Combined molecular and spin dynamics simulation of bcc iron with lattice vacancies

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Abstract. Using an atomistic model that treats both translational and spin degrees of freedom, we have performed combined molecular and spin dynamics simulations to study dynamic properties of BCC iron with varying vacancy concentrations. Atomic interactions are described by an empirical many-body potential while spin interactions are handled with a Heisenberg-like Hamiltonian with a coordinate dependent exchange interaction. By calculating the Fourier transform of spatial and temporal correlation functions, vibrational and magnetic excitations have been studied. The creation of vacancies in the material has shown splitting of the characteristic transverse spin-wave excitations, indicating the production of additional excitation modes. By merging two vacancies to form a nearest neighbor pair, we find that these modes become more distinct. Investigation of longitudinal spin-wave excitations reveals interactions between constituent components of the split transverse excitations.

1. Introduction

Computer simulation methods have been utilized for decades to study dynamic properties of materials at finite temperature. The molecular dynamics (MD) method [1, 2] has been widely used to investigate structural properties including diffusion, dislocations, and surface phenomena. To investigate time-dependent properties of magnetic systems, the spin dynamics (SD) method [3, 4] has given insight into propagating spin waves [5] and longitudinal two-spin-wave modes. However, the coupling of lattice vibrations with spin waves has only been investigated in recent years [6], revealing a strong interplay [7] between the two subsystems. Therefore, models attempting to describe a real magnetic material must handle both the lattice and spin subsystems on equal footing. Recent work using the combined molecular and spin dynamics (MDSD) framework has only investigated these systems for pure conditions, while impurities such as vacancies and interstitial defects are common in metallic materials. Vacancy defects are of importance in nuclear energy production, as radiation damage and hydrogen-vacancy interactions [8] may cause a metal to weaken over time.
2. Model and methods

2.1. Hamiltonian and equations of motion

For a system of $N$ atoms of mass $m$ with positions $\{r_i\}$, velocities $\{v_i\}$ and classical atomic spins $\{S_i\}$, the MDSD Hamiltonian is written

$$H = \sum_{i=1}^{N} \frac{mv_i^2}{2} + U(\{r_i\}) - \sum_{i<j} J_{ij}(\{r_k\})S_i \cdot S_j,$$

(1)

where the first term represents the kinetic energy of the atoms, and $U(\{r_i\})$ is a many-body interatomic potential. In this work, the potential used is an embedded atom potential parameterized for iron by Dudarev and Derlet [9]. The third term determines the exchange coupling between the spins, and is Heisenberg-like with a coordinate-dependent exchange interaction $J_{ij}(\{r_k\})$ parameterized for iron by first-principles calculations [10]. In the case of a vacancy at site $i$, the atom corresponding to the position of site $i$ is removed from the system. This Hamiltonian has true dynamics, described by the classical equations of motion

$$\frac{dr_i}{dt} = v_i,$$

$$\frac{dv_i}{dt} = f_i/m,$$

$$\frac{dS_i}{dt} = \frac{1}{\hbar} H_i^{\text{eff}} \times S_i,$$

(2)

where $f_i = -\nabla r_i H$ and $H_i^{\text{eff}} = \nabla S_i H$ represent the interatomic force and effective field felt by atom $i$, respectively.

2.2. Integration scheme

The time evolution of phase variables is written as

$$\frac{dq(t)}{dt} = \hat{L}q(t),$$

(3)

where $q(t) = \{r_i(t), v_i(t), e_i(t)\}$ represents the complete set of positions, velocities, and spin orientations at time $t$. The Liouville operator $\hat{L}$ is of the form

$$\hat{L} = \sum_{i=1}^{N} \left( v_i \cdot \frac{\partial}{\partial r_i} + \frac{f_i}{m_i} \cdot \frac{\partial}{\partial v_i} + \left( \frac{g\mu_B}{\hbar M_i} \right) (H_i^{\text{eff}} \times e_i) \cdot \frac{\partial}{\partial e_i} \right).$$

(4)

The solution to equation 3 is given by

$$q(t + \tau) = e^{\hat{L}\tau}q(t),$$

(5)

where $\tau$ represents the finite time step and $e^{\hat{L}\tau}$ is the operator which produces the time evolution of the phase variables. Utilization of a second-order Suzuki-Trotter decomposition [11] allows for the decomposition of the exponential operator in Eq. (5). The equations in Eq. (2) can then be solved numerically, producing trajectories for the atomic and spin degrees of freedom.

2.3. Dynamic structure factor

During the simulation, the microscopic spin density is calculated and the spin-spin intermediate scattering function is computed after each time step,
where \( k = x, y, z \) and \( \rho^k_s(q, t) \) is the \( k \)-component of the microscopic spin density. Using the choice of a Cartesian coordinate system such that the \( z \)-axis is parallel to the magnetization vector, spin excitations that propagate parallel and perpendicular to this symmetry axis are differentiated. The components of \( F_{ss}(q, t) \) are regrouped into a longitudinal component

\[
F_{ss}^L(q, t) = F^z_{ss}(q, t),
\]

and a transverse component

\[
F_{ss}^T(q, t) = \frac{1}{2} (F^x_{ss}(q, t) + F^y_{ss}(q, t)).
\]

The temporal Fourier transform of \( F_{ss}^{L,T}(q, t) \) yields the dynamic structure factor,

\[
S_{ss}^{L,T}(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F_{ss}(q, t)e^{-i\omega t} dt,
\]

for momentum transfer \( q \) and frequency \( \omega \), an experimentally accessible quantity [12]. In each of the included figures, data have been smoothed for clarity using a moving average.

3. Results

3.1. Randomly distributed vacancies

To investigate the effects of randomly distributed vacancies, MDSD simulations have been performed on \( L=8 \) simulation cells (1024 lattice sites) with 5% of lattice sites left vacant and compared to results from pure lattice simulations. At a temperature of \( T = 300 \)K, pure lattice results display a well defined single excitation peak [13] in the transverse component of the spin-spin dynamic structure factor \( S^T_{ss}(q, \omega) \). The introduction of vacancies distributed throughout the lattice causes a dampening of transverse dynamic structure factor peaks as well as a shift to lower frequency. For small values of \( |q| \), the peak in the dynamic structure factor is shown to exhibit splitting into multiple peaks as seen in Fig. 1.

3.2. Vacancy pair formation

The effect of merging vacant sites from distant positions outside of the interaction cut-off into nearest neighbor lattice positions in a small system is shown in Fig. 2. Removing two atoms from distant sites results in a dampening of the characteristic spin wave peak and a broadening toward lower frequency. As these vacancies are brought closer together, the single peak becomes split into two distinct peaks, located at frequencies higher and lower than the pure lattice excitation. This splitting behavior is most pronounced when the vacancies occupy nearest neighbor lattice positions.

Excitations in the longitudinal component of the dynamic structure factor \( S^L_{ss}(q, \omega) \) represent two-spin-wave annihilation processes [14]. These excitations are typically much lower in intensity than transverse peaks. Frequencies of longitudinal excitations can be predicted by subtracting the frequencies of constituent transverse spin waves. In the case of a nearest neighbor vacancy pair, the longitudinal spin wave spectrum displays more excitations due to the increased number of transverse spin waves as indicated by the peak splitting behavior shown in Fig. 2. These new excitations can be identified as the interaction between constituent components of the split transverse peaks, and their locations are predicted as shown in Fig. 3.
Figure 1. Transverse component of the spin-spin dynamic structure factor \( S_{SS}^{T}(q, \omega) \) in MDSD simulation at temperature \( T = 300\text{K} \) for \(|q| = 0.274\text{Å}^{-1} \) along the \((q, 0, 0)\) direction for an \( L = 8 \) simulation cell.

Figure 2. Transverse spin-spin dynamic structure factor for \(|q| = 0.365\text{Å}^{-1} \) along the \((q, 0, 0)\) direction in an \( L=6 \) system showing the merging of two defects into a nearest neighbor vacancy pair.

4. Summary
Using the combined molecular and spin dynamics simulation method, we have studied the effects of lattice vacancies on spin waves in BCC iron. The introduction of randomly distributed vacancies throughout the lattice results in a dampening of the small \(|q|\) characteristic transverse spin-spin dynamic structure factor peak as well as a shift of these peaks to lower frequency. Splitting of the low \(|q|\) excitation peaks occurs at 5\% vacancy concentration, and this behavior is shown to be caused by the formation of vacancy pairs. The constituent components of split transverse excitations are shown to interact with those of differing \(|q|\) through observation of the longitudinal dynamic structure factor.
Figure 3. Longitudinal spin-spin dynamic structure factor for $|q| = 0.365\text{Å}^{-1}$ along the $(q, 0, 0)$ direction in an $L=8$ system. Arrows indicate the predicted locations of the two-spin-wave annihilation peaks for pure lattice simulations. The dashed vertical lines (---) indicate predicted locations of two such peaks in the system containing a nearest neighbor vacancy pair.

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