Dynamical structure factor of the three-dimensional quantum spin liquid candidate NaCaNi$_2$F$_7$

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We study the spin-1 pyrochlore material NaCaNi$_2$F$_7$ with a combination of molecular dynamics simulations, stochastic dynamical theory and linear spin wave theory. The dynamical structure factor from inelastic neutron scattering is well described with a near-ideal Heisenberg Hamiltonian incorporating small anisotropic terms and weak second-neighbor interactions. We find that all three approaches reproduce remarkably well the momentum dependence of the scattering intensity as well as its energy dependence with the exception of the lowest energies. These results are notable in that (i) the data show a complete lack of sharp quasiparticle excitations in momentum space over much, if not all, of the energy range; (ii) linear spin-wave theory appears to apply in a regime where it would be expected to fail for a number of reasons. We elucidate what underpins these surprises, and note that basic questions about the nature of quantum spin liquidity in such systems pose themselves as a result.

Introduction: Quantum spin liquids [1] are enigmatic phases of matter characterized by the absence of symmetry breaking and conventional quasiparticles (magnons). The search for their realisation in actual magnetic materials has targeted, but is not limited to, materials involving the geometrically frustrated [2] triangular, kagome [3] and pyrochlore [4] geometries with low spins.

Indeed, while there have been significant efforts to synthesise quantum spin liquid materials in spin-1/2 systems in two dimensions, fewer efforts have been devoted to three dimensions, see Ref. [3] for a review. This strategic choice is not without reason: high lattice coordination number and high spin typically suppress quantum fluctuations, and thus in particular favor conventional forms of magnetic order over quantum spin liquids in three dimensions. However, it is now clear that this perspective is too pessimistic: as a matter of principle, we know that certain types of spin liquid – in particular, Coulombic U(1) spin liquids – can exist in $d = 3$ but not in $d = 2$ [5, 6]; and as a matter of practice, it looks as if quantum spin liquid phases need by no means be restricted to $S = 1/2$ exclusively [7].

Despite several recent advances in the field, however, our understanding of the actual properties of low-spin Heisenberg spin liquids in three dimensions is very limited, as they are beyond the scope of practically all exact or controlled approximate theoretical schemes. We are at a loss to describe either their ground states or excitation spectra, unlike Ising models like spin ice, where the simplest quantum versions [5, 6] are amenable to quantum Monte Carlo (QMC) simulations [8, 9]. Experimental data is therefore a particularly indispensable guide for our understanding of these magnets, for an early review see [10].

In the quest to identify quantum spin liquids in real materials [11], one relies heavily on characteristic signatures in the magnetic excitation spectra, as their ground states are often largely featureless. By contrast, the excitations of spin liquids can be downright spectacular, including in particular fractionalised [12] and other unusual emergent quasiparticles such as spinons in the spin-1/2 Heisenberg antiferromagnet chain [13–15], Majorana fermions in the Kitaev honeycomb model [16–18], and magnetic monopoles [19] and photons in the U(1) spin liquid [5, 6, 9].

The dual challenge is thus to identify novel behaviour in experimental data on candidates quantum spin liquid materials in $d = 3$, and to devise a theoretical framework for understanding the underlying behaviour. Here, we report progress for the fluoride pyrochlore NaCaNi$_2$F$_7$ [20], a prime $S = 1$ quantum spin liquid candidate.

In NaCaNi$_2$F$_7$, the magnetic Ni$^{2+}$ ions reside on the three-dimensional pyrochlore lattice (Fig. 1), where what little is known theoretically about quantum Heisenberg models for $S = 1/2$ and $S = 1$ points towards quantum spin liquid behavior [7, 21], while the classical case is well-established to be a Coulomb spin liquid [22–24], whose many-body dynamics is by now fairly well understood [23–25].

We analyze the magnetic excitation spectrum obtained by inelastic neutron scattering on NaCaNi$_2$F$_7$ in Ref. [26], which we supplement with new data from a different experiment. We present three tractable complementary theoretical approaches that reproduce the dynamical structure factor $S(q, \omega)$ for all momenta $q$ and for a broad range of energies $\omega$. At the highest energies, the quality of the agreement differs between models (and becomes harder to assess on account of a considerable phonon background). At low energies, we find the well-known pinch-point motifs, while at intermediate energies, characteristic structures complementary to the pinch points appear [27, 28]. Overall, the main disagreement between experiment and theory appears at the lowest energies, as discussed below.

In the light of the abovementioned challenges posed by three-dimensional quantum spin liquids, the capacity of our relatively simple approaches to yield a wide-ranging account of the observed dynamics is as striking as it is encouraging for the study of other yet unexplored systems and models in this class. We therefore include a discussion of the broader implications of our results about the nature of the quantum dynamics in such a setting, which we believe may be of importance well beyond the material studied here.
The dynamical structure factor obtained experimentally for the pyrochlore NaCaNi$_2$F$_2$ is presented in the form of a comparison of scattering intensities as a function of momentum (Fig. 2) and energy (Figs. 3, 4). Besides their interpretation and discussion, for the methodologically interested reader, we collate all necessary technical information in a set of self-contained technical appendices.

**Model and methods:** We use the Hamiltonian (Fig. 1)

\[ H = \frac{1}{2} \sum_{ij} \sum_{\mu\nu} J_{ij}^{\mu\nu} \mathbf{s}_i^{\mu} \cdot \mathbf{s}_j^{\nu}, \]

where subscripts $i$ and $j$ refer to lattice sites and superscripts $\mu$ and $\nu$ refer to Cartesian components of spins in the global frame. The interaction matrix is parameterized by four exchange parameters between nearest neighbors $J_{01} = (J_2, J_3, J_4; -J_1, J_3, -J_4, J_1)$ with $J_1 = J_2 = 3.2(1)$ meV, $J_3 = 0.019(3)$ meV, $J_4 = -0.070(4)$ meV, and isotropic between next-nearest-neighbors $J_{NNN} = -0.025(5)$ meV, obtained by fitting to the equal-time correlations by some of us in a previous study [26]. The interaction matrices for other pairs follow from appropriate symmetry transformations.

The methods utilized are, firstly, molecular dynamics (MD) simulations of the pyrochlore magnet [23] where the semi-classical Landau-Lifshitz equations of motion for the spins are integrated numerically, averaged over initial conditions obtained from Monte Carlo simulations of our Hamiltonian at the temperature $T = 1.8$ K. Secondly, we employ a self-consistent Gaussian approximation adapted to frustrated magnets [30] and extended into a stochastic model for their dynamics by Conlon and Chalker [25], which we refer to as stochastic large-$N$ (SLN). Thirdly, we use the linear spin-wave theory (LSWT) to describe spin dynamics near a low-energy state (again averaged over an ensemble obtained from Monte Carlo simulations). Details of these are provided in the appendix.

The central object of investigation are the dynamical spin correlations as captured by the structure factor in dynamical-momentum space

\[
S(\mathbf{q},\omega) = \sum_{\mu\nu}(\delta_{\mu\nu} - \frac{q_{\mu}q_{\nu}}{q^2}) \\
\times \frac{1}{2\pi N} \sum_{i,j=1}^N \int_{-\infty}^\infty dt e^{-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} e^{i\omega t} \langle \mathbf{s}_i^{\mu}(t) \mathbf{s}_j^{\nu}(0) \rangle.
\]

The classical expression is given above and the quantum expression is sensitive to time order of the spin operators (see Appendix A 2). Throughout this work, we rescale the two "classical" approaches MD and SLN by $\beta\omega$ to make comparison with LSWT. The factor essentially arises from the classical equipartition-based suppression of the low-$T$ intensity, as opposed to the non-vanishing matrix elements in the quantum case, see Eq. (A21).

**Results:** The dynamical structure factor obtained experimentally and by the three theories is depicted as a function of wavevector in a set of cuts at various energies, Fig. 2, and as a function of energy along a set of paths through reciprocal space, Fig. 3.

Fig. 2 displays normalized momentum cuts in the [HHL] and [HL0] planes at energies 0.5, 2, 4 and 8 meV. At low energies, the pinch points characteristic of Heisenberg pyrochlore magnets are clearly visible. This is in itself interesting, as the presence of well-defined pinch points implies that each tetrahedron has vanishing total magnetization [31, 32]. In general, however, adjacent tetrahedra cannot both be in spin singlet states, as their total spin operators do not commute. Therefore, while for the classical theories, the pinch points sharpen as $\sqrt{T}$ as $T$ is lowered [33], for $S = 1/2$ they were found to be quite smeared out [21], becoming sharper as $S$ increases. For $S = 1$, a theoretical prediction for the full-width at half maximum of the pinch point in the static correlations at [002] (located at $(0, 0, 4\pi)$ in reciprocal space) of $\mathbf{q}_{FWHM}^S = 4\pi/3$ is comparable to the value $\pi$ extracted from the low-$T$ experimental data.

As the energy increases, the overall intensity distribution changes little initially, but whatever sharp features were present wash out; e.g., the intensity minimum in the scattering rhombus around [202] is slowly filled in and the pinch points broaden. At higher energies, the experimental signal is increasingly polluted by the phonon background at large $q$, but it is still possible to identify a qualitative rearrangement of the weight, especially in the [HHL] data, with the area around the pinch-points growing into prominent pairs of "half-moons" features at 8 meV. These have recently been identified as a dispersing complement to the pinch points [27, 28]. This feature is present in MD and LSWT, but not in SLN, which is relaxational and does not capture the spin precession at high frequencies.

We next turn to the energy dependence of the data, depicted in Fig. 3, with additional cuts from a different neutron instrument (see Appendix C) presented in Fig. 4. The general shapes of experiment and MD/LSWT are very similar—a broad signal with a vertical appearance reminiscent of a foun-
We next address several more general questions arising from our central observation of what we believe is remarkable agreement between theory and experiments at all but the lowest energies on one hand, and between MD and LSWT on the other. We start with the latter, which is quite unremarkable: the spin length, $S = 1$, really is not particularly large in our setting, so that one would generically expect at least considerable quantum renormalization effects, all the more so since the classical local exchange field, a central feature in suppressing fluctuations, is reduced as a result of geometric frustration.

Discussion: We next address several more general questions arising from our central observation of what we believe is remarkable agreement between theory and experiment at all but the lowest energies on one hand, and between MD and LSWT on the other. We start with the latter, which is quite unexpected: the $S = 1$ Heisenberg pyrochlore antiferromagnet unifies several reasons why LSWT should break down. In- stead, it works (un)reasonably well, as evidenced in the comparison by eye with experiment as well as in the detailed quantitative agreement with MD, Fig. 4. The inauspicious ingredients are, firstly, the absence of a state with long-range order around which to perturb, the existence of which would disagreeing mainly at the lowest energies, while SLN fails to capture high-energy structure.

Figure 2. (Color) Momentum dependent dynamical structure factor in [HHL] plane (a) and [H0L] plane (b) at constant energies: inelastic neutron experiment compared to linear spin wave theory, molecular dynamics, and the stochastic model. The data in panel (a) were collected on CNCS and the data in panel (b) were collected on MACS. Raw neutron scattering intensity has been corrected by the magnetic form-factor for Ni$^{2+}$ [29]. To focus on the wavevector dependence, the data are rescaled for each value of energy, for the experimental data, by the maximum magnetic scattering intensity; and by the maximum intensity in the MD simulations for the six theory panels, with an additional factor $\beta \omega$ between MD/SLN and LSWT (Eq. (A21), see text), $\hat{N}(\omega) = \beta \omega \hat{S}_{\text{max}}(\omega)$, where $\beta = 1/k_B T$.

Figure 3. (Color) Energy dependence of dynamical structure factor along momentum cuts [22L] and [HH2]. Neutron scattering intensity is in absolute units (see Appendix C). Rescaled MD and LSWT in particular reproduce well the shape of the broad dispersive curve, disagreeing mainly at the lowest energies, while SLN fails to capture high-energy structure.
from $6S$ in a ferromagnet to $2S$. Finally, a finite fraction of the spin-wave modes live at or near zero energy in LSWT, which implies the onset of the many-particle continuum already at the bottom of the single-particle spectrum. Above this onset, spin waves are generally expected to cease to be a useful description of the excitation spectrum [34].

So why does linear spin wave theory nonetheless work so well? LSWT actually finds another route to work—it is not a theory of universal low-energy hydrodynamic excitations, but more a description of the statistically typical short-to-intermediate time behavior, which in fact does not do a good job precisely at the lowest energies; thus in the end conforming to at least a subset of the above expectations.

To see this, think of the (near-)zero frequency modes responsible for motion between (near-)degenerate ground states, and oscillatory excitations around these as driving this motion [23–25]. The latter have finite frequency and finite scattering weight. Therefore, unlike in the case of an initially sharp mode, lifetime broadening is insignificant.

Regarding the low-$T$ limit, the zero modes mentioned above have no dynamics in LSWT (that is just the statement that their frequency is zero). The motion along the ground-state manifold is thus essentially frozen out, and LSWT in fact fails completely to capture their motion arising from scattering high-energy excitations, which is present in (not rescaled) MD and SLN theories.

From the preceding paragraph, it is clear that our comparison is not particularly sensitive to the detailed nature of the low-frequency behavior. Indeed, it has been a common theme of several recent studies of exotic magnetic dynamics that scattering away from low energies is most instructive. While this part of the spectrum is not universal, it may permit simple models, e.g. in terms of deconfined spinons in the case of the Heisenberg chain [14] which in its detailed agreement with experiment may be more convincing than the relatively featureless, and fragile, low-energy universal features. This is all the more so since, like here, this portion is often experimentally harder to access. Furthermore, the most characteristic aspects of the spin liquid ground states are topological in nature and as such invisible to experimental probes that couple to local correlations anyway [11].

Further complicating the low-energy analysis is the presence...
ence of disorder and (partial) freezing [20, 35], which will need to be included in a separate nontrivial modeling effort [36]. Also, further small terms in the Hamiltonian to which the previous fitting procedure may be insensitive, can additionally lead to shifts of weight on a scale which is small in absolute units but nonetheless notable at low energies. Further, to accurately model a low-energy window comparable in size to the temperature, a more detailed correspondence between classical and quantum calculations than our simple rescaling ansatz would be needed.

While bearing all of this in mind, we emphasize the complete absence of sharp quasiparticle peaks characteristic of magnons with well-defined momenta and energies both in theory and experiment. This reflects the spatially disordered nature of the spin configurations in our classical theory, while posing the question about the appropriate description of the corresponding low-temperature quantum state. In particular, it will be interesting to know if the small-spin pyrochlore Heisenberg antiferromagnet exhibits no well-defined quasiparticle excitations at all.

The final basic issue raised by our study is the role of the “quantumness” in this compound. The relative success of fully classical modeling across a broad range of energies, at temperatures far below the Curie-Weiss scale, is rather unexpected. The low-energy discrepancies discussed above seem like a small price to pay for the huge simplicity of the theoretical approaches we have employed. This calls for an experiment on analogous compounds with larger spin, to investigate whether the low-energy regime will be better modeled while retaining the other features already successfully accounted for.

Employing semi-classical modelling for what “ought to be” a quantum spin liquid is not without precedent. This was done for the Kitaev honeycomb model [16], which has the benefit that the availability of an exact solution of the dynamical structure factor [37] of the spin liquid allows for a reliable comparison in detail. There [38], the high-frequency portion of the response was accounted for modulo a reasonable amount of data post-processing, while the physics related to the emergent fluxes at low energies—the most direct manifestation of fractionalization—remained inaccessible.

This of course suggests a similar scenario here, namely that qualitative signatures of a quantum spin liquid are visible only at the lowest energies, perhaps even only below the scope of the experimental data. In this case, the challenge is to identify a framework which can account for such a rapid crossover into a classical regime, where quantum mechanics mainly enters in the mode occupation numbers. An alternative would be the absence of a qualitatively distinct low-frequency quantum spin liquid regime altogether. This could either happen intrinsically, if the emergent low-energy description is amenable to a semi-classical description; or extrinsically, in that the quantum spin liquid behavior is so fragile in practice that disorder or coupling to phononic degrees of freedom destroys it entirely. There are many tantalizing open questions. The minimal next step for which experimental input would be most valuable would be to consider materials with other values of spin—ideally both $S = 1/2$ and higher spin values—as well as extending the experimental window further down towards the asymptotic low-frequency behavior, if possible in a sample including minimal disorder.

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Appendix A: Correspondence between classical and quantum spin wave theories

We discuss linear spin wave theory from the classical and quantum perspectives. We begin with a classical ground state (or generally a local minimum of energy), so that every spin $s_i$ is in a state of equilibrium. It is convenient to define a local frame with three mutually orthogonal unit vectors $u_i$, $v_i$, and $w_i$, where $u_i = s_i/S$ points along the equilibrium direction. Small deviations of $s_i$ from its equilibrium position can be parametrized in terms of two coordinates $x_i$ and $y_i$ as follows:

$$s_i = \sqrt{S^2 - S(x_i^2 + y_i^2)} u_i + \sqrt{S} (x_i v_i + y_i w_i)$$

$$\approx (S - \frac{x_i^2 + y_i^2}{2}) u_i + \sqrt{S} (x_i v_i + y_i w_i).$$

The dynamics of variables $x_i$ and $y_i$ is governed by the Lagrangian

$$L = \sum_i \frac{1}{2} \left( y_i \frac{dx_i}{dt} - x_i \frac{dy_i}{dt} \right) - U,$$

where $U$ is the potential energy encoding the spin interactions. Upon expanding it to the second order in the deviations from equilibrium, we obtain

$$L = \frac{1}{2} \sum_{i} \tilde{z}^T \Gamma \tilde{z} - \frac{1}{2} \tilde{z}^T H \tilde{z},$$

where $H$ is a symmetric matrix, $\Gamma$ is a skew-symmetric matrix and $\tilde{z}$ is a column vector:

$$\tilde{z} \equiv \begin{pmatrix} x_1 \\ y_1 \\ \vdots \\ x_N \\ y_N \end{pmatrix}, \quad \Gamma = \begin{pmatrix} 0 & -1 & \cdots & 0 & 0 \\ 1 & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & 0 & -1 \\ 0 & 0 & \cdots & 1 & 0 \end{pmatrix}.$$
1. Classical approach

In the classical approach, the momentum- and energy-dependent spin correlation is defined as

\[ S_{\text{classical}}^{\mu\nu}(q, \omega) = \frac{1}{2\pi N} \sum_{i,j=1}^{N} \int_{-\infty}^{\infty} dt \, e^{-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j) + i\omega t} \times \langle \psi_{i}^{\dagger}(t) \psi_{j}^{\dagger}(0) \rangle. \]  

(A5)

Here \( i, j = 1, \ldots, N \) are indices labeling lattice sites and \( \mu, \nu = x, y, z \) are indices for Cartesian spin components.

The classical equations of motion for the deviations \( z \) are given by the Lagrangian (A3), which correctly describe the precession of spins (B1),

\[ \Gamma \frac{d}{dt} z = \mathcal{H} z. \]  

(A6)

The solution to this equation (A6)

\[ z(t) = \sum_{\alpha} c_{\alpha} \psi_{\alpha} e^{-i\omega_{\alpha} t} \]  

(A7)

is a superposition with amplitude \( c_{\alpha} \) of the normal modes \( \psi_{\alpha} \) of the eigenproblem

\[ (i\omega_{\alpha} \Gamma + \mathcal{H}) \psi_{\alpha} = 0. \]  

(A8)

This eigenproblem has the following properties: the eigenvalues come in pairs of real numbers \( -\omega_{\alpha} \) and the eigenvectors \( \psi_{\alpha}^{\dagger} \Gamma \psi_{-\alpha} = -\psi_{\alpha}^{\dagger} \Gamma \psi_{\alpha} \); we thus choose the orthonormalization

\[ \psi_{\alpha}^{\dagger}(-i\Gamma) \psi_{\beta} = \text{sgn}(\omega_{\alpha}) \delta_{\alpha\beta}. \]  

(A9)

As a result,

\[ \psi_{\alpha}^{\dagger} \mathcal{H} \psi_{\alpha} = \text{sgn}(\omega_{\alpha}) \omega_{\alpha} \delta_{\alpha\beta} = |\omega_{\alpha}| \delta_{\alpha\beta}. \]  

(A10)

and the potential energy is diagonalized in \( c_{\alpha} \)

\[ U = \frac{1}{2} \sum_{\alpha} \omega_{\alpha} c_{\alpha}^{*} c_{\alpha}. \]  

(A11)

The Boltzmann distribution gives the thermal average of the amplitudes \( \langle c_{\alpha}^{2} c_{\alpha}^{\dagger} \rangle = \delta_{\alpha\beta} / |\omega_{\alpha}| \), thus

\[ \langle z_{k}(t) z_{l}(0) \rangle = \sum_{\alpha} \frac{\langle \psi_{\alpha}^{\dagger} \rangle}{\beta |\omega_{\alpha}|} e^{-i\omega_{\alpha} t}, \]  

(A12)

where \( k, l = 1, \ldots, 2N \). Denote \( \psi_{\alpha}^{i} = (\psi_{\alpha}, \psi_{\alpha+1})^{T} \) and \( \eta_{\alpha}^{i} = (\eta_{\alpha}, \eta_{\alpha+1})^{T} \), The spin correlation function (A5) can be expressed as

\[ S_{\text{classical}}^{\mu\nu}(q, \omega) = \frac{S}{N} \sum_{i,j=1}^{N} e^{-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \times \sum_{\alpha} \frac{(\eta_{\alpha}^{i}, \psi_{\alpha}^{j})}{\beta |\omega_{\alpha}|} \delta(\omega - \omega_{\alpha}). \]  

(A13)

2. Quantum statistics

In the quantum approach, the spin correlation can be computed as the imaginary part of the retarded response function

\[ G_{\mu\nu}^{\mu\nu} = \frac{1}{N} \sum_{i,j=1}^{N} \int_{-\infty}^{\infty} dt \, e^{-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j) + i\omega t} \left\langle \psi_{i}^{\dagger}(t) \psi_{j}^{\dagger}(0) \right\rangle. \]  

(A14)

As the temperature goes to zero,

\[ S_{\text{quantum}}^{\mu\nu}(q, \omega) = \frac{1}{\pi} \lim_{T \to 0} \text{Im} G_{\mu\nu}^{\mu\nu} = \frac{1}{\pi} \text{Im} G_{\mu\nu}^{\mu\nu}. \]  

(A15)

To evaluate the functional average over the ensemble, we take \( t \to -i\tau \) in (A3) to get the imaginary-time partition function

\[ Z = \int Dz \exp \left\{ -\frac{1}{2} \int_{0}^{\beta} d\tau \, z^{T} (-i\Gamma \frac{d}{d\tau} + \mathcal{H}) z \right\}. \]  

(A16)

In the representation of Matsubara frequencies \( \omega_{n} = 2\pi n / \beta \) (\( n \in \mathbb{Z} \)),

\[ z(\tau) = \frac{1}{\sqrt{\beta}} \sum_{\omega_{n}} \zeta_{n} e^{-i\omega_{n} \tau}. \]  

(A17)

We diagonalize the action in the partition function (A16) by decomposing \( \zeta_{n} \) into orthonormal vectors \( \psi_{\alpha} \) (A9) and calculate the matrix elements of the propagator:

\[ \langle \zeta_{k}(\omega) \zeta_{l}(-\omega) \rangle = -\sum_{\alpha} \frac{\langle \psi_{\alpha}^{\dagger} \rangle}{\omega - \omega_{\alpha} + i0^{+}} \delta(\omega - \omega_{\alpha}) \text{sgn}(\omega_{\alpha}). \]  

(A19)

The spin correlation function (A15) is thus

\[ S_{\text{quantum}}^{\mu\nu}(q, \omega) = \frac{S}{N} \sum_{i,j=1}^{N} e^{-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \times \sum_{\alpha} (\eta_{\alpha}^{i}, \psi_{\alpha}^{j}) (\eta_{\alpha}^{j}, \psi_{\alpha}^{i})^{*} \delta(\omega - \omega_{\alpha}) \text{sgn}(\omega_{\alpha}), \]  

(A20)

with the same notation as in (A13).

3. Correspondence

Comparing Eqs. (A13) and (A20), we arrive at a relation between the finite temperature classical calculation and the zero temperature quantum calculation for spin correlations under the linear spin wave framework,

\[ \beta \omega S_{\text{classical}}^{\mu\nu}(q, \omega) = S_{\text{quantum}}^{\mu\nu}(q, \omega), \]  

(A21)

which is applicable at low temperature and positive energy transfer (\( \beta \omega \gg 1 \)).
In this work, we have studied the dynamical structure factor of the spin-1 pyrochlore material NaCaNi$_2$F$_7$ with a combination of classical Monte Carlo and molecular dynamics simulations (MD), stochastic "large-N" (SLN) and real-space linear spin wave theory (LSWT). Here we provide additional details needed to reproduce our data in the main text.

1. Monte Carlo-molecular dynamics

We study the dynamics of interacting classical spins by integrating the Landau-Lifshitz equation [39]

\[
\frac{d}{dt} s_i(t) = -s_i \times \frac{\partial H}{\partial s_i},
\]

(B1)

which describes the precession of the spin in the local exchange field. Here time \( t \) is in the unit of meV$^{-1}$.

Following previous work [23–25], we perform Monte Carlo plus molecular dynamics simulations with the Hamiltonian \( H \) derived previously by some of us for NaCaNi$_2$F$_7$ [26] (see main text). The initial configuration (IC) of spins is drawn by a Monte Carlo (MC) run from the Boltzmann distribution \( \exp(-\beta H) \) at temperature \( T = 1.8 K \). Then, for each starting configuration the spins are deterministically evolved according to Eq. (B1). This is done for many independent initial configurations and the result is averaged,

\[
\langle s_i^t(t)s_j^0(0) \rangle = \sum_{\text{IC from MC}} s_i^t(t)s_j^0(0) |_{\text{IC}}.
\]

(B2)

We simulated spins on the pyrochlore lattice with \( N = 16L^3 \) sites, where \( L \) is the number of cubic unit cells and we show the results for \( L = 8 \). 6000 initial configurations were used from independent Monte Carlo runs.

To compute the dynamical spin structure factor in practice, we evolve the Landau-Lifshitz equation (B1) for a long but finite time \( T_s = 60 \) meV$^{-1}$, using the fourth-order Runge Kutta method with discretized time steps. The time step \( \delta t = 0.02 \) meV$^{-1}$ is chosen to be large enough to allow us to reach large \( T_s \) efficiently, yet small enough to ensure that the energy is constant during the entire time evolution (to an accuracy of roughly six digits in the energy per site).

In order to compute energy-momentum spin correlations computationally efficiently, we perform a Fourier transform of the spin configurations during the time evolution

\[
\tilde{s}_i^\mu(q, \omega) = \frac{1}{\sqrt{N_c}} \sum_r e^{-iq \cdot r} s_i^\mu(r, t).
\]

(B3)

Then (A5) is equivalent to

\[
S^{\mu\nu}(q, \omega) = \frac{T_s}{2\pi} \langle \tilde{s}_i^{\mu}(q, \omega) \tilde{s}_i^{\nu}(-q, -\omega) \rangle.
\]

(B4)

As an overall check, we took the integration \( \int d\omega S^{\mu\nu}(q, \omega) \) to compare with the static spin correlations \( S^{\mu\nu}(q) \) of the spin configurations sampled from Monte Carlo runs. They are consistent with each other.

2. Stochastic model

In the stochastic model, we study the hydrodynamic motion of the spins under the large-N approximation (\( N \) as of spin components). The spin configuration drifts under a generalized force, while a noise with Gaussian distribution provides thermal fluctuations [25]:

\[
\frac{d}{dt} s_i^{\mu}(t) = \gamma \sum_j \Delta_{ij} \frac{\partial E}{\partial s_j^{\nu}} + \xi_i^{\mu}(t),
\]

(B5)

where \( \gamma \) is a dynamical parameter to fit to the MD data (Fig. 6) and \( \Delta_{ij} = A_{ij}^{(1)} - z\delta_{ij} \) is the lattice Laplacian (\( A_{ij}^{(1)} \) is the first-order adjacency matrix and \( z \) is the coordination number).

The Boltzmann factor is

\[
\beta E \equiv \sum_{ij} \sum_{\mu\nu} \frac{1}{2} (\beta J_{ij}^{\mu\nu} + \lambda \delta_{ij}\delta^{\mu\nu}) s_i^{\mu}s_j^{\nu},
\]

(B6)

where \( \lambda \) is the Lagrange multiplier fixing the average length of the "soft" spins. As is the case in the self-consistent Gaussian approximation [26, 30], \( \lambda \) is solved self-consistently from

\[
NS^2 = \sum_{q \in BZ} \sum_{\rho} \frac{1}{\beta \epsilon_{\rho}(q) + \lambda}.
\]

(B7)

where \( \epsilon_{\rho}(q) \) are the eigenvalues of the interaction matrix in the reciprocal space.

The noise variables follow the independent Gaussian distribution \( \langle \xi_i^{\mu}(t) \rangle = 0 \) and \( \langle \xi_i^{\mu}(t)\xi_j^{\nu}(t') \rangle = -(2\gamma/\beta) \delta_{ij}\delta^{\mu\nu}\delta(t-t') \), whose amplitude is determined by the fluctuation-dissipation theorem.

The lattice Fourier transform is performed on each of the four fcc sublattices (\( a = 1, \ldots, 4 \)),

\[
\tilde{s}_i^\mu(q) = \frac{1}{\sqrt{N_c}} \sum_{i \in a} e^{-iq \cdot r} s_i^\mu(r),
\]

(B8)

where \( N_c \) is the number of up- or down- tetrahedra and \( 4N_c = N \) is the number of sites. The lattice Laplacian and the interaction matrix transform accordingly into momentum space, denoted by \( \Delta(q) \) and \( J(q) \) respectively. Define \( P = -\Delta(q) \otimes I_3 \) and \( Q = J(q) + (\lambda/\beta)I_{12} \), where \( I_n \) is an \( n \times n \) identity matrix; the equation of motion in the momentum-energy space of the 12-component vector \( \hat{S} \equiv (\hat{s}_1^x, \hat{s}_1^y, \hat{s}_1^z, \ldots, \hat{s}_4^x, \hat{s}_4^y, \hat{s}_4^z)^T \) can be expressed by matrix multiplication:

\[
\hat{S}(q, \omega) = G(q, \omega) \hat{\xi}(q, \omega),
\]

(B9)

where the Green’s function is

\[
G^{-1}(q, \omega) = -i\omega I_{12} + \gamma P Q.
\]

(B10)

Because \( P \) and \( Q \) are real and symmetric, \( Q \) is positive definite and \( P \) is semi-positive definite, there exists a similarity transformation under matrix \( V \) to obtain a diagonal matrix \( \Lambda \) with real and non-negative entries (generally \( PQ \neq QP \)),

\[
QP = VAV^{-1}.
\]

(B11)
It can then be derived
\[
\langle \tilde{S}_\alpha(q, \omega) \tilde{S}_\beta(-q, -\omega) \rangle = 2{\gamma \over \beta} \langle GPG^\dagger \rangle_{\alpha\beta}
= 2{\gamma \over \beta} \left[ PV(\omega^2 + \gamma^2 \Lambda^2)^{-1} V^{-1} \right]_{\alpha\beta}.
\]
(B12)

The classical spin correlations (A5) thus evaluate to be
\[
S^{\mu\nu}(q, \omega) = {1 \over 8\pi} \sum_{\alpha\beta} \kappa_{\mu\alpha} \kappa_{\nu\beta} \langle \tilde{S}_\alpha(q, \omega) \tilde{S}_\beta(-q, -\omega) \rangle,
\]
(B13)

where \(\kappa_{\mu\alpha} = (1, 1, 1, 1) \otimes \hat{e}_{\mu}\) and the factor from \(N = 4N_c\) is accounted.

We further confirm the fluctuation-dissipation theorem is obeyed despite the subtlety from the non-commutation of the matrices. The static spin correlations upon integration of (B13) over energies is analytically the same as in our previous work [26].

3. Real space linear spin wave theory

A typical application of linear spin wave theory is usually based on a classical ground state candidate that is derived or postulated. Often, the simplest ground states have a small unit cell of \(n\) spins (say a pattern on a single tetrahedron, \(n = 4\), for the pyrochlore lattice [40]), which repeats in real space, so the wavevector is a good quantum number. The Hamiltonian in momentum space is block diagonalized and gives \(n\) bands with sharp dispersions. However, the situation is markedly different for inhomogeneous ground states or states with very large unit cells. It becomes hard to track bands for large unit cells and for inhomogeneous states the loss of translational invariance means momentum is no longer a good quantum number.

This latter situation is typical for the classical Heisenberg model on the pyrochlore lattice. It has many ground states which satisfy the condition \(\sum_{i\in\mathbb{Z}^3} s_i = 0\), and most of them are inhomogeneous. (Small anisotropic and further-neighbor interactions lift this degeneracy, but can still lead to the formation of many low-energy minima.) Thus here we consider finite lattice clusters and perform linear spin wave theory in real space directly using the formalism given by Eq. (A20). A former general consideration can be found in Ref. [41].

To closely mimic the situation in MD, we first assemble an ensemble of classical ground (or metastable low-energy) states for the NaCaNi\(_2\)F\(_7\) Hamiltonian by performing replica Monte Carlo runs ranging from very low temperature (\(T = 0.1\) K) to high temperature (\(T = 10\) K). This allows for good equilibration of spin configurations and largely prevents from the simulation getting "stuck". (Formally, if all independent runs are run for infinitely long they must all find the true ground state, this is not the case in practical finite runs.) The last spin configuration encountered in each run at the lowest temperature is used as the starting configuration for an iterative algorithm. This algorithm works by aligning one spin with its local exchange field; keeping all the other spins in the configuration fixed. One sweep consists of \(N\) such moves (one for each spin). Multiple sweeps are performed until the spin directions stop changing completely, which guarantees that a stable low-energy minimum has been achieved.

Then given a low-energy stable classical spin configuration, we construct and then directly diagonalize the potential \(H\) in real-space. To evaluate the spin correlations (A20) with discrete eigenvalues \(\omega_\alpha\), we use a very narrow Gaussian function as an approximation to the Dirac delta function,
\[
\delta(\omega - \omega_\alpha) = \lim_{\epsilon \to 0} {1 \over \sqrt{2\pi}\epsilon} \exp \left[ -{\left( \omega - \omega_\alpha \right)^2 \over 2\epsilon^2} \right],
\]
(B14)

with \(\epsilon = 0.01\).

Finally, we average the dynamical structure factor over \(N_s\) low-energy spin configurations. The data in the main text is collected for \(N_s = 250\) and \(N_s = 16L^3\) with \(L = 8\). Fig. 7(a) shows our results for the dynamical structure factor along two different momentum cuts as a function of energy for \(L = 4, 6, 8\). The finite size effects are small. Fig. 7(b) shows the same cuts for different numbers of spin configurations used in the average, all with \(L = 8\).

It can be shown that for a spin configuration with translational symmetry, our real-space LSWT is equivalent to the result in momentum-space, which presents sharp dispersions. Yet even for a single spin configuration (see Fig. 7(b)), the branches are broad. This confirms that the classical local minima found in the Monte Carlo simulation are indeed inhomogeneous.

We have also analyzed the inverse participation ratio (IPR) of the spin wave modes to understand the localization and delocalization effects. In analogy to the density distribution \(\rho_\epsilon(r) = |\psi_\epsilon(r)|^2\) of a given electron wavefunction, which is normalized \(\int d^3r \rho_\epsilon(r) = 1\), we consider the normalization (A9) and define the density distribution of the spin wave modes at energy \(\omega_\alpha\) to be
\[
\rho_\alpha(r_i) = (\psi_{\alpha}^i)^\dagger (-i\Gamma_2) \psi_{\alpha}^i,
\]
(B15)

where \(\Gamma_2 = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}\) and \(\psi_{\alpha}^i \equiv (|\psi_{\alpha}|_{2i}, |\psi_{\alpha}|_{2i+1})^T\), corre-
responding to the two transverse spin deviations from the equilibrium direction. The IPR is given by

$$\text{IPR}(\omega_n) = \sum_{i=1}^{N} |\rho_i(\mathbf{r}_i)|^2.$$  \hspace{1cm} (B16)

For a delocalized mode, we expect IPR($\omega_n$) \(\sim 1/N\) while for a localized mode IPR($\omega_n$) \(\sim O(1)\). In the main text Fig. 5, we show the IPR multiplied by the number of sites, i.e. \(N \times \text{IPR}(\omega)\). The collapse of the values for different lattice sizes (except perhaps at the edges of the spectrum, especially the upper edge) indicates the delocalization of spin wave modes for a wide energy range.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{(Color) Real space linear spin wave theory results for different lattice sizes \(N = 16L^3\) (a) and different numbers of samples \(N_s\) with \(L = 8\) (b).}
\end{figure}

**Appendix C: Experimental data**

The nonpolarized inelastic neutron scattering experiment probes the sum of the components of the spin correlation function that is perpendicular to the momentum transfer \(\mathbf{q}\):

$$S(\mathbf{q}, \omega) = \sum_{\mu,\nu} \left( \delta_{\mu\nu} - \frac{q_\mu q_\nu}{q^2} \right) S^{\mu\nu}(\mathbf{q}, \omega).$$  \hspace{1cm} (C1)

The measured intensity in the unit of scattering cross-section is given by

$$I(\mathbf{q}, \omega) = \left( \frac{\gamma r_0}{2} \right)^2 |g f(q)|^2 S(\mathbf{q}, \omega),$$  \hspace{1cm} (C2)

where \(f(|q|)\) is the magnetic form factor, \(g\) is the g-factor, and \(\gamma r_0 = 0.539 \times 10^{-12} \text{ cm}\) is the neutron magnetic scattering length. Throughout this work we use the dipole approximation to the Ni\(^{2+}\) form-factor [29] and an estimation of \(g = 2.28\) [42].

Data presented in Fig. 2(b) and Fig. 3 is identical to the published data set in Ref. [26]. In addition to the previously published data set, we have also collected a new complementary data set with finer momentum and energy resolution. The inelastic neutron scattering data presented in Fig. 2(a) and Fig. 4 was collected on the cold neutron chopper spectrometer (CNCS) at Oak Ridge National Lab using fixed incident neutron energies of 2.5 meV, 6.59 meV, and 12 meV providing energy resolution (FWHM) at the elastic lines of 0.07 meV, 0.4 meV, and 0.95 meV respectively. The same single crystal sample used for previous studies was mounted with the [HH0] and [00L] directions in the horizontal scattering plane of the instrument. Data was collected with [00L] initially directed along the incident neutron beam and the sample rotated over 180°. The sample was cooled to 350 mK for all measurements. (No phase transition happens between 350 mK and 1.8 K and the dynamical structure factor at finite energy (> 0.1 meV) is mostly temperature independent under the freezing temperature \(T_f = 3.6 \text{ K}\).) Data in Fig. 2(a) has been symmetrized by folding about the [HH0] and [00L] axes.

The data contains energy-dependent non-magnetic background intensity arising from incoherent nuclear scattering and scattering from the sample environment. This background contribution is estimated by taking a cut around the point \(\mathbf{q} = [0.03.65]\) and subtracted from the data in Fig. 4.
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