Experimental Observation of Lee-Yang Zeros

Xinhua Peng,[1,*] Hui Zhou,[1] Bo-Bo Wei,[2] Jiangyu Cui,[1] Jiangfeng Du,[1,†] and Ren-Bao Liu[2,‡]
[1] *Hefei National Laboratory for Physical Sciences at Microscale, Department of Modern Physics, and Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China, Hefei 230026, China*
[2] *Department of Physics, Centre for Quantum Coherence, and Institute of Theoretical Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China*
(Received 11 September 2014; published 5 January 2015)

Lee-Yang zeros are points on the complex plane of physical parameters where the partition function of a system vanishes and hence the free energy diverges. Lee-Yang zeros are ubiquitous in many-body systems and fully characterize their thermodynamics. Notwithstanding their fundamental importance, Lee-Yang zeros have never been observed in experiments, due to the intrinsic difficulty that they would occur only at complex values of physical parameters, which are generally regarded as unphysical. Here we report the first observation of Lee-Yang zeros, by measuring quantum coherence of a probe spin coupled to an Ising-type spin bath. The quantum evolution of the probe spin introduces a complex phase factor and therefore effectively realizes an imaginary magnetic field. From the measured Lee-Yang zeros, we reconstructed the free energy of the spin bath and determined its phase transition temperature. This experiment opens up new opportunities of studying thermodynamics in the complex plane.

DOI: 10.1103/PhysRevLett.114.010601 PACS numbers: 05.70.-a, 03.65.Yz, 33.25.+k, 64.60.De

After the pioneering works by van der Waals [1,2], Mayer [3,4], and van Hove [5], it has been known that different phases (e.g., liquid and gas phases) of a thermodynamic system have the same microscopic interactions but the free energy of the system encounters a singularity (nonanalytic) point in the physical parameter space where the phase transition occurs. A rigorous relation between the analytic properties of free energies and thermodynamics (in particular, phase transitions) was established by Yang and Lee in a seminal paper published in 1952 through continuation of the free energy to the complex plane of physical parameters [6]. Lee and Yang considered a general Ising model with the ferromagnetic interaction $J_{ij} > 0$ under a magnetic field h with the Hamiltonian $H(h) = -\sum_{i,j} J_{ij} s_i s_j - h \sum_j s_j$, where the spins s_j take values $\pm 1/2$. The partition function of N spins at temperature T (or inverse temperature $\beta \equiv 1/T$) $\Xi(\beta, h) \equiv \sum_{\text{all states}} \exp(-\beta H)$ can be written into an Nth order polynomial of $z \equiv \exp(-\beta h)$ as $\Xi = \exp(\beta N h/2) \sum_{n=0}^{N} p_n z^n$, where $\exp(-\beta H)$ is the Boltzmann factor (the probability in a state with energy H, up to a normalization factor) and the coefficients p_n can be interpreted as the partition function in a zero magnetic field under the constraint that n spins are at state $-1/2$. The free energy F is related to the partition function by $F = -T \ln(\Xi)$. Obviously, the zeros of the partition function (where $\Xi = 0$) are the singularity points of the free energy and hence fully determine the analytic properties of the free energy. If the Lee-Yang zeros are determined, the partition function can be readily reconstructed as $\Xi = p_0 \exp(\beta N h/2) \prod_{n=1}^{N} (z - z_n)$. Since the Boltzmann factor is always positive for real interaction parameters and real temperature, zeros of the partition function would occur only on the complex plane of the physical parameters. Lee and Yang proved that for the ferromagnetic Ising model the N zeros of the partition function all lie within an arc on the unit circle in the complex plane of z (corresponding to pure imaginary values of the external field) [7]. At sufficiently low temperature ($T \leq T_C$), the end points of the arc, i.e., the Yang-Lee singularity edges [8,9] approach the real axis of h at the thermodynamic limit ($N \to \infty$). Thus the free energy encounters a singularity point on the real axis of the magnetic field, which means the onset of a phase transition.

The Lee-Yang zeros exist universally in many-body systems. These include a broad range of physical systems described by the Ising models, such as anisotropic magnets, alloys, and lattice gases. The Lee-Yang theorem, first proved for ferromagnetic Ising models of spin-$1/2$, was later generalized to general ferromagnetic Ising models of arbitrarily high spin [10–12] and to other interesting types of interactions [13–16]. For general many-body systems, the Lee-Yang zeros may not be distributed along a unit circle but otherwise present similar features as in ferromagnetic Ising models. Lee-Yang zeros have also been generalized to zeros of partition functions in the complex plane of other physical parameters (such as Fisher zeros in the complex plane of temperature [17]). The Lee-Yang zeros (or their generalizations) fully characterize the analytic properties of free energies and hence thermodynamics of the systems. Therefore, determining the Lee-Yang zeros is not only fundamentally important for a complete picture of thermodynamics and statistical physics (by continuation to the complex plane) but also technically useful for studying thermodynamics of many-body systems.

Experimental observation of Lee-Yang zeros, however, has not been made before. The previous experiments could only indirectly derive the densities of Lee-Yang zeros from susceptibility measurement plus analytic continuation [18,19]. The difficulty is intrinsic: The Lee-Yang zeros would occur only at complex values of external fields or temperature, which are unphysical.

A recent theoretical discovery about the relation between partition functions and probe spin coherence [20] makes it experimentally feasible to access the complex plane of physical parameters. Wei and Liu found that the coherence of a central spin embedded in an Ising-type spin bath is equivalent to the partition function of the Ising bath under a complex magnetic field. The imaginary part of the magnetic field is realized by the time since the quantum coherence of the central spin is a complex phase factor as a function of time. The Lee-Yang zeros of the partition function are one-to-one mapped to the zeros of the central spin coherence, which are directly measurable. Related to the connection between central spin decoherence and Lee-Yang zeros [20], recent theoretical studies have revealed the profound links between thermodynamics in the complex plane and dynamical properties of quantum systems, such as quantum quenches of cold atom systems [21], trajectories in quantum optics [22], and work distributions of quantum nanoengines [23,24]. To reveal the full picture of thermodynamics in the complex plane of parameters [25], experimental observation of thermodynamic functions of complex variables is highly desirable.

Here we make the first observation of Lee-Yang zeros by measuring quantum coherence of a probe spin coupled to an Ising-type spin bath, following the proposal in Ref. [20]. We used liquid-state nuclear magnetic resonance (NMR) of trimethylphosphite (TMP) molecules [26] to simulate a coupled probe-bath system. The measured zeros of the central spin coherence agree very well with the Lee-Yang zeros of the partition function of the bath spins. From the measured Lee-Yang zeros, we reconstructed the free energy of the spin bath and determined its phase transition temperature. This experiment demonstrates quantum coherence probe as a useful approach to studying thermodynamics in the complex plane [25], which may reveal a broad range of new phenomena that would otherwise be inaccessible if physical parameters are restricted to be real numbers.

The trimethylphosphite (TMP) molecule [Fig. 1(a)] used in the liquid-state NMR experiments contains nine equivalent ^{1}H nuclear spins ($\mathbf{s}_1, \mathbf{s}_2, \ldots \mathbf{s}_9$, regarded as the bath in our experiments) and one ^{31}P nuclear spin ($\mathbf{s}_0$, the probe spin) [26]. In the liquid state, the three ^{1}H spins in each methyl group have Heisenberg interaction with strength $2\pi \times 16.75\ \mathrm{sec}^{-1}$ between each other while the interaction between ^{1}H spins in different methyl groups is negligible,

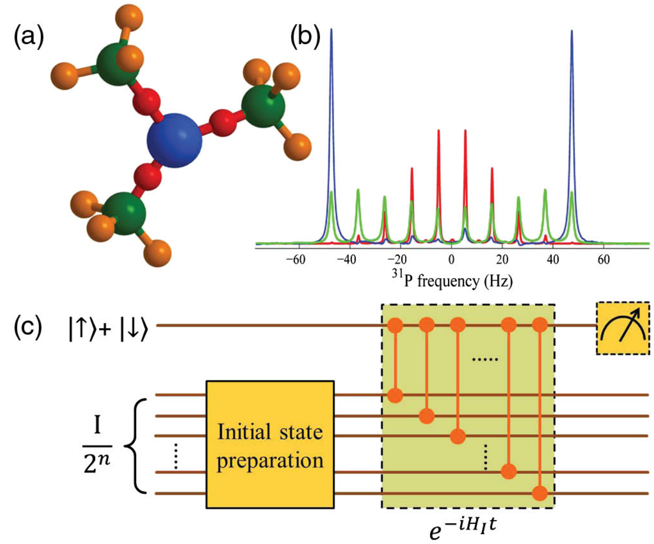

FIG. 1 (color online). System and methods for observation of Lee-Yang zeros. (a), Schematic structure of a TMP molecule. The molecule consists of one ^{31}P nuclear spin (the blue ball) as the probe and nine equivalent ^{1}H spins (the orange balls) as the bath. (b) Liquid-state ^{31}P NMR spectra of TMP molecules at $T = 300$ K or $T_{\mathrm{eff}} = \infty$ (red), for the nine ^{1}H spins at a simulated temperature $T_{\mathrm{eff}} = 15J/8$ (green) and $T_{\mathrm{eff}} = 9J/40$ (blue). The coupling ($\lambda = 2\pi \times 10.57$ sec) between the ^{1}H spins and the ^{31}P nuclear spin shifts the resonance frequency of the ^{31}P by $(9/2 - n)\lambda/(2\pi)$, where n is the number of ^{1}H spins with $s_j^z = -1/2$. (c) Quantum circuit for measuring the ^{31}P spin coherence $L(t)$, with vertical red lines representing the interaction between the probe spin and the bath spins.

and the ^{31}P spin has Ising-type interaction with the nine bath spins with a uniform coupling constant $\lambda = 2\pi \times 10.57\ \mathrm{sec}^{-1}$. The probe-bath Hamiltonian $H_{\mathrm{TMP}} = -\nu_{\mathrm{H}} \sum_{j=1}^{9} s_j^z - \nu_{\mathrm{P}} s_0^z - \sum_{1\le i<j\le 9} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j + \lambda s_0^z \sum_{j=1}^{9} s_j^z$, where $J_{ij} = 2\pi \times 16.75\ \mathrm{sec}^{-1}$ for ^{1}H spins in the same methyl group and $J_{ij} = 0$ otherwise, and $\nu_{\mathrm{H}} = 2\pi \times 400.25 \times 10^6$ and $\nu_{\mathrm{P}} = 2\pi \times 161.92 \times 10^6\ \mathrm{sec}^{-1}$ are the Larmor frequencies of the ^{1}H and ^{31}P nuclear spins under a magnetic field 9.4 T, respectively. The coupling to the ^{1}H nuclear spins splits the NMR resonance of the ^{31}P nuclear spin into 10 peaks corresponding to the 10 quantized polarizations of the 9 ^{1}H spins [Fig. 1(b)]. Note that the microscopic Hamiltonian above is not of the ferromagnetic Ising type and the magnetic field is strong.

To facilitate observation of the Lee-Yang zeros on the unit circle, we need to simulate a ferromagnetic model under zero magnetic field. Quantum simulation of a general Hamiltonian for a 10-spin system is highly demanding. Instead of directly simulating an effective Hamiltonian, we used the quantum simulation method to prepare ensembles of the bath that are described by the effective density matrix [27]

$$\rho_{\mathrm{eff}} \propto \exp(-\beta_{\mathrm{eff}} H_{\mathrm{eff}}), \tag{1}$$

We chose the effective Hamiltonian to be a ferromagnetic Ising model with global coupling, namely, $H_{\mathrm{eff}} = -J\sum_{1\le i<j\le 9} s_i^z s_j^z - h\sum_{1\le i\le 9} s_i^z$, where $\beta_{\mathrm{eff}} = 1/T_{\mathrm{eff}}$ is the effective inverse temperature, and h is the effective magnetic field. Note that the absolute value of J is irrelevant since the effective temperature is scaled by J. This choice of effective Hamiltonian greatly simplified the experiments due to two features. First, the effective Ising Hamiltonian commutes with the microscopic interactions of the coupled probe-bath system, so the prepared ensembles would stay unchanged during the evolution. Second, all states with the same total spin polarization along the z axis have the same probability to appear in the ensembles, so the density matrix can be simply simulated by choosing different excitation strengths of different ^{31}P resonances in Fig. 1(b) [27].

We initially prepared the probe spin in a superposition state as $|\Psi(0)\rangle = |\uparrow\rangle + |\downarrow\rangle$ and detected its coherence $L(t) \equiv \langle s_0^x\rangle + i\langle s_0^y\rangle$ as a function of time. The experimental scheme is schematically illustrated in Fig. 1(c). The coupling between the probe and the bath results in a local magnetic field $b = -\lambda\sum_{j=1}^{j} s_j^z$, which during the quantum evolution of the probe spin induces a phase factor to the state: $|\Psi(t)\rangle = |\uparrow\rangle + \exp(-ibt)|\downarrow\rangle$. The random distribution of the local field b leads to the probe spin decoherence. The coherence, as characterized by the spin polarization in the $x-y$ plane, is the ensemble average of the phase factor, that is [20],

$$L(t) = \langle e^{-ibt}\rangle = \frac{\mathrm{Tr}[\exp(-\beta_{\mathrm{eff}} H_{\mathrm{eff}} - ibt)]}{\mathrm{Tr}[\exp(-\beta_{\mathrm{eff}} H_{\mathrm{eff}})]} = \frac{\Xi(\beta_{\mathrm{eff}}, h + it\lambda/\beta_{\mathrm{eff}})}{\Xi(\beta_{\mathrm{eff}}, h)}. \tag{2}$$

The probe spin coherence, except for the normalization factor $\Xi(\beta_{\mathrm{eff}}, h)$, is equivalent to the partition function of the spin bath with a complex magnetic field $h + i\lambda t/\beta_{\mathrm{eff}}$. It becomes zero when the evolution time t is such that $z = \exp(-\beta_{\mathrm{eff}} h - i\lambda t)$ equals to a Lee-Yang zero. For the ferromagnetic Ising model, all the Lee-Yang zeros lie on the unit circle of z, where $h = 0$. Thus in our experiment we set the effective magnetic field h to be zero. The effective density matrix ρ_{eff} was created (up to a trivial strength factor) by the temporal averaging method [32]. The states created were confirmed by partial state tomography [33] and the final fidelity [34] was ≈0.99. The probe spin coherence was measured by the free induction decay (FID) [35] of the ^{31}P spin in NMR. The coherence zeros t_n of $L(t)$ and hence the corresponding Lee-Yang zeros $z_n = \exp(-i\lambda t_n)$ were extracted by fitting these experimental data via a polynomial function (or by interpolation).

Figure 2 shows the measured probe spin coherence and the Lee-Yang zeros. For the nine-spin Ising bath, there are

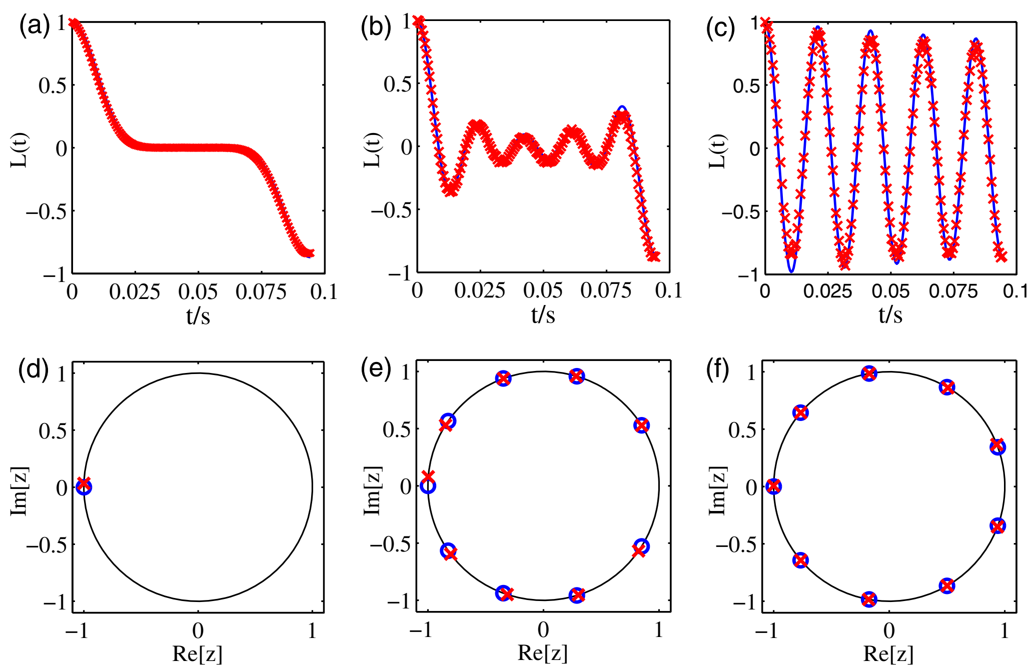

FIG. 2 (color online). Coherence of the ^{31}P probe spin and the Lee-Yang Zeros. The effective magnetic field was $h = 0$. (a), (b), and (c) are the measured probe spin coherence $L(t)$ (red symbols) as functions of time for (a) laboratory temperature ($T = 300$ K), (b) simulated temperature $T_{\mathrm{eff}} = 15J/8$ and (c) simulated temperature $T_{\mathrm{eff}} = 9J/40$. The solid lines are the numerically calculated probe spin coherence. (d), (e), and (f) show the Lee-Yang zeros (by red crosses) measured from the zeros of probe spin coherence corresponding to (a), (b), and (c). The theoretical predictions of the Lee-Yang zeros are shown as blue circles for comparison. The unit circles are plotted as a guide to the eye.

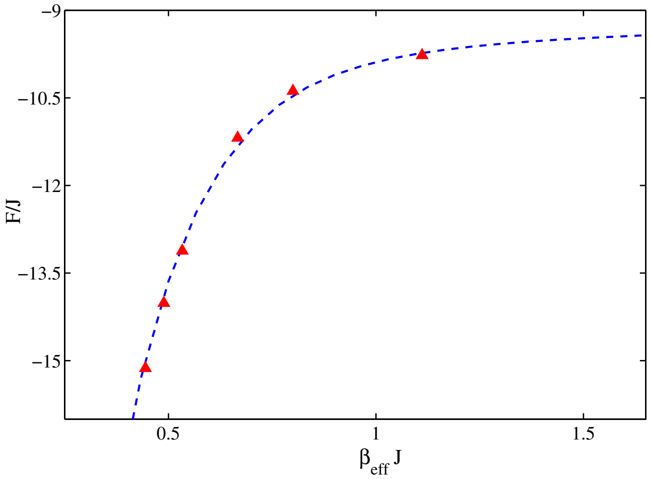

FIG. 3 (color online). Free energy of the ^{1}H spin bath reconstructed from the measured Lee-Yang zeros. The red symbols are the experimentally determined free energy as a function of the simulated inverse temperature. The dashed line is the theoretical calculation.

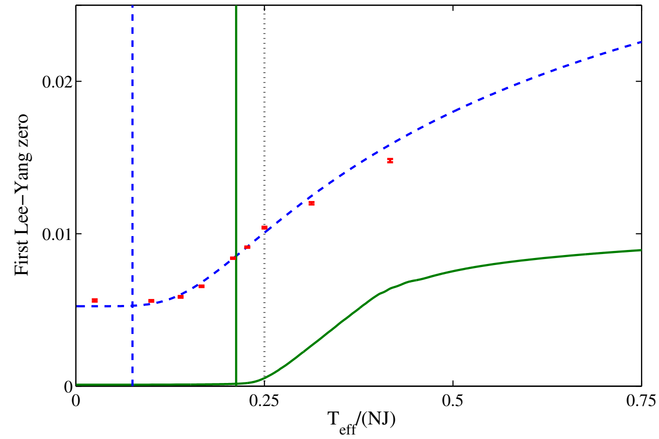

FIG. 4 (color online). Phase transition of the long-range coupling Ising model determined by measurement of Lee-Yang zeros. The red symbols are the first Lee-Yang zero, i.e., the Yang-Lee singularity edge (given by the first time t_1 when the probe spin coherence became zero) as a function of the simulated temperature. The blue dashed line is the numerically calculated result for comparison. The green solid line represents the theoretical curve for a large bath size ($N = 500$) that approximates the thermodynamic limit. Note that the phase transition temperature for the long-range coupling system is proportional to the number of spins N (so the x axis is scaled by N). Below the critical temperature, the first Lee-Yang zero is almost constant as a function of temperature. The measured critical temperature (indicated by vertical dashed line) deviates from the theoretical predictions for $N = 500$ (the vertical solid line) and for $N \to \infty$ (the vertical dotted line) due to the finite size effect.

9 zeros t_n for $L(t_n) = 0$ within a period of coherence evolution ($0 \leq t \leq 2\pi/\lambda = 0.0946$ sec), which determine the 9 Lee-Yang zeros $z_n = \exp(-i\lambda t_n)$. At room temperature (the laboratory temperature, at which $T/J \to \infty$), all of the nine Lee-Yang zeros are degenerate at $z_n = -1$ or, correspondingly, $t_n = \pi/\lambda$, as observed in Figs. 2(a) and 2(d). When the simulated temperature T_{eff} was comparable to or less than the coupling strength of the bath (J), the nine zeros were clearly resolved in the probe spin coherence [Figs. 2(b), 2(c), 2(e), and 2(f)]. The measured coherence zeros agree well with the theoretically determined Lee-Yang zeros [27].

The Lee-Yang zeros fully determine the partition functions or free energy of spin systems, and in turn the thermodynamic properties of the systems. This is fundamentally rooted in the fact that the free energies are analytic functions of the physical parameters, except for the singularity points corresponding to the Lee-Yang zeros. Thus we determined the free energies of the Ising model for various temperatures, by measuring the coherence of just one probe spin. The results are shown in Fig. 3, which compares very well to the theoretical calculation of the free energies of the Ising model. It should be pointed out that there exist other proposals for evaluating the partition functions or free energies of thermodynamic systems [36–40]. These schemes, however, require either control gates over multiple qubits [36,37] or repeated quench of the systems [38–40], and, moreover, all of them involve quantum measurement of many qubits. The Lee-Yang zero method in this Letter is much simpler and more experimentally implementable since it needs control and measurement of only one probe spin.

Phase transitions are intimately connected to the Lee-Yang zeros. At or below the phase transition temperature, the Yang-Lee singularity edges (the Lee-Yang zeros with the smallest imaginary part of the magnetic field) [8,9] approach the real axis of the magnetic field in the thermodynamic limit ($N \to \infty$). The critical temperature of the long-range Ising model is $T_C = NJ/4$. Our finite spin bath had only nine spins, which is far from the thermodynamic limit. But still the phase transition temperature can be inferred from the fact that below the critical temperature, the Lee-Yang zeros become almost uniformly distributed along the unit circle. The uniform distribution of the Lee-Yang zeros at low temperature ($T_{\mathrm{eff}} \ll J$) was indeed observed in Figs. 2(c) and 2(f). The uniform distribution of Lee-Yang zeros led to periodic oscillation of the probe spin coherence. Such periodic oscillation can be understood from the fact that below the critical temperature the bath spins were mostly in the two degenerate, polarized ground states, which led to interference between probe spin precessions under two opposite local fields. As shown in Fig. 4, below the transition temperature, the measured Yang-Lee edge (the first Lee-Yang zero) is almost constant as a function of temperature. The measured phase transition temperature agrees reasonably well with the theoretical calculation considering the small size of our system [27].

In summary, we have directly observed the Lee-Yang zeros in experiments for the first time, which conceptually completes the analytic description of statistical physics and thermodynamics. We also demonstrated the feasibility of using probe spin coherence to determine the thermodynamic properties of the baths and, more generally, to access thermodynamics on the complex plane of physical parameters [25].

This work was supported by The National Key Basic Research Program of China (Grants No. 2014CB848700 and No. 2013CB921800), National Natural Science Foundation of China (Grants No. 11375167, No. 11227901, and No. 91021005), the Strategic Priority Research Program (B) of The Chinese Academy of Sciences (Grant No. XDB01030400), Hong Kong Research Grants Council–General Research Fund Project 401413, and The Chinese University of Hong Kong Focused Investments Scheme.

*xhpeng@ustc.edu.cn
†djf@ustc.edu.cn
‡rbliu@phy.cuhk.edu.hk

[1] J. D. Van der Waals, Ph.D. thesis, Leiden University (1873) [English translation J. D. van der Waals, *On the Continuity of the Gaseous and Liquid States* (Dover, Mineola, NY, 1988)].
[2] J. C. Maxwell and J. D. Van der Waals, Nature (London) **10**, 477 (1874).
[3] J. E. Mayer, J. Chem. Phys. **5**, 67 (1937).
[4] J. E. Mayer and P. G. Ackermann, J. Chem. Phys. **5**, 74 (1937).
[5] L. Van Hove, Physica (Amsterdam) **15**, 951 (1949).
[6] C. N. Yang and T. D. Lee, Phys. Rev. **87**, 404 (1952).
[7] T. D. Lee and C. N. Yang, Phys. Rev. **87**, 410 (1952).
[8] P. J. Kortman and R. B. Griffiths, Phys. Rev. Lett. **27**, 1439 (1971).
[9] M. E. Fisher, Phys. Rev. Lett. **40**, 1610 (1978).
[10] T. Asano, Prog. Theor. Phys. **40**, 1328 (1968).
[11] M. Suzuki, J. Math. Phys. (N.Y.) **9**, 2064 (1968).
[12] R. B. Griffiths, J. Math. Phys. (N.Y.) **10**, 1559 (1969).
[13] M. Suzuki, Prog. Theor. Phys. **40**, 1246 (1968).
[14] M. Suzuki and M. E. Fisher, J. Math. Phys. (N.Y.) **12**, 235 (1971).
[15] D. A. Kurtze and M. E. Fisher, J. Stat. Phys. **19**, 205 (1978).
[16] I. Bena, M. Droz, and A. Lipowskil, Int. J. Mod. Phys. B **19**, 4269 (2005).
[17] M. E. Fisher, in *Lectures in Theoretical Physics*, edited by W. E. Brittin (University of Colorado Press, Boulder, CO, 1965), Vol. 7c, p. 1.
[18] C. Binek, Phys. Rev. Lett. **81**, 5644 (1998).
[19] C. Binek, W. Kleemann, and H. A. Katori, J. Phys. Condens. Matter **13**, L811 (2001).
[20] B. B. Wei and R. B. Liu, Phys. Rev. Lett. **109**, 185701 (2012).
[21] M. Heyl, A. Polkovnikov, and S. Kehrein, Phys. Rev. Lett. **110**, 135704 (2013).
[22] C. Flindt and J. P. Garrahan, Phys. Rev. Lett. **110**, 050601 (2013).
[23] R. Dorner, S. R. Clark, L. Heaney, R. Fazio, J. Goold, and V. Vedral, Phys. Rev. Lett. **110**, 230601 (2013).
[24] L. Mazzola, G. D. Chiara, and M. Paternostro, Phys. Rev. Lett. **110**, 230602 (2013).
[25] B. B. Wei, S. W. Chen, H. C. Po, and R. B. Liu, Sci. Rep. **4**, 5202 (2014).
[26] J. A. Jones, S. D. Karlen, J. Fitzsimons, A. Ardavan, S. C. Benjamin, G. A. D. Briggs, and J. J. L. Morton, Science **324**, 1166 (2009).
[27] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.114.010601 for details of the system, the experimental and theoretical methods, and error analysis, which includes Refs. [28–31].
[28] J. Wilms, J. Vidal, F. Verstraete, and S. Dusuel, J. Stat. Mech. P01023 (2012).
[29] M. H. Levitt, *Spin Dynamics: Basics of Nuclear Magnetic Resonance*, 2nd ed. (Wiley, New York, 2008).
[30] C. Bauer, R. Freeman, T. Frenkiel, J. Reeler, and A. J. Shaka, J. Magn. Reson. **58**, 442 (1984).
[31] H. Geen and R. Freeman, J. Magn. Reson. **93**, 93 (1991).
[32] E. Knill, I. Chuang, and R. Laflamme, Phys. Rev. A **57**, 3348 (1998).
[33] J.-S. Lee, Phys. Lett. A **305**, 349 (2002).
[34] E. M. Fortunato, M. A. Pravia, N. Boulant, G. Teklemariam, T. F. Havel, and D. G. Cory, J. Chem. Phys. **116**, 7599 (2002).
[35] R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Oxford University Press, Oxford, 1987).
[36] D. A. Lidar and O. Biham, Phys. Rev. E **56**, 3661 (1997).
[37] D. Poulin and P. Wocjan, Phys. Rev. Lett. **103**, 220502 (2009).
[38] G. Hummer and A. Szabo, Proc. Natl. Acad. Sci. U.S.A. **98**, 3658 (2001).
[39] J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco, and C. Bustamante, Science **296**, 1832 (2002).
[40] D. Collin, F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco, and C. Bustamante, Nature (London) **437**, 231 (2005).