at $r = \sigma_0 = 2^{1/6} \sigma$

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Lennard-Jones model properties

Lennard-Jones model:

- Interactions between spherical non polar particles,
- Very good model for noble gas,
- Good model for liquids,
- simple \implies fast and robust.

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Atoms are modeled by interacting points.



Verlet algorithm:

$$\mathbf{x}(t+\delta t) = 2\mathbf{x}(t) - \mathbf{x}(t-\delta t) + \frac{\mathbf{f}(t)}{m}\delta t^2 + O(\delta t^4)$$

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with $\mathbf{f} = -\nabla V$

http://lammps.sandia.gov

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Crystallization box

In a periodic box, we fix the volume *V*, the density ρ , the rates of each kinds of atoms, and the evolution of the temperature.



We observe the crystallization process and the resulting structures of the alloys.

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Crystallization box

Numerical experiment figures:

- 4 000 atoms,
- 200 000 time steps,
- \sim 2 hours of computing.

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Lennard-Jones parameters

- energy of the link ε ,
- specific distance of interaction σ from:

$$V(r) = \varepsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right)$$

- mass *m* of the atom,
- density ρ of atoms in the box.

From ρ and σ we define the compactness $\kappa = \rho \sigma^3$.

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Lennard-Jones parameter calibration

Then we obtain numerically:

- the mass per volume $M = \rho m$
- the temperature of fusion $T_f = \varepsilon f(\kappa)$
- the pressure $P = P(\kappa, \sigma, \varepsilon, m, T)$

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LJ approximation of AI, Cu, Sn and Mg

We simulate AI, Cu, Sn and Mg atoms which have the following properties:

	Al	Cu	Sn	Mg
<i>m</i> (g/mol)	27.0	63.6	118.7	24.3
<i>M</i> (kg/m ³)	2719	8978	7310	1738
T_f (K)	934	1358	505	923

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Periodic table

H	Periodic Table of the Elements										2 He						
Li	Be		hydro alkali	ogen i meta	ls		■ p ■ n	oor me onmet	etals als		2	B	C ⁶	N ⁷	08	9 F	10 Ne
11 Na	12 Mg	alkali earth metals Transition metals				 noble gases rare earth metals 			AI	Si	15 P	16 S	CI CI	Ar Ar			
19 K	20 Ca	21 Sc	22 Ti	V ²³	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	Te Te	53	Xe Xe
Cs Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								

Ce	59 Pr	60 Nd	61 Pm	62 Sm	Eu 63	64 Gd	Tb ⁶⁵	66 Dy	67 Ho	68 Er	69 Tm	Yb	71 Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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LJ parameters for AI, Cu, Sn and Mg

	Al	Cu	Sn	Mg
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	Al	Cu	Sn	Mg
ε	2.748	4.715	0.504	2.027
σ	1.1336	1.0023	1.4554	1.2977
ρ	0.7654	1.0726	0.46787	0.5435
κ	1.1150	1.0800	1.4424	1.1877

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Solidification of pure Al, Cu, Sn and Mg

	Al	Cu	Sn	Mg
T_f (K)	934	1358	505	923



Rate of crystallization during time for AI (in black), Cu (in blue), Sn (in red) and Mg (in dark blue).

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Crystal lattice

In a crystal, atoms are located at:

$$\mathbf{x}_{\lambda} = a\lambda_1\mathbf{e}_1 + a\lambda_2\mathbf{e}_2 + a\lambda_3\mathbf{e}_3$$
 with $\lambda \in \mathbb{Z}^3$

for some basis $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ of \mathbb{R}^3 .

In cubic centered-face, each atoms *A* have 12 neighbors A_i , and the next closest atoms are at a distance of $\sqrt{2}a$ of *A*.

We take $\mathbf{e}_i = AA_i$. We write all atoms *B* in a neighborhood N(A) of *A* such that $d(A, B) \leq 3a$, in the $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ coordinates centered on *A*:

$$\vec{AB} = x_1(B)\vec{AA_1} + x_2(B)\vec{AA_2} + x_3(B)\vec{AA_3}$$

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Then we compute the criterion μ :

$$\mu = \frac{1}{\#N(A)} \sum_{B \in N(A)} \frac{1}{3} \left(\cos(2\pi x_1(B)) + \cos(2\pi x_2(B)) + \cos(2\pi x_3(B)) \right)$$

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If $\mu \ge \mu_0$ (with $\mu_0 \approx$ 0.5), *A* is considered as being inside a crystal structure.

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Cu crystallization



Solidification of LJ atoms with the Cu characteristics. In blue: liquid atoms. In green: ccf crystal atoms.

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Cu-Sn crystallization



Solidification of LJ atoms with the Cu characteristics. In blue: liquid Cu, in red: liquid Sn. In green: ccf crystal Cu, in orange: ccf crystal Sn. Introduction ccf spot rates Experiments on alloys Diffusion Numerical results Strain-stress response

Comparison for various concentration in Cu-Sn alloys



Rate of ccf crystal locus for various concentrations in Sn: $\rho_{Sn} = 0, 0.05, 0.1, 0.15 \text{ and } 0.2$

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Green-Kubo diffusion

Green-Kubo formula:

$$D = \frac{1}{3} \int_0^\infty < \mathbf{v}(0) \cdot \mathbf{v}(t) > dt$$

where we noted $\langle y \rangle$ the space average of *y*.

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Diffusion for Al, Cu, Sn and Mg



Noisy Green-Kubo diffusion computed for AI, Cu, Sn and Mg in the crystallization process.

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Mechanical properties of crystal

- $\bullet\,$ big atoms (Sn) \rightarrow pressure force coherence
- small atoms (Cu) \rightarrow stirring force coherence

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Strain-stress response

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Alloying improvement



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Experimental numerical test



Experimental numerical device to measure the deformation of a crystal under a shear stress force.

Erwan Deriaz Erwan.Deriaz@ippt.gov.pl

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Stress = F

Strain = $\frac{dx}{L}$

Hence we obtain the following stress-strain relation:

$$\frac{dx}{L} = \alpha F$$

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with α the elasticity constant of the material.



Location of the probes on the device (top). The material undergoes a shear stress (bottom).

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Result for pure LJ crystal



Example of shear stress / strain deformation result for a crystal with Lennard-Jones potential model.

Erwan Deriaz Erwan.Deriaz@ippt.gov.pl

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Conclusion

From solidification experiments we would like to:

- observe the segregation of atoms during the crystallization process,
- observe the variations on *T_f* depending on the concentration of alloying components,
- recreate the crystal structures of alloys,
- test for the mechanical properties.