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2137-7

# Joint ICTP-IAEA Advanced Workshop on Multi-Scale Modelling for Characterization and Basic Understanding of Radiation Damage Mechanisms in Materials

*12 - 23 April 2010*

## Modelling of liquid metals for fusion reactors

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# Liquid (Pb-Li) Molecular Dynamics simulation: Multiscale approach
## (from Quantum to Classical).


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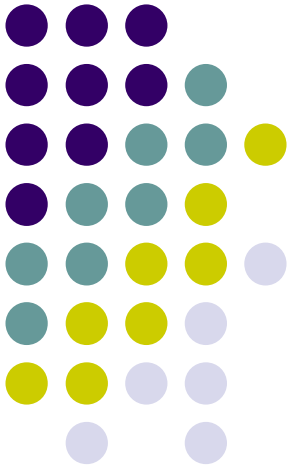

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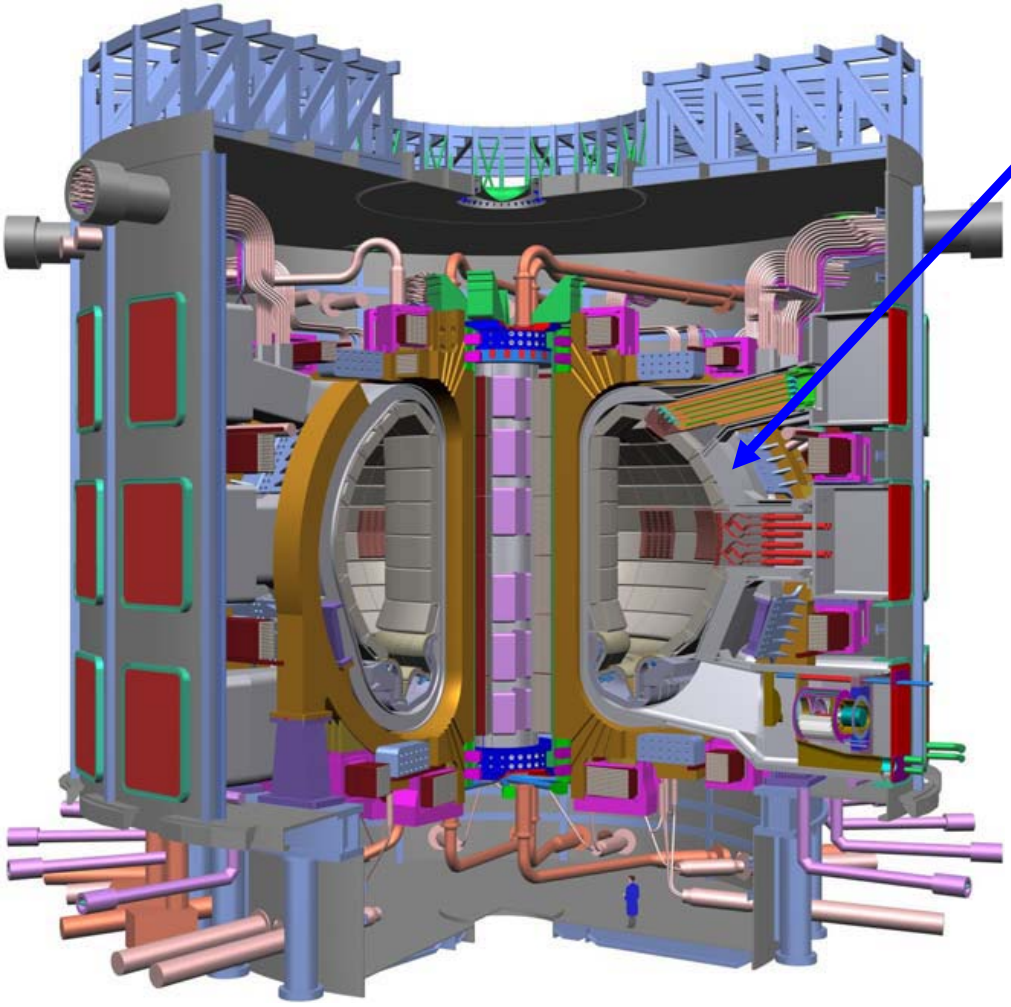
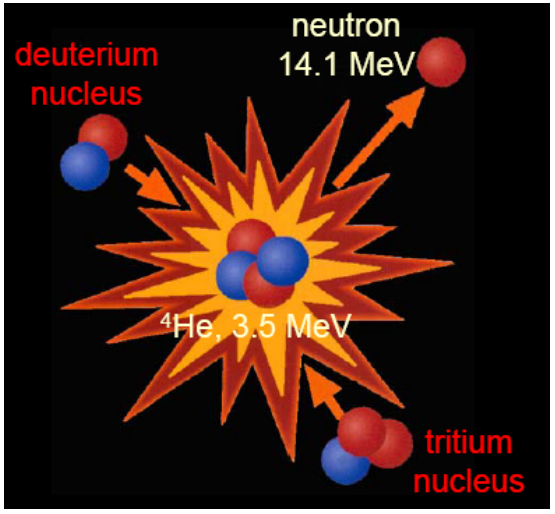
# Test Blanket Module (TBM)





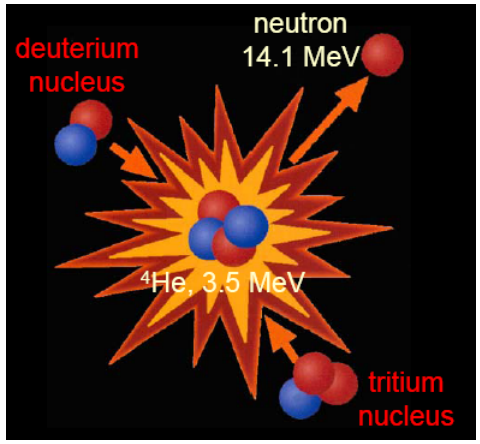
# Test Blanket Module

**Breeding Blanket:** the kinetic energy of 14 MeV neutrons is transformed into heat that is transferred to a coolant.

- Absorbs the 14 MeV neutrons, transforming their energy to provide most of the reactor power output.
- Shields the superconducting coils and other outer components.
- Allows for neutron multiplication and breeding of Tritium to fuel the reactor.

# TBM candidates

- A breeding blanket consists of:
  - A tritium breeding material (Li-containing alloy)
  - A neutron multiplier (Be or Pb)
  - A coolant (water, He and/or Pb-Li)
  - A structural material (to separate and contain the different materials)



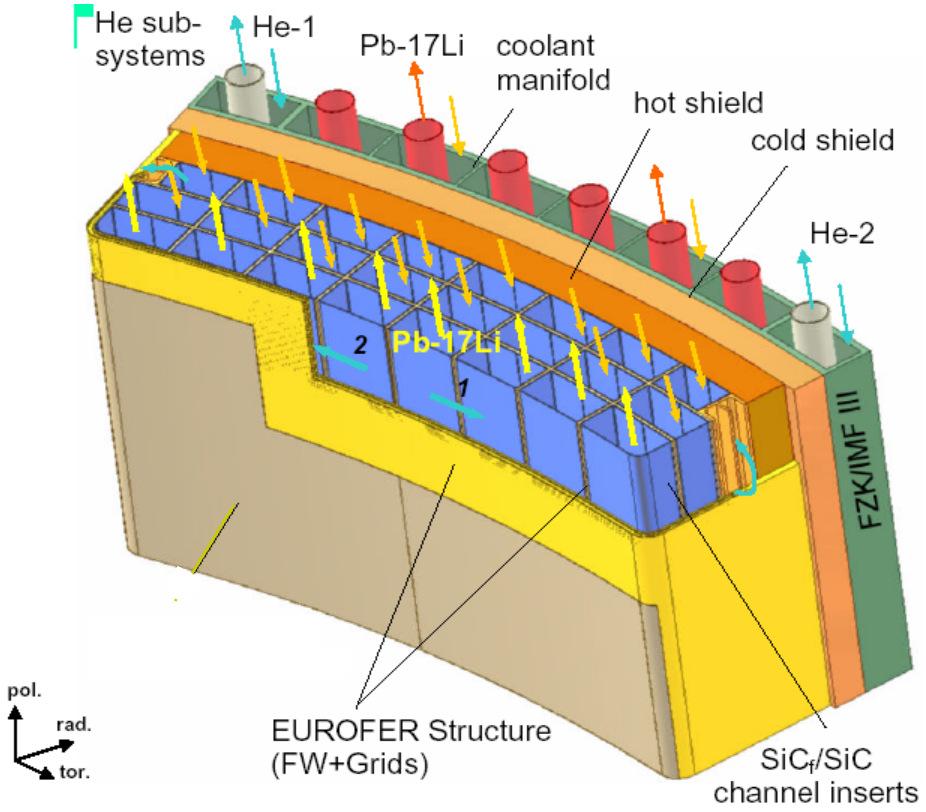

**Candidates:**

Ceramic Breeder
Molten Salt
FLiBe
**Pb-Li eutectic**
SnLi
Etc..

# PbLi TMB

**Table 1**
Main parameters of tritium system.

| | |
|---|---|
| LiPb flow rate (kg/s) | $5.5 \times 10^4$ |
| Blanket He flow rate (kg/s) | 1700 |
| Turbine He flow rate (kg/s) | 1500 |
| Blanket LiPb inlet/out $T$ (°C) | 480/700 |
| Blanket He inlet/out $T$ (°C) | 300/450 |
| Turbine He inlet/out $T$ (°C) | 680/300 |
| LiPb volume ($m^3$) | 550 |
| He mass in the primary loop (kg) | $1.0 \times 10^4$ |
| He mass in the secondary loop (kg) | $1.0 \times 10^4$ |

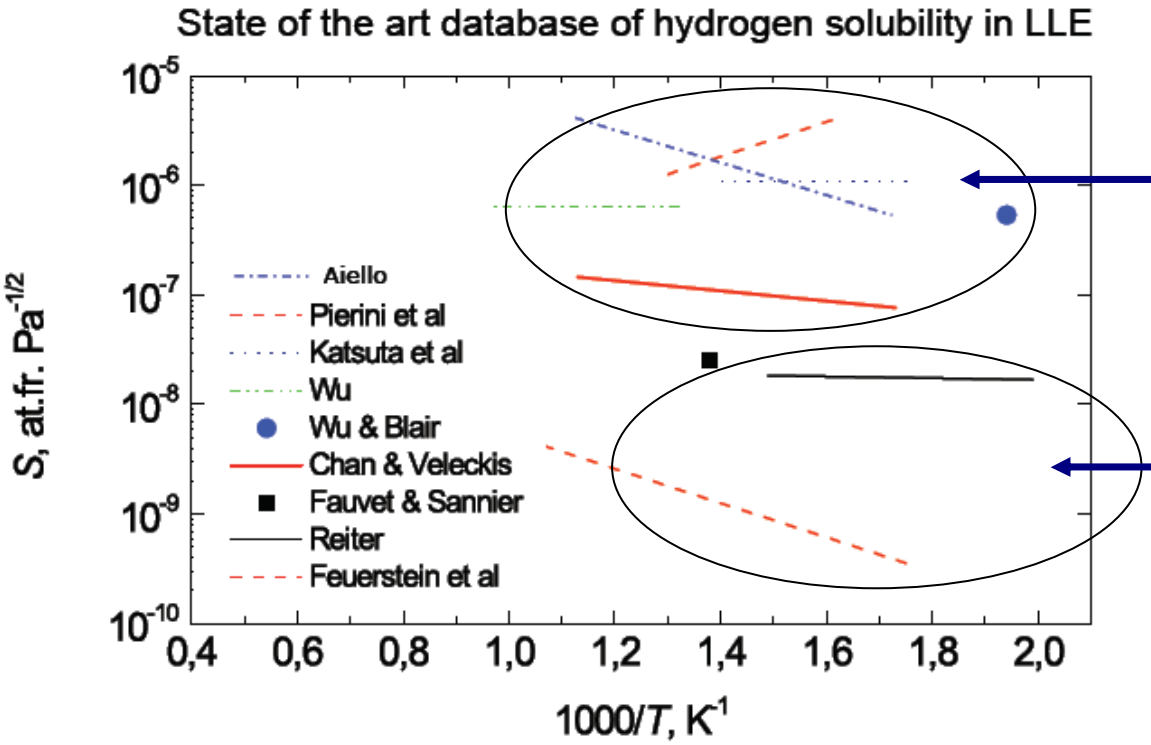



Main parameters of tritium system [1]

Dual coolant (He+ PbLi) blanket

[1] Y. Song *et al*, Fusion Engineering and Design 84 (2009) 1779–1783

# PbLi TBM




Absorption technique

Desorption technique

**Solubility database is inadequate for design.**

Scatter reflects experimental approaches and measurement techniques applied. Knowledge of dynamic transport properties (difussion, mass transfer, interface processes) is much more limited.

# $Pb_{83}Li_{17}$ advantages:

| **Liquid Breeder** | Li | **$Li_{17}Pb_{83}$** | Flibe | $Li_{20}Sn_{80}$ |
|---|---|---|---|---|
| Melting point (ºC) | 180 | 235 | 459 | 320 |
| Density (g/cm$^3$) 873K | 0.48 | 8.98 | 2.0 | 6.0 |
| Li Density (g/cm$^3$) 873K | 0.48 | 0.061 | 0.28 | 0.09 |
| Breeding property | Good | **Fairly good** | Neutron multiplier required | Neutron multiplier required |
| Chemical stability | **Active** | Middle | Almost stable | Almost stable |
| Corrosion | **Severe** | Middle | **HF exist**, severe | ? |
| Tritium release form | HT, $T_2$ | HT, $T_2$ | HT, $T_2$, **TF** | HT, $T_2$ |

Ref, Y. Kang, T. Terai / Fusion Engineering and Design 81 (2006) 519–523

# $Pb_{83}Li_{17}$ disadvantages:

| | Li | $Li_{17}Pb_{83}$ | Flibe | $Li_{20}Sn_{80}$ |
|---|---|---|---|---|
| **Tritium solibility** * (atom frac $Pa^{-0.5}$) (873K) | Very high $7.49x10^{-3}$ | Very low $1.93x10^{-8}$ | Very low HT/$T_2$ $1.77x10^{-11}$ $Pa^{-1}$ TF $1.77x10^{-11}$ $Pa^{-1}$ | Middle $2x10^{-7}$-$1x10^{-5}$ |
| **Tritium diffusivity order** ($m^2/s$) (873K) | Relatively high $10^{-9}$ | Relatively high $10^{-9}$ | Relatively high $10^{-9}$ | Relatively high $10^{-9}$ |
| **Thermal conductivity** | **Li**>$Li_{20}Sn_{80}$> $Li_{17}Pb_{83}$ > Flibe | | | |
| **Dynamic viscosity** | Flibe>$Li_{20}Sn_{80}$~$Li_{17}Pb_{83}$ >**Li** | | | |

Ref, Y. Kang, T. Terai / Fusion Engineering and Design 81 (2006) 519–523

# PbLi MD simulations:

- Liquid Pb and Li MD simulation.

- **Liquid $Pb_xLi_{1-x}$ MD simulation.**
  - $Pb_xLi_{1-x}$ eutectic title determination.
  - $Pb_xLi_{1-x}$ Physical properties.
  - Evolution with concentration and Temp.
  - Magnetic field effect? (QMD)
- **He and T solubility in $Pb_xLi_{1-x}$.**
  - Nucleation, cavitation etc

X = 15.7 – 17%

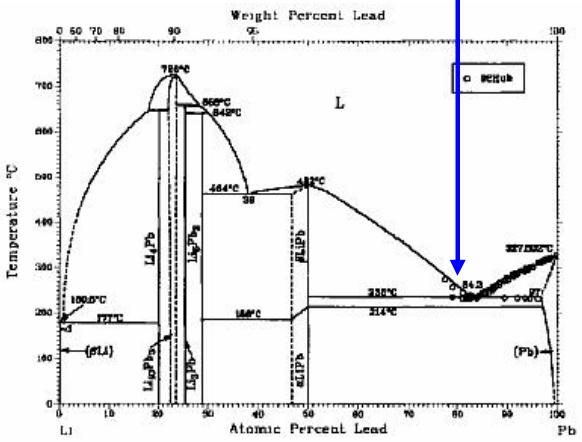



Fig. 1: Pb-Li phase diagram [1]

[1] P. Hubberstey, T. Sample and M. G. Barker, J. Nucl, Mater 191-194, 283-287 (1992)

# Liquid Pb and Li MD simulation:

1. Development of suitable potentials for Pb and Li:

**EAM (Embedded Atom Method)**,
MEAM (Modified EAM)
FS (Finnis-Sinclair)
…

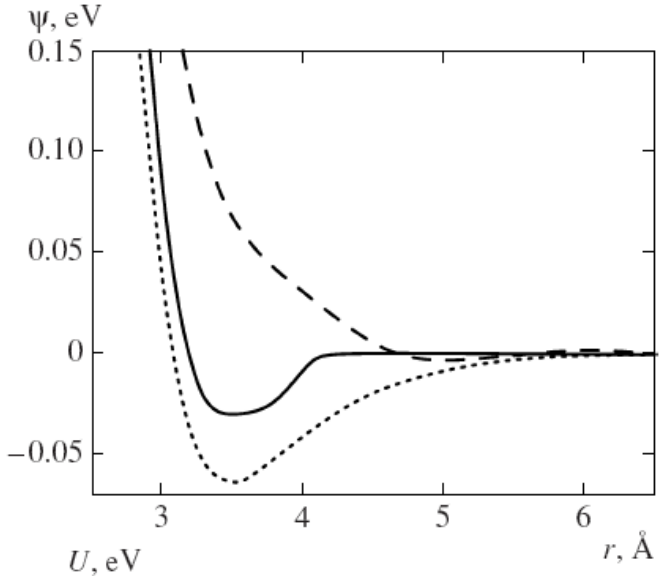


Fig. 2: Different Pb interatomic potentials [1]

2. Implementation in LAMMPS. Testing the code. Checking with the experimental database [2]

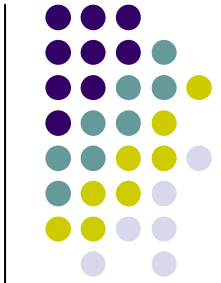

[1] Khusnutdinov et al, *Journal of Experimental and Theoretical Physics, 2009, Vol. 108, No. 3, pp. 417–427.*
[2] M. Vals, L. A. Sedano *et al*, Journal of Nuclear Materials 376 (2008) 353-357

# Why EAM?

Effective medium theories (EAM) do better than pair potentials.

- But EAM does not give you subtle hybridization effects.
- So, there will be always subtle **electronic changes** that you simply will not get right.
- You cannot get complex crystal structure differences in metals with EAM.

# EAM formalism:



In the EAM formalism the energy *E* of atom *i* is written as

$$E_i = \sum_j \phi(r_{ij}) + F_{embed}\left(\sum_j \rho(r_{ij})\right)$$

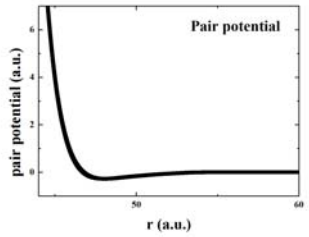
Where φ is a pair-potential interaction between atoms *i* and *j* and *F* is an embedding function, namely the energy to embed atom *i* in the electron density ρ provided by its surrounding *j* atoms. The φ, ρ, and *F* functions are analytic expressions with coefficients fit to various experimentally determined quantities [1].

[1] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).

# Zhou EAM Pb potential:

- Total energy:

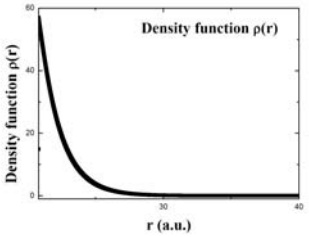
$$E_m = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=i_1}^{i_N}\phi_{ij}(r_{ij}) + \sum_{i=1}^{N}F_i(\rho_i),$$




Pair potential →

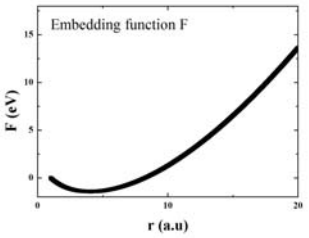
$$\phi(r) = \frac{A\exp\left[-\alpha\left(\frac{r}{r_e}-1\right)\right]}{1+\left(\frac{r}{r_e}-\kappa\right)^{20}} - \frac{B\exp\left[-\beta\left(\frac{r}{r_e}-1\right)\right]}{1+\left(\frac{r}{r_e}-\lambda\right)^{20}}.$$

[2]




Electron density function →

$$f(r) = \frac{f_e\exp\left[-\beta\left(\frac{r}{r_e}-1\right)\right]}{1+\left(\frac{r}{r_e}-\lambda\right)^{20}}$$




$$F(\rho) = \sum_{i=0}^{3} Fn_i\left(\frac{\rho}{\rho_n}-1\right)^i \quad \rho < \rho_n \qquad \rho_n = 0.85\,\rho_e$$

Embedding function →

$$F(\rho) = \sum_{i=0}^{3} F_i\left(\frac{\rho}{\rho_e}-1\right)^i \quad \rho_n \leqslant \rho < \rho_o \qquad \rho_o = 1.15\rho_e$$

$$F(\rho) = F_o\left[1-\ln\left(\frac{\rho}{\rho_e}\right)^{\eta}\right]\left(\frac{\rho}{\rho_e}\right)^{\eta} \quad \rho_o \leqslant \rho$$

[2] Zhou *et al*, Acta Materialia (2000).

# Hoyt-Ercolessi-Lim PbCu Alloy

- The interatomic potential used is due to Lim, Ong, and Ercolessi [18]. This is a many-body glue-type potential, given by

$$V = \frac{1}{2} \sum_{ij} \phi(r_{ij}) + \sum_{i} U(n_i),$$

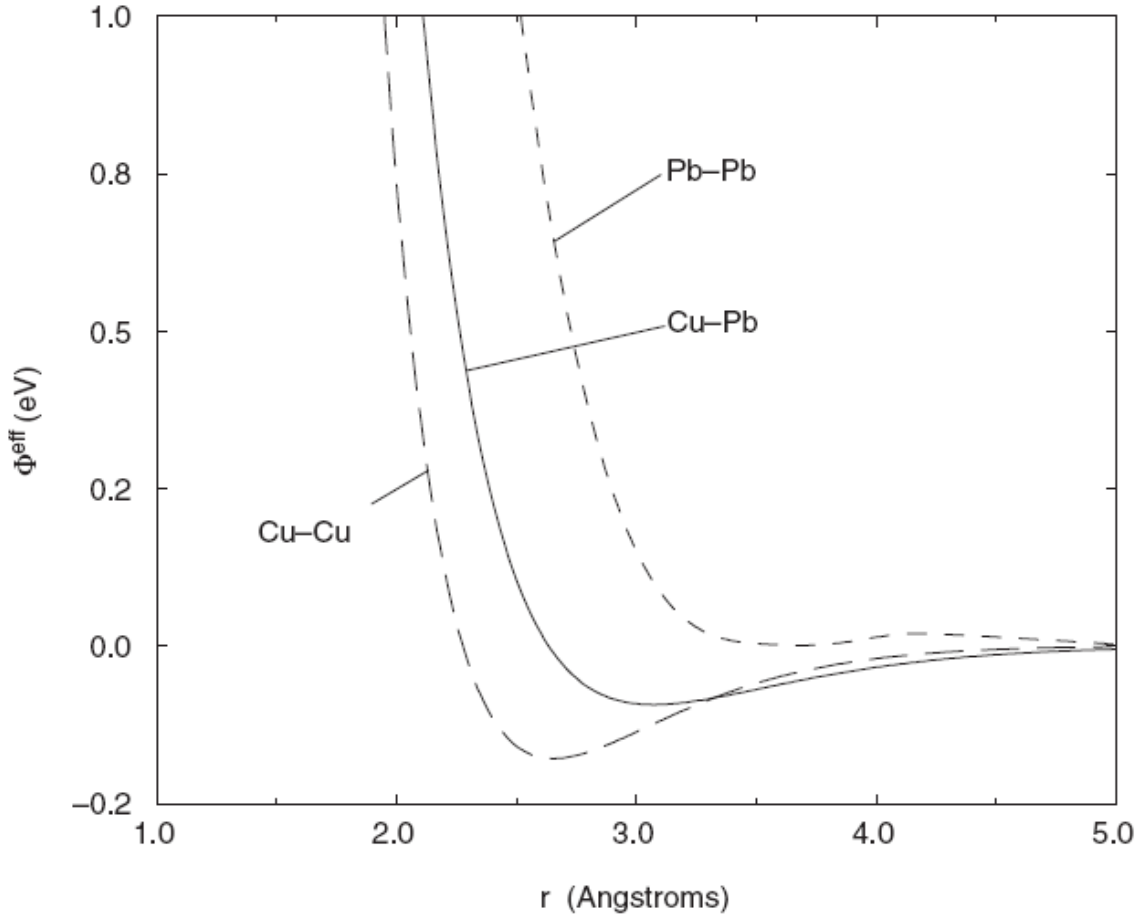
where $\phi$ is a short-range two-body potential and *U* is a many-body glue term which reflects the effects of the conduction electrons in the metal.

$$n_i = \Sigma_j \rho(r_{ij})$$

is a generalized coordination where $\rho(r)$ is some short-ranged function.

[18] Lim H S, Ong C K and F Ercolessi 1992 *Surf. Sci.* **269/270** 1109

# Hoyt-Ercolessi-Lim PbCu Alloy




The effective pair potentials for Cu–Cu, Pb–Pb and Cu–Pb of the optimized EAM potential.

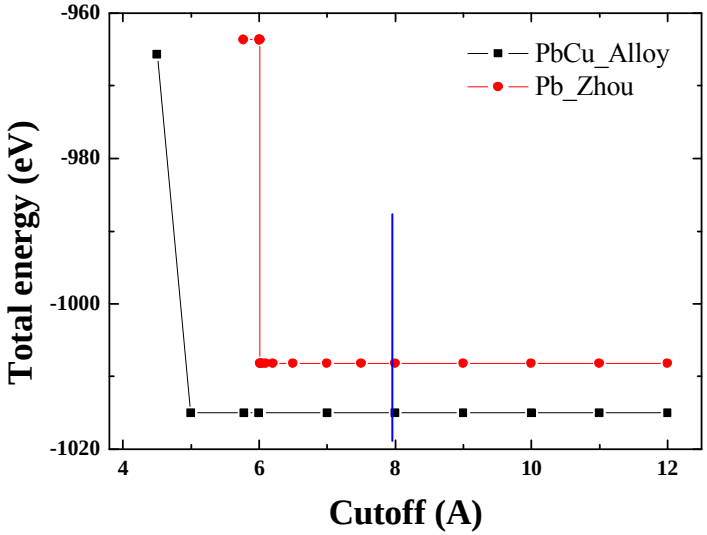
Lim H S, Ong C K and F Ercolessi 1992 *Surf. Sci.* **269/270** 1109

# Pb EAM potentials

- Two Pb EAM potentials are being carefully tested [1, 2].

Total energy variation depending on the cutoff for both potentials.

Down, number of neighbours for both potentials in a 500 atoms simulation




| | Cutoff (A) | N neighbours. |
|---|---|---|
| PbCu | 5.77 | 16615 |
| Pb | 12.27 | 99645 |

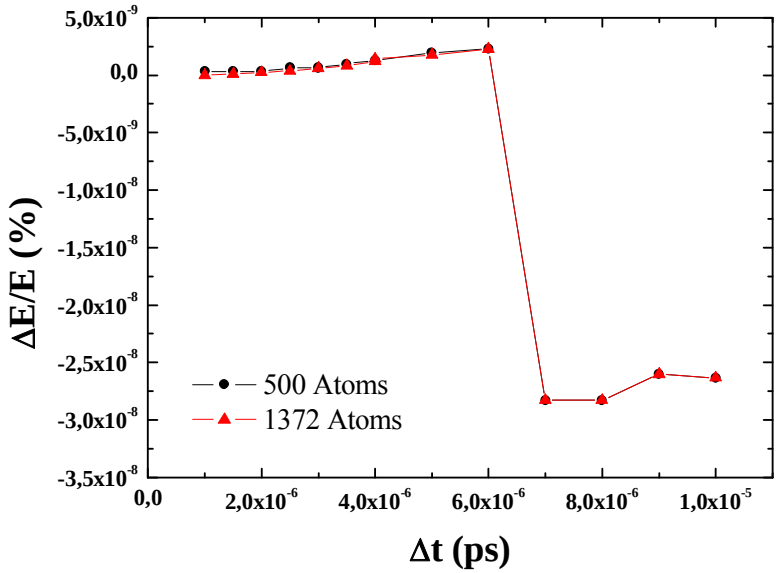

[1] Zhou et al, Acta Materalia (2000).
[2] J.J. Hoyt, J.W. Garvin, E.B. Webb III, and M. Asta, "An Embedded Atom Method Interatomic Potential for the Cu-Pb System", Model. Simul. Mater. Sci. Eng., 11, 287 (2003).

# Pb EAM potentials

- Two Pb EAM potentials are being carefully tested [1, 2].

Scaling properties are being checked for our EAM potentials.

Both Pb potentials give similar results independently of N




Total energy lost depending on timestep Δt, for two different number of atoms, N, in the simulation box.


[1] Zhou et al, Acta Materalia (2000).
[2] J.J. Hoyt, J.W. Garvin, E.B. Webb III, and M. Asta, "An Embedded Atom Method Interatomic Potential for the Cu-Pb System", Model. Simul. Mater. Sci. Eng., 11, 287 (2003).

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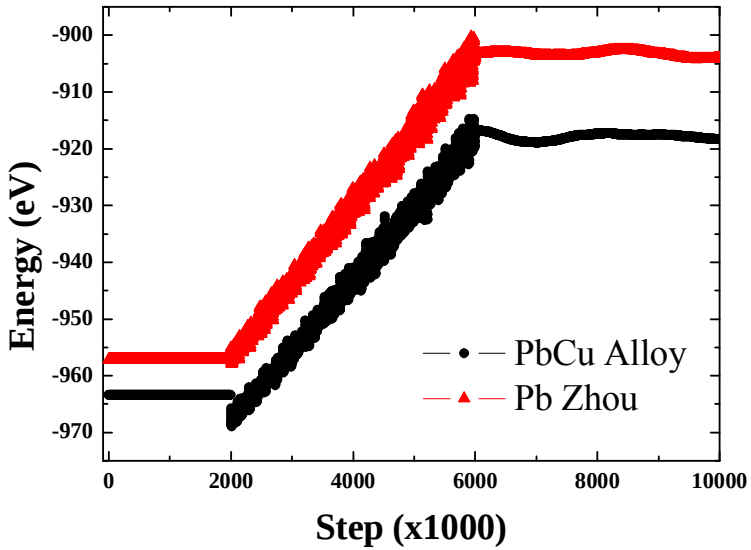



Total Energy for Pb simulation in initial heating equilibration. Red triangles E calculated with Pb EAM potential (Zhou) setfl format, black squares idem using Pb EAM potential for PbCu alloys (Hoyt).

[1] Zhou et al, Acta Materalia (2000).
[2] J.J. Hoyt, J.W. Garvin, E.B. Webb III, and M. Asta, "An Embedded Atom Method Interatomic Potential for the Cu-Pb System", Model. Simul. Mater. Sci. Eng., 11, 287 (2003).

# Limitations of the EAM potential:

It can neither be fitted to fcc metals with negative Cauchy pressure nor to hcp metals with a negative Cauchy and/or $C_{12}–C_{44} > (3C_{12}–C_{11})/2$.

The lack of three-body terms also makes it challenging to apply the EAM to metals with strong covalent effects.

Consequently, some modified embedding-atom methods (MEAM) [1] are being studied.

[1] B. Lee, J-H. Shim, and M. I. Baskes. Phys Rev B 68, 144112 (2003) Semiempirical atomic potentials for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, Al, and Pb based on first and second nearest-neighbor modified embedded atom method

# MEAM potentials.

- The modified embedded atom method (MEAM) [3, 4] was developed by Baskes *et al* by introducing

  an angular-dependent term into the EAM, which comes from the symmetry of electronic wavefunctions.

The MEAM parameters are published in [4] for 10 kinds of fcc material and 10 kinds of bcc material.

Although some other versions of MEAM have also been developed, the theory and parameters (MEAM92) described in [4] are most commonly used.

[3] Baskes M I, Nelson S J and Wright A F 1989 *Phys. Rev.* B **40** 6085
[4] Baskes M I 1992 *Phys. Rev.* B **46** 2727

# MEAM potentials

- In the MEAM model, an energy **modification term** was added to the total energy expression for the EAM to describe the energy changes caused by the **non-spherical distribution of electrons** and deviation from the linear superposition of atomic electron density:

$$E_{tot} = \sum F(\rho_i) + \frac{1}{2}\sum \phi(r_{ij}) + \sum M(P_i)$$

- The energy modification term is empirically taken as:

$$M(P) = \alpha\left(\frac{P}{P_e}\right)^2 \exp\left[-\left(\frac{P}{P_e}\right)^2\right]$$

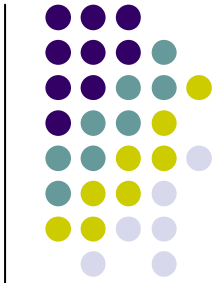
- where $F(\rho_i)$ is the embedding function, $\Phi(r_{ij})$ is the potential between atoms i and j with separation distance $r_{ij}$ and $\rho_i$ is the electron density induced at site i by all other atoms in the system and is taken in the original form [1]:

$$\rho_i = \sum f(r_{ij})$$

- And P in the energy modification term M(P) is taken as: $P = \sum f^2(r_{ij})$

[1] R.A. Johnson, Phys. Rev. B39 (1988) 3924.

# MEAM potentials: Pb



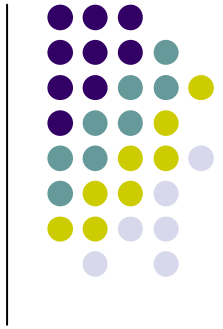
Pb MEAM parameters:

TABLE I. Parameters for the MEAM potential of Cu, Ag, Au, Ni, Pd, Pt, Al, and Pb. The units of the sublimation energy $E_c$, the equilibrium nearest-neighbor distance $r_e$, and the bulk modulus $B$ are eV, Å, and $10^{12}$ dyn/cm$^2$, respectively.

| | $E_c$ | $r_e$ | $B$ | $A$ | $\beta^{(0)}$ | $\beta^{(1)}$ | $\beta^{(2)}$ | $\beta^{(3)}$ | $t^{(1)}$ | $t^{(2)}$ | $t^{(3)}$ | $C_{max}$ | $C_{min}$ | $d$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 3.54 | 2.555 | 1.420 | 0.94 | 3.83 | 2.2 | 6.0 | 2.2 | 2.72 | 3.04 | 1.95 | 2.80 | 1.21 | 0.05 |
| Ag | 2.85 | 2.880 | 1.087 | 0.94 | 4.73 | 2.2 | 6.0 | 2.2 | 3.40 | 3.00 | 1.50 | 2.80 | 1.38 | 0.05 |
| Au | 3.93 | 2.880 | 1.803 | 1.00 | 5.77 | 2.2 | 6.0 | 2.2 | 2.90 | 1.64 | 2.00 | 2.80 | 1.53 | 0.05 |
| Ni | 4.45 | 2.490 | 1.876 | 0.94 | 2.56 | 1.5 | 6.0 | 1.5 | 3.10 | 1.80 | 4.36 | 2.80 | 0.81 | 0.05 |
| Pd | 3.91 | 2.750 | 1.955 | 0.94 | 5.15 | 2.2 | 6.0 | 2.2 | 4.50 | 1.47 | 4.85 | 2.80 | 1.69 | 0.05 |
| Pt | 5.77 | 2.770 | 2.884 | 0.90 | 4.92 | 2.2 | 6.0 | 2.2 | 3.94 | −2.20 | 3.84 | 2.80 | 1.53 | 0.05 |
| Al | 3.36 | 2.860 | 0.794 | 1.16 | 3.20 | 2.6 | 6.0 | 2.6 | 3.05 | 0.51 | 7.75 | 2.80 | 0.49 | 0.05 |
| Pb | 2.04 | 3.500 | 0.488 | 1.01 | 5.42 | 2.2 | 6.0 | 2.2 | 3.10 | 3.91 | 1.25 | 2.80 | 0.81 | 0.00 |

[1] B. Lee, J-H. Shim, and M. I. Baskes. Phys Rev B 68, 144112 (2003) Semiempirical atomic potentials for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, Al, and Pb based on first and second nearest-neighbor modified embedded atom method

# MEAM potentials: Li



Li MEAM parameters:

**Table 2.** MEAM parameters for Li. The values listed are: the sublimation energy $E_0$ (eV), the equilibrium nearest-neighbour distance $R_0$ (Å), the exponential decay factor for the universal energy function $\alpha$, the scaling factor for the embedding energy $A$, the adjustment parameter for the embedding function $\kappa$, the exponential decay factors for the atomic densities $\beta^{(l)}$, and the weighting factors for the atomic densities $w^{(l)}$.

| $E_0$ | $R_0$ | $\alpha$ | $A$ | $\kappa$ | $\beta^{(0)}$ | $\beta^{(1)}$ | $\beta^{(2)}$ | $\beta^{(3)}$ | $w^{(0)}$ | $w^{(1)}$ | $w^{(2)}$ | $w^{(3)}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.65 | 3.04 | 2.97 | 0.87 | −1.3933 | 1.4570 | 2.1248 | 2.0316 | 1.0196 | 1.0 | 0.0082 | 0.1857 | 1.8526 |

X. Yuan *et al*, 2003 Modelling Simul. Mater. Sci. Eng. 11 447 Development of modified embedded atom method for a bcc metal: lithium

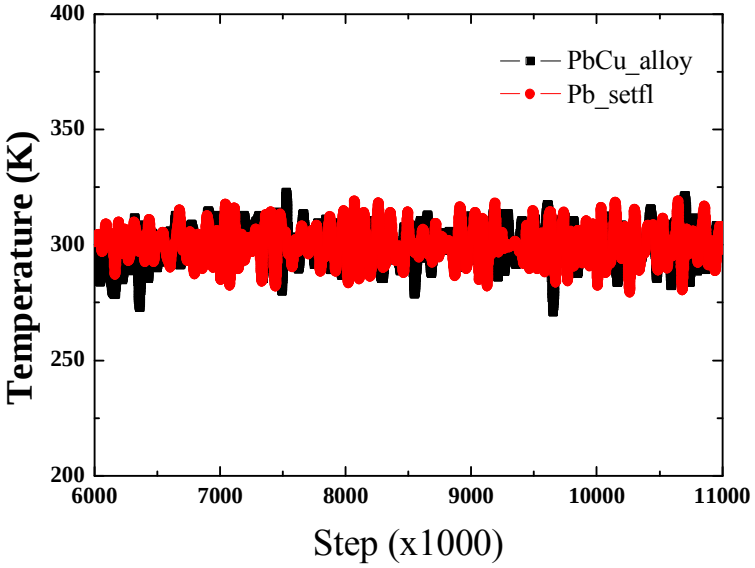
# Thermodynamic properties

**Heat capacity:**

$$C_V = \frac{1}{k_B T^2}\left(\left\langle E^2 \right\rangle - \left\langle E \right\rangle^2\right)$$

**Isothermal compresibility:**

$$\beta_T = -\frac{1}{\langle V \rangle}\left(\frac{\partial \langle V \rangle}{\partial P}\right)_T = \frac{1}{k_B T \langle V \rangle}\left(\left\langle V^2 \right\rangle - \left\langle V \right\rangle^2\right)$$

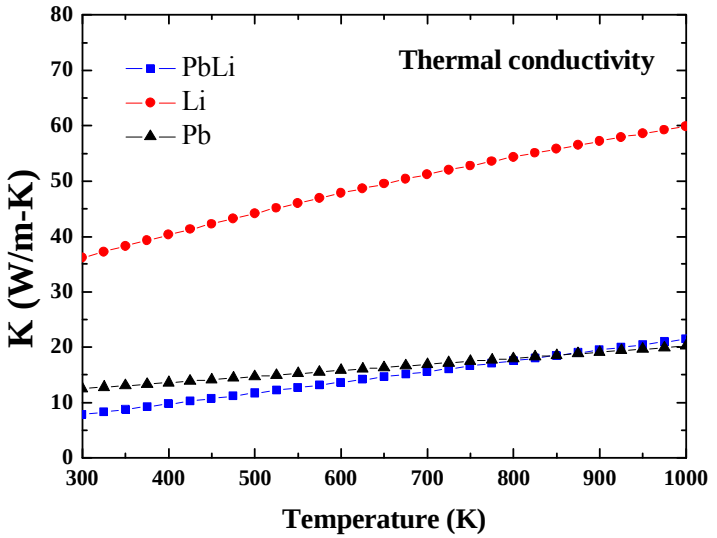


# Thermodynamic properties

- **Thermal conductivity**

  The expression of the spectral thermal conductivity is a consequence of the fluctuation-dissipation theorem [1, 2]:

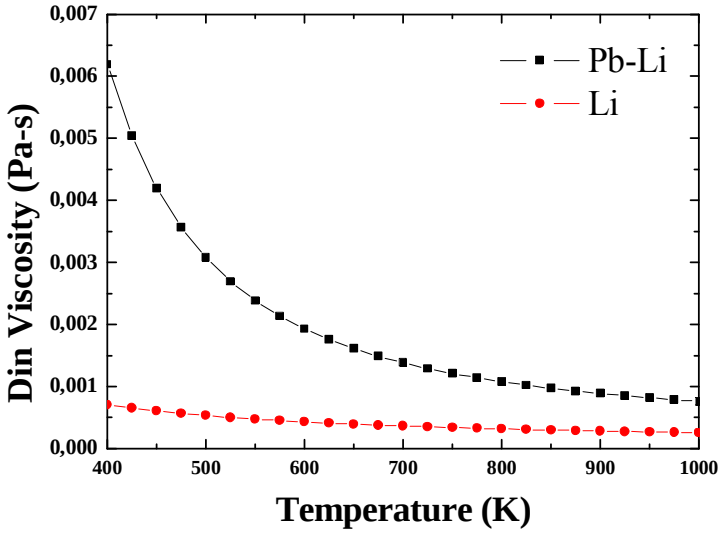
$$\lambda(k,\omega) = \frac{V}{3k_B T_0^2} \int_0^\infty \langle q_0(k,0) q_0(k,t) \rangle e$$

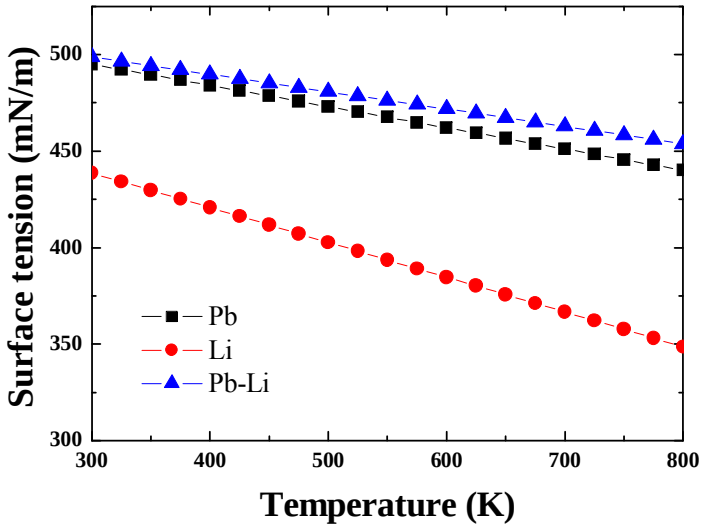



Experimental thermal conductivity of Pb, Li and $Pb_{83}Li_{17}$.


[1] R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[2] R. Kubo and M. Yokota, J. Phys. Soc. Jpn. **12**, 1203 (1957).

# Thermodynamic properties




Experimental viscosity (left) and surface tension (right) in funtion of temperature for Pb, Li and Pb-Li eutectic alloy.

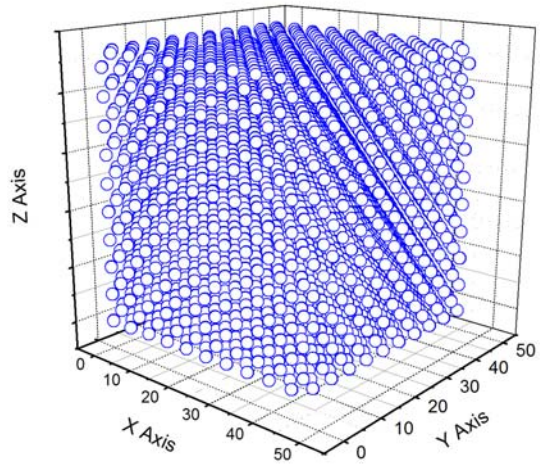
## Viscosity

$$\eta = \frac{V}{k_B T}\int_0^\infty dt < P_{\alpha\beta}(t)P_{\alpha\beta}(0) >$$

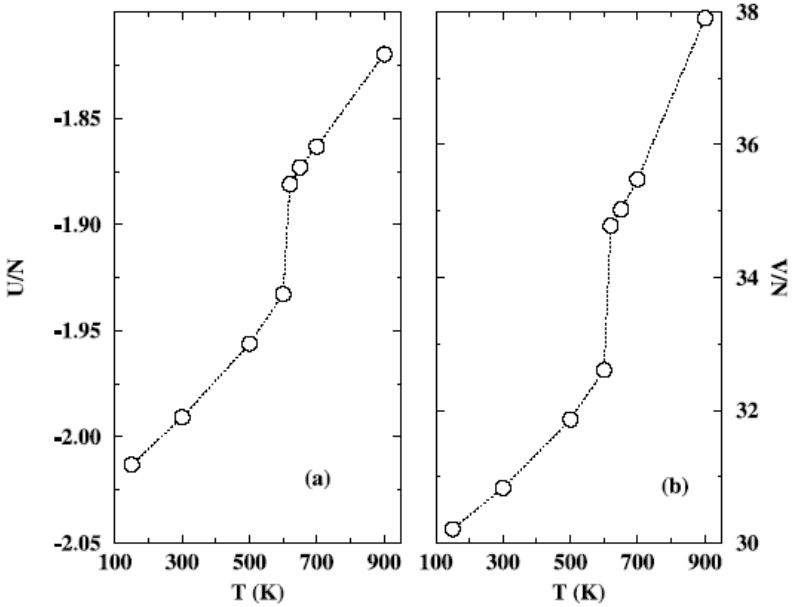
$P_{\alpha\beta}$ –off-diagonal components of the stress tensor

# Melting point

Potential energy jump overstimates melting point.



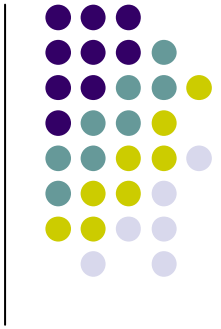

Pb lattice at 300K. (500 atoms)




Thermal behavior of the potential energy (left) and the volume (right) per atom, for the pure Pb system. Potential energy U=N in eV/atom; atomic volume V =N in $A^3$.

[1] L. Vofiadlo and G.D. Price Phys Chem Minerals (1996) 23:42-49

# Melting point



According to the **Lindemann melting criterion**, a solid melts when the ratio of the mean amplitude *u* of the atomic thermal vibrations to the distance $d_{NN}$ between the nearest neighbors reaches a certain critical value *L* identical for all substances,

$$\sqrt{\left\langle u^2(T_m)\right\rangle} = L d_{NN}$$

where *L* is the **Lindemann constant**.
The pressure dependence of $T_m$ is usually estimated under the assumption that the constant *L* is almost invariable along the melting curve $T_m(p)$.

The preferred method of obtaining the $T_m$ in MD simulations is the **coexistence technique** [42–44], which employs bulk systems containing crystal and liquid phases separated by a flat interface and long runs in the *NVE* ensemble to stabilize the temperature at the melting point.

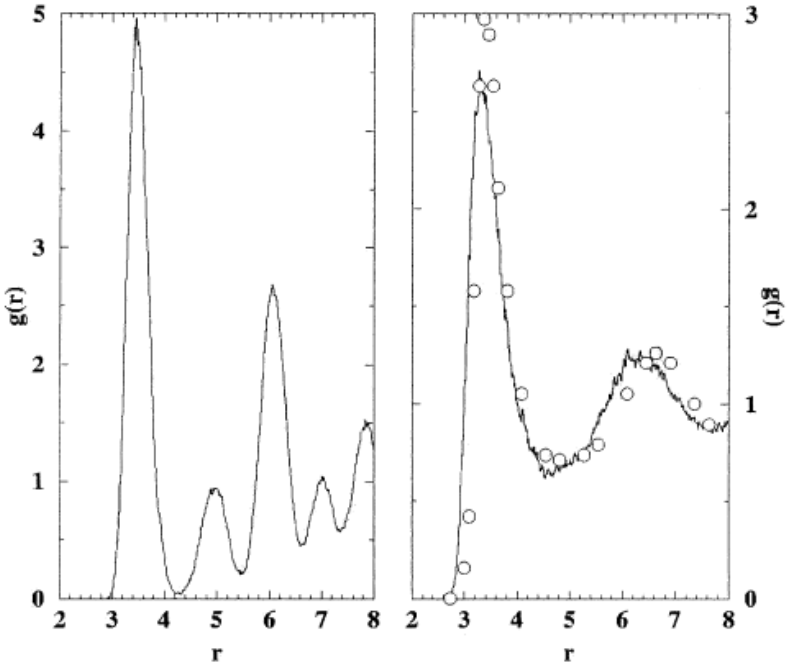

[42] J. R. Morris, C. Z. Wang, K. M. Ho, and C. T. Chan, Phys. Rev. B **49**, 3109 1994.
[43] J. R. Morris and X. Song, J. Chem. Phys. **116**, 9352 2002.
[44] J. J. Hoyt, M. Asta, and A. Karma, Mater. Sci. Eng., R. **R41**, 121 2003.

# Structural properties

- Structural properties are under progress.

Radial distribution function (RDF) g(r)

$$g(r,t) = \frac{1}{4\pi r^2}\frac{dn(r,t)}{dr}$$




Radial distribution functions of the Pb system at different temperatures: T = 300 K (left panel); T =700 K (right panel) [1]. In the latter panel, the experimental RDF g(r) of pure Pb, taken from Ref.[11], is also reported (o). Distances r in A.


[1] M. Celino et al. / Journal of Nuclear Materials 301 (2002) 64–69
[11] W.Gudowsk i, A. Mellergard, M. Dzugutov, W.S.Howells, P.Zetterstrom, J.Non-Cr yst.Solids 156–158 (1993) 130.

# PbLi eutectic alloy:

- Pb-Li binary system requires **7 functions**:

  $\varphi_{Pb\text{-}Pb}(r)$, $\varphi_{Li\text{-}Li}(r)$, $\varphi_{Pb\text{-}Li}(r)$ Interatomic potential

  + $\rho_{Pb}(r)$, $\rho_{Li}(r)$, electron densities

  + $F_{Pb}[\rho]$, and $F_{Li}[\rho]$ embedding energy functions

**Pb-Li cross potential [1, 2] ?**

$$\Phi^{PbLi}(r) = \frac{1}{2}\left(\frac{\rho^{Pb}}{\rho^{Li}}\Phi^{Li}(r) + \frac{\rho^{Li}}{\rho^{Pb}}\Phi^{Pb}(r)\right) \quad [1]$$

$$\Phi^{PbLi}(r) = \frac{1}{2}\left(\frac{\Omega^{Pb} f^{Pb}(r)}{\Omega^{Li} f^{Li}(r)}\Phi^{Li}(r) + \frac{\Omega^{Li} f^{Li}(r)}{\Omega^{Pb} f^{Pb}(r)}\Phi^{Pb}(r)\right) \quad [2]$$


[1] Landa A. *et al* Acta mater. 48 (2000) 1753-1761

[2] W. Hu et al, J. Phys. D: Appl. Phys. 33 (2000) 711.

# PbLi eutectic alloy:

- Wu *et al*, [2]

$$\Phi^{Li-Pb}(r)=\frac{1}{2}\left(\frac{\Omega^{Pb}f^{Pb}(r)}{\Omega^{Li}f^{Li}(r)}\Phi^{Li}(r)+\frac{\Omega^{Li}f^{Li}(r)}{\Omega^{Pb}f^{Pb}(r)}\Phi^{Pb}(r)\right)$$

where $\Omega_{Al}$ and $\Omega_{Pb}$ are the **atomic volume** of atom **Al and Pb**, respectively.

$$f(r)=f_e\left(\frac{r_{le}}{r}\right)^6$$

subscript *e* indicates **equilibrium state**

$r_{le}$ is the nearest neighbour distance in equilibrium. ***¿?*** → ← ***Ab initio*** **(QMD)**

[2] W. Hu et al, J. Phys. D: Appl. Phys. 33 (2000) 711.

# First principles calculations:

- Pb, Li and PbLi alloys QMD simulations [1, 2].
  - 1. Structural properties of PbLi alloys.

**QUESTIONS:**
Solid structure of PbLi eutectic?
$Li_4Pb$ and $Pb_n$ clusters.
Hard melting phases ($Li_5Pb_2$, LiPb, $Li_3Pb$)?

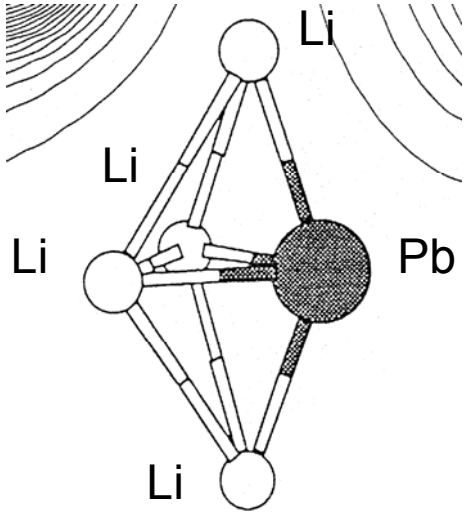


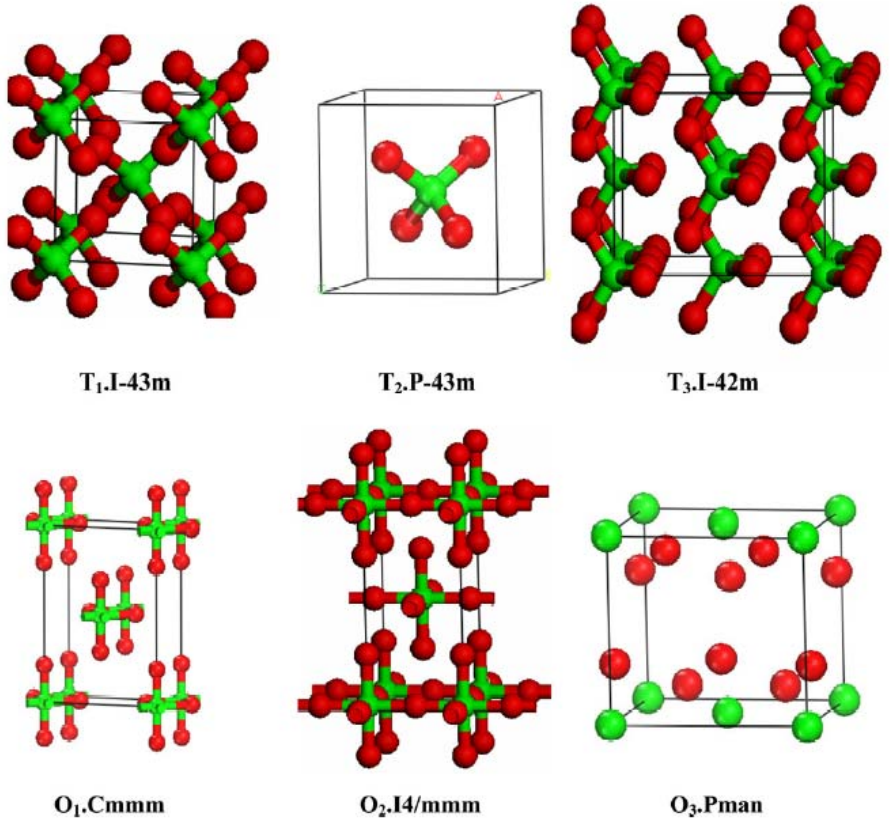

Fig. 3: $Li_4Pb$ (Zintl ions).

  - 2. Pb-Li Phase diagram.
  - 3. Pb-Li potential for CMD simulations

**[1] VASP:** Kresse G. and Hafner J. 1994 *Phys. Rev.* B **49** 14 251
**[2] WIEN2K:** P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, J. Luitz, WIEN2K, An Augmented-Plane-Wave+Local Orbitals Program for Calculating Crystal Properties, Karlheinz Schwarz, Techn. Wien, Austria, 2001, ISBN 2-9501031-1-2.

# First principles calculations:

$Li_4Pb$ posible crystal structures [1]



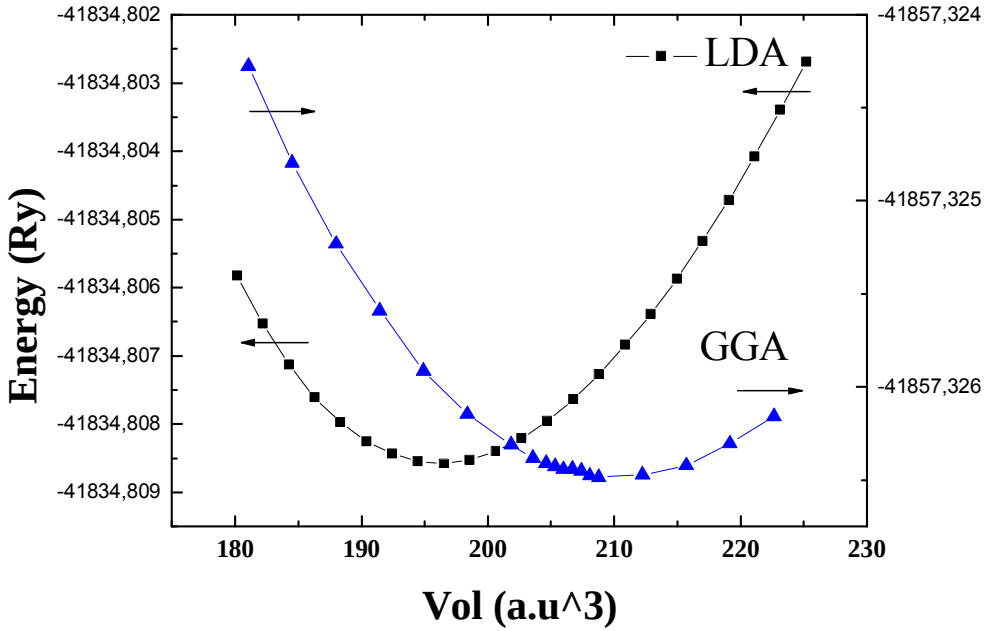

[1] Z. Li et al. / Solid State Communications 143 (2007) 353–357

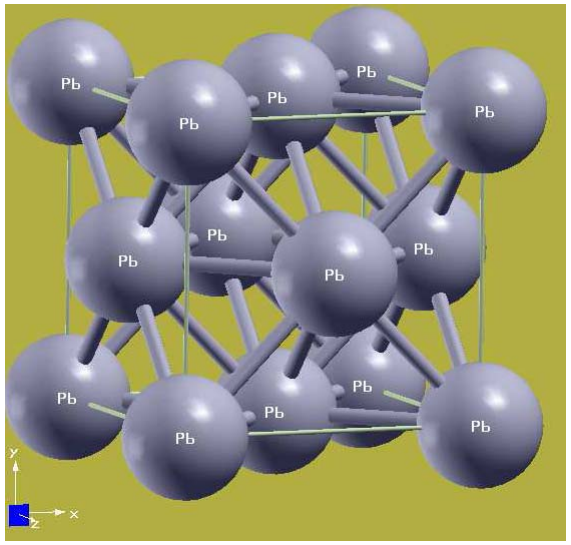
# First principles calculations:

- The self-consistent calculation is performed within the local density approximation [54] (LDA) for the exchange-correlation functional, and, in addition to the LDA, the total energy was calculated using the generalized gradient approximation [55] (GGA).

[54] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[55] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865(1996).

# First principles calculations (Pb):



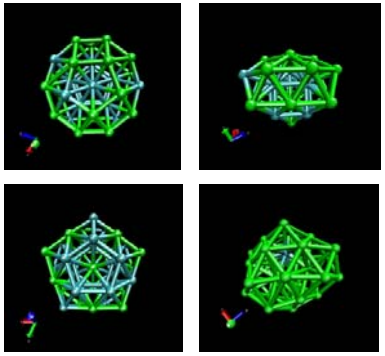




**Left: Pb volume minimization with two different approximations to the exchange-correlation (XC) energy functional in DFT. Right Pb FCC cubic crystal struture.**

# First principles calculations (Pb): Pb clusters?

The structure of $Pb_{83}Li_{17}$ eutectic melt seems to be rather inhomogeneous with two kind structural units: $Li_4Pb$ associates and $Pb_n$ clusters [3].

Coexistence of solid and liquid phases in atomic clusters [4]**?**



Four different Pb clusters.

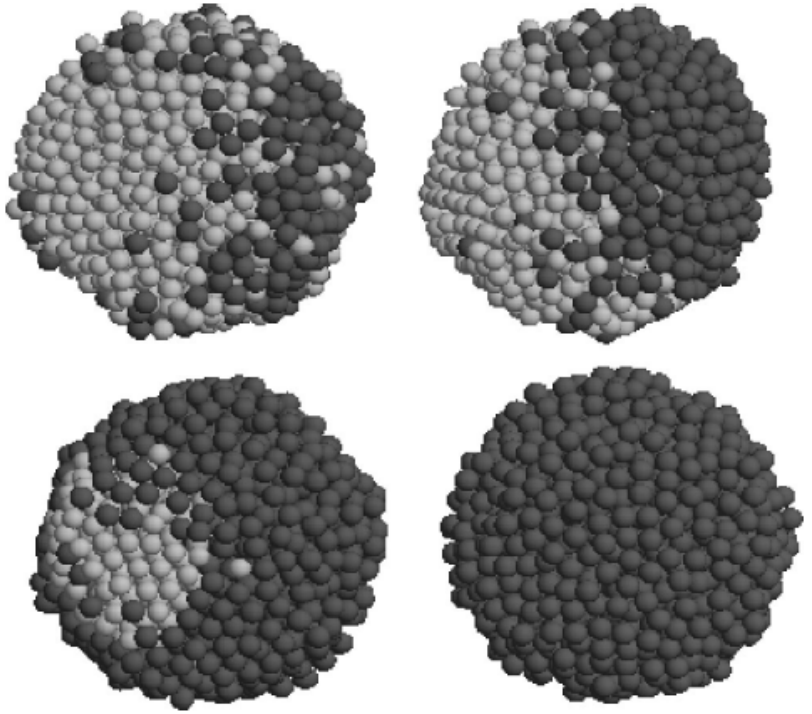


FIG. 3. A sequence of snapshots showing the coexisting solid-liquid state as the energy is increased from $E=-1.712$ eV/atom (top left) to $E=-1.706$ eV/atom (bottom right). Atoms are classified by their mobilities: the dark gray atoms are liquid (high mobility) while the light gray atoms are solid (low mobility).

[3] Journal of Nuclear Materials 376 (2008) 371–374
[4] Hendy S. C. *et al*, Phys. Rev. B, Vol 64, 085425 (2005)

# First principles calculations (Li):

- **Structure of Li**

  BCC structure at room temperature but BCC and HCP at 78K (transition temperature)(C. Kittel (1976).

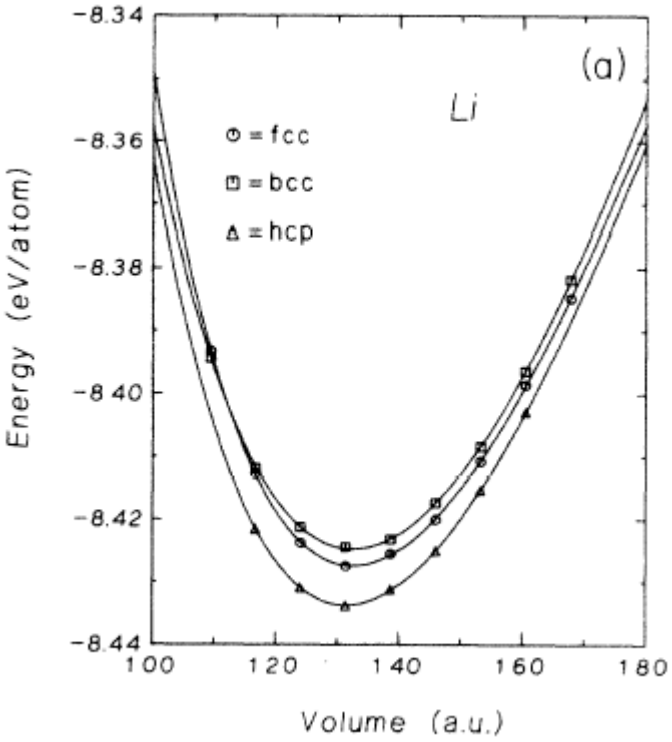
  BCC plastic deformation → FCC at around 77K (C. S. Barrett (1947)).

  BCC, 9R and disordered polytype phases below the transition temperature (Schwarz et al. (1990) [21]).

  Close-packed rhombohedral 9R: (a) at 4.2K (Overhauser (1984) [22]); (b) at 20K (Berliner and Werner (1986) [23]); (c) below transition (Smith (1987) [24]).

  *Ab initio* calculations → FCC (Das et al. (1996) [25], Staikov et al. (1997) [26], and Doll et al. (1999) [27]).

**Conclusion:** the ground state structure of Li is "not clear" [1, 2]!!!




Volume minimization [X]


[1] G. P. Purja Pun and Y. Mishin, Defects and Diffusion, (2007), vol. 266, pp. 49-62

[2] Rodriguez-Prieto A, Bergara A, Silkin V M and Echenique P M (2006) *Phys. Rev.* B **74** 172104

# He & T behaviour in liquid PbLi

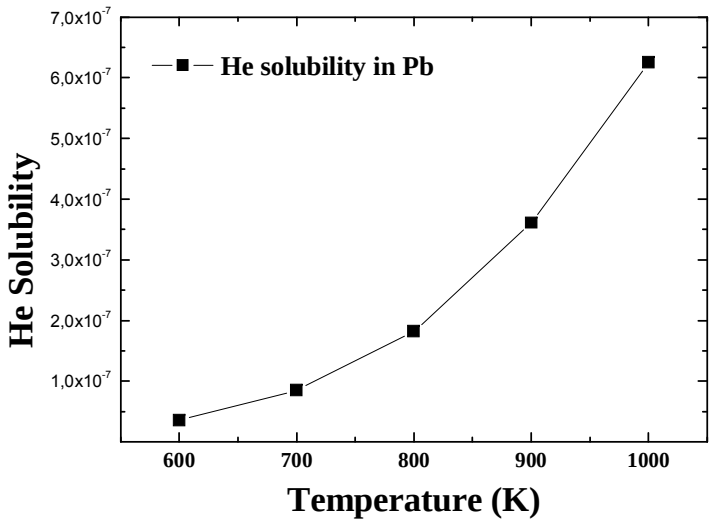
- Diffusion coefficient and Sievert's constants for H (D and T) has been measured but **consensous is poor** [1].

$$D_{PbLi} = 4{,}03 \cdot 10^{-8} \exp(-19500/RT_{PbLi}) \left[m^2 / s\right]$$

- Sievert's constant largely depend on the experimental technique used.

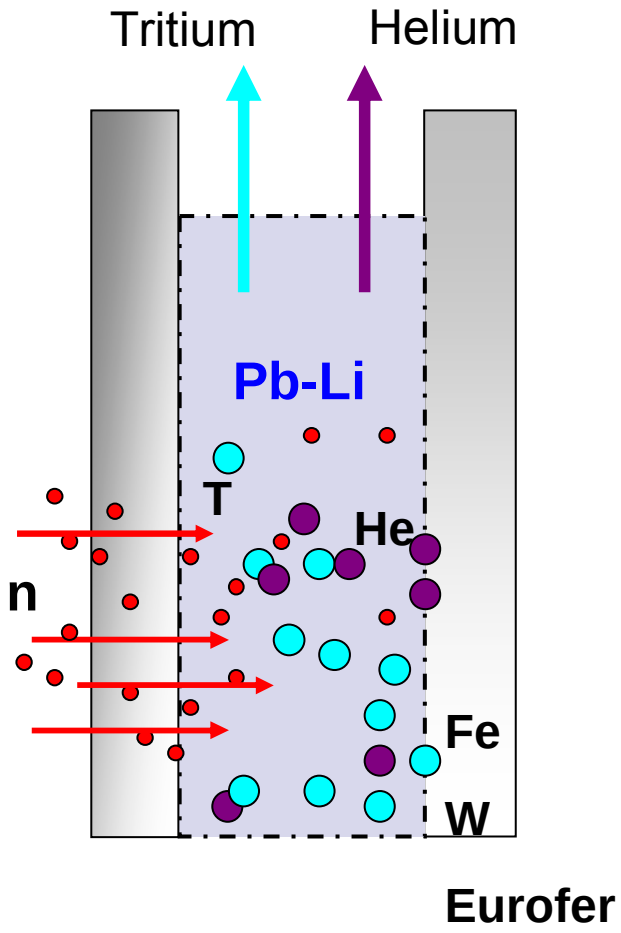
$$Ks_{PbLi} = 2{,}32 \cdot 10^{-8} \exp(-1350/RT_{PbLi}) \cdot Nav \cdot 9800 \cdot 1000/173 \left[at - T / m^3 \sqrt{Pa}\right]$$

- He solubility in PbLi is unknown.




[1] L. A. Sedano *et al*, (2007)

# He & T behaviour in liquid PbLi



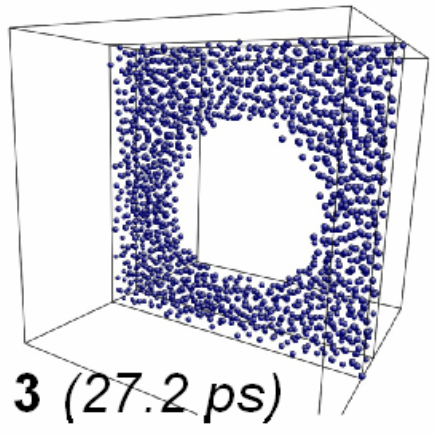

$^{6}Li + n \rightarrow {}^{4}He + {}^{3}H + 4.78\ MeV$

$^{7}Li + n \rightarrow {}^{4}He + {}^{3}H + n + 2.47\ MeV$

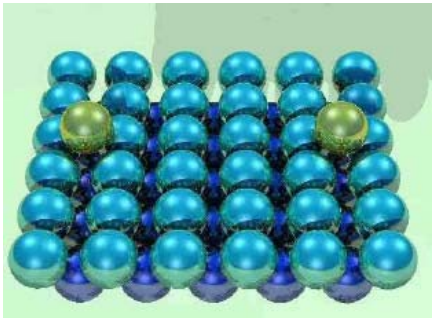
- Tritium is absorbed into **He bubbles**, where it can only exist as **molecular tritium**.
- Molecular tritium has a larger energy than He gas phase, therefore it is **desorbed** from the bubble into the bulk liquid, where it dissociates into **atomic tritium** again.
- Mass transfer coefficients are not accurate and equilibrium constant is unknown.

# Critical physico-chemical problems:

- Bubble nucleation & grow phenomena.
- Bubble diffusion and behaviour. Coalescence phenomena.

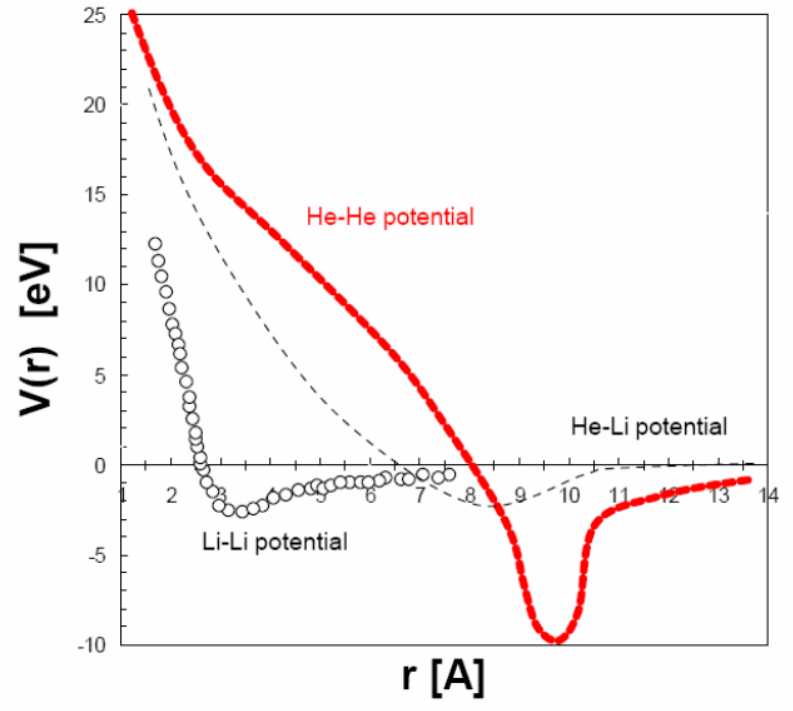



- Adsorption/permeability of a surface (i.e. Fe, Al layer).
- Atomistic diffusion of other species (i.e He, H) in the eutectic. Rates of adsorption and diffusion.

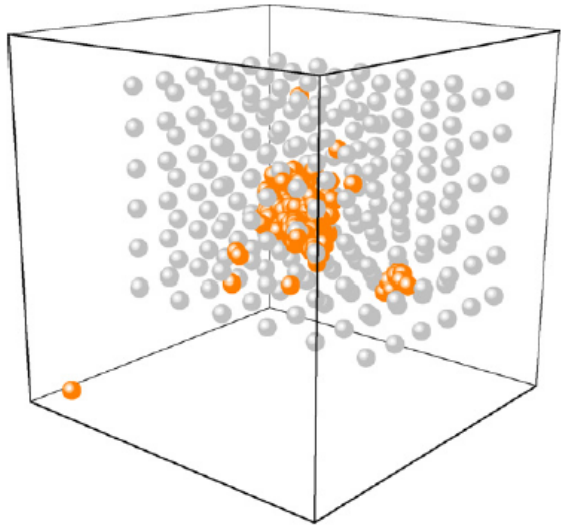


- Residence time of eutectic atoms in a material surface. Diffusion inside the structural material.

# He (+T) PbLi simulations




**Bubble formation!**



Ranges and profiles in He Li system:
Li-Li potential from [6], Li-He from [7] and He-He from [8]

3D configuration of He atoms before and after bubble formation. The light gray balls represent the initial sites of He atoms, while the equilibrium sites of these He atoms are indicated by orange balls [9].


[**6**] González L E, Gonzá lez. D J, Silbert M and Alonso J A 1993 *J. Phys.: Condens. Matter* **5** 4283.
[**7**] P. Soldán *et al.*, Chem. Rev. Letters, 343 (2001) 429-436.
[**8**] J.S. Murday and R.M. Cotts, 2. Naturforsch. 26a (1971) 85.
[9] B.Y. Ao et al. Atomistic study of small helium bubbles in plutonium Journal of Alloys and Compounds 444–445 (2007) 300–304

# He bubble formation simulation:

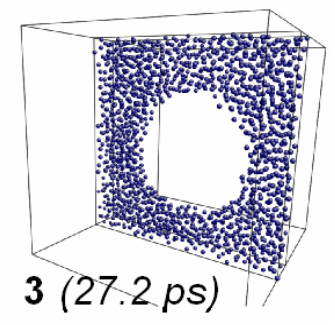
- **An initial stage of bubble formation takes a long time compared to a typical MD-time scale, ~ $10^{-9}$ sec.**

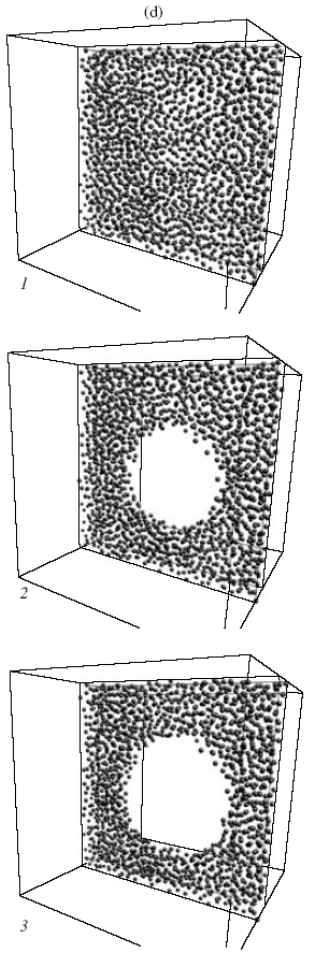
**Two processes, with different time scales:**

**1. Slow process – formation of a critical nucleus.**

**2. Fast process – Bubble collapse and sputtering.**

**→ Huge computation task.**



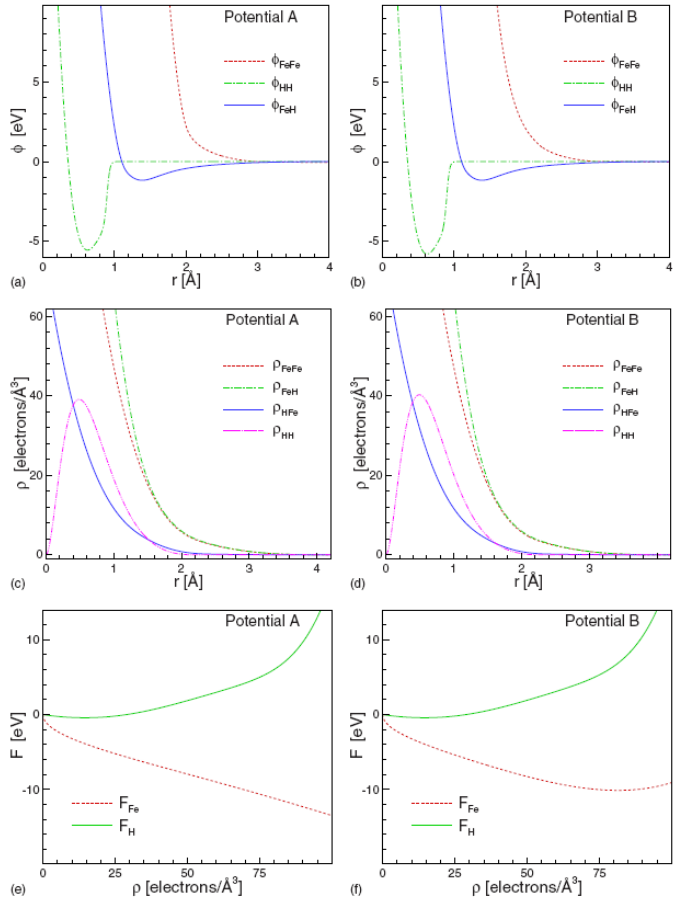




Section *1* contains a metastable liquid phase before cavity formation, section *2* corresponds to the beginning of cavity formation, and section *3* shows the cavity formed [1]

[1] T. T. Bazhirov, G. E. Norman, and V. V. Stegailov "Molecular Dynamics Simulation of Cavitation in a Lead Melt at Negative Pressures" Russian Journal of Physical Chemistry, 2006, Vol. 80, Suppl. 1, pp. S90–S97 (2006).

# Tritium MD simulations

- Very few studies about hydrogen isotopes (D or T) are published [1].
- An EAM potential for H is being implemented [2, 3].




a) Two-body interaction potential, b) electron density, and c) embedding functions **for H** Potentials A and B [4].


[1]Thin Solid Films Volume 516, Issue 19, 1 August 2008, Pages 6553-6559, 20th Symposium on Plasma Science for Materials (SPSM-20), Hydrogen isotope sputtering of graphite by molecular dynamics simulation A. Ito and H. Nakamura
[2] M. Ruda, D. Farkas, and J. Abriata, Phys. Rev. B 54, 9765 (1996).
[3] M. Wen, X.-J. Xu, S. Fukuyama, and K. Yokogawa, J. Mater. Res. 16, 3496 2001.
[4] Ramasubramaniam et al, Phys. Rev. B 79, 174101 (2009):

# *Magnetic field effect & MHD

**There is no available information on magnetic permeability (nor magnetic susceptibility) of the eutectic.**

Even for Pb and Li separately it is difficult to obtain a general consensus. Is generally accepted that Li is paramagnetic ($\chi_v$>0) and Pb diamagnetic ($\chi_v$<0), but even in this aspect there are still discrepancies [2]

| | |
|---|---|
| Mag. Perm. [N.A$^{-2}$]<br>$\mu_m = \mu_{m0}(1 + C/T)$ | $\mu_m = 1.257 \cdot 10^{-5} + 5.485 \times 10^{-4}/T$ |

Pb data, very poor database (Li contents effects unkonwns) [1]

[1] M. Vals, L. A. Sedano *et al*, Journal of Nuclear Materials 376 (2008) 353-357
[2] F. Sears and M.Zemansky, "Física", Ed. Aguilar, 1979.

# Conclusions

- To clarify all questions and doubts about suitability of PbLi for liquid breeder blanket in fusion reactors MD, (both Classical and Quantum) simulations of PbLi (+He+T) are extremely necessary from a tecnologyc point of wiev and also of great interest from a purely scientific one.

# Thank you for your attention.