38th International Conference on Plasma Science (ICOPS)
and 24th Symposium on Fusion Engineering (SOFE)
Chicago, USA June 26 - 30, 2011.

Li & Pb MD Simulations

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Outline

- Motivation
- MD, potentials and methods
- Results
- Conclusions
- LiPb EAM/alloy/cd results
- Future work

- **Motivation**
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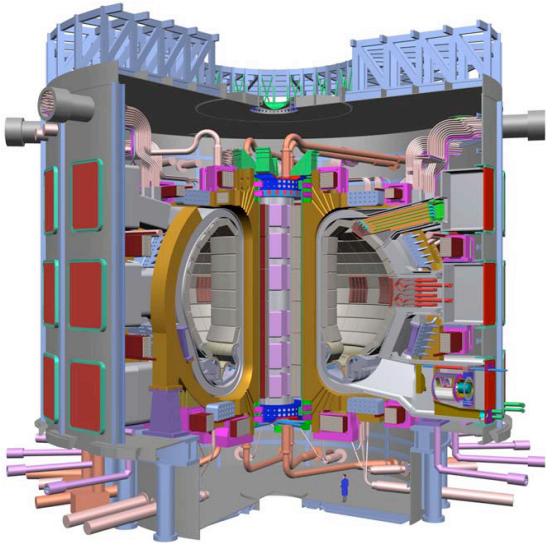
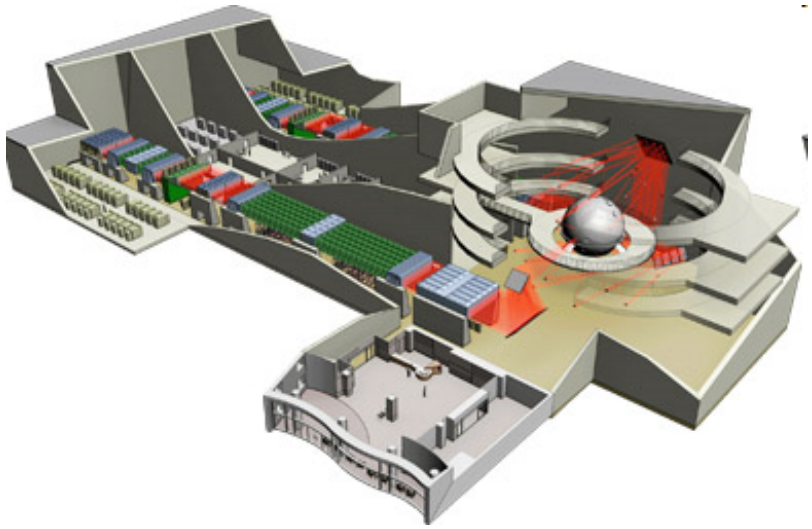
Fusion Reactor Technologies

- ITER, HiPER etc





We will need a blanket…

Blanket solutions I

- LiPb & other possible candidates

Liquid breeder	**Li**	**$Li_{17}Pb_{83}$**	**Flibe**	**$Li_{20}Pb_{80}$**
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 multipler required	Neutron multipler 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

Blanket solutions II

- LiPb & other possible candidates

Liquid breeder	**Li**	**$Li_{17}Pb_{83}$**	**Flibe**	**$Li_{20}Pb_{80}$**
Tritium solubility (atom frac $Pa^{-0.5}$ T=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			

Tritium (& He) behaviour

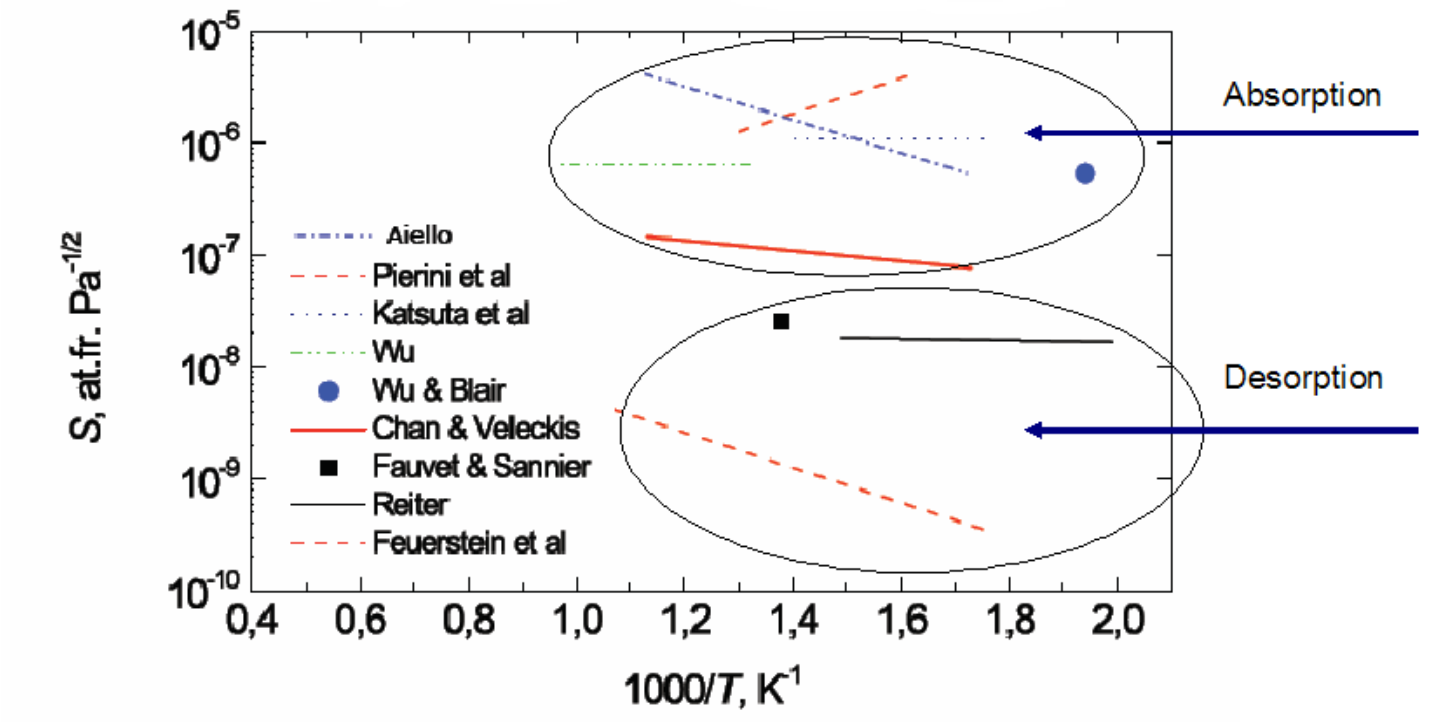
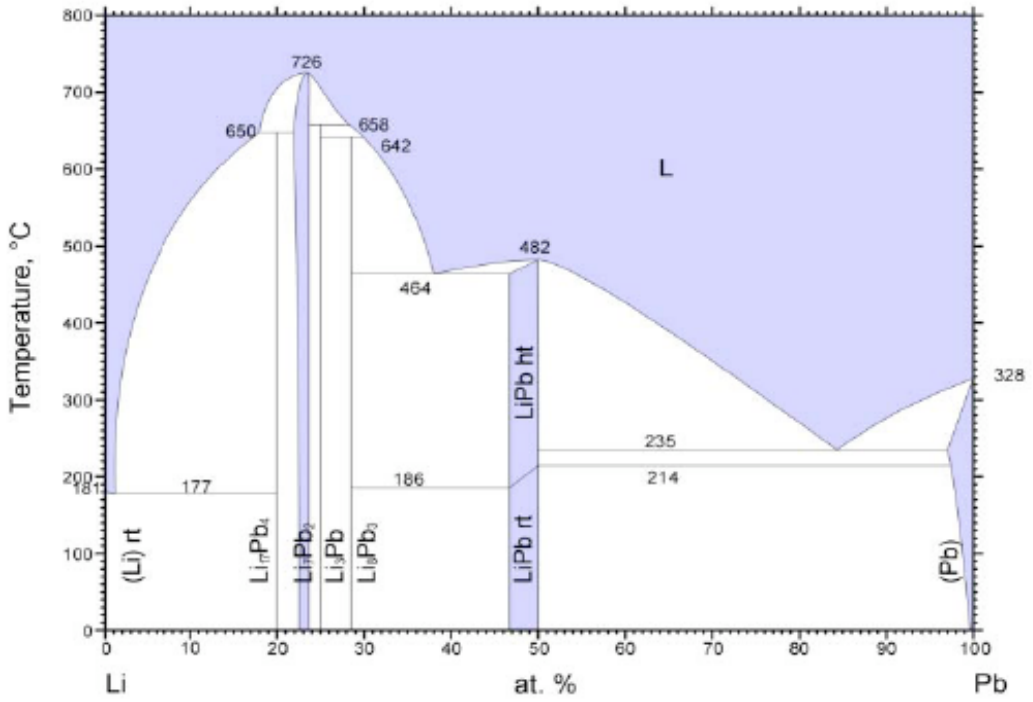


Figure 1: Solubility database is inadequate for design. Scatter reflects experimental approaches and measurement techniques applied. Knowledge of dynamic transport properties (diffusion, mass transfer, interface processes) is much more limited [1].

[1] RICAPITO I. Liquid Meatal Blankets for Fusion Reactors, Fusion Summer School, 10 Sept (2010)

LiPb system

- Phase diagram



[2] P. Hubberstey, et al, J. Nucl, Mater 191-194, 283-287 (1992), P. Hubbertey. Journal of Nuclear Materials 247 (1997) 208-214

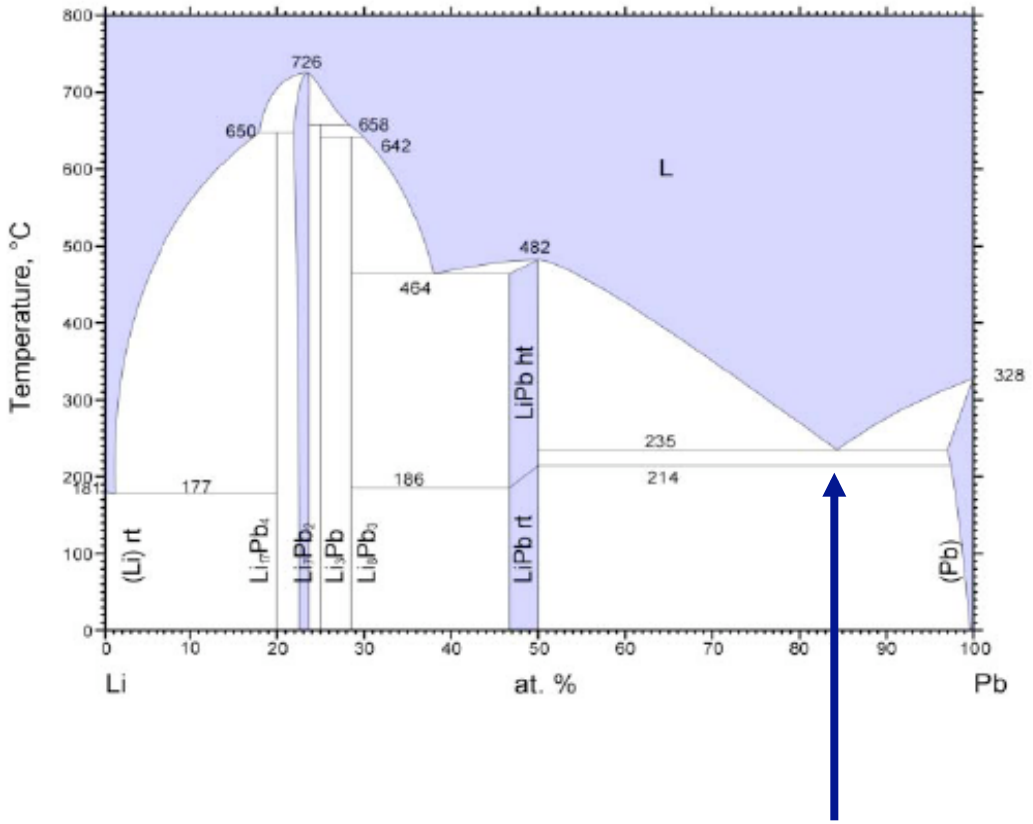
LiPb system

- Phase diagram

Eutectic point is still to be determined.

Structural properties of liquid phase remain unclear.

Magnetic fied effects?



Eutectic Li = 15,7 – 17 % (to be determined!)

[2] P. Hubberstey, et al, J. Nucl, Mater 191-194, 283-287 (1992), P. Hubbertey. Journal of Nuclear Materials 247 (1997) 208-214

- Motivation
- **MD, potentials and methods**
- Results
- Conclusions
- LiPb EAM/alloy/cd results
- Future work

Li & Pb EAM potentials

The total internal energy of the system of *N* atoms is described as the energy required to embed these *N* atoms into the homogeneous electron gas caused by surrounding atoms plus a correction of energy from two-body interactions. Thus this total energy can be expressed as:

$$E_i = \frac{1}{2}\sum_{i,j,i\neq j}\phi_{ij}(r_{ij}) + \sum_i F_i(\rho_i)$$

where ϕ_{ij} represents the pair energy between atoms i and j separated by r_{ij}, and F_i stands for the embedding energy to embed an atom i into a local site with electron density r_i.

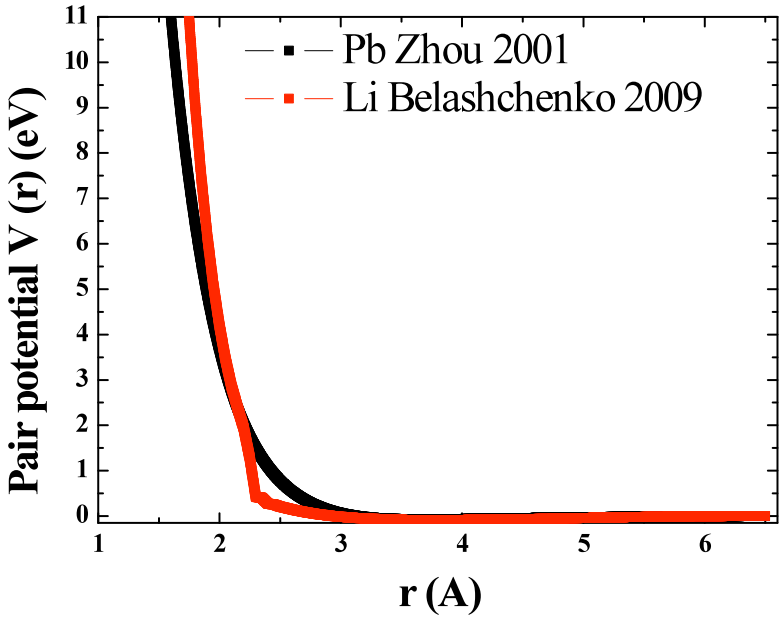


Fig. 2. Pair potentials for lead and lithium following references [3], [4].

[3] Zhou *et al* Acta Materialia Vol 49, Issue 19, 14 November 2001, 4005-4015
[4] D. Belashchenko *et al.* High Temperature 2009 vol 47 No 2 211-218.

- Motivation
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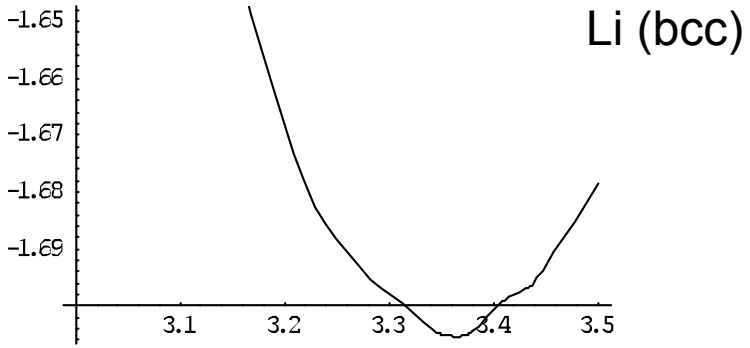
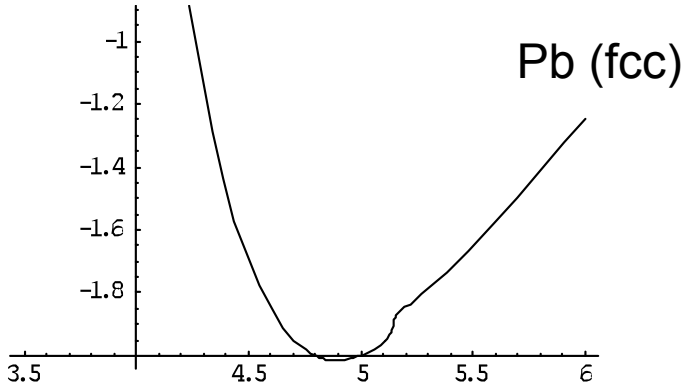
Testing Li & Pb potentials I

- Cohesive energy & Lattice parameter



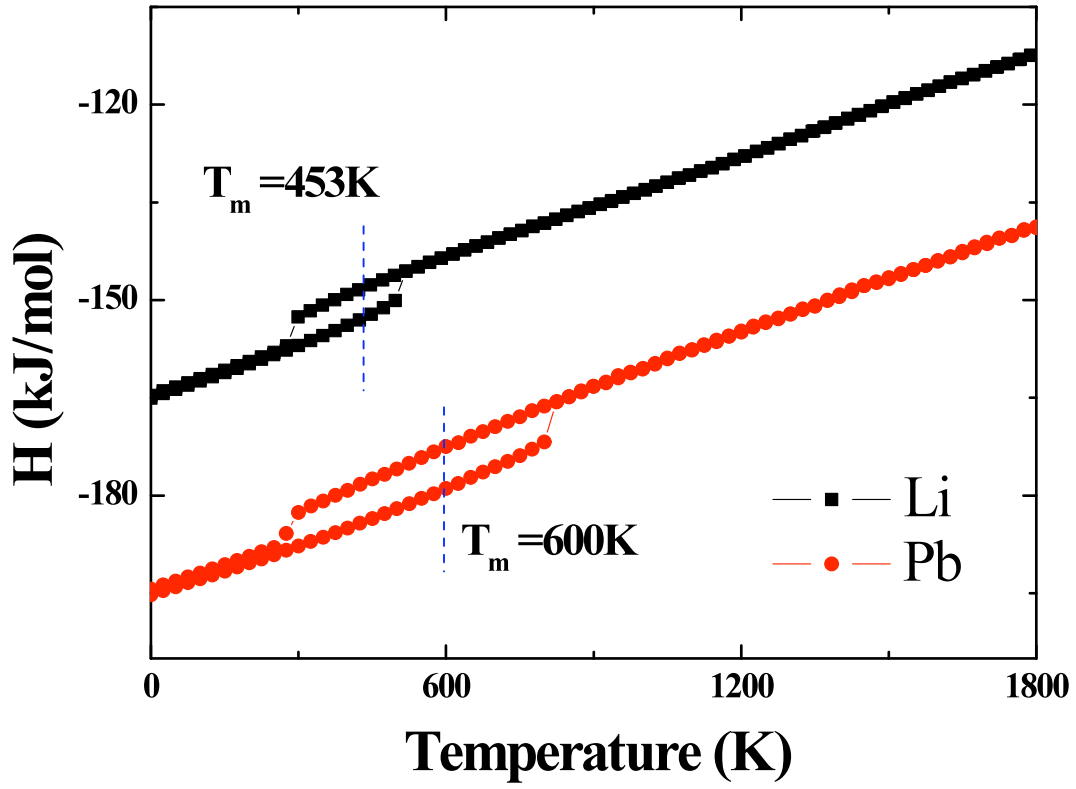


	Theoretical calculation		Experiment	
Element	E_c (eV/at)	Cell parameter (A)	E_c (eV/at)	Cell parameters (A)
Pb (fcc)	-2.014	a= 4.894	-2.03	a= 4.9095
Li (bcc)	-1.705	a= 3.3648	-1.63	a= 3.355

Table 1. Calculated cohesive energy, Ec, and lattice parameter, a, for Pb and Li in fcc and bcc phases. All values have been calculated **using Pb and Li EAM potentials** in the **effective representation.** The results are exactly the same that those obtained with the original potentials.

Testing Li & Pb potentials II

- Melting point



Experimental: T_m(Pb) = 600 K, T_m(Li) =453 K

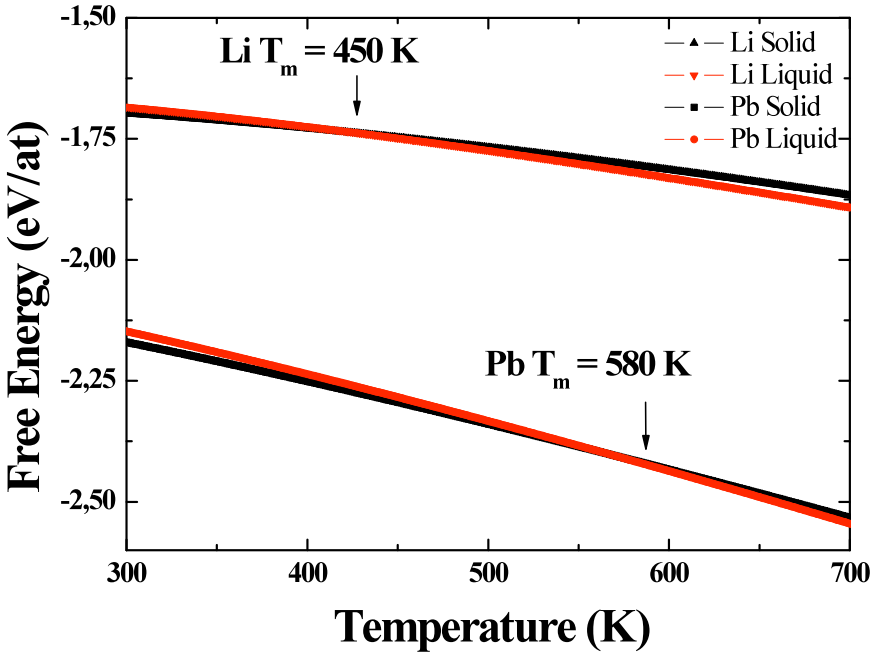
Testing Li & Pb potentials II

- Melting point

Free energies can be calculated using the Gibbs-Duhem integral:

$$f(T) = f(T_0)\frac{T}{T_0} - T\int_{T_0}^{T}\frac{h(\tau)}{\tau^2}d\tau$$

where h(τ) is the enthalpy per particle. The coupling-constant integration method, or switching Hamiltonian method, [5] is used to calculate $f(T_0)$ [6].



Melting point from free energy calculations.
Experimental: T_m(Pb) = 600 K, T_m(Li) =453 K

[5] Molecular Dynamics Simulation of Statistical Mechanical Systems, edited by G. Ciccotti and W. G. Hoover. (North Holland Amsterdam 1986)
[6] a) E. Ogando Arregui M. Caro and A. Caro. Phys Rev B 66 054201 (2002) b)E. Lopasso, A. Caro et al. Phys Rev B 68 21425 (2003)

Testing Li & Pb potentials III

- Structural properties

$$R(r) = \frac{1}{N}\sum_{\nu}\sum_{\mu}\frac{b_\nu b_\mu}{\langle b\rangle^2}\delta(r - r_{\nu\mu})$$

$$\rho(r) = \frac{1}{4\pi r^2}R(r)$$

Radial distribution function

$$g(r) = \rho(r)/\rho_0 = \frac{R(r)}{4\pi\rho_0 r^2} \qquad \text{thus } g(r) \to 1 \text{ for } r \to \infty$$

$$G(r) = 4\pi r\rho_0(g(r) - 1)$$

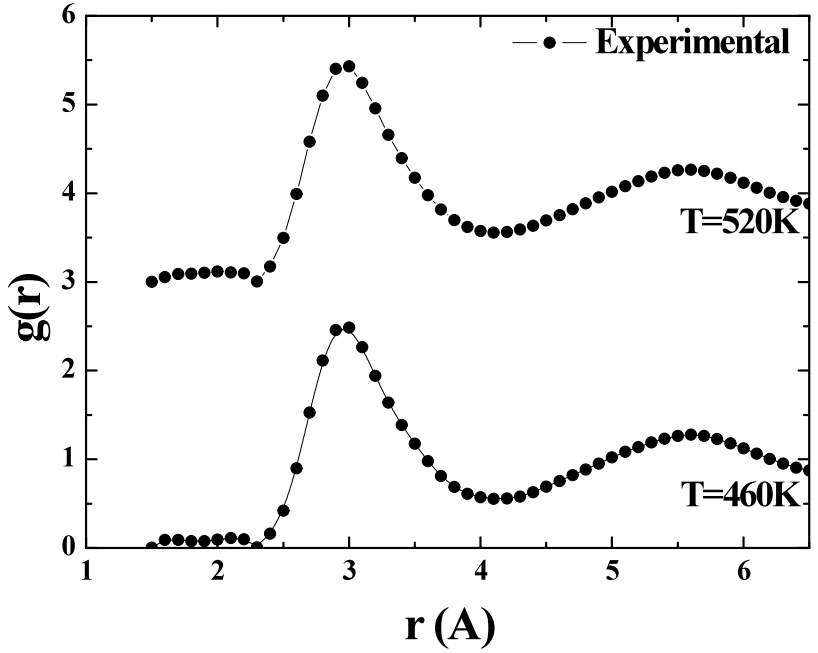
$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q) - 1]\sin(Qr)\mathrm{d}Q$$

Total structural factor

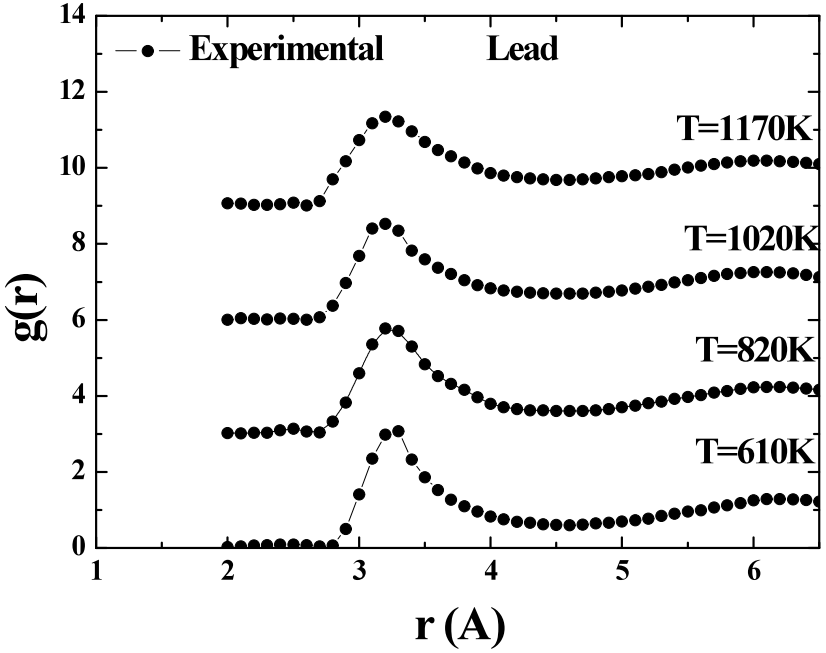
$$S(Q) = 1 + \frac{1}{Q}\int_0^\infty G(r)\sin(Qr)\mathrm{d}r$$

Testing Li & Pb potentials IIIb

- Structural properties (g(r))



Lithium g(r) experimental results.

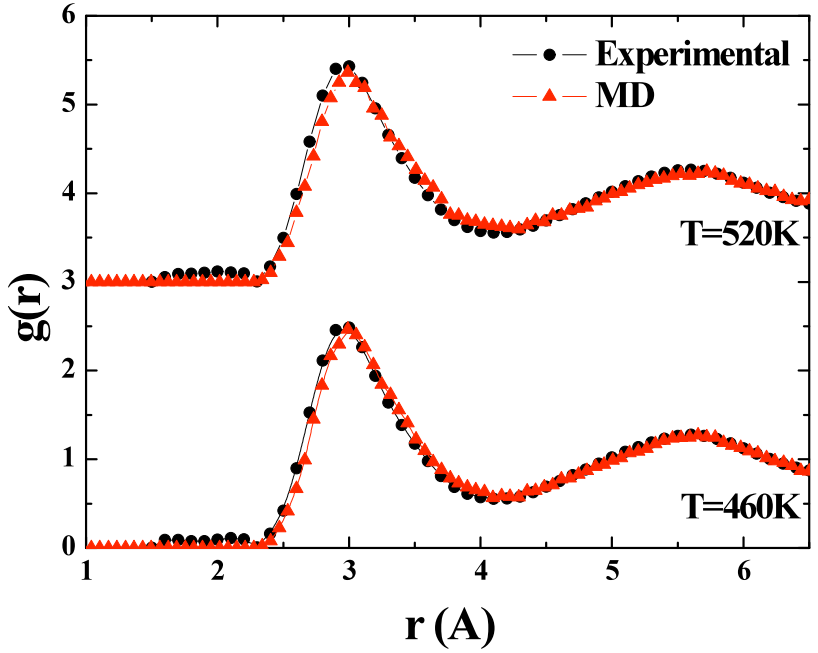


Lead g(r) experimental data.

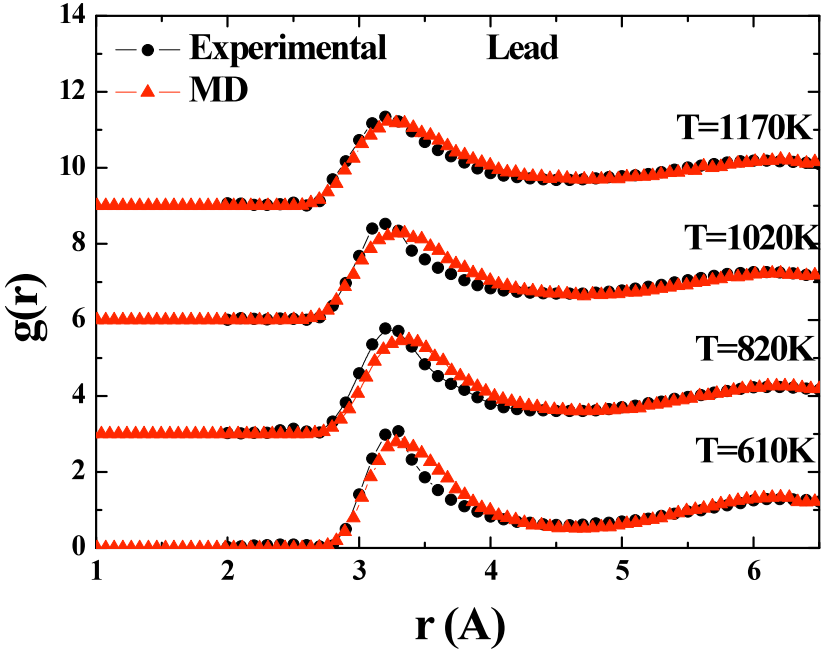
[7] Experimental data: http://res.tagen.tohoku.ac.jp/~waseda/scm/AXS/index.html

Testing Li & Pb potentials IIIb

- Structural properties (g(r))



Lithium g(r) calculated (red triangles) compared with experimental results (black circles).



Lead g(r) calculated (red triangles) compared with experimental (black circles)

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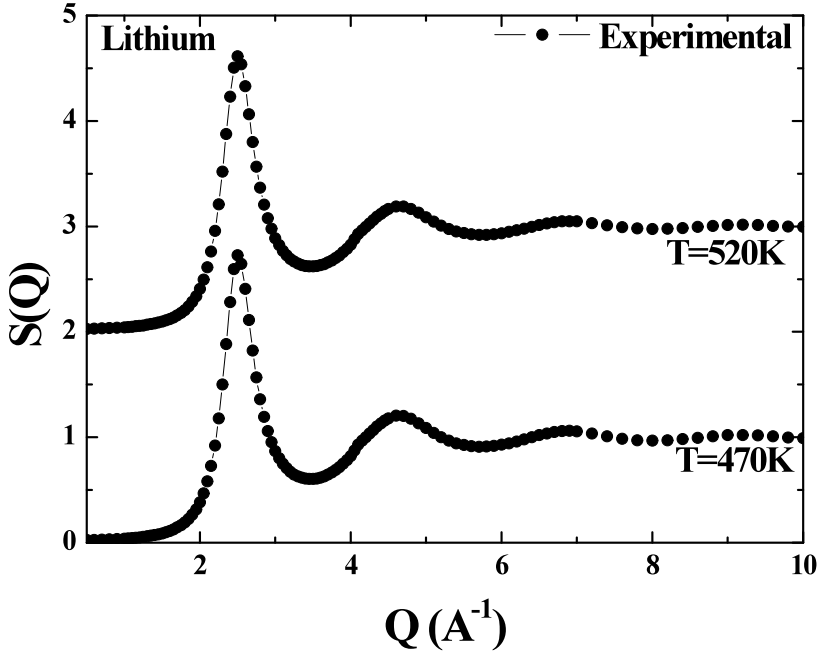
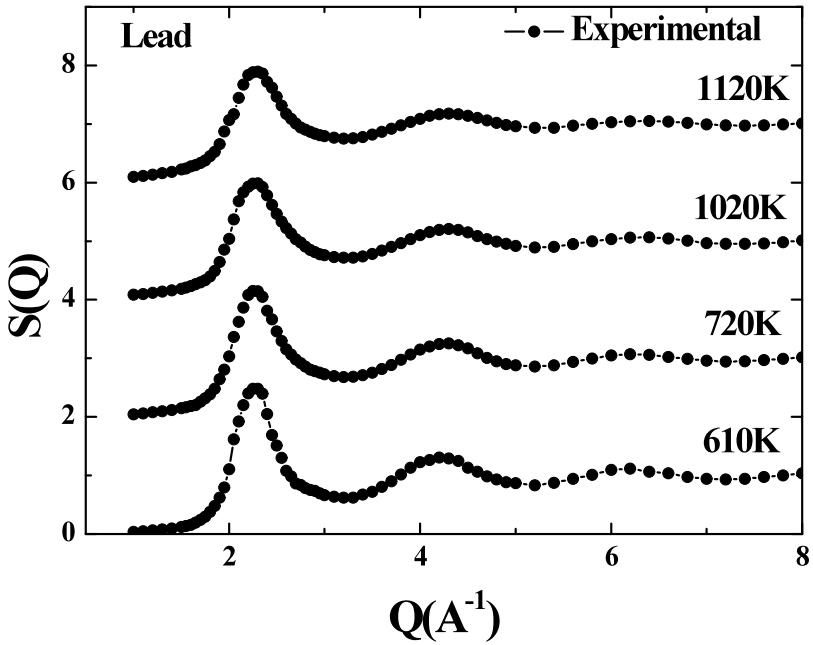
Testing Li & Pb potentials IIIc

- Structural properties (S(Q))



Lithium S(Q) experimental data.



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Testing Li & Pb potentials IIIc

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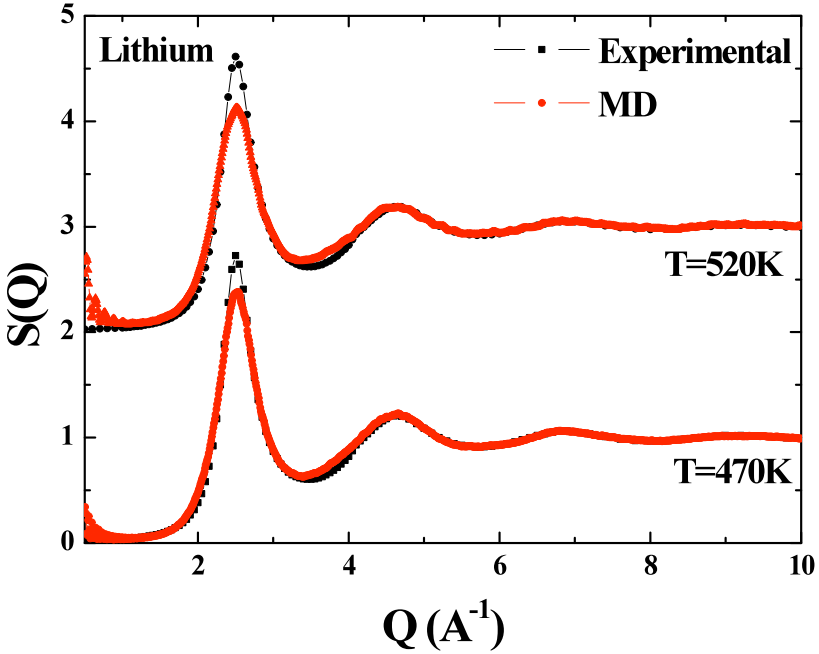
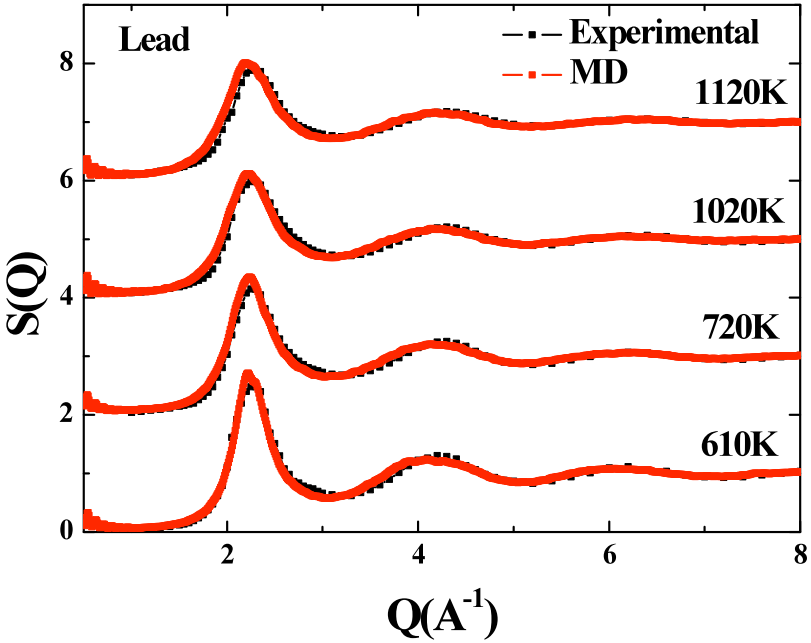


Lithium S(Q) calculated (red) compared with experimental results (black).



Lead S(Q) calculated (red) compared with experimental (black)

[7] Experimental data: http://res.tagen.tohoku.ac.jp/~waseda/scm/AXS/index.html

Testing Li & Pb potentials IV

- Density (ρ)

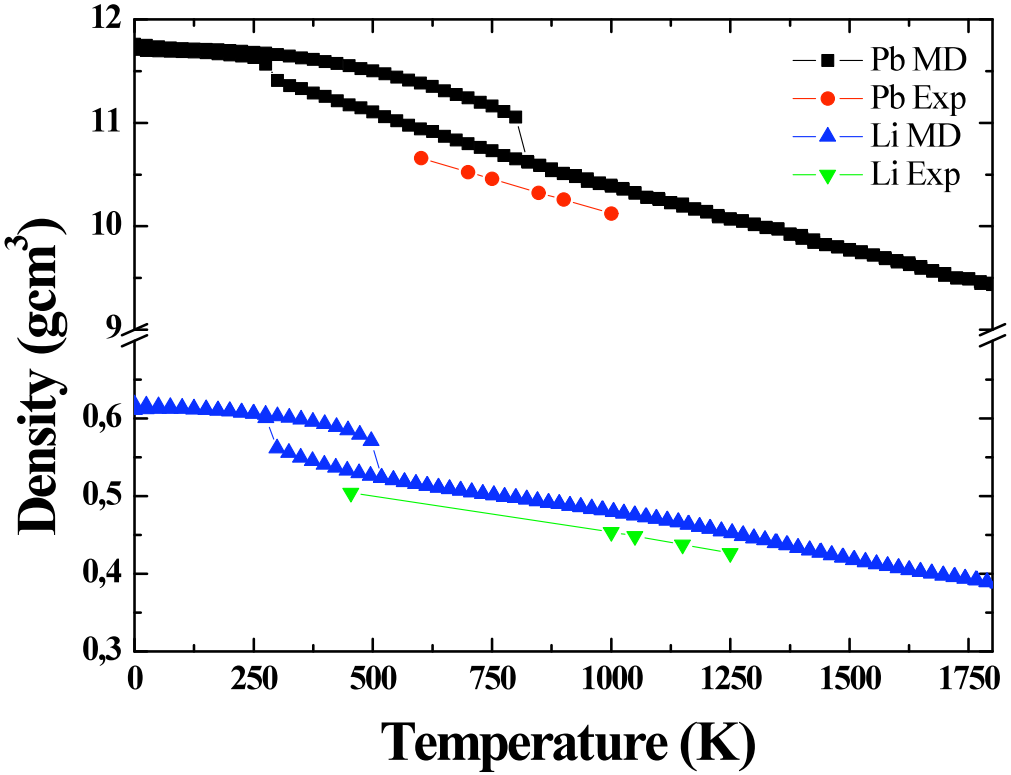


Figure 3. Density, ρ, calculated from MD simulations (black squares for lead and blue triangles for lithium) compared with experimental values in liquid phase, red circles for Pb and inverted green triangles for Li.

Testing Li & Pb potentials IV

- Density (ρ) & dρ/dT

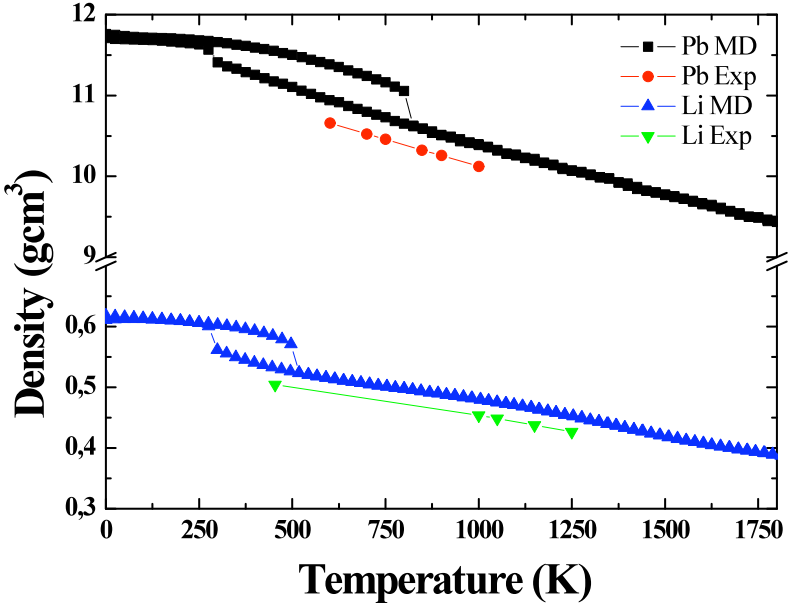


Figure 3. Density, ρ, calculated from MD simulations (black squares for lead and blue triangles for lithium) compared with experimental values in liquid phase, red circles for Pb and inverted green triangles for Li.

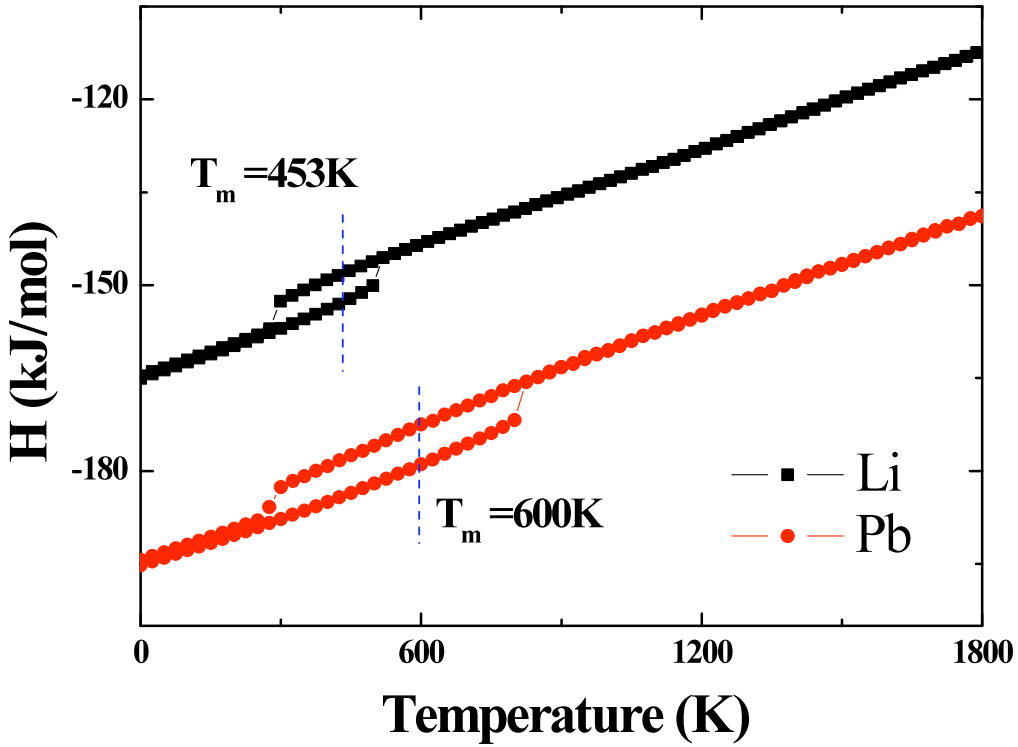
	Experimental		**MD**	
	ρ (Liq Temp) g/cm^3	∂ρ/dT (g/ cm^{3}K)	ρ (Liq Temp) g/cm^3	∂ρ/dT (g/ cm^{3}K)
Li	0,51	-9,6x10^{-5}	0,53	-8,6x10^{-5}
Pb	10,64	-0.0013	10,96	-0.0013

Table 2. Density, ρ, and density variation with temperature, ∂ρ/dT, of liquid lead and lithium compared with experimental values.

Testing Li & Pb potentials V

- Heat capacity (C_p)

$$C_p = \left(\partial H / \partial T\right)_p$$



Testing Li & Pb potentials V

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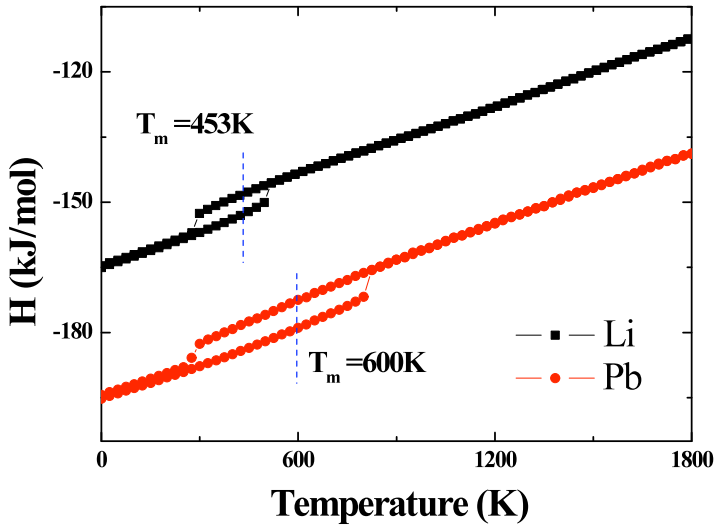

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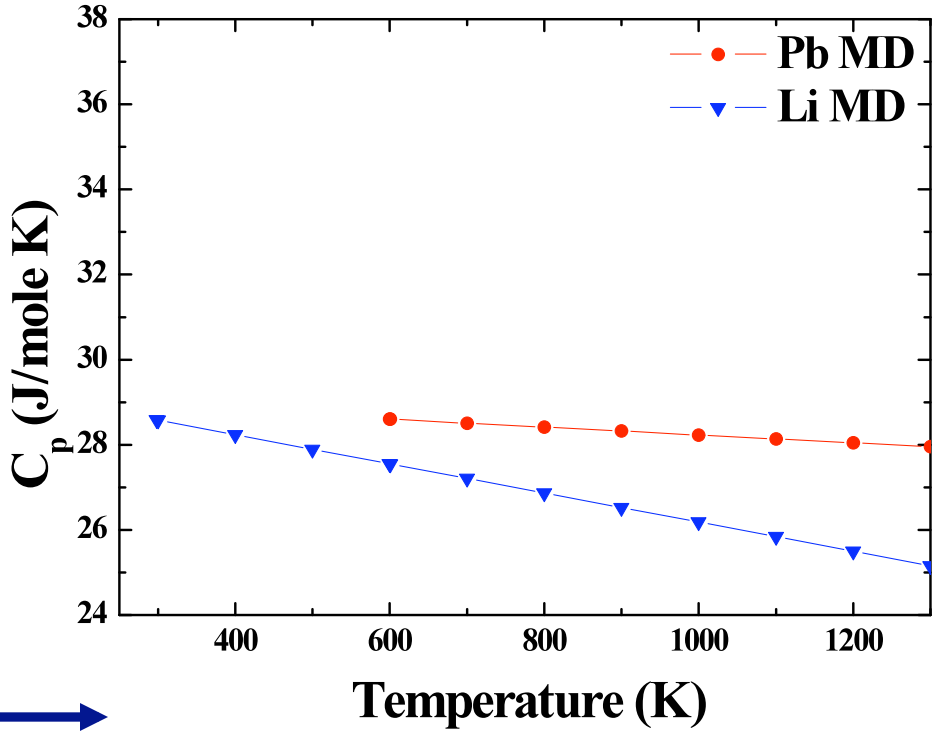
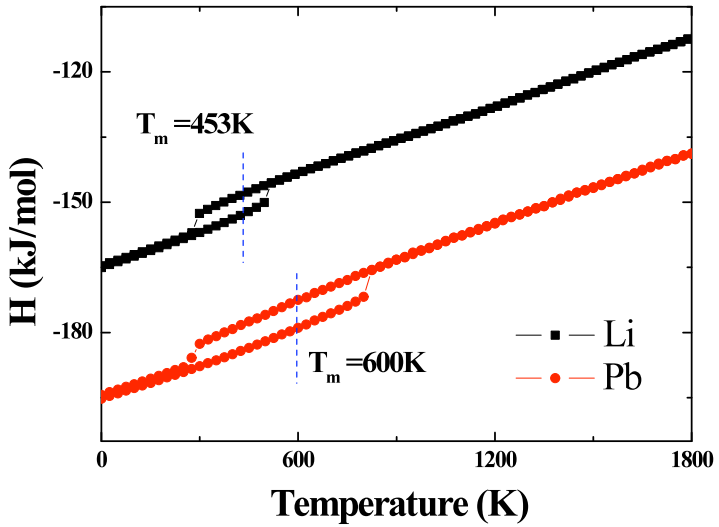


[8] Summary of Physical Properties for Lithium, Pb-17Li, and (LiF)n•BeF2 Coolants S.J. Zinkle, ORNL. APEX Study Meeting, July 27-28, 1998

Testing Li & Pb potentials V

- Heat capacity (C_p)



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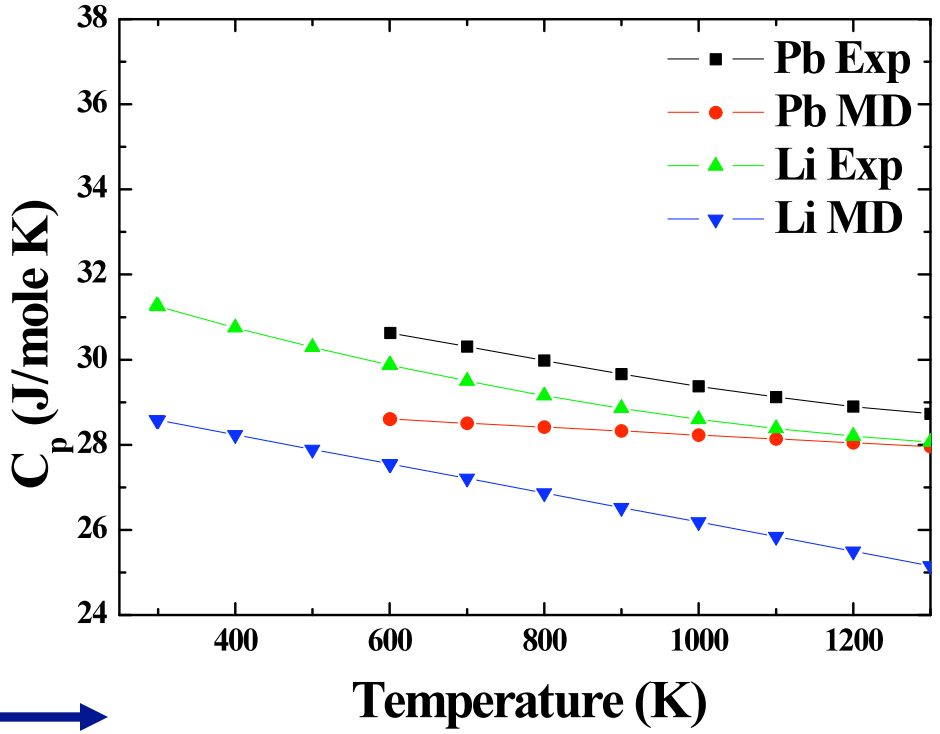

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Testing Li & Pb potentials VI

- Pressure

Experimentally, lithium presents a structural phase transition (from bcc to fcc lattice) at high pressures [9] at 7.5 GPa. **Will be our potential good enough to acount on that transformation?**

[9] Olinger B. and Shaner J. W. (1983) Science 219 107

Testing Li & Pb potentials VI

- Pressure

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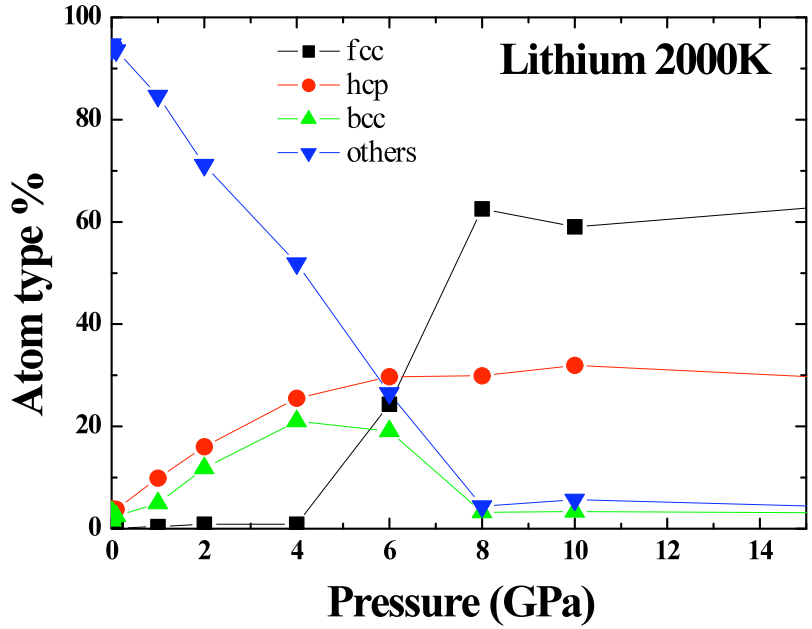
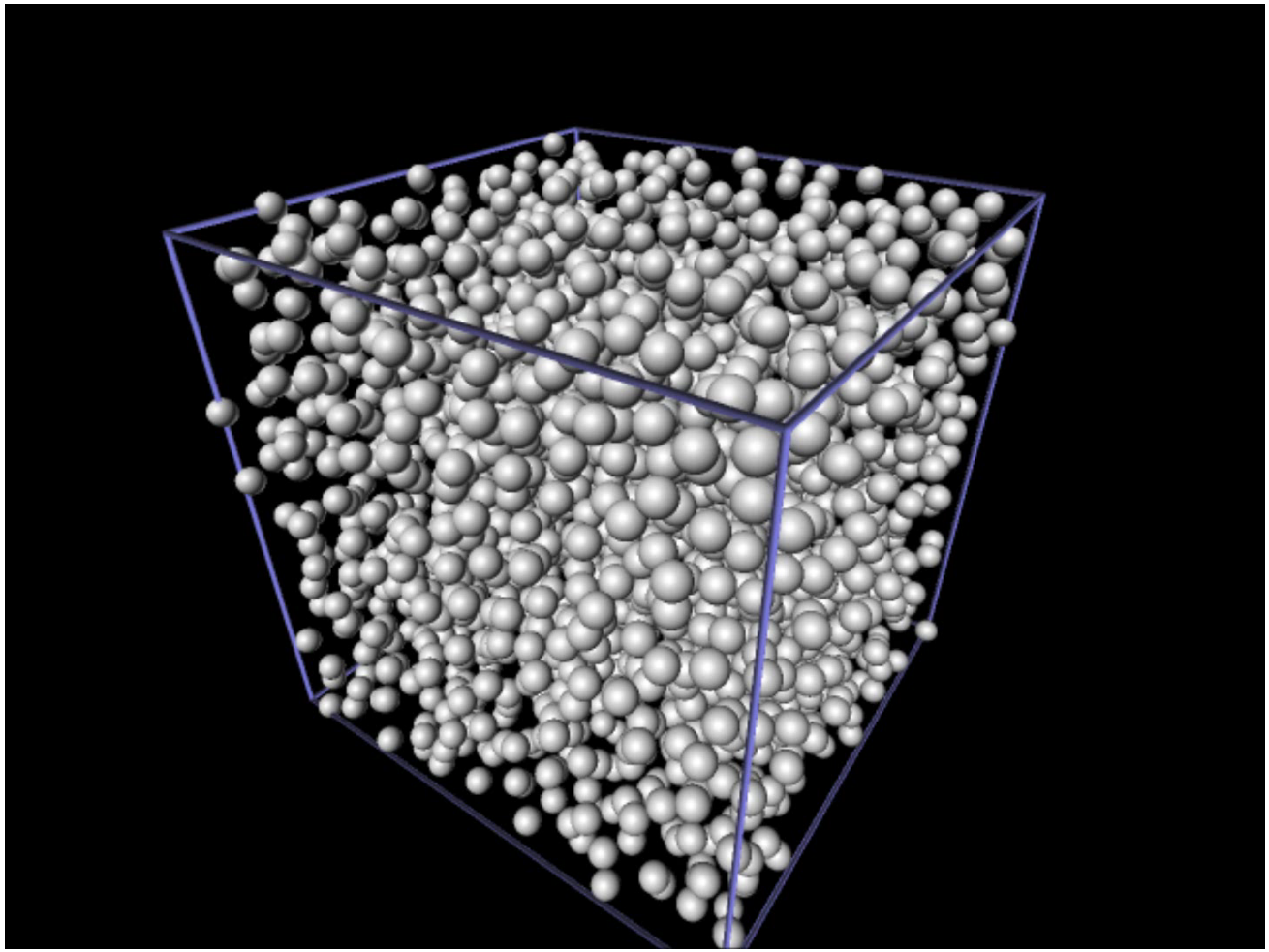


[9] Olinger B. and Shaner J. W. (1983) Science 219 107

Testing Li & Pb potentials VI

- Pressure

Lithium
MD Simulations
T= 1000K
Final Pressure
20 GPa



Testing Li & Pb potentials VII

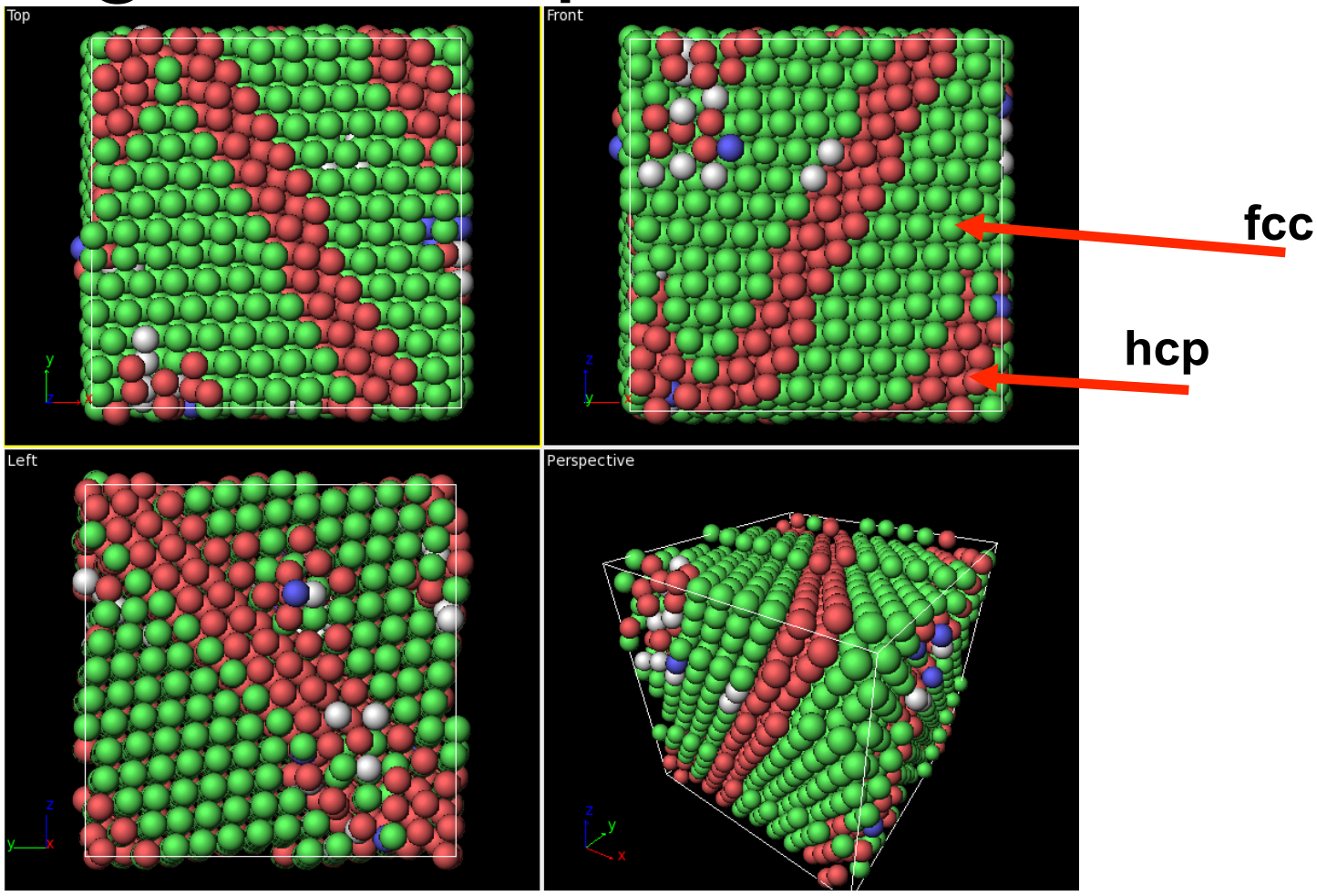
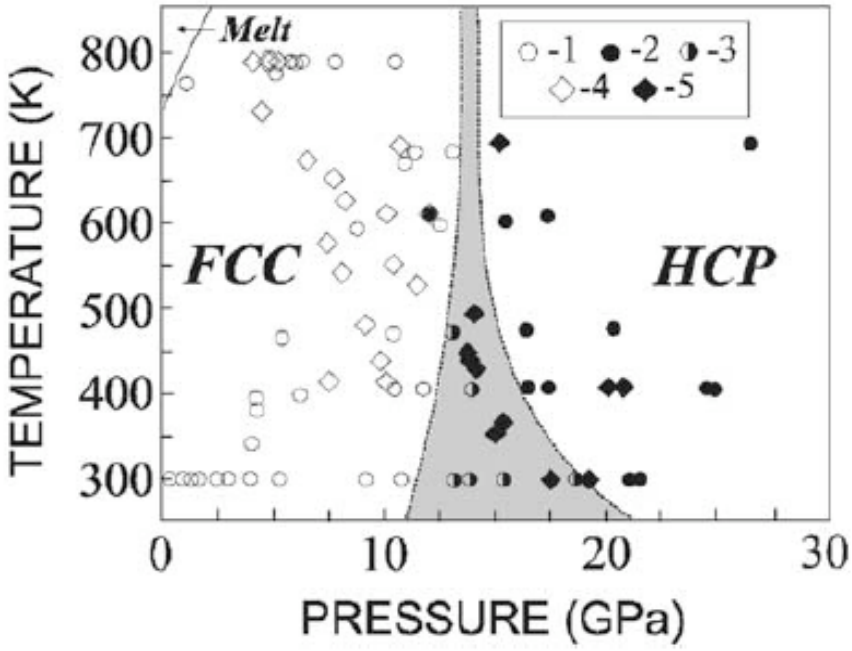


Figure 4. Lithium CNA analysis visualization at 2000K and P= 8Gpa. (N=2000 Atoms). Green spheres correspond to fcc atoms, red ones to hcp, blue to bcc and white to others.

Testing Li & Pb potentials VII

Pb crystallizes in the fcc structure under normal conditions. A **transition to the hcp** structure is observed **at 14 GPa** (Takahashi 1969). At about **110 GPa a further transition to the bcc** structure is observed (Mao 1990; Vanderborgh, 1990).

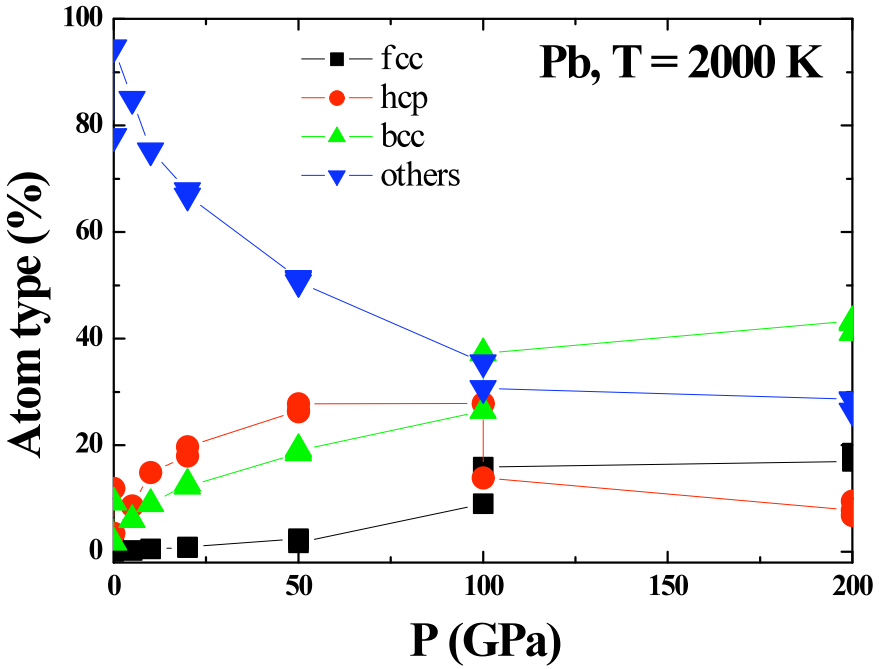
In both cases the volume reduction is very small and there is a large region of **phase coexistence**, consistent with a very small enthalpy difference between the phases over a large pressure interval.

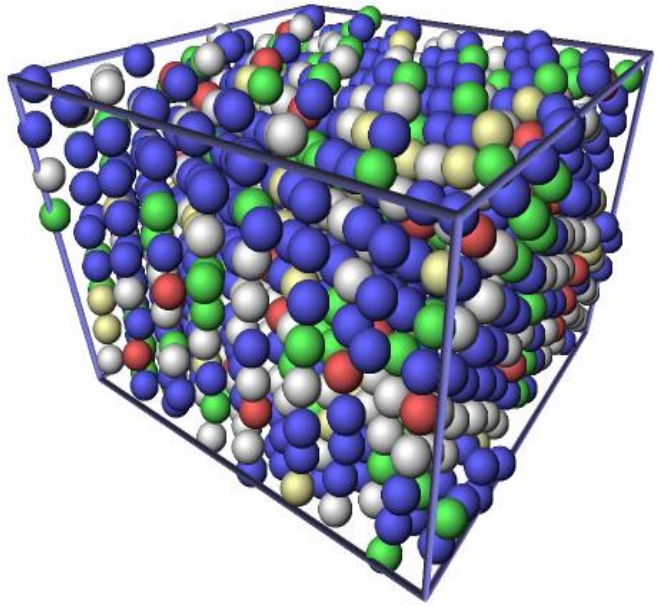


[10] A. Mujica *et al*. High-pressure phases of group-IV, III–V, and II–VI compounds. Reviews of Modern Physics, Vol. 75, 2003

Testing Li & Pb potentials VII

A **transition to the hcp** structure is observed **at 14 GPa**. At about **110 GPa a further transition to the bcc** structure is observed.
In both cases the volume reduction is very small and there is a large region of **phase coexistence**, consistent with a very small enthalpy difference between the phases over a large pressure interval [10].





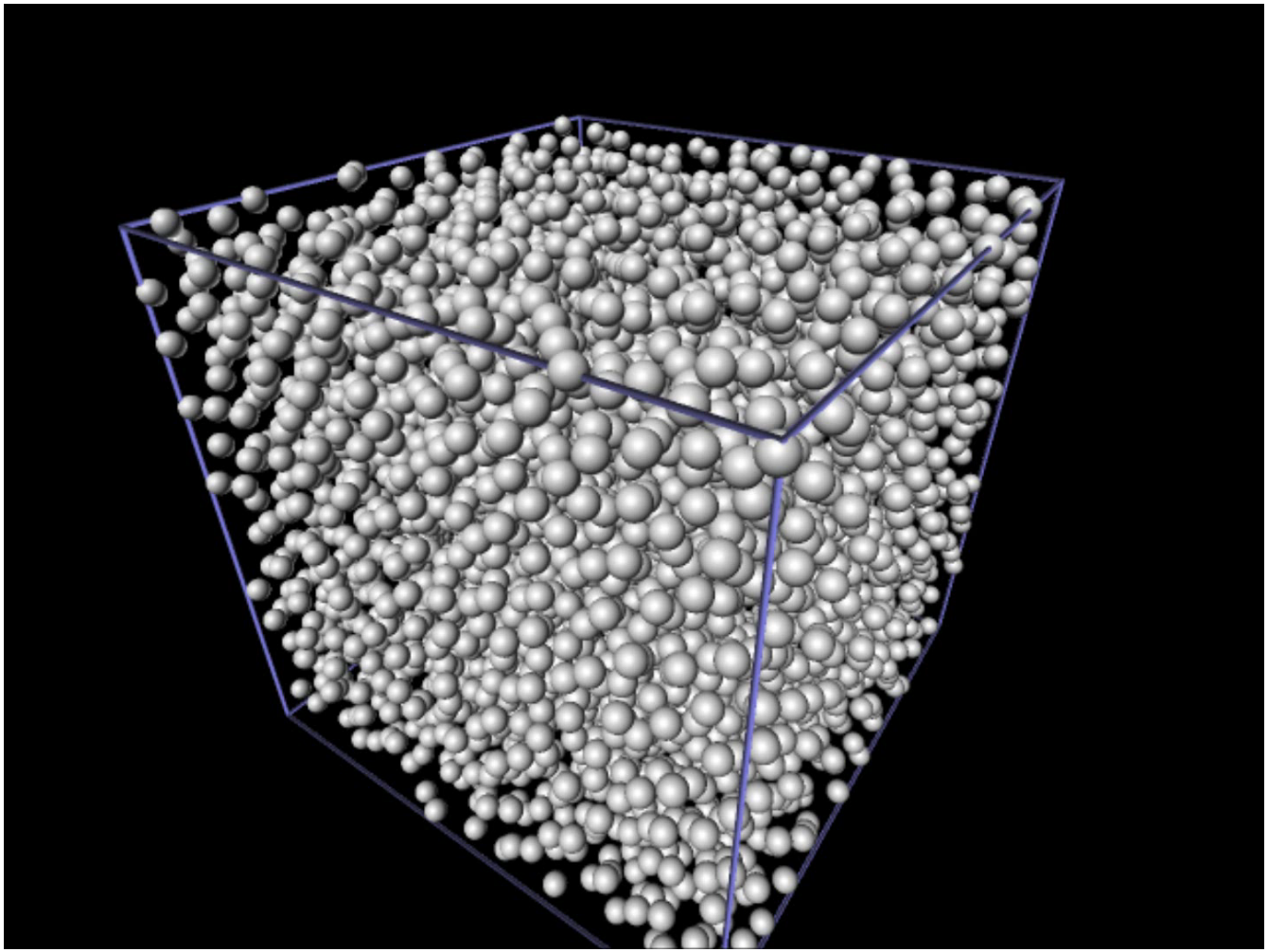
P=200 GPa T=2000 K. Blue = bcc type atoms, green = fcc, red = hcp white = others

[10] A. Mujica *et al*. High-pressure phases of group-IV, III–V, and II–VI compounds. Reviews of Modern Physics, Vol. 75, 2003

Testing Li & Pb potentials VII

- Pressure

Lead
MD Simulations
T= 1000K
Final Pressure
200 GPa



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Conclusions

- We trust in our EAM potentials to simulate **liquid** Pb and Li **in a wide range of temperatures** ***(and pressures)***

- **… And to create a new LiPb cross potential**

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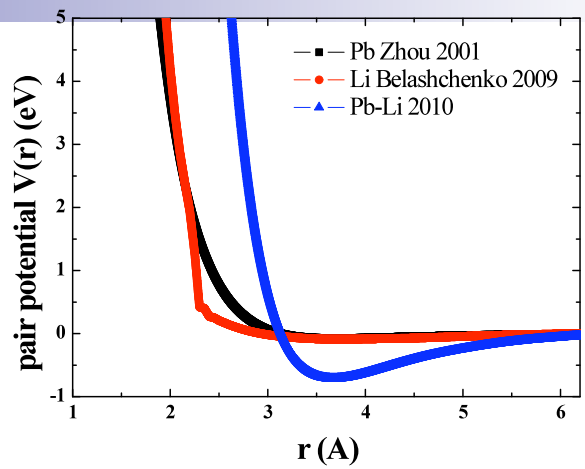
- **LiPb EAM/alloy/cd results**
- Future work

LiPb cross potential



- EAM/cd

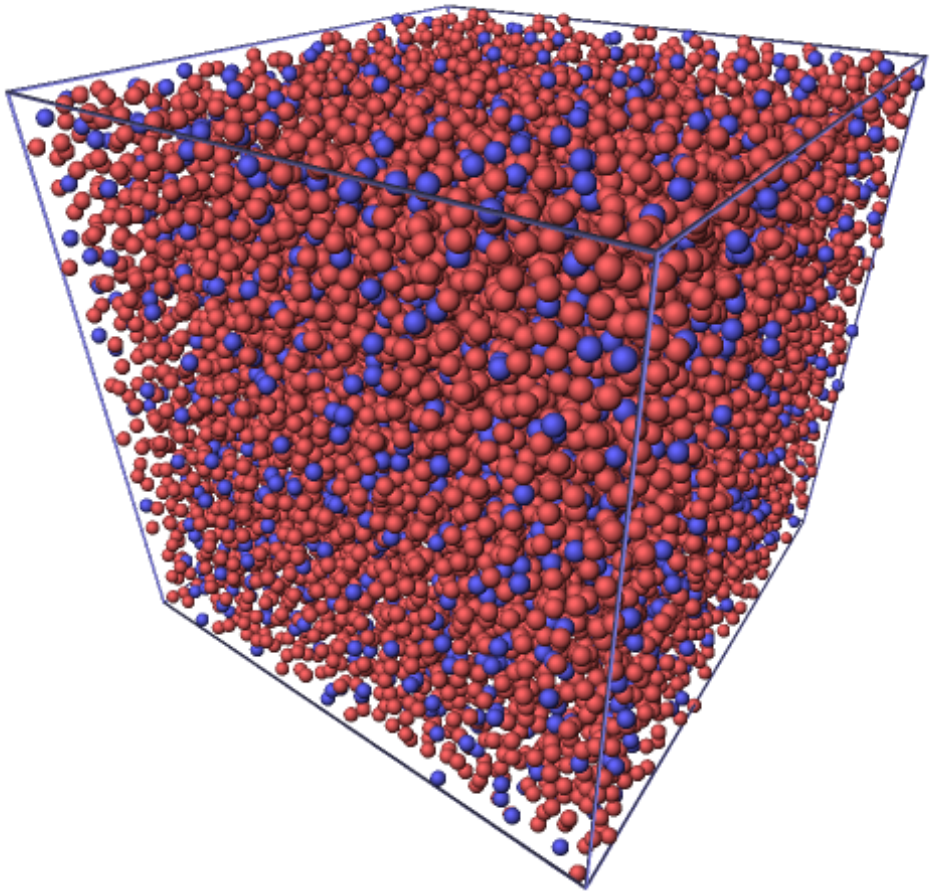
In an EAM model, for a binary alloy system with type a atoms and type-b atoms, there exist two kinds of electron density functions $\rho_a(r)$ **and** $\rho_b(r)$**,** two kinds of embedding energy functions $F_a(\rho)$ **and** $F_b(\rho)$**,** and three kinds of pair potential functions $\phi_{aa}(r)$**,** $\phi_{bb}(r)$**, and** $\phi_{ab}(r)$**.**

Usually the six functions $\rho_a(r)$, $\rho_b(r)$, $F_a(r)$, $F_b(r)$, $\phi_{aa}(r)$, and $\phi_{bb}(r)$ are assumed to be **transferable** from monatomic systems to alloy systems.

In our case we have made use of the **effective representation** [11] and develop a LiPb cross potential in the **EAM alloy composition dependent** framework [11].

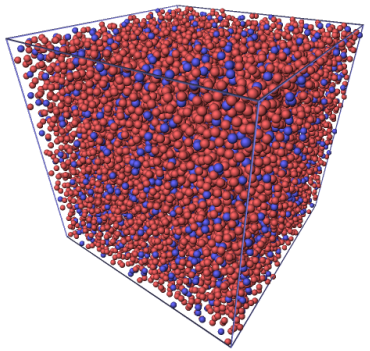
[11] A.Caro, D. A. Crowson, and M. Caro Classical Many-Body Potential for Concentrated Alloys and the Inversion of Order in Iron-Chromium Alloys. PRL 95, 075702 (2005)

LiPb preliminary results I

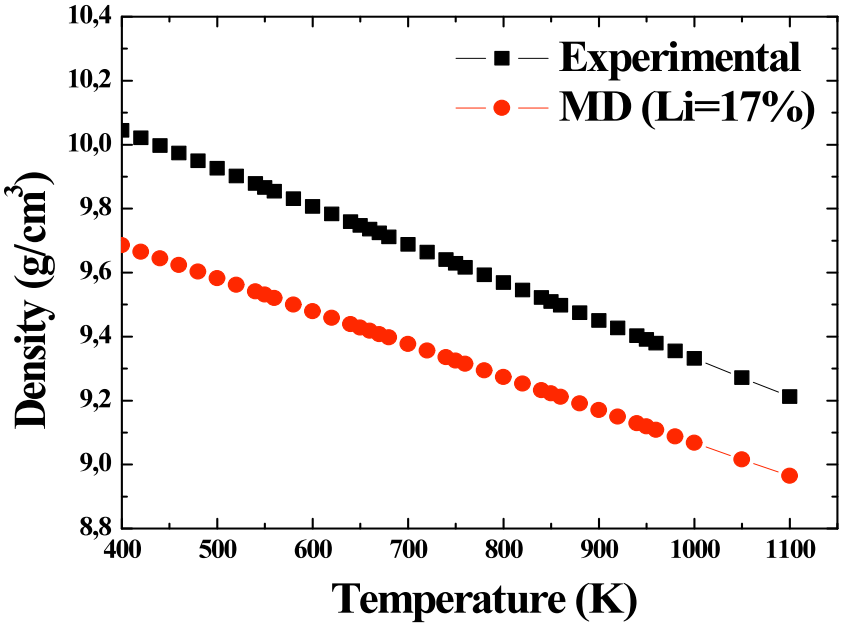


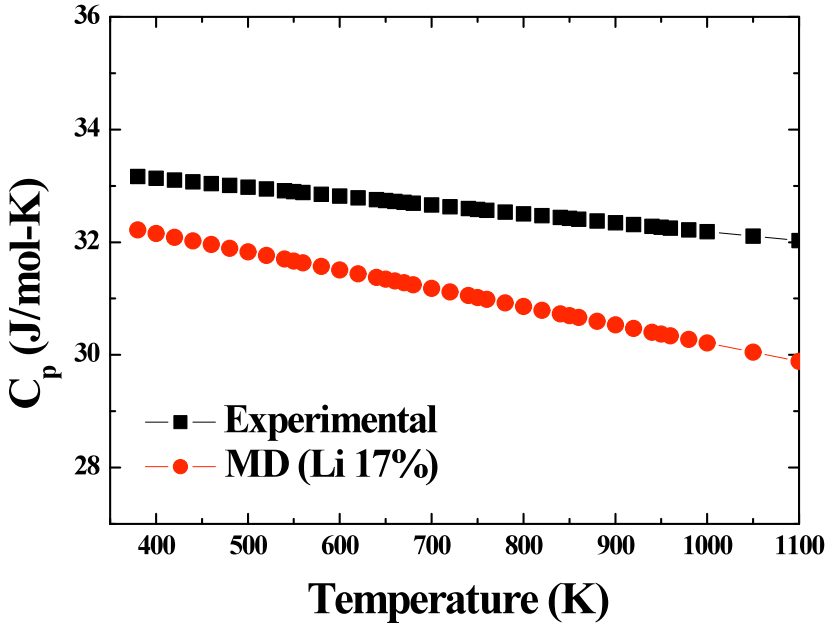
Eutectic LiPb (17%), T=1000K, N= 100000 atoms.

LiPb preliminary results I



- Eutectic $\rho(T)$ and C_p





[12] Database: E. Mas de les Vall *et al*. Lead-lithium eutectic material database for nuclear fusion technology. Journal of Nuclear Materials 376 (2008) 353-357.

LiPb preliminary results II

CMD
vs
ab initio [13]

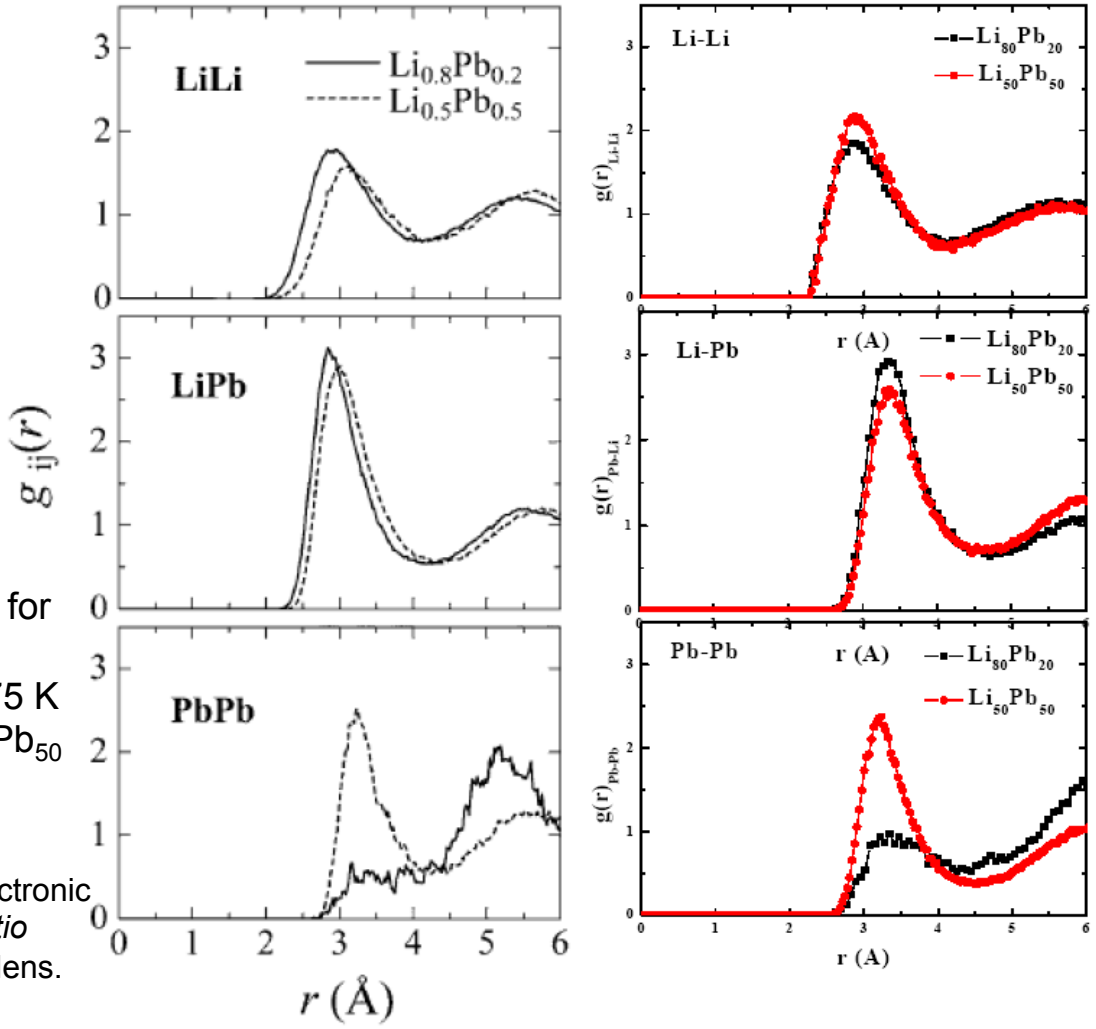


Figure 5. RDF $g_{LiLi}(r)$, $g_{LiPb}(r)$ and $g_{PbPb}(r)$ for the liquid $Li_{80}Pb_{20}$ (solid line - black) and $Li_{50}Pb_{50}$ (broken line - red) alloys. T= 1075 K and 805 K for the liquid $Li_{80}Pb_{20}$ and $Li_{50}Pb_{50}$ alloys, respectively [13].

[13] Senda et al. The ionic structure and the electronic states of liquid Li-Pb alloys obtained from *ab initio* molecular dynamics simulations. J. Phys.: Condens. Matter 12, 6101 (2000)

Structural properties

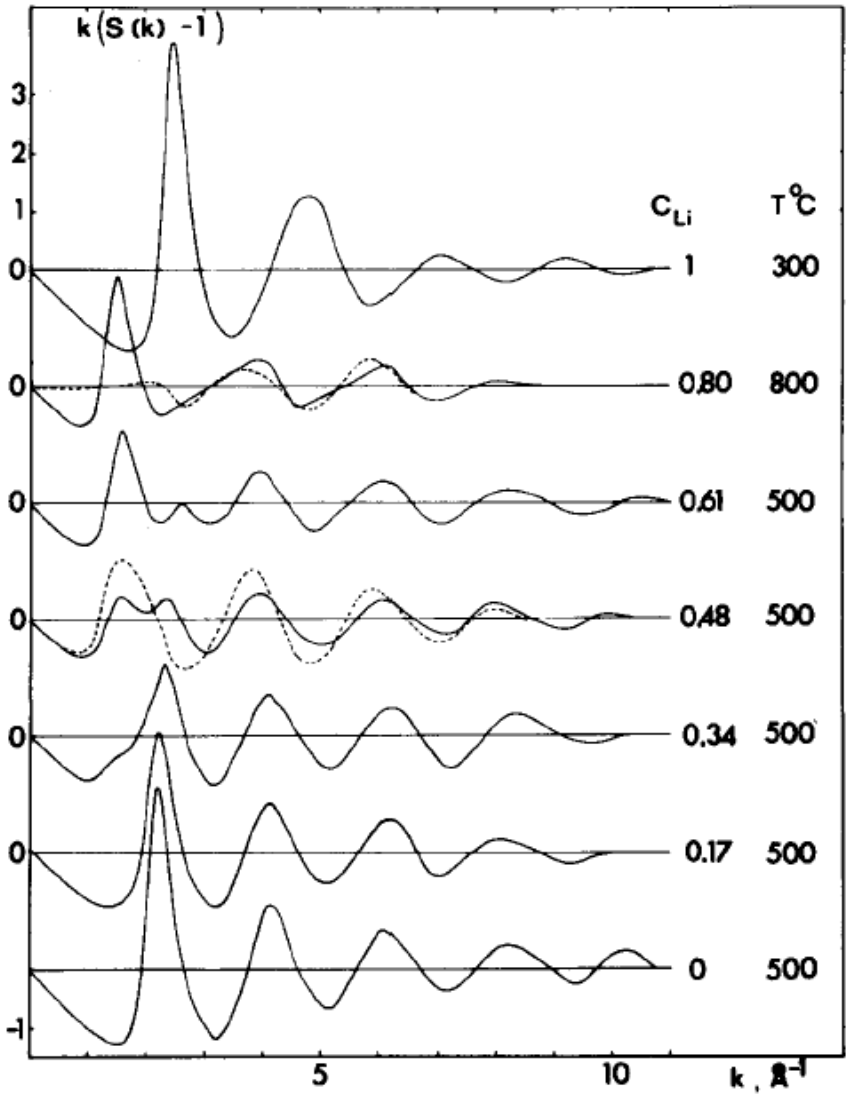
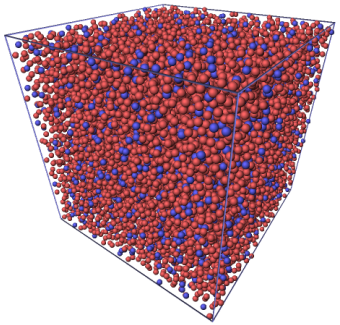
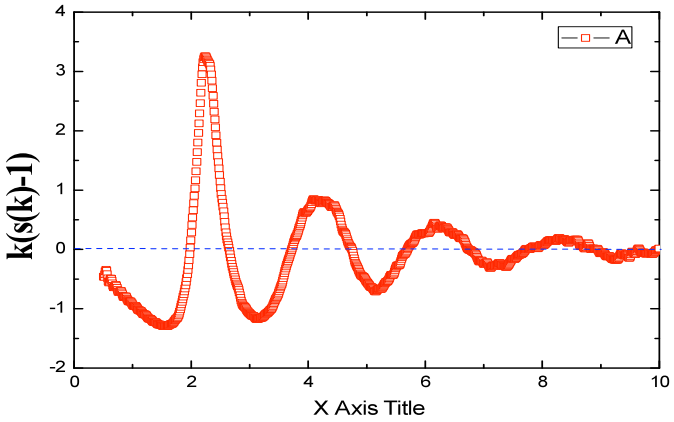


FIG. 4. $k(S(k)-1)$ curves of liquid ^{7}LiPb alloys, obtained by neutron diffraction. ------: 80 Li, theoretical curve for a random hard sphere mixture (rhs).[2] ------: 48 Li, "zero-alloy curve" calculated by separating a rhs $S_{NN}(k)$ contribution from the measured curve.



Li17 T = 800K



[14] H. Ruppersberg and H. Egger. The Journal of Chemical Physics, Vol. 63, No.1 0, 15 (1975)

Structural properties

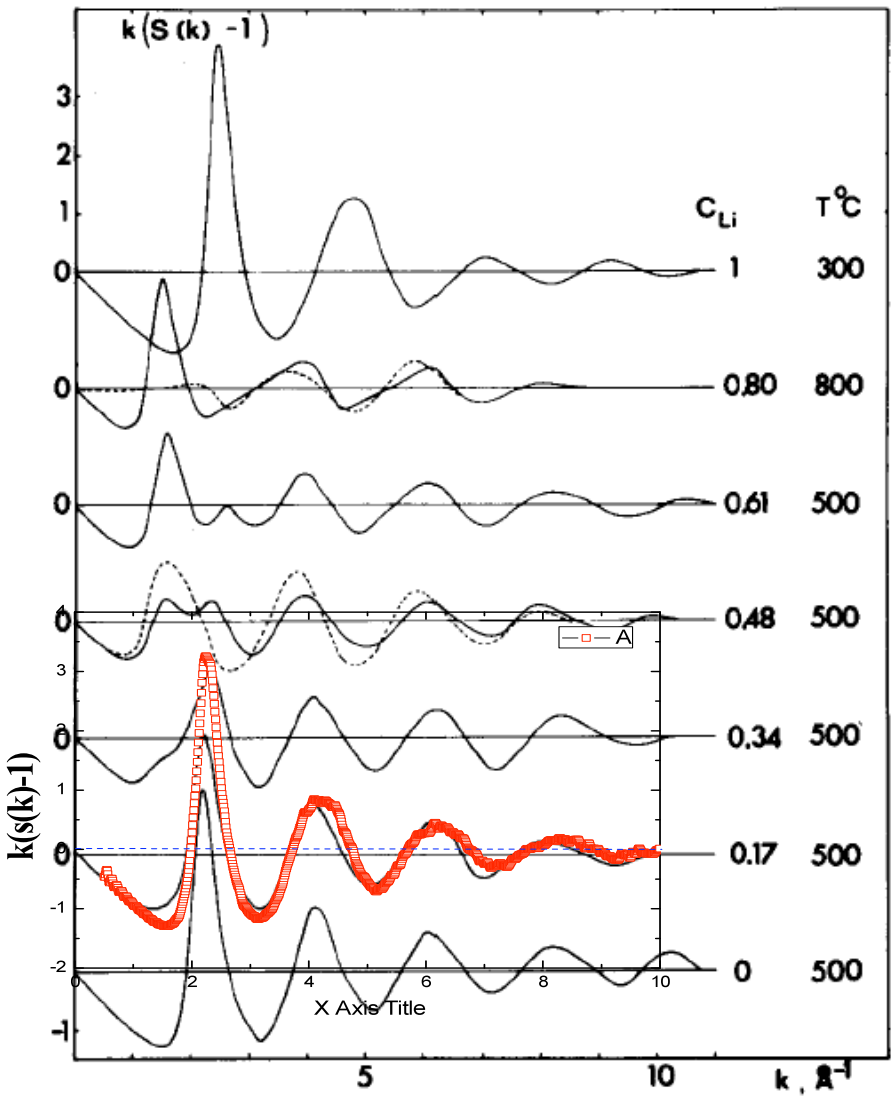
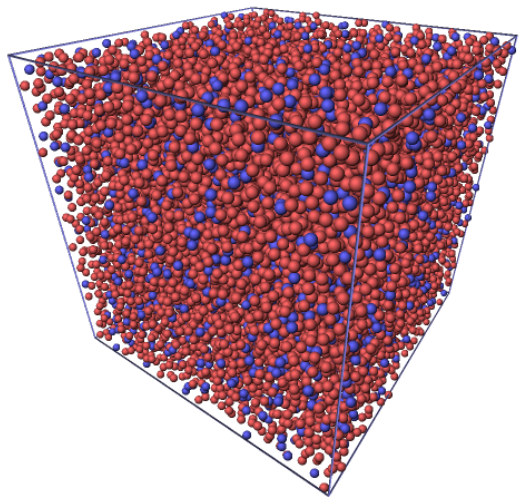


FIG. 4. $k(S(k)-1)$ curves of liquid ^{7}LiPb alloys, obtained by neutron diffraction. -------: 80 Li, theoretical curve for a random hard sphere mixture (rhs).[2] -------: 48 Li, "zero-alloy curve" calculated by separating a rhs $S_{NN}(k)$ contribution from the measured curve.

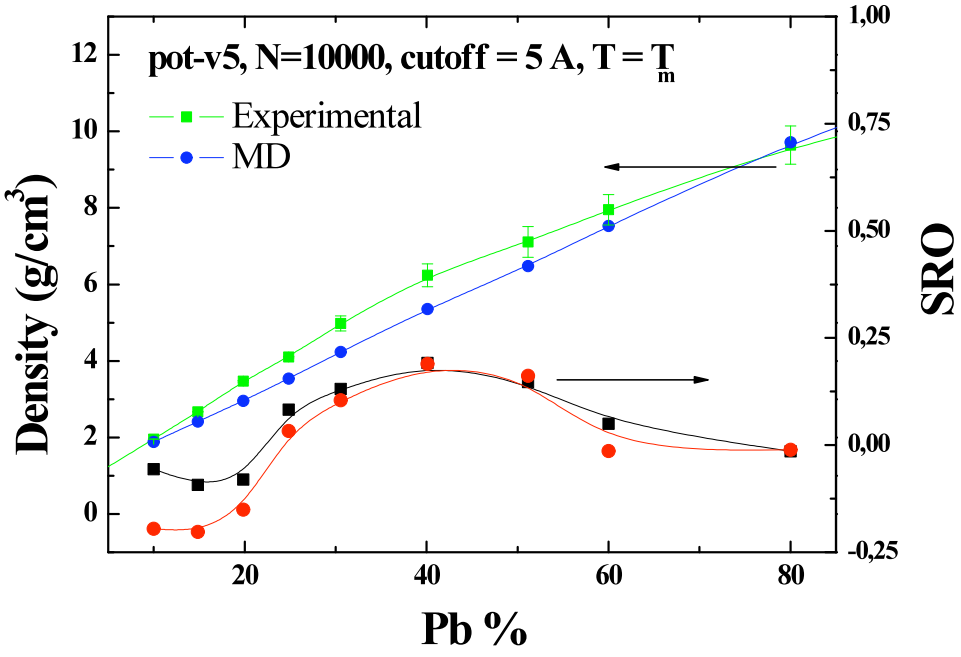
S(Q) $Li_{17}Pb_{83}$ OK



- Motivation
- MD, potentials and methods
- Results
- Conclusions
- LiPb EAM/alloy/cd results
- **Future work**

Future plans (LiPb)

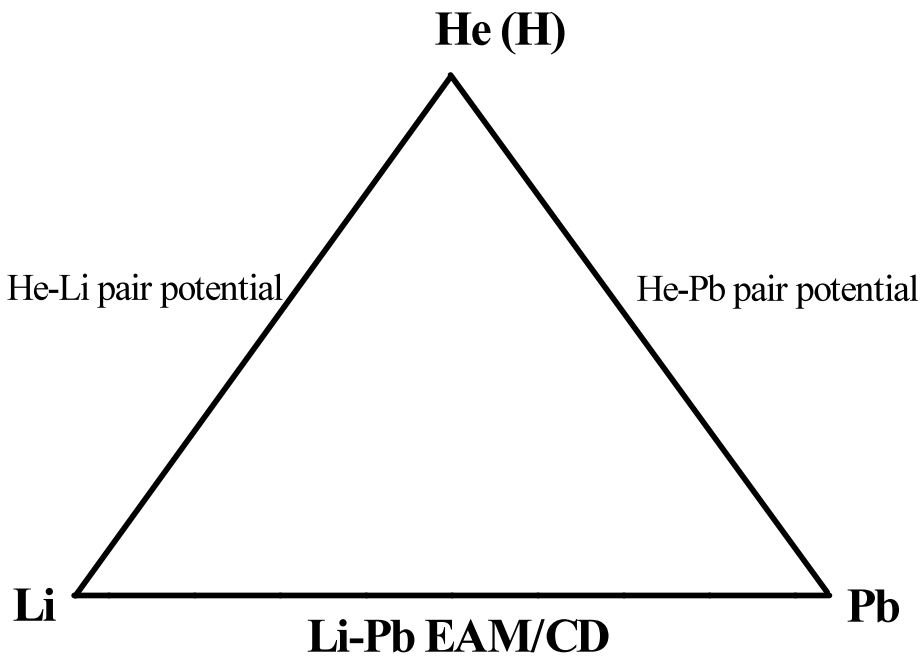
- Final tunning of LiPb cross potential.
- Determine eutectic point.
- Study SRO in liquid LiPb system.



SRO calculated from our MD data. Around eutectic composition SRO is 0.

Future plans (Li-Pb-He)

- He (and/or T) will be introduced in LiPb.
- He(T)-Pb and He(T)-Li potentials must be developed.



Schematic picture of the ternary potential for Li-Pb-He.

ACKNOWLEDGEMENTS

- This work is partially funded by the European CONSOLIDER Program.
- The work of the first author is part of their PhD Thesis and has been supported by the *Universidad Politécnica de Madrid* (Spain).

- We are grateful to Professor D. Belaschenko for providing us with his lithium potential.

Thank you for your attention