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Theory of the spatial resolution of (scanning) transmission electron microscopy in liquid water or ice layers

Niels de Jonge

INM – Leibniz Institute for New Materials, Department of Physics, Saarland University, Saarbrücken 66123, Germany

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ABSTRACT

The sample dependent spatial resolution was calculated for transmission electron microscopy (TEM) and scanning TEM (STEM) of objects (e.g., nanoparticles, proteins) embedded in a layer of liquid water or amorphous ice. The theoretical model includes elastic- and inelastic scattering, beam broadening, and chromatic aberration. Different contrast mechanisms were evaluated as function of the electron dose, the detection angle, and the sample configuration. It was found that the spatial resolution scales with the electron dose to the −1/4th power. Gold- and carbon nanoparticles were examined in the middle of water layers ranging from 0.01—10 µm thickness representing relevant classes of experiments in both materials science and biology. The optimal microscope settings differ between experimental configurations. STEM performs the best for gold nanoparticles for all layer thicknesses, while carbon is best imaged with phase-contrast TEM for thin layers but bright field STEM is preferred for thicker layers. The resolution was also calculated for a water layer enclosed between thin membranes. The influence of chromatic aberration correction for TEM was examined as well. The theory is broadly applicable to other types of materials and sample configurations.

1. Introduction

Obtaining morphological information of specimens at the nanoscale is essential for developments in materials science, and nanotechnology, to understand chemical processes at interfaces, and to gain insights into the molecular machinery of life enclosed in the three-dimensional (3D) structure of proteins and the ultrastructure of cells. Transmission electron microscopy (TEM) has traditionally been associated with the study of ultra-thin solid samples in vacuum, achieving atomic resolution. Sub-Angstrom spatial resolution is even possible using scanning TEM (STEM) [1]. Already since the early days of electron microscopy, scientists recognized the importance to image under hydrated conditions such to maintain samples in realistic conditions [2], which is of particular importance for biological cells, proteins, water batteries, catalytic nanoparticles, and biominerals [3–7]. TEM and STEM under hydrated conditions is achieved by maintaining the specimen in amorphous ice [8], and also electron microscopy of liquid water has become available with nanometer resolution in the past decade [4]. Of advantage for obtaining nanometer resolution in liquid-phase STEM is that the anticipated broadening effect on the resolution of Brownian motion appears to be largely reduced under certain experimental conditions [9].

But despite the broad usage of STEM and TEM, it is often unknown what spatial resolution is possible for a specific sample, and, in addition, the choice between TEM or STEM is not always obvious. The optimal spatial resolution of TEM is traditionally calculated for a thin sample in vacuum imaged with phase contrast [10]. For STEM, the point spread function in vacuum is usually considered, which is of sub-Angstrom dimensions for aberration-corrected instruments [11]. For specimens in water, however, it is often impossible or undesirable to prepare an ultra-thin sample, so that the resolution becomes limited by other factors, such as spatial broadening and broadening of the energy spread of the electron beam due to electron scattering in the water layer. Moreover, these specimens are typically dose sensitive so that the signal-to-noise-ratio *SNR* and not the intrinsic resolution of the electron optics becomes the limiting factor [4,12] .

Here, a theoretical framework is provided for calculating the optimal spatial resolution for TEM and STEM in liquid water or amorphous ice as function of the different microscope settings and sample parameters. The aim of these calculation is to estimate the achievable resolution within a factor of two, which will be sufficient in many instances to optimize experimental designs for the best possible resolution for a given sample. Higher precision would require more complex theoretical models [13,14]. The model includes the electron optical resolution, the signal-to-noise limited resolution, beam broadening, the type of material, and the

E-mail address: niels.dejonge@leibniz-inm.de

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sample geometry. The calculations are based on analytical expressions of elastic- and inelastic electron scattering in a specimen [10]. For certain experimental configurations full analytical solutions are possible [15] but typically these solutions involve approximations, such as applying Taylor series or neglecting inelastic scatting [16]. Alternatively, it is possible to simulate the scanning of an electron beam over a three-dimensional (3D) sample using Monte Carlo simulations [17,18]. Monte Carlo simulations provide precise calculations of the spatial resolution of, for example, bright field- or dark field STEM in thick specimens [19]. However, these are more time consuming, and require a fixed sample geometry so that they are less flexible, and moreover they are not applicable to TEM. The approach shown here is to numerically solve the analytical expressions. This is quicker and more flexible than Monte Carlo simulations but more precise than deriving full analytical solutions. The following section will introduce scattering contrast, beam broadening, and energy broadening. The optimal resolution for STEM and TEM will then be determined including the electron dose as important factor. Examples will be calculated for both dark field- and bright field STEM, and for TEM of nanoparticles of either gold or carbon in a water layer. These represent two key classes of relevant experiments, namely the study of nanomaterials of high atomic number (Z) in water, and the imaging of low-Z biological- or polymeric samples. The resolution will be examined as function of the water thickness, the vertical position of the nanoparticles in the sample, and the electron dose. These examples serve as guide for choosing between TEM and dark field- or bright field STEM. The influence of enclosing a water layer by membrane windows on the resolution will be calculated, and the possible benefit of chromatic aberration correction in TEM will be discussed as well.

2. Theory

2.1. Electron microscopy configurations

Two electron microscopy modalities are available, STEM and TEM, for observing nanoscale objects (e.g., nanoparticle, protein) embedded in a layer of water. Each modality requires a different optimization of the experimental setup (Fig. 1). Liquid water layers are enclosed by thin windows [4], and these are included in the calculations for precision. For STEM, the highest resolution is obtained for objects in the top of the water layer with respect to a downward traveling electron beam [4,12]. The STEM images are primarily formed by electrons that are elastically scattered by an angle larger than the opening semi-angle β of the annular dark field (ADF) detector. The probe size of the STEM in vacuum is typically much smaller than the achieved resolution, because the resolution is limited by the signal-to-noise-ratio in the image for objects in the top of the water layer and by beam broadening due to electron scattering for objects deeper in the water layer [12]. For the calculations below, it is assumed that the objects under observation are in the focal plane for STEM so that geometric beam broadening can be neglected.

The highest resolution is obtained for objects at the bottom of the water layer for TEM [4]. The opening semi-angle of the scattered electron beam α is set by the objective aperture. The resolution is determined by several factors including chromatic aberration of the objective lens and the energy spread of the beam that is broadened by scattering in the water layer [4]. It is assumed in the following that the defocus is adjusted at the Scherzer optimum.

2.2. Electron scattering principles

2.2.1. Electron scattering cross sections

In order to calculate scattering contrast in TEM or STEM, both elastic- and inelastic electron scattering are considered. Elastic scattering dominates dark field contrast for larger detection angles. Inelastic scattering mostly leads to small angular deviations and needs to be included for calculations involving small angles (below 10 mrad). For typical settings, elastic scattering is calculated using the partial cross section for elastic scattering $\sigma_{el}(\theta)$ assuming a screened Rutherford scattering model based on a Wentzel potential for single scattering events by an angle θ or larger [10]:

$$\sigma_{el}(\theta) = (1/\pi)Z^{4/3}\lambda^2(1+E/E_0)^2\frac{1}{1+(\theta/\theta_0)^2} \quad (1)$$

with atomic number Z, electron energy E, and the relativistic wavelength of the electron:

$$\lambda = \frac{hc}{\sqrt{2EE_0+E^2}} \quad (2)$$

with Planck's constant h, the speed of light c, and the rest energy given by:

$$E_0 = m_0c^2 \quad (3)$$

with the rest mass of the electron m_0. The characteristic angle is given by:

$$\theta_0 = \frac{\lambda Z^{1/3}}{2\pi a_H} \quad (4)$$

with Bohr radius a_H.

The scattering cross section for inelastic scattering is given by Reimer and Kohl [10]:

$$\sigma_{inel}(\theta) = (4/\pi)Z^{1/3}\lambda^2(1+E/E_0)^2 \times\left[\frac{-1}{4(1+(\theta/\theta_0)^2)}+\ln\sqrt{1+(\theta_0/\theta)^2)}\right] \quad (5)$$

The total cross section is then obtained via [10]:

$$\sigma(\theta) = \sigma_{el}(\theta)+\sigma_{inel}(\theta) \quad (6)$$

2.2.2. Scattering by a specimen

To calculate dark field scattering contrast, the amount of electrons N scattered by θ or larger for a certain thickness of a material t is obtained as follows [10]:

$$\frac{N}{N_0} = 1-e^{-t/l(\theta)} \quad (7)$$

with N_0 the number of incident electrons, and the mean-free-path length for elastic scattering $l(\theta)$ given by:

$$l(\theta) = \frac{W}{\sigma(\theta)\rho N_A} \quad (8)$$

with mass density ρ, the atomic weight W and Avogadro's number N_A. Note that $l(\theta)$ depends on the detector opening angle because scattering events leading to scattering at higher angles occur less frequently. Thus, a longer mean free path between scattering events applies for scattering into larger angles. Eq. (8) not only applies for single elements but also for molecules comprising of different elements. The mean-free-path length for molecules is calculated from averaging the different values of W weighted by molar fractions, ρ is usually known in literature, and an average σ is calculated from $\sigma(\theta)$ for each element and accounting for the molecular fractions [12,15,20,21]. For water one thus obtains:

$$\sigma_{el,H_2O}(\theta) = 0.67\sigma_{el,H}(\theta)+0.33\sigma_{el,O}(\theta) \quad (9)$$

Alternatively, the average $\langle Z\rangle$ value of a molecule can be used, which equals 4.7 for water, and was shown to accurately describe experimental data [12,20].

Bright field scattering contrast is calculated from the amount of electrons *not* scattered by θ or larger M [10]:

$$\frac{M}{N_0} = e^{-t/l(\theta)} \quad (10)$$