

Prédiction de propriétés volumétriques et thermodynamiques de solides organiques et minéraux des roches sédimentaires par modélisation moléculaire

Philippe Ungerer, Xavier Rozanska, Marianna Yiannourakou, Erich Wimmer
Materials Design, S.A.R.L., Montrouge, France

SFGP – Thermodynamique des phases solides, 8 décembre 2014

Materials Design Company Profile

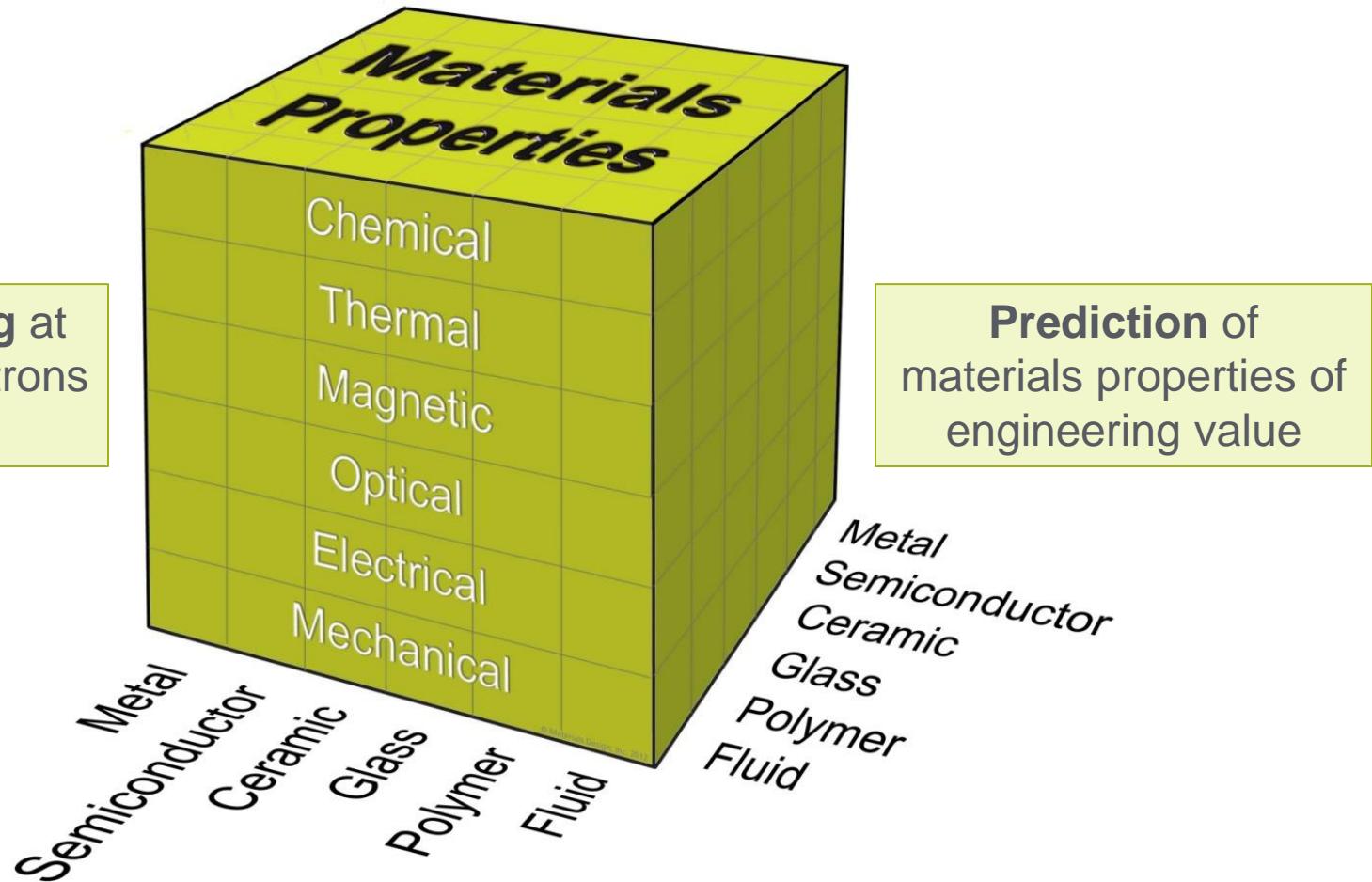
- Since 1998
- Activity: Creation and support of atomistic simulation software
- Product: **MedeA®** software, support and consulting services
- Global presence: USA (San Diego CA, Angel Fire NM), Europe (Paris, Stockholm); distributors in Japan, Korea, China, Taiwan, and India
- Over 400 customers in Industry, Universities, and Government Laboratories

- Energy
- Metals & alloys
- Chemicals
- Oil & Gas
- Electronics
- Automotive & aerospace
- Glass and ceramics
- Mining & drilling



Purpose of MedeA®

Understanding and Prediction



Plan

- Introduction : les solides dans l'environnement MedeA
 - Méthodes de simulation atomistiques:
 - Mécanique quantique : DFT (VASP), MOPAC
 - Mécanique statistique : UNCLE, PHONON, LAMMPS, GIBBS
 - Types d'application
 - Solides cristallins : métaux, semi-conducteurs, minéraux
 - Solides amorphes : organiques (polymères, kérrogènes...), inorganiques
 - Bases de données (exemple = Uranium carbides)
- Exemples d'application :
 - Stockage d'électricité : propriétés d'équilibre et de transport de Li₂O (coll. Toyota)
 - Pétrole et Gaz : propriétés et structure des kérrogènes et des charbons (coll. Total)
 - Minéraux argileux (stage S. Naseem-Khan, UPMC)
- Conclusions



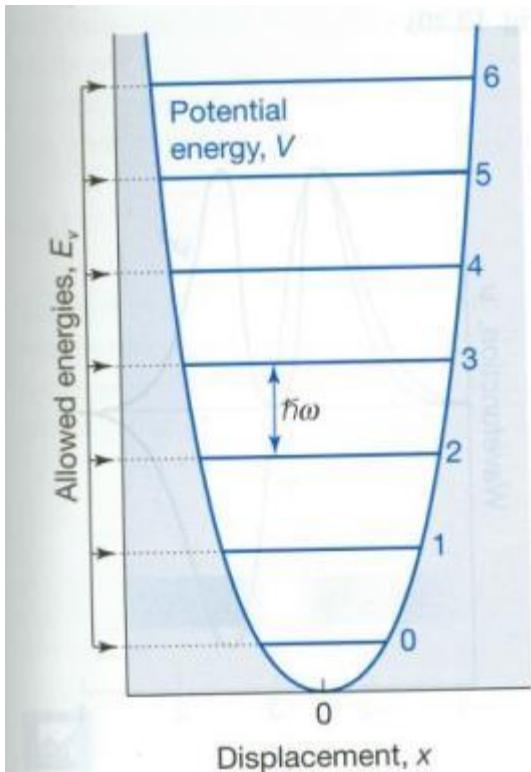
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INTRODUCTION



Quantization of vibrational energy

- Harmonic oscillator of mass m



12.17 The energy levels of a harmonic oscillator are evenly spaced with separation $\hbar\omega$, with $\omega = (k/m)^{1/2}$. Even in its lowest state, an oscillator has an energy greater than zero.

Instantaneous
potential energy

$$V(x) = \frac{1}{2} k x^2$$

Spring Constant

Characteristic
frequency

$$\nu = \frac{1}{2\pi} (k/m)^{1/2}$$

Average energy at
temperature T for
 N harmonic
oscillators of
identical Θ_ν

$$E_\nu(T) = N k_B \left(\frac{\Theta_\nu}{2} + \frac{\Theta_\nu}{e^{\Theta_\nu/T} - 1} \right)$$

where $\Theta_\nu = h\nu/k_B$ is the
characteristic vibrational temperature of the mode

References : Atkins, Physical chemistry, 7th ed. (2002);
Mc Quarrie, Statistical mechanics (2000)

Variation of vibrational energy with temperature for N harmonic oscillators

- Contribution to total energy :

$$E_{vib}(T) = N k_B \left(\frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T} - 1} \right)$$

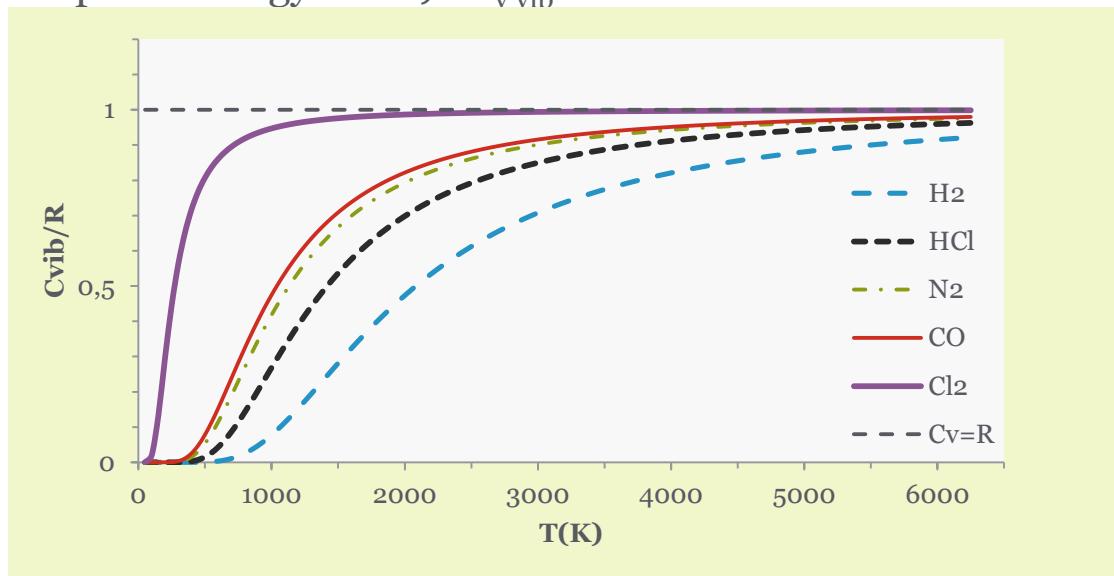
- Contribution to $C_{p\ id}$:

$$C_{vib}(T) = N k_B \left(\frac{\Theta_v}{T} \right)^2 \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2}$$

- If $T \gg \Theta_v$ $E_{vib}(T) \rightarrow N k_B T$ $C_{vib}(T) \rightarrow N k_B$ (classical approximation)
- If $T = \Theta_v$ $E_{vib}(T) = N k_B T \left(\frac{e+1}{2(e-1)} \right) \approx 1,082 N k_B T$ $C_{vib}(T) = \frac{e}{(e-1)^2} N k_B \approx 0,921 N k_B$
- If $T=0\ K$ $E_v = N k_B \frac{\Theta_v}{2}$ (Zero point energy level) $C_{vib} = 0$

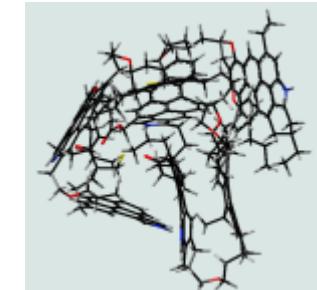
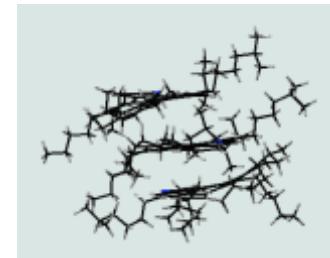
- Ex. diatomic molecules

$$R = N_A k_B = 8,314 \text{ J/mol/K}$$



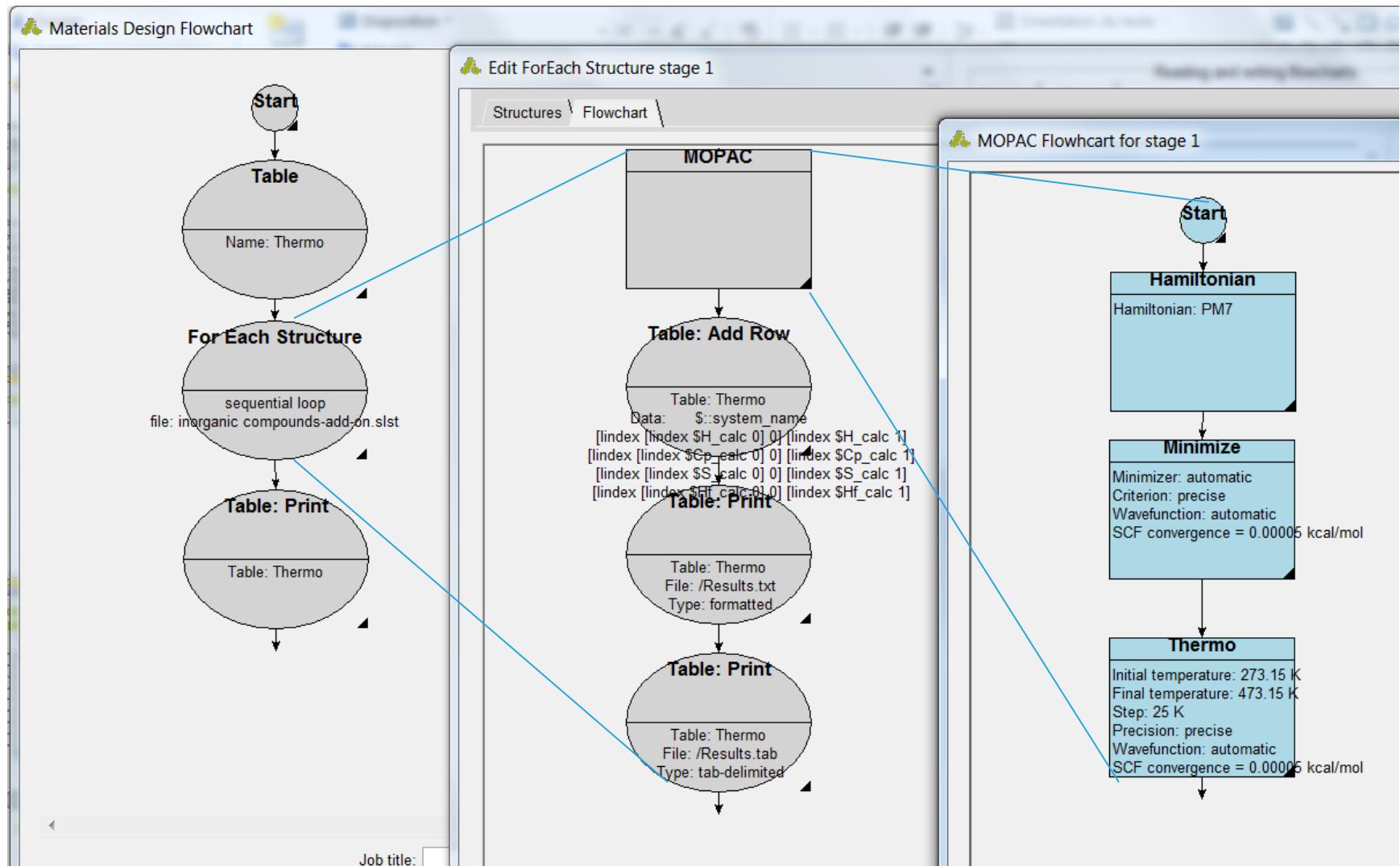
Ideal thermodynamic properties of MedeA-MOPAC (molecular quantum chemistry + optimization + vibrational analysis)

- Accuracy
 - Std Heats of formation :
 - Organics : 2.5 %
 - Inorganics : 1-3 times larger deviations
 - Heat capacity (273-700K):
 - Organic molecules : 3%
 - Inorganic molecules : 1-3 times larger uncertainty
 - Expected uncertainty on ΔG_f° : 15-30 kJ/mol in the range 300-1000 K
(Rozanska et al., J. Chem. Eng Data, 2014)
- Coverage and efficiency:
 - Organic and organo-metallic systems
 - Applicable to molecular aggregates (non-covalent)
 - CPU time per cycle $\sim n^{2,6}$
 - Small molecules (up to n=35 atoms ie C11) : seconds
 - Medium size molecules (C10-C30) : minutes
 - Heavy molecules (C30-C100) : hours
 - Macromolecules (C100-C250) : days
 - Practical limitation :
 - 600 atoms on a laptop,
 - more on parallel computers



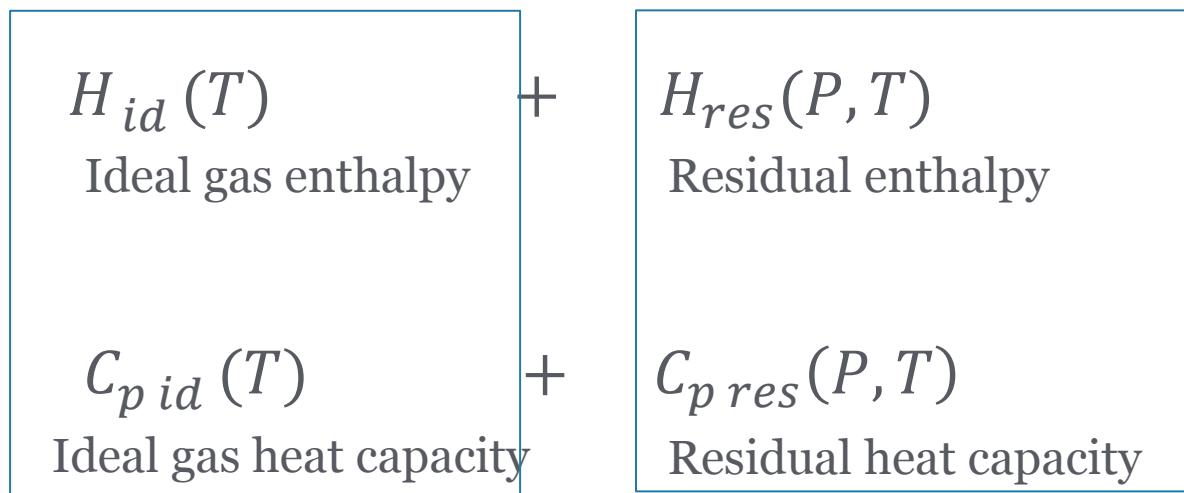
Ideal thermodynamic properties in MedeA-MOPAC

Flowchart for several compounds or conformers



Property prediction for organic macromolecules by combined use of Quantum chemistry and classical Molecular dynamics

- $H(P, T) =$
Total enthalpy
- $C_p(P, T) =$
Total heat capacity



From Quantum
Mechanics (MOPAC)
on isolated molecule
or fragments



From Molecular
Dynamics (LAMMPS)
with pcff + on a
condensed phase (8- 32
molecules)

Use of crystal structure databases in MedeA – example of Uranium Carbides

Materials Design: InfoMaticA -- Search

File Edit Options MPM Pauling

| ID | completeness | space group | sum |
|-------------|--------------|-------------|-----------------------|
| ICSD.44142 | Complete | R3-MH | C1 B2 U1 |
| ICSD.20743 | Complete | P121/N1 | C3 H6 N2 O7 Se1 U1 |
| ICSD.109752 | Complete | C12/C1 | C2 Cs2 O10 Se1 U1 |
| ICSD.27053 | Complete | | C1 O5 U1 |
| ICSD.26476 | Complete | | C1 U1 |
| ICSD.77560 | Complete | | C1 U1 |
| ICSD.60822 | Complete | | C4 Cr4 U1 |
| ICSD.26477 | Complete | | C3 U2 |
| ICSD.77561 | Complete | | C3 U2 |
| ICSD.26478 | Complete | | C2 U1 |
| ICSD.109207 | Complete | | C1 B1 U1 |
| ICSD.240742 | Complete | | C4 H5 Na1 O15 U2 |
| ICSD.250382 | Complete | | C5 H6 K3 N1 O13 S1 U1 |
| ICSD.151876 | Complete | I | C3 Cs4 O11 U1 |
| ICSD.87760 | Complete | | C1 O5 U1 |
| ICSD.109210 | Complete | I4-3D | C3 U2 |
| ICSD.65202 | Complete | P4/MBM | C8 Re3 U5 |
| ICSD.280581 | Complete | P3-C1 | C3 Na4 O11 U1 |
| ICSD.23742 | Complete | PNMA | C2 U1 V1 |

Search Criteria | Detailed Info

Require that []
 Require that []
 Require that []
 Require that []

try [] Coords []
 any number [] any number []
 delete []

Displaying 247 of 247 hits

U₂C₃

UC

MedeA®-InfoMaticA

name systematic

- Uranium boride carbide (1/2/1) - HT
- Melanatediamide selenitouranyl
- Dicesium selenato(VI)oxalatodioxouranate
- Uranium(VI) carbonate dioxide
- Uranium carbide
- Uranium carbide (1/1)

(C) gra + UC₂ ht2

Temperature, °C

at. %

UC₂ ht2

UC

UC₂ ht

(C) gra + U₂C₃ ht

U₂C₃ ht

L

(U) ht1

(U) ht2

(U) rt

1120

773

660

660

1520

1795

1825

2050

2435

2540

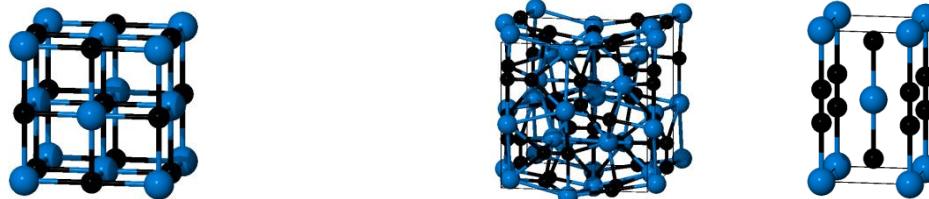
2490

1773

C

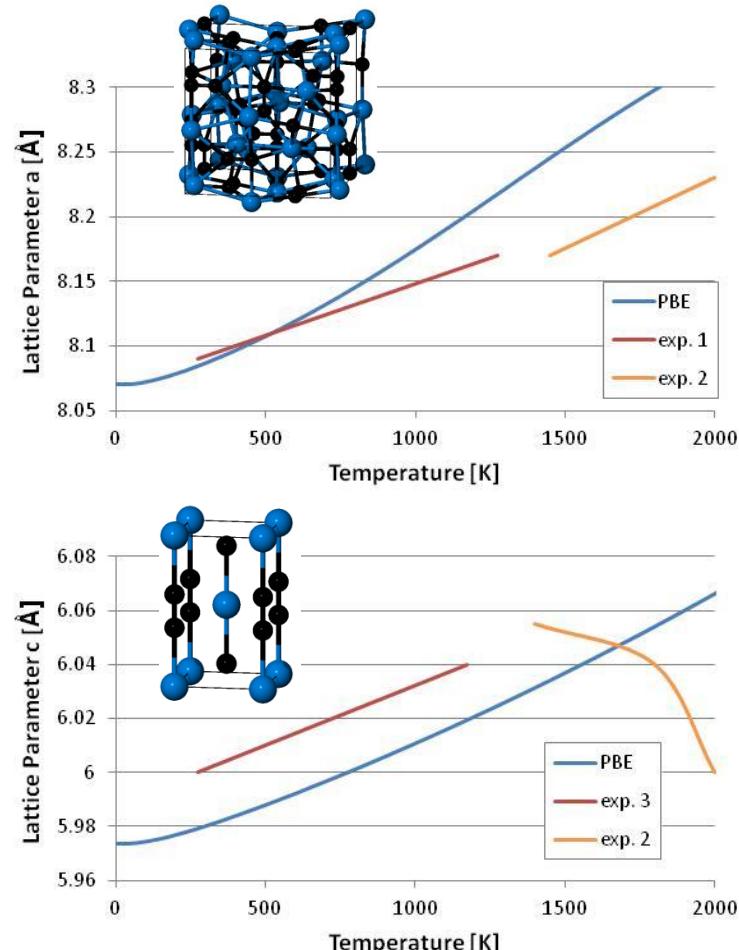
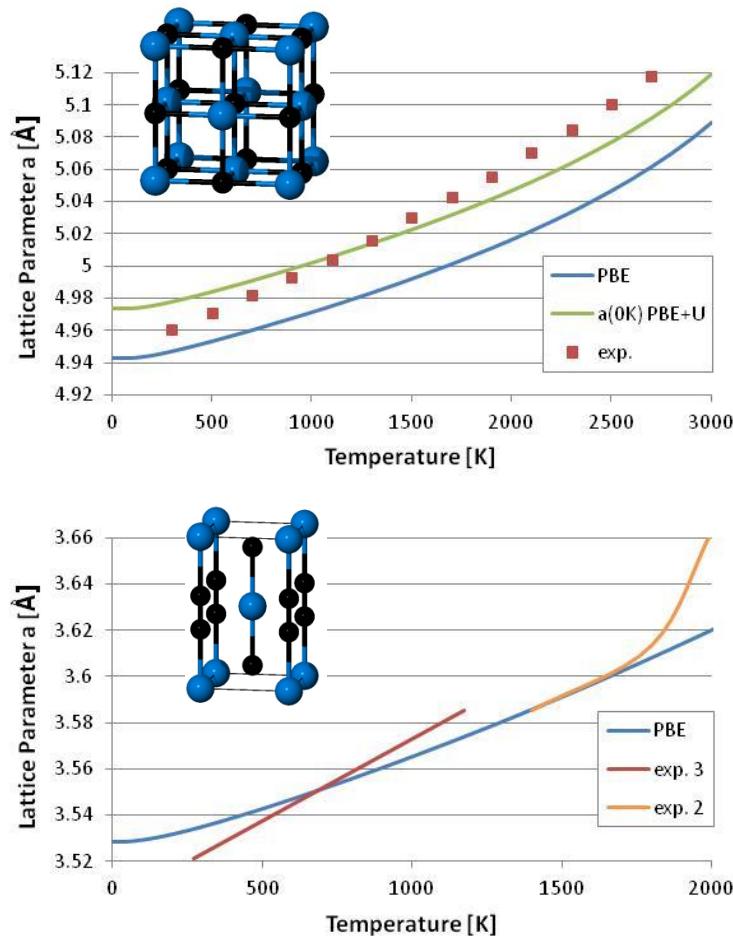
U

Structure and elastic properties of uranium carbides from quantum DFT with periodic boundary conditions (MedeA- VASP)



| Compound | UC | | | | U_2C_3 | α - UC_2 | |
|-----------------------|----------------|---------------------------|--------------------------|-------------------------|---------------|-------------------|---------------|
| Property | a | c_{11} | c_{12} | c_{44} | a | a | c |
| Units | Å | GPa | GPa | GPa | Å | Å | Å |
| Experiment References | 4.9598 [33] | 315-344 [45,34,5 5] | 77-105 [45,34,5 5] | 61-65 [45,34,5 5] | 8.089 [43] | 3.519 [42] | 5.979 [42] |
| LDA | 4.8551 | 331 | 148 | 3 | 7.9140 | 3.4503 | 5.886 |
| GGA | 4.9359 | 275 | 139 | 16 | 8.0479 | 3.5176 | 5.9578 |
| GGA LS | 4.9296 | 252 | 117 | 12 | 8.0627 | 3.5300 | 5.9763 |
| LDA+U 3eV | 4.8991 | 348 | 156 | 46 | 8.1693 | 3.5153 | 6.0330 |
| LDA+U 4eV | 4.9104 | 333 | 163 | 48 | | | |
| GGA+U 3eV | 4.9736 | 308 | 140 | 68 | | | |
| GGA+U 4eV | 4.9807 | 304 | 123 | 73 | | | |
| HSE06 | 4.9894 | 322 | 170 | 80 | | | |
| HSE06 LS | 4.9847 | | | | | | |

Thermal expansion of uranium carbides - Quantum DFT vs experiment comparison



R. Méndez-Peña and R. E. Taylor, J. Am. Ceram. Soc. **47**, 101 (1964), taken from C. B. Basak, Comp. Mat Sci. **40**, 562 (2007)
 R. S Street and M. H. Rand, UKAEA report AERE-M1327 (1963), taken from Ref. 78

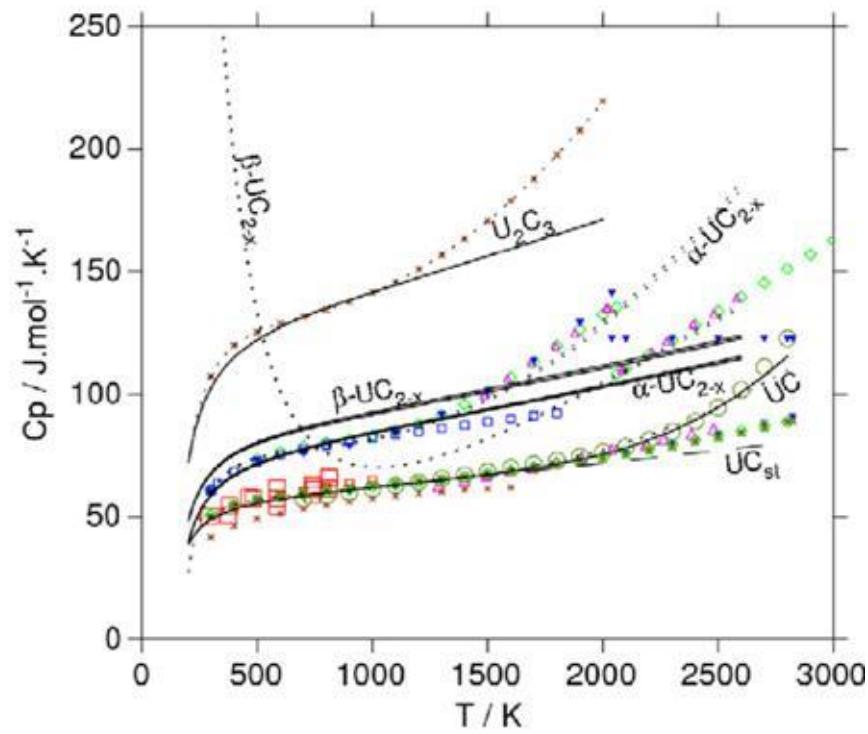
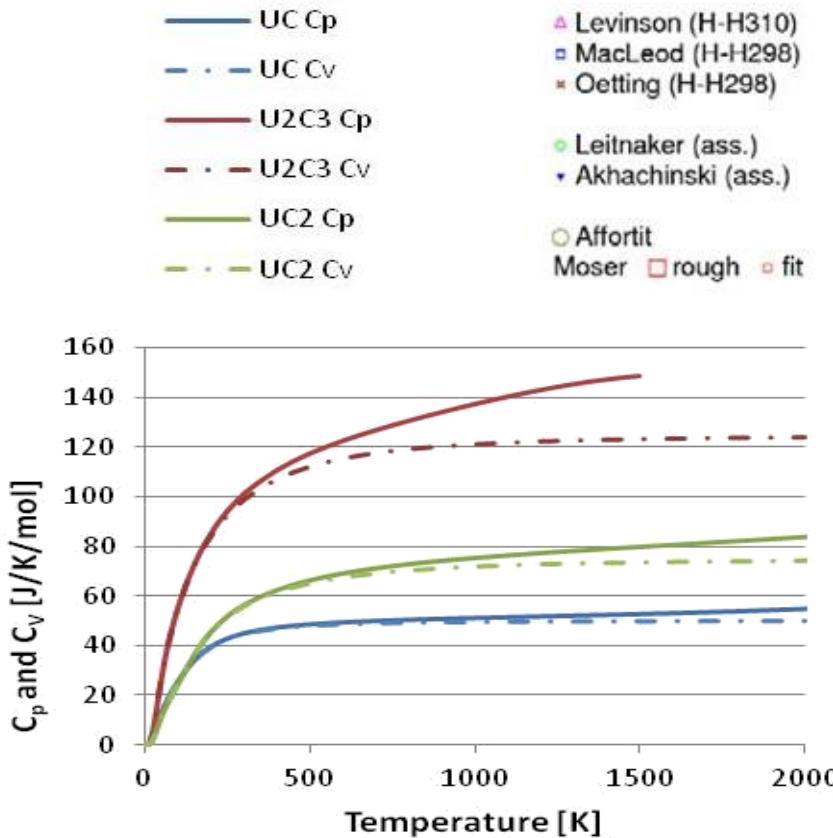
A. L. Bowman, G. P. Arnold, W. G. Witteman, and T. C. Wallace, J. Nuc. Mat. **19**, 111 (1966)

I. F. Ferguson, R.S. Street, and T. N. Waters, UKAEA report AERE-M819 (1961) , taken from Ref. 78



Heat capacities of uranium carbides

DFT vs Experiment comparison



2

Applications

Lithium Oxide for electricity storage applications



Thermal expansion, diffusion and melting of Li₂O using a compact forcefield derived from *ab initio* molecular dynamics

Ryoji Asahi¹, Clive M. Freeman², Paul Saxe²
and Erich Wimmer²

¹ Toyota Central Research and Development Laboratories, Inc., Nagakute, Aichi,
480-1192 Japan

² Materials Design, Inc., Angel Fire, NM 87710, USA

General motivation

Diffusion of lithium ions in oxides and the thermo-mechanical properties of these materials are currently of major interest, especially for batteries but also in other energy-related areas such as nuclear fusion. In the quest for improved electrochemical performance, longer lifetimes and improved safety, the atomic-scale understanding and prediction of materials properties plays

.....



Structure of Li₂O from Crystal databases in MedeA

Materials Design: InfoMaticA -- Search

File Edit Options MPM Pauling

| ID | completeness | space group | sum | structural | name systematic |
|----------------------|--------------|-------------|--------|------------|----------------------------------|
| ICSD.173180 | Complete | FM3-M | Li2 O1 | Li2 O1 | Lithium oxide |
| ICSD.173193 | Complete | FM3-M | Li2 O1 | Li2 O1 | Lithium oxide |
| ICSD.642219 | Complete | FM3-M | Li2 O1 | Li2 O1 | Lithium oxide |
| ICSD.22402 | Complete | FM3-M | Li2 O1 | Li2 O1 | Lithium oxide |
| ICSD.54368 | Complete | FM3-M | Li2 O1 | Li2 O1 | Dilithium oxide |
| ICSD.57411 | Complete | FM3-M | Li2 O1 | Li2 O1 | Dilithium oxide |
| ICSD.60431 | Complete | FM3-M | Li2 O1 | Li2 O1 | Lithium oxide |
| ICSD.108886 | Complete | R3-MH | Li2 O1 | Li2 O1 | Dilithium oxide |
| ICSD.173206 | Complete | FM3-M | Li2 O1 | Li2 O1 | Lithium oxide |
| NCD_Inorganic_035826 | Unknown | | Li2 O | Li2 O | Lithium oxide (2 ⁴ 1) |
| NCD_Inorganic_024799 | Unknown | Fm3m | Li2 O | Li2 O | Lithium oxide (2 ⁴ 1) |
| Pauling.458322 | Complete | Fm-3m | Li2O | Li2O | |
| Pauling.530333 | Complete | Fm-3m | Li2O | Li2O | |
| Pauling.530334 | Complete | Fm-3m | Li2O | Li2O | |
| Pearson.458322 | Complete | Fm-3m | Li2O | Li2O | |
| Pearson.1704305 | Complete | Fm-3m | Li2O | Li2O | |
| Pearson.530333 | Complete | Fm-3m | Li2O | Li2O | |
| Pearson.1704449 | Complete | Fm-3m | Li2O | Li2O | |
| Pearson.308438 | Complete | Fm-3m | Li2O | Li2O | |
| Pearson.530334 | Complete | Fm-3m | Li2O | Li2O | |
| Pearson.1014709 | Complete | Pnma | Li2O | Li2O | |

Search Criteria: Detailed Information | Coordinates | Geometry | Coordination | Pair Correlation | Powder pattern

MedeA - [* (Li2 O)4 (Fm-3m) – Lithium oxide (ICSD #173180)_1]

File Edit Builders View Tools Job Control Forcefields Gibbs InfoMaticA Analysis

Lithium oxide

Symmetry

Spacegroup: **FM3-M** Z: 4.
SpGrp Number: Volume: 98.23
Pearson symbol: cF12 Calculated density:

Cell

a: 4.614±0. α: 90.±0.
b: 4.614±0. β: 90.±0.
c: 4.614±0. γ: 90.±0.

Reference

(1) David, W.I.F., Jones, M.O., Gregory, D.H., Jewell, C.M., Johnson, S.R., Walton, A. and Edwards, P.P., A mechanism for non-stoichiometry in the lithium amide/lithium imide hydrogen storage reaction, *Journal of the American Chemical Society* (6) 129, 1594 - 1601 (2007).

Mobility of O in Li_2O from molecular dynamics using a forcefield parameterized on Tf and ab initio MD results

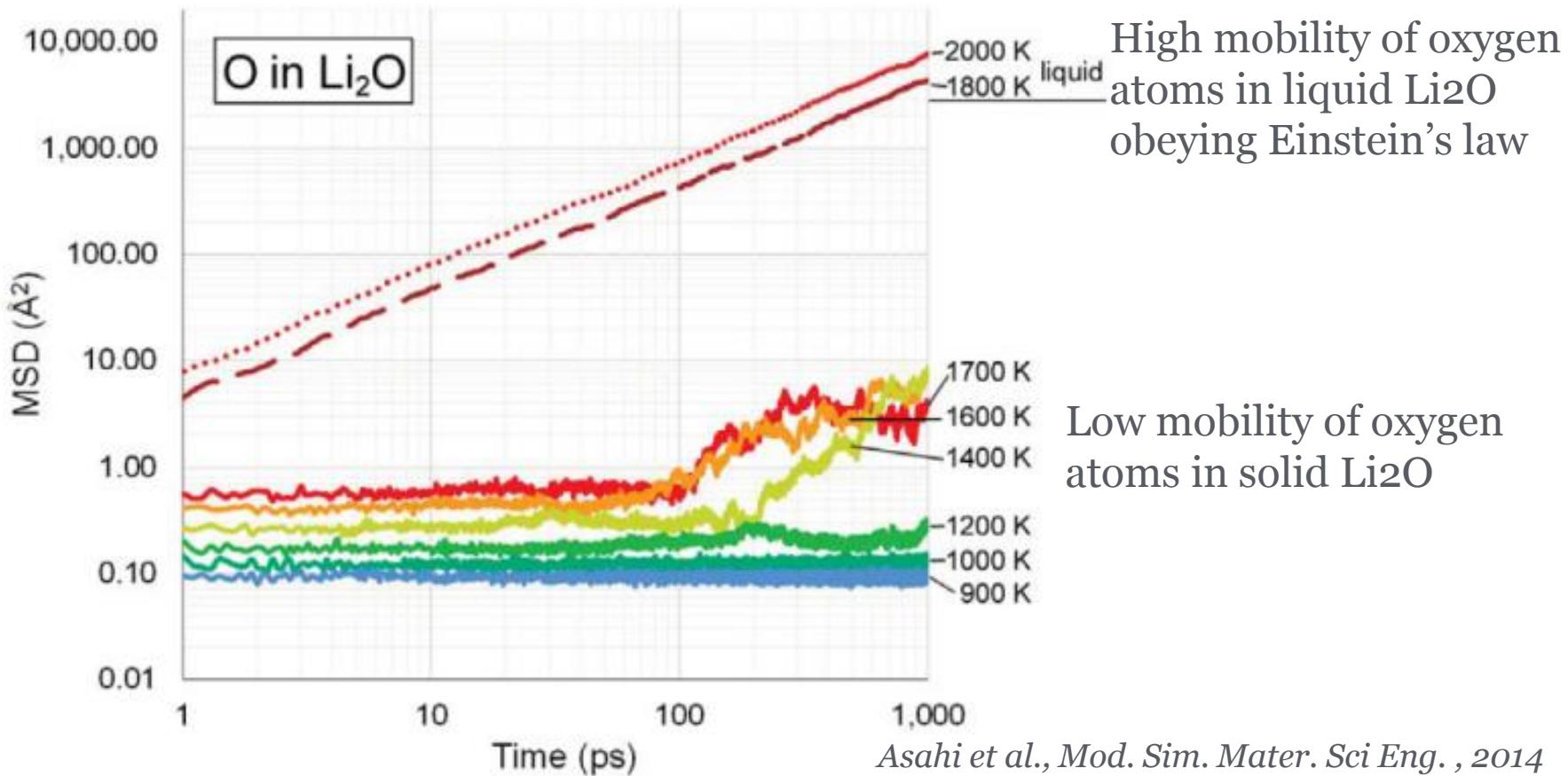
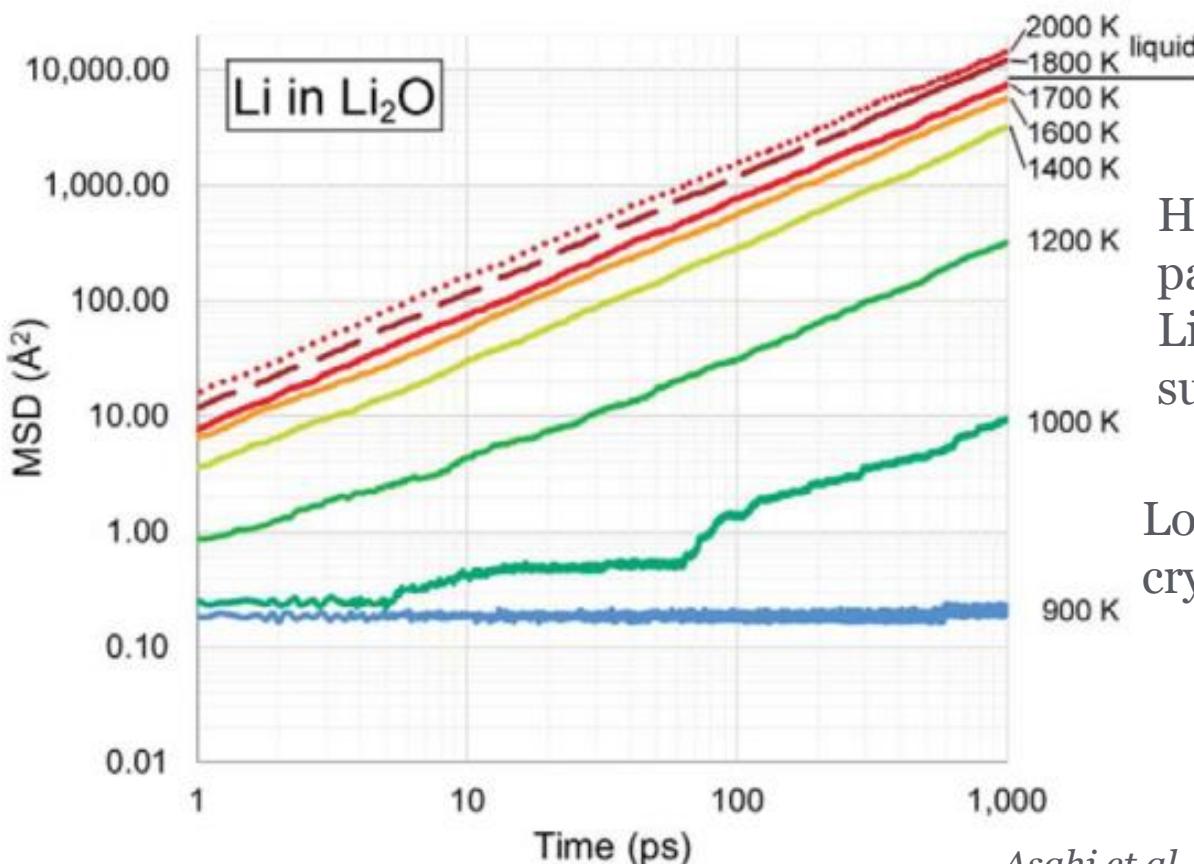


Figure 11. Computed mean square displacement (MSD) of oxygen ions in Li_2O as a function of temperature. Note the lack of mobility up to 1700 K.

Diffusivity of Li in Li_2O from classical molecular dynamics



Asahi et al., Mod. Sim. Mater. Sci Eng. , 2014

Figure 10. Computed mean square displacement (MSD) of lithium ions in Li_2O as a function of temperature. Note the onset of diffusion between 900 and 1000 K and the gradual increase in mobility towards the value of liquid Li_2O .

High mobility of Li atoms in liquid Li_2O ($T > 1700 \text{ K}$)

High mobility of Li atoms in partly disordered crystalline Li_2O ($T = 1200-1700 \text{ K}$) ie superionicity

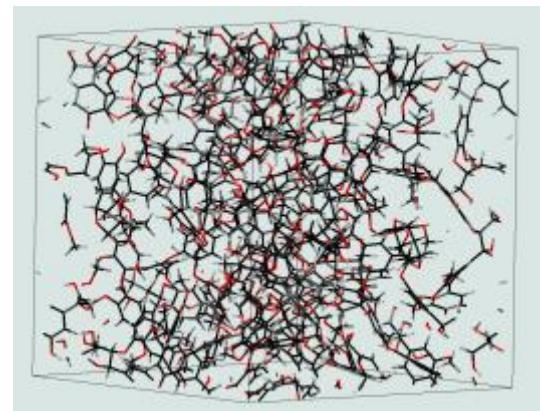
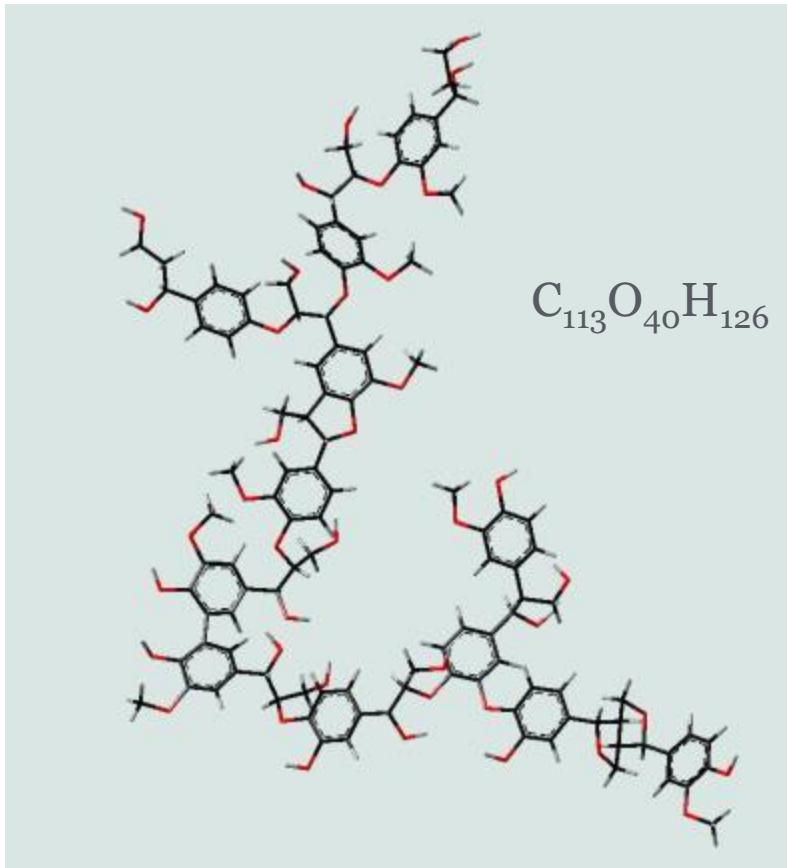
Low mobility of Li atoms in crystalline Li_2O ($T < 1200 \text{ K}$)

3

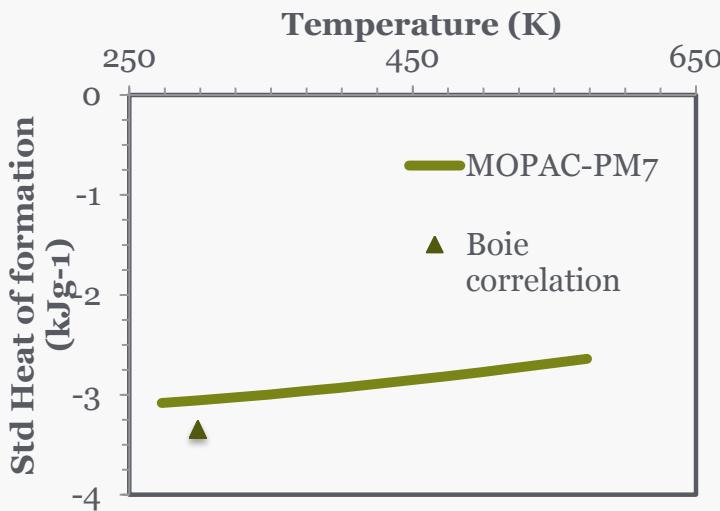
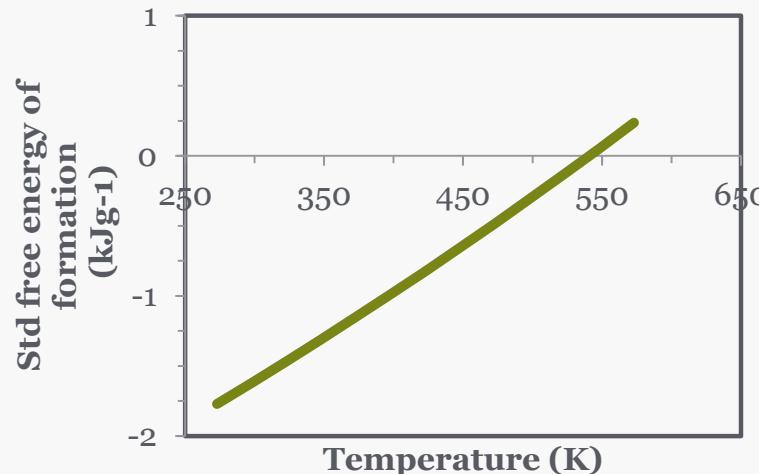
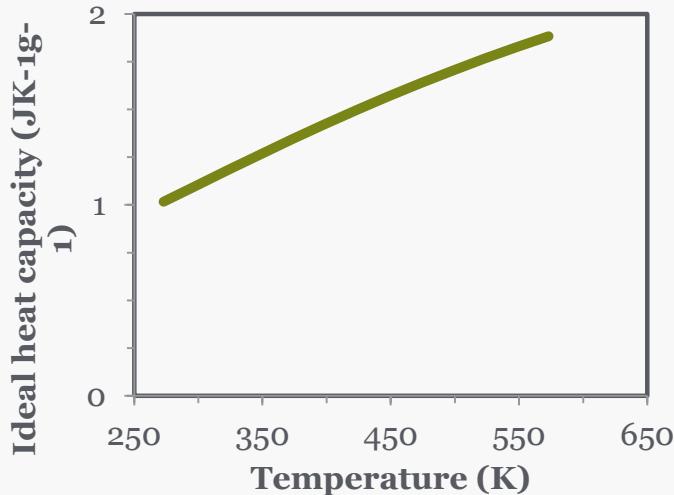
APPLICATIONS STRUCTURE AND THERMODYNAMIC PROPERTIES OF LIGNIN



Lignin structure

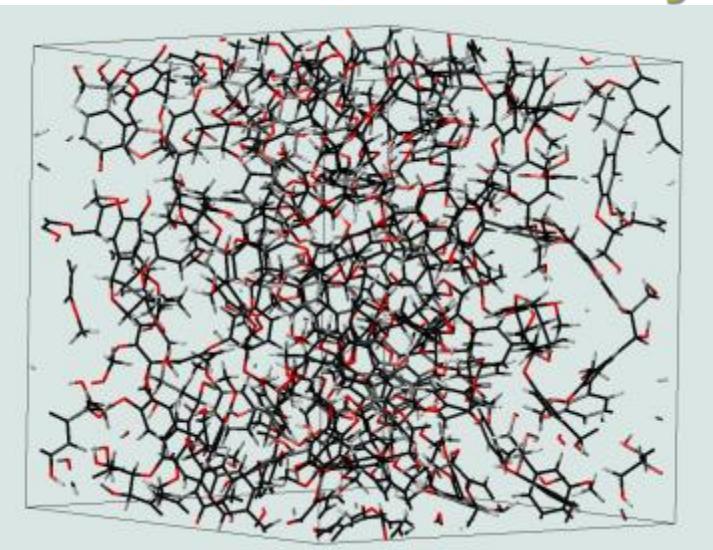


MOPAC simulation of lignin properties from vibrational analysis



- Heat capacity increase with T is a non-classical effect linked with the quantization of vibrational energy
- Good prediction of the strongly negative Std heat of formation, a consequence of the high oxygen content

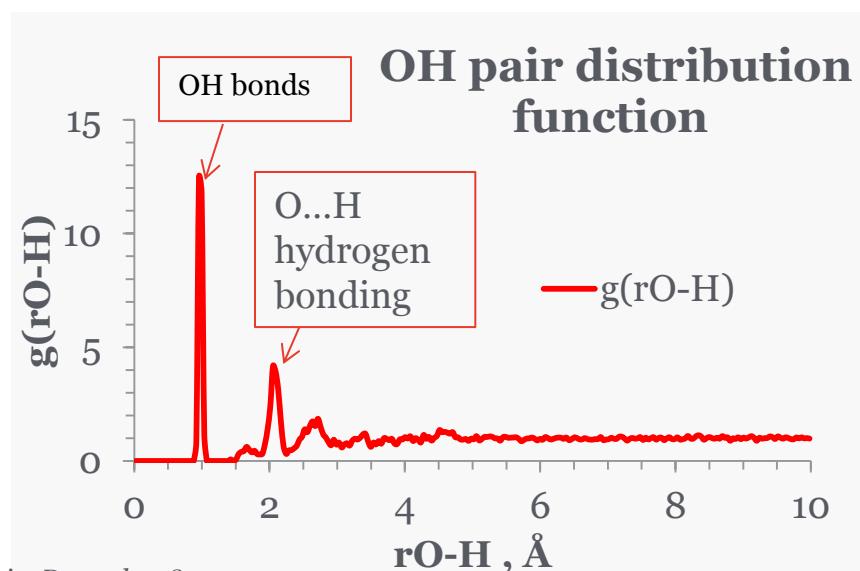
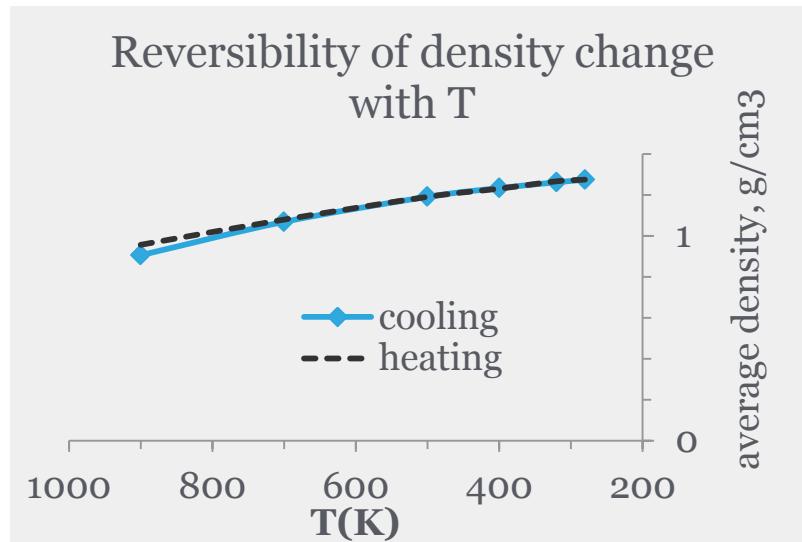
LAMMPS simulation of lignin structure and density with 8 model units



Final configuration after NPT relaxation from 900K to 280K in 1 ns

Average density at 300 K, 1 bar:
 $\rho = 1.266 \text{ g/cm}^3$ (LAMMPS pcff+)
 $\rho = 1.28 \text{ g/cm}^3$ (Zhang-Lebeuf, Energy&Fuels, 2009)

Residual heat capacity at 300 K :
 $C_{\text{pres}} \approx -0.03 \pm 0.06 \text{ J/g/K}$
Therefore $|C_{\text{pres}}| \ll C_{\text{pid}}$



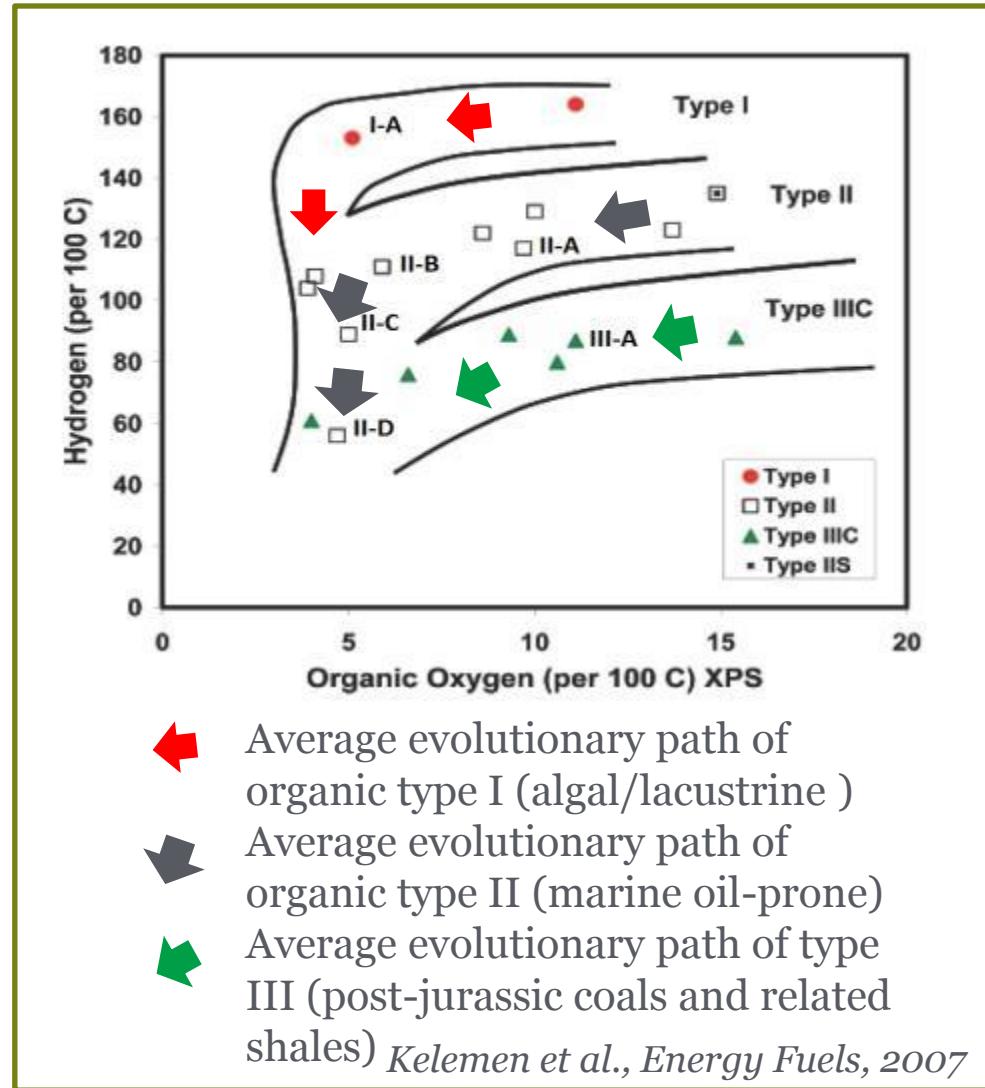
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APPLICATIONS THERMOCHEMICAL PROPERTIES OF KEROGEN

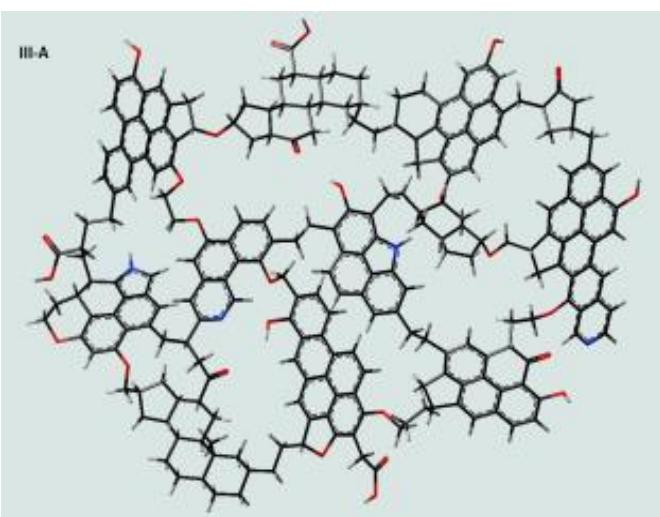


Chemical structure and properties of kerogen (organic matter of oil shales)

- Kerogen definition = fraction of the sedimentary organic matter insoluble in a good solvent (ex. dichloromethane)
- Oil & gas have been generated by kerogen maturation in a million-year long process
- Kerogen composition varies depending on i) the origin of organic matter (types I, II, III) and ii) maturation (A immature; B, C hydrocarbon generation ; D post-mature, gas generation)
- Better understanding of hydrocarbon retention and transport in kerogen is desired for the production of shale oil and shale gas.



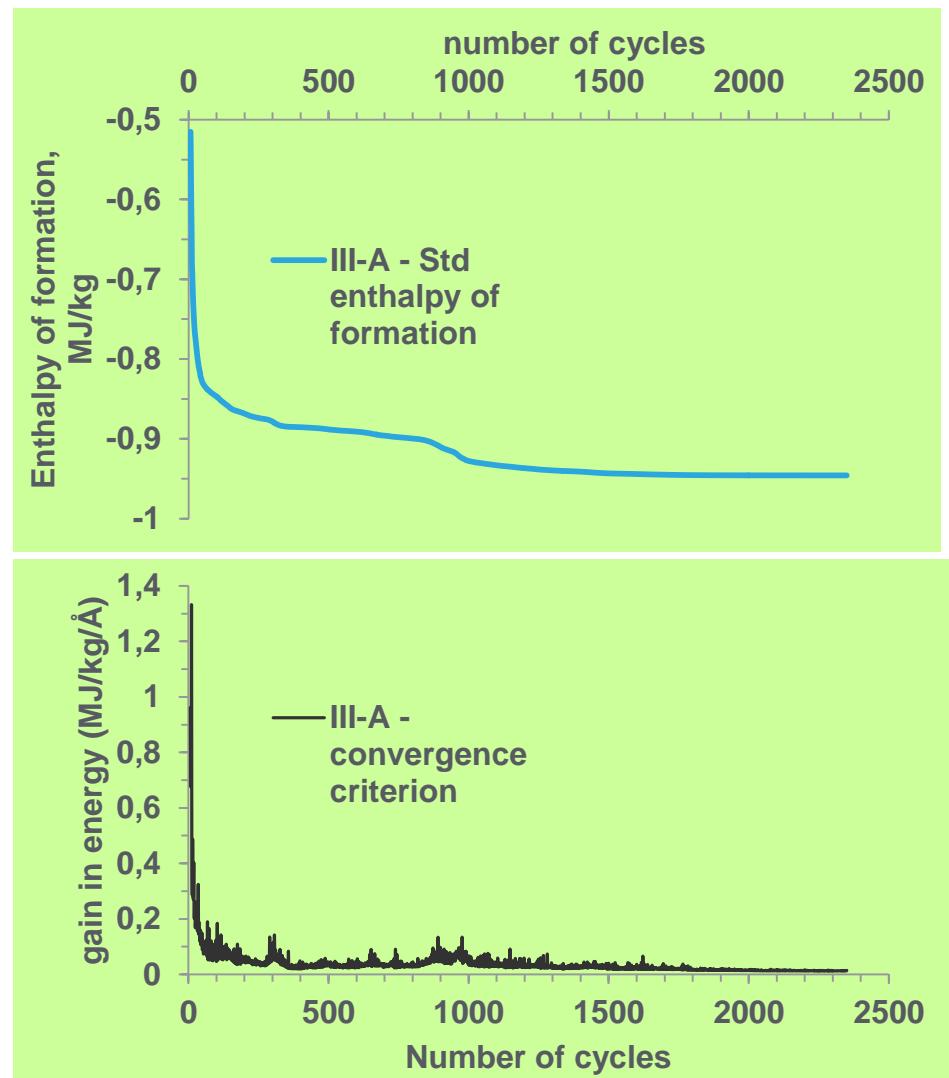
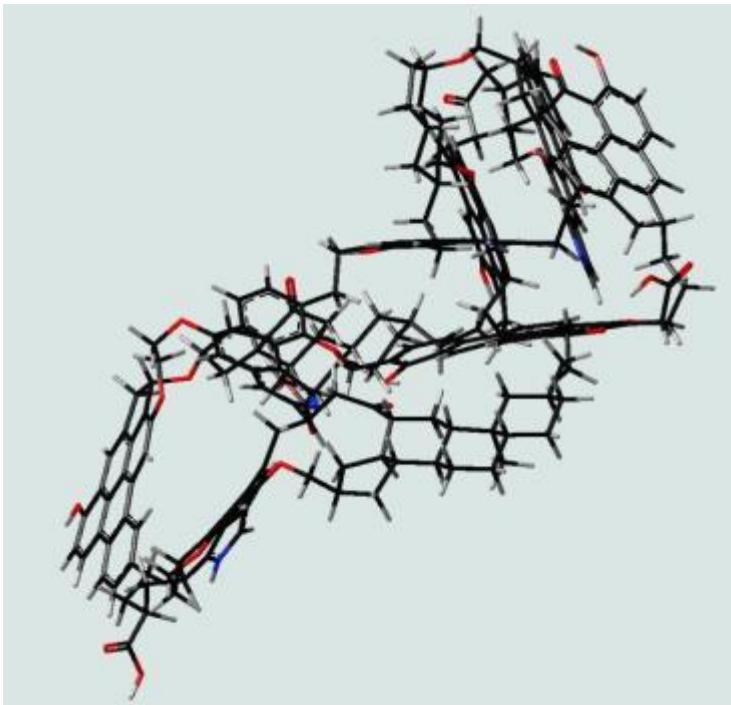
Example of kerogen structure based on analytical data (elemental analysis, ^{13}C NMR, XPS,...)



| | III-A | |
|--|---|-------|
| | Analytical data | Model |
| H/C | 0.87 | 0.886 |
| O/C | 0.111 | 0.116 |
| N/C | 0.017 | 0.017 |
| S/C | 0.002 | 0.000 |
| f_a' , % of aromatic carbon | 52% (XPS) 57% (^{13}C NMR) | 57% |
| Average number of C atoms per polyaromatic cluster | 16 | 16.5 |
| f_a' Fraction of aromatic carbons with attachments | 0.35 | 0.36 |
| f_a^S number of aromatic carbons linked with sp^3 C , per 100 C | 0.12 | 0.11 |
| f_a^H number of protonated aromatic carbons, per 100 C | 0.21 | 0.18 |
| f_a^P number of phenolic- phenoxy C, per 100 C | 0.07 | 0.065 |
| number of O in carboxylic groups (-COOH) per 100 C | 2.1 | 2.4 |
| f_a^C number of carbonyl – carboxyl aromatic carbons, per 100 C | 0.04 | 0.03 |
| Pyrrolic (mol % of N) | 57 | 50 |
| Pyridinic (mol % of N) | 31 | 50 |
| Quaternary (mol % of N) | 11 | 0 |
| Amino (mol % of N) | 0 | 0 |
| aromatic S (% of organic S) | 42% | - |
| aliphatic S (sulfides & thiols) (% of organic S) | 58% | - |

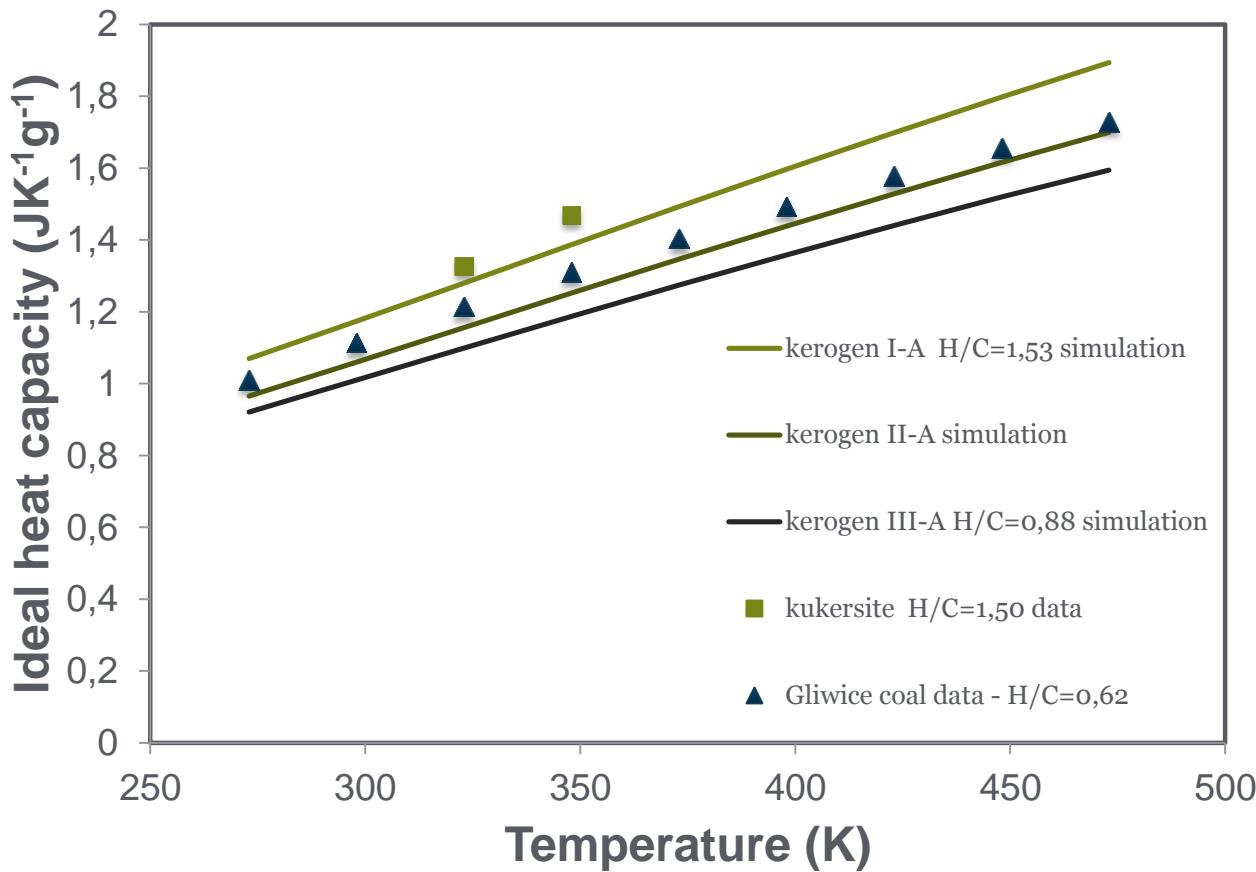


Structure optimization (ie energy minimization) of a kerogen unit (III-A) with MOPAC



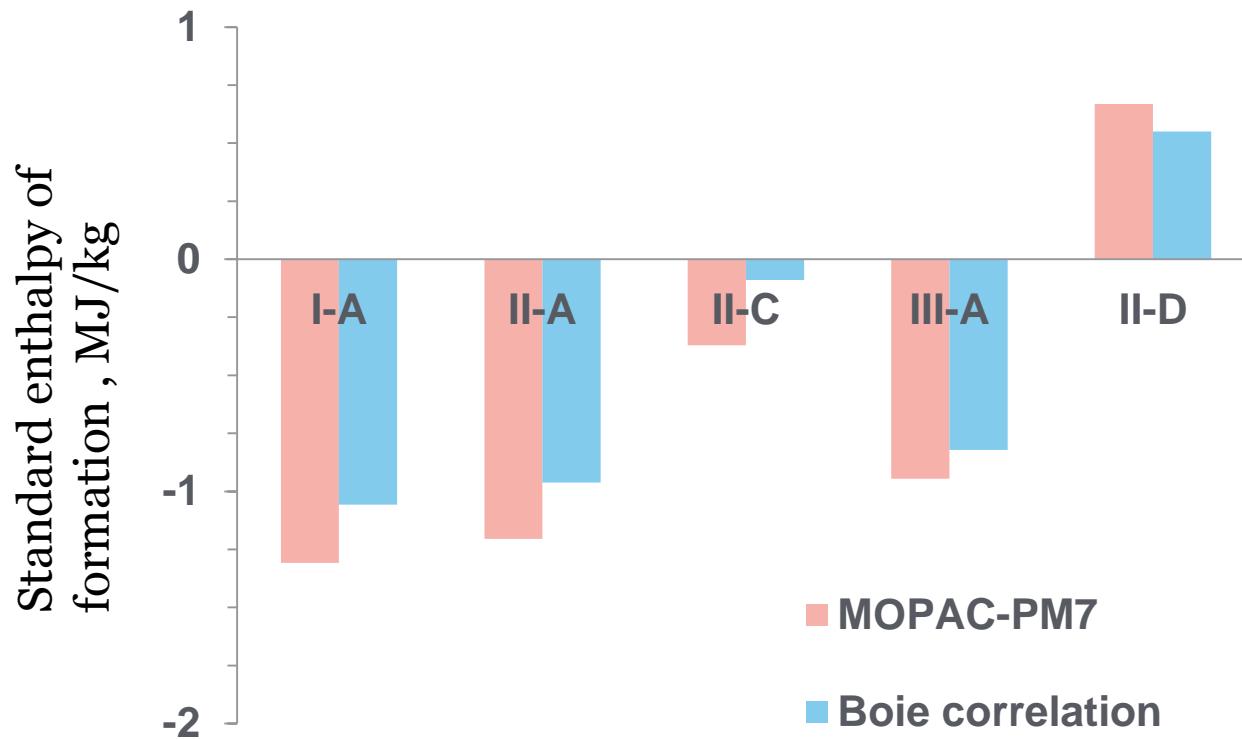
Ungerer et al., Energy & Fuels, 2014

Ideal heat capacity of kerogen



NB : from molecular dynamics residual heat capacity is < 0.2 kJ/g/K .

Std enthalpy of formation of kerogen – influence of organic type and maturity



Ungerer et al., Energy & Fuels, 2014

Density of kerogen predicted from molecular dynamics using MedeA-LAMMPS

Comparison of density predictions (g/cm³) from molecular dynamics at 300 K and 1 bar with experimental data from the literature .

| | | Maturity stage | | |
|-------------------------------------|---------------------------------|-----------------|----------------------------|-------------------|
| | | A (immature) | C (peak oil generation) | D (overmature) |
| Type I (GRS) | Experiment | 0.95 | | |
| | Simulation | 1.00 | | |
| Type II | Experiment | 1.18-1.29 | 1.18-1.25 | 1.3 – 1.4 |
| | Simulation | 1.13 | | 1.21 – 1.28 |
| Type III (higher plants) | Experiment-based correlation | 1.25 | | |
| | Simulation | 1.16-1.20 | | |

Ungerer et al., Energy & Fuels, 2014

5 Applications: Clay minerals



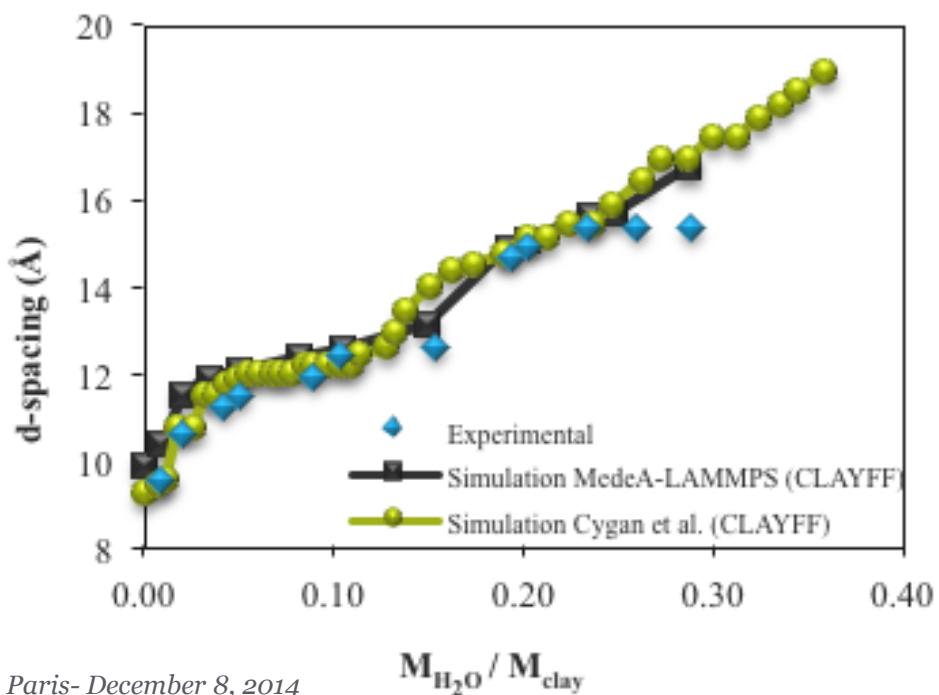
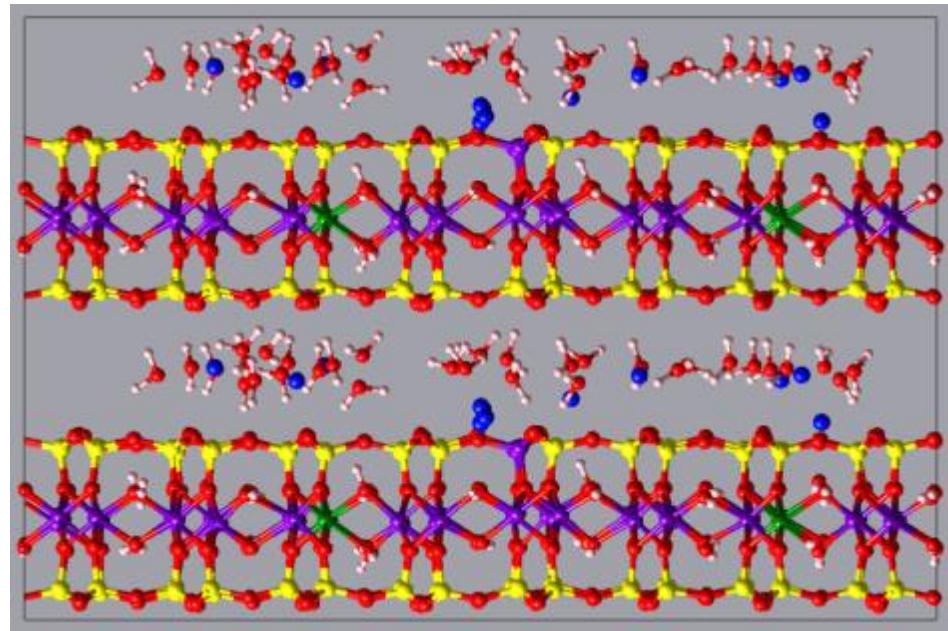
Adsorption of H_2O on Na-Montmorillonite and swelling

Acknowledgement : S. Naseem-Khan (Masters UPMC)

CLAYFF force field
(Cygan et al., JPCB, 2004)
implemented in MedeA
NPT LAMMPS simulations for
different loadings

T = 300 K, P = 1 bar

d



7 CONCLUSIONS



Conclusions

- Efficiency of the MedeA environment to simulate solid phases
 - Crystalline (Uranium carbides), superionic (LiO_2), layered (montmorillonite)
 - Amorphous (lignin, kerogen, coal)
- Controlled accuracy of Quantum methods
 - Prediction of standard thermochemical properties with MOPAC-PM7, including heat capacity increase with T for organic macromolecules (a quantum effect !)
 - Robust way of predicting thermochemical properties of dense systems by coupling QM results and forcefield – based methods
- Insight in the structure of alloys, condensed matter and minerals at the nanoscale
- Industrial applications aiming at strategic advantage
 - Hybrid vehicles
 - Oil and gas
 - Nuclear
 - Etc.

