



Curtin University

# Introduction to atomistic modeling

**Paolo Raiteri**

# 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

# 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

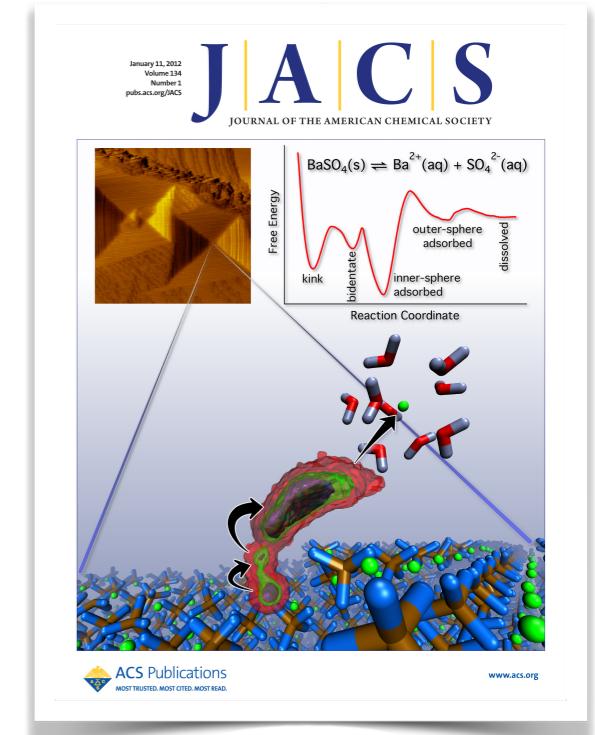
- **Approaches:**

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

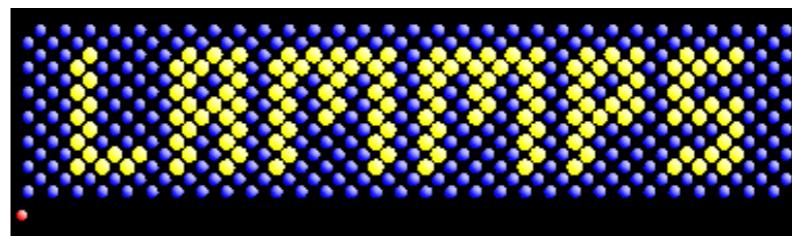
- **Extras:**

- Free energy methods

## GULP



## PLUMED



## CP2K

OpenMM

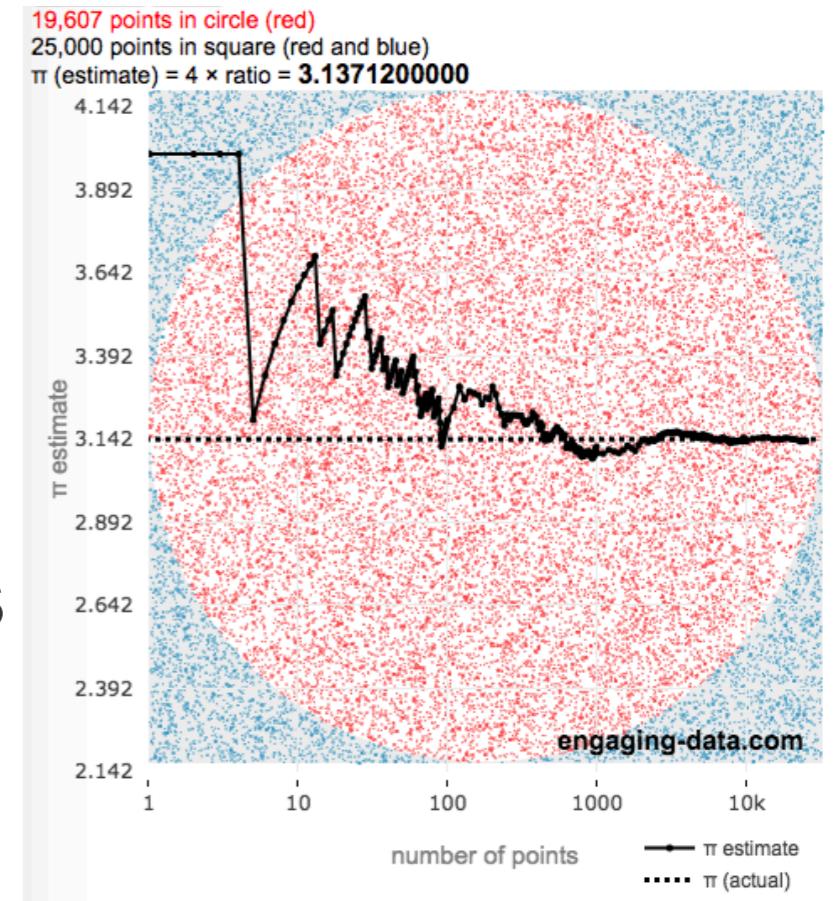
# Monte Carlo simulations

- 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

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



# Lattice Dynamics

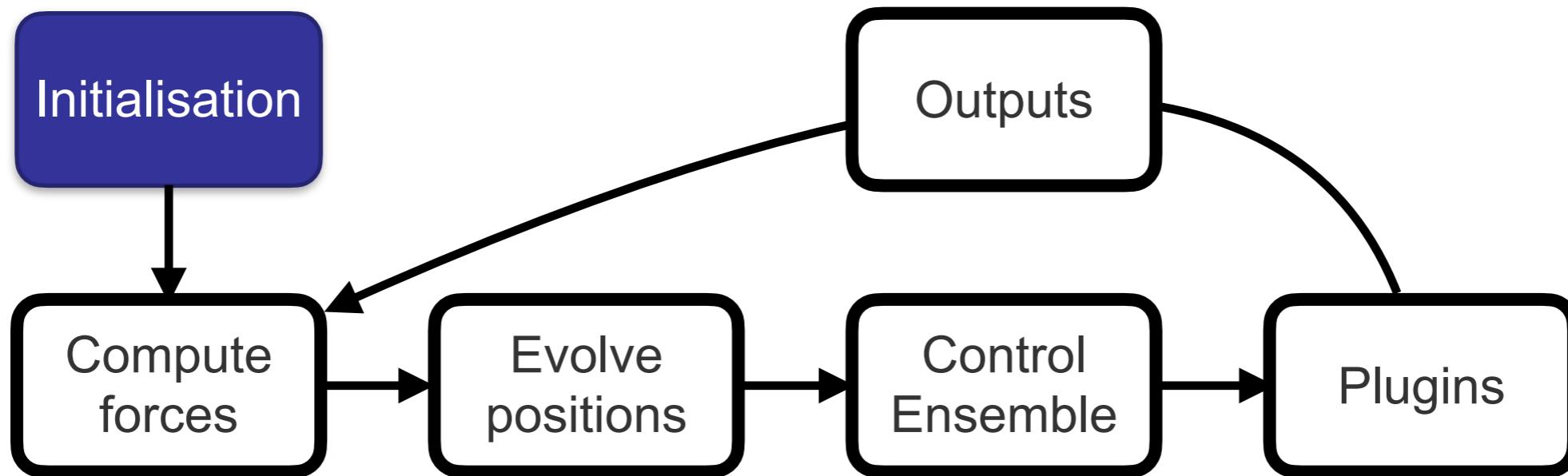
- Based on statistical thermodynamics
- Useful to describe crystals below the Debye temperature  
(and isolated molecules)
- Free energies can be computed using quasi-harmonic approximations from the phonons/vibrations
- Limited applications to liquids and amorphous materials
- We use it routinely to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

# Molecular Dynamics

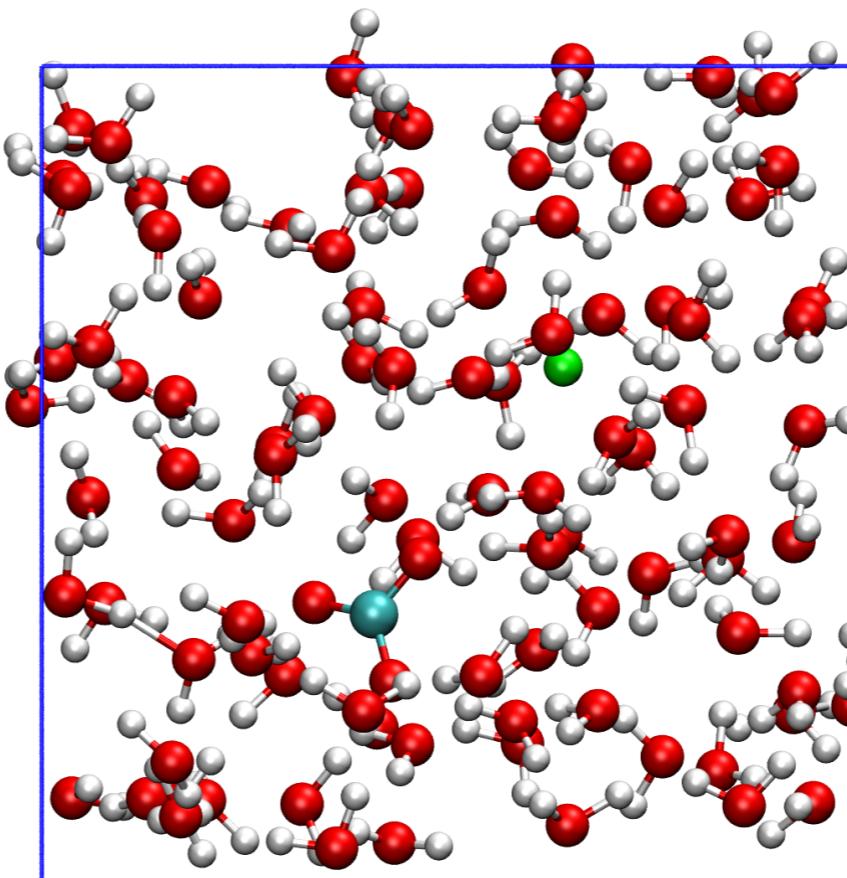
- Most widely used computational tool for atomistic simulations
- Based on Newtonian dynamics
- Statistical mechanics can be used to compute properties
- Atomic trajectories can give access to kinetics
- Only difference is how the energy and forces are computed

# Molecular Dynamics

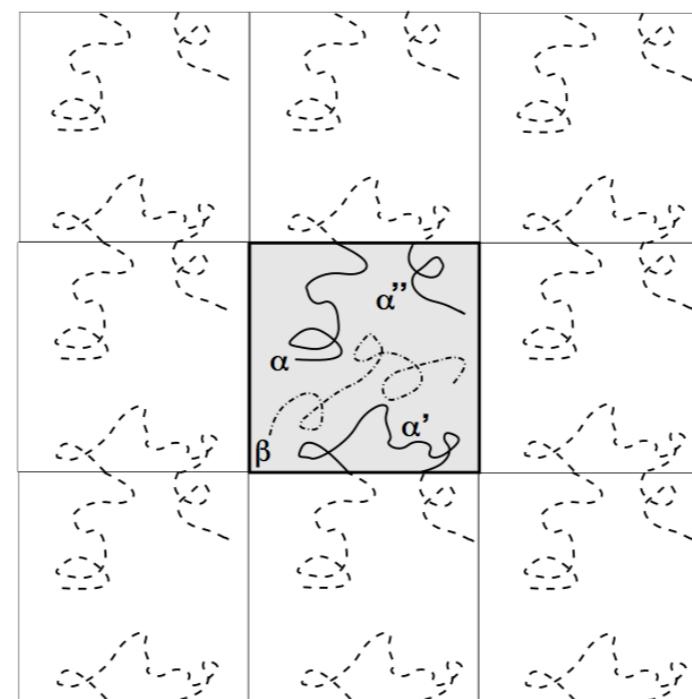
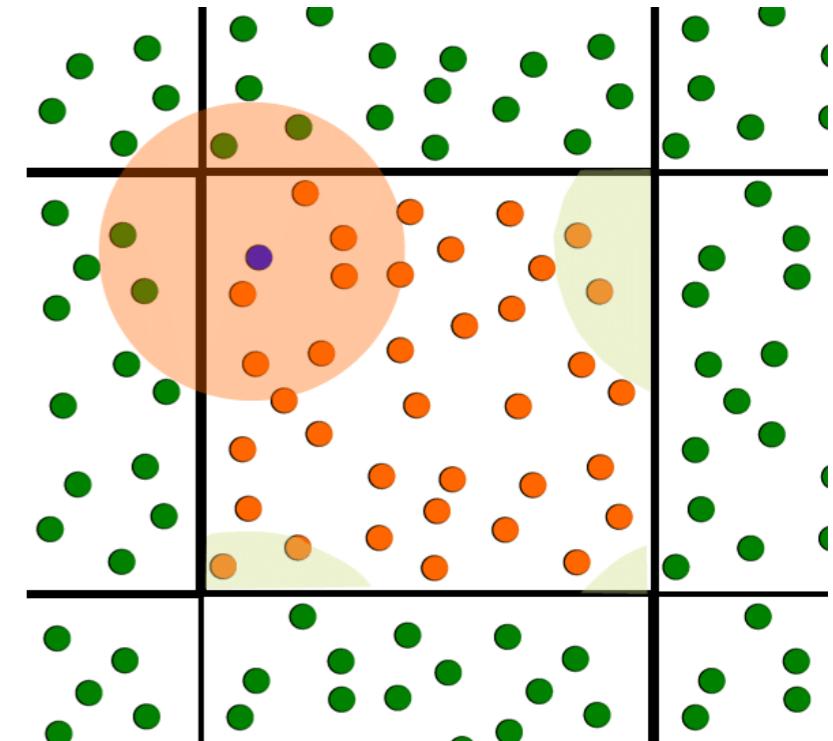
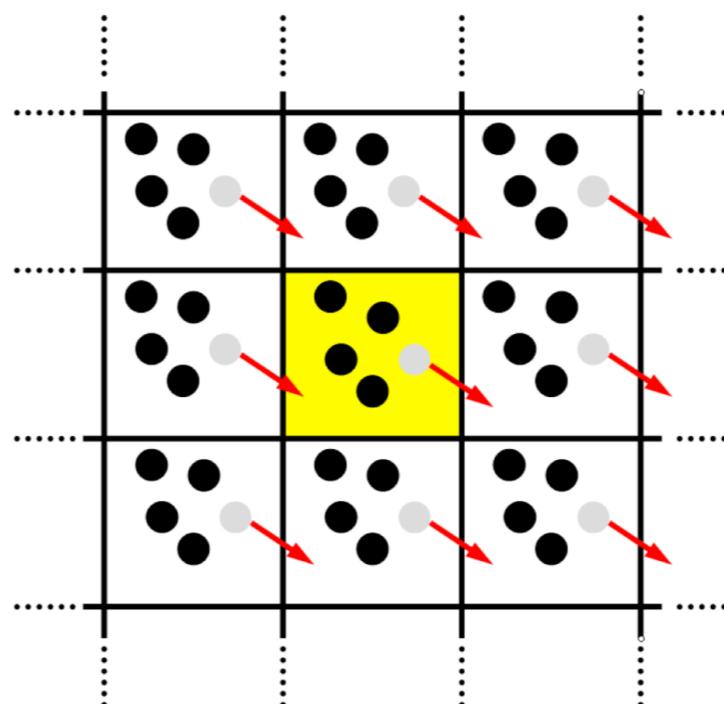
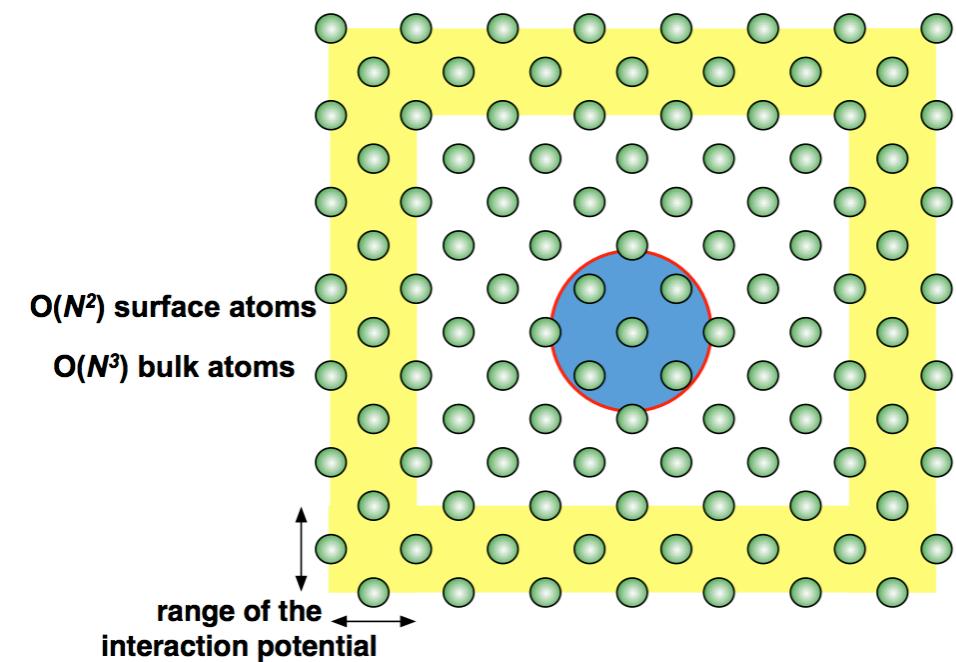
Each cycle propagates the system forward in time



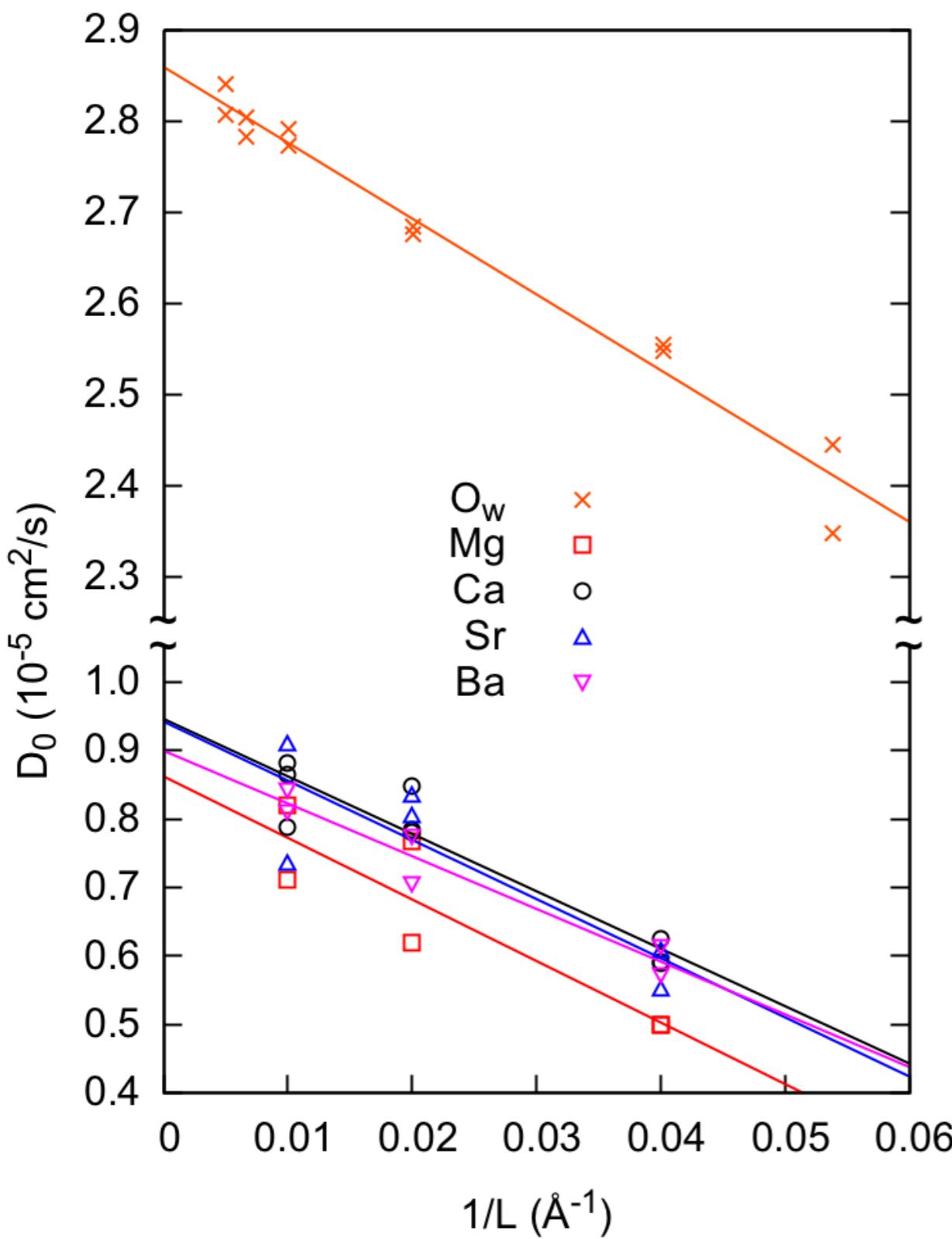
- Box size
- Positions
- Temperature
  - Velocities
- Simulation parameters



# Finite size and boundary conditions



# Finite size - Diffusion



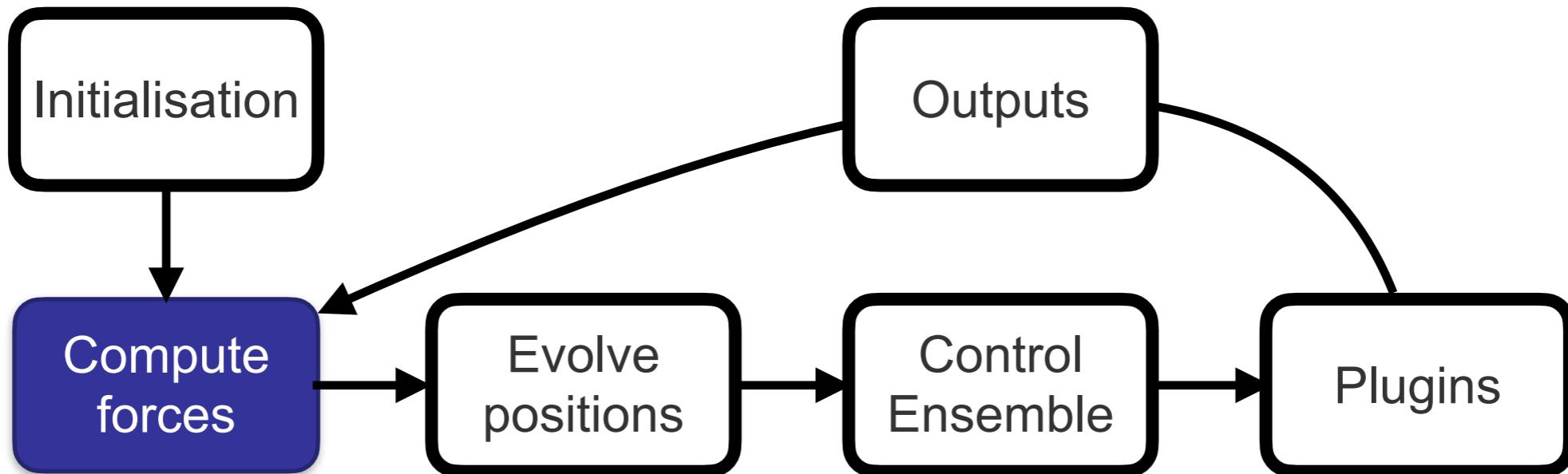
*J. Phys. Chem. B* (2004), **108**, 15873–15879.

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

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

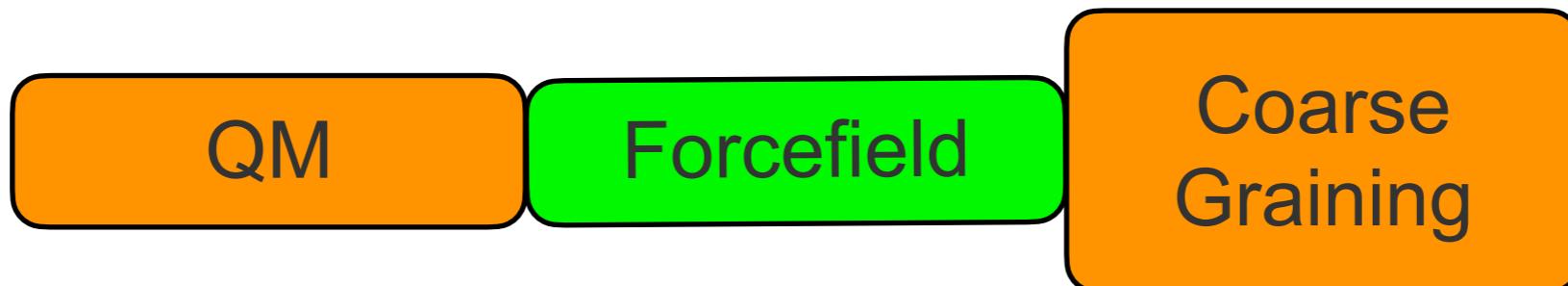
$D_0$ ( $10^{-5} \text{ cm}^2/\text{s}$ )	Exp [1]	Theory
Mg	0.71	0.86
Ca	0.79	0.95
Sr	0.79	0.94
Ba	0.84	0.90
H <sub>2</sub> O	2.30	2.86

# Molecular Dynamics

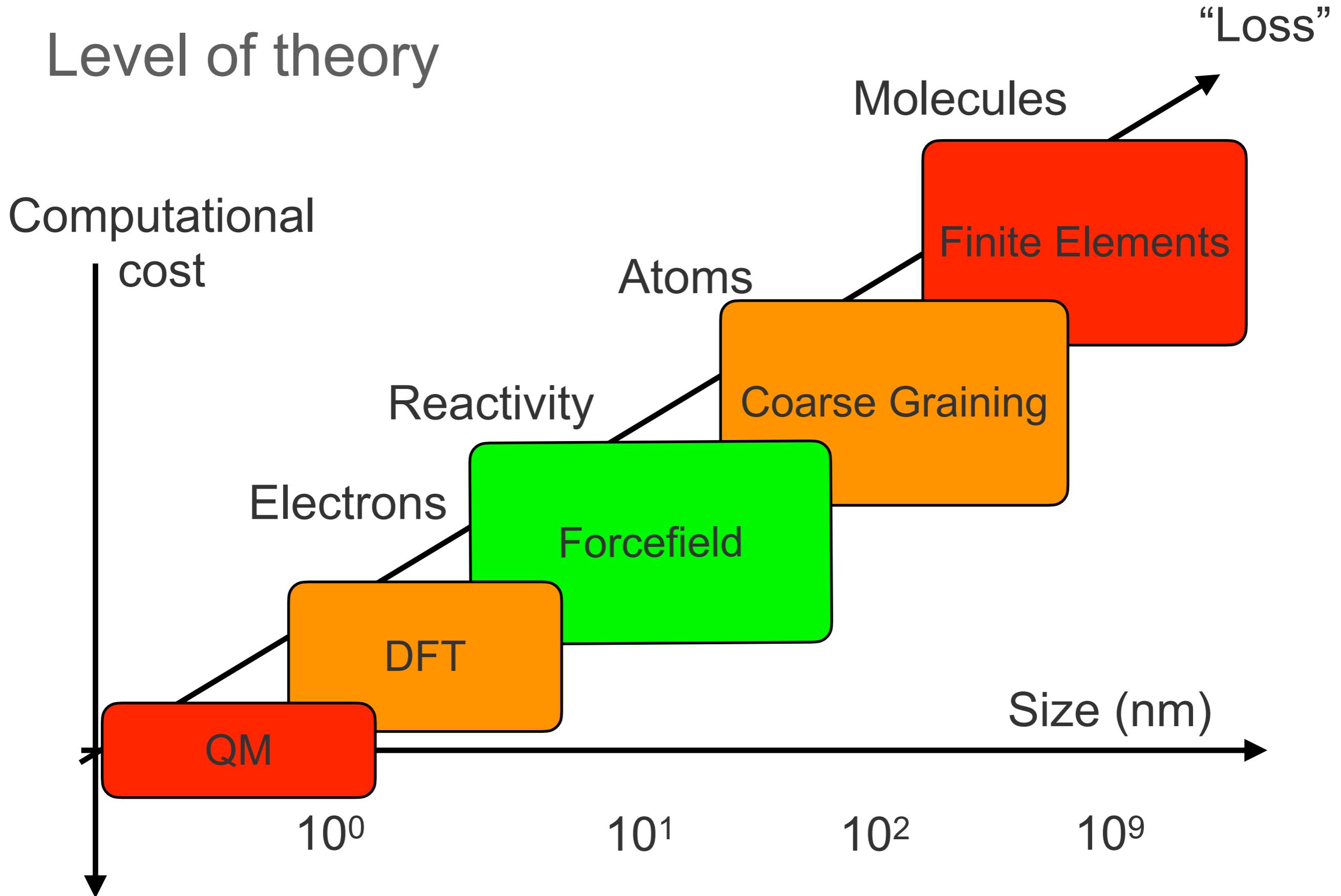


**Newton's second law**

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



# Level of theory



# Ab initio methods

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

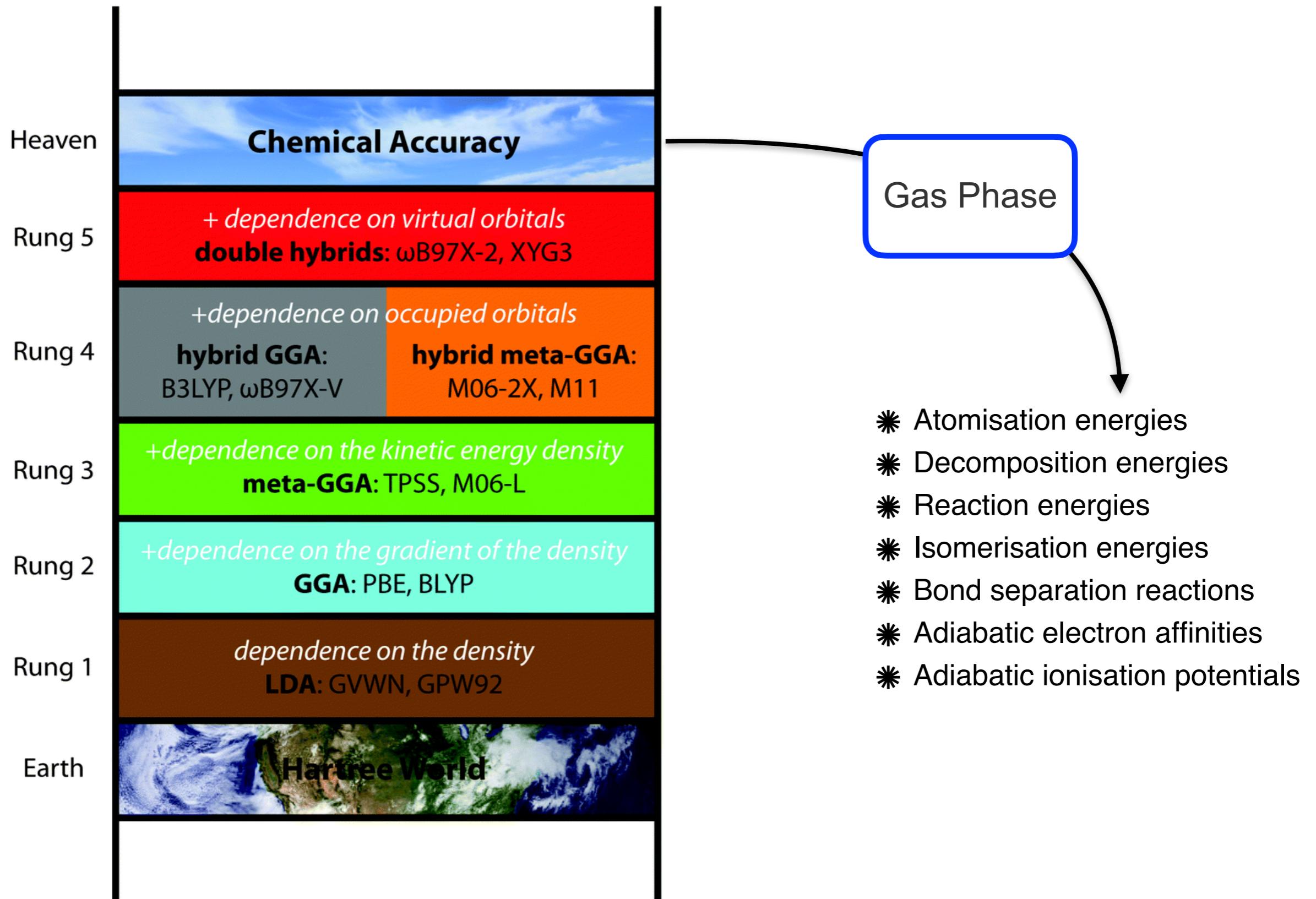
- Schrödinger equation

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

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

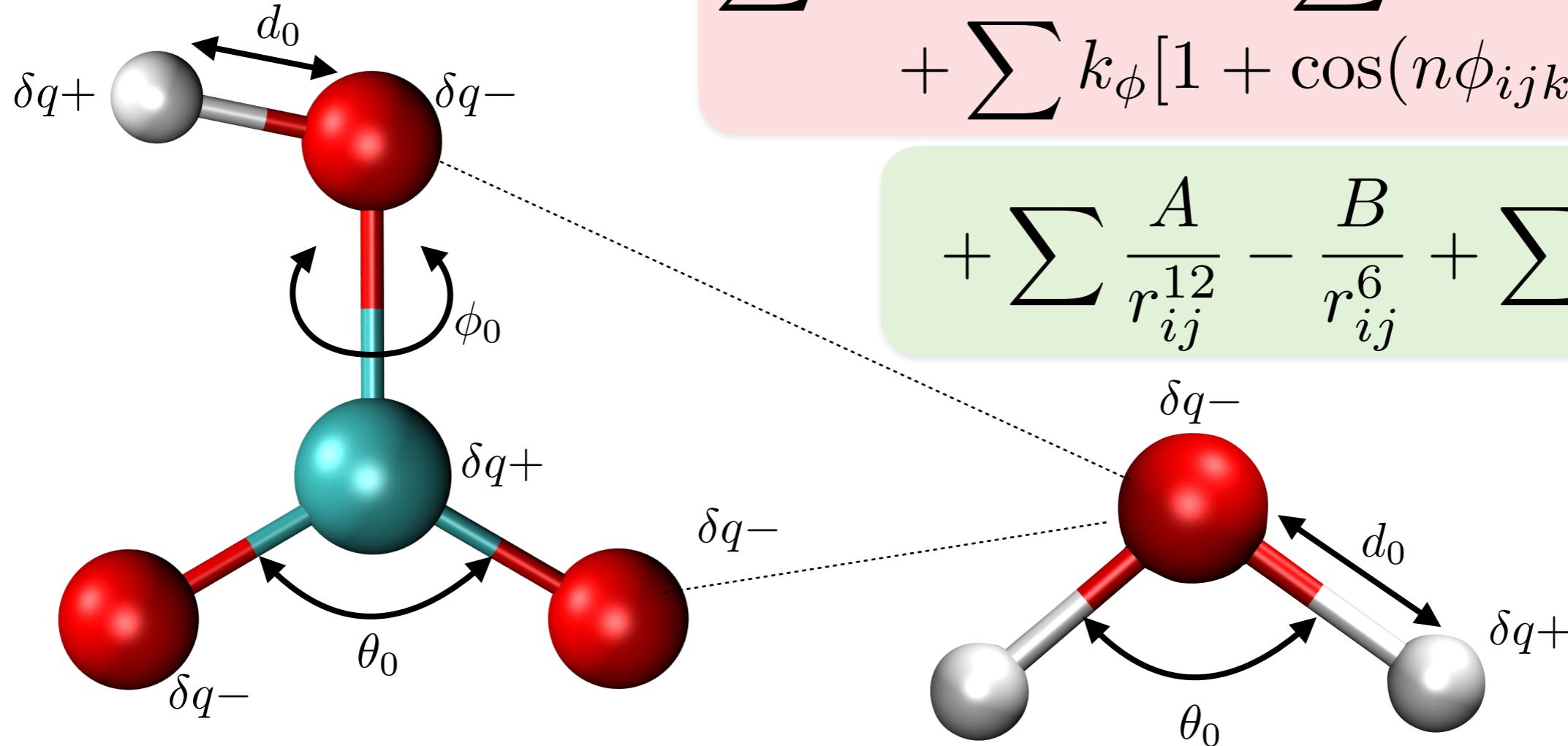
$$\rho = \int \cdots \int d\mathbf{x}^{3N} \Psi^* \Psi$$

# Jacob's ladder of DFT



# Force field

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

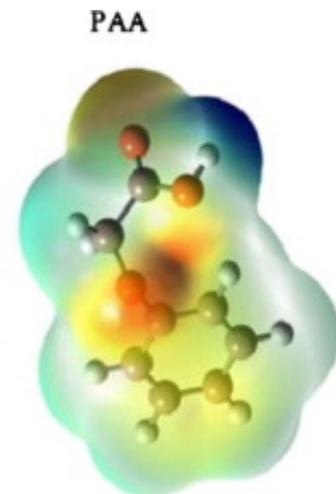
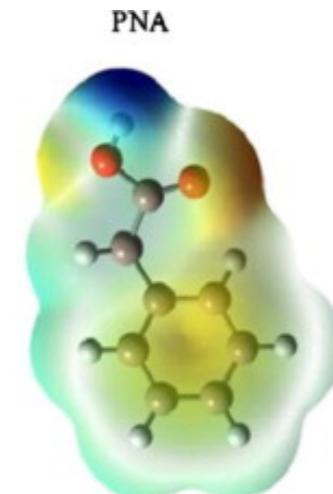
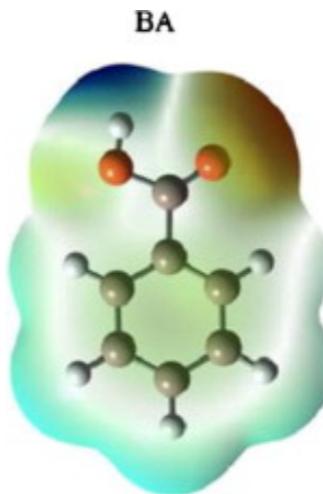


$$U = \sum k_b(b_{ij} - b_0)^2 + \sum k_\theta(\theta_{ijk} - \theta_0)^2$$
$$+ \sum k_\phi[1 + \cos(n\phi_{ijkl} - \phi_0)]^2$$

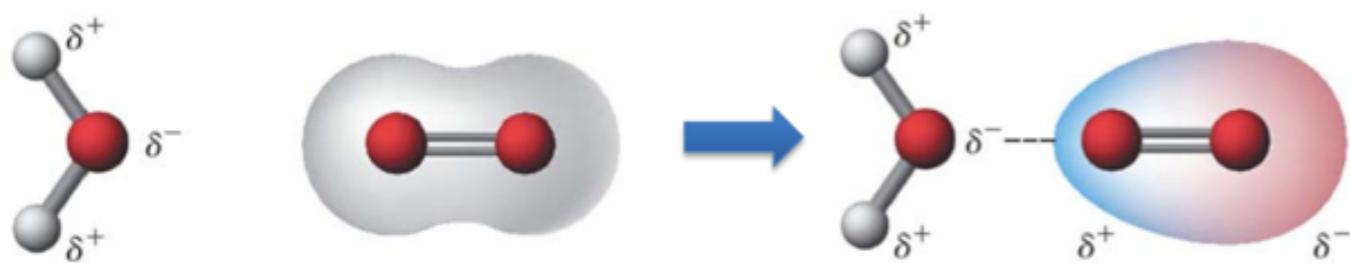
$$+ \sum \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^6} + \sum \frac{q_i q_j}{r_{ij}}$$



# Polarisable forcefield

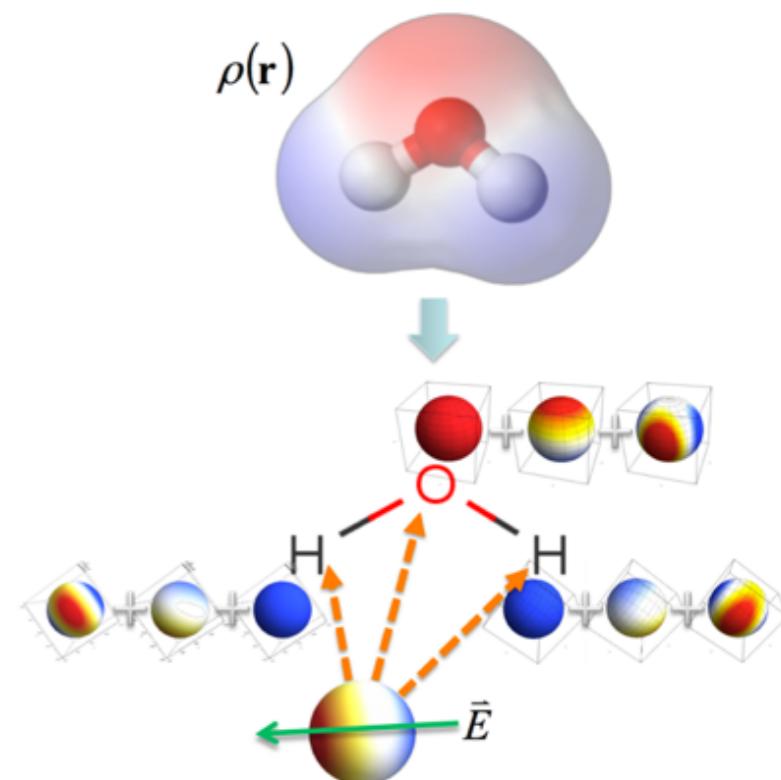


DOI: j.saa.2013.09.127

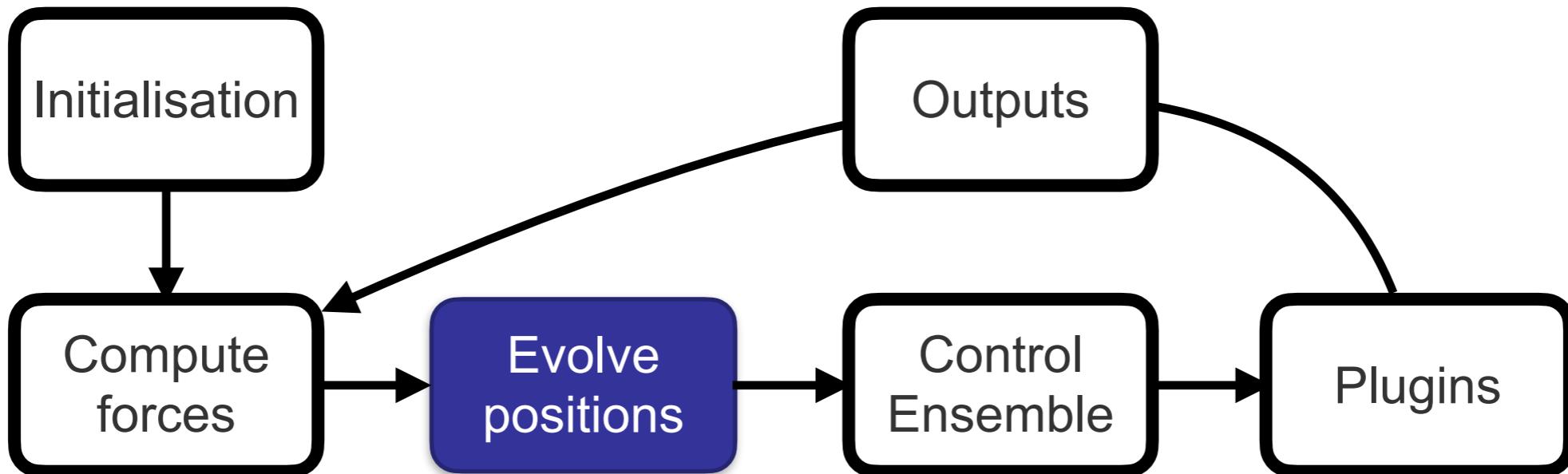


$$U = \sum k_b (b_{ij} - b_0)^2 + \sum k_\theta (\theta_{ijk} - \theta_0)^2 + \sum k_\phi [1 + \cos(n\phi_{ijkl} - \phi_0)]^2$$

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



# Molecular Dynamics



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

**Verlet algorithm**       $\vec{v}(t + \Delta t) = \vec{v}(t) + \vec{a}(t)\Delta t$        $\Delta t \approx 0.5 - 5 \text{ fs}$

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

# Time scale perspective

AFM

NMR

IR/Raman

MD

$10^{-18}$        $10^{-15}$        $10^{-12}$        $10^{-9}$        $10^{-8}$        $10^{-7}$        $10^{-6}$        $10^{-3}$        $10^0$        $10^3$

femto

pico

nano

micro

milli

10<sup>0</sup>

$10^3$

light absorption

electron transfer

water exchange

step migration

bond vibrations

proton transfer

dielectric relaxation

diffusion limited reactions

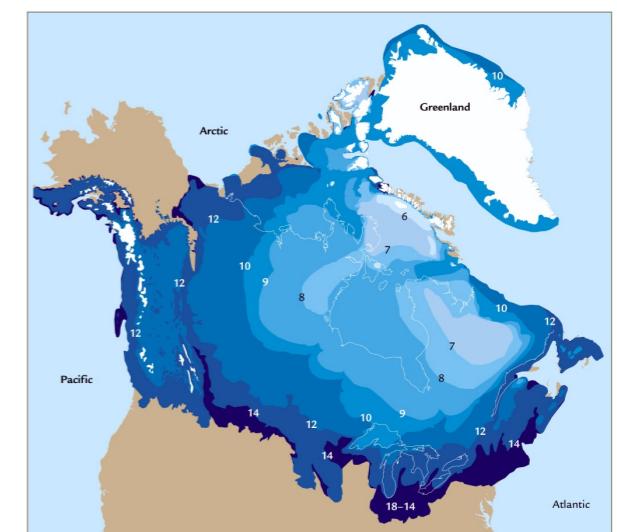
## Experimental time scale

## Phenomenon

## Simulation time

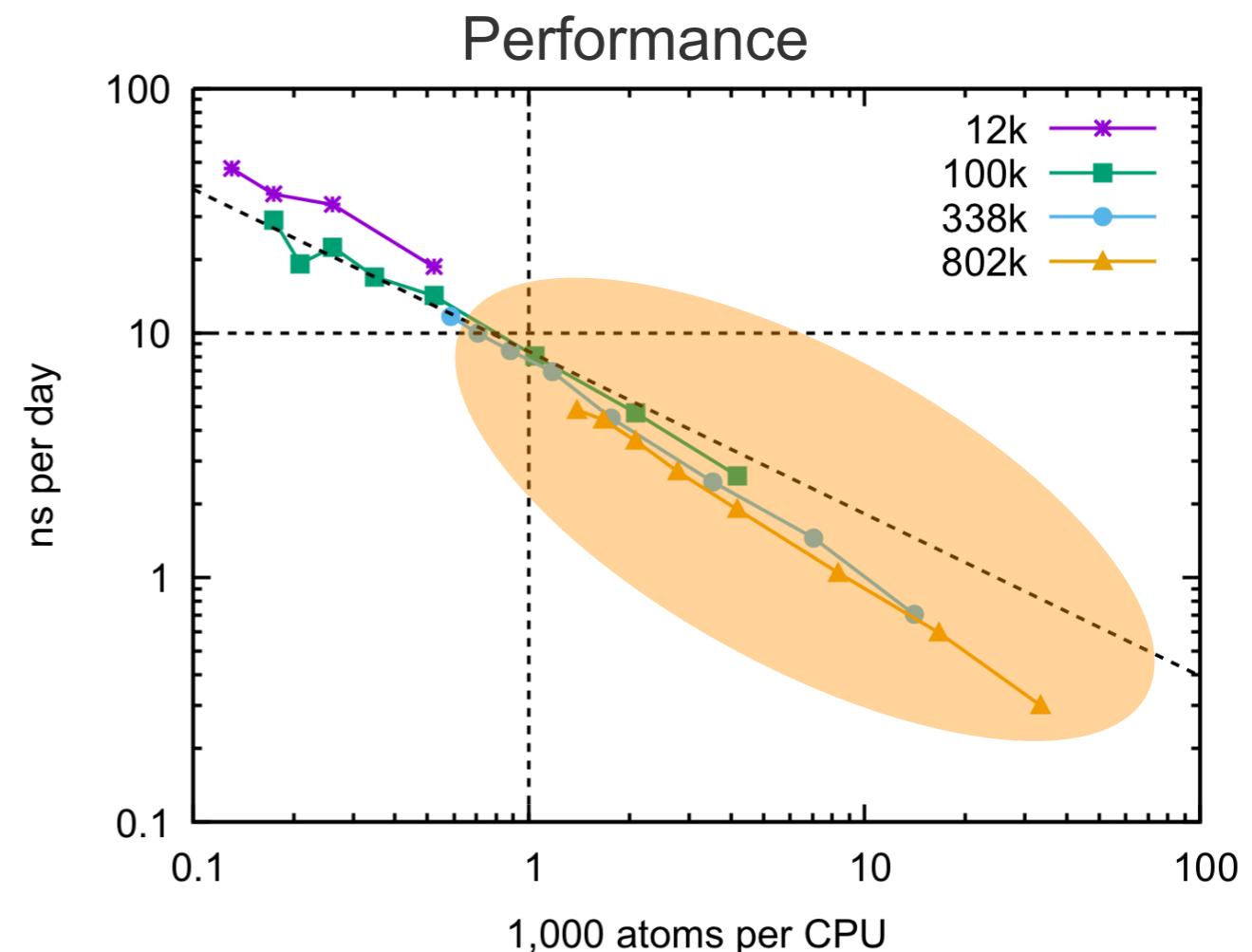
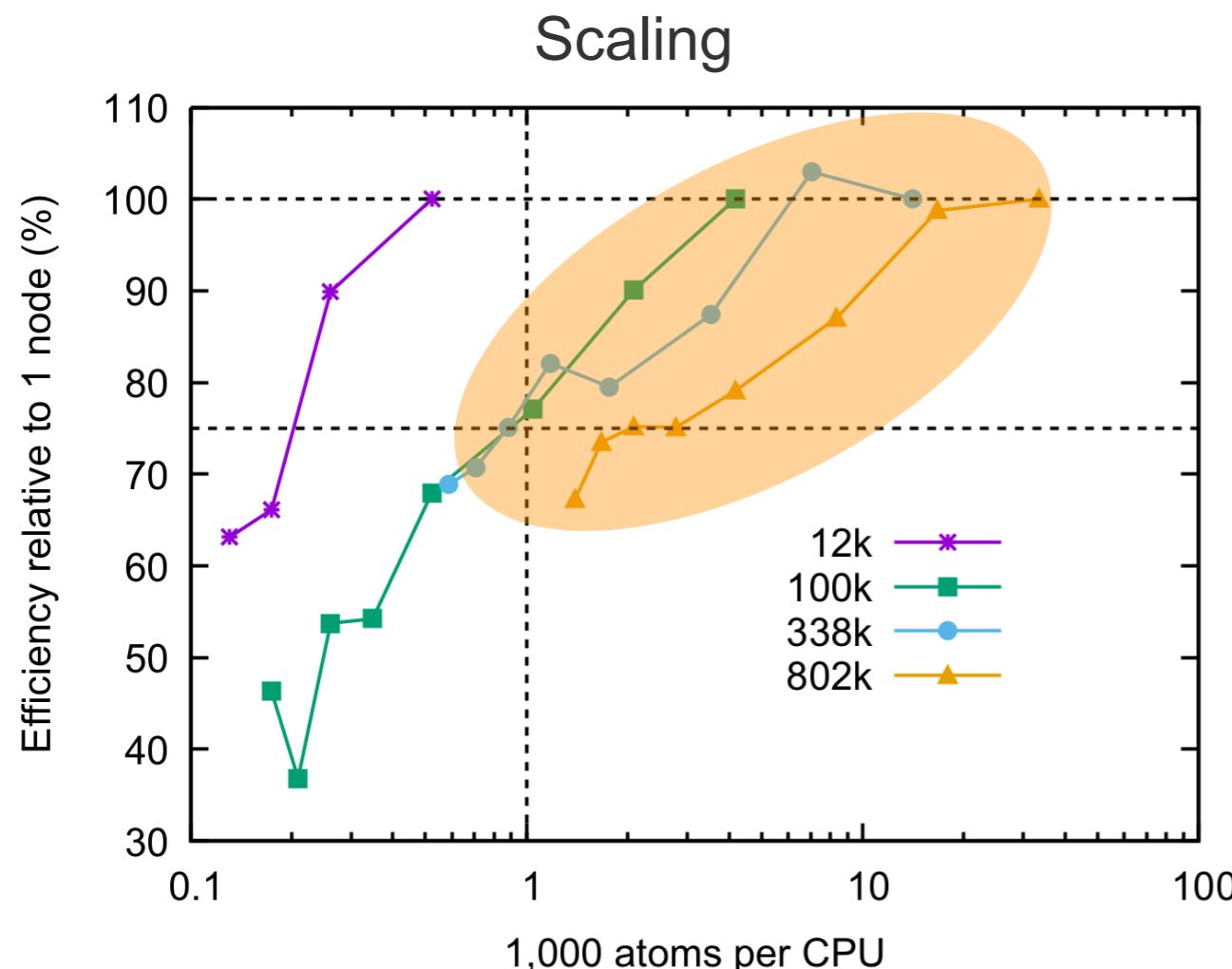
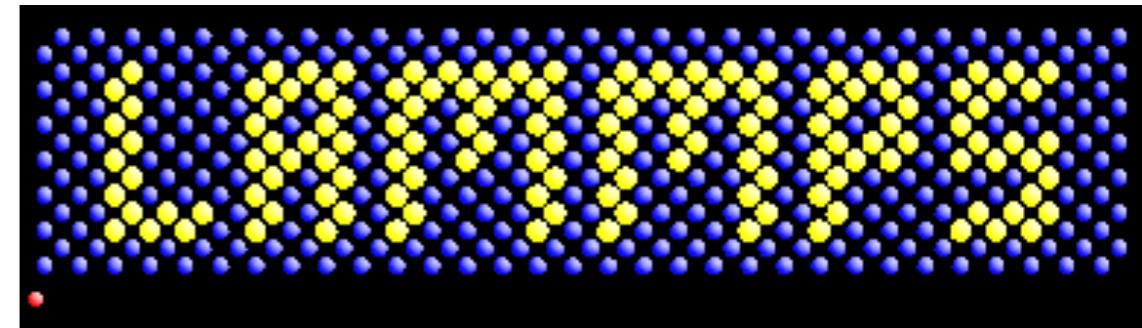
10 fs	O-H vibration	0.1 s
1 ps	H-bond persistence	10 s
1 ns	Ion permeation through a membrane	3 hours
1 $\mu$ s	Conformational rearrangement	115 days
1 ms	Protein folding (fast)	317 years
1 s	Protein folding (typical)	317,000 years

Assuming 10 ms per MD cycle



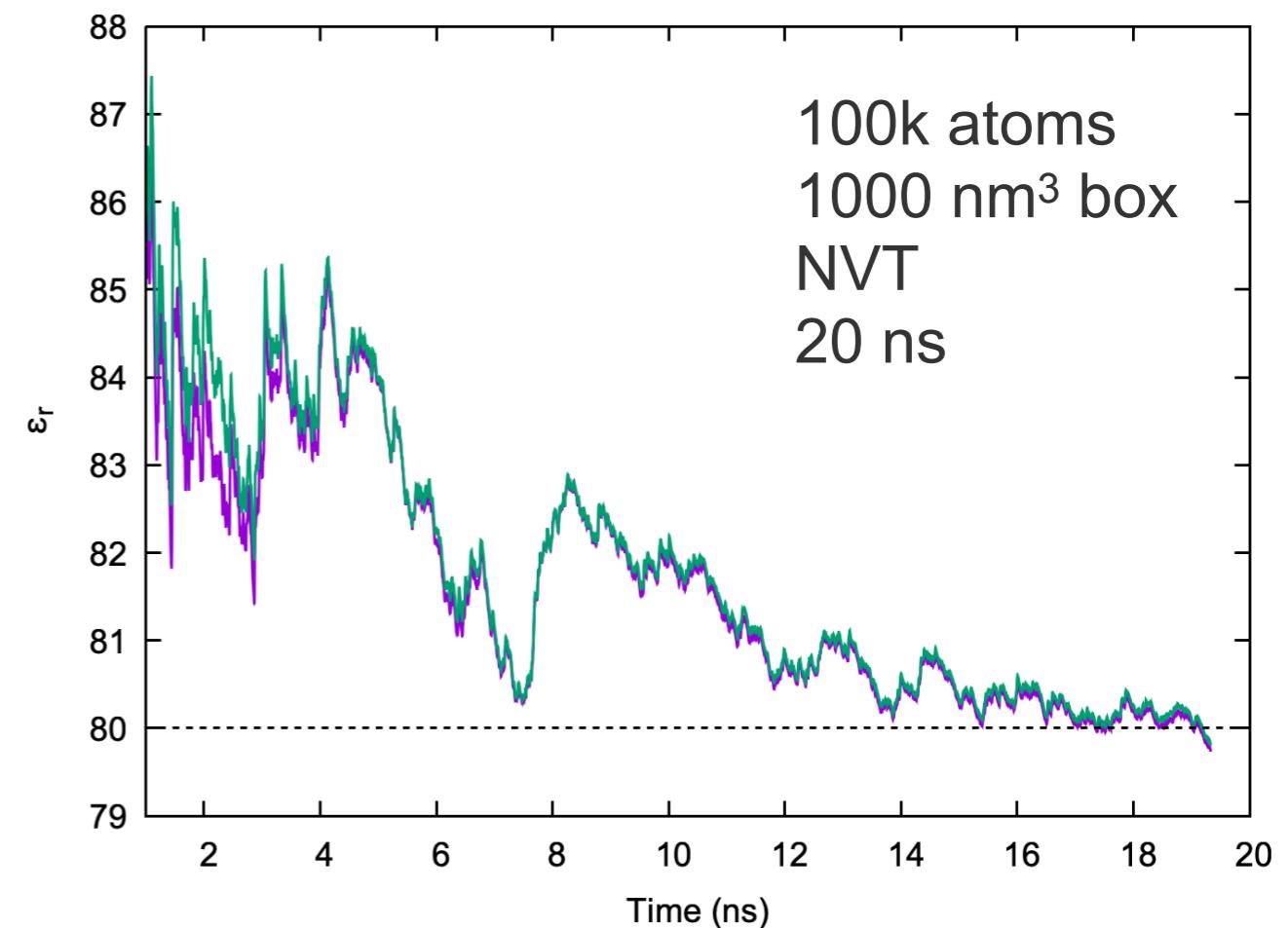
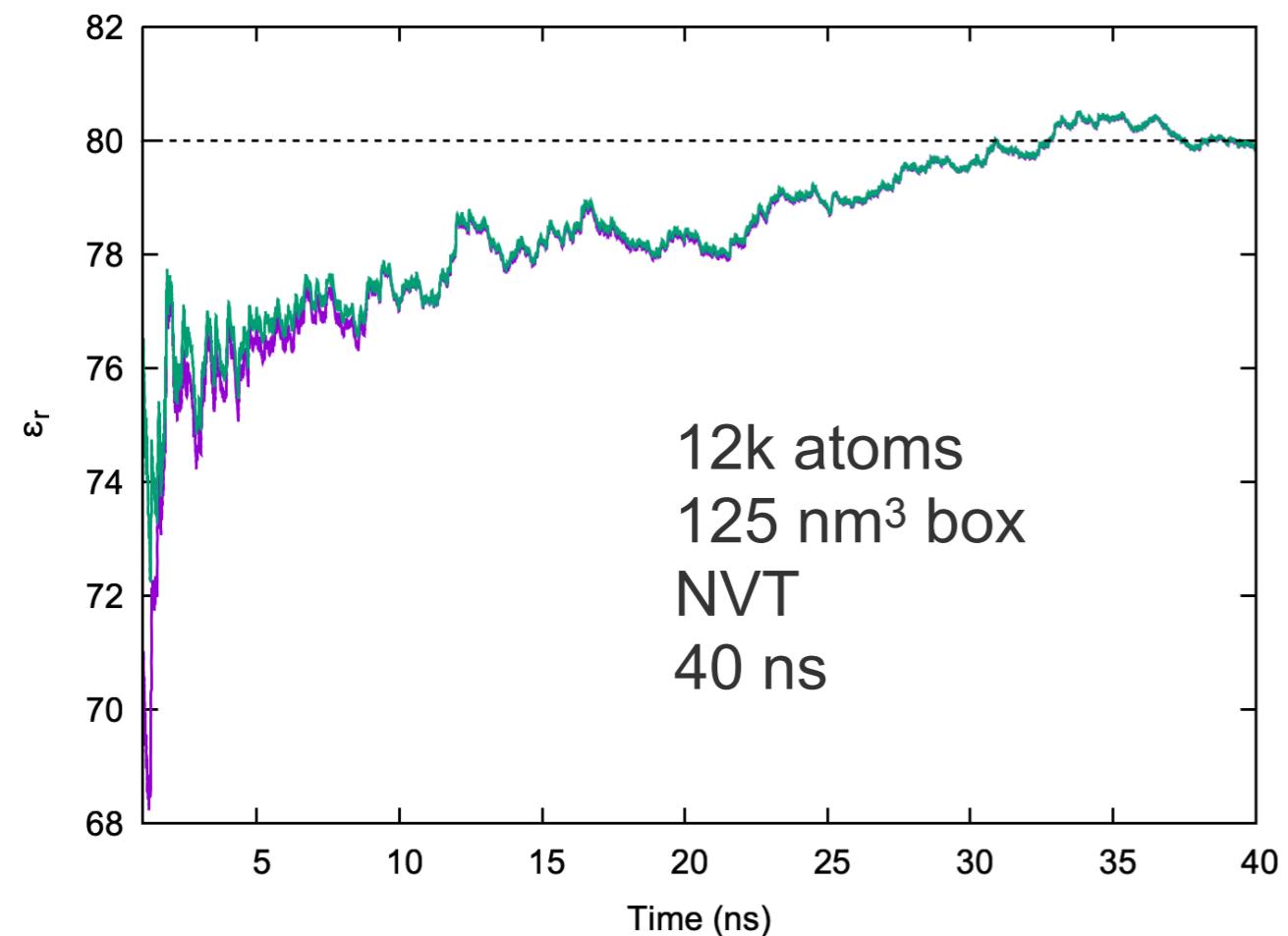
Last ice age:  
115,000-11,700 years ago

# LAMMPS on magnus

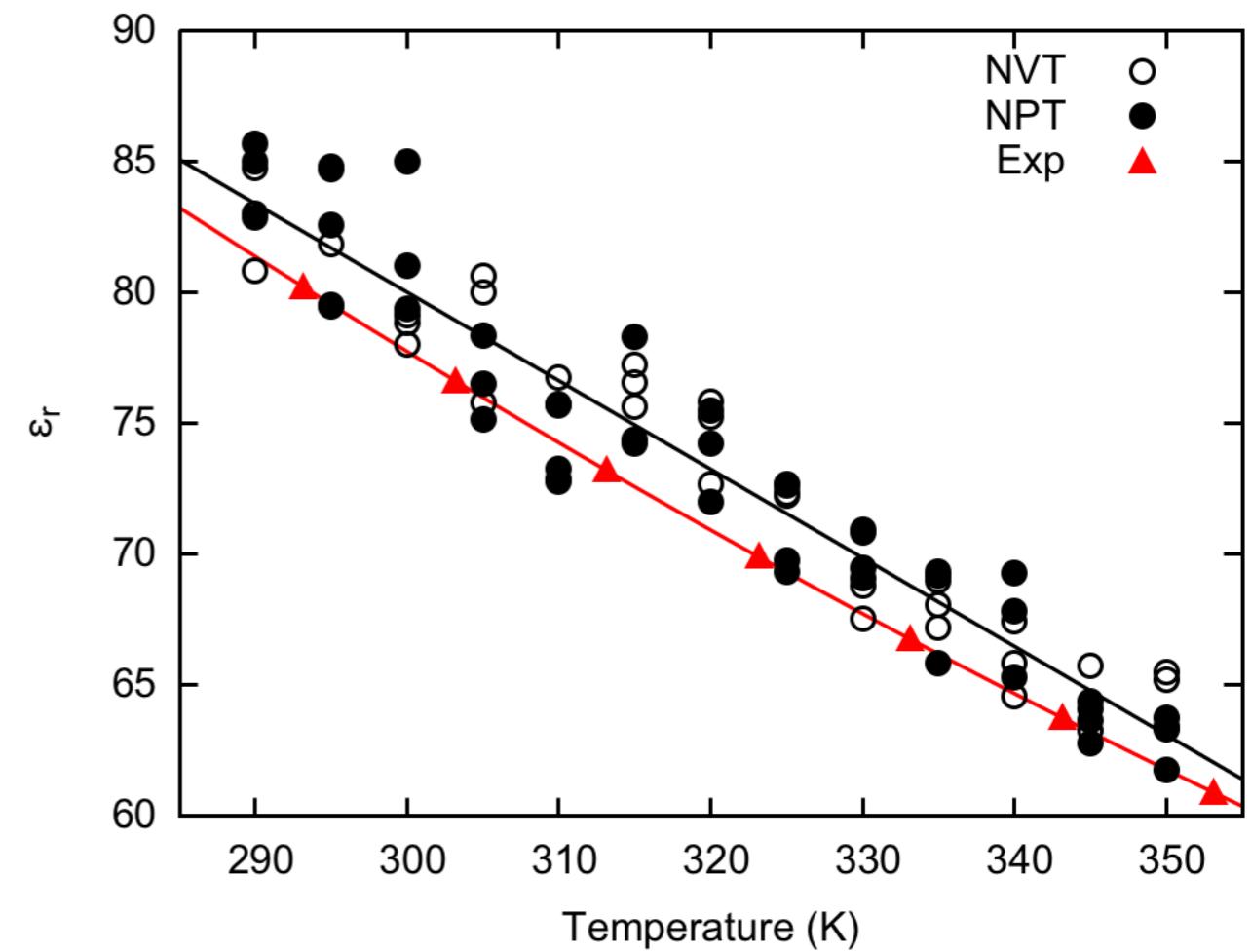
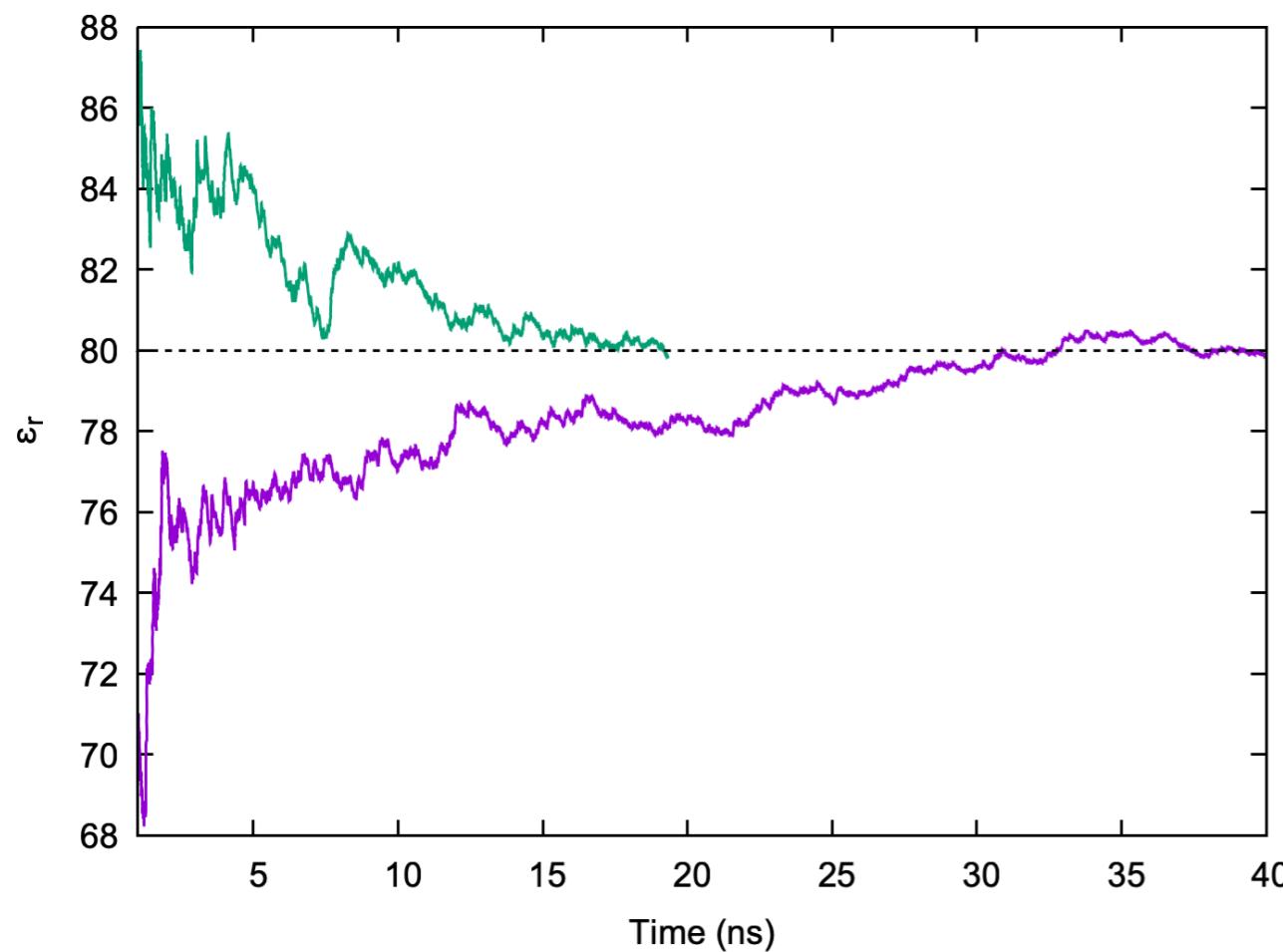


Number of nodes used:  
1 - 2 - 3 - 4 - 8 - 12 - 16 - 20 - 24

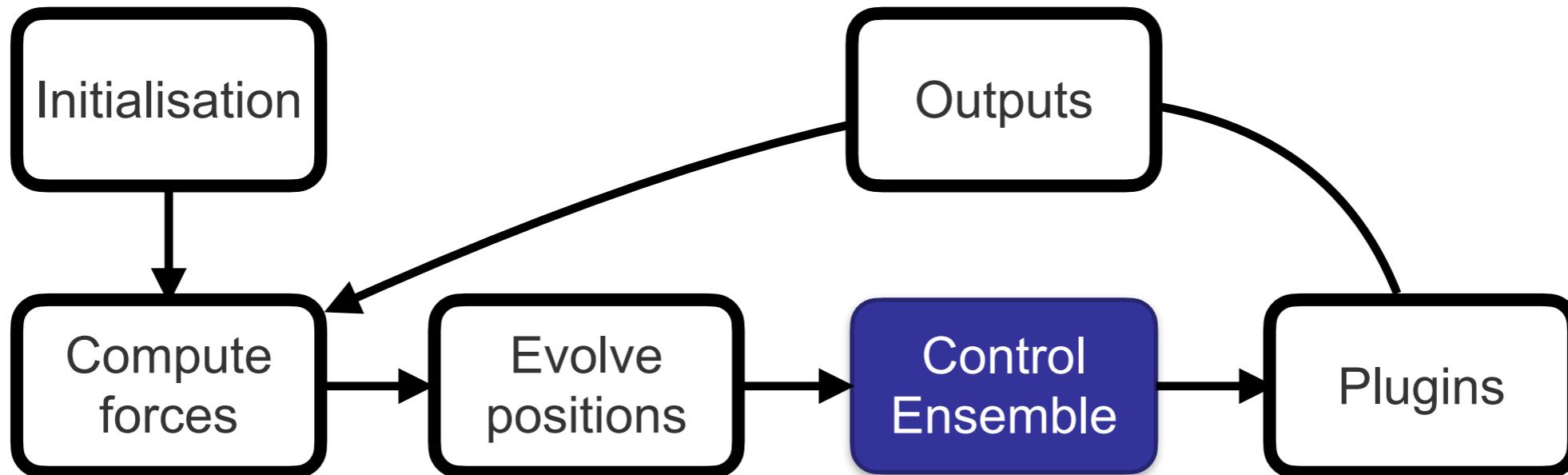
# Finite time - Dielectric constant



# Finite time - Dielectric constant



# Molecular Dynamics



$N$  : Number of atoms

$\mu$  : Chemical potential

$V$  : Volume

$P$  : Pressure

$E$  : Energy

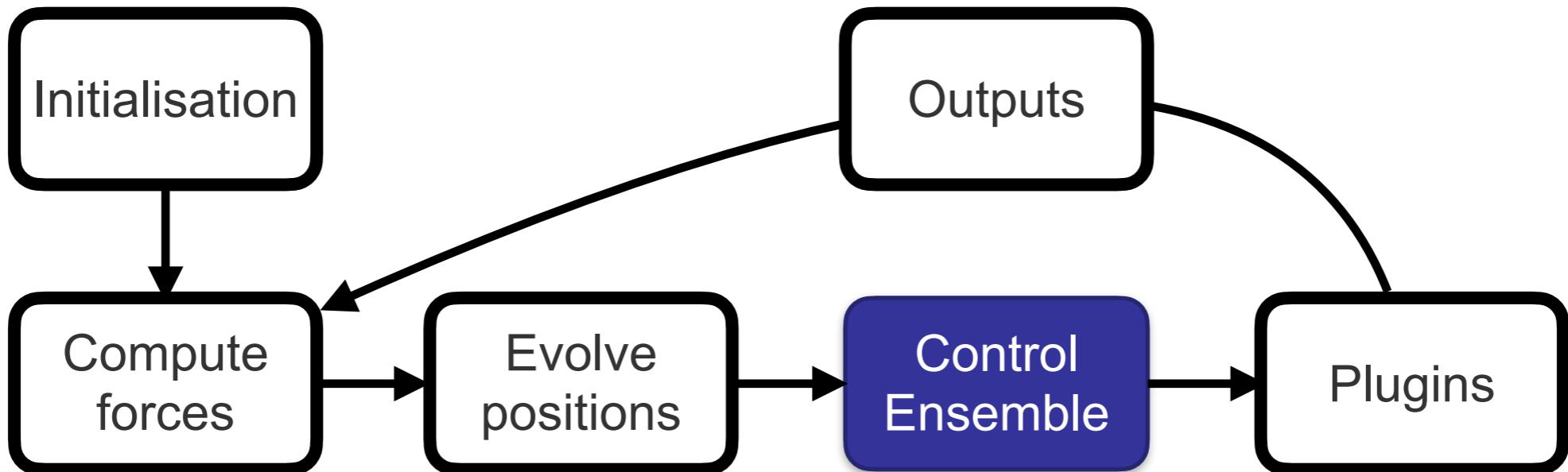
$H$  : Entalpy

$T$  : Temperature

Choose (any) 3

$NVE$	$\rightarrow$	Isolated system	
$NVT$	$\rightarrow$	Isothermal – Isochoric	C S L Y
$NPH$	$\rightarrow$	Isoenthalpic – Isobaric	O S S T
$NPT$	$\rightarrow$	Isothermal – Isobaric	E E D M
$\mu PT$	$\rightarrow$	Open system	

# 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

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

$$\lambda = \sqrt{\frac{T_{NVT}}{T(t)}}$$

# Specific heat

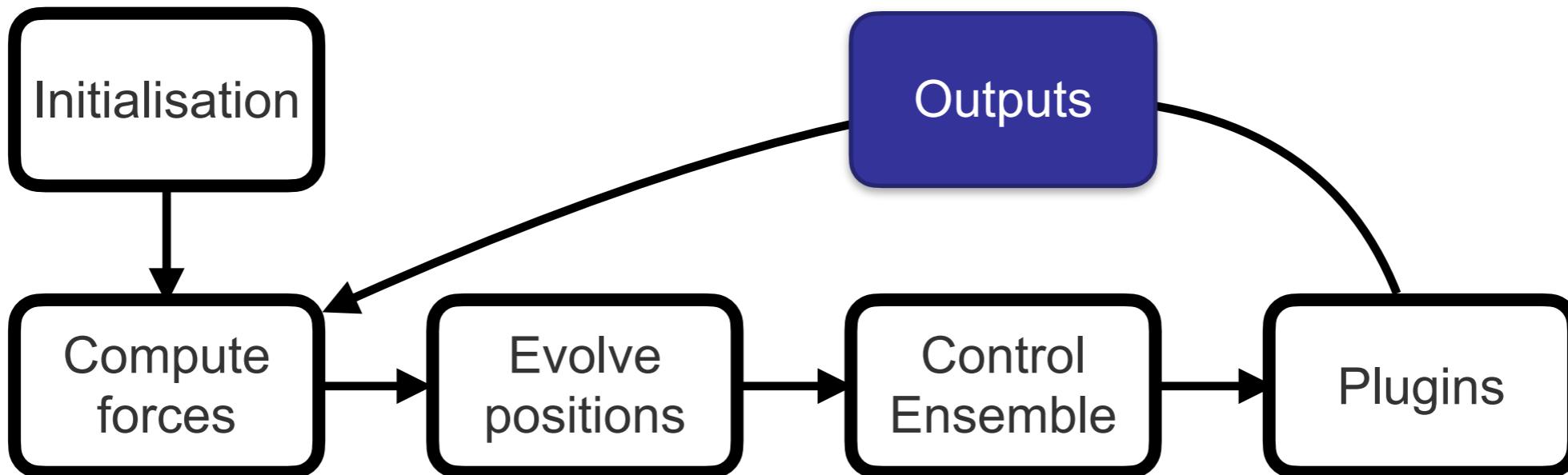
	slope	fluct.
Berendsen	31.98	4.36
Andersen	31.89	24.76
CSVR	32.07	32.80
Langevin	32.16	34.83
Exp.	29.71	

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

# Self Diffusion coefficient

	D [10 <sup>-5</sup> cm <sup>2</sup> /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*

# Molecular Dynamics



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

Post-processing

- *Density*
- *Structural properties [g(r)]*
- *Dynamical properties [D<sub>0</sub>]*
- ...
- *Phase changes*
- ...
- *Free energies*
- *Reaction rates*

# How to read the methods section of a paper?

- Do you know any of the authors ?

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- Gauge the results rather than the method !
- Any obvious red flags ?
- Often trends are more reliable than absolute numbers

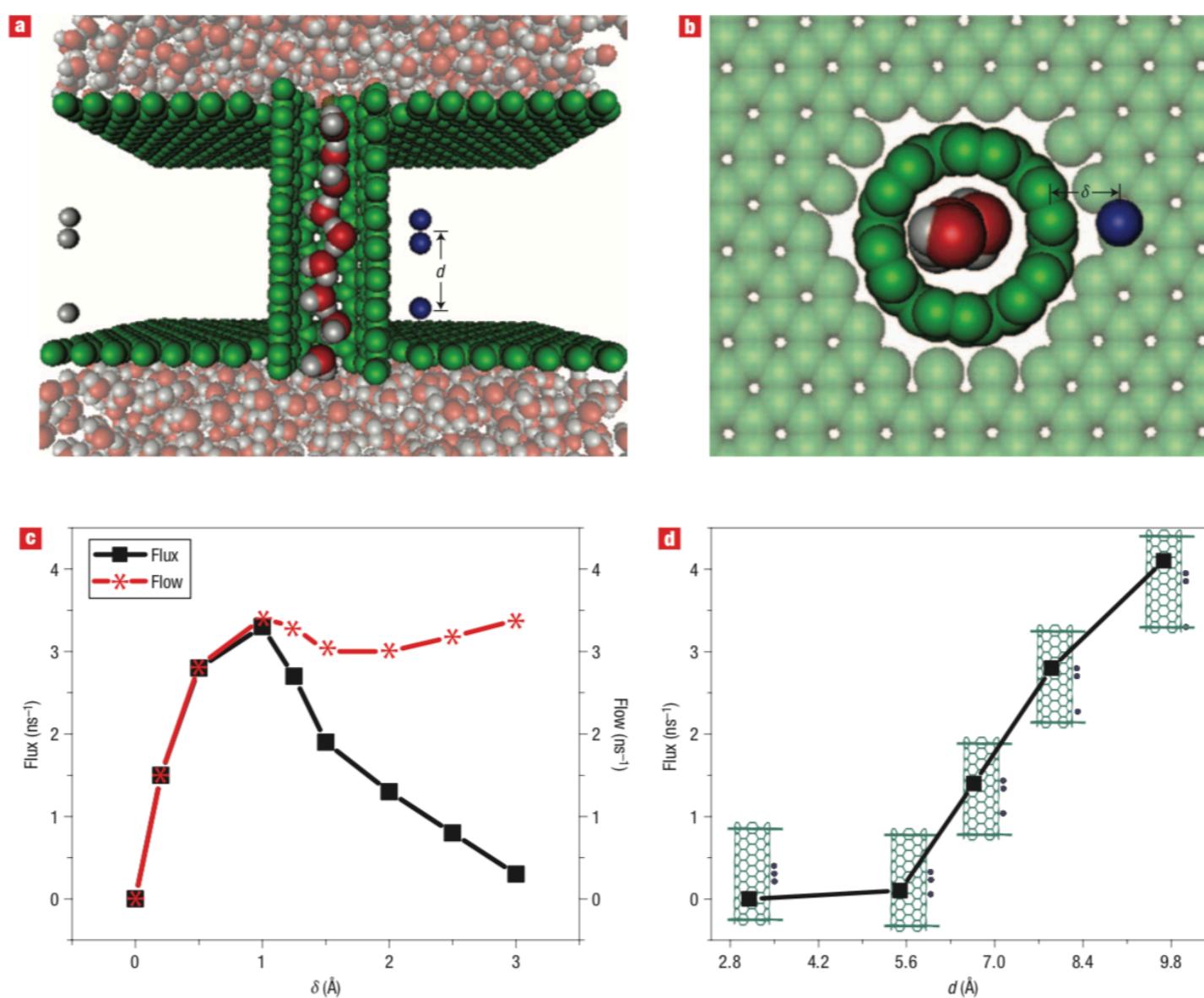
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- Identify the level of theory (*ab initio*, forcefield...)
- System size and simulation length appropriateness

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- Any “special” techniques used (Metadynamics) ?

# Thermodynamics works!

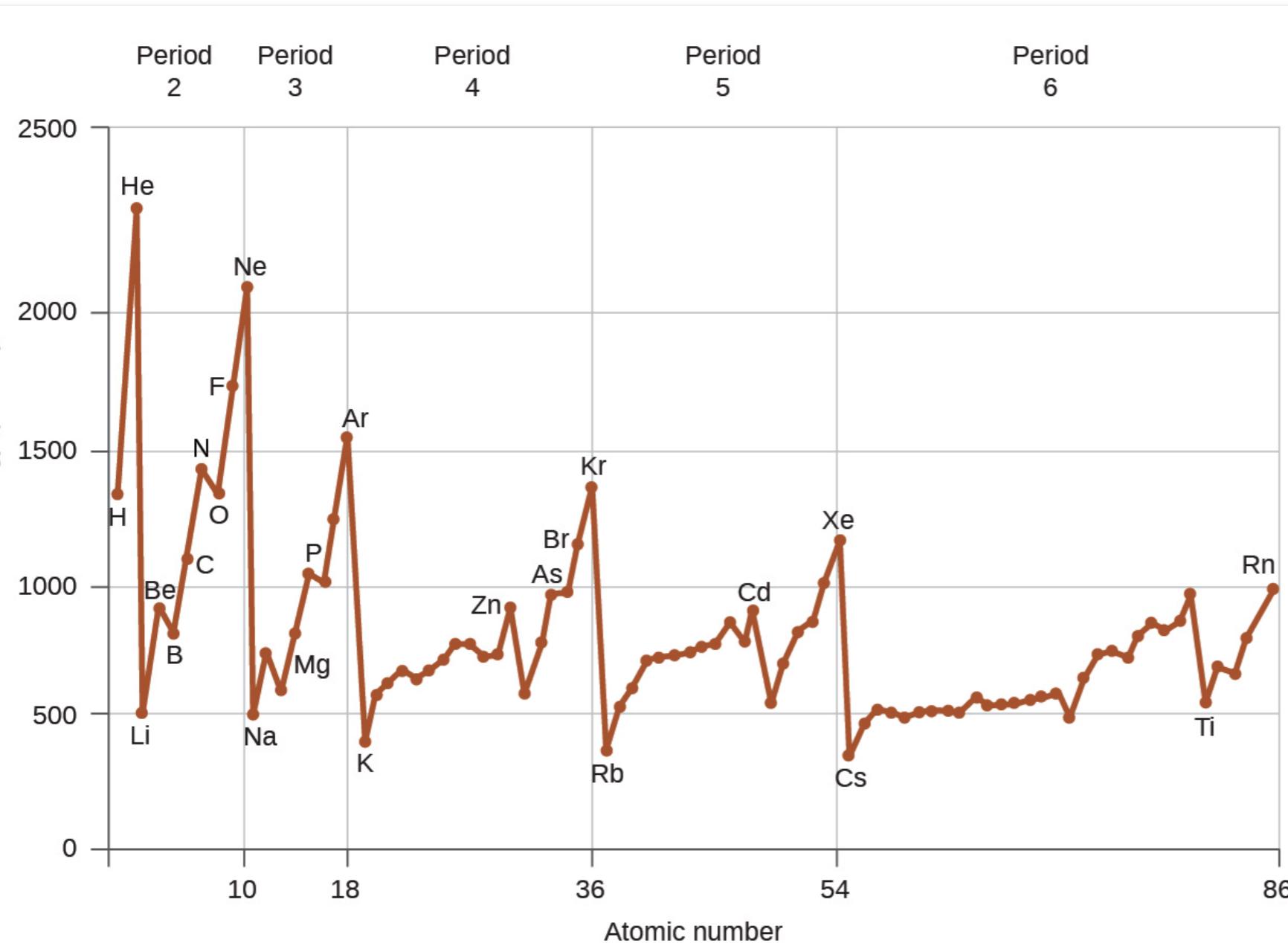


**Figure 1** Introduction to the main system and the flows and fluxes for different charge arrangements in the main system. **a**, Side view of the main system. The green spheres are the carbon atoms of the nanotube and the graphite sheets (note that the figure is not drawn to scale). The blue points 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  $\delta$  for  $d = 7.9 \text{ \AA}$ . **d**, Flux with respect to  $d$  for  $\delta = 0.5 \text{ \AA}$ .

# Put the numbers into context



**Table 1. Summary of Binding Residues and Interaction Energies<sup>a</sup> 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

<sup>a</sup> (the position of the end of the second water molecule in the last 15 ns. <sup>c</sup>Any atom of the residue located on the calcite surface for a period of time (~5 ns)

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

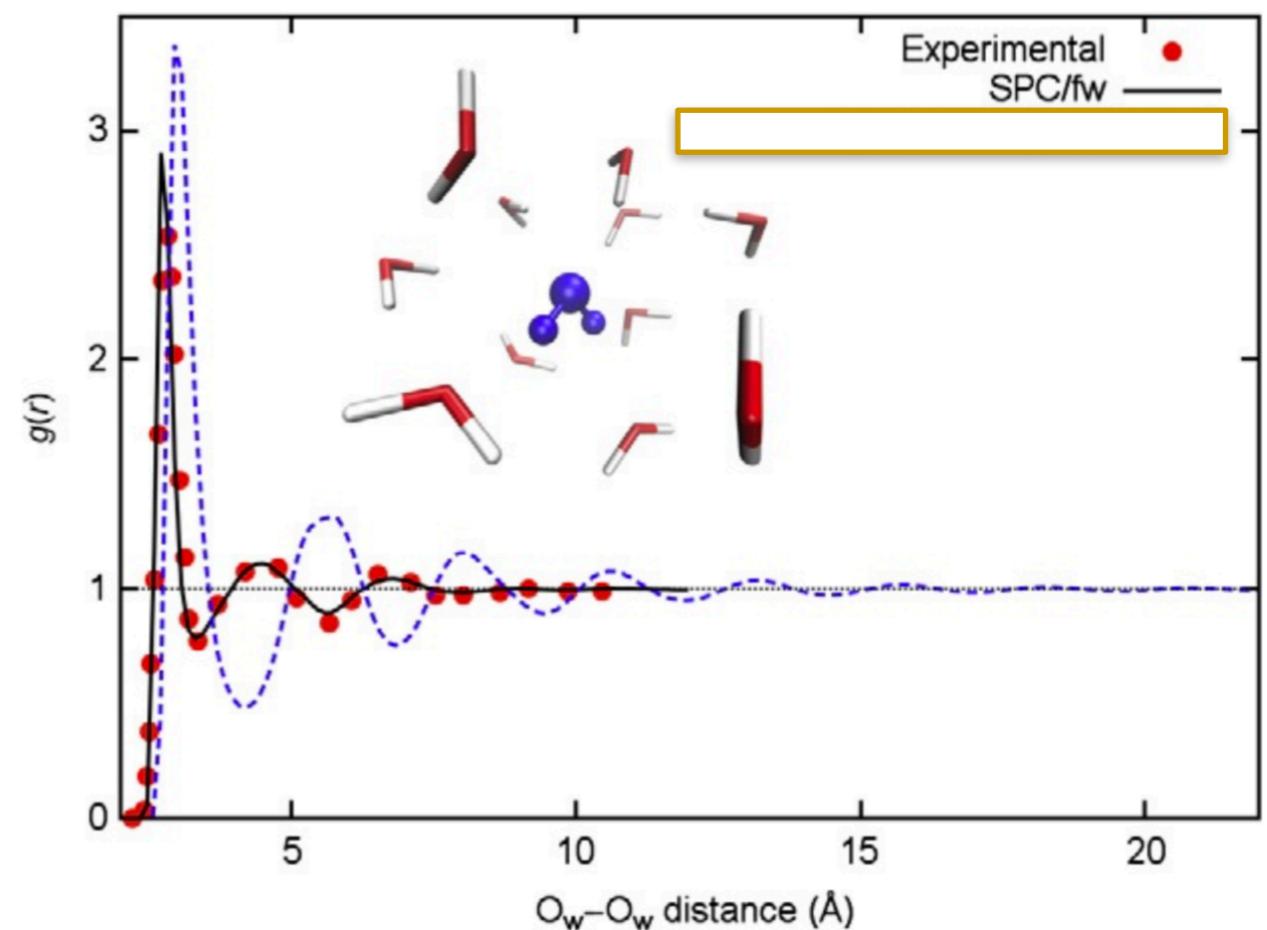
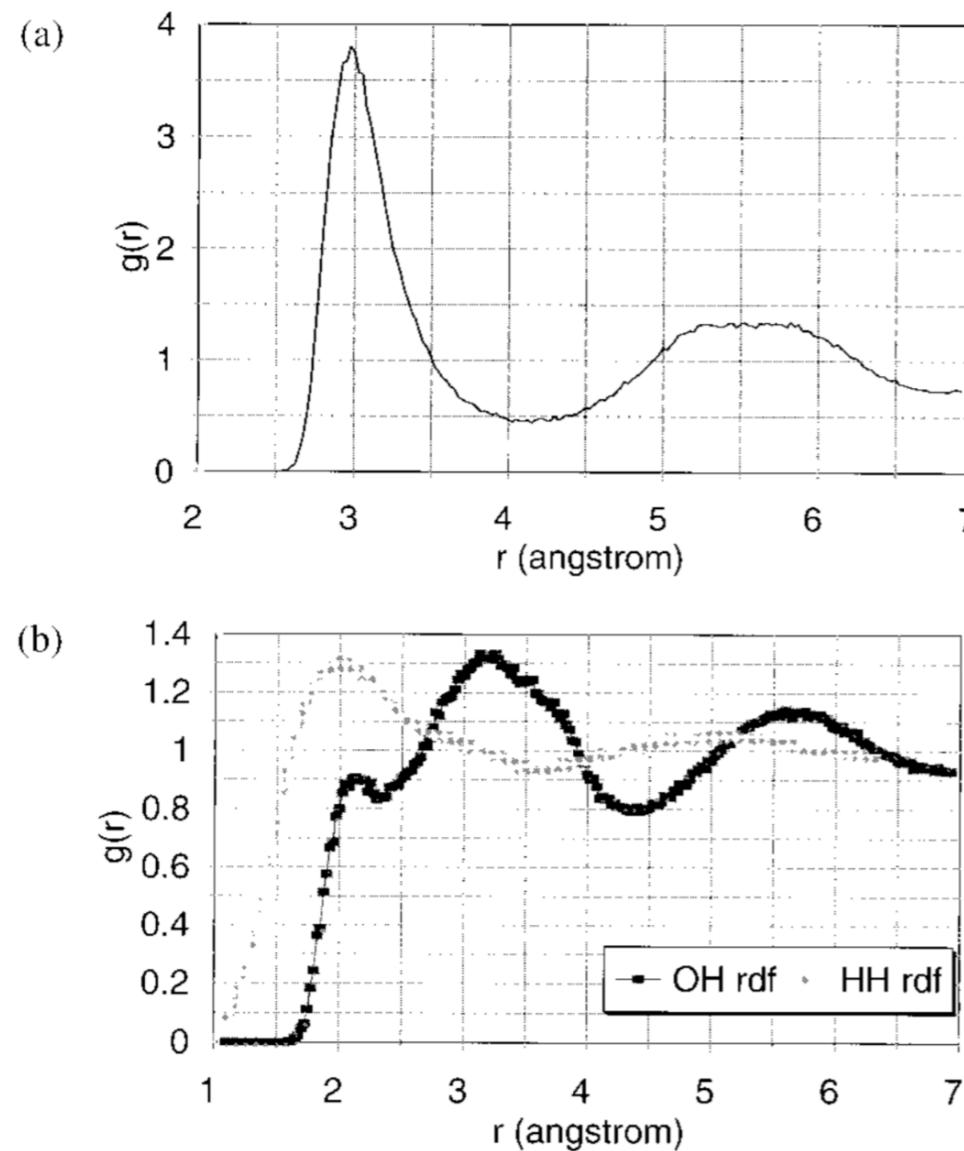


FIG. 3. (a) O-O and (b) O-H and H-H radial distribution functions, omitting intramolecular OH and HH interactions.

# Simplistic model

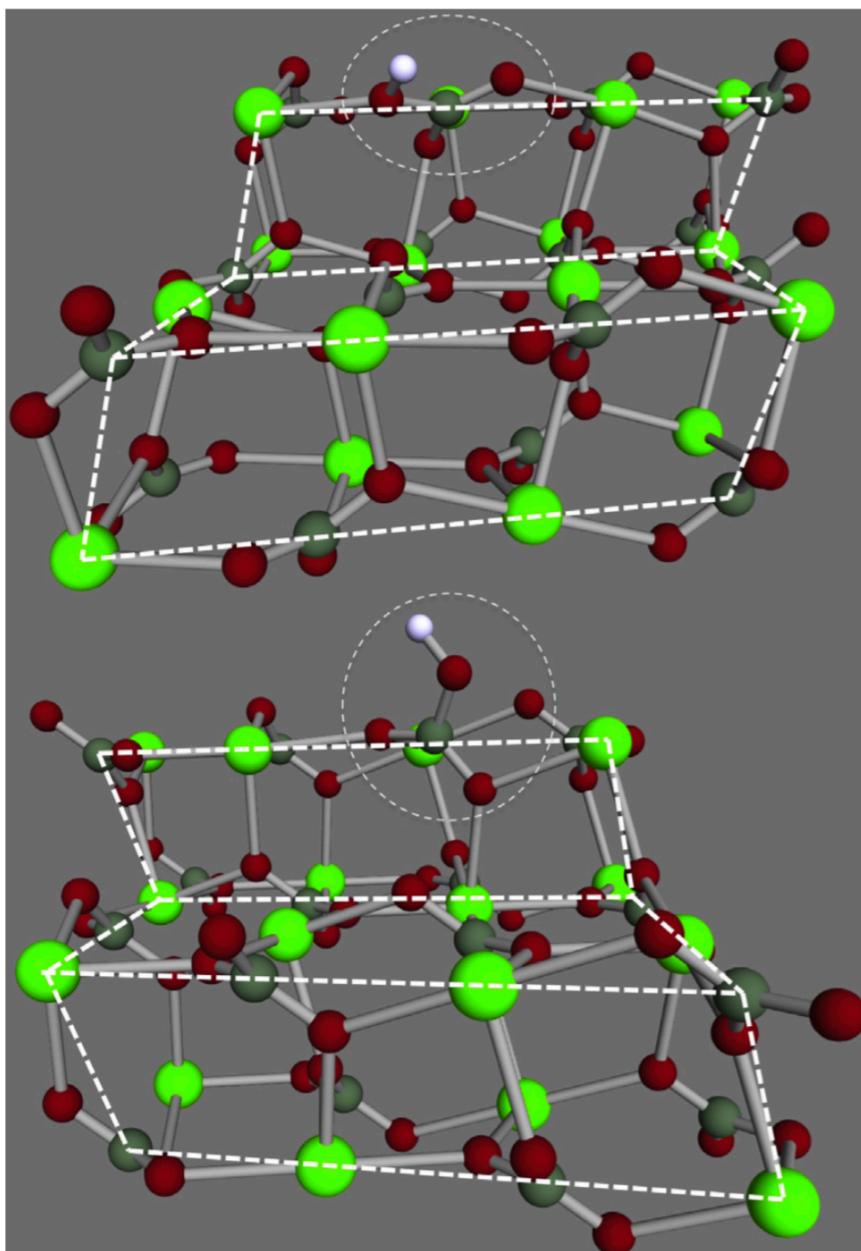


Table 1

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	$\Delta G_{\text{ads}}$ (kJ/mol)
$\text{CO}_3^{2-}$ on calcite {10.4}, outer shell	-50
$\text{HCO}_3^-$ on calcite {10.4}, outer shell	-18
$\text{CO}_3^{2-}$ on calcite {10.4}, inner shell	4
$\text{HCO}_3^-$ on calcite {10.4}, inner shell	34



Trends probably reasonable

More from Julian about this

# Computational chemistry works!



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

Hanyu Liu<sup>a</sup>, Ivan I. Naumov<sup>a</sup>, Roald Hoffmann<sup>b</sup>, N. W. Ashcroft<sup>c</sup>, and Russell J. Hemley<sup>d,e,1</sup>

<sup>a</sup>Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015; <sup>b</sup>Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853; <sup>c</sup>Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853; <sup>d</sup>Department of Civil and Environmental Engineering, The George Washington University, Washington, DC 20052; and <sup>e</sup>School 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)

PNAS

We predict that  $\text{YH}_{10}$  is the energetically stable phase from 250 to 300 GPa, and is dynamically stable down to 220 GPa.

The predicted  $T_c$  for  $\text{YH}_{10}$  is very high (Fig. 7) using similar EPC calculations. At 250 GPa, the  $\lambda$  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  $\text{YH}_{10}$  increased by ~30 K relative to  $\text{YH}_6$  (30) despite the fact that  $\lambda$  decreases (from 2.93 to 2.56). But, this change is offset by the higher average  $\omega_{\log}$  calculated for  $\text{YH}_{10}$  compared with  $\text{YH}_6$  (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,<sup>1,\*</sup> Muhtar Ahart,<sup>1</sup> Ajay K. Mishra,<sup>2,†</sup> Zachary M. Geballe,<sup>2</sup> Maria Baldini,<sup>2,§</sup> Yue Meng,<sup>3</sup> Viktor V. Struzhkin,<sup>2</sup> and Russell J. Hemley<sup>1,†</sup>

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

<sup>2</sup>Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA

<sup>3</sup>HPCAT, X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

In summary, we report four-probe, ac resistance measurements on  $\text{LaH}_{10\pm x}$  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  $\text{LaH}_{10}$  at comparable pressures.

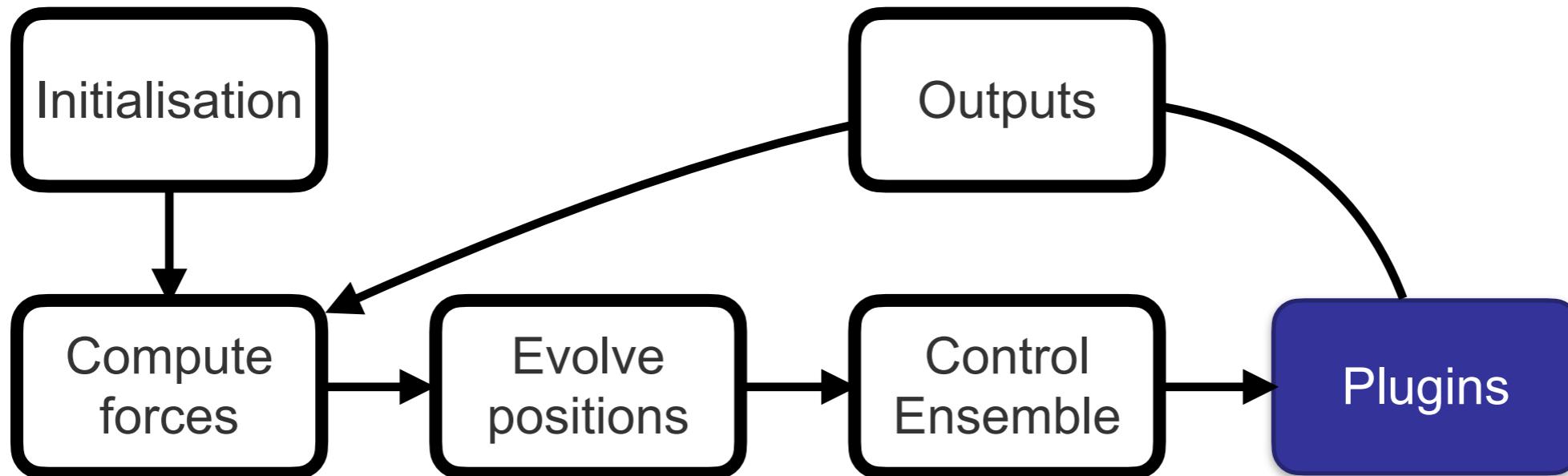
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- 
- Identify the level of theory (*ab initio*, forcefield...)
  - System size and simulation length appropriateness
  - Molecular dynamics, Monte Carlo, lattice dynamics...
- 
- Any “special” techniques used (Metadynamics) ?

# 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) ?

# Molecular Dynamics



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

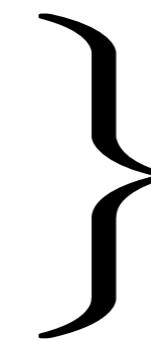
$$\begin{aligned} G &= -k_B T \ln Z \\ &= -k_B T \ln \sum_i e^{-\beta E_i} \end{aligned}$$

# Free energy methods (and friends)

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

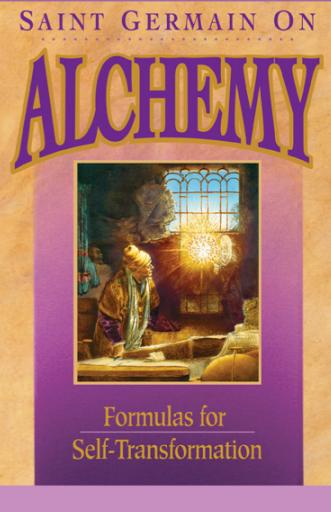


$$\Delta G = \Delta H - T\Delta S$$

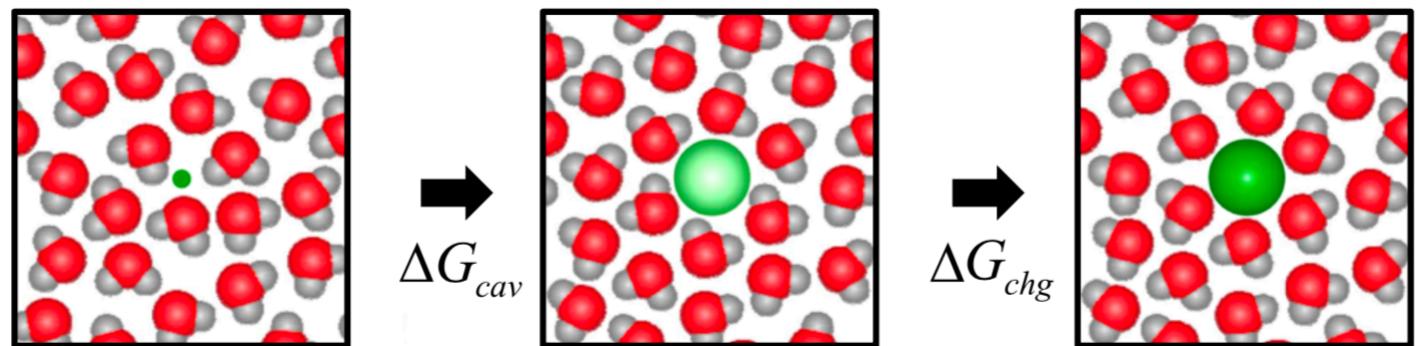


$$\nu = k \prod [I]^i$$

$$k = A \exp(-\beta \Delta G)$$



# Free Energy Perturbation

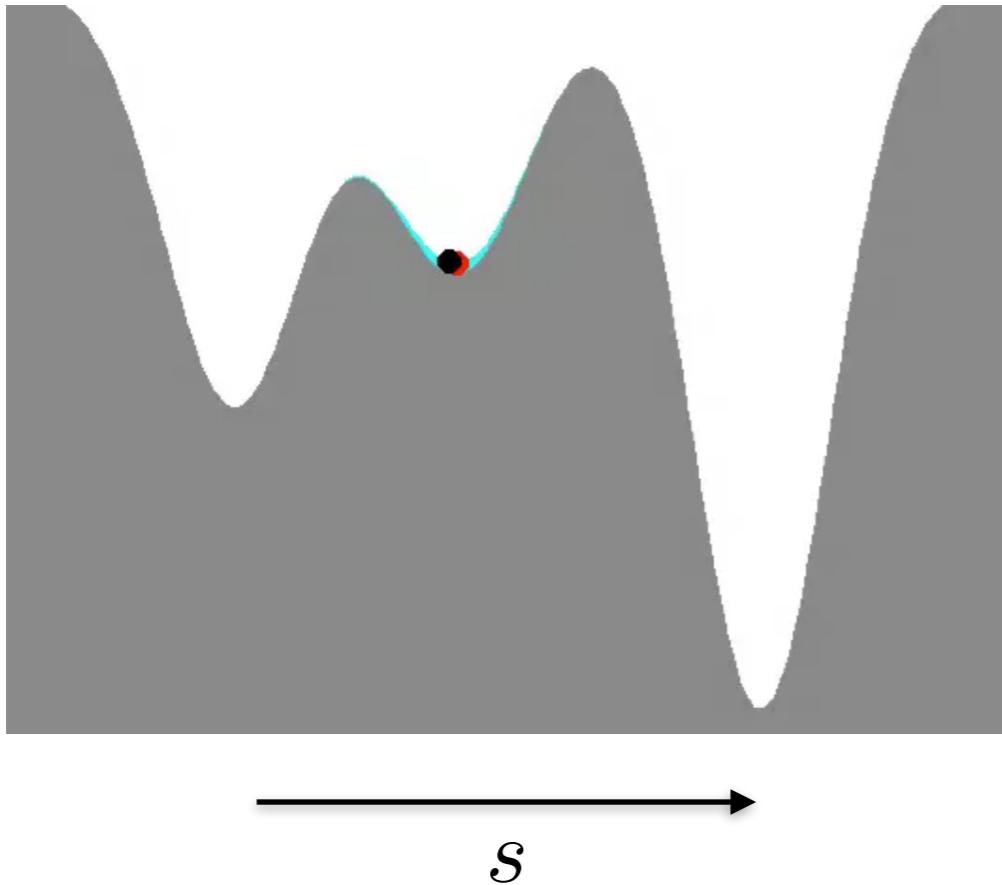


$$\Delta G = \sum_{i=0}^{N-1} \Delta G_{i,i+1} = -k_B T \sum_{i=0}^{N-1} \ln \left\langle \exp[-\beta \Delta U_{i,i+1}] \right\rangle_i$$

---

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

# Metadynamics

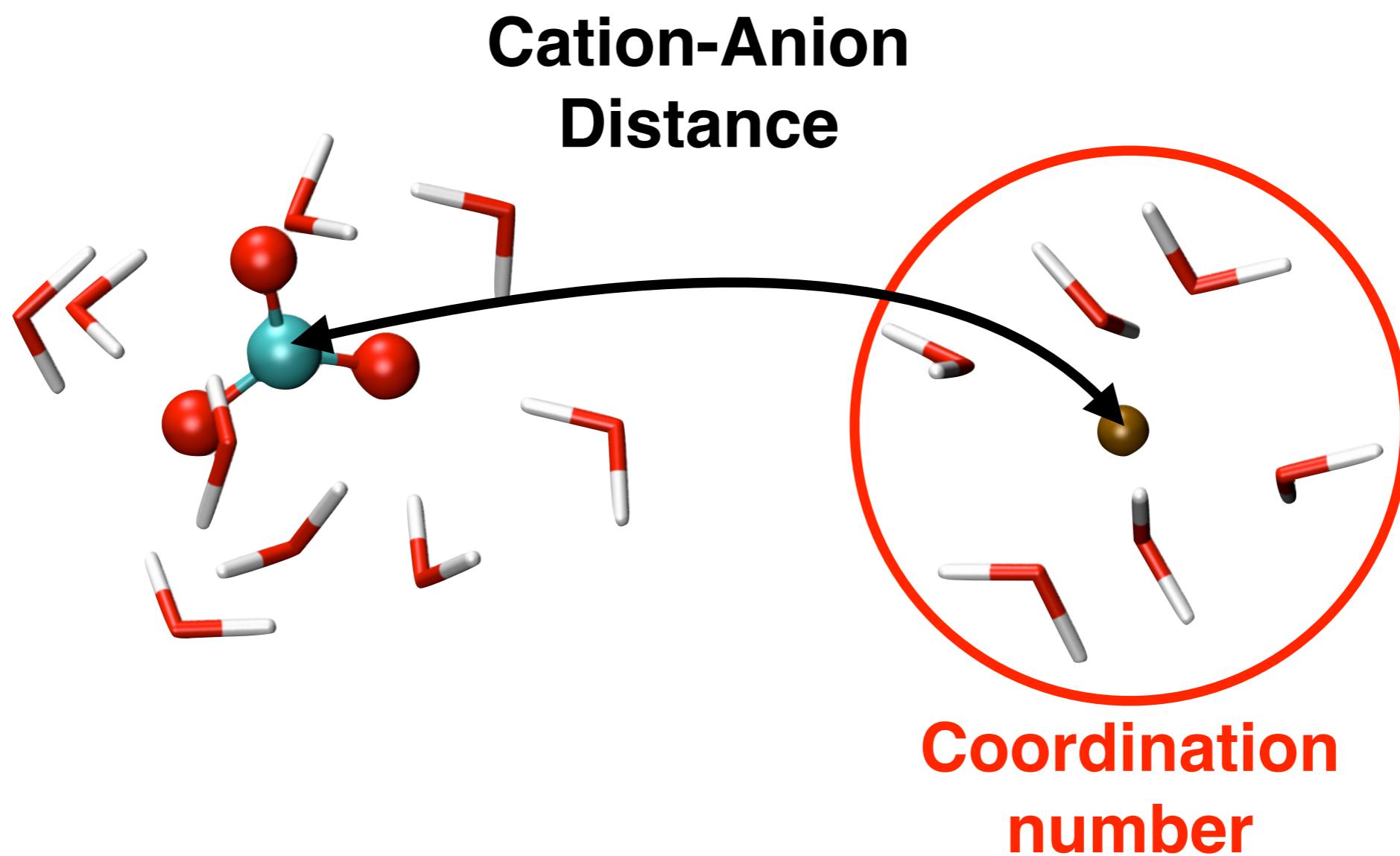


Well Tempered  
Multiple Walkers  
Trivially Parallel - Task Farming

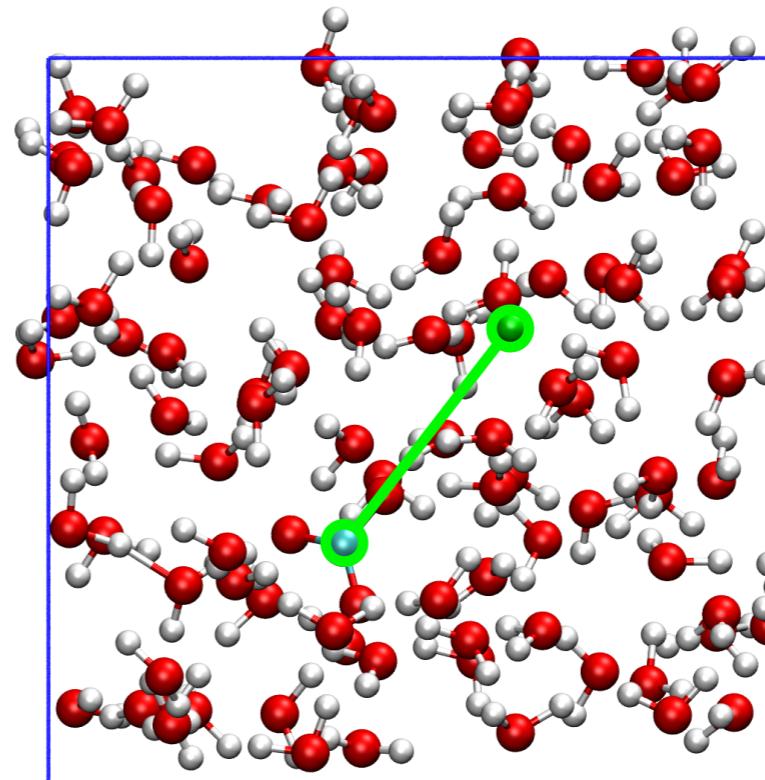
“Accurate” collective variables

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

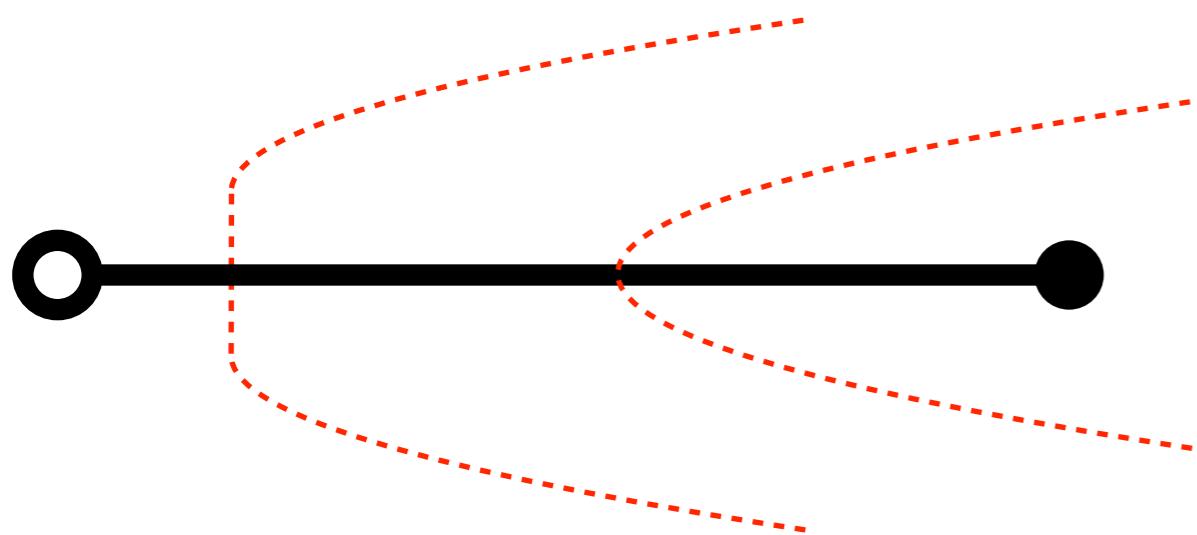
# The case of ion-pairing



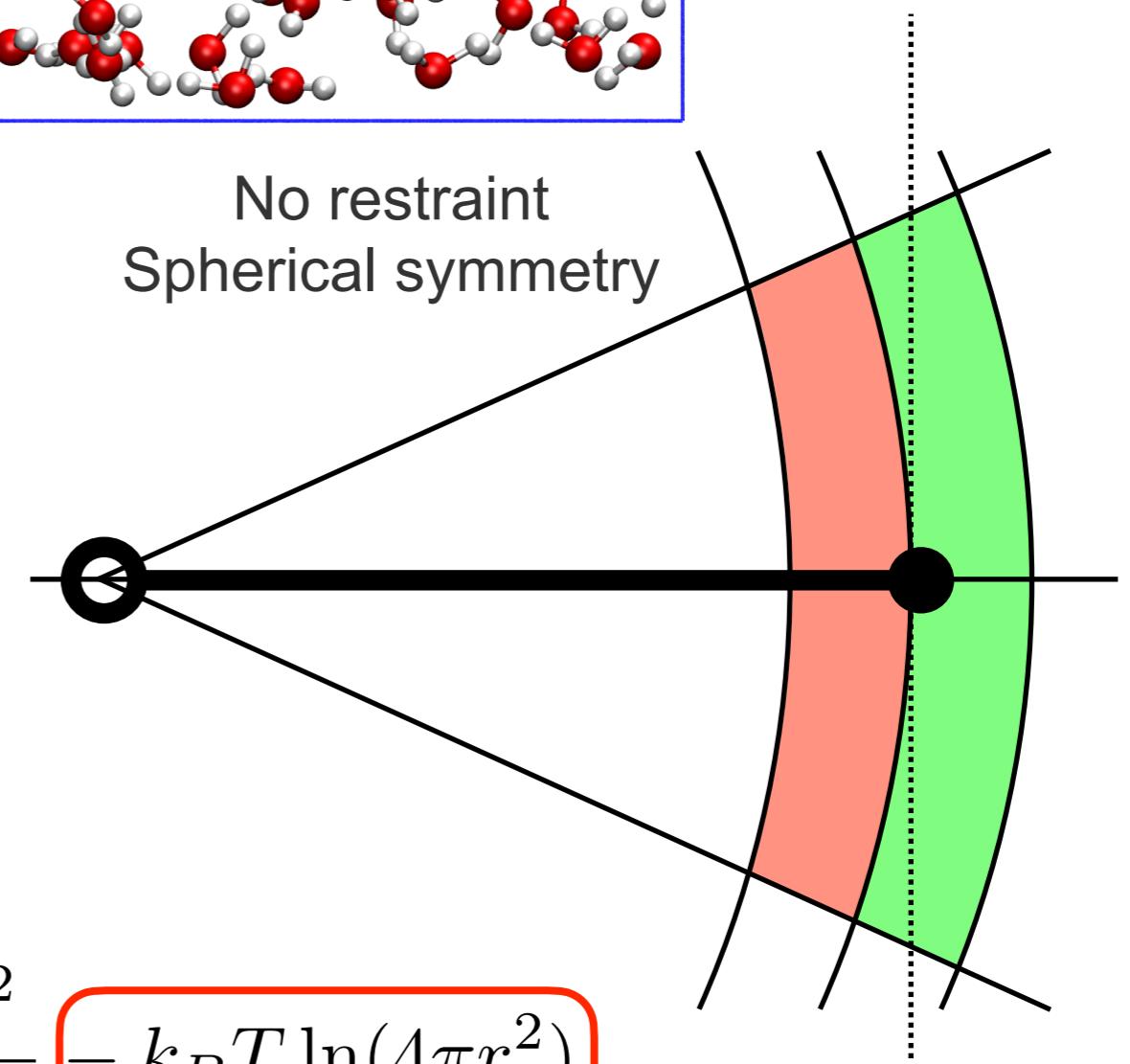
# Pairing free energy simulation setup



Line restraint  
Cylindrical      Harmonic

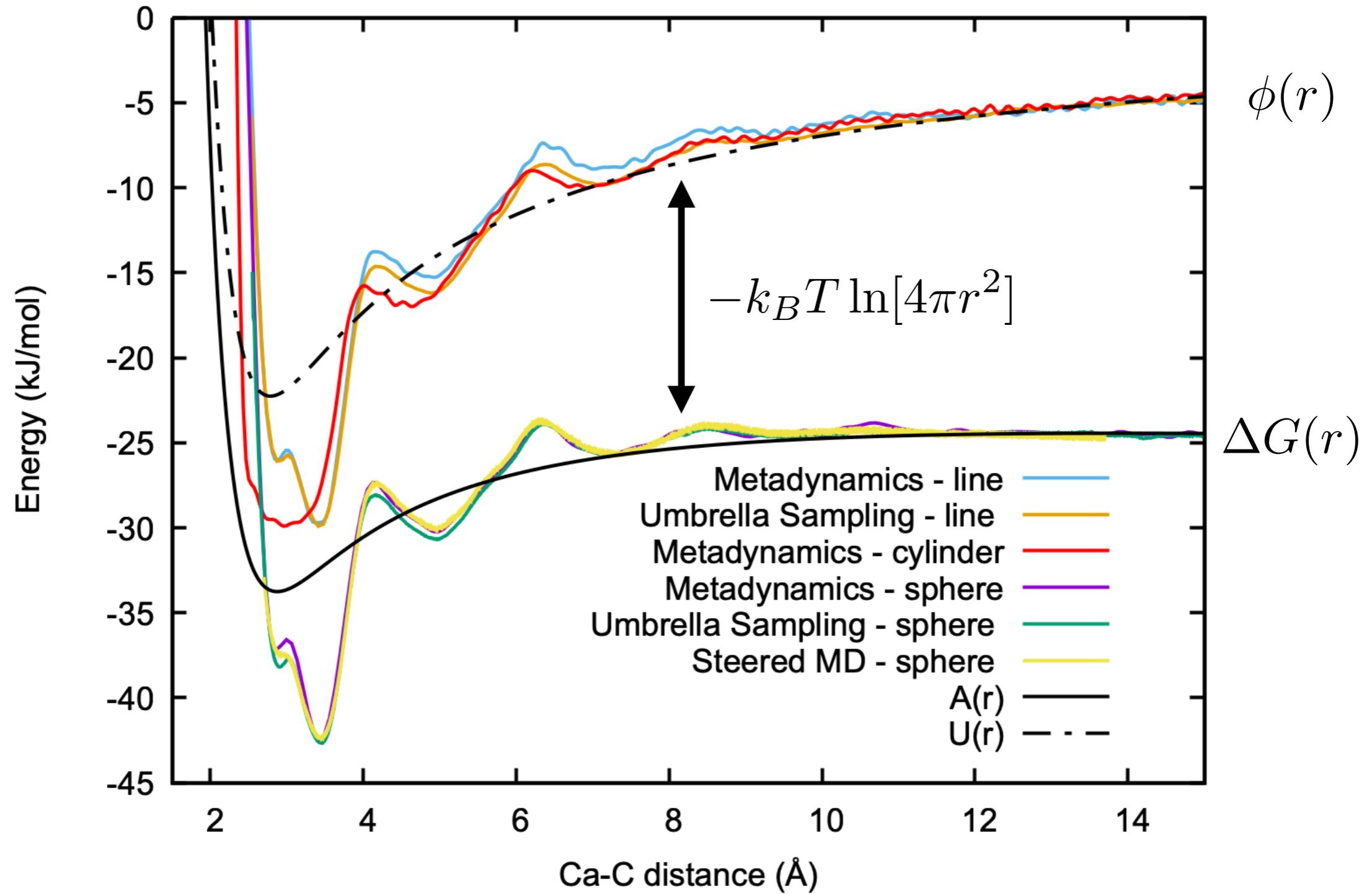


No restraint  
Spherical symmetry

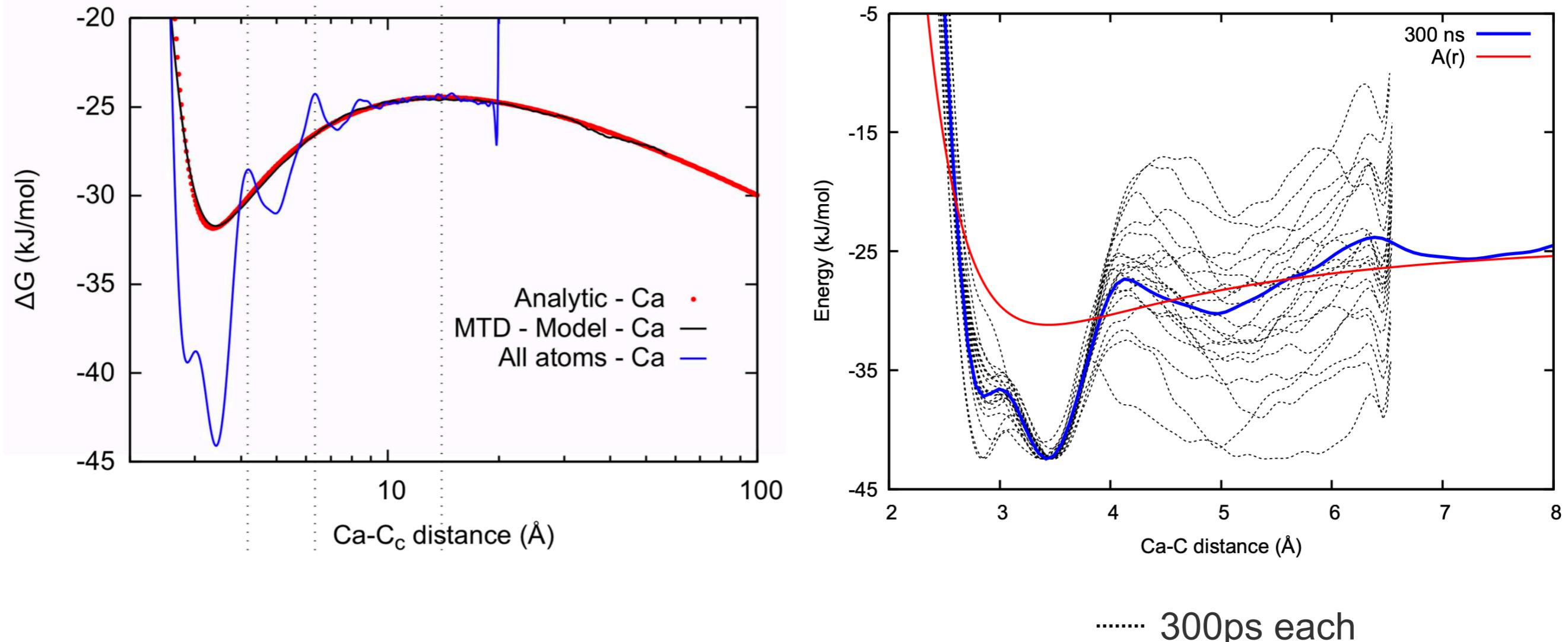


$$\Delta G(r) = \frac{1}{4\pi\epsilon_0 \epsilon_r r} \frac{q^2}{-k_B T \ln(4\pi r^2)}$$

# Pairing free energy - simulation setup

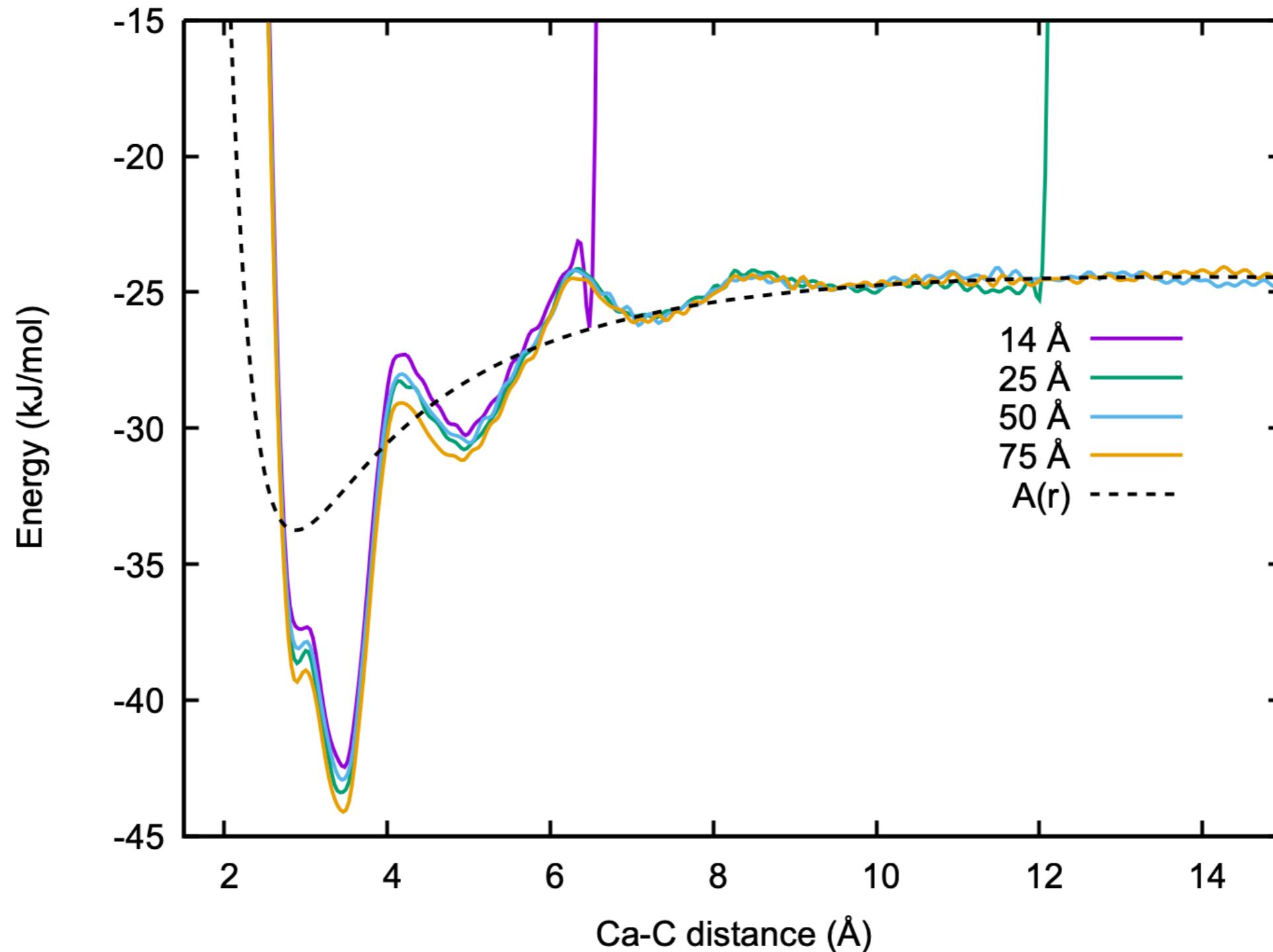


# Pairing free energy - simulation time

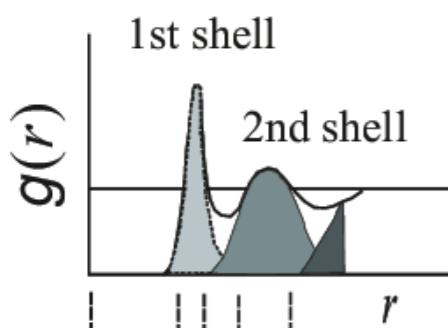


More from Julian about this

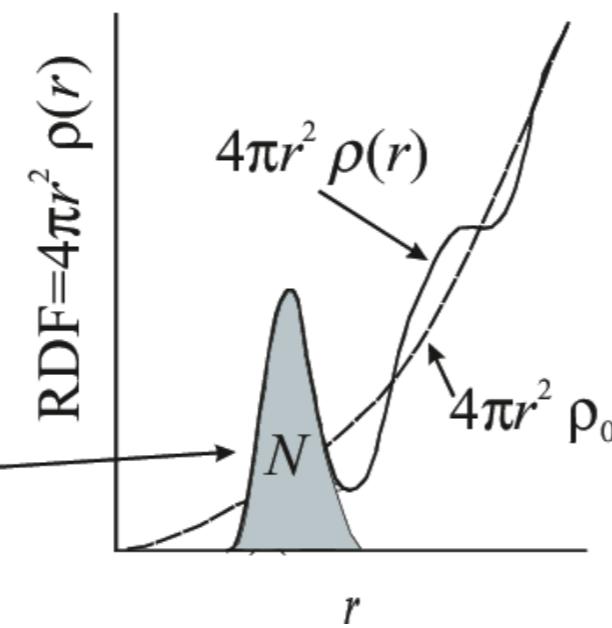
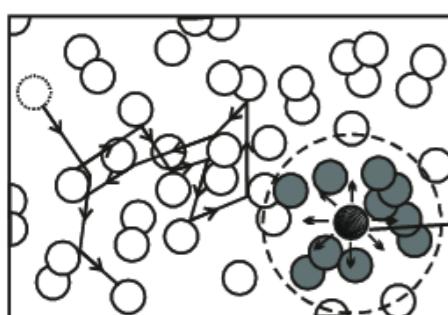
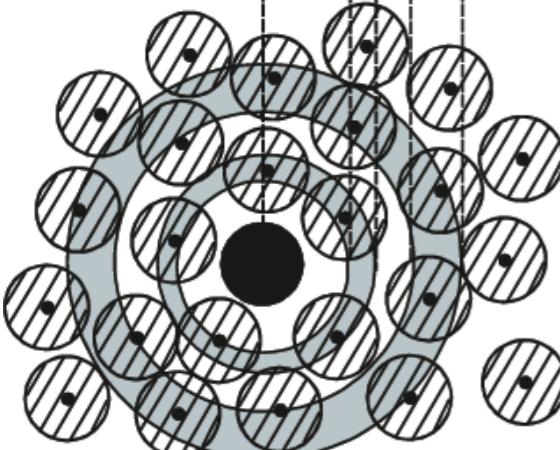
# Pairing free energy - system size



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



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



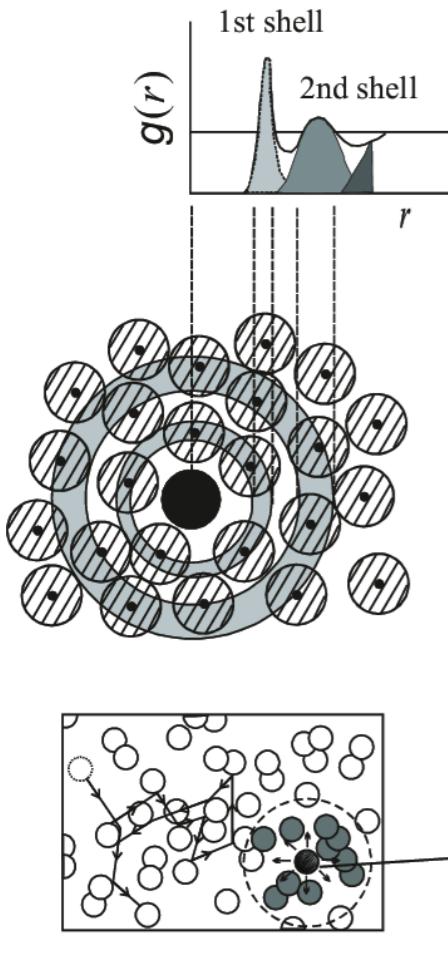
$$K_{eq} = \frac{[\text{AB}]c^\phi}{[\text{A}][\text{B}]}$$

$$[\text{AB}] = \frac{N_{\text{AB}}}{V} = \frac{N_{\text{A}} n_{\text{B}}}{V} = \rho \alpha$$

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

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

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



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

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

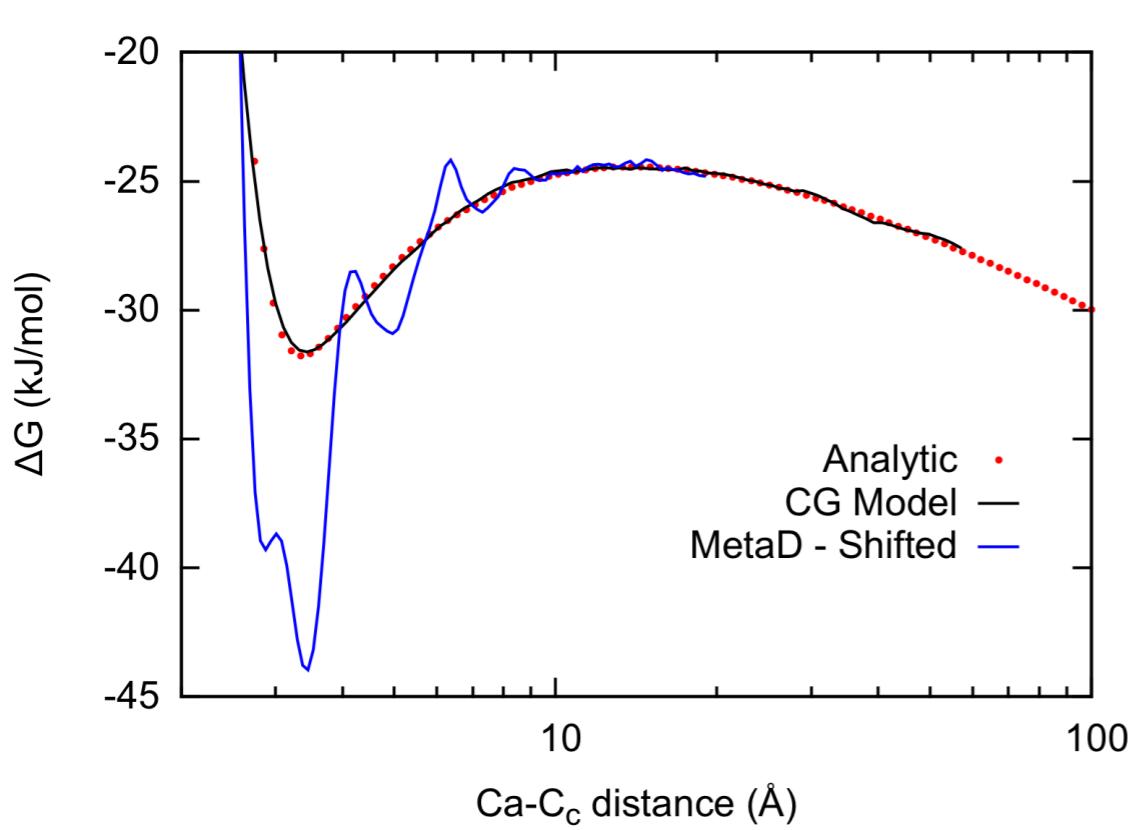
$$[\text{AB}] = \frac{N_{\text{AB}}}{V} = \frac{N_A n_B}{V} = \rho^2 \int_0^{R_c} 4\pi r^2 g(r) \, dr$$

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

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

# 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

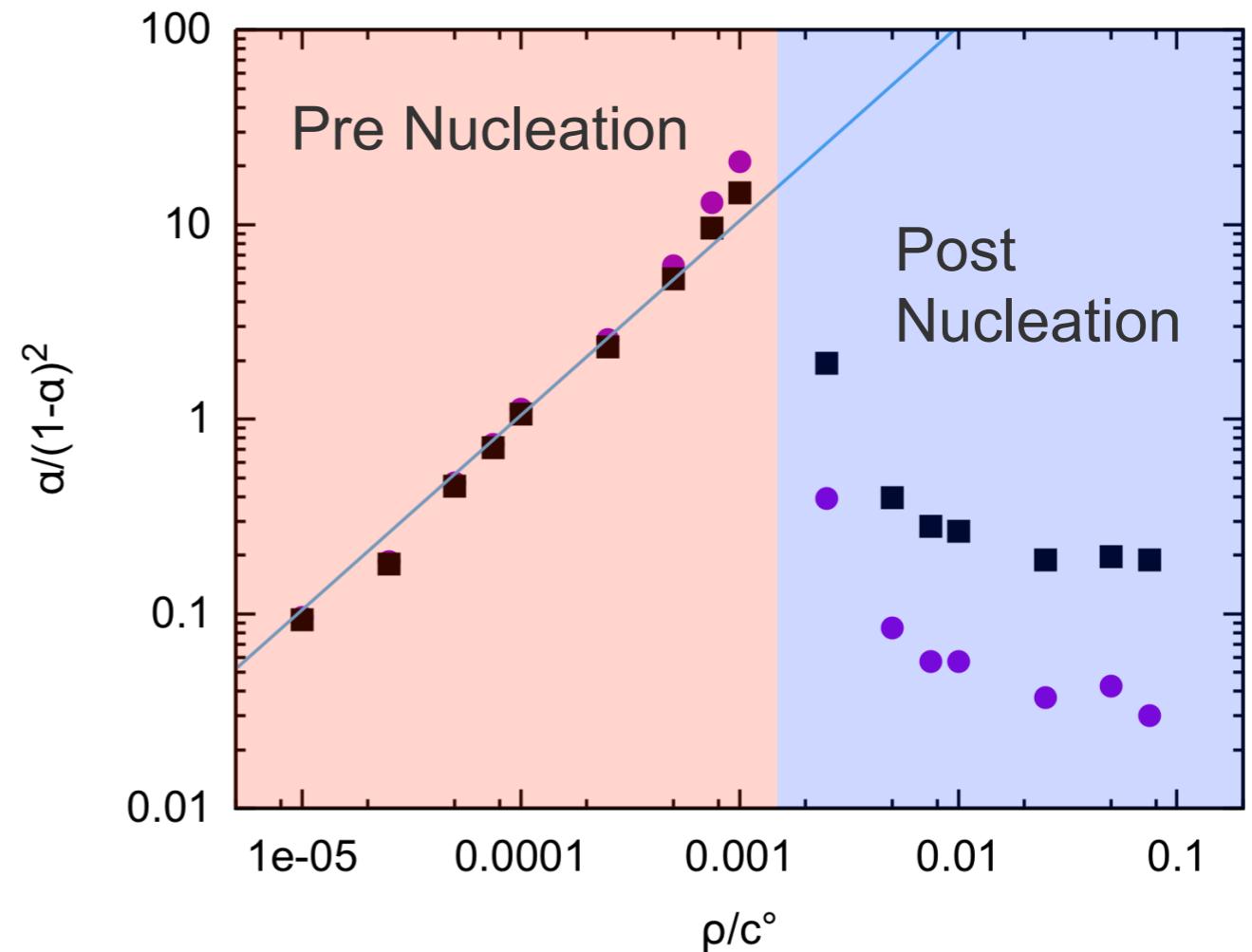
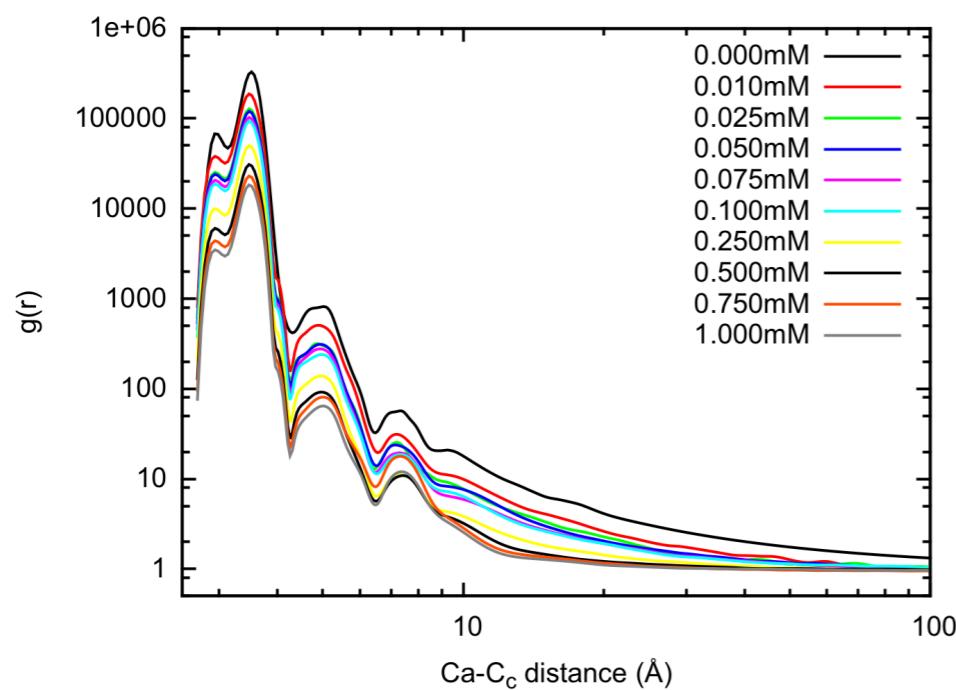
$$\Delta G(r) = \phi(r) - k_B T \ln(4\pi r^2) + \text{C}$$

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

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

# Association constant - CG model

$$K_a = \frac{c^\ominus \alpha}{\rho(1 - \alpha)^2}$$
$$\alpha = \int_0^{R_B} 4\pi \rho r^2 g(r) \, dr$$



# 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

# 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
- ...
-