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Generation of phonon density of states and thermal scattering law using ab initio molecular dynamics

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ABSTRACT

The operation and safety of thermal nuclear reactors is dependent on the ability to accurately predict the thermal neutron spectrum; a distribution which is correlated to the inelastic thermal neutron scattering cross-section of the neutron moderator. The inelastic thermal neutron scattering law, $S(\alpha,\beta)$, of a moderator is a fundamental property of the material describing the permitted vibrational excitations of the atoms, i.e. phonons, and may be calculated using atomistic methods. The current state-of-the-art *ab initio* lattice dynamics (AILD) methods have been used to calculate phonon density of states (DOS) at 0 K for use in the generation of $S(\alpha,\beta)$ under reactor conditions. Modern computational power, however, has made accessible *ab initio* molecular dynamics (AIMD) methods. The AIMD technique captures temperature effects and permits the calculation of the phonon DOS from first principles. This is in contrast to AILD, where temperature effects are lacking, and classical molecular dynamics methods that use semi-empirical force fields. The aim of this work is to demonstrate the use of AIMD in the generation of the phonon DOS for beryllium as an exemplar moderating material. The phonon DOS was computed from AIMD simulations at 300 K and compared to AILD. Subsequently, $S(\alpha,\beta)$ and the inelastic scattering cross-section were generated using the NJOY package for both methods. The predicted phonon DOS and inelastic scattering cross-section for the AIMD method were found to be consistent with those predicted using AILD.

1. Introduction and theory

The ability to accurately predict the thermal neutron spectrum in thermally driven nuclear reactors is paramount to its operation and safety. Thermal neutrons have de Broglie wavelengths on the order of the interatomic distance in matter and are therefore strongly influenced by the atomic structure and dynamics of the material. Consequently, the double-differential thermal neutron scattering cross-section, using the first Born approximation and Fermi's pseudo potential is given by (Squires, 1978),

$$\frac{\partial^2\sigma}{\partial\Omega\partial E'} = \frac{1}{4\pi k_B T}\sqrt{\frac{E'}{E}}[\sigma_{coh}S(\alpha,\beta) + \sigma_{inc}S_s(\alpha,\beta)] \quad (1)$$

is a function of the thermal scattering law (TSL, i.e., $S(\alpha,\beta)$). The 'self-part' of the TSL is S_s. The bound coherent and incoherent nuclear cross-sections are σ_{coh} and σ_{inc}, respectively. For typical solid nonhydrogenous reactor materials (e.g. Be, graphite, BeO) the nuclear incoherent cross-section is negligible (Sears, 1992). The double differential scattering cross-section of a neutron of incident energy E, describes the probability that a neutron scatters to energy E' through solid angle Ω by an exchange of energy and momentum with the atomic structure of a material with a bulk temperature, T. Momentum and energy exchange between neutrons and atoms are represented by α and β, respectively. These dimensionless variables are defined as,

$$\beta = \frac{E' - E}{k_B T}$$
$$\alpha = \frac{E' + E - 2\mu\sqrt{EE'}}{Ak_B T} \quad (2)$$

where A is the nucleus to neutron mass ratio, and μ is the scattering cosine.

The TSL has contributions from non-interference effects (self-part S_s) and interference effects (distinct-part S_d) (Hawari et al., 2004; Hehr, 2010),

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$$S(\alpha,\beta) = S_s(\alpha,\beta) + S_d(\alpha,\beta). \quad (3)$$

Although both the self-part and distinct parts have elastic and inelastic contributions, the distinct contributions to inelastic scattering are generally negligible (Hawari, 2014; MacFarlane, 1994). Consequently, inelastic scattering is often predicted from the self-part. In crystalline materials the self-part is dependent on the behavior of lattice vibrations (i.e. phonons). The resulting scattering law may be evaluated using the phonon expansion (Rössler, 2004; Hawari et al., 2004; Hawari, 2014; MacFarlane, 1994; Koppel and Houston, 1968),

$$S(\alpha,\beta) = ({}^0S_s + {}^0S_d) + \sum_{P>0} {}^PS_s \quad (4)$$

where, the superscript indicates the number of phonons emitted or absorbed during a single scattering event. The 0-phonon contributions are elastic, whereas $P > 0$ are inelastic. Typically atomic motion in a crystalline material may be assumed to be nearly harmonic. Furthermore, each atom may be assumed to vibrate in a manner which is relatively independent of other atoms (incoherent approximation) and to be isotropic (cubic approximation). Within these approximations the scattering law of a moderating material may be estimated with the vibrational or phonon density of states (DOS), through the phonon expansion as (MacFarlane, 1994)

$${}^PS_s(\alpha,\beta) = \exp(-\alpha\lambda)\frac{(\alpha\lambda)^P}{P!} \times F_P(\rho(\beta),\beta,T) \quad (5)$$

where the functional F_P describes the phonon emission and absorption processes. Each functional is a temperature dependent convolution of the phonon DOS, $\rho(\beta)$, to the corresponding phonon order. The Debye-Waller factor, λ, is a measure of the mean-squared displacement of the atom due to thermodynamic vibration and T is the bulk crystal temperature. The 1-phonon functional F_1 and the general form of the functional F_P are formulated for an atom of mass M as

$$F_1(\rho(\beta),\beta,T) = \frac{\rho(\beta)\exp(-\beta/2)}{2\lambda\sinh(\beta/2)} \quad (6)$$

$$F_P(\rho(\beta),\beta,T) = \int_{-\infty}^{\infty} \mathrm{d}\beta' F_1(\rho(\beta'),\beta',T) F_{P-1}(\rho(\beta-\beta'),\beta-\beta',T) \quad (7)$$

The phonon DOS is a fundamental property of a material which describes the available vibrational states for atoms within the crystal lattice. Although atomic vibrations in solids are assumed to be harmonic creating a 'free' phonon gas, due to anharmonicity from phonon-phonon scattering, the phonon DOS is a function of the bulk crystal temperature.

2. Methods of generating the phonon density of states

The phonon DOS, which is the fundamental input to the scattering law, may be calculated from atomistic models. In particular, *ab initio* lattice dynamics (AILD) and classical molecular dynamics (MD) represent predictive approaches that may be utilized to calculate the phonon DOS for generation of the scattering law in crystalline materials (Hawari, 2014). Modern computational power and techniques have now made *ab initio* molecular dynamics (AIMD) accessible for calculations of the phonon DOS. This method represents an emerging technique for the calculation of phonon DOS for use in the generation of the TSL.

2.1. Ab initio lattice dynamics

Lattice dynamics techniques calculate the phonon DOS using the dynamical matrix method in which interatomic forces are assumed to be approximately harmonic. Historically, lattice dynamics has been utilized to calculate the phonon DOS for the generation of TSL by parameterizing the harmonic force constants to obtain reasonable agreement with measured dispersion relations (Koppel and Houston, 1968). These relations map the phonon frequencies to the phonon wave vectors within the crystal. In recent years AILD has been utilized to calculate the phonon DOS (Hawari, 2014). This method is a predictive approach where the forces for a static atomic lattice (i.e. approximating 0 K conditions) are calculated from the electronic structure of the crystal using the Hellmann-Feynman force theorem (Hawari, 2014; Feynman, 1939; Hawari et al., 2004). In this case, forces may be generated from predictive density functional theory (DFT) simulations within the Born-Oppenheimer approximation, which treats the dynamics of atoms and electrons as separable. While the AILD technique has been successfully utilized in the process of calculating thermal neutron scattering cross sections, the predicted phonon DOS do not capture the effects of anharmonicity with increasing bulk moderator temperature.

2.2. Classical molecular dynamics

Molecular dynamics methods may be utilized to capture the effects of temperature on the phonon DOS or to treat materials which contain non-vibrational contributions to the TSL. In traditional MD the Born-Oppenheimer approximation is assumed and the atomic trajectories (i.e. time dependent atomic positions) are molecularly dynamically evolved using classical mechanics and semi-empirical interatomic force fields (Haile, 1997). In these simulations, the phonon DOS which results from vibrational motion is calculated from the dynamics of atom velocities in thermal equilibrium using the velocity auto-correlation function (Rahman et al., 1976). In this case, the phonon DOS is the Fourier transform of the velocity auto-correlation function,

$$\rho(\omega) = \int_{-\infty}^{\infty} dt' \sum_j \frac{\langle \mathbf{v}_j(t'+t)\cdot\mathbf{v}_j(t)\rangle}{\langle \mathbf{v}_j(t)\cdot\mathbf{v}_j(t)\rangle}\exp(i\omega t'). \quad (8)$$

where ω is the phonon frequency (i.e. energy, $E = \hbar\omega$) and $\mathbf{v}_j(t)$ are the atom velocities at a time t. Although the traditional MD technique may capture the temperature effects not present in AILD simulations, the semi-empirical nature of the interatomic forces results in this technique being less predictive.

2.3. Ab initio molecular dynamics

Ab initio molecular dynamics is a first principles technique and an evolution of the AILD and MD techniques. In contrast to traditional MD, which uses semi-empirical interatomic force-fields, forces in AIMD are predicted directly from the electronic structure. Equilibrium dynamics of a system may be simulated by AIMD using the Car-Parrinello method (Car and Parrinello, 1985). In Car-Parrinello AIMD, the Born-Oppenheimer approximation is invoked such that the dynamics of the simulation are defined on the time scale of fluctuations in the atomic system. Within this computational scheme, DFT is used to establish a self-consistent solution to the electronic structure (i.e. electron density and wave-functions) at each simulation time step; from which the interatomic forces may be derived using Hellmann-Feynman force theory (Feynman, 1939). Classical Newtonian mechanics is then

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