Structure of CdSe nanocrystals studied by Total Scattering (PDF) supported by Molecular Dynamics simulations

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Experimental and methodology

CdSe nanocrystals 2.5-3.5 nm in diameter were examined. Diffraction patterns were collected up to Q_{max} of 22 A^{-1} using Bruker D8 Advance with Ag tube. Total Scattering Analysis was applied to determine the structure of the examined samples in direct space.

A package of software NanoPDF was developed to build atomistic models of nanocrystals, to calculate theoretical $S(Q)$ and $G(r)$ functions, and to find best matched atomistic models based on comparison of experimental and theoretical $G(r)$ values.

Atomic structure of CdSe nanocrystals was simulated by Molecular Dynamics using POLY-classic software.

Single crystals of CdSe show hexagonal 2H structure. Nanocrystals show always a disorder structure which is intermediate between hexagonal 2H (AB) and cubic 3C polytype (ABC). Theoretical calculations were made for 4H modification with ABAC layer stacking (50% hexagonality).

5 nm
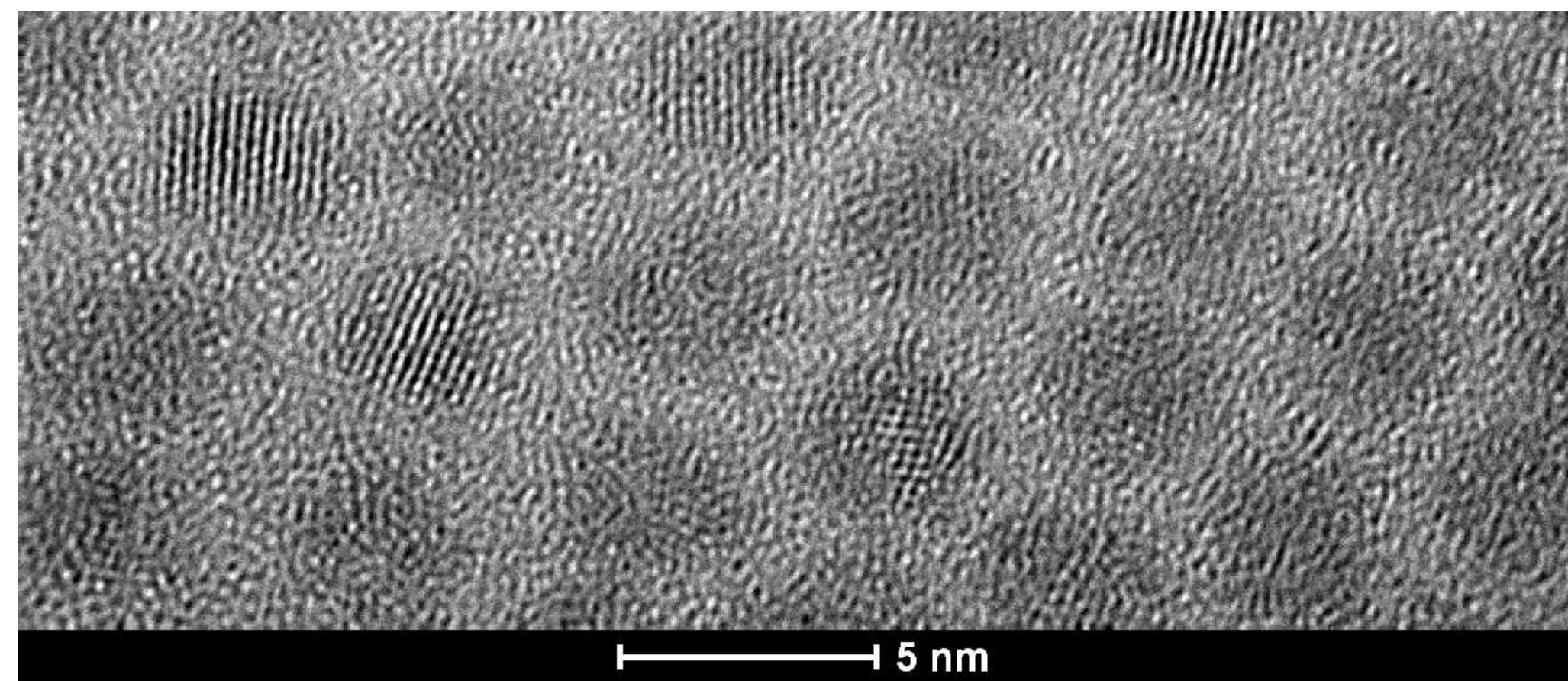
Projection of CdSe nanocrystal in Reciprocal Space
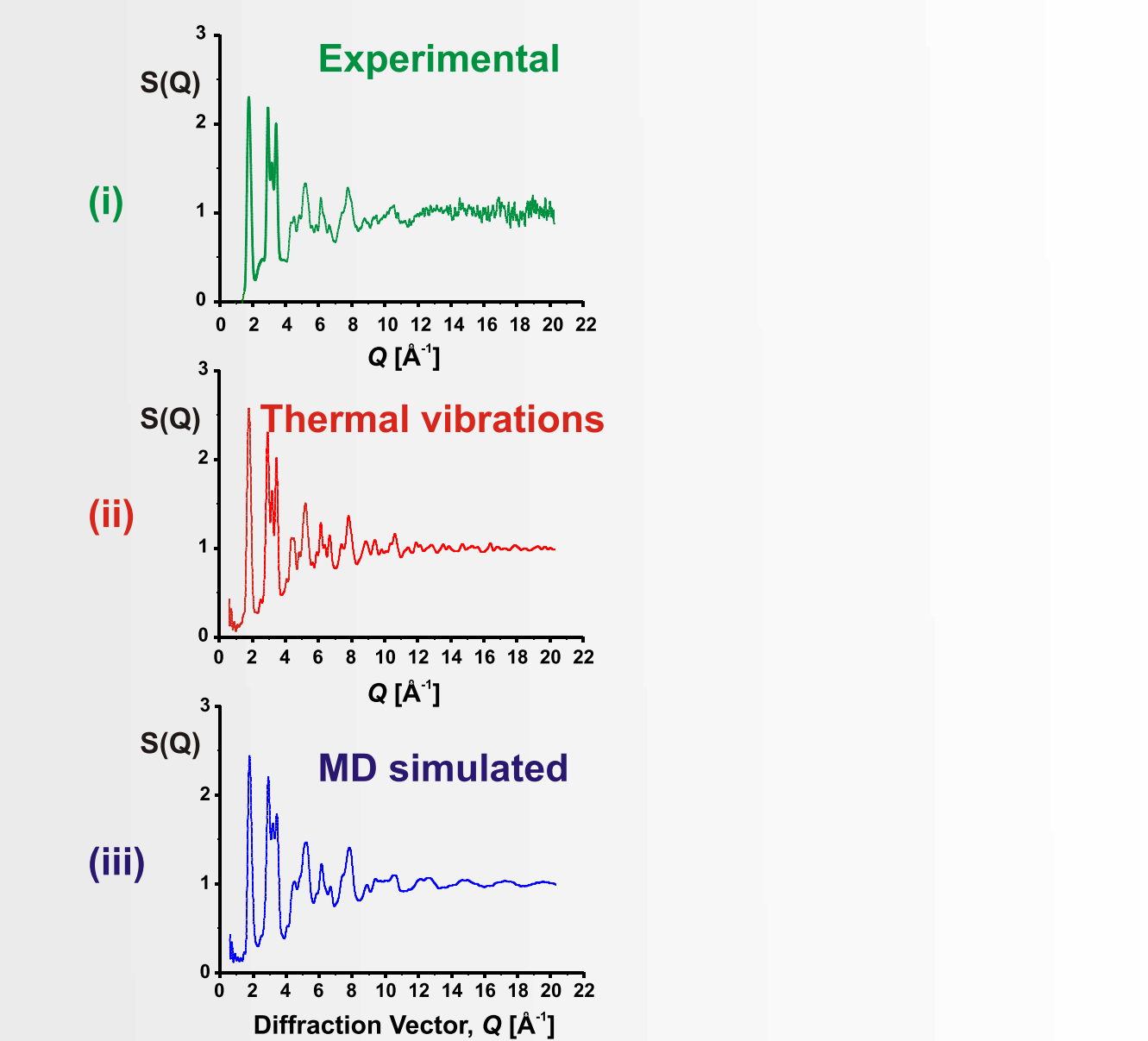
Fig.1(a) Experimental and theoretical structure factors of 3.5 nm CdSe nanocrystals: (i) experimental, (ii) calculated for a perfect CdSe 4H lattice with 0.3 Å amplitude of atomic thermal vibrations, (iii) MD simulated model.
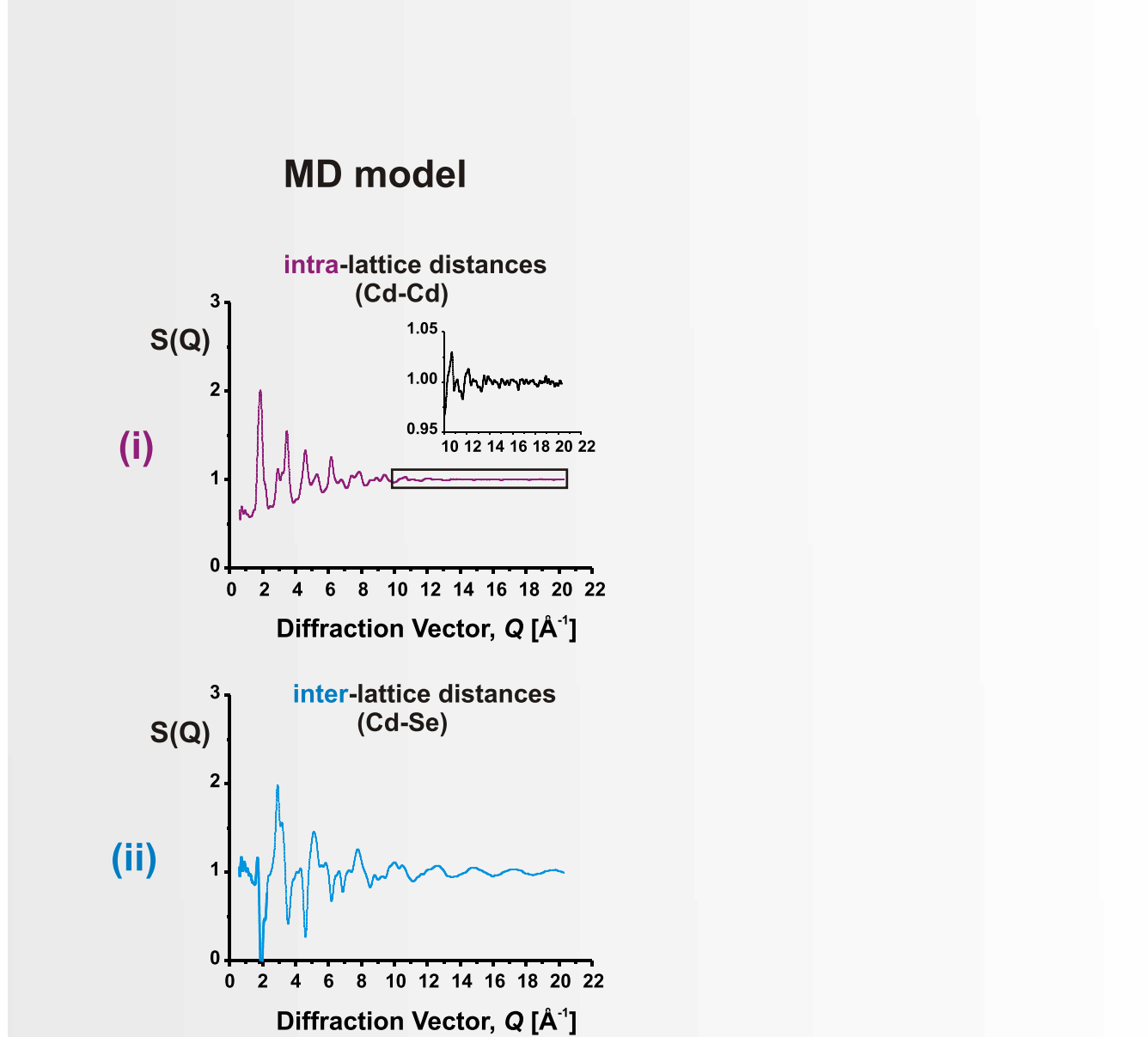
Fig. 1(b) Partial structure factors S(Q) calculated for MD simulated model for (i) intra- and (ii) inter-atomic distances.

On experimental S(Q)s the Bragg reflections are well "visible" up to Q about 10-12 A^{-1}. Above this Q range there is observed a characteristic "waving of intensity" what results from disordering/disturbance of long range order within the grain volume. Similar intensity waves is present on S(Q) calculated for MD simulated model, Fig.1(a)-(iii). This is an indication that MD simulation reproduces the real atomic structure of nano CdSe.

Fig.1(b) shows "partial" S(Q)s calculated for MD model accounting (i) only for **intra**-lattice (Cd-Cd) distances and (ii) only for **inter**-lattice (Cd-Se) distances. While intra-lattice S(Q) shows Bragg reflections up to large Q, the inter-lattice S(Q) shows a strong intensity waving starting from Q about 10 A^{-1}. We conclude that while within each individual sublattice coherence is well preserved, there occurs a unique correlation between Cd and Se sub-lattices which leads to/is responsible for the intensity waves.

## Projection of CdSe nanocrystal in Real Space
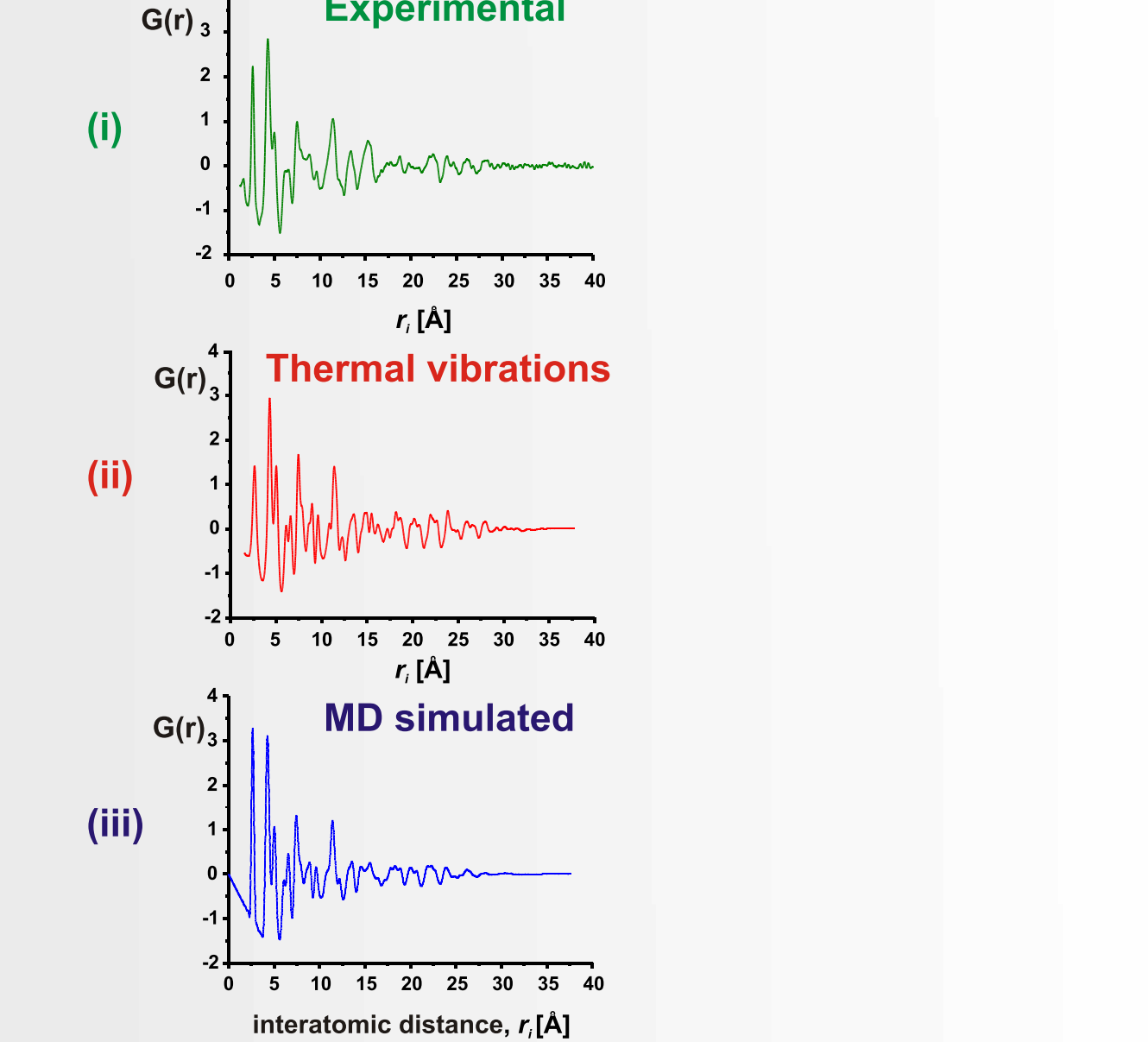
Fig.2(a) Experimental and theoretical Pair Distribution Functions G(r) of 3.5 nm CdSe nanocrystals: (i) experimental, (ii) calculated for a perfect CdSe 4H lattice with 0.3 Å amplitude atomic thermal vibrations, (iii) MD simulated model.
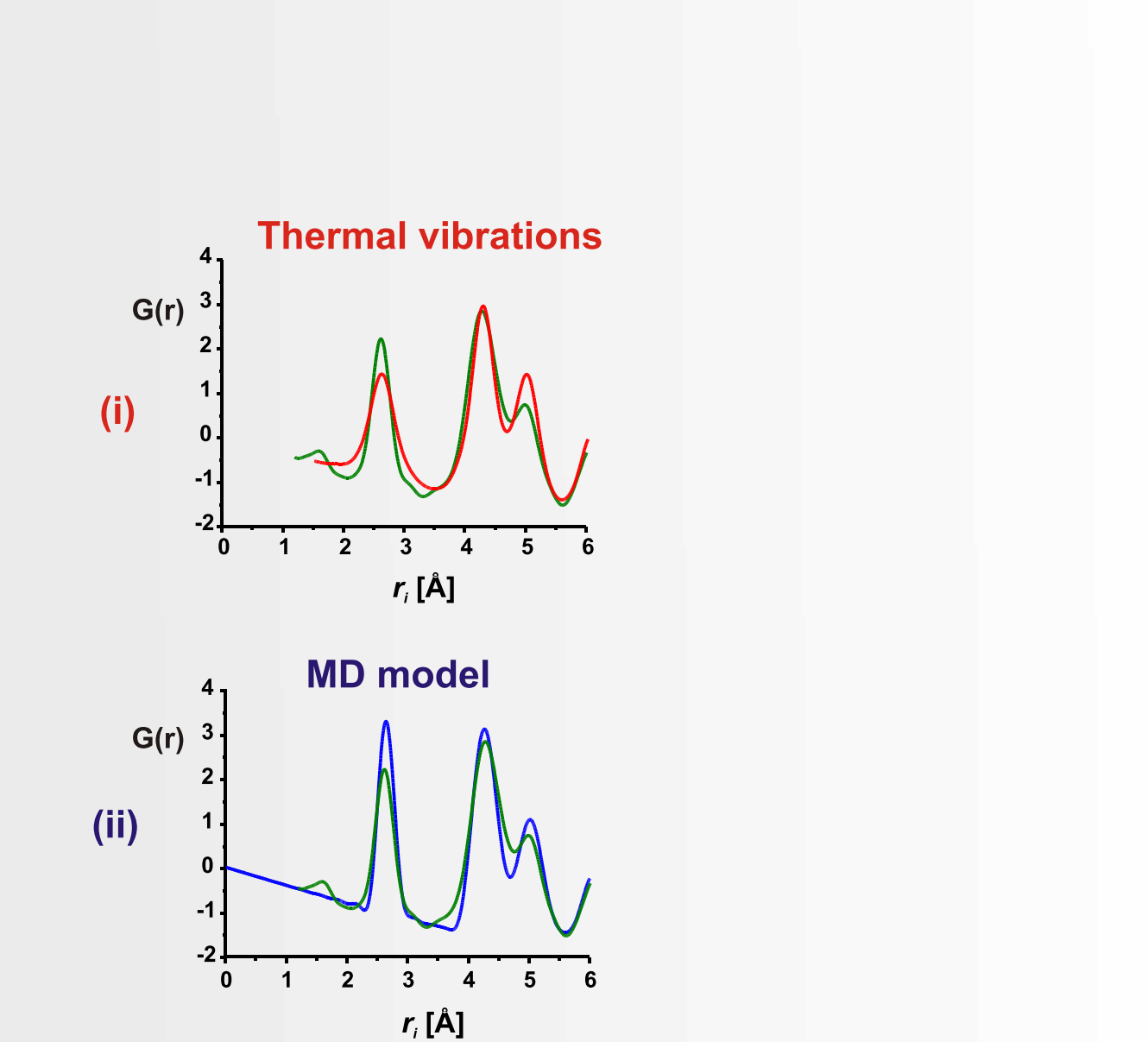
Fig.2 (b) Comparison of first three peaks (inter-atomic distances r_1, r_2 and r_3) at experimental and theoretical G(r)s calculated for (i) a perfect CdSe lattice with atomic thermal vibrations and (ii) MD model.

The overall shape of G(r) of both Fig.2(a) (ii) and (iii) models match well the experimental one. On experimental G(r) width of individual lines is differentiated and the first peak (r_1 distance) is narrower than all other peaks. When searching for an appropriate model matching the real structure of a nanocrystals line width is one of critical criterions. Presence of atomic thermal vibrations leads to same broadening of all G(r) lines, Fig.2(b) and it is evident that such model with thermal vibrations is inappropriate. The MD simulated model reproduces much better experimental G(r) function.

Distribution of inter-planar spacings perpendicular to hexagonal planes
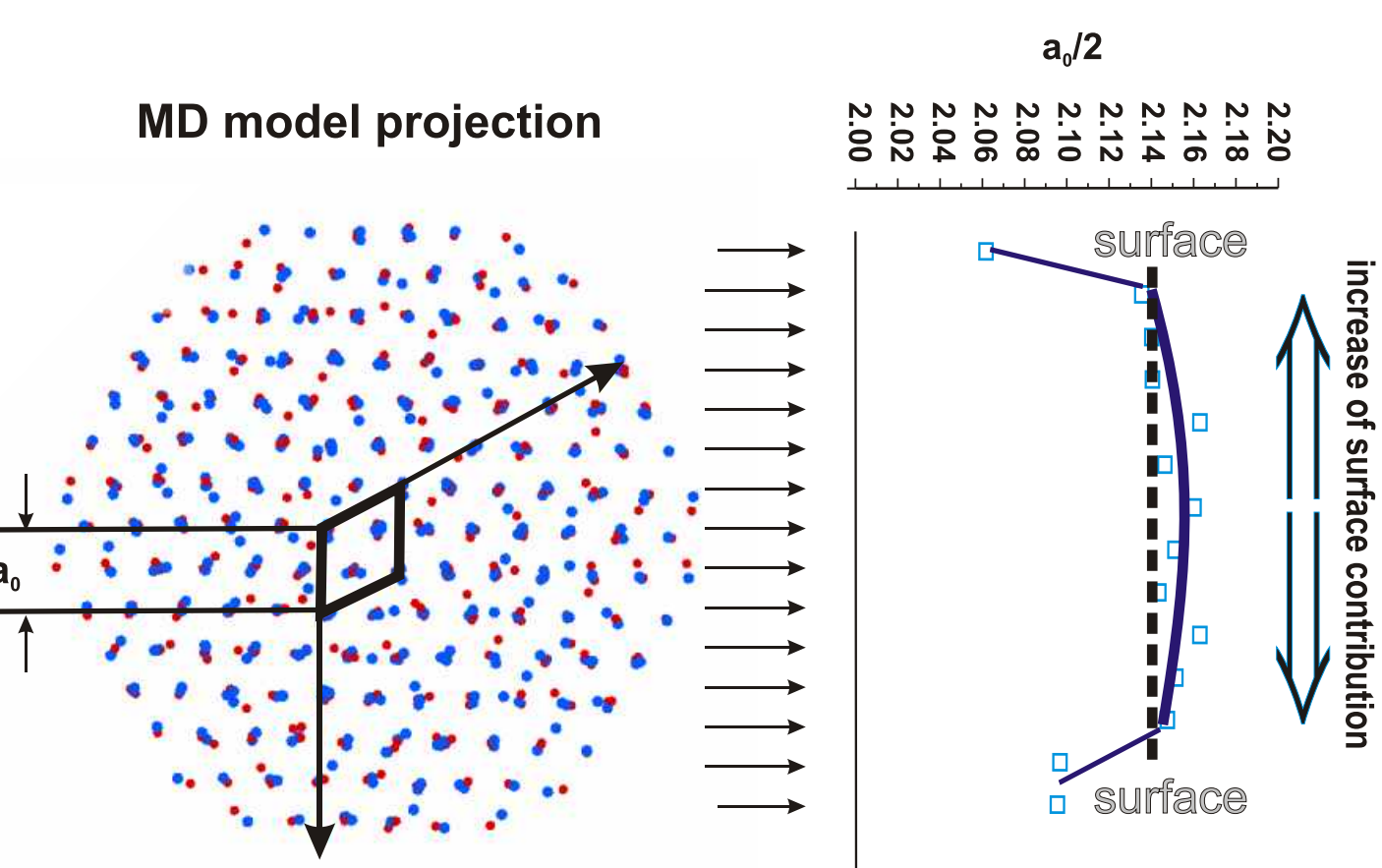
Fig.3 (a) Projection of 3.5 nm CdSe model (4H) along trigonal axis and plot of changes of the inter-planar spacings between the nearest atomic planes which are parallel to trigonal a-axis. Calculations made for all atoms present in the grain. *Note: dotted line corresponds to inter-planar spacing in CdSe crystal*
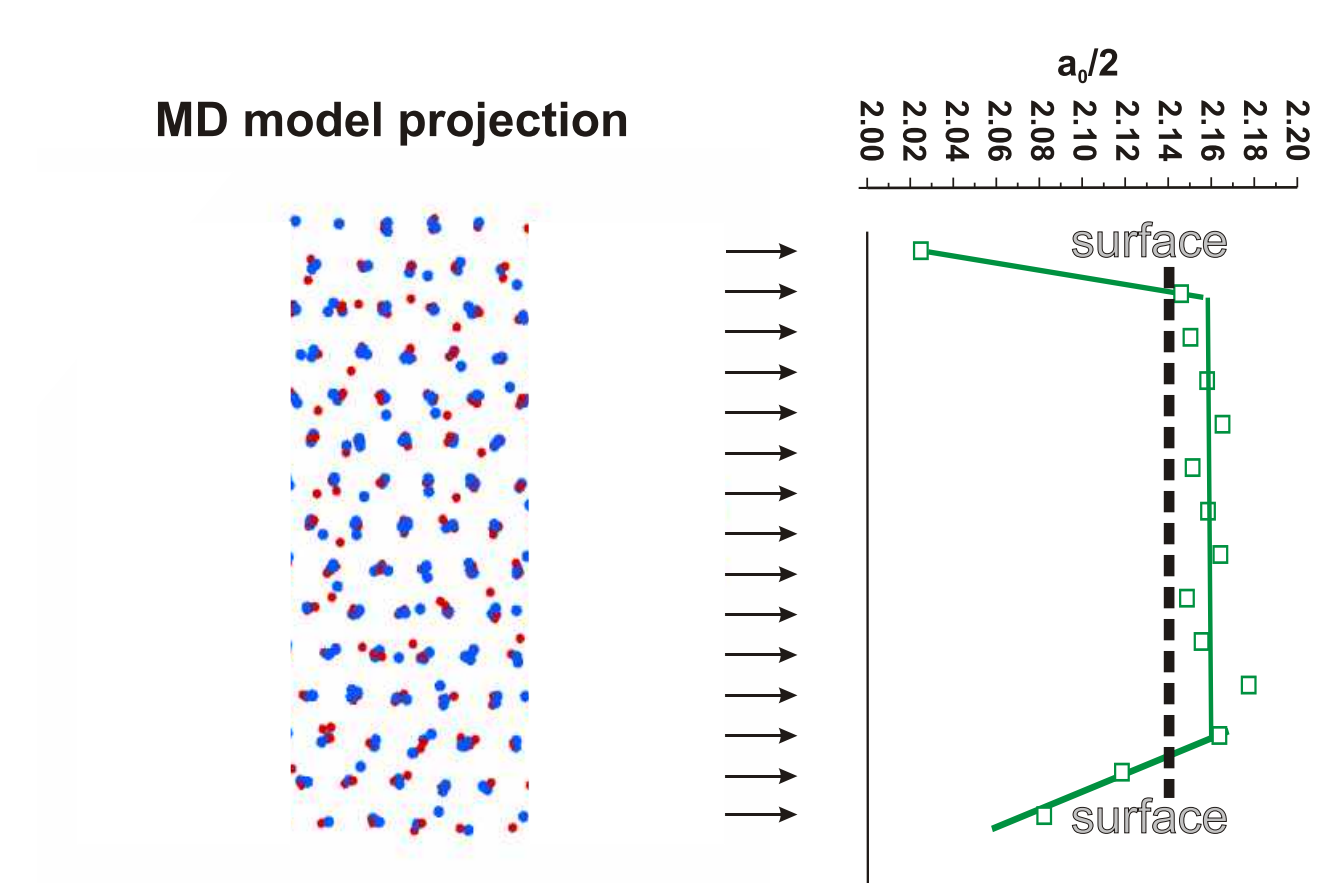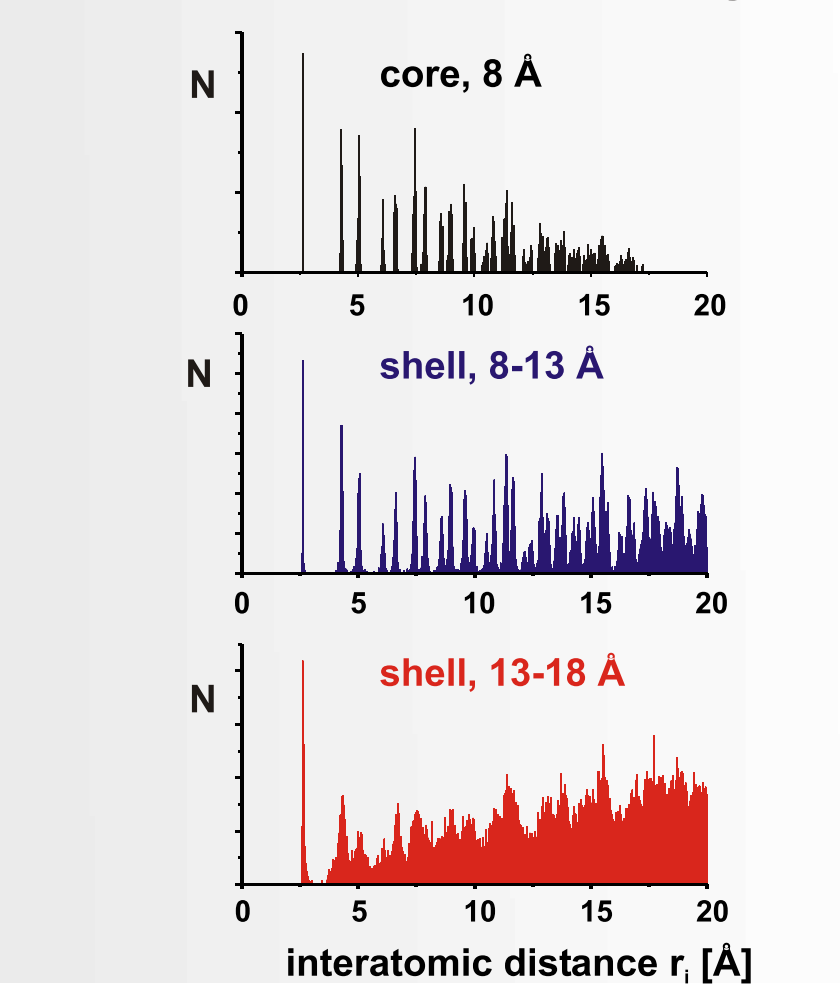
Fig. 3 (b) Projection of 3.5 nm CdSe model (4H) along trigonal axis and plot of changes of the inter-planar spacings between the nearest atomic planes which are parallel to trigonal a-axis. Calculations were made only for the atoms present within cylinder of 12 Å diameter.

Comparison of the calculation procedures applied to Figs. (a) and (b) allows one to evaluate the effect of presence of surface atoms on the calculated positions (centers of gravity) of individual atomic planes, and on evaluation of structure of the surface. The planes which are close to the grain center consist mainly from the atoms located in the inner part of the grain, with relatively small contribution of the surface atoms. Assuming that the surface thickness is the same in all directions, with an increase of the distance of given atomic plane from the center (their overall area decreases) the contribution of the surface atoms increases, up to the last one or two central planes which form the surface. The last points in the plots presented in Figs. 3(a) and (b) correspond to inter-planar spacing within the surface. Figs.3(a) and (b) show that the inter-planar spacing at the surface is about 5% shorter than in core of CdSe grain. In Fig.3(a) the increasing contribution of the surface atoms leads to a little decrease of the calculated average distances between the planes. In Fig.3(b) where the surface atoms are removed, the inter-planar spacings in the direction perpendicular to trigonal axis are same accros the whole grain, up to the surface.
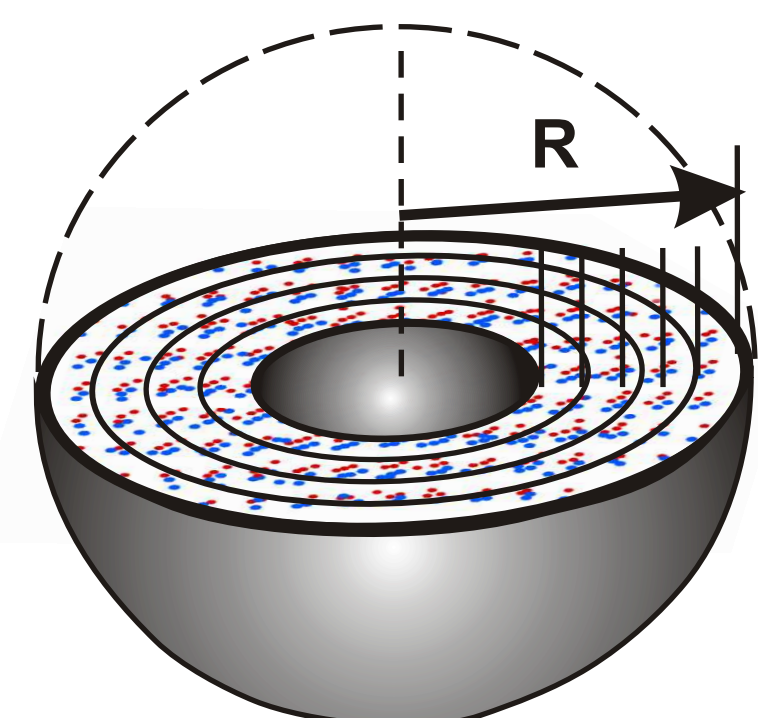
In conclusion, Fig.3 shows very clearly that within the grain volume the average a-distances are well preserved what might be interpreted as that there are no strains present within individual hexagonal atomic planes, except the very last atoms terminating the grains. This observation cannot be interpreted however, that the individual hexagonal planes are strictly flat (planes).

Distribution of inter-layer spacings perpendicular to trigonal axis
(between hexagonal atomic layers)

Fig.4 (a) Projection of 3.5 nm CdSe model (4H) along hexagonal atomic planes and plots of (i) changes of the inter-layer spacings and (ii) u-parameter. Calculations were made for all atoms present in the grain including surface atoms. *Note: dotted line corresponds to distance in CdSe crystal*

Fig.4 (b) Projection of 3.5 nm CdSe model (4H) along hexagonal atomic planes and plots of (i) changing the inter-layer spacings and (ii) u-parameter. Calculations were made for all atoms present in the grain. Calculations were made only for the atoms present within cylinder of 12 Å diameter.

Presence of surface atoms has always an effect on the average inter-layer spacings calculated as distances of "center of gravity" of neighboring atomic layers. However, accounting only for surface atoms is insufficient for explanation of the calculated inter-layer spacings presented in Fig.4.

In Fig.4(a) the largest inter-layer distance is calculated for the layers located close to the grain center, about 3.52 Å. In Fig.4(b) where the surface atoms are rejected, the calculated inter-layer distance is the smallest, about 3.46 Å. Obviously, the real inter-layer distance in the core of the grain is that calculated for Fig.4(b). This is less than that of the reference CdSe crystal and less than in other parts of the grain what shows that the inner core of CdSe grain is compressed relative to its environment; it might look like that there is an internal pressure present in the grain. The distance between the layers which terminate the grain, thus which form the grain surface, is also less than the layers closer to the grain core. This looks again like the surface itself is compressed, relative to the grain volume underneath the surface. The large inter-layer distance showed in Fig.4(b) is clearly not coming from contribution of the surface atoms but from bending (waving) of the hexagonal layers for which the centers of gravity are calculated.

Additional information comes from plots presenting u-parameter which is calculated from inter-layer distances determined separately for Cd and Se hexagonal layers. These plots are similar at Figs.4(a) and (b) what means that they reflect real deformation of CdSe$_4$/SeCd$_4$ tetrahedra.

Shortest inter-atomic distances: *change of bond length in radial direction*

Fig.5 (a) Pair Distribution Histogram (PDH) of different parts of 35Å MD simulated CdSe model

Fig.5 (b) Changes of length and width of first four inter-atomic distanced with the distance from the grain center for MD CdSe model.
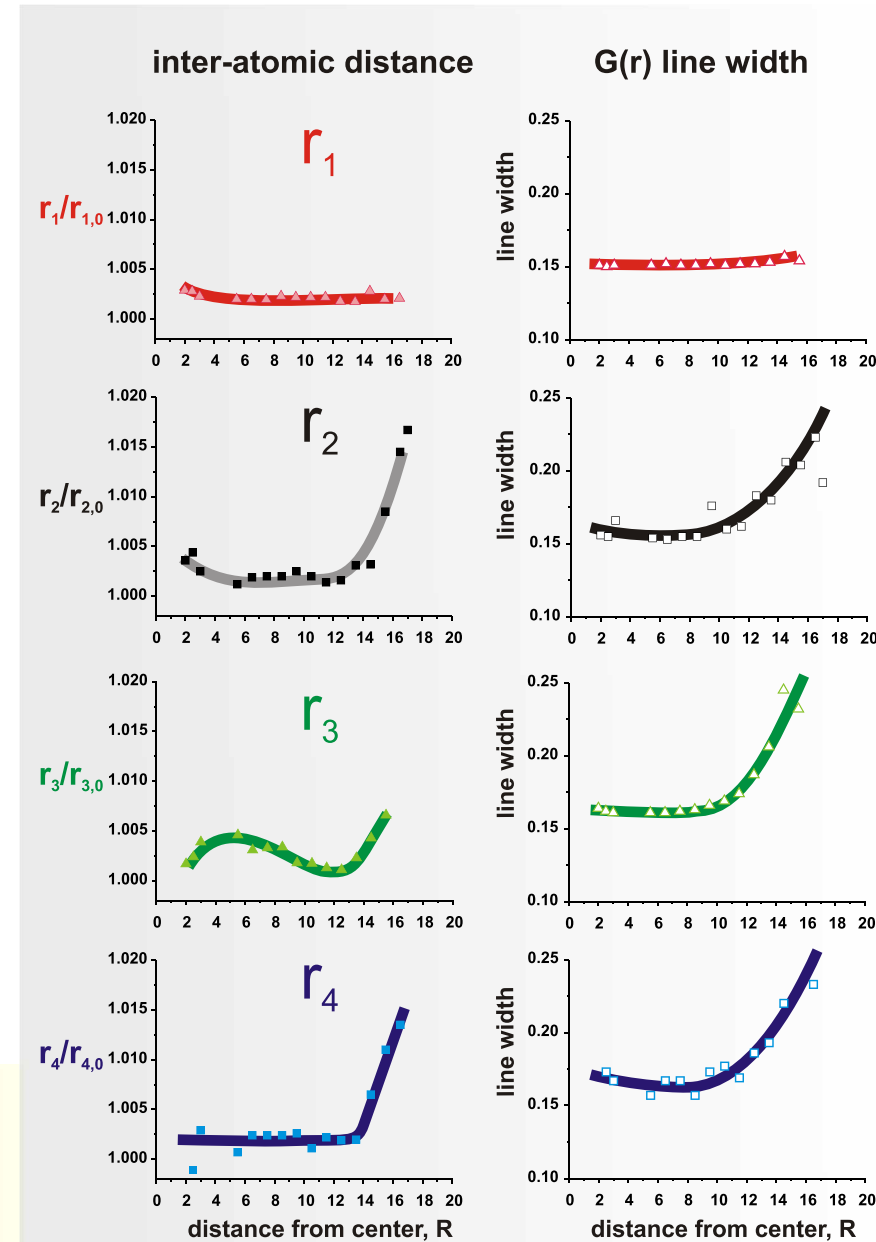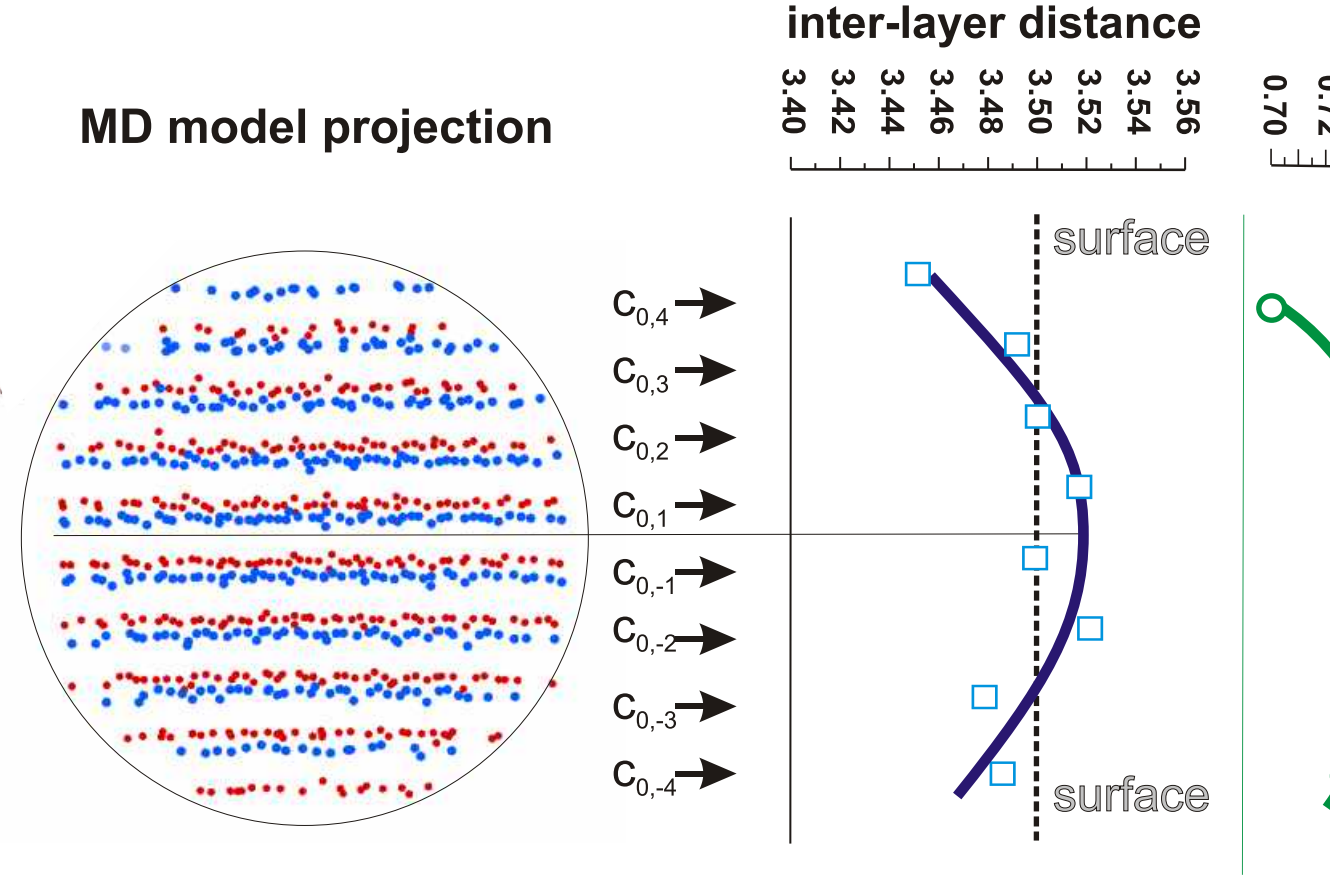
Fig.5(a) shows Pair Distribution Histogram presenting numbers of inter-atomic distances present in given volume part of the grain. In the core all the r-distances are well defined and show nearly no dispersion about the average value. In the 5Å shell around 8Å core there appears a small dispersion about the average r's. In the 5Å thick surface shell there is a very large dispersion which is about 0.5Å, and its much much larger for larger interatomic distances. One cannot discern individual peaks for distances above grain radius.
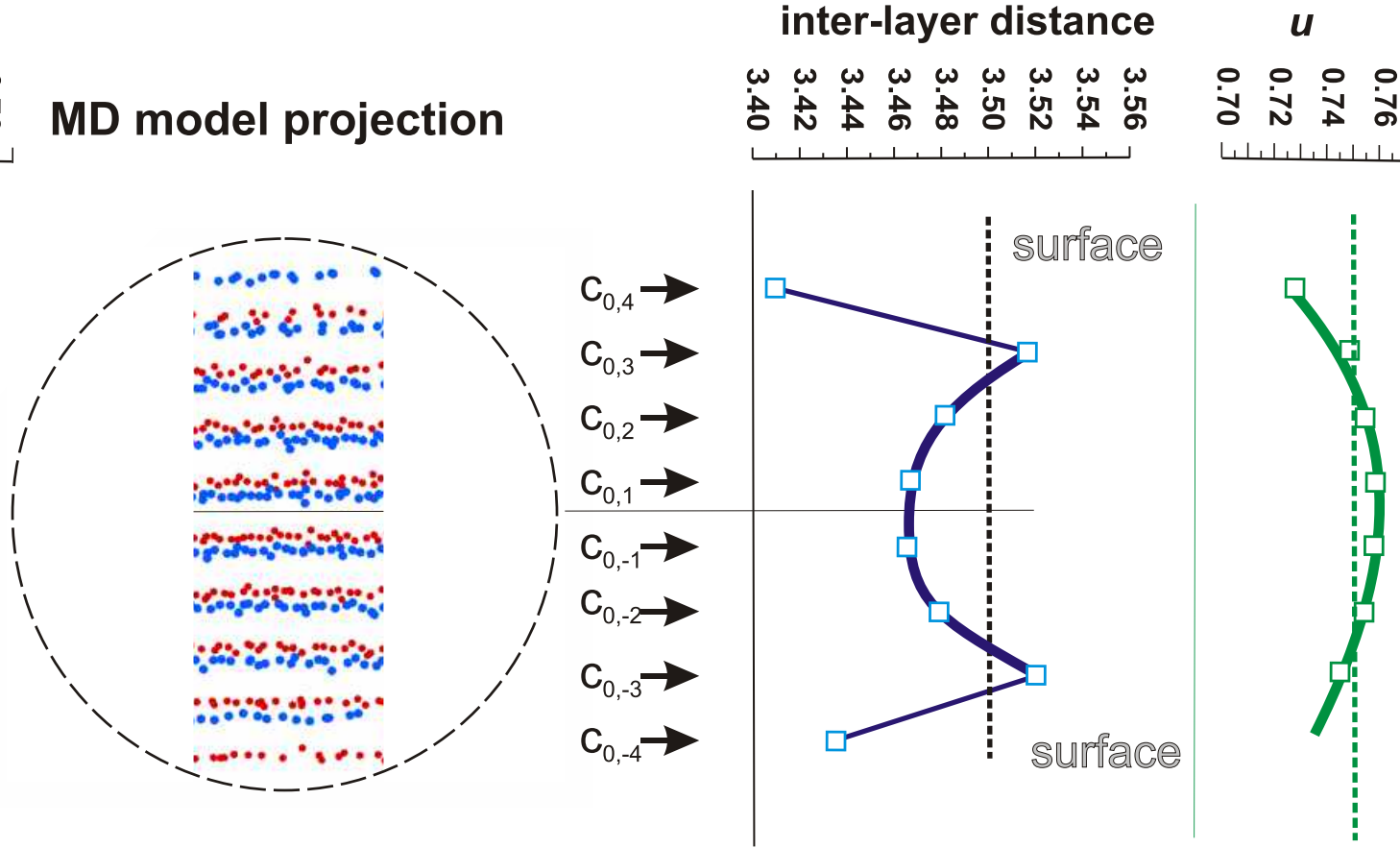
On G(r) a few shortest inter-atomic distances are represented by individual well separated peaks, for which one can determine/refine positions and width with a good accuracy. We subdivided MD models into few Å thick shells and for each shell individually we determined position and width.
Fig.5(b) shows that the shortest inter-atomic distance between Cd and Se, r_1, is same in the whole grain volume. Also width of peak of this atomic pair is same. Larger r-distances show complex shapes what obviously results from anisotropy of the internal structure of CdSe nanograin. Their length increases starting from about 5 Å underneath the grain surface; they are larger at the surface by about 1-2% comparing with the corresponding distances in the grain interior. Along with increase of length of these distances their width also strongly increases what means that their positions are strongly dispersed about the average/equilibrium positions. This is a clear proof of presence of a very strong disorder which increases towards the grain surface. The largest inter-atomic distances are formed by strongly dispersed atoms belonging to the surface and, that's why they appear on G(r) as very broad peaks; broadening of G(r) peaks increase with an increase of the r-distances.

Summary

MD simulated atomic models of CdSe nanocrystals reproduce pretty well the shape of both experimental structure factor $S(Q)$ and $G(r)$ functions.

Analysis of inter-planar spacings shows very clearly presence of anisotropy of the atomic structure of CdSe nanocrystals where individual inter-planar spacings change differently in different directions. There is an indication that hexagonal atomic layers are not planes but are modulated/bent at the surface but also in the grain core. Definitely, the internal structure cannot be described by a single function of density/inter-atomic distances fluctuations with spherical symmetry.

Different relations describe changes of inter-planar spacings and different ones apply to changes of small and large inter-atomic distances within the grain volume. Larger r-distances at $G(r)$ are not well constrained and, therefore, in no case the structure of a nanograin can be „refined" with reference to a single crystal lattice. In the surface layer (~5A thick) short-range order is preserved, while long-range order nearly completely disappears; one might describe the surface as being in an amorphous-like state.

Software

NanoPDF is a program to calculate diffraction patterns and Pair Distribution Functions of nanocrystals and analyze experimental PDF data.

http://www.unipress.waw.pl/soft/crystallography/nanopdf/

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