Spin-Lattice Dynamics Simulations of Ferromagnetic Iron

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Abstract. We develop a Spin-Lattice Dynamics (SLD) simulation model for ferromagnetic iron where atoms are treated as classical particles with spins. The atoms interact *via* many-body forces as well as *via* spin-orientation-dependent forces of the Heisenberg form. The coupling between the lattice and the spin degrees of freedom is described by a *coordinate-dependent* exchange function. An algorithm for integrating the spin-lattice dynamics equations of motion is based on the 2nd order Suzuki-Trotter decomposition for the non-commuting Liouville evolution operators for atomic coordinates and spins. The notions of the spin thermostat and the spin temperature are introduced through a combined application of the Langevin spin dynamics and the fluctuation-dissipation theorem. Several applications of the new method described in the paper illustrate the significant effect of the spin degrees of freedom on the dynamics of atomic motion in iron and iron-based alloys, and confirm that the Spin-Lattice Dynamics approach provides a viable framework for performing realistic large-scale simulations of magnetic materials.

Keywords: Spin-Lattice Dynamics, Molecular Dynamics, Ferromagnetic Iron, Magnetic Relaxation, Spin-Phonon Interaction, Magnetic Potential
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INTRODUCTION

Modelling dynamical processes occurring in steels at high temperature or/and under irradiation is one of the major mathematical challenges in the field of advanced nuclear and fusion materials. Steels are very unusual systems in that their properties are determined by the magnetism of iron and solute (e.g. chromium or nickel) atoms or, in other words, by the effects of electron exchange and correlations. Probably the most convincing argument confirming the pivotal role played by the exchange and correlation effects comes from the fact that the body-centred cubic (bcc) crystal structure of iron itself is *anomalous*. A simple examination of the Periodic Table shows that in the absence of magnetism iron would adopt the hexagonal closed packed (hcp) structure, and hence the stabilization of its bcc structure is a magnetic phenomenon [1, 2, 3]. The structure of radiation defects in transition metals also reflects this magnetic anomaly, with a self-interstitial atom defect in iron adopting the $\langle 110 \rangle$ dumbbell configuration whereas in all the non-magnetic bcc metals a self-interstitial atom defect is a $\langle 111 \rangle$ crowdion [4, 5].

The main challenge associated with modelling steels is the fact that their structural and mechanical properties are determined by magnetism. This requires developing new physical approximations and mathematical algorithms capable of describing the entire complexity of phenomena resulting from the interplay between magnetism and elastic deformations, phase transformations, the finite temperature effects, excitation of spin waves and spin-phonon interactions, and the presence of magnetic solute atoms and impurities. In this paper we make the first step towards addressing this complexity by implementing a new method for the treatment of linked dynamics of kinematic motion of atoms and precession of spins.

In a transition metal the angular moments (spins) of atoms and the associated magnetic moments are formed due to the intra-atomic exchange interaction between d-electrons in the partially filled atomic d-shells, see e.g. [6]. According to Hund's rule, the total moment of an isolated atom is maximum subject to the constraint that the total number of d-electrons in an atom is constant. For example, an individual iron atom containing seven d-electrons has the magnetic moment of $3\mu_B$ in agreement with the fact that the difference between the total number of electrons in the full spin-up sub-shell, containing five d-electrons, and the spin-down sub-shell containing the remaining two electrons, equals three. In a transition metal, the d-electrons (or, more precisely, s- and d-electrons) are hybridized and hence become itinerant, hopping (or tunneling) from one lattice site to another. The interplay between the effect of intra-atomic exchange and inter-atomic quantum hopping affects the magnitudes of atomic moments and results in ordering the directions of moments, which adopt a ferromagnetic, or an antiferromagnetic, or a complex non-collinear magnetic configuration.

In this paper, we develop a reformulation of molecular dynamics that includes the spin degrees of freedom, and treats the coupled spin and lattice excitations within a unified simulation framework, taking into account the coordinates of atoms and the orientations of atomic spins as independent variables. The equations of motion are derived from the generalized Heisenberg Hamiltonian where the exchange coupling function is fitted to the *ab-initio* data, and where the scalar part of the interatomic interaction is given by the magnetic potential [8, 9, 10]. These equations form the basis for the Spin-Lattice Dynamics (SLD) algorithm. They are integrated using the 2nd order Suzuki-Trotter decomposition (STD) scheme for the non-commuting Liouville evolution operators for the lattice and the spin degrees of freedom. The position of each atom and the direction vector of the atomic spin are determined at each simulation time step. The coordinate dependence of the exchange coupling function links evolution of the spin and the lattice subsystems, and is responsible for the spin-orientation-dependent part of the inter-atomic forces. The "spin temperature" is introduced using the stochastic Langevin dynamics approach combined with the fluctuation-dissipation theorem.

In this paper we describe the fundamentals of the SLD algorithm and apply it to a micro-canonical ensemble simulation of adiabatic relaxation of a periodic array of $180°$ domain-walls in ferromagnetic bcc iron, and then to a canonical ensemble simulation of various finite-temperature magnetic properties, investigated using a method that treats the exchange of energy and angular momentum with the thermal bath (reservoir). We show that the SLD approach provides a suitable framework for evaluating the equilibrium nearest-neighbour atom spin-spin correlation functions as well as time-dependent autocorrelation functions of spin orientations.

THE SPIN-LATTICE DYNAMICS EQUATIONS

Magnetism is a signature of the fact that electrons in a material interact. For a non-interacting system of electrons the Hamiltonian is independent of the spin variable. The energies of eigenstates of this Hamiltonian are also independent of the spin of electrons, and so is the density of states

$$D(E) = \sum_\alpha \delta(E - E_\alpha). \tag{1}$$

Here E_α are the spin-independent energies of eigenstates, and summation is performed over all the eigenstates $\{\alpha\}$ of the system. The energy of the system of non-interacting electrons can be trivially evaluated by integrating the density of states up to the Fermi energy, viz.

$$E_{tot} = 2 \int^{\varepsilon_F} D(E) dE, \tag{2}$$

where ε_F is the Fermi energy, and the factor of 2 comes from summation over spins. The only practical problem associated with the evaluation of E_{tot} and with the development of a numerical scheme for molecular dynamics simulations consists in finding a suitable approximation for $D(E)$. This may be accomplished for example by using the tight-binding approximation and the Green's functions approach, see for example [1].

The treatment of interacting electrons presents an incomparably more difficult problem and hence "*few subjects in science are more difficult to understand than magnetism*[1]" [11]. A general property of an interacting electron system, as opposed to a non-interacting one, is the appearance of low energy scales [12]. This remarkable phenomenon is based on the fact that in an ordinary non-magnetic metal the characteristic energy scale for electronic excitations is provided by the bandwidth. This quantity is of the order of 5 eV and the associated temperature scale is of the order of 50000K. Excitations in a system of interacting electrons are characterized by temperatures many orders of magnitude lower, for example the Curie temperature of iron is 1043K. Hence, to model the microscopic behaviour of iron at a finite temperature one must include in the treatment both the coordinate and the spin degrees of freedom.

The collective coordinate degrees of freedom in a system of interacting atoms are the low energy phonon excitations, whereas the collective low-energy excitations in a system of interacting electrons are spin waves. Hence the (relatively) low temperature dynamics of iron can be well described using the coordinate and spin variables representing these excitations. The above argument also highlights the limitations of the mean-field Stoner model that does not describe the low-energy collective magnetic excitations. For example the relation between the electronic structure and the magnetic susceptibility is entirely different from that predicted by the Stoner model [13].

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[1] Encyclopedia Britannica, 15th Edition, 1989

The Spin-Lattice Dynamics model investigated in this paper uses the classical spin-lattice Hamiltonian function [6, 7]

$$H(\{\mathbf{p}_i\}, \{\mathbf{R}_i\}, \{\mathbf{e}_i\}) = \sum_k \frac{\mathbf{p}_k^2}{2m_k} + U(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N) - \frac{1}{2} \sum_{i,j,i\neq j} J_{ij}(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N)\mathbf{e}_i \cdot \mathbf{e}_j,$$
(3)

where $\mathbf{R}_i$ and $\mathbf{p}_i$ are the coordinates and the momentum of atom i, and $\mathbf{e}_i$ is the unit vector of atomic spin. $J_{ij}(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N)$ is the coordinate-dependent exchange function. The dynamics of the system is now 8-dimensional since in addition to the six degrees of freedom per atom in the coordinate and the momentum space we now have two additional degrees of freedom for the direction of the atomic angular momentum. The equations of motion for atoms and spins (the Spin-Lattice Dynamics, or SLD, equations) now have the form

$$\frac{d\mathbf{R}_k}{dt} = \frac{\mathbf{p}_k}{m_k}$$

$$\frac{d\mathbf{p}_k}{dt} = -\frac{\partial U}{\partial \mathbf{R}_k} + \frac{1}{2}\frac{\partial}{\partial \mathbf{R}_k} \sum_{i,j,i\neq j} J_{ij}(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N)\mathbf{e}_i \cdot \mathbf{e}_j$$

$$\Pi_k \frac{d\mathbf{e}_k}{dt} = \mathbf{e}_k \times \mathbf{H}_k,$$
(4)

where $\mathbf{H}_k = \sum_{i,i\neq k} J_{ik}(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N)\mathbf{e}_i$ and Π_k is the classical intrinsic *mechanical* angular momentum associated with atom k. These equations may be derived quantum-mechanically using the Heisenberg operator formalism. In the classical limit where the magnitude of atomic spin Π_k is many times the spin of a single electron, the system of atoms *and* spins evolves along the classical trajectories given by the solutions of differential equations (4).

CONSTRAINTS IMPOSED BY THE CONSERVATION LAWS

In this section we show that solutions of the SLD equations (4) satisfy the total energy and total angular momentum conservation laws, which in some cases strongly affect the dynamical behaviour of the system, preventing it from approaching a thermodynamically equilibrium configuration even in the macroscopic limit. First, consider the energy conservation law. The energy of the system is given by an expression similar to (3) where $\mathbf{R}_i(t)$, $\mathbf{p}_i(t)$, and $\mathbf{e}_i(t)$ are now the solutions of the SLD equations (4), namely

$$E(t) = \sum_k \frac{\mathbf{p}_k^2(t)}{2m_k} + U(\mathbf{R}_1(t), ..., \mathbf{R}_N(t)) - \frac{1}{2} \sum_{i,j,i\neq j} J_{ij}(\mathbf{R}_1(t), ..., \mathbf{R}_N(t))\mathbf{e}_i(t) \cdot \mathbf{e}_j(t). \quad (5)$$

The time derivative of $E(t)$ is

$$\frac{dE(t)}{dt} = \sum_k \frac{\mathbf{p}_k(t)}{m_k}\frac{d\mathbf{p}_k}{dt} + \sum_l \frac{\partial U}{\partial \mathbf{R}_l}\frac{d\mathbf{R}_l}{dt} - \frac{1}{2}\sum_{i,j,i\neq j}\sum_l \frac{\partial J_{ij}}{\partial \mathbf{R}_l}\frac{d\mathbf{R}_l}{dt}\mathbf{e}_i(t) \cdot \mathbf{e}_j(t)$$

$$- \frac{1}{2} \sum_{i,j,i\neq j} J_{ij} \frac{d}{dt} \left(\mathbf{e}_i(t) \cdot \mathbf{e}_j(t) \right). \tag{6}$$

The first three terms in the right-hand side of this equation cancel each other in accord with the SLD equations of motion (4) for $\mathbf{R}_i(t)$, $\mathbf{p}_i(t)$, and $\mathbf{e}_i(t)$. The fourth term is

$$
\begin{aligned}
\frac{1}{2} \sum_{i,j} J_{ij} \frac{d}{dt} \left(\mathbf{e}_i(t) \cdot \mathbf{e}_j(t) \right) &= \frac{1}{2} \sum_{i,j} J_{ij} \left[\frac{1}{\Pi_i} \sum_l J_{li} (\mathbf{e}_i \times \mathbf{e}_l) \cdot \mathbf{e}_j + \frac{1}{\Pi_j} \sum_l J_{lj} \mathbf{e}_i \cdot \left(\mathbf{e}_j \times \mathbf{e}_l \right) \right] \\
&= \frac{1}{2} \sum_{i,j} J_{ij} \frac{1}{\Pi_i} \sum_l J_{li} (\mathbf{e}_i \times \mathbf{e}_l) \cdot \mathbf{e}_j + \frac{1}{2} \sum_{i,j} J_{ij} \frac{1}{\Pi_j} \sum_l J_{lj} \mathbf{e}_i \cdot (\mathbf{e}_j \times \mathbf{e}_l) \\
&= \frac{1}{2} \sum_{i,j} J_{ij} \frac{1}{\Pi_i} \sum_l J_{li} (\mathbf{e}_i \times \mathbf{e}_l) \cdot \mathbf{e}_j + \frac{1}{2} \sum_{i,j} J_{ji} \frac{1}{\Pi_i} \sum_l J_{li} \mathbf{e}_j \cdot (\mathbf{e}_i \times \mathbf{e}_l) \\
&= \sum_{i,j,l} \frac{1}{\Pi_i} J_{il} J_{ij} (\mathbf{e}_i \times \mathbf{e}_l) \cdot \mathbf{e}_j = \sum_i \frac{1}{\Pi_i} \left(\mathbf{e}_i \times \left[\sum_l J_{il} \mathbf{e}_l \right] \right) \cdot \left[\sum_j J_{ij} \mathbf{e}_j \right] \\
&= \sum_i \frac{1}{\Pi_i} (\mathbf{e}_i \times \mathbf{H}_i) \cdot \mathbf{H}_i = 0. \tag{7}
\end{aligned}
$$

In the last equation, we used the fact that $J_{ij} = J_{ji}$ and that for any two vectors $\mathbf{A}$ and $\mathbf{B}$ the scalar vector product of the form $\mathbf{A} \cdot (\mathbf{B} \times \mathbf{A})$ vanishes. This shows that the total energy of the system remains constant while the individual energies of the lattice or the spin subsystems vary as a function of time.

Similarly, by considering the time derivative of the total angular momentum of the system $\sum_i \Pi_i \mathbf{e}_i(t)$ we find that for pure spin dynamics this quantity is also conserved. We prove this by a series of transformations involving the transposition of summation indices, namely

$$\frac{d}{dt} \sum_i \Pi_i \mathbf{e}_i(t) = \sum_{i,l} J_{li} (\mathbf{e}_i \times \mathbf{e}_l) = \sum_{i,l} J_{il} (\mathbf{e}_l \times \mathbf{e}_i) = -\sum_{i,l} J_{il} (\mathbf{e}_i \times \mathbf{e}_l) = -\sum_{i,l} J_{li} (\mathbf{e}_i \times \mathbf{e}_l) = 0, \tag{8}$$

where we noted that $J_{li} = J_{il}$ and that for any two vectors $\mathbf{A}$ and $\mathbf{B}$ their vector product changes sign if the vectors are transposed $\mathbf{A} \times \mathbf{B} = -\mathbf{B} \times \mathbf{A}$.

The total angular momentum conservation law imposes an unusually severe constraint on the dynamics of evolution of the spin system. Indeed, imagine a case where initially all the atomic spins pointed upwards. Since this configuration corresponds to the maximum possible vertical projection of the total angular momentum, and since the dynamics of the system, even in the case where interaction with the lattice is present, conserves the total angular momentum, the spin of every atom is constrained and has to remain stationary and independent of time during the entire simulation. Numerical studies performed for a microcanonical ensemble and described below confirm this finding.

In terms of the general methodology of atomistic simulations this is a very unusual point. In the field of molecular dynamics simulations, it is generally believed that the best strategy for maintaining accuracy is to perform a microcanonical simulation for a very large system. The argument about the conservation of the total angular momentum given above shows that fundamentally this strategy does not apply to Spin-Lattice Dynamics.

The fact that the SLD equations (4) conserve the total energy and, in the case of the spin subsystem, the total spin angular momentum, shows that interaction between a system of magnetic atoms and the thermostat (i.e. the thermal bath or the thermal reservoir) has to involve the exchange of energy *and* angular momentum. Since the spin and the lattice subsystems are linked, it is natural that this interaction should proceed through the spin rather than through the lattice subsystem. Indeed, the spin subsystem can exchange both the angular momentum and energy with the thermal reservoir while the lattice subsystem can only exchange energy. We consider this point in detail below, after investigating a microcanonical ensemble simulation where dynamical evolution of a closed large system of magnetic atoms is followed on a nanosecond timescale.

THE INTEGRATION ALGORITHM

A prime criterion for the choice of a numerical integration algorithm is its performance with respect to the energy and angular momentum conservation in a large-scale simulation performed over a relatively long interval of time. Our preliminary studies showed that that standard predictor-corrector methods did not conserve the energy and angular momentum satisfactorily. In this work we adopt the symplectic Suzuki-Trotter decomposition (STD) integration algorithm investigated in connection with spin dynamics by Omelyan *et al.* [14, 15] and Tsai *et al.* [16, 17]. Omelyan *et al.* and Tsai *et al.* used integration schemes based on the 2nd order STD for the non-commuting Liouville evolution operators describing the spin and the lattice degrees of freedom. In comparison with the 4th-order Runge-Kutta method, the 2nd order STD has superior performance in terms of the total energy and the total angular momentum conservation.

Consider the differential equations of motion of the form $d\mathbf{x}/dt = \hat{L}\mathbf{x}$, where $\hat{L}$ is the Liouville operator. The vector solution of these equations is given by the matrix exponent $\mathbf{x}(t) = \exp\left(\hat{L}(t-t_0)\right)\mathbf{x}(t_0) = \exp\left(\hat{L}(t-t_N)\right)\exp\left(\hat{L}(t_N-t_{N-1})\right)...\exp\left(\hat{L}(t_1-t_0)\right)\mathbf{x}(t_0)$, where $t > t_N > t_{N-1} > ... > t_1 > t_0$. The second-order Suzuki-Trotter decomposition formula states that if $\hat{L} = \hat{L}_A + \hat{L}_B$ then for a small time step δt

$$\exp\left((\hat{L}_A + \hat{L}_B)(\delta t)\right) = \exp\left(\hat{L}_A(\delta t)/2\right)\exp\left(\hat{L}_B(\delta t)\right)\exp\left(\hat{L}_A(\delta t)/2\right) + O\left((\delta t)^3\right). \quad (9)$$

Alternatively we may also write

$$\exp\left((\hat{L}_A + \hat{L}_B)(\delta t)\right) = \exp\left(\hat{L}_B(\delta t)/2\right)\exp\left(\hat{L}_A(\delta t)\right)\exp\left(\hat{L}_B(\delta t)/2\right) + O\left((\delta t)^3\right).$$

For example, the velocity Verlet algorithm, which is one of the most often used methods for integrating equations of conventional molecular dynamics, where the evolution of the system involves only the coordinates $\mathbf{R}_i$ and momenta $\mathbf{p}_i$ of atoms, is equivalent to the SDT of the form [16, 17]

$$\exp\left((\hat{L}_\mathbf{p} + \hat{L}_\mathbf{R})(\delta t)\right) = \exp\left(\hat{L}_\mathbf{p}(\delta t)/2\right)\exp\left(\hat{L}_\mathbf{R}(\delta t)\right)\exp\left(\hat{L}_\mathbf{p}(\delta t)/2\right) + O\left((\delta t)^3\right), \tag{10}$$

where

$$\exp\left(\hat{L}_\mathbf{p}(\delta t)\right)\{\mathbf{R}(t),\mathbf{p}(t)\} = \{\mathbf{R}(t),\mathbf{p}(t+\delta t)\} = \{\mathbf{R}(t),\mathbf{p}(t)+\mathbf{F}(t)\delta t\}$$

$$\exp\left(\hat{L}_{\mathbf{R}}(\delta t)\right)\{\mathbf{R}(t),\mathbf{p}(t)\} \;=\; \{\mathbf{R}(t+\delta t),\mathbf{p}(t)\} = \left\{\mathbf{R}(t)+\frac{\mathbf{p}(t)}{m}\delta t,\mathbf{p}(t)\right\}. \quad (11)$$

In the case of SLD equations (4) the Liouville operator is given by the sum of three terms $\hat{L} = \hat{L}_{\mathbf{e}} + \hat{L}_{\mathbf{p}} + \hat{L}_{\mathbf{R}}$, and now several possible forms of the STD can be used. Depending on how we order the Liouville evolution operators in the formula for the STD, we can arrive at either the $(\mathbf{p},\mathbf{R},\mathbf{e},\mathbf{R},\mathbf{p})$ decomposition [14, 15] corresponding to the choice of the single-time-step Liouville operator of the form $\exp\left(\hat{L}_{\mathbf{p}}(\delta t)/2\right)\exp\left(\hat{L}_{\mathbf{R}}(\delta t)/2\right)\exp\left(\hat{L}_{\mathbf{e}}(\delta t)\right)\exp\left(\hat{L}_{\mathbf{R}}(\delta t)/2\right)\exp\left(\hat{L}_{\mathbf{p}}(\delta t)/2\right)$, or at the $(\mathbf{e},\mathbf{p},\mathbf{R},\mathbf{p},\mathbf{e})$ decomposition used in [16, 17]. Our simulations use the $(\mathbf{e},\mathbf{R},\mathbf{p},\mathbf{R},\mathbf{e})$ decomposition that minimizes the frequency of evaluation of $\hat{L}_{\mathbf{p}}$, which is the most time consuming step of the algorithm. It is important to keep track of the non-commuting spin evolution operators, since the correct application of the STD requires ordering spins in accord with the way how they enter the Liouville operator. As opposed to conventional molecular dynamics, in SLD each degree of freedom is coupled to all the other degrees of freedom, making parallelizing the algorithm a challenging task. In this work we have been able to address this problem, and all the calculations described below were performed using an efficient parallel numerical integration scheme based on the second-order STD.

MICROCANONICAL ENSEMBLE SIMULATIONS

We start with a simple case of a closed (microcanonical ensemble) system and investigate the dynamics of adiabatic spin-lattice relaxation of a periodic array of 180° domain walls. The scalar part of interatomic potential, which we take in the form given in [8], together with the exchange function, fully define the dynamics of evolution of positions and velocities of atoms and their spins, as well as how the magnitude of the magnetic moments of an atom varies as a function of its position in a lattice. Evolution of a closed system follows the conservative dynamics equations where both the energy of the system and the total angular momentum stay constant during the simulation. The simulations were performed for a system of 54000 atoms initially forming a regular bcc lattice with lattice parameter $a = 2.8665$ Å. The initial dimensions of the cubic simulation cell are $30a \times 30a \times 30a$ with periodic boundary conditions applied along x, y and z. To follow the dynamics of adiabatic relaxation of a domain wall we chose the initial spin configuration in the form where all the spins in the left hand side of the simulation cell $(0 < x < 15a)$ pointed upwards whereas the spins in the right hand side of the cell $(15a < x < 30a)$ pointed downwards. A full description of these simulations is given elsewhere [18].

A microcanonical simulation provides a convenient means for investigating the transfer of energy between the lattice and the spin subsystems. Figure 1 shows an example of classical trajectories for the direction vector of an atomic spin and for the position vector of an atom in the crystal lattice followed by integrating the SLD equations (4).

The simulations also show how the coordinate dependence of the exchange parameter facilitates the transfer of energy between the two subsystems. In a simulation of the dynamics of adiabatic relaxation of a domain wall considered here we assumed that
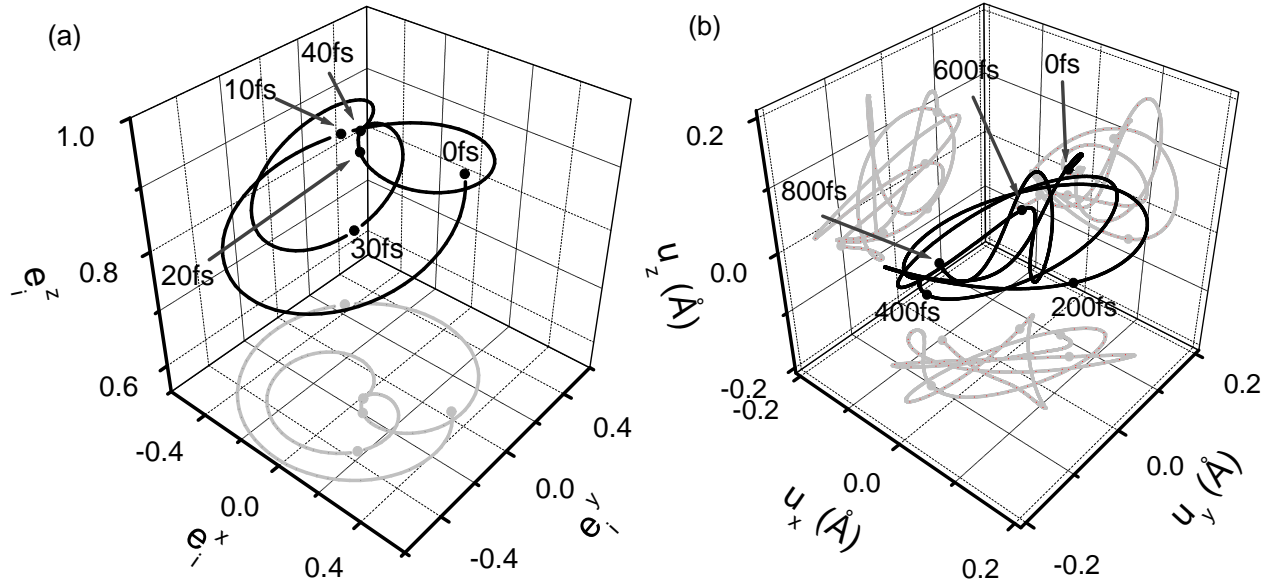
FIGURE 1. Trajectories of the two-dimensional direction vector of an atomic spin (a) and the three-dimensional vector of atomic displacement from an equilibrium position in the lattice (b) calculated by solving the SLD equations for a closed system of 54000 atoms initially thermalised at 300K and then evolved according to the system of equations (4) integrated using the 2nd order Suzuki-Trotter decomposition method. Note that the characteristic period of precession of an atomic spin is approximately an order of magnitude shorter than the period of oscillations of an atom near an equilibrium position in the crystal lattice.

initially the velocities of all the atoms were set to zero, and the energy was stored purely in the spatially heterogeneous spin configuration of the domain wall. Fig. 2 shows that initially the force associated with the spin-spin exchange term excites lattice vibrations at the domain boundary. These vibrations remain coherent on the timescale of approximately two periods of oscillations, each occurring on the Debye timescale of ~ 0.1 ps. The lattice perturbation propagates through the simulation cell in the form of sound waves which collide in the centre of the cell at $t \sim 0.3$ ps. The subsequent lattice relaxation gives rise to the rapid equipartitioning of the kinetic and the potential energy of the lattice occurring on the 10 to 20 ps timescale. This equipartitioning of energy in the lattice subsystem is driven primarily by the anharmonicity of the *scalar* interatomic potential, and the resulting phonon-phonon interactions [19]. On this 10 to 20 ps timescale the spin subsystem remains coupled to the lattice, but the effect of this coupling on the rate of the intra-lattice equipartitioning of energy is relatively weak. On the same 10 to 20 ps timescale the spin subsystem evolves into a quisi-equilibrium configuration that can be approximately described as an incoherent superposition of spin waves. Fig. 2 shows that the equipartitioning of energy in the combined spin-lattice system is characterized by a much longer relaxation timescale of the order of a nanosecond. On this timescale the two subsystems exchange energy, and this results in the eventual thermalisation of both the spins and the lattice. The process of spin-lattice thermalisation is driven by the spin-phonon interaction occurring because the exchange parameter varies as a function of the interatomic distance. The nanosecond timescale of the spin-phonon
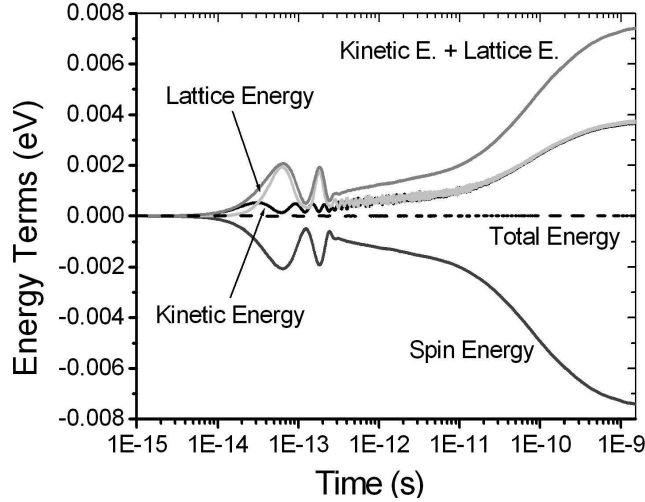
FIGURE 2. Time evolution of the kinetic, potential and spin energies in a microcanonical ensemble simulation of evolution of an initially atomically sharp domain wall. All the terms are shown with respect to their initial values at the start of the simulation. Equipartitioning of the kinetic and potential energies in the lattice subsystem results in that the two terms become almost indistinguishable for $t \geq 20$ ps. The weak coupling between the lattice and the spin subsystems results in that the process of spin-lattice relaxation found in this simulations occurs on a much longer timescale ~ 1 ns.

thermalisation found in our simulations agrees with analytical estimates given in [20]. This final slow spin-lattice thermalisation occurs subject to the condition that the total angular momentum of the spin subsystem remains constant, as the total angular momentum conservation law in the case of a microcanonical ensemble simulation imposes a constraint on the possible modes of evolution of the spin subsystem.

THE LANGEVIN DYNAMICS OF SPINS

in addition to the use of an efficient integration algorithm, to perform a canonical ensemble simulation we need to develop a method for controlling the temperature of the system. We have already noted above that the spin subsystem does not thermalise on its own in a microcanonical ensemble simulation because of the constraint imposed by the law of conservation of the total angular momentum. In this respect, the dynamics of a large closed system of interacting atomic spins is fundamentally different from the dynamics of a large closed system of interacting atoms, where collisions between the atoms eventually result in the statistical equilibration of positions and velocities. To introduce the notion of the spin temperature, we replace the deterministic spin dynamics equations considered above by the the stochastic Langevin-type equations of the form

$$\Pi_k \frac{d\mathbf{e}_k}{dt} = \mathbf{e}_k \times (\mathbf{H}_k + \mathbf{h}_k) - \eta \mathbf{e}_k \times (\mathbf{e}_k \times \mathbf{H}_k),$$

(12)

where $\mathbf{h}_k$ is a fluctuating random vector field satisfying the condition

$$\langle h_\alpha(t') h_\beta(t'') \rangle = \mu \delta_{\alpha\beta} \delta(t' - t'').$$
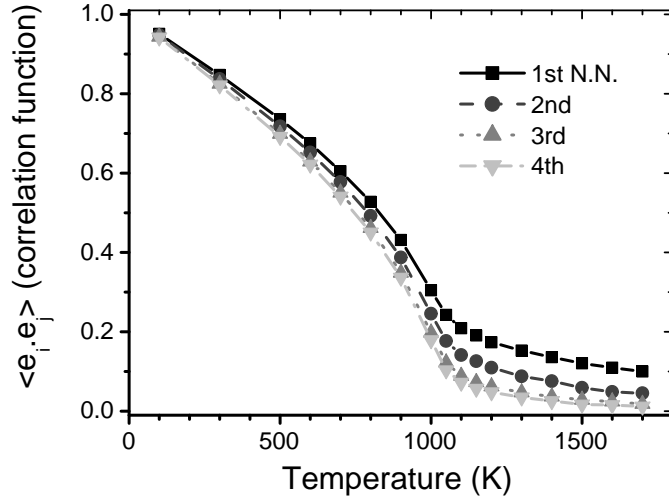
(13)

FIGURE 3. The spin-spin $\langle \mathbf{e}_i \cdot \mathbf{e}_j \rangle$ equilibrium correlation functions evaluated for pairs of neighbouring atoms using dynamical microcanonical simulations performed for spin-lattice systems initially equilibrated at a given temperature. The spin-spin correlations vanish above the Curie temperature as the distance between the pairs of atoms increases.

Here indices α and β refer to the Cartesian coordinates, and η is a dimensionless damping constant. In practical simulations the value of this damping constants was chosen in the interval $10^{-4} < \eta < 10^{-3}$. The random field and the damping term together describe interaction between the spin subsystem and the thermal reservoir. This gives rise to the exchange of energy and angular momentum between the spin subsystem and the thermostat. The temperature of the spin subsystem is defined through the application of the fluctuation-dissipation theorem. Following Brown, Jr. [21], we define the value of the damping coefficient η by finding the energy distribution for the spin subsystem from the corresponding Fokker-Planck equation, and by requiring that this distribution is identical to the Gibbs distribution corresponding to a given temperature. This results in a condition relating the amplitude of the random field and the damping term,

$$\mu = 2\Pi_k k_B T \eta, \tag{14}$$

where T is the absolute temperature of the spin thermostat. In the numerical implementation of the method, the fluctuating field is modelled using Gaussian random numbers.

CANONICAL ENSEMBLE SIMULATIONS

The critical temperature of a ferro-/paramagnetic phase transition corresponds to the disappearance of long-range order in spin orientations. To investigate the short-range directional order in the spin subsystem at equilibrium we investigated the spatial spin-spin correlation functions in a fully thermalized ensemble. Fig. 3 shows the spatial spin-spin correlation functions evaluated dynamically using the SLD algorithm for several nearest neighbour (NN) atomic shells. Even for temperatures higher than the Curie temperature correlations between directions of atomic spins persist for the 1st and 2nd
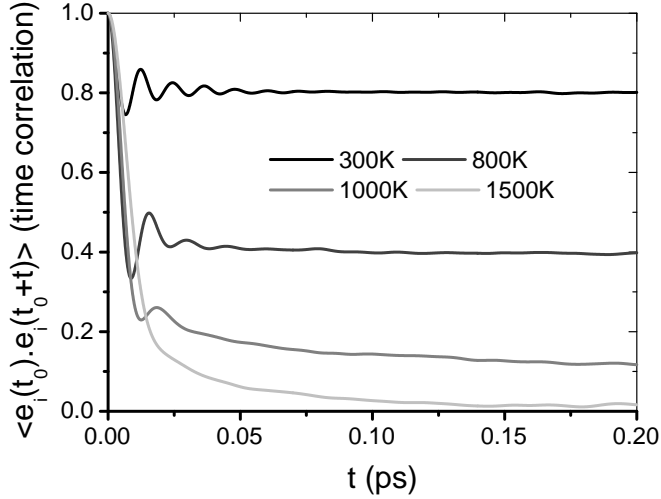
FIGURE 4. The time autocorrelation functions of atomic spin direction vectors evaluated using micro-canonical ensemble simulations for systems that were initially thermally equilibrated at a given temperature. Note the fluctuating behaviour of autocorrelation functions at short times.

nearest neighbours. The spin-spin correlation functions remain non-negative for all the sites up to the 12th nearest neighbour investigated in this work.

To investigate the temporal fluctuations of directions of atomic spins at thermal equilibrium, we evaluated the time-dependent spin direction autocorrelation functions by performing NVE simulations for a thermally equilibrated ensemble. Fig. 4 shows the oscillating behavior observed for short times, and associated with the rotation of spins illustrated in Fig. 1. In the limit $t \rightarrow \infty$ the autocorrelation functions asymptotically approach the square of the equilibrium value of the spin direction vector corresponding to a given temperature. The amplitude of fluctuations increases with temperature due to larger transverse projections spanned by the rotating spins. At around 700K the fluctuations reach maximum and then gradually die out due to the ever increasing precession angle and the increasing frequency of events of flipping of the spin direction vector. The profiles of the time correlation functions vary depending on absolute temperature.

CONCLUSIONS

Large-scale molecular dynamics simulations of magnetic materials, such as ferromagnetic iron, often neglect coupling between the spins (or magnetic moments) and the lattice degrees of freedom of atoms. This restricts the applicability of simulations to short timescales or to systems where the spin-lattice coupling is very small. A thermodynamically accurate simulation of a ferromagnetic material at a high temperature requires treating the flow of energy between the lattice and the spin subsystems. This in turn requires that the coupling between the spin and lattice dynamics should be explicitly considered in the treatment of dynamics of the system. In this paper the equations of motion for both the coordinates of atoms and the direction vectors of atomic spins are derived from a Hamiltonian expressed in terms of the magnetic interatomic poten-

tial and the Heisenberg spin-spin interaction with a pair-wise exchange function. Each atom is considered as a classical particle with an intrinsic spin. The dynamics of atoms is partially similar to that described by the conventional Molecular Dynamics equations, but with additional degrees of freedom associated with the evolution of directions of atomic spins. We call the new simulation approach the Spin-Lattice Dynamics (SLD) to differentiate it from MD where the dynamics of atomic spins is neglected. The equations of motion are integrated using the 2nd order Suzuki-Trotter decomposition for the non-commuting Liouville evolution operators, and the spin temperature is introduced via a combination of the Langevin spin dynamics and the fluctuation-dissipation theorem.

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REFERENCES

1. D. G. Pettifor, *Bonding and Structure of Molecules and Solids* (Oxford Universiy Press, Oxford, 1995).
2. M. Friák, M. Šob, and V. Vitek, Phys. Rev. B**63**, 052405 (2001).
3. H. C. Herper, E. Hoffmann, and P. Entel, Phys. Rev. B**60**, 3839–3848 (1999).
4. D. Nguyen-Manh, A. Horsfield, and S. L. Dudarev, Phys. Rev. B**73**, 020101 (2006).
5. P. M. Derlet, D. Nguyen-Manh, and S. L. Dudarev, Phys. Rev. B**76**, 054107 (2007)
6. S. L. Dudarev and P. M. Derlet, J. Computer-Aided Mater. Des. (2008) in the press; DOI 10.1007/s10820-007-9073-x
7. U. Nowak, "Classical Spin Models," in *Handbook of Magnetism and Advanced Magnetic Materials*, edited by H. Kronmueller, Wiley, New York, 2007.
8. S. L. Dudarev and P. M. Derlet, Journ. Phys. Cond. Matt. **17**, 7097–7118 (2005); ibid. **19**, 239001 (2007)
9. P. M. Derlet and S. L. Dudarev, Prog. Mater. Sci. **52**, 299–318 (2007)
10. P. W. Ma, W. C. Liu, C. H. Woo and S. L. Dudarev, J. Appl. Phys. **101**, 073908 (2007)
11. P. Mohn, *Magnetism in the Solid State* (Springer, Heidelberg, 2003).
12. P. Fulde, "Origins of Heavy Quasiparticles," in *Electron Correlations and Materials Properties 2*, edited by A. Gonis, N. Kioussis, and M. Ciftan, Kluwer Academic/Plenum Publishers, New York, 2003, pp. 111-118.
13. Duk Joo Kim, *New Perspectives in Magnetism of Metals* (Kluwer Academic/Plenum Publishers, New York, 1999), pp. 63-67.
14. I. P. Omelyan, I. M. Mryglod, and R. Folk, Phys. Rev. Lett. **86**, 898–901 (2001)
15. I. P. Omelyan, I. M. Mryglod, and R. Folk, Phys. Rev. E **64**, 016105 (2001)
16. S. H. Tsai, M. Krech, and D. P. Landau, Brazil. J. Phys. **34**, 382–391 (2004)
17. S. H. Tsai, H. K. Lee, and D. P. Landau, Am. J. Phys. **73**, 615–624 (2005)
18. P. W. Ma, C. H. Woo, and S. L. Dudarev, (2008) in preparation
19. J. H. Van Vleck, Phys. Rev. **59**, 730–736 (1941)
20. K. P. Sinha and U. N. Upadhyaya, Phys. Rev. **127**, 432–439 (1962)
21. W. F. Brown Jr., Phys. Rev. **130**, 1677–1686 (1963)