Hydrodynamic approach to coherent nuclear spin transport

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We develop a linear response formalism for nuclear spin diffusion in a dipolar coupled solid. The theory applies to the high-temperature, long-wavelength regime studied in the recent experiments of Boutis et al. [Phys. Rev. Lett. 92, 137201 (2004)], which provided direct measurement of interspin energy diffusion in such a system. A systematic expansion of Kubo’s formula in the flip-flop term of the Hamiltonian is used to calculate the diffusion coefficients. We show that this approach is equivalent to the method of Lowe and Gade [Phys. Rev. 156, 817 (1967)] and Kaplan [Phys. Rev. B 2, 4578 (1970)], but has several calculational and conceptual advantages. Although the lowest orders in this expansion agree with the experimental results for magnetization diffusion, this is not the case for energy diffusion. Possible reasons for this disparity are suggested.

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I. INTRODUCTION

Spin diffusion occurs for conserved quantities in paramagnetic spin systems. For dipolar-coupled nuclear spins in high external magnetic fields, these quantities are the interaction energy and the spin component along the field. In a solid, diffusive behavior arises from energy-conserving two-spin flips of anti-aligned spins, which produce a dynamics analogous to a random walk. Recent experiments have provided the first direct measurements of magnetization and energy diffusion in a dipolar-coupled spin system. These experiments were carried out on very pure single crystal samples of the insulator calcium fluoride, a substance that has been studied extensively by the NMR community for the past sixty years, and whose structural properties are well known. Calcium fluoride is an ideal material to study because of its very long spin-lattice relaxation time \( T_1 \sim 100 \) s at room temperature in these experiments, its simple structure (the fluorine sublattice is simple cubic), and the high accuracy to which the spin-1/2 nuclei behave as ideal magnetic dipoles. Since the timescale on which diffusion was observed (on the order of seconds) was much shorter than \( T_1 \), the spin system was well isolated and the evolution coherent. This is the regime in which Waugh and co-workers demonstrated that spin diffusion is reversible (by a sign change of an effective Hamiltonian via multiple-pulse NMR methods). Nevertheless, the transport of magnetization in three dimensions appears indistinguishable from an incoherent process, as many calculations and experiments have shown.

In contrast, we find that this does not seem to hold for energy transport, where despite diffusive behavior the use of thermally averaged correlation functions leads to results that are inconsistent with the experiments of Boutis et al.

This paper is organized as follows. In Secs. II and III we outline the linear response formalism for spin diffusion in a dipolar-coupled solid, including a derivation of the energy and magnetization current operators. This formalism applies to the high-temperature, long-wavelength regime studied experimentally. It is equivalent to the density matrix approach of Lowe and Gade and Kaplan (LGK), as we prove in the Appendix. Our formulation has the advantages that the long-wavelength limit is built-in and the application to inter-spin energy is straightforward. In Sec. IV, we derive the expansion of the Kubo formula in powers of the flip-flop term of the dipolar Hamiltonian, which we use for numerical evaluation of the diffusion coefficients. The diffusion coefficients of magnetization and inter-spin energy obtained from this expansion to two leading orders in the flip-flop are given in Sec. V. Their numerical values are calculated in Sec. VI, along with an estimate of the errors. Our main finding is that, although the expansion for the magnetization diffusion coefficient reproduces the experimental results, the series for inter-spin energy does not. In Sec. VII we discuss this result and comment on how our method complements previous approaches to the problem.

II. KUBO FORMULA

The linear response diffusion coefficients of a continuous system may be obtained from Kubo’s formula:

\[
D = \frac{\int_0^\infty dt \int d^3r \int d^3r' \langle j_z(r, t) j_z(r', 0) \rangle_{eq}}{\int d^3r \int d^3r' \langle S(r, 0) S(r', 0) \rangle_{eq}},
\]

where \( S(r) \) is the operator representing the local density of a globally conserved quantity. In our case this is either the energy \( S = \mathcal{H} \) or the component of spin magnetization along an external field \( S = M \), and \( j_z(r) \) is the corresponding current density along the transport direction. The angular brackets denote averaging over an equilibrium statistical ensemble at the appropriate temperature, which is infinite for the case we consider. The discrete version of this formula is more directly applicable to our problem since the spins reside on a lattice, and is given by replacing \( r \) with a lattice site index. However,
the continuum representation is more useful for derivations, and is completely equivalent.

Eq. (11) is the correct formula for the diffusion coefficient of the quantity $S$ if the following assumptions hold.

(1) The correlation function of $S$ is known to have a diffusive form (i.e. a diffusive pole).

(2) The system may at all times be described by a statistical ensemble that is sufficiently close to equilibrium (linear response regime).

Assumption (1) may be checked experimentally, and has been verified for both spin-spin and energy-energy correlators of dipolar-coupled spins in a solid. Assumption (2) is more subtle, as it rests on the validity of the ergodic hypothesis, which has received much attention recently in the context of lattice spin systems in dimensions 1 − 3. As discussed below, we believe that it may not be valid for the diffusion of energy.

Experimentally, spin diffusion has been measured by observing the relaxation of initial states varying sinusoidally in real space with a given wavevector $k$. Spatially-inhomogeneous states are represented mathematically as perturbations on the infinite temperature equilibrium state, $\rho_\infty = 1/2N$, where $N$ is the number of spins. We have

$$\rho(0) = \rho_\infty + \delta \rho(0).$$  (2)

Two possibilities exist for $\delta \rho(0)$, corresponding to long-wavelength fluctuations in the two conserved quantities,

$$\delta \rho_M(k,0) = \epsilon \int d^3r \cos(k \cdot r) M(r),$$  (3)

$$\delta \rho_H(k,0) = \epsilon \int d^3r \cos(k \cdot r) H(r),$$  (4)

where $\epsilon$ is a small quantity of order $\gamma h B_0/2N k_B T$. Here $B_0$ is the external field, and $\gamma$ is the gyromagnetic ratio of the nuclear species of interest ($\gamma = 2.51 \times 10^4$ Hz/Oe for $^{19}$F). Using typical experimental values of $B_0 = 1$ T, $T = 300$ K, we estimate $\epsilon \sim 10^{-5} - 10^{-6}$. The important length scales are related by $L >> k^{-1} >> a$, where $L$ is the sample size and $a$ is the lattice spacing. $a = 2.73 \times 10^{-8}$ cm for the Fluorines in CaF$_2$, and $L \sim 0.1$ cm, $k^{-1} \sim 10^{-4}$ cm in the experiments. The realization of such states is discussed in detail by Boutis et al. In practice, $k$ is parallel to the external magnetic field, and transport is measured in the same direction. As shown in the Appendix, expectation values taken with respect to the states in Eqs. (2) and (3) give rise to the equilibrium-averaged correlation functions appearing in Eq. (11).

We find it plausible that assumption (2) is valid when the spatial profile of magnetization or energy in the initial state varies sufficiently slowly, and when this state has no long range correlations. While this is possible for magnetization, the creation of spatial inhomogeneities in the interaction energy requires NMR techniques that introduce short - ranged correlations between the spins. Some of these correlations persist due to energy conservation, and these are the ones relevant to energy transport. Other correlations are assumed to decay rapidly and to be unobservable. A careful analysis of the initial state involved in the energy diffusion measurements is needed to determine whether assumption (2) is satisfied. On the other hand, the extent to which our results agree with experiment may be viewed as a constraint on its validity.

### III. CURRENT OPERATORS

In order to use Eq. (11) we need to obtain expressions for the current operators $j_i(r)$. We start with the rotating – frame Hamiltonian of interacting magnetic dipoles in a large external magnetic field.

$$\mathcal{H} = \sum_{i,j(i\neq j)} \mathcal{H}_{ij},$$  (5)

$$\mathcal{H}_{ij} = b_{ij} \left( I_{iz} I_{jz} - \frac{1}{4} (I_i + I_j + I_i - I_i + I_j - I_j) \right).$$  (6)

The Latin indices run over all lattice sites and the $I_{ij}$ are operators for spin-1/2, satisfying the commutation relations $[I_{i\alpha}, I_{j\beta}] = \delta_{ij} \hbar \gamma$, where $\alpha, \beta, \gamma$ is any cyclic permutation of $x, y, z$. The $I_{ij} \equiv I_{jz} \pm i I_{jy}$ are raising and lowering operators. The coupling constants are given by

$$b_{ij} = \frac{\gamma \hbar^2}{2} - \frac{3 \hbar^2}{r_{ij}^3},$$  (7)

where $r_{ij}$ is the displacement vector between lattice sites $i$ and $j$, and unit vectors are denoted by a caret. We take the $z$-direction to be along the external magnetic field.

The total $z$-component of spin and total energy are conserved quantities of the Hamiltonian, Eqs. (5) and (6). This implies that they satisfy a local continuity equation. We define spin and interaction energy densities that depend on continuous variables.

$$I_\alpha(r,t) \equiv \sum_i \delta(r - r_i) I_{i\alpha}(t), \quad \alpha = z, +, -$$  (8)

$$\mathcal{H}(r,t) \equiv \sum_{i,j(i\neq j)} \delta(r - r_i) \mathcal{H}_{ij}(t).$$  (9)

The operators in these equations and throughout this section are in the Heisenberg representation.

The densities of magnetization and interaction energy are given in terms of the spin densities as

$$M(r) = \gamma \hbar z(r),$$  (10)

$$\mathcal{H}(r) = \int d^3r' \delta(r - r') \{ I_z(r) I_z(r') - \frac{1}{4} [I_z(r) I_i(-r') + I_i(r') I_i(-r)] \}.$$  (11)
where $b(r - r') = \sum_{i,j} \delta(r - r_i) \delta(r' - r_j) b_{ij}$. We avoid writing the time dependence of the operators where there is no possibility of confusion. Next, we use the Heisenberg equation of motion,

$$\frac{\partial M(r, t)}{\partial t} = -\frac{i}{\hbar}[M(r, t), H],$$

$$\frac{\partial H(r, t)}{\partial t} = -\frac{i}{\hbar}[H(r, t), H],$$

and to obtain

$$\frac{\partial M(r)}{\partial t} = \frac{i\hbar}{2} \int d^3r' b(r - r') (I_+(r) I_- (r') - I_+(r') I_- (r)),$$

$$\frac{\partial H(r)}{\partial t} = -\frac{i}{\hbar} \int d^3r' d^3r'' b(r' - r) b(r'' - r') \times \{I_+(r') [I_+(r) I_-(r') - I_+(r') I_- (r)] + 2I_z(r) [I_+(r') I_-(r'') - I_+(r'') I_-(r')] + 2I_z(r') [I_+(r) I_-(r') - I_+(r') I_- (r)]\}.$$

In order to write Eqs. (14) and (15) as continuity equations, they may be integrated over an arbitrary volume and the result expressed in terms of a surface integral, whose integrand is the current density. This gives the current density operators,$

j^{(M)}(r, t) = \frac{i\hbar}{2} \int d^3r' b(r - r')(r' - r') \times \{I_+(r') I_-(r') - I_+(r') I_- (r)\},$

$$j^{(H)}(r, t) = \frac{i}{8} \int d^3r' d^3r'' b(r' - r) b(r'' - r') \times \{I_+(r') [I_+(r) I_-(r'') - I_+(r'') I_- (r)] + 2I_z(r) [I_+(r') I_-(r'') - I_+(r'') I_- (r')] + 2I_z(r') [I_+(r) I_-(r') - I_+(r') I_- (r)]\}.$$

where the superscripts $M$ and $H$ denote magnetization and energy current, respectively. The continuity equations then take their usual form,

$$\frac{\partial S(r, t)}{\partial t} + \nabla \cdot j^{(S)}(r, t) = 0, \quad S = M, H.$$

Similar results have been obtained by Furman and Goren by a different method.\textsuperscript{24,25}

IV. PERTURBATION THEORY

Using an interaction representation introduced by Lowe and Norberg,\textsuperscript{26} we can expand Eq. (11) in powers of the flip-flop term of the Hamiltonian. Following Ref. 13 we define

$$H_1 = \sum_{i,j(i\neq j)} b_{ij} I_i z I_j z,$$

$$H_2 = -\frac{1}{4} \sum_{i,j(i\neq j)} b_{ij} (I_i + I_j - + I_i - I_j +).$$

Using the notation $\tilde{A}(t) = e^{-iH_1 t/\hbar} A(0) e^{iH_1 t/\hbar}$, we may write any operator in the Heisenberg representation as an infinite series in $H_2$,

$$A(t) = e^{iH_1 t/\hbar} \left\{ A(0) + \frac{i}{\hbar} \int_0^t dt_1 [\tilde{H}_2(t_1), A(0)] + \left( \frac{i}{\hbar} \right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 [\tilde{H}_2(t_1), [\tilde{H}_2(t_2), A(0)]] + \cdots \right\} e^{-iH_1 t/\hbar}.$$

Using this expansion for $j_z(t)$ in Eq. (1) gives a perturbation series for the diffusion coefficient.

$$D = \left( \int_0^\infty dt \langle j_z(0) j_z(t) \rangle \right) + \frac{i}{\hbar} \int_0^\infty dt \int_0^t dt_1 \langle [\tilde{H}_2(t_1), j_z(0)] j_z(t) \rangle + \left( \frac{i}{\hbar} \right)^2 \int_0^\infty dt \int_0^t dt_1 \int_0^{t_1} dt_2 \langle [\tilde{H}_2(t_1), [\tilde{H}_2(t_2), j_z(0)] \rangle + \cdots \right) / \langle S(0)^2 \rangle,$$

where the spatial integrations have been suppressed, and angular brackets denote an equilibrium average. The operators $\tilde{H}_2(t)$ and $\tilde{j}_z(t)$ can be evaluated using the identity.\textsuperscript{13,26}

$$\exp \left( it \sum_{m,n(m\neq n)} b_{mn} I_m z I_n z \right) I_i + I_j \exp \left( -it \sum_{m,n(m\neq n)} b_{mn} I_m z I_n z \right) = I_i + I_j - L_{ij}(t),$$

where

$$L_{ij}(t) = \prod_{l(l\neq i,j)} e^{2it(b_{il} - b_{lj}) I_l z}.$$\textsuperscript{24}

It is advantageous to approximate the operator $L_{ij}(t)$ by a c-number, equal to its thermal average, $L_{ij}(t) \approx G_{ij}(t)$. At infinite temperature,

$$G_{ij}(t) = \prod_{m(m\neq i,j)} \cos(b_{im} - b_{jm}) t.$$\textsuperscript{25}

The neglected q-number terms are expected to be approximately $20 - 25\%$ smaller, as discussed at the end of Sec. IV.

It turns out that $G_{ij}(t)$ depends very weakly on its indices. In order to make the calculation of higher order terms in the perturbation series tractable, we therefore replace $G_{ij}(t)$ by $G(t)$. $G$ is a suitably defined average over all the $G_{ij}$’s, as discussed in Sec. VI. The overall error introduced by approximating the higher order terms in this way is therefore small (we shall see in Sec. VI that it is less than 10%). The resulting perturbation series
contains only even-order terms,

\[ D = \sum_{n=0}^{\infty} \left( \frac{1}{n!} \right) F^{2n+1} \frac{\langle \mathcal{H}_{ij}(t_0) \rangle^2}{(2n+1)! (S(0)^2)^n}, \]  

\[ F = \int_0^{\infty} G(t) \, dt, \]  

where \([A, B]_n \equiv [A, [A, ..., [A, B]_n]]\) is a commutator with \(A\) taken \(n\) times. It is worth noting that this series may be written in a simple closed form,

\[ D = \int_0^F dF' \langle e^{iH_2F'/h} \mathcal{J}_0(0) e^{-iH_2F'/h} \mathcal{J}_0(0) \rangle / (S(0)^2), \]  

which shows that our system is approximately equivalent to one with purely flip-flop interaction, evolving for a finite time, \(F\).

V. ANALYTICAL RESULTS

In this section we give analytic expressions for the diffusion coefficients to the two leading orders using Eq. 22 and 20. We are interested in the infinite temperature case. Therefore, \(\langle \cdots \rangle_{eq} = \text{tr} \langle \cdots \rangle / 2^N\), where \(N\) is the number of lattice sites. Each term in Eq. 20 then contains a trace over a product of spin operators at different lattice sites. The evaluation of such traces is a tedious but straightforward task. We do not discuss it further here.

A. Magnetization Diffusion

The denominator of Eq. 11 for \(S = M\) at \(T = \infty\) is \(\int d^3r \int d^3r' \mathcal{H}(r, 0) M(r', 0) / 2^N = N\gamma^2 h^2 / 4\).

The lowest order term is calculated exactly, by inserting the expressions for the Hamiltonian, Eq. 12, and the magnetization current, Eq. 15, into the first line of Eq. 22, and applying the identity, Eq. 20. We obtain

\[ D_M^{(0)} = \frac{1}{4} \sum_{i \neq 0} b_{0i}^2 \zeta_i^2 F_{0i}, \]  

\[ z_{ij} = z_i - z_j, \]  

where \(F_{ij}\) is given by Eq. 21 with \(G_{ij}(t)\) replacing \(G(t)\). The lattice site labelled 0 is arbitrary, due to the translational invariance of an infinite lattice. This result is identical to LGK’s, as expected from the equivalence of the two methods (see Appendix).

The next term, obtained from Eq. 20, using all of the approximations discussed in the last section, is

\[ D_M^{(2)} = \frac{1}{8} F^3 \left( 2 \sum_{i \neq 0} b_{0i}^2 \zeta_i^2 - \sum_{i, j, (i, j) \neq 0} b_{0i}^2 b_{0j}^2 \zeta_i^2 \zeta_j^2 \right). \]  

B. Energy Diffusion

For \(S = \mathcal{H}\), the denominator is \(\int d^3r \int d^3r' \text{tr} \{ \mathcal{H}(r, 0) \mathcal{H}(r', 0) \} = (3/16) \times 2^N \times \sum_{i, j (i \neq j)} b_{ij}^2\). The lowest order term is

\[ D_\mathcal{H}^{(0)} = \frac{1}{48} \sum_{i, j (i \neq j)} b_{ij}^2 \left( \sum_{i, k (i \neq k)} B_{ij}^2 F_{ik} \right), \]  

where

\[ B_{ij} \equiv b_{ij} b_{jz} z_i + 2 b_{ij} b_{kz} z_j + 2 b_{ik} b_{jk} z_i. \]  

\[ R_{kl,ij} = \int_0^{\infty} dt K_{kl,ij}(t), \]  

\[ K_{kl,ij}(t) = -4 \text{tr} \{ I_z I_z L_k(t) \} \sin(\Delta_{k\ell,t}) \sin(\Delta_{kj,t}) \cos(\Delta_{kl,t}). \]  

\[ \Delta_{k\ell,p} = b_{pk} - b_{pl}. \]

It is useful to have approximate analytic expressions for the integrals in Eq. 22 and Eq. 20. It has been shown that the saddle point approximation to \(F_{ij}\) is quite accurate. It is equivalent to replacing \(G_{ij}\) in the integrand by a Gaussian,

\[ G_{ij}(t) \approx \exp \left( -\frac{1}{2} \sum_{k (k \neq i, j)} (b_{ki} - b_{kj})^2 t^2 \right). \]

To evaluate \(R_{kl,ij}\), we replace the product of cosines in \(K_{kl,ij}(t)\) by a Gaussian, as above. Since this Gaussian cuts off the integral at times \(t \ll h / b\), where \(b\) is of the order of the nearest neighbor coupling strength, we can expand the sine terms around \(t = 0\), which yields

\[ K_{kl,ij}(t) \approx (b_{ik} - b_{id})(b_{jk} - b_{jd}) t^2 \]  

\[ \times \exp \left( -\frac{1}{2} \sum_{p (p \neq i, j, k, l)} (b_{pk} - b_{pl})^2 t^2 \right). \]

These approximations give

\[ F_{ij} = \frac{\sqrt{\pi}}{\sqrt{2} \sum (k (k \neq i, j)) (b_{ki} - b_{kj})^2} \]  

\[ R_{kl,ij} = \frac{\sqrt{\pi}}{2} \left( \frac{b_{ik} - b_{id})(b_{jk} - b_{jd})}{(b_{pk} - b_{pl})^2 \sum (p (p \neq i, j, k, l)) (b_{pk} - b_{pl})^2} \right)^{3/2}. \]

Equation 48 has been derived previously.13,14 Equations 13 and 14 allow a more rapid numerical evaluation of the expressions for the diffusion coefficients than
by numerical integration of Eqs. (25) and (31). By numerical integration on cubic lattices of between 5³ and 11³ spins, we have verified that Eq. (25) approximates the exact value with an error that is less than 2% and Eq. (31) approximates the exact value to within 10%.

We found numerically that the sum over R terms in Eq. (29) was about 20 – 25% in magnitude of the sum over F terms, for both the (001) and (111) directions. The R terms arise from the lowest order (in $L_{ij}$) q-number correction to the approximation, Eq. (25), to $L_{ij}(t)$. We therefore expect this same number to also be a good estimate of the error in this approximation.

Using Eq. (26) for the next order term, we obtain

$$D^{(2)}_{ij} = \frac{F^3}{(3!)(192)} \sum_{k,l,(k\neq l)} b_{kl}^2 \times \left( \sum_{u,q,l}(u \neq q \neq l) \left[ b_{uq}^2 - B_{qkl}^2 + 2B_{kql}B_{kul} \right] + b_{uq}b_{kl} - 4B_{uql}B_{qul} + 6B_{uql}B_{qkl} + 3B_{ukl}B_{qkl} - 3B_{uql}B_{qul} + b_{uq}b_{kl} \right)$$

VI. NUMERICAL RESULTS

Because Eqs. (29), (31), (32), and (40) can be evaluated numerically only for finite lattice sizes, we use finite size scaling to extract the infinite lattice limit. The approach to the infinite lattice value is expected to follow a power law. For example, if we approximate the sums by integrals in Eq. (29),

$$D^{(0)}_{ij} \approx \frac{1}{4} \int_{a \leq r \leq L} d^3r b(r)^2 z^2 F(r).$$

As $r \to \infty$, $F \to \text{const}$. Therefore,

$$D^{(0)}_{ij} \sim \text{const} \times \int_{a}^{L} r^2 dr \left( \frac{1}{r^2} \right)^2 r^2 = \text{const} \times \frac{1}{a^2} \left( \frac{1}{L} \right).$$

A least squares fit to a power law describes very well the scaling with finite lattice size. For diffusion of magnetization, we were able to vary the lattice size, in increments of 2 lattice sites, between 1 and 81 lattice sites on an edge. For energy diffusion, we studied lattices with up to 27 sites on an edge.

The constant $F$ in Eqs. (31) and (40) was taken as the mean value of the $F_{ij}$ over three layers of nearest neighbors. This averaging procedure works well since contributions from far-apart indices are suppressed by the $b$ factors in the summations. In dimensionless units, this gave

$$\frac{\gamma^2 \hbar}{a^2} \times F = \{ 0.48 \pm 0.05, \text{(001) direction}, 1.17 \pm 0.14, \text{(111) direction}. \}$$

The error, taken to be one standard deviation from the mean, is 10% for the (001) direction and 12% for the (111) direction. Therefore, the error in $F^3$ is about three times as much, or between 30% and 40%. As the magnitude of the second order terms is between 10% and 20% that of the zero order terms, the overall error in approximating $F_{ij} \approx F$ is less than 10%.

The results, including errors due to fitting and approximations, are summarized in Table I. Our magnetization diffusion coefficient agrees well with experimental values. However, the energy diffusion coefficient that we obtain is significantly smaller than observed experimentally, albeit larger than the magnetization diffusion coefficient. The relative orientation dependence is within the experimental range for magnetization, but disagrees drastically for energy.

### Table I: Summary of the theoretical and experimental results for the spin diffusion rate of energy, $D_M$, and magnetization, $D_N$, for a single crystal of calcium fluoride. Theoretical values have been obtained by numerically evaluating Eqs. (29) and (40), and Eqs. (29) and (31), using Eq. (25) for $F_{ij}$ and Eq. (30) for $R_{ikmj}$, and using finite size scaling to extrapolate to the infinite lattice limit.

| Theory | [001] | [111] | $D_{001}/D_{111}$ |
|--------|-------|-------|-------------------|
| $D^{(0)}_{M}$ | $(10^{-12}\text{cm}^2/\text{s})$ | 8.4 ± 0.2 | 7.9 ± 0.2 |
| $D^{(0)}_{N}$ | $(10^{-12}\text{cm}^2/\text{s})$ | -0.3 ± 0.1 | -0.5 ± 0.2 |
| $D^{(1+2)}_{M}$ | $(10^{-12}\text{cm}^2/\text{s})$ | 8.1 ± 0.3 | 7.4 ± 0.4 |
| $D^{(1+2)}_{N}$ | $(10^{-12}\text{cm}^2/\text{s})$ | 19.8 ± 0.7 | 12.5 ± 0.3 |
| $D^{(1+2)}_{N}$ | $(10^{-12}\text{cm}^2/\text{s})$ | -0.7 ± 0.3 | -1.1 ± 0.5 |
| $D^{(0)}_{H}$ | $(10^{-12}\text{cm}^2/\text{s})$ | 19.1 ± 1.0 | 11.4 ± 0.8 |
| $D^{(1+2)}_{H}$ | $(10^{-12}\text{cm}^2/\text{s})$ | 29 ± 3 | 33 ± 4 |

VII. CONCLUSION

We have presented a hydrodynamic approach to study the long-wavelength spin dynamics in a lattice of dipolar-coupled spins-1/2 in high magnetic field and at high temperature, motivated by recent experiments on coherent nuclear spin transport in calcium fluoride. The Kubo formula, Eq. (11), for the diffusion coefficients applies to the physical regime probed experimentally and rests on the assumption that the time evolution of the system is ergodic. We developed a perturbation theory for Eq.
that is equivalent to the approach of LGK but simplifies the calculations enormously. This allowed us to obtain the diffusion coefficients for magnetization as well as energy to leading order in the flip-flop term of the Hamiltonian, and estimate the first perturbative correction. The result for magnetization diffusion agrees with experiment to within its degree of accuracy. The result for inter-spin energy diffusion is larger than that for magnetization diffusion, in qualitative agreement with the experiment. It does not, however, describe the experiment quantitatively.

One possible reason for the disparity is the ergodicity assumption, which is implicit in our choice of how to take the average in the correlation functions appearing in Eq. (1). Our assumption of Eq. (2) leads to the equivalence of the non-equilibrium average of the conserved density to its equilibrium correlation function, as is usual in linear response theory. For magnetization diffusion, the low polarization results in a very low density of polarized spins in a completely randomly polarized background. The sparsity of polarized spins means that their effect on each other is negligible, and they can be treated as independent. This suggests that statistical averaging over a complete infinite temperature ensemble is the correct procedure. For energy diffusion, the correlations inherent to the initial states used in the experiments of Boutis et al. may require the use of an ensemble that is a subset of the full Hilbert space. This would imply a modification of Eq. (2) for the density matrix at finite time, and needs to be investigated further.

The most evident source of inaccuracy in our calculation is our truncation of the perturbation series. Our estimate of the next-to-leading order correction to energy diffusion does not rule out the possibility that a resummation of our perturbation series would explain the experiment quantitatively. However, currently available non-perturbative (e.g. Bennet and Martin) and resummation (e.g. Borckmans and Walgraef) methods are much too cumbersome to treat the diffusion of inter-spin energy. They are also plagued by their own uncontrolled approximations, such as the ad-hoc replacement of certain correlation functions by gaussians in order to simplify the calculations. This state of affairs, coupled with the great success of LGK at predicting the magnetization diffusion coefficient based on an expansion in the flip-flop term, and earlier that of Lowe and Norberg at fitting the shape of the FID by a similar expansion, motivated us to systematize their approach and apply it to inter-spin energy diffusion. For the final word on this problem, we await either a new non-perturbative method or a tractable technique for summing our perturbation series to all orders.

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APPENDIX: EQUIVALENCE TO LGK METHOD

LGK compute the time evolution of the average density, \( \langle S(k, t) \rangle = \text{tr} \{ \delta \rho(-k, t) S(k) \} \), starting from one of the non-equilibrium states, Eq. (3) or Eq. (4). In general, we write

\[
\delta \rho(t = 0) = \epsilon \int d^3r \cos(k \cdot r) S(r) = \frac{\epsilon}{2} S(k) + \frac{\epsilon}{2} S(-k). \tag{A.1}
\]

The average of any Schrödinger operator \( A \) at time \( t \) is

\[
\langle A(t) \rangle = \text{tr} \{ \delta \rho(t) A \}. \tag{A.2}
\]

If \( \langle S(r, t) \rangle \) satisfies a diffusion equation,

\[
\frac{\partial}{\partial t} \langle S(r, t) \rangle = D \nabla^2 \langle S(r, t) \rangle, \tag{A.3}
\]

then the time dependence of \( \langle S(k, t) \rangle \) [the Fourier transform of \( \langle S(r, t) \rangle \) at wavevector \( k \)] is given by

\[
\frac{\partial}{\partial t} \langle S(k, t) \rangle = -D k^2 \langle S(k, t) \rangle \implies \langle S(k, t) \rangle = e^{-k^2Dt} \langle S(k, 0) \rangle. \tag{A.4}
\]

Taking the time derivative of the last equation and rearranging terms, we obtain LGK’s expression for the diffusion coefficient,

\[
D = \lim_{k \to 0} \left( \frac{1}{k^2} \frac{\langle \dot{S}(k, t) \rangle}{\langle S(k, 0) \rangle} \right). \tag{A.5}
\]

The right hand side is in fact independent of time for \( t \) greater than the short timescale defined by the inverse spin-spin coupling. We keep the explicit time dependence to remind us that \( t \) is long, but finite, while \( k \) tends to zero. In other words, we take the \( t \to \infty \) limit after the \( k \to 0 \) limit.

In the Heisenberg representation, we have

\[
\langle S(k, t) \rangle = \text{tr} \{ e^{-i\mathcal{H}t} \delta \rho(0) e^{i\mathcal{H}t} S(k) \} = \frac{\epsilon}{2} \text{tr} \{ S(k, -t) S(k, 0) \} + \frac{\epsilon}{2} \text{tr} \{ S(-k, -t) S(k, 0) \}. \tag{A.6}
\]

Because of translational invariance, only the second term on the right side of Eq. (A.6) contributes, and we have

\[
\langle S(k, t) \rangle = \frac{\epsilon}{2} \text{tr} \{ S(-k, -t) S(k, 0) \}. \tag{A.7}
\]

We take the time derivative of Eq. (A.7), and use \( \partial S(t)/\partial t = i[\mathcal{H}, S(t)] \), to find

\[
\langle \dot{S}(k, t) \rangle = -\frac{\epsilon}{2} \text{tr} \{ e^{-i\mathcal{H}t}[\mathcal{H}, S(-k, 0)] e^{i\mathcal{H}t} S(k, 0) \}. \tag{A.8}
\]
\[ = -\frac{\epsilon}{2} \text{tr} \{ \dot{S}(-k,0)S(k,t) \} \]
\[ = -\frac{\epsilon}{2} \int_0^t dt' \text{tr} \{ \dot{S}(-k,0)S(k,t') \} \]
\[ -\frac{\epsilon}{2} \text{tr} \{ \dot{S}(-k,0)S(k,0) \}. \quad (A.8) \]

The second term on the right-hand side of the last equation vanishes. Substituting the continuity equation,
\[ \dot{S}(k,t) + i k \cdot \mathbf{j}(k,t) = 0, \]
and taking \( k = k \hat{z} \), we obtain
\[ \langle \dot{S}(k,t) \rangle = -\frac{\epsilon}{2} k^2 \int_0^t dt' \text{tr} \{ j_z(k,t')j_z(-k,0) \}. \quad (A.9) \]

According to Eq. \[ A.6 \], we further have
\[ \langle S(k,0) \rangle = \frac{\epsilon}{2} \text{tr} \{ S(k,0)S(-k,0) \}. \quad (A.10) \]

Substituting Eqs. \[ A.9 \] and \[ A.10 \] into Eq. \[ A.5 \] gives
\[ D = \lim_{k \to 0} \int_0^t dt' \frac{\text{tr} \{ j_z(k,t')j_z(-k,0) \}}{\text{tr} \{ S(k,0)S(-k,0) \}}. \quad (A.11) \]

Taking the limit \( t \to \infty \), we obtain the standard form of the Kubo formula, Eq. \[ 1 \], which proves the equivalence of the two approaches.

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