A new software package to stimulate the pattern of proposed transient chemical structures using the multislice simulation of the Debye-Scherrer diffraction pattern for gold nanoparticles

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ABSTRACT

Introduction: Much recent work in physical chemistry focuses on the ultrafast structural dynamics using new experimental tools like femtosecond electron diffraction. Due to theoretical limitations, an efficient modelling methodology is necessary to help identify and extract information on the structure of the sample under study. **Methods**: A software package was created to implement the multislice method for the purpose of dynamically simulating electron scattering in specimens with arbitrary structure. **Results**: We showed that the simulated Debye-Scherrer diffraction patterns of gold nanoparticles are consistent with experimental results. **Discussion**: Our paper demonstrates a reliant and versatile tool that experimenters can use to simulate the pattern of proposed transient chemical structures. These structures can be compared with data.

KEYWORDS

Ultrafast structural dynamics, Multislice method, electron scattering, Debye–Scherrer diffraction patterns

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INTRODUCTION

Given a substance in some physical state and under a certain set of environmental conditions, describe its properties at any later time when a perturbation is applied. Such is the general form of the riddles that natural scientists face. If the changes are of a chemical nature, the problem can be rewritten in the atomistic framework of a chemical reaction—the transformation of an initial system of molecules (reactants) to a final one composed of alternate molecules (products) via some reaction mechanism. Indeed, one of the grand goals of all theoretical and experimental chemists is to provide a real time view of chemical reactions by resolving nuclear motions that accompany the breaking and forming of chemical bonds in the transition state region of a reaction coordinate diagram (1, 2). However, the challenge lies in the extremely rapid speed at which chemical processes operate.

Two notable techniques exist for characterizing the structural properties of chemical reactions on short timescales: X-ray and electron ultrafast diffraction. Like the strobe lights used in slow motion photography, the periodic ultrafast pulses of probing particles illuminate and capture the atomic structure of matter at an instant in time. Typically, chemical dynamics are initiated with an ultrashort (pump) light pulse and then, at various delay times, the sample is probed in transmission or reflection with an ultrashort electron (5, 4) or x-ray pulse (6). By recording diffraction patterns as a function of the pump-probe delay, it is possible to follow various aspects of the real space atomic configuration of the sample as it evolves during photoinduced structural transformations (Fig. 1). Researchers recently discovered new properties of solid-to-liquid phase transitions using this technique (5).



Fig. 1. Illustration of an ultrafast electron diffraction experiment.

Complementary to these novel experimental techniques is the need for an efficient and robust simulation capability. Computer models allow researchers to generate simulated electron diffraction patterns that are based on suggested structures of transient species (7). These results are compared with those obtained experimentally. To perform a simulation, researchers need a numerical method for solving the electron wavefunction in imperfect crystals using a form of the Schrödinger wave equation. Fortunately, many functional algorithms already exist, among which the multislice theory (9) and the Bloch wave method (10) are the most popular.

In this article, we describe a software package developed to take atomic structural data of a sample as input and generate the resulting electron diffraction pattern using the multislice method. We use our software to investigate the structure of gold nanocrystals as a way to test the software's applicability and consistency. We modelled various structural shapes of gold and compared the resulting diffraction images. We chose gold for the ready accessibility of its published data (11). Although much work has been done previously on the simulation of such images (12, 13, 14, 15), the main interest here lies in the development of reliable simulation software that permits direct and complete control over atomic configuration inputs. Such capability could be applied to experiments involving macromolecules, including biological systems (16).

METHODS

KINEMATICAL DIFFRACTION THEORY

The traditional general diffraction theory starts with a plane wave incident on an atom, ψ_{inc} , of wave vector **k**, which gives rises to another plane wave and an outgoing spherical wave ψ_{scar} :

$$\psi_{scatt}(\mathbf{r}) = f(\Delta \mathbf{k}) \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{|\mathbf{r}|}$$
[1]

$$f(\Delta \mathbf{k}) = -\frac{m}{2\pi\hbar^2} \int V(\mathbf{r}') e^{-i\Delta \mathbf{k} \cdot \mathbf{r}'} d^3 \mathbf{r}' \qquad [2]$$

where $f(\Delta \mathbf{k})$ is the scattering factor for a single scatterer with potential $V(\mathbf{r})$.

In the case of diffraction from a material, the coherently scattered wavelet amplitude from all N atoms in the material can be summed over to get the total diffracted wave $\psi(\Delta \mathbf{k})$:

$$\psi(\Delta \mathbf{k}) = \sum_{j=1}^{N} f(\mathbf{R}_{j}) e^{-i\Delta \mathbf{k} \cdot \mathbf{R}_{j}}$$
^[3]

where \mathbf{R}_{j} is the position vector of atom *j*. This is the kinematical theory of diffraction.

DYNAMICAL DIFFRACTION THEORY

Since the kinematical theory only considers single scattering of electrons, a different approach to scattering is needed in order to include the effects of multiple interactions. To do so, the dynamical theory of diffraction is derived by solving for the electron wavefunction $\psi(x, y, z)$ in the Schrödinger wave equation in a periodic electrostatic potential V(x, y, z):

$$\left[\frac{-\hbar^2}{2m}\nabla^2 - eV(x, y, z)\right]\psi(x, y, z) = E\psi(x, y, z) \quad [4]$$

with $E = \frac{\hbar^2}{2m\lambda^2}$ for purely elastic collisions. By assuming that the specimen is only a minor perturbation to the electron's motion along the z direction, this equation can be approximated in operator form as

$$\frac{\partial \psi}{\partial z} = [A + B]\psi(x, y, z)$$
^[5]

$$A = \frac{i\lambda}{4\pi} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)$$
[6]

$$B = i\sigma V(x, y, z)$$
^[7]

where A, B are non-commuting operators and σ is an interaction parameter. As suggested by Kirkland (21), this equation has the formal operator solution of

$$\psi(x, y, z) = \exp[\int_0^z [A(z') + B(z')]dz']\psi(x, y, 0)$$
[8]

After some further algebraic manipulations, a compact iterative solution can be found in terms of a convolution:

$$\psi_{n+1}(x,y) = p_n(x,y,\Delta z_n)^* [t_n(x,y)\psi_n(x,y)]$$
[9]

where $\psi_n(x,y)$ is the wavefunction after the nth layer of atoms, t(x,y,z) is the transmission function and $p(x,y,\Delta z)$ is the propagator function. Such is the form of the solution that the multislice method is implemented numerically. The action of each steps of the algorithm on the wavefunction is illustrated in Fig. 2.



Fig. 2. Simplified diagram of the multislice method for solving the dynamical scattering problem..

In the software implementation, the wavefunction is recursively transmitted and propagated through each slice until it is all the way through the specimen. The diffraction pattern is simply the modulus square of the Fourier transform $\Psi(k_x, k_y)$ of the exit wavefunction $\psi(x, y)$:

$$\Psi(k_x, k_y) = \mathsf{F}[\psi(x, y)]$$
^[10]

$$I(k_x, k_y)) = |\Psi(k_x, k_y)|^2$$
[11]

DEBYE-SCHERRER DIFFRACTION

If the crystal structure of the specimen is known, the exit wavefunction of the probe electrons can be reliably simulated, and we can compute the resulting diffraction pattern from a particular zone axis. The width of a typical pulse of electrons is 100 μ m while that of a nanoparticle is 10 Å. Thus, the cross sectional area of a pulse can cover on the order of 10⁵ particles. Therefore, such an experimental setup would not generate the spotted diffraction pattern of any particular crystal orientation, but a *Debye-Scherrer diffraction pattern* (22), which consists of a series of concentric rings resulting from summing over the diffraction image of randomly oriented particles (Fig. 4). Such patterns arise for polycrystalline and powdered samples.

The Debye scattering equation of kinematical diffraction elegantly describes the radial intensity density function in powder diffraction patterns:

$$I(\Delta k) = |f(\Delta k)|^2 \sum_{m=1}^{N} \sum_{n=1}^{N} \frac{\sin(\Delta k R_{mn})}{\Delta k R_{mn}}$$
[12]

where the summation is performed over all possible pairs of atoms m, n in the specimen.

In the dynamical theory of diffraction, there is no equivalent expression to Equation [12] for simply computing the scattering intensity function for a random orientation. The multislice method produces the diffraction pattern for a specific orientation (b,k,l) only, $I_{bkl}(\Delta k)$. As illustrated in Fig. 2, an integration over all possible orientations (ϕ,θ) is necessary. This is approximated by a Monte Carlo integration scheme:

$$\bar{I}(\Delta k) = \int_0^{\pi} \int_0^{2\pi} I(\Delta k, \phi, \theta) d\phi d\theta$$
[13]

$$\approx \frac{4\pi^2}{N} \sum_{m=1}^{N} I(\Delta k, \phi_m, \theta_m)$$
[14]

where (ϕ_m, θ_m) are randomly and uniformly selected points on the unit sphere, and N is the number of orientations over which the powder average is taken.

A STRUCTURAL MODEL FOR OUR SPECIMEN

Generating a description of the sample in a form that can be used in a multislice program is the most difficult part of simulating a diffraction pattern. The specimen needs to be described as a sequence of layers (in the x,y-plane), with a spacing between each layer (along the z-axis). Clearly, not all crystals have such convenient structures. Thus, there is no general procedure to generate its multislice description. Fortunately, gold has a relatively simple structure at standard conditions, with a face centered cubic (fcc) unit cell (24).



Fig. 3. A ball-and-stick model of a face-centered cubic (fcc) unit cell with lattice parameter *a*. Adapted from (8).

SIMULATING THERMAL VIBRATIONS IN OUR SPECIMEN At room temperature, the atoms in the specimen vibrate slighty. Even for heavy gold atoms, the root mean square displacement \bar{u} is 0.1414 Å at 300 K (17). Therefore, it is important to be able to model the effects of thermal energy on atomic structures.

A general theory of diffraction in the presence of thermal vibrations is complicated (18, 19). A rigorous treatment would involve the quantization of these oscillations into quasi-particles (phonons) and apply Bose-Einstein statistics. Given such complexity, the frozen phonon approximation is used to numerically simulate the effects of thermal vibrations in the specimen. Here, each atomic position is displaced by a random amount. However, the outputs of a random number generator cannot be used as the thermal displacement directly since they have an uniform distribution. For the technique to be equivalent to the Debye model of the density of states for phonons, the random offsets need to have a standard Gaussian distribution (20) with \bar{u} as its standard deviation. This is accomplished by applying a Box-Muller transformation on the numbers generated.

OUR SOFWARE PACKAGE

We developed a software package using the multislice method to model the electron diffraction patterns of gold nanoparticles, taking into account dynamical effects. To simulate the electron diffraction patterns for the gold nanoparticles that take into account dynamical scattering effects, a software package based on the multislice method was developed in the C language while making use of some pre-existing code published by Kirkland (21). Specifically, our code includes his implementation for parameterizing the Hartree-Fock atomic potentials and for computing the two dimensional discrete fast Fourier transform.

RESULTS AND DISCUSSION

Through a direct application of kinemetical diffraction theory, we computed the position and intensity of all the diffraction peaks of gold. Our results consistently match theory. In particular, the diffraction spots are correctly positioned and have the relative intensity profile as predicted by the equations of the kinematical diffraction theory. Therefore, we argue that our implementation of the dynamical multislice theory is sufficiently capable of generating accurate data at each step of the simulation.

Fig. 5 compares the radial intensity density from experimental measurements with results from our software. The actual data was extracted from Fig. 4, a powder diffraction image of 15 nm gold nanoparticles taken in a transmission electron microscope



Fig. 4. Experimental data (A) TEM image of 15 nm gold nanoparticles (B) the corresponding powder powder diffraction pattern.



Fig. 5. Comparison of radial intensity density from experimental and simulated diffraction patterns.

(TEM). The simulations were made for 50 Å model gold particles at 300 K in a rectangular array. This graph demonstrates our software's ability to match the radial distance and height of the diffraction peaks in experimental data. However, the kinematical peak intensity decreases too rapidly, leading to significant discrepancy for higher order diffractions such as (200). In this aspect, the multislice method seems to provide a better fit with experimental results. Both approaches fail to emulate the decaying background that is featured in the actual diffraction pattern, but this is acceptable as a known consequence of inelastic electron scattering, a type of interaction not included in either kinematical or dynamical theories. Another potential problem is the broadness of the measured peaks in comparison with the relatively narrow peaks of the simulated pattern. This disparity is probably due to the energy and spatial spread of the incoming electron beam, which tends to broaden diffraction peaks (20). These effects were not included in the current simulation since our software assumes the initial wavefunction is a perfectly monochromatic planar wave.

The central peak, denoted with the Miller index (000), is caused either by the part of the electron beam that has directly transmitted through the sample or by fowardly scattered electrons. Figure 6 shows a plot of the central peak's intensity for several elements as a function of specimen thickness. The onset of these oscillations occurs later for aluminum (Z = 13) than for gold (Z = 79) or uranium (Z = 92). Similarly, the smallest overal decay rate of the intensity occurs for aluminum, and the largest for uranium. This limiting behaviour is consistent with the expectation that the kinematic approach to scattering remains valid for a thicker specimen that consists of lighter atoms with a weaker scattering potential.

Figure 6 also depicts the decaying oscillation of the diffraction intensity. Such behaviour is not predicted by the kinematical theory of diffraction. This reflects the need for a dynamical approach to simulating diffraction in thick specimens. The Debye scattering equation assumes that each atom is a single scatterer and that the final wavefunction is just a sum over the scattered wavelets; therefore, the intensity ought to be constant for any specimen depth. In multislice theory, electrons can scatter multiple times. This causes the forward beam to lose intensity as it leaks out and into diffracted beams. However, the diffracted beam can scatter back into the main beam. This leads to the observed oscillations in intensity at (000) (11). Given these multiple scattering events, low order diffractions, which are nominally forbidden, do occur and rapidly sap away the intensity of main beam. However, as the main beam loses intensity, these unusual scattering events become less likely, leading to a stabilization of the beam intensities.



Fig. 6. Comparative plot of the intensity at the (000) point in the simulated diffraction pattern from multislice theory for a film of Al, gold and U. The same lattice structure (fcc unit cell at 4.0782 Å) was used for all three elements.

In Figure 7, we plot the dynamical radial intensity density for different particle diameters. As expected, the overall trend is the progressive sharpening of the diffraction peaks as the size of particles increases. As the number of atoms increases, diffractions favoured by the structure factor rules tend to occur more frequently and thus become increasingly better defined when compared with the kinematically forbidden ones.

Figure 8 plots the dynamical radial intensity density for different interparticle distances. Although no quantitative analysis was made, the main effect of changing the large scale structure of the specimen is an expected broadening of the diffraction peaks. In particular, a decrease in the interparticle distance causes the interference between trans-particle pairs of atoms, and the appearance of high frequency envelope. This peak envelope is simply a sinc function whose frequency is proportional to the interparticle distance.

Figure 9 illustrates the effects of thermal vibrations by comparing the radial intensity density function simulated at different temperatures (0 K, 300 K, 1337 K). Here, the diffraction peaks are observed to be increasingly suppressed as the specimen temperature rises. In addition, the intensity suppression is stronger for higher order diffractions. This is clearly shown in Figure 10, where the intensity of several prominent diffraction peaks is plotted on a logarithmic scale. On this plot, the intensities decrease linearly and do so more strongly for higher order peaks. Both plots are consistent with the effects of the Debye-Waller factor, which has the exponential form e^{-2M} , $M = \Delta k^2 \langle u^2 \rangle$. Therefore, the multislice method, supplemented by the frozen phonon approximation, has correctly reproduced the predicted diffraction features due to thermal vibrations.



Fig. 7. Comparison of dynamical radial intensity density for different gold particle diameters.



Fig. 8. Comparison of dynamical radial intensity density for different gold interparticle distances.

CONCLUSION

Our results demonstrate that our implementation of the multislice approach is sufficient in attaining our stated goal of generating powder diffraction patterns for gold nanoparticles. In particular, comparison between the dynamical and kinematical results show that the former provides a better fit with experimental results. Further analysis shows that the simple Debye scattering equation is not sufficient for modelling diffraction in 50 Å gold clusters since there are significant dynamical corrections. The main corrections were seen to be progressive peak broadening, suppression of (111) peak intensity, enhancement of higher order peak intensity, and inward peak shift.





Fig. 9. Comparison of dynamical radial intensity density for different specimen temperatures.



Fig. 10. Comparison of dynamical peak intensity for different diffraction peaks and specimen temperatures.

Future work entails improving the software package introduced in this article. Some improvements include using complex electron scattering factors (25) to model inelastic scattering, simulating an imperfect initial electron beam by averaging the multislice diffraction pattern over a range of illumination angles to take into account a partially coherent beam (21).

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