



Introduction to atomistic modeling

Paolo Raiteri

Curtin University is a trademark of Curtin University of Technology
CRICOS Provider Code 00301J

Why computer simulations ?

- Reproduce experiments - sometimes...
- Replace experiments
- Interpret experiments
- Test theories
- Make predictions
- Guide future experiments
- It's fun
- It's easy
- It's cheap

exa	E	10^{18}
peta	P	10^{15}
tera	T	10^{12}
giga	G	10^9
mega	M	10^6
kilo	k	10^3
hecto	h	10^2
deca	da	10^1

Computational science 70M\$ (each)



@Pawsey Centre (Perth)

Architecture: Cray XE

Computing Power: circa 50 PetaFLOPS

1,600 CPU nodes, 750 GPU nodes

Memory: 548 Terabytes

Interconnect: Slingshot

Local storage: 3 Petabytes



@NCI (Canberra)

Architecture: Intel Xeon Platinum

Computing Power: 2 PetaFLOPS, from 3000 nodes

Memory: 576 TBytes (192 Gigabytes per node)

Interconnect: Infiniband FDR

Local storage: 10 Petabytes

1 PetaFLOP: circa 10,000 times more computing power than a desktop computer

3

Computer simulations (of minerals)

• *Objectives:*

- Atomistic picture
- Thermodynamics
- Connect with experiments

• *Challenges:*

- Timescale ($> \mu\text{s}$)
- Concentration ($< 1 \text{ mM}$)
- Reactivity
- Accuracy of the methods

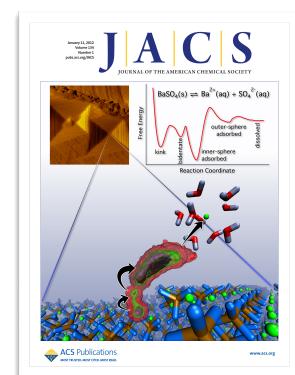
• *Approaches:*

- *Ab initio* methods
- Forcefields methods
- Monte Carlo
- Lattice dynamics
- Molecular dynamics

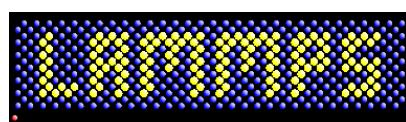
• *Extras:*

- Free energy methods

GULP



PLUMED



CPMD

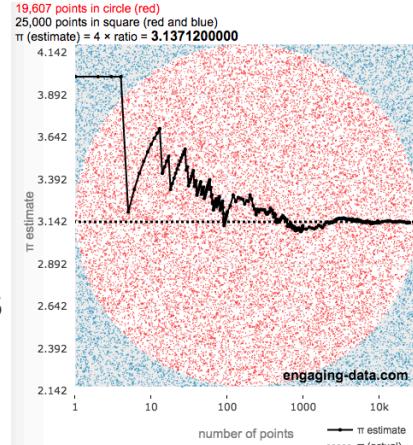


4

Monte Carlo simulations

- Many useful applications in science
- Not widely used in atomistic simulations
- Stochastic method

$$\langle A \rangle \approx \frac{1}{M} \sum_{i=1}^M A(\mathbf{x}_i^N)$$



- No dynamics or kinetics
- “Random” movements - importance sampling

$$acc(\mathbf{x}^N \rightarrow \mathbf{y}^N) = \min \left(1, \exp\{-\beta[U(\mathbf{y}^N) - U(\mathbf{x}^N)]\} \right)$$

5

Lattice Dynamics

- Based on statistical thermodynamics
 - Useful to describe crystals below the Debye temperature (and isolated molecules)
 - Free energies can be computed using quasi-harmonic approximations from the phonons/vibrations
 - Limited applications to liquids and amorphous materials
-
- We use it routinely to develop forcefields that accurately reproduce the solid phases and their solubilities

6

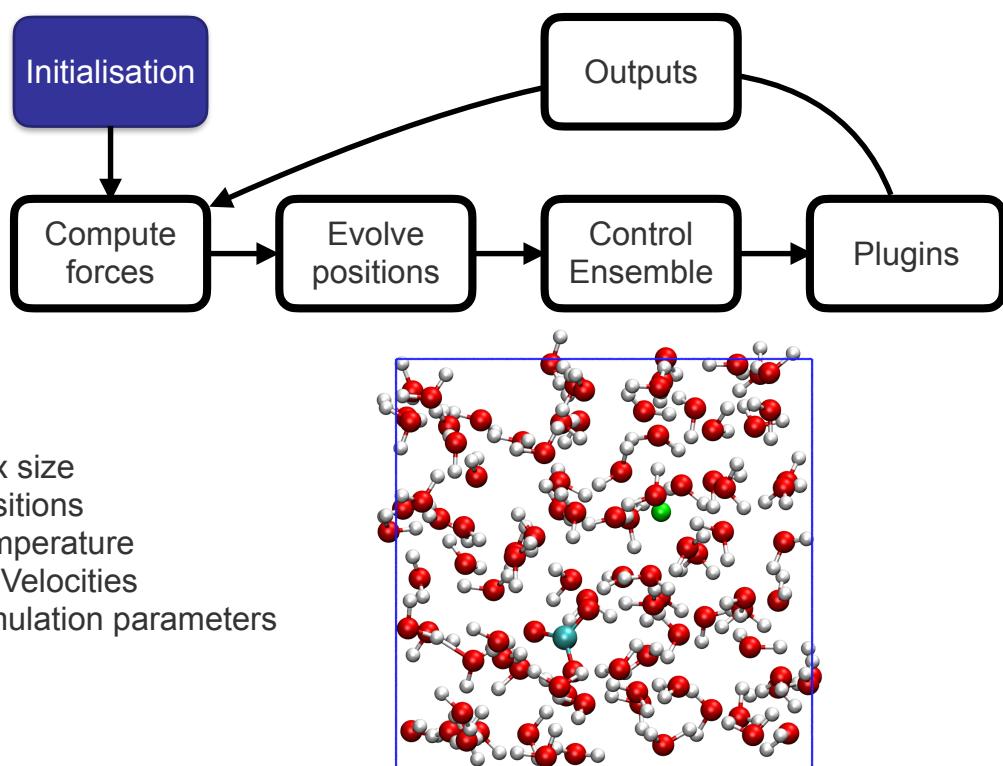
Molecular Dynamics

- Most widely used computational tool for atomistic simulations
- Based on Newtonian dynamics
- Statistical mechanics can be used to compute properties
- Atomic trajectories can give access to kinetics
- Only difference is how the energy and forces are computed

7

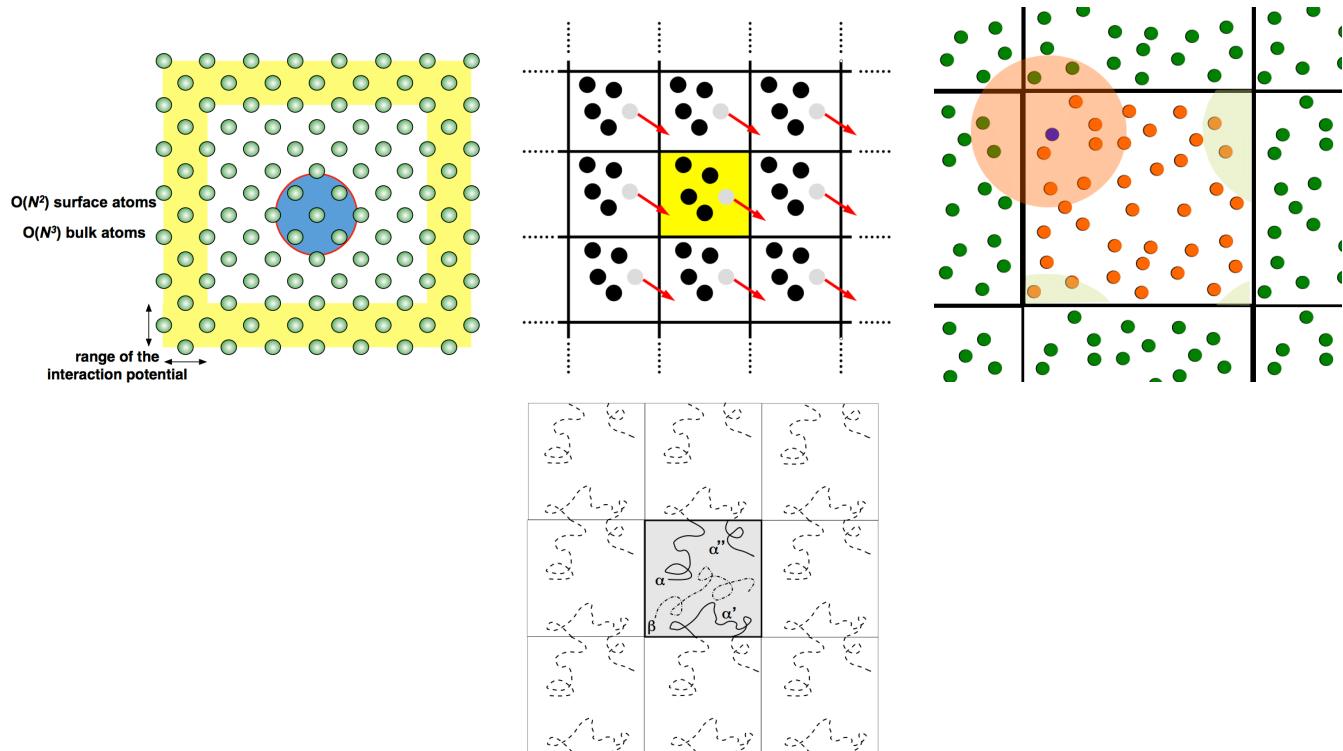
Molecular Dynamics

Each cycle propagates the system forward in time



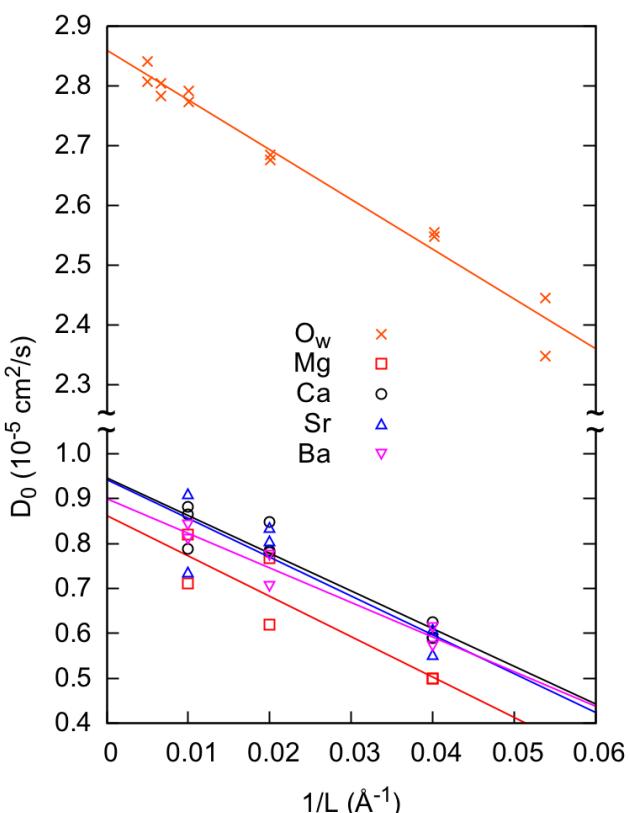
8

Finite size and boundary conditions



9

Finite size - Diffusion



J. Phys. Chem. B (2004), **108**, 15873–15879.

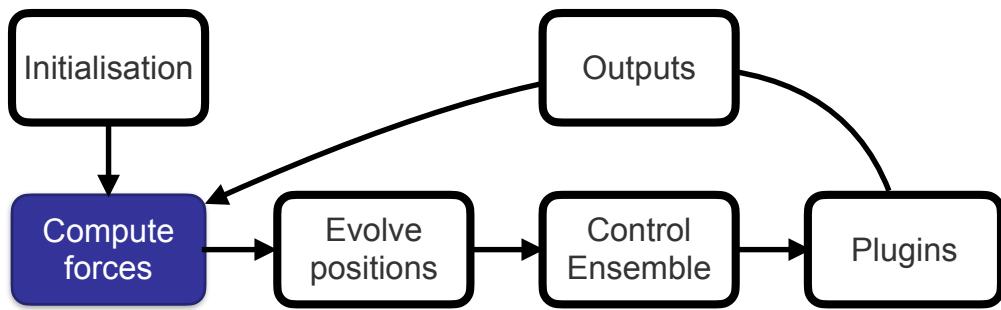
$$D_{PBC} = D^\infty - \frac{k_B T \xi}{6\pi \eta L}$$

[1] Atkinson *et al.*; *J. Phys. Chem.* (1974), **78**, 1913–1917.

D_0 ($10^{-5} \text{ cm}^2/\text{s}$)	Exp [1]	Theory
Mg	0.71	0.86
Ca	0.79	0.95
Sr	0.79	0.94
Ba	0.84	0.90
H_2O	2.30	2.86

10

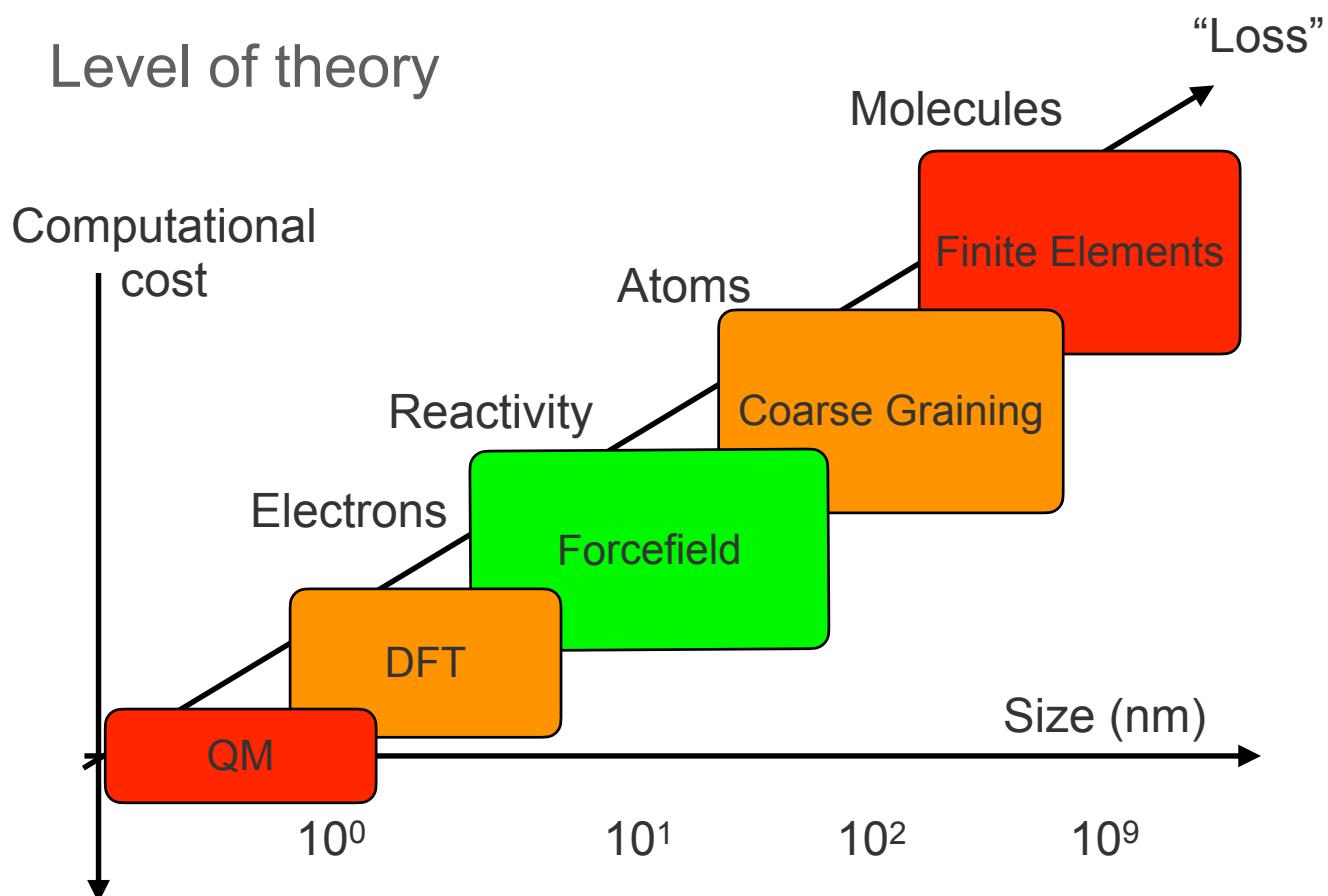
Molecular Dynamics



Newton's second law $\vec{F}_i = -\frac{\partial U}{\partial \vec{x}_i} + q_i \vec{E} = m_i \vec{a}_i$



11



12

Ab initio methods

$$\vec{F}_i = -\frac{\partial \varepsilon}{\partial \vec{x}_i} = m_i \vec{a}_i$$

Schödinger equation

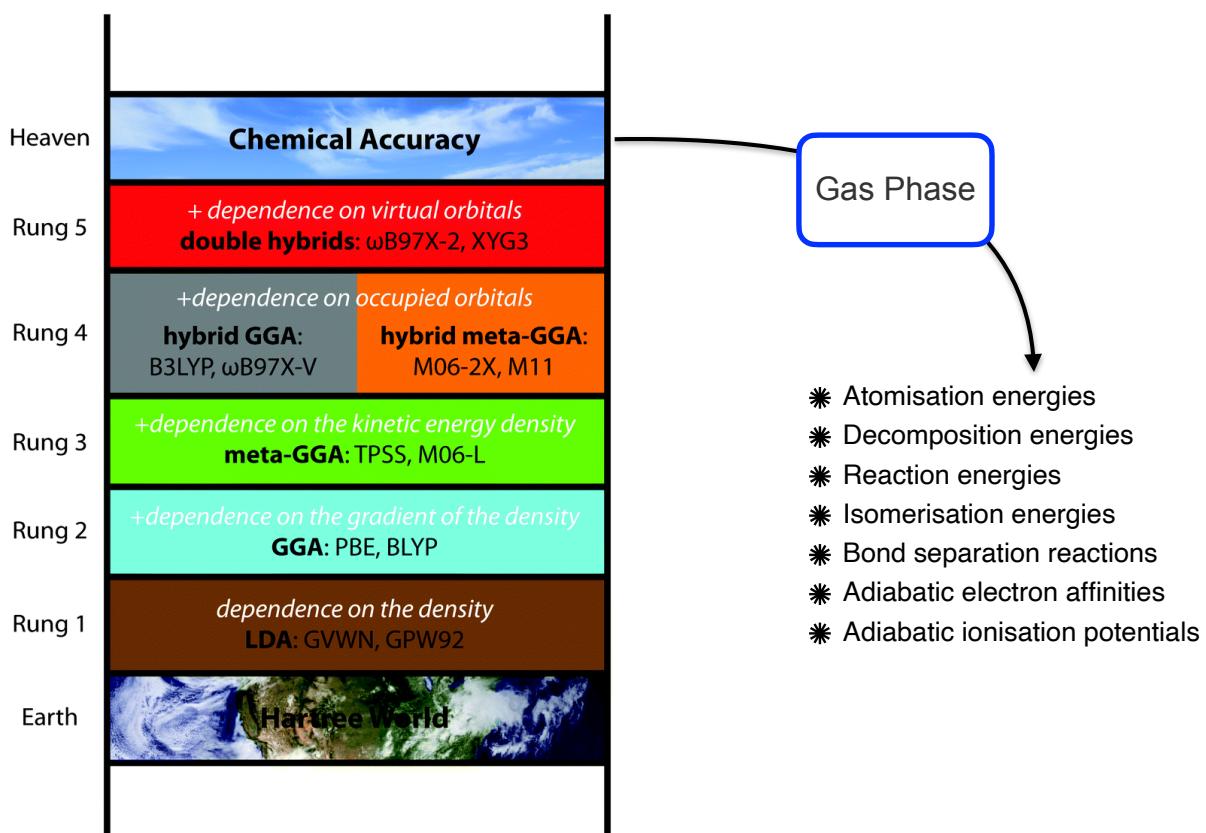
$$\hat{H}\Psi = \left[\sum_i^N \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 \right) + \sum_i^N V(\vec{r}_i) + \sum_{i < j}^N U(\vec{r}_i, \vec{r}_j) \right] \Psi = \varepsilon \Psi$$

- Born–Oppenheimer approximation
- Density Functional Theory
- Basis set
- Exchange and Correlation
- Huge zoo of methods (B3LYP, PBE0...)
- Poor treatment of the vdw interactions

$$\rho = \int \cdots \int d\mathbf{x}^{3N} \Psi^* \Psi$$

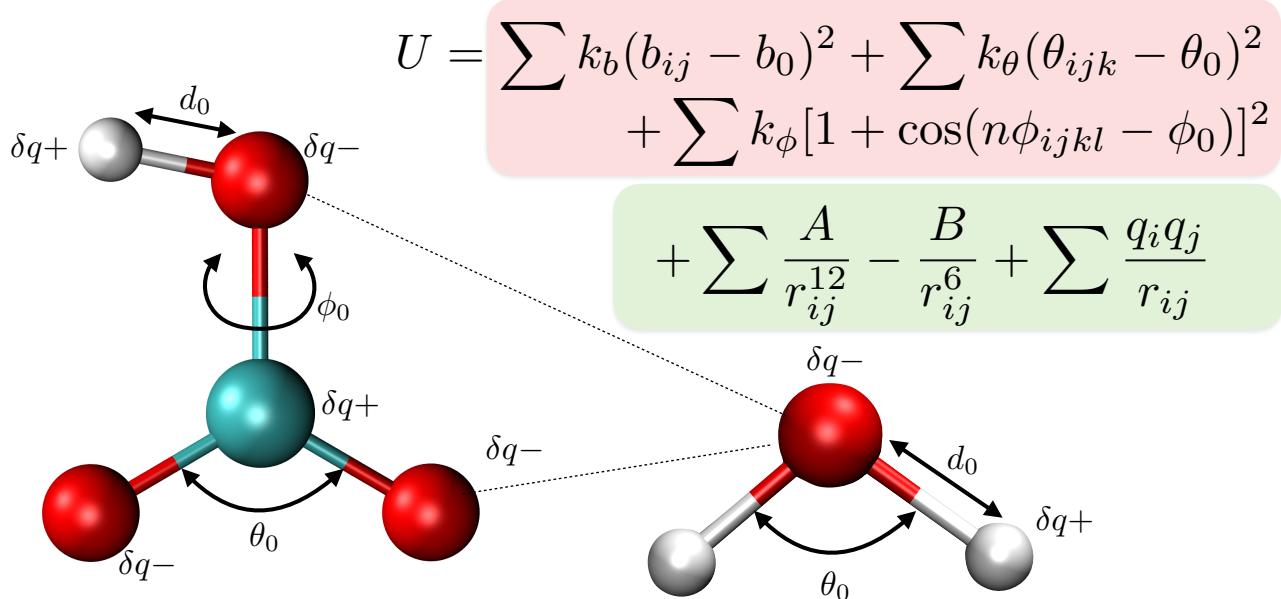
13

Jacob's ladder of DFT



Force field

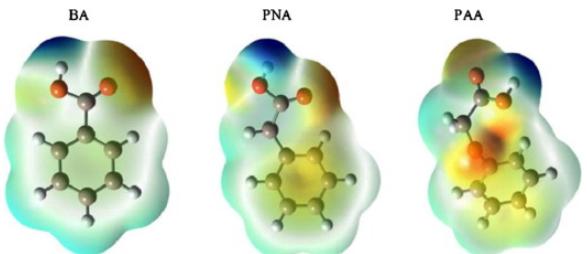
$$\vec{F}_i = -\frac{\partial U}{\partial \vec{r}_i} + q_i \vec{E} = m_i \vec{a}_i$$



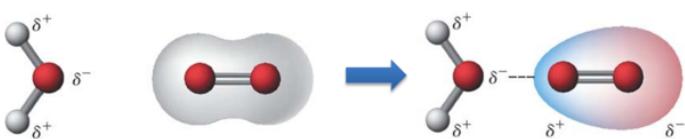
15



Polarisable forcefield

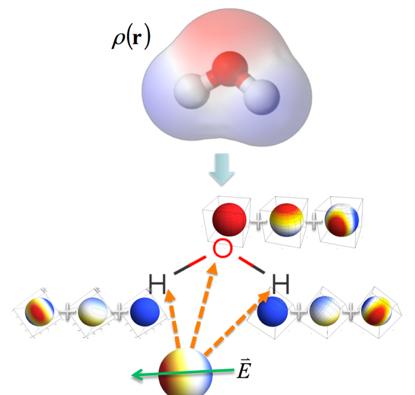


DOI: j.saa.2013.09.127

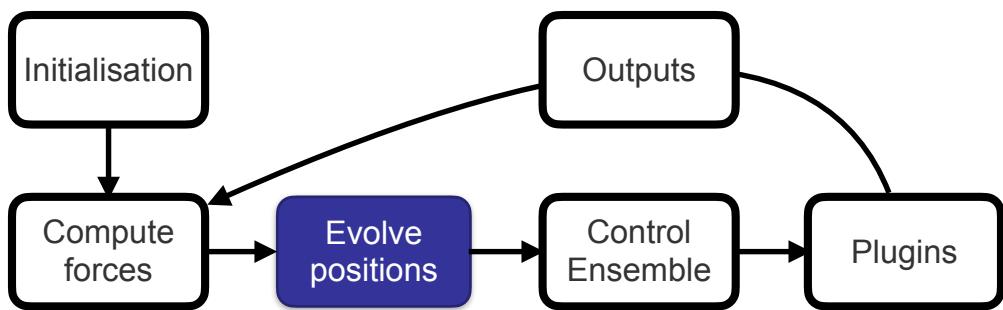


$$U = \sum k_b(b_{ij} - b_0)^2 + \sum k_\theta(\theta_{ijk} - \theta_0)^2 + \sum k_\phi[1 + \cos(n\phi_{ijkl} - \phi_0)]^2$$

$$+ U_{vdW} + U_{elec}^{perm} + U_{elec}^{ind}$$



Molecular Dynamics

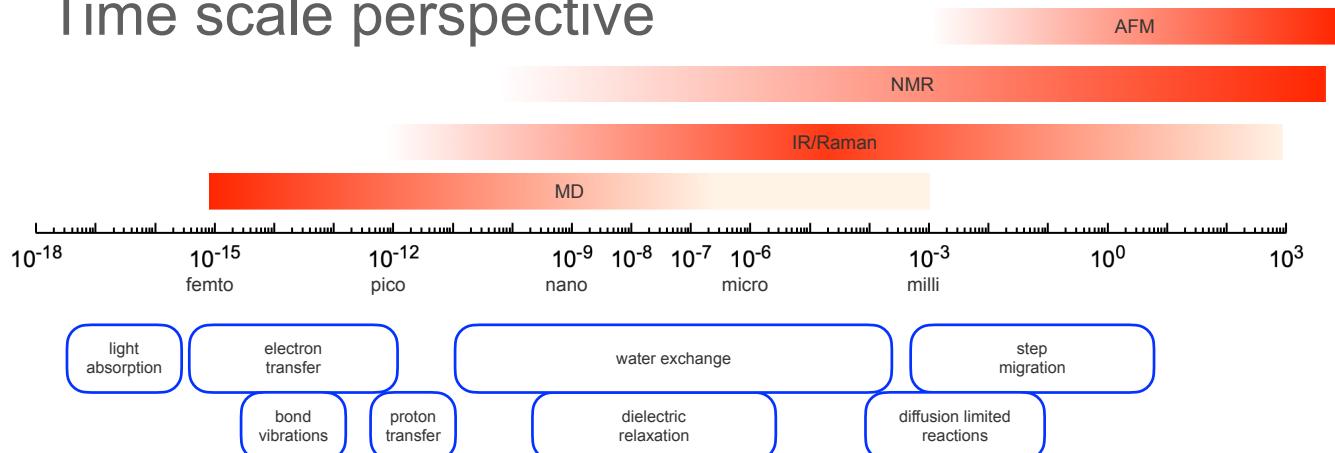


$$\vec{a}(t) = F(t) = -\frac{\partial U}{\partial \vec{r}} \quad \text{timestep}$$

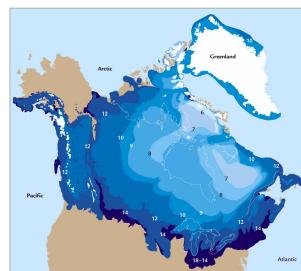
$$\vec{r}(t + \Delta t) = \vec{r}(t) + \vec{v}(t) \Delta t + \frac{1}{2} \vec{a}(t) \Delta t^2$$

17

Time scale perspective



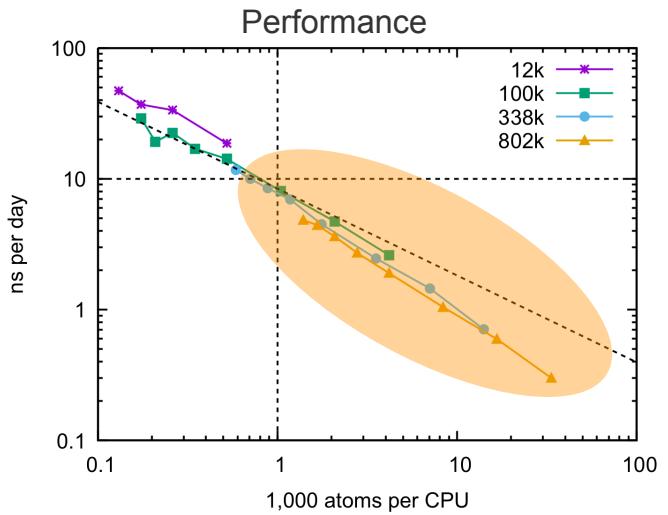
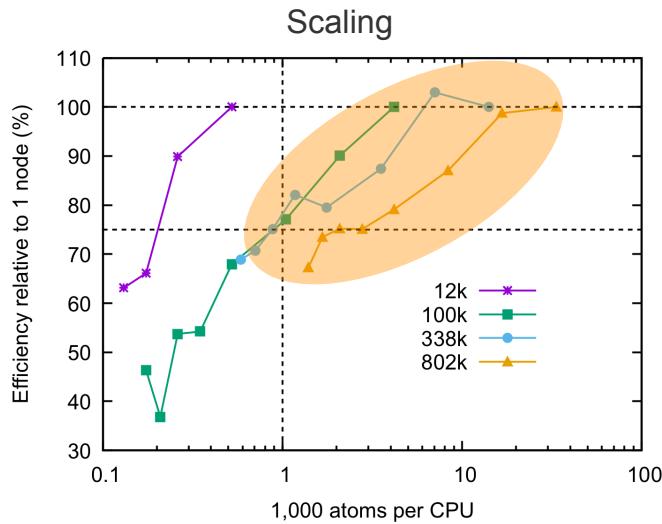
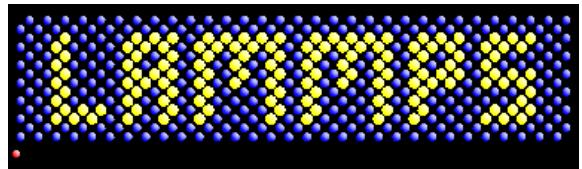
Experimental time scale	Phenomenon	Simulation time
10 fs	O-H vibration	0.1 s
1 ps	H-bond persistence	10 s
1 ns	Ion permeation through a membrane	3 hours
1 μ s	Conformational rearrangement	115 days
1 ms	Protein folding (fast)	317 years
1 s	Protein folding (typical)	317,000 years



Last ice age:
115,000-11,700 years ago

Assuming 10 ms per MD cycle

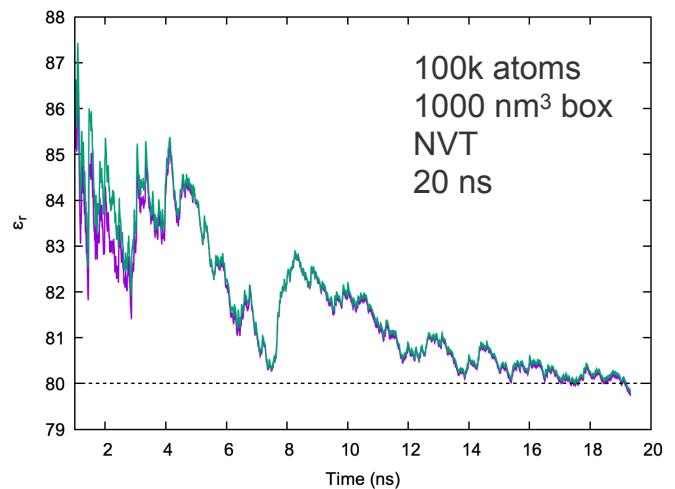
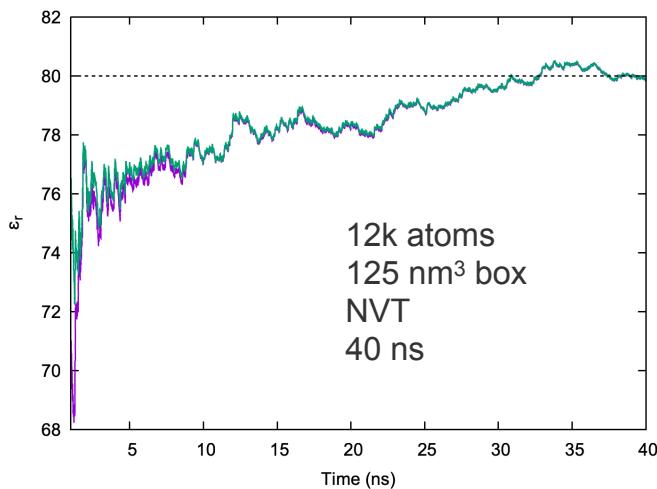
LAMMPS on magnus



Number of nodes used:
1 - 2 - 3 - 4 - 8 - 12 - 16 - 20 - 24

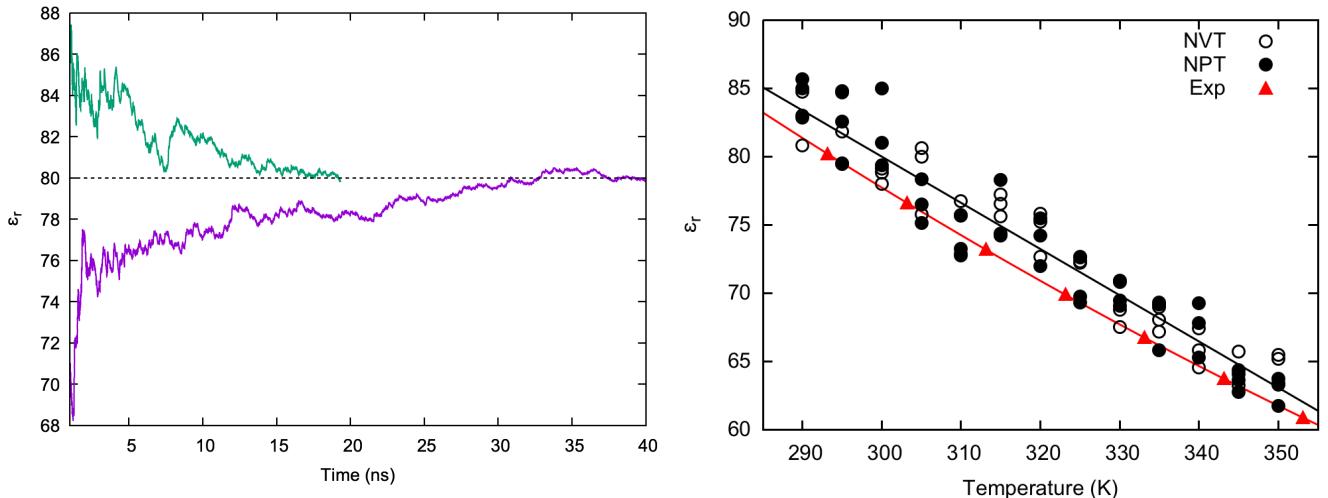
19

Finite time - Dielectric constant



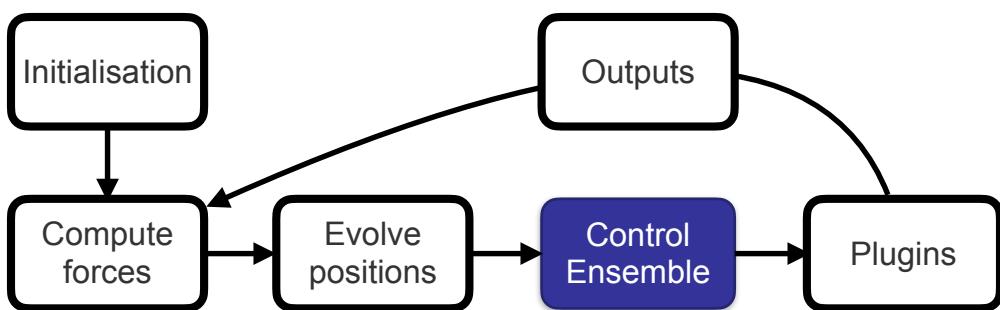
20

Finite time - Dielectric constant



21

Molecular Dynamics



N : Number of atoms

μ : Chemical potential

V : Volume

P : Pressure

E : Energy

H : Entalpy

T : Temperature

Choose (any) 3

$NVE \rightarrow$ Isolated system

$NVT \rightarrow$ Isothermal – Isochoric

$NPH \rightarrow$ Isoenthalpic – Isobaric

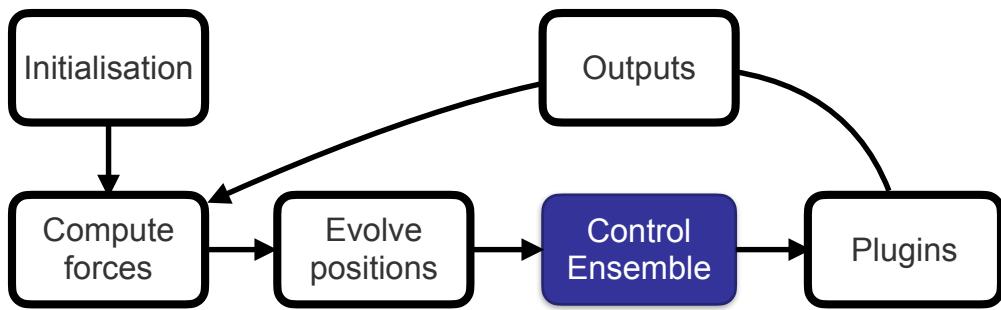
$NPT \rightarrow$ Isothermal – Isobaric

$\mu PT \rightarrow$ Open system

C S Y
L O T
S E E
D M

22

Molecular Dynamics



$$K(t) = \frac{1}{2} \sum_{i=1}^N m_i v_i^2(t) = \frac{3}{2} N k_B T(t)$$

Velocity Rescaling

$$\frac{1}{2} \sum_{i=1}^N m_i \lambda^2 v_i^2(t) = \frac{3}{2} N k_B T_{NVT} \quad \lambda = \sqrt{\frac{T_{NVT}}{T(t)}}$$

23

Specific heat

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = \frac{\langle \delta H^2 \rangle_{NPT}}{k_B T^2}$$

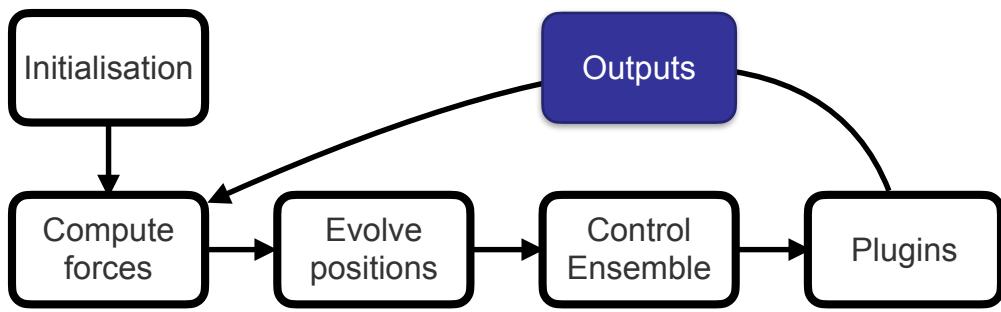
	slope	fluct.
Berendsen	31.98	4.36
Andersen	31.89	24.76
CSVR	32.07	32.80
Langevin	32.16	34.83
Exp.	29.71	

Self Diffusion coefficient

	D [10 ⁻⁵ cm ² /s]
Experiment	2.30
NVE	2.45
NVT - Berendsen	2.4
NVT - CSVR	2.47
NVT - Nosé-Hoover	2.46
NPT - MTTK	2.44
NVT - Langevin	1.09*

24

Molecular Dynamics



- Energy
- Temperature
- Pressure
- Volume
- ...
- Atomic coordinates
- ...

Post-processing

- Density
- Structural properties [$g(r)$]
- Dynamical properties [D_0]
- ...
- Phase changes
- ...
- Free energies
- Reaction rates

25

How to read the methods section of a paper?

- Do you know any of the authors ?
- Gauge the results rather than the method !
- Any obvious red flags ?
- Often trends are more reliable than absolute numbers
- Identify the level of theory (*ab initio*, forcefield...)
- System size and simulation length appropriateness
- Any “special” techniques used (Metadynamics) ?

26

Thermodynamics works!

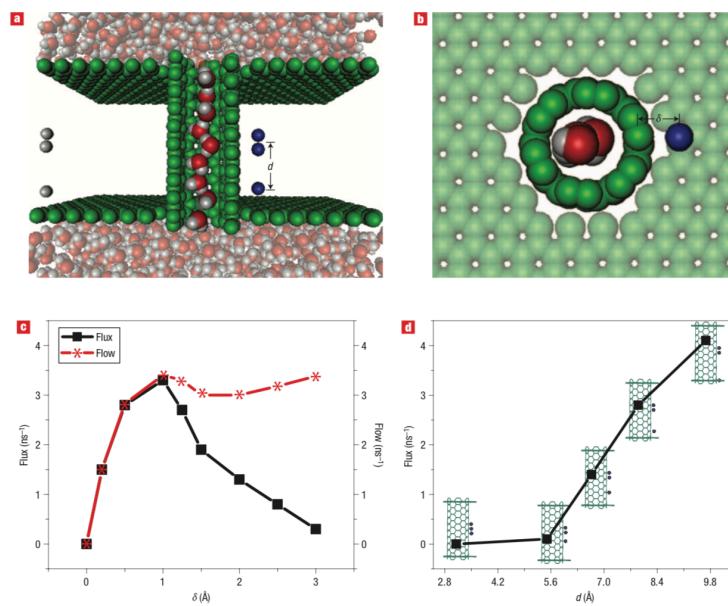


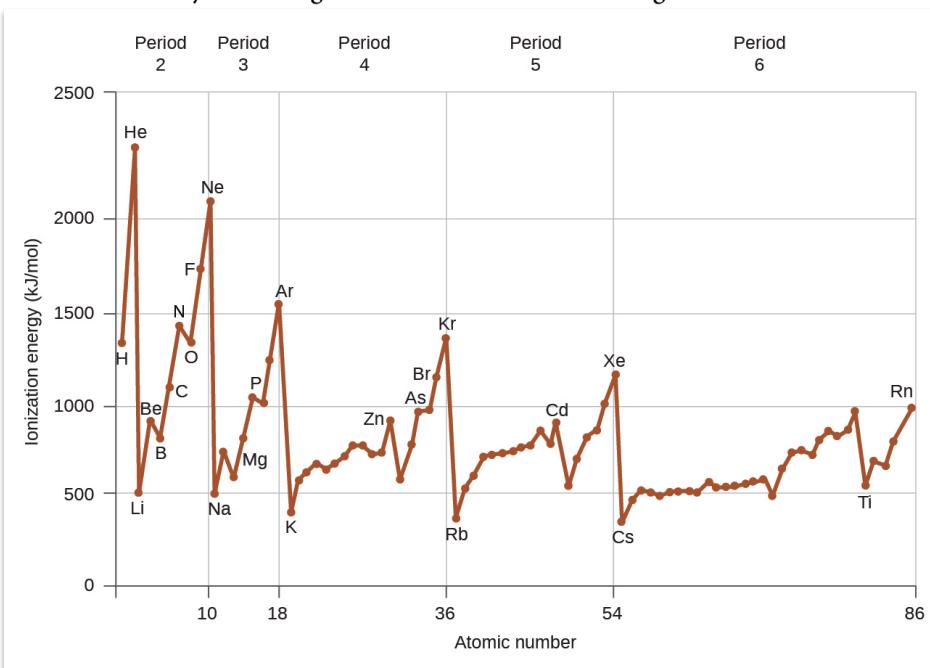
Figure 1 Introduction to the main system and the flows and fluxes for different charge arrangements in the main system. **a**, Side view of the main system. The green spheres are the carbon atoms of the nanotube and the graphite sheets (note that the figure is not drawn to scale). The blue points are the positive charges (0.5e, 0.5e and 1.0e, from top to bottom), and the grey ones are negative charges to neutralize the positive charges near the channel. Water molecules are shown in sphere representation with oxygen in red and hydrogen in grey. **b**, Top view of the same arrangement. **c**, Flow and flux for different radial distance δ for $d = 7.9 \text{ \AA}$. **d**, Flux with respect to d for $\delta = 0.5 \text{ \AA}$.

27

Put the numbers into context



Table 1. Summary of Binding Residues and Interaction Energies^a between SCA-1 and the Calcite (104) Surface for All Systems



E_{ele} , kJ/mol	E_{vdW} , kJ/mol	E_{tot} , kJ/mol
-385.95	-3.45	-389.40
-377.32	5.69	-371.63
-798.95	-5.62	-804.57
-329.59	-7.53	-337.12
-582.08	-33.77	-615.85
-354.18	-27.92	-382.11
-337.78	10.78	-327.00

^a (the position of the end of the second water molecule at the last 15 ns. ^cAny atom of the residue located near the calcite surface for a period of time (~5 ns)

28

No comparison with readily available experiments [water g(r)]

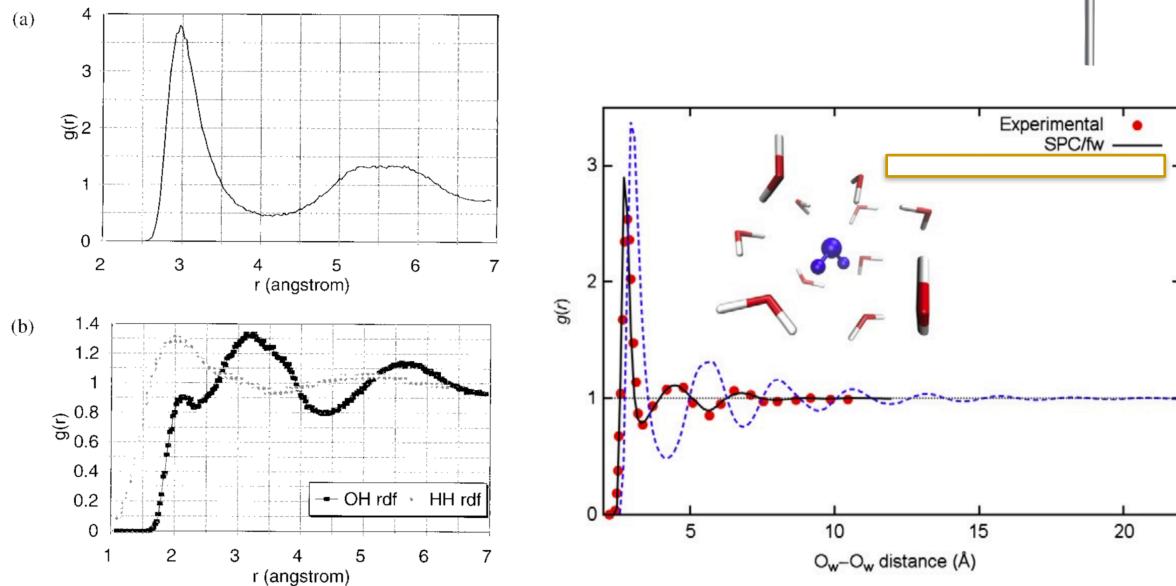


FIG. 3. (a) O-O and (b) O-H and H-H radial distribution functions, omitting intramolecular OH and HH interactions.

29

Simplistic model

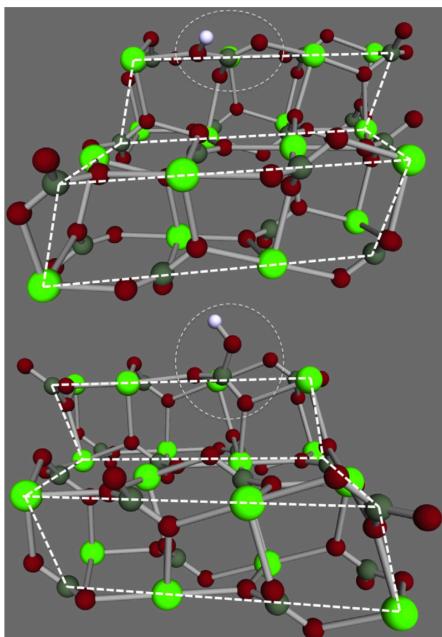


Table 1

Predicted pK_a for the bicarbonate deprotonation reaction to carbonate, $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$, at various surface sites of calcite. For the step and kink sites, there are two different orientations of the carbonate group and both pK_a values are presented. The values are calculated for the case where there is no surface potential.

Site	pK_a
Free in solution	10.35
Adsorbed on {10.4} (outer shell)	7.4
Adsorbed on {10.4} (inner shell)	7.5
{10.4} terrace	-6.0
Acute step	-5.6, -3.7
Obtuse step	-5.0, -4.4
Kink site acute step, long $\text{CO}_3^- \text{CO}_3$	-2.6, -1.7
Kink site acute step, short $\text{CO}_3^- \text{CO}_3$	-4.0, 2.4
Kink site obtuse step, long $\text{CO}_3^- \text{CO}_3$	-2.4, -1.8
Kink site obtuse step, short $\text{CO}_3^- \text{CO}_3$	-0.1, 0.0



Table 2

Adsorption energy of carbonate from aqueous solution onto calcite {10.4}, modelled by an 80 atom calcite cluster in inner and outer sphere geometry.

Adsorption geometry	ΔG_{ads} (kJ/mol)
CO_3^{2-} on calcite {10.4}, outer shell	-50
HCO_3^- on calcite {10.4}, outer shell	-18
CO_3^{2-} on calcite {10.4}, inner shell	4
HCO_3^- on calcite {10.4}, inner shell	34

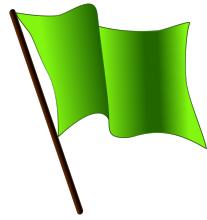
Trends probably reasonable



More from Julian about this

30

Computational chemistry works!



PNAS

Potential high- T_c superconducting lanthanum and yttrium hydrides at high pressure

Hanyu Liu^a, Ivan I. Naumov^a, Roald Hoffmann^b, N. W. Ashcroft^c, and Russell J. Hemley^{d,e,f}

^aGeophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015; ^bDepartment of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853; ^cLaboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853; ^dDepartment of Civil and Environmental Engineering, The George Washington University, Washington, DC 20052; and ^eSchool of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853

Contributed by Russell J. Hemley, May 5, 2017 (sent for review March 20, 2017; reviewed by Panchapakesan Ganesh, Jeffrey M. McMahon, and Dimitrios Papaconstantopoulos)

We predict that YH_{10} is the energetically stable phase from 250 to 300 GPa, and is dynamically stable down to 220 GPa.

The predicted T_c for YH_{10} is very high (Fig. 7) using similar EPC calculations. At 250 GPa, the λ is 2.56 and gives a T_c of 305–326 K with $\mu^* = 0.1\text{--}0.13$ based on numerically solving the Eliashberg equations. The T_c of YH_{10} increased by ~30 K relative to YH_6 (30) despite the fact that λ decreases (from 2.93 to 2.56). But, this change is offset by the higher average ω_{log} calculated for YH_{10} compared with YH_6 (1,282 K versus 1,124 K), as a result of the higher hydrogen content in the former.

PHYSICAL REVIEW LETTERS 122, 027001 (2019)

Editors' Suggestion | Featured in Physics

Evidence for Superconductivity above 260 K in Lanthanum Superhydride at Megabar Pressures

Maddury Somayazulu,^{1,*} Muhtar Ahart,¹ Ajay K. Mishra,^{2,‡} Zachary M. Geballe,² Maria Baldini,^{2,§}

Yue Meng,³ Viktor V. Struzhkin,³ and Russell J. Hemley^{1,†}

¹Institute for Materials Science and Department of Civil and Environmental Engineering, The George Washington University, Washington, DC 20052, USA

²Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA

³HPCAT, X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

In summary, we report four-probe, ac resistance measurements on LaH_{10+x} synthesized at pressures of 180–200 GPa by a modulated, pulsed laser heating technique that preserves the integrity of multiprobe electrical contacts on the sample after synthesis. Our multiple measurements reveal the signature of superconductivity at temperatures above 260 K at pressures of 180–200 GPa. The transition temperature is close to that predicted for the superconducting T_c based on BCS-type calculations for LaH_{10} at comparable pressures.

31

How to read the methods section of a paper?

- Do you know any of the authors ?
- Gauge the results rather than the theory section !
- Any obvious red flags ?
- Often trends are more reliable than absolute numbers

- Identify the level of theory (*ab initio*, forcefield...)
- System size and simulation length appropriateness
- Molecular dynamics, Monte Carlo, lattice dynamics...

- Any “special” techniques used (Metadynamics) ?

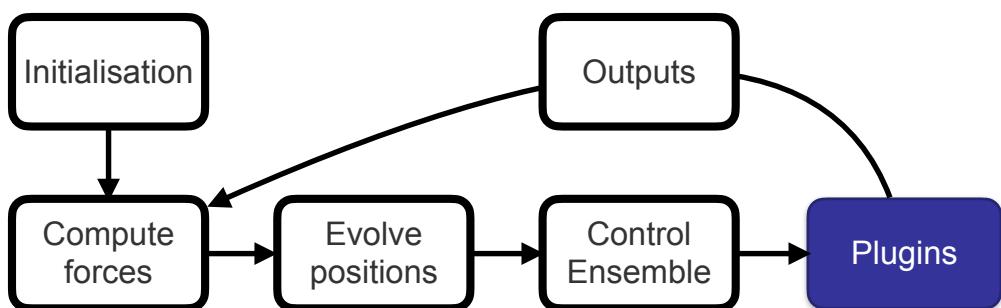
32

How to read the methods section of a paper?

- Do you know any of the authors ?
- Gauge the results rather than the theory section !
- Any obvious red flags ?
- Often trends are more reliable than absolute numbers
- Identify the level of theory (*ab initio*, forcefield...)
- System size and simulation length appropriateness
- Molecular dynamics, Monte Carlo, lattice dynamics...
- Any “special” techniques used (Metadynamics) ?

33

Molecular Dynamics



- *Umbrella Sampling*
- *Metadynamics*
- *Free Energy Perturbation*
- *Steered MD (Jarzynski)*
- *AFED*
- ...
- *Transition Path Sampling*
- *Forward Flux*
- ...

$$\begin{aligned} G &= -k_B T \ln Z \\ &= -k_B T \ln \sum_i e^{-\beta E_i} \end{aligned}$$

34

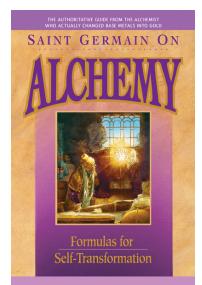
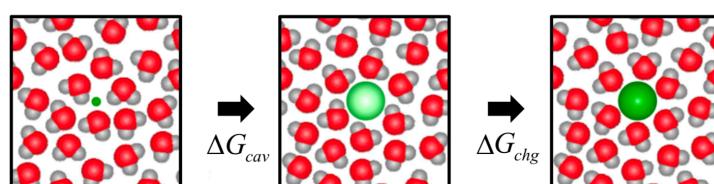
Free energy methods (and friends)

- Umbrella sampling
- Metadynamics
- Free Energy Perturbation
- Steered MD (Jarzynski)
- AFED
- ...
- Transition Path Sampling
- Forward Flux

$$\left. \begin{array}{l} \Delta G = \Delta H - T\Delta S \\ \nu = k \prod [I]^i \\ k = A \exp(-\beta \Delta G) \end{array} \right\}$$

35

Free Energy Perturbation



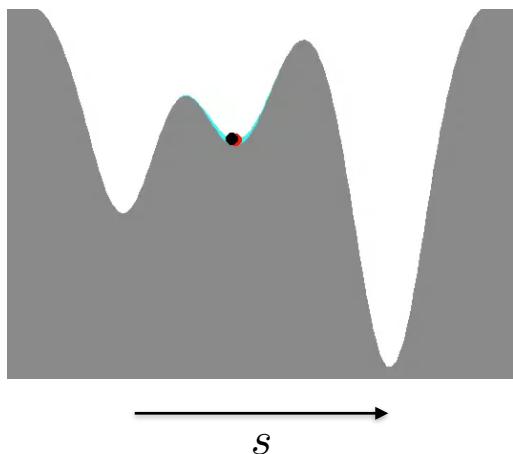
$$\Delta G = \sum_{i=0}^{N-1} \Delta G_{i,i+1} = -k_B T \sum_{i=0}^{N-1} \ln \left\langle \exp[-\beta \Delta U_{i,i+1}] \right\rangle_i$$

$$\Delta G = -k_B T \sum_{i=0}^{N-1} \ln \left\langle \exp[-\beta \Delta \lambda_{i,i+1} U] \right\rangle$$

36

Metadynamics

PLUMED



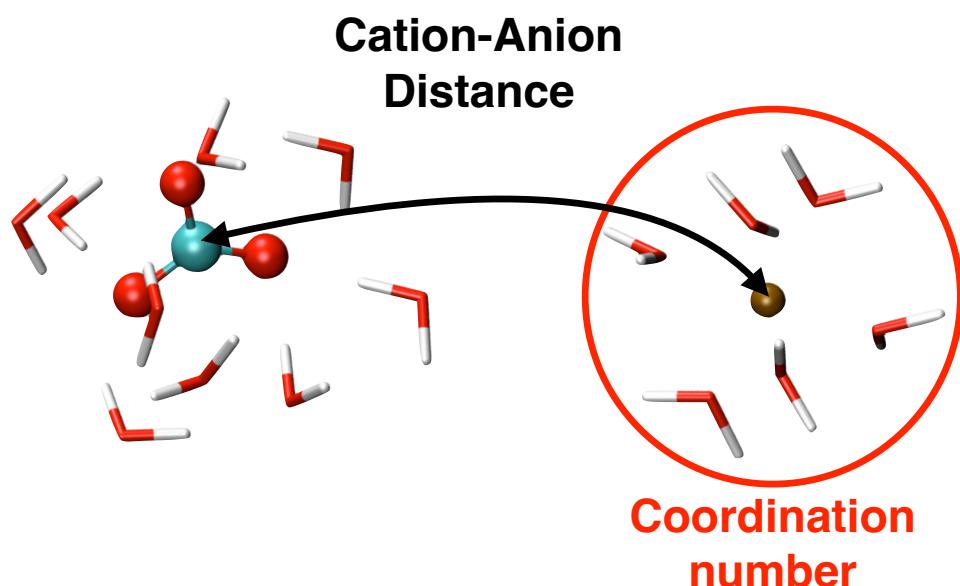
Well Tempered
Multiple Walkers
Trivially Parallel - Task Farming

"Accurate" collective variables

$$\Delta G(s) = - \sum_i w_i \exp \left[-(s - s_i)^2 / 2\sigma^2 \right]$$

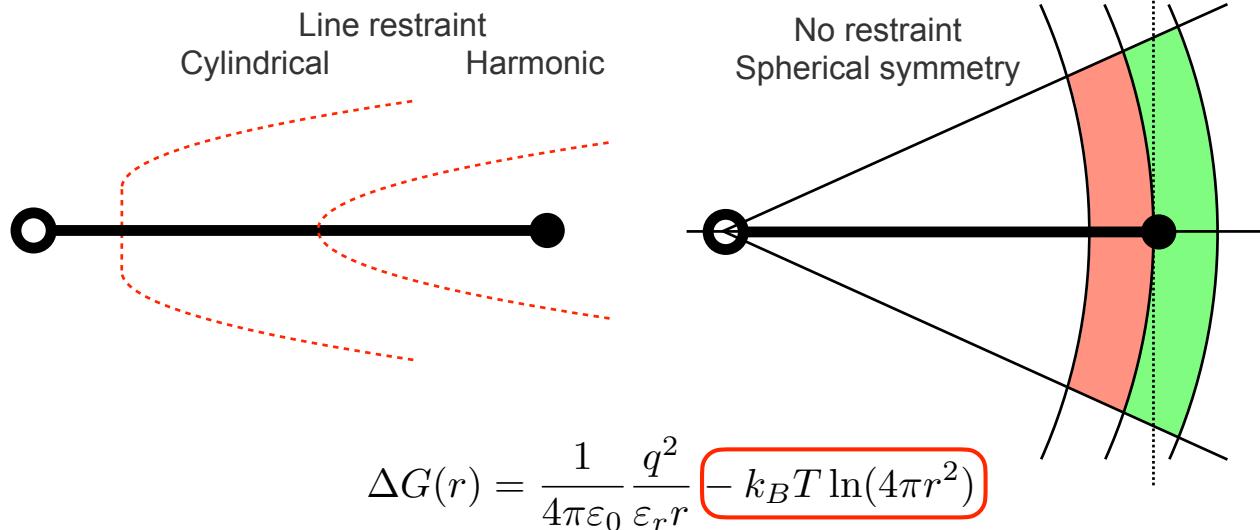
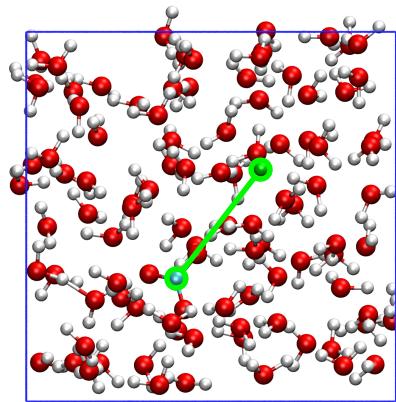
37

The case of ion-pairing



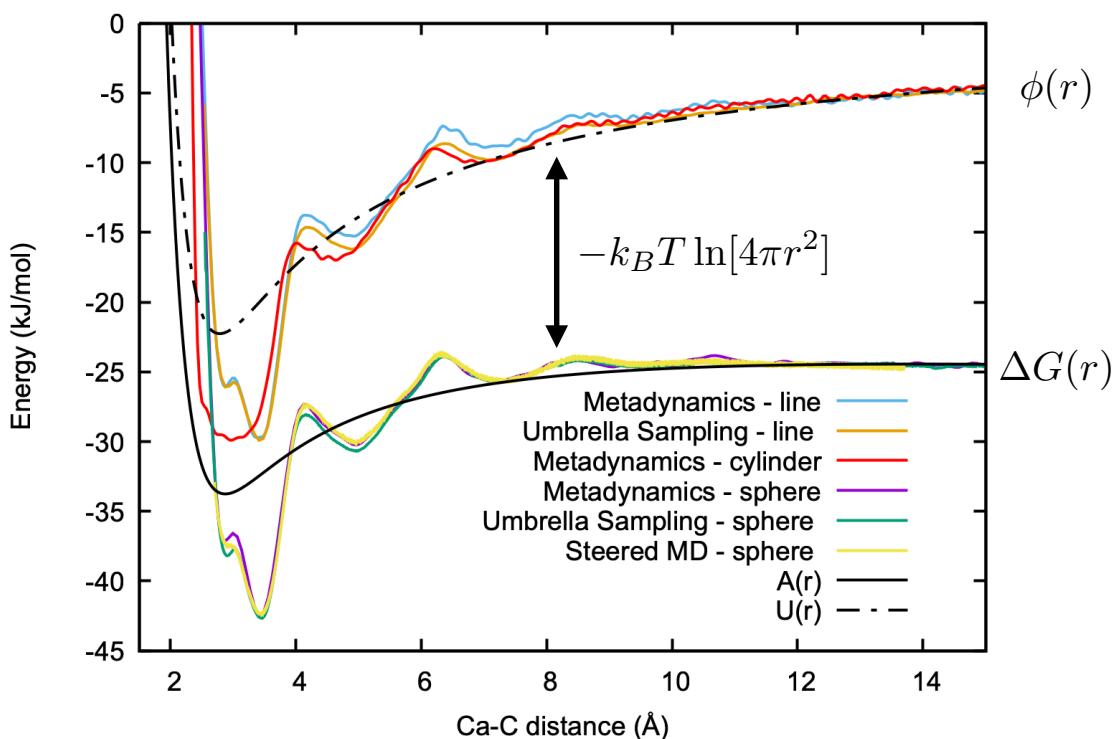
38

Pairing free energy simulation setup



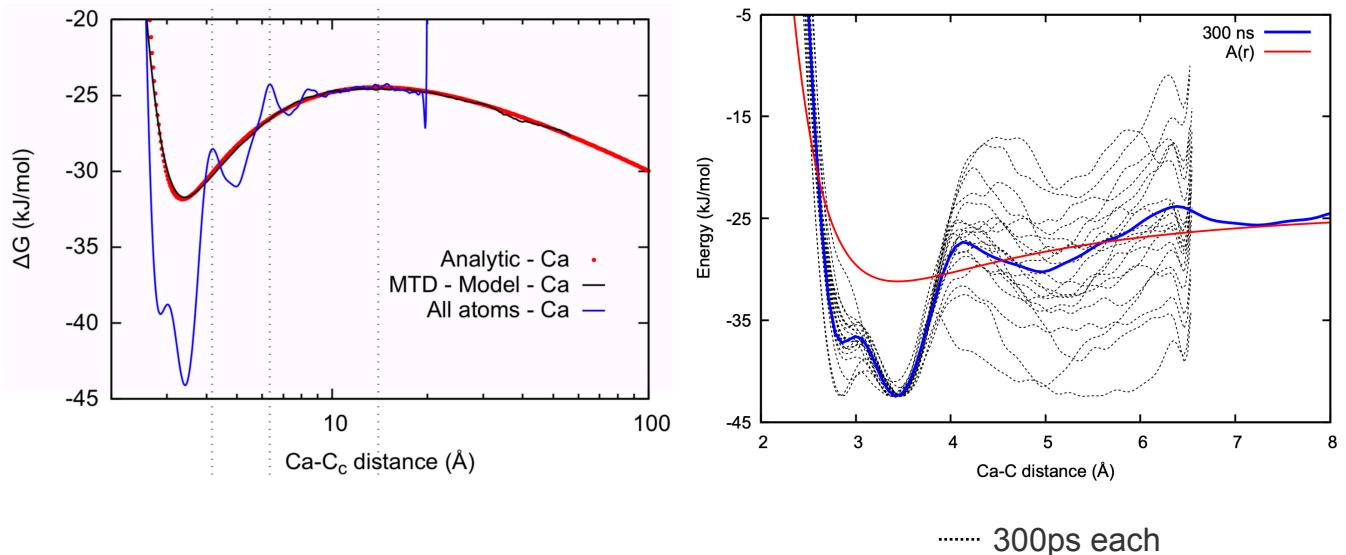
39

Pairing free energy - simulation setup



40

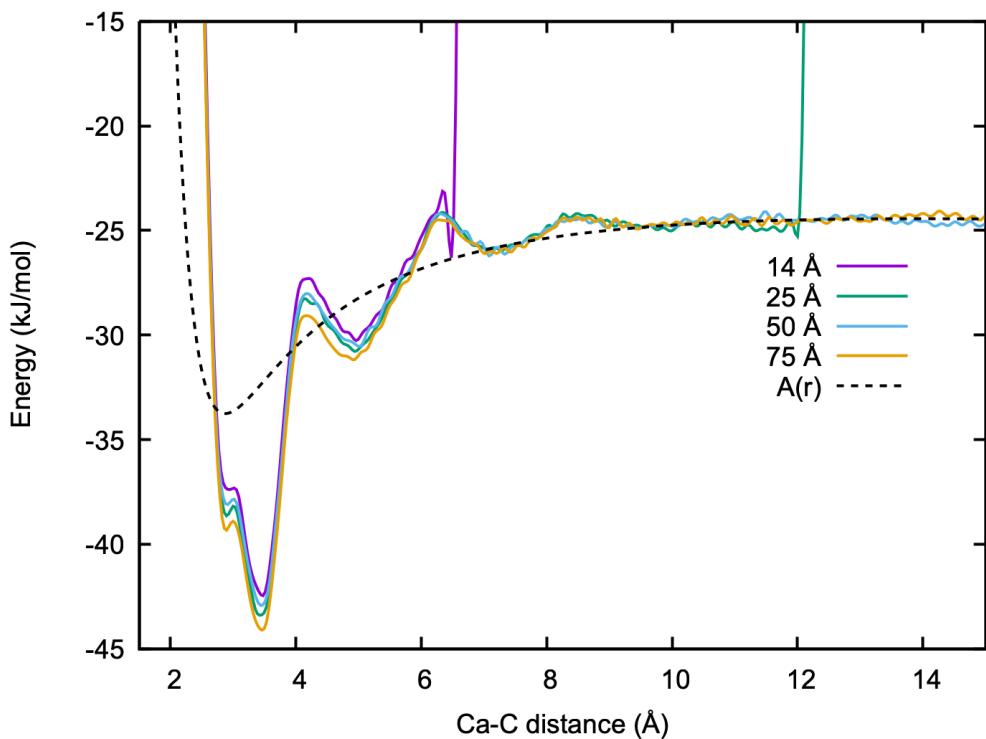
Pairing free energy - simulation time



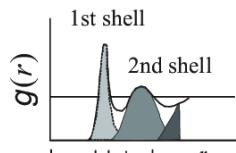
More from Julian about this

41

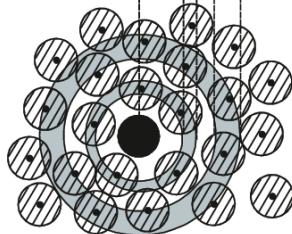
Pairing free energy - system size



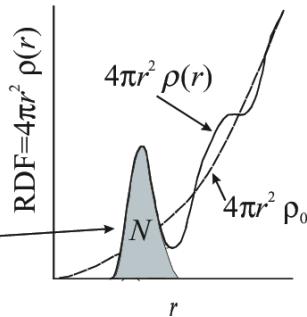
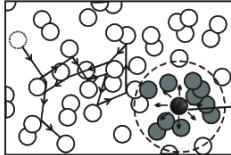
42



$$\rho = \rho_A = \rho_B = \frac{N_A}{V} = \frac{N_B}{V}$$



$$n_B = \rho \int_0^{R_c} 4\pi r^2 g(r) dr = \alpha$$



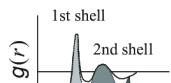
$$K_{eq} = \frac{[AB]c^\ominus}{[A][B]}$$

$$[AB] = \frac{N_{AB}}{V} = \frac{N_A n_B}{V} = \rho \alpha$$

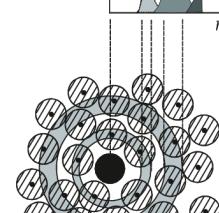
$$[A] = [B] = \rho - [AB] = \rho(1 - \alpha)$$

$$K_a = \frac{c^\ominus \alpha}{\rho(1 - \alpha)^2}$$

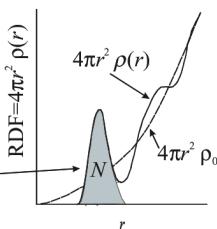
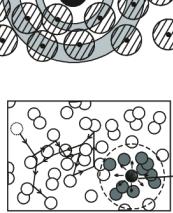
43



$$\rho = \rho_A = \rho_B = \frac{N_A}{V} = \frac{N_B}{V}$$



$$n_B = \rho \int_0^{R_c} 4\pi r^2 g(r) dr = \alpha$$



$$K_{eq} = \frac{[AB]c^\ominus}{[A][B]}$$

$$[AB] = \frac{N_{AB}}{V} = \frac{N_A n_B}{V} = \rho^2 \int_0^{R_c} 4\pi r^2 g(r) dr$$

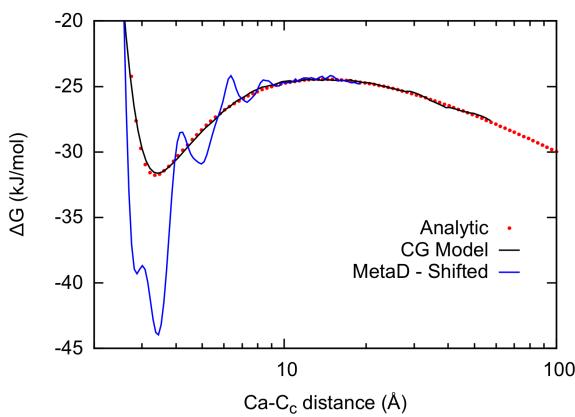
$$[A] = [B] = \rho - [AB] \approx \rho \quad \text{Weak association}$$

$$K_{eq} \approx \frac{c^\ominus \rho^2 \int_0^{R_c} 4\pi r^2 g(r) dr}{\rho^2} = c^\ominus \int_0^{R_c} 4\pi r^2 g(r) dr$$

44

Association constant

$$K_a = \frac{[AB]c^\ominus}{[A][B]}$$



Brute force

$$K_a = \frac{c^\ominus \alpha}{\rho(1-\alpha)^2}$$

$$\alpha = \int_0^{R_B} 4\pi\rho r^2 g(r) dr$$

all-atom MD - free energy

$$\Delta G(r) = \phi(r) - k_B T \ln(4\pi r^2) + C$$

$$g(r) = e^{-\beta\phi(r)}$$

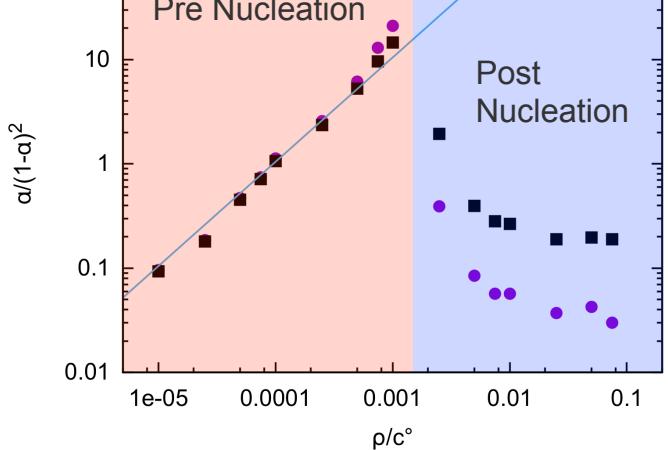
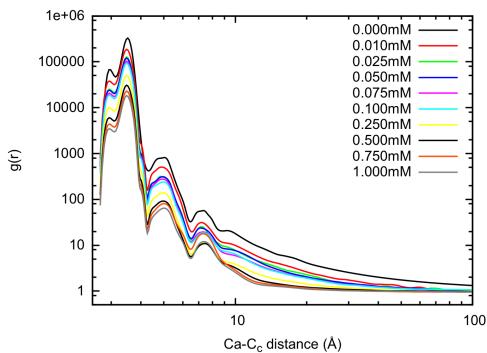
$$K_a \approx c^\ominus \int_0^{R_B} 4\pi r^2 e^{-\beta\phi(r)} dr = c^\ominus \frac{\alpha}{\rho}$$

45

Association constant - CG model

$$K_a = \frac{c^\ominus \alpha}{\rho(1-\alpha)^2}$$

$$\alpha = \int_0^{R_B} 4\pi\rho r^2 g(r) dr$$



46

Importance of the free energy alignment

$$\Delta G^\dagger(r) + \mathbf{C} = \Delta G(r) = \phi(r) - k_B T \ln(4\pi r^2)$$

$$g(r) = e^{-\beta\phi(r)} \quad 4\pi r^2 g(r) = e^{-\beta\Delta G(r)}$$

$$\begin{aligned} K_{eq} &\approx c^\Theta \int_0^{R_c} 4\pi r^2 g(r) \, dr \\ &= c^\Theta \int_0^{R_c} e^{-\beta\Delta G(r)} \, dr \\ &= c^\Theta \int_0^{R_c} e^{-\beta\Delta G^\dagger(r)} e^{-\beta\mathbf{C}} \, dr \end{aligned}$$

$$K_{eq} = K_{eq}^\dagger e^{-\beta\mathbf{C}}$$

\mathbf{C} (kJ/mol)	$\exp(-\beta\mathbf{C})$
1.0	1.5
2.5	2.7
5.0	7.4

47

Conclusions

- It is often difficult to gauge papers outside your field
- Every computational (and experimental) method has limitations
- Attend as many seminars outside your field as you can
- ...
-

48