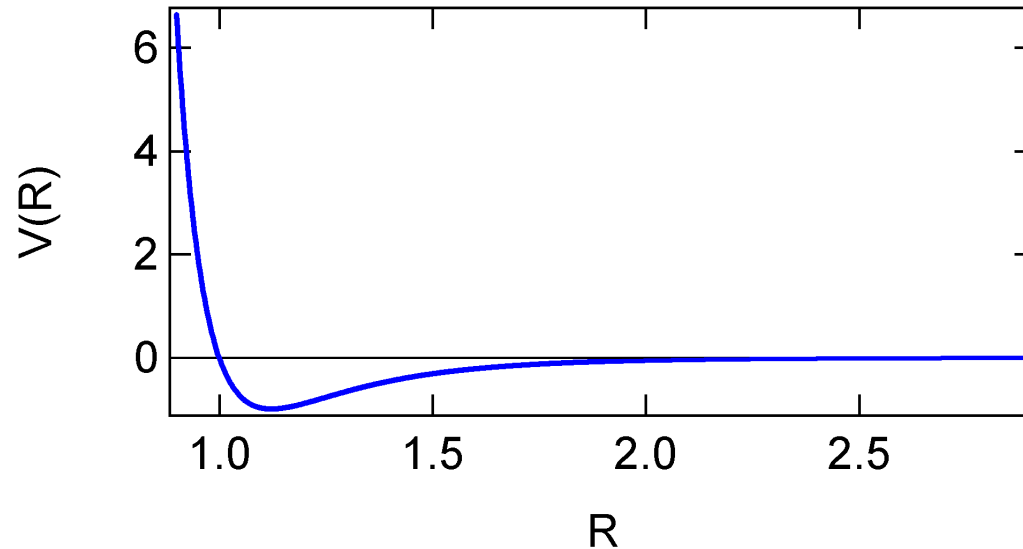# Lecture 7: Force fields and limitations of MD

- Potentials: which one and why ?
- Limitations

Remember (lecture 4)

Force calculation

1) Starting point is the interaction potential V(R). e.g. the Lennard-Jones potential
   All the model approximations are contained in the parameters of V(R) !

2) Calculation of the force acting on every particle.
   For the x-component of the force, we have :

$$F_x(R) = -\frac{\partial V(R)}{\partial x} = -\left(\frac{x}{R}\right)\frac{\partial V(R)}{\partial R}$$

❑ **Consider the types of possible interactions** between two molecules or atoms

❖ <u>Electrostatic interactions</u>
    Between charges/ions (Coulomb).
    Partial charges are allowed (q_O=-2.4 in SiO_2)
    Dipoles (permanent-induced, Debye)
    Induced-induced dipoles (London dispersion interaction)
    Effective way taking into account electronc delocalization
    (embedded atom, metals)

❖ <u>Bonding interactions</u>
    Effective way taking into account electronic delocalization
    (embedded atom, metals)
    Valence (overlap) interactions
    Covalent bonds
    Bond stretch, bond-angle bending, torsional potential

❖ <u>Weak interactions</u>
    Specific chemical forces giving rise to association and complex formation
    Hydrogen bonding

A. POTENTIALS: WHICH ONE AND WHY ?

❑ We are looking for a function which takes into account all possible interactions from neighbors on a given atom/molecule

$$\mathcal{V}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \sum_{i>j} V_{ij}(\vec{r}_i, \vec{r}_j)$$

❑ In practice, however, potentials are usually limited to 2- or 3-body interactions with some obvious rules.

   ❖ Repulsive core : $V(R = 0) = +\infty$

   ❖ Zero negative interaction at infinite distance $V(R = +\infty) = 0$
      Definition of a interaction cut-off (computational efficiency)

❑ Having set these 2 limits, there is an infinite variety of potentials. **The question of why is left to author's imagination.**

A. POTENTIALS: WHICH ONE AND WHY ?

❑ **Classes of potentials** which have been found to be more adapted to given materials or elements.

❑ The interaction V(R) is the sum of different contributions

$$V_{ij} = V_{ij}^{Rep} + V_{ij}^{Elec} + V_{ij}^{Disp} + V_{ij}^{Cov}$$

V_{ij}^{Rep} = repulsion energy ($\approx e^{-r/\rho}$, $1/r^{12}$)   **Born-Mayer** (electronic overlap**)**

V_{ij}^{Elec} = electrostatic energy ($\approx z_i z_j / r_{ij}$)   **Coulombic**

V_{ij}^{Disp} = dispersion energy ($\approx -1/r^6$)

V_{ij}^{Cov} = covalent bond ($\approx D_e [(1- e^{-(r-l)/\lambda})^2 -1])$ **Morse**

A. POTENTIALS

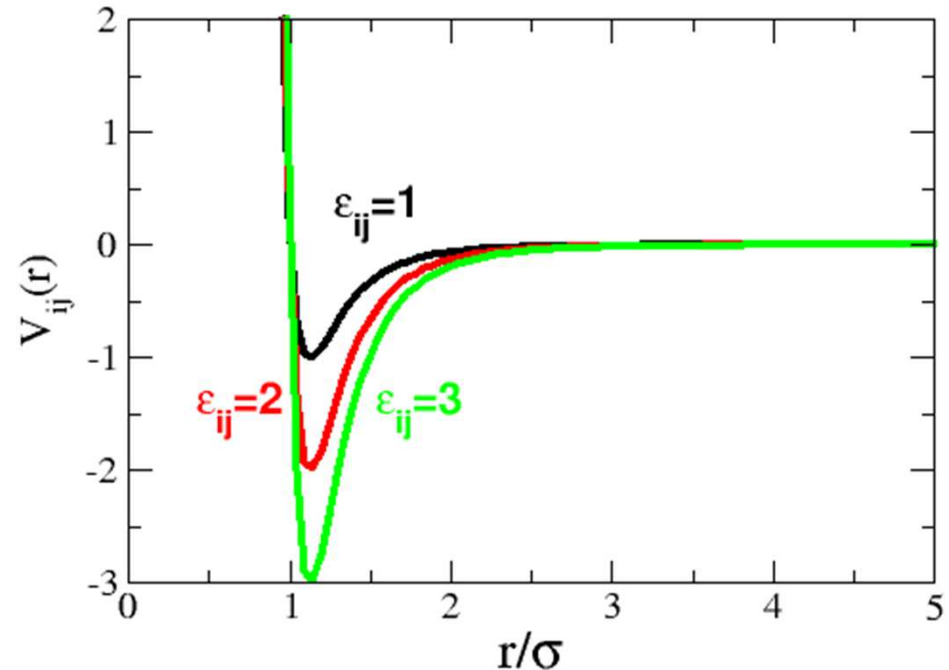## 1. Lennard-Jones potential (pair potential)

$$V_{ij}(r) = 4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6} \right\}$$

❑ Repulsive in $-1/r^{12}$

❑ Attractive in $-1/r^{6}$

❑ Defined by 2 parameters

Collision diameter σ_{ij}
Energy level ϵ_{ij}

❑ Minimum found at r_{ij}/σ_{ij} =1.122

❑ Typical cut-off at r_{ij}/σ_{i}=2.5 (avoid computing V_{ij} for all pairs)
❑ Starting point for many investigation or new potentials

A. POTENTIALS

2. Simple silicon potentials (Stillinger-Weber, 1985)

❑ One of the first attempts to model a semiconductor with a classical model.
2- and **3-body term** :

$$E_{SW}(1,2,...,N) = \Sigma_{(i,j)}(A.r_{ij}^{-4} - B).e^{(r_{ij}-a)^{-1}} + \Sigma_{i,j,k}\lambda.\left(\cos\theta_{jik} + \frac{1}{3}\right).e^{\gamma.(r_{ij}-a)^{-1}+\gamma.(r_{ik}-a)^{-1}}$$

❑ 3-body interaction forces the tetrahedral geometry (cos(109º)=-1/3).

❑ Successful modelling of c-Si (lattice parameter of the diamond structure, bond distance, vibrations)

❑ Pressure polymorphs of c-Si have too high energies
    Transferrability problems
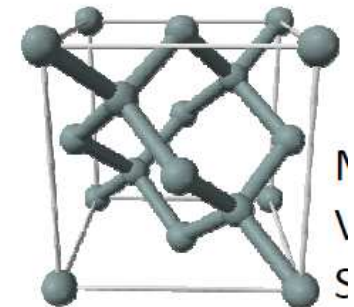
A. POTENTIALS

2. Simple silicon potentials (Stillinger-Weber, 1985)

Computer simulation of local order in condensed phases of silicon

Frank H. Stillinger and Thomas A. Weber
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 7 November 1984)

A model potential-energy function con... to describe interactions in solid and liqu... plored by molecular-dynamics computer... tions. Starting with the diamond-structu... nucleation and melting. The resulting liq... steepest-descent mappings of system co... clusions emerge: (1) a temperature-indep... for "simple" liquids with only pair inter... apparently can be supplemented by a fr... values of appropriately defined mean disp...

We have carried out a limited search over the seven parameters A, B, p, q, a, λ, and γ to identify a reasonable choice of f_2 and f_3. An important component of this diamond structure was indeed the most stable periodic arrangement of particles at low pressure, at least among simple alternatives. However, after this lattice-sum criterion was satisfied, it was still necessary that the melting point and the liquid structure inferred for the tentative interaction by the molecular-dynamics simulation also be in reasonable accord with experiment. These latter criteria served to contribute to our rejection of several of our initial choices for parameter sets.

Overall, the most satisfactory parameter set thus far discovered is the following:

$$A = 7.049\,556\,277 \,, \quad B = 0.602\,224\,558\,4 \,,$$

$$p = 4 \,, \quad q = 0 \,, \quad a = 1.80 \,, \qquad (2.7)$$

$$\lambda = 21.0 \,, \quad \gamma = 1.20 \,.$$

A. POTENTIALS

2. Simple silicon potentials (Stillinger-Weber, 1985)

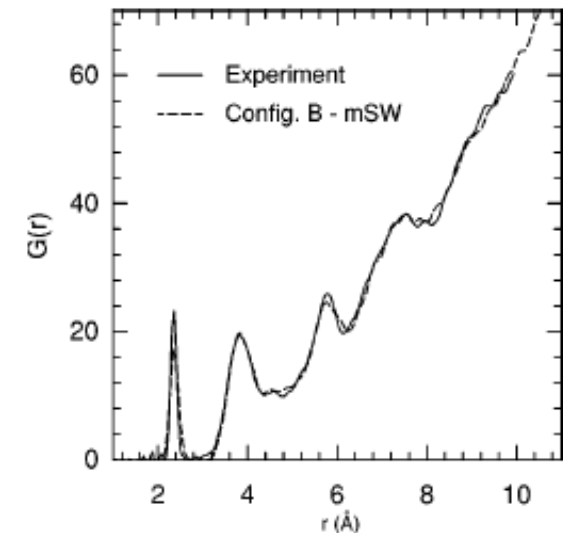❑ **Modified Interactions:**

Marder et al. (1999): 3 body term enhanced

Mousseau et al. (2001): energy decreased, 3 body term enhanced.

Fusco et al. (2010): continuous change of 3 body term

$$E = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk})$$

$$\phi_2(r_{ij}) = A_{ij}\epsilon_{ij} \left[B_{ij}(\frac{\sigma_{ij}}{r_{ij}})^{p_{ij}} - (\frac{\sigma_{ij}}{r_{ij}})^{q_{ij}} \right] \exp\left(\frac{\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}} \right)$$

$$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk}\epsilon_{ijk} [\cos\theta_{ijk} - \cos\theta_{0ijk}]^2 \exp\left(\frac{\gamma_{ij}\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}} \right) \exp\left(\frac{\gamma_{ik}\sigma_{ik}}{r_{ik} - a_{ik}\sigma_{ik}} \right)$$

❑ Successful modeling of the structure of amorphous Si

Barkema, Mousseau, PRB 2000

A new parametrization of the Stillinger–Weber potential for an improved description of defects and plasticity of silicon

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[3] Department of Physics, University of Helsinki and Helsinki Institute of Physics, FIN-00014 Helsinki, Finland
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Abstract

A new parametrization of the widely used Stillinger–Weber potential is proposed for silicon, allowing for an improved modelling of defects and plasticity-related properties. The performance of the new potential is compared to the original version, as well as to another parametrization (Vink *et al* 2001 *J. Non-Cryst. Solids*, **282** 248), in the case of several situations: point defects and dislocation core stability, threshold displacement energies, bulk

A. POTENTIALS

3. Silica potentials (ionic systems)

❑ Oxydes involve important electronegativity differences leading to charge separation.

❑ Systems can be treated with fixed (fractional) charges.

$$V_{ij}(r) = \frac{q_i q_j}{r} + A_{ij} e^{-B_{ij} r} - \frac{C_{ij}}{r^6}$$

❑ Most of the parametrizations involve a Born-Mayer form: attractive dispersion term ($-C_{ij}/r^6$) and short-range interaction ($A_{ij} \exp(-B_{ij}/r)$)

❑ Valid also for germania (GeO_2, Oeffner and Elliott, PRB 1996, Matsui et al. 1991) Fitting of the α-quartz-rutile transformation under pressure + cell lengths and vibrations of both polymorphs

A. POTENTIALS

3. Silica potentials (ionic systems)

❑ **Ewald summation:** allows computing the weakly decaying <u>Coulombic interaction</u> in an infinte lattice or under periodic boundary conditions.

❑ **Idea:** split the function into a rapidly decaying and slowly decaying function as:

$$\frac{1}{r} = \frac{\mathbf{erf}(\alpha\, r)}{r} + \frac{\mathbf{erfc}(\alpha\, r)}{r}$$
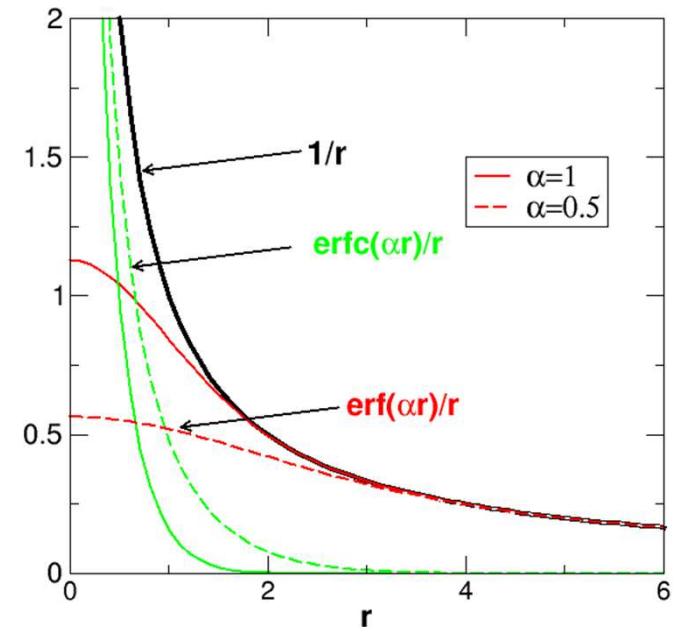
Slow decay
Compute in Fourier space where it has a rapid decay.
Particle Mesh Ewald
k-sum is not computed for atom positions, but for fixed positions on a grid.

Rapid decay
Compute in real space

❑ α sufficiently large to have all interactions of the primary simulation box contributing to the **erfc** term.

A. POTENTIALS

3. Silica potentials (ionic systems)

❑ **Various parametrizations:**

Fitted to match the quantum mechanical calculated potential energy surface of an isolated cluster H_4SiO_4 « *representative* » of the bulk silica. Lasaga and Gibbs (1987); Tsuneyuki et al. (**TTAM**, 1988); Van Beest, Kramer, Van Santen (**BKS**, 1991)
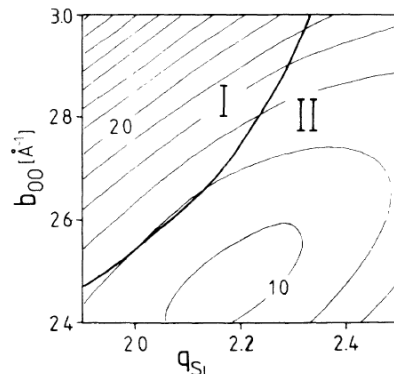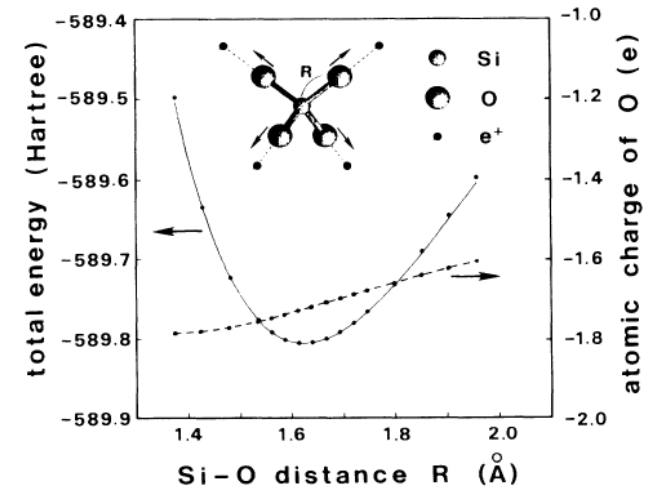
FIG. 1. Total energy and the Mulliken charge on an oxygen atom for T_d deformation of a $SiO_4^{4-}-4e^+$ cluster shown in the inset. The solid circles are the cluster calculation, full curve is the fitted potential, and the broken curve is a guide to the eye.

Tsuneyuki et al, PRL 1988

FIG. 1. Two-dimensional phase diagram of quartz in "bulk" parameter space ($c_{OO}=0$). The contour plots represent the χ^2 values of the fit to the *ab initio* data. The minimum corresponds to an average difference of 0.01 eV between force-field prediction and SCF energy. The thick line denotes the α-β phase boundary obtained when the force fields are applied to quartz (I denotes α; II is β).

TABLE I. Force-field parameters.

| i-j	Short-range parameters A_{ij} (eV)	b_{ij} (Å^{-1})	c_{ij} (eV Å^6)	Atomic charges
O-O	1388.7730	2.76000	175.0000	$q_O = -1.2$
Si-O	18003.7572	4.87318	133.5381	$q_{Si} = 2.4$
Al-O	16008.5345	4.79667	130.5659	$q_{Al} = 1.4$
P-O	9034.2080	5.19098	19.8793	$q_P = 3.4$

Van Beest et al. PRL 1991

A. POTENTIALS
3. Silica potentials

Spurious effects and short corrections

❑ For some parametrizations (e.g. TTAMM, BKS), the O-O interaction becomes highly attractive at short distance

❑ At T=6000 K, $k_B T$=0.5 eV

❑ At high densities and HT, there is the possibility that particles overcome the repulsive V_{O-O} barrier. **Collapse !**

❑ To avoid such spurious effects, a highly repulsive potential is added for $r<r_0$, of the form: $(r/r_0)^n$
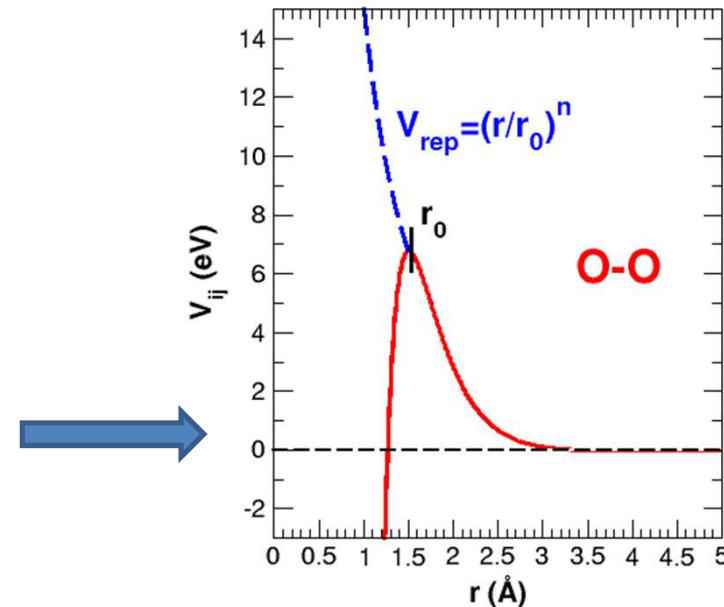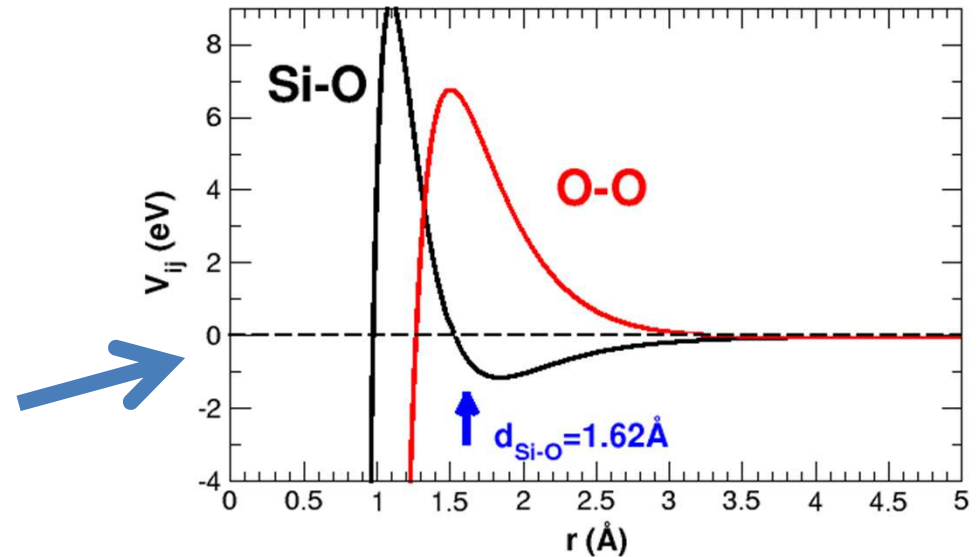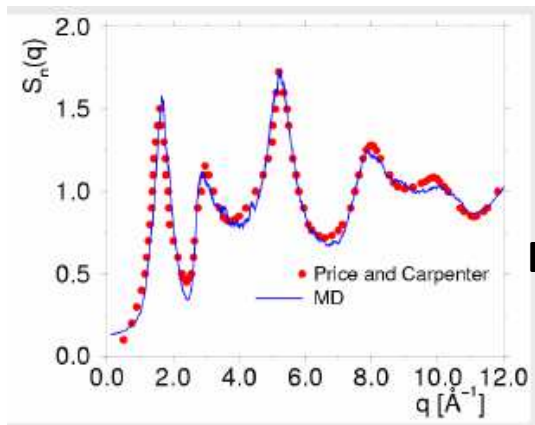
A. POTENTIALS

3. Silica potentials (ionic systems)
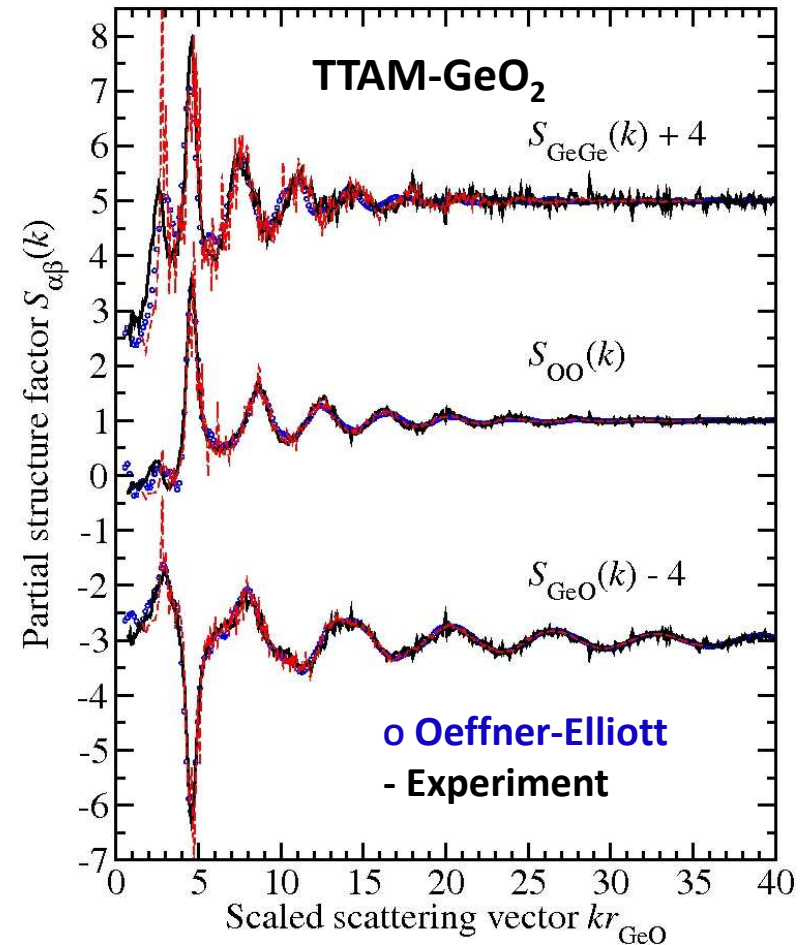
❑ Most potentials succeed in reproducing accurately the structure of amorphous silica or germania.
  ❑ d_{Si-O}=1.62 A
  ❑ d_{Ge-O}=1.73 A

❑ Thermodynamics (equation of state) not always well reproduced.
  « *BKS pathology* » in silica
P=0 for ρ=2.5 g/cm^3 and ρ$_{exp}$=2.2 g/cm^3

TTAM-GeO$_2$

$S_{GeGe}(k) + 4$

$S_{OO}(k)$

$S_{GeO}(k) - 4$

o **Oeffner-Elliott**
- **Experiment**

BKS-SiO$_2$

P. Salmon et al., JPCM 2006

Kob and Horbach, PRB 1999
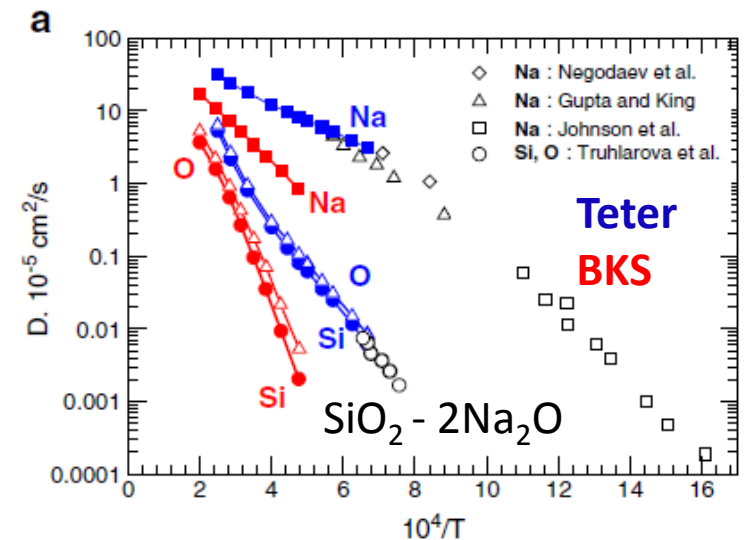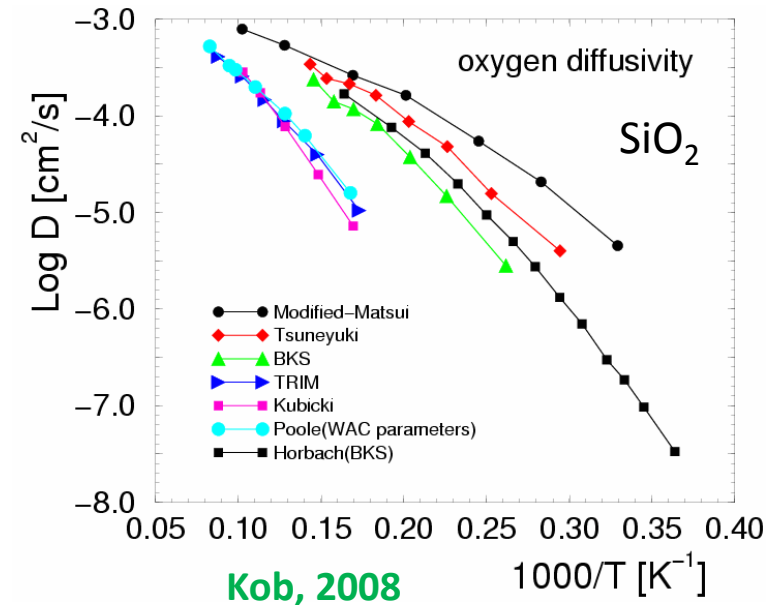
A. POTENTIALS

4. Silicate potentials

❑ Build in the same spirit as the silica potentials (BKS type or any other parametrization).

$$V_{ij}(r) = \frac{q_i q_j}{r} + A_{ij} e^{-B_{ij} r} - \frac{C_{ij}}{r^6}$$

Alkali silicates: BKS-like, (Horbach et al. Chem. Geol 2001) Teter (not published, Du and Cormack, 2003) …

Alkaline earth silicates: Du and Cormack, Pedone…

❑ Na-Na, Na-O and Si-Si limited to Coulombic interaction

❑ **Agreement on structure does not reflect the quality of the potential. Dynamics !**

Kob, 2008

Bauchy et al. Chem. Geol. 2013

A. POTENTIALS

5. Borosilicates

❑ In glasses containing B_2O_3, presence of B_3 and B_4 units. B_4 units are hardly obtained from a simple 2-body pair potential (Born-Mayer-Huggins).

❑ Addition to BMH of a 3-body term (inspired from Stillinger-Weber) forces angles to acquire a tetrahedral angle.

$$V_3 = \lambda_{jik} \exp\left\{\left(\gamma_{ij}/\left(r_{ij} - r_{ij}^0\right) + \gamma_{ik}/\left(r_{ik} - r_{ik}^0\right)\right)\right\}$$

$$\times \left(\cos\theta_{jik} - \cos\theta_{jik}^0\right)^2,$$

$$\text{for } r_{ij} \le r_{ij}^0, \text{ and } r_{ik} \le r_{ik}^0.$$

❑ This relatively weak contribution energetically penalizes the system when the angle formed by an atomic triplet, *jik,* deviates from the tetrahedral angle.
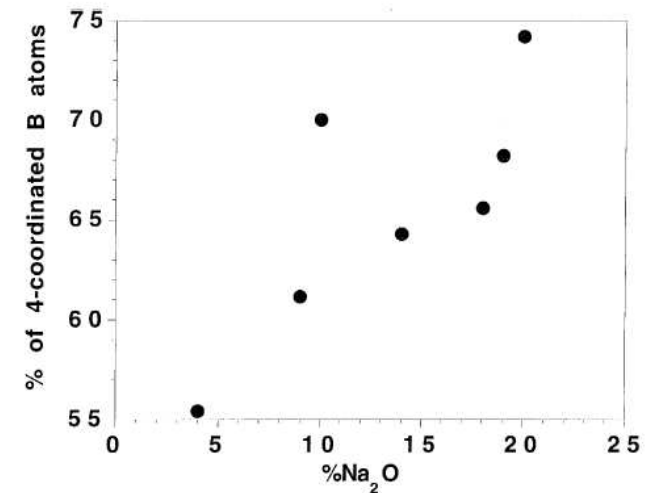
❑ Used in all simulations involving B_2O_3 and Na_2O

Fig. 3. Percentage of 4-coordinate B versus Na_2O percentage.

Delaye et al., JNCS 1997

A. POTENTIALS

5. Generalized (multicomponent)

❑ Reproduce crystal structure and atomic positions

❑ Crystal properties that contain information about the shape of the energy surface

   Elastic constants, high-frequency and static dielectric constants, lattice energy, phonon frequencies.

❑ Conventional fitting procedure consists usually in the following

   - The structural crystal properties and the initial guess for the potential parameters are read.
   - The six cell strains or individual strains and properties of the initial structures are calculated with the guess potentials.
   - A functional of type $(Prop_{calc}-Prop_{exp})^2$ is calculated and the parameters are changed to minimize the functional.

❑ GULP package (Oeffner-Elliott, Pedone,…) **http://projects.ivec.org/gulp/**

A. POTENTIALS
5. Generalized (multicomponent)

- ❑ **Pedone potential**: potential fitted for more than 40 different crystals
  $Ca_2ZnSi_2O_7$, $BaBeSi_2O_7$, $CaSiO_3$, …

- ❑ Functional form:
Coulombic+Morse (iono-covalent)+repulsion

$$U(r) = \frac{z_i z_j e^2}{r} + D_{ij}[\{1 - e^{-a_{ij}\cdot(r-r_0)}\}^2 - 1] + \frac{C_{ij}}{r^{12}}$$

- ❑ Allows excellent reproduction of mechanical, structural properties of binary silicates

TABLE 2: Potential Parameters of Eq 4 Derived from Binary Oxides[a]

	D_{ij} (eV)	a_{ij} (Å^{-2})	r_0 (Å)	C_{ij} (eV Å^{12})
Li$^{0.6}$–O$^{-1.2}$	0.001114	3.429506	2.681360	1.0
Na$^{0.6}$–O$^{-1.2}$	0.023363	1.763867	3.006315	5.0
K$^{0.6}$–O$^{-1.2}$	0.011612	2.062605	3.305308	5.0
Be$^{1.2}$–O$^{-1.2}$	0.239919	2.527420	1.815405	1.0
Mg$^{1.2}$–O$^{-1.2}$	0.038908	2.281000	2.586153	5.0
Ca$^{1.2}$–O$^{-1.2}$	0.030211	2.241334	2.923245	5.0
Sr$^{1.2}$–O$^{-1.2}$	0.019623	1.886000	3.328330	3.0
Ba$^{1.2}$–O$^{-1.2}$	0.065011	1.547596	3.393410	5.0
Sc$^{1.8}$–O$^{-1.2}$	0.000333	3.144445	3.200000	2.6
Ti$^{2.4}$–O$^{-1.2}$	0.024235	2.254703	2.708943	1.0
Zr$^{2.4}$–O$^{-1.2}$	0.206237	2.479675	2.436997	1.0
Cr$^{1.8}$–O$^{-1.2}$	0.399561	1.785079	2.340810	1.0
Mn$^{1.2}$–O$^{-1.2}$	0.029658	1.997543	2.852075	3.0
Fe$^{1.2}$–O$^{-1.2}$	0.078171	1.822638	2.658163	2.0
Fe$^{1.8}$–O$^{-1.2}$	0.418981	1.620376	2.382183	2.0
Co$^{1.2}$–O$^{-1.2}$	0.012958	2.361272	2.756282	3.0
Ni$^{1.2}$–O$^{-1.2}$	0.029356	2.679137	2.500754	3.0
Cu$^{0.6}$–O$^{-1.2}$	0.090720	3.802168	2.055405	1.0
Ag$^{0.6}$–O$^{-1.2}$	0.088423	3.439162	2.265956	1.0
Zn$^{1.2}$–O$^{-1.2}$	0.001221	3.150679	2.851850	1.0
Al$^{1.8}$–O$^{-1.2}$	0.361581	1.900442	2.164818	0.9
Si$^{2.4}$–O$^{-1.2}$	0.340554	2.006700	2.100000	1.0
Ge$^{2.4}$–O$^{-1.2}$	0.158118	2.294230	2.261313	5.0
Sn$^{2.4}$–O$^{-1.2}$	0.079400	2.156770	2.633076	3.0
P$^{3.0}$–O$^{-1.2}$	0.831326	2.585833	1.800790	1.0
Nd$^{1.8}$–O$^{-1.2}$	0.014580	1.825100	3.398717	3.0
Gd$^{1.8}$–O$^{-1.2}$	0.000132	2.013000	4.351589	3.0
Er$^{1.8}$–O$^{-1.2}$	0.040448	2.294078	2.837722	3.0
O$^{-1.2}$–O$^{-1.2}$	0.042395	1.379316	3.618701	22.0[b]

Pedone et al., JPC B 2006

**TABLE 3: Structural Parameters for Fitted Binary Oxides**

oxide		a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	V_{cell} (Å³)	<M−O>	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{14}	C_{23}	B
										lattice parameters										
Cu₂O	expt	4.2696	4.2696	4.2696	90	90	90	77.833	1.8488	11.60			1.10			10.50				11.20
cuprite	calcd	4.2704	4.2704	4.2704	90	90	90	77.875	1.8491	10.58			1.94			11.38				11.12
	% error	0.02	0.02	0.02	0	0	0	0.05	0.02	−8.80			79			8.38				−0.71
Ag₂O	expt	4.7200	4.7200	4.7200	90	90	90	105.154	2.0438											
	calcd	4.7200	4.7200	4.7200	90	90	90	105.154	2.0438											
	% error	0.00	0.00	0.00	0	0	0	0.00	0.00											
BeO	expt	2.6750	2.6750	4.3410	90	90	120	26.901	1.6347	47.0		49.4	15.30			16.8	11.9			25.1
bromellite	calcd	2.6984	2.6984	4.3349	90	90	120	27.336	1.6439	47.58		48.1	14.39			17.87	14.39			26.27
	% error	0.87	0.87	−0.14	0	0	0	1.62	0.56	1.2		−2.6	−5.9			6.4	20.9			1.62
ZnO	expt	3.2494	3.2494	5.2038	90	90	120	47.584	1.9775	20.90		21.80	4.41			12.00	10.4			14.35
zincite	calcd	3.2463	3.2463	5.0974	90	90	120	46.522	1.9637	21.29		17.77	4.31			13.99	12.1			14.90
	% error	−0.1	−0.1	−2.0	0	0	0	−2.2	−0.7	1.87		−18.5	−2.2			16.6	16.3			3.8
MgO	expt	4.2170	4.2170	4.2170	90	90	90	74.991	2.1086	29.40			15.5			9.30				16.0
periclase	calcd	4.2394	4.2394	4.2394	90	90	90	76.192	2.1197	29.46			10.53			10.53				16.84
	% error	0.53	0.53	0.53	0	0	0	1.60	0.53	0.20			−32			13				5.3
CaO	expt	4.8105	4.8105	4.8105	90	90	90	111.319	2.4052	22.40			8.06			6.00				11.47
lime	calcd	4.7748	4.7748	4.7748	90	90	90	108.861	2.3874	26.87			4.56			4.56				11.96
	% error	−0.74	−0.74	−0.74	0	0	0	−2.2	−0.74	20			43			24				4.27
SrO	expt	5.1500	5.1500	5.1500	90	90	90	136.591	2.5750	17.00			5.56			4.6				8.73
	calcd	5.1453	5.1453	5.1453	90	90	90	136.213	2.5726	17.13			2.84			2.84				7.60

matthieu.micoulaut@upmc.fr **Atomic modeling of glass – LECTURE 7 FORCE FIELDS**

B. BEYOND SIMPLE POTENTIALS
1. Taking into account polarization effect

☐ Metallization of ionic solids at high pressure and high temperature (geosciences).

☐ Transferability of the models at extreme conditions . Need to account for a lot of many-body effects. Polarizable Ion Model (**Madden, Salanne, Jahn, Wilson,…**).

☐ Atomic motion creates short range changes in the induced dipolear momentum. Induces changes in the interaction potential.

☐ Polarizable model: Coulomb+repulsion+dipolar momentum dependent dispersion term.

$$V_{\text{repulsion}} = \sum_{i,j>i} B^{ij} \exp(-a^{ij} r^{ij})$$

$$V_{\text{dispersion}} = -\sum_{i,j>i} \left[f_6^{ij}(r^{ij}) \frac{C_6^{ij}}{(r^{ij})^6} + f_8^{ij}(r^{ij}) \frac{C_8^{ij}}{(r^{ij})^8} \right]$$

μ_{SR}

μ_{AS}
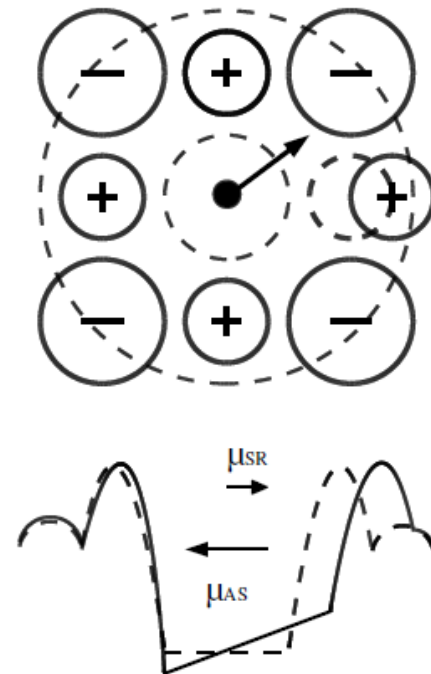
B. BEYOND SIMPLE POTENTIALS
1. Taking into account polarization effect

❑ In addition, one has a charge-dipole and dipole-dipole interaction

$$V_{\text{polarization}} = \sum_{i,j>i} \left(q^i \mu_\alpha^j g_D^{ij}(r^{ij}) - q^j \mu_\alpha^i g_D^{ji}(r^{ij}) \right) \nabla_\alpha \frac{1}{r^{ij}}$$

$$\sum_{i,j>i} -\mu_\alpha^i \mu_\beta^j \nabla_\alpha \nabla_\beta \frac{1}{r^{ij}}$$

$$+ \sum_i \frac{1}{2\alpha^i} \mid \vec{\mu}^i \mid^2$$

❑ μ_i (i=1..N) are induced dipoles on each ion. Computed at each time step.

❑ To obtain the parameters
  ❑ Force fitting (forces and dipoles from first principles MD)
  ❑ Minimization of $\quad \chi_F^2 = \sum_i \frac{|\vec{F}_{fp}^i - \vec{F}_{pim}^i|^2}{|\vec{F}_{fp}^i|^2}$

$$\chi_D^2 = \sum_i \frac{|\vec{\mu}_{fp}^i - \vec{\mu}_{pim}^i|^2}{|\vec{\mu}_{fp}^i|^2}$$
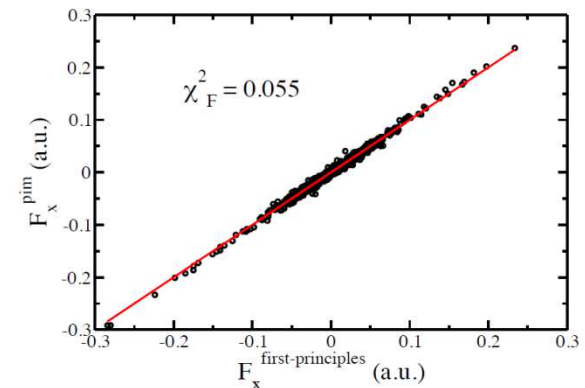
B. BEYOND SIMPLE POTENTIALS

1. Taking into account polarization effect

Polarizable ion model

Salmon et al., JPCM 2012

MD
Salmon et al.

GeO$_2$

Oeffner-Elliott model

MD
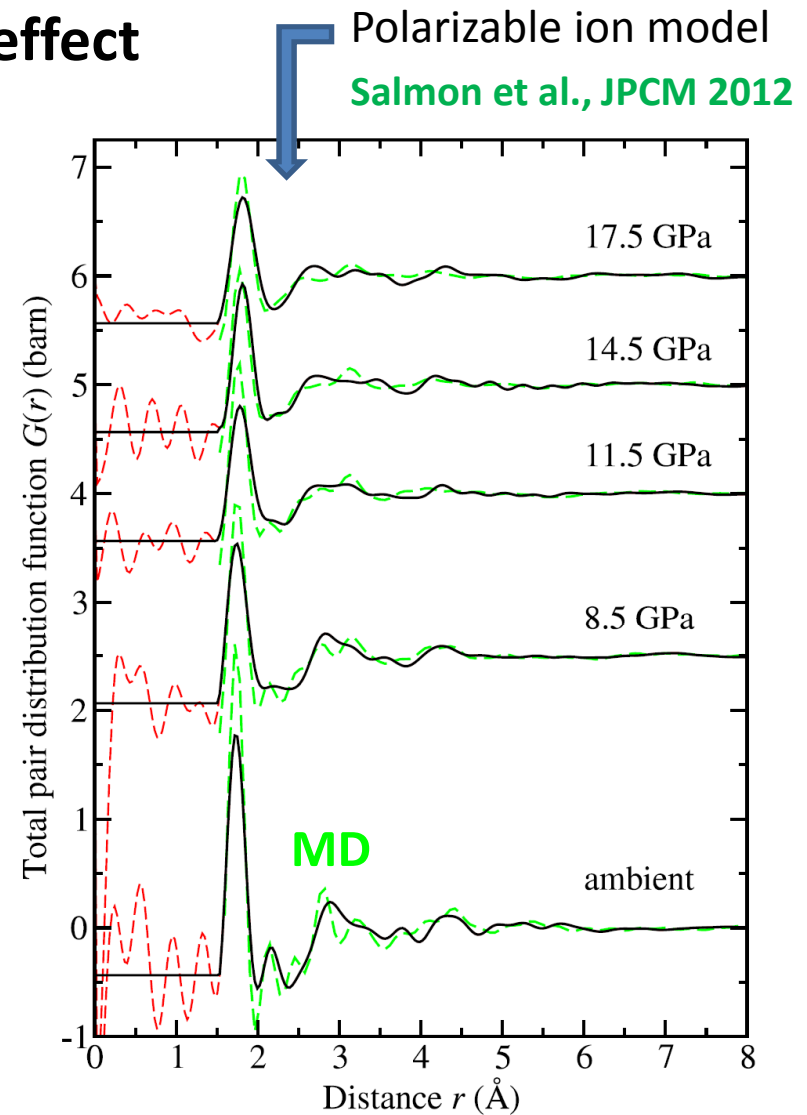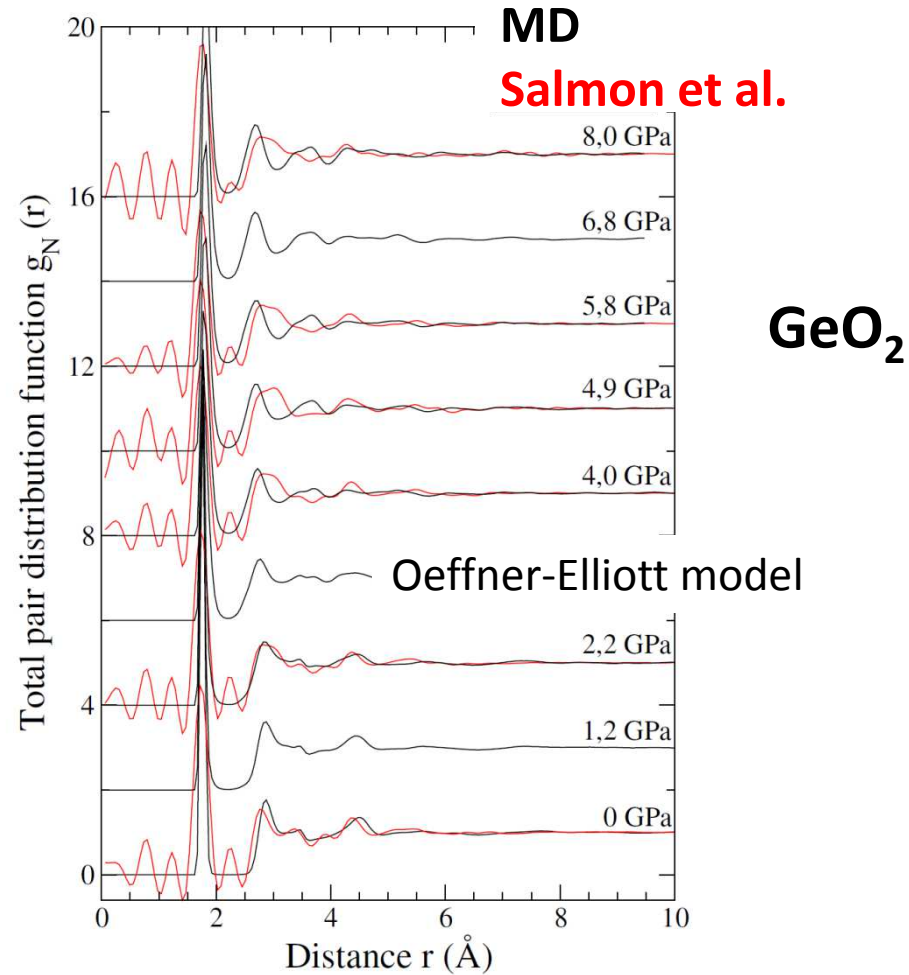
B. BEYOND SIMPLE POTENTIALS
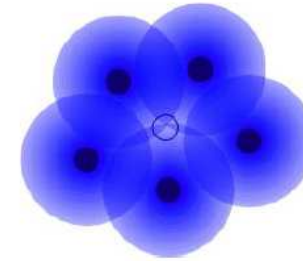
2. Embedded atom potentials (EAM)

❑ Designed for the simulation of metals for which electronic delocalization is taken into account in an effective way.

❑ Potential of the form:

$$U_{metal} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} V_{ij}(r_{ij}) + \sum_{i=1}^{N} F(\rho_i)$$

where $V_{ij}(r_{ij})$ is a pair potential incorporating repulsive electrostatic and overlap interaction.

$F(\rho_i)$ is a functional describing the energy of embedding an atom in the electron cloud bulk density, ρ_i, which is defined by pairs of atoms as:

$$\rho_i = \sum_{j=1, j \neq i}^{N} \rho_{ij}(r_{ij})$$

One form for
$$F(\rho) = -E_c \left(1 - \ln \left(\rho / \rho_e \right)^{\alpha/\beta} \right) \left(\rho / \rho_e \right)^{\alpha/\beta} - 6\phi_e \left(\rho / \rho_e \right)^{\gamma/\beta}$$

with model parameters that are determined base on lattice parameter, bulk modulus, cohesive energy E_c, average electron density ρ_e.

C. LIMITATIONS

1. Physical properties

❑ Vibrational properties fail to be properly described by classical MD.

❑ Difficulty in reproducing physical properties
Vibration > Dynamics > Structure

❑ Using either dipole-induced dipole interactions or Hessian matrix (vibrational eigenmodes), computation of Raman spectra.

❑ No possibility to compute electronic (band structure, eDOS) or magnetic properties (NMR spectra)
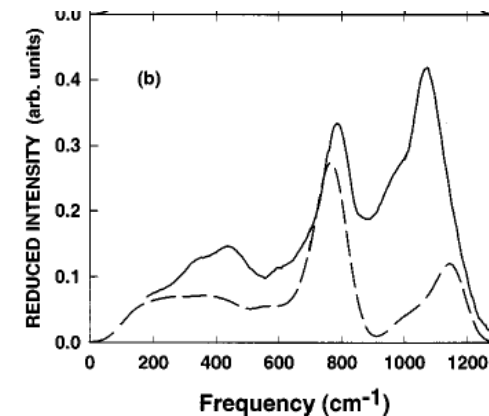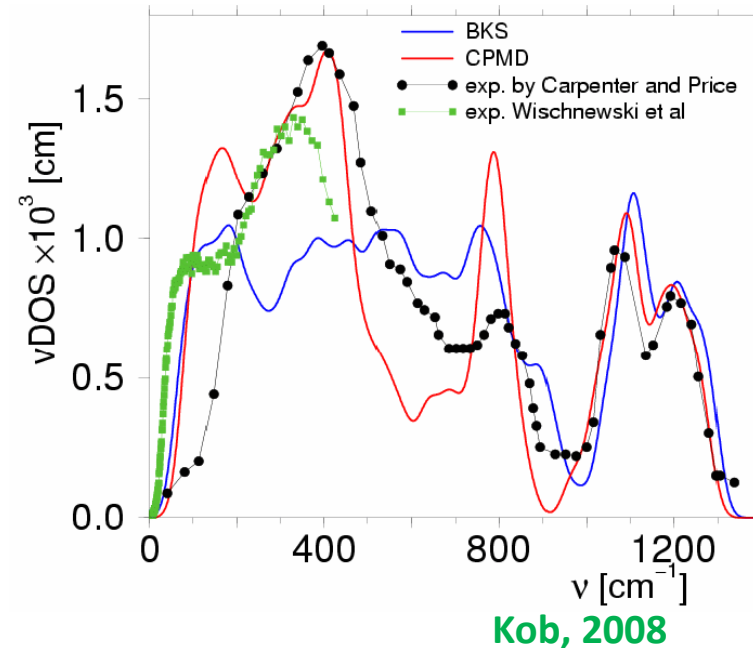
Zotov et al., PRB 1999

Kob, 2008

FIG. 9. VH polarized experimental (———) and calculated (— — —) spectra of NS4 glasses: (a) NS4_I; (b) NS4_II model.

C. LIMITATIONS

2. Systems

Molecular simulation of chalcogenides

➢In e.g. GeSe$_2$, presence of homopolar defects

➢Charge transfer
 (covalent character of chemical bonding)

➢ Even worse in semi-metallic tellurides

➢Attempts with complex 3-body potentials (Mauro et al. 2009) or PIMs (Wilson, 2008)
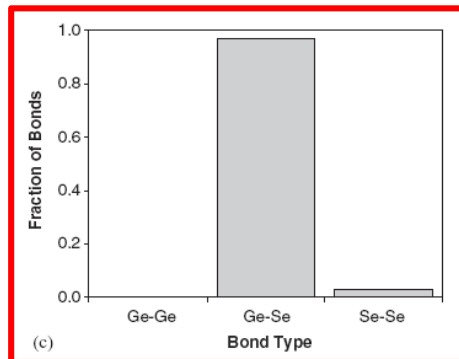
Mauro et al. J. Ceram. Soc. 2006

Expt. Salmon et al. 1991
MD Vashishta potential

Ge-Ge

Se-Se
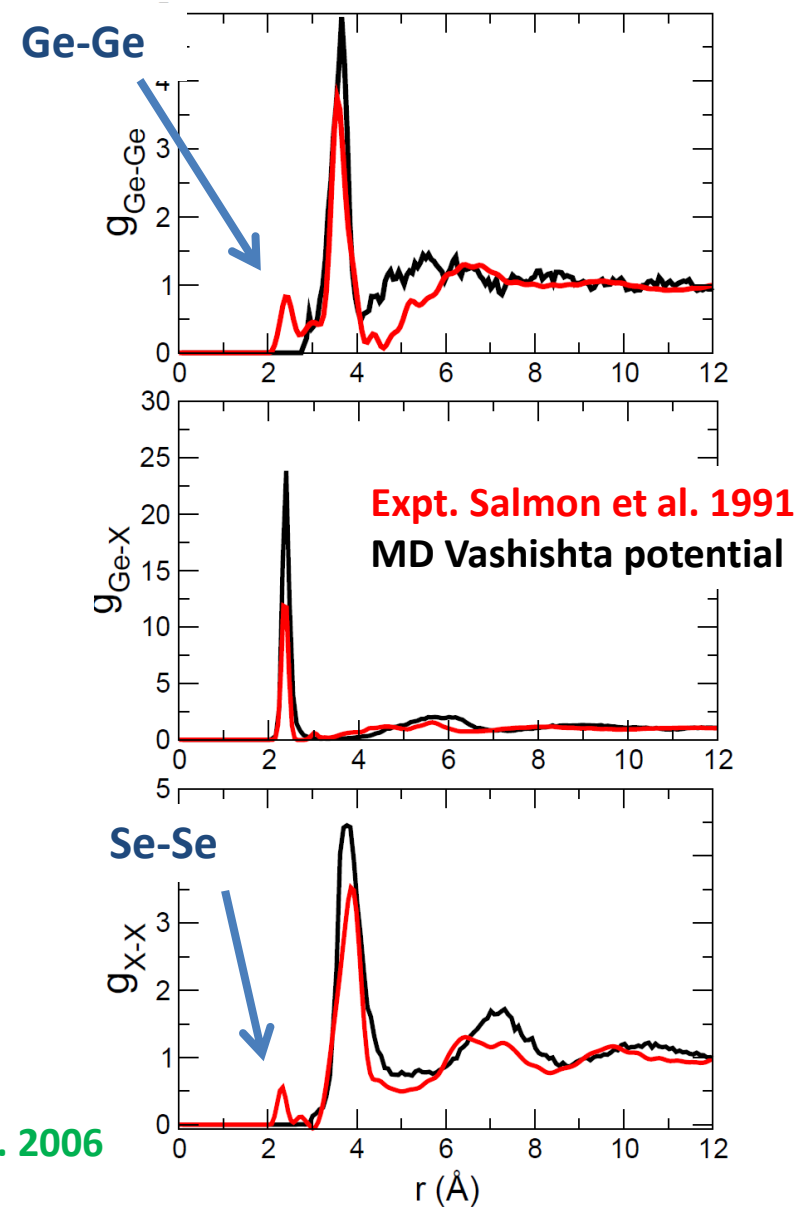
C. LIMITATIONS

3. Glass transition and computational limit

❑ To ensure conservation of energy (see lecture 4), typical time step of an MD run is **2 fs**. For a (small) 3000 atomic system and on a monoprocessor, this needs 0.12 s.

❑ A simulation time of **2ns will require 10^6** steps, i.e. 1.3 days. For this system, a simulation time (typical timescale at Tg) of a second would require **$1.36.10^6$ years**.

❑ Leads to unrealistic quenching rates.

q ~ 4000K/2ns=2. 10^{12} K/s !!

q_{exp} ~ 10^{-3} – 10^6 K/s
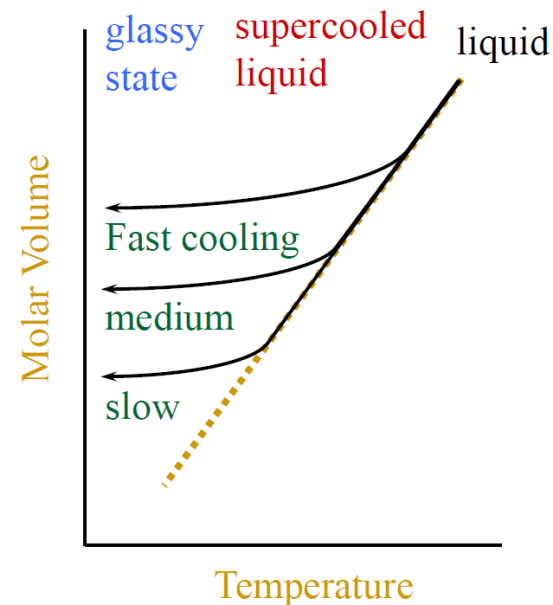
C. LIMITATIONS

3. Glass transition and computational limit

❑ Certain timescales cannot be probed by computer simulations. Still, features of the glass transition are visible.
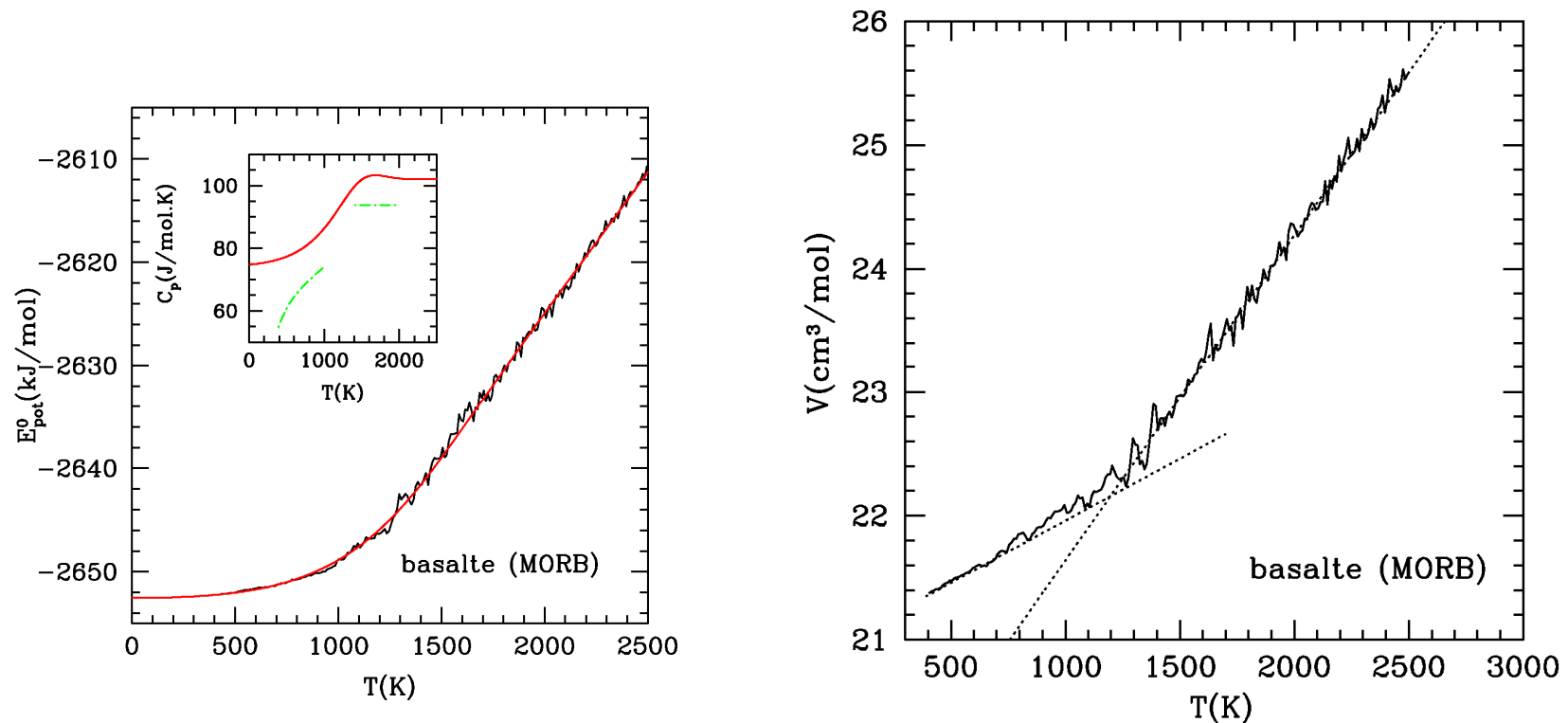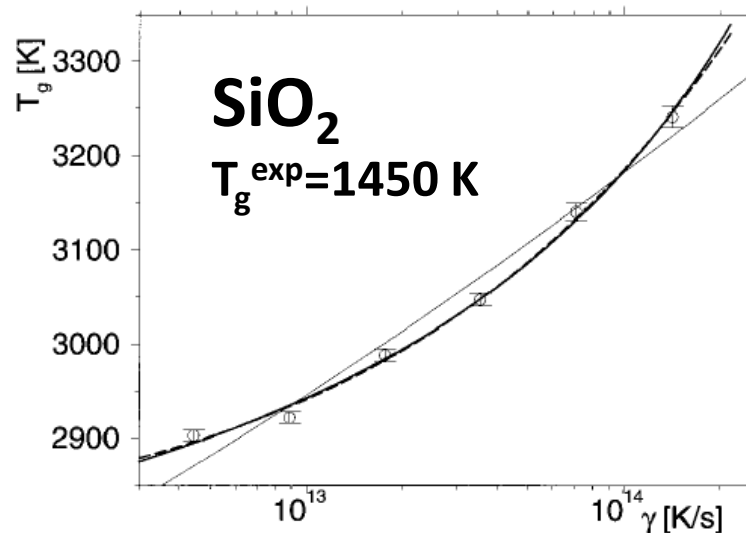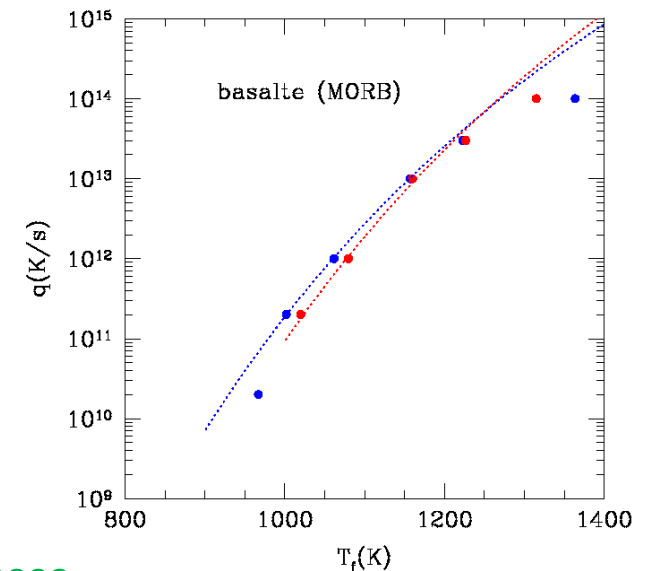
Guillot et al. GCA 2012

C. LIMITATIONS
3. Glass transition and computational limit

❑ Too high quenching rates lead to unrealistic high glass transition temperatures.

❑ Collision of flaws : $T_g^{MD}(GeO_2)$=900 K and $T_g^{exp}(GeO_2)$=900 K but $D^{MD}=10^3 D^{exp}$
(**Micoulaut et al. PRE 2006**)

❑ Absence of full relaxation. Not enough time found for a full relaxation over the potential energy landscape.

SiO$_2$

T_g^{exp}=1450 K

Vollmayr et al. PRB 1996

basalte (MORB)

Guillot et al. GCA 2009

3. Viscosity, consistency and Tg definition

❑ The maximum time available: $N=10^3 - 10^4$ atoms, $t_{max} \sim 1000$ ns

❑ The diffusion constant is about

$$D_{min} = <R_{min}^2>/6t_{max} = 2. \ 10^{-14} \ m^2/s$$

for a mean square displacement of 10 A^2

❑ Using Eyring $\eta_{max} = k_B T/\lambda D_{min} = 3000$ Pa.s with $\lambda=2.8$ A for silicates

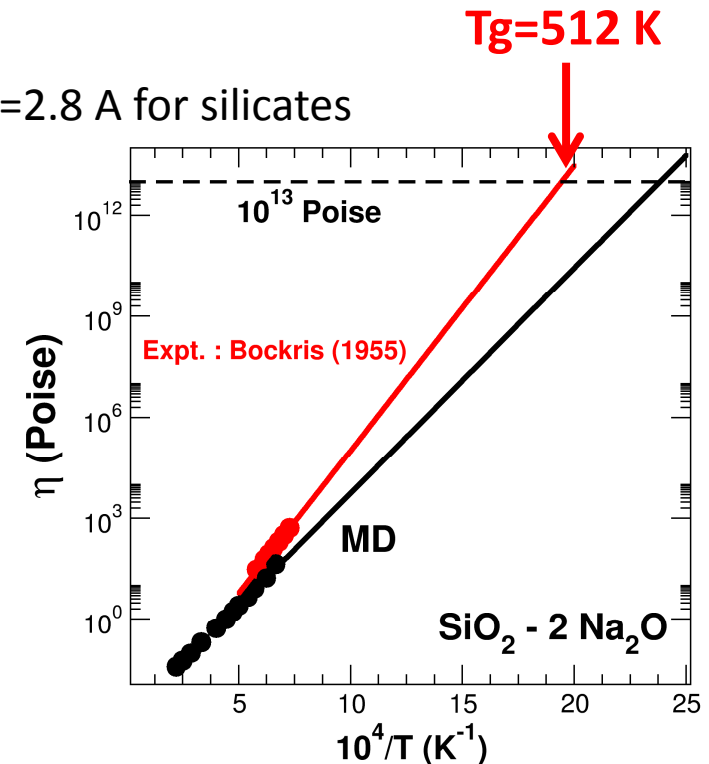❑ Check with Maxwell $\tau_{relax} = \eta/G_\infty = 100 - 1000$ ns with $G_\infty = 0.3 \ 10^{10} - 3. \ 10^{10}$ Pa

❑ Check the timescale of 1000 ns, one can only probe a high temperature liquid viscosity and its associated relaxation.

T$_g$(viscosity, Bockris)=512 K
T$_g$(viscosity, MD)=418 K
Tg(calorimetry)=733 K **(Mazurin)**
Arrhenius assumed

Tg=512 K

10^{13} Poise

10^{12}

10^9

Expt. : Bockris (1955)

10^6

η **(Poise)**

10^3

MD

10^0

SiO$_2$ - 2 Na$_2$O

5   10   15   20   25

10^4/T (K^{-1})

C. LIMITATIONS
3. Simulation size and consistency

❑ The size of a system imposes a typical cooling rate which obeys a log-log relation
(Guillot, 2009; Zasadzinski , J. Microsc. 1988)

$$ln\ q \sim -\ ln\ (Volume/Area)$$

❑ For a micrometric ($1\mu m^3$) water sample, one has 10^6 K/s.

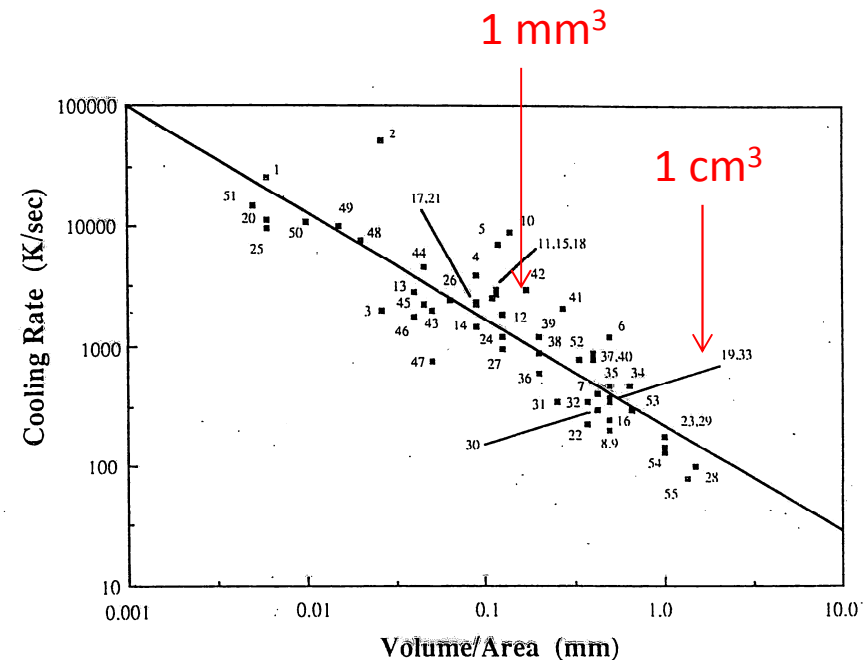❑ For a nanometer sized numerical sample $(20\ A)^3$, extrapolation gives the typical MD cooling rate 10^9K/s

Fig. 3. Literature values of the measured cooling rate (Table 1) versus volume/area ratio. Linear regression fit shows slope of $-0\cdot9\pm0\cdot1$, indicating cooling rates are limited by convection and Bi<1.
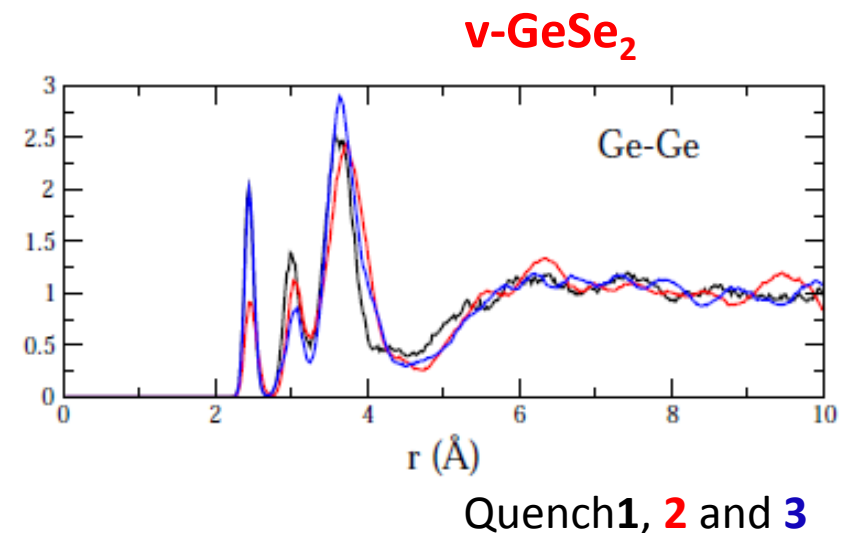
C. LIMITATIONS

3. Size effect and energy landscape sampling

❑ Although periodic boundary conditions are used, there are obvious size effects in MD simulations (apparent during relaxation processes). Weak effect on structural properties.

❑ Limited time does not allow to sample all the phase space. A good reproduction consist in quenching from the HT liquid to different **inherent structures** (minima of the potential energy landscape) and averaging.

v-GeSe$_2$

Quench**1**, **2** and **3**
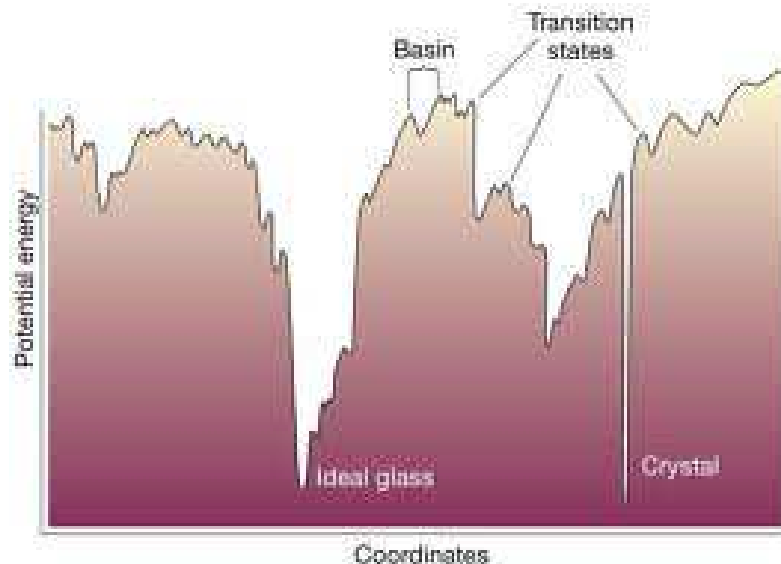
Debenedetti and Stillinger, Nature 2001

C. LIMITATIONS

4. Quantum effects

❑ **Validity of the replacement of Schrödinger equation** with the classical Newton equation. Indicator is the Broglie wavelength:

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

❑ Quantum effects are expected to become significant when Λ is much larger than interparticle distance (d_{Si-O}=1.62 A)

❑ For T=300 K, one has
   ❖ Λ=1 A for a H atom (m_H=1 amu)
   ❖ Λ=0.19 A for a Si atom (m_{Si}=28 amu)
   ❖ Λ=0.07 A for a Au atom (m_{Au}=197 amu)

❑ All atoms (except for the lightest ones) can be treated classically. However, with T becoming lower, quantum corrections may be needed.

❑ $\Lambda \sim d_{Si-O}$ at 120 K.

Conclusion

❑ Most of the modeling of glass structure and properties is contained in the force field (potential).

❑ Mostly adapted for ionic systems (silicates). Classical potentials fail for chalcogenide glasses.

❑ Library of potentials available. Accurate reproduction of glass properties.

❑ Difficulty: Vibrations > Dynamics/transport > Structure

❑ Computer timescale limits the investigation of a true glass transition.

Next lecture (8): Practical MD and applications

Homework assignement: setting up you personal simulation