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.
  - As we saw in the discussion on molecular mechanics, 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 of the ions z_i are often fractional charges, depending on the degree of ionicity of a material (e.g. in NaCl it is essentially 1, in GaN roughly 0.5, in GaAs roughly 0.2 and in pure Si 0.0). The short-range potential contains the repulsion of the electron shells and possibly also an attractive van der Waals-interaction.

- Some common representations for V_{SR}

  - 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: $$V_{\mathrm{SR}}(r) = De^{-2\alpha(r-r_0)} - 2De^{-\alpha(r-r_0)}$$

  So the Buckingham and Born-Huggins-Mayer potentials have a Lennard-Jones-like van der Waals-part.

- 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 ionic compounds the interactions are also partly covalent, or even a mixture of ionic, covalent and metallic bonding. In this case it may become important to add a many-body term into the potential.

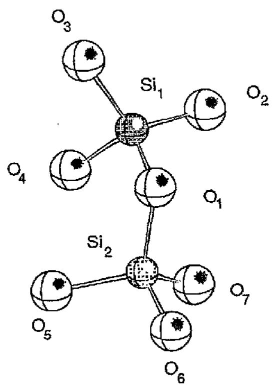
- Such potentials have been formed for many ionic compounds. We present here briefly the potential by Vashista *et al.* for SiO_2, [Phys. Rev. B 41 (1990) 12197] which comes up in many different contexts (glass, sand, quartz, the dielectric in Si-based semiconductors etc. etc.).

  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, ⟨Si—O⟩, represent the average bond length. In the last column values of bond angles Si—O—Si, average value ⟨Si—O—Si⟩, bond angle O—Si—O, and its average value ⟨O—Si—O⟩ 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 ($Fd3m$) 8 mol/u.c.	$d_{Si—O} = 1.611$ $\langle d_{Si—O} \rangle = 1.611$	∢Si—O—Si = 146.7 ⟨∢Si—O—Si⟩ = 146.7 ∢O—Si—O = 107.8,112.8
α-cristobalite[b]	2.35 (7.088)	tetragonal ($P4_12_1$) 4 mol/u.c.	$d_{Si—O}(1) = 1.602$ $d_{Si—O}(2) = 1.617$	∢Si—O—Si = 144.7 ⟨∢Si—O—Si⟩ = 144.7 ∢O—Si—O = 108.1–111.3 ⟨∢O—Si—O⟩ = 109.5
keatite[c]	2.50 (7.526)	tetragonal ($P4_12$) 12 mol/u.c.	$d_{Si—O} = 1.56–1.62$ $\langle d_{Si—O} \rangle = 1.590$	∢Si—O—Si = 148.2–159.5 ⟨∢Si—O—Si⟩ = 155.2 ∢O—Si—O = 103.7–113.8
β-quartz[d]	2.52 (7.57)	hexagonal ($P6_22$) 3 mol/u.c.	$d_{Si—O}(1) = 1.591$ $d_{Si—O}(2) = 1.606$	∢Si—O—Si = 150.9 ⟨∢Si—O—Si⟩ = 150.9 ∢O—Si—O = 108.0–110.5
α-quartz[e]	2.65 (7.956)	trigonal ($P3_221$) 3 mol/u.c.	$d_{Si—O}(1) = 1.605$ $d_{Si—O}(2) = 1.614$ $\langle d_{Si—O} \rangle = 1.609$	∢Si—O—Si = 143.7 ⟨∢Si—O—Si⟩ = 143.7 ∢O—Si—O = 108.7–110.4
coesite[f]	2.92 (8.784)	monoclinic ($P21/a$) 16 mol/u.c.	$d_{Si—O} = 1.60–1.62$ $\langle d_{Si—O} \rangle = 1.609$	∢Si—O—Si = 137.4–180 ⟨∢Si—O—Si⟩ = 148.4 ∢O—Si—O = 107.9–110.5 ⟨∢O—Si—O⟩ = 109.5
stishovite[g]	4.29 (12.88)	tetragonal ($P4_2/mnm$) 2 mol/u.c.	$d_{Si—O}(1) = 1.809$ $d_{Si—O}(2) = 1.757$	∢Si—O—Si = 81,90,106[h] ∢O—Si—O = 100,130

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:



The potential is of the familiar form:

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

and the two-body part V_2 is

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

where 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 is of the relatively simple form

$$V_3=B_{jik}f(r_{ij},r_{ik})p(\theta_{jik},\overline{\theta}_{jik}) \ , \qquad (3)$$

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

$$f(r_{ij},r_{ik})=\begin{cases}\exp\left[\dfrac{l}{r_{ij}-r_0}+\dfrac{l}{r_{ik}-r_0}\right] & \text{for } r_{ij},r_{ik}<r_0\\ 0 \text{ for } r_{ij},r_{ik}>r_0 \ , & \end{cases} \tag{4}$$

$$p(\theta_{jik},\overline{\theta}_{jik})=(\cos\theta_{jik}-\cos\overline{\theta}_{jik})^2 \ , \tag{5}$$

and the parameters are

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, $\overline{\theta}$, and r_0 pertain to the three-body part of the interaction potential, where B is the strength, and l, $\overline{\theta}$, 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	$\overline{\theta}$	r_0
A-X-A	1.40	1.0	141.00	2.60
X-A-X	0.35	1.0	109.47	2.60

where 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.

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

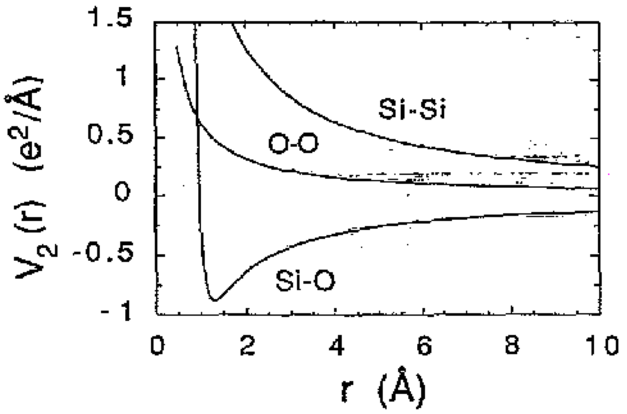


FIG. 1. Si-Si, Si-O, and O-O contributions to the two-body part of the interaction potentials, Eq. (2), for SiO_2. Total interaction potential is a sum of two-body, Eq. (2), and three-body contributions, Eq. (3). Unit of length is Å and of energy $e^2/\text{Å}=14.39$ eV.

but the potential still does describe well the most common forms of SiO_2 :

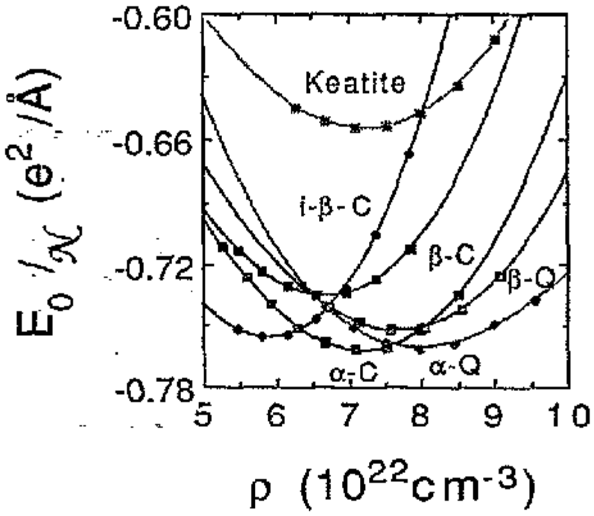
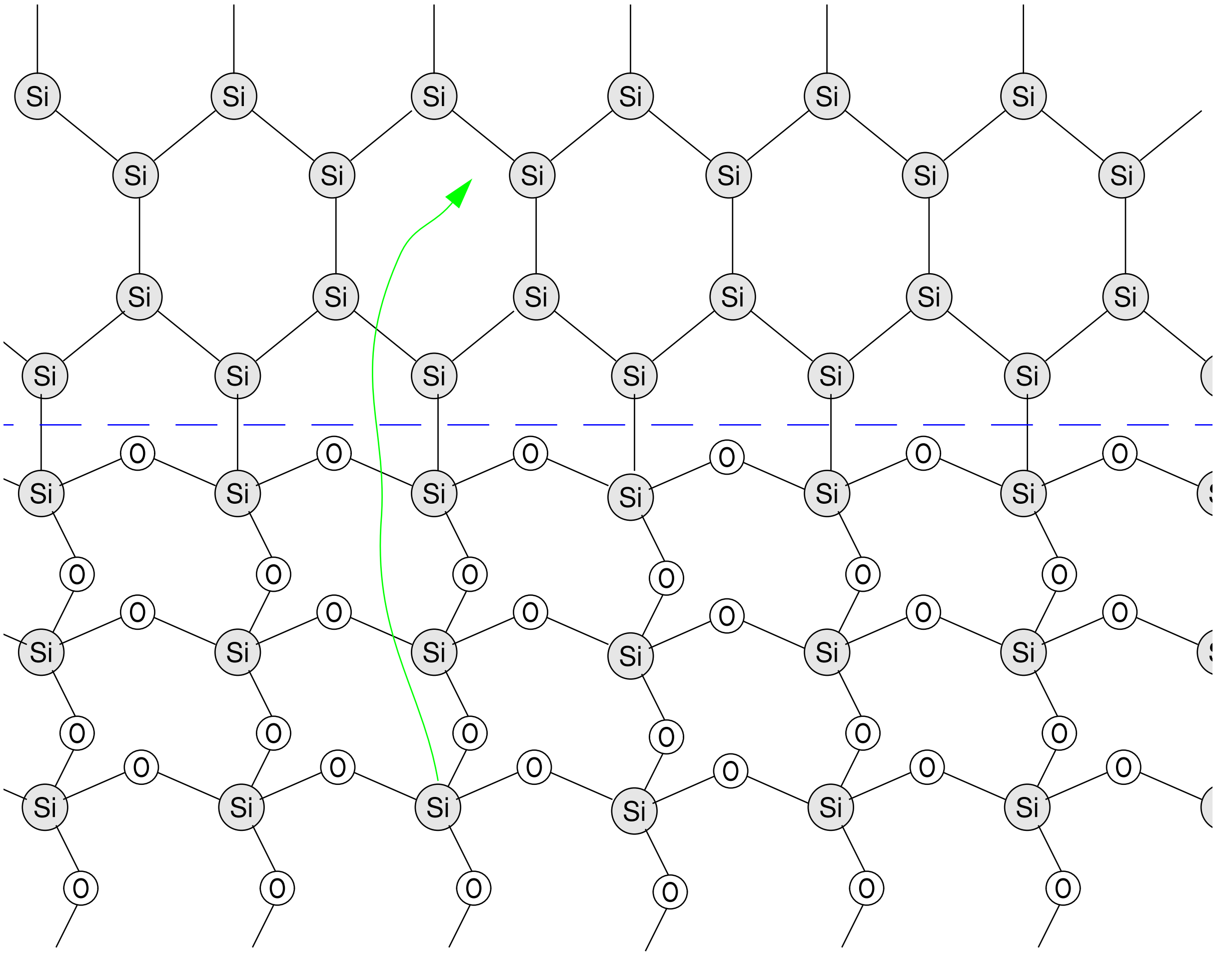


FIG. 2. Total potential energy (two plus three body) per particle, $E_0/\mathcal{N}$ in units of $e^2/\text{Å}=14.39$ eV, for various crystalline phases of SiO_2 as a function of density: ideal β-cristobalite (i-β-C), β-cristobalite (β-C), α-cristobalite (α-C), β-quartz (β-Q), α-quartz (α-Q), and keatite.

Charge-transfer potential models

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



- On the Si side of the interface, the charge state of the Si atoms is 0, and the interactions can be described with ordinary Si potentials, e.g. SW or Tersoff. On the SiO_2 side on the other hand the Si atoms have a charge of almost +2.0 (+1.6 in the Vashishta model), so an ionic model like Vashishtas could be used.

- Consider now 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??

- The easy answer would be to make the model a function of the distance to the interface. But this is not a very satisfactory, as an interaction model which depends explicitly on a coordinate is obviously unphysical. And this of course would only work if we know where our interface is.

- The better way to describe this would be to formulate a charge transfer model for the atoms, which would predict the degree of ionicity of an atom.

- There are extremely few models like this, since charge transfer processes are difficult to deal with and poorly understood (remember that even plain DFT or HF only calculates the ground state electron configurations). But 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 (similar in formalism to the electron density in EAM) which gives the charge state of atoms. I.e.

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

where $f_{AB}(r_{ij})$ 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.

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. Here V_{manybody} could be some many-body potential for an uncharged system, say ordinary Tersoff. The function $g(z_i)$ would be used to switch this potential on and off depending on the ionicity. So it should have the property

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

- 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. For instance in the SiO_2 case presented above, it obviously should be constructed such that if an Si atom has two O atoms at the equilibrium distance, it should give $z_i \approx 1.6$ .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

$$
\begin{aligned}
f_{Si-Si} &= 0 \\
f_{O-O} &= 0 \\
f_{Si-O}(r_0) &= +0.4 \\
f_{O-Si}(r_0) &= -0.4
\end{aligned}
$$

and

$$Z(x) = x \text{ at least when } x < 2$$

- 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 (I actually made most of the above up as I went along since I didn't have the Alavi publication handy) there is not much more to say, except that this is a wide-open topic with lots of room for new and interesting research. Go beat 'em all!

Repulsive potentials for high energies

- When talking about repulsive potentials there is first reason to clarify the concepts:

  In equilibrium potentials there is always a **repulsive part**. This part is usually constructed to obtain a minimum in the potential, and to describe states close to equilibrium, at energies ~ 0.1 - 100 eV above the minimum. The short-range potentials V_{SR} mentioned above belong to this category.

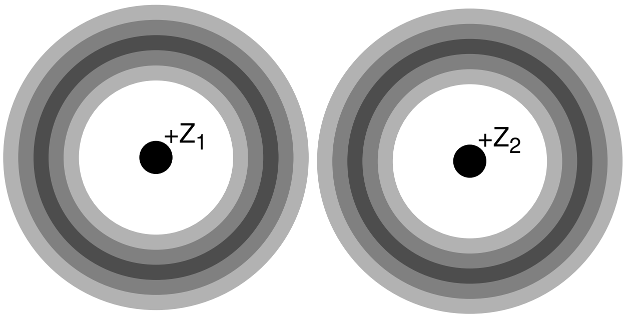
  Ion ion irradiation and nuclear physics one frequently is interested in very high-energy collisions. Say if an ion with a kinetic energy of 100 keV make a head-on collision with a target atom, the interaction energy in center-of-mass coordinates is 50 keV ! In this regime the equilibrium potentials are not valid, and there is a reason to fit a high-energy **repulsive potential** to them.

- Good high-energy repulsive potentials are usually written in the form

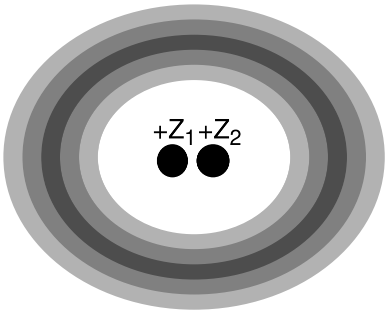
$$V(r) = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 r}\Phi\left(\frac{r}{a}\right) ,$$

  where $\Phi(x)$ is a screening function and $a = a(Z_1, Z_2)$ a screening length. The idea here is that Φ is formed such that Φ -> 1 when x -> 0, so the potential reduces to the Coulomb potential between the nuclei at high energies.

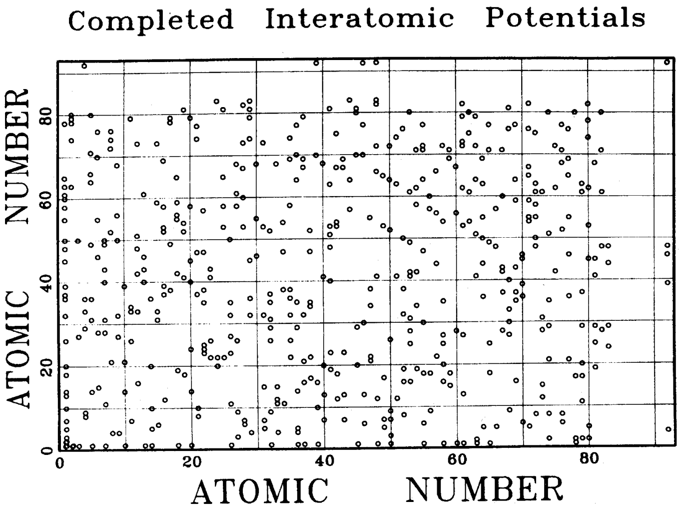
  So the screening function describes the fact that at normal interatomic distances the electron shells screen the nuclei so that the nucleus don't "see" each other almost at all. Then $\Phi \approx 0$ and the low-energy interaction effects dominate.



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

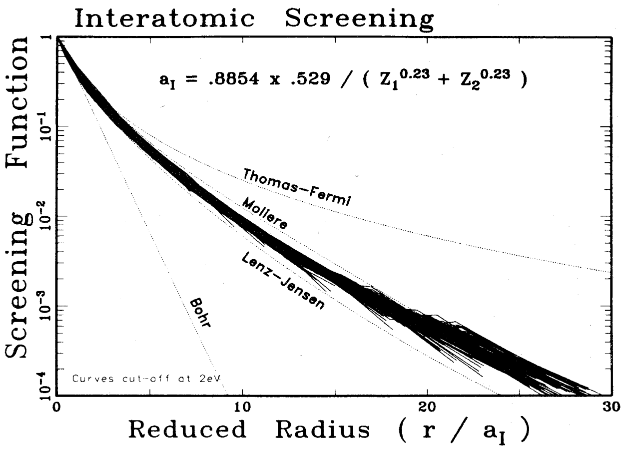


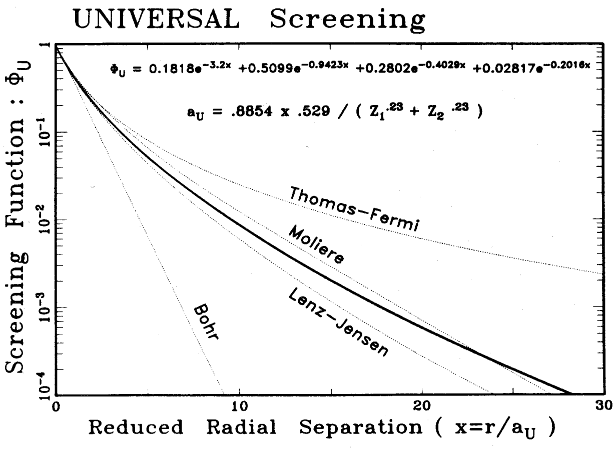
- The nowadays most used repulsive potential is that formulated by Ziegler, Biersack and Littmark (ZBL). They used simple quantum mechanical so called free-electron gas (FEG)-calculations to obtain the repulsive interatomic potential for 522 randomly chosen atom pairs, and sought a shape for the screening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



They obtained

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





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

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.

- 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 we have shown that 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

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

  This vanishes in infinity only if $d > 3$. So in three dimensions we obtain convergence trivially only if the potential -> 0 faster than r^{-3}.

  This is of course true for all exponentially reducing potentials (Morse, Tersoff etc.), as well as LJ potentials with the usual longer-range exponents 5 or 6, but obviously not for the Coulomb potential, or gravitational potential for that matter, which are r^{-1} !

- When one simulates a periodic system with an ionic potential one can not use a simple cutoff distance < cell size/2 and assume the system behaves well using it.

- To circumvent this many methods have been developed. The oldest and probably still most used one is Ewald summation [Ann. Phys. **64** (1921) 253]. It is much more efficient than direct summation, but is still an $O(N^2)$ method. A newer method is the so called Fast Multipole Method, which can be parallelized and is O(N).

Ewald-summation

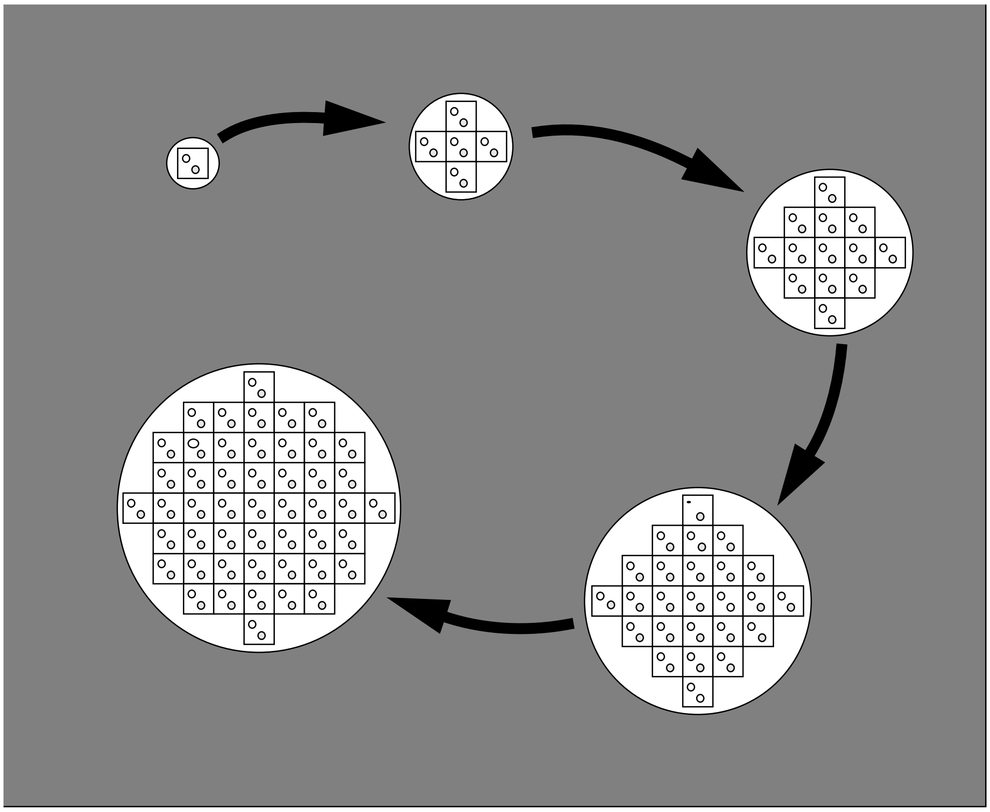
- In Ewald summation one takes into account all interactions to an atom both from the MD cell itself as well as all the periodic image cells.

- The potential energy due to the Coulomb interaction is

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

  Here 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_xL, n_yL, n_zL), where $n_x = -\infty, ..., -1, 0, 1, ..., \infty$ 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! The crucial thing us to do the summation in such an order that it does converge, and preferably as fast as possible. 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 (otherwise things would quickly blow up, both in the simulation and reality), the charges in it give at along distance a dipole, quadrupole etc. interaction, which vanishes during symmetric summation.

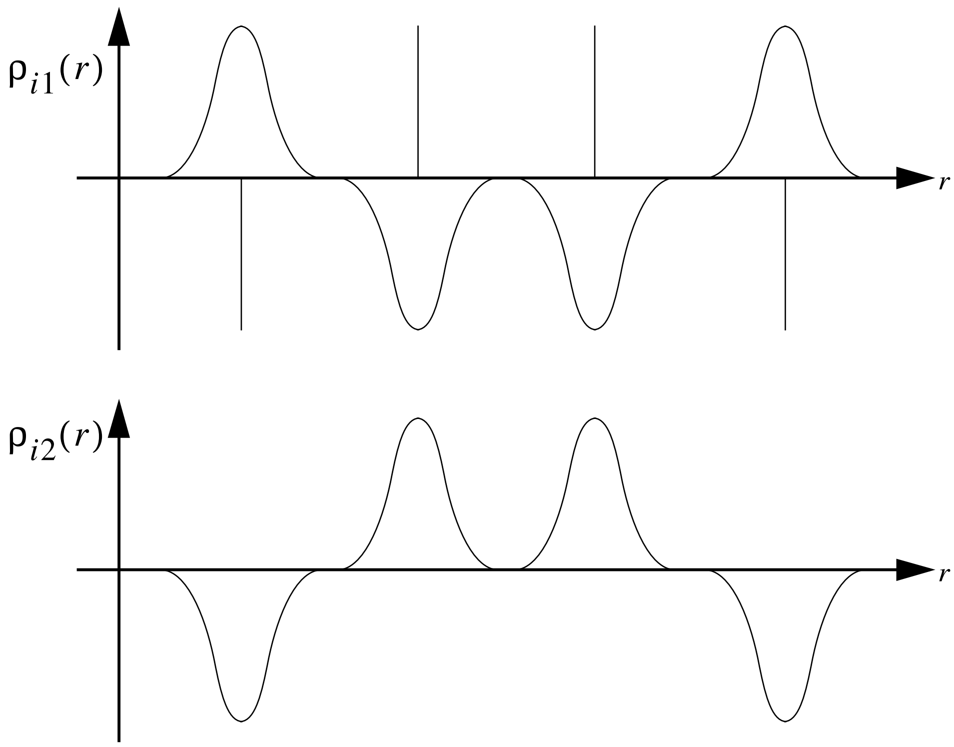
- The surrounding medium also affects the energy of this ball. In a perfect conductor (metal) ($\varepsilon = \infty$) and in vacuum ($\varepsilon = 1$) the results are different; in vacuum a dipole layer will form at the surface. The correspondence between the two quantities is:

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

- 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.

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.

- 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:

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

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

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

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

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

- Here $\operatorname{erfc}(x) = (2/\pi^{1/2})\int_x^{\infty} e^{-t^2}dt$ 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 $\mathbf{n} = 0$.

- The second term is the sum over reciprocal space vectors $\mathbf{k} = (2\pi/L)\mathbf{n}$

- The third term 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.

- The last term 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

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

- 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

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

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

- Does this sound highly complicated? Fortunately there are several applications of Ewald summation easily available, see e.g. Allen-Tildesley program **F.22** (available from below the course home page).

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

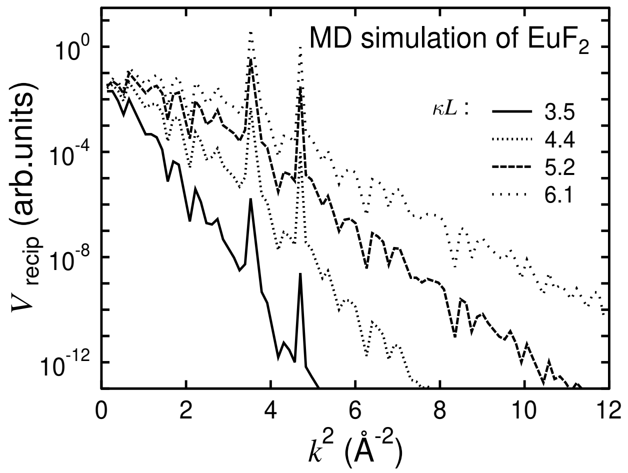
- In applying the method one has to choose three parameters:

cutoff radius	r_c
width of Gaussian charge densities	κ
upper limit for $\mathbf{k}$ summation	$\|\mathbf{k}\|^2_{max}$

- 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.

- Example: EuF_2 :

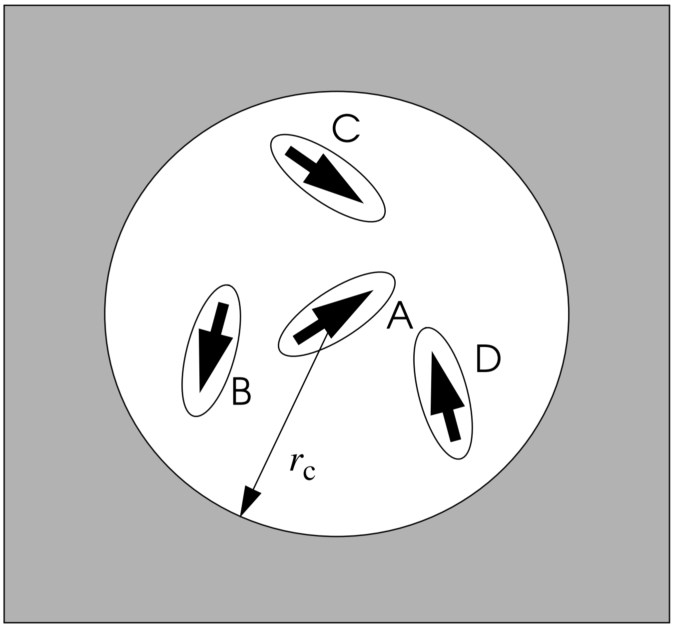
$$N = 324$$
$$L = 17.4 Å$$
$$\kappa L = 5.2$$
$$r_c = L/2$$
$$|\mathbf{k}|^2_{max} = 5 Å^{-2}$$



- If the periodicity of the Ewald summation causes trouble, one can use the **particle-lattice** 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

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

- 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) 181]

- The method uses an electrical multipole method to describe the influence of a region far away on an atom. In 2 dimensions the method can be described as follows.

  Consider points in complex space $z = x + iy$, which describe points (x,y) in ordinary 2D cartesian space. Let a set of points be $\{z_i, i = 1, \ldots, m\}$ and the corresponding charges q_i inside some radius r. Then the multipole expansion ϕ^p of this set of points outside the radius r is

$$\phi^p(z) = Q\log(z) + \sum_{k=1}^{p} \frac{a_k}{z^k} \qquad \text{(FMM.1)}$$

  where

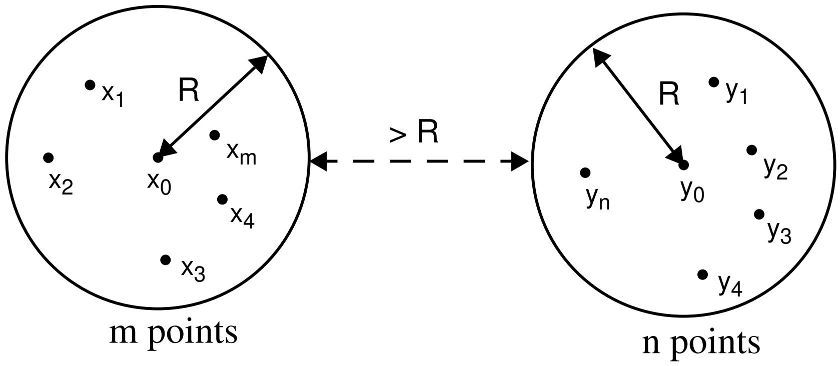
$$Q = \sum_{i=1}^{m} q_i \quad \text{ja} \quad a_k = \sum_{i=1}^{m} \frac{-q_i z_i^k}{k} \qquad \text{(FMM.2)}$$

  If in these equations $p = \infty$ this is exact, otherwise an error ϕ_{err} will result, which is

$$\phi_{\mathrm{err}} \le \frac{\sum_{i=1}^{m} |q_i|}{1 - \left|\frac{r}{z}\right|} \left|\frac{r}{z}\right|^{p+1}$$

  So the larger the p the smaller the error. On the other hand, the larger the z, the smaller the error. So for points farther away it is enough to use less terms p in the expansion.

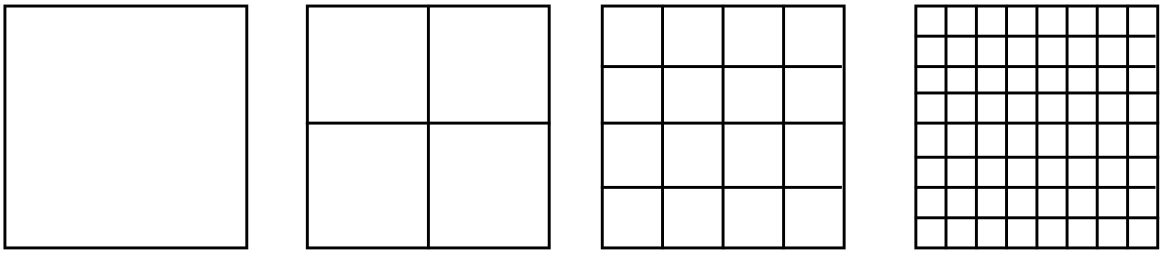
- Why is this useful, then ? Let us consider as a simple example two sets of points x_i and y_j which are inside two circles of radius *R:*



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* factors a_k in equation (FMM.1) using equation (FMM.2), this requires *mp* operations. After this we could calculate the sum (FMM.1) for all points *y*, which requires *n p* operations. Hence this method is *O(mp + np)*. If the two circles are far away, *p* can be relatively small. If the number of points is large then clearly $mp + np << nm$, so we can gain lots of simulation time.

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



Level 0 Level 1 Level 2 Level 3

- Level 0 is the normal, ordinary simulation cell, and the lower levels finer divisions of it. The idea now is that the interactions from the small, far cells are calculated with a coarse multipole expansion and the closer ones with a more accurate one. The closest interactions are calculated as in ordinary MD.

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

- The level structure is utilized for instance so that a lowest-level multipole expansion is calculated directly from atoms. Then the higher-order multipoles can be calculated from the lower-level multipoles, reducing the need for summations over all atoms.

.

		x	x	x	x	x	x
		x				x	x
		x		*i*		x	x
		x				x	x
		x	x	x	x	x	x
		x	x	x	x	x	x

Interaction list of cell *i*. The cells “x” are *far neighbours* of *i*.

- Somewhat simplified the algorithm for calculating the potential at some given time is roughly as follows, **assuming as an example** that the number of levels is 3. This also does not account for periodic boundaries

  1. Calculate the multipole expansions at level 3 by summing over all atoms

  2. Calculate multipole expansions on levels 2, 1, 0 using the expansion at the previous level as a help.

  3. Calculate at levels 1, 2 a *local* multipole expansion for all cells *i* for each *far neighbour* cell of this cell, always going down to finer levels.

  4. Calculate the local multipole expansion at the finest level 3.

  5. Using the result of step 4 get the potential on an atom from its *far neighbours*.

  6. Calculate the potential for atoms from its nearest neighbours as a sum over atoms.

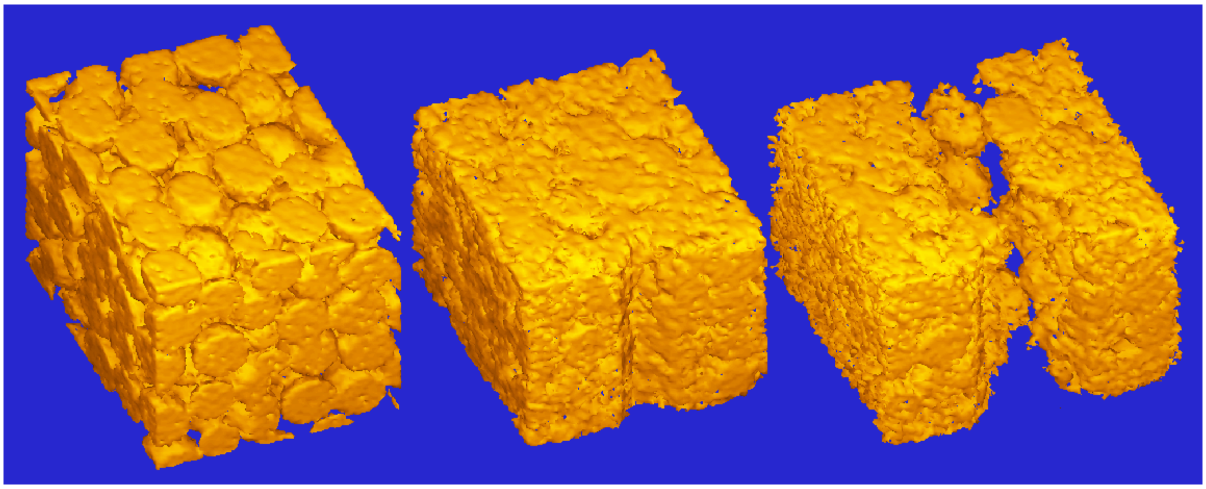
  7. Combine the results of levels 5 and 6 to get the total potential and force, which gives the final force on each atom

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

- 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!

- 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.

  - Exhaustive documentation and a downloadable code available from Duke University, http://www.ee.duke.edu/research/SciComp/software.html