

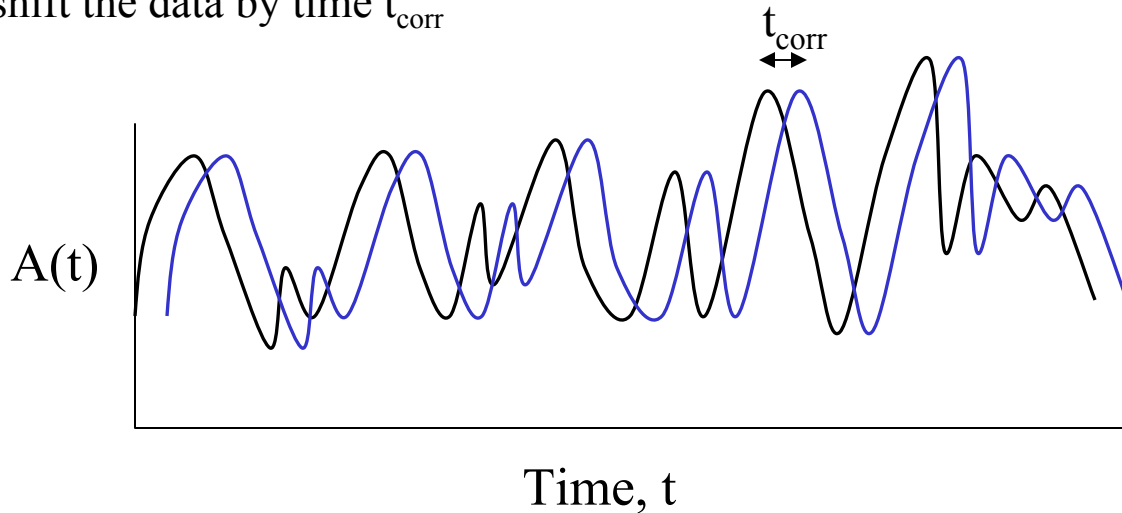
Correlation functions and their application for the analysis of MD results

1. Introduction. Intuitive and quantitative definitions of correlations in time and space.
2. Velocity-velocity correlation function.
 - the decay in the correlations in atomic motion along the MD trajectory.
 - calculation of generalized vibrational spectra.
 - calculation of the diffusion coefficient.
3. Pair correlation function (density-density correlation).
 - analysis of ordered/disordered structures, calculation of average coordination numbers, etc.
 - can be related to structure factor measured in neutron and X-ray scattering experiments.

What is a correlation function?

Quantitative definition of correlation

Let us shift the data by time t_{corr}



and multiply the values in new data set to the values of the original data set.

Now let us average over the whole time range and get a single number $G(t_{\text{corr}})$. If the two data sets are lined up, the peaks and troughs are aligned and we will obtain a big value from this multiply-and-integrate operation. As we increase t_{corr} the $G(t_{\text{corr}})$ declines to a constant value.

The operation of multiplying two curves together and integrating them over the x-axis is called an overlap integral, since it gives a big value if the curves both have high and low values in the same places.

The overlap integral is also called the Correlation Function $G(t_{\text{corr}}) = \langle A(t_0)A(t_0+t_{\text{corr}}) \rangle$. This is not a function of time (since we already integrated over time), this is function of the shift in time or correlation time t_{corr} .

Decay of the correlation function is occurring on the timescale of the fluctuations of the measured quantity undergoing random fluctuations.

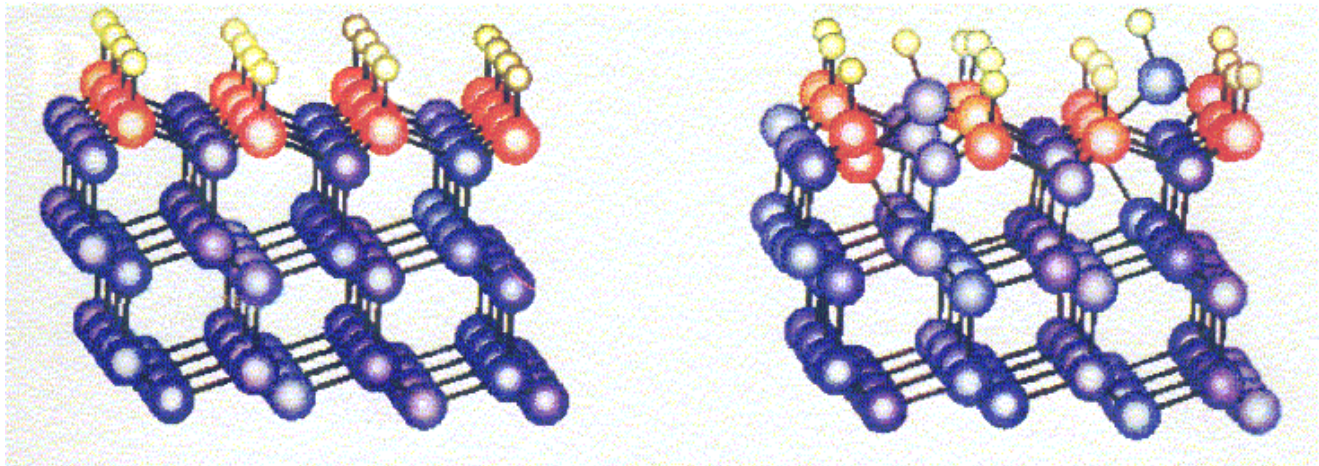
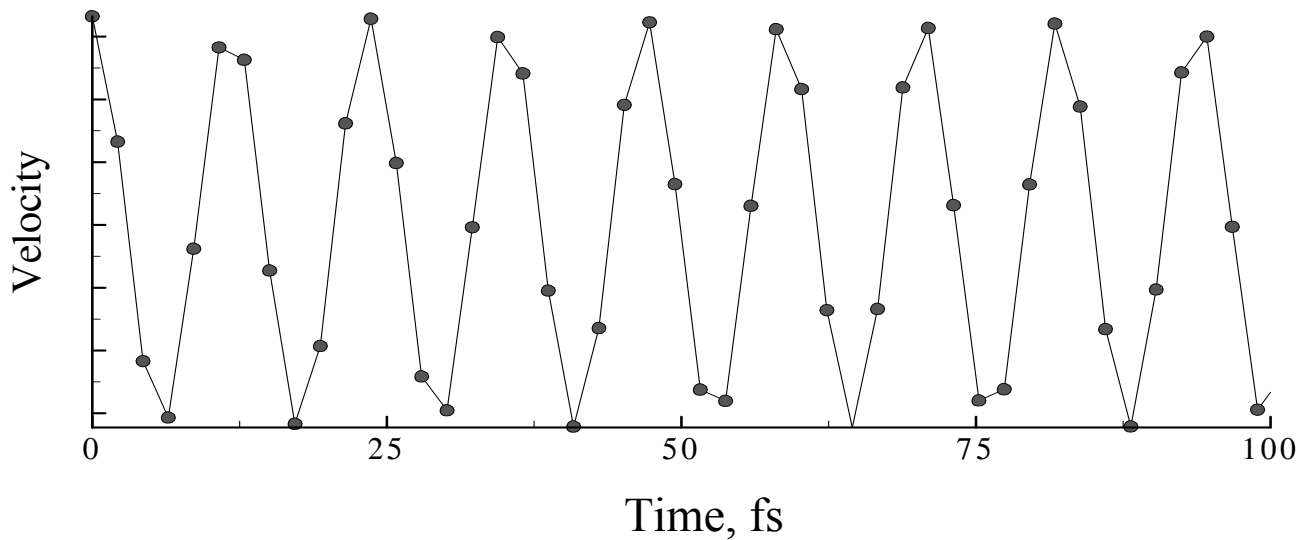
All of the above considerations can be applied to correlations in space instead of time $G(\mathbf{r}) = \langle A(\mathbf{r}_0)A(\mathbf{r}_0+\mathbf{r}) \rangle$.

Time correlations along the MD trajectory

1

Example: Vibrational dynamics on H-terminated diamond surface

Below is a time dependence of the velocity of a H atom on a H-terminated diamond surface recorded along the MD trajectory.



Snapshots of hydrogenated diamond surface reconstructions.

L. V. Zhigilei, D. Srivastava, B. J. Garrison, Phys. Rev. B **55**, 1838 (1997).

Time correlations along the MD trajectory

Example: Vibrational dynamics on H-terminated diamond surface

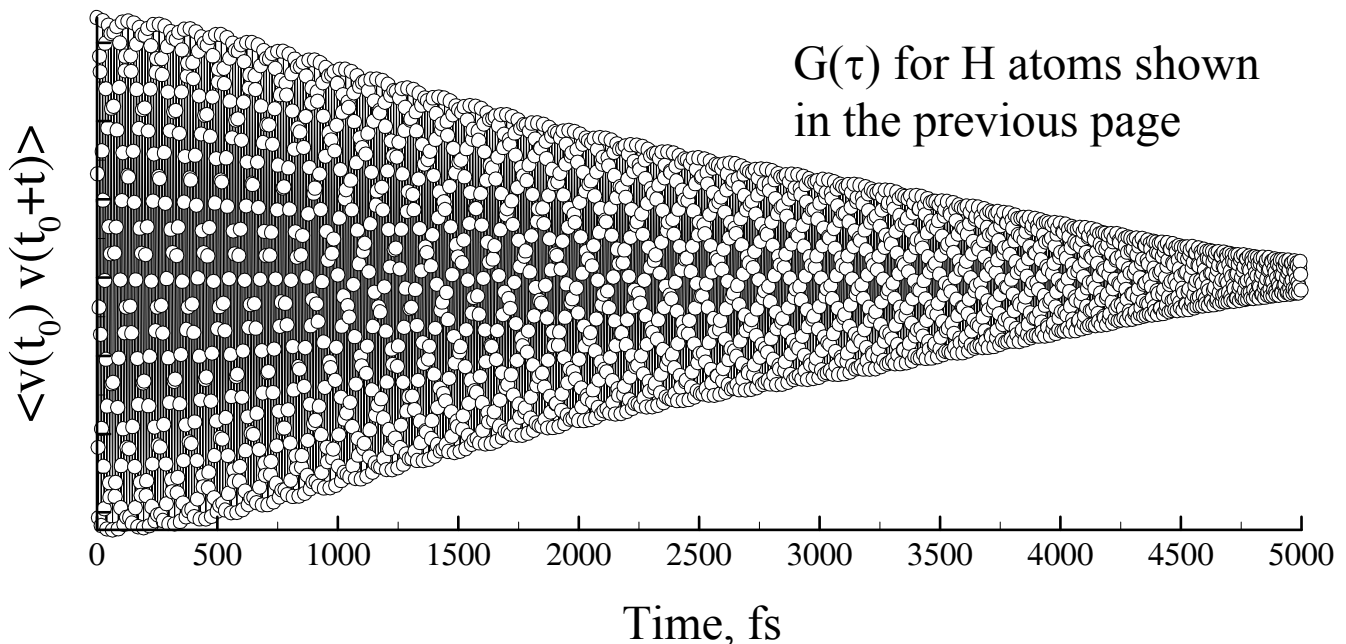
Velocity-velocity autocorrelation function

For an ensemble of N particles we can calculate velocity-velocity correlation function,

$$G(\tau) = \langle \vec{v}_i(t_0) \cdot \vec{v}_i(t_0 + \tau) \rangle_{i,t_0} = \frac{1}{N} \sum_{i=1}^N \frac{1}{t_{\max}} \sum_{t_0=1}^{t_{\max}} \vec{v}_i(t_0) \cdot \vec{v}_i(t_0 + \tau)$$

In this calculation of $G(\tau)$ we perform

- averaging over the starting points t_0 . MD trajectory used in the calculation should be $t_{\max} + \text{range of the } G(\tau)$.
- averaging over trajectories of all atoms.



The resulting correlation function has the same period of oscillations as the velocities. The decay of the correlation function reflects the decay in the correlations in atomic motion along the trajectories of the atoms, not decay in the amplitude!

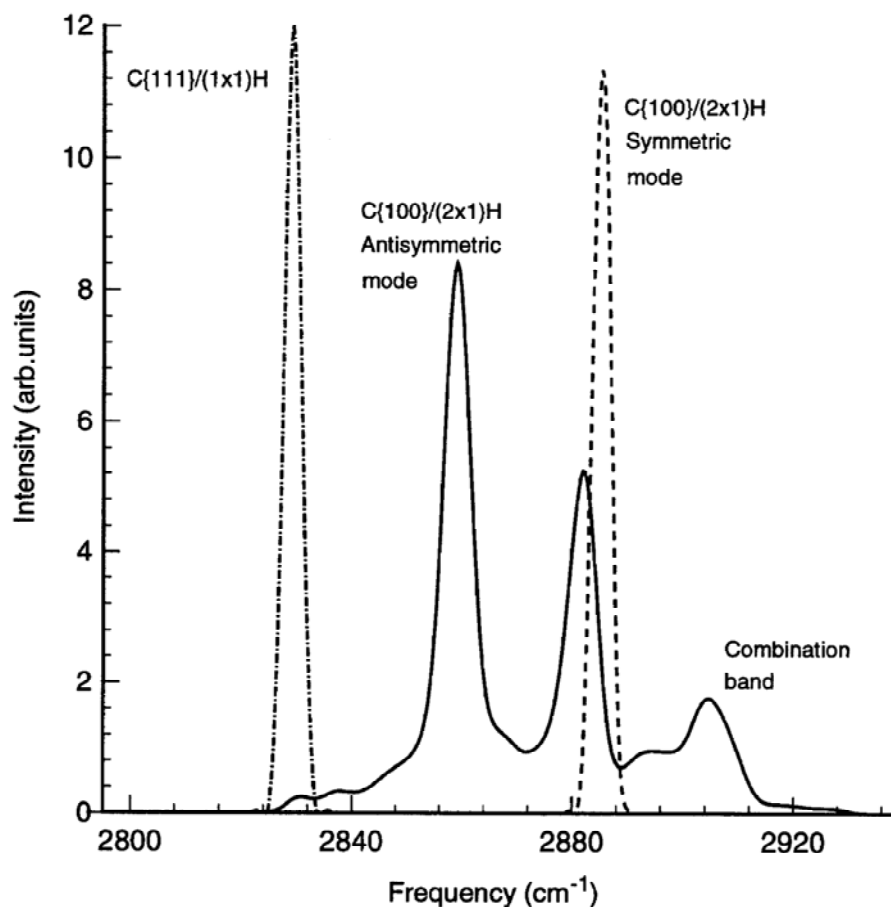
Time correlations along the MD trajectory

Example: Vibrational dynamics on H-terminated diamond surface

Vibrational spectrum

Vibrational spectrum for the system can be calculated by taking the Fourier Transform of the correlation function, $G(\tau)$ that transfers the information on the correlations along the atomic trajectories from time to frequency frame of reference.

$$I(\nu) = \int_{-\infty}^{\infty} \exp(-2\pi i\nu\tau)G(\tau)d\tau$$



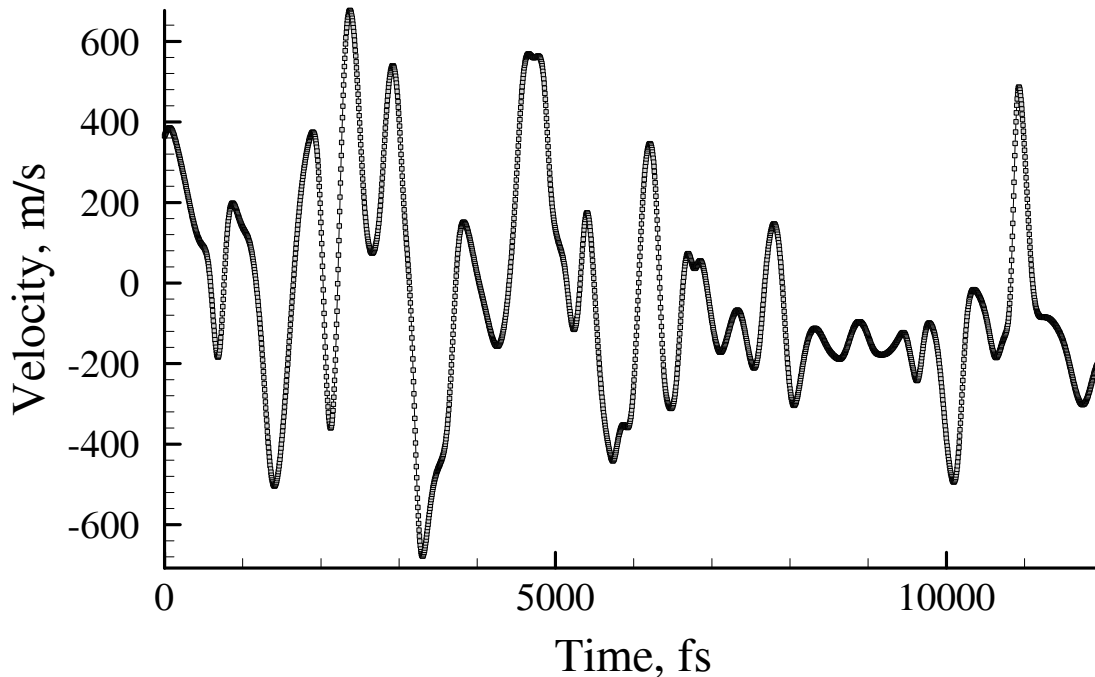
Spectral peaks corresponding to the specific CH stretching modes on the H-terminated {111} and {100} diamond surfaces.

L. V. Zhigilei, D. Srivastava, B. J. Garrison, *Surface Science* **374**, 333 (1997).

Velocity-velocity autocorrelation function

Example: organic liquid, molecular mass is 100 Da,
intermolecular interaction - van der Waals.

1

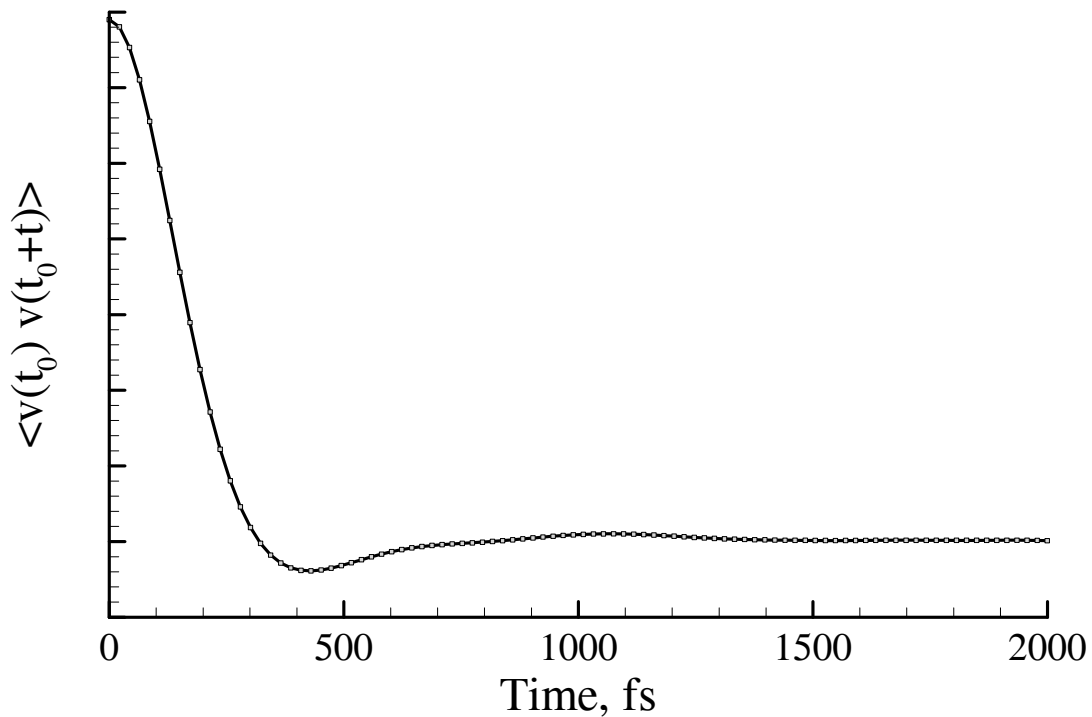


Velocity of one molecule in an organic liquid. In the liquid phase molecules/atoms “lose memory” of their past within one/several periods of vibration. This “short memory” is reflected in the velocity-velocity autocorrelation function, see next page.

Velocity-velocity autocorrelation function

Example: organic liquid, molecular mass is 100 Da,
intermolecular interaction - van der Waals.

2

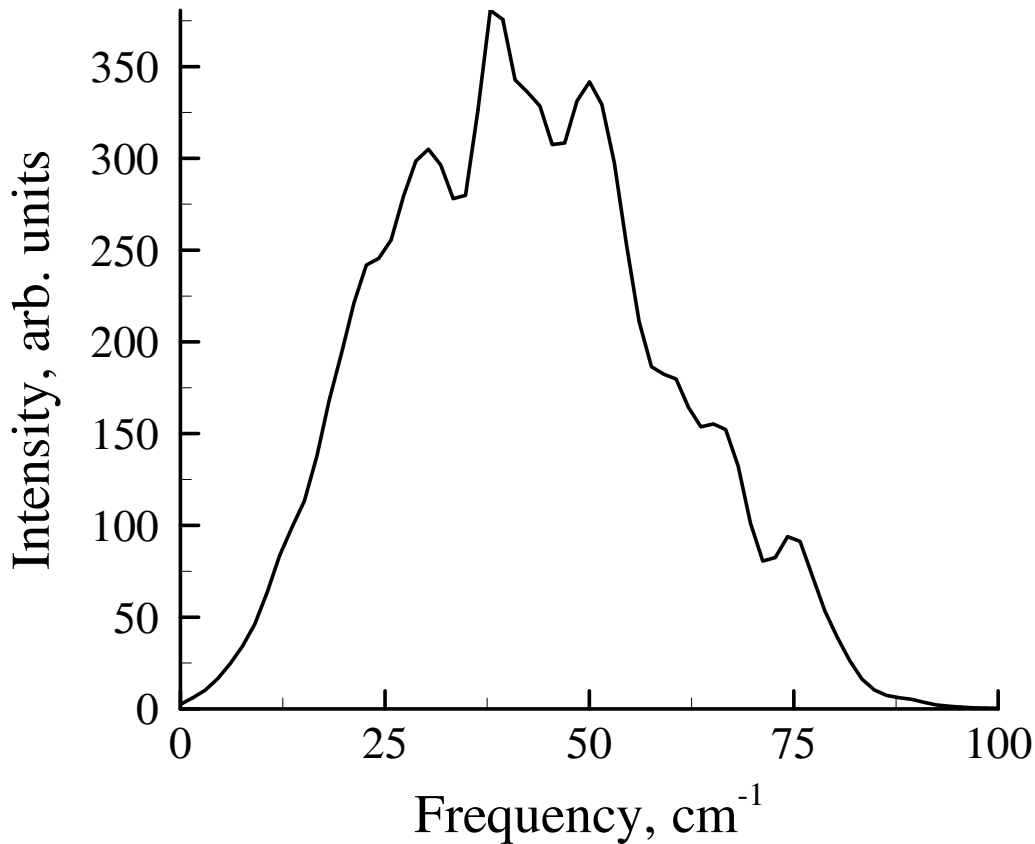


The decay of the velocity-velocity autocorrelation function has the same timescale as the characteristic time of molecular vibrations in the model organic liquid, see previous page.

Velocity-velocity autocorrelation function

Example: organic liquid, molecular mass is 100 Da,
intermolecular interaction - van der Waals.

3



Vibrational spectrum, calculated by taking the Fourier transform of the velocity-velocity autocorrelation function can be used to

- relate simulation results to the data from spectroscopy experiments,
- understand the dynamics in your model,
- choose the timestep of integration for the MD simulation (the timestep is defined by the highest frequency in the system).

How to describe the correlation in real space?



Photo by Mike Skeffington (www.skeff.com), cited by *Nature* 435, 75-78 2005.

Density-density correlation function I

Pair correlation function, $g(r)$

Let's define $g(\mathbf{r})$, density – density correlation function that gives us the probability to find a particle in the volume element $d\mathbf{r}$ located at \mathbf{r} if at $\mathbf{r} = 0$ there is another particle.

At atomic level the density distribution in a system of N particles can be described as

$$\rho(\vec{r}) = \sum_j^N \delta(\vec{r} - \vec{r}_j)$$

Then, by definition, the density – density autocorrelation function is

$$C(\vec{r}) = \langle \rho(\vec{r}_i) \rho(\vec{r}_i + \vec{r}) \rangle_i \quad \text{where} \quad \rho(\vec{r}_i) = \sum_j^N \delta(\vec{r}_i - \vec{r}_j) = 1$$

$$\text{and} \quad \rho(\vec{r}_i + \vec{r}) = \sum_j^N \delta(\vec{r}_i + \vec{r} - \vec{r}_j) = \sum_j^N \delta(\vec{r} - \vec{r}_{ij})$$

Therefore

$$C(\vec{r}) = \langle \rho(\vec{r}_i) \rho(\vec{r}_i + \vec{r}) \rangle_i = \left\langle \sum_j^N \delta(\vec{r} - \vec{r}_{ij}) \right\rangle_i = \frac{1}{N} \sum_i^N \sum_j^N \delta(\vec{r} - \vec{r}_{ij})$$

To relate the probability to find a particle at \mathbf{r} to what is expected for a uniform random distribution of particles of the same density, we can normalize to the average density in the system, $\rho_0 = N/V$:

$$c(\vec{r}) = \frac{C(\vec{r})}{\rho_0} = \frac{V}{N^2} \sum_i^N \sum_j^N \delta(\vec{r} - \vec{r}_{ij})$$

Density-density correlation function II

Pair correlation function, $g(r)$

$$c(\vec{r}) = \frac{1}{N\rho_0} \sum_i^N \sum_j^N \delta(\vec{r} - \vec{r}_{ij}) = \frac{V}{N^2} \sum_i^N \sum_j^N \delta(\vec{r} - \vec{r}_{ij})$$

For isotropic system $g(r)$ can be averaged over angles and calculated from MD data by calculating an average number of particles at distances $r - r + \Delta r$ from any given particle:

$$N_r(r) = \langle c(\vec{r}) \rangle_{\text{angle}}$$

To define the probability to find a particle at a distance r from a given particle we should divide N_r by the volume of a spherical shell of radius r and thickness Δr :

$$g(r) = N_r / (4\pi r^2 \Delta r)$$

Thus, we can define the **pair distribution function**, which is a real-space representation of correlations in atomic positions:

$$g(r) = \frac{1}{4\pi N r^2 \rho_0} \sum_{j=1}^N \sum_{\substack{i=1 \\ i \neq j}}^N \delta(r - r_{ij}) = \frac{1}{2\pi N r^2 \rho_0} \sum_{j=1}^N \sum_{i>j}^N \delta(r - r_{ij})$$

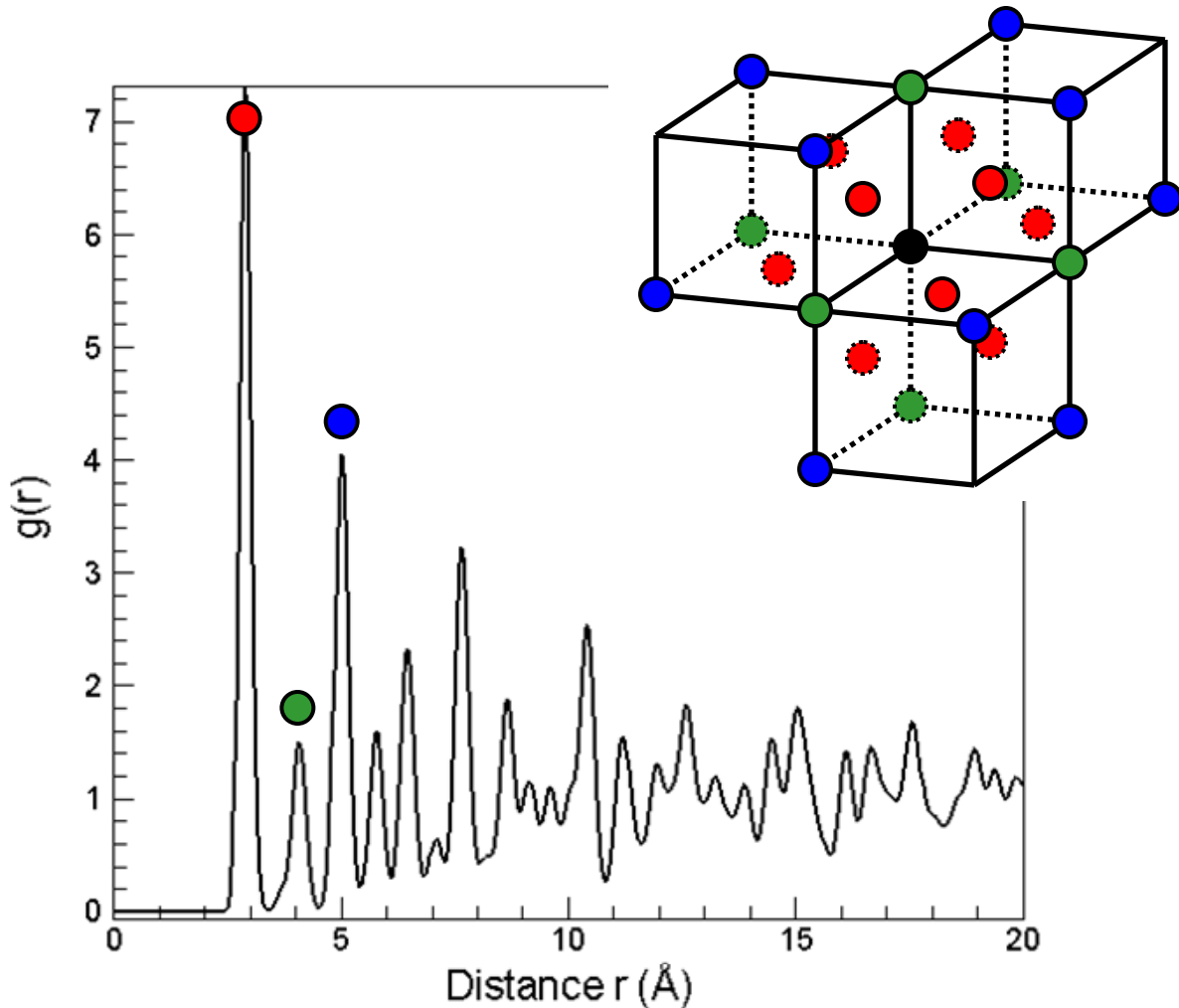
$g(r)$ can be calculated up to the distance r_g that should not be longer than the half of the size of the computational cell.

Although $g(r)$ has the same double sum as in the force subroutine, the range r_g is commonly greater than the potential cutoff r_c and $g(r)$ is usually calculated separately from forces.

Calculation of $g(r)$ for a particular type of atom in a system can give information on the chemical ordering in a complex system.

Pair distribution function, $g(r)$. Examples.

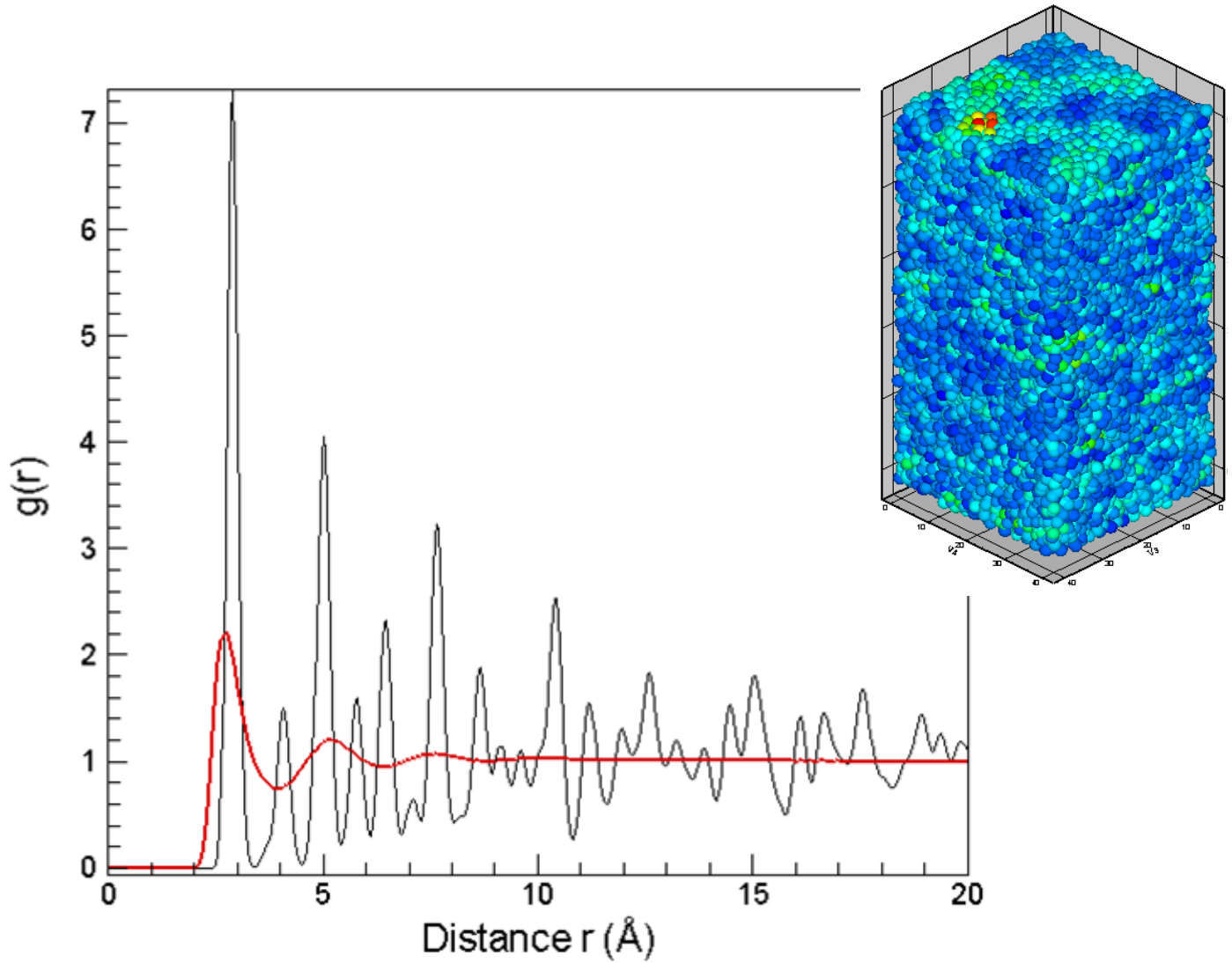
Pair Distribution Function $g(r)$ for fcc Au at 300 K



Terminology suggested in [T. Egami and S. J. L. Billinge, *Underneath the Bragg Peaks. Structural analysis of complex material* (Elsevier, Amsterdam, 2003)] is used in this lecture notes.

Pair distribution function, $g(r)$. Examples.

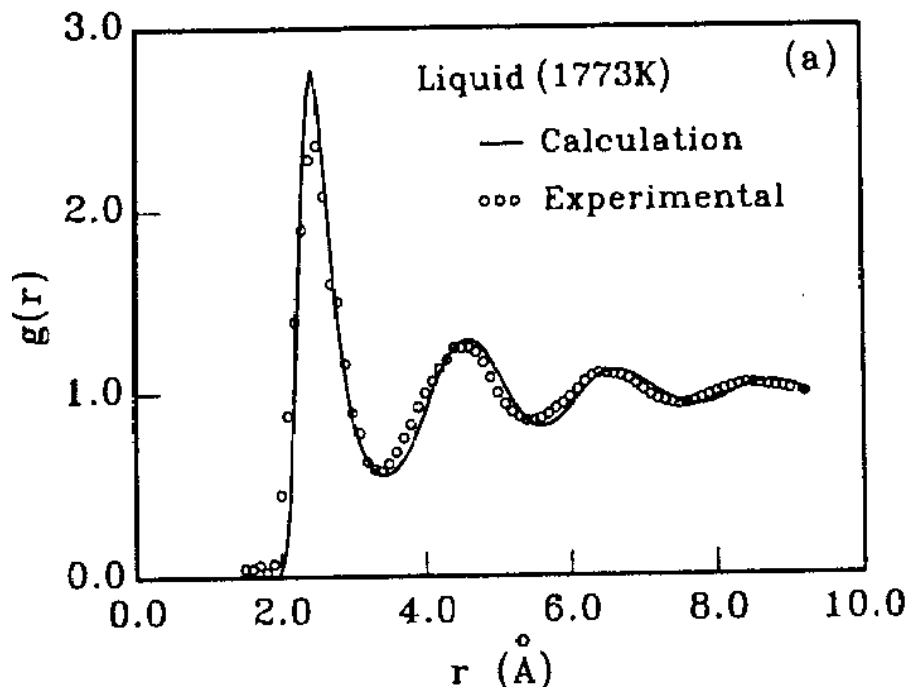
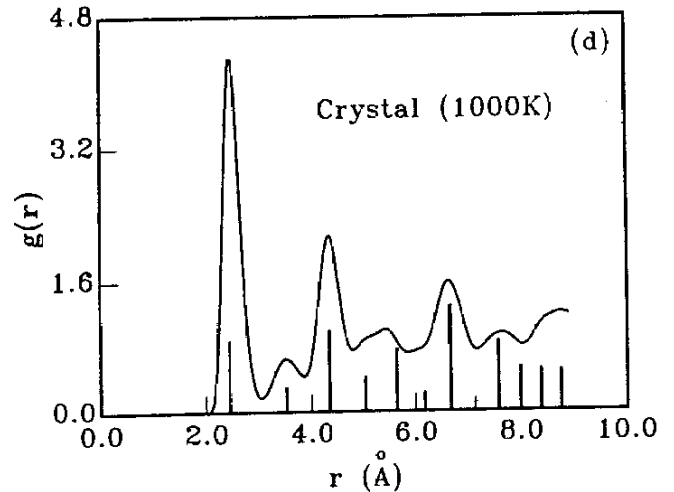
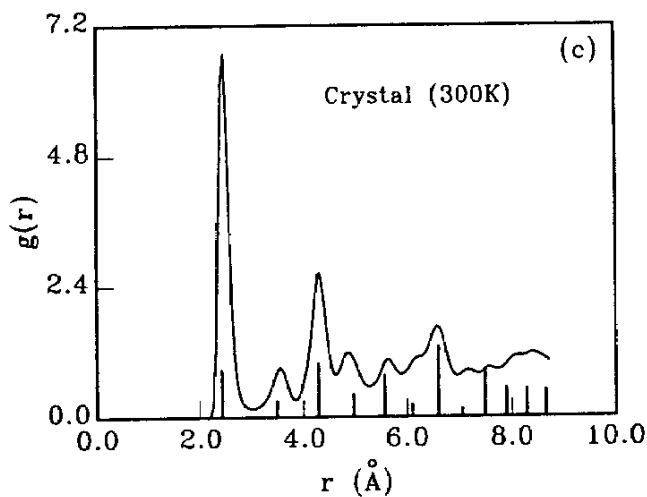
Pair Distribution Function $g(r)$ for liquid Au



Pair distribution function, $g(r)$. Examples.

Figures below are $g(r)$ calculated for MD model of crystalline and liquid Ni.

[J. Lu and J. A. Szpunar, Phil. Mag. A **75**, 1057-1066 (1997)].



$g(r)$ for pure Ni in a liquid state at 1773 K (46 K above T_m). Experimental data points are obtained by Fourier transform of the experimental structure factor.

Family of Pair Distribution Functions

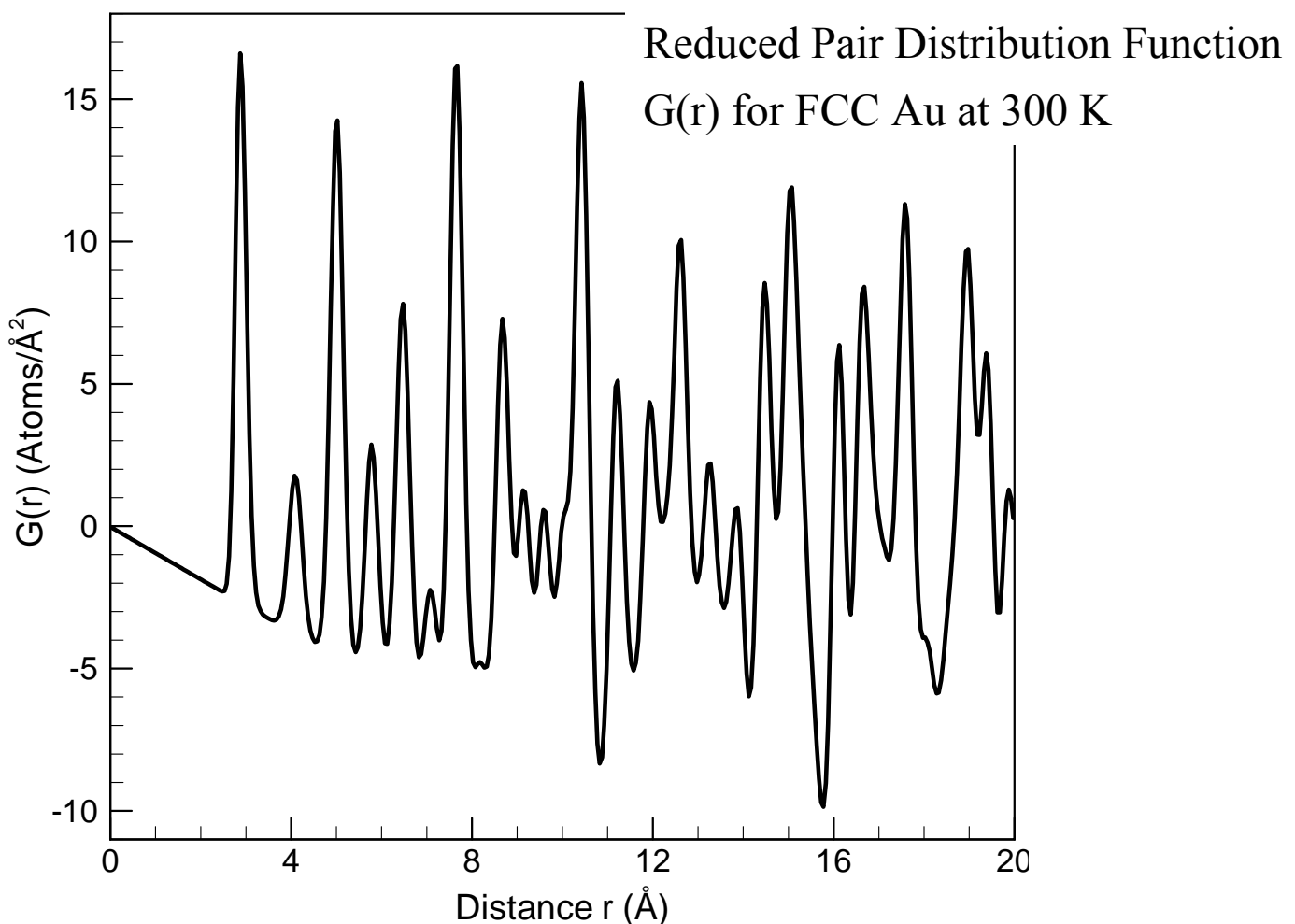
Pair distribution function (PDF):

$$g(\mathbf{r}) = \frac{1}{4\pi N r^2 \rho_0} \sum_{j=1}^N \sum_{\substack{i=1 \\ i \neq j}}^N \delta(\mathbf{r} - \mathbf{r}_{ij}) = \frac{1}{2\pi N r^2 \rho_0} \sum_{j=1}^N \sum_{i>j}^N \delta(\mathbf{r} - \mathbf{r}_{ij})$$

also often defined as $\tilde{g}(\mathbf{r}) = g(\mathbf{r}) - 1$

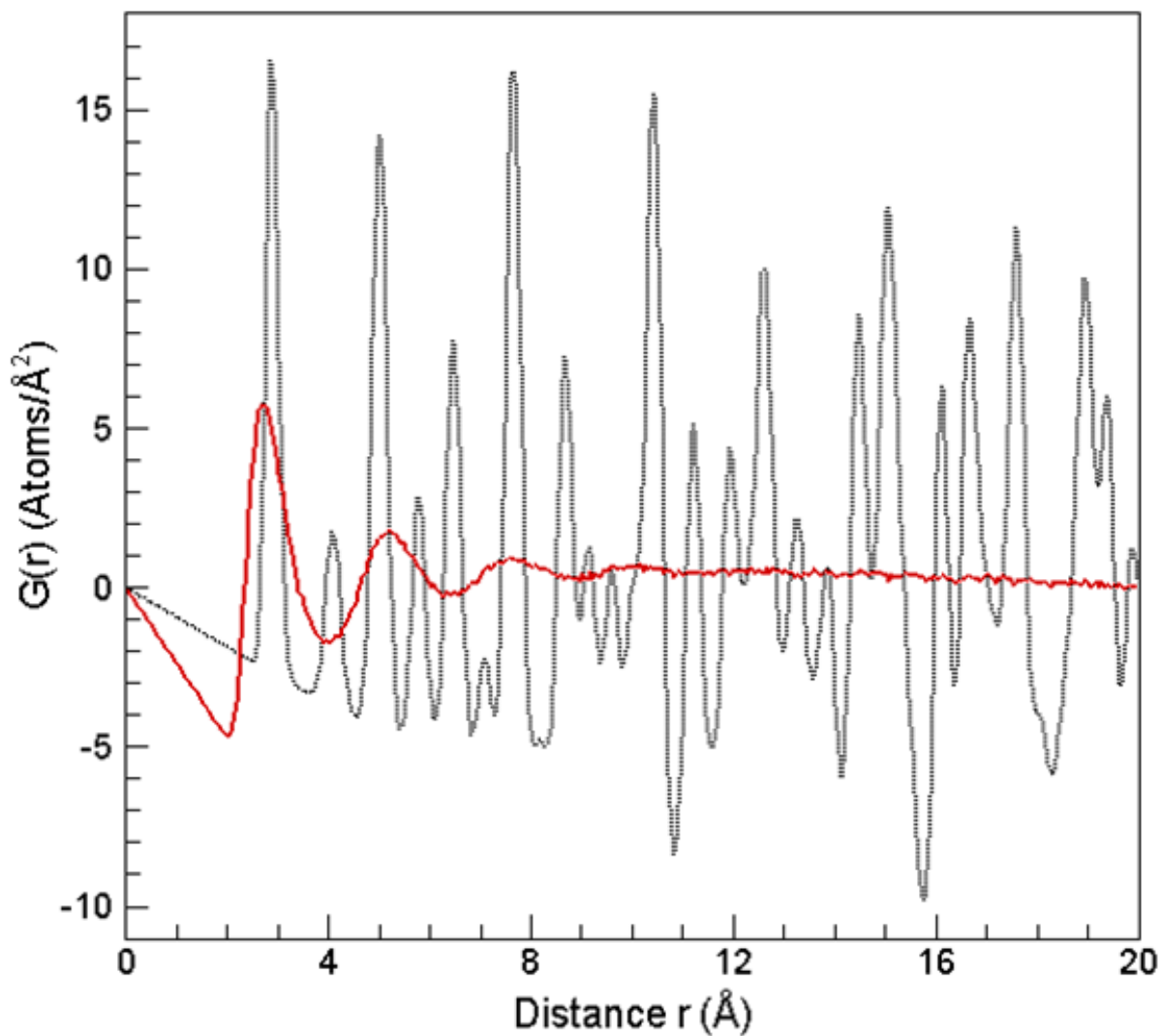
Reduced PDF:

$$G(r) = 4\pi r \rho_0 \tilde{g}(r) \quad \text{or} \quad H(r) = 4\pi r^2 \rho_0 \tilde{g}(r)$$



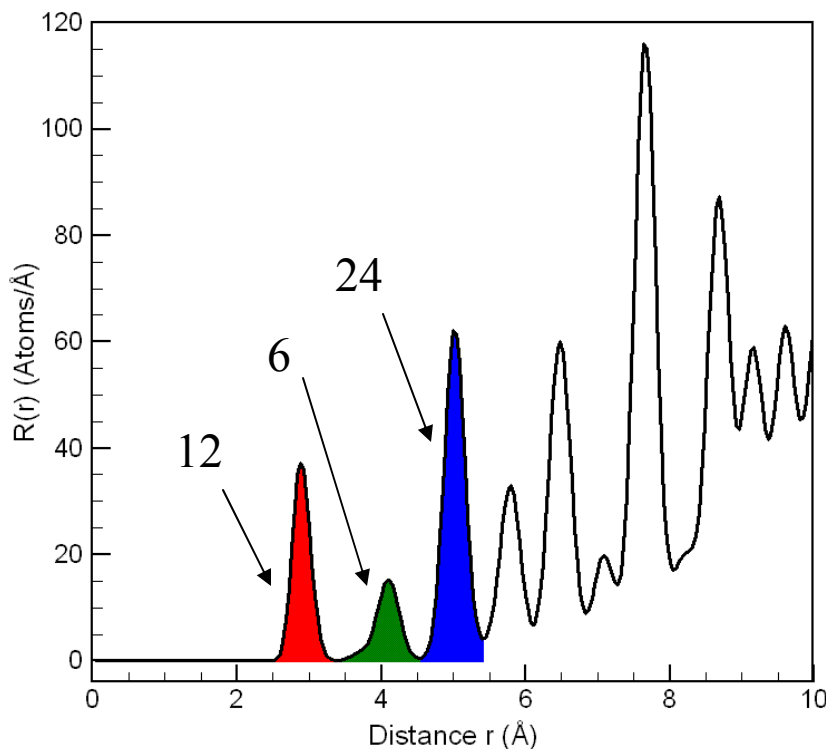
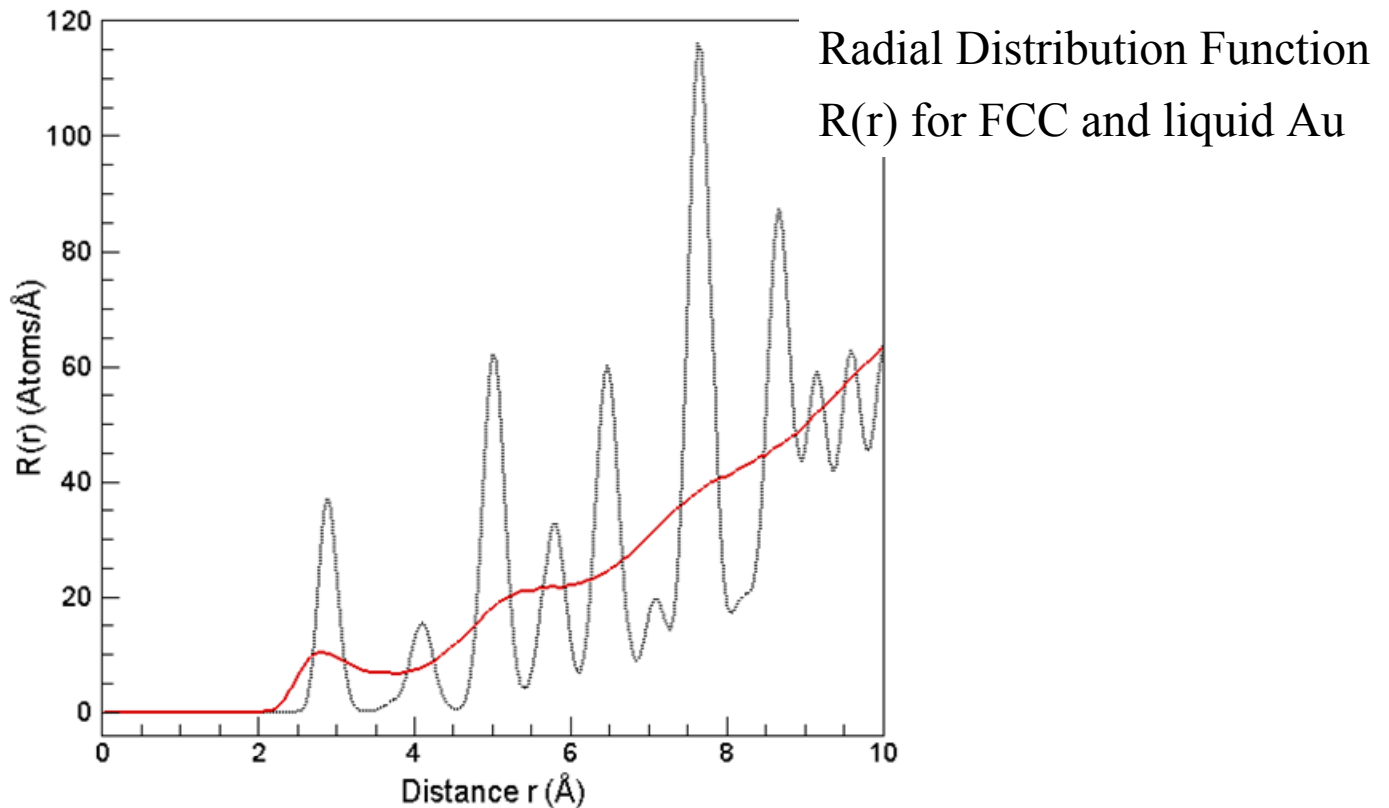
Family of PDF: Reduced Pair Distribution Function

Reduced Pair Distribution Function $G(r)$ for liquid Au



Family of PDF: Radial distribution function

Radial distribution function: $R(r) = 4\pi r^2 \rho_0 g(r)$



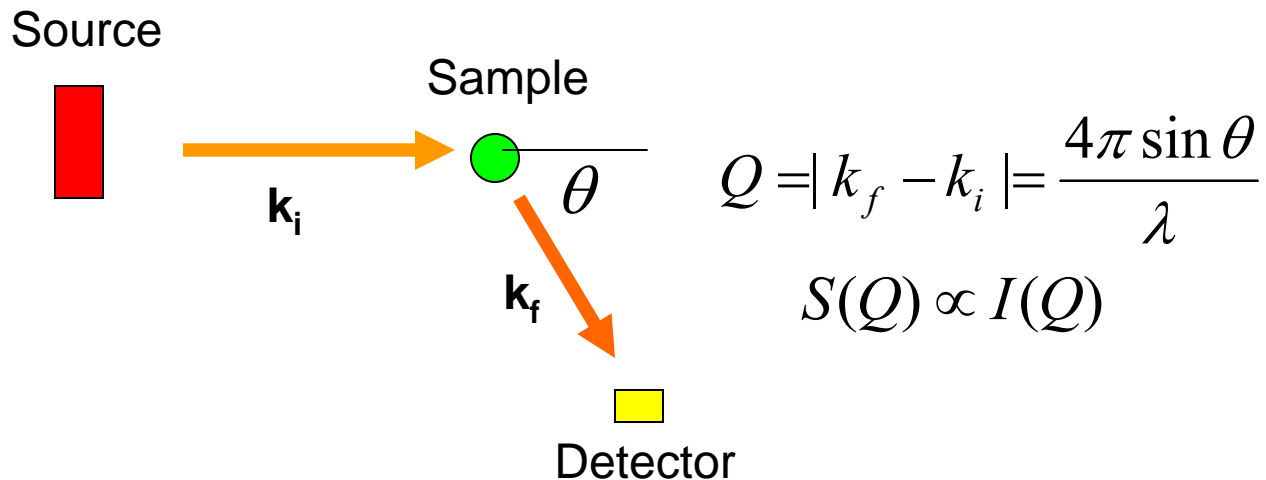
$g(r)$ can be used to calculate the average number of atoms located between r_1 and r_2 (define coordination numbers even in disordered state).

$$n = \int_{r_1}^{r_2} R(r) dr$$

$$n = \frac{N}{V} \int_{r_1}^{r_2} g(r) 4\pi r^2 dr$$

Experimental measurement of PDFs

$g(r)$ can be obtained by Fourier transformation of the total structure factor that is measured in neutron and X-ray scattering experiments. Analysis of liquid and amorphous structures is often based on $g(r)$.



$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^{\infty} Q [S(Q) - 1] \sin(Qr) dQ$$

ρ_0 is average number density of the samples
 Q is the scattering vector

Software package for Neutron/X-rays experiments:
PDFGETN, PDFGETX at <http://nirt.pa.msu.edu/software.php>

Analysis of liquid and amorphous structures is often based on $g(r)$.

Structure function $S(Q)$

[1]

The amplitude of the wave scattered by the sample is given by summing the amplitude of scattering from each atom in the configuration:

$$\Psi_s(\vec{Q}) = \sum_{i=1}^N f_i \exp(-i\vec{Q} \cdot \vec{r}_i)$$

where \vec{Q} is the scattering vector, \vec{r}_i is the position of atom i
 f_i is the x-ray or electron atomic scattering form factor for the i^{th} atom.

The magnitude of \vec{Q} is given by $Q = 4\pi \sin \theta / \lambda$, where θ is half the angle between the incident and scattered wave vectors, and λ is the wavelength of the incident wave.

The intensity of the scattered wave can be found by multiplying the scattered wave function by its complex conjugate:

$$I(\vec{Q}) = \Psi_s(\vec{Q}) \cdot \Psi_s^*(\vec{Q}) = \sum_{j=1}^N \sum_{i=1}^N f_i f_j \exp(-i\vec{Q} \cdot (\vec{r}_i - \vec{r}_j))$$

Spherically-averaged powder-diffraction intensity profile is obtained by integration over all directions of interatomic separation vector:

$$I(Q) = \sum_{j=1}^N \sum_{i=1}^N f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}}$$

By dividing this equation by $\sum_{i=1}^N f_i^2$ we obtain the structure function

$$S(Q) = \frac{I(Q)}{\sum_{i=1}^N f_i^2} = 1 + \frac{2}{\sum_{i=1}^N f_i^2} \sum_{j=1}^N \sum_{i<j}^N f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}}$$

Or, for monatomic system:

$$S(Q) = 1 + \frac{2}{N} \sum_{j=1}^N \sum_{i<j}^N \frac{\sin(Qr_{ij})}{Qr_{ij}}$$

Phys. Rev. B **73**, 184113 2006

$$S(Q) = 1 + \frac{2}{N} \sum_{j=1}^N \sum_{i<j}^N \frac{\sin(Qr_{ij})}{Qr_{ij}}$$

This equation can be used to calculate the structure function from an atomic configuration.

The calculations, however, involve the summation over all pairs of atoms in the system, leading to the quadratic dependence of the computational cost on the number of atoms and making the calculations expensive for large systems.

An alternative approach to calculation of $S(Q)$ is to substitute the double summation over atomic positions by integration over pair distribution function

$$g(r) = \frac{1}{2\pi N r^2 \rho_0} \sum_{j=1}^N \sum_{i>j}^N \delta(r - r_{ij})$$

The expression for the structure function can be now reduced to the integration over r (equivalent to Fourier of $g(r)$):

$$S(Q) = 1 + \int_0^{\infty} 4\pi r^2 \rho_0 g(r) \frac{\sin(Qr)}{Qr} dr$$

The calculation of $g(r)$ still involves $N^2/2$ evaluations of interatomic distances r_{ij} , but it can be done much more efficiently than the direct calculation of $S(Q)$, which requires evaluation of the sine function and repetitive calculations for each value of Q .

Structure function $S(Q)$

[3]

$$S(Q) = 1 + \int_0^{\infty} 4\pi r^2 \rho_0 g(r) \frac{\sin(Qr)}{Qr} dr$$

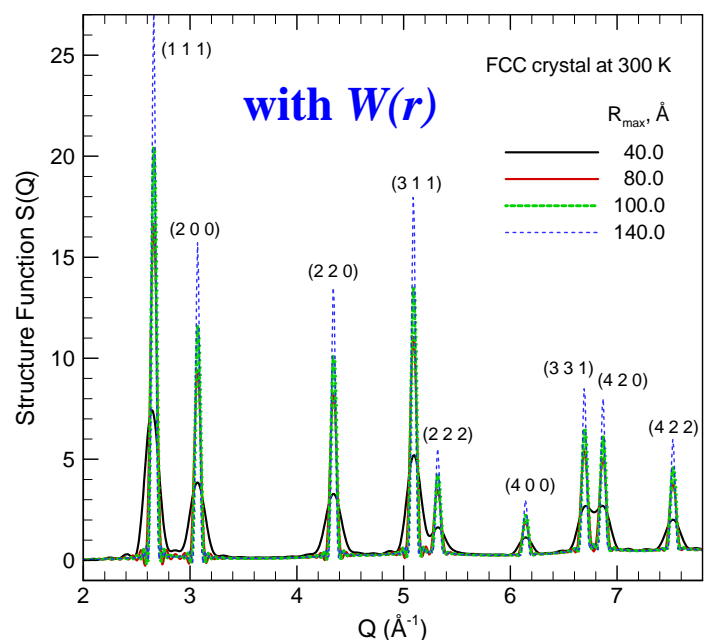
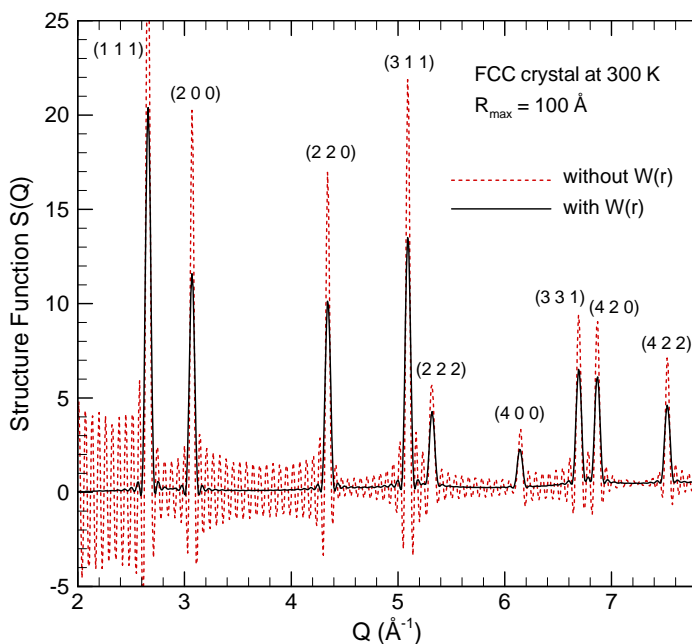
In calculation of $g(r)$, the maximum value of r , R_{\max} , is limited by the size of the MD system.

The truncation of the numerical integration at R_{\max} induces spurious ripples (Fourier ringing) with a period of $\Delta = 2\pi/R_{\max}$.

Several methods have been proposed to suppress these ripples [Peterson et al., J. Appl. Crystallogr. **36**, 53 (2003); Gutiérrez and Johansson, Phys. Rev. B **65**, 104202 (2002); Derlet et al., Phys. Rev. B **71**, 024114 (2005)]. E. g., a damping function $W(r)$ can be used to replace the sharp step function at R_{\max} by a smoothly decreasing contribution from the density function at large interatomic distances and approaching zero at R_{\max} :

$$S(Q) = 1 + \int_0^{R_{\max}} 4\pi r^2 \rho(r) \frac{\sin(Qr)}{Qr} W(r) dr$$

$$W(r) = \frac{\sin\left(\pi \frac{r}{R_{\max}}\right)}{\pi \frac{r}{R_{\max}}}$$

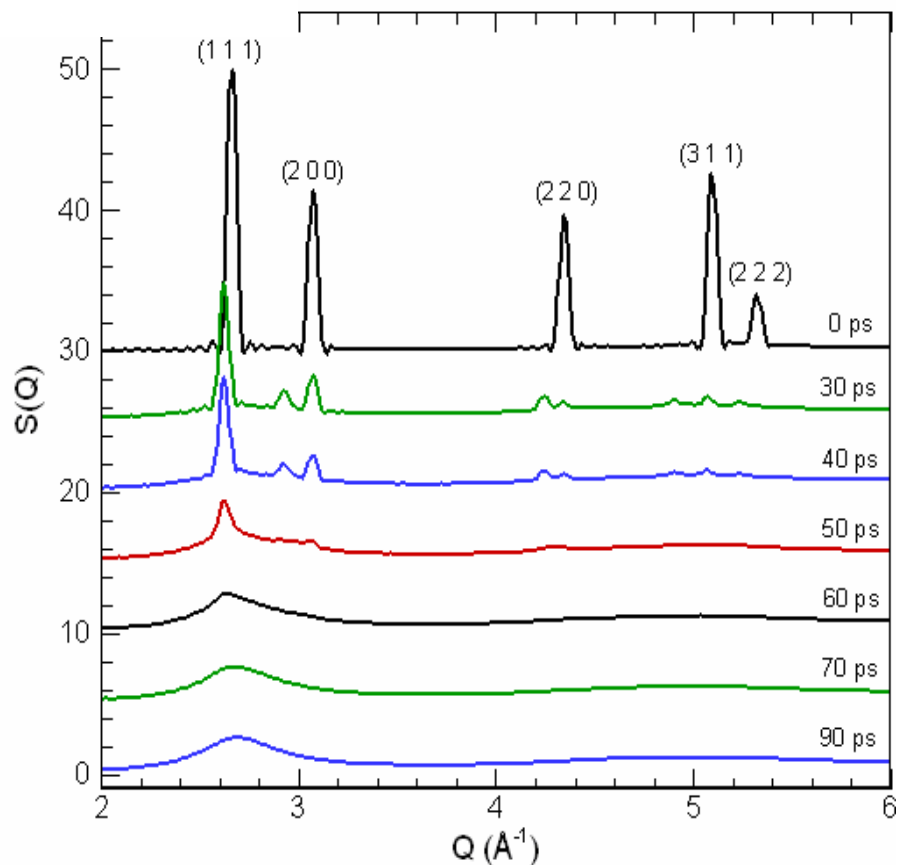
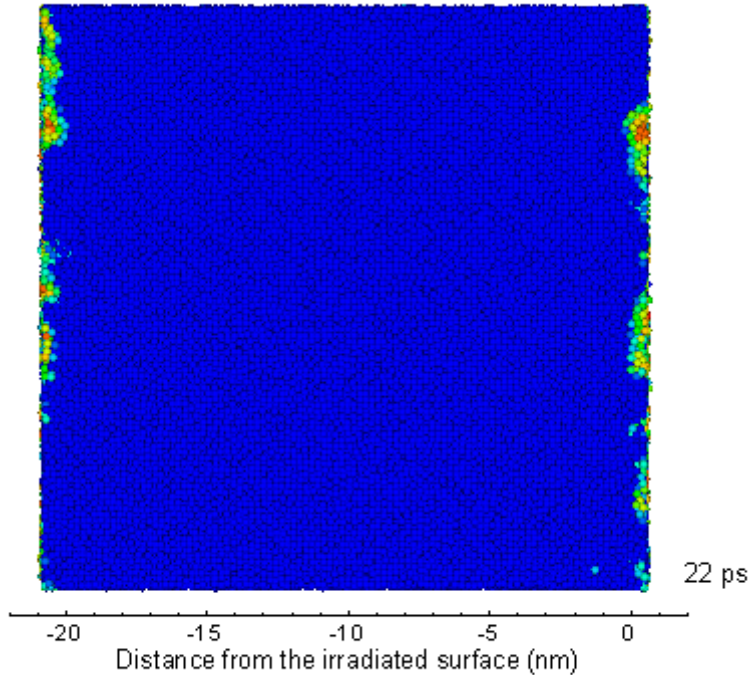


Phys. Rev. B **73**, 184113 2006

Example: MD simulation of laser melting of a Au film irradiated by a 200 fs laser pulse at an absorbed fluence of 5.5 mJ/cm²

Competition between heterogeneous and homogeneous melting

Phys. Rev. B **73**, 184113 2006

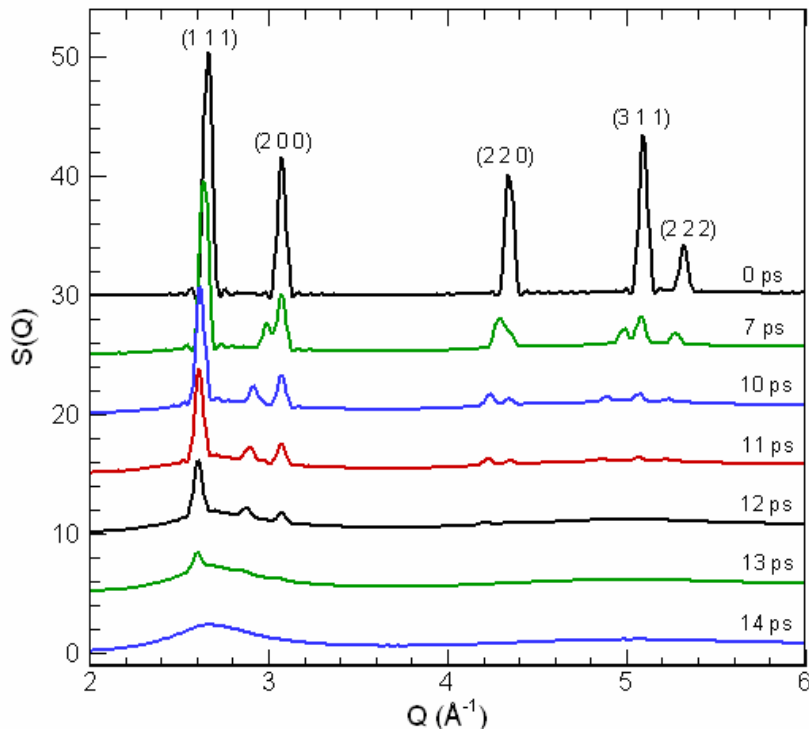


Relevant time-resolved electron diffraction experiments:

Dwyer et al., *Phil. Trans. R. Soc. A* **364**, 741, 2006; *J. Mod. Optics* **54**, 905, 2007.

University of Virginia, MSE 4270/6270: Introduction to Atomistic Simulations, Leonid Zhigilei

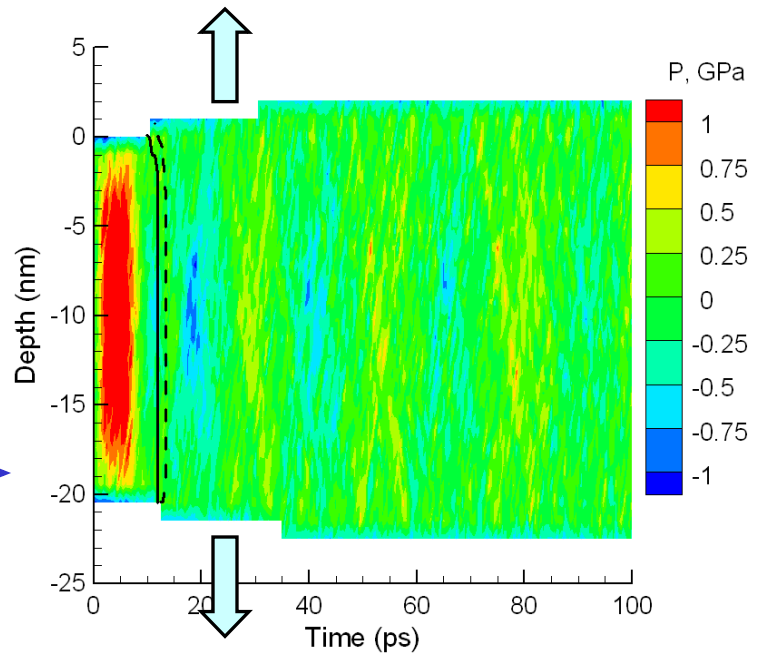
Example: Au film irradiated by a 200 fs laser pulse at an absorbed fluence of 18 mJ/cm²



- The height of the crystalline peaks
- decrease before melting
 - disappear during melting

Splitting and shift of the peaks

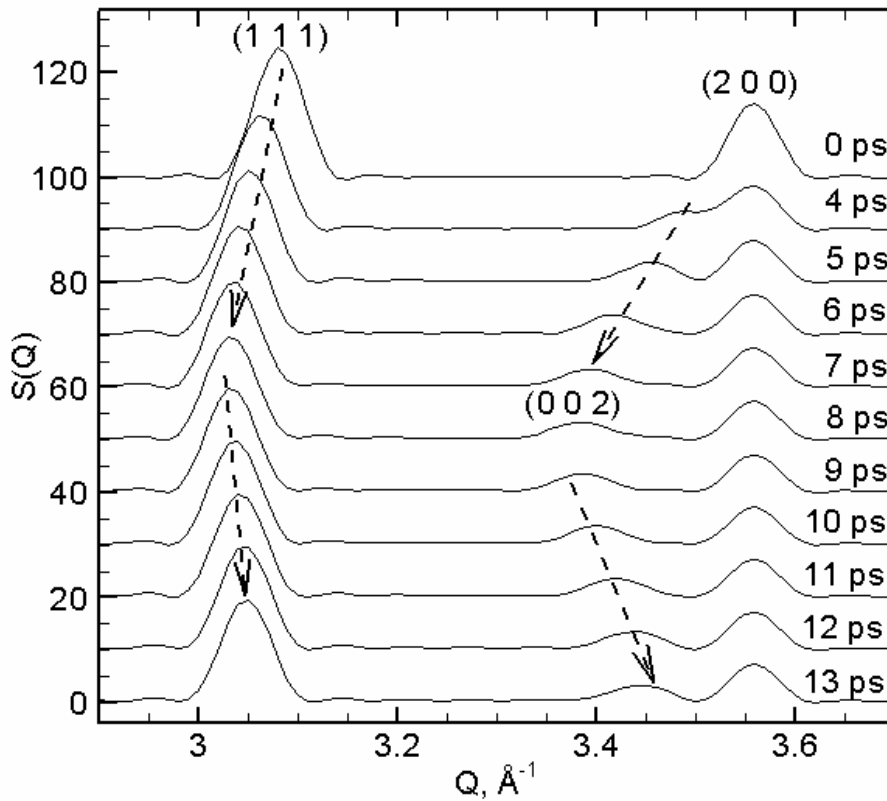
Thermoelastic stresses lead to the uniaxial expansion of the film along the [001] direction



Phys. Rev. B **73**, 184113 2006

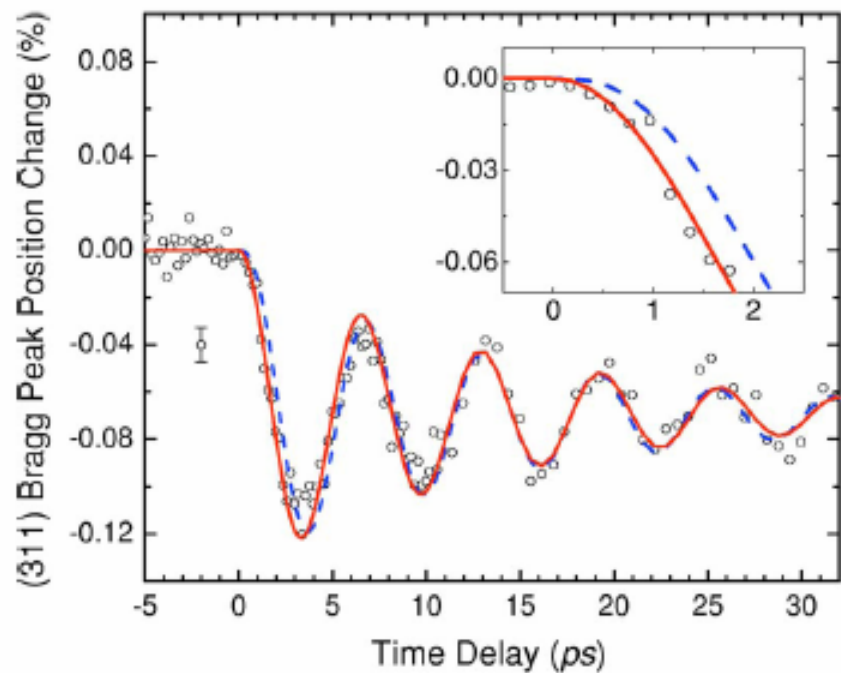
Cubic lattice → Tetragonal lattice

Example for a 21 nm Ni film irradiated by a 200 fs laser pulse at an absorbed fluence of 10 mJ/cm² (below the melting threshold)



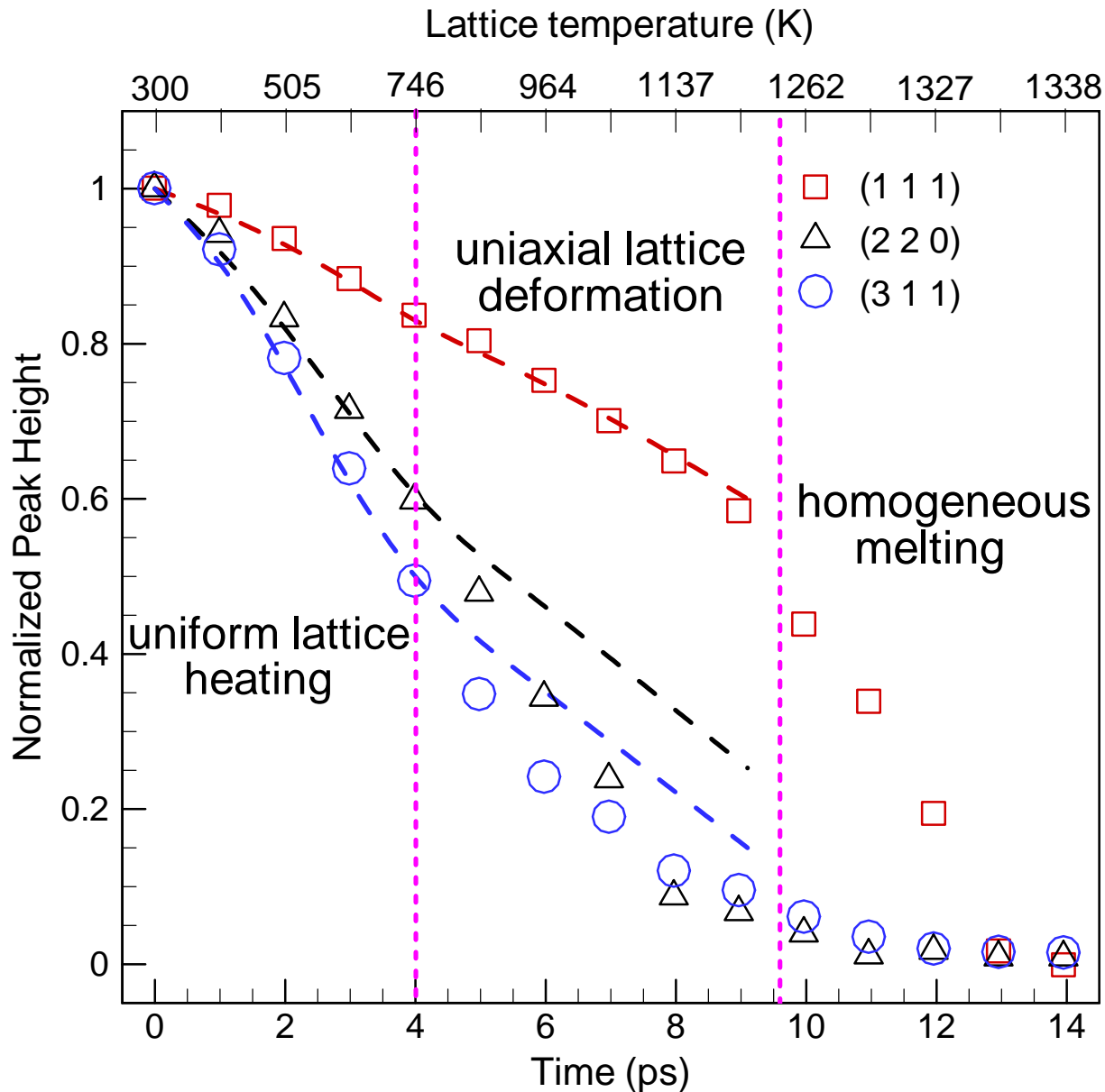
Simulation:
Z. Lin and L. V. Zhigilei,
J. Phys.: Conf. Series **59**,
11, 2007.

Shifts of diffraction peaks reflect transient uniaxial thermoelastic deformations of the film → **an opportunity for experimentally probing ultrafast deformations.**



H. Park et al. *Phys. Rev. B* **72**, 100301, 2005.

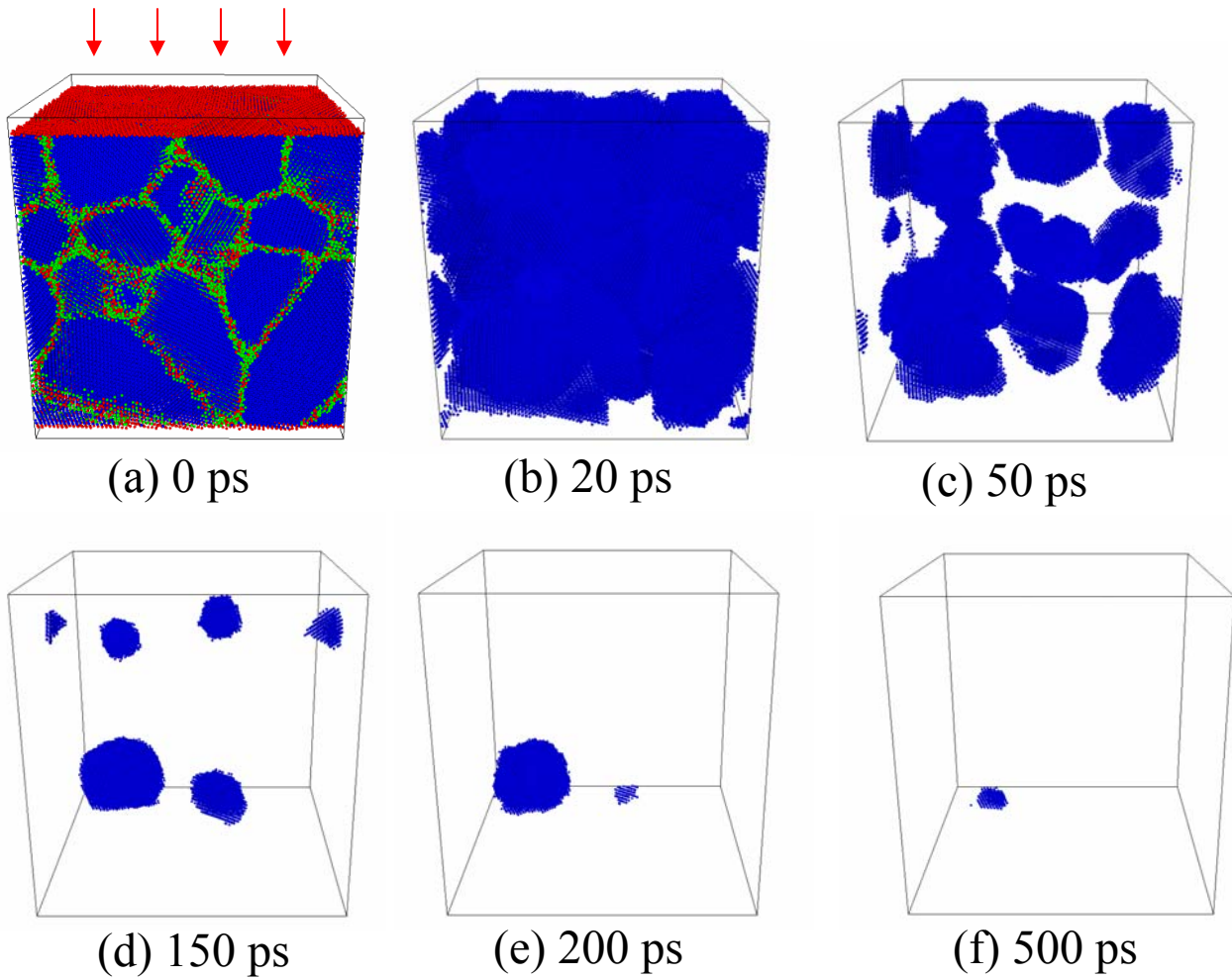
Example: Au film irradiated by a 200 fs laser pulse at 18 mJ/cm²
Three stages in the evolution of the diffraction profiles



- (1) 0 to 4 ps: thermal vibrations of atoms (Debye-Waller factor)
- (2) 4 to 10 ps: Debye-Waller + uniaxial lattice expansion
- (3) 10 to 14 ps: homogeneous melting

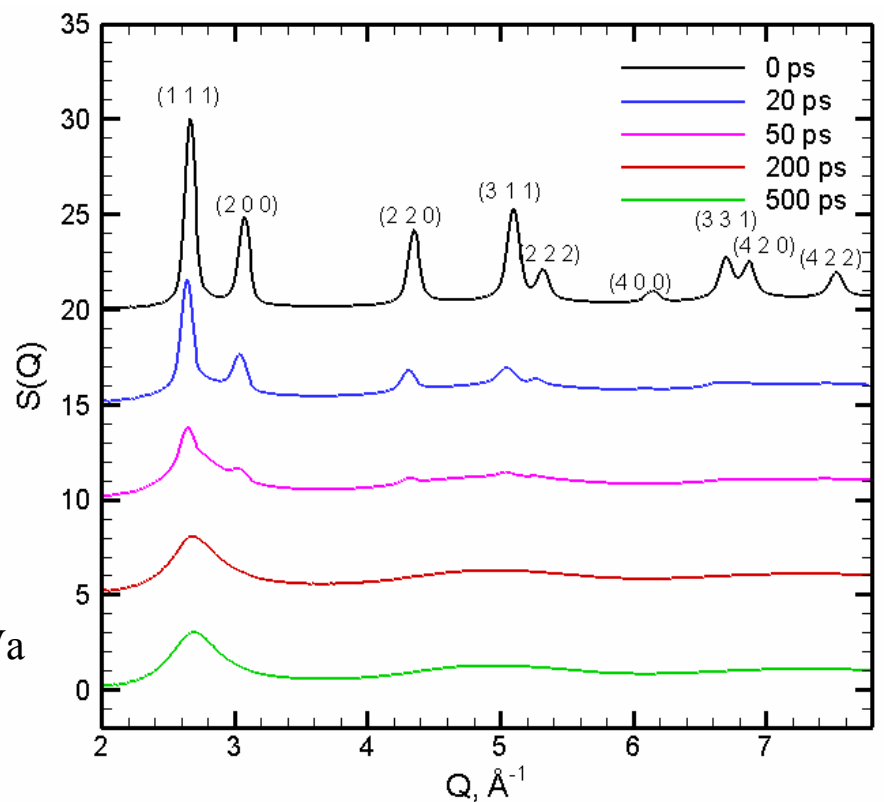
Phys. Rev. B **73**, 184113 2006

Example for melting of a nanocrystalline Au film

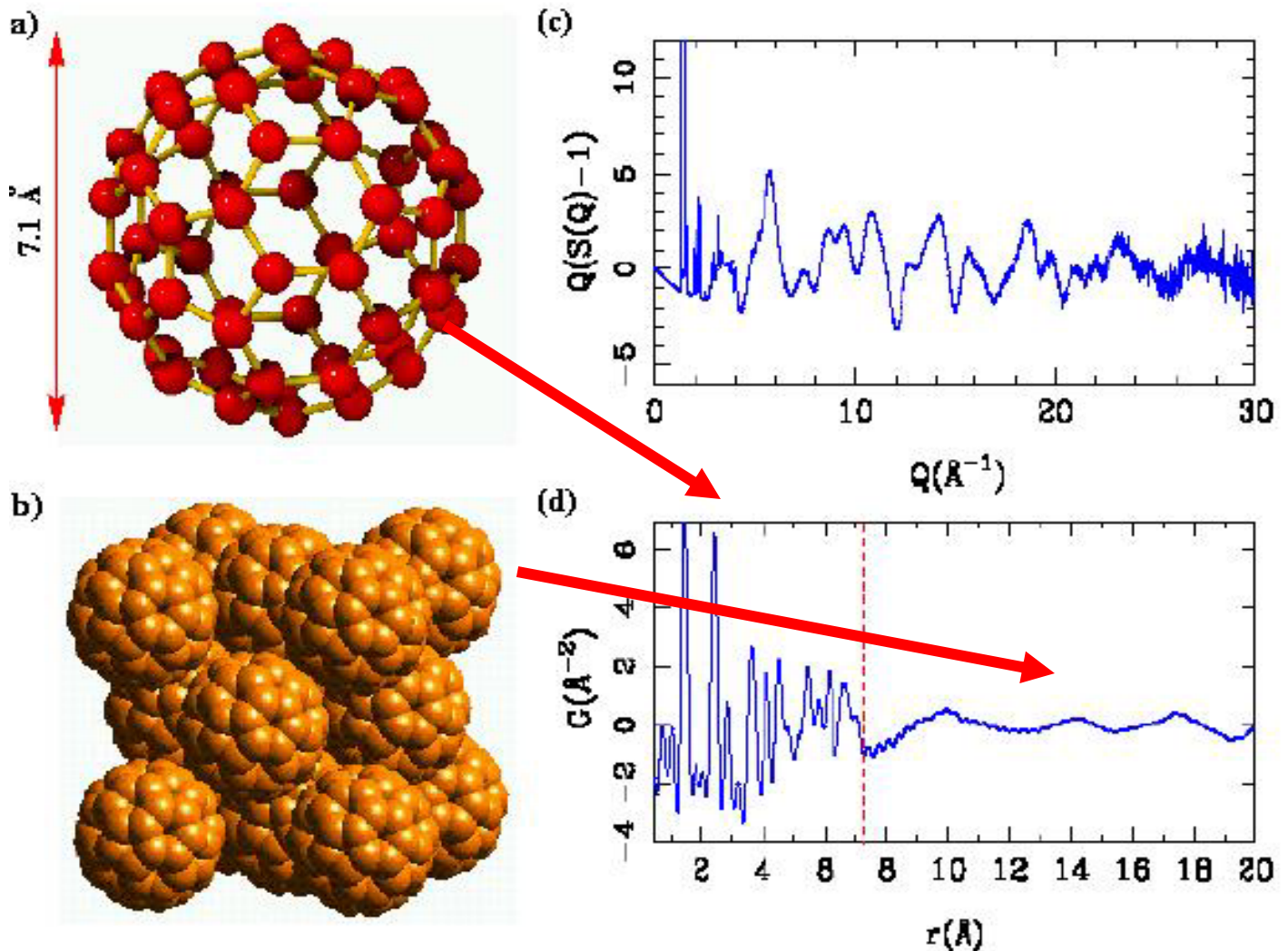


Evolution of diffraction profiles can be related to time-resolved pump-probe experiments, with connections made to the microstructure of the target.

calculations by Zhibin Lin, UVa



Example for a complex material (e.g. solid C_{60})



C_{60} correlations: The nearest neighbor is at 1.4 \AA distance, the second neighbor at 2.2 \AA and so on. There are sharp peaks in $G(r)$ at these positions.

Inter-particle correlations: There are no sharp peaks beyond 7.1 \AA , the diameter of the ball. PDF shows the long-range order.

T. Egami and S. J. L. Billinge, *Underneath the Bragg Peaks. Structural analysis of complex material* (Elsevier, Amsterdam, 2003)

Juhás et al., *Nature*, **440**, 655, 2006

Some additional ways to use PDFs in MD simulations

For pairwise interaction, $g(r)$ can be used to calculate the potential energy per particle,

$$\text{P.E.} = \frac{1}{N} \sum_{i=1}^N \sum_{j>i}^N U(|\vec{r}_{ij}|) = 2\pi \frac{N}{V} \int_0^{\infty} r^2 U(r) g(r) dr$$

- This calculation can be used to check the consistency of the calculation of energy and $g(r)$. Integration should be done from 0 to r_c .
- Integrating from r_c to infinity gives the energy correction due to the potential cutoff.

For pairwise interaction, $g(r)$ can be used to calculate the pressure in the system,

$$P = \frac{Nk_B T}{V} - \frac{2\pi N^2}{3V^2} \int_0^{\infty} \frac{dU(r)}{dr} r^3 g(r) dr$$