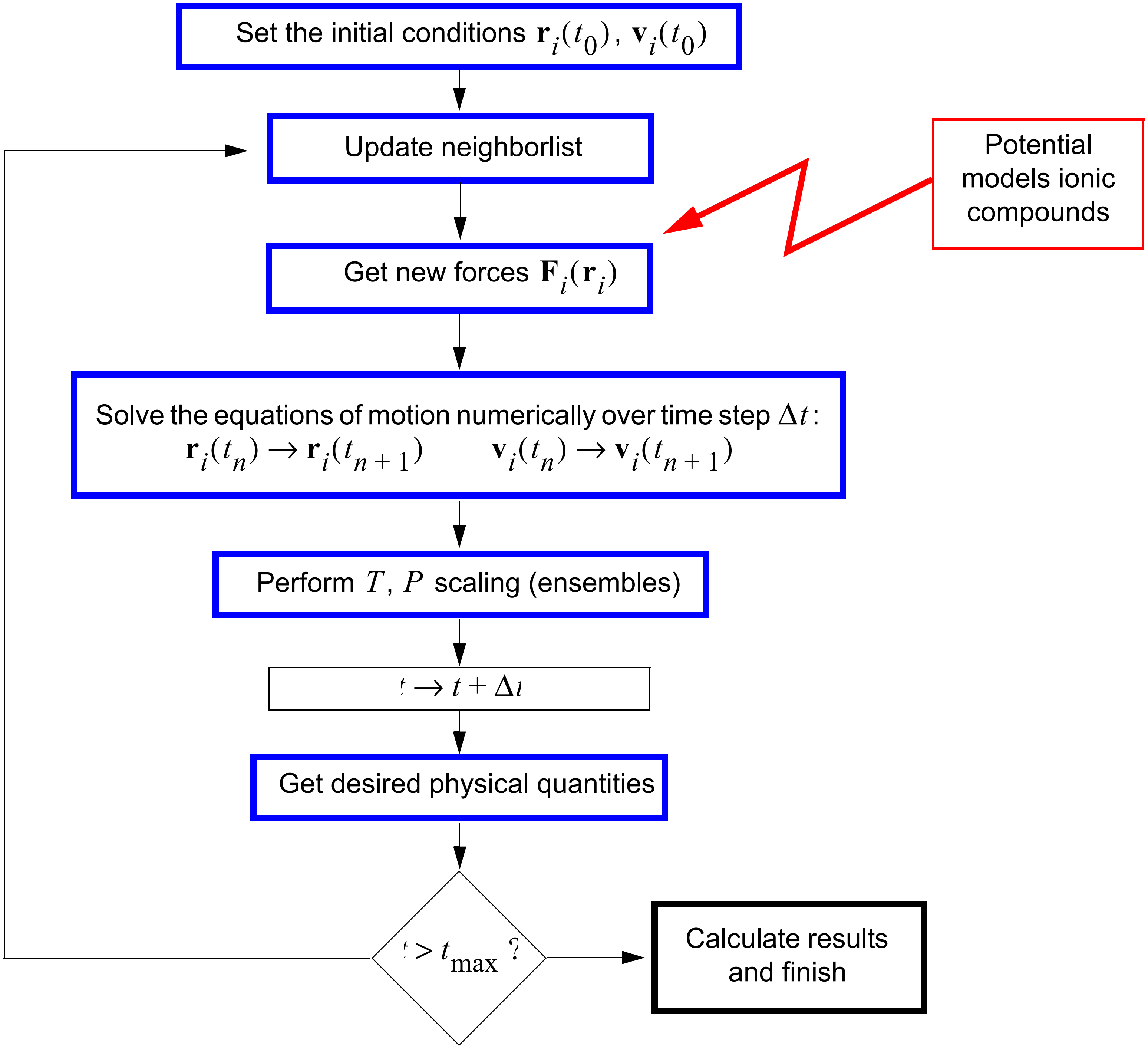


Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Update neighborlist

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Potential models ionic compounds

Solve the equations of motion numerically over time step Δt:

$$\mathbf{r}_i(t_n) \to \mathbf{r}_i(t_{n+1}) \qquad \mathbf{v}_i(t_n) \to \mathbf{v}_i(t_{n+1})$$

Perform T, P scaling (ensembles)

$t \to t + \Delta t$

Get desired physical quantities

$t > t_{max}$?

Calculate results and finish

Potentials for ionic compounds

- There is a wide range of materials where ionic interactions are important:
  - In hard condensed matter many, if not most, compounds have at least some degree of ionicity.
  - Partial ionic charges are also very important for organic materials

- In ionic compounds one can simply describe the long-range interaction with a Coulomb pair potential. But one should add a short-range interaction V_{SR} to describe repulsion at short distances:

$$V(r_{ij}) = V_{\mathrm{SR}}(r_{ij}) + \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_{ij}};$$

  - The charges z_i are often fractional charges, depending on the degree of ionicity of a material (e.g. NaCl: 1, GaN: 0.5, GaAs: 0.2, Si 0.0).

  - V_{SR} contains the repulsion of the electron shells and possibly an attractive van der Waals-interaction. Common forms:
    - Buckingham: $V_{\mathrm{SR}}(r) = Ae^{-r/\rho} - \frac{C}{r^6}$
    - Born-Huggins-Mayer: $V_{\mathrm{SR}}(r) = Ae^{-B(r-\sigma)} - \frac{C}{r^6} - \frac{D}{r^8}$
    - Morse: $V_{\mathrm{SR}}(r) = De^{-2\alpha(r-r_0)} - 2De^{-\alpha(r-r_0)}$

Potentials for ionic compounds

- The repulsion is usually significant only for nearest neighbours, and the van der Waals interaction for the 2-nd neighbours. In oxides frequently the interaction between cations is assumed to be only the Coulomb repulsion.

- In many real compounds the interactions are a mixture of covalent, metallic and ionic interactions (e.g. many carbides and nitrodes).

Potentials for ionic compounds

- Such potentials have been formed for many ionic compounds. We present here briefly the potential by Vashista *et al.* for SiO_2, [*Phys. Rev. B* **41** (1990) 12197.] which comes up in many different contexts.
  - Silicon dioxide also has many different structures, which makes it difficult to model:

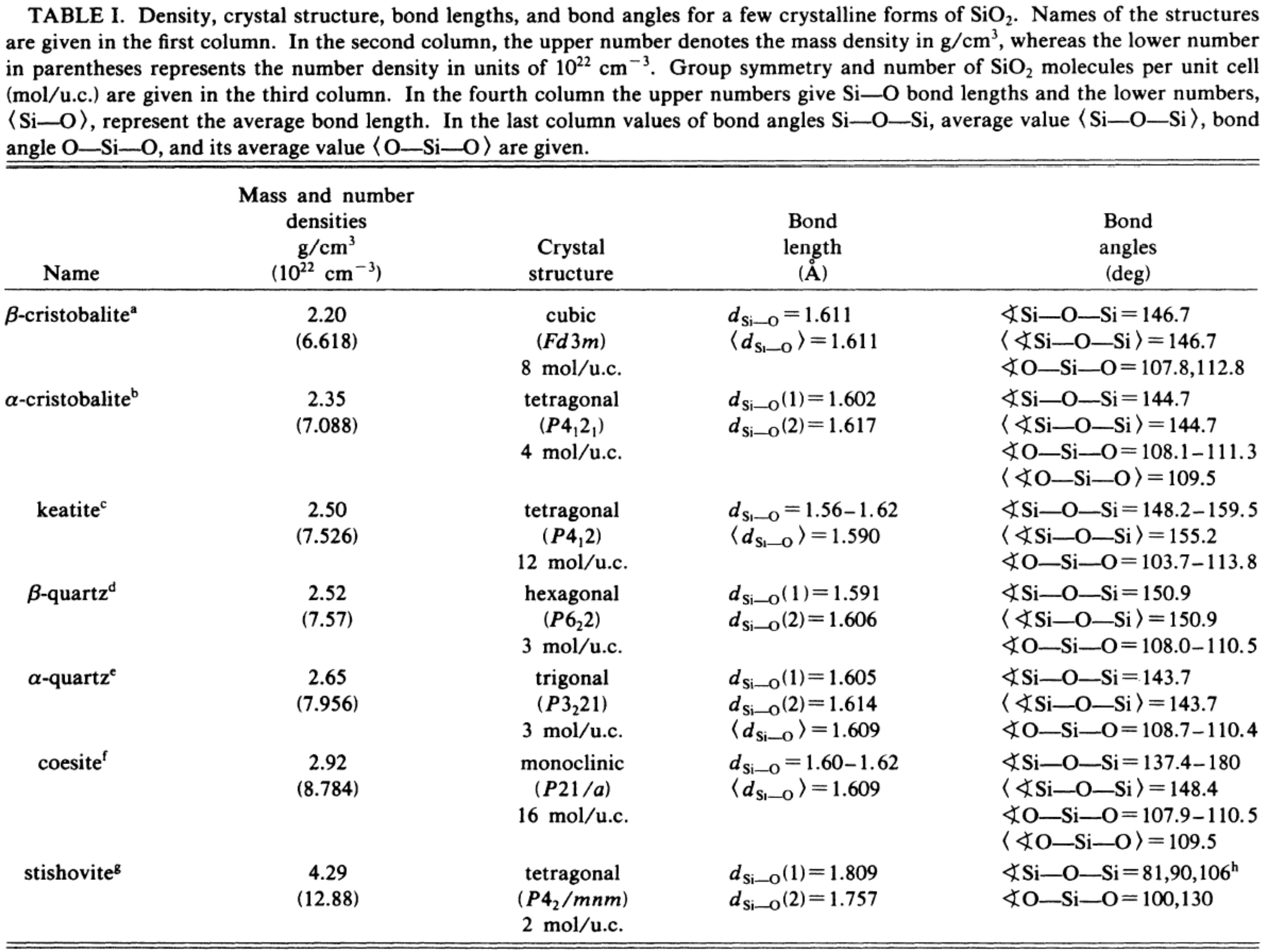


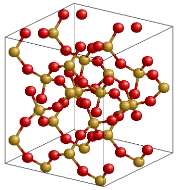
TABLE I. Density, crystal structure, bond lengths, and bond angles for a few crystalline forms of SiO_2. Names of the structures are given in the first column. In the second column, the upper number denotes the mass density in g/cm^3, whereas the lower number in parentheses represents the number density in units of 10^{22} cm^{-3}. Group symmetry and number of SiO_2 molecules per unit cell (mol/u.c.) are given in the third column. In the fourth column the upper numbers give Si—O bond lengths and the lower numbers, $\langle$Si—O$\rangle$, represent the average bond length. In the last column values of bond angles Si—O—Si, average value $\langle$Si—O—Si$\rangle$, bond angle O—Si—O, and its average value $\langle$O—Si—O$\rangle$ are given.

Name	Mass and number densities g/cm^3 (10^{22} cm^{-3})	Crystal structure	Bond length (Å)	Bond angles (deg)
β-cristobalite[a]	2.20 (6.618)	cubic (*Fd*3*m*) 8 mol/u.c.	$d_{Si—O}=1.611$ $\langle d_{Si—O}\rangle=1.611$	$\sphericalangle$Si—O—Si$=146.7$ $\langle\sphericalangle$Si—O—Si$\rangle=146.7$ $\sphericalangle$O—Si—O$=107.8,112.8$
α-cristobalite[b]	2.35 (7.088)	tetragonal ($P4_12_1$) 4 mol/u.c.	$d_{Si—O}(1)=1.602$ $d_{Si—O}(2)=1.617$	$\sphericalangle$Si—O—Si$=144.7$ $\langle\sphericalangle$Si—O—Si$\rangle=144.7$ $\sphericalangle$O—Si—O$=108.1-111.3$ $\langle\sphericalangle$O—Si—O$\rangle=109.5$
keatite[c]	2.50 (7.526)	tetragonal ($P4_12$) 12 mol/u.c.	$d_{Si—O}=1.56-1.62$ $\langle d_{Si—O}\rangle=1.590$	$\sphericalangle$Si—O—Si$=148.2-159.5$ $\langle\sphericalangle$Si—O—Si$\rangle=155.2$ $\sphericalangle$O—Si—O$=103.7-113.8$
β-quartz[d]	2.52 (7.57)	hexagonal ($P6_22$) 3 mol/u.c.	$d_{Si—O}(1)=1.591$ $d_{Si—O}(2)=1.606$	$\sphericalangle$Si—O—Si$=150.9$ $\langle\sphericalangle$Si—O—Si$\rangle=150.9$ $\sphericalangle$O—Si—O$=108.0-110.5$
α-quartz[e]	2.65 (7.956)	trigonal ($P3_221$) 3 mol/u.c.	$d_{Si—O}(1)=1.605$ $d_{Si—O}(2)=1.614$ $\langle d_{Si—O}\rangle=1.609$	$\sphericalangle$Si—O—Si$=143.7$ $\langle\sphericalangle$Si—O—Si$\rangle=143.7$ $\sphericalangle$O—Si—O$=108.7-110.4$
coesite[f]	2.92 (8.784)	monoclinic ($P21/a$) 16 mol/u.c.	$d_{Si—O}=1.60-1.62$ $\langle d_{Si—O}\rangle=1.609$	$\sphericalangle$Si—O—Si$=137.4-180$ $\langle\sphericalangle$Si—O—Si$\rangle=148.4$ $\sphericalangle$O—Si—O$=107.9-110.5$ $\langle\sphericalangle$O—Si—O$\rangle=109.5$
stishovite[g]	4.29 (12.88)	tetragonal ($P4_2/mnm$) 2 mol/u.c.	$d_{Si—O}(1)=1.809$ $d_{Si—O}(2)=1.757$	$\sphericalangle$Si—O—Si$=81,90,106$[h] $\sphericalangle$O—Si—O$=100,130$

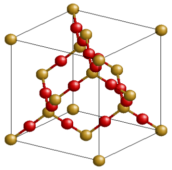
Potentials for ionic compounds

- But all of these have the common feature that they can be understood as tetrahedra with Si in the centre and O atoms in the joint corners:

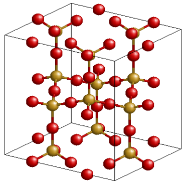
α cristobalite



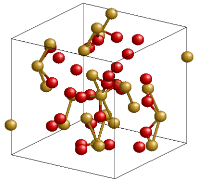
β cristobalite



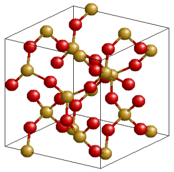
β tridymite



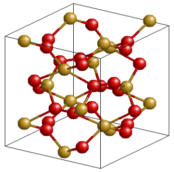
keatite



α quartz



β quartz



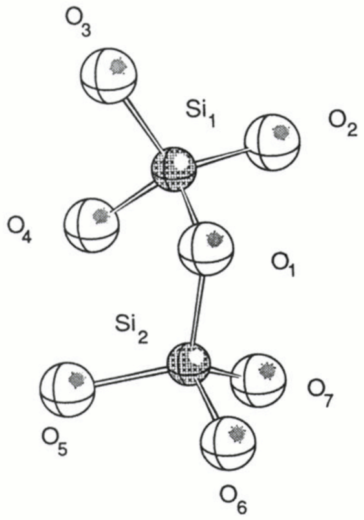
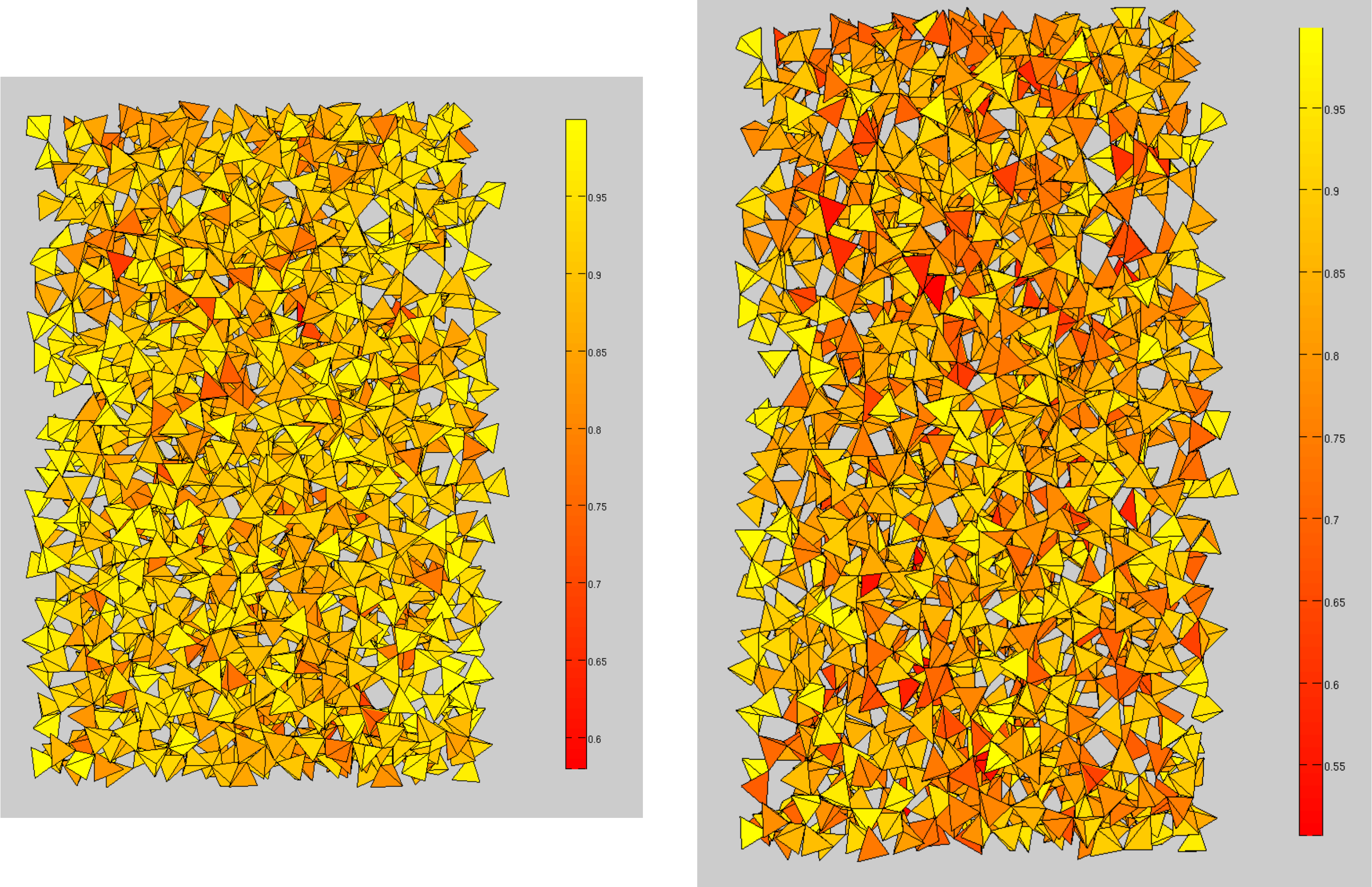


FIG. 9. A schematic view of corner-sharing tetrahedra in *a*-SiO_2.

Potentials for ionic compounds

- Simulation of a 40-Å diameter SiO_2 beam in equilibrium (left) and strained.
  - Colorcoded is the ratio between the shortest and longest edge of a face of a tetrahedron.



Potentials for ionic compounds

- The potential is of the familiar form:

$$V = \sum_{1 \le i < j \le N} V_2(r_{ij}) + \sum_{1 \le i \le j \le k \le N} V_3(\mathbf{r}_{ij}, \mathbf{r}_{jk}, \mathbf{r}_{ik}) \, .$$

- The two-body part V_2:

$$V_2 = \frac{H_{ij}}{r^{\eta_{ij}}} + \frac{Z_i Z_j}{r} - \frac{\frac{1}{2}(\alpha_i Z_j^2 + \alpha_j Z_i^2)}{r^4} e^{-r/r_{4s}} \, ,$$

The first part is the “steric” repulsion due to the ion size, the second the Coulomb term and the third a charge-dipole term, which takes into account the large polarizability of O.

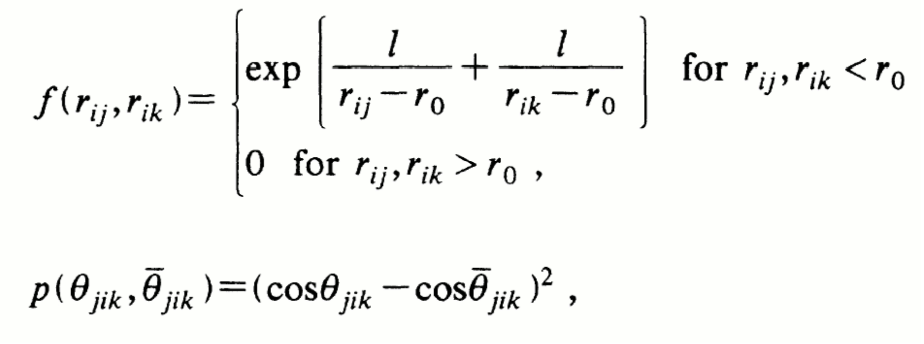
- The three-body term:

$$V_3 = B_{jik} f(r_{ij}, r_{ik}) p(\theta_{jik}, \bar{\theta}_{jik}) \, ,$$

where the f-function describes how the bond lengths and the p-term how a change of the bond angle affects the interaction.

Potentials for ionic compounds

- These are



$$f(r_{ij},r_{ik})=\begin{cases}\exp\left[\dfrac{l}{r_{ij}-r_0}+\dfrac{l}{r_{ik}-r_0}\right] & \text{for } r_{ij},r_{ik}<r_0\\ 0 \quad \text{for } r_{ij},r_{ik}>r_0\ , & \end{cases}$$

$$p(\theta_{jik},\bar{\theta}_{jik})=(\cos\theta_{jik}-\cos\bar{\theta}_{jik})^2\ ,$$

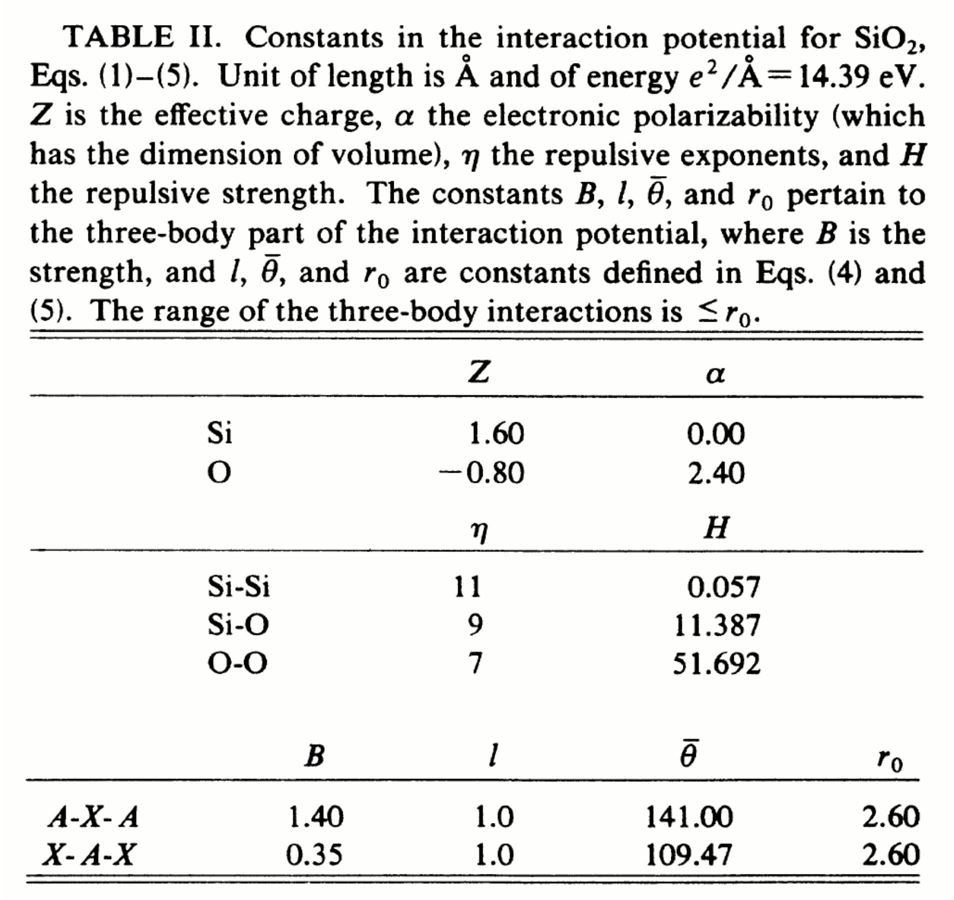


TABLE II. Constants in the interaction potential for SiO_2, Eqs. (1)–(5). Unit of length is Å and of energy $e^2/\text{Å}=14.39$ eV. Z is the effective charge, α the electronic polarizability (which has the dimension of volume), η the repulsive exponents, and H the repulsive strength. The constants B, l, $\bar{\theta}$, and r_0 pertain to the three-body part of the interaction potential, where B is the strength, and l, $\bar{\theta}$, and r_0 are constants defined in Eqs. (4) and (5). The range of the three-body interactions is $\leq r_0$.

	Z	α
Si	1.60	0.00
O	−0.80	2.40

	η	H
Si-Si	11	0.057
Si-O	9	11.387
O-O	7	51.692

	B	l	$\bar{\theta}$	r_0
A-X-A	1.40	1.0	141.00	2.60
X-A-X	0.35	1.0	109.47	2.60

- Parameters are shown on the right.
  - *A* corresponds to Si and *X* to O in the three-body parts. Note that only the *AXA*- and *XAX*-three-body terms are defined - the potential would not describe sensibly e.g. pure Si since there is no *AAA*-term.

Potentials for ionic compounds

- The Si-Si and O-O-interaction are just a purely repulsive pair potential:

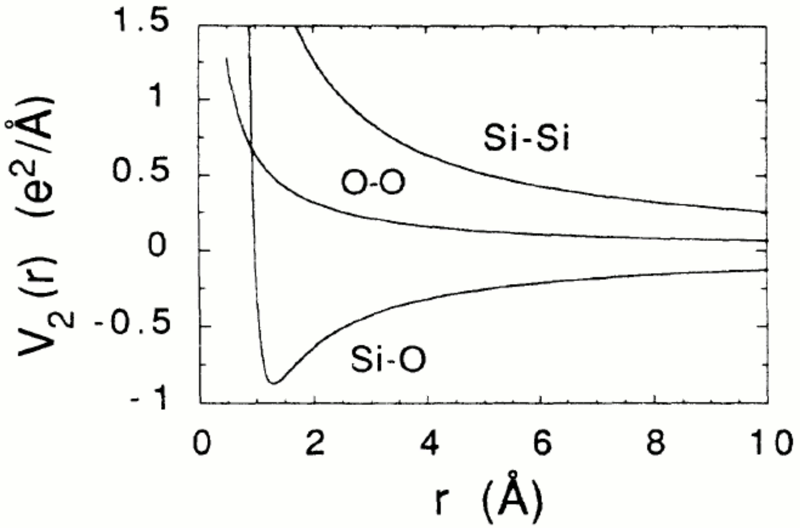


FIG. 1. Si-Si, Si-O, and O-O contributions to the two-body part of the interaction potentials, Eq. (2), for SiO_2. Total interaction potential is a sum of two-body, Eq. (2), and three-body contributions, Eq. (3). Unit of length is Å and of energy $e^2/\text{Å} = 14.39$ eV.

Potentials for ionic compounds

- The potential describes well the most common forms of SiO_2 :

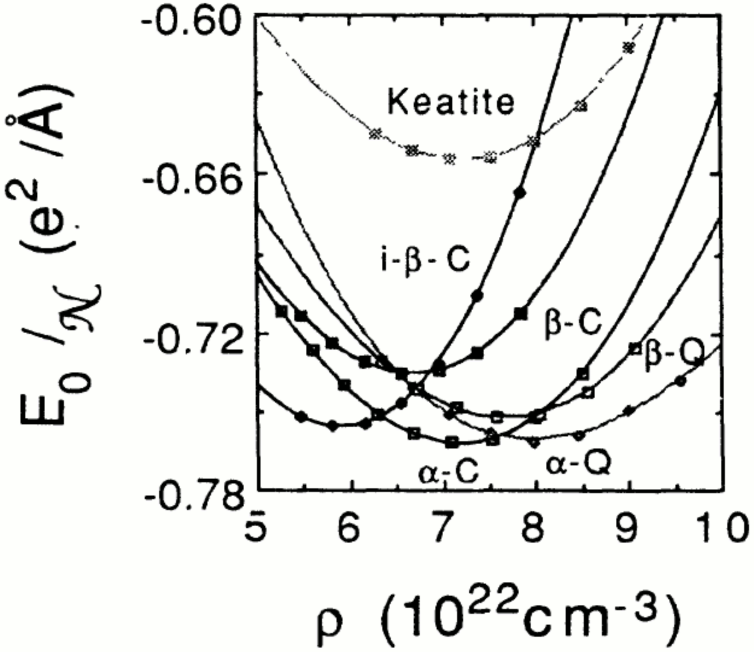


FIG. 2. Total potential energy (two plus three body) per particle, $E_0/\mathcal{N}$ in units of $e^2/\text{Å}=14.39$ eV, for various crystalline phases of SiO_2 as a function of density: ideal *β*-cristobalite (*i-β-C*), *β*-cristobalite (*β-C*), *α*-cristobalite (*α-C*), *β*-quartz (*β-Q*), *α*-quartz (*α-Q*), and keatite.

Potentials for ionic compounds

- A newer potential was developed by Watanabe et al. [*Appl. Surf. Sci.* **234** (2004) 207.].
  - One of its strengths is the ability to describe also the so called sub-oxides of SiO_2; e.g. SiO.
  - Because of this it is suitable for describing interfaces between Si and SiO_2 and to be used in defect studies and ion bombardment simulations.
  - The potential is based on the Stillinger-Weber potential and the Si-Si interaction is the original Si-SW.
  - Examples of its use in nanocluster bombardment can be found in J. Samela's PhD thesis[1].
  - However, its elastic properties are not very good, strongly overestimates e.g. bulk modulus

- An SiO2 potential in the Tersoff formalism: [Munetoh et al, Comput. Mater. Sci. 39 (2007) 334]: better than Watanabe in some elastic and melting properties

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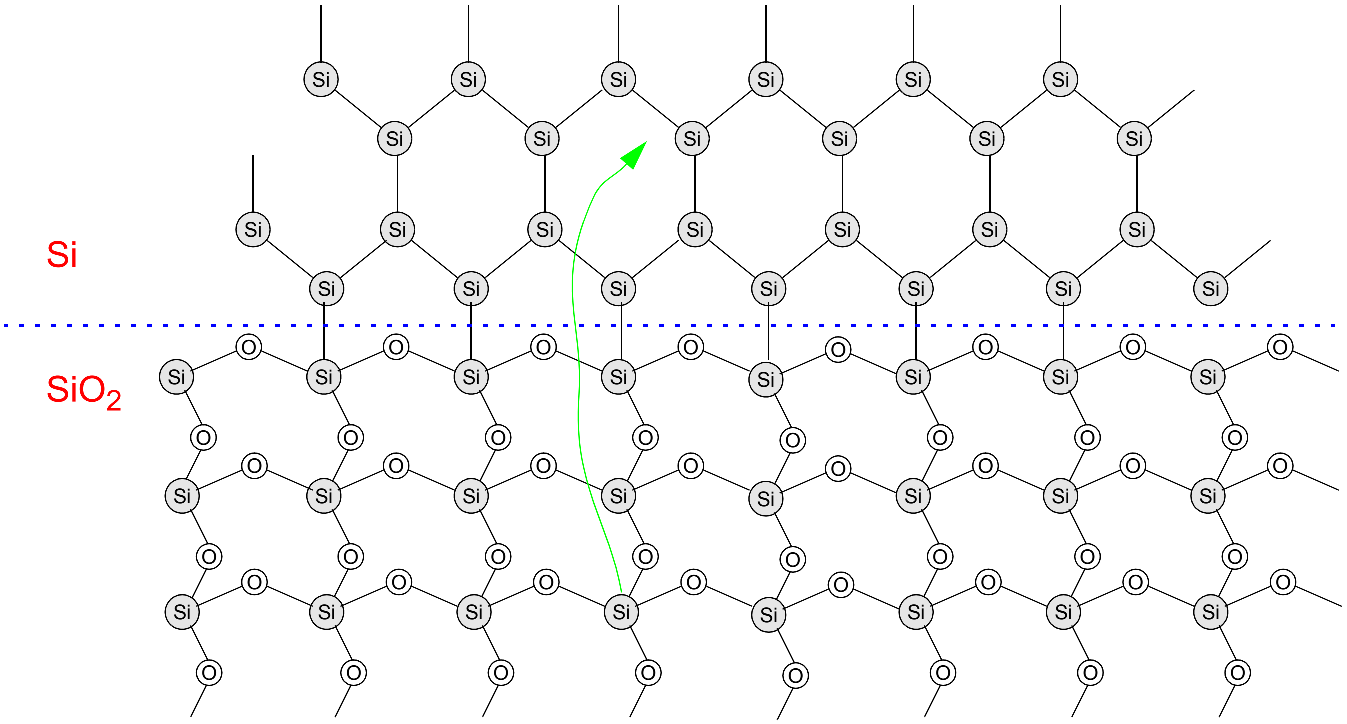
[1] Electronically available at http://urn.fi/URN:ISBN:978-952-10-3927-0

Charge-transfer potential models

- There is a clear fundamental problem with the description of ionic bonding and covalent bonding described above.
  - Consider the following (schematic 2D representation) of an Si-SiO_2 interface system:



  - On the Si side of the interface, $z_{\mathrm{Si}} = 0$ → ordinary Si potentials.
  - On the SiO_2 side $z_{\mathrm{Si}} \approx 2$ → ionic model.

To be more precise, ab initio calculations give for SiO_2:

$$Z_{\mathrm{Si}} \approx 1.4e, \ \ Z_{\mathrm{O}} \approx -0.7e$$

- What happens if we move an Si atom from the SiO_2 to the Si side (green line). This could easily occur in reality by diffusion or a radiation process. Which model should be used to describe the interactions of this atom??

Charge-transfer potential models

- Here we get to the charge transfer model for the atoms, where the environment-dependence of the ionicity of the atom is built into the model.
  - There are extremely few models like this, since charge transfer processes are difficult to deal with and poorly understood.
  - One fairly well motivated approach is that of Alavi *et al.,* Phil. Mag. B **65** (1992) 489.
  - The idea is to formulate an environment-dependent term which gives the charge state of atoms:

$$z_i = Z\left(\sum_{j \neq i} f_{A_i B_j}(r_{ij})\right)$$

    - $f_{AB}(r_{ij})$ is some function of the atom distances and types A_i and B_j
    - $Z(x)$ is a function which could e.g. limit the charge state to reasonable values (like say between -4 and +4 for Si).
  - Some thought reveals that the f_{AB} functions would be likely to have the properties

$$\begin{aligned} f_{AA} &= 0 \\ f_{BB} &= 0 \\ f_{AB}(r_{ij}) &= -f_{BA}(r_{ij}) \end{aligned}$$

    - The first two criteria ensure charge neutrality in a pure elemental region, the latter one global charge neutrality.

Charge-transfer potential models

- Once the z_i have been determined, one could use an expression of e.g. the form

$$V_i = \sum_j \frac{z_i z_j e^2}{4\pi\varepsilon_0 r_{ij}} + g(z_i)\sum_{jk} V_{\text{manybody}}$$

to obtain the total interaction energy of an atom i.

- V_{manybody} could be some many-body potential for an uncharged system.
- The function $g(z_i)$ would be used to switch this potential on and off depending on the ionicity:

$$g(z_i) \begin{cases} = 1 \text{ when } z_i = 0 \\ \rightarrow 0 \text{ when } z_i \neq 0 \end{cases}$$

- The big and difficult question is how to choose $f(r_{ij})$. It should be constructed to ensure global charge neutrality, and give correct ionicities in known environments.

Charge-transfer potential models

- For instance in the SiO_2 case presented above, it obviously should be constructed such that if an Si atom has four O atoms at the equilibrium distance, it should give $z_i \approx 1.4e$. Since every Si atom has 4 O neighbours and every O atom 2 Si neighbours this would mean that in case only nearest-neighbour interactions are counted and the equilibrium atom distance is r_0, one could have

$$\begin{cases} f_{\text{Si-Si}} = 0 \\ f_{\text{O-O}} = 0 \\ f_{\text{Si-O}} = +0.35 \\ f_{\text{O-Si}} = -0.35 \\ Z(x) = x, \quad \text{when } x \le 4 \end{cases}$$

(remember: $Z_{\text{Si}} \approx 1.4e$, $Z_{\text{O}} \approx -0.7e$)

- One way to deduce the functional form could be to use quantum mechanical schemes to deduce ionicity, such as Mulliken charge analysis.

- Since little work has been done on this topic there is not much more to say, except that this is a wide-open topic with lots of room for new and interesting research.

- See also F. H. Streitz, J. W. Mintmire, *Phys. Rev. B* **50** (1994) 11996; X. W. Zhou *et al.*, *Phys. Rev. B* **69** (2004) 035402.

Potential models for ionic compounds

- Sometimes rather simple models may be sufficient.
  - An example: Si/SiO_2 interface (again!) [Y. Tu, J. Tersoff, *Phys. Rev. Lett.* **84** (2000) 4393.]
    - Simple VFF potential (sum over bonds; only Si-O and Si-Si bonds; no defects: continuous network of bonds):

$$E_{\{\mathbf{r}\}} = \frac{1}{2}\sum_i k_b(b_i - b_0)^2 + \frac{1}{2}\sum_{i,j} k_\theta(\cos\theta_{ij} - \cos\theta_0)^2 + U$$

    - Suboxide penalty U allows to study other environments of Si atoms than the perfect SiO_2. It gives the energy cost of having less than 4 O neighbors:

Number of O neighbors	U/eV
0	0.00
1	0.47
2	0.51
3	0.24
4	0.00

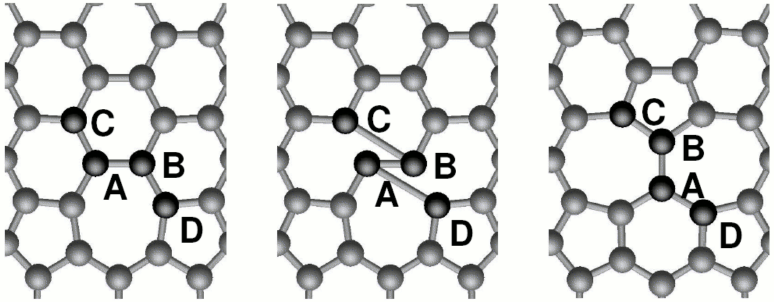


FIG. 1: The bond-switch move in a 2D example. *On the left:* The situation before the switch. *Center:* The bonds have been switched. *On the right:* The atoms have been moved to their minimum energy position.

    - Interface structure was optimized using bond-switching Monte Carlo.

    - For every **bond topology** the atom positions $\{\mathbf{r}\}$ were obtained by minimizing the potential energy

$$E = \min_{\{\mathbf{r}\}}(E_{\{\mathbf{r}\}})$$

Phase space = ensemble of bond topologies

Potential models for ionic compounds

Results: interfaces Si—amorphous SiO2 and Si—tridymite

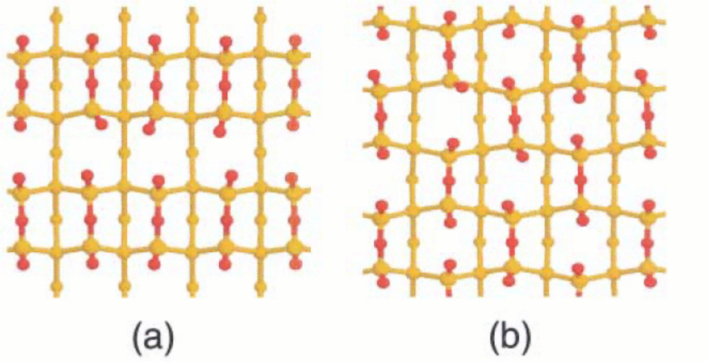


FIG. 1 (color). Plan view illustrating two Si-SiO_2 interface structures. The last three layers of Si are shown in gold, with atoms farther from the interface shown smaller. The first layer of O is shown in red. (a) Stripe phase, having (2 × 1) symmetry. (b) Check phase, having $c(2 \times 2)$ symmetry.

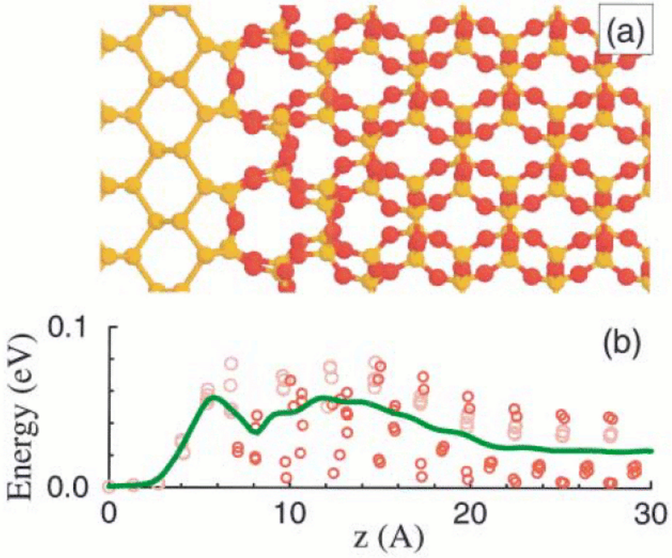


FIG. 4 (color). Interface between Si and tridymite, as in Fig. 3, to illustrate similarity of interface regions.

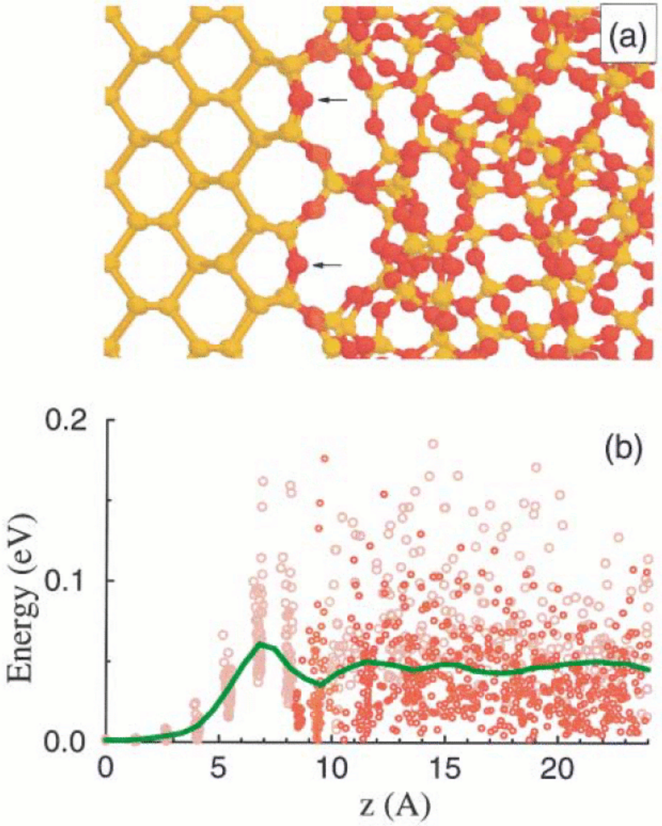


FIG. 3 (color). (a) Side view of canonical interface, for 4 × 4 cell of stripe phase, in [110] projection. The Si and O atoms are represented by gold and red spheres, respectively. Each arrow points to a row of oxygen atoms that form the bridges at the interface. Notice the substantial voids above each bridge bond. (b) Energy of each atom versus its z coordinate. Red circles represent oxygen atoms and gold circles represent silicon atoms. The green line is the local energy per atom, averaged over 20 configurations (and over a z range of $\sim$1 Å for smoothness).

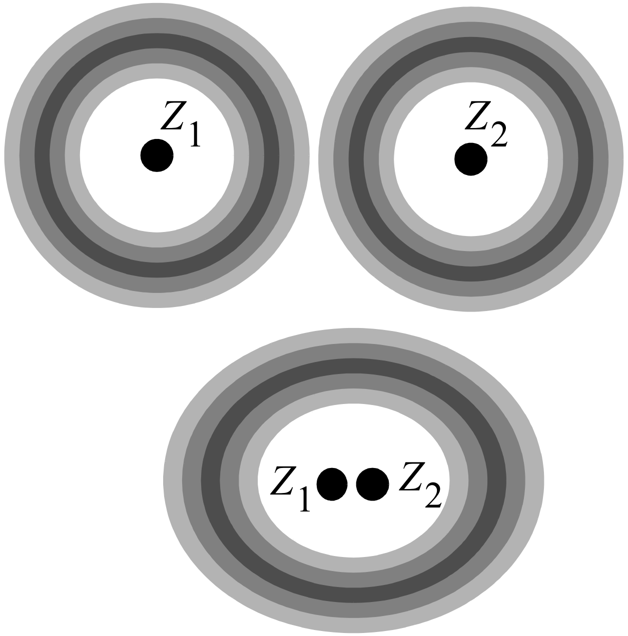
Repulsive potentials for high energies

- When talking about repulsive potentials there is first reason to clarify the concepts:
  - **Repulsive part** of equilibrium potentials: Constructed to obtain a minimum in the potential, and to describe states close to equilibrium, at energies ~ 0.1 - 100 eV above the minimum.
    - E.g. the short-range potentials V_{SR} mentioned above belong to this category.
  - Ion ion irradiation and nuclear physics one frequently is interested in very high-energy collisions.
    - An ion with a kinetic energy of 100 keV makes a head-on collision with a target atom → the C.M. energy is 50 keV
    - In this regime the equilibrium potentials are not valid, and there is a reason to fit a high-energy **repulsive potential** to them.
- Repulsive potentials are usually written in the form

$$V(r) = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 r}\Phi\left(\frac{r}{a}\right) \quad ,$$

where $\Phi(x)$ is a **screening function** and $a = a(Z_1, Z_2)$ a **screening length**.

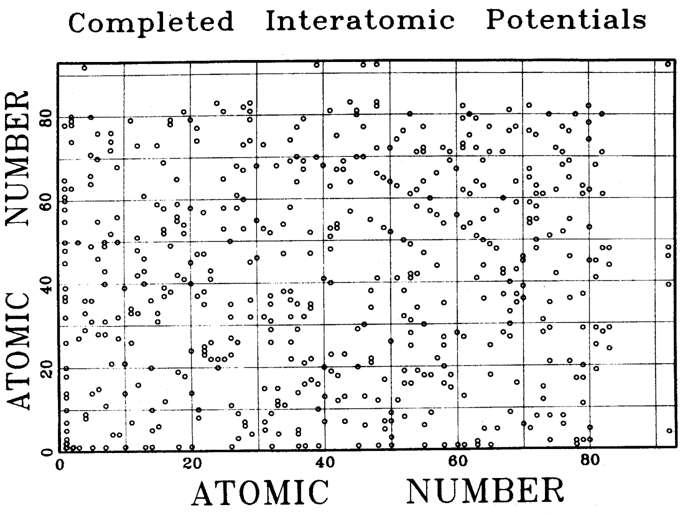
  - Φ is formed such that $\Phi \to 1$ when $x \to 0$, so the potential reduces to the Coulomb potential between the nuclei at high energies.
  - At normal interatomic distances the electron shells screen the nuclei so that the nucleus don't "see" each other almost at all ($\Phi \approx 0$).



Repulsive potentials for high energies

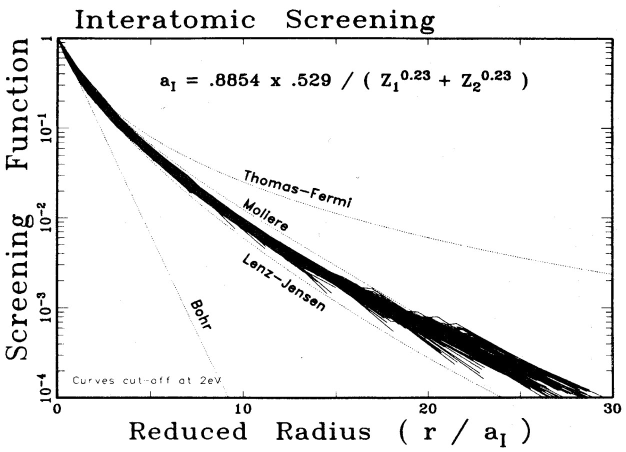
- At very small distances the nuclei are so close that the electron clouds do not screen them. The interaction is then purely Coulombic and $\Phi \approx 1$.

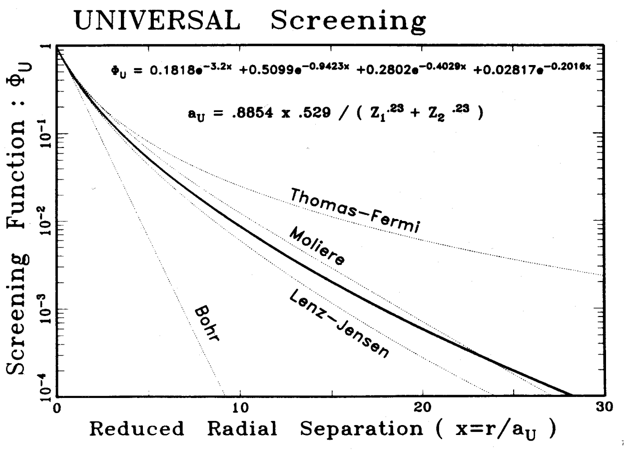
- The most used repulsive potential is that formulated by Ziegler, Biersack and Littmark (ZBL).
  - They used free-electron gas (FEG)-calculations to obtain the repulsive interatomic potential for 522 randomly chosen atom pairs, and sought a shape for the screening length which makes the screening function be as similar as possible for the different atoms:



$$a = \frac{0.8856 \times a_0}{Z_1^{0.23} + Z_2^{0.23}}$$, where $a_0 = 0.529\text{Å}$ is the Bohr length.

Repulsive potentials for high energies





- Onto these curves they fit a universal function (right figure above) of the form

$$\Phi(x) = \sum_{i=1}^{4} a_i e^{-b_i x} .$$

and obtained the parameter values shown on the right.

i	a_i	b_i
1	0.1818	3.2
2	0.5099	0.9423
3	0.2802	0.4029
4	0.02817	0.2016

- This potential is generally called the **ZBL universal potential**. The advantage of using it is that it is extremely easy: the only information needed of it are the atom numbers Z_1 and Z_2 . The disadvantage is that this is an average potential, from which each specific case can vary easily 5-10 %.

- It is also possible to reproduce the FEG calculations for any atom pair based on information in the ZBL book *The Stopping and Range of Ions in Matter* (Pergamon, New York, 1985). This gives so called **ZBL pair-specific potentials.** These seem to be accurate to a few % or so.

Repulsive potentials for high energies

- In case the best possible accuracy is desired, one can use Hartree-Fock- or DFT-calculations of the energy of a dimer, or even better an atom inside a solid.
  - With dimer calculations by using certain HF- , HFS- and DFT methods it is possible to obtain the high-energy repulsive potential to ~ 1 % accuracy [Nordlund, Runeberg and Sundholm, *Nucl. Instr. Meth. Phys. Res. B* **132** (1997) 45].

Efficient ways to calculate ionic interactions

- So far we have assumed that the sum giving the energy of each atom always converges easily. This is not true always, however.
  - Let us consider potentials of the form $V \sim r^{-d}$. Far from the central atom in a homogeneous material the number of atoms in a thin shell dr is $4\pi r^2 \rho dr$, where ρ is the atom density, so the total potential in this layer is proportional to $4\pi r^2 \rho dr r^{-d}$. If we now integrate the total potential for all r, we obtain

$$V = \int_{r_{\min}}^{\infty} 4\pi\rho r^2 r^{-d} dr = 4\pi\rho \frac{1}{3-d} r^{3-d} \bigg|_{r_{\min}}^{\infty}$$

  - This vanishes in infinity only if $d > 3$. So in three dimensions we obtain convergence trivially only if the potential decays faster than r^{-3}.
  - Exponentially decaying potentials (Morse, Tersoff etc.), as well as LJ potentials are OK in this respect, but not the Coulomb potential which is r^{-1}
    → **When one simulates a periodic system with an ionic potential one can not use a simple cutoff distance < cell size/2.**
  - To circumvent this many methods have been developed: 1) Ewald summation [*Ann. Phys.* **64** (1921) 253]. It is much more efficient than direct summation, but is still an $O(N^2)$ method. 2) A newer method is the so called Fast Multipole Method, which can be parallelized and is $O(N)$.

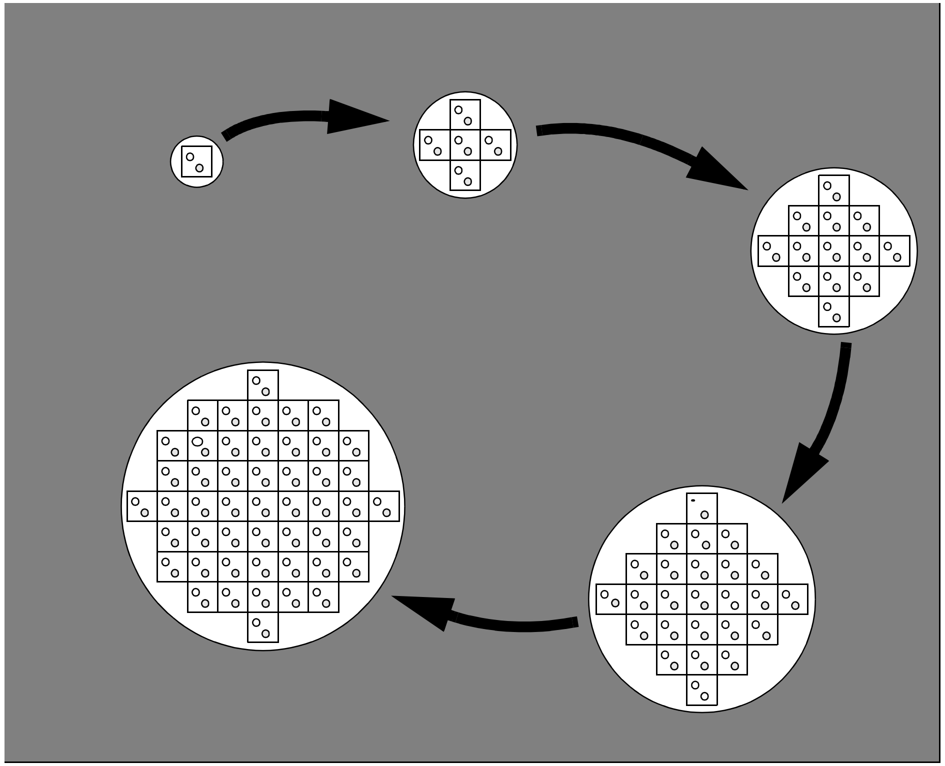
Ewald-summation

- Take into account all interactions to an atom both from the MD cell itself as well as all the periodic image cells.
- The potential energy due to the Coulomb interaction is

$$V^{zz} = \frac{1}{2}\sum_{\mathbf{n}}\left[\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{z_1 z_2}{|\mathbf{r}_{ij}-\mathbf{n}|}\right]$$

Note: cgs units

- z_1 and z_2 are the atom charges, and cgs units are used for brevity. The vector $\mathbf{n}$ is now in principle a sum over all image cells $(n_x L, n_y L, n_z L)$, where $n_x = -\infty, \ldots, -1, 0, 1, \ldots, \infty$ and the indices i and j loop over atom pairs inside the cell (except of course not $i = j$ when $\mathbf{n} = 0$).



- This sum does not necessarily converge!
- Change the summation order: A natural way to achieve this is to add image cells radially outwards from the origin.
- Physically the reason this leads to convergence is easy to understand: since each cell has to be charge neutral the charges in it give at a long distance a dipole, quadrupole etc. interaction, which vanishes during symmetric summation.

Ewald-summation

- The surrounding medium also affects the energy of this ball. In a perfect conductor (metal) ($\varepsilon = \infty$) and in vacuum ($\varepsilon = 1$) the results are different; in vacuum a dipole layer will form at the surface. The correspondence between the two quantities is:

$$V^{zz}(\varepsilon = \infty) = V^{zz}(\varepsilon = 1) - \frac{2\pi}{3L^3}\left|\sum_i z_i \mathbf{r}_i\right|^2$$

  - Ewald summation enables calculation of $V^{zz}(\varepsilon = \infty)$.
  - If we want our system to be surrounded by vacuum, we can add the dipole term.

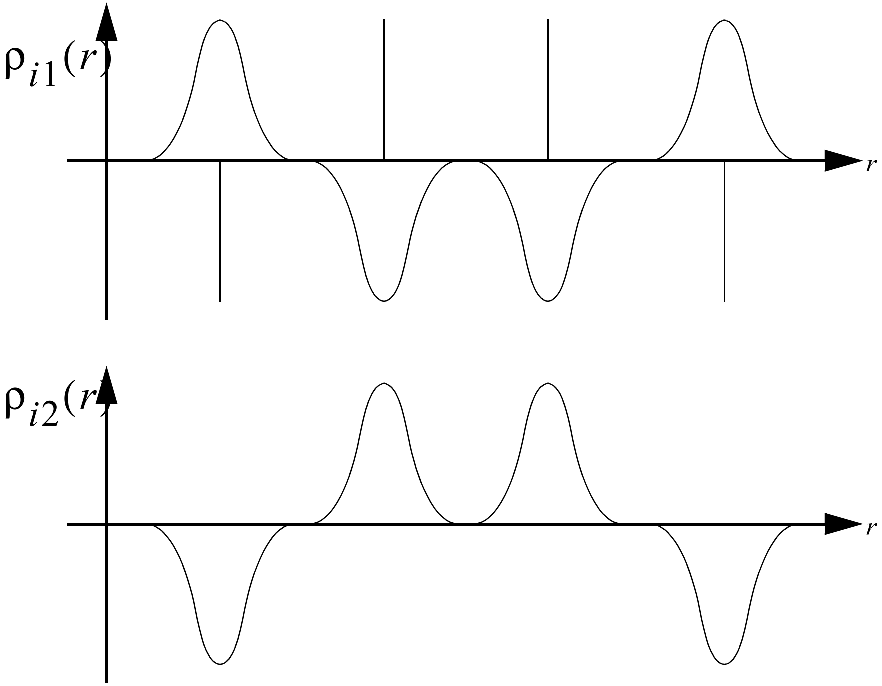
Ewald-summation

- In the Ewald method the charges z_i are given in the form of a charge density ρ_i^z. This ρ_i^z is given us the sum of a Gaussian and delta function electron density:

$$\rho_i^z(\mathbf{r}) = \rho_{i1}^z(\mathbf{r}) + \rho_{i2}^z(\mathbf{r})$$

$$\rho_{i1}^z(\mathbf{r}) = z_i[\delta(\mathbf{r} - \mathbf{r}_i) - \kappa^3\pi^{-3/2}e^{-\kappa^2(\mathbf{r} - \mathbf{r}_i)^2}]$$

$$\rho_{i2}^z(\mathbf{r}) = z_i\kappa^3\pi^{-3/2}e^{-\kappa^2(\mathbf{r} - \mathbf{r}_i)^2}$$



- ρ_{i1}^z is now a sum of delta functions located at the atom positions, and Gaussian-shaped densities of centered on the same position but of opposite signs, formed so that the integral is 0. Because ρ_{i1}^z now has a finite range, we can calculate the energy and force due to is using a cutoff radius.

- On the other hand, we also use the function ρ_{i2}^z to correct for the error made in introducing the Gaussian functions. But this function is now smooth, and can be calculated in reciprocal space: the Fourier-transformation of ρ are summed, and then an inverse Fourier transformation is used to obtain back the real-space answer.

Ewald-summation

- The result (“after a few steps of algebra”) is an equation which has a real-space term $\mathbf{r}$, a $\mathbf{k}$-space term and the inverse value of the self-energy and the surface energy:
  - Term 1 is the short-range part. $\operatorname{erfc}(x) = (2/\pi^{1/2})\int_x^{\infty} e^{-t^2}dt$ is the complementary error function and L the side length of the MD-cell. We assume here that the cell is cubic. Again in the $\mathbf{n}$ sum the term $i = j$ when $\mathbf{n} = 0$.
  - Term 2 is the sum over reciprocal space vectors $\mathbf{k} = (2\pi/L)\mathbf{n}$.
  - Term 3 V_{self} is the self-energy of ρ^{z}_{i2} which has to be removed because it is included in the $V^{zz}_{\text{recipr.}}$ part.
  - Term 4 is the surface term of the sphere.
- By setting κ (the width of the Gaussians) large enough we can restrict ourselves to the term $\mathbf{n} = 0$, which corresponds to the normal ‘minimum image’ convention.
- The real-space term can be calculated in the some loop as the short-range forces. Then V^{zz}_{real} is of the form

$$V^{zz}_{\text{real}} = \sum_{i<j}\left[z_i z_j \frac{\operatorname{erfc}(\kappa r_{ij})}{r_{ij}}\right].$$

$$V^{zz}(\varepsilon = 1) = V^{zz}_{\text{real}} + V^{zz}_{\text{recipr.}} - V^{zz}_{\text{self}} + V^{zz}_{\text{surf}}$$

$$= \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\Bigg[\sum_{|\mathbf{n}|=0}^{\infty} z_i z_j \frac{\operatorname{erfc}(\kappa|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|} \qquad 1$$

$$+ \frac{1}{\pi L^3}\sum_{\mathbf{k}\neq 0} z_i z_j \frac{4\pi^2}{k^2} e^{-k^2/4\kappa^2}\cos(\mathbf{k}\cdot\mathbf{r}_{ij})\Bigg] \qquad 2$$

$$- \frac{\kappa}{\pi^{1/2}}\sum_{i=1}^{N} z_i^2 \qquad 3$$

$$+ \frac{2\pi}{3L^3}\left|\sum_{i=1}^{N} z_i \mathbf{r}_i\right|^2 \qquad 4$$

Ewald-summation

- Using complex numbers the reciprocal-space term can be written in the simpler form

$$V^{zz}_{\text{recip}} = \sum_{\mathbf{k}} A(\mathbf{k}) \left| \sum_i z_i e^{i\mathbf{k}\cdot\mathbf{r}_i} \right|^2$$

$$A(\mathbf{k}) = \frac{2\pi}{L^3} \frac{\exp(-k^2/4\kappa^2)}{k^2}$$

- The force acting on atom i is

$$\mathbf{f}^i_{\text{recip}} = -2z_i \sum_{\mathbf{k}\neq 0} \mathbf{k}A(\mathbf{k})\,\text{Im}\left\{ e^{-i\mathbf{k}\cdot\mathbf{r}_i} \sum_j z_j e^{i\mathbf{k}\cdot\mathbf{r}_j} \right\}$$

- Note that the force calculation takes time as $O(N^2)$.

- Does this sound highly complicated? Fortunately there are several implementations of Ewald summation easily available, see e.g. Allen-Tildesley program **F.22** or N. Anastasiou and D. Fincham, *Comput. Phys. Commun.* **25** (1981)159.

- It is easy to generalize the equations to non-cubic cells.

Ewald-summation

- In applying the method one has to choose three parameters:

  cutoff radius r_c

  width of Gaussian charge densities κ

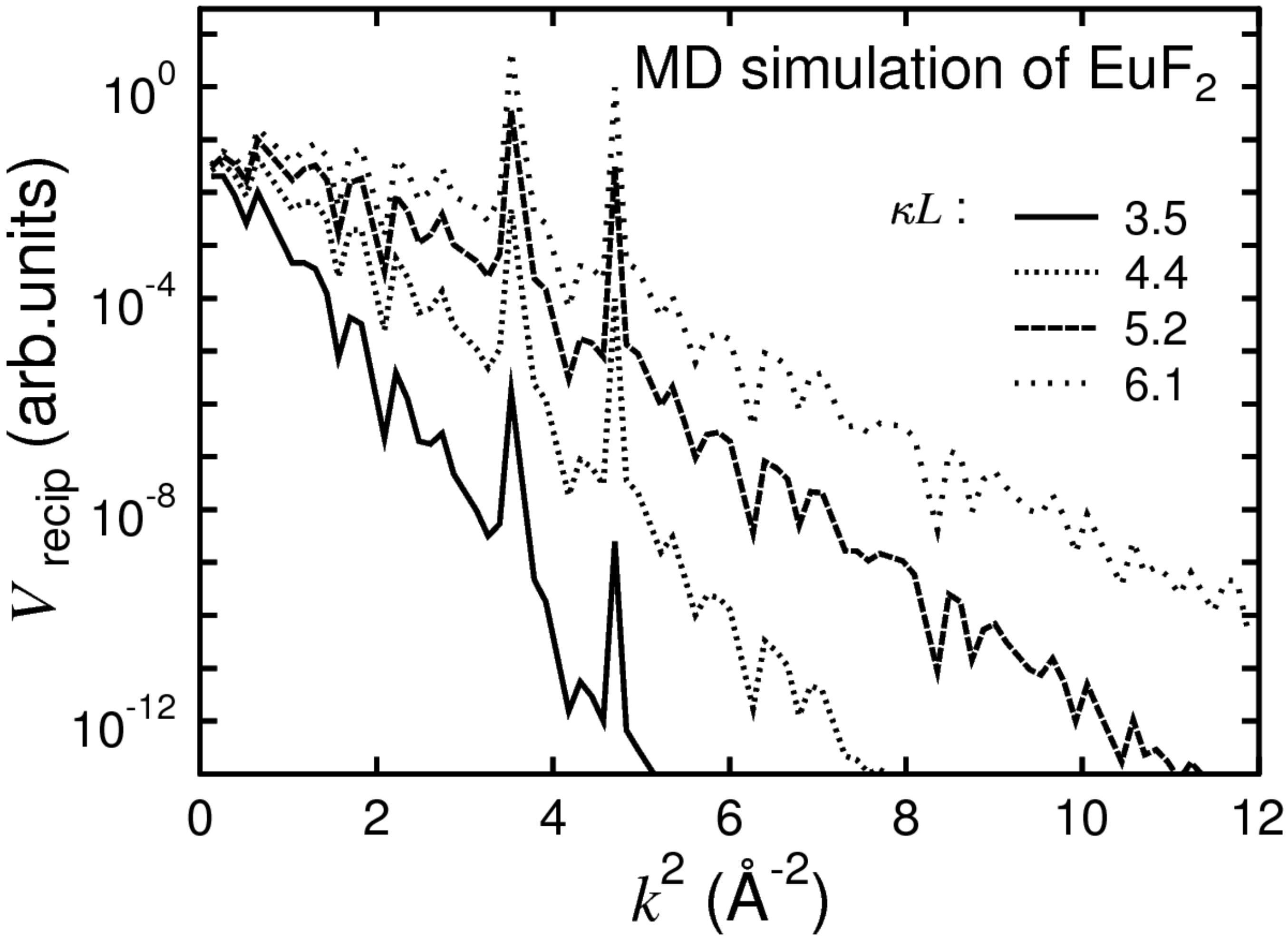
  upper limit for $\mathbf{k}$ summation $|\mathbf{k}|^2_\mathrm{max}$.

  - It is best to start by setting r_c fairly large, e.g. $L/2$. From this a suitable value of κ can be obtained, on the basis of which a suitable limit for the $\mathbf{k}$-summation can be obtained. Typically $\kappa \sim 5/L$, in which case the calculation is concentrated in $\mathbf{k}$-space. The $\mathbf{k}$-summation would then involve 100-200 vectors.

Ewald-summation

- Example: EuF_2 :

$$
\begin{aligned}
N &= 324 \\
L &= 17.4\text{Å} \\
\kappa L &= 5.2 \\
r_c &= L/2 \\
|\mathbf{k}|^2_{\max} &= 5\text{Å}^{-2}
\end{aligned}
$$



Ewald-summation

- Application of MD in neutrino-induced Doppler broadening (NID) [A. Kuronen, *et al. Phys. Rev. B* 52, (1995) 12640.]: *K* electron capture of ^{152}Eu → ν emission → 3.0-eV recoil energy to ^{152}Sm → γ rays Doppler broadened

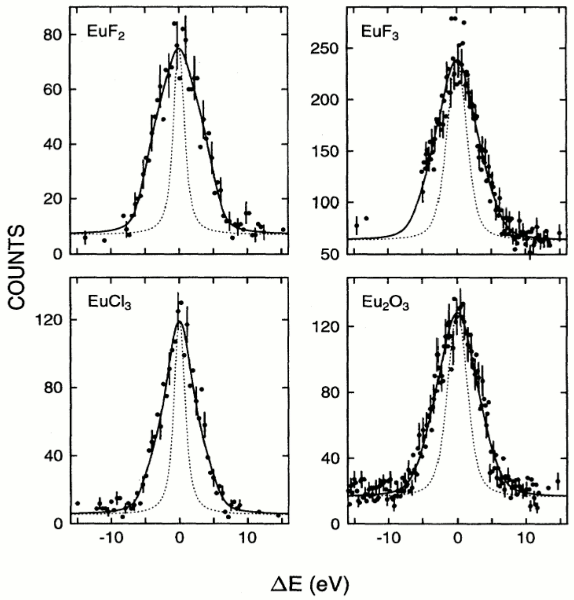


FIG. 1. Experimental (filled circles) and simulated (solid line) γ-ray line shapes for the 842-keV transition in ^{152}Sm measured in different target materials. The instrumental response function is also shown (dashed line). The simulations were performed with the recoil charge equal to the charge of the Eu atom in each lattice.

TABLE I. Parameters for the short-range potential (1) used in the simulations. For Sm, same values as for Eu were used.

Interaction	A (eV)	ρ (Å)	C (eVÅ^6)
Eu–Eu	1715.0	0.317	0.0
Eu–F	3429.1	0.280	14.0
F–F	369.1	0.280	12.5
Eu–Cl	3886.0	0.349	169.6
Cl–Cl	7911.5	0.383	2026.8
Eu–O	5045.4	0.290	34.0
O–O	22764.3	0.149	27.9

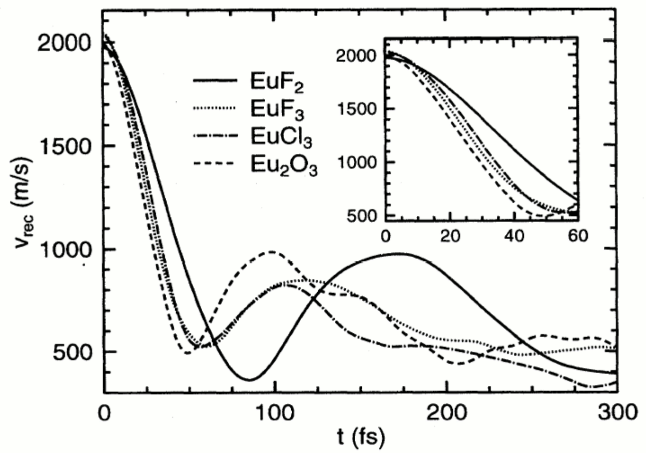


FIG. 2. Average magnitude of the velocity vector of the recoiling Sm ion as a function of time after the nuclear decay of ^{152}Eu as obtained from the MD simulations for different target materials.

TABLE II. Lifetime of the 963-keV state in ^{152}Sm obtained from NID measurements in different target materials using the equilibrium charges of Eu (2+ for EuF$_2$ and 3+ for the others) for the Sm ion in simulations. Lifetimes are weighted averages of the values for the 842- and 963-keV transitions. In addition to the statistical uncertainty, the quoted errors include uncertainties of the target temperature (0.9 fs), simulation statistics (2.0 fs), and instrumental response function (1.2 fs for EuF$_3$ and Eu$_2$O$_3$).

Target material	Lifetime (fs)
EuF$_2$	24.2±2.7
EuF$_3$	22.4±2.9
EuCl$_3$	36.8±2.8
Eu$_2$O$_3$	27.8±2.8

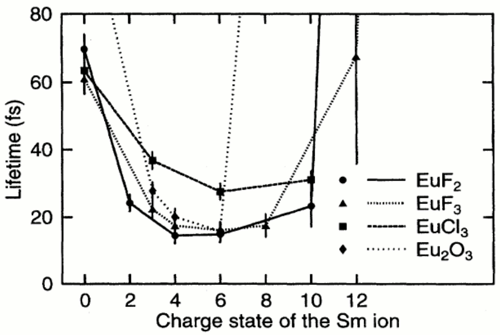


FIG. 3. Dependence of the fitted lifetime of the 963-keV level in ^{152}Sm on the charge state of recoiling ion in different target materials.

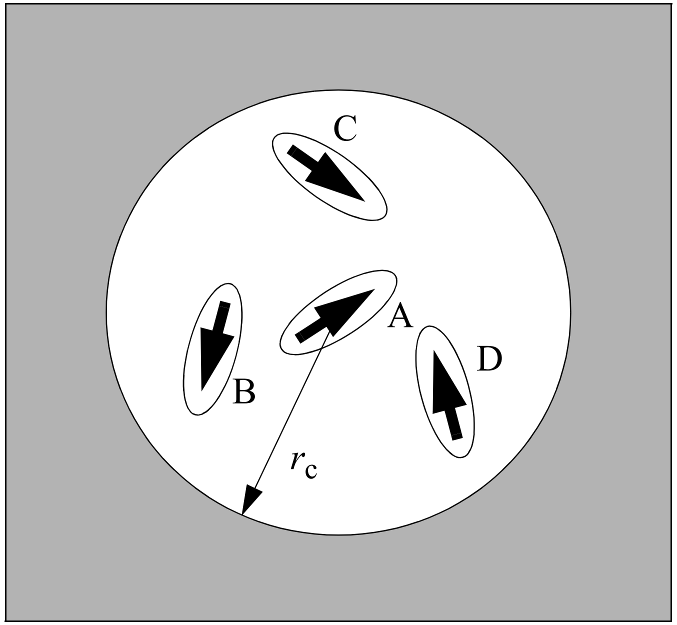
Ewald-summation

- If the periodicity of the Ewald summation causes trouble, one can use the particle-lattice (or particle-mesh) method:
  - The reciprocal space part is calculated by smoothing the ion charges in a regular lattice and solving the potential from the Poisson equation $\nabla^2\phi = -\rho/\varepsilon_0$ with Fourier methods.
    - The advantage is that this scales as $O(N)$.
    - The disadvantage is that the program gets more complicated
    -

Reaction field method

- In this method neighbours farther than r_c are approximated as continuous medium with some ε_s.

- The forces and energies inside the cavity are calculated normally.



- The continuous medium polarizes, which leads to a force on molecule i in the cavity R

$$E_i = \frac{2(\varepsilon_s - 1)}{2\varepsilon_s + 1} \frac{1}{r_c^3} \sum_{j \in R} \mu_j \quad \text{(sum includes } i\text{)}$$

- The problem here is ε_s, which has to be known in advance.

Field Multipole Method (FMM)

- The FMM method [Greengard and Rokhlin, *J. Comput. Physics* **73** (1987) 325.] is based on looking at different regions of space with different resolutions.

- The advantage of the method is that it is $O(N)$ and also can be parallelized [Nakano *et al*. *Comput. Physics Commun.* **83** (1994) 197.]

- The method uses an electrical multipole method to describe the influence of a region far away on an atom.
  - Potential outside a localized charge distribution $\rho(\mathbf{r})$ can be written as a multipole expansion:

$$\Phi(\mathbf{r}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}q_{lm}\frac{Y_{lm}(\theta,\phi)}{r^{l+1}},$$

where the multipole moments are defined as

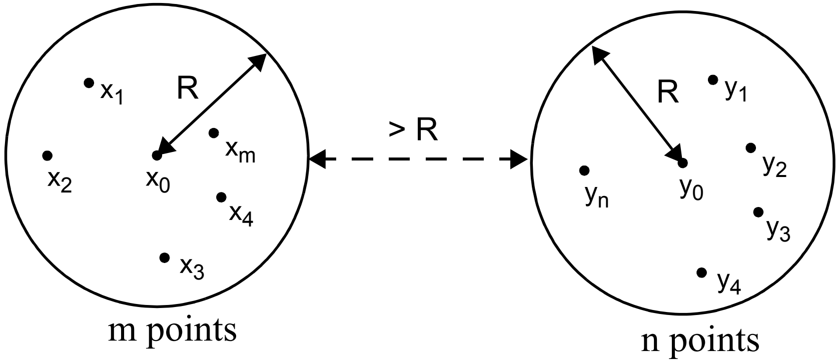
$$q_{lm} = \int Y^*_{lm}(\theta',\phi')r'^{l}\rho(\mathbf{r}')d\mathbf{r}'.$$

  - In practice, the sum over l can be truncated to some finite value:

$$\Phi(\mathbf{r}) = \sum_{l=0}^{p}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}q_{lm}\frac{Y_{lm}(\theta,\phi)}{r^{l+1}}$$

Field Multipole Method (FMM)

- Why is this useful, then ? Let us consider as a simple example two sets of points x_i and y_j which are inside two circles of radius R:

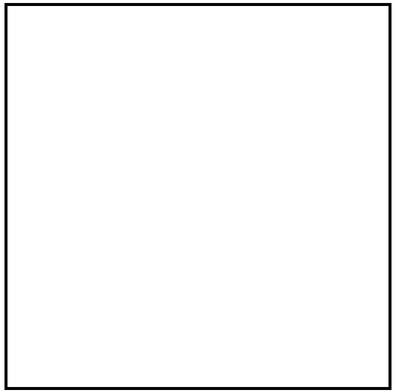


- Let the points x_i have charges q_i . If we now want to calculate the forces from points x_i on the points y_j we could of course calculate the Coulomb interaction from all the m y-points to all the n x-points. This would require nm interaction calculations, i.e. the algorithm is $O(nm)$.

- But if we, instead of this, first calculate the p^2 factors q_{lm}, requiring mp^2 operations. After this we could calculate the sum for all points y, which requires np^2 operations. Hence this method is $O(mp^2 + np^2)$. If the two circles are far away, p can be relatively small. If the number of points is large then clearly $mp^2 + np^2 \ll nm$, so we can gain lots of simulation time.

Field Multipole Method (FMM)

In the actual *FMM*-method space is divided into different levels of cell sizes.



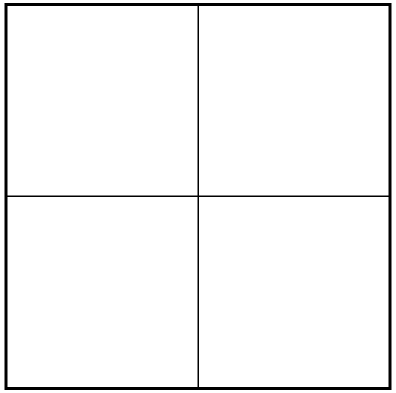
Level 0

🟦 cell b

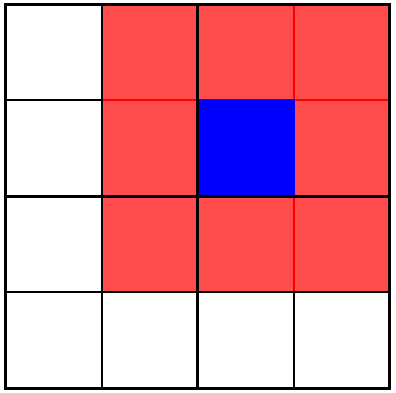
🟥 b‘s **near neighbors**: cell at the same level as b that have a common point with b

🟩 b‘s **far neighbors**: cells at the same level as b that are children of b‘s parent’s near neighbors but are not b‘s near neighbors

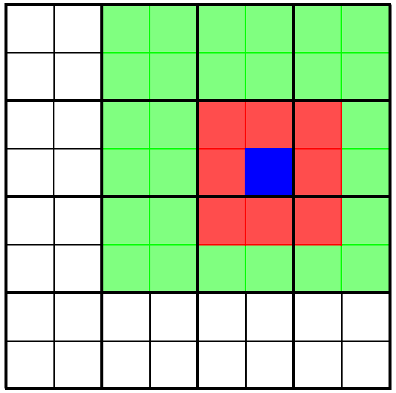
Cells that are not each others near neighbors are **well separated**.



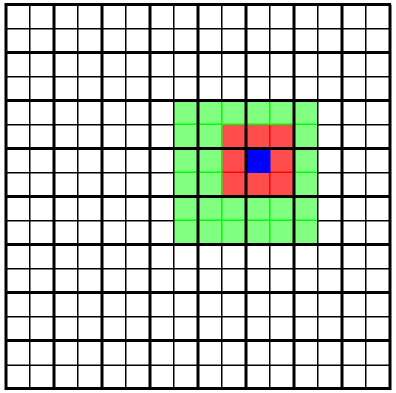
Level 1



Level 2



Level 3



Level 4

- Level 0 is the normal, ordinary simulation cell, and the higher index levels finer divisions of it.
- Multipole expansion is used to calculate interactions between cells that are well separated.
- At level 1 (see above) there are no well separated cell pairs, so that we have to go to level 2 to be able to use the expansion.
- At level 2, in order to calculate interactions between a cell and its near neighbors, we divide the box further to smaller cells. Now each new cell has far neighbors for which the multipole expansion is applied. (Note that interaction between a cell and those cells that are not its near or far neighbors has been taken care of in previous levels.)
- At some stage division is so fine that interaction between near neighbors can be calculated by normal sum over atom pairs.

Field Multipole Method (FMM)

- This calculation scales as $O(N\log N)$ (where N is the number of atoms):
  1) at every level the calculation of multipole expansions scales as $O(p^2N)$
  2) number of levels is $O(\log N)$

- To obtain the $O(N)$ behavior multipole expansion is calculated from atom positions only at the smallest scale divisions.
  - These results can be compined to calculate the expansions in coarser levels by so called translation of a multipole expansion.

- An accurate algorithm, the equations and boundary condition solutions can be found from the paper of Greengard and Rokhlin.

- In practical calculations numerical noise may become a problem.

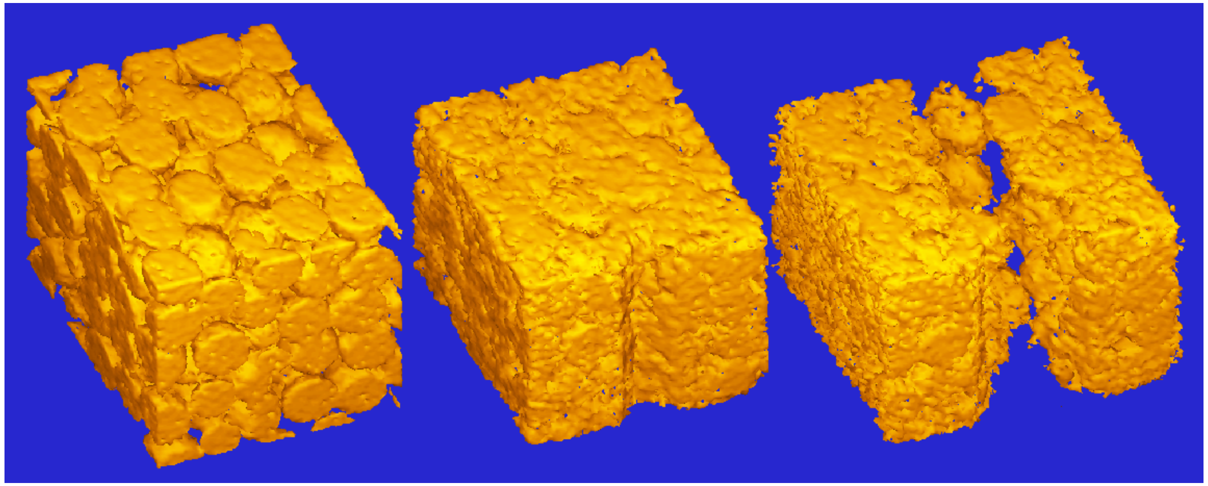
- In addition, as in Ewald summation it is also possible to take into account the effect of periodic image cells with the same principle.

- It is also evident that this algorithm can be parallelized well, since for the far cells it is enough to know only the multipole expansion, which is relatively easy to pass around.

- The FMM-model is also very general: in addition to the calculation of atomic interactions it can also be used in plasma dynamics, fluid mechanics and in astronomy!

Field Multipole Method (FMM)

- Sample application: R. Kalia et. al. simulated the fracture of about a million atom Si_3N_4 crystal [R. Kalia, TMS conference proceedings 1997].



Note that in the picture above the atoms are so small they can not be distinguished from each other!!

- After the original FMM formulation, variations often called **Fast Multipole Algorithms (FMA)** have been developed.
  - Basic idea same as in FMM, but tree-like data structures and FFT’s are used to optimize the interactions even further.
  - E.g.: **dpmta** method, W. T. Rankin, PhD Thesis, Duke University, 1995
  - In principle better, but very complex leading to numerical accuracy problems (“numerical noise”

- A comparison: [J. A Board, C. W. Humphres, C. G. Lambert, W. T. Rankin and A. Y. Toukmaji, "Ewald and multipole methods for periodic N-body problems", "Proceedings of the Eighth SIAM Conference on Parallel Processing for Scientific Computing 1997]; says that for small numbers of particles and processors, PArticle-Mesh Ewald (PME) faster than dpmta