Finite-size effects on the dynamic susceptibility of CoPhOMe
single-chain molecular magnets in presence of a static magnetic field

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The static and dynamic properties of the single-chain molecular magnet \( [\text{Co(hfac})_2\text{NTPhOMe}] \) are investigated in the framework of the Ising model with Glauber dynamics, in order to take into account both the effect of an applied magnetic field and a finite size of the chains. For static fields of moderate intensity and short chain lengths, the approximation of a mono-exponential decay of the magnetization fluctuations is found to be valid at low temperatures; for strong fields and long chains, a multi-exponential decay should rather be assumed. The effect of an oscillating magnetic field, with intensity much smaller than that of the static one, is included in the theory in order to obtain the dynamic susceptibility \( \chi(\omega) \). We find that, for an open chain with \( N \) spins, \( \chi(\omega) \) can be written as a weighted sum of \( N \) frequency contributions, with a sum rule relating the frequency weights to the static susceptibility of the chain. Very good agreement is found between the theoretical dynamic susceptibility and the ac susceptibility measured in moderate static fields (\( H_{dc} \leq 2 \text{ kOe} \)), where the approximation of a single dominating frequency turns out to be valid. For static fields in this range, new data for the relaxation time, \( \tau \) versus \( H_{dc} \), of the magnetization of CoPhOMe at low temperature are also well reproduced by theory, provided that finite-size effects are included.

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I. INTRODUCTION

It is commonly admitted that the plain Ising Hamiltonian does not contain any dynamics. In fact, when considering a system of Ising spins, \( \sigma_i \), localized at the sites, \( i \), of a lattice
\[
\mathcal{H} = -J \sum_{i<j} \sigma_i \sigma_j, \quad \sigma_i = \pm 1
\]
the physically interesting quantities, \( \sigma_i \)'s, commute with \( \mathcal{H} \). However, for a system in contact with a heat bath, a stochastic dynamics can be introduced by means of a master equation which assumes Markovian processes inducing random flips between different states. One of the few cases in which the problem can be solved analytically is for a one-dimensional lattice, zero external magnetic field, and an opportune choice of the transition probability, as devised by Glauber some decades ago. He calculated the dynamic susceptibility within a linear response framework, and found that the uniform magnetization decays exponentially, with a relaxation time given by an Arrhenius law
\[
\tau(T) = \tau_0 e^{\frac{g J}{k_B T}}, \quad (2)
\]
where \( 1/\tau_0 \) is the relaxation rate for an isolated spin. Considering that, at low temperatures, the correlation length for model (1) in one dimension is given by \( \xi \propto e^{\frac{2 g J}{k_B T}} \), the dynamic critical exponent results in \( z = 2 \). Glauber’s dynamics has been ever since applied in very different areas, comprising structural phase transitions, neural networks, chemical reactivity, and even bio-socio-econo-physics.

The recent discovery of single-chain magnets (SCMs) spurred renewed interest for Glauber’s dynamics in magnetic nanomaterials. Such systems show magnetic hysteretic without the onset of three-dimensional magnetic ordering. At very low temperatures, the relaxation of the magnetization is so slow that also other very interesting dynamic phenomena have been observed with unprecedented clarity, including collective reversals and quantum tunneling. As a result, after the discovery of the archetypal SCM \( [\text{Co(hfac})_2\text{NTPhOMe}] \) (hereafter denoted CoPhOMe) the number of SCM compounds has been rapidly increasing.

The strong exchange interaction and one-dimensional character of CoPhOMe make it the ideal system where to observe the long-predicted slow relaxation of the magnetization. In CoPhOMe, owing to the very high value of the exchange constant \( J/I/k_B = 80 \text{ K} \), the correlation length \( \xi \) is huge, at low temperatures, in a zero magnetic field. Consequently, the unavoidable presence of even a small density of defects causes the chain to break into finite segments whose average length, \( \bar{L} \), can be much smaller than the correlation length, \( \xi \). In such a finite-size regime, \( \bar{L} \ll \xi \), the dynamics of the system in zero field is modified with respect to Glauber’s analysis of the infinite chain. In particular the relaxation time, measured in CoPhOMe using ac susceptibility and SQUID magnetization decay techniques, was found to follow an
Arrhenius law with a halved energy barrier:  
\[ \tau(T) = \tau_0(L) e^{\frac{2J_1}{k_B T}}, \]  
(3)  
in agreement with theoretical predictions of finite-size effects.  

These effects were systematically investigated in CoPhOMe by introducing non-magnetic impurities. For nominally pure and impure samples, the complex susceptibility \( \chi(\omega) = \chi'(\omega) + i\chi''(\omega) \) was measured in presence of a moderate static magnetic field \( (H_{dc} = 2 \text{kOe}) \) and of a much smaller ac field oscillating at frequency \( \omega \).  

A two-peaked structure was found in \( \chi'(\omega) \) as a function of temperature: the low temperature peak is frequency-dependent, while the high temperature one is not. On the basis of transfer matrix calculations for the static susceptibility of the doped chain, the low temperature peak was attributed to finite-size effects. Anyway, the frequency dependence of the peak for \( \chi'(\omega) \) and \( \chi''(\omega) \) remains unexplained. Static and dynamic susceptibilities with a similar behavior have also been observed in different cobalt-organic single-chain magnets in presence of a moderate static magnetic field \( (H_{dc} = 0.5 \text{kOe}) \) and of lattice imperfections. The explanation of such features is thus becoming more pressing, as it can constitute an important tool for the analysis of the properties of a whole class of magnetic systems.  

In systems with a very large correlation length, like the one-dimensional Ising model at low temperatures, the introduction of an external magnetic field can have dramatic consequences. A static field \( H_{dc} \) strongly depresses the correlation length \( \xi \), and this fact, in turn, should also strongly affect the dynamic susceptibility. The Glauber dynamics of the infinite Ising chain model in an external magnetic field was studied some years ago in order to describe the kinetics of the helix-coil transition in biopolymers. For single-chain magnets, a theoretical and experimental study was recently performed by Coulon et al. focusing on the relaxation time of the magnetization fluctuations. In addition to a static magnetic field, their theoretical analysis considered finite-size effects, relevant in SCMs. A local-equilibrium approximation was adopted in order to truncate the infinite hierarchy of kinetic equations for finite open Ising chains in \( H_{dc} \neq 0 \). The main advantages of this approximation, first proposed by Huang for infinite chains, are: (i) it provides the exact steady-state solution in contrast with the mean field approximation; (ii) it is valid for any value of the applied field, in contrast with perturbation methods.  

In this work, we develop the theoretical framework necessary to analyze the ac susceptibility measurements of single-chain magnets in presence of a static magnetic field \( H_{dc} \). We include in the theory the effect of an oscillating magnetic field with intensity much smaller than that of the static one, using a linear response framework. With these theoretical tools, we can account for the dynamic behavior of CoPhOMe and other single-chain magnets. We directly compare the calculated behavior to previous and new experimental measurements of both the relaxation time and the ac susceptibility in presence of a static magnetic field \( H_{dc} \). In this way, we can reproduce the temperature and frequency dependence of the ac susceptibility of SCMs, measured in moderate static fields \( (H_{dc} \leq 2 \text{kOe}) \) and in presence of crystal defects and/or non-magnetic impurities. For static fields in this range, new data for the relaxation time of the magnetization of CoPhOMe, \( \tau \) versus \( H_{dc} \), are analyzed at low temperature. They are well reproduced by theory, provided that finite-size effects are included.  

The paper is organized as follows. In Section II we present both the real system and the simplified model that we adopt to catch the essentials of its stochastic dynamics. In Section III we calculate, for pure and doped chain systems, the temperature dependence of the magnetization and static susceptibility in presence of a static magnetic field. In Section IV the theoretical framework for the calculation of the dynamic susceptibility in presence of a static magnetic field is first developed for the infinite chain, and then generalized to an open, finite chain with \( N \) spins; next we present and discuss the approximation of a single dominating contribution, with characteristic frequency \( \Omega \), to the dynamic susceptibility. In Section V the results of our explicit calculations, performed using parameters suitable for describing CoPhOMe, are shown and discussed. Finally, the conclusions are drawn in Section VI and some technical details are reported in the Appendices, for the reader’s convenience.  

II. THE MODEL  
The magnetic properties of CoPhOMe are determined by Co(II) ions, with an Ising character and effective \( S = 1/2 \), and by NITPhOMe organic radicals, magnetically isotropic and with \( s = 1/2 \). The primitive magnetic cell is made up of three cobalt ions and three radicals. The spins are arranged in a helical structure, with the helix axis coincident with the crystallographic c axis of the chain. Although the effective spins of the two types of magnetic centers have the same value \((1/2)\), the gyromagnetic factors are different. The gyromagnetic factor \( g_R \) of the organic radical is isotropic, while cobalt is strongly anisotropic and \( g_{Co} = \frac{g}{|g|} = g \), with \( g_{Co} \gg g_R \). The Hamiltonian currently used to describe a CoPhOMe chain of \( N \) spins reads  
\[
\mathcal{H} = -\sum_{l=1}^{N/6} \sum_{m=1}^{3} \left\{ J \sigma_{l,2m} [\sigma_{l,2m-1} + \sigma_{l,2m+1}] + \mu_B H \right\} + g_R \sigma_{l,2m-1} (\hat{z}_{2m-1} \cdot \hat{e}_H) + g_{Co} \sigma_{l,2m} (\hat{z}_{2m} \cdot \hat{e}_H),
\]  
(4)  
where \( \sigma \) is the spin variable, \( l \) is the magnetic cell index and \( m \) the site label. The nearest neighbor exchange is antiferromagnetic and rather strong, \( |J|/k_B \approx 80 \text{ K} \), \( \hat{e}_H \) denotes the direction of the applied magnetic field \( \hat{H} \);
finally, all local axes along which the spins are aligned, \( z_k \) \((k = 1, \ldots, 6)\), form the same angle \( \theta \approx 55^\circ \) with the \( c \) axis. It follows that the sublattice magnetizations are not compensated along \( c \), whereas they are compensated within the plane perpendicular to the chain axis. Thanks to its ferrimagnetic and quasi-one-dimensional character (the ratio between interchain and intrachain exchange constants is less than \( 10^{-6} \)), \( \text{CoPhOMe} \) was the first magnetic molecular compound to display slow relaxation of the magnetization at low temperatures for \( H = 0 \) and a feature which was predicted long time ago by Glauber in the one-dimensional model of Ising spins, coupled by a nearest neighbor ferromagnetic exchange and interacting with a heat reservoir, causing them to change their states randomly with time.

In this paper we are primarily concerned with analyzing finite-size effects on the spin dynamics of \( \text{CoPhOMe} \) in presence of a non-negligible static magnetic field. Since model (3) is too involved, in the following we adopt a simplified model, yet able to catch the essentials of the dynamic behavior. Namely, we make the approximation of an open Ising chain with \( N \) equal spins, all with \( \sigma = \pm 1 \) and the same (isotropic) gyromagnetic factor \( g \), coupled by an effective nearest neighbor ferromagnetic exchange \( J_1 > 0 \) and subject to a time-dependent external magnetic field \( H(t) \)

\[
\mathcal{H} = - \sum_{j=1}^{N} J_1 \sigma_j \sigma_{j+1} + g \mu_B H(t) \sigma_j.
\]  

(5)

### III. Static Properties

For pure \( \text{CoPhOMe} \), static magnetization measurements were originally performed in single-crystal samples\([10]\) with a static magnetic field \( H_{dc} = 1 \) kOe applied parallel to the chain direction. A strong increase in the quantity \( T \cdot M/H_{dc} \) is found on decreasing \( T \) below 100 K, with a maximum reached around 25 K and a subsequent decrease. Such a behavior, typical of ferrimagnetic and ferrimagnetic systems, was also observed in the case of poly-crystalline powder samples of pure\([3,34]\) and Zn(II)-doped \( \text{CoPhOMe} \)\([14]\) at different static magnetic fields and different concentrations of Zn(II) non-magnetic impurities. It is also a common feature of all SCMs identified so far\([14]\).

For an open chain of \( N \) spins in an applied field, described by Eq. (3), the static properties can be calculated analytically in terms of the two eigenvalues, \( \lambda_0 \) and \( \lambda_1 \), and of the corresponding eigenvectors of the transfer matrix\([14]\). Denoting the concentration of quenched non-magnetic impurities by \( c \), the magnetization per spin of the doped chain is

\[
M_{\text{doped}} = \sum_{N=1}^{\infty} c^2 (1-c)^N M_N
\]  

(6)

and the static susceptibility per spin is

\[
\chi_{\text{doped}} = \sum_{N=1}^{\infty} c^2 (1-c)^N \chi_N,
\]  

(7)

where the explicit expression for \( M_N \) and \( \chi_N \) are reported in Appendix A.

For the infinite chain (i.e. \( c = 0 \) and \( N \to \infty \)), the static properties can be calculated analytically in terms only of the larger eigenvalue \( \lambda_0 \)

\[
\lambda_0 = e^K (\cosh h_0 + \sqrt{\sinh^2 h_0 + e^{-4K}}),
\]  

(8)

where \( K = J_1/k_B T \) and \( h_0 = g \mu_B H_{dc}/k_B T \). The magnetization per spin is

\[
M = k_B T \frac{1}{\lambda_0} \frac{\partial \lambda_0}{\partial H_{dc}} = \frac{\sinh h_0}{\sqrt{\sinh^2 h_0 + e^{-4K}}} \equiv m_{eq}
\]  

(9)

and the susceptibility per spin is

\[
\chi = k_B T \left[ - \frac{1}{\lambda_0} \left( \frac{\partial \lambda_0}{\partial H_{dc}} \right)^2 + \frac{1}{\lambda_0^2} \frac{\partial^2 \lambda_0}{\partial H_{dc}^2} \right].
\]  

(10)

In Fig. 1 the calculated quantity \( T \cdot M/H_{dc} \), see Eq. (6), is reported versus \( T \) for different values of \( c \) (including \( c = 0 \)) and for a fixed value of the dc field \( (H_{dc} = 1 \) kOe). In Fig. 2 the same quantity is reported for different values of the static applied magnetic field and for a fixed, rather small, value of the non-magnetic impurities concentration \( (c = 0.01) \). It is worth observing that,
at low fields and low temperatures, the curves calculated for $c = 0.01$ resemble the experimental ones, obtained by Lascialfari et al.\textsuperscript{25} for a powder sample of nominally pure CoPhOMe (see inset). In contrast, according to Eq. (6), the theoretical curves for the pure system (not shown here) are found to undergo a much stronger increase at such low fields and temperatures (as it can also be inferred from the concentration dependence of $T \cdot M/H_{dc}$ shown in Fig. 1). Previous suggestions\textsuperscript{24,26} about the presence of lattice imperfections, or impurities that limit the chain size even in pure CoPhOMe, appear thus to be confirmed.

In Fig. 3 we show new experimental data for the temperature dependence of $\chi'(\omega)$, the real part of the ac susceptibility of a different cobalt-organic single-chain magnet, for $H_{dc} = 0.5$ kOe. As in the case of CoPhOMe, the higher-temperature peak, due to the infinite chain, did not present any dynamic effect, while the lower temperature shoulder, related to finite-size effects, was found to be frequency-dependent.

In the following we will show that the latter feature can be well accounted for by a calculation of the dynamic susceptibility in the framework of the simplified model ($I = 0$) powder sample.

**IV. DYNAMIC PROPERTIES**

In ac magnetic measurements, a small ac drive magnetic field is superimposed on the dc field, causing a time-dependent moment in the sample. Therefore we are faced with the theoretical problem of determining how the kinetic equations of motion for the time-dependent spin averages of a finite, open chain in zero magnetic field\textsuperscript{21,22} are modified by the presence of magnetic field of the general form

$$H(t) = H_{dc} + H_1 e^{-i\omega t}$$

i.e. the sum of a static dc field of any intensity, $H_{dc}$, and of an ac field, oscillating at the angular frequency $\omega$. In the following we will make use of the reduced fields $h_0 = \frac{g \mu_B H_1}{k_B T}$ and $h_1 = \frac{g \mu_B H_1}{k_B T}$. As the experimental oscillating fields are usually much smaller than the static field, we will consider the case $H_1 \ll H_{dc}$, which allows us to use the expansion ($h(t) = \frac{g \mu_B B(t)}{k_B T}$)

$$\tanh h(t) \approx \tanh h_0 + h_1 e^{-i\omega t}(1 - \tanh^2 h_0).$$

Generally speaking, the susceptibility induced by a field as in Eq. (11) will have a real and an imaginary part

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$$

from which the dynamic behavior of molecular materials is usually extracted. In the following we will thus focus on calculating these experimentally relevant quantities, which are compared to data in the next section.

Typical values of the frequencies, $\nu = \frac{\omega}{2\pi}$, used in ac susceptibility measurements\textsuperscript{20,26} on pure and doped CoPhOMe, range between 0.1 and 10000 Hz. In contrast, one has $\nu \approx$ MHz for proton nuclear magnetic resonance (NMR) and muon spin relaxation ($\mu$SR) experiments.\textsuperscript{25,26} In the following, before passing to the...
comparison with experimental data, we first examine the properties of an infinite chain (subsection A), then include finite-size effects (subsection B), and eventually explore the single-frequency approximation (subsection C).

A. Infinite chain

Before considering finite-size effects, it is instructive to calculate first the ac susceptibility of an infinite Ising chain in presence of a static magnetic field. The kinetic equation for the site-independent average \( m(t) = \langle \sigma(t) \rangle \) of a spin in the infinite chain is

\[
\tau_0 \frac{dm(t)}{dt} = -(1 - \gamma)m(t) + \left[1 - \gamma \Gamma_1(t)\right] \tanh h(t)
\]

(14)

where \( \gamma = \tanh(2K) \) and \( \Gamma_1(t) \) is the nearest neighbor spin-pair time-dependent correlation function. The kinetic equation for \( \Gamma_1(t) \), on its turn, involves higher order time-dependent correlation functions, so that eventually an infinite sequence of equations is obtained as a consequence of \( h(t) \neq 0 \). In order to truncate this hierarchy, we adopt the local-equilibrium approximation29,30 i.e., the relation holding at equilibrium37 between the nearest neighbor correlation function and the magnetization (where \( m_{eq} \) is defined in Eq. 9),

\[
\Gamma_{1,eq} = m_{eq}^2 + \frac{1 - m_{eq}^2}{1 - \frac{\cosh h_0 - \sqrt{\sinh^2 h_0 + e^{-4K}}}{\cosh h_0 + \sqrt{\sinh^2 h_0 + e^{-4K}}} \tanh h_0 + e^{-4K}} \tag{15}
\]

is assumed to hold locally also at any time \( t \neq 0 \). The main advantages of this approximation, first proposed by Huang38 for an infinite Ising chain model with Glauber dynamics in \( H_{dc} \neq 0 \), are: (i) it provides the exact steady-state solution38 in contrast with the mean field approximation, which assumes simply \( \Gamma_{1,eq} = m_{eq}^2 \); (ii) it is valid for any value of the applied field, in contrast with the perturbation method, which assumes \( h_0 \ll 1 \).

In this way, a nonlinear equation for \( m(t) \) is obtained, where the approximation of a linear response of the chain applies only to the ac field, \( H \). We thus assume \( \delta m(t) = m(t) - m_{eq} \), i.e. small departures of the magnetization from its equilibrium value \( m_{eq} \). Likewise, we expand \( \Gamma_1(t) \approx \Gamma_{1,eq} + \frac{d\Gamma_1(t)}{dm(t)} m_{eq} \delta m(t) \) and, taking into account that \( \frac{d\Gamma_1(t)}{dm(t)} m_{eq} = 2 \tanh h_0 \) at equilibrium38 we finally obtain a linear non-homogeneous differential equation for \( \delta m(t) \)

\[
\tau_0 \frac{d}{dt} \delta m(t) = -(1 - \gamma + 2\gamma \tanh^2 h_0) \delta m(t) + h_1 e^{-i\omega t} \left(1 - \tanh^2 h_0\right) \left(1 - \gamma \Gamma_{1,eq}\right). \tag{16}
\]

In absence of the ac field (\( h_1 = 0 \)), one finds an exponential time decrease for the magnetization fluctuation

\[
\delta m(t) = \delta m(t_0) e^{-\lambda_{\infty}(t-t_0)/\tau_0}. \tag{17}
\]

Thus, for the infinite Ising chain, there is a single relaxation time, \( \tau_{\infty} \), related to the a-dimensional parameter \( \lambda_{\infty} \) by

\[
\lambda_{\infty} = \frac{\tau_0}{\tau_{\infty}} = 1 + 2\gamma \tanh^2 h_0. \tag{18}
\]

Notice that, for \( h_0 \to 0 \), Glauber’s result2 of an exponentially diverging relaxation time at low temperatures (\( \tau_{\infty} \approx \frac{1}{2} \tau_0 e^{4K} \) for \( k_B T \ll J_1 \)) is correctly recovered, while for \( H_{dc} \neq 0 \) the relaxation time of the infinite chain does not diverge any more.

In presence of the ac field (\( h_1 \neq 0 \), the general solution of Eq. (16) is

\[
\delta m(t) = \delta m(t_0) e^{-\lambda_{\infty}(t-t_0)/\tau_0} + h_1 \left(1 - \tanh^2 h_0\right)
\]
\[ x(1 - \gamma \Gamma_{1,eq}) \int_{t_0}^{t} e^{-i\omega t'} e^{-\lambda_\infty(t-t')/\tau_0} \, dt'. \]  

(19)

Taking into account that \( \lambda_\infty \neq 0 \), one can safely let \( t_0 \to -\infty \) in order to find a solution that does not depend on the initial conditions\(^{2,38}\).

\[ \delta m(t) = (1 - \tanh^2 h_0)(1 - \gamma \Gamma_{1,eq}) \frac{h_1 e^{-i\omega t}}{\lambda_\infty - i\omega \tau_0}. \]  

(20)

The fluctuation of the total magnetization of the infinite Ising chain is obtained summing over all the \( N \) spins and letting \( N \to \infty \)

\[ \delta\langle M(t) \rangle = N g \mu_B \delta\langle \sigma(t) \rangle = \chi(\omega) H_1 e^{-i\omega t}, \]  

(21)

so that the dynamic susceptibility, \( \chi(\omega) \), is

\[ \chi(\omega) = \frac{g^2 \mu_B^2 N}{k_B T} \frac{1 - \tanh^2 h_0)(1 - \gamma \Gamma_{1,eq})}{1 - \lambda_\infty - i\omega \tau_0} = \frac{1}{1 - i\omega \tau_0 / \lambda_\infty} \]  

(22)

where \( \lambda_\infty \) denotes the static susceptibility of the infinite Ising chain for \( H_{dc} \neq 0 \).

\[ \chi_\infty = \frac{g^2 \mu_B^2 N}{k_B T} \frac{1 - \tanh^2 h_0)(1 - \gamma \Gamma_{1,eq})}{1 - \gamma + 2\gamma \tanh^2 h_0}. \]  

(23)

For \( h_0 \to 0 \), Glauber’s result\(^2\)

\[ \chi(\omega) = \frac{g^2 \mu_B^2 N}{k_B T} \frac{1 + \eta}{1 - \tanh^2 h_0) / (1 - \gamma + 2\gamma \tanh^2 h_0)} \]  

(24)

is correctly recovered, by taking into account that \( \lambda_\infty \to 1 - \gamma, \Gamma_{1,eq} \to \eta = \text{tanh} K, \) and \( \gamma = \frac{2\eta}{1 + \eta} \).

**B. Finite chain**

In the case of an open Ising chain with a finite number \( N \) of spins, the lack of translational invariance leads to \( N \) kinetic equations for the \( N \) site-dependent spin averages \( \delta\langle \sigma_p(t) \rangle \) \((p = 1, \cdots, N)\)\(^{21,22,29}\). As in the case of the infinite chain, we can introduce the local-equilibrium approximation\(^{28,39}\) in order to truncate the infinite sequence of equations for the higher-order time-dependent spin correlation function. Next we perform the linearization of the kinetic equations, in the hypothesis of a linear response to the ac magnetic field. We then obtain a set of \( N \) linear differential equations, which can be written in matrix form

\[ \tau_0 \frac{d \Sigma}{dt} = -Y \cdot \Sigma + h_1 e^{-i\omega t}(1 - \tanh^2 h_0) \Psi. \]  

(25)

where \( \Sigma \) and \( \Psi \) are \( N \times 1 \) vectors containing the spin fluctuations and the non-homogeneous terms, respectively (see Appendix B for details). \( Y \) is a real, symmetric, tridiagonal, \( N \times N \) matrix, with nonzero \( a \)-dimensional eigenvalues \( \lambda_j \) \((j = 1, \cdots, N)\), while \( \Phi^{(\lambda_j)} \) are the corresponding \( N \times 1 \) eigenvectors. In the limiting case \( h_0 \to 0 \), the numerical solutions for \( \lambda_j \) coincide with the ones obtained\(^{21,22}\) in the framework of a finite-size scaling calculation of the Glauber dynamics in a zero static field. In particular, the low-temperature expansion \((k_B T \ll J_1)\) for the eigenvalue of a finite open chain with \( N \) spins is

\[ \lambda_1(H_{dc} = 0) \approx \frac{1}{\tau_0} e^{\frac{2\eta}{1 + \eta}} \]  

(26)

to be compared with \( \lambda_\infty(H_{dc} = 0) \approx 2e^{-\eta} \) for the eigenvalue of the infinite chain\(^2\).

We are interested in the long time behavior of the system, characterized for being independent on the initial condition. Thus, solving Eq. \(^{23}\) by the method of eigenfunctions\(^{39}\) and letting \( t_0 \to -\infty \), we obtain for the fluctuation of a single-spin average \((p = 1, \cdots, N)\)

\[ \delta\langle \sigma_p(t) \rangle = h_1 e^{-i\omega t}(1 - \tanh^2 h_0) \]  

(27)

\[ \chi_N(\omega) = g \mu_B \sum_{p=1}^{N} \delta\langle \sigma_p(t) \rangle = \chi_N(\omega) H_1 e^{-i\omega t} \]  

(28)

where the angular frequencies are

\[ \Omega_j = \frac{\lambda_j}{\tau_0} \]  

(29)

and the corresponding frequency weights are

\[ A_j(\lambda_j, T, H_{dc}) = \frac{1}{\lambda_j} \sum_{p=1}^{N} \Phi^{(\lambda_j)}_p \]  

(30)

The angular frequencies\(^{23}\) are expressed in terms of the \( a \)-dimensional eigenvalues, \( \lambda_j \), of the matrix \( Y \) and of the characteristic time, \( \tau_0 \), for the spin flip of an isolated spin. The latter is a free parameter which is expected to depend, in general, on the intensity of the applied magnetic field\(^{29}\). The general expression for the dynamic susceptibility per spin of a doped chain is thus

\[ \chi(\omega) = \sum_{N=1}^{\infty} c^2(1 - \eta)^N \chi_N(\omega). \]  

(31)
FIG. 4: (Color online) Temperature dependence of the first three eigenvalues $\lambda_j = \Omega_j \tau_0$ ($j = 1$, red full circles; $j = 2$, green full squares; $j = 3$, blue full triangles) of an open Ising chain, calculated for a finite number of spins ($N=11$ and $N=101$) in presence of a nonzero static field ($H_{dc} = 2$ kOe and $H_{dc} = 10$ kOe). For comparison, the eigenvalue $\lambda_\infty$ (black open circles) of an infinite chain in nonzero field is also reported. Dashed lines denote the zero-field, low-temperature expansions for the smallest eigenvalue of a finite chain, $\lambda_1(H_{dc} = 0) \approx 2e^{-\frac{2J}{g^2\mu_B^2}}$ and for the eigenvalue of an infinite chain, $\lambda_\infty(H_{dc} = 0) \approx 2e^{-\frac{2J}{g^2\mu_B^2}}$. The horizontal lines, from bottom to top, denote the quantity $2\pi\nu\tau_0$, calculated for three different frequencies: $\nu = 1$ kHz, $\nu$ (MHz) = 4.26 $H_{dc}$ (kOe), and $\nu$ (MHz) = 13.55 $H_{dc}$ (kOe), typically used in ac susceptibility, proton NMR, and $\mu$SR measurements, respectively. Insets: calculated temperature dependence of the frequency weights, $A_j(\lambda_j, T, H_{dc})$ with $j = 1$ and $j = 3$ (red full circles and blue full triangles, respectively); for odd $N$, the weights of the even modes are zero. The curves denoted by black open circles and black dashed lines represent the frequency weights of an infinite chain in $H_{dc} \neq 0$ and in $H_{dc} = 0$, respectively. The parameters used for the calculations were $J/I/k_B = 80$ K, $g = 2$, and $\tau_0 = 4 \cdot 10^{-13}$ s.

C. Single-frequency approximation

Let us start deriving a quite general sum rule for the frequency weights, which is readily obtained letting zero frequency ($\omega = 0$) in Eq. (28)

$$\sum_{j=1}^{N} A_j(\lambda_j, T, H_{dc}) = \frac{k_B T}{g^2 \mu_B^2} \chi_N$$  \hspace{1cm} (32)

where $\chi_N$, the static susceptibility of a finite open Ising chain with $N$ spins, subject to the dc field $H_{dc}$, is given...
by Eq. (A5). Next we observe that, in the approximation of a single characteristic frequency, \( \Omega_c \), dominating the relaxation of the magnetization fluctuations, the equation (28) for the dynamic susceptibility of a finite, open, Ising chain with \( N \) spins assumes the simple form

\[
\chi_N(\omega) \approx \chi_N \frac{\Omega_c^2 + i\omega\Omega_c}{\Omega_c^2 + \omega^2}. \tag{33}
\]

In principle, the characteristic frequency is not necessarily \( \Omega_c = \lambda_1/\tau_0 \), i.e. related to the smallest eigenvalue of \( Y \). Rather, in order to determine the dominating frequency, the temperature dependence of the frequency weights must be taken into account.

In the single-frequency approximation, the dynamic susceptibility per spin of a doped chain also simplifies greatly

\[
\chi(\omega) \approx \chi_{\text{doped}} \frac{\Omega_c^2 + i\omega\Omega_c}{\Omega_c^2 + \omega^2}, \tag{34}
\]

where \( \chi_{\text{doped}} \) is given by Eq. (7).

Finally we observe that, using the fluctuation-dissipation theorem, the linear response \( S_N(\omega) \) of a finite open Ising chain with \( N \) spins can be expressed as a weighted sum of \( N \) Lorentzian functions centered at zero frequency with widths \( \Omega_j \)

\[
S_N(\omega) = \frac{2k_B T}{\omega} \chi''_N(\omega) = 2g^2\mu_B^2 \sum_{j=1}^{N} \frac{\Omega_j}{\Omega_j^2 + \omega^2} A_j(\lambda_j, T, H_{dc}). \tag{35}
\]

When the approximation of a single dominating frequency \( \Omega_c \) holds, the linear response is simply the product of \( T \chi_N \) and of a single Lorentzian function, centered at zero frequency, with width equal to the characteristic frequency \( \Omega_c \)

\[
S_N(\omega) = \frac{2k_B T}{\omega} \chi''_N(\omega) \approx 2k_B T \chi_N \frac{\Omega_c}{\Omega_c^2 + \omega^2}. \tag{36}
\]

It is worth noticing that expressions quite similar to Eqs. (35) and (36) were obtained for the spectrum of fluctuations of a cluster magnetization by Santini et al.\textsuperscript{40} in the framework of an exact calculation of the energy levels of three important classes of magnetic molecules in contact with a phonon heat bath: namely, antiferromagnetic rings, grids, and nanomagnets. Moreover,
Bianchi et al. recently showed that, while for antiferromagnetic homometallic rings the approximation of a single dominating frequency is valid, it does not hold for heterometallic rings, due to the presence of inequivalent ions which prevent mapping local-spin correlations with the corresponding total-spin ones.

V. RESULTS

In this section we compare the theoretical results derived in IV with experimental ac susceptibility data, obtained in nominally pure and zinc-doped CoPhOMe for different values of $H_{dc}$ and of the frequency of the oscillating field. Also, new experimental data for the relaxation time of the magnetization, measured as a function of the static magnetic field at fixed temperature, will be discussed and compared with theoretical calculations.

Let us first provide evidence for the correctness of the single frequency approximation, Eq. (41), by showing the temperature dependence of the eigenvalues and weights of a finite, open, Ising chain in an applied dc field. The value of the exchange constant we assumed for the calculations, $J_1/k_B = 80$ K, is known to provide the correct temperature dependence for the static and dynamic properties of CoPhOMe. The characteristic time for the spin flip of an isolated spin, $\tau_0$, was left as a free parameter (see later on). Moreover the field dependence of $\tau_0$, though expected in principle, was neglected for the sake of simplicity.

In Fig. 4 some of the $N$ calculated a-dimensional eigenvalues, $\lambda_j$, of the real tridiagonal matrix $Y$, defined in Eq. (25) and Eq. (B10), are reported as a function of inverse temperature for different values of the number of spins, $N$, and of the applied static field, $H_{dc}$. For the sake of comparison, also the temperature dependence of the eigenvalue $\lambda_\infty$, see Eq. (18), of an infinite chain in the same field is shown. Except for the case of long chains and strong fields, at sufficiently low temperatures a single mode dominates the low-frequency dynamics of a finite, open, Ising chain with $N$ spins: namely, the mode with characteristic frequency $\Omega_c = \lambda_1/\tau_0$, where $\lambda_1$ is the smallest eigenvalue of $Y$. The temperature dependence of the frequency weights corresponding to the various modes is displayed in the insets of Fig. 4. For not too long chains and not too strong fields, one can see that the frequency related to the smallest eigenvalue $\lambda_1$ has the strongest weight.
A. Ac susceptibility

Some years ago, the ac susceptibility of CoPhOMe was measured versus $T$ in single crystals, both for $H_{dc} = 0$ Oe in a nominally pure sample\textsuperscript{10} and for $H_{dc} = 2$ kOe in a doped one.\textsuperscript{26} In this work, we present some new data for $\chi(\omega)$ versus $T$. Data were obtained, using an homemade ac probe and a Cryogenics magnetometer, on a collection of nominally pure single crystals of CoPhOMe. The crystals were all aligned with the chain axis along the magnetic field direction. The frequencies in an ac susceptibility experiment typically range between 0.1 and 10 kHz, and we can safely adopt the single-frequency approximation in order to account for the temperature dependence of $\chi(\omega)$ in moderate fields ($H_{dc} \leq 2$ kOe). Additionally the oscillating fields used were always below 8 Oe, and the condition $H_{dc} \gg H_1$ is also fulfilled.

In Fig. [a](b) we show the temperature dependence of the real and imaginary part of the dynamic susceptibility calculated for an infinite chain with $H_{dc} = 0$, while analogous quantities calculated for a zinc-doped chain ($c = 0.047$) in $H_{dc} = 2$ kOe are reported in Fig. [c](d).

In the pure system ($c = 0$) with $H_{dc} = 0$, see Eq. (24), a single, resonating peak is found both for $\chi'(\omega)$ and $\chi''(\omega)$ versus $T$, whose position gradually shifts to higher temperature with increasing the frequency of the tiny oscillating field, see Fig. [a](b). The phenomenon can be interpreted as a manifestation of stochastic resonance in a set of coupled bistable systems: i.e. there is an optimal value of noise, for which the response of the dynamic system to the driving field is maximum. In a ferromagnetic or ferrimagnetic chain, the role of stochastic noise is played by thermal fluctuations, and a resonance peak occurs when the deterministic time scale of the oscillating magnetic field matches the statistical time scale associated with the spontaneous decay of the net magnetization.

For the doped system in $H_{dc} = 2$ kOe, we find that a frequency-dependent peak in the calculated $\chi'(\omega)$ and $\chi''(\omega)$ versus $T$ (the colored curves in Fig. [c](d)) develops at substantially lower temperatures with respect to the peak in the static susceptibility of an infinite chain (the full black curve in Fig. [c]), see Eq. (23). This can be easily understood by looking at Fig. [1] for a finite, open Ising chain in a moderate field, the fulfillment of the resonance condition ($\omega = \Omega_c$ in Eq. (24)), occurs at low temperatures, as signaled by the crossing between the full horizontal line (which represents a typical value, 1 kHz, of the frequency $\nu$ in an ac susceptibility measurement) and the curve (red full circles) representing the $T$ dependence of the smallest frequency mode, $\lambda_1$. In contrast,
the crossing does not occur in the case of an infinite chain (black open circles) subject to the same dc field; i.e. the relaxation rate of the infinite chain does not fulfill the resonance condition $(\omega \tau_0 = \lambda_{\infty}$ in Eq. 22) at the low frequencies involved in the ac susceptibility experiment: thus, the infinite chain does not present any dynamic response. As already observed in Sect. III, nominally pure samples are non-homogeneous and consequently, at low temperatures, only the regions with dilute chains contribute to the dynamic properties in a significant way. This explains the experimental results 10,11,23–25 in which the measured relaxation rate, for $H = 0$, was always found to follow the modified Arrhenius law with a halved energy barrier, $\tau(T) = \tau_0(\bar{L}) e^{2J/I k_B T}$, where $\bar{L}$ is the mean length of a chain.

In Fig. 8 we present new experimental data for the temperature dependence of the ac susceptibility of CoPhOMe, measured for a fixed value of the frequency ($\nu = 1$ kHz) at different values of the static magnetic field ($H_{dc} \leq 1$ kOe), see (a)(b), and for a fixed value of the dc field ($H_{dc} = 1$ kOe) at different values of the frequency ($\nu \leq 1$ kHz). In Fig. 9 we plot the real and imaginary part of the dynamic susceptibility, calculated using Eqs. (34) and (7) for a doped chain ($c = 0.047$) at just the same values of frequency and dc field as in Fig. 8. For the sake of comparison, also the dynamic susceptibil-
ity of the infinite chain \((c = 0)\) was calculated: for fixed \(H_{dc} = 1\) kOe, at the chosen values of \(\nu\), this quantity was not found to display any frequency dependence (see the black line in Fig. 7(c)), in fine agreement with experimental observations (see the higher temperature peak in Fig. 7(c)). Thus we can conclude that, for the moderate values of \(\nu\) and \(H_{dc}\) exploited in the present ac susceptibility experiments: (i) the frequency dependence of \(\chi(\omega)\) can be attributed solely to finite-size effects; (ii) the approximation of a single dominating frequency is a good one for the calculation of the dynamic susceptibility.

B. Relaxation time

In Fig. 8(a) we show the frequency dependence of the imaginary part of the ac susceptibility, measured for a sample of five crystals of nominally pure CoPhOMe, at a fixed temperature of 9 K and for \(H_{dc}\) ranging from 0.1 to 2 kOe. Fitting of the curves was performed using an extended Debye model to extract the peak frequency of the magnetization of CoPhOMe (both at \(T = 5.1\) K and 9 K), one has to assume a value \(\tau_0 \approx 4 \cdot 10^{-13}\) s for the characteristic time of spin flip of an isolated spin (the only free parameter in Glauber’s theory\(^2\)). For the sake of simplicity, the same field-independent value was assumed in all calculations throughout the paper.

As regards the dc field dependence of the relaxation time of the magnetization, \(\tau\), we can conclude that it is well reproduced by theory, provided that finite-size effects are included. In fact, in a measurement performed for an inhomogeneous CoPhOMe sample, no appreciable contribution to the relaxation time, \(\tau\), is expected from the infinite chain at low temperatures, owing to the high value of the exchange coupling \((J_1/k_B = 80\) K). For example from Eq. (15), putting \(\tau_0 = 4 \cdot 10^{-13}\) s, at \(T = 5\) K one has \(\tau_\infty = 1.25 \cdot 10^{15}\) s for \(H_{dc} = 0\), while in a static field \(H_{dc} = 10\) Oe the relaxation time reduces to \(\tau_\infty = 2.77 \cdot 10^{-6}\) s. In contrast, an experimentally appreciable relaxation time is associated with finite-size chains.

VI. CONCLUSIONS

In this paper, the spin dynamics of the archetypal molecular magnetic chain, CoPhOMe, in presence of an external magnetic field of any intensity, was investigated using a simplified model, consisting of a one-dimensional Ising ferromagnet with a stochastic dynamics caused by the interaction of the spins with a heat reservoir\(^2\).

In the framework of a local-equilibrium approximation, devised to truncate the infinite sequence of kinetic equations originated by the presence of a nonzero static magnetic field, and of a linear response of the system to a small oscillating field, we first calculated the dynamic susceptibility of an infinite chain. Next, the theory was generalized to a finite, open Ising chain. We showed that the dynamic susceptibility of an open chain with a finite number \(N\) of spins can be expressed as a weighted sum of \(N\) frequency contributions, related to the \(N\) relaxation rates of the magnetization fluctuations. From the comparison with the ac susceptibility data obtained for nominally pure samples we can draw two conclusions: i) the pure samples are really non-homogeneous, because regions with very low density of defects coexist with regions with relevant density of defects; ii) only the latter regions show a contribution to the dynamic relaxation, in the frequency range conventionally investigated by ac susceptibility measurements.

For doped CoPhOMe chains, the approximation of a single dominating frequency was found to be quite satisfactory in order to account for ac susceptibility data\(^2\) in a moderate static magnetic field \((H_{dc} = 2\) kOe\), both as a function of temperature and of the frequency of the small oscillating field.

Finally, it is worth observing that, on the basis of our calculation of the \(T\)- and \(H\)-dependence of the relaxation rates (and corresponding frequency weights), we do not
expect that the approximation of a single dominating frequency will be able to account for $^1$H nuclear magnetic resonance (NMR) and muon spin rotation ($\mu$SR) experimental data\textsuperscript{32,33,35,36} in pure and zinc-doped CoPhOMe, because these techniques probe the local spin dynamics at frequencies ($\nu \approx$ MHz) substantially higher than the typical frequencies ($\nu \approx$ kHz) used in an ac susceptibility experiment. Anyway, the present results constitute a fundamental background for the future theoretical investigation of such high-frequency regimes.

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**Appendix A: Analytical expressions of the magnetization $M_N$ and the static susceptibility $\chi_N$ of an open Ising chain of $N$ spins in a dc magnetic field $H_{dc}$**

Following Wortis\textsuperscript{21} the free energy $F_N$ of a finite chain of $N$ spins, coupled by the Hamiltonian\textsuperscript{13} with $H = H_{dc}$ and subject to open boundary conditions, can be expressed as the sum of a bulk, a surface, and a finite-size contribution

$$ F_N = -k_B T \left\{ N \ln \lambda_0 + \ln \left( A_0 \lambda_0 \right) + \ln \left[ 1 + A_1 \left( \frac{\lambda_1}{\lambda_0} \right)^{N-1} \right] \right\} $$

(A1)

where

$$ \lambda_{0,1} = e^K \left( \cosh h \pm \sqrt{\sinh^2 h + e^{-2K}} \right) $$

(A2)

$$ A_{0,1} = \cosh h \pm \frac{\sinh^2 h + e^{-2K}}{\sqrt{\sinh^2 h + e^{-2K}}} $$

(A3)

with $K = \frac{h}{k_B T}$, $h_0 = \frac{g\mu_B H_{dc}}{k_B T}$. For the reader’s convenience, explicit expressions for the static magnetization, $M_N$, and static susceptibility, $\chi_N$, of a finite open Ising chain with $N$ spins in presence of a magnetic field are reported hereafter. The magnetization is

$$ M_N = -\frac{\partial F_N}{\partial H_{dc}} = g \mu_B \left\{ N \left[ \frac{1}{\lambda_0} \frac{\partial \lambda_0}{\partial h_0} + \left( \frac{1}{A_0} \frac{\partial A_0}{\partial h_0} - \frac{1}{\lambda_0} \frac{\partial \lambda_0}{\partial h_0} \right) \right] \right\} $$

(A4)

$$ + \frac{1}{(\lambda_1/\lambda_0)^{N-1} + A_1 A_0} \left\{ \left( \frac{1}{A_0} \frac{\partial A_1}{\partial h_0} - \frac{A_1}{A_0^2} \frac{\partial A_0}{\partial h_0} \right) + \left( N - 1 \right) \frac{A_1}{A_0} \left( \frac{1}{\lambda_1} \frac{\partial \lambda_1}{\partial h_0} - \frac{1}{\lambda_0} \frac{\partial \lambda_0}{\partial h_0} \right) \right\} $$

and the static susceptibility is

$$ \chi_N = -\frac{\partial^2 F_N}{\partial H_{dc}^2} = g \mu_B \left\{ N \left[ - \frac{1}{\lambda_0} \left( \frac{\partial \lambda_0}{\partial h_0} \right)^2 + \frac{1}{\lambda_0} \frac{\partial^2 \lambda_0}{\partial h_0^2} \right] \right\} $$

$$ + \left[ - \frac{1}{A_0^2} \left( \frac{\partial A_0}{\partial h_0} \right)^2 + \frac{1}{A_0} \frac{\partial^2 A_0}{\partial h_0^2} + \frac{1}{\lambda_0^2} \left( \frac{\partial \lambda_0}{\partial h_0} \right)^2 - \frac{1}{\lambda_0} \frac{\partial^2 \lambda_0}{\partial h_0^2} \right] $$

$$ - \frac{1}{(\lambda_1/\lambda_0)^{N-1} + A_1 A_0} \left\{ \left( N - 1 \right) \frac{\lambda_0}{\lambda_1} (N-2) \left( \frac{1}{\lambda_1} \frac{\partial \lambda_1}{\partial h_0} - \frac{\lambda_0}{\lambda_1^2} \frac{\partial \lambda_0}{\partial h} \right) + \frac{1}{A_0} \frac{\partial A_1}{\partial h_0} - \frac{A_1}{A_0^2} \frac{\partial A_0}{\partial h_0} \right\} $$
\[ \times \left[ \left( \frac{1}{A_0} \frac{\partial A_1}{\partial h_0} - \frac{A_1}{A_0^2} \frac{\partial A_0}{\partial h_0} \right) + (N-1) \frac{A_1}{A_0} \left( \frac{1}{\lambda_1} \frac{\partial \lambda_1}{\partial h_0} - \frac{1}{\lambda_0} \frac{\partial \lambda_0}{\partial h_0} \right) \right] \]

\[ + \left( - \frac{1}{A_0} \frac{\partial A_1}{\partial h_0} + \frac{A_1}{A_0^2} \frac{\partial A_0}{\partial h_0} \right) \left( \frac{1}{\lambda_1} \frac{\partial \lambda_1}{\partial h_0} - \frac{1}{\lambda_0} \frac{\partial \lambda_0}{\partial h_0} \right) \]

\[ + (N-1) \left( \frac{1}{A_0} \frac{\partial A_1}{\partial h_0} - \frac{A_1}{A_0^2} \frac{\partial A_0}{\partial h_0} \right) \left( \frac{1}{\lambda_1} \frac{\partial \lambda_1}{\partial h_0} - \frac{1}{\lambda_0} \frac{\partial \lambda_0}{\partial h_0} \right) \]

\[ + (N-1) \frac{A_1}{A_0} \left( - \frac{1}{\lambda_1^2} \left( \frac{\partial \lambda_1}{\partial h_0} \right)^2 + \frac{1}{\lambda_1} \left( \frac{\partial \lambda_1}{\partial h_0} \right) \left( \frac{\partial \lambda_1}{\partial h_0} \right) \right) \]

The derivatives with respect to the magnetic field in Eq. (A3) and Eq. (A5) are expressed as

\[ \frac{k_B T}{g \mu_B} \frac{\partial \lambda_{0,1}}{\partial H_{dc}} = e^K \left( \sinh h \pm \frac{\sinh(2h_0)}{2\sqrt{\sinh^2 h_0 + e^{-2K}}} \right) \]

\[ \frac{k_B T}{g \mu_B} \frac{\partial A_{0,1}}{\partial H_{dc}} = \sinh h \pm \frac{\sinh(2h_0)}{\sqrt{\sinh^2 h_0 + e^{-2K}}} \left[ 1 - \frac{\sinh^2 h_0 + e^{-2K}}{2(\sinh^2 h_0 + e^{-4K})} \right] \]

\[ (k_B T)^2 \frac{\partial^2 \lambda_{0,1}}{g \mu_B H_{dc}^2} = e^K \cosh h_0 \pm \left[ \frac{e^{2K} \cosh(2h_0)}{\sqrt{e^{2K} \sinh^2 h_0 + e^{-2K}}} - \frac{1}{4} \left( e^{2K} \sinh^2(2h_0) \right)^{3/2} \right] \]

\[ (k_B T)^2 \frac{\partial^2 A_{0,1}}{g \mu_B H_{dc}^2} = \cosh h_0 \pm \left\{ \frac{2 \cosh(2h_0)}{\sqrt{\sinh^2 h_0 + e^{-4K}}} - \frac{\sinh^2(2h_0)}{\left( \sinh^2 h_0 + e^{-4K} \right)^{3/2}} \right\} + \frac{3}{4} \frac{\sinh^2 h_0 + e^{-2K}}{\left( \sinh^2 h_0 + e^{-4K} \right)^{3/2}} \sinh^2(2h_0) + \frac{e^{2K} \sinh^2(2h_0)}{\left( \sinh^2 h_0 + e^{-4K} \right)^{3/2}} \cosh(2h_0) \}

### Appendix B: Relaxation times of an open chain of N Ising spins in an applied magnetic field

In order to calculate the relaxation times of an open chain of N spins coupled by the Ising exchange Hamiltonian and subject to a static magnetic field \( H \), Eq. (B0), following Glauber one starts by writing the kinetic equation of motion for the time-dependent average of an interior spin \( \langle \sigma_p \rangle \) with \( 1 < p < N \)

\[ \tau_0 \frac{d \langle \sigma_p \rangle}{dt} = -\langle \sigma_p \rangle + \frac{\gamma}{2} \left( \langle \sigma_{p-1} \rangle + \langle \sigma_{p+1} \rangle \right) + \tanh h(t) \left[ 1 - \frac{\gamma}{2} \left( \langle \sigma_{p-1} \sigma_p \rangle + \langle \sigma_p \sigma_{p+1} \rangle \right) \right] \]

where \( \tau_0 \) is the characteristic time for the spin flip of an isolated spin, \( \gamma = \tanh(2K) \) and \( h(t) = \frac{g \mu_B H(t)}{k_B T} \). For the two spins \( p = 1 \) and \( p = N \) located at the ends of the open chain, following Coulon et al., one has instead

\[ \tau_0 \frac{d \langle \sigma_1 \rangle}{dt} = -\langle \sigma_1 \rangle + \eta \langle \sigma_2 \rangle + \tanh h(t) \left[ 1 - \eta \langle \sigma_1 \sigma_2 \rangle \right] \]

\[ \tau_0 \frac{d \langle \sigma_N \rangle}{dt} = -\langle \sigma_N \rangle + \eta \langle \sigma_{N-1} \rangle + \tanh h(t) \left[ 1 - \eta \langle \sigma_{N-1} \sigma_N \rangle \right] \]

where \( \eta = \tanh K \). In our case, see Eq. (11), the time-dependent magnetic field is assumed to be \( H(t) = H_{dc} + H_1 e^{-i\omega t} \) i.e. the sum of a static dc field of any intensity, \( H_{dc} \), and of a much lower AC field, \( H_1 \ll H_{dc} \), oscillating at the
angular frequency $\omega$. Thus we can expand $\tanh h(t) \approx \tanh h_0 + h_1 e^{-i\omega t}(1 - \tanh^2 h_0)$, where $h_0 = \frac{\mu B_{\text{ext}}}{k_B T}$ and $h_1 = \frac{g\mu B_{\text{ext}}}{k_B T}$.

Following Coulon et al.\textsuperscript{29} a linearization of the equations \textsuperscript{[B1], [B2], and [B3]} around the spin equilibrium values is next performed in the framework of linear response theory (i.e. small departures from thermal equilibrium are assumed)

$$
\langle \sigma_p \rangle \approx \langle \sigma_p \rangle_{N,\text{eq}} + \delta \langle \sigma_p \rangle,
\langle \sigma_p \rangle_{p+1} \approx \langle \sigma_p \sigma_{p+1} \rangle_{N,\text{eq}} + \delta \langle \sigma_p \sigma_{p+1} \rangle
$$

In this way, we obtain a system of $N$ differential equations in the spin fluctuations ($\delta \langle \sigma_p \rangle$ with $p = 1, \ldots, N$) where, on the right hand sides, the presence of the field involves the presence of variations of time-dependent nearest neighbors spin-spin correlation functions ($\delta \langle \sigma_p \sigma_{p+1} \rangle$)

$$
\tau_0 \frac{d\delta \langle \sigma_1 \rangle}{dt} = -\delta \langle \sigma_1 \rangle + \eta \left[ \delta \langle \sigma_2 \rangle - \tanh h_0 \delta \langle \sigma_1 \sigma_2 \rangle \right] + h_1 e^{-i\omega t}(1 - \tanh^2 h_0) \left[ 1 - \eta \langle \sigma_1 \sigma_2 \rangle_{N,\text{eq}} \right]
\tau_0 \frac{d\delta \langle \sigma_p \rangle}{dt} = -\delta \langle \sigma_p \rangle + \frac{\eta}{2} \left[ \delta \langle \sigma_{p-1} \rangle + \delta \langle \sigma_{p+1} \rangle \right] - \tanh h_0 \left[ \delta \langle \sigma_{p-1} \sigma_p \rangle + \delta \langle \sigma_p \sigma_{p+1} \rangle \right] + h_1 e^{-i\omega t}(1 - \tanh^2 h_0) \left[ 1 - \eta \langle \sigma_{p-1} \sigma_p \rangle_{N,\text{eq}} \right]
\tau_0 \frac{d\delta \langle \sigma_N \rangle}{dt} = -\delta \langle \sigma_N \rangle + \eta \left[ \delta \langle \sigma_{N-1} \rangle - \tanh h_0 \delta \langle \sigma_{N-1} \sigma_N \rangle \right] + h_1 e^{-i\omega t}(1 - \tanh^2 h_0) \left[ 1 - \eta \langle \sigma_{N-1} \sigma_N \rangle_{N,\text{eq}} \right]
$$

If one writes down the kinetic equations for $\delta \langle \sigma_p \sigma_{p+1} \rangle$, one finds an infinite sequence of equations involving other, higher-order spin correlation functions. Such an infinite hierarchy of equations can be decoupled by resorting to the local-equilibrium approximation first proposed by Huang in the case of the kinetic equation of an infinite Ising chain in a magnetic field\textsuperscript{29} i.e. the relation existing between the magnetization and the correlation function at thermal equilibrium\textsuperscript{32} is assumed to hold locally although the system is not in equilibrium ($t \neq 0$). The advantage of the local-equilibrium approximation with respect to perturbative methods\textsuperscript{45} or mean field approximation is that it provides an exact steady-state solution\textsuperscript{46}.

In the case of a finite chain with $N$ spins, the local-equilibrium approximation was implemented, following Coulon et al.\textsuperscript{29} by expressing the variations of two-spin correlation functions in terms of a linear combination of the variations of single-spin averages

$$
\delta \langle \sigma_p \sigma_{p+1} \rangle = A_{N,p} \delta \langle \sigma_p \rangle + B_{N,p} \delta \langle \sigma_{p+1} \rangle.
$$

The coefficients are\textsuperscript{29}

$$
A_{N,p} = \frac{\langle \sigma_{N-p} \rangle_{N-p,\text{eq}} - \eta \langle \sigma_{p} \rangle_{p,\text{eq}}}{1 - \eta \langle \sigma_{p} \rangle_{p,\text{eq}} \langle \sigma_{N-p} \rangle_{N-p,\text{eq}}}, \quad B_{N,p} = \frac{\langle \sigma_{p} \rangle_{p,\text{eq}} - \eta \langle \sigma_{N-p} \rangle_{N-p,\text{eq}}}{1 - \eta \langle \sigma_{p} \rangle_{p,\text{eq}} \langle \sigma_{N-p} \rangle_{N-p,\text{eq}}}
$$

where the average spin values can be calculated, at thermal equilibrium, by using the recursive relation\textsuperscript{45}

$$
\langle \sigma_p \rangle_{p,\text{eq}} = \frac{\tanh h_0 + \eta \langle \sigma_{p-1} \rangle_{p-1,\text{eq}}}{1 + \eta \tanh h_0 \langle \sigma_{p-1} \rangle_{p-1,\text{eq}}}
$$

with the initial condition $\langle \sigma_1 \rangle_{1,\text{eq}} = \tanh h_0$. The set of $N$ linear differential equations in the $N$ variables $\delta \langle \sigma_p \rangle$ can be rewritten in matrix form as

$$
\tau_0 \frac{d\Sigma}{dt} = -Y \cdot \Sigma + h_1 e^{-i\omega t}(1 - \tanh^2 h_0) \Psi.
$$

The $N \times 1$ vector $\Sigma$ has elements $\Sigma_p = \delta \langle \sigma_p \rangle$ ($p = 1, \ldots, N$). $Y$ is a real, symmetric, tridiagonal, $N \times N$ matrix whose nonzero elements are (1 < $p$ < $N$)

$$
Y_{1,1} = 1 + \eta A_{N,1} \tanh h_0, \quad Y_{1,2} = \eta \left( B_{N,1} \tanh h_0 - 1 \right),
Y_{p-1,p} = \frac{\eta}{2} \left( A_{N,p-1} \tanh h_0 - 1 \right), \quad Y_{p,p} = 1 + \frac{\eta}{2} \left( A_{N,p} + B_{N,p} \right) \tanh h_0, \quad Y_{p,p+1} = \frac{\eta}{2} \left( B_{N,p} \tanh h_0 - 1 \right),
Y_{N,N-1} = \eta \left( A_{N,N-1} \tanh h_0 - 1 \right), \quad Y_{N,N} = 1 + \eta B_{N,N-1} \tanh h_0
$$

The $N \times 1$ vector $\Psi$ in Eq. \textsuperscript{[B9]} has elements

$$
\Psi_1 = 1 - \eta \langle \sigma_1 \sigma_2 \rangle_{N,\text{eq}}
$$
This equation can be solved, e.g. using the method of eigenfunctions, as described in Section IV.B.