Finite temperature properties of molecules and materials → Molecular dynamics

- **Which interatomic potential?**
  - **Fitted to experiment → a potential energy function**
  - **Computed using electronic structure methods**

- **How do we compute thermodynamic and dynamical properties ? Some examples:**
  - **Pair correlation functions of liquids and amorphous systems**
  - **Diffusion coefficient of liquids**

- **Error analysis**

Interatomic potentials

How do we derive/compute inter-atomic potentials?

1. ***Ab initio* quantum-mechanical calculations**: these usually consist in studying a quantum-mechanical system of few atoms, in which the individual electrons and atomic nuclei are considered separately, and the energy of the system at various nuclear separations is computed and tabulated.

2. **Quantum Simulations:** The *inter-atomic potential is computed on the fly* at each step from DFT calculations

3. Often for 'big' systems one chooses a relatively simple, **parametric form for the potential,** incorporating some physical effects deemed relevant, and **adjusts the parameters in a phenomenological fashion**, by fitting numerical predictions to known experimental results. Typically, scattering experiments are good sources of quantitative information, as well as specific heat, compressibility, sound velocity measurements etc.

Good Reference: M. P.Allen and D. J. Tildesley, Computer Simulation of Liquids, Oxford University Press (1994)

Inter-atomic Potentials (I)

Pair-wise" potentials:
$$V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} v(\mathbf{r}_i, \mathbf{r}_j)$$

Note that if the potential is **central**, we can write $v(\mathbf{r}_i, \mathbf{r}_j)$ as $v(\mathbf{r}_{ij})$ where $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r_j}|$

Higher order terms, such as a three-body $v(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_l)$ are preferably avoided, as they increase considerably the computational workload (the calculation of three-body forces require a number of operations proportional to N^3, four-body to N^4, etc.).

In those cases where three-body effects are too large to be neglected, one may attempt to incorporate them into an *effective* two-body potential, by modifying the 2-body potential so as to include some of the effects due to three-body terms.

Inter-atomic Potentials (II)

What determines the interaction between two molecules, or two atoms?

Atoms and molecules consist of electrically charged particles, protons and electrons, which, to a very large extent, are responsible for the interaction between them, which is predominantly **electrostatic.**

The distribution of negative charge associated with the electron cloud is usually not spherically symmetric, resulting in a nonzero *dipole moment* of the atom (molecule).

The electric field generated by a single electrostatic dipole is proportional to $1/r^3$, and this can be shown to lead to a weak inter-atomic (intermolecular) attraction proportional to **$1/r^6$,** which is dominant at large distances.

If two atoms or two molecules are brought very close together, the interaction between them becomes more complicated; quantum effects start playing a more important role, resulting in an effective **"hard-core" repulsion of atoms** and molecules at sufficiently short distances.

Lennard-Jones (LJ) Potential

One of the most important and popular potentials is the Lennard-Jones potential:
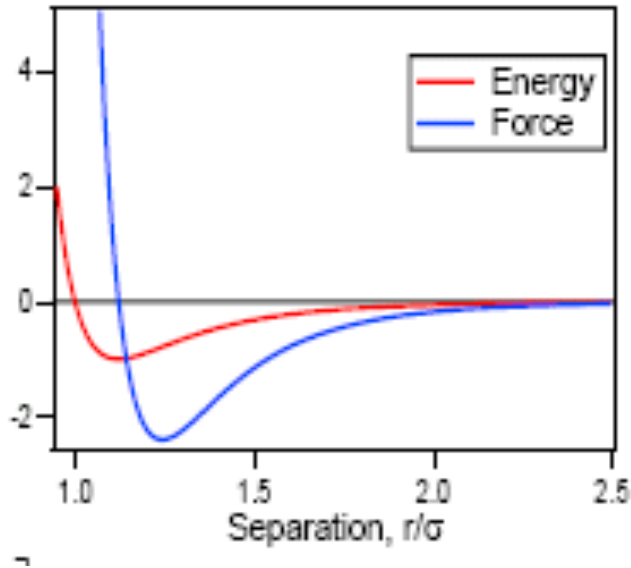
$$v(r_{12}) = 4\varepsilon \left\{ \left(\frac{\sigma}{r_{12}} \right)^{12} - \left(\frac{\sigma}{r_{12}} \right)^{6} \right\}$$

Two adjustable parameters, σ (length) and ε (energy)

Usually one takes σ as the length unit and 4ε as the energy unit.

The mass unit is simply the mass of the particles; with only one component in the system, the mass disappears (formally) from the calculation.

All other units are derivable from the above ones. For example: $t = \sqrt{\dfrac{m\sigma^2}{4\varepsilon}}$

LJ potentials: examples

Atom	Source	ε/k (^{0}K)	σ(nm)
H	Murad and Gubbins[2]	8.6	0.281
He	Maitland, et al[3]	10.2	0.228
C	Tildesley and Madden[4]	51.2	0.335
N	Cheung and Powles[5]	37.3	0.331
O	English and Venables[6]	61.6	0.295
F	Singer et al[7]	52.8	0.283
Ne	Maitland et al[8]	47.0	0.272
S	Tildesley and Madden	183.0	0.352
Cl	Singer et al	173.5	0.335
Ar	Maitland et al	119.8	0.341
Br	Singer et al	257.2	0.354
Kr	Maitland et al	164.0	0.383

[1] M.P.Allen and D.J. Tildesley, **Computer Simulation of Liquids,** Oxford Science Publications, (1987,1989).

[2] S.Murad and K.E. Gubbins, "Molecular dynamics simulation of methane using a singularity free algorithm". In **Computer modelling of matter, (**ed. P. Lykos) ACS Symposium Series Vol. 86, pp. 62-712. American Chemical Society, Washington.

[3] G.C. Maitland, et al, **Intermolecular forces: their origin and determination,** Clarendon Press, Oxford (1981)

[4] D.J. Tildesley and P.A. Madden, Mol. Phys. **42**, 1137-1156 (1981)

[5] Mol. Phys. **30,** 921-49 (1975)

[6] Proc. R. Soc. Lond. **A340,** 57-80 (1974)

[7] Mol. Phys. **33,** 1757-95 (177)

[8] G.C. Maitland,M.Rigby,E.B.Smith,W.A. Wakeham, **Intermolecular forces: their origin and determination,** Clanendon, Oxford (1981)

The LJ Potential

The long-range part, proportional to $1/r^6$ attempts to describe the dipole-dipole attractive interaction.

The short-range part is only aimed at representing a hard-core repulsion between two atoms.

In fact, the short-range part of LJ may be unphysical and typically must be softened to obtain a closer description of the short-range properties of the interaction.

The Lennard-Jones potential is rather ubiquitous in the simulation literature, and it is widely considered a paradigmatic potential to simulate most atomic liquids.

It is occasionally "hidden" behind other appearances. For example, the so-called "3-9" potential, aimed at representing the interaction of an atom with a surface is simply the LJ potential where one of the two atoms is replaced with an infinite, two dimensional uniform atomic distribution.

The LJ Potential

Another important advantage of the LJ potential is its relatively simple analytical expression, which permits its evaluation with few computer operations.

This is an important aspect, as the calculation of the forces from the potential is the most expensive part of the simulation.

If a more sophisticated potential is required, involving more terms and/or more involved analytical expressions, making use of transcendental functions such as fractional powers, trigonometric functions and exponentials, the toll to be paid in terms of execution time is substantial.

This is not to say that more complicated potentials cannot be used, but that appropriate strategies have to be considered, such as the use of *spline-fit potentials* based on *look-up table*.

Beyond the Pair Potential

A central potential may be an acceptable approximation for atomic systems, but when one is dealing with complex molecules, often it is necessary to consider explicitly their spatial extension as well as their detailed chemical structure.

This typically involves considering potentials that have a well-defined angular part, i. e. they depend on the relative orientation of the molecules.

One possibility of dealing with molecular systems consists of representing molecules as a collection of individual "units", where chemical bonds are represented by further inter-atomic potentials.

In other words, molecules would lose their identity as far as the simulation is concerned, as only individual "units" appear.

Beyond the Pair Potential

- It is often the case that the energy scale corresponding to chemical bonds within a molecule is much different than the one corresponding to the self-bonding of the molecular liquid or solid.

- The classical approach might be acceptable to describe a molecular liquid, but a full quantum mechanical description is needed to characterize intra-molecular bonds.

A possible remedy to the first point consists of simply eliminating intra-molecular potential and replacing them with rigid "dumbbells" or with flexible "springs", whose characteristic frequencies are chosen to match the experimentally observed vibrational spectra of the molecules.

In this case, the molecule has a center of mass and the constituent atoms move together with it while rotating around it.The second problem can only be addressed by attempting to incorporate quantum-mechanical effects in the motion of the molecules.

# Example: interactions in simulations of "classical" molecules

Van der Waals forces	$V(r) \sim \dfrac{1}{r^6}$	Polarization force (e.g., induced dipole-dipole interactions)
Coulombic interactions	$V(r) \sim \dfrac{1}{r}$	Electrostatic force
Steric repulsion	$V(r) \sim \dfrac{1}{r^{12}}$	QM steric/exchange interaction
Harmonic interactions between two bodies	$V(r) \propto (r - r_0)^2$	Mutual interactions between atoms bonded to one another, QM
Three-body bending interactions	$V(r) \propto (\theta_{ijk} - \theta_{ijk}^0)^2$	
Four-body torsional interactions	$V(r) = V(\theta_{ijkl})$	

Example: interactions in simulations of ionic materials

μ asymptotic
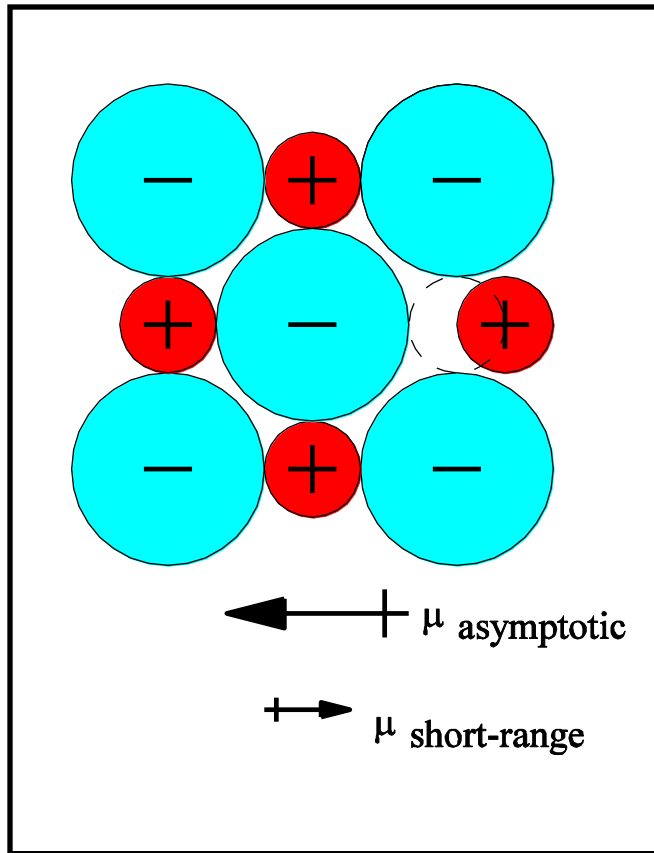
μ short-range

- **Potential with 20-30 parameters inclusive of**
  - **Coulomb interaction**
  - **short-range repulsion**
  - **dispersion (van der Waals)**
  - **polarization**
  - **spherical breathing, dipolar + quadrupolar shape deformations**
- **Optimized by fitting to reference DFT calculations**

Potential fitting
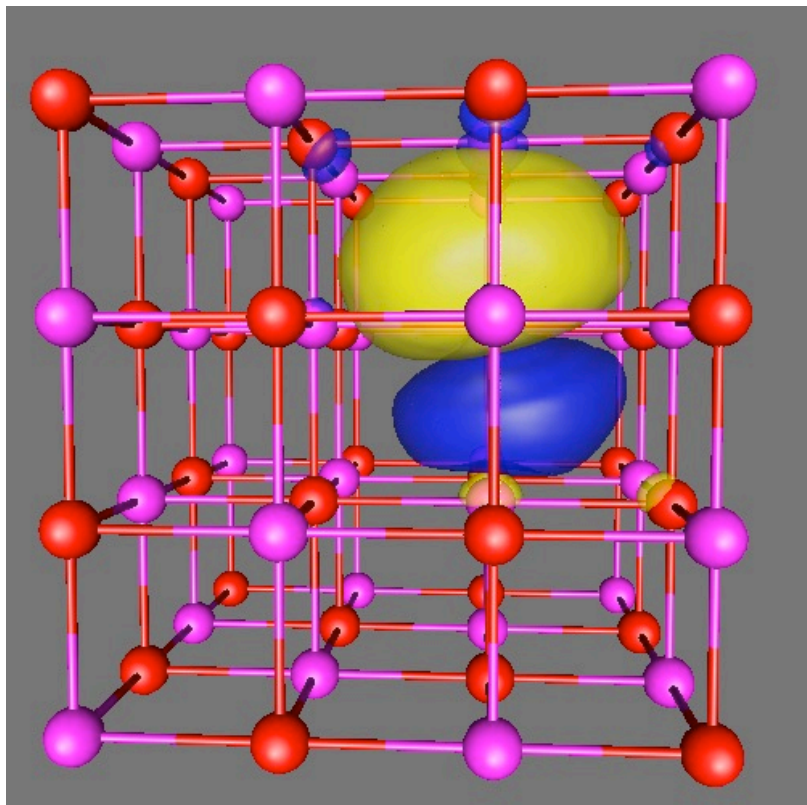
Aguado et al, Faraday Discuss. **124**, 171 (2003)

- **Al_2O_3**
  - **bixbyite, corundum, melt, ortho-perovskite, $Rh_2O_3(II)$**
- **MgO**
  - **rocksalt, CsCl, sphalerite**
- **SiO_2**
  - **α-quartz, α-cristobalite, stishovite**
- **$MgAl_2O_4$**
  - **spinel, Ca-ferrite, Ca-titanite**
- **$MgSiO_3$**
  - **ortho-perovskite, post-perovskite**

Example of popular empirical potentials for Si

- **Stillinger-Weber (1985)**
  basic empirical potential, initially for bulk structure, with pair-wise (sum of two exponentials) and three-body terms (quadratic well in the angle with an exponential cutoff in radius)
    - **F. H. Stillinger and T. A. Weber, Phys. Rev. B, 31, 5262, 1985.**

- **Tersoff (1988)**
    - **J.Tersoff, Phys.Rev.B 38, 9902 (1988)**

$$E = \sum_i E_i = \tfrac{1}{2} \sum_{i \neq j} V_{ij} \,,$$

$$V_{ij} = f_C(r_{ij})[a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})]$$

$$f_R(r) = A \exp(-\lambda_1 r) \,,$$

$$f_A(r) = -B \exp(-\lambda_2 r) \,,$$

$$f_C(r) = \begin{cases} 1, & r < R - D \\ \tfrac{1}{2} - \tfrac{1}{2}\sin\left[\dfrac{\pi}{2}(r-R)/D\right], & R - D < r < R + D \\ 0, & r > R + D \end{cases}$$

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-1/2n} \,,$$

$$\zeta_{ij} = \sum_{k\,(\neq i,j)} f_C(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] \,,$$

$$g(\theta) = 1 + c^2/d^2 - c^2/[d^2 + (h - \cos\theta)^2] \,,$$

$$a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-1/2n} \,,$$

$$\eta_{ij} = \sum_{k\,(\neq i,j)} f_C(r_{ik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] \,.$$

- **EDIP (1997)**
  Environmentally Dependent Inter-atomic Potential
    - **M. Z. Bazant and E. Kaxiras, Phys. Rev. Lett. 77, 4370 (1996).**
    - **M. Z. Bazant, E. Kaxiras, J. F. Justo, Phys. Rev. B 56, 8542 (1997).**
    - **J. F. Justo, M. Z. Bazant, E. Kaxiras, V. V. Bulatov, and S. Yip, Phys. Rev. B 58, 2539 (1998).**

Calculation of physical properties

Computing physical quantities

Averages are computed as: $< A >= \dfrac{1}{n}\sum_{i=1}^{n} A_i$

- We have seen how to compute total energies, temperature, pressure.

- We now look at **partial correlation functions and structure factors (→ structural properties)** and **diffusion coefficients (the simplest dynamical property)**

Analogies with Experiment

- The goal is to obtain a (hopefully) reliable numerical estimate for some relevant physical quantity **A** characterizing a system of interest, such as a liquid, or a solid, or a biological molecule.

- Once a mathematical model, deemed suitable, has been defined for the system of interest, the simulation consists in performing an ***experiment on the model***, i. e. on a ***fictitious* system,** described by the mathematical model specified.

- A simulation allows one to investigate numerically the behavior that the ideal or fictitious system would have if it existed, and rendering it possible to make "measurements" on it.

Simulations as Computer Experiments

Just as in an experiment, the estimate of the quantity **A** is obtained by measuring its value a sufficiently large number of times during the simulation, and averaging the results.

An important difference between a real experiment and the simulation is that the latter may make it possible to "measure" quantities that cannot be easily (or at all) measured in a real experiment (for example, the trajectory of a single particle).

This way of "solving" the problem has obvious methodological and deep *philosophical* differences with respect to tackling the problem analytically.

Some Important Issues with Simulations

- Results are *numbers*, as opposed to elegant equations; thus, one has to make sense out of a set of numbers, i. e. interpret the results.

- Results are obtained for *finite systems* only, whereas often one is seeking estimates for infinite systems, to eliminate surface effects; thus, one has to assess the sensitivity of the results to the system size (finite-size scaling).

- Even if simulation were free from approximations, the results are usually affected by *statistical errors*, which have to be estimated.

- Because the field of computer simulations is no more than 50 years old, most interesting techniques have likely not yet been invented or tried.

Pair distribution functions

Liquids and Disordered Systems : Pair Distribution Functions
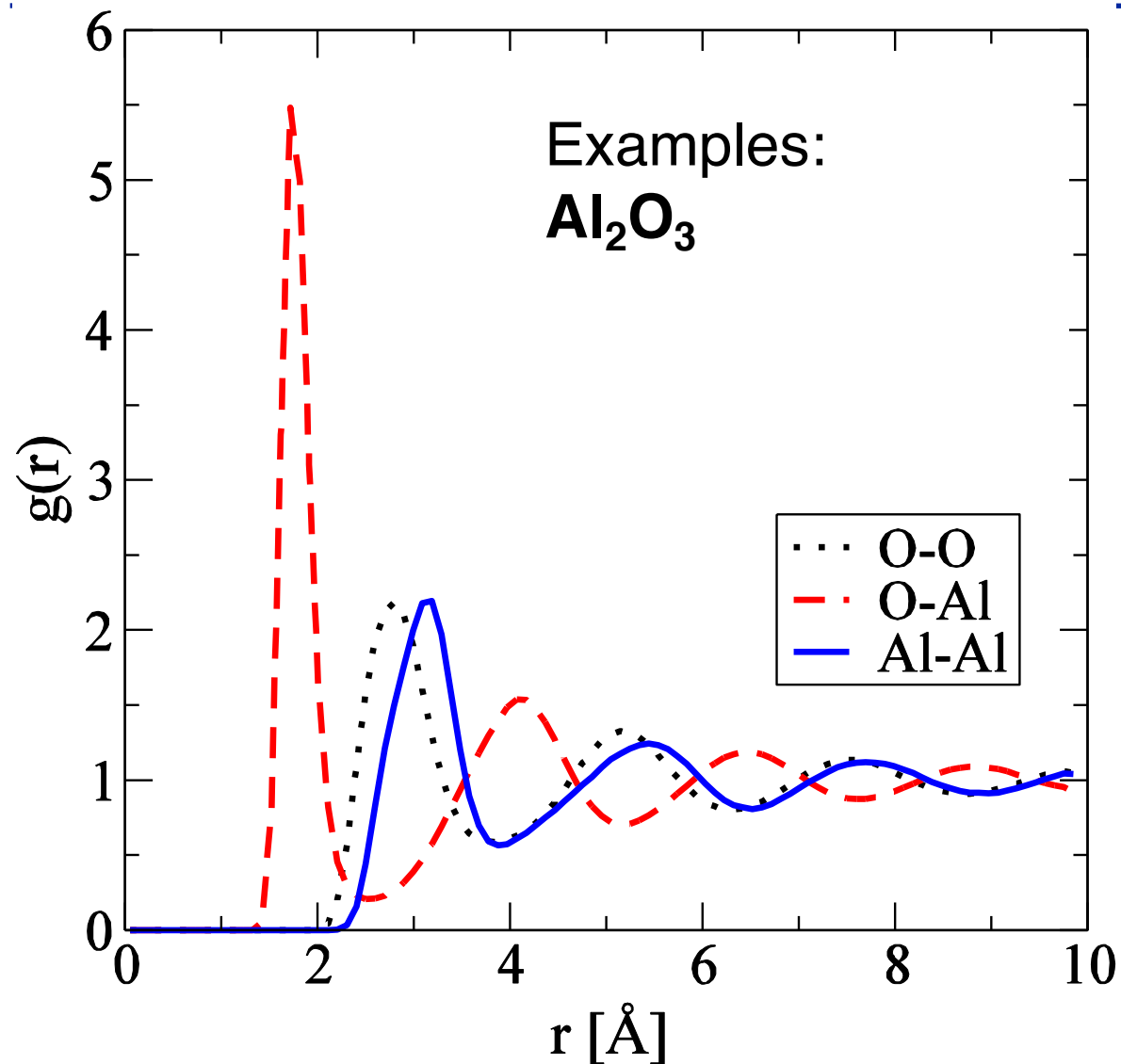
The pair distribution function provides a measure of the probability of finding any two particles at a given physical distance.

Typically, this is defined (in 3 dimensions) as:

$$g(r) = (N-1)\frac{p(r)}{r^2}$$

The pre-factor is defined in such a way so that:

$$\frac{\int r^2 g(r)dr}{\int r^2 dr} = 1 - \frac{1}{N}$$
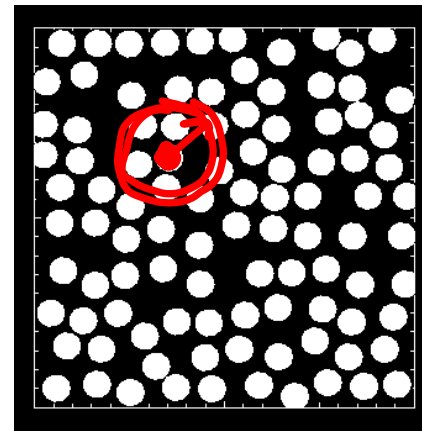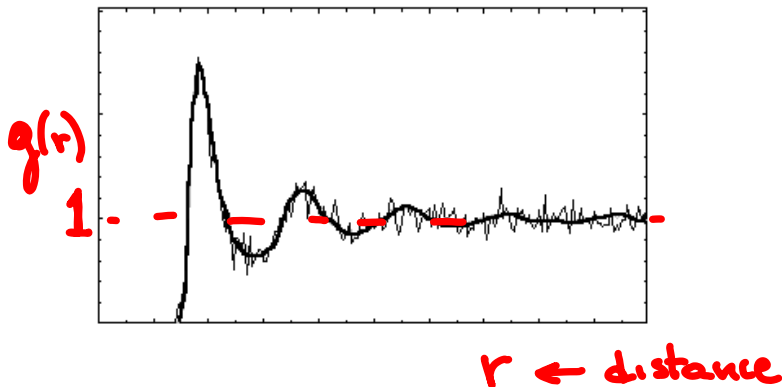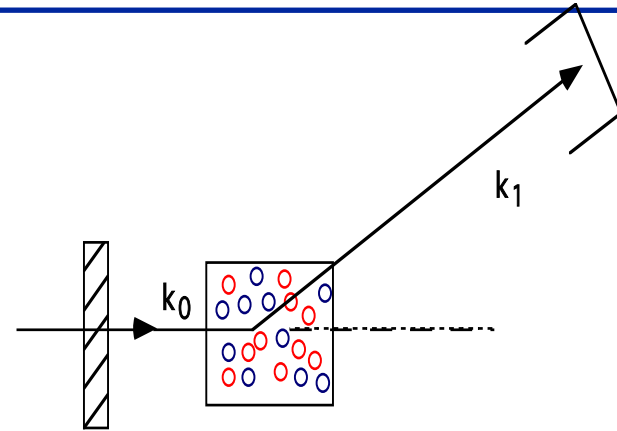
Partial radial distribution functions

Examples:
Al_2O_3

Comparison with experiment is indirect as diffraction measurements yield structure factors not partial correlation functions

The scattering cross section (or intensity) is given in terms of a *weighted average structure factor*:

$$\frac{d\sigma}{d\Omega}(Q) = \langle \bar{b} \rangle^2 S(Q) + \langle \bar{b}^2 \rangle - \langle \bar{b} \rangle^2$$

where

$$S(Q) = \sum_{ij} W_{ij} S_{ij}(Q)$$

$$Q = |\mathbf{k_1} - \mathbf{k_0}|$$

The weighting factors are (*Faber-Ziman definition*) :

for neutrons:
$$W_{ij}^N = \frac{c_i c_j \overline{\bar{b}_i \bar{b}_j}}{\langle \bar{b} \rangle^2}$$
; *for x-rays:*
$$W_{ij}^X = \frac{c_i c_j f_i(Q) f_j(Q)}{\langle f(Q) \rangle^2}$$

Relation between structure factors and real space correlation functions

The partial structure factors are related to partial pair distribution functions

through the Fourier transform

$$S_{ij}(Q) = 1 + \frac{4\pi\rho}{Q} \int_0^\infty [g_{ij}(r) - 1] \sin Qr \, . r dr$$

These have a direct physical interpretation:

$4\pi r^2 c_j g_{ij}(r)\Delta r = \text{average number of } j \text{ atoms in a}$
$\text{range } (r, \ r + \ \Delta r) \text{ from an } i \text{ atom at the origin}$

For i, j = 1, …. n there are n(n+1)/2 partial pair distribution functions

Neutron Diffraction with Isotope Substitution

If two measurements are made with different isotopes for element A:

$$\Delta \bar{b}_A = \bar{b}_A(1) - \bar{b}_A(2)$$

The difference in scattering cross sections is given in terms of the *difference structure factor*:

$$\Delta \frac{d\sigma}{d\Omega}(Q) = 2c_A \Delta b_A \langle \bar{b} \rangle S_A(Q) + \Delta \langle \bar{b}_2 \rangle - 2c_A \Delta b_A \langle \bar{b} \rangle$$

where

$$S_A(Q) = \sum_j W_j' S_{Aj}(Q)$$

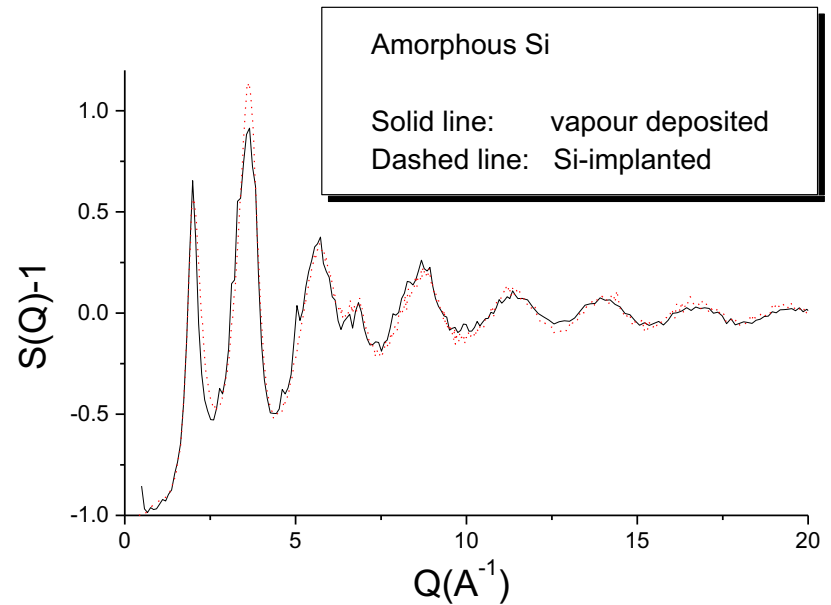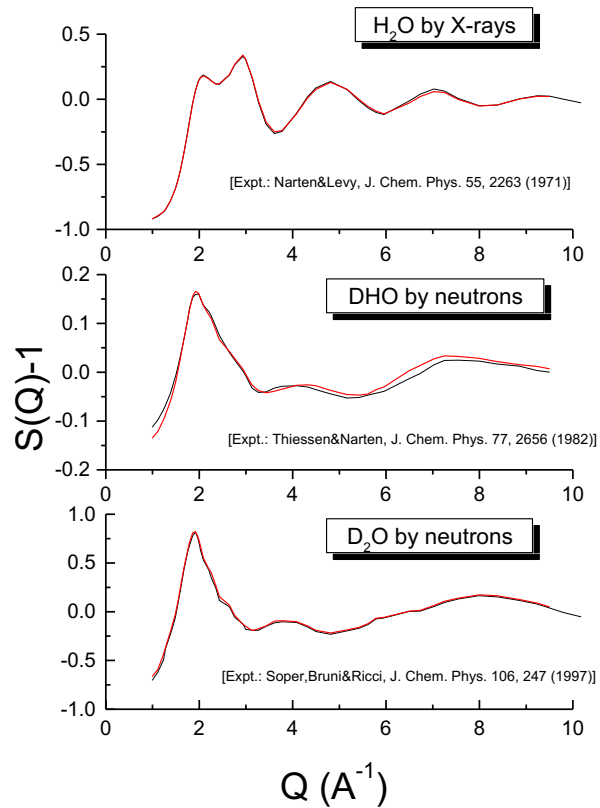The corresponding *difference pair distribution function*

$$g_A(r) = 1 + \frac{1}{2\pi_2 \rho_0 r} \int_0^\infty [S_A(Q) - 1] \sin Qr \cdot Q dQ$$

gives the structure about *the A atoms only*.

The difference weighting factors are

$$W_J = \frac{c_j \bar{b}_j}{\langle \bar{b} \rangle}$$

Examples of structure factors

Water

Diffusion coefficient and other transport properties

Diffusion Coefficient

The pair distribution function is an example of *correlation function*, i. e. a measure of the relationship of the value of a physical quantity at a given point in time/space for a system under study and the value of the same quantity (or, possibly, of another one) at a different point.

The pair distribution function is appropriate to characterize a system in thermal equilibrium, and it is a *static*, **or time-independent, quantity.**

One of the big advantages of MD is that it permits to calculate time-dependent quantities; these are typically *dynamic correlation functions*, of great practical interest as they describe the behavior of a system under the influence of an external probe.

For example, physically relevant quantities such as transport coefficients can be determined by studying the long-time behavior of appropriate dynamic correlations.

Diffusion Coefficient

It is usually of interest to determine the capability of a system to allow *diffusion of matter* throughout itself.

Diffusion can be modeled microscopically; Fick's first law of diffusion associates the *diffusion coefficient D* (or *self-diffusion coefficient*), to the average square displacement of particles from their initial positions as follows (*see also next lecture*):

$$\lim(t \to \infty) \frac{\left\langle \{\mathbf{r}(t) - \mathbf{r}(t=0)\}^2 \right\rangle}{2dt} = 3D$$

commonly known as "Einstein relation"

This relation permits to evaluate the coefficient *D* straightforwardly using MD, by simply averaging the mean square displacement of all particles.

Note that the time-formulation of MD is crucial in permitting to follow the time displacement of all the particles; this is not possible in any other computational scheme, such as Monte Carlo, if not very indirectly, as the time disappears from the formulation.

Transport Properties

- **Differential Equations**

Mass	Energy	Momentum
$$\frac{\partial c(r,t)}{\partial t} + \nabla \bullet \mathbf{j} = 0$$	$$c_p \frac{\partial T(r,t)}{\partial t} + \nabla \bullet \mathbf{q} = 0$$	$$\rho \frac{D\mathbf{v}(r,t)}{Dt} + \nabla \bullet \underline{\underline{\tau}} = 0$$

- **Constitutive Equations**

| Fick's Law	Fourier's Law	Newton's Law
$$\mathbf{j} = -D\nabla c$$	$$q = -k\nabla T$$	$$\tau_{xy} = -v\nabla_y (\rho v_x)$$

Transport Properties

— **Not that the Fick's, Fourier's and Newton's laws only apply for "not-too-large gradients"**

• Green-Kubo Relation

— **Relation between transport properties and integral over time-correlation function.**

Transport Properties

- Consider self-diffusion in a pure substance

- Consider mass current when initial configurations are given as Dirac delta functions

- Combine mass balance eqn. with Fick's Law
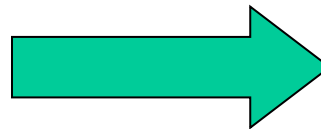
d = Dimensionality of the system

$$\frac{\partial c(\mathbf{r},t)}{\partial t} - D\nabla^2 c(\mathbf{r},t) = 0$$

$$c(\mathbf{r},t) = \delta(\mathbf{r})$$

$$c(\mathbf{r},t) = (2\pi Dt)^{-d/2}\exp(-\frac{r^2}{2Dt})$$

Transport Properties

$$<r^2(t)> = \int c(\mathbf{r},t)r^2\,dr$$

$$\int c(\mathbf{r},t)dr = 1$$

$$\frac{\partial <r^2(t)>}{\partial t} = 2dD$$
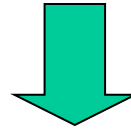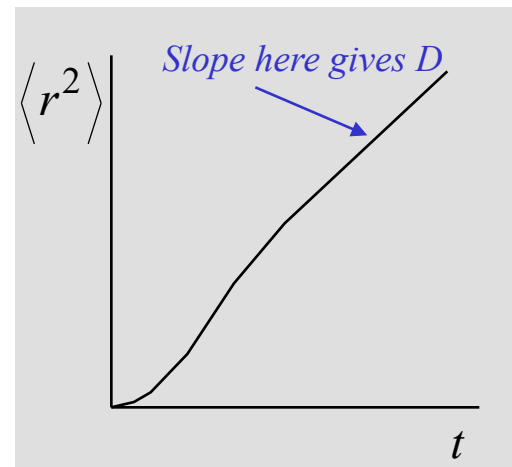
Note: in 3D, dr → d**r and integration is carried out in spherical coordinates**

$$\frac{\partial c(\mathbf{r},t)}{\partial t} - D\nabla^2 c(\mathbf{r},t) = 0$$
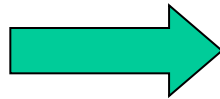
$$<r^2(t)> = \frac{1}{N}\sum (r_i(t))^2 = 2dDt$$

$$<r^2(t)> = \frac{1}{N}\sum (r_i(t))^2 = 2dDt$$

Slope here gives D

$\langle r^2 \rangle$

t

Transport Properties

- **An alternative formulation using velocity instead of particle position**

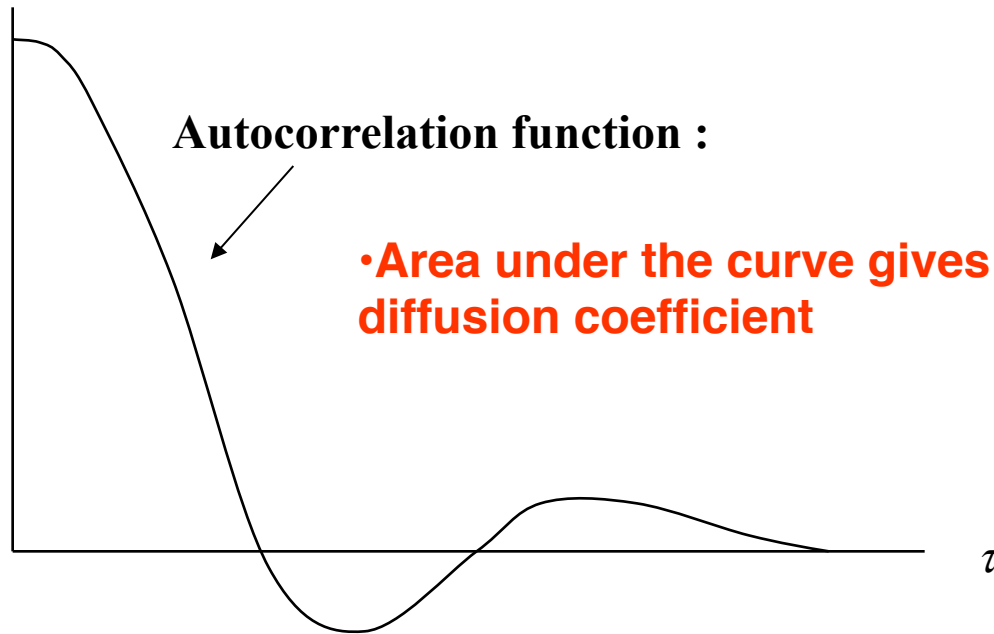$$\mathbf{r}_i(t) = \int\limits_0^t \mathbf{v}(\tau)\,d\tau$$

$$\left\langle r^2(t) \right\rangle = \left\langle \int\limits_0^t \mathbf{v}(\tau_1)\,d\tau_1 \cdot \int\limits_0^t \mathbf{v}(\tau_2)\,d\tau_2 \right\rangle$$

$$= \int\limits_0^t d\tau_1 \int\limits_0^t d\tau_2 \left\langle \mathbf{v}(\tau_2) \cdot \mathbf{v}(\tau_1) \right\rangle$$

$$= 2\int\limits_0^t d\tau_1 \int\limits_0^{\tau_1} d\tau_2 \left\langle \mathbf{v}(\tau_2) \cdot \mathbf{v}(\tau_1) \right\rangle$$

$$= 2\int\limits_0^t d\tau_1 \int\limits_0^{\tau_1} d\tau_2 \left\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau_1 - \tau_2) \right\rangle$$

$$= 2\int\limits_0^t d\tau_1 \int\limits_0^t d\tau \left\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \right\rangle$$

$$2dDt = 2t\int\limits_0^t d\tau \left\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \right\rangle$$

Transport Properties

$$2dDt = 2t\int_0^t d\tau <\mathbf{v}(0)\mathbf{v}(\tau)>$$

$$\xrightarrow{\quad t\to\infty\quad}$$

$$D = \frac{1}{d}\int_0^\infty d\tau <\mathbf{v}(0)\mathbf{v}(\tau)>$$

$$<\mathbf{v}(0)\mathbf{v}(\tau)> \qquad\qquad <\mathbf{v}(0)\mathbf{v}(\tau)> = <v(t')v(t'')>$$

Autocorrelation function :

•**Area under the curve gives the value of self-diffusion coefficient**

Error analysis

Sources of Error

Just like in a real experiment, in computer simulations the measured quantity is assigned a numerical value, which is in principle affected by *statistical and systematic errors*.

Statistical errors

They affect numerical simulations, just like they affect experimental measurements. This is because the experiment (or the simulation) necessarily takes a finite time.

Assigning statistical errors is a rather delicate part of a simulation.

Systematic Errors

Systematic errors can be generally associated with "lack of calibration", or "incomplete calibration", even when discussing computer simulations, for which the word "calibration" takes a slightly generalized meaning.

In a computer simulation, typical sources of systematic errors are:
- The finite size of the simulation sample
- A defective random number generator in Monte Carlo simulations
- The finite time-step in Molecular Dynamics simulations
- Round-off errors due to the finite precision of the computer (any numerical calculation suffers from this)
- Sometimes, approximations in the numerical procedure

There are, with the sole exception of the last item in the above list, well-defined methods to deal with systematic errors in the context of computer simulations.

Error Bars

Many simulation results are not meaningful without an associated error bar

Once a robust procedure is defined to calculate error bars reliably, then one can empirically attempt to establish how many initial data points should be discarded, in other words how long the transient is, before the system reaches equilibrium.

Typically, one wants to make sure that as little data as possible from the transient region is included in the average, but at the same time one does not want to throw away too much data.

What is usually done is to calculate the average < **A** > by discarding an increasing number of initial data points until the average does not change, within error bars. Occasionally, one may fail to reach such a limit: in this case, the simulation should be carried on for a longer time, as the transient extends through most of it.

Review: Error Bars

Averages are computed as:

$$< A >= \frac{1}{n} \sum_{i=1}^{n} A_i$$

Statistical error is then:

$$(\sigma)^2 \approx (\delta A)^2 \left(1 \pm \sqrt{\frac{2}{(n-1)}}\right)$$

where:

$$(\delta A)^2 = \frac{\sum_i (A_i - < A >)^2}{n(n-1)}$$

Actually, this is only true when two criteria are met: (1) the data is drawn from a gaussian probability distribution, and (2) the data are uncorrelated

Re-blocking Transformation

Blocking or "binning" method is the simplest way to eliminate data correlation.

In this method, the data set is transformed, for example into one that is 1/2 the size:

$$\{A_1, A_2, A_3, \ldots, A_n\} \rightarrow \{A_1', A_2', A_3', \ldots, A_{n/2}'\}$$

The statistical error is then recomputed, and the re-blocking is repeated.

One can derive the following result (*):

$$\sigma^2 \geq (\delta A^{(n/2)})^2 \geq (\delta A^{(n/2-1)})^2 \geq \cdots \geq (\delta A'')^2 \geq (\delta A')^2 \geq (\delta A)^2$$

 * see, for example, H. Flyvbjerg and H. G. Petersen, *J. Chem. Phys.* **91**, 461 (1989).