An introduction to classical molecular dynamics

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Outline

- ***Introduction***
- **1st Part : Basic Molecular Dynamics methodology**
- **2nd Part : Different Ensembles**
- **3rd Part : Computing Properties**

Introduction : Computer simulations

- An established tool to study complex systems and gain insight into their behaviour
- Simulations fill the gaps between real experiments and theories, and microscopic and macroscopic

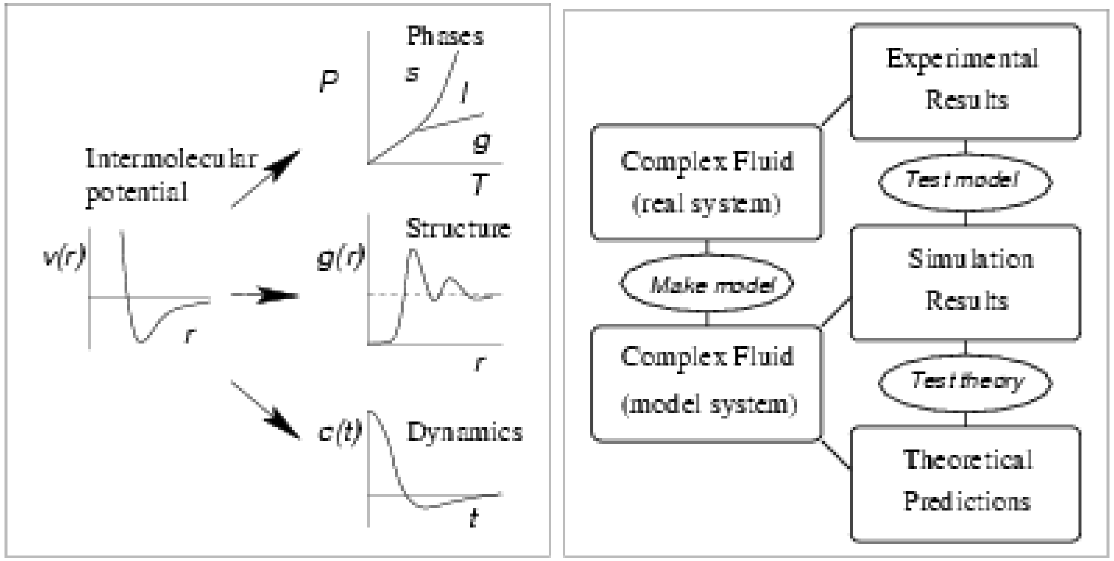


Figure 1. Simulations as a bridge between (a) microscopic and macroscopic; (b) theory and experiment.

from M. P. Allen, NIC Series, Vol. 23, 1 (2004)

Computer simulations - *in silico* experiments

- Simulations are relatively simple, inexpensive, and everything can be measured (in principle)
- Help to understand the experimental results and/or to propose new experiments
- Test of theoretical predictions
- Investigate systems on a level of detail which is not possible in real experiments or analytical theories (local structure, mechanism of transport, surfaces, ...)
- Creating new materials (not yet in glassy science)

Computer simulation techniques

Given : an interesting phenomenon or a theoretical prediction
→ choose Hamiltonian, i.e. the model of atomic interactions
→ choose size of the simulation box and boundary conditions
→ choose length of the run (=time window investigated)

⇒ **Two main families of simulation techniques**

1. Molecular Dynamics **(MD)** : solve Newton's equations of motion
   - realistic trajectories of the particles, in principle
   - propagation in phase space is relatively slow
2. Monte Carlo : pick a random configuration and apply the Boltzmann criterion
   - trajectory is not realistic
   - unphysical moves can be used to accelerate

1st Part : Basic Molecular dynamics

- MD principle and flowchart
- Periodic boundary conditions
- Interaction potential : short- and long-range interactions, truncation, smoothening, neighbor list, very short range interaction
- Integrator
- Measurements : T and P

MD principle

→ For a set of N interacting particles, one generates their trajectory by numerical integration of Newton's equation of motion, for a specific interatomic potential $\mathcal{U}(\mathbf{r}^N)$

$$m_i\ddot{\mathbf{r}}_i = \mathbf{f}_i; \quad \mathbf{f}_i = -\nabla_i\mathcal{U}(\mathbf{r}^N) \tag{1}$$

$\mathbf{r}^N = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_\mathrm{N})$ is the complete set of $3N$ particle coordinates.

→ Given initial condition $\{\mathbf{r}_i(0), \dot{\mathbf{r}}_i(0)\}_{i=1,2,\ldots,N}$ and boundary condition, one solves the set (1) of coupled 2^{nd} order differential equations to yield positions and velocities at later times $t = l\delta t$: $\{\mathbf{r}_i(l\delta t), \dot{\mathbf{r}}_i(l\delta t)\}$, $l = 1, 2, \ldots, L$.

→ In principle, all physical properties of the numerical sample (i.e. collection of N particles) can be computed from the knowledge of its phase space trajectory $\{\mathbf{r}_i(t), \mathbf{p}_i(t) = m_i\dot{\mathbf{r}}_i(t), \mathbf{f}_i(t)\}_{i=1,2,\ldots,N}$.

Integrator

Integration of the coupled set (1) of Newton equations :
(1) discretization of the time in interval δt, and
(2) a suitable algorithm, called *integrator*, to propagate step-by-step

$$\{\mathbf{r}_i(t), \mathbf{p}_i(t)\} \rightarrow \{\mathbf{r}_i(t+\delta t), \mathbf{p}_i(t+\delta t)\}$$

Requirements for a good, well-behaved integrator :

1. be simple and fast enough
2. stable trajectories with enough long timestep
3. the temporal evolution must be reversible
4. conserving energy and preserve phase space volume according to Liouville theorem

Integrator (2)

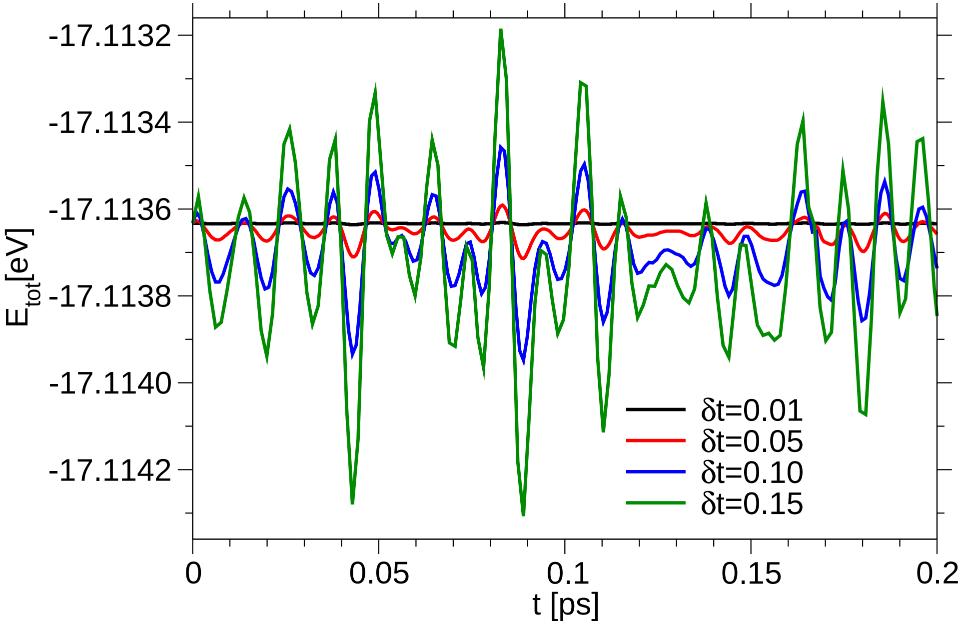
- Well-behaved and widely used integrators : the Verlet class
- *Velocity Verlet* integrator

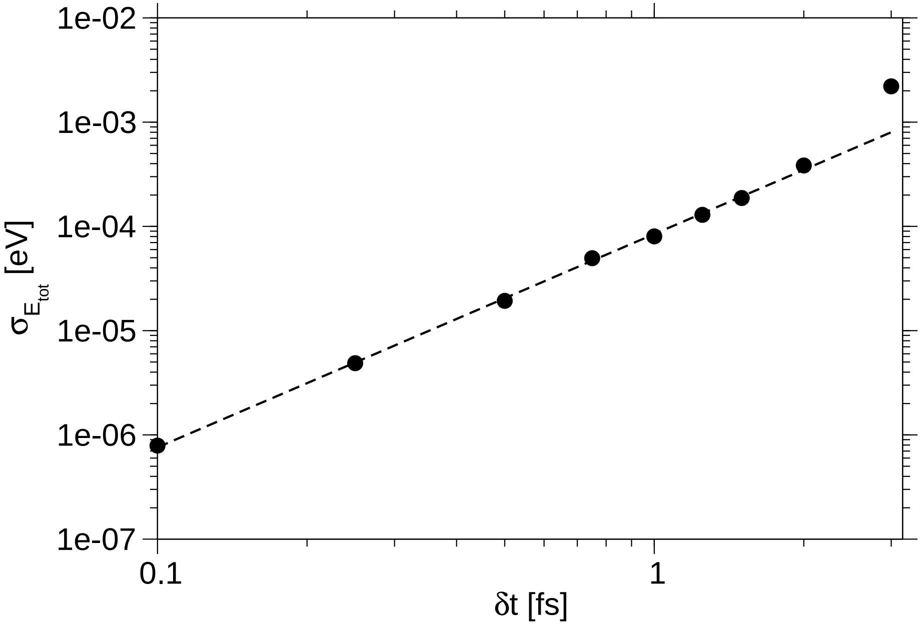
$$\begin{aligned}
\mathbf{r}_i(t+\delta t) &= \mathbf{r}_i(t) + \mathbf{v}_i(t)\delta t + \frac{\mathbf{f}_i(t)}{2m_i}\delta t^2 \\
\mathbf{f}_i(t+\delta t) &= \mathbf{f}_i(\mathbf{r}_i(t+\delta t)) \\
\mathbf{v}_i(t+\delta t) &= \mathbf{v}_i(t) + \frac{\mathbf{f}_i(t+\delta t)+\mathbf{f}_i(t)}{2m_i}\delta t
\end{aligned}$$

Integrators : careful choice of δt

Velocity-Verlet integrator : compromise between energy conservation and any waste of CPU time

$$\sigma^2_{E_{\mathrm{tot.}}} = \langle E^2_{\mathrm{tot.}} \rangle - \langle E_{\mathrm{tot.}} \rangle^2 \propto \delta t^2$$





Example : SiO_2 liquid, 1152 atoms sample, 6100K, BKS potential

$\Rightarrow \delta t = 2$ fs inadequate choice!

Flowchart for a typical run of an MD program

step 1	initialization : reading state parameters
	(e.g. density, temperature)
	set initial $\mathbf{r}_i(0)$ and assign $\dot{\mathbf{r}}_i(0)$
	start **MD-loop**, `do n=1, Nb of time-steps`
step 2	calculate force on each particle
step 3	move particles by one time-step δt
step 4	collect data, i.e. save current positions and velocities
	go back to step 2 if the preset Nb. of timesteps not reached
	end **MD-loop**, `enddo`
step 5	analyse results

A MD simulation study for network glasses

Melt-and-quench typical flowchart

1. System setup : potential, nb of atoms, time step δt and initial configuration $\{\mathbf{r}_i(0), \dot{\mathbf{r}}_i(0)\}$, $i = 1, 2, \ldots, N$

   e.g. positions on a lattice and velocities drawn from a Boltzmann distribution - the precise choice is irrelevant as the system will ultimately lose all memory of the initial state
2. Equilibration(s) run(s) at high temperature(s): achieve definite mean values of T, P (fixed nb of atoms)
3. Production run (M steps) : computation of quantities of interest along the trajectory $\{\mathbf{r}_i(j\delta t), \dot{\mathbf{r}}_i(j\delta t), \mathbf{f}_i(j\delta t)\}$, $j = 1, 2, \ldots, M$
4. Cooling run
5. Propagation run for a waiting time at room temperature and collecting data run in order to compute average properties

Choice of the interatomic potential $\mathcal{U}(\mathrm{r}^N)$

$\Rightarrow$ Main alternatives : classical and *ab initio* approaches

Ab initio approach (see M. Salanne's lecture) :

- interactions are calculated numerically from the instantaneous positions of the ions, and taking into account the electronic structure of the system, obtained using the density functional theory (Kohn-Sham, DFT)
- universality
- it can handle relatively complex systems
- computationally very expensive
- typical system sizes : 100 - 1000 atoms
- short trajectories

Interatomic potential $\mathcal{U}(\mathrm{r}^N)$: Classical approach

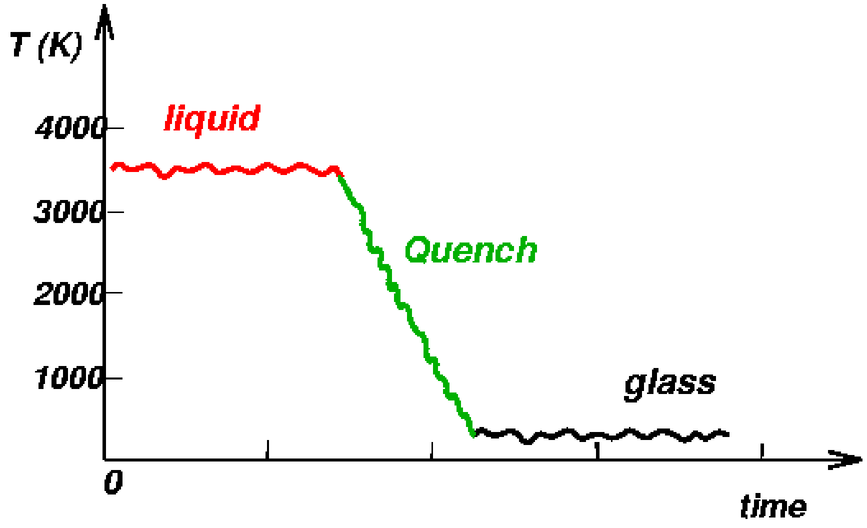
- atoms are considered as interacting point particles, and electrons not explicitely taken into account
- an effective picture is adopted, i.e. introduction of a *force field*, defined by a set of parameters and (most often) analytical functions, depending on the mutual position of particles :
- a force field generally fitted to experimental data or to results from quantum mechanics calculations, corresponding to specific conditions of temperature and pressure, and often based on a formal decomposition :

$$\mathcal{U}(\mathbf{r}^N) = \sum_i \sum_{j>i} u^{(2)}(\mathbf{r}_i, \mathbf{r}_j) + \text{3-body terms} + \ldots \quad \textit{(isolated system)}$$

- an effective potential is rather specific to a material, i.e. not transferable when composition changes and/or physical conditions ;
- simulations relatively cheap

MD simulations of network glasses

Typical time and length scales, and quench rates



	Classical MD	*Ab Initio* MD
Size	1 000 - 500 000 atoms	100 - 1000 atoms
	∼ 100Å	∼ 15Å
Trajectory length	∼ 1 ns	∼ 20 - 30 ps
Quench rate	10^{10} to 10^{14} K/s	10^{14} to 10^{15} K/s

Other approaches : – combined classical and *ab initio* simulations

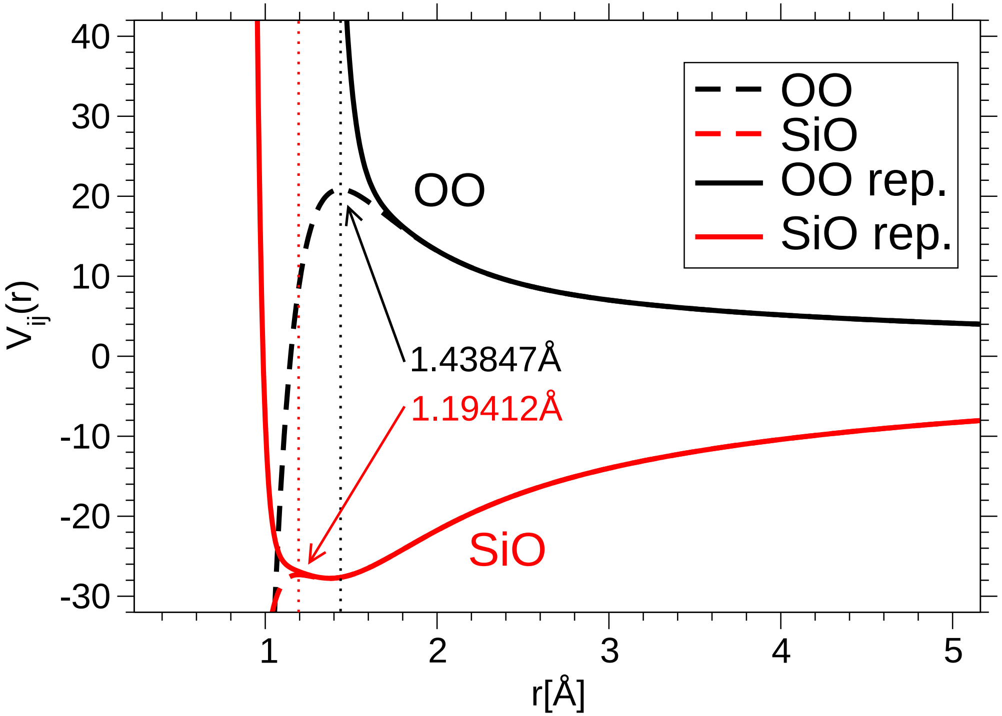
– hybrid or QM/MM simulations [e.g. like fracture in Si, see Csanyi, Albaret, et al. PRL **93** (2004)]

Classical approach : an example

The so-called BKS (van Beest, Kramer and van Santen) potential for $\mathrm{SiO_2}$

$$u^{(2)}(\mathbf{r}_i, \mathbf{r}_j) = V_{ij}(r = |\mathbf{r}_i - \mathbf{r}_j|) = \frac{q_i q_j e^2}{r} + A_{ij}\exp(-B_{ij} r) - \frac{c_{ij}}{r^6}$$

for $i,\ j =$ Si, O .



$$V_{ij}(r) \rightarrow V_{ij}^{rep.=repulsive}(r)$$

(dashed line) ⟶ (solid line)

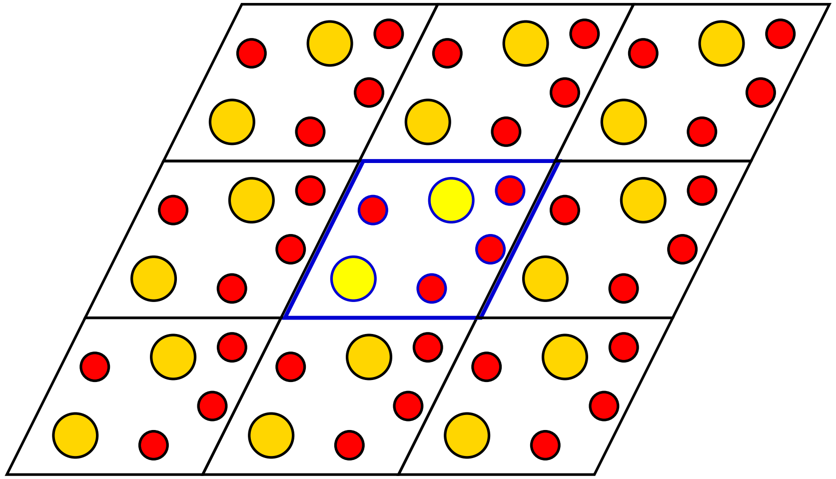
$$V_{ij}^{rep.}(r) = V_{ij}(r) + 4\epsilon_{ij}\frac{\sigma_{ij}}{r^{24}}$$

Periodic Boundary Conditions (PBC)

- Given a system having a limited number of particles N, confined in a finite box with specific geometry (called **MD cell**), important contributions on the measured properties would come from the surfaces.

e.g $\frac{E_{surface}}{E_{bulk}} \approx 6N^{-1/3}$ for a cubic box (i.e. 6% for $N = 10^6$)

-Solution : impose PBC, i.e. the basic cell is surrounded by infinitely replicated periodic images of itself



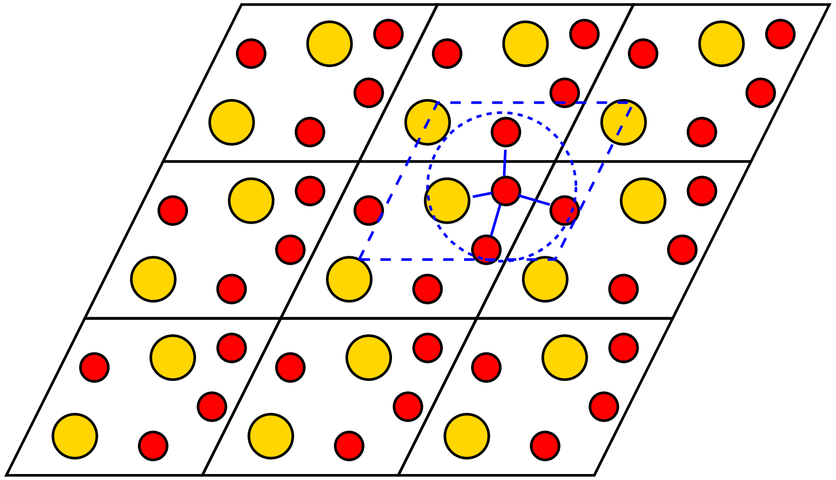
Consequences :

- The imposed artificial periodicity should be bear in mind when considering properties influenced by long-range correlations.
- PBC inhibits the occurrence of long-wavelength fluctuations.
- Normal modes of wavelength $>$ L are meaningless

PBC (2)

- When using PBC , if a particle crosses a surface of the basic cell, it re-enters through the opposite wall with unchanged velocity, and, for any observable, we have : $\boldsymbol{A}(\mathbf{r}) = \boldsymbol{A}(\mathbf{r} + \mathbf{n}\boldsymbol{L})$, $\mathbf{n} = (\boldsymbol{n_1}, \boldsymbol{n_2}, \boldsymbol{n_3})$, $\boldsymbol{n_i}$ integers
- The potential energy is affected, e.g. for a 2-body potential :

$$\mathcal{U}(\mathbf{r}^N) = \sum_{i<j} u^{(2)}(r_{ij}) + \sum_{\mathbf{n}} \sum_{i<j} u(|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L|) \Rightarrow \text{infinite summation!!}$$



Minimum image convention (MIC) :

distance $r_{ij} = \min|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L|$ over all $\mathbf{n}$. A particle interacts only with each of the $(N-1)$ other particules in the basic MD cell or their *nearest images*.

$\Rightarrow$ cut off of the potential by the condition $r_{cut} \leq L/2$

$\Rightarrow$ The use of **PBC+MIC** affects the computed properties.

Interaction potential : spatial extent

Short *vs* long range : case of the BKS potential

$$V_{ij}(r) = \frac{q_i q_j e^2}{r} + A_{ij}\exp(-B_{ij}r) - \frac{c_{ij}}{r^6} = V_{ij}^{C}(r) + V_{ij}^{BM}(r)$$

where $V_{ij}^{BM}(r) = A_{ij}\exp(-B_{ij}) - \frac{c_{ij}}{r^6}$ and $V_{ij}^{C}(r) = \frac{q_i q_j e^2}{r}$

- Short range term V_{BM} (falls off faster than $\approx \frac{1}{r^3}$), is truncated and shifted

$$V_{BM}(r_{ij}) = \begin{cases} V_{BM}(r_{ij}) - V_{BM}(r_{cut}) & \text{if } r_{ij} \leq r_{cut} \\ 0 & \text{if } r_{ij} > r_{cut} \end{cases}$$

- Value of r_{cut} consistent with energy conservation and computational efficiency

- Long range term V_C , Coulomb interaction, requires special methods for computation (Ewald method, etc)

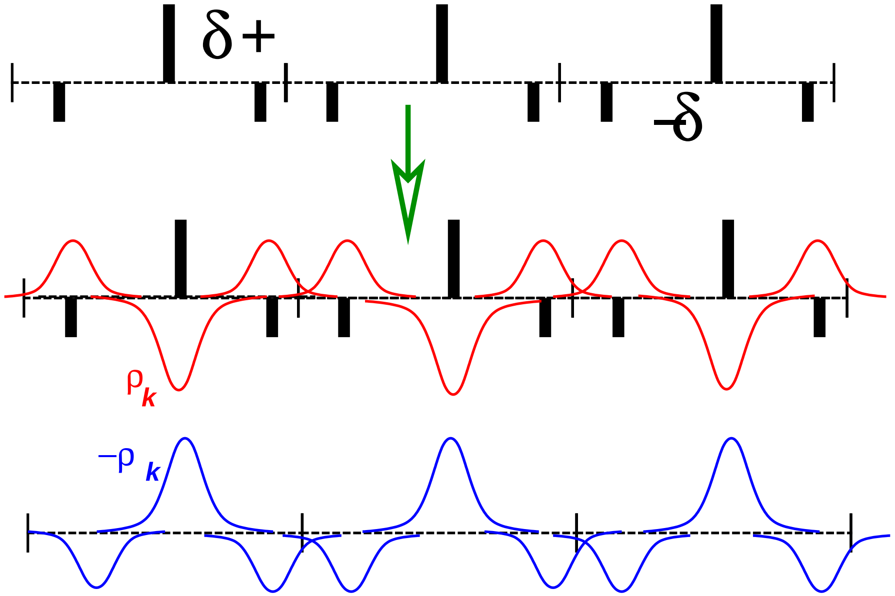
Coulomb interaction : Ewald method

Total electrostatic energy of a system of point charges (PBC) :

$$V^{\text{Coul.}} = \sum_{\mathbf{n}} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{n}L|}$$

a conditionally convergent series

Ewald approach : widely employed method to compute $V^{\text{Coul.}}$



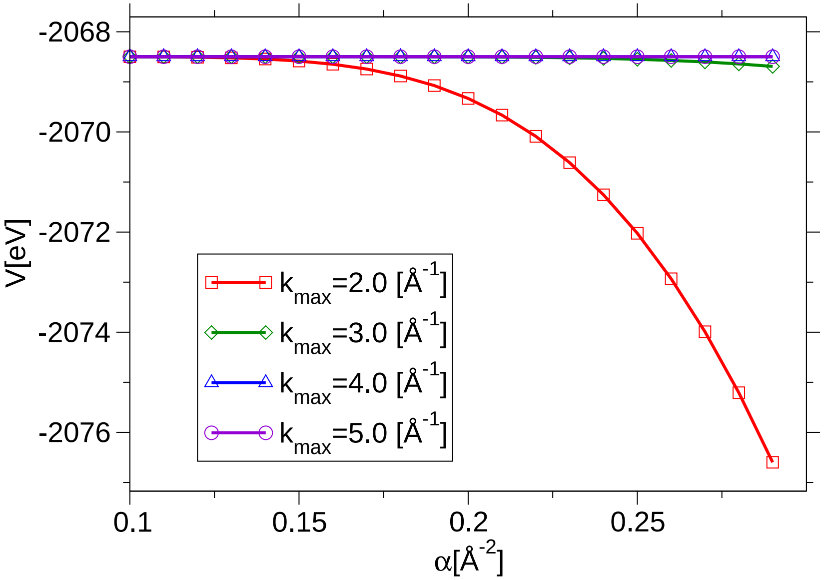
$$\rho_k(r) = \frac{\alpha^3}{\pi^{3/2}} \sum_{i=1}^{N} q_i \exp(-\alpha^2 |\mathbf{r} - \mathbf{r}_i|^2)$$

Coulomb interaction : Ewald method (2)

- Splitting of the Coulomb potential in a sum of two fast converging contributions :

$$V^{\text{Coul.}} = \frac{1}{2}\sum_{i\neq j} q_i q_j \frac{\text{erfc}(\sqrt{\alpha} r_{ij})}{r_{ij}} - (\alpha/\pi)^{\frac{1}{2}} \sum_i q_i^2 + \frac{1}{2}\sum_{\mathbf{k}\neq 0}\sum_{i,j} \frac{4\pi q_i q_j}{\Omega k^2} \exp\left[i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)\right] \exp\left(-k^2/4\alpha\right)$$

Practical aspects : α, k_{max}, r_{cut}^{ew} chosen in order to ensure a good balancing of the error and of the computation time in both real and reciprocal space for a given specified accuracy.

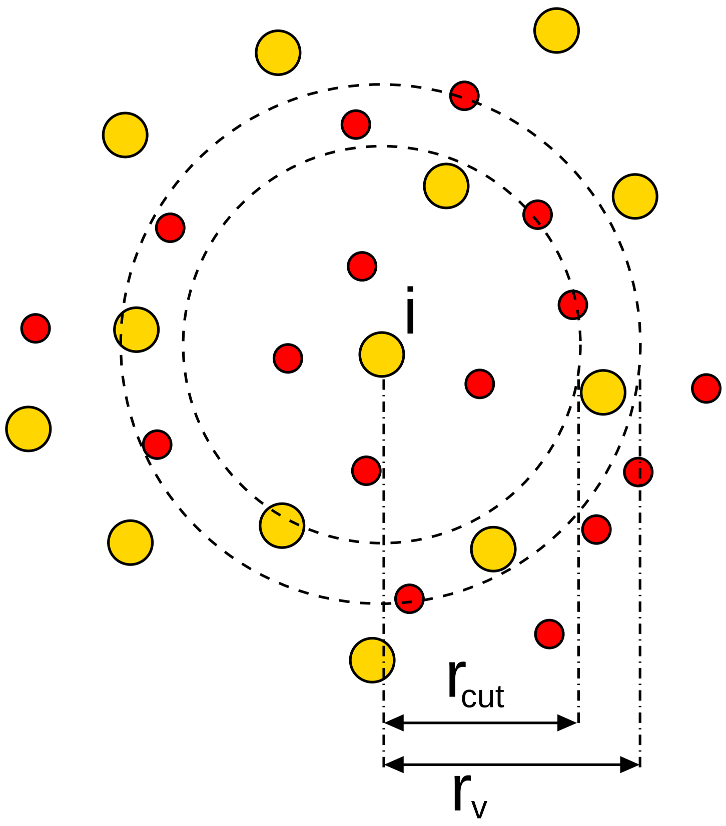


Neighbour list

- Forces calculation is the most CPU time consuming stage in a MD run.

e.g. for a short range pair-potential, such $u^{(2)}(r_{ij}) = 0$ if $r_{ij} > r_{cut}$, CPU time $\approx \frac{1}{2}N(N-1)$

- The speed of the code is improved if one constructs list of nearest neighnbor pairs‘; Verlet scheme, *cell list* method, etc...



Verlet scheme :

- 1st MD step : construction of a neighbour list for each particle i, i.e. of all pairs (i, j) such that $r_{ij} \leq r_v$

- next MD steps : only pairs appearing in the list are checked in the force routine

- list refreshing : when a particle has moved by more than $(r_v - r_{cut})/2$ or after of a given number of steps, depending on the ’skin’ width $(r_v - r_{cut})$ and temperature

$\Rightarrow$ reducing the CPU time, scaling now with N instead of $\approx N^2$

Thermodynamic quantities : equation of state

Routinely calculated, by time averaging $< A >_M = \frac{1}{M}\sum_{t=1}^{M} A_t$ over M time steps:

- *total energy*, conserved quantity apart from errors due to the integration algorithm, cut-offs and round-off errors,

$$E = E_{kin} + \mathcal{U}$$

-*temperature* T

$$< T > = \frac{2 < E_{kin} >}{(3N-3)k_B} \Leftrightarrow < E_{kin} > = \langle \sum_{i=1}^{N} \frac{m_i \mathbf{v}_i^2}{2} \rangle$$

- instantaneous *pressure* P, from virial theorem :

$$P = \frac{Nk_BT}{V} + \frac{1}{3V}\sum_{i=1}^{N} \mathbf{r}_i \nabla_{\mathbf{r}_i} \mathcal{U}$$

For a pairwise force field : $P = \frac{Nk_BT}{V} + \frac{1}{3V}\sum_{i<j} \mathbf{r}_{ij}\mathbf{f}_{ij}$

Estimating errors

- For a given model, computer simulation generates "exact" data if one can perform an infinitely long simulation.
- Or, in practice, one usually don't carry out such a simulation!
- Consequence : the simulation results are subjected to statistical errors, which may (and have to) be estimated.

- Statistical errors :
  - static properties
  - correlation function
- Block averages

Estimating errors : static properties

Given a simulation of total length $T = N\delta t$ and an observable $\mathcal{A}$

"Time" average

$$\mathcal{A}_T = \frac{1}{T}\int_0^T \mathcal{A}(t)\mathrm{d}t = \frac{1}{N}\sum_{i=1}^{N} \mathcal{A}_i$$

Ergodic hypothesis : $\lim\limits_{T\to\infty} \mathcal{A}_T \to < \mathcal{A} >$, i.e. ensemble average

Estimating the variance in $\mathcal{A}_T$:

$$\sigma^2(\mathcal{A}_T) = \frac{1}{N}\sigma^2(\mathcal{A}) \quad \text{– if } \mathcal{A}_i \text{ were statistically indepedent}$$

Or configurations are stored quite frequently, i.e. they are highly correlated.

$$\Rightarrow \sigma^2(\mathcal{A}_T) = \frac{2N_\mathcal{A}}{N}\sigma^2(\mathcal{A})$$

with $2t^c_\mathcal{A} = 2N_\mathcal{A}\delta t$ a 'correlation time', i.e. the time for which the correlation persist.

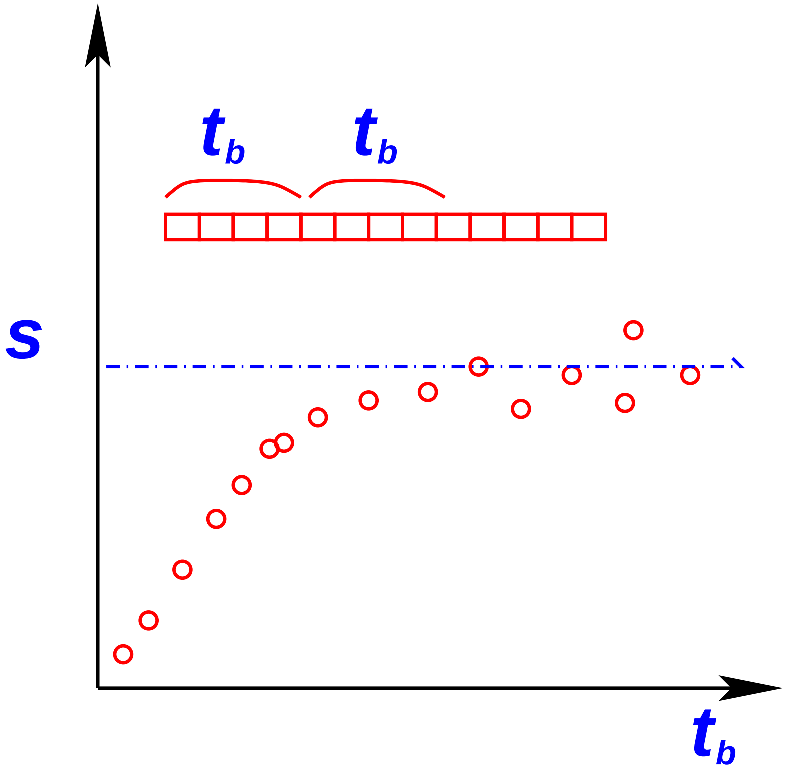
Problem : $t^c_\mathcal{A}$ is unknown before starting the analysis of the results!!

Estimating errors : static properties(2)

Solution : Block analysis, i.e. break down the set of configurations into a series of n_b blocks of t_b succesive steps : $N = n_b t_b$

$$< \mathcal{A} >_b = \frac{1}{t_b}\sum_{i=1}^{t_b}\mathcal{A}_i \quad \text{and } \sigma^2(< \mathcal{A}_b >) = \frac{1}{n_b}\sum_{b=1}^{n_b}(< \mathcal{A} >_b - < \mathcal{A} >)^2$$

Expectation : $\sigma^2(< \mathcal{A}_b >) \approx s\frac{1}{t_b}$ when t_b large.



$$s = \lim_{t_b\to\infty}\frac{t_b\sigma^2(< \mathcal{A}_b >)}{\sigma^2(\mathcal{A}_T)}$$

s – the 'statistical inefficiency'

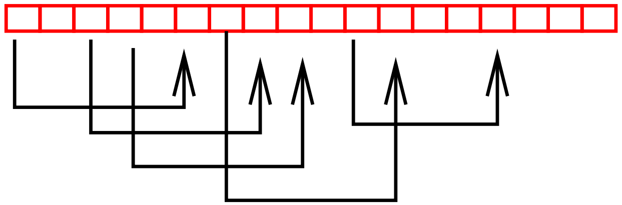
$$\Rightarrow \sigma(\mathcal{A}_T) \approx \sqrt{\frac{s}{N}}\sigma(\mathcal{A})$$

Time dependent properties

- Time dependent properties computed as *time correlation coefficients*

$$C_{\mathcal{AB}} = \frac{1}{M}\sum_{i=1}^{M}\mathcal{A}_i\mathcal{B}_i \equiv < \mathcal{A}_i\mathcal{B}_i > \Leftrightarrow C_{\mathcal{AB}}(t) = < \mathcal{A}(t)\mathcal{B}(0) >$$

- Expected behavior : $C_{\mathcal{AB}}(0) = < \mathcal{AB} >$ and $C_{\mathcal{AB}}(t) = < \mathcal{A} >< \mathcal{B} >$ when $t \rightarrow \infty$
- Usually one defines a correlation or relaxation time, τ_c, the time taken to loose the correlation
- Simulation time T should be significantly longer than τ_c
- In practice, use different time origins improve the accuracy when computing a time depedent quantity : $C_{\mathcal{AA}}(t) = \frac{1}{M}\sum_{j=1}^{M}\mathcal{A}(t_j)\mathcal{A}(t_j + t)$



2nd Part : Different Ensembles

- NVE
- NVT
- NPT

NVE- microcanonical ensemble

- NVE is the natural ensemble in an MD simulation, i.e. a computational method to propagate a system along a path of constant energy in the phase space.
- Constants of motion : N, V, $E = <\mathcal{H} = \sum_i \frac{1}{2} m_i \mathbf{v}_i^2 + \mathcal{U}(\mathbf{r}^N)>$, and $\mathbf{P}_{tot} = \sum_{i=1}^{N} m_i \mathbf{v}_i = 0$
- To adjust the system to a given energy, reasonable initial conditions are supplied and then energy is either removed or added, usually by an adhoc reajustement of the velocities.
- In practice : (1) one performs equilibrations until an average temperature (or equivalently the desired energy), is reached;
  (2) one performs NVE production run

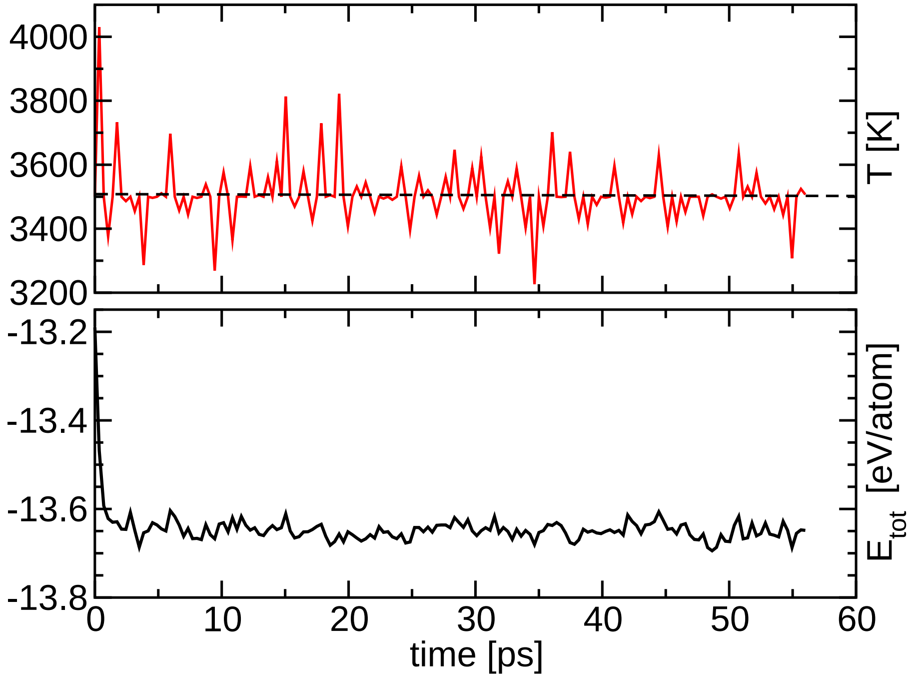
NVE (2)

- The total energy in an NVE-MD simulation is not constant : due to cutoffs and approximation when integrateting the eqs of motion, to round-off errors, it fluctuates around a mean value, at the best, and, at long times, this might introduce a drift
- "Advantage" of having a finite size system : fluctuations of the intensive properties, e.g. temperature ⇒ specific heat C_V

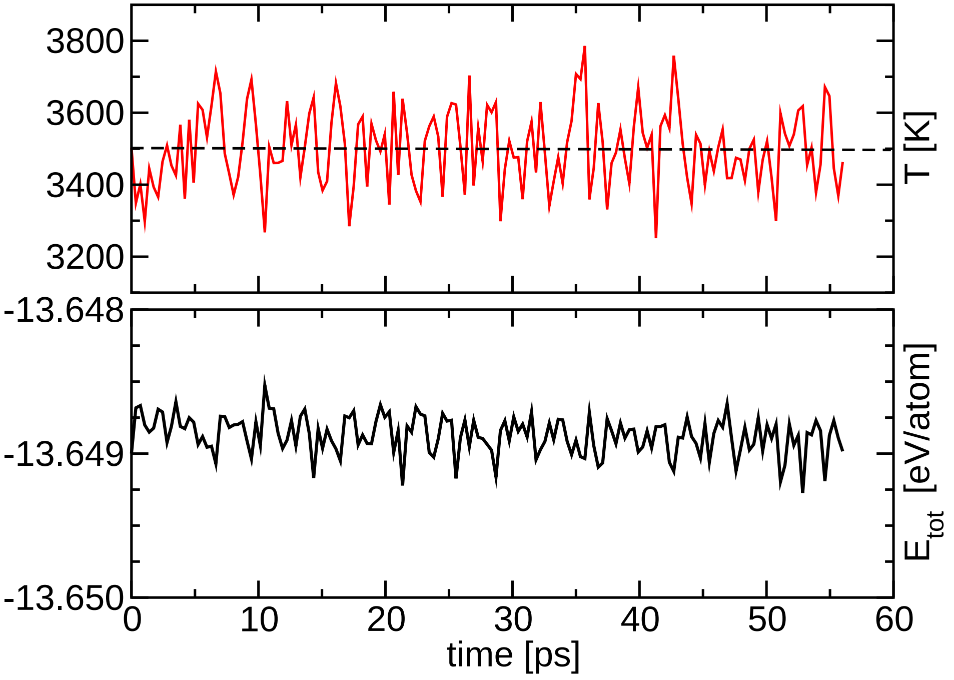
$$\frac{< \delta E_{kin}^2 >}{< E_{kin}^2 >} = \frac{2}{3N}\left(1 - \frac{3Nk_B}{2C_V}\right)$$

NVE (3) - MD of a liquid NS2 at 3500 K

Sodium disilicate (NS2) : Na_2O - 2 SiO_2, 450 atoms, BKS-like potential, Horbach et al. Chem. Geol. **174** 81 (2001)



(1) Equilibration run



(2) NVE run

NVT- canonical ensemble

- The system is coupled to an external heat bath imposing the target T
- Various thermostats : Andersen, Nosé-Hooever, Berendsen, $\dots$

• Andersen thermostat - atomic velocities are periodically reselected at random from the Maxwell-Boltzmann distribution (like an occasional random coupling with a thermal bath)
• Berendsen thermostat : corrects deviations of the $T(t)$ from the target T_0 :

$$\mathbf{v}_i \rightarrow \lambda \mathbf{v}_i, \text{ with } \lambda = [1 + \frac{\delta t}{\tau_T}(\frac{T_0}{T} - 1)]^{1/2}$$

τ_T - coupling time constant, $\propto$ time scale on which the target temperature is reached.

NVT (2)

- Nosé-Hoover thermostat - introduction of an additional variable, ν representing the heat bath and having the effect to renormalise the time :

$$\mathbf{r}'_i = \mathbf{r}_i \,, \mathbf{p}'_i = \mathbf{p}_i/\nu \,, \nu' = \nu \,, t' = t/\nu$$

with t' is the real time and t is the virtual one, etc. The extended Lagrangian of the new system [Nosé , JCP **81** (1984)]

$$\mathcal{L}_{\text{Nosé}} = \sum_i \frac{1}{2} m_i \nu^2 \dot{\mathbf{r}}_i^2 - V(\{\mathbf{r}_i\}) + \frac{1}{2} Q \dot{\nu}^2 - \frac{g}{k_B T} \ln \nu$$

Q - effective "mass" associated to ν, $g = 3N + 1$ - nb of degrees of freedom of the system. $\Rightarrow$ eqs of motion drawn from the resulting Hamiltonian

$$\mathcal{H}_{\text{Nosé}} = \sum_i \frac{1}{2} m_i \nu^2 \dot{\mathbf{r}}_i^2 + V(\{\mathbf{r}_i\}) + \frac{\mathbf{p}_\nu}{2Q} + \frac{g}{k_B T} \ln \nu$$

NPT- isobaric-isothermal ensemble

- The system is coupled to a barostat imposing the target pressure P (and to an external heat bath imposing the target T)
- Various barostats : Andersen, Berendsen, Parrinello-Rahman
- Andersen barostat : → simulation box with variable volume, but fixed shape
  - introduction of an additional variable, the volume $\mathcal{V}$ and use of reduced units : $\mathbf{s}_i = \mathbf{r}_i / \mathcal{V}^{1/3}$
  - the equations of motion are drawn from

$$\mathcal{H} = \frac{1}{\mathcal{V}^{2/3}} \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \sum_{i<j=1}^{M} \mathcal{U}(\left\{\mathcal{V}^{2/3}\mathbf{s}_i\right\}) + \frac{1}{2} M \dot{\mathcal{V}}^2 + P\mathcal{V}$$

NPT (2)

- Berendsen barostat : $\frac{dP(t)}{dt} = \frac{1}{\tau_p}(P - P_{bath})$ with scaling $\mathbf{r}'_i = \lambda^{1/3}\mathbf{r}_i$, and $\lambda = 1 - \kappa\frac{\delta t}{\tau_P}(P - P_{target})$
- Parrinello-Rahman method
  - generalization in order to change both volume and cell shape
  - appropriate to study structural phase transitions in crystaline solids

  Parrinello & Rahman - PRL, **45** 1196 (1980), and J. Appl. Phys. **56** 7182 (1981)

- the isothermal compressibility can be calculated

$$< \delta V^2 >_{NPT} = < V^2 > - < V >^2 = V k_B T \kappa_T$$

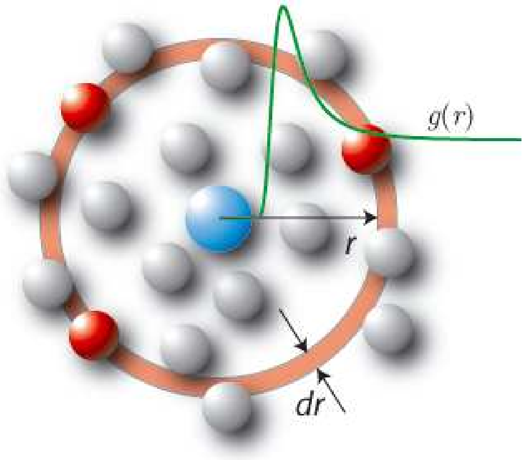
3rd Part : Computing properties

- Structure : $g_{\alpha\beta}(r)$, coordination $z_{\alpha\beta}$, total structure factor $S(q)$ (neutrons and X-ray), partial structure factors $S_{\alpha\beta}(q)$, bond angle distribution (BAD), rings, ...
- Dynamics : diffusion constants
- Auto-correlation functions, vibrational density of states
- Dependence on cooling rate, potential

Structure : pair distribution functions (PDF) $g_{\alpha\beta}(r)$

$dn_{\alpha\beta}$ = nb. of atomic pairs (α, β) separated by

a distance btw r and $r + dr$



$$dn_{\alpha\beta} = \frac{\mathcal{N}_{\alpha\beta}}{V} g_{\alpha\beta}(r) 4\pi r^2 dr$$

$$\mathcal{N}_{\alpha\beta} = \begin{cases} N_\alpha \left(N_\alpha - 1\right) & \text{if } \alpha = \beta \\ N_\alpha N_\beta & \text{if } \alpha \neq \beta \end{cases}$$

Or alternatively, using the local (particle) density :

$$(2) \qquad \rho_{\alpha\beta}(\mathbf{r}) = \sum_{i=1}^{N_\alpha} \sum_{j=1, j\neq i}^{N_\beta} \delta(\mathbf{r} - \mathbf{r}_i + \mathbf{r}_j) \Rightarrow g_{\alpha\beta}(r) = \frac{V}{\mathcal{N}_{\alpha\beta}} \langle \rho_{\alpha\beta}(\mathbf{r}) \rangle$$

PDF $g_{\alpha\beta}(r)$ - recipe for computing (1)

```
      dr=box/(2*nbins)                  bin size
      do i =1, nbins                    nbins, total nb of bins
      gab (i)=0
      enddo
      ncfg=0
1     [Reading positions]
      ncfg=ncfg+1                       reading a configuration
      do i =1, napart                   loop over all pairs (α, β)
      do j =1, nbpart
      dx=x(i) - x(j)
      dx=dx-anint(dx/box)*box           periodic boundary conditions
idem   dy =y(i)-y(j), dz=z(i)-z(j)
      r=dx*dx+dy*dy +dz*dz
      r=sqrt(r)
      ig=nint(r/dr)
      gab (ig)=gab (ig)+1
      enddo
      enddo
      go to 1                           (see next page)
```

PDF $g_{\alpha\beta}(r)$ - recipe for computing (2)

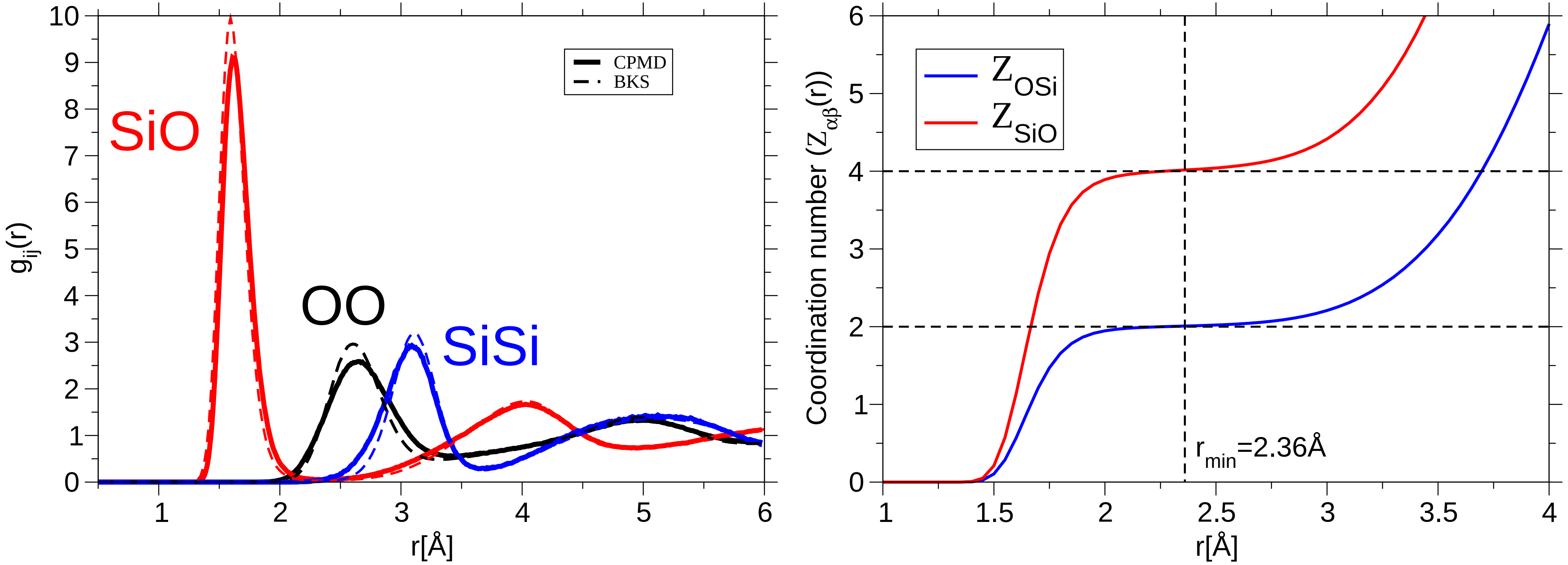
And finally $g_{\alpha\beta}$ calculation

```
factor=box**3/(4*pi*napart*nbpart)/ncfg
do i =1, nbins
r=dr*i
vdr=(dr*r**2)
gab (i)=gab (i)*factor/vdr
write(10,*)r, gab (i)

enddo
```

PDF → coordination

Liquid silica - A. Carré, PhD thesis



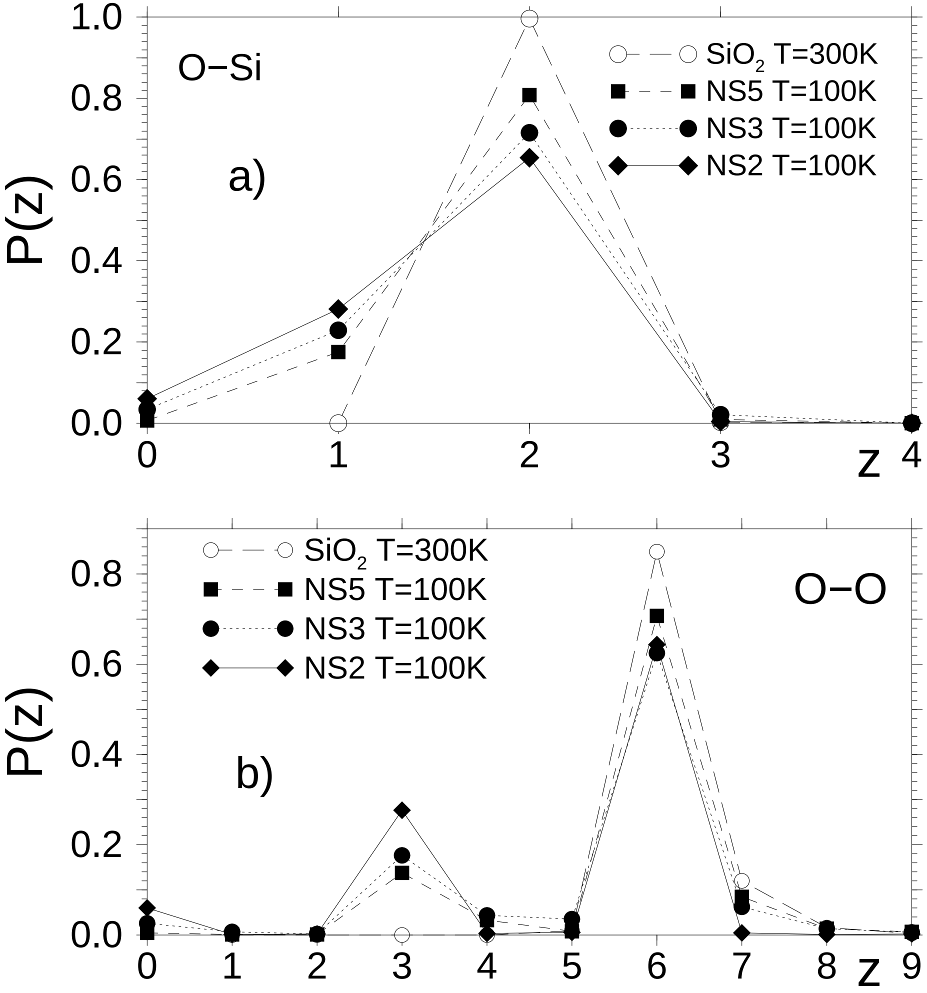
PDF → $z_{\alpha\beta}$, pair coordination number, (#neighbors β surrounding an atom α within a distance $r \leq r_{min}$)

$$z_{\alpha\beta} = \frac{N_\beta}{V} \int_0^{r_{min}} 4\pi r^2 g_{\alpha\beta}(r) dr$$

(i.e. a geometrical criterion)

Distribution of the pair coordination number (3)

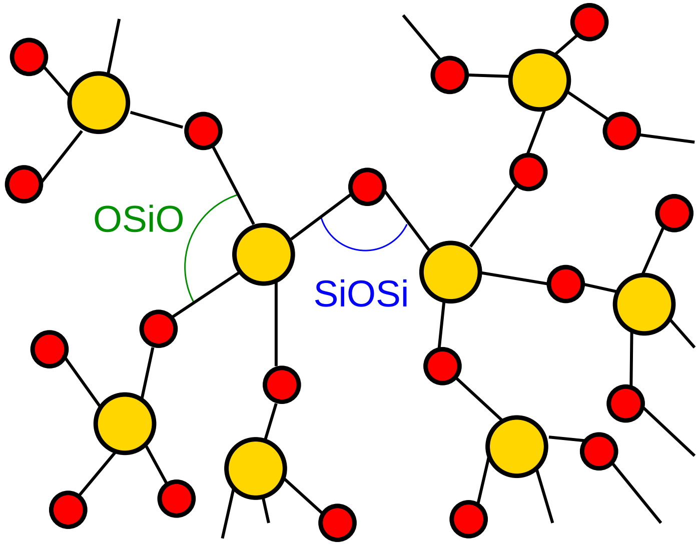
BKS-like potential, A. Winkler, PhD thesis (2002)

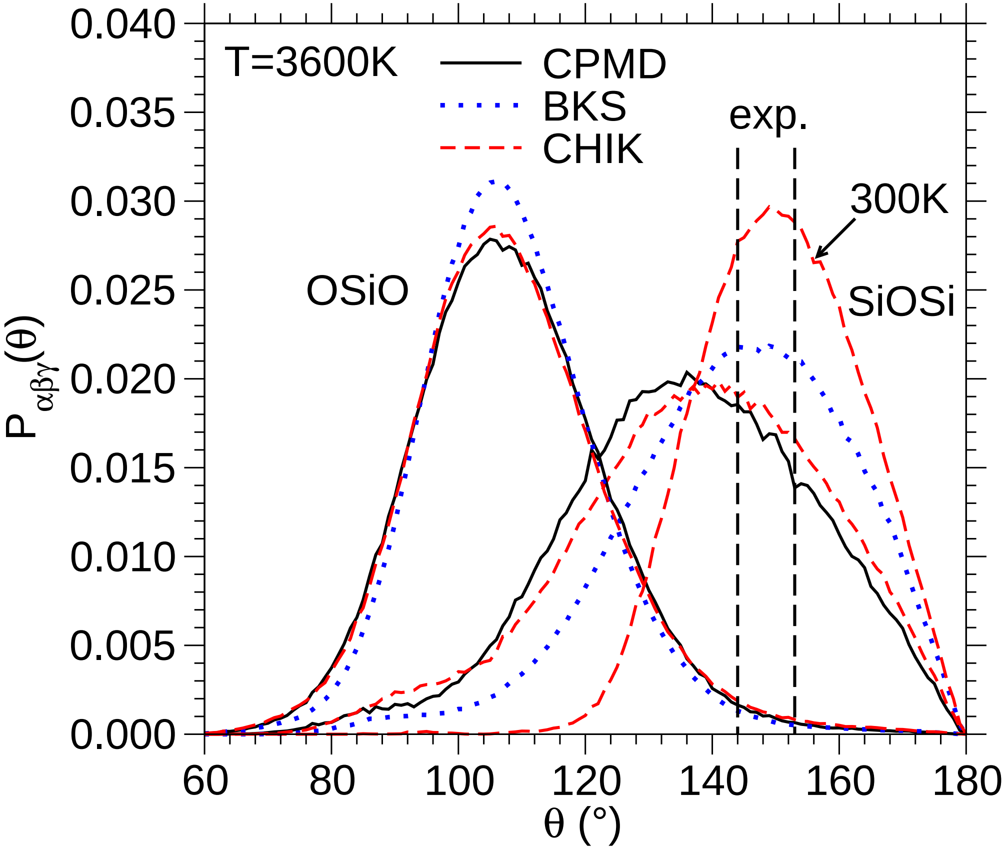


The introduction of Na atoms affects the local coordination of the SiO network

Bond angle distribution (BAD)

Recipe : for computing the $P_{\alpha\beta\gamma}$ distribution look after the α and γ neighbors of β so that $r_{\alpha\beta} \leq r_{min}$ and $r_{\beta\gamma} \leq r_{min}$ (don't forget the PBC!)



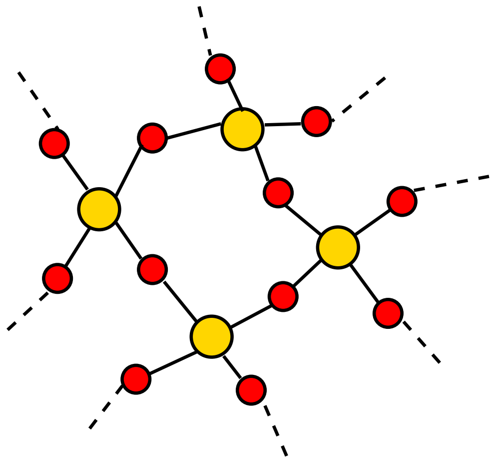


CHIK potential - a BKS-like potential with parameters adjusted on ab initio data

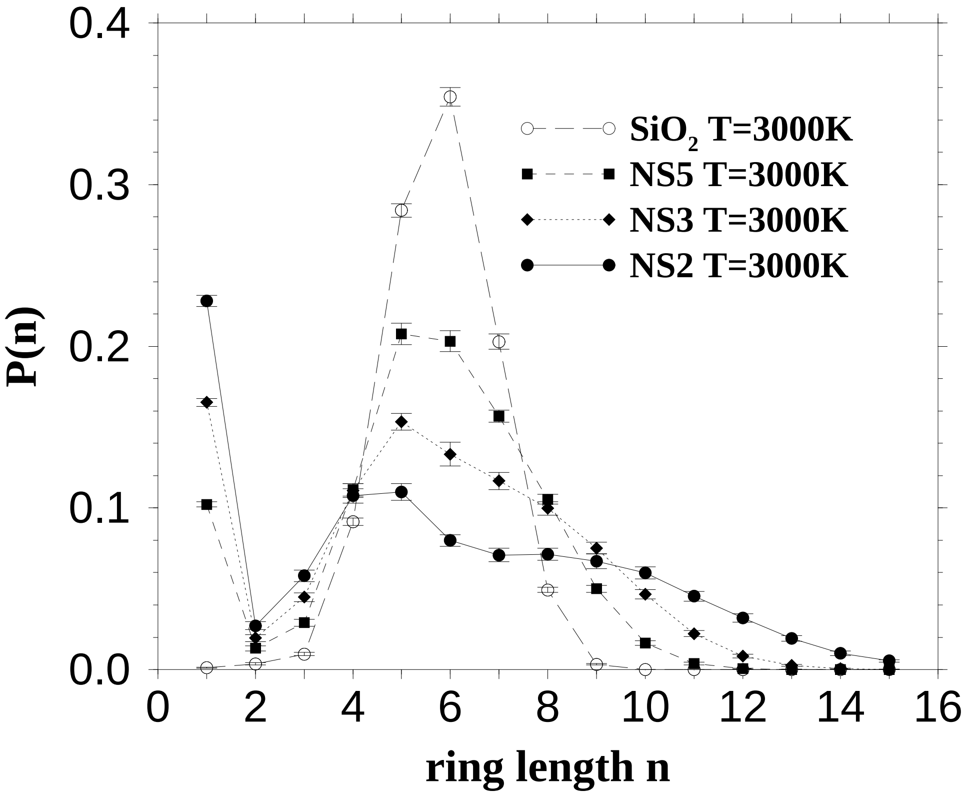
Carré et al. EPL (2008)

Rings

probability to find a ring of length n ($n = 2, 3, \ldots, 14$) (don't forget the PBC!)



Ring of size $n = 4$

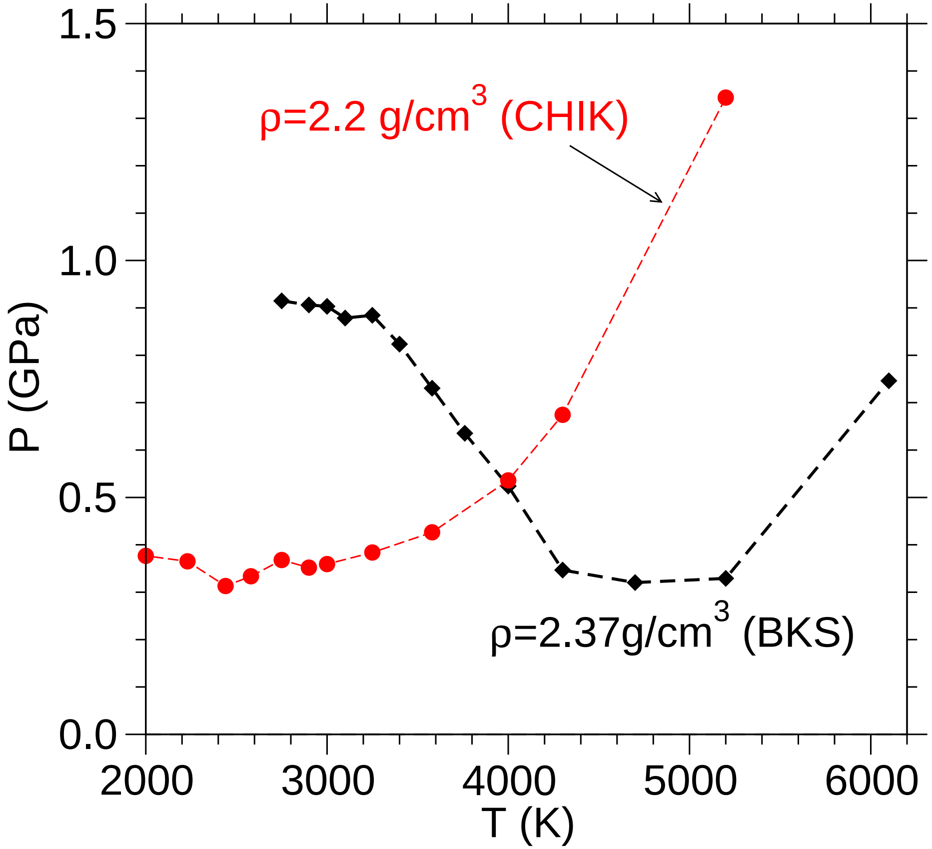


- The introduction of Na atoms affects the local structure of the SiO network as well as that on intermediate length scale

BKS-like potential, A. Winkler, PhD thesis (2002)

Pressure, $P = P(T)$

Example : occurrence of a density maximum at 1820 K of amorphous SiO_2, seen in $P = P(T)$

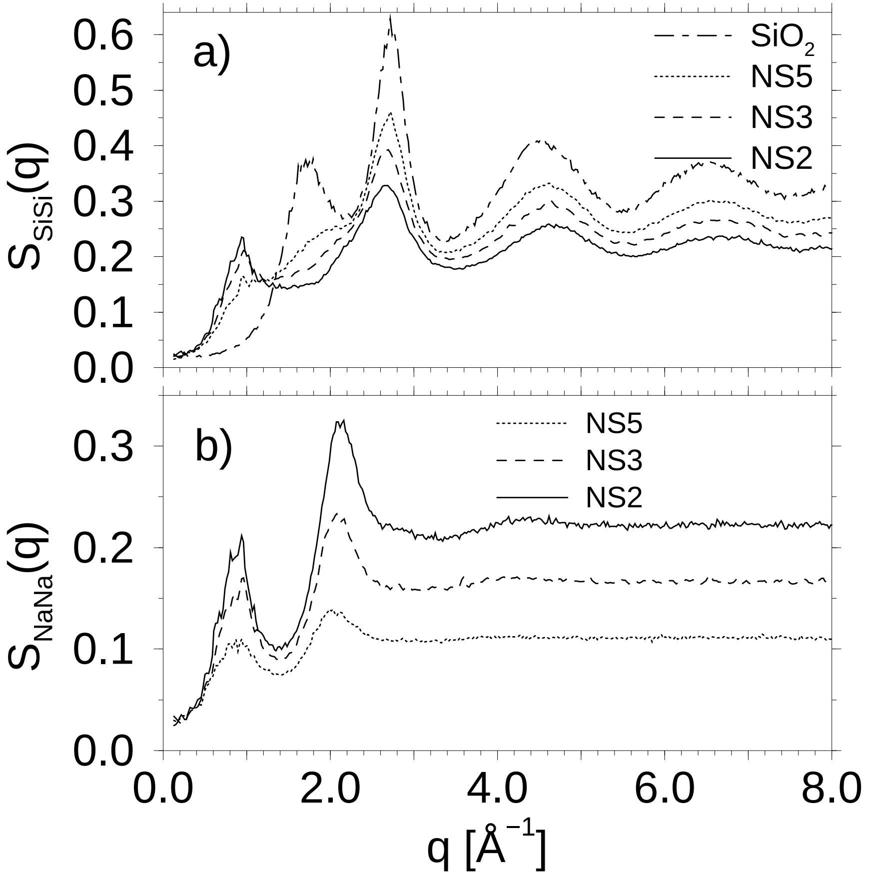


- Both BKS and CHIK show a minimum pressure at about 4800 K and 2300 K, respectively, but the CHIK data are in better agreement with experiment with respect to the location of the minimum and the density. [Carré et al. EPL (2008)]

Reciprocal space : partial structure factors

$$S_{\alpha\beta}(q) = \frac{f_{\alpha\beta}}{N}\left\langle \sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta} \exp\left[i\mathbf{q}\cdot\mathbf{r}_{ij}\right]\right\rangle$$

$f_{\alpha\beta} = 1/2$ for $\alpha \neq \beta$, $f_{\alpha\beta} = 1$ for $\alpha = \beta$



- Effect of introducing Na atoms :

from SiO_2 to NS5, NS3 and NS2

MD simulation with a BKS-like potential,

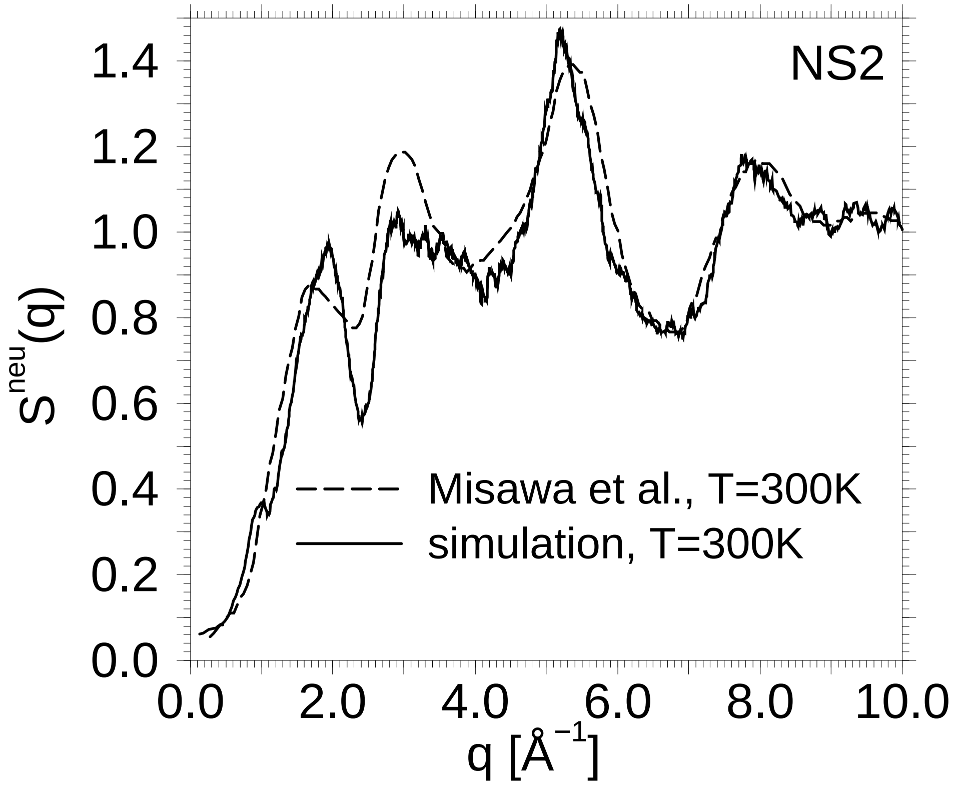
A. Winkler, PhD thesis (2002)

Remark : when using PBC, results could not depend on the choice of a particular particle image, i.e. the allowed wavevectors are quantized $\mathbf{q} = \frac{2\pi}{L}(n_x, n_y, n_z)$, with n_x, n_y, n_z integers.

Reciprocal space : comparison to experiments

- Neutron total structure factor : $S_n(q) = \frac{1}{\sum_\alpha c_\alpha b_\alpha^2} \sum_{\alpha,\beta} b_\alpha b_\beta S_{\alpha\beta}(q)$

b_α neutron scattering lengths, $c_\alpha = N_\alpha / N$

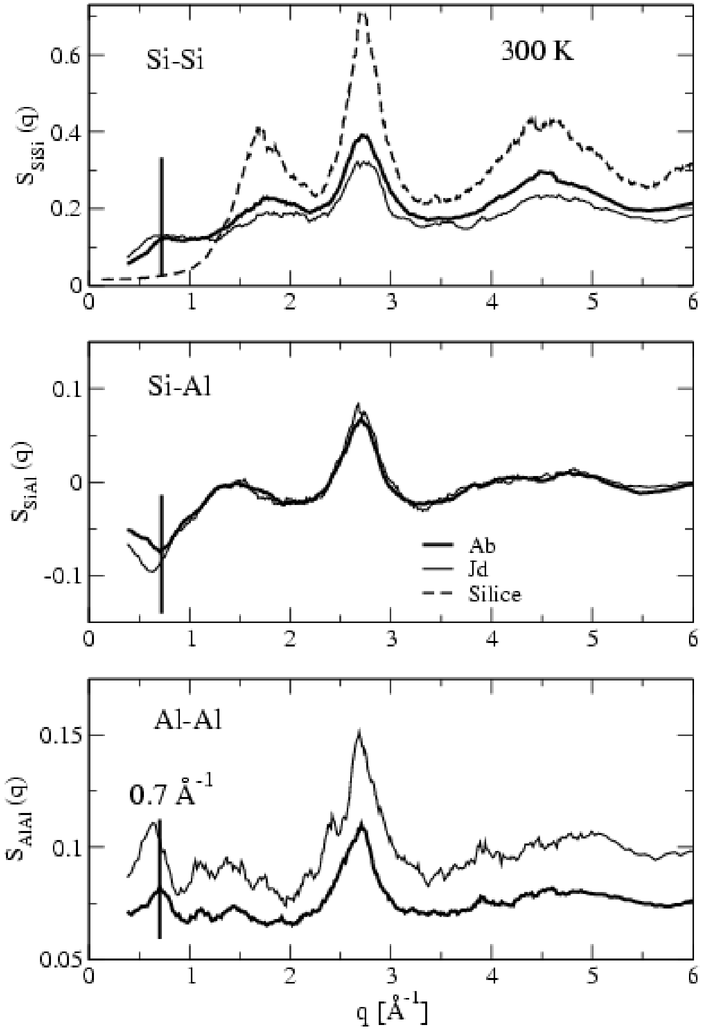


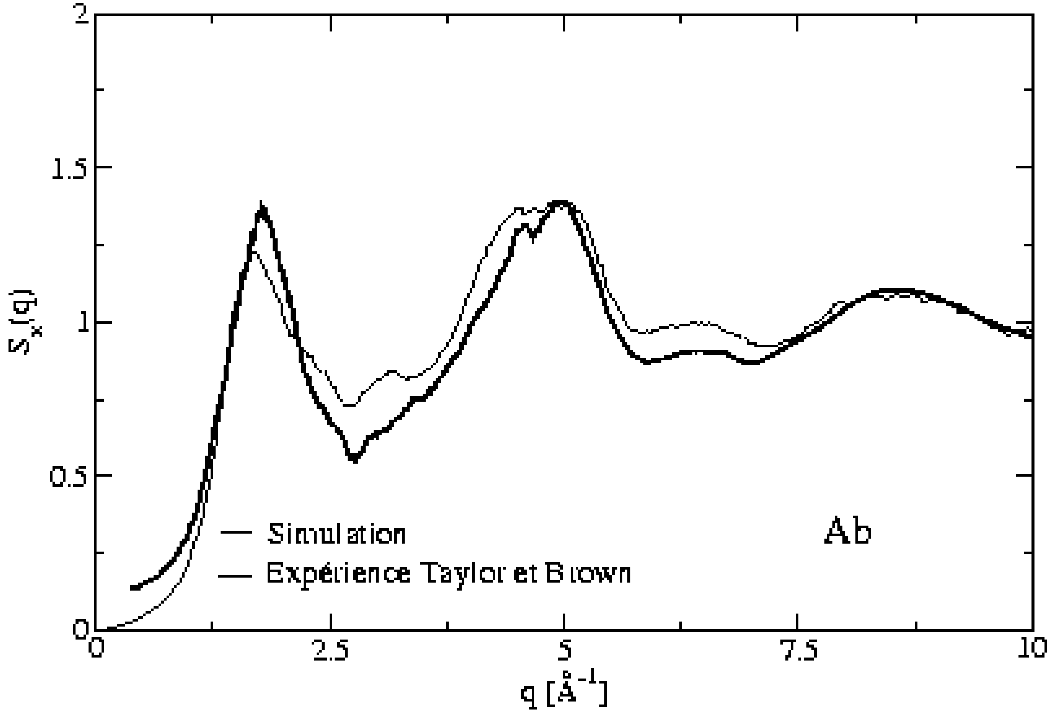
Horbach et al. Chem. Geol. (2001)

Reciprocal space : comparison to experiments (2)

- X-ray structure factor (f_α - form factors) :

$$S_n(q) = \frac{1}{\sum_\alpha c_\alpha f_\alpha(q/4\pi)} \sum_{\alpha,\beta} f_\alpha(q/4\pi) f_\beta(q/4\pi) S_{\alpha\beta}(q)$$





MD simul. BKS-like potential

Albite (Ab) - $NaAlSi_3O_8$, Jadeite (Jd) -$NaAlSi_2O_6$

S. de Wispeleare, PhD thesis (2005)

Dynamics : MSD

Simplest quantity : Mean Square Displacement (MSD) of particles of type α

$$\left\langle r_\alpha^2(t)\right\rangle = \frac{1}{N_\alpha}\sum_{l=1}^{N_\alpha}\left\langle\left|\mathbf{r}_l(t)-\mathbf{r}_l(0)\right|^2\right\rangle\,, \quad \mathbf{r}_l(t) - \text{ uncorrected PBC position}$$

Main regimes for a liquid :

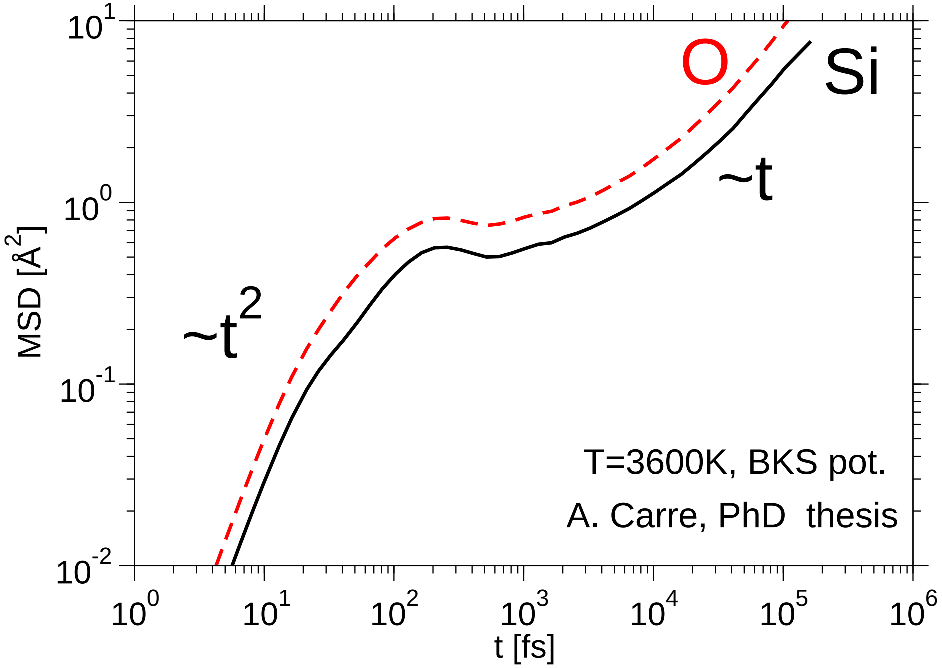
1. short time scale → ballistic regime : $\left\langle r_\alpha^2(t)\right\rangle \propto t^2$
2. intermediate time scale → a plateau-like region due to cage effect, and becoming more pronounced with decreasing temperature
3. long time scale → diffusive regime : $\left\langle r_\alpha^2(t)\right\rangle \propto t$

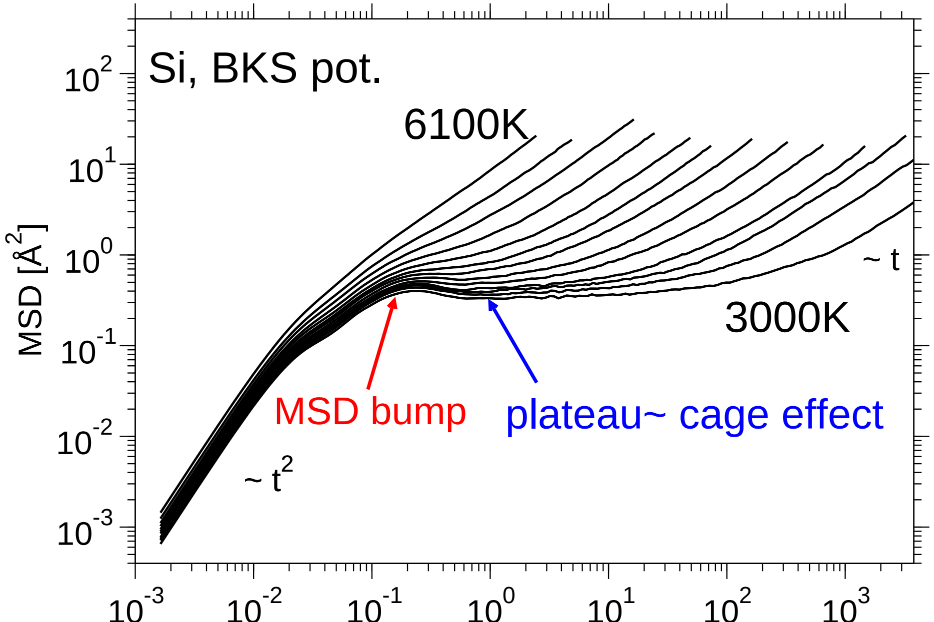
Main regimes for a glass (at temperatures $< T_g$) :

1. short time scale → ballistic regime : $\left\langle r_\alpha^2(t)\right\rangle \propto t^2$
2. a plateau region : particles oscillate around their equilibrium positions

Dynamics : MSD (2)

Example : Liquid silica, BKS potential (A Carré, PhD thesis, 2007)





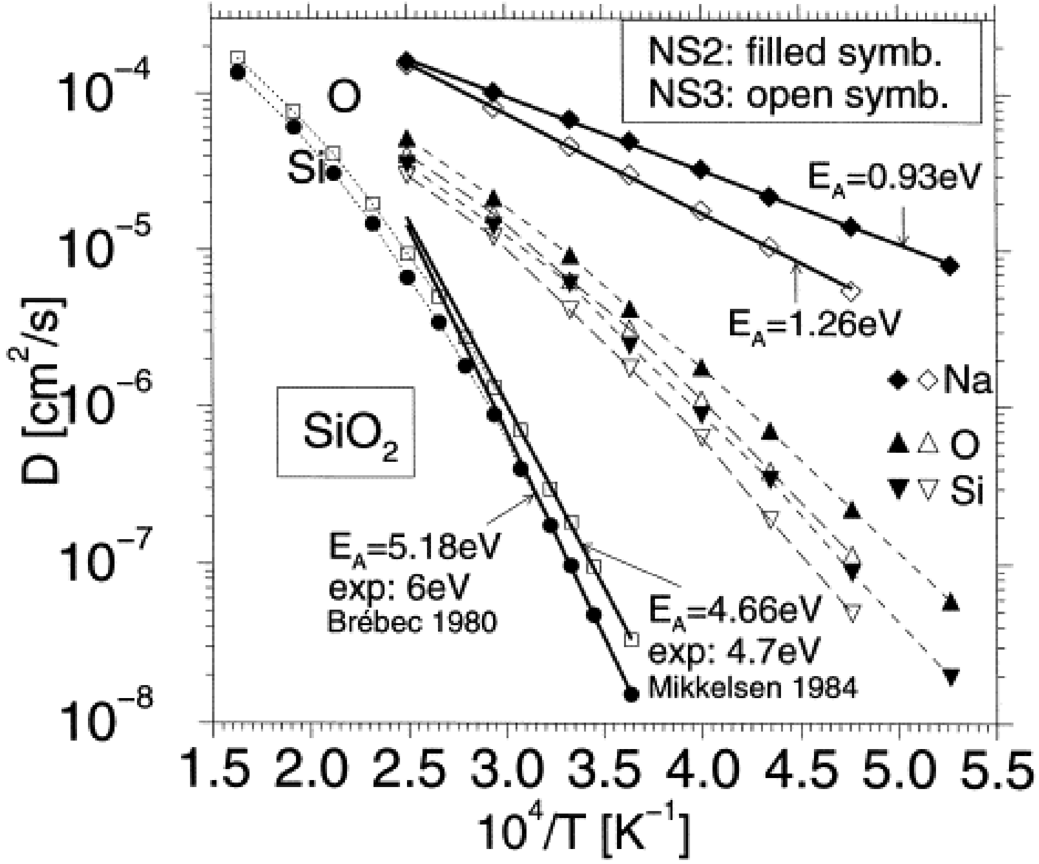
MSD of silicon atoms, [Horbach & Kob, PRB **60**, (1999)]

Dynamics : Diffusion constant

Self-diffusion constant D_α : Einstein relation (long time scale)

$$\lim_{t\to\infty} \frac{\left\langle r_\alpha^2(t) \right\rangle}{t} = 6D_\alpha$$

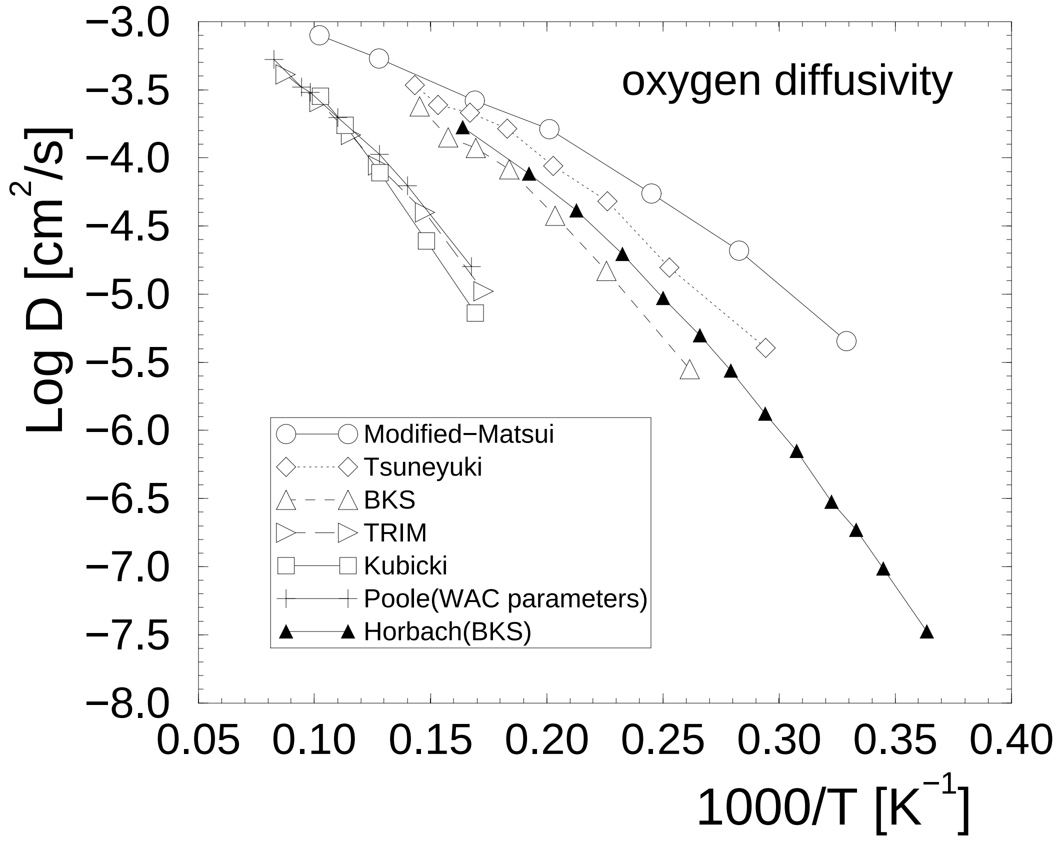
Activation energies : $D_\alpha \propto \exp\left(-\frac{E_{a,\alpha}}{k_B T}\right)$ (Arrhenius plot of D_α)



BKS - like potential
[Horbach et al. Chem. Geol. (2001)]

Diffusion constant (2)

Temperature dependence of the O-diffusion constant (Hemmati and Angell, 2000)



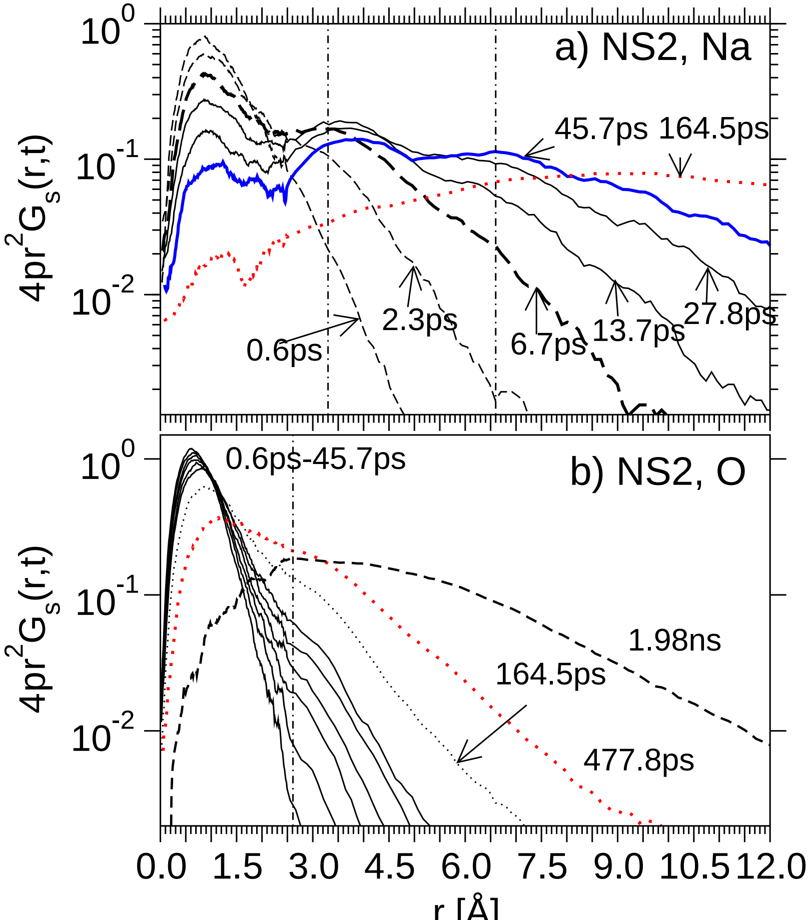
For silica : many different potentials, essentially equivalent from the structural point of view, BUT various potentials make very different predictions for the dynamical properties.

Dynamics : insight into microscopic diffusion

Self part of the van Hove correlation function

$$G_s^{\alpha}(r,t) = \frac{1}{N_\alpha}\sum_{i=1}^{N_\alpha} \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_i(0)|)\rangle \qquad \alpha \in \{\mathrm{Si}, \mathrm{Na}, \mathrm{O}\} \quad .$$

$4\pi r^2 G_s^{\alpha}(r,t)$ - probability to find a particle a distance r away from the place it was at $t = 0$



Sodium disilicate NS2 (2100 K)

Horbach et al., Chem. Geol. (2001)

- The diffusion of sodium atoms is discontinous, by hopping in average over a distance $\bar{r}_{\mathrm{Na-Na}} = 3.3$.
- At $t = 45.7$ ps, Na atoms have performed **2** elementary diffusion steps while most of the Oxygens sit in the cage formed by the neighboring atoms and only rattle around in this cage.

Viscosity η

- Green-Kubo relation

$$\eta = \frac{1}{k_B T V} \int_0^\infty dt \langle \dot{A}_{\alpha\beta}(t) \dot{A}_{\alpha\beta}(0) \rangle$$

with pressure tensor

$$\dot{A}_{\alpha\beta} = \sum_{i=1}^{N} m_i v_i^\alpha v_i^\beta + \sum_{i=1}^{N} \sum_{j>i}^{N} F_{ij}^\alpha r_{ij}^\beta \quad \alpha \neq \beta$$

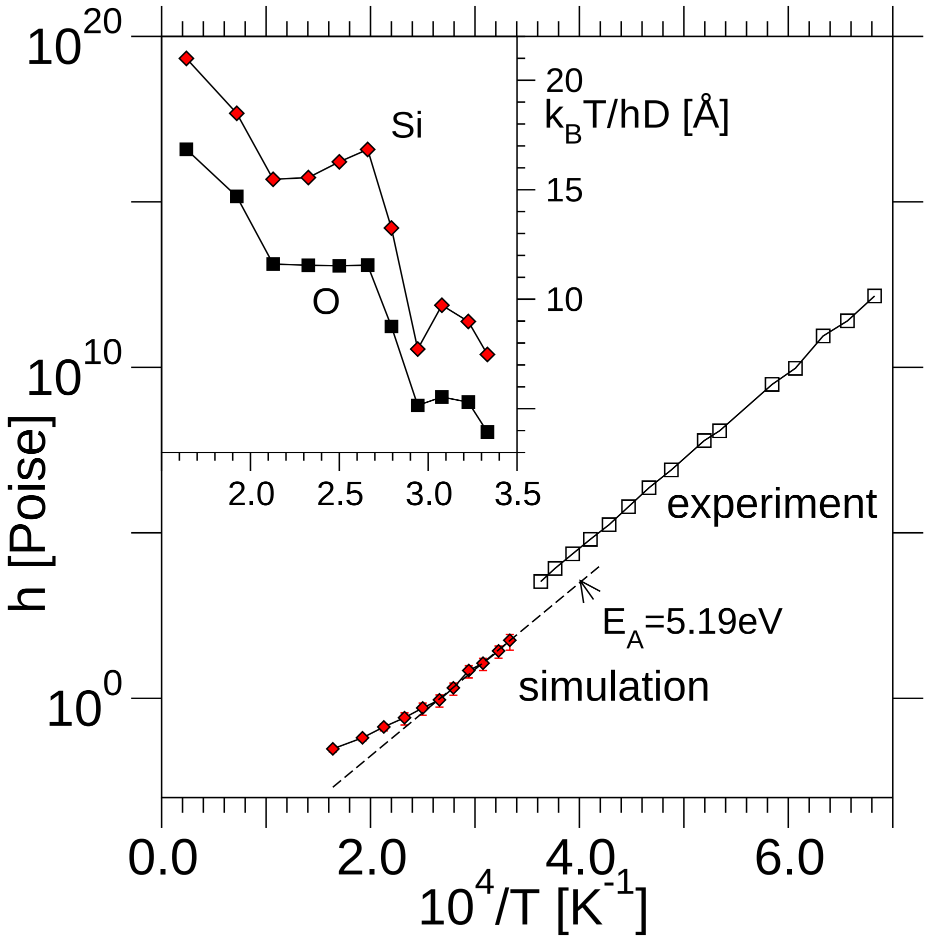
- Einstein formula:

$$\eta = \frac{1}{k_B T V} \lim_{t \to \infty} \langle (A_{\alpha\beta}(t) - A_{\alpha\beta}(0))^2 \rangle$$

where $A_{\alpha\beta}(t) = \sum_{i=1}^{N} m_i v_i^\alpha(t) r_i^\beta(t)$ and $A_{\alpha\beta}(t) - A_{\alpha\beta}(0)$ computed as $\int_0^t dt' \dot{A}_{\alpha\beta}(t')$ (Allen et al. 1994)

Viscosity η (2)

- Silica - temperature dependence of the viscosity in an Arrhenius plot [Horbach and Kob (1999)]



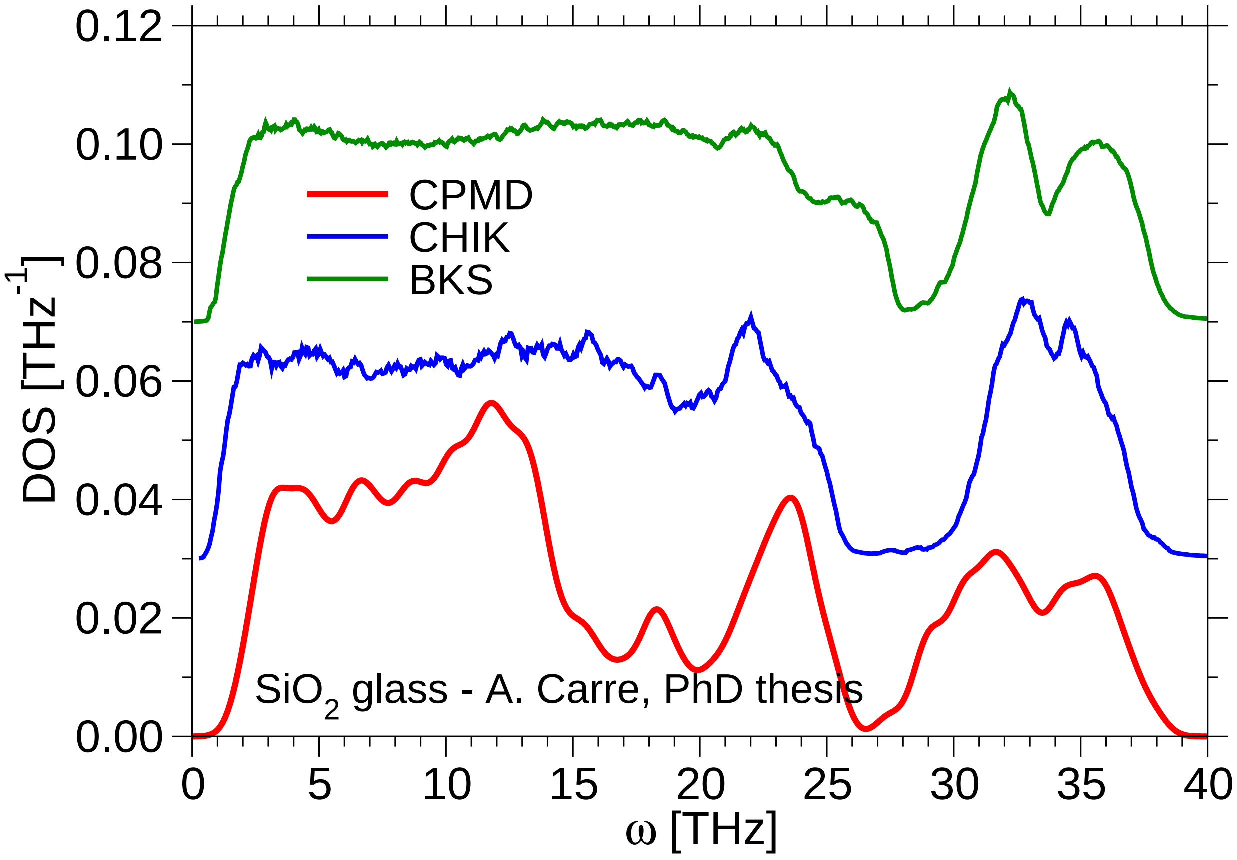
- Stokes-Einstein relation $\frac{k_B T}{\eta D} = \lambda = const.$ not always a good way to convert viscosity data into diffusivities or vice versa!!

Vibrational density of states (VDOS)

Fourier transform of the velocity auto-correlation function :

$$g(\omega) = \int_0^{\infty} \frac{1}{k_B T} \sum_j m_j \langle \mathbf{v}_j(t) \cdot \mathbf{v}_j(0) \rangle \exp(-\imath w t) dt \propto \sum_\nu \delta(\omega - \omega_\nu)$$

w_ν frequencies of the normal modes



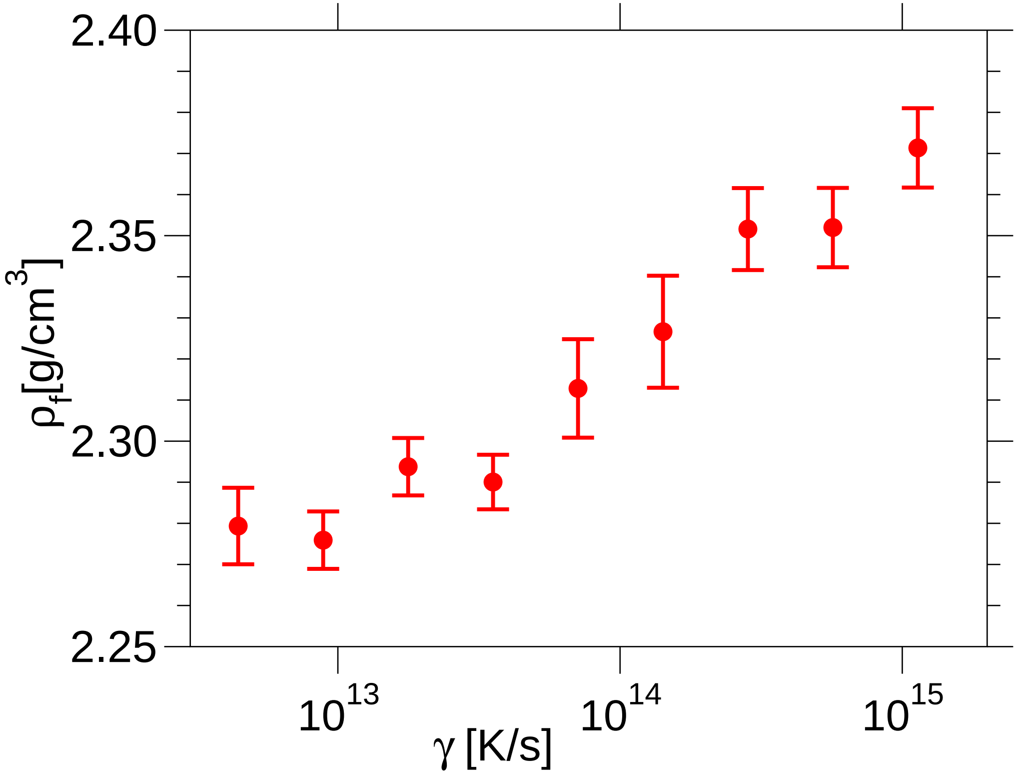
Silica - A. Carré PhD thesis

Cooling rate dependence

The properties of the simulated glass samples depend on the cooling rates : density, vibrational density of states, local and medium range structure

Example:

Density of SiO_2 glass at 0 K, Vollmayr et al. PRB 54 15808 (1996), using BKS potential

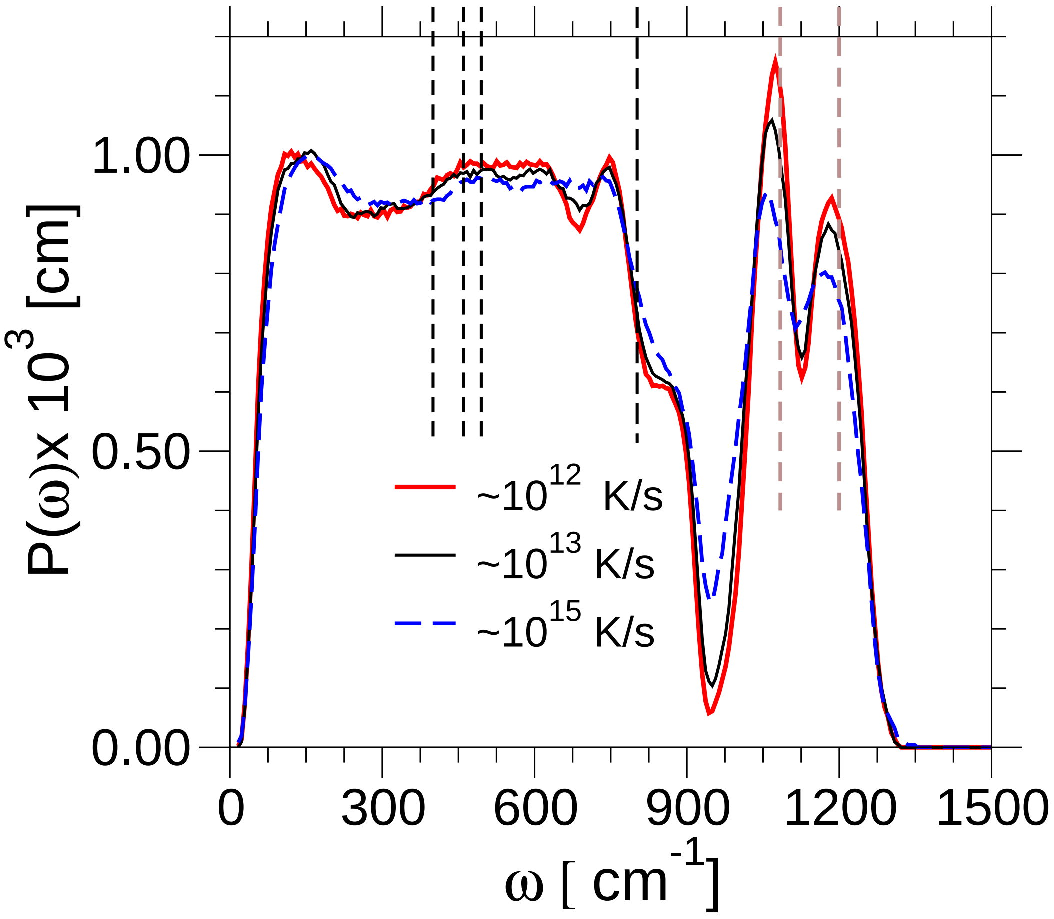


Cooling rate dependence (2)

The properties of the simulated glass samples depend on the cooling rates : Vibrational density of states (VDOS)

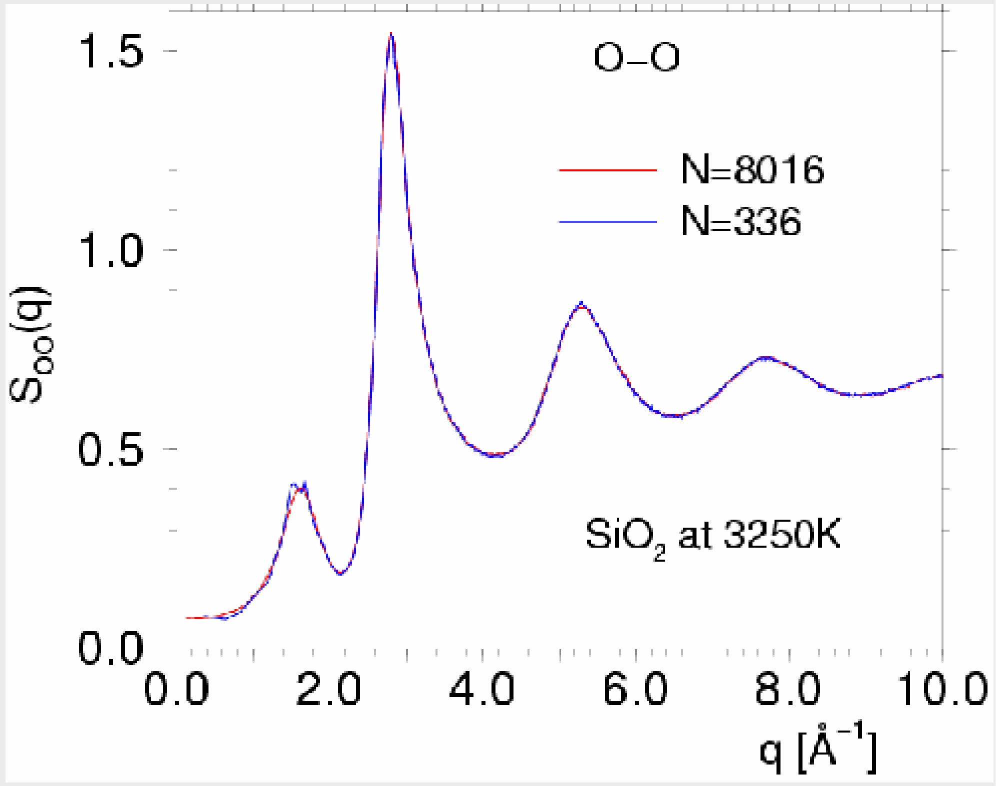
Example:

VDOS of SiO_2 glass at 0K, (diagonalization of the dynamical matrix), Vollmayr et al. PRB **54** 15808 (1996), using BKS potential



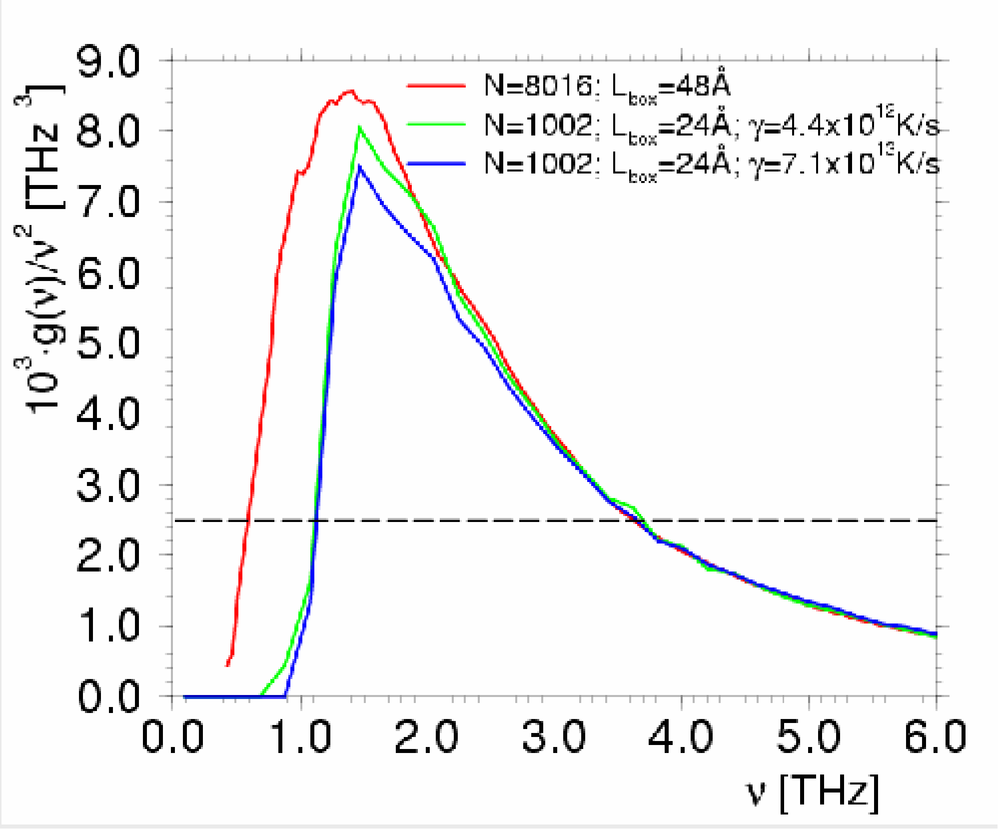
System size : static and dynamics properties

- Usually the static properties show almost no finite size effects.
- Substantial finite size effects are presented by the dynamic quantities, and they become more pronounced with temperature.



Finite size effects : vdos

- At small ν , $g(\nu)$ is expected to scale like ν^2 , (Debye); many glass-forming systems shown an anomalous increase of $g(\nu)$ over the Debye-level $\Rightarrow$ Boson peak



SiO_2 glass, BKS potential, Horbach et al. J.Phys. Chem. B (1999)

- Even for the largest systems $g(\nu)$ does not show the expected Debye behavior at small ν
- $\Rightarrow$ Strong dependence of $g(\nu)$ on system size and on cooling rate

MD codes

- How does one choose a code for performing MD ?
  Some criteria :
  - the chemical composition of the system and phenomena under consideration ;
  - the properties we are interested in ;
  - trade-off between accuracy, performance, and computational effort
  - distribution : freeware or commercial
  - platforms and/or computer facilities at hand
  - user-friendly or not
- Some codes used by the physics/biophysics/chemistry communities :
  - DL_POLY, LAMMPS, GROMOS, CHARMM, NAMD, POLY-MD
  - home-made codes

Summary

- MD simulations : an unified study of the physical properties : thermodynamic, structural, dynamic, and transport properties
- Direct link between potential model and physical properties
- Complete control on the input, initial and boundary conditions
- Access to atomic trajectories
- Don't forget the various approximations, conventions, etc. when discussing the reliability of the MD results
- Glasses are overall quite difficult to simulate : potential equivalent for the structure give completely different dynamical results!

Further reading : a non-exhaustive list

- M. P. Allen and D. J. Tildesley,
  "Computer Simulation of Liquids" (Clarendon Press, Oxford, 1987)
- D. Frenkel and B. Smit,
  "Understanding Molecular Simulation From Algorithms to Applications"
- D.W. Hermann,
  "Computer Simulation Methods"
- K. Binder and W. Kob
  "Glass Materials and disordered solids: an introduction to their statistical mechanics"
- . . .