



Predicting EXAFS signals from shock compressed iron by use of molecular dynamics simulations

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ABSTRACT

Simulated EXAFS signals from ab initio models and configurational averaging of molecular dynamics (MD) data are compared for α -Fe, and configurationally averaged MD EXAFS signals are compared with experimental data for iron shock compressed to pressures above the α - ϵ transition pressure. It is shown that molecular dynamics potentials and ab initio models capable of recreating similar vibrational density of states lead to EXAFS signals in good mutual agreement. The effects of the classical nature of the phonon distribution in the MD and the anharmonicity of the potential give rise to noticeable differences between ab initio models and configurational averaging of MD data. However, the greatest influence on the spectra is the form of the potential itself. We discuss the importance of these effects in simulating EXAFS spectra for shock compressed polycrystalline iron. It is shown that EXAFS is an insensitive probe for determining the nature of the close packed product phase in this system.

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1. Introduction

One method to produce matter with high energy densities is through shock compression where the application of transient pressures close to a megabar in solids typically impart a good fraction of 10^{11} J m⁻³ to the sample. Over recent years molecular dynamics (MD) has become an important tool for studying material under such conditions [1,2]. These simulations, although based on semi-empirical inter-atomic potentials, show phenomena which are in qualitative, and often quantitative agreement with experiment. The continued growth in computing power has allowed simulation of the lattice response in crystals of over 10^8 atoms in size for times of order up to hundreds of picoseconds [3]. These time and length scales are starting to become directly comparable with those employed in experiments that use ultra-short pulses of X-rays to interrogate the lattice response of materials subject to shock compression, with the lattice response being diagnosed by either X-ray diffraction or the recording of extended X-ray

absorption fine structure (EXAFS) [4,5]. Given this convergence of conditions between experiment and simulation, several authors have started to make direct comparisons between the instantaneous diffraction signals that one can predict from the MD, and experimentally recorded diffraction patterns [3,6–8]. However, despite a wealth of extant research on liquid and gaseous systems [9], relatively little work has been undertaken in calculating the EXAFS signals from solids by directly using the atomic positions supplied from MD simulations.

From the standpoint of studying shock or ramp-compressed solids, the motivation to use MD simulations to predict EXAFS signals, rather than (or as well as) conventional methods, stems from the fact that the compressed state can be highly defective [1], contain regions of rapidly varying shear strain (especially throughout the shock or ramp front), or it can be in a mixture of phases with considerable structure on the nanoscale [10]. All of these effects make it difficult to determine exactly what parameters should be used in a conventional EXAFS simulation (which is based on the coordinates of a ‘typical’ unit cell). Such conditions are far from those pertaining in a perfect crystal, and thus, at least under certain conditions, we might expect a more accurate representation of an experimentally recorded EXAFS signal to be made by

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exploiting predictions of atomic coordinates, rather than by the conventional methods that assume perfection of the crystal, save for thermal effects. Of course, such conditions need not necessarily only pertain to shocked solids, but to many other systems of mixed phase solids or polycrystals where significant effects due to grain or crystallite boundaries may prevent simple methods such as the summation of perfect crystalline EXAFS signals from being used.

The purpose of this paper is twofold: first we give further details of how we calculate simulated EXAFS for iron shock compressed above the α - ϵ (bcc to hcp) transition pressure. Such calculations have recently been compared with experimental data, recorded on nanosecond time-scales, of laser-shocked iron [10]. Second, given that direct calculation of EXAFS from solid state MD is a relatively undeveloped approach (although the differences between predictions based on MD data have been explored elsewhere for liquid/glass systems [11], and homogeneous solid systems [12], often by cumulant analysis), we note the differences that may arise between ab initio approaches and MD due to the classical nature of the potentials. As we show below, by far the largest uncertainty in the accuracy of the MD approach for shocked solids is likely to be associated with the potential used, given that potentials that correctly model the room temperature phonon distribution may fail to capture the pertinent physics under shock compression, and the potentials that are used under shock conditions for iron are difficult to experimentally verify at the relevant conditions.

The paper is laid out in the following manner: in Section 2 we discuss the underlying theory of predicting EXAFS signals via both ab initio and configurational averaging from MD. Section 3 discusses the simulation of EXAFS signals from single crystal Fe, in particular the difficulties arising at low temperature and when using a potential which may not accurately recreate the material's vibrational density of states. Section 4 applies the findings of the previous sections to a poly-morphic shocked product phase in Fe and compares the results to experimental data.

2. FEFF and MD calculations

EXAFS is often used to probe structural properties of condensed matter and so direct simulation of EXAFS signals could be a powerful diagnostic tool [13,14]. This technique involves observing the modulation of the X-ray absorption cross-section at wave numbers a few \AA^{-1} above an absorption edge caused by interference between the outgoing and the back-scattered components of the photoelectron wave function. The back-scattered component contains information on the structural, dynamic and chemical state of the surrounding atoms and so the EXAFS signal contains a wealth of information on the microscopic environment within the crystal. The standard result for the modulation to the susceptibility seen in EXAFS as a function of the incident X-ray wave vector, k , is of the form

$$\chi(k) = \sum_j S_0^2 F_j(k) e^{-2\sigma_j^2 k^2} e^{-r_j/\lambda_i} \frac{\sin(2kr_j + \phi_{ij}(k))}{kr_j^2} \quad (1)$$

where r_j is the displacement between the core atom and its j th neighbour, S_0^2 is an amplitude reduction factor accounting for multi-electron effects on the ionised core, $F_j(k)$ is a backscattering amplitude, σ is a mean square relative displacement of atoms in the scattering path, with $e^{-2\sigma_j^2 k^2}$ being the Debye–Waller factor accounting for temperature effects and static disorder, λ is the photoelectron mean free path, e^{-r_j/λ_i} being an amplitude reduction factor for inelastic scattering losses and $\phi_{ij}(k)$ represents the phase shifts of the photoelectron wave function due to scattering.

It is an implementation of an equation of the form of Eq. (1) which constitutes the core of the FEFF code – a standard ab initio EXAFS package used in both prediction and post-processing of EXAFS signals [15]. Although FEFF is, strictly speaking, a code for calculating the amplitude and phase contributions from the various scattering paths within the sample, FEFF8 provides numerous models to account for thermal motion in the crystal. The simplest such approach uses a correlated Debye model to account for temperature effects on the EXAFS spectrum [19]. The size of the RMS deviation of the atoms is determined by Debye theory and is therefore based on the quantum mechanical Bose–Einstein statistics. We must supply the code with both a temperature for the sample and the material's Debye temperature to allow the Debye–Waller factor to be calculated. In this model the thermal displacement of atoms is assumed to have a spherically symmetric distribution with a Gaussian cross-section, which will clearly be a poor approximation in applications where anisotropy is of importance. Furthermore, the correlated Debye model is not directionally dependent.

Two methods designed to address the issue of directionality are the equation of motion method (EMM) and recursion method (RM), the details of which are described elsewhere [16,17,27]. Both of these methods calculate a vibrational density of states (VDOS) based on a number of force constants provided to the FEFF code. The force constants are parameterized by inter-atomic distance allowing an effective directional dependence to be applied. EMM proceeds by a simple integration of Schrödinger's equation not dissimilar in principle to a quantum MD. The recursion method constructs a delta function representation of the VDOS based on eigenstates of the Hamiltonian of the system. These methods allow for directionality but still do not address the issue of anharmonicity as each bond is treated as being harmonic in the current implementation of FEFF (although suggestions on how to account for anharmonicity have been put forward [18]).

Although it is clear that none of the extant models are fully adequate to describe a solid state system, it has been shown that RM and EMM both produce estimates of vibrational amplitude consistent with experiment [19] leading to EXAFS signals comparable to those obtained experimentally, at least when within the harmonic limit. Although EMM may be considered the more natural choice for crystals, the recursion method implementation in FEFF is more mature. For the remainder of this paper all theoretical EXAFS signals not directly calculated from MD will have their thermal effects accounted for by the recursion method using force constants derived from neutron scattering data [20].

These approaches based on a single FEFF scattering calculation in a perfect crystal are comparatively fast, requiring only one pass through the code to generate a complete EXAFS signal. However, systems with more than one inequivalent atomic site will require, to a first approximation, a weighted summation of the EXAFS signals for each absorbing atom type.

In contrast, in the MD approach we supply both initial positions and velocities for all of the atoms in the system. The initial velocities will usually be randomly generated with a distribution consistent with the desired initial temperature of the system. The trajectories of the atoms are then calculated over a few picoseconds by integration of Newton's equations until a stable (thermalised) state has been reached. In order to determine an EXAFS signal from the MD data we perform a configurational average over a representative sample of the atoms (usually of order a few thousand in this paper). Each atom is taken in turn to be the core ion for an FEFF scattering calculation and the resultant spectra are summed incoherently to give a simulated signal for the whole sample. In this case the Debye–Waller factors are not added into Eq. (1), but accounted for by the ensemble averaging. This approach is very

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