Application and extension of Glauber Ising-spin dynamics in the context of a single chain magnet system

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APPLICATION AND EXTENSION OF GLAUBER ISING-SPIN DYNAMICS
IN THE CONTEXT OF A SINGLE CHAIN MAGNET SYSTEM

by

Ryan T. Kristensen

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Abstract

The Glauber Ising-spin dynamic with a local equilibrium approximation is applied to
infinite and finite one-dimensional (anti-)ferromagnetic Ising chains with classic nearest
neighbor interactions. The application of the Glauber dynamic and local equilibrium
approximation is then extended to the one-dimensional ferrimagnetic chain with nearest
neighbor interactions. Time dependant behavior and equilibrium states of the one-
dimensional ferrimagnetic chain are then discussed in terms of the single chain magnet
referred to as CoPhOMe, whose behavior empirical data to date suggest is consistent
with a one-dimensional Ising ferrimagnet.
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Appendix B: Computer Model Code for One-Dimensional Ferrimagnetic Lattice with Nearest Neighbor Interactions
Listing of Frequently Used Symbols

$\alpha$ is a parameter describing the time scale on which transitions take place [s$^{-1}$]
$B$ is the applied magnetic flux density [T]
$b$ is the non-dimensional applied magnetic field energy, $\mu B / k_B T$
$\beta$ is a parameter related to the applied magnetic field energy
$g$ is the non-dimensional coupling energy, $J / k_B T$
$\gamma$ is a parameter related to the coupling between adjacent spins inside a spin chain
$\gamma'$ is a parameter related to the coupling between adjacent spins at the ends of a spin chain
$J$ is the nearest neighbor coupling energy [J]
$k_B$ is Boltzmann's constant [1.3807x10$^{-23}$ J / K]
$\mu$ is the magnetic moment of spins at each lattice site, or at specific sites denoted by
Subscript present [Am$^2$ or J / T]
$\mu_B$ is the Bohr magneton [9.274x10$^{-24}$ Am$^2$ or J / T]
$N$ is the total number of spins [integer]
$p(\sigma)$ is the probability that the spin at site $i$ will have the value $\sigma$
$p(-\sigma)$ is the probability that the spin at site $i$ will have the value $-\sigma$
$p(\sigma_1, \cdots, \sigma_N, t)$ is the probability of the system being in a particular configuration at time $t$
$P(\sigma, \sigma')$ is the probability that a site will take a value $\sigma$ and an adjacent site will take a value of $\sigma'$
$P(\sigma)$ is the probability that a site has a value $\sigma$
\( P(\sigma|n_1) \) is the probability that \( n_1 \) nearest neighbors of a site (that has a value \( \sigma \)) are up

\( P_c(\sigma|n_1) \) is the conditional probability that \( n_1 \) nearest neighbors of a site are up, if that site has a value \( \sigma \)

\( P_c(\sigma, \sigma') \) is the conditional probability that the nearest neighbor site will have the value \( \sigma' \) if that site’s nearest neighbor has the value \( \sigma \)

\( P_{oe}(\sigma, \sigma') \) is the probability that an odd site will take a value \( \sigma \) and an adjacent even site will take a value of \( \sigma' \)

\( P_e(\sigma) \) is the probability that an even site has a value \( \sigma \)

\( P_e(\sigma|n_1) \) is the probability that \( n_1 \) nearest neighbors of an even site (that has a value \( \sigma \)) are up

\( P_{c,e}(\sigma|n_1) \) is the conditional probability that \( n_1 \) nearest neighbors of an even site are up, if that even site has a value \( \sigma \)

\( P_{c,eo}(\sigma, \sigma') \) is the conditional probability that the odd nearest neighbor site will have the value \( \sigma' \) if the even site has the value \( \sigma \)

\( Q \) is the average single-spin expectation value

\( q_i(t) \) is the expectation value of the spin at site \( i \)

\( R \) is the average two-spin product expectation value

\( r_{ij}(t) \) is the expectation value of the product of the spin at site \( i \) and the spin at site \( j \)

\( s_{ijk}(t) \) is the expectation value of the product of the spins at sites \( i, j, \) and \( k \)

\( \sigma_i \) is the orientation of the spin at site \( i \) \([\pm 1]\)

\( T \) is the temperature \([\text{K}]\)

\( \tau_0 \) is the exponential prefactor of the thermally activated (Arrhenius) behavior \([\text{s}]\)

\( w(\sigma) \) is the transition probability, or probability per unit time, that the spin at site \( i \) flips from \( \sigma \) to \(-\sigma\) while the spins at other sites remain momentarily fixed
$w(-\sigma_i)$ is the transition probability, or probability per unit time, that the spin at site $i$ flips from $-\sigma_i$ to $\sigma_i$ while the spins at other sites remain momentarily fixed.
Chapter One

Introduction

The Ising model, despite its seemingly simple nature, has demonstrated a remarkable ability to describe static and dynamic physical phenomena in applications as disparate as the modeling of polymers\(^1\), binary alloys\(^2,3\), liquid/gas phase transitions\(^2,3\), and magnetism. The latter application involving the description of the equilibria and dynamics of the constituent portions of magnetic materials is the subject of this study. Specifically, the Ising model will be employed to describe, in part, the magnetic behavior of the single chain magnet \((\text{Co(hfac)}_2[\text{NIT(C}_6\text{H}_4\text{p-OMe})])\), where hfac is hexafluoroacetylacetonate and NIT(C\(_6\)H\(_4\)p-OMe) is the 4'-methoxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide radical\(^4\). This compound is generally referred to as CoPhOMe.

1.1 Ising Model of Magnetization

Many different lattice models have been used to study magnetization. In each of these, a system of interacting 'particles' is modeled by locating the particles in a 1D, 2D, or 3D lattice of points. Such models include\(^5\):

- the vector, or Heisenberg, model where the particles are represented by a vector quantity that may take any 3D direction. Note that while the classical Heisenberg model employs a traditional scalar component vector representation of the particles, the quantum Heisenberg model explicitly incorporates the Pauli
spin matrices (for spin ½ particles) as each component of the quantum mechanical spin operators.

- the X-Y model, where the particles are represented by a vector quantity that may take any 2D direction that is limited to a defined X-Y plane

- the Ising model, where the particles are represented by a binary scalar quantity that indicates an ‘up’ or ‘down’ orientation associated with the particle

The particles in the Ising model of magnetization are commonly referred to as spins, each having a magnetic moment oriented in an up or down sense. This two-state restriction of the magnetic moments is analogous to the two states allowed by a (quantum) spin ½ particle in an applied magnetic field, where the magnetic field orientation defines the direction of up and down. This representation is particularly useful when considering spins with significant anisotropy, where an energy barrier promotes alignment along a particular axis while prohibiting intermediate orientations. While a rigorously correct quantum description of spin ½ particles must use the quantum Heisenberg model, the Ising model often presents a means to obtain a physically meaningful description of a system without requiring as complex a mathematical representation. In the case of a 1D lattice with an applied magnetic field, the classic nearest neighbor Ising Hamiltonian is:

$$H = -J \sum_{i}^{N} \sigma_i \sigma_{i+1} - \mu B \sum_{i}^{N} \sigma_i$$

(1.1)

where $J$ is the nearest neighbor coupling energy $[J]$.
$N$ is the total number of spins [integer]

$\sigma_i$ is the orientation of the spin at site $i$ $[\pm 1]$

$\mu$ is the magnetic moment of spins at each lattice site [$\text{Am}^2$ or $J / \text{T}$]

$B$ is the applied magnetic flux density [$\text{T}$]

When the nearest neighbor coupling energy, or exchange energy, is positive, a tendency toward ferromagnetic order results because the system of parallel oriented spins is least energetic. The second term of the Hamiltonian then determines whether the common orientation of the system is up or down, consistent with the orientation of the applied magnetic field. However, when the coupling energy is negative the system tends toward an anti-ferromagnetic order of oppositely oriented adjacent spins. This configuration is least energetic in the absence of an applied magnetic field, and is thus the preferred state of the system. In this case, the applied magnetic field only disrupts the anti-ferromagnetic order when the second term’s energy (the energy associated with the magnetic moments in the applied field) is on the order of or greater than the nearest neighbor coupling energy.

The Ising model can be considerably extended to include higher dimensional lattices\textsuperscript{6,7,8} and more sophisticated coupling between particles\textsuperscript{9,10}. However, these models rarely have exact solutions and are often extremely complicated. In fact, the exact solution to the simple 2D Ising model in zero applied field obtained by Lars Onsager in 1944 is considered one of his great contributions to Physics, and he was later awarded the 1968 Nobel Prize in chemistry.
A thoroughly studied variant of the 1D Ising model incorporates a random-field term representing the effects of compositional and morphological disorder.\textsuperscript{11}

\[ H = -J \sum_{i} \sigma_i \sigma_{i+1} - \mu B \sum_{i} \sigma_i - \sum_{i} b_i \sigma_i \]  

(1.2)

where \( b_i \) represents a random energy field defined by a given probability distribution \[ J \]

This random-field Ising model (RFIM) has been employed to study hysteresis\textsuperscript{12}, disorder\textsuperscript{13}, avalanche phenomena\textsuperscript{14} (Barkhausen noise) and other applications. While an exact solution to the classic 1D Ising model introduced above is readily obtained, exact descriptions of the RFIM have been demonstrated only with the application of more complicated methods and simplifying assumptions\textsuperscript{15,16,17}.

### 1.2 Dynamics of the Ising Model

Numerous approaches have been developed to extend the Ising model to the study of dynamic phenomena. Traditional stochastic approaches include the Metropolis\textsuperscript{18}, Glauber\textsuperscript{19}, and heat bath\textsuperscript{20} dynamics, where the flipping of a spin from one orientation to the other is determined by a probabilistic assessment of the energy associated with the spin.

- In the Metropolis dynamic, the change in energy \( \Delta E \) of the system caused by the potential spin flip is calculated. If \( \Delta E < 0 \), i.e., if the flip would bring the system to a state of lower energy, the flip is allowed. If \( \Delta E > 0 \), the flip is allowed with probability \( \exp(-\Delta E/k_B T) \), where \( k_B \) is Boltzmann’s constant (1.3807x10\textsuperscript{-23} J / K)
and $T$ is temperature in Kelvin. This dynamic is specifically intended for use in obtaining computationally (numerically) determined solutions.

- In the Glauber dynamic, the probability of a spin flipping can be expressed in terms of the change in energy associated with the two possible actions the spin may take\textsuperscript{21} – either the spin flips (change in energy is $\Delta E$) or it does not (change in energy is zero). This spin-flip probability is expressed as:

\[
\frac{\exp(-\Delta E / k_B T)}{1 + \exp(-\Delta E / k_B T)}
\]  

In contrast to the Metropolis dynamic, the Glauber dynamic can be incorporated into an analytical description of the system of interest.

- In the heat bath dynamic\textsuperscript{2}, each spin is determined to be up or down with probabilities given by the fixed orientation of the neighbor spins. In the absence of an applied magnetic field this is written as:

\[
p(up) = \frac{\exp(-E_+ / k_B T)}{\exp(-E_+ / k_B T) + \exp(-E_- / k_B T)} 
\]  

and

\[
p(down) = \frac{\exp(-E_- / k_B T)}{\exp(-E_+ / k_B T) + \exp(-E_- / k_B T)}
\]
In each of these approaches, several computational methods may be implemented for selecting spins to evaluate (e.g. random or series selection) and defining the associated time stepping (e.g. single or multiple rounds of evaluating each spin). Each dynamic can also be utilized in more sophisticated numerical simulations such as the Monte Carlo method\textsuperscript{20}, though the Glauber dynamic presents a structure that can be leveraged to gain insight into the dynamic processes present (including the effect of inter-spin coupling on the overall magnetization process). The Glauber dynamic has been exactly solved in the absence of an applied magnetic field\textsuperscript{19}.

However, the Glauber dynamic model (even in one dimension) has not been solved where there is an applied magnetic field. The complication is that the magnetic field energy interacts with the spin coupling energy to create an open system of mixed multi-spin dynamic equations. This complication has generally been avoided by limiting studies to magnetic susceptibility with the assumptions that the applied magnetic field is very small and that the two-spin correlations are not changed by the small applied magnetic field\textsuperscript{22,23}.

An alternative approach circumvents the complications presented by the open system of mixed multi-spin dynamic equations by introducing a local equilibrium approximation\textsuperscript{24,25}. If the microscopic collision time is much shorter than the macroscopic relaxation time, the system will relax through a range of temporary local equilibrium states. In each Ising
model temporary equilibrium state, the thermodynamic properties and multi-spin correlations can be determined solely in terms of the single-spin expectation value and temperature. This allows for the multi-spin dynamic equations to be expressed in terms of the single-spin expectation value, thus closing the system of dynamic equations and allowing a study of the system in response to an applied magnetic field of arbitrary amplitude. Now the dynamic magnetic behavior of systems described by an Ising model can be interrogated throughout its entire magnetization range (hysteresis cycle).

The lack of a restriction on the magnetic field amplitude enables the Glauber dynamic solution of the Ising model to be employed for such analogous studies as polymer kinetics (where the magnetic field corresponds to a chemical potential), the denaturation of DNA molecules, the activity of allosteric enzymes, and ion adsorption on protein molecules. The local equilibrium approximation method as applied to the Glauber dynamic solution of the Ising model was tested against experimental data on the potassium-sodium exchange in human lymphocytes with good agreement between kinetic data and model results.

1.3 Experimental Investigations

The single chain magnet (SCM) referred to as CoPhOMe has been studied with much interest since the demonstration of its slow dynamics and hysteresis behavior at low temperatures. CoPhOMe has a pseudo one-dimensional helicoidal structure, with repeated pairings of adjacent Co$^{2+}$ ions and NITPhOMe organic radicals forming three pairs for each turn of the helix. The Co ions have a strong easy axis anisotropy (that makes an angle of ~50 degrees with the axis of the helical chain), while the spin $\frac{1}{2}$ radical ions are essentially isotropic and serve to transmit the exchange coupling from
The exchange coupling energy between Co and radical sites is anti-ferromagnetic, and is estimated to be on the order of 80K to 220K (in temperature units), while the ratio of interchain to intrachain coupling energies is estimated\textsuperscript{29,30} to be $< 10^{-4}$. Each ion possesses different Lande values ($g_{Co} \sim 7.4\mu_B$ to $9\mu_B$ and $g_{R} \sim 2\mu_B$)\textsuperscript{29}, but the Co ion is effectively spin $\frac{1}{2}$ at low temperatures since just the lowest lying doublet of the anisotropic Co ion is populated below $\sim$50K. Thus, despite the fact that this SCM system is not truly spin $\frac{1}{2}$, it lends itself to description by use of a one-dimensional ferrimagnetic Ising model below $\sim$50K. As opposed to ‘ferromagnetic’ materials where all the magnetic centers have the same magnetic moment and tend to align with each other, ‘ferrimagnetic’ materials consist of alternating magnetic centers with two different magnetic moments where adjacent moments tend to align opposite each other.

The low temperature slowing down of the CoPhOMe spin dynamics was first quantified by studies of the imaginary component of the magnetic susceptibility. It was found that the relaxation time of the CoPhOMe magnetization follows a thermally activated (Arrhenius) behavior below $\sim$15K\textsuperscript{27}. The relaxation time was thus observed to obey:

$$\tau = \tau_0 \exp \left( \frac{\Delta}{k_B T} \right) \quad (1.6)$$

where $\tau$ is the relaxation time [s]
$\tau_0$ is the exponential prefactor [\sim$4\times10^{-11}$ seconds]
$\Delta/k_B$ is the energy barrier [\sim152K]
Subsequent studies\textsuperscript{31} of the time decay of the magnetization in zero field have roughly corroborated this finding, and indicate an energy barrier $\Delta / k_B$ of 186±5K and an exponential prefactor $\tau_0$ of $\sim 7 \times 10^{-12}$ seconds.

Along with the slowing down phenomenon below $\sim 15$K, a complex series of hysteresis loops (similar to those observed in single molecule magnets\textsuperscript{32,33} and magnetostrictive thin films\textsuperscript{34}) present themselves in response to magnetic fields applied along the axis of the CoPhOMe chain\textsuperscript{27,31}. As the temperature is reduced from 7K to 1.5K, the coercivity is observed to increase, and plateaus develop at zero magnetization (at coercive field) and approximately 1/3 to 1/2 the saturation magnetization (at zero field). The plateaus are observed to be reversible, do not vary with the sweeping rate of the field (nominally 0.068 T/s) when the sweeping rate is faster than the spin relaxation rate, and are present above the blocking temperature ($\sim 7$K) when the hysteresis disappears. Neither hysteresis nor any plateau phenomena are observed for magnetic fields applied perpendicular to the chain axis, and paramagnetic behavior is present down to 1.8K. Theoretical studies\textsuperscript{27,35,36} indicate that the plateaus may be the result of the helicoidal nature of the chain and subtle variations in the angle of the easy axis of the Co ion. Specific variations can introduce next-nearest neighbor interactions that are not accounted for in the standard Ising model Hamiltonian.

The blocking of the magnetization at low temperature is not attributed to a phase transition to 3D order, but is dynamical in nature as indicated by the measured slowing down of the spin dynamics. The 3D ordering in Ising systems results from the correlation length $\zeta \sim \exp\left(\frac{2J}{k_B T}\right)$ exponentially diverging at low temperatures and.
enhancing the weak interchain coupling energy$^{37}$. The absence of the diverging correlation length is attributed to the presence of diamagnetic impurities or defects that inhibit long range ordering (i.e. dramatically reduce the 3D ordering temperature) and can affect the static and dynamic properties of magnetization$^{38}$. The presence of a defect effectively removes one bond from each of its adjacent Ising spins, thus reducing the energy associated the flipping of the adjacent spins relative to inner spins with no adjacent defects. Thus spin inversion will preferentially occur close to the defects, or at the ends of a finite chain of spins.

Studies of the magnetic susceptibility of CoPhOMe with various concentrations of diamagnetic impurities indicate a strong sensitivity to geometric limitations of the correlation length$^{37,38,39}$. Peaks in the real part of the susceptibility are observed at \(\sim 14\)K and \(\sim 33\)K. The high temperature peak is strongest in the pure sample and is roughly consistent with that expected for an infinite 1D Ising system. As the defect concentration is increased, the high temperature peak is diminished while the low temperature peak becomes pronounced. This behavior is qualitatively reproduced by solving a randomly diluted ferrimagnetic Ising chain in field for distributions of chain lengths consistent with the experimental defect concentrations. Analysis of the imaginary portion of the magnetic susceptibility between 7-10K indicate that the relaxation time energy barrier is unchanged (160±8K) while the exponential pre-factor varies from \(3.5\times10^{-11}\) seconds in the pure sample to \(1\times10^{-12}\) seconds for the 4.7% defect concentration. Experimental results at the highest concentrations studied also suggest coherent reversal of all spins in the shortened chains as an additional mode of spin reversal (as opposed to the traditional mode of individual spin reversal). Nuclear spin-lattice relaxation rate data obtained for pure$^{40,30}$ and defect-doped$^{29}$ samples indicate dual peaks similar to the
susceptibility data discussed above. This is consistent with the presence of a second relaxation mechanism.

1.4 References


Chapter Two

Application of Glauber Ising-Spin Dynamics to a One-Dimensional (Anti-) Ferromagnetic Lattice with Nearest Neighbor Interactions

The classic one-dimensional ferromagnetic lattice of Ising spins represents a foundation from which a more physically representative model will be constructed in Chapter 3. This chapter details the equilibrium per-spin magnetization and zero-field static magnetic susceptibility in the infinite chain limit, as well as a brute force approach to the calculation of the per-spin magnetization of a finite number of spins in an open chain. The application of the Glauber dynamic is then discussed, with the local equilibrium approximation being evaluated relative to the infinite and finite chain equilibrium results.

2.1 Infinite Chain and Finite Chain Equilibrium Solutions

Expressions for the equilibrium per-spin magnetization and zero-field static magnetic susceptibility in the infinite chain limit are developed using the transfer matrix formalism. In the finite chain case, a method is detailed for calculating the equilibrium per-spin magnetization by explicit construction of the multi-spin partition function.

2.1.1 Infinite Chain Equilibrium Solution

Recall the Hamiltonian for a one-dimensional chain of spins with nearest neighbor interactions:
\[ H = -J \sum_i^N \sigma_i \sigma_{i+1} - \mu B \sum_i^N \sigma_i \]  \hspace{1cm} (2.1)

Note that when applying this formalism to spin \( \frac{1}{2} \) particles, the correct energy units for the magnetic field portion of the Hamiltonian are contained in the magnetic moment \( \mu \).

The coupling (or exchange) energy \( J \) expresses the energy associated with adjacent spins being either parallel or anti-parallel, which is expressed by the product of the \( \pm 1 \) spin orientation variables. Thus, no additional factors related to the quantum spin number of the particles need be applied.

Assume a closed boundary condition such that \( \sigma_{N+1} = \sigma_1 \). This allows for a simplified calculation of the thermodynamic properties of the chain in the infinite chain limit with no loss of generality. The partition function for the system can now be expressed as:

\[ Z = \sum_{\sigma_1} \sum_{\sigma_2} \cdots \sum_{\sigma_N} \exp \left[ \frac{1}{k_B T} \sum_i^N (J \sigma_i \sigma_{i+1} + \mu B \sigma_i) \right] \]  \hspace{1cm} (2.2)

where each summation is taken over the two values (\( \pm 1 \)) each spin can take. For convenience in notation, let \( g = J / k_B T \) and \( b = \mu B / k_B T \). Now let a 2x2 transfer matrix \( T \) be defined such that the matrix elements are given by

\[ \langle \sigma | T | \sigma' \rangle = \exp[g \sigma \sigma' + b \sigma] \]  \hspace{1cm} (2.3)

where
\[ T = \begin{bmatrix} \exp[g + b] & \exp[-g + b] \\ \exp[-g - b] & \exp[g - b] \end{bmatrix} \] (2.4)

The partition function can now be written as:

\[
Z = \sum_{\sigma_1} \cdots \sum_{\sigma_N} \langle \sigma_1 \mid T \mid \sigma_2 \rangle \langle \sigma_2 \mid T \mid \sigma_3 \rangle \cdots \langle \sigma_{N-1} \mid T \mid \sigma_N \rangle \langle \sigma_N \mid \sigma_1 \rangle \\
= \sum_{\sigma_1} \langle \sigma_1 \mid T^N \mid \sigma_1 \rangle = \text{Trace}(T^N) = \lambda_+^N + \lambda_-^N
\] (2.5)

where \( \lambda_\pm \) are the two eigenvalues of \( T \).

These eigenvalues are determined by solving \( \det(T - \lambda \mathbb{I}) = 0 \):

\[
\det(T - \lambda \mathbb{I}) = \det \begin{pmatrix} \exp[g + b] - \lambda & \exp[-g + b] \\ \exp[-g - b] & \exp[g - b] - \lambda \end{pmatrix} \\
= \exp[2g] + \lambda^2 - \lambda \{\exp[g + b] + \exp[g - b] - \exp[-2g]\}
\] (2.6)

Recall that \( \sinh(x) = \frac{e^x - e^{-x}}{2} \) and \( \cosh(x) = \frac{e^x + e^{-x}}{2} \). Now,

\[
\det(T - \lambda \mathbb{I}) = \lambda^2 - \lambda \{2 \exp[g] \cosh(b)\} + 2 \sinh(2g) = 0
\] (2.7)
The eigenvalues are determined using the quadratic formula:

\[
\lambda_z = \frac{2\exp[g] \cosh(b) \pm \sqrt{4\exp[2g] \cosh^2(b) - 8\sinh(2g)}}{2} 
\]

Recall that \( \cosh^2(x) - \sinh^2(x) = 1 \). Now,

\[
\lambda_z = \exp[g] \cosh(b) \pm \exp[g] \sqrt{\cosh^2(b) - 1 + \exp[-4g]} 
\]

As \( N \) approaches infinity, the larger eigenvalue dominates the partition function.

Therefore, the Helmholtz free energy \( F \) can be written as:

\[
\lim_{N\to\infty} F = -k_B T \ln(\lambda_z^N) = -k_B T N \ln(\lambda_z) 
\]

And the free energy per spin is

\[
\lim_{N\to\infty} \frac{F}{N} = -k_B T \ln(\exp[g]) - k_B T \ln(\cosh(b) + \sqrt{\sinh^2(b) + \exp[-4g]}) 
\]

\[
= -J - k_B T \ln(\cosh(b) + \sqrt{\sinh^2(b) + \exp[-4g]}) 
\]

The magnetization per spin \( m \) is determined from the free energy per spin:
\[ m = - \frac{\partial F}{\partial B} \bigg|_r \]
\[ = k_B T \left[ \frac{1}{\cosh(b) + \sqrt{\sinh^2(b) + \exp[-4g]}} \right] \times \]
\[ \left[ \left( \frac{\mu}{k_B T} \right) \sinh(b) + \frac{1}{2} \sinh^2(b) + \exp[-4g] \right]^{1/2} \times \]
\[ \left[ \left( \frac{2\mu}{k_B T} \right) \sinh(b) \cosh(b) \right] \]
\[ (2.12) \]

To simplify notation, let \( R = \sqrt{\sinh^2(b) + \exp[-4g]} \). Now,
\[ m = k_B T \left[ \frac{1}{\cosh(b) + R} \right] \left[ \left( \frac{\mu}{k_B T} \right) \sinh(b) + \frac{1}{2} \left( \frac{1}{R} \right) \left[ \frac{2\mu}{k_B T} \right] \sinh(b) \cosh(b) \right] \]
\[ (2.13) \]
\[ = \left[ \frac{\mu}{\cosh(b) + R} \right] \frac{R \sinh(b) + \sinh(b) \cosh(b)}{R} = \frac{\mu \sinh(b)}{R} \]

The magnetization per spin in the infinite chain limit is then
\[ m = \frac{\mu \sinh(b)}{\sqrt{\sinh^2(b) + \exp[-4g]}} \]
\[ (2.14) \]

This result, with the magnetization normalized by \( \mu \), is displayed for a range of \( \mu B / k_B T \) and \( J / k_B T \) below in Figure 2.1:
The static magnetic susceptibility is found from the magnetization:

\[ \chi = \frac{\partial m}{\partial H} \]
Thus, the static magnetic susceptibility is

\[ \chi = \frac{\mu}{k_B T} \frac{\cosh(b) \exp(-4g)}{\sinh^2(b) \cosh(b) - \exp(-4g)} \]

(2.15)

\[ \chi = \frac{\mu}{k_B T} \frac{R^2 \cosh(b) - \sinh(b) \cosh(b)}{R^2} \left( \frac{1}{k_B T} - \frac{\mu}{k_B T} \sinh^2(b) \cosh(b) \right) \]

(2.16)

\[ \chi = \frac{3m_B}{2B} \]

(2.17)
And the static magnetic susceptibility in the zero field \((B\to 0)\) limit is

\[
\lim_{B\to 0} \chi = \left(\frac{\mu}{k_B T}\right)\exp\left[2g\right]
\]

The static magnetic susceptibility, normalized by \(\mu\), is displayed for a range of \(\mu B / k_B T\) and \(J / k_B T\) below in Figure 2.2:

```
Figure 2.2: Static susceptibility of infinite chain vs. \(\mu B / k_B T\)
for \(J / k_B T = 0.1, 1, \) and 10
```
2.1.2 Finite Chain Equilibrium Solution

In calculating the equilibrium per spin magnetization of an open chain of finite length, the partition function of a six-spin ferromagnetic chain with nearest neighbor interactions will be explicitly constructed. From this partition function, the equilibrium properties can be calculated. The Hamiltonian for this chain is:

\[ H = -J \sum_i \sigma_i \sigma_{i+1} - \mu_B \sum_i \sigma_i \]  

(2.18)

The chain of six Ising spins may take any of \(2^6 = 64\) possible configurations, though many of the configurations are degenerate (have the same energy). The various configurations, their degeneracy, and their energy are detailed below in Table 2.1.

Table 2.1: Energy and degeneracy of various configurations of a six-spin ferromagnetic chain

<table>
<thead>
<tr>
<th>Description</th>
<th>Example</th>
<th>Degeneracy</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Up</td>
<td>↑↑↑↑↑↑</td>
<td>1</td>
<td>(-5J - 6\mu B)</td>
</tr>
<tr>
<td>One Down (End)</td>
<td>↓↑↑↑↑↑</td>
<td>2</td>
<td>(-3J - 4\mu B)</td>
</tr>
<tr>
<td>One Down (Inside)</td>
<td>↑↓↑↑↑↑</td>
<td>4</td>
<td>(-J - 4\mu B)</td>
</tr>
<tr>
<td>Two Adjacent Down (End)</td>
<td>↓↓↑↑↑↑</td>
<td>2</td>
<td>(-3J - 2\mu B)</td>
</tr>
<tr>
<td>Two Adjacent Down (Inside) - and -</td>
<td>↑↓↓↑↑↑</td>
<td>3 + 1</td>
<td>(-J - 2\mu B)</td>
</tr>
<tr>
<td>Two Non-Adjacent Down (Both Ends)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Two Non-Adjacent Down (One End)</td>
<td>↓↑↓↑↑↑</td>
<td>6</td>
<td>(J - 2\mu B)</td>
</tr>
<tr>
<td>Configuration</td>
<td>Result</td>
<td>Energy</td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------------</td>
<td>----------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>Two Non-Adjacent Down (Inside)</td>
<td>↑↓↑↓↑↑↑↑</td>
<td>3</td>
<td>$3J - 2\mu B$</td>
</tr>
<tr>
<td>Three Adjacent Down (End)</td>
<td>↓↓↓↑↑↑↑↑</td>
<td>2</td>
<td>$-3J$</td>
</tr>
<tr>
<td>Three Adjacent Down (Inside)</td>
<td>↑↓↓↓↑↑↑↑</td>
<td>2 + 2</td>
<td>$-J$</td>
</tr>
<tr>
<td>- and -</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>One Non-Adjacent and Two Adjacent Down (Both Ends)</td>
<td>↓↑↑↑↓↓↓↓</td>
<td></td>
<td>$J$</td>
</tr>
<tr>
<td>One Non-Adjacent (One End) and Two Adjacent Down</td>
<td>↓↑↓↓↑↑↑↑</td>
<td>4 + 4</td>
<td>$J$</td>
</tr>
<tr>
<td>- and -</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>One Non-Adjacent and Two Adjacent (One End) Down</td>
<td>↓↓↑↑↑↑↑↑</td>
<td></td>
<td>$J$</td>
</tr>
<tr>
<td>One Non-Adjacent and Two Adjacent Down (Inside)</td>
<td>↑↓↑↓↓↓↑↑</td>
<td>2 + 2</td>
<td>$3J$</td>
</tr>
<tr>
<td>Three Non-Adjacent Down (Both Ends)</td>
<td>↓↑↓↑↑↑↑↑</td>
<td>2</td>
<td>$5J$</td>
</tr>
</tbody>
</table>

Note that the table above identifies 22 states with zero, one, or two spins down and 20 states with three spins down. An additional 22 states are found by reversing the orientation of the 22 zero, one, or two spin down configurations. These reversed configurations have the same degeneracy as their original counterparts, and the energy is found by reversing the sign of the $B$ term in the energy associated with the original configuration. Thus, all 64 possible states of the six spin chain are described.
The partition function is defined as

$$Z = \sum_j N_j \exp\left[ -\frac{E_j}{k_B T} \right]$$

(2.19)

where $j$ is the index ascribed to each unique energy state

$N_j$ is the degeneracy of state $j$

$E_j$ is the energy of state $j$

The contribution from the 20 states with three spins down is

$$Z_{3\text{spin down}} = 2\exp[3g] + 4\exp[g] + 8\exp[-g] + 4\exp[-3g] + 2\exp[-5g]$$

(2.20)

The contribution from the 22 states with zero, one, or two spins down is

$$Z_{<3\text{spin down}} = \exp[5g] \exp[6b] + 2\exp[3g] \exp[4b] + 4\exp[g] \exp[4b] +$$

$$+ 2\exp[3g] \exp[2b] + 4\exp[g] \exp[2b] + 6\exp[-g] \exp[2b] +$$

$$+ 3\exp[-3g] \exp[2b]$$

(2.21)

The contribution from the 22 states with zero, one, or two spins up is
\[ Z_{\text{spin-up}} = \exp[5g] \exp[-6b] + 2 \exp[3g] \exp[-4b] + 4 \exp[g] \exp[-4b] + 2 \exp[3g] \exp[-2b] + 4 \exp[g] \exp[-2b] + 6 \exp[-g] \exp[-2b] + 3 \exp[-3g] \exp[-2b] \]

After factoring and collecting terms into appropriate \( \cosh \) functions, the complete partition function is

\[
Z = Z_{-5} \exp[-5g] + Z_{-3} \exp[-3g] + Z_{-1} \exp[-g] + Z_{5} \exp[5g] + Z_{3} \exp[3g] + Z_{1} \exp[g]
\]

where

\[
Z_{-5} = 2
\]

\[
Z_{-3} = 4 + 2 \cosh(-2b) + 4 \cosh(2b)
\]

\[
Z_{-1} = 8 + 4 \cosh(-2b) + 8 \cosh(2b)
\]

\[
Z_{1} = 4 + 8 \cosh(4b) + 8 \cosh(2b)
\]

\[
Z_{3} = 2 + 4 \cosh(4b) + 4 \cosh(2b)
\]

\[
Z_{5} = 2 \cosh(6b)
\]

Similar to the infinite chain case discussed above, the magnetization of the finite chain is determined from the Helmholtz free energy:
\[ m = -\left( \frac{1}{6} \frac{\partial F}{\partial B} \right)_r = \left( \frac{1}{6} \right) (k_B T) \frac{\partial}{\partial B} \ln(Z) = \left( \frac{1}{6} \right) (k_B T) \left( \frac{1}{Z} \right) \frac{\partial Z}{\partial B} \quad (2.25) \]

where the factor of 1/6 is introduced to provide the magnetization on a per spin basis. A straightforward evaluation of the derivative of the partition function defined above yields

\[
m = \left( \frac{\mu}{6Z} \right) \left\{ \exp(-3g)[-4\sinh(-2b) + 8\sinh(2b)] + \exp(-g)[-8\sinh(-2b) + 16\sinh(2b)] + \exp(3g)[16\sinh(4b) + 8\sinh(2b)] + \exp(5g)[12\sinh(6b)] \right\} \quad (2.26)\]

This result, with the magnetization normalized by \( \mu \), is displayed for a range of \( \mu B / k_B T \) and \( J / k_B T \) below in Figure 2.3:
Figure 2.3: Equilibrium magnetization of finite (six spin) chain vs. $\mu B / k_B T$ for $J / k_B T = 0.1$, 1, and 10

### 2.1.3 Comparison of Equilibrium Solutions

For convenience, the equilibrium magnetizations obtained for the infinite chain and finite chain are directly compared below in Figure 2.4, Figure 2.5, and Figure 2.6.
Equilibrium Magnetization of Infinite and Finite Chains with $J / k_B T = 0.1$

Figure 2.4: Equilibrium magnetization of infinite and finite chains vs. $\mu B / k_B T$ for $J / k_B T = 0.1$
Figure 2.5: Equilibrium magnetization of infinite and finite chains vs. $\mu B / k_B T$ for $J / k_B T = 1$
2.2 Derivation of Spin Dynamic Equations

The previously discussed equilibrium solutions for the magnetization and susceptibility of one-dimensional Ising chains provides the magnetic behavior of the system in the limit of long times. In order to assess the dynamic processes taking place during the approach to equilibrium, the appropriate spin dynamic equations must be obtained. The Glauber approach\(^2\) to determining this behavior is detailed below. Subsequently, a local equilibrium approximation is applied to model the infinite chain and finite chain cases.

In the absence of an applied magnetic flux density \((B = 0)\), the Hamiltonian for an arbitrary site \(i\) contains the following terms:
From these terms, the portion of the system energy associated with spin $\sigma_i$ is:

\[
H(\sigma_i) = -J(\sigma_{i-1} + \sigma_i, \sigma_{i+1}) = -J\sigma_i(\sigma_{i-1} + \sigma_{i+1})
\]  

(2.28)

Changing the sign of $\sigma_i$ represents the change in energy resulting from a switch in orientation of the spin at site $i$. The ratio of probabilities of the spin at site $i$ taking the value $-\sigma_i$ as opposed to $\sigma_i$ is given by the ratio of the respective Maxwell-Boltzmann factors as the system approaches equilibrium at temperature $T$. Thus:

\[
\frac{p(-\sigma_i)}{p(\sigma_i)} = \frac{\exp[-(H(-\sigma_i)/k_B T)]}{\exp[-(H(\sigma_i)/k_B T)]} = \frac{\exp[-g\sigma_i(\sigma_{i-1} + \sigma_{i+1})]}{\exp[g\sigma_i(\sigma_{i-1} + \sigma_{i+1})]}
\]  

(2.29)

where $p(\sigma_i)$ is the probability that the spin at site $i$ will have the value $\sigma_i$.

$p(-\sigma_i)$ is the probability that the spin at site $i$ will have the value $-\sigma_i$.

Recalling the identities

\[\sinh x + \cosh x = e^x\]

\[\cosh x - \sinh x = e^{-x}\]

the exponentials above may be expanded as
Since $\sigma$ can only be $\pm 1$, cosh is an even function, and sinh is an odd function, the above expression may be further simplified as

$$\exp[-g \sigma_i (\sigma_{i-1} + \sigma_{i+1})] = \cosh[g \sigma_i (\sigma_{i-1} + \sigma_{i+1})] \mp \sigma_i \sinh[g \sigma_i (\sigma_{i-1} + \sigma_{i+1})]$$

(2.31)

Noting that $\tanh x = \frac{\sinh x}{\cosh x}$ and that tanh is an odd function, the exponentials can be written as:

$$\exp[-g \sigma_i (\sigma_{i-1} + \sigma_{i+1})] = \cosh[g \sigma_i (\sigma_{i-1} + \sigma_{i+1})][1 \mp \sigma_i \tanh[g \sigma_i (\sigma_{i-1} + \sigma_{i+1})]]$$

$$= \cosh[g \sigma_i (\sigma_{i-1} + \sigma_{i+1})]\left[1 \mp \frac{1}{2} \sigma_i (\sigma_{i-1} + \sigma_{i+1}) \tanh[2g] \right]$$

(2.32)

Now,

$$\frac{p(-\sigma_i)}{p(\sigma_i)} = \frac{1 - \frac{1}{2} \sigma_i (\sigma_{i-1} + \sigma_{i+1}) \tanh[2g]}{1 + \frac{1}{2} \sigma_i (\sigma_{i-1} + \sigma_{i+1}) \tanh[2g]}$$

(2.33)

If the spins at all other sites are considered fixed, an equilibrium will be approached where the ratio of probabilities of the spin at site $i$ taking the value $-\sigma$ as opposed to $\sigma$ is...
equal to the ratio of transition probabilities of $\sigma_i$ flipping to $-\sigma_i$ as opposed to $-\sigma_i$ flipping to $\sigma_i$. For the spin at site $i$, this means

$$\frac{p(-\sigma_i)}{p(\sigma_i)} = \frac{w(\sigma_i)}{w(-\sigma_i)}$$

(2.34)

where $w(\sigma_i)$ is the transition probability, or probability per unit time, that the spin at site $i$ flips from $\sigma_i$ to $-\sigma_i$ while the spins at other sites remain momentarily fixed.

$w(-\sigma_i)$ is the transition probability, or probability per unit time, that the spin at site $i$ flips from $-\sigma_i$ to $\sigma_i$ while the spins at other sites remain momentarily fixed.

For an Ising model with nearest neighbor interactions and no applied magnetic flux density, Glauber identified\(^2\) a convenient form to assume for the transition probability of the spin at site $i$:

$$w(\sigma_i) = \frac{1}{2} \alpha \left[ 1 - \frac{1}{2} \gamma \sigma_i \left( \sigma_{i-1} + \sigma_{i+1} \right) \right]$$

(2.35)

where $\alpha$ is a parameter describing the time scale on which transitions take place [s\(^{-1}\)]

$\gamma$ is a parameter related to the coupling between adjacent spins.

Now, for the spin at site $i$.
\[
\frac{p(-\sigma_i)}{p(\sigma_i)} = \frac{w(\sigma_i)}{w(-\sigma_i)} = \frac{1 - \frac{1}{2} \gamma \sigma_i (\sigma_{i-1} + \sigma_{i+1})}{1 + \frac{1}{2} \gamma \sigma_i (\sigma_{i-1} + \sigma_{i+1})}
\] (2.36)

Comparison with the previously determined ratio of spin probabilities yields

\[
\gamma = \tanh[2g]
\] (2.37)

In the presence of an applied magnetic flux density \((B \neq 0)\), the portion of the system energy associated with spin \(\sigma_i\) receives an additional term and becomes:

\[
H(\sigma_i) = -J \sigma_i (\sigma_{i-1} + \sigma_{i+1}) - \mu B \sigma_i
\] (2.38)

By the method described above, it is found that:

\[
\frac{p(-\sigma_i)}{p(\sigma_i)} = \frac{\exp[-(H(-\sigma_i)/k_B T)]}{\exp[-(H(\sigma_i)/k_B T)]} = \frac{\exp[-g \sigma_i (\sigma_{i-1} + \sigma_{i+1})]\exp[-b \sigma_i]}{\exp[g \sigma_i (\sigma_{i-1} + \sigma_{i+1})]\exp[b \sigma_i]}
\] (2.39)

\[
= \frac{w(\sigma_i)}{w(-\sigma_i)} \frac{\exp[-b \sigma_i]}{\exp[b \sigma_i]} = \frac{w(\sigma_i)}{w(-\sigma_i)} \left( \frac{1 - \sigma_i \tanh[b]}{1 + \sigma_i \tanh[b]} \right)
\]

Including the applied magnetic flux density requires the assumed form of the transition probability to be augmented such that

\[
w'(\sigma_i) = w(\sigma_i)(1 - \sigma_i \beta_{\text{even}}) = \frac{1}{2} \alpha \left[ 1 - \sigma_i \beta - \frac{1}{2} \gamma \sigma_i (\sigma_{i-1} + \sigma_{i+1}) + \frac{1}{2} \beta \sigma_i (\sigma_{i-1} + \sigma_{i+1}) \right]
\] (2.40)
where

\[ \beta = \tanh[b] \]  

(2.41)

The transition probabilities defined above can be used to describe the time evolution of the expectation values of the spins, as well as multiple-spin products. For example, the expectation values of a single spin and a product of two spins are respectively defined as

\[ q_i(t) = \langle \sigma_i(t) \rangle = \sum_{\{\sigma\}} \sigma_i p(\sigma_1, \ldots, \sigma_N, t) \]  

(2.42)

and

\[ r_{i,j}(t) = \langle \sigma_i(t)\sigma_j(t) \rangle = \sum_{\{\sigma\}} \sigma_i\sigma_j p(\sigma_1, \ldots, \sigma_N, t) \]  

(2.43)

where \( \{\sigma\} \) denotes summation over all \( 2^N \) possible configurations of the \( N \) spins

- \( t \) is time
- \( p(\sigma_1, \ldots, \sigma_N, t) \) is the probability of the system being in a particular configuration at time \( t \)

Note that \( r_{i,i}(t) = 1 \) for \( i = j \), and that \( r_{i,j}(t) = r_{j,i}(t) \).

The time rate of change of the single spin expectation value can then be written as
\[
\frac{d}{dt} q_i(t) = \frac{d}{dt} \sum_{[\sigma]} \sigma_i p(\sigma_i, \ldots, \sigma_N, t) = \sum_{[\sigma]} \sigma_i \frac{d}{dt} p(\sigma_i, \ldots, \sigma_N, t)
\] (2.44)

Using the transition probability introduced above, the time rate of change of the spin configuration probability can be expressed as\(^2\)

\[
\frac{d}{dt} p(\sigma_i, \ldots, \sigma_N, t) = -\left[ \sum_m w(\sigma_m) \right] p(\sigma_i, \ldots, \sigma_m, \ldots, \sigma_N, t) + \\
\sum_m w(-\sigma_m) p(\sigma_i, \ldots, -\sigma_m, \ldots, \sigma_N, t)
\] (2.45)

The first term represents how a change in orientation (transition from \(\sigma_m\) to \(-\sigma_m\)) of any of the spins in the configuration will destroy that configuration, resulting in a negative contribution to the change in configuration probability with time. Alternatively, the second term represents how a change in orientation (transition from \(-\sigma_m\) to \(\sigma_m\)) of an oppositely oriented spin in a configuration that is otherwise identical will serve to create that configuration, resulting in a positive contribution to the change in configuration probability with time. The rate of change of configuration probability can be alternately written as\(^2\)

\[
\frac{d}{dt} p(\sigma_i, \ldots, \sigma_N, t) = -\sum_m \sigma_m \sum_{\sigma_m'} w(\sigma_m') p(\sigma_i, \ldots, \sigma_m, \ldots, \sigma_N, t)
\] (2.46)

where the inner summation over \(\sigma_m'\) represents a summation over the two possible values \(\sigma_m\) may take, 1 and -1. Depending on the value that \(\sigma_m\) takes in the configuration
(the outer summation), one of the two terms in the inner summation represents the
destruction term while the other represents the creation term. Upon substitution into the
time rate of change of the single spin expectation value:

\[
\frac{d}{dt} q_i(t) = \sum_{\sigma_i} \left\{ -\sum_{\sigma_m} \sigma_m \sum_{\sigma_m'} w(\sigma_m') p(\sigma_i, \cdots, \sigma_m', \cdots, \sigma_N, t) \right\}
\]

(2.47)

Since the expectation value is specific to the spin at site \(i\), the transition probabilities
pertaining to spins at other sites are not relevant. This is borne out in detailed
calculations and is consistent with the use of the transition probability to represent the
spin flip probability per unit time of a specific site, while regarding the spins at other sites
as being momentarily fixed. Now, the summation over \(m\) can be replaced with the \(i\)th
term:

\[
\frac{d}{dt} q_i(t) = \sum_{\sigma_i} \left\{ -\sigma_i \sum_{\sigma_i'} w(\sigma_i') p(\sigma_i, \cdots, \sigma_i', \cdots, \sigma_N, t) \right\}
\]

\[
= \sum_{\sigma_i} \left\{ -\sigma_i \left( w(1) p(\sigma_i, \cdots, 1, \cdots, \sigma_N, t) - w(-1) p(\sigma_i, \cdots, -1, \cdots, \sigma_N, t) \right) \right\}
\]

(2.48)

When (in the sum over the \(2^N\) possible configurations) \(\sigma_i\) is 1, the first term is the
destruction term while the second is the creation term (and vice versa when \(\sigma_i\) is -1).

Note that since \(\sigma_i\) can only take two values, the transition probabilities between the two
states must be equal and opposite:

\[
w(1) p(\sigma_i, \cdots, 1, \cdots, \sigma_N, t) = -w(-1) p(\sigma_i, \cdots, -1, \cdots, \sigma_N, t)
\]

(2.49)
Then

\[ \sigma_i \left\{ w(1) p(\sigma_i, \cdots, 1, \cdots, \sigma_N, t) - w(-1) p(\sigma_i, \cdots, -1, \cdots, \sigma_N, t) \right\} = \]

\[
\begin{cases} 
(1)(2w(1) p(\sigma_i, \cdots, 1, \cdots, \sigma_N, t)) \text{ when } \sigma_i = 1 \\
(-1)(-2w(-1) p(\sigma_i, \cdots, -1, \cdots, \sigma_N, t)) \text{ when } \sigma_i = -1 
\end{cases}
\]

\[ = 2w(\sigma_i) p(\sigma_i, \cdots, \sigma_i, \cdots, \sigma_N, t) \] (2.50)

Therefore, the time evolution of the expectation value of a spin at site \( i \) may now be expressed as (using the augmented transition probability):

\[
\frac{d}{dt} q_i(t) = -2 \sum_{\sigma} \sigma w'(\sigma_i) p(\sigma_i, \cdots, \sigma_N, t) \] (2.51)

Applying the augmented transition probability determined above yields:

\[
\frac{d}{dt} q_i(t) = -\alpha \sum_{\sigma} \sigma \left\{ 1 - \sigma \beta - \frac{1}{2} \gamma \sigma_i (\sigma_{i-1} + \sigma_{i+1}) + \frac{1}{2} \gamma \beta \sigma_i (\sigma_{i-1} + \sigma_{i+1}) \right\} p(\sigma_i, \cdots, \sigma_N, t) \]

\[
= -\alpha \sum_{\sigma} \sigma \left\{ \sigma_i - \beta - \frac{1}{2} \gamma (\sigma_{i-1} + \sigma_{i+1}) + \frac{1}{2} \gamma \beta (\sigma_{i-1} + \sigma_{i+1}) \right\} p(\sigma_i, \cdots, \sigma_N, t) \] (2.52)

\[
= -\alpha \left\{ q_i(t) - \beta - \frac{1}{2} \gamma (q_{i-1}(t) + q_{i+1}(t)) + \frac{1}{2} \gamma \beta (r_{i-1}(t) + r_{i+1}(t)) \right\} \]
The dynamic equations for the single spin expectation values depend on the expectation values of the nearest neighbor spins as well as the products of the spin with each of its nearest neighbors. By a process similar to that detailed above, the time evolution of the expectation value of a product of two spins is:

\[
\frac{d}{dt} r_{i,j}(t) = -2 \sum_{[\sigma]} \sigma_i \sigma_j \left\{ w'(\sigma_i) + w'(\sigma_j) \right\} p(\sigma_i, \cdots, \sigma_N, t) \]

\[
= -\alpha \left\{ 2r_{i,j}(t) - \beta q_j(t) - \frac{1}{2} \gamma (r_{i,j-1}(t) + r_{i,j+1}(t)) + \frac{1}{2} \eta \beta (s_{i,j-1}(t) + s_{i,j+1}(t)) \right\} \tag{2.53}
\]

where

\[
s_{i,j,k}(t) = \langle \sigma_i(t) \sigma_j(t) \sigma_k(t) \rangle = \sum_{[\sigma]} \sigma_i \sigma_j \sigma_k p(\sigma_1, \cdots, \sigma_N, t) \tag{2.54}
\]

is the expectation value of the product of the three spins at lattice sites \(i, j, \) and \(k.\)

The dynamic equation describing the time evolution of the two-spin product expectation value depends on the expectation value of the product of three spins. As expected, this trend continues such that the three-spin expectation value dynamic is dependant upon the four-spin expectation value, and so on. This system of equations has no exact solution when a non-zero applied magnetic field is present.
2.3 Infinite Chain Application of Local Equilibrium Approximation

A local equilibrium approximation will be implemented to model the infinite chain. The dynamic equation representing the time evolution of the expectation value of a spin on lattice site \( i \) was previously found to be:

\[
\frac{d}{dt} q_i(t) = -\alpha \left( q_i(t) - \beta - \frac{1}{2} \gamma (q_{i+1}(t) + q_{i-1}(t)) + \frac{1}{2} \gamma \beta (r_{i-1}(t) + r_{i+1}(t)) \right) \tag{2.55}
\]

As a simplification, the average value of the expectation value will be considered. The dynamic equation can then be written as:

\[
\frac{d}{dt} Q(t) = -\alpha \left( Q(t) - \beta - \frac{1}{2} \gamma (Q(t) + Q(t)) + \frac{1}{2} \gamma \beta (R(t) + R(t)) \right) \tag{2.56}
\]

\[
= -\alpha \left( Q(t) - \beta - \gamma Q(t) + \gamma \beta R(t) \right)
\]

with

\[
Q(t) = \frac{1}{N} \sum_{i=1}^{N} q_i(t) \tag{2.57}
\]

\[
R(t) = \frac{1}{N} \sum_{i=1}^{N} r_{i+1}(t) \tag{2.58}
\]
where \( Q \) is the average single-spin expectation value

\[ R \] is the average two-spin product expectation value

Alternatively, \( R \) can be expressed as:

\[
R(t) = \sum_{\sigma, \sigma'} [P(\sigma, \sigma') \sigma \sigma']
\]  

(2.59)

where \( P(\sigma, \sigma') \) is the probability that a site will take a value \( \sigma \) and an adjacent site will take a value of \( \sigma' \)

Since \( \sigma \) takes a value of \( \pm 1 \), \( P(\sigma, \sigma') \) is four different quantities: \( P(+,+), P(+,-), P(-,+), \) and \( P(-,-) \). Three equations describing the required consistency amongst these probabilities are apparent:

\[
Q(t) = P(+,+) - P(-,-)
\]  

(2.60)

\[
P(+,-) = P(-,+)
\]  

(2.61)

\[
1 = P(+,+)+P(+,-)+P(-,+)+P(-,-)
\]  

(2.62)

The fourth equation required to determine the four unknowns above is found using the local equilibrium approximation\(^3\), where the local neighborhood of any spin is considered to exist in a temporary equilibrium state for time scales less than the macroscopic relaxation time. Recall that for a given lattice site, the ratio of probabilities of the spin at
site $i$ taking the value $-\sigma_i$ as opposed to $\sigma_i$ is given by the ratio of the respective Maxwell-Boltzmann factors as the system approaches equilibrium at temperature $T$:

$$\frac{p(-\sigma_i)}{p(\sigma_i)} = \frac{\exp[-(H(-\sigma_i)/k_B T)]}{\exp[-(H(\sigma_i)/k_B T)]} = \frac{\exp[-g\sigma_i(\sigma_{i+1} + \sigma_{i-1}) - b\sigma_i]}{\exp[g\sigma_i(\sigma_{i+1} + \sigma_{i-1}) + b\sigma_i]} \quad (2.63)$$

Let $n_i$ be the number of nearest neighbor sites that have a value of $+1$. Then it is observed that:

$$\begin{align*}
(\sigma_{i+1} + \sigma_{i-1}) &= \begin{cases} 
-2 & n_i = 0 \\
0 & n_i = 1 \\
2 & n_i = 2
\end{cases} \quad (2.64)
\end{align*}$$

Following the non-standard notation introduced for this method, let:

$P(\sigma)$ be the probability that a site has a value $\sigma$

$P(\sigma|n_i)$ be the probability that $n_i$ nearest neighbors of a site (that has a value $\sigma$) are up

$P_c(\sigma|n_i)$ be the conditional probability that $n_i$ nearest neighbors of a site are up, if that site has a value $\sigma$

and note that

$$P(\sigma | n_i) = P(\sigma) P_c(\sigma | n_i) \quad (2.65)$$

Now,
Since the nearest neighbor spins do not influence each other in the case of an infinite chain,}

\[ P_c(\sigma \mid n_i) = \binom{2}{n_i} [P_c(\sigma, +)]^{n_i} [P_c(\sigma, -)]^{2-n_i} \]  

(2.68)

where \( P_c(\sigma, \sigma') \) is the conditional probability that the nearest neighbor site will have the value \( \sigma' \) if that site's nearest neighbor has the value \( \sigma \)
\[ P(\sigma, \sigma') = P(\sigma)P_\sigma(\sigma, \sigma') \] (2.70)

Now

\[ \frac{P_\sigma(- \mid 0)}{P_\sigma(+ \mid 0)} = \frac{[P(-, -)/P(-)]^2}{[P(+)/P(+)]^2} = \frac{[P(+)P(-, -)]^2}{[P(-)P(-, +)]^2} \] (2.71)

and

\[ \frac{P_\sigma(- \mid 1)}{P_\sigma(+ \mid 1)} = \frac{[P(-, +)/P(-)]^2}{[P(+)P(+)][P(+)P(+)]} = \frac{[P(+)P(-, -)]^2}{[P(-)P(-, +)]^2} \] (2.72)

Equating this with the previously obtained result

\[ \frac{\exp[2g - b]}{\exp[-2g + b]} = \frac{P(+)P(-, -)}{P(-)P(-, +)} \] (2.73)

and

\[ \frac{\exp[-b]}{\exp[b]} = \frac{P(+)P(-, -)}{P(-)P(+, +)} \] (2.74)

And substituting yields
This simplifies to

$$\exp[4g] = \frac{P(++,+)P(---)}{P(++,+)P(---)}$$  \hspace{1cm} (2.76)$$

This result is the fourth equation required to solve for the four unknown two-spin probabilities $P(++,+)P(++,+)P(++,+)P(++,+)$, and $P(-,-)$. The solutions can be written as:

$$P(++,+) = \frac{1}{2}(1 + Q(t)) + \frac{1 - \sqrt{Q(t)^2 - (Q(t)^2 - 1)\exp(4g)}}{2(\exp(4g) - 1)}$$  \hspace{1cm} (2.77)$$

$$P(++,-) = P(++,+) = \frac{1 - \sqrt{Q(t)^2 - (Q(t)^2 - 1)\exp(4g)}}{2(\exp(4g) - 1)}$$  \hspace{1cm} (2.78)$$

$$P(++,+) = \frac{1}{2}(1 - Q(t)) + \frac{1 - \sqrt{Q(t)^2 - (Q(t)^2 - 1)\exp(4g)}}{2(\exp(4g) - 1)}$$  \hspace{1cm} (2.79)$$

where a non-physical second solution has been eliminated, as determined by inspection of the two-spin probabilities in the limit $Q(t) \rightarrow \pm 1$. Now, $R(t)$ can be expressed in terms of $Q(t)$ and $g$ as:
\[ R(t) = \sum_{\sigma, \sigma'} \left[ P(\sigma, \sigma') \sigma \sigma' \right] = P(+, +) - P(+, -) - P(-, +) + P(-, -) \]

\[ = 1 + \frac{2 - 2\sqrt{Q(t)^2 - (Q(t)^2 - 1)} \exp(4g)}{(\exp(4g) - 1)} \]

The time evolution of \( Q(t) \) can now be expressed purely in terms of \( Q(t) \), \( J / k_B T \), and \( \mu_B / k_B T \):

\[ \frac{d}{dt} Q(t) = -\alpha \left[ Q(t) - \beta - \gamma Q(t) + \gamma \left( 1 + \frac{2 - 2\sqrt{Q(t)^2 - (Q(t)^2 - 1)} \exp(4g)}{(\exp(4g) - 1)} \right) \right] \]

This differential equation is solved numerically for parameters of interest, where the magnetic moment per site \( M(t) \) and the average spin expectation value are related by \( M(t) = \mu Q(t) \). Note that the time evolution of \( Q(t) \) described by the equation above reduces to the exact equilibrium solution when \( dQ(t)/dt = 0 \) is evaluated. This indicates how the numerical implementation of the local equilibrium approximation is expected to provide very good equilibrium results, while providing a dynamic response that is approximated in accordance with the assumed temporary local equilibrium states existing for time scales less than the macroscopic relaxation time.

### 2.3.1 Correspondence with Infinite Chain Equilibrium Solution

The dynamic equation obtained for the time rate of change of the single spin expectation value using the local equilibrium approximation is now evaluated for various values of \( J / k_B T \), and \( \mu B / k_B T \). For illustrative purposes, a nominal value of 1000 s\(^{-1}\) is chosen for \( \alpha \),
the parameter representing the time scale of the process, and the spins are all assumed to have initial expectation values of zero.

The time response of the one-dimensional infinite chain to an applied magnetic field with $\mu B / k_B T = 0.1$ is provided below in Figure 2.7, where the solid lines indicate the results of the numerical solution of the dynamic equation and the dotted lines represent the equilibrium solution previously established for the infinite chain limit.

For each value of $J / k_B T$ considered, the dynamic model approaches the correct equilibrium magnetization. Consistent with the equilibrium solution previously presented, the equilibrium magnetization increases with increasing $J / k_B T$, owing to the increasing
energy benefit associated with adjacent spins aligning with each other. Also demonstrated in Figure 2.7 is the increasing resistance to magnetization changes (time to reach equilibrium) as $J / k_B T$ increases. This is intuitively explained by how the larger energies associated with spin orientation serve to reduce the probability of spin flip transitions to such a degree that larger and larger time periods are required for the system to reach equilibrium.

![Magnetization of Infinite Chain vs. Time](image)

Figure 2.8: Equilibrium (dotted line) and dynamic (solid line) magnetization of infinite chain vs. time for $\mu B / k_B T = 1$ and for $J / k_B T = 0.1, 1, \text{ and } 10$

The time response with an applied magnetic field with $\mu B / k_B T = 1$ is indicated in Figure 2.8 above. Similar behavior is observed, with the higher values of $J / k_B T$ resulting in responses that reach higher equilibrium magnetizations (with a magnetization of 1 being the maximum possible, i.e. all spins are up) while also requiring longer times. The
increase in $\mu B / k_B T$ relative to the previous figure has the effect of increasing the equilibrium magnetization and speeding the approach to equilibrium, which is expected as an increased $\mu B / k_B T$ provides a reduced minimum energy state for the system to evolve towards. In effect, the greater the drop into a valley, the faster a cart will roll down the slope.

![Magnetization of Infinite Chain vs. Time](image)

**Figure 2.9:** Equilibrium (dotted line) and dynamic (solid line) magnetization of infinite chain vs. time for $\mu B / k_B T = 10$ and for $J / k_B T = 0.1, 1,$ and $10$.

The time response with an applied magnetic field with $\mu B / k_B T = 10$ is indicated in Figure 2.9 above. Now, all values of $J / k_B T$ considered approach an equilibrium magnetization of 1, with approach times still less than that of Figure 2.8 (where $\mu B / k_B T = 1$).
The hysteresis response to a time-varying applied magnetic field can also be calculated and compared with that obtained with the equilibrium solution. Similar to the previous calculations, a nominal value of $\alpha = 1000 \text{ s}^{-1}$ is chosen and the expectation value of the spins is initially zero. Due to the large difference in relaxation time scales between $J / k_B T = 0.1, 1$ and $J / k_B T = 10$ (as indicated in the figures above), only $J / k_B T = 0.1$ and 1 are shown together below in Figure 2.10. An applied field of amplitude $\mu B / k_B T = 3$ is sinusoidally cycled at a frequency of 0.01 Hz for 100 seconds, effectively tracing a hysteresis cycle from initial magnetization to saturation in both directions.

Figure 2.10: Equilibrium (dotted line) and dynamic (solid line) magnetization of infinite chain vs. $\mu B / k_B T$ (cycled at 0.01 Hz) for $J / k_B T = 0.1$, and 1
The solid lines indicate the results of the numerical solution of the dynamic equation and the dotted lines represent the equilibrium solution previously established for the infinite chain limit. Good agreement is shown, and the paramagnetic behavior is consistent with the period of the applied field being much longer than the relaxation time of the spins.

From the hysteresis behavior above, the static susceptibility is obtained by a straightforward numerical differentiation of the magnetization with respect to the applied field. This result is compared to the equilibrium static susceptibility in Figure 2.11 below, where the solid lines indicate the results of the numerical solution and the dotted lines represent the equilibrium solution.

![Static Susceptibility vs. Applied Magnetic Field](image)

Figure 2.11: Equilibrium (dotted line) and dynamic (solid line) static susceptibility of infinite chain vs. $\mu B / k_B T$ (cycled at 0.01 Hz) for $J / k_B T = 0.1$, and 1
Good agreement is observed. Note that the vertical line observed at zero applied field is the result of the low susceptibility associated with the low field initial magnetization portion of the hysteresis curve.

As a demonstration of the hysteresis resulting from an applied field whose period is closer to the spin relaxation time, the hysteresis and susceptibility are calculated with an applied magnetic field frequency of 1 Hz for a duration of 1.5 seconds (while other parameters remain the same as discussed above).

![Magnetization vs. Applied Magnetic Field](image)

Figure 2.12: Equilibrium (dotted line) and dynamic (solid line) magnetization of infinite chain vs. $\mu B / k_B T$ (cycled at 1 Hz) for $J / k_B T = 0.1$, and 1

The hysteresis of the $J / k_B T = 1$ chain is observed to increase significantly, while the $J / k_B T = 0.1$ chain is only slightly beginning to show hysteresis in Figure 2.12 above. This
is consistent with the $J / k_B T = 1$ chain having a longer relaxation time and effectively lagging behind the applied magnetic field.

The susceptibility associated with the hysteresis above is indicated in Figure 2.13 below.

![Static Susceptibility vs. Applied Magnetic Field](image)

Figure 2.13: Equilibrium (dotted line) and dynamic (solid line) static susceptibility of infinite chain vs. $\mu B / k_B T$ (cycled at 1 Hz) for $J / k_B T = 0.1$, and 1

As expected, the $J / k_B T = 0.1$ susceptibility is largely unchanged and similar to the equilibrium result. The $J / k_B T = 1$ susceptibility now presents a double peak response, with each peak corresponding to the coercivity field of the full hysteresis loop presented previously. Note that the lower peak on the right side is from the initial magnetization response (starting from a randomized state), which has shifted and broadened relative to the vertical line it presented when the applied field had a much slower frequency.
2.4 Finite Chain Application of Local Equilibrium Approximation

The methodology described above for applying the local equilibrium approximation to the infinite chain can similarly be applied to the finite chain. In this case, the expectation value of each spin and the expectation value of the product of adjacent spins will not be averaged over the length of the chain, rather a form for explicitly calculating these quantities on a per spin basis will be obtained. Also, the Glauber dynamic equation will be modified to account for the end spins, which only have one nearest neighbor.

Recall the dynamic equation previously obtained:

\[
\frac{d}{dt} q_i(t) = -\alpha q_i(t) - \beta \left( \gamma (q_{i-1}(t) + q_{i+1}(t)) + \frac{1}{2} \gamma (r_{i-1}(t) + r_{i+1}(t)) \right)
\]

(2.82)

where \( r_{ij} \) can be expressed as

\[
r_{ij}(t) = \sum_{\sigma, \sigma'} [P_{ij}(\sigma, \sigma')\sigma\sigma']
\]

(2.83)

and \( P_{ij}(\sigma, \sigma') \) is the probability that site \( i \) will take a value \( \sigma \) and the adjacent site \( j \) will take a value of \( \sigma' \).

Analogous to the infinite chain case, the four equations describing the four possible values of \( P_{ij} \) will be obtained and solved in terms of the single spin expectation value and coupling energy. This process will be detailed for the case of the end spin and its
nearest neighbor, noting that both the process and the result are the same in the case of
two adjacent inner spins. In the following, the subscript $e$ will denote the end spin while
the subscript $i$ will denote the end spin’s inner adjacent nearest neighbor. Now, three of
the four equations describing the spin product expectation value are:

$$q_e(t) = P_{e,j}(+,+) + P_{e,j}(-,+)-P_{e,j}(-,-)-P_{e,j}(+,-)$$  \hspace{1cm} (2.84)

$$q_i(t) = P_{e,j}(+,+) + P_{e,j}(-,+)-P_{e,j}(+,-)-P_{e,j}(-,-)$$  \hspace{1cm} (2.85)

$$1 = P_{e,j}(+,+) + P_{e,j}(-,+)+P_{e,j}(-,+)+P_{e,j}(-,-)$$  \hspace{1cm} (2.86)

The fourth equation is obtained using the local equilibrium approximation. The ratio of
probabilities of the end spin taking the value $-\sigma_e$ as opposed to $\sigma_e$ is given by:

$$\frac{p(-\sigma_e)}{p(\sigma_e)} = \frac{\exp\left[-(\mathcal{H}(-\sigma_e)/k_B T)\right]}{\exp\left[-(\mathcal{H}(\sigma_e)/k_B T)\right]} = \frac{\exp\left[-(J/k_B T)\sigma_e \sigma_i - (\mu B/k_B T)\sigma_e\right]}{\exp\left[(J/k_B T)\sigma_e \sigma_i + (\mu B/k_B T)\sigma_e\right]}$$  \hspace{1cm} (2.87)

Now,

$$\frac{P(-|0)}{P(+|0)} = \frac{\exp[g-b]}{\exp[-g+b]} = \frac{P(-)P_i(-|0)}{P(+)P_i(+|0)}$$  \hspace{1cm} (2.88)

and
\[
\frac{P(-|1)}{P(+|1)} = \frac{\exp[-g-b]}{\exp[g+b]} = \frac{P(-)P_c(-|1)}{P(+)P_c(+|1)}
\]  
(2.89)

Similar to the infinite chain, the nearest neighbors of an inner spin in an open finite chain do not influence each other. However, the end spin of a finite chain has only a single nearest neighbor. Thus,

\[
P_c(\sigma | n_i) = [P_c(\sigma_{i,+})]^n_i [P_c(\sigma_{i,-})]^{1-n_i}
\]  
(2.90)

Now,

\[
\frac{P_c(-|0)}{P_c(+|0)} = \frac{P_{c,i}(-,-)/P(-)}{P_{c,i}(+,+)/P(+)} = \frac{P(+)P_{c,i}(-,-)}{P(-)P_{c,i}(+,+)}
\]  
(2.91)

and

\[
\frac{P_c(-|1)}{P_c(+|1)} = \frac{P_{c,i}(-,+)/P(-)}{P_{c,i}(+,+)/P(+)} = \frac{P(+)P_{c,i}(-,+)}{P(-)P_{c,i}(+,+)}
\]  
(2.92)

Upon equating these equations with those obtained from the Maxwell-Boltzmann ratios and substituting to eliminate \(b\), the fourth equation is found to be:

\[
\exp[4g] = \frac{P_{c,i}(+,+)P_c(-,-)}{P_{c,i}(-,+)P_c(+,-)}
\]  
(2.93)

The solutions for the four \(P_{c,i}(\sigma,\sigma')\) can be written as:
\[
P_{e,j}^{(+,+)} = \frac{\exp(4g)(2 + q_x + q_z) - q_x - q_z}{4\exp(4g) - 4}
\]
\[
\left(\exp(4g)(2 + q_x + q_z) - q_x - q_z\right)^2 - \frac{\exp(4g)(4\exp(4g) - 4)(q_x q_z + q_x + q_z + 1)}{4\exp(4g) - 4}
\]

(2.94)

\[
P_{e,j}^{(+,-)} = \frac{1}{2}(q_x + 1 - 2P_{e,j}^{(+,+))})
\]

(2.95)

\[
P_{e,j}^{(-,+)} = \frac{1}{2}(q_j + 1 - 2P_{e,j}^{(+,+))})
\]

(2.96)

\[
P_{e,j}^{(-,-)} = \frac{1}{2}(-q_x - q_z + 2P_{e,j}^{(+,+))})
\]

(2.97)

Noting that the result obtained above for the end spin and its neighbor is also obtained in the case of two adjacent inner spins, the expectation value of the product of two adjacent spins can be written in terms of the above probabilities.

\[
\tau_{i,j}(t) = \sum_{\sigma,\sigma'}[P_{i,j}(\sigma,\sigma')\sigma\sigma'] = P_{e,j}^{(+,+)} - P_{e,j}^{(+,-)} - P_{e,j}^{(-,+)} + P_{e,j}^{(-,-)}
\]

(2.98)

In order to account for the boundary condition required for the end spins that have no nearest neighbor (and associated coupling energy) on one side, the Glauber dynamic equation must be modified accordingly. By inspection of the previously detailed
determination of the dynamic equation, this results in the dynamic equation for the end spins taking the form:

\[
\frac{d}{dt} q_e(t) = -\alpha \{ q_e(t) - \beta - \gamma' \dot{q}_e(t) \} + \gamma' \beta \dot{r}_e(t) \tag{2.99}
\]

where

\[
\gamma' = \tanh \left( \frac{J}{k_B T} \right) \tag{2.100}
\]

The differential equations for each spin in the finite chain can now be solved numerically for parameters of interest, and the results compared with the corresponding equilibrium solutions.

### 2.4.1 Correspondence with Finite Chain Equilibrium Solution

Similar to the infinite chain case, the dynamic equations for the spin expectation values are solved for various values of \(J / k_B T\) and \(\mu B / k_B T\), while a nominal value of 1000 s\(^{-1}\) is chosen for \(\alpha\). In the finite chain case, it is appropriate to compare the average expectation value of the spins in the chain to the equilibrium solution obtained previously.

Note that in implementing the equations detailed in the previous section for the finite chain, numerical instabilities are encountered for large values of \(J / k_B T\) and \(\mu B / k_B T\). This is attributed to the increased number of mathematical operations required to be performed on the large numbers that result from the exponential functions. This results
in a limitation of the range of parameters that may be studied, though an approximation will be introduced that provides good agreement with the equilibrium solution while providing for results with improved stability.

The time response of the one-dimensional finite chain to an applied magnetic field with $\mu B / k_B T = 0.1$ is provided in Figure 2.14 below, where the solid lines indicate the results of the numerical solution of the dynamic equation and the dotted lines represent the equilibrium solution previously established for the finite chain limit.

![Figure 2.14: Magnetization of Finite Chain vs. Time](image)

Figure 2.14: Equilibrium (dotted line) and dynamic (solid line) magnetization of finite (six spin) chain vs. time for $\mu B / k_B T = 0.1$ and for $J / k_B T = 0.1, 1, 5$.

Though values of $J / k_B T$ greater than 5 had issues converging to a stable equilibrium, it is observed that very good agreement with the finite chain equilibrium solution is
obtained. Similar results are indicated in Figure 2.15 below for $\mu B / k_B T = 1$, though convergence to equilibrium was limited for values of $J / k_B T$ greater than 2.

![Magnetization ofFinite Chain vs. Time](image)

**Figure 2.15:** Equilibrium (dotted line) and dynamic (solid line) magnetization of finite (six spin) chain vs. time for $\mu B / k_B T = 1$ and for $J / k_B T = 0.1, 1,$ and 2

Finally, the time response with $\mu B / k_B T = 10$ is provided in Figure 2.16 below.
In order to simplify the implementation of the dynamic equations so as to enhance the convergence to equilibrium for larger values of $\mu B / k_B T$ and $J / k_B T$, the expression obtained for the two spin product expectation value in the infinite chain case is implemented in the modified dynamic equations for the finite chain. This approximation is implemented on a per spin basis, in that the infinite chain expression is calculated using the single spin expectation value for each individual location in the finite chain. Using this approximation, the time response of the one-dimensional finite chain to an applied magnetic field with $\mu B / k_B T = 0.1$ is provided in Figure 2.17 below.
Figure 2.17: Equilibrium (dotted line) and dynamic (solid line) magnetization of finite (six spin) chain vs. time for $\mu_B/k_B T = 0.1$ and for $J/k_B T = 0.1, 1, \text{ and } 10$. The dynamic magnetization is calculated using the infinite chain two spin product expectation value as an approximation.

Good agreement is obtained relative to the finite chain equilibrium solution, though the agreement is better at lower $J/k_B T$ than at higher $J/k_B T$. In this case, the error for $J/k_B T = 1$ is 0.59% while the error for $J/k_B T = 10$ is 2.4%. This reduction in the magnetization at higher $J/k_B T$ and lower $\mu_B/k_B T$ with inclusion of the infinite chain two spin product expectation value is consistent with the assumptions inherent in the development of the infinite chain solution. In an infinite chain, the expectation value of each spin is the same at each site. Similarly, the two spin product expectation values between adjacent sites are all the same. Thus, when the infinite chain expression is applied to the finite chain that has a lower equilibrium magnetization at higher $J/k_B T$. 

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and lower $\mu B / k_B T$ (as previously indicated in the infinite chain vs. finite chain equilibrium solution comparison, Figure 2.5 and Figure 2.6), the two spin product portion of the finite spin dynamic equation is biased toward a smaller product, which similarly biases the resulting single spin expectation value that the dynamic equation converges to.

This is corroborated by inspection of the equilibrium value each spin in the finite chain converges to, provided below in Figure 2.18. The difference between inner and outer spin values is essentially the same when the full finite chain solution is implemented and when the approximation is implemented. However, comparisons of the same sites between the two solutions reveal an almost constant difference in spin value, regardless of site.
The time response for $\mu B / k_B T = 1$ is provided below in Figure 2.19, where better agreement is obtained for $J / k_B T = 1$ and 10 (each having an error of 0.19% relative to the equilibrium solution).
Figure 2.19: Equilibrium (dotted line) and dynamic (solid line) magnetization of finite (six spin) chain vs. time for $\mu_B/k_B T = 1$ and for $J/k_B T = 0.1, 1, \text{ and } 10$. The dynamic magnetization is calculated using the infinite chain two spin product expectation value as an approximation.

Finally, the time response for $\mu B/k_B T = 3$ is provided below in Figure 2.20, where very good agreement is obtained with the equilibrium solution.
Figure 2.20: Equilibrium (dotted line) and dynamic (solid line) magnetization of finite (six spin) chain vs. time for $\mu B / k_B T = 3$ and for $J / k_B T = 0.1$, $1$, and $10$. The dynamic magnetization is calculated using the infinite chain two spin product expectation value as an approximation.

Similar to the infinite chain discussion above, the hysteresis response to a time-varying applied magnetic field can also be calculated for the finite chain and compared with that obtained with the equilibrium solution. As in previous calculations, the infinite chain two spin product approximation is applied, a nominal value of $\alpha = 1000 \text{ s}^{-1}$ is chosen, and the expectation value of the spins is initially zero. Due to the large difference in relaxation time scales between $J / k_B T = 0.1, 1$ and $J / k_B T = 10$ (as indicated in the figures above), only $J / k_B T = 0.1$ and $1$ are shown together below. In Figure 2.21 below, an applied field of amplitude $\mu B / k_B T = 3$ is sinusoidally cycled at a frequency of $0.01 \text{ Hz}$ for $100$
seconds, effectively tracing a hysteresis cycle from initial magnetization to saturation in both directions.

![Magnetization vs. Applied Magnetic Field](image)

Figure 2.21: Equilibrium (dotted line) and dynamic (solid line) magnetization of finite (six spin) chain vs. $\mu B / k_B T$ (cycled at 0.01 Hz) for $J / k_B T = 0.1$, and 1. The dynamic magnetization is calculated using the infinite chain two spin product expectation value as an approximation.

With the relatively slow cycling frequency of the applied field, no hysteresis is observed and good agreement with the equilibrium solution is obtained.

The calculated response with an applied magnetic field frequency of 1 Hz for a duration of 1.5 seconds (while other parameters remain the same as discussed above) is provided in Figure 2.22 below.
Figure 2.22: Equilibrium (dotted line) and dynamic (solid line) magnetization of finite (six spin) chain vs. $\mu B / k_B T$ (cycled at 1 Hz) for $J / k_B T = 0.1$, and 1. The dynamic magnetization is calculated using the infinite chain two spin product expectation value as an approximation.

Similar to the infinite chain, little hysteresis is observed for $J / k_B T = 0.1$ since the relaxation time to equilibrium is relatively small. The $J / k_B T = 1$ response exhibits appreciable hysteresis since the relaxation time is larger, thus causing the magnetization to lag behind the sweeping applied magnetic field.

### 2.5 Summary

This chapter has detailed the calculation of the equilibrium per-spin magnetization and zero-field static magnetic susceptibility in the infinite chain limit, as well as the calculation of the per-spin magnetization of a finite number of spins in an open chain via explicit
construction of the partition function of a six-spin ferromagnetic chain with nearest neighbor interactions. The Glauber dynamic was then applied to obtain dynamic equations describing the time response of the single spin expectation values, and the local equilibrium approximation was leveraged to generate numerically soluble systems of equations describing the infinite and finite chains. Good agreement was obtained between these numerical solutions and the previously obtained equilibrium solutions.

2.6 References


Chapter Three

Extension of Glauber Ising-Spin Dynamics to a One-Dimensional Ferrimagnetic Lattice with Nearest Neighbor Interactions

The techniques described in Chapter 2 for the one-dimensional (anti-) ferromagnetic Ising model with nearest neighbor interactions will now be extended to describe the dynamic behavior of a ferrimagnetic lattice, where alternating sites have magnetic moments of different strength. The response of the resulting dynamic equations for the infinite chain and finite chain will be compared with previous results in the ferromagnetic limit as a check, and will also be employed to describe the empirically determined magnetization dynamics of the ferrimagnetic single chain magnet CoPhOMe.

3.1 Derivation of Spin Dynamic Equations

A 1D ferrimagnetic lattice may be considered as a superposition of sublattices identified separately by odd and even site indices, where the odd and even sites are occupied by magnetic moments of different magnitudes. This system, with nearest neighbor (odd-even site) coupling is described by:

\[
H = -J \sum_i^{N} \sigma_i \sigma_{i+1} - \mu_{\text{even}} B \sum_i^{N/2} \sigma_{2i} - \mu_{\text{odd}} B \sum_i^{N/2} \sigma_{2i-1} \tag{3.1}
\]

where \( \mu_{\text{even}} \) is the magnetic moment of spins at even lattice sites \([\text{Am}^2 \text{ or J/T}]\)

\( \mu_{\text{odd}} \) is the magnetic moment of spins at odd lattice sites \([\text{Am}^2 \text{ or J/T}]\)
Alternatively,

\[
H = - \sum_{i}^{N/2} \left\{ J\left(\sigma_{2i-1}\sigma_{2i} + \sigma_{2i}\sigma_{2i+1}\right) + \mu_{\text{even}} B\sigma_{2i} + \mu_{\text{odd}} B\sigma_{2i-1} \right\}
\]  (3.2)

In the absence of an applied magnetic flux density \((B = 0)\), the Hamiltonian for an arbitrary site \(i\) contains the following terms:

\[
H = \cdots - J\left(\sigma_{2i-3}\sigma_{2i-2} + \sigma_{2i-2}\sigma_{2i-1}\right) - J\left(\sigma_{2i-4}\sigma_{2i} + \sigma_{2i}\sigma_{2i+1}\right) - \\
J\left(\sigma_{2i+1}\sigma_{2i+2} + \sigma_{2i+2}\sigma_{2i+3}\right) - \cdots
\]  (3.3)

From these terms, the portion of the system energy associated with even spin \(\sigma_{2i}\) is:

\[
H(\sigma_{2i}) = -J\left(\sigma_{2i-1}\sigma_{2i} + \sigma_{2i}\sigma_{2i+1}\right) = -J\sigma_{2i}\left(\sigma_{2i-1} + \sigma_{2i+1}\right)
\]  (3.4)

Similarly, the portion associated with odd spin \(\sigma_{2i-1}\) is:

\[
H(\sigma_{2i-1}) = -J\left(\sigma_{2i-2}\sigma_{2i-1} + \sigma_{2i-1}\sigma_{2i}\right) = -J\sigma_{2i-1}\left(\sigma_{2i-2} + \sigma_{2i}\right)
\]  (3.5)

The ratio of probabilities of the spin at site \(i\) taking the value \(-\sigma\) as opposed to \(\sigma\) is given by the ratio of the respective Maxwell-Boltzmann factors as the system approaches equilibrium at temperature \(T\). Thus, for spins on even \((2i)\) lattice sites:
\[
\frac{p(-\sigma_{2i})}{p(\sigma_{2i})} = \frac{\exp[-(H(-\sigma_{2i})/k_BT)]}{\exp[-(H(\sigma_{2i})/k_BT)]} = \frac{\exp[-g\sigma_{2i}(\sigma_{2i-1} + \sigma_{2i+1})]}{\exp[g\sigma_{2i}(\sigma_{2i-1} + \sigma_{2i+1})]}
\]  

(3.6)

where \( p(\sigma_{2i}) \) is the probability that the spin at site 2i will have the value \( \sigma_{2i} \).

\( p(-\sigma_{2i}) \) is the probability that the spin at site 2i will have the value \(-\sigma_{2i}\).

By expanding the exponential terms using the appropriate hyperbolic trigonometric functions as in Chapter 2, the ratio of even site probabilities can be written as:

\[
\frac{p(-\sigma_{2i})}{p(\sigma_{2i})} = \frac{1 - \frac{1}{2} \sigma_{2i}(\sigma_{2i-1} + \sigma_{2i+1}) \tanh[2g]}{1 + \frac{1}{2} \sigma_{2i}(\sigma_{2i-1} + \sigma_{2i+1}) \tanh[2g]} = \frac{w(\sigma_{2i})}{w(-\sigma_{2i})}
\]  

(3.7)

where \( w(\sigma_{2i}) \) is the transition probability, or probability per unit time, that the spin at site 2i flips from \( \sigma_{2i} \) to \(-\sigma_{2i}\).

\( w(-\sigma_{2i}) \) is the transition probability, or probability per unit time, that the spin at site 2i flips from \(-\sigma_{2i}\) to \( \sigma_{2i} \).

The same form of transition probability as employed previously (Equation 2.35) is applicable to the even and odd site descriptions in the ferrimagnetic lattice. We now have for the even and odd sites respectively:

\[
\frac{p(-\sigma_{2i})}{p(\sigma_{2i})} = \frac{w(\sigma_{2i})}{w(-\sigma_{2i})} = \frac{1 - \frac{1}{2} \gamma \sigma_{2i}(\sigma_{2i-1} + \sigma_{2i+1})}{1 + \frac{1}{2} \gamma \sigma_{2i}(\sigma_{2i-1} + \sigma_{2i+1})}
\]  

(3.8)
\[
\frac{p(-\sigma_{2i-1})}{p(\sigma_{2i-1})} = \frac{w(\sigma_{2i-1})}{w(-\sigma_{2i-1})} = \frac{1 - \frac{1}{2} \gamma \sigma_{2i-1}(\sigma_{2i-2} + \sigma_{2i})}{1 + \frac{1}{2} \gamma \sigma_{2i-1}(\sigma_{2i-2} + \sigma_{2i})}
\] (3.9)

Where, upon comparison with the previously determined ratio of spin probabilities (Equation 3.7), it is found that

\[
\gamma = \tanh(2g)
\] (3.10)

Note that this is the same expression as found in Chapter 2 for the (anti-) ferromagnetic lattice (see Equation 2.37).

In the presence of an applied magnetic flux density \((B \neq 0)\), the portion of the system energy associated with spin \(\sigma_{2i}\) becomes:

\[
H(\sigma_{2i}) = -J \sigma_{2i} (\sigma_{2i-1} + \sigma_{2i+1}) - \mu_{\text{even}} B \sigma_{2i}
\] (3.11)

Similarly, the portion associated with spin \(\sigma_{2i-1}\) becomes:

\[
H(\sigma_{2i-1}) = -J (\sigma_{2i-2} \sigma_{2i-1} + \sigma_{2i-1} \sigma_{2i}) - \mu_{\text{odd}} B \sigma_{2i-1}
\] (3.12)

By the method described in Chapter 2, the appropriate augmented transition probabilities for even and odd sites become:
\[ w'(\sigma_{2i}) = w(\sigma_{2i})(1 - \sigma_{2i}\beta_{even}) = \frac{1}{2} \alpha \left( 1 - \sigma_{2i}\beta_{even} - \frac{1}{2} \gamma \sigma_{2i}(\sigma_{2i-1} + \sigma_{2i+1}) + \frac{1}{2} \gamma \beta_{even}(\sigma_{2i-1} + \sigma_{2i+1}) \right) \tag{3.13} \]

\[ w'(\sigma_{2i-1}) = w(\sigma_{2i-1})(1 - \sigma_{2i-1}\beta_{odd}) = \frac{1}{2} \alpha \left( 1 - \sigma_{2i-1}\beta_{odd} - \frac{1}{2} \gamma \sigma_{2i-1}(\sigma_{2i-2} + \sigma_{2i}) + \frac{1}{2} \gamma \beta_{odd}(\sigma_{2i-2} + \sigma_{2i}) \right) \tag{3.14} \]

where \( \beta_{even} = \tanh[b_{even}] \) and \( \beta_{odd} = \tanh[b_{odd}] \)

Note how the transition probabilities for odd and even sites contain terms dependant on the values of adjacent spins, which are on even and odd sites. This coupling of the transition probabilities requires that the dynamics of the odd and even sublattices be solved as a dependant system, in lieu of pursuing independent dynamic solutions.

The transition probabilities defined above can be used to describe the time evolution of the expectation values of the even and odd site spins, as well as multiple-spin products, just as accomplished in Chapter 2. This yields the even site and odd site dynamic equations developed below:
\[
\frac{d}{dt} q_{2i}(t) = -\alpha \sum_{\{\sigma\}} \left\{ -1 - \sigma_{2i} \beta_{\text{even}} - \frac{1}{2} \gamma \sigma_{2i} (\sigma_{2i-1} + \sigma_{2i+1}) + \frac{1}{2} \gamma \beta_{\text{even}} (\sigma_{2i-1} + \sigma_{2i+1}) \right\} \times p(\sigma_1, \ldots, \sigma_N, t) \\
= -\alpha \sum_{\{\sigma\}} \left\{ -1 - \sigma_{2i} \beta_{\text{even}} - \frac{1}{2} \gamma (\sigma_{2i-1} + \sigma_{2i+1}) + \frac{1}{2} \gamma \beta_{\text{even}} (\sigma_{2i-1} + \sigma_{2i+1}) \right\} \times p(\sigma_1, \ldots, \sigma_N, t)
\]

(3.15)

\[
\frac{d}{dt} q_{2i-1}(t) = -\alpha \sum_{\{\sigma\}} \left\{ -1 - \sigma_{2i-1} \beta_{\text{odd}} - \frac{1}{2} \gamma \sigma_{2i-1} (\sigma_{2i-2} + \sigma_{2i}) + \frac{1}{2} \gamma \beta_{\text{odd}} (\sigma_{2i-2} + \sigma_{2i}) \right\} \times p(\sigma_1, \ldots, \sigma_N, t) \\
= -\alpha \sum_{\{\sigma\}} \left\{ -1 - \sigma_{2i-1} \beta_{\text{odd}} - \frac{1}{2} \gamma (\sigma_{2i-2} + \sigma_{2i}) + \frac{1}{2} \gamma \beta_{\text{odd}} (\sigma_{2i-2} + \sigma_{2i}) \right\} \times p(\sigma_1, \ldots, \sigma_N, t) \\
= -\alpha \left\{ q_{2i-1}(t) - \beta_{\text{odd}} - \frac{1}{2} \gamma (q_{2i-2}(t) + q_{2i}(t)) + \frac{1}{2} \gamma \beta_{\text{odd}} (r_{2i-1,2i-2}(t) + r_{2i-1,2i}(t)) \right\} 
\]

(3.16)

Note how the dynamic equations for the single spin expectation values contain both a coupling between the odd and even sublattices and a dependence on the expectation values of the products of the spin with each of its nearest neighbors on the opposite sublattice. Since the two-spin products in the single-spin expectation value dynamic
equations above involve adjacent spin pairs, where one spin is on an even site and the other spin is on an odd site, the dynamic equation for this expectation value is:

$$\frac{d}{dt} r_{\text{even}, \text{odd}}(t) = -2 \sum_{\{\sigma\}} \sigma_{\text{even}} \sigma_{\text{odd}} \left\{ w'(\sigma_{\text{even}}) + w'(\sigma_{\text{odd}}) \right\} p(\sigma_1, \ldots, \sigma_N, t)$$

\[
\begin{align*}
\frac{d}{dt} r_{\text{even}, \text{odd}}(t) &= \left[ 2r_{\text{even}, \text{odd}}(t) - \beta_{\text{even}} q_{\text{odd}}(t) - \frac{1}{2} \mathcal{H}_{\text{odd}, \text{even}-1}(t) + r_{\text{odd}, \text{even}+1}(t) \right] \\
&\quad + \frac{1}{2} \eta \beta_{\text{even}} \left( s_{\text{even}, \text{odd}, \text{even}-1}(t) + s_{\text{even}, \text{odd}, \text{even}+1}(t) \right) \\
&\quad - \beta_{\text{odd}} q_{\text{even}}(t) - \frac{1}{2} \mathcal{H}_{\text{even}, \text{odd}-1}(t) + r_{\text{even}, \text{odd}+1}(t) \\
&\quad + \frac{1}{2} \eta \beta_{\text{odd}} \left( s_{\text{even}, \text{odd}, \text{odd}-1}(t) + s_{\text{even}, \text{odd}, \text{odd}+1}(t) \right)
\end{align*}
\]

(3.17)

where

$$s_{i,j,k}(t) = \langle \sigma_i(t) \sigma_j(t) \sigma_k(t) \rangle = \sum_{\{\sigma\}} \sigma_i \sigma_j \sigma_k p(\sigma_1, \ldots, \sigma_N, t)$$

(3.18)

is the expectation value of the product of the three spins at lattice sites $i$, $j$, and $k$.

The dynamic equation describing the time evolution of the even-odd two-spin product expectation value depends on the expectation value of the product of three spins. As expected, this trend continues and the three-spin expectation value dynamic depends on the four-spin expectation value, etc.

It is also seen in the two-spin expectation value dynamic equation that a dependency exists between the time evolution of the two-spin expectation value between even and
odd sublattices \((r_{\text{even,odd}})\) and the two-spin expectation values involving spins on common odd \((r_{\text{odd,odd}})\) and even \((r_{\text{even,even}})\) sublattices. Each common sublattice two-spin expectation value dynamic equation is obtained in similar fashion as the dynamic for \(r_{\text{even,odd}}\), resulting in further dependencies on additional combinations of two and three spin products. Clearly, a complicated system of differential equations describes the ferrimagnetic lattice. In the next section, the local equilibrium approximation will be employed to close and simplify this system of equations.

### 3.2 Infinite Chain Application of Local Equilibrium Approximation

The dynamic equations representing the time evolution of the expectation value of spins on even and odd lattice sites respectively were previously found to be:

\[
\frac{d}{dt} q_{2i}(t) = -\alpha \begin{cases} q_{2i}(t) - \beta_{\text{even}} - \frac{1}{2} \gamma (q_{2i-1}(t) + q_{2i+1}(t)) + \\ \frac{1}{2} \gamma \beta_{\text{even}} \left( r_{2i-1,2i-1}(t) + r_{2i,2i}(t) \right) \end{cases} \quad (3.19)
\]

and

\[
\frac{d}{dt} q_{2i-1}(t) = -\alpha \begin{cases} q_{2i-1}(t) - \beta_{\text{odd}} - \frac{1}{2} \gamma (q_{2i-2}(t) + q_{2i}(t)) + \\ \frac{1}{2} \gamma \beta_{\text{odd}} \left( r_{2i-1,2i-2}(t) + r_{2i-1,2i}(t) \right) \end{cases} \quad (3.20)
\]
As a simplification, the average value of the odd and even site expectation values will be considered. The dynamic equations can then be written as:

\[
\frac{d}{dt} Q_{\text{even}}(t) = -\alpha \left\{ Q_{\text{even}}(t) - \beta_{\text{even}} - \frac{1}{2} \gamma (Q_{\text{odd}}(t) + Q_{\text{odd}}(t)) + \right. \\
\left. \frac{1}{2} \gamma \beta_{\text{even}} \left( R_{\text{even,odd}}(t) + R_{\text{even,odd}}(t) \right) \right\} 
\]

(3.21)

and

\[
\frac{d}{dt} Q_{\text{odd}}(t) = -\alpha \left\{ Q_{\text{odd}}(t) - \beta_{\text{odd}} - \frac{1}{2} \gamma (Q_{\text{even}}(t) + Q_{\text{even}}(t)) + \right. \\
\left. \frac{1}{2} \gamma \beta_{\text{odd}} \left( R_{\text{odd,even}}(t) + R_{\text{odd,even}}(t) \right) \right\} 
\]

(3.22)

with

\[
Q_{\text{even}}(t) = \frac{1}{N_{\text{even}}} \sum_{i=1}^{N_{\text{eq}}} q_{2i}(t) 
\]

(3.23)

\[
Q_{\text{odd}}(t) = \frac{1}{N_{\text{odd}}} \sum_{i=1}^{N_{\text{eq}}} q_{2i-1}(t) 
\]

(3.24)
\[ R_{\text{even,odd}}(t) = R_{\text{odd,even}}(t) = \frac{1}{N} \sum_{i=1}^{N} r_{2i-1,2i}(t) \] (3.25)

where \( Q_{\text{even}} \) is the average even site expectation value
\( Q_{\text{odd}} \) is the average odd site expectation value
\( R_{\text{even,odd}} \) is the average two-spin product expectation value
\( N_{\text{even}} \) is the number of even sites
\( N_{\text{odd}} \) is the number of odd sites
\( N \) is the total number of sites

Alternatively, \( R_{\text{odd,even}} \) can be expressed as:

\[ R_{\text{odd,even}}(t) = \sum_{\sigma, \sigma'} [P_{\text{oe}}(\sigma, \sigma') \sigma \sigma'] \] (3.26)

where \( P_{\text{oe}}(\sigma, \sigma') \) is the probability that an odd site will take a value \( \sigma \) and an adjacent even site will take a value of \( \sigma' \)

Since \( \sigma \) takes a value of \( \pm 1 \), \( P_{\text{oe}}(\sigma, \sigma') \) can only be expressed in four possible ways: \( P_{\text{oe}}(+,+) \), \( P_{\text{oe}}(+,-) \), \( P_{\text{oe}}(-,+) \), and \( P_{\text{oe}}(-,-) \). Three equations describing the required consistency amongst these probabilities are apparent:

\[ Q_{\text{odd}} = P_{\text{oe}}(+,+) + P_{\text{oe}}(+,-) - P_{\text{oe}}(-,+) - P_{\text{oe}}(-,-) \] (3.27)

\[ Q_{\text{even}} = P_{\text{oe}}(+,+) - P_{\text{oe}}(+,-) + P_{\text{oe}}(-,+) - P_{\text{oe}}(-,-) \] (3.28)
The fourth equation required to determine the four unknowns above is found using Huang’s local equilibrium approximation, just as in Chapter 2. Recall that for a given even lattice site, the ratio of probabilities of the spin at site $2i$ taking the value $-\sigma_{2i}$ as opposed to $\sigma_{2i}$ is given by the ratio of the respective Maxwell-Boltzmann factors as the system approaches equilibrium at temperature $T$:

$$p(-\sigma_{2i}) \over p(\sigma_{2i}) = \exp[-(H(-\sigma_{2i})/k_B T)] \over \exp[-(H(\sigma_{2i})/k_B T)] = \exp\left[\frac{g \sigma_{2i}(\sigma_{2i-1} + \sigma_{2i+1}) - b_{even} \sigma_{2i}}{k_B T}\right] \over \exp\left[\frac{g \sigma_{2i}(\sigma_{2i-1} + \sigma_{2i+1}) + b_{even} \sigma_{2i}}{k_B T}\right] \tag{3.30}$$

Letting $n_1$ be the number of nearest neighbor sites that have a value of +1, it is observed that:

$$\left(\sigma_{2i-1} + \sigma_{2i+1}\right) = \begin{cases} -2 & n_1 = 0 \\ 0 & n_1 = 1 \\ 2 & n_1 = 2 \end{cases} \tag{3.31}$$

and with a minor change in notation such that:

$P_e(\sigma)$ is the probability that an even site has a value $\sigma$

$P_e(\sigma|n_1)$ is the probability that $n_1$ nearest neighbors of an even site (that has a value $\sigma$) are up

$P_{ee}(\sigma|n_1)$ is the conditional probability that $n_1$ nearest neighbors of an even site are up, if that even site has a value $\sigma$
and

\[ P_e (\sigma | n_i) = P_e (\sigma) P_{ce} (\sigma | n_i) \]  

(3.32)

It can now be written that:

\[
\frac{P_e (-|0)}{P_e (+|0)} = \frac{\exp[2g - b_{even}]}{\exp[-2g + b_{even}]} = \frac{P_e (-P_{ce}(-|0)}}{P_e (+P_{ce}(+|0))}
\]  

(3.33)

and

\[
\frac{P_e (-|1)}{P_e (+|1)} = \frac{\exp[-b_{even}]}{\exp[b_{even}]} = \frac{P_e (-P_{ce}(-|1)}}{P_e (+P_{ce}(+|1))}
\]  

(3.34)

Since the nearest neighbor spins do not influence each other directly:

\[
P_{ce} (\sigma | n_i) = \binom{2}{n_1} [P_{ceo} (\sigma, +)]^{n_1} [P_{ceo} (\sigma, -)]^{2-n_1}
\]  

(3.35)

where \( P_{ceo} (\sigma, \sigma') \) is the conditional probability that the odd nearest neighbor site will have the value \( \sigma' \) if the even site has the value \( \sigma \)

and
\[
\binom{2}{n_1} = \begin{cases} 
1 & n_1 = 1 \\
2 & n_1 = 2 \\
1 & n_1 = 1 
\end{cases} \quad (3.36)
\]

Note that

\[
P_{ee} (\sigma, \sigma') = P_e (\sigma) P_{ee} (\sigma, \sigma')
\]

and

\[
P_{e,ee} (\sigma, \sigma') = P_{e,ee} (\sigma', \sigma)
\]

Now

\[
\frac{P_{ee} (- | 0)}{P_{ee} (+ | 0)} = \left[ \frac{P_{ee} (-,-)/P_e (-)}{P_{ee} (+,-)/P_e (+)} \right] = \left[ \frac{P_e (+) P_{ee} (-,-)}{P_e (-) P_{ee} (+,-)} \right] = \left[ \frac{P_e (+) P_{ee} (-,-)}{P_e (-) P_{ee} (+,-)} \right] \quad (3.39)
\]

and

\[
\frac{P_{ee} (- | 1)}{P_{ee} (+ | 1)} = \left[ \frac{P_{ee} (-,+)/P_e (-)}{P_{ee} (+,+)/P_e (+)} \right] = \left[ \frac{P_e (+) P_{ee} (-,+)}{P_e (-) P_{ee} (+,+)} \right] = \left[ \frac{P_e (+) P_{ee} (-,+)}{P_e (-) P_{ee} (+,+)} \right] \quad (3.40)
\]

Equating with the previously obtained result
\[
\frac{\exp[2g - b_{\text{even}}]}{\exp[-2g + b_{\text{even}}]} = \frac{P_e (+)[P_{oe} (-,-)]^2}{P_e (-)[P_{oe} (-,+) ]^2}
\] (3.41)

and

\[
\frac{\exp[-b_{\text{even}}]}{\exp[b_{\text{even}}]} = \frac{P_e (+)P_{oe} (+,-)P_{oe} (-,-)}{P_e (-)P_{oe} (-,+)P_{oe} (+,+)}
\] (3.42)

And substituting yields

\[
\frac{\exp[2g]}{\exp[-2g]} \frac{P_e (+)P_{oe} (+,-)P_{oe} (-,-)}{P_e (-)P_{oe} (-,+)P_{oe} (+,+)} = \frac{P_e (+)[P_{oe} (-,-)]^2}{P_e (-)[P_{oe} (-,+) ]^2}
\] (3.43)

which simplifies to

\[
\exp[4g] = \frac{P_{oe} (+,+)P_{oe} (-,-)}{P_{oe} (+,-)P_{oe} (-,+)}
\] (3.44)

This result is the fourth equation required to solve for the four unknown two-spin probabilities \( P_{oe}(+,+), P_{oe}(+,+), P_{oe}(-,+), \) and \( P_{oe}(-,-) \). The same result is obtained when applying the above methodology to an odd lattice site. The fourth equation is also similar in structure to that obtained for the finite ferromagnetic chain in Chapter 2. This is the result of the inequality of \( P_{\text{even}}(+,-) \) and \( P_{\text{even}}(-,+ \) common to both cases. The solutions can be written as:
\[ P_{oe}(+,+) = \frac{\exp(4g)(2 + Q_{odd} + Q_{even}) - Q_{odd} - Q_{even}}{4 \exp(4g) - 4} \]

\[ \sqrt{\left(\frac{\exp(4g)(2 + Q_{odd} + Q_{even}) - Q_{odd} - Q_{even}}{4 \exp(4g) - 4}\right)^2 - \frac{\exp(4g)(4 \exp(4g) - 4)(Q_{odd}Q_{even} + Q_{odd} + Q_{even} + 1)}{4 \exp(4g) - 4}} \]

\[ P_{oe}(+,-) = \frac{1}{2} \left( Q_{odd} + 1 - 2P_{oe}(+,+) \right) \]  \hfill (3.46)

\[ P_{oe}(-,+) = \frac{1}{2} \left( Q_{even} + 1 - 2P_{oe}(+,+) \right) \]  \hfill (3.47)

\[ P_{oe}(-,-) = \frac{1}{2} \left( -Q_{odd} - Q_{even} + 2P_{oe}(+,+) \right) \]  \hfill (3.48)

Now, \( R_{odd,even}(t) \) can be expressed in terms of \( Q_{even}(t) \), \( Q_{odd}(t) \), and \( g \) using the equations above as:

\[ R_{odd,even}(t) = \sum_{\sigma, \sigma'} [P_{oe}(\sigma, \sigma')\sigma\sigma'] = P_{oe}(+,+) - P_{oe}(+,-) - P_{oe}(-,+) + P_{oe}(-,-) \]  \hfill (3.49)

Finally, the coupled equations describing the time evolution of \( Q_{even}(t) \) and \( Q_{odd}(t) \) can be expressed purely in terms of \( Q_{even}(t) \), \( Q_{odd}(t) \), \( J / k_B T \), and \( \mu B / k_B T \) such that they present a closed system of equations that can be solved numerically for parameters of interest.
3.2.1 Correspondence with Infinite Ferromagnetic Chain

Solution

Solutions of the dynamic equations developed above will be compared to the infinite chain equilibrium solutions determined in Chapter 2. This involves evaluating the dynamic equations in the ferromagnetic limit, where the odd and even sites have equivalent magnetic moments.

In Figure 3.1 below, the magnetization per spin is indicated for a time-varying magnetic field applied at a frequency of 0.01 Hz for 100 seconds. Similar to previous calculations, the time scale parameter $\alpha$ is chosen to be 1000 s$^{-1}$ and all spins have an initial expectation value of zero (corresponding to an initial randomization without nearest neighbor correlations).
The dynamic solution obtained from the ferrimagnetic differential equations (in the ferromagnetic limit) is shown to agree very well with the equilibrium solution obtained previously. Additionally, the same hysteresis behavior is observed in the ferromagnetic limit (in the ferromagnetic infinite chain detailed in Chapter 2) when the frequency of the applied field is increased to 1 Hz and the duration extended to 1.5 seconds. This is shown in Figure 3.2 below.
3.3 Finite Chain Application of Local Equilibrium Approximation

The dynamic equations describing the finite ferrimagnetic chain are similar to those describing the infinite ferrimagnetic chain. However, one can no longer average over the length of the chain and one must account for the boundary conditions at the end spins. Similar to Chapter 2, the dynamic equations will be applied separately to each odd and even spin. Also, since the end spins only have one nearest neighbor, their dynamic equations must be modified, just as with the finite (anti-) ferromagnetic chain. This results in odd and even end spins being described by:
The differential equations for each spin in the finite chain can now be solved numerically for parameters of interest, and the results compared with the corresponding equilibrium solutions in the ferromagnetic limit.

### 3.3.1 Correspondence with Finite Ferromagnetic Chain Solution

The dynamic solution for a ferromagnetic chain of six spins is calculated using the equations above, but in the limit of a ferromagnetic chain. This result is then compared to the equilibrium solution obtained in Chapter 2. In Figure 3.3 below, the magnetization per spin is indicated for a time-varying magnetic field applied at a frequency of 0.01 Hz for 100 seconds. Similar to previous calculations, the time scale parameter $\alpha$ is chosen to be 1000 s$^{-1}$ and all single-spin and two-spin product expectation values are assumed to be initially zero.

\[
\frac{d}{dt} q_{\text{even}}(t) = -\alpha \{q_{\text{even}}(t) - \beta_{\text{even}} - \gamma'(q_{\text{even}}(t)) + \gamma' \beta_{\text{even}}(r_{\text{even},\text{even}}(t))\} \tag{3.50}
\]

and

\[
\frac{d}{dt} q_{\text{odd}}(t) = -\alpha \{q_{\text{odd}}(t) - \beta_{\text{odd}} - \gamma'(q_{\text{odd}}(t)) + \gamma' \beta_{\text{odd}}(r_{\text{odd},\text{odd}}(t))\} \tag{3.51}
\]

where $\gamma' = \tanh[J / k_B T]$. 

The differential equations for each spin in the finite chain can now be solved numerically for parameters of interest, and the results compared with the corresponding equilibrium solutions in the ferromagnetic limit.
Figure 3.3: Equilibrium (dotted line) and dynamic (solid line) magnetization of finite (six spin) chain vs. $\mu B / k_B T$ (cycled at 0.01 Hz) for $J / k_B T = 0.1$, and $1$

The dynamic solution (solid line) is shown to agree very well with the equilibrium solution obtained previously (dotted line). Additionally, the same hysteresis behavior is observed in the ferromagnetic limit (as in the finite ferromagnetic chain discussed in Chapter 2) when the frequency of the applied field is increased to 1 Hz and the duration extended to 1.5 seconds. This is shown in Figure 3.4 below.
3.4 Application to Single Chain Magnet CoPhOME

As discussed in Section 1.3, much empirical data has been accumulated on the single chain magnet referred to as CoPhOME. These data suggest that CoPhOME may be well characterized by a one-dimensional ferrimagnetic Ising chain with nearest neighbor interactions. As such, the ferrimagnetic dynamic Ising model detailed above will be employed to determine how well the empirical magnetization dynamics may be represented.
Estimates for the coupling energy between the radical lattice sites and the cobalt lattice sites vary, but are generally less than 100K in magnitude. Thus, this parameter will be considered free to be tuned to better represent the empirical data available. Additionally, the estimated values of the magnetic moments for the radical and cobalt spin \( \frac{1}{2} \) sites vary slightly, but will be taken to be \( 2\mu_B \) and \( 9\mu_B \) respectively for this study\(^1\). Note that since the easy axis of magnetization for the helically structured CoPhOMe forms an angle of approximately 54.74° (cos\(^{-1}\)(1/\(\sqrt{3}\))) relative to the principle axis of the chain\(^2\), and the orientation of the weaker radical spins is predominantly governed by the orientation of the cobalt neighbor spins, a factor of \( \cos(54.74\,\degree) \) is applied to the magnetic moments to indicate the resultant magnetization along the chain axis. The resulting “saturation” magnetization for applied field strengths of interest is then 2.02\(\mu_B\) per formula unit (radical-cobalt pair), or approximately 11,300 emu per mol, which agrees well with the experimentally determined saturation magnetization\(^3,4\). True saturation would occur only if the applied field were strong enough to overcome the ferrimagnetic nearest neighbor coupling (and the anisotropy of the cobalt spins) such that all spins are oriented in the direction of the applied field. However, such fields would be on the order of hundreds of Tesla in magnitude, and are not of interest for this study\(^5\). The energy \( (\mu B / k_B T) \) associated with the radical and cobalt spins can then be expressed as 0.3878 x \( (B / T) \) and 1.7449 x \( (B / T) \) respectively, where B is in Tesla and T is in Kelvin.

There are also varying estimates for the time scale parameter \( \alpha \), which is a measure of the relaxation time of the spins. The relaxation time obeys (approximately) a temperature-dependant Arrhenius behavior\(^3,4\):
\[ \tau = \tau_0 \exp\left( \frac{\Delta}{k_B T} \right) \]  \hspace{1cm} (3.52)

where different estimates for \( \tau_0 \) and \( \Delta \) have been made. Through studies of the effect of impurities on the dynamics of CoPhOMe, \( \tau_0 \) has been shown to be dependant on the length of the chain, while \( \Delta \) shows no such dependence. Estimates for \( \tau_0 \) vary from 7x10\(^{-12}\) seconds to 3.5x10\(^{-11}\) seconds for relatively pure samples (with chain lengths of approximately 2000 spins\(^4,6\), to 1x10\(^{-12}\) seconds for samples with an impurity concentration of 4.7\% (with chain lengths of approximately 20 spins\(^6\). A relationship between \( \tau_0 \) and \( \alpha \) has been proposed through a theoretical treatment of the slow relaxation mode dominating the magnetization behavior at low temperature\(^3\):

\[ \alpha = \frac{1}{2\tau_0} \]  \hspace{1cm} (3.53)

For the infinite chain modeling discussed below, a \( \tau_0 \) value of 3.5x10\(^{-11}\) seconds is assumed.

### 3.4.1 Relaxation Response

Experimental data have been obtained for the relaxation of CoPhOMe after being saturated in a high applied magnetic field, then having that field quickly removed\(^4\). Though not explicitly stated, these data are taken to be from a relatively pure sample. Thus, this relaxation process is modeled by utilizing the infinite chain ferrimagnetic dynamic and associated parameters detailed above, with an initial condition of all even site (cobalt) spins up and all odd site (radical) spins down and the applied magnetic field
having zero magnitude. The result (with a coupling energy of -43.3945K) is provided in Figure 3.5 below:

Figure 3.5: Normalized CoPhOMe magnetization vs. time for an infinite chain dynamic solution (solid lines) with an initially saturated state, a coupling energy of -43.3945K, and zero applied magnetic field and the corresponding selected experimental data (dots) at $T = 5K, 6K, \text{and } 7K$

Good agreement is obtained with the experimental data, though the result is found to be very sensitive to the value of the coupling energy. The experimental data indicate a leveling off at low temperatures and long times that may be due to ferromagnetic impurities in the test setup or the presence of interchain coupling. A one-dimensional Ising chain must eventually equilibrate at zero magnetization.
The finite chain dynamic is now used to compare to the infinite chain result and the same experimental results shown above in Figure 3.5. The response of a 2000 spin chain (corresponding to estimates for relatively pure samples) with the same coupling energy as used for the infinite chain is provided below in Figure 3.6.

![Normalized Magnetization vs. Time](image)

Figure 3.6: Normalized CoPhOMe magnetization vs. time for a finite chain (2000 spins) dynamic solution (solid lines) with an initially saturated state, a coupling energy of -43.3945K, and zero applied magnetic field and the corresponding selected experimental data (dots) at T = 5K, 6K, and 7K

The calculated relaxation of the 2000 spin chain is observed to occur approximately two to four orders of magnitude faster in time than that shown experimentally and calculated for the infinite chain. Calculations for the 2000 spin system at higher values (>+5%) of coupling energy are computationally expensive, but extrapolations of the change in dynamic response with small changes in coupling energy indicate that a coupling energy
of approximately 65K will result in better agreement with the experimental results. This value of the coupling energy is consistent with previously published estimates of approximately 58K to 90K\textsuperscript{6,7}.

The change in dynamic response between the infinite chain and finite chain at the same coupling energy can be understood by considering how the finite chain is limited in extent, with the end spins only having a single nearest neighbor. This results in the effective nearest neighbor coupling energy for the finite chain system being less than that for the infinite chain system, where every spin has two nearest neighbors. This lesser coupling energy results in a faster response, similar to the behavior observed for the ferromagnetic chain in Section 2.3.1 and Section 2.4.1 of Chapter 2.

### 3.4.2 Hysteresis Behavior

The magnetization response associated with an applied oscillating magnetic field is investigated for the infinite chain dynamic model, consistent with the available experimental data being obtained from presumably pure samples. In the infinite chain, the coupling energy of approximately -43K is used since that value provided agreement with the empirical relaxation response. The applied field has a peak magnitude of 35,000 Oersted (or 3.5T in free space) and is cycled at a frequency of 0.005Hz (or a sweep rate of 0.07 T/s) for 300 seconds (or 1.5 cycles). These applied field parameters are consistent with those used for the experimental determination of the CoPhOMe hysteresis response\textsuperscript{4}. The calculated time evolution of the average odd and even spin expectation values are shown below in Figure 3.7 and Figure 3.8 with the normalized applied magnetic field superposed.
Average Spin Expectation Value vs. Time at $T = 7K$

Figure 3.7: Odd (dotted line) and even (solid line) site average expectation values vs. time for an infinite chain dynamic solution at 7K (with normalized applied magnetic field superposed (dash-dot line))
Figure 3.8: Odd (dotted line) and even (solid line) site average expectation values vs. time for an infinite chain dynamic solution at 15K (with normalized applied magnetic field superposed (dash-dot line))

In the 7K response, where a slight hysteresis is observed, the even and odd spins are shown to resist reversing their orientation until the applied magnetic field has reversed direction. In contrast, the 15K response indicates how the spins begin their reorientation in advance of the applied field changing direction. The hysteresis responses and corresponding selected experimental data at 7K and 15K are shown below in Figure 3.9 and Figure 3.10.
Figure 3.9: Calculated infinite chain hysteresis response at 7K (solid line) and 15K (dotted line) and the corresponding selected experimental data at 7K (squares) and 15K (circles)
Figure 3.10: Zoomed view of calculated infinite chain hysteresis response at 7K (solid line) and 15K (dotted line) and the corresponding selected experimental data at 7K (squares) and 15K (circles).

Both responses approach the correct saturation magnetization of approximately $2.02\mu_B$, though much more quickly than the experimental results. The calculated responses also have coercive fields (applied field at which the magnetization becomes zero) close to zero, whereas the experimental data for the 7K and 15K responses have coercivities of approximately 0.1T and 0T respectively (these data points are indicated on the zero magnetization axis in Figure 3.10). The 7K data points along the zero applied field axis in Figure 3.10 also indicate how the calculated response has a remanent magnetization (magnetization remaining as the applied field is reduced to zero) that is substantially larger than that observed experimentally. Thus the lower temperature response is not capturing some aspect of the true physical dynamics. This is also evidenced by how the
lower temperature response fails to indicate the characteristic magnetization plateaus observed in the CoPhOMe hysteresis response at a little less than one half the saturation magnetization (near zero applied field) and at zero magnetization (near ±1T).

Several approaches have been investigated to enable an understanding of the CoPhOMe hysteresis behavior. It has been postulated that the additional dynamic mechanism may be the result of intra-sublattice interactions (i.e. Co-Co spin coupling). This may be due to either individual Co spins having distinct anisotropy axes that are all slightly offset from the nominal 54.74° (where adjacent Co spins are orthogonal and no interactions are present) as investigated by Chandra et al\textsuperscript{5}, or rather all the Co spins having the same anisotropy axis angle with a common offset from the nominal value as investigated by Vindigni et al\textsuperscript{2}.

The Chandra model is phenomenologically based, and relies on specific periodicities and magnitudes of individual Co axis offsets to obtain magnetization plateau phenomena. These particulars notwithstanding, the non-zero and saturation magnetization plateaus are only obtained for applied magnetic flux densities of several Tesla (versus <1T in experiment) and at temperatures below approximately 2K (versus <7K in experiment).

The Vindigni model is simpler and more general in how it treats all the Co spins as having a common axis angle that may be offset from the nominal value. This offset theoretically results in the system being in proximity to a disorder point on either side of which the Co spins interact either ferromagnetically or antiferromagnetically. With a small angular offset of the anisotropy axes, it is shown that the applied magnetic field can serve to drive the system from one side of the disorder point to the other. A jump in
the magnetization results from the transition in ordering associated with the Co spin interaction.

Alternatively, explicit finite chain partition function calculations with a Co spin interaction that does not transition ordering with applied magnetic field have failed to reproduce the plateau phenomena demonstrated in experiment. The potential also exists for unaccounted extraneous magnetic moments in the experimental sample to exhibit the gradual approach to saturation with applied magnetic field.

**3.4.3 Susceptibility**

The AC susceptibility of CoPhOME has been experimentally investigated for nearly pure samples as well as samples doped with varying concentrations of diamagnetic impurities. A dual-peak character is observed for the in-phase susceptibility, with a higher temperature peak (~33K) being most prominent for the relatively pure sample and a lower temperature peak (~14K) being dominant for the more highly doped samples. The higher temperature peak is consistent with that expected for an infinite one-dimensional Ising chain, and decreases and shifts to lower temperatures as the impurity concentration increases, disappearing altogether at higher impurity concentrations.

The AC susceptibility of the highest impurity concentration studied (4.7%) is modeled using the ferrimagnetic finite chain model, with a chain length of 20 spins (corresponding to the nominal segment length of a 2000 spin chain with 4.7% impurities) and a \( \tau_0 \) value of \( 1 \times 10^{12} \) seconds. An exchange interaction of approximately 65K was used. This is consistent with the relaxation discussion above. In accordance with the experimental technique, the applied magnetic field is the superposition of a DC field of 2000 Oe and
an AC field of 10 Oe applied at a frequency of 2700 Hz. The resulting in-phase and out-of-phase susceptibility, together with the experimentally determined in-phase susceptibility, is presented below in Figure 3.11.

![Figure 3.11: Calculated finite chain in-phase (filled squares) and out-of-phase (filled diamonds) susceptibility and experimentally determined in-phase susceptibility (open squares) for CoPhOMe with 4.7% impurity concentration (chain length of 20 spins).](image)

Very good qualitative agreement is obtained between the calculated and empirical in-phase susceptibilities, with the low temperature peak being well-represented and the high temperature peak absent. Note that the out-of-phase susceptibility is only substantially present below the blocking temperature of approximately 12K, where the Glauber slow dynamics become manifest. Note that the out-of-phase susceptibility for the 4.7% doped sample is not presented in the literature.
The AC susceptibility of the relatively pure sample is modeled using a chain length of 2000 spins and a $\tau_0$ value of $3.5 \times 10^{-11}$ seconds. All other parameters remain the same. This result as well as the experimentally determined in-phase susceptibility are presented below in Figure 3.12.

![Figure 3.12: Calculated finite chain in-phase (filled squares) and out-of-phase (filled diamonds) susceptibility and experimentally determined in-phase susceptibility (open squares) for relatively pure CoPhOMe (chain length of 2000 spins).](image)

In the case of relatively pure CoPhOMe, the agreement between calculations and experiment are less straightforward, though the results are not altogether inconsistent. The high temperature peak is present in the calculated result, but it is significantly larger in magnitude and slightly lower in temperature than the experimental result. The experiment shows a low temperature peak that is absent in the calculated result.
The difference in temperatures of the upper peaks can be attributed to the exchange energy used in the calculation being slightly low. The magnitude discrepancy and lower peak can be attributed to the presence of uncharacterized defects (crystalline, chemical, etc.) in the relatively pure sample that effectively break the CoPhOMe chains into a distribution of longer and shorter length segments. Thus, the empirical susceptibility for the relatively pure sample will contain features resulting from a superposition of the calculated higher and lower impurity AC susceptibilities. This is consistent with the calculations performed by Bogani et al to understand the effect of varying length chains on AC susceptibility.  

3.5 Summary

Using the local equilibrium approximation, a closed set of dynamic equations has been developed to describe the time-evolution of the magnetization of infinite and finite length ferrimagnetic Ising chains. In the limit of a ferromagnetic chain with nearest neighbor interactions, this dynamic was shown to correspond with the equilibrium solution obtained previously. In comparisons with the empirical studies of the Ising ferrimagnet CoPhOMe, the dynamic model shows good agreement with the zero-field relaxation response, but fails to capture the plateau features and coercivity observed in hysteresis experiments. However, the calculated AC susceptibility shows good quantitative agreement with experiment for high impurity level samples and good qualitative agreement with experiment for relatively pure samples.
3.6 References


Appendix A

Computer Model Code for One-Dimensional (Anti-)
Ferromagnetic Lattice with Nearest Neighbor Interactions

The equations describing the behavior of the finite and infinite length one-dimensional (anti-) ferromagnetic Ising chains with nearest neighbor interactions are detailed in Chapter 2. This appendix contains the computer model code that was used to implement those equations, and post-process the associated results. The computer language used is MATLAB version 7.7.0.471 (R2008b), a product of The MathWorks, Inc. Three separate codes are provided for the finite length chain, as well as for the infinite length chain. For each chain type, one of the three codes calculates the response to an AC applied field (with or without a superposed DC field), one calculates the response to a DC applied field only, and the third code calculates the differential change in single-spin expectation values.
A.1 Infinite_Local_EQ_AC.m

% Infinite_Local_EQ_AC.m
% Implementation of local equilibrium approximation for one-dimensional
% (anti-) ferromagnetic infinite chain with nearest neighbor
% interactions.
% AC response post-processing.
% Ryan Kristensen
% 16 April 2009

% Initialize and clear workspace
close all
clear all
clc

%% Physical Constants
% Boltzmann's constant (J/degK)
k_B = 1.3807e-23;

%% Principal Inputs
% Applied magnetic field (mu B / k T)
% DC
b_DC = 0;
% AC
b_max_AC = 3;

% Coupling energy (J / k T)
g = [0.1 1];
% Glauber gamma parameter
gamma = tanh(2*g);

% Time duration to simulate (sec)
tmax = 1.5;

% Initial condition
Q1 = 0;

% Frequency (Hz)
f = 1;

% Time scale parameter
a = 1000; % (1/sec)
%% Solution of Differential Equation

ODE15s is a variable order, multi-step, solver based on the numerical differentiation formulas and is appropriate for stiff problems

\[ [T_{sol\_g01}, Q_{sol\_g01}] = \text{ode15s(@(t, Q) Infinite\_Local\_EQ\_dQ(t, Q, ... \quad a, g(1), \gamma(1), b_{DC}(1), b_{max\_AC}(1), f), [0 tmax], Qi); } \]

\[ [T_{sol\_g1}, Q_{sol\_g1}] = \text{ode15s(@(t, Q) Infinite\_Local\_EQ\_dQ(t, Q, ... \quad a, g(2), \gamma(2), b_{DC}(1), b_{max\_AC}(1), f), [0 tmax], Qi); } \]

%% Post-Processing Solution

% Infinite chain equilibrium magnetization and static susceptibility

% Applied field points
b_EQ = linspace(-3,3,101);

% Equilibrium magnetization
Q_EQ_g01 = sinh(b_EQ)/sqrt((sinh(b_EQ)).^2 + exp(-4*g(1)));
Q_EQ_g1 = sinh(b_EQ)/sqrt((sinh(b_EQ)).^2 + exp(-4*g(2)));

% Infinite chain static susceptibility ( / k T)
Chi_EQ_g01 = ((cosh(b_EQ)*exp(-4*g(1)))/(sinh(b_EQ)).^2 + exp(-4*g(1))).^(3/2);
Chi_EQ_g1 = ((cosh(b_EQ)*exp(-4*g(2)))/(sinh(b_EQ)).^2 + exp(-4*g(2))).^(3/2);

%% Plot magnetization with equilibrium solution

figure
plot(b_DC + b_max_AC*sin(2*pi*f*T_sol_g01), Q_sol_g01, 'k', 'linewidth', 2)
hold on
plot(b_EQ, Q_EQ_g01, 'k:', 'linewidth', 3)
plot(b_DC + b_max_AC*sin(2*pi*f*T_sol_g1), Q_sol_g1, 'r', 'linewidth', 2)
plot(b_EQ, Q_EQ_g1, 'r:', 'linewidth', 3)
ggrid on
title('Magnetization vs. Applied Magnetic Field')
ylabel('Magnetization per Spin (a.u. -1 to +1)')
ylim([-1.1 1.1])
xlabel('Applied Magnetic Field (\mu B / k\_B T)')
xlim([-3 3])
text(-1.1, 0.65, '\text{J} / k\_B T = 1', 'backgroundcolor', [1 1 1])
text(1, 0.65, '\text{J} / k\_B T = 0.1', 'backgroundcolor', [1 1 1])
%% Plot susceptibility with equilibrium solution

% Calculate susceptibility from magnetization
Chi_g01 = gradient(Q_sol_g01,b_DC + b_max_AC*sin(2*pi*f*T_sol_g01));
Chi_g1 = gradient(Q_sol_g1,b_DC + b_max_AC*sin(2*pi*f*T_sol_g1));

figure
plot(b_DC + b_max_AC*sin(2*pi*f*T_sol_g01),Chi_g01,'k','linewidth',2)
hold on
plot(b_DC + b_max_AC*sin(2*pi*f*T_sol_g1),Chi_g1,'r','linewidth',2)
plot(b_EQ,Chi_EQ_g01,'k:','linewidth',3)
plot(b_EQ,Chi_EQ_g1,'r:','linewidth',3)
grid on

title('Static Susceptibility vs. Applied Magnetic Field')
ylabel('Susceptibility per Spin ($\chi x k_B T$) (a.u.)')
ylim([0 8])
xlabel('Applied Magnetic Field ($\mu B / k_B T$)')
xlim([-3 3])

text(0.3,5,'J / k_B T = 1','backgroundcolor',[1 1 1])

text(1,0.7,'J / k_B T = 0.1','backgroundcolor',[1 1 1])

% End of file
A.2 Infinite_Local_EQ_DC.m

% Infinite_Local_EQ_DC.m
% Implementation of local equilibrium approximation for one-dimensional
% (anti-) ferromagnetic infinite chain with nearest neighbor
% interactions.
% DC response post-processing.
% Ryan Kristensen
% 16 April 2009

% Initialize and clear workspace
close all
clear all
clc

%% Physical Constants
% Boltzmann's constant (J/degK)
k_B = 1.3807e-23;

%% Principal Inputs
% Applied magnetic field (mu B / k T)
% DC
b_DC = [0.1 1 10];
% AC
b_max_AC = [0 0 0];

% Coupling energy (J / k T)
g = [0.1 1 10];
% Glauber gamma parameter
gamma = tanh(2*g);

% Time duration to simulate (sec)
tmax = 1e7;

% Initial condition
Q1 = 0;

% Frequency (Hz)
f = 0;

% Time scale parameter
a = 1000; % (1/sec)
%% Solution of Differential Equation

% ODE15s is a variable order, multi-step, solver based on the numerical
% differentiation formulas and is appropriate for stiff problems

% b = 0.1, all g

[T_sol_b01_g01,Q_sol_b01_g01] = ode15s(@(t,Q)
    Infinite_Local_EQ_dQ(t,Q,...
    a,g(1),gamma(1),b_DC(1),b_max_AC(1),f),[0 tmax],Qi);

[T_sol_b01_g1,Q_sol_b01_g1] = ode15s(@(t,Q)
    Infinite_Local_EQ_dQ(t,Q,...
    a,g(2),gamma(2),b_DC(1),b_max_AC(1),f),[0 tmax],Qi);

options = odeset('MaxStep',0.001*tmax);
[T_sol_b01_g10,Q_sol_b01_g10] = ode15s(@(t,Q)
    Infinite_Local_EQ_dQ(t,Q,...
    a,g(3),gamma(3),b_DC(1),b_max_AC(1),f),[0 tmax],Qi,options);

% b = 1, all g

[T_sol_b1_g01,Q_sol_b1_g01] = ode15s(@(t,Q)
    Infinite_Local_EQ_dQ(t,Q,...
    a,g(1),gamma(1),b_DC(2),b_max_AC(2),f),[0 tmax],Qi);

[T_sol_b1_g1,Q_sol_b1_g1] = ode15s(@(t,Q)
    Infinite_Local_EQ_dQ(t,Q,...
    a,g(2),gamma(2),b_DC(2),b_max_AC(2),f),[0 tmax],Qi);

options = odeset('MaxStep',0.0001*tmax);
[T_sol_b1_g10,Q_sol_b1_g10] = ode15s(@(t,Q)
    Infinite_Local_EQ_dQ(t,Q,...
    a,g(3),gamma(3),b_DC(2),b_max_AC(2),f),[0 tmax],Qi,options);

% b = 10, all g

[T_sol_b10_g01,Q_sol_b10_g01] = ode15s(@(t,Q)
    Infinite_Local_EQ_dQ(t,Q,...
    a,g(1),gamma(1),b_DC(3),b_max_AC(3),f),[0 tmax],Qi);

[T_sol_b10_g1,Q_sol_b10_g1] = ode15s(@(t,Q)
    Infinite_Local_EQ_dQ(t,Q,...
    a,g(2),gamma(2),b_DC(3),b_max_AC(3),f),[0 tmax],Qi);

options = odeset('MaxStep',0.0001*tmax);
[T_sol_b10_g10,Q_sol_b10_g10] = ode15s(@(t,Q)
    Infinite_Local_EQ_dQ(t,Q,...
    a,g(3),gamma(3),b_DC(3),b_max_AC(3),f),[0 tmax],Qi,options);

%% Post-Processing Solution

% Infinite chain equilibrium solutions
% b = 0.1, all g
Q_EQ_b01_g01 = sinh(b_DC(1))./sqrt((sinh(b_DC(1))).^2 + exp(-4*g(1)));
Q_EQ_b01_g1 = sinh(b_DC(1))./sqrt((sinh(b_DC(1))).^2 + exp(-4*g(2)));
Q_EQ_b01_g10 = sinh(b_DC(1))./sqrt((sinh(b_DC(1))).^2 + exp(-4*g(3)));

% b = 1, all g
Q_EQ_b1_g01 = sinh(b_DC(2))./sqrt((sinh(b_DC(2))).^2 + exp(-4*g(1)));
Q_EQ_b1_g1 = sinh(b_DC(2))./sqrt((sinh(b_DC(2))).^2 + exp(-4*g(2)));
Q_EQ_b1_g10 = sinh(b_DC(2))./sqrt((sinh(b_DC(2))).^2 + exp(-4*g(3)));

% b = 10, all g
Q_EQ_b10_g01 = sinh(b_DC(3))./sqrt((sinh(b_DC(3))).^2 + exp(-4*g(1)));
Q_EQ_b10_g1 = sinh(b_DC(3))./sqrt((sinh(b_DC(3))).^2 + exp(-4*g(2)));
Q_EQ_b10_g10 = sinh(b_DC(3))./sqrt((sinh(b_DC(3))).^2 + exp(-4*g(3)));

% Plot dynamic solution with equilibrium solution

%% b = 0.1
figure
semilogx(T_sol_b01_g01,Q_sol_b01_g01,'k','linewidth',2)
hold on
semilogx([1e-9 tmax],[Q_EQ_b01_g01 Q_EQ_b01_g01],'k:','linewidth',3)
semilogx(T_sol_b01_g1,Q_sol_b01_g1,'k','linewidth',2)
semilogx([1e-9 tmax],[Q_EQ_b01_g1 Q_EQ_b01_g1],'k:','linewidth',3)
semilogx(T_sol_b01_g10,Q_sol_b01_g10,'k','linewidth',2)
semilogx([1e-9 tmax],[Q_EQ_b01_g10 Q_EQ_b01_g10],'k:','linewidth',3)

text(1e0,0.05,'J / k_B T = 0.1','backgroundcolor',[1 1 1])
text(1e0,0.52,'J / k_B T = 1','backgroundcolor',[1 1 1])
text(1e0,0.93,'J / k_B T = 10','backgroundcolor',[1 1 1])
grid on

title('Magnetization of Infinite Chain vs. Time')
ylabel('Magnetization per Spin (a.u. -1 to +1)')
ylim([-0.1 1.1])
xlabel('Time (s)')
xlim([1e-5 1e7])
xticklabel_rotate([1e-5 1e-3 1e-1 1e1 1e5 1e7],0,...
    {'10^(-5)';'10^(-3)';'10^(-1)';'10^1';'10^3';'10^5';'10^7'},...
    'HorizontalAlignment','center');

%% b = 1
figure
semilogx(T_sol_b1_g01,Q_sol_b1_g01,'k','linewidth',2)
hold on
semilogx([1e-9 tmax],[Q_EQ_b1_g01 Q_EQ_b1_g01],'k:','linewidth',3)
semilogx(T_sol_b1_g1,Q_sol_b1_g1,'k','linewidth',2)
semilogx([1e-9 tmax],[Q_EQ_b1_g1 Q_EQ_b1_g1],'k:','linewidth',3)
semilogx(T_sol_b1_g10,Q_sol_b1_g10,'k','linewidth',2)
semilogx([1e-9 tmax],[Q_EQ_b1_g10 Q_EQ_b1_g10],'k:','linewidth',3)

text(1e-2,0.75,'J / k_B T = 0.1','backgroundcolor',[1 1 1])
text(1e-2,0.93,'J / k_B T = 1','backgroundcolor',[1 1 1])
text(1e3,0.93,'J / k_B T = 10','backgroundcolor',[1 1 1])

grid on

title('Magnetization of Infinite Chain vs. Time')
ylabel('Magnetization per Spin (a.u -1 to +1)')
xlabel('Time (s)')
xlim([1e-5 1e7])
xticklabel_rotate([1e-5 1e-3 1e-1 1e1 1e3 1e5 1e7],0,...
{'10^-5';'10^-3';'10^-1';'10^1';'10^3';'10^5';'10^7'},...
'HorizontalAlignment','center');

%% b = 10
figure
semilogx(T_sol_b10_g01,Q_sol_b10_g01,'k','linewidth',2)
hold on
semilogx([1e-9 tmax],[Q_EQ_b10_g01 Q_EQ_b10_g01],'k:','linewidth',3)
semilogx(T_sol_b10_g1,Q_sol_b10_g1,'k','linewidth',2)
semilogx([1e-9 tmax],[Q_EQ_b10_g1 Q_EQ_b10_g1],'k:','linewidth',3)
semilogx(T_sol_b10_g10,Q_sol_b10_g10,'k','linewidth',2)
semilogx([1e-9 tmax],[Q_EQ_b10_g10 Q_EQ_b10_g10],'k:','linewidth',3)

text(1.15e-5,0.93,'J / k_B T = 0.1','backgroundcolor',[1 1 1])
text(1e-2,0.93,'J / k_B T = 1','backgroundcolor',[1 1 1])
text(1e3,0.93,'J / k_B T = 10','backgroundcolor',[1 1 1])

grid on

title('Magnetization of Infinite Chain vs. Time')
ylabel('Magnetization per Spin (a.u -1 to +1)')
xlabel('Time (s)')
xlim([1e-5 1e7])
xticklabel_rotate([1e-5 1e-3 1e-1 1e1 1e3 1e5 1e7],0,...
{'10^-5';'10^-3';'10^-1';'10^1';'10^3';'10^5';'10^7'},...
'HorizontalAlignment','center');

% End of file
A.3 Infinite_Local_EQ_dQ.m

function dQ = Infinite_Local_EQ_dQ(t,Q,a,g,gamma,b_DC,b_max_AC,f)

% Infinite_Local_EQ_dQ.m
% Function calculating differential change in average single spin
% expectation value (dQ) for one-dimensional (anti-) ferromagnetic
% infinite chain with nearest neighbor interactions
% Inputs: t is the value of time (s)
%         Q is the average single spin expectation value
%         a is alpha (1/s)
%         g is J / k T
%         gamma is tanh(2g)
%         b_DC is DC amplitude of mu B / k T
%         b_max_AC is the AC zero to peak amplitude of mu B / k T
%         f is the frequency of the applied field (Hz)
%
% Ryan Kristensen
% 16 April 2009

% Screen out invalid values of Q that ODE solver stepping investigates
% (otherwise, complex results can be returned)
if Q > 1
    Q = 1;
elseif Q < -1
    Q = -1;
end

% Glauber beta parameter
if f == 0
    beta = tanh(b_DC);
else
    b = b_DC + b_max_AC*sin(2*pi*f*t);
    beta = tanh(b);
end

% Average two-spin product expectation value
R = 1 + (2-2*sqrt(Q^2 - (Q^2 - 1)*exp(4*g)))/(exp(4*g)-1);

% Differential change in Q with time
dQ = -a*(Q - beta - gamma*Q + gamma*beta*R);

% End of file
% A.4 Finite_Local_EQ_AC.m
% Finite_Local_EQ_AC.m
% Implementation of local equilibrium approximation for one-dimensional
% (anti-)ferromagnetic finite chain with nearest neighbor
% interactions.
% AC response post-processing.
% Ryan Kristensen
% 14 June 2009

% Initialize and clear workspace
clear all
close all
clc

%% Physical constants
% Boltzmann's constant (J/degK)
k_B = 1.3807e-23;

%% Principal Inputs
% Number of spins
N = 6;

% Applied magnetic field (mu B / k T)
% DC
b_DC = 0;
% AC
b_max_AC = 3;

% Coupling energy (J / k T)
g = [0.1 1];
% Glauber gamma parameter (inner spins)
gamma = tanh(2*g);
% Glauber gamma parameter (end spins)
gamma1 = tanh(g);

% Time duration to simulate (sec)
tmax = 1.5;

% Frequency (Hz)
f = 1;

% Time scale parameter
a = 1000; % (1/sec)
% Initial condition
qi = zeros(1,N);

%% Solution of Differential Equation
% ODE15s is a variable order, multi-step, solver based on the numerical
% differentiation formulas and is appropriate for stiff problems

% g = .1
[T_sol_g01,Y_sol_g01] = ode15s(@(t,y) Finite_Local_EQ_dy(t,y,...
a,g(1),gamma(1),gamma1(1),b_DC,b_max_AC,f,N),[0 tmax],qi);

% g = 1
[T_sol_g1,Y_sol_g1] = ode15s(@(t,y) Finite_Local_EQ_dy(t,y,...
a,g(2),gamma(2),gamma1(2),b_DC,b_max_AC,f,N),[0 tmax],qi);

% Transpose solution vectors
q_g01 = Y_sol_g01';
q_g1 = Y_sol_g1';

%% Post-Processing Solution
figure
% imagesc(T_sol_g1,1:N,q_g1),[-1 1])
% surf(T_sol_g1,1:N,q_g1)
% colormap(gray)
contourf(T_sol_g1,1:N,q_g1,100)
shading flat
colorbar
title('Spin Expectation Value vs. Time')
ylabel('Spin Index')
set(gca,'ytick',1:N,'yticklabel',num2str([1:N]))
xlabel('Time (s)')

% Calculate average single spin expectation value
for ti = 1:length(T_sol_g01)
    M_avg_g01(ti) = sum(q_g01(:,ti))/N;
end
for ti = 1:length(T_sol_g1)
    M_avg_g1(ti) = sum(q_g1(:,ti))/N;
end

% Finite chain equilibrium magnetization
% Applied field points
b_EQ = linspace(-3,3,101);
% Equilibrium magnetization
Q_EQ_01 = Finite_Spin_EQ(b_EQ,g(1));
Q_EQ_1 = Finite_Spin_EQ(b_EQ,g(2));

%% Plot magnetization with equilibrium solution
figure
plot(b_DC + b_max_AC*sin(2*pi*f*T_sol_g01),M_avg_g01,'k','linewidth',2)
hold on
plot(b_EQ,Q_EQ_01,'k:','linewidth',3)
plot(b_DC + b_max_AC*sin(2*pi*f*T_sol_g1),M_avg_g1,'r','linewidth',2)
plot(b_EQ,Q_EQ_1,'r:','linewidth',3)
grid on

title('Magnetization vs. Applied Magnetic Field')
ylabel('Magnetization per Spin (a.u. -1 to +1)')
ylim([-1.1 1.1])
xlabel('Applied Magnetic Field (\mu B / k_(B)T)')
xlim([-3 3])

text(-1.1,0.65,'J / k_(B)T = 1','backgroundcolor',[1 1 1])
text(1,0.65,'J / k_(B)T = 0.1','backgroundcolor',[1 1 1])

% End of file
A.5 Finite_Local_EQ_DC.m

% Finite_Local_EQ_DC.m
% Implementation of local equilibrium approximation for one-dimensional
% (anti-) ferromagnetic finite chain with nearest neighbor
% interactions.
% DC response post-processing.
% Ryan Kristensen
% 14 June 2009

% Initialize and clear workspace
clear all
close all
clc

%% Physical constants

% Boltzmann's constant (J/degK)
k_B = 1.3807e-23;

%% Principal Inputs

% Number of spins
N = 6;

% Applied magnetic field (mu B / k T)
% DC
b_DC = 0.1;
% AC
b_max_AC = 0;

% Coupling energy (J / k T)
g = [0.1 1 10];
% Glauber gamma parameter (inner spins)
gamma = tanh(2*g);
% Glauber gamma parameter (end spins)
gamma1 = tanh(g);

% Time duration to simulate (sec)
tmax = 1e8;

% Frequency (Hz)
f = 0;

% Time scale parameter
a = 1000; % (1/sec)
% Initial condition
qi = zeros(1,N);

%% Solution of Differential Equation
% ODE15s is a variable order, multi-step, solver based on the numerical differentiation formulas and is appropriate for stiff problems

% g = .1
[T_sol_g01,Y_sol_g01] = ode15s(@(t,y) Finite_Local_EQ_dy(t,y,...
    a,g(1),gamma(1),gamma1(1),b_DC,b_max_AC,f,N),[0 tmax],qi);

% g = 1
[T_sol_g1,Y_sol_g1] = ode15s(@(t,y) Finite_Local_EQ_dy(t,y,...
    a,g(2),gamma(2),gamma1(2),b_DC,b_max_AC,f,N),[0 tmax],qi);

% g = 10
[T_sol_g10,Y_sol_g10] = ode15s(@(t,y) Finite_Local_EQ_dy(t,y,...
    a,g(3),gamma(3),gamma1(3),b_DC,b_max_AC,f,N),[0 tmax],qi);

% Transpose solution vectors
q_g01 = Y_sol_g01';
q_g1 = Y_sol_g1';
q_g10 = Y_sol_g10';

%% Post-Processing Solution
figure
% imagesc(T_sol,1:N,q),[-1 1])
% surf(T_sol,1:N,q)
% colormap(gray)
contourf(T_sol_g10,1:N,q_g10,100)
shading flat
colorbar
title('Spin Expectation Value vs. Time')
ylabel('Spin Index')
set(gca,'ytick',[1:N],'yticklabel',num2str([1:N]))
xlabel('Time (s)')

% Calculate average single spin expectation value
for ti = 1:length(T_sol_g01)
    M_avg_g01(ti) = sum(q_g01(:,ti))/N;
end

for ti = 1:length(T_sol_g1)
    M_avg_g1(ti) = sum(q_g1(:,ti))/N;
end

for ti = 1:length(T_sol_g10)
    M_avg_g10(ti) = sum(q_g10(:,ti))/N;
% Finite chain equilibrium solutions
Q_EQ_01 = Finite_Spin_EQ(b_DC,g(1));
Q_EQ_1 = Finite_Spin_EQ(b_DC,g(2));
Q_EQ_10 = Finite_Spin_EQ(b_DC,g(3));

% % b = 0.1 g = 0.1,1,5
% figure
% semilogx([1e-9 tmax], [Q_EQ_01 Q_EQ_01], 'k:', 'linewidth', 3)
% hold on
% semilogx(T_sol_g01, M_avg_g01, 'k', 'linewidth', 2)
% semilogx([1e-9 tmax], [Q_EQ_1 Q_EQ_1], 'k:', 'linewidth', 3)
% semilogx(T_sol_g1, M_avg_g1, 'k', 'linewidth', 2)
% semilogx([1e-9 tmax], [Q_EQ_10 Q_EQ_10], 'k:', 'linewidth', 3)
% semilogx(T_sol_g10, M_avg_g10, 'k', 'linewidth', 2)
% grid on
% text(1e-4, 0.18, 'J / k_B T = 0.1', 'backgroundcolor', [1 1 1])
% text(1e-3, 0.42, 'J / k_B T = 1', 'backgroundcolor', [1 1 1])
% text(1e1, 0.6, 'J / k_B T = 5', 'backgroundcolor', [1 1 1])
% title('Magnetization of Finite Chain vs. Time')
% ylabel('Magnetization per Spin (a.u. -1 to +1)')
% ylim([-0.1 1.1])
% xticklabel_rotate([1e-5 1e-4 1e-3 1e-2 1e-1 1e0 1e1 1e2 1e3], 0, ...
%     {'10^-5';'10^-4';'10^-3';'10^-2';'10^-1';'10^0';'10^1';...
%     '10^2';'10^3'},'HorizontalAlignment','center');

% % b = 1 g = 0.1,1,2
% figure
% semilogx([1e-9 tmax], [Q_EQ_01 Q_EQ_01], 'k:', 'linewidth', 3)
% hold on
% semilogx(T_sol_g01, M_avg_g01, 'k', 'linewidth', 2)
% semilogx([1e-9 tmax], [Q_EQ_1 Q_EQ_1], 'k:', 'linewidth', 3)
% semilogx(T_sol_g1, M_avg_g1, 'k', 'linewidth', 2)
% semilogx([1e-9 tmax], [Q_EQ_10 Q_EQ_10], 'k:', 'linewidth', 3)
% semilogx(T_sol_g10, M_avg_g10, 'k', 'linewidth', 2)
% grid on
% text(5e-5, 0.75, 'J / k_B T = 0.1', 'backgroundcolor', [1 1 1])
% text(3e-4, 0.93, 'J / k_B T = 1', 'backgroundcolor', [1 1 1])
% text(3e-2, 0.5, 'J / k_B T = 2', 'backgroundcolor', [1 1 1])

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%% Magnetization of Finite Chain vs. Time
% ylabel('Magnetization per Spin (a.u. -1 to +1)')
% xlim([1e-5 1e3])
% set(gca,'XMinorGrid','off','XMinorTick','off')
% xticklabel_rotate([1e-5 1e-4 1e-3 1e-2 1e-1 1e0 1e1 1e2 1e3],0,...
%   '10^(-5)';'10^(-4)';'10^(-3)';'10^(-2)';'10^(-1)';'10^0';'10^1';...
%   '10^(2)';'10^3'),'HorizontalAlignment','center');

%% b = 10 g = 0.1,1,4
% figure
% semilogx([1e-9 tmax],[Q_EQ_01 Q_EQ_01],'k:','linewidth',3)
% hold on
% semilogx(T_sol_g01,M_avg_g01,'k','linewidth',2)
% semilogx([1e-9 tmax],[Q_EQ_1 Q_EQ_1],'k:','linewidth',3)
% semilogx(T_sol_g1,M_avg_g1,'k','linewidth',2)
% semilogx([1e-9 tmax],[Q_EQ_10 Q_EQ_10],'k:','linewidth',3)
% semilogx(T_sol_g10,M_avg_g10,'k','linewidth',2)
% grid on
% text(5e-5,0.93,'J / k_{B}T = 0.1','backgroundcolor',[1 1 1])
% text(1e-2,0.93,'J / k_{B}T = 1','backgroundcolor',[1 1 1])
% text(3e-2,0.5,'J / k_{B}T = 4','backgroundcolor',[1 1 1])
% title('Magnetization of Finite Chain vs. Time')
% ylabel('Magnetization per Spin (a.u. -1 to +1)')
% xlim([1e-5 1e3])
% set(gca,'XMinorGrid','off','XMinorTick','off')
% xticklabel_rotate([1e-5 1e-4 1e-3 1e-2 1e-1 1e0 1e1 1e2 1e3],0,...
%   '10^(-5)';'10^(-4)';'10^(-3)';'10^(-2)';'10^(-1)';'10^0';'10^1';...
%   '10^(2)';'10^3'),'HorizontalAlignment','center');

%% APPROX b = 0.1 g = 0.1,1,10
% figure
% semilogx([1e-9 tmax],[Q_EQ_01 Q_EQ_01],'k:','linewidth',3)
% hold on
% semilogx(T_sol_g01,M_avg_g01,'k','linewidth',2)
% semilogx([1e-9 tmax],[Q_EQ_1 Q_EQ_1],'k:','linewidth',3)
% semilogx(T_sol_g1,M_avg_g1,'k','linewidth',2)
% semilogx([1e-9 tmax],[Q_EQ_10 Q_EQ_10],'k:','linewidth',3)
% semilogx(T_sol_g10,M_avg_g10,'k','linewidth',2)
% grid on
% text(2e-5,0.18,'J / k_{B}T = 0.1','backgroundcolor',[1 1 1])
\% text(1e-3,0.42,'J / k_{B}T = 1','backgroundcolor',[1 1 1])
\% text(5e4,0.6,'J / k_{B}T = 10','backgroundcolor',[1 1 1])
\% title('Magnetization of Finite Chain vs. Time')
\% ylabel('Magnetization per Spin (a.u. -1 to +1)')
\% ylim([-1 1.1])
\% xlabel('Time (s)')
\% set(gca,'XMinorGrid','off','XMinorTick','off')
\% xlim([1e-5 1e7])
\% xticklabel_rotate([1e-5 1e-3 1e-1 1e1 1e3 1e5 1e7],0,...
\%   {'10^{-5}';'10^{-3}';'10^{-1}';'10^1';'10^3';'10^5';'10^7'},...
\%   'HorizontalAlignment','center');
\% \% APPROX b = 1 g = 0.1,1,10
\% figure
\% semilogx([1e-9 tmax],[Q_EQ_01 Q_EQ_01],'k:','linewidth',3)
\% hold on
\% semilogx(T_sol_g01,M_avg_g01,'k','linewidth',2)
\% semilogx([1e-9 tmax],[Q_EQ_1 Q_EQ_1],'k:','linewidth',3)
\% semilogx(T_sol_g1,M_avg_g1,'k','linewidth',2)
\% semilogx([1e-9 tmax],[Q_EQ_10 Q_EQ_10],'k:','linewidth',3)
\% semilogx(T_sol_g10,M_avg_g10,'k','linewidth',2)
\% grid on
\% text(1.2e-5,0.75,'J / k_{B}T = 0.1','backgroundcolor',[1 1 1])
\% text(5e-5,0.92,'J / k_{B}T = 1','backgroundcolor',[1 1 1])
\% text(9e2,0.5,'J / k_{B}T = 10','backgroundcolor',[1 1 1])
\% title('Magnetization of Finite Chain vs. Time')
\% ylabel('Magnetization per Spin (a.u. -1 to +1)')
\% ylim([-1 1.1])
\% xlabel('Time (s)')
\% set(gca,'XMinorGrid','off','XMinorTick','off')
\% xlim([1e-5 1e7])
\% xticklabel_rotate([1e-5 1e-3 1e-1 1e1 1e3 1e5 1e7],0,...
\%   {'10^{-5}';'10^{-3}';'10^{-1}';'10^1';'10^3';'10^5';'10^7'},...
\%   'HorizontalAlignment','center');
\% \% APPROX b = 3 g = 0.1,1,10
\% figure
\% semilogx([1e-9 tmax],[Q_EQ_01 Q_EQ_01],'k:','linewidth',3)
\% hold on
\% semilogx(T_sol_g01,M_avg_g01,'k','linewidth',2)
\% semilogx([1e-9 tmax],[Q_EQ_1 Q_EQ_1],'k:','linewidth',3)
\% semilogx(T_sol_g1,M_avg_g1,'k','linewidth',2)
\% semilogx([1e-9 tmax],[Q_EQ_10 Q_EQ_10],'k:','linewidth',3)
\% semilogx(T_sol_g10,M_avg_g10,'k','linewidth',2)
\% grid on
\% text(1.2e-5,0.92,'J / k_{B}T = 0.1','backgroundcolor',[1 1 1])
text(1e-2,0.92,'J / k(B)T = 1','backgroundcolor',[1 1 1])
text(7e2,0.5,'J / k(B)T = 10','backgroundcolor',[1 1 1])
title('Magnetization of Finite Chain vs. Time')
ylabel('Magnetization per Spin (a.u. -1 to +1)')
ylim([-1 1.1])
xlabel('Time (s)')
set(gca,'XMinorGrid','off','XMinorTick','off')
xlim([1e-5 1e7])
xTickLabel_Rotate([1e-5 1e-3 1e-1 1e1 1e3 1e5 1e7],0,...
    {'10^-5';'10^-3';'10^-1';'10^1';'10^3';'10^5';'10^7'},...
    'HorizontalAlignment','center');

% End of file
function dy = Finite_Local_EQ_dy(t,y,a,g,\gamma,\gamma_1,b_DC, b_{\text{max}_{\text{AC}}}, f, N)
%
% Finite_Local_EQ_dy.m
%
% Function calculating differential change in individual single spin expectation value (dy) for one-dimensional (anti-) ferromagnetic finite chain with nearest neighbor interactions
%
% Inputs: t is the value of time (s)
% y is the vector of individual single spin expectation values
% a is alpha (1/s)
% g is J / k T
% \gamma is \tanh(2g)
% \gamma_1 is \tanh(g)
% b_{\text{DC}} is DC amplitude of \mu B / k T
% b_{\text{max}_{\text{AC}}} is the AC zero to peak amplitude of \mu B / k T
% f is the frequency of the applied field (Hz)
% N is the number of spins in the finite chain
%
% Ryan Kristensen
% 14 June 2009

% Screen out invalid values of Q that ODE solver stepping investigates (otherwise, complex results can be returned)
for i = 1:length(y)
    if y(i) > 1
        y(i) = 1;
    end
    if y(i) < -1
        y(i) = -1;
    end
end

% Glauber beta parameter
if f == 0
    beta = \tanh(b_{DC});
else
    b = b_{DC} + b_{\text{max}_{\text{AC}}} \sin(2\pi f t);
    beta = \tanh(b);
end

% Initialize dy vector
dy = zeros(N,1);

% Loop i over N spins
for i = 1:N

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\[ \text{im1} = i-1; \quad \text{Value of } i-1 \]
\[ \text{ipl} = i+1; \quad \text{Value of } i+1 \]

\[
\% \text{ Calculate } r \text{ using finite chain two-spin product expectation value}
\]

\[
\text{if } i == 1 \quad \% \text{ For end spin}
\]
\[
\% \text{ Two spin probabilities}
\]
\[
\text{Pi_ip1_pp} = \frac{(\exp(4*g)*(2+y(i)+y(ipl)) - y(i) - y(ipl) - \ldots
\quad \sqrt{(\exp(4*g)*(2+y(i)+y(ipl)) - y(i) - y(ipl))^2 - \ldots
\quad \exp(4*g)*\left(4*\exp(4*g)-4\right)\left(y(i)*y(ipl) + y(i)+y(ipl)+1\right)}\ldots
\quad \ldots
\quad \ldots
\quad / (4*\exp(4*g)-4);}
\]
\[
\text{Pi_ip1_pm} = 0.5*(y(i) + 1 - 2*\text{Pi_ip1_pp});
\]
\[
\text{Pi_ip1_mp} = 0.5*(y(ipl) + 1 - 2*\text{Pi_ip1_pp});
\]
\[
\text{Pi_ip1_mm} = 0.5*(-y(i) - y(ipl) + 2*\text{Pi_ip1_pp});
\]
\[
% \text{ Two spin product expectation value}
\]
\[
r_i_ip1 = \text{Pi_ip1_pp} - \text{Pi_ip1_pm} - \text{Pi_ip1_mp} + \text{Pi_ip1_mm};
\]

\[
\text{elseif } i == N \quad \% \text{ For end spin}
\]
\[
% \text{ Two spin probabilities}
\]
\[
\text{Pi_im1_pp} = \frac{(\exp(4*g)*(2+y(i)+y(im1)) - y(i) - y(im1) - \ldots
\quad \sqrt{(\exp(4*g)*(2+y(i)+y(im1)) - y(i) - y(im1))^2 - \ldots
\quad \exp(4*g)*\left(4*\exp(4*g)-4\right)\left(y(i)*y(im1) + y(i)+y(im1)+1\right)}\ldots
\quad \ldots
\quad \ldots
\quad / (4*\exp(4*g)-4);}
\]
\[
\text{Pi_im1_pm} = 0.5*(y(i) + 1 - 2*\text{Pi_im1_pp});
\]
\[
\text{Pi_im1_mp} = 0.5*(y(im1) + 1 - 2*\text{Pi_im1_pp});
\]
\[
\text{Pi_im1_mm} = 0.5*(-y(i) - y(im1) + 2*\text{Pi_im1_pp});
\]
\[
% \text{ Two spin product expectation value}
\]
\[
r_i_im1 = \text{Pi_im1_pp} - \text{Pi_im1_pm} - \text{Pi_im1_mp} + \text{Pi_im1_mm};
\]

\[
\text{else} \quad \% \text{ For inner spins}
\]
\[
% \text{ Two spin probabilities}
\]
\[
\text{Pi_ip1_pp} = \frac{(\exp(4*g)*(2+y(i)+y(ipl)) - y(i) - y(ipl) - \ldots
\quad \sqrt{(\exp(4*g)*(2+y(i)+y(ipl)) - y(i) - y(ipl))^2 - \ldots
\quad \exp(4*g)*\left(4*\exp(4*g)-4\right)\left(y(i)*y(ipl) + y(i)+y(ipl)+1\right)}\ldots
\quad \ldots
\quad \ldots
\quad / (4*\exp(4*g)-4);}
\]
\[
\text{Pi_ip1_pm} = 0.5*(y(i) + 1 - 2*\text{Pi_ip1_pp});
\]
\[
\text{Pi_ip1_mp} = 0.5*(y(ipl) + 1 - 2*\text{Pi_ip1_pp});
\]
\[
\text{Pi_ip1_mm} = 0.5*(-y(i) - y(ipl) + 2*\text{Pi_ip1_pp});
\]
\[
% \text{ Two spin product expectation value}
\]
\[
r_i_ip1 = \text{Pi_ip1_pp} - \text{Pi_ip1_pm} - \text{Pi_ip1_mp} + \text{Pi_ip1_mm};
\]

\[
% \text{ Two spin probabilities}
\]
\[
\text{Pi_im1_pp} = (\exp(4*g)*(2+y(i)+y(im1)) - y(i) - y(im1) - \ldots
\quad \sqrt{(\exp(4*g)*(2+y(i)+y(im1)) - y(i) - y(im1))^2 - \ldots
\quad \exp(4*g)*\left(4*\exp(4*g)-4\right)\left(y(i)*y(im1) + y(i)+y(im1)+1\right)}\ldots
\quad \ldots
\quad \ldots
\quad / (4*\exp(4*g)-4);}
\]
sqrt((exp(4*g)*(2+y(i)+y(im1)) - y(i) - y(im1))^2 - ...
exp(4*g)*(4*exp(4*g)-4)*(y(i)*y(im1) + y(i)+y(im1)+1)) ... 
/ (4*exp(4*g)-4);

Pi_im1_pm = 0.5*(y(i) + 1 - 2*Pi_im1_pp);
Pi_im1_mp = 0.5*(y(im1) + 1 - 2*Pi_im1_pp);
Pi_im1_mm = 0.5*(-y(i) - y(im1) + 2*Pi_im1_pp);

% Two spin product expectation value
r_i_im1 = Pi_im1_pp - Pi_im1_pm - Pi_im1_mp  + Pi_im1_mm;

end

%% Calculate r using infinite chain two-spin product expectation value
% Q = y(i);
% if i == 1 % For end spin
%   r_i_ip1 = 1 + (2-2*sqrt(Q^2 - (Q^2 - 1)*exp(4*g)))/(exp(4*g)-1);
% elseif i == N % For end spin
%   r_i_im1 = 1 + (2-2*sqrt(Q^2 - (Q^2 - 1)*exp(4*g)))/(exp(4*g)-1);
% else % For inner spins
%   r_i_im1 = 1 + (2-2*sqrt(Q^2 - (Q^2 - 1)*exp(4*g)))/(exp(4*g)-1);
%   r_i_ip1 = r_i_im1;
% end

%% Differential change in single spin expectation value with time
if i == 1 % For end spin
  dy(i) = -a*(y(i) - beta - ...
    gamma*(y(ip1)) + ...
    gamma*beta*(r_i_ip1));
elseif i == N % For end spin
  dy(i) = -a*(y(i) - beta - ...
    gamma*(y(im1)) + ...
    gamma*beta*(r_i_im1));
else % For inner spins
  dy(i) = -a*(y(i) - beta - ...
    0.5*gamma*(y(im1) + y(ip1)) + ...
    0.5*gamma*beta*(r_i_im1 + r_i_ip1));
end

% Continue looping i from 1 to N
end

% End of file
Appendix B

Computer Model Code for One-Dimensional Ferrimagnetic Lattice with Nearest Neighbor Interactions

The equations describing the behavior of the finite and infinite length one-dimensional ferrimagnetic Ising chains with nearest neighbor interactions are detailed in Chapter 3. This appendix contains the computer model code that was used to implement those equations, and post-process the associated results. The computer language used is MATLAB version 7.7.0.471 (R2008b), a product of The MathWorks, Inc. Three separate codes are provided for the finite length chain, as well as for the infinite length chain. For each chain type, one of the three codes calculates the response to an AC applied field (with or without a superposed DC field), one calculates the response to a DC applied field only, and the third code calculates the differential change in single-spin expectation values.
B.1 Infinite_Local_EQ_AC.m

% Infinite_Local_EQ_AC.m
% Implementation of local equilibrium approximation for one-dimensional
% ferrimagnetic infinite chain with nearest neighbor interactions.
% AC response post-processing.
% Ryan Kristensen
% 2 July 2009

% Initialize and clear workspace
close all
clear all
clc

%% Physical Constants
% Permeability of free space (H/m or T*m / A)
mu_0 = 4*pi*(10^(-7));

% Bohr magneton unit magnetic moment (A*m^2 or J/T)
mu_B = 9.274e-24;

% Boltzmann's constant (J/degK)
k_B = 1.3807e-23;

%% Principal Inputs
% Temperature (K)
Temp = [7 15];

% Nearest neighbor coupling energy (eV)
% Note: 40K = 0.0034eV, 80K = 0.0069eV, 100K=0.0086,
% 220K = 0.019eV, 400K = 0.0345eV
J_eV = -0.00374
% J_eV = -0.00374 (43.3945K) with tau_0 = 3.5e-11 and a = 1/2tau_0
% for infinite chain (2004 Bogani, pure)

% Applied magnetic field (Oe)
% DC
H_DC_Oe = 0;
% AC
H_AC_Oe = 35000;

% Time duration to simulate (sec)
tmax = 1.5*(1/0.005);
% Frequency (Hz)
f = 0.005;

% Initial condition
Qo_i = 0;
Qe_i = 0;
Qi = [Qo_i; Qe_i];

%% Time Scale Parameter Definition
% Exponential prefactor (sec)
tau_0 = 3.5e-11;
% 3.5e-11 from 2004 Bogani (pure, ~2000 spins per chain)
% 1e-12 from 2004 Bogani (c = 0.047, ~20 spins per chain)
% Time scale parameter
a = 1/(2*tau_0) % (1/sec)  a = 1/(2*tau_0) per 2002 Caneschi

%% Coupling Energy Conversions and Definitions
% Convert nearest neighbor coupling energy from eV to Joules
J_J = J_eV*(1.602e-19);

% Local equilibrium g parameter (J / k T)
g = (J_J)./(k_B*Temp)
% g = [0.1 1] % For comparison with Section 2

% Glauber gamma parameter
gamma = tanh(2*g)

%% Magnetic Moment Conversions and Definitions
% Odd Site Spin
% Lande g-factor for spin
g_spin_o = 2*cos(54.74*pi/180);
% Spin value of spin
m_s_spin_o = 0.5;
% Magnetic moment of spin (Bohr magnetons)
mu_spin_o = g_spin_o*m_s_spin_o;
% Magnetic moment of spin (A*m^2 or J/T)
mu_eff_spin_o = mu_spin_o*mu_B;

% Even Site Spin
% Lande g-factor for spin
g_spin_e = 9*cos(54.74*pi/180);
% Spin value of spin
m_s_spin_e = 0.5;
% Magnetic moment of spin (Bohr magnetons)
mu_spin_e = g_spin_e*m_s_spin_e;
% Magnetic moment of spin (A*m^2 or J/T)
mu_eff_spin_e = mu_spin_e*mu_B;
Convert applied DC field from Oe to A/m

\[ H_{DC} = H_{DC\_Oe} \times \frac{1000}{4\pi}; \]

Convert applied AC field from Oe to A/m

\[ H_{AC} = H_{AC\_Oe} \times \frac{1000}{4\pi}; \]

Odd Site
Local equilibrium b parameter (\( \mu B / k T \))

\[ b_{o\_max\_AC} = \frac{(\mu_{eff\_spin\_o} \times \mu_0 \times H_{AC})}{(k_B \times Temp)} \]

\[ b_{o\_DC} = \frac{(\mu_{eff\_spin\_o} \times \mu_0 \times H_{DC})}{(k_B \times Temp)}; \]

\% b_{o\_max\_AC} = 3 \% For comparison with Section 2
\% b_{o\_DC} = 0 \% For comparison with Section 2

Even Site
Local equilibrium b parameter (\( \mu B / k T \))

\[ b_{e\_max\_AC} = \frac{(\mu_{eff\_spin\_e} \times \mu_0 \times H_{AC})}{(k_B \times Temp)} \]

\[ b_{e\_DC} = \frac{(\mu_{eff\_spin\_e} \times \mu_0 \times H_{DC})}{(k_B \times Temp)}; \]

\% b_{e\_max\_AC} = 3 \% For comparison with Section 2
\% b_{e\_DC} = 0 \% For comparison with Section 2

Solution of Differential Equation

ODE15s is a variable order, multi-step, solver based on the numerical differentiation formulas and is appropriate for stiff problems

Solver options

\[ \text{options} = \text{odeset}(\text{'InitialStep'}, 1e-6, \text{'MaxStep'}, 1/(10*f), ...) \]

\% Base
\% tic
\% [T\_sol, Q\_sol] = ode15s( @(t,Q) Infinite\_Local\_EQ\_dQ(t,Q,...
\% a,g,gamma,b\_o\_max\_AC,b\_o\_DC,b\_e\_max\_AC,b\_e\_DC,f),...
\% [0 tmax],Qi,options);
\% toc

\% For dual temperature evaluation
\% tic
\% [T\_sol\_T1, Q\_sol\_T1] = ode15s( @(t,Q) Infinite\_Local\_EQ\_dQ(t,Q,...
\% a,g(1),gamma(1),b\_o\_max\_AC(1),b\_o\_DC(1),b\_e\_max\_AC(1),b\_e\_DC(1),f),...
\% [0 tmax],Qi,options);
\% toc

\% For comparison with Section 2
\% tic
\% [T\_sol\_g01, Q\_sol\_g01] = ode15s( @(t,Q) Infinite\_Local\_EQ\_dQ(t,Q,...
\% a,g(1),gamma(1),b\_o\_max\_AC,b\_o\_DC,b\_e\_max\_AC,b\_e\_DC,f),...
% [0 tmax],Qi,options);
% % For comparison with Section 2
% [T_sol_g1,Q_sol_g1] = ode15s(@(t,Q) Infinite_Local_EQ_dQ(t,Q,...
% a,g(2),gamma(2),b_o_max_AC,b_o_DC,b_e_max_AC,b_e_DC,f),...
% [0 tmax],Qi,options);

%% Post-Processing Solution

% Base
% Qo_sol = Q_sol(:,1);
% Qe_sol = Q_sol(:,2);

% For dual temperature evaluation
Qo_sol_T1 = Q_sol_T1(:,1);
Qe_sol_T1 = Q_sol_T1(:,2);
Qo_sol_T2 = Q_sol_T2(:,1);
Qe_sol_T2 = Q_sol_T2(:,2);

% 7K: Plot odd and even site average
% single spin expectation values vs. time
figure
plot(T_sol_T1,Qo_sol_T1,'k:','linewidth',2)
hold on
plot(T_sol_T1,Qe_sol_T1,'k','linewidth',2)
plot(T_sol_T1,H_AC*sin(2*pi*f*T_sol_T1)/H_AC,'b-.','linewidth',2)
grid on
title('Average Spin Expectation Value vs. Time at T = 7K')
ylim([-1.1 1.1])
ylabel('Average Spin Expectation Value')
legend('Odd Sites','Even Sites','Normalized Applied Magnetic Field')
xlabel('Time (s)')

% 15K: Plot odd and even site average
% single spin expectation values vs. time
figure
plot(T_sol_T2,Qo_sol_T2,'k:','linewidth',2)
hold on
plot(T_sol_T2,Qe_sol_T2,'k','linewidth',2)
plot(T_sol_T2,H_AC*sin(2*pi*f*T_sol_T2)/H_AC,'b-.','linewidth',2)
grid on
title('Average Spin Expectation Value vs. Time at T = 15K')
ylim([-1.1 1.1])
ylabel('Average Spin Expectation Value')
legend('Odd Sites','Even Sites','Normalized Applied Magnetic Field')
xlabel('Time (s)')

% % Calculate magnetization per formula unit vs. time
% m_fu = mu_spin_o*Qo_sol + mu_spin_e*Qe_sol;
% % Plot magnetization per formula unit
% % figure
% % plot(T_sol,m_fu,'k','linewidth',2)
% % grid on
% % title('Magnetization vs. Time')
% % ylim([-2.1 2.1])
% % ylabel('Magnetization ((\mu)_B per formula unit)')
% % xlim([0 tmax])
% % xlabde('Time (s)')

% Magnetization per formula unit
m_fu_T1 = mu_spin_o*Qo_sol_T1 + mu_spin_e*Qe_sol_T1;

m_fu_T2 = mu_spin_o*Qo_sol_T2 + mu_spin_e*Qe_sol_T2;

% Point picked data from 2004 Rolland
m_fu_7K_data = [-0.1 0; 0 0.72; 0.1 0.33 .98; 0.5 1.61; 1 1.69; ... 
                  1.5 1.77; 2 1.85; 2.5 1.93; 3 2.006];

m_fu_15K_data = [0 0; 0.25 0.89; 0.5 1.07; 1 1.43; 1.5 1.65; 2 1.88; ... 
                  2.5 1.97; 3 2.006];

% Plot magnetization per formula unit vs. applied magnetic field
figure
plot(H_AC*sin(2*pi*f*T_sol_T1)*mu_0,m_fu_T1,'b','linewidth',2)
hold on
plot(m_fu_7K_data(:,1),m_fu_7K_data(:,2),'ws','... 
     'markeredgecolor','k','markerfacecolor','b','markersize',5)
plot(H_AC*sin(2*pi*f*T_sol_T2)*mu_0,m_fu_T2,'r','linewidth',2)
plot(m_fu_15K_data(:,1),m_fu_15K_data(:,2),'wo','... 
     'markeredgecolor','k','markerfacecolor','r','markersize',5)

% Plot symmetric data on other side of hysteresis loop
plot(-m_fu_7K_data(:,1),-m_fu_7K_data(:,2),'ws','... 
     'markeredgecolor','k','markerfacecolor','b','markersize',5)
plot(-m_fu_15K_data(:,1),-m_fu_15K_data(:,2),'wo','... 
     'markeredgecolor','k','markerfacecolor','r','markersize',5)
grid on
title('Magnetization vs. Applied Magnetic Field')
ylim([-2.1 2.1])
ylabel('Magnetization ((\mu)_B per formula unit)')
xlabel('Applied Magnetic Field, \mu_0H (T)')
xlim([-3.5 3.5])
legend('7K Calculation','7K Data','15K Calculation','15K Data','... 
       'location','southeast')

%% Section 2 Comparison: Plot magnetization with equilibrium solution

% g = 0.1
% Qo_sol_g01 = Q_sol_g01(:,1);
% Qe_sol_g01 = Q_sol_g01(:,2);
% Q_sol_g01 = 0.5*(Qo_sol_g01 + Qo_sol_g01);
% 
% g = 1
% Qo_sol_g1 = Q_sol_g1(:,1);
% Qe_sol_g1 = Q_sol_g1(:,2);
% Q_sol_g1 = 0.5*(Qo_sol_g1 + Qo_sol_g1);
% Load solution data
% load infinite_spin_sol.mat

% figure
% plot(b_o_DC + b_o_max_AC*sin(2*pi*f*T_sol_g01),Q_sol_g01,'k','linewidth',2)
% hold on
% plot(mu_B_k_T_inf,M_01_inf,'k:','linewidth',3)
% plot(b_o_DC + b_o_max_AC*sin(2*pi*f*T_sol_g1),Q_sol_g1,'r','linewidth',2)
% plot(mu_B_k_T_inf,M_1_inf,'r:','linewidth',3)
% grid on
% title('Magnetization vs. Applied Magnetic Field')
% ylim([-1.1 1.1])
% xlabel('Applied Magnetic Field (\(\mu\)B / k_{B}T)')
% ylabel('Magnetization per Spin (a.u. -1 to +1)')
% xlim([-3 3])
% text(-1.1,0.65,'J / k_{B}T = 1','backgroundcolor',[1 1 1])
% text(1,0.65,'J / k_{B}T = 0.1','backgroundcolor',[1 1 1])

% End of file
B.2 Infinite_Local_EQ_DC.m

% Infinite_Local_EQ_DC.m
% Implementation of local equilibrium approximation for one-dimensional
% ferrimagnetic infinite chain with nearest neighbor interactions.
% DC response post-processing.
% Ryan Kristensen
% 2 July 2009

% Initialize and clear workspace
close all
clear all
clc

%% Physical Constants

% Permeability of free space (H/m or T*m / A)
mu_0 = 4*pi*(10^(-7));

% Bohr magneton unit magnetic moment (A*m^2 or J/T)
mu_B = 9.274e-24;

% Boltzmann's constant (J/degK)
k_B = 1.3807e-23;

%% Principal Inputs

% Temperature (K)
Temp = [5 6 7];

% Nearest neighbor coupling energy (eV)
% Note: 40K = 0.0034eV, 80K = 0.0069eV, 100K=0.0086,
% 220K = 0.019eV, 400K = 0.0345eV
J_eV = -0.00374
% J_eV = -0.00374 (43.3945K) with tau_0 = 3.5e-11 and a = 1/2tau_0
% for infinite chain (2004 Bogani, pure)

% Applied magnetic field (Oe)
% DC
H_DC_Oe = 0;
% AC
H_AC_Oe = 0;

% Time duration to simulate (sec)
tmax = 1e4;
% Frequency (Hz)
f = 0;

% Initial condition
Qo_i = -1;
Qe_i = 1;
Qi = [Qo_i; Qe_i];

%% Time Scale Parameter Definition
% Exponential prefactor (sec)
tau_0 = 3.5e-11;
% 3.5e-11 from 2004 Bogani (pure, ~2000 spins per chain)
% 1e-12 from 2004 Bogani (c = 0.047, ~20 spins per chain)
% Time scale parameter
a = 1/(2*tau_0) % (1/sec) a=1/(2*tau_0) per 2002 Caneschi

%% Coupling Energy Conversions and Definitions
% Convert nearest neighbor coupling energy from eV to Joules
J_J = J_eV*(1.602e-19);
% Local equilibrium g parameter (J / k T)
g = (J_J)./(k_B*Temp)
% Glauber gamma parameter
gamma = tanh(2*g);

%% Magnetic Moment Conversions and Definitions
% Odd Site Spin
% Lande g-factor for spin
g_spin_o = 2*cos(54.74*pi/180);
% Spin value of spin
m_s_spin_o = 0.5;
% Magnetic moment of spin (Bohr magnetons)
mu_spin_o = g_spin_o*m_s_spin_o;
% Magnetic moment of spin (A*m^2 or J/T)
mu_eff_spin_o = mu_spin_o*mu_B;

% Even Site Spin
% Lande g-factor for spin
g_spin_e = 9*cos(54.74*pi/180);
% Spin value of spin
m_s_spin_e = 0.5;
% Magnetic moment of spin (Bohr magnetons)
mu_spin_e = g_spin_e*m_s_spin_e;
% Magnetic moment of spin (A*m^2 or J/T)
mu_eff_spin_e = mu_spin_e*mu_B;
% Convert applied DC field from Oe to A/m
H_DC = H_DC_Oe*1000/(4*pi);

% Convert applied AC field from Oe to A/m
H_AC = H_AC_Oe*1000/(4*pi);

% Odd Site
% Local equilibrium b parameter (mu B / k T)
b_o_max_AC = (mu_eff_spin_o*mu_0*H_AC)./(k_B*Temp)
b_o_DC = (mu_eff_spin_o*mu_0*H_DC)./(k_B*Temp);

% Even Site
% Local equilibrium b parameter (mu B / k T)
b_e_max_AC = (mu_eff_spin_e*mu_0*H_AC)./(k_B*Temp)
b_e_DC = (mu_eff_spin_e*mu_0*H_DC)./(k_B*Temp);

%% Solution of Differential Equation

% ODE15s is a variable order, multi-step, solver based on the numerical
% differentiation formulas and is appropriate for stiff problems

% Solver options
options = odeset('InitialStep',1e-6,'AbsTol',2.23e-7,'RelTol',2.23e-7);
tic
[T_sol_T1,Q_sol_T1] = ode15s(@(t,Q) Infinite_Local_EQ_dQ(t,Q,...
a,g(1),gamma(1),b_o_max_AC(1),b_o_DC(1),b_e_max_AC(1),b_e_DC(1),f),...
[0 tmax],Qi,options);
toc
tic
[T_sol_T2,Q_sol_T2] = ode15s(@(t,Q) Infinite_Local_EQ_dQ(t,Q,...
a,g(2),gamma(2),b_o_max_AC(2),b_o_DC(2),b_e_max_AC(2),b_e_DC(2),f),...
[0 tmax],Qi,options);
toc
tic
[T_sol_T3,Q_sol_T3] = ode15s(@(t,Q) Infinite_Local_EQ_dQ(t,Q,...
a,g(3),gamma(3),b_o_max_AC(3),b_o_DC(3),b_e_max_AC(3),b_e_DC(3),f),...
[0 tmax],Qi,options);
toc

%% Post-Processing Solution

Qo_sol_T1 = [Q_sol_T1(:,1)];
Qe_sol_T1 = [Q_sol_T1(:,2)];

Qo_sol_T2 = [Q_sol_T2(:,1)];
Qe_sol_T2 = [Q_sol_T2(:,2)];

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Qo_sol_T3 = Q_sol_T3(:,1);
Qe_sol_T3 = Q_sol_T3(:,2);

% Plot odd and even site average single spin expectation values vs. time
figure
semilogx(T_sol_T1,Qo_sol_T1,'b:','linewidth',3)
hold on
semilogx(T_sol_T1,Qe_sol_T1,'b','linewidth',2)
semilogx(T_sol_T2,Qo_sol_T2,'g:','linewidth',3)
semilogx(T_sol_T2,Qe_sol_T2,'g','linewidth',2)
semilogx(T_sol_T3,Qo_sol_T3,'r:','linewidth',3)
semilogx(T_sol_T3,Qe_sol_T3,'r','linewidth',2)
grid on
title('Average Spin Expectation Value vs. Time')
ylim([-1.1 1.1])
ylabel('Average Spin Expectation Value')
%legend('Odd Sites','Even Sites')
xlim([5e-1 1e4])
xlabel('Time (s)')

% Calculate magnetization per formula unit vs. time
m_fu_T1 = mu_spin_o*Qo_sol_T1 + mu_spin_e*Qe_sol_T1;
m_fu_T2 = mu_spin_o*Qo_sol_T2 + mu_spin_e*Qe_sol_T2;
m_fu_T3 = mu_spin_o*Qo_sol_T3 + mu_spin_e*Qe_sol_T3;

% Calculate normalized magnetization per formula unit vs. time
m_fu_max = (mu_spin_e - mu_spin_o);
m_fu_T1_norm = m_fu_T1/m_fu_max;
m_fu_T2_norm = m_fu_T2/m_fu_max;
m_fu_T3_norm = m_fu_T3/m_fu_max;

% Plot normalized magnetization per formula unit
figure
semilogx(T_sol_T1,m_fu_T1_norm,'b','linewidth',2)
hold on
semilogx(T_sol_T2,m_fu_T2_norm,'g','linewidth',2)
semilogx(T_sol_T3,m_fu_T3_norm,'r','linewidth',2)
grid on
title('Normalized Magnetization vs. Time')
ylim([-0.1 1.1])
ylabel('Normalized Magnetization')
%legend('Odd Sites','Even Sites')
xlabel('Time (s)')

% Rolland data
Roland_2004_5K = [1e4 0.82; 0.5 1; 100 0.98];
plot(Roland_2004_5K(:,1),Roland_2004_5K(:,2), 'wo',
    'markeredgecolor','k','markerfacecolor','b','markersize',7)
Roland_2004_6K = [1e4 0.05; 2000 0.05; 0.5 0.99; 100 0.57];
plot(Roland_2004_6K(:,1),Roland_2004_6K(:,2), 'wo',
    'markeredgecolor','k','markerfacecolor','b','markersize',7)
Roland_2004_7K = [1e4 0; 0.5 0.72; 100 0; 20 0.2; 2 0.3];
plot(Roland_2004_7K(:,1),Roland_2004_7K(:,2), 'wo',
    'markeredgecolor','k','markerfacecolor','b','markersize',7)
grid on
title('Normalized Magnetization vs. Time')
ylim([-0.1 1.1])
ylabel('Normalized Magnetization')
%legend('Odd Sites','Even Sites')
xlabel('Time (s)')
```matlab
xlim([5e-1 1e4])
xlabel('Time (s)')
text(1e3,0.9,'T = 5K','backgroundcolor',[1 1 1])
text(30,0.5,'T = 6K','backgroundcolor',[1 1 1])
text(1,0.2,'T = 7K','backgroundcolor',[1 1 1])

% legend('5K','6K','7K','location','southeast')

% End of file
function dQ = Infinite_Local_EQ_dQ(t,Q,a,g,gamma,b_o_max_AC,b_o_DC,...
        b_e_max_AC,b_e_DC,f)

  \% Infinite_Local_EQ_dQ.m
  \% Function calculating differential change in average single spin
  \% expectation values (dQ(1) and dQ(2)) for for odd and even sites
  \% respectively of one-dimensional ferrimagnetic infinite
  \% chain with nearest neighbor interactions
  \%
  \% Inputs: t is the value of time (s)
  \%         Q(1) is the average single spin expectation value
  \%              for odd sites
  \%         Q(2) is the average single spin expectation value
  \%              for even sites
  \%         a is alpha (1/s)
  \%         g is J / k T
  \%         gamma is tanh(2g)
  \%         b_o_max_AC is the AC zero to peak amplitude of \mu B / k T
  \%              for odd sites
  \%         b_o_DC is DC amplitude of \mu B / k T for odd sites
  \%         b_e_max_AC is the AC zero to peak amplitude of \mu B / k T
  \%              for even sites
  \%         b_e_DC is DC amplitude of \mu B / k T for even sites
  \%         f is the frequency of the applied field (Hz)
  \%
  \% Ryan Kristensen
  \% 2 July 2009

  \% Separate 2-element input Q into separate variables for odd and
  \% even site average single spin expectation values
  Qo = Q(1);
  Qe = Q(2);

  \% Screen out invalid values of Q that ODE solver stepping investigates
  \% (otherwise, complex results can be returned)
  if Qo > 1
      Qo = 1;
  elseif Qo < -1
      Qo = -1;
  end
  if Qe > 1
      Qe = 1;
  elseif Qe < -1
      Qe = -1;
  end

  \% Glauber beta parameter
if \( f == 0 \)
    \[
    \beta_o = \tanh(b_o_{DC});
    \beta_e = \tanh(b_e_{DC});
    \]
else
    \[
    b_o = b_o_{DC} + b_o_{max}_{AC}\sin(2\pi f t);
    \beta_o = \tanh(b_o);
    b_e = b_e_{DC} + b_e_{max}_{AC}\sin(2\pi f t);
    \beta_e = \tanh(b_e);
    \]
end

% Two-spin probabilities
% Note: Poe_pp is simplified form of solution presented in Chapter 3
\[
\theta = Q_o + Q_e;
\]
\[
G = \exp(4g);
\]
Poe_pp = \[
\frac{(\exp(4g)*(2+Qo+Qe) - Qo - Qe - \ldots
\quad \sqrt{G^2\theta^2 + \theta^2 - 2G\theta^2 - 4G^2QoQe + \ldots
\quad 4GQoQe + 4G}}}{(4G-4)};
\]
Poe_pm = 0.5*(Qo + 1 - 2*Poe_pp);
Poe_mp = 0.5*(Qe + 1 - 2*Poe_pp);
Poe_mm = 0.5*(-Qo - Qe + 2*Poe_pp);

% Average two-spin product expectation value
\[
Roe = Poe_pp - Poe_pm - Poe_mp + Poe_mm;
\]

% Differential change in Qo with time
\[
dQo = -a*(Qo - \beta_o - gamma*Qe + gamma*\beta_o*Roe);
\]

% Differential change in Qe with time
\[
dQe = -a*(Qe - \beta_e - gamma*Qo + gamma*\beta_e*Roe);
\]

% Define 2 element output variable dQ
\[
dQ = [dQo; dQe];
\]

% End of file
% Finite_Local_EQ_AC.m
%
% Implementation of local equilibrium approximation for one-dimensional
% ferrimagnetic finite chain with nearest neighbor interactions.
%
% AC response post-processing.
%
% Ryan Kristensen
% 2 July 2009

% Initialize and clear workspace
close all
clear all
clc

%% Physical Constants
% Permeability of free space (H/m or T*m / A)
u0 = 4*pi*(10^(-7));

% Bohr magneton unit magnetic moment (SI) (A*m^2 or J/T)
u_B = 9.274e-24;

% Bohr magneton unit magnetic moment (CGS) (emu)
u_B_cgs = 9.274e-21;

% Boltzmann's constant (J/degK)
k_B = 1.3807e-23;

% Avogadro's Number (#/mol)
N_A = 6.02e23;

%% Principal Inputs
% Number of spins
N = 2000;

% Temperature (K)
Temp = 10;
% Temp = [5 6 7]; % For comparison with Section 2

% Nearest neighbor coupling energy (eV)
% Note: 40K = 0.0034eV, 65K = 0.0056eV, 80K = 0.0069eV,
% 100K=0.0086, 220K = 0.019eV, 400K = 0.0345eV
J_eV = -0.0056
% J_eV = -0.00374 (43.3945K) with tau_0 = 3.5e-11 and a = 1/2tau_0
% for infinite chain (2004 Bogani, pure)
% Applied magnetic field (Oe)
% DC
H_DC_Oe = 2000;
% AC
H_AC_Oe = 10;

% Time duration to simulate (sec)
tmax = 40*(1/2700);

% Frequency (Hz)
f = 2700;

% Initial condition
Qo_i = 0; % Odd sites initial orientation
Qe_i = 0; % Even sites initial orientation
qi = zeros(1,N); % Initialize initial condition vector
for i = 1:N
    if i/2 ~= floor(i/2) % For odd spins
        qi(i) = Qo_i;
    else % For even spins
        qi(i) = Qe_i;
    end
end

% Time Scale Parameter Definition
% Exponential prefactor (sec)
tau_0 = 3.5e-11;
% 3.5e-11 from 2004 Bogani (pure, ~2000 spins per chain)
% 1e-12 from 2004 Bogani (c = 0.047, ~20 spins per chain)

% Time scale parameter
a = 1/(2*tau_0) % (1/sec) a=1/(2*tau_0) per 2002 Caneschi
% a = 1000 % For comparison with Section 2

% Coupling Energy Conversions and Definitions
% Convert nearest neighbor coupling energy from eV to Joules
J_J = J_eV*(1.602e-19);

% Local equilibrium g parameter (J / k T)
g = (J_J)./(k_B*Temp)
% g = [0.1 1] % For comparison with Section 2

% Glauber gamma parameter (inner spins)
gamma = tanh(2*g);
% Glauber gamma parameter (end spins)
gamma1 = tanh(g);

% Magnetic Moment Conversions and Definitions
% Odd Site Spin
% Lande g-factor for spin
\( g_{spin\_o} = 2 \times \cos(54.74\times\pi/180); \)
% Spin value of spin
\( m_s_{spin\_o} = 0.5; \)
% Magnetic moment of spin (Bohr magnetons)
\( \mu_{spin\_o} = g_{spin\_o} \times m_s_{spin\_o}; \)
% Magnetic moment of spin (A*m^2 or J/T)
\( \mu_{eff\_spin\_o} = \mu_{spin\_o} \times \mu_B; \)

% Even Site Spin
% Lande g-factor for spin
\( g_{spin\_e} = 9 \times \cos(54.74\times\pi/180); \)
% Spin value of spin
\( m_s_{spin\_e} = 0.5; \)
% Magnetic moment of spin (Bohr magnetons)
\( \mu_{spin\_e} = g_{spin\_e} \times m_s_{spin\_e}; \)
% Magnetic moment of spin (A*m^2 or J/T)
\( \mu_{eff\_spin\_e} = \mu_{spin\_e} \times \mu_B; \)

% Convert applied DC field from Oe to A/m
\( H_{DC} = H_{DC\_Oe} \times 1000/(4\pi); \)
% Convert applied AC field from Oe to A/m
\( H_{AC} = H_{AC\_Oe} \times 1000/(4\pi); \)

% Odd Site
% Local equilibrium b parameter (mu B / k T)
\( b_{o\_max\_AC} = (\mu_{eff\_spin\_o} \times \mu_0 \times H_{AC})/(k_B \times Temp); \)
\( b_{o\_DC} = (\mu_{eff\_spin\_o} \times \mu_0 \times H_{DC})/(k_B \times Temp); \)
% b_{o\_max\_AC} = 3 % For comparison with Section 2
% b_{o\_DC} = 0 % For comparison with Section 2

% Even Site
% Local equilibrium b parameter (mu B / k T)
\( b_{e\_max\_AC} = (\mu_{eff\_spin\_e} \times \mu_0 \times H_{AC})/(k_B \times Temp); \)
\( b_{e\_DC} = (\mu_{eff\_spin\_e} \times \mu_0 \times H_{DC})/(k_B \times Temp); \)
% b_{e\_max\_AC} = 3 % For comparison with Section 2
% b_{e\_DC} = 0 % For comparison with Section 2

%% Solution of Differential Equation

% ODE15s is a variable order, multi-step, solver based on the numerical
% differentiation formulas and is appropriate for stiff problems

% Solver options
options = odeset('InitialStep',1e-6,'MaxStep',1/(30*f),...
'AbsTol',2.23e-11,'RelTol',2.23e-11);

% Base
tic
[T_sol,Y_sol] = ode15s(@(t,y) Finite_Local_EQ_dy(t,y,...
a,g,gamma,gamma1,b_o_max_AC,b_o_DC,b_e_max_AC,b_e_DC,f,N),...
[0 tmax],qi,options);
toc

% For comparison with Section 2
[T_sol_g01,Y_sol_g01] = ode15s(@(t,y) Finite_Local_EQ_dy(t,y,...
    a,g(1),gamma(1),gamma1(1),b_o_max_AC,b_o_DC,...
    b_e_max_AC,b_e_DC,f,N),[0 tmax],qi,options);
%
% For comparison with Section 2
[T_sol_g1,Y_sol_g1] = ode15s(@(t,y) Finite_Local_EQ_dy(t,y,...
    a,g(2),gamma(2),gamma1(2),b_o_max_AC,b_o_DC,...
    b_e_max_AC,b_e_DC,f,N),[0 tmax],qi,options);

% Transpose solution vectors
q = Y_sol';

% For comparison with Section 2
q_g01 = Y_sol_g01';
q_g1 = Y_sol_g1';

%% Post-Processing Solution

% Compensate for different moments on odd/even sites
spin_multipliers = zeros(1,N);
for ss = 1:N
    if ss/2 ~= floor(ss/2) % For odd sites
        spin_multipliers(ss) = mu_spin_o;
    else
        spin_multipliers(ss) = mu_spin_e;
    end
end

% Calculate magnetization per spin (m) and per formula unit (m_fu)
m = zeros(N,length(T_sol)); % Initialize vector
m_fu = zeros(length(T_sol),1); % Initialize vector
for ti = 1:length(T_sol)
    m(:,ti) = spin_multipliers'.*q(:,ti);
    m_fu(ti) = 2*sum(m(:,ti))/N;
end

% Calculate normalized magnetization per formula unit vs. time
m_fu_max = (mu_spin_e - mu_spin_o);
m_fu_norm = m_fu/m_fu_max;

% Plot magnetization per formula unit over last half of time record
t_half_i = floor(length(T_sol)/2);
figure
plot(T_sol(t_half_i:length(T_sol)),...
m_fu(t_half_i:length(T_sol)) -
mean(m_fu(t_half_i:length(T_sol)));
    % 'k', 'linewidth', 2)
hold on
plot(T_sol(t_half_i:length(T_sol)),
    0.001*sin(2*pi*f*T_sol(t_half_i:length(T_sol)));
    'b')
grid on
title('Magnetization vs. Time')

% ylim([-2.1 2.1])
ylabel('Magnetization ((\mu)_B per formula unit)')
% xlim([0 tmax])
xlabel('Time (s)')

% Plot magnetization per formula unit vs. applied magnetic field
figure
plot(H_AC*sin(2*pi*f*T_sol)*mu_0,m_fu)
grid on
title('Magnetization vs. Applied Magnetic Field')
% ylim([-2.1 2.1])
ylabel('Magnetization ((\mu)_B per formula unit)')
% xlim([5e-1 1e4])
xlabel('Applied Magnetic Field, (\mu)_0H (T)')

% Calculate susceptibility from magnetization
% Note: emu/(mol Oe) = emu/mol

% Convert magnetization to emu/mol
m_emu_mol = m_fu*N_A*mu_B_cgs;
% Calculate mean magnetization over last half of time record
mean_m = mean(m_emu_mol(t_half_i:length(T_sol)));  

% In-phase AC susceptibility
m_in_ph = (2/(max(T_sol) - T_sol(t_half_i)))*...
    trapz(T_sol(t_half_i:length(T_sol)),
        (m_emu_mol(t_half_i:length(T_sol)) - mean_m).*...
        sin(2*pi*f*T_sol(t_half_i:length(T_sol))));
Chi_in_ph = m_in_ph/H_AC_Oe

% Out-of-phase AC susceptibility
m_out_ph = (2/(max(T_sol) - T_sol(t_half_i)))*...
    trapz(T_sol(t_half_i:length(T_sol)),
        (m_emu_mol(t_half_i:length(T_sol)) - mean_m).*...
        cos(2*pi*f*T_sol(t_half_i:length(T_sol))));
Chi_out_ph = -m_out_ph/H_AC_Oe % Reverse sign for display purposes

% Qo_sol = Q_sol(:,1);
% Qe_sol = Q_sol(:,2);
% % % Plot odd and even site average single spin
% % % expectation values vs. time
% % figure
% % Calculate magnetization per formula unit vs. time
% % m_fu = mu_spin_o*Qo_sol + mu_spin_e*Qe_sol;
% % Plot magnetization per formula unit
% % figure
% % semilogx(T_sol,m_fu,'r','linewidth',2)
% % grid on
% % ylim([-0.1 2])
% % ylabel('Magnetization (\mu_B per formula unit)')
% % xlim([5e-1 1e4])
% % xlabel('Time (s)')
%
% Section 2 Comparison: Plot magnetization with equilibrium solution
%
% Calculate average magnetization at each time
% for ti = 1:length(T_sol_g01)
%     Q_sol_g01(ti) = sum(q_g01(:,ti))/N;
% end
% for ti = 1:length(T_sol_g1)
%     Q_sol_g1(ti) = sum(q_g1(:,ti))/N;
% end
%
% Load solution data
% load finite_spin_sol.mat
% figure
% plot(b_o_DC + b_o_max_AC*sin(2*pi*f*T_sol_g01),Q_sol_g01,'k','...'
%      'linewidth',2)
% hold on
% plot(mu_B_k_T_fin,M_01_fin,'k:','linewidth',3)
% plot(b_o_DC + b_o_max_AC*sin(2*pi*f*T_sol_g1),Q_sol_g1,'r',...'
%      'linewidth',2)
% plot(mu_B_k_T_fin,M_1_fin,'r:','linewidth',3)
% grid on
% title('Magnetization vs. Applied Magnetic Field')
% ylabel('Magnetization per Spin (a.u. -1 to +1)')
% ylim([-1.1 1.1])
% xlabel('Applied Magnetic Field (\mu_B / k_(B)T)')
% xlim([-3 3])
% text(-1.1,0.65,'J / k_(B)T = 1','backgroundcolor',[1 1 1])
% text(1,0.65,'J / k_(B)T = 0.1','backgroundcolor',[1 1 1])

% End of file
B.5 Finite_Local_EQ_DC.m

% Finite_Local_EQ_DC.m
% Implementation of local equilibrium approximation for one-dimensional
% ferrimagnetic finite chain with nearest neighbor interactions.
% DC response post-processing.
% Ryan Kristensen
% 2 July 2009

% Initialize and clear workspace
close all
clear all
clc

%% Physical Constants

% Permeability of free space (H/m or T*m / A)
mu_0 = 4*pi*(10^(-7));

% Bohr magneton unit magnetic moment (A*m^2 or J/T)
mu_B = 9.274e-24;

% Boltzmann's constant (J/degK)
k_B = 1.3807e-23;

%% Principal Inputs

% Number of spins
N = 2000;

% Temperature (K)
Temp = [5 6 7];

% Nearest neighbor coupling energy (eV)
% Note: 40K = 0.0034eV, 80K = 0.0069eV, 100K=0.0086,
% 220K = 0.019eV, 400K = 0.0345eV
J_eV = -0.00374
% J_eV = -0.00374 (43.3945K) with tau_0 = 3.5e-11 and a = 1/2tau_0
% for infinite chain (2004 Bogani, pure)

% Applied magnetic field (Oe)
% DC
H_DC_Oe = 0;
% AC
H_AC_Oe = 0;
% Time duration to simulate (sec)
tmax = 1e4;

% Frequency (Hz)
f = 0;

% Initial condition
Qo_i = -1; % Odd sites initial orientation
Qe_i = 1; % Even sites initial orientation
qi = zeros(1,N); % Initialize initial condition vector
for i = 1:N
    if i/2 ~= floor(i/2) % For odd spins
        qi(i) = Qo_i;
    else % For even spins
        qi(i) = Qe_i;
    end
end

%% Time Scale Parameter Definition

% Exponential prefactor (sec)
tau_0 = 3.5e-11;
% 3.5e-11 from 2004 Bogani (pure, ~2000 spins per chain)
% 1e-12 from 2004 Bogani (c = 0.047, ~20 spins per chain)

% Time scale parameter
a = 1/(2*tau_0) % (1/sec) a=1/(2*tau_0) per 2002 Caneschi

%% Coupling Energy Conversions and Definitions

% Convert nearest neighbor coupling energy from eV to Joules
J_J = J_eV*(1.602e-19);

% Local equilibrium g parameter (J / k T)
g = (J_J)./(k_B*Temp)

% Glauber gamma parameter (inner spins)
gamma = tanh(2*g);
% Glauber gamma parameter (end spins)
gammal = tanh(g);

%% Magnetic Moment Conversions and Definitions

% Odd Site Spin
% Lande g-factor for spin
g_spin_o = 2*cos(54.74*pi/180);
% Spin value of spin
m_s_spin_o = 0.5;
% Magnetic moment of spin (Bohr magnetons)
mu_spin_o = g_spin_o*m_s_spin_o;
% Magnetic moment of spin (A*m^2 or J/T)
mu_eff_spin_o = mu_spin_o*mu_B;

% Even Site Spin
% Lande g-factor for spin
g_spin_e = 9*cos(54.74*pi/180);
% Spin value of spin
m_s_spin_e = 0.5;
% Magnetic moment of spin (Bohr magnetons)
mu_spin_e = g_spin_e*m_s_spin_e;
% Magnetic moment of spin (A*m^2 or J/T)
mu_eff_spin_e = mu_spin_e*mu_B;

% Convert applied DC field from Oe to A/m
H_DC = H_DC_Oe*1000/(4*pi);
% Convert applied AC field from Oe to A/m
H_AC = H_AC_Oe*1000/(4*pi);

% Odd Site
% Local equilibrium b parameter (mu B / k T)
b_o_max_AC = (mu_eff_spin_o*mu_0*H_AC)./(k_B*Temp)
b_o_DC = (mu_eff_spin_o*mu_0*H_DC)./(k_B*Temp);

% Even Site
% Local equilibrium b parameter (mu B / k T)
b_e_max_AC = (mu_eff_spin_e*mu_0*H_AC)./(k_B*Temp)
b_e_DC = (mu_eff_spin_e*mu_0*H_DC)./(k_B*Temp);

%% Solution of Differential Equation

% ODE15s is a variable order, multi-step, solver based on the numerical
% differentiation formulas and is appropriate for stiff problems

% Solver options
options = odeset('InitialStep',1e-6,'AbsTol',1e-3,'RelTol',1e-3);

tic
[T_sol_T1,Y_sol_T1] = ode15s(@(t,y) Finite_Local_EQ_dy(t,y,...
a,g(1),gamma(1),gamma1(1),b_o_max_AC(1),b_o_DC(1),... b_e_max_AC(1),b_e_DC(1),f,N),[0 tmax],qi,options);
toc

tic
[T_sol_T2,Y_sol_T2] = ode15s(@(t,y) Finite_Local_EQ_dy(t,y,...
a,g(2),gamma(2),gamma1(2),b_o_max_AC(2),b_o_DC(2),... b_e_max_AC(2),b_e_DC(2),f,N),[0 tmax],qi,options);
toc

tic
[T_sol_T3,Y_sol_T3] = ode15s(@(t,y) Finite_Local_EQ_dy(t,y,...
a,g(3),gamma(3),gamma1(3),b_o_max_AC(3),b_o_DC(3),... b_e_max_AC(3),b_e_DC(3),f,N),[0 tmax],qi,options);
toc

% Transpose solution vectors
q_T1 = Y_sol_T1';
q_T2 = Y_sol_T2';
q_T3 = Y_sol_T3';

%% Post-Processing Solution

% Compensate for different moments on odd/even sites
spin_multipliers = zeros(1,N);
for ss = 1:N
    if ss/2 ~= floor(ss/2) % For odd sites
        spin_multipliers(ss) = mu_spin_o;
    else
        spin_multipliers(ss) = mu_spin_e;
    end
end

% Calculate magnetization per spin (m) and per formula unit (m_fu)
m_T1 = zeros(N,length(T_sol_T1));
m_fu_T1 = zeros(length(T_sol_T1),1);
for ti = 1:length(T_sol_T1)
    m_T1(:,ti) = spin_multipliers'.*q_T1(:,ti);
    m_fu_T1(ti) = 2*sum(m_T1(:,ti))/N;
end
m_T2 = zeros(N,length(T_sol_T2));
m_fu_T2 = zeros(length(T_sol_T2),1);
for ti = 1:length(T_sol_T2)
    m_T2(:,ti) = spin_multipliers'.*q_T2(:,ti);
    m_fu_T2(ti) = 2*sum(m_T2(:,ti))/N;
end
m_T3 = zeros(N,length(T_sol_T3));
m_fu_T3 = zeros(length(T_sol_T3),1);
for ti = 1:length(T_sol_T3)
    m_T3(:,ti) = spin_multipliers'.*q_T3(:,ti);
    m_fu_T3(ti) = 2*sum(m_T3(:,ti))/N;
end

% Calculate normalized magnetization per formula unit vs. time
m_fu_max = (mu_spin_e - mu_spin_o);
m_fu_T1_norm = m_fu_T1/m_fu_max;
m_fu_T2_norm = m_fu_T2/m_fu_max;
m_fu_T3_norm = m_fu_T3/m_fu_max;

% Plot normalized magnetization per formula unit
figure
semilogx(T_sol_T1,m_fu_T1_norm,'b','linewidth',2)
hold on
semilogx(T_sol_T2,m_fu_T2_norm,'g','linewidth',2)
semilogx(T_sol_T3,m_fu_T3_norm,'r','linewidth',2)
% Plot point picked data from 2004 Rolland
Rolland_2004_5K = [1e4 0.82; 0.5 1; 100 0.98];
plot(Rolland_2004_5K(:,1),Rolland_2004_5K(:,2), 'wo', ... 
    'markeredgecolor','k','markerfacecolor','b','markersize',7)
Rolland_2004_6K = [1e4 0.05; 2000 0.05; 0.5 0.99; 100 0.57];
plot(Rolland_2004_6K(:,1),Rolland_2004_6K(:,2), 'wo', ... 
    'markeredgecolor','k','markerfacecolor','g','markersize',7)
Rolland_2004_7K = [1e4 0; 0.5 0.72; 100 0; 20 0; 2 0.3];
plot(Rolland_2004_7K(:,1),Rolland_2004_7K(:,2), 'wo', ... 
    'markeredgecolor','k','markerfacecolor','r','markersize',7)
grid on
title('Normalized Magnetization vs. Time')
ylim([-0.1 1.1])
xlabel('Normalized Magnetization')% (μ_B per formula unit)
xlim([5e-1 1e4])
text(1e3,0.9,’T = 5K’,'backgroundcolor',[1 1 1])
text(30,0.5,’T = 6K’,'backgroundcolor',[1 1 1])
text(1,0.2,’T = 7K’,'backgroundcolor',[1 1 1])
legend('5K','6K','7K', 'location','southeast')

% End of file
function dy = Finite_Local_EQ_dy(t,y,a,g,gamma,gamma1,...
    b_o_max_AC,b_o_DC,b_e_max_AC,b_e_DC,f,N)

  % Finite_Local_EQ_dy.m
  % Function calculating differential change in individual single spin expectation value (dy) for one-dimensional ferrimagnetic finite chain with nearest neighbor interactions
  % Inputs: t is the value of time (s)
  % y is the vector of individual single spin expectation values
  % a is alpha (1/s)
  % g is J / k T
  % gamma is tanh(2g)
  % gamma1 is tanh(g)
  % b_o_max_AC is the AC zero to peak amplitude of mu B / k T for odd sites
  % b_o_DC is DC amplitude of mu B / k T for odd sites
  % b_e_max_AC is the AC zero to peak amplitude of mu B / k T for even sites
  % b_e_DC is DC amplitude of mu B / k T for even sites
  % f is the frequency of the applied field (Hz)
  % N is the number of spins in the finite chain
  %
  % Ryan Kristensen
  % 2 July 2009

  % Screen out invalid values of y that ODE solver stepping investigates (otherwise, complex results can be returned)
  for i = 1:length(y)
    if y(i) > 1
      y(i) = 1;
    end
    if y(i) < -1
      y(i) = -1;
    end
  end

  % Glauber beta parameter
  if f == 0
    beta_o = tanh(b_o_DC);
    beta_e = tanh(b_e_DC);
  else
    b_o = b_o_DC + b_o_max_AC*sin(2*pi*f*t);
    beta_o = tanh(b_o);
    b_e = b_e_DC + b_e_max_AC*sin(2*pi*f*t);
    beta_e = tanh(b_e);
  end
% Initialize dy vector
dy = zeros(N,1);

% Intermediate value used below
G = exp(4*g);

% Loop i over N spins
for i = 1:N
    im1 = i-1; % Value of i-1
    ip1 = i+1; % Value of i+1

    %% Calculate r using finite chain two-spin product expectation value
    if i == 1 % For first end spin (odd)
        % Two spin probabilities
        % Pi_ip1 = Poe from Section 3, a simplified form of which is used
        theta = y(i) + y(ip1);
        Pi_ip1_pp = (G*(2+theta) - theta - ...
                     sqrt(G^2*theta^2 + theta^2 - ...
                        2*G*theta^2 - 4*G^2*y(i)*y(ip1) + ...)
                   / (4*G-4);
        Pi_ip1_pm = 0.5*(y(i) + 1 - 2*Pi_ip1_pp);
        Pi_ip1_mp = 0.5*(y(ip1) + 1 - 2*Pi_ip1_pp);
        Pi_ip1_mm = 0.5*(-y(i) - y(ip1) + 2*Pi_ip1_pp);
        r_i_ip1 = Pi_ip1_pp - Pi_ip1_pm - Pi_ip1_mp + Pi_ip1_mm;
    elseif i == N % For last end spin (N must be even)
        % Two spin probabilities
        % Pi_im1 = Poe from Section 3, but here i is even, so swap i & im1
        theta = y(i) + y(im1);
        Pi_im1_pp = (G*(2+theta) - theta - ...
                     sqrt(G^2*theta^2 + theta^2 - ...
                        2*G*theta^2 - 4*G^2*y(i)*y(im1) + ...)
                   / (4*G-4);
        Pi_im1_pm = 0.5*(y(i) + 1 - 2*Pi_im1_pp);
        Pi_im1_mp = 0.5*(y(im1) + 1 - 2*Pi_im1_pp);
        Pi_im1_mm = 0.5*(-y(im1) - y(i) + 2*Pi_im1_pp);
        r_i_im1 = Pi_im1_pp - Pi_im1_pm - Pi_im1_mp + Pi_im1_mm;
    end

end
else % For inner spins

if i/2 ~= floor(i/2) % For odd inner spins

% Two spin probabilities
theta = y(i) + y(ip1);
P_ipl_pp = (G*(2+theta) - theta - ...
    sqrt(G^2*theta^2 + theta^2 - ...
        2*G*theta^2 - 4*G^2*y(i)*y(ip1) + ...
        4*G*y(i)*y(ip1) + 4*G)) ... /
    (4*G-4);
P_ipl_pm = 0.5*(y(i) + 1 - 2*P_ipl_pp);
P_ipl_mp = 0.5*(y(ip1) + 1 - 2*P_ipl_pp);
P_ipl_mm = 0.5*(-y(i) - y(ip1) + 2*P_ipl_pp);

% Two spin product expectation value
r_i_ip1 = P_ipl_pp - P_ipl_pm - P_ipl_mp + P_ipl_mm;

% Two spin probabilities
theta = y(i) + y(ip1);
P_ipl_pp = (G*(2+theta) - theta - ...
    sqrt(G^2*theta^2 + theta^2 - ...
        2*G*theta^2 - 4*G^2*y(i)*y(ip1) + ...
        4*G*y(i)*y(ip1) + 4*G)) ... /
    (4*G-4);
P_ipl_pm = 0.5*(y(ip1) + 1 - 2*P_ipl_pp);
P_ipl_mp = 0.5*(y(i) + 1 - 2*P_ipl_pp);
P_ipl_mm = 0.5*(-y(ip1) - y(i) + 2*P_ipl_pp);

% Two spin product expectation value
r_i_ip1 = P_ipl_pp - P_ipl_pm - P_ipl_mp + P_ipl_mm;

else % For even inner spins

% Two spin probabilities
theta = y(i) + y(ip1);
P_ipl_pp = (G*(2+theta) - theta - ...
    sqrt(G^2*theta^2 + theta^2 - ...
        2*G*theta^2 - 4*G^2*y(i)*y(ip1) + ...
        4*G*y(i)*y(ip1) + 4*G)) ... /
    (4*G-4);
P_ipl_pm = 0.5*(y(ip1) + 1 - 2*P_ipl_pp);
P_ipl_mp = 0.5*(y(i) + 1 - 2*P_ipl_pp);
P_ipl_mm = 0.5*(-y(ip1) - y(i) + 2*P_ipl_pp);

% Two spin product expectation value
r_i_ip1 = P_ipl_pp - P_ipl_pm - P_ipl_mp + P_ipl_mm;

% Two spin probabilities
theta = y(i) + y(im1);
Pi_im1_pp = (G*(2+theta) - theta - ... 
    sqrt(G^2*theta^2 + theta^2 - ... 
        2*G*theta^2 - 4*G^2*y(i)*y(im1) + ... 
        4*G*y(i)*y(im1) + 4*G)) ... 
    / (4*G-4);
Pi_im1_pm = 0.5*(y(im1) + 1 - 2*Pi_im1_pp);
Pi_im1_mp = 0.5*(y(i) + 1 - 2*Pi_im1_pp);
Pi_im1_mm = 0.5*(-y(im1) - y(i) + 2*Pi_im1_pp);

% Two spin product expectation value
r_i_im1 = Pi_im1_pp - Pi_im1_pm - Pi_im1_mp + Pi_im1_mm;
end
end

%% Differential change in single spin expectation value with time
if i == 1 % For first end spin (odd)
    dy(i) = -a*(y(i) - beta_o - gamma1*(y(ip1)) + ... 
        gamma1*beta_o*(r_i_ip1));
elseif i == N % For last end spin (N must be even)
    dy(i) = -a*(y(i) - beta_e - gamma1*(y(im1)) + ... 
        gamma1*beta_e*(r_i_im1));
else % For inner spins
    if i/2 ~= floor(i/2) % For odd inner spins
        dy(i) = -a*(y(i) - beta_o - 0.5*gamma*(y(im1) + y(ip1)) + ... 
            0.5*gamma*beta_o*(r_i_im1 + r_i_ip1));
    else % For even inner spins
        dy(i) = -a*(y(i) - beta_e - 0.5*gamma*(y(im1) + y(ip1)) + ... 
            0.5*gamma*beta_e*(r_i_im1 + r_i_ip1));
    end
end
end % Continue looping i from 1 to N

% End of file