

Unveiling the scaling laws behind spin-phonon enhanced decorrelation in spin chains

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To study the spin-Peierls transition at finite temperatures, we use path integral molecular dynamics (PIMD) in combination with stochastic series expansion or exact diagonalization to sample the quantum Boltzmann distribution of the spin-phonon-coupled one-dimensional isotropic Heisenberg chains. The use of PIMD in this context has apparently been overlooked up to now and offers several advantages over other approaches, including no restriction on the functional forms of the phonon potential or the exchange coupling. This approach allows us to study the spin-spin correlation in such systems in detail. Looking at $S = 1/2$, we find that it exhibits algebraic decay in the undimerized phase and exponential decay in the dimerized phase, but with many nuanced trends present. The decay exponentials in all cases roughly obey the scaling of $(g^2/(m\omega_\pi^2))^\nu$, where g is the spin-phonon coupling constant, m is mass, and ω_π is the frequency of the $k = \pi$ phonon.

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I. INTRODUCTION

Spin-phonon coupled systems combine several of the most challenging aspects of electronic structure theory. To begin with, the “spin” aspect of the systems, which result from the strongly open-shell nature of the underlying electronic structure, often leads to “strongly correlated” systems for which the electronic states cannot be well described by mean-field-type wave functions (Hartree-Fock or density functional theory). Instead, the wave functions usually require exponentially long configuration-interaction expansions to describe them exactly. Associated with this phenomenon is the fact that the electronic spectrum close to the ground-state is very dense (and potentially gapless). This allows for the possibility of nonadiabatic coupling to the nuclear motion, at finite temperature, where vibrations can be expected to be excited. This means that the entire system, i.e., electrons, as described through their spin degrees of freedom, and phonons may need to be treated on the same quantum footing, at finite temperature, drastically expanding the Hilbert space yet further when compared to the spin-only system.

Spin-phonon coupling can lead to structural transitions such as spin-Peierls dimerization, with accompanying change in spin order, which have been observed experimentally from one-dimensional systems (including CuGeO_3 [1], α' - NaV_2O_5 [2], π -donor-acceptor compounds [3], and Würster’s blue perchlorate [4]) up to three-dimensional ones (such as pyrochlores [5]). There is in addition a vast theoretical literature [6–15]. Many studies up to now have used model

Hamiltonians with Einstein-dispersion phonons [16–18], which neglect anharmonicity and, even within the harmonic approximation, are not as realistic as cosine-dispersion phonons. In the present study we present a method to treat the spin-phonon problem which largely overcomes difficulties in earlier formulations, including severe sign problems arising from second-quantized descriptions of the spin-coupled phonons, and is not limited to particular phonon potentials or exchange couplings. The methodology enables us to explore in unprecedented detail the effect of spin-phonon coupling on spin correlations and dimerization near the spin-Peierls transition in a wide range of parameters (exchange coupling, phonon dispersion, mass, and temperature) of the problem.

The key feature of the approach we employ that distinguishes it from earlier approaches is the use of molecular dynamics to sample the exact quantum Boltzmann distribution of the nuclei. Earlier approaches typically used Monte Carlo with small discrete steps [19] or global resampling from a known approximate distribution [16–18]. Although earlier approaches also used imaginary-time path integrals to represent the quantum Boltzmann distribution, here molecular dynamics has been explored instead of Monte Carlo. This is surprising given how routine and efficient path integral molecular dynamics (PIMD) has become (albeit in chemistry) and the advantages of molecular dynamics compared to Monte Carlo [20–27].

The spin-phonon Heisenberg model we consider is

$$\hat{\mathcal{H}} = \sum_i \frac{\hat{p}_i^2}{2m_i} + V(\hat{\mathbf{q}}) + \sum_i J_i(\hat{\mathbf{q}}) \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} = \hat{T} + \hat{V} + \hat{h}, \quad (1)$$

where m_i is the mass of atom i , p_i its momentum, q_i its displacement from equilibrium, $\mathbf{S}_i$ its associated spin, V is the phonon potential [which is commonly taken to be of Einstein form $V = \sum_i \frac{1}{2} m \omega^2 q_i^2$ or cosine-dispersion form $V = \sum_i \frac{1}{2} m \omega^2 (q_i - q_{i+1})^2$ with periodic boundary conditions], and J_i

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is the exchange coupling between spins i and $i + 1$ in the Heisenberg Hamiltonian $\hat{h}$ defined as

$$\hat{h}(\mathbf{q}) = \sum_i J_i(\mathbf{q}) \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1}. \quad (2)$$

In the present one-dimensional (1D) applications, each atom is constrained to move along the chain, though this restriction can be easily lifted in our formalism to allow the phonons to have more degrees of freedom. The unit system used here sets the elementary charge, Boltzmann constant, reduced Planck's constant, and Bohr radius to 1, which makes kelvin the unit of energy.

II. PATH-INTEGRAL MOLECULAR DYNAMICS FORMALISM

We write the partition function as the following path integral [20], exact in the $P \rightarrow \infty$ limit,

$$\begin{aligned} Q &= \frac{1}{(2\pi\hbar)^{PN}} \int d\mathbf{q} d\mathbf{p} \\ &\times \sum_{\Omega} e^{-\beta_P(\sum_{\tau}^P \frac{|\mathbf{p}_{\tau}|^2}{2m} + \sum_{\tau}^P \frac{m}{2\hbar^2\beta_P} |\mathbf{q}_{\tau+1} - \mathbf{q}_{\tau}|^2 + V(\mathbf{q}))} \\ &\times \langle \Omega | \prod_{\tau}^P e^{-\beta_P \hat{h}(\mathbf{q}_{\tau})} | \Omega \rangle, \end{aligned} \quad (3)$$

where P is the number of imaginary time points (the number of ring-polymer “beads” for each atom in the PIMD jargon), the sum over $|\Omega\rangle$ covers the complete set of 2^N spin states, $\beta_P = \beta/P$, and $\mathbf{q}_{\tau}$ denotes the positions of all the atoms at imaginary time point τ . Note that the classical limit for the phonons corresponds to $P = 1$.

An important feature of Eq. (3) is that the exponent of the first exponential is real, so the exponential is strictly positive. Thus using path integrals for the phonons introduces no additional sign problem to the spin-only problem (no spin-phonon coupling). This is an advantage over approaches that treat the phonons in second quantization, which often suffer from a worse sign problem, the severity of the sign problem depending on the form of the phonon potential and exchange coupling [16]. In addition, the rest of the integrand is also positive, which allows us to write

$$\begin{aligned} Q &= \frac{1}{(2\pi\hbar)^{PN}} \int d\mathbf{q} d\mathbf{p} \\ &\times e^{-\beta_P(\sum_{\tau}^P \frac{|\mathbf{p}_{\tau}|^2}{2m} + \sum_{\tau}^P \frac{m}{2\hbar^2\beta_P} |\mathbf{q}_{\tau+1} - \mathbf{q}_{\tau}|^2 + V(\mathbf{q}) + \mathcal{F}_P(\mathbf{q}))}, \end{aligned} \quad (4)$$

in which the spin free energy $\mathcal{F}_P(\mathbf{q})$ defined as

$$\mathcal{F}_P(\mathbf{q}_1, \dots, \mathbf{q}_P) = -\beta_P^{-1} \ln \sum_{\Omega} \langle \Omega | \prod_{\tau}^P e^{-\beta_P \hat{h}(\mathbf{q}_{\tau})} | \Omega \rangle \quad (5)$$

is real [28]. The ring-polymer positions $\mathbf{q}$ can be sampled using the path-integral molecular dynamics (PIMD) method, which has become a powerful and versatile simulation method [24] since its introduction by Parrinello and Rahman [21,29] in the 1980s. Note that the distribution of atom positions at any imaginary time point $\rho(\mathbf{q}_{\tau})$ is the same as the exact quantum Boltzmann distribution of the atom positions, so this approach is not an approximation (provided P is large enough) and allows us to calculate exact expectation values of phonon-only properties such as the bond length distribution. Properties depending on spin, for example spin-spin correlations, can also be calculated without approximation by using the same approach: it is possible to sample from a joint distribution by sampling from a marginal distribution and a conditional distribution. In the present context, molecular dynamics is used to sample ring-polymer positions $\mathbf{q}$, followed by the observables being calculated at each such geometry using a spin-only method such as stochastic series expansion (SSE) [30–32]. This two-step approach has been used in earlier works, which, however, sample ring-polymer positions $\mathbf{q}$ differently, e.g., SSE with perturbation of the Hamiltonian in the interaction picture [18,33] and continuous imaginary time path integrals to formulate a joint probability distribution for positions [16,17]. In contrast to earlier approaches, no particular form of phonon potential $V(\mathbf{q})$ and exchange coupling $J(\mathbf{q})$ is required for computational efficiency. This means that the present approach is not limited to the harmonic approximation and, furthermore, within the harmonic approximation it is not limited to a particular phonon dispersion. These are appealing features, but in this work we make the harmonic approximation (Einstein or cosine dispersion) and assume the exchange coupling is linear $J_i(\mathbf{q}) = J_0[1 - g(q_{i+1} - q_i)]$, where g is the spin-phonon coupling) to aid comparison with earlier works.

The question that now needs to be addressed is how to calculate the spin force, the contribution to the force that comes from the spin free energy $\mathcal{F}_P(\mathbf{q})$. Using an identity for the derivative of a matrix exponential [34], it is straightforward to show that the components of the force are

$$\begin{aligned} &-\frac{\partial \mathcal{F}_P(\mathbf{q}_1, \dots, \mathbf{q}_P)}{\partial q_{i,\tau}} \\ &= -\frac{\partial J_i(\mathbf{q}_{\tau})}{\partial q_{i,\tau}} \langle \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} \rangle_{\tau}(\mathbf{q}_1, \dots, \mathbf{q}_P) \\ &+ \frac{\partial J_{i-1}(\mathbf{q}_{\tau})}{\partial q_{i,\tau}} \langle \hat{\mathbf{S}}_{i-1} \cdot \hat{\mathbf{S}}_i \rangle_{\tau}(\mathbf{q}_1, \dots, \mathbf{q}_P), \end{aligned} \quad (6)$$

where

$$\langle \hat{A} \rangle_{\tau}(\mathbf{q}_1, \dots, \mathbf{q}_P) = \text{Tr} \left[\left(\prod_{\tau'=1}^{\tau} e^{-\beta_P \hat{h}(\mathbf{q}_{\tau'})} \right) \hat{A} \left(\prod_{\tau'=\tau+1}^P e^{-\beta_P \hat{h}(\mathbf{q}_{\tau'})} \right) \right] / \text{Tr} \left[\left(\prod_{\tau'=1}^P e^{-\beta_P \hat{h}(\mathbf{q}_{\tau'})} \right) \right] \quad (7)$$

and the trace is over a complete set of spin states $|\Omega\rangle$ [35]. This expectation value, and thus the force, can be calculated with

a slight extension of SSE or another spin-only technique. We refer to the combination of discrete path integrals and SSE as

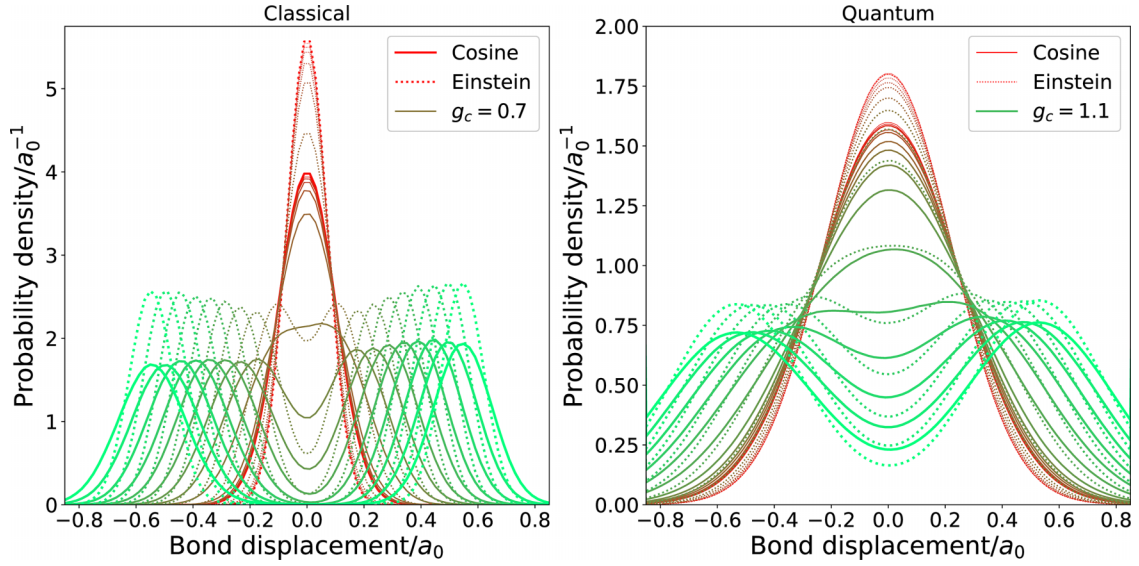


FIG. 1. Bond length distributions for the classical and quantum systems with cosine (full line) and Einstein (dotted line) dispersions. As the color changes from red to green, the spin-phonon coupling is changing from 0 to 1.5 in increments of 0.1. Classical (left) $P = 1$ versus quantum (right) $P = 50$ in a system of $N = 128$ copper atoms ($m = 0.36$) with a force constant of $k = 5.6 \text{ N m}^{-1}$ ($\omega_\pi = 244 \text{ cm}^{-1}$) and an exchange constant of $J_0 = 278 \text{ K}$ at $T = 2.78 \text{ K}$. One can see how the curves continuously change shape from unimodal to bimodal at critical spin-phonon coupling, which is around $g_c = 0.7$ in the classical case for both cosine and Einstein dispersion and $g_c = 1.1$ in the quantum, again for both types of dispersion.

ring polymer stochastic series expansion (RPSSE). Of course, instead of SSE, the force and the spin partition function can also be calculated easily if each $\hat{h}(\mathbf{q}_r)$ can be diagonalized. To this end, one would diagonalize all imaginary time slices and use the eigenbases to insert the resolution of the identity between the operators and reduce the problem to matrix multiplication. We analogously refer to this method as ring polymer exact diagonalization (RPED).

Since the latter involves the diagonalization of matrices growing exponentially in size with the number of spins, RPED is on the face of it too computationally expensive. However, we have found that the spin force is relatively local, meaning that the spin force for atom i can be accurately obtained by diagonalizing the Hamiltonian for a subsystem centered on atom i instead of the entire system. This approximation makes RPED more computationally efficient than RPSSE as the thermodynamic limit is approached and scales linearly with the number of sites. Detailed analysis on the accuracy of the subsystem length ranging from 6 to 64 atoms is presented in the Supplemental Material (SM). Based on our analysis presented in the SM, we decided it is justified to use subsystem length of 8 atoms in all the RPED results presented here. This subsystem length leads to underestimation of the spin force along the Peierls mode (wave number $k = \pi$). We correct for this underestimation using a scaling procedure, which is described in detail in the Appendixes and justified later in the text using features of the spin-spin correlation.

III. RESULTS AND DISCUSSION

Turning now to computational results, we consider the bond length distribution and spin-spin correlation. The bond length distribution (distance between neighboring atoms) is a phonon-only property that describes the extent of dimer-

ization. In contrast, the spin-spin correlation is a spin-only property that describes the range of spin interactions and is defined as the expectation value $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = 3 \langle S_i^z S_j^z \rangle$ as a function of $|i - j|$.

We have investigated the effect of the choice of dispersion (Einstein versus cosine) on the bond length distribution and the quantitative importance of treating the phonons quantum mechanically. For a sensible comparison, the single Einstein dispersion frequency was chosen to agree with the cosine-dispersion-Peierls-mode frequency ω_π . We chose a set of parameters where both the classical and the quantum system, which is in the ground vibrational state, undergo spin-Peierls transition at $T/J = 0.01$. The method can also handle sign change in $J_i(\mathbf{q})$ at large displacements. Results are shown in Fig. 1. Prior to the spin-Peierls transition, at low spin-phonon coupling g , the bond length distribution has a single sharp peak because all bonds are roughly the same length. Beyond the spin-Peierls transition, a dimerized phase with bimodal bond length distribution appears, resulting from alternating long and short bonds. There is a clear difference between the Einstein dispersion and the cosine dispersion results. The bond length distribution peaks are significantly sharper for the Einstein dispersion system. This is because the spin-phonon coupling softens the phonons around $k = \pi$ so only they become thermally accessible, whereas the cosine dispersion always has phonons around $k = 0$ which have low frequencies and are thermally accessible even at low temperatures. Although the peaks are sharper for the Einstein dispersion, the positions of the maxima are essentially the same, and so are the Einstein and cosine critical spin-phonon couplings, $g_c \approx 1.1$ (quantum) and $g_c \approx 0.7$ (classical). The discrepancy between the quantum and classical critical spin-phonon couplings shows the importance of treating the phonons quantum mechanically. The

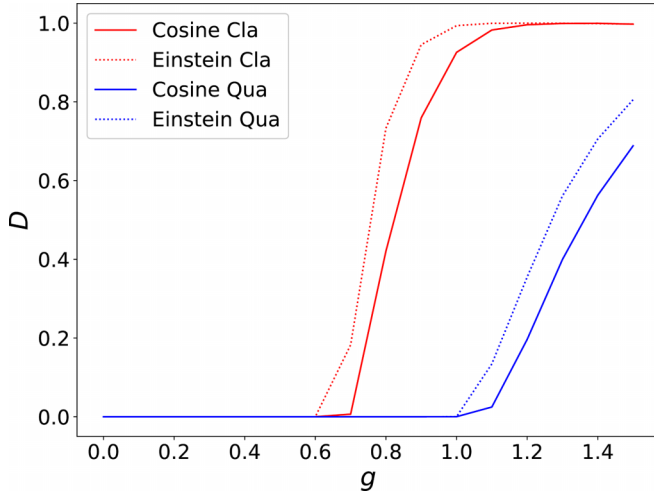


FIG. 2. Dimerization extent for the systems considered in Fig. 1 as defined by Eq. (8). The effects of Einstein dispersion enhancing the dimerization compared to the cosine dispersion, as well as nuclear quantum effects hindering dimerization, are clearly visible.

quantum critical coupling is larger because quantum delocalization (zero point energy) makes the system more resistant to dimerization.

In addition, we make use of the following metric to quantify the extent of the dimerization:

$$D = 1 - \frac{2\rho_0}{\rho_L + \rho_R}, \quad (8)$$

where D is the dimerization extent, ρ is the probability density, and subscripts refer to origin (0) and maximal binned values on the left (L) and on the right (R) of the origin. In

Fig. 2 we see that the onset of the dimerization for the two types of dispersion happens at a similar value of g , which is slightly lower for the Einstein dispersion. The differences between classical and quantum cases are more pronounced, much larger g is needed to achieve dimerization in the quantum case, and the change of the dimerization extent D with g is not as steep and achieving saturation $D = 1$ is much more difficult.

In the thermodynamic limit, the short range spin-spin correlation of the ground state of the Heisenberg model decays slightly differently for even and odd numbers of site distances, but both show an algebraic decay with exponents of -0.820 for even and -0.975 for odd site distances [36,37]. We found that 128 atoms at $T/J = 0.01$ is enough to reach the behavior seen in the thermodynamic limit, as shown in the Supplemental Material [38]. All of the calculations in the remainder of the paper were performed at this temperature.

Including the spin-phonon interaction affects the decay laws, as shown in Fig. 3. One can see that there are two main behaviors. At low couplings, before the dimerization takes place, the dependence is still algebraic and the greater the spin-phonon coupling, the faster the decay. Beyond the critical coupling g_c , the decay becomes exponential. In the intermediate range of coupling strengths, the correlation decay does not fall in either of the two categories. In our simulations we have found that these results are fairly insensitive to the form of the exchange coupling and the phonon dispersion, i.e., the decay exponentials for the cosine and Einstein dispersion with the same $k = \pi$ mode frequency are almost identical, so we focus on the Einstein dispersion in the remainder of the article.

A straight line in the log-log plot indicates an algebraic decay of the form

$$\langle S_i^z S_{i+x}^z \rangle = \beta_1 x^{\alpha_0 + \kappa}, \quad (9)$$

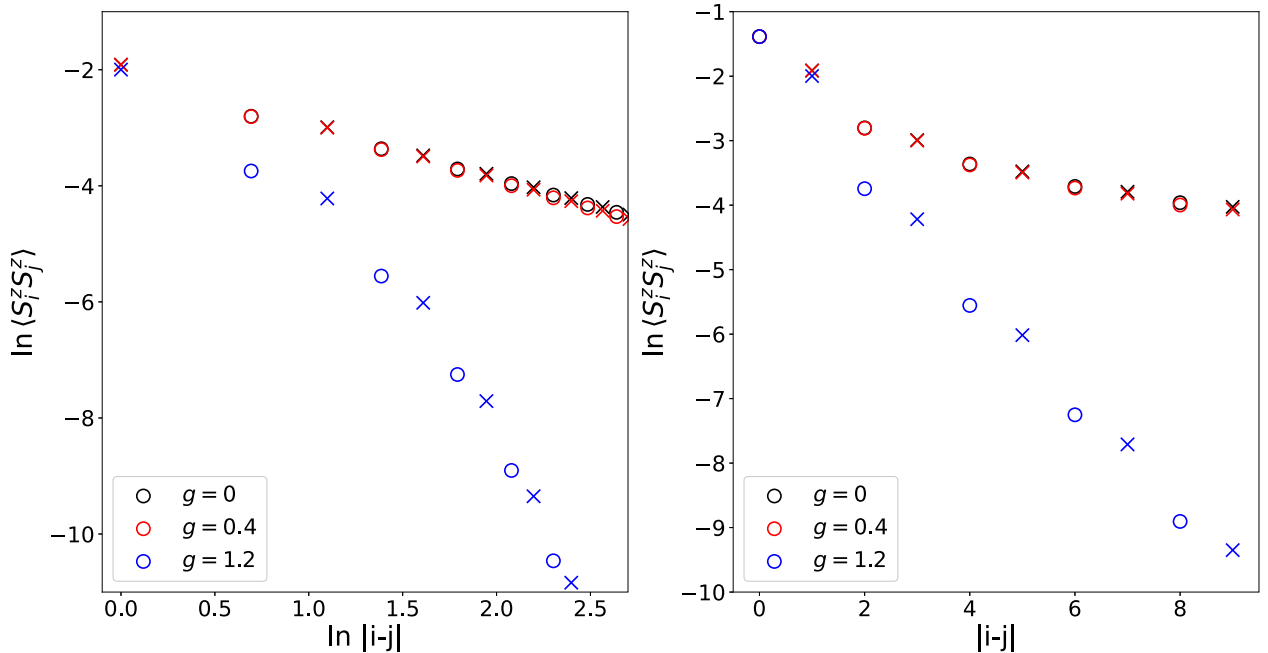


FIG. 3. Spin-spin correlation decay trends for the linear coupling for the uncoupled system (black), nondimerized system (red, $g = 0.4$), and dimerized (blue, $g = 1.2$), for the log-log (left) and log-linear (right) plots. Circles represent the even site distances and crosses the odd site distances.

where x is the difference in the number of sites and α_0 is the decay exponent of the uniform chain, α_0 being much larger than κ , whereas a straight line in the log-linear plot indicates an exponential decay,

$$\langle S_i^z S_{i+x}^z \rangle = \beta_2 e^{\epsilon x}. \quad (10)$$

Interestingly, we find the dependence of the exponents on the system parameters takes the form

$$\kappa, \epsilon \propto g^{\epsilon_1} m^{\epsilon_2} \omega^{2\epsilon_3}, \quad (11)$$

i.e., the exponents κ, ϵ depend on only one independent variable, even though on the face of it there are four independent variables: m, J_0, ω , and g , β being fixed, and furthermore that $c_1 \approx -2c_2 \approx -2c_3$, i.e., $\frac{g^2}{m\omega^2}$ is the independent variable.

To understand this result, note that the partition function and expectation values are invariant under the following transformation involving a factor α ,

$$m \rightarrow \alpha m, \quad \beta \rightarrow \alpha \beta, \quad J_0 \rightarrow J_0/\alpha, \quad \omega \rightarrow \omega/\alpha, \quad (12)$$

which reduces the number of independent variables by one. We accounted for this in our calculations by fixing J_0 relative to β . In the classical case, since the momenta can be integrated out, time-independent position and spin observables, like the spin-spin correlation, can only depend on the spring constant $m\omega^2$, not separately on m and ω , which further reduces the number of independent variables by one, but this reduction does not apply to the quantum case due to the ring-polymer springs.

At low coupling strengths, we have found numerically that the spin force is sufficiently small that the distribution $\rho(\mathbf{q})$ is essentially the same as with no spin-phonon coupling at all. In this regime one can make a change of variables $gq_i = X_i$, which is the only variable that the exchange coupling constants depend on. The potential is then $V(X) = \frac{m\omega^2}{2g^2} X^2$. The values of X follow a normal distribution with a variance $\frac{g^2}{\beta m\omega^2}$. This decreases the number of independent variables by one, leaving two independent variables in the quantum case and $g/m\omega^2$ as the only independent variable in the classical case. Why the quantum spin-spin correlation nevertheless depends on only one independent variable at low coupling strengths is the subject of ongoing work.

On the other hand, at high coupling strengths where the system is dimerized, we have found numerically, in both classical and quantum regimes, that the spin-spin correlation is the same as the spin-spin correlation at the fixed geometry corresponding to the minimum in the total free energy, i.e., fluctuations are unimportant. Because of the particular dependence of the spin force on g [see Eq. (6)], the minimum satisfies the condition

$$gf(gq_{\text{eq}}) = m\omega^2 q_{\text{eq}}, \quad (13)$$

where the form of f is unimportant. Therefore, gq_{eq} depends only on $g^2/m\omega^2$, so the exchange coupling at the minimum is given by

$$J_i/J_0 = 1 \pm 2\tilde{f}\left(\frac{g^2}{m\omega^2}\right), \quad (14)$$

so the spin-spin correlation only depends on $g^2/m\omega^2$ through a function $\tilde{f}$ which is the solution of Eq. (13) and whose

TABLE I. Fitted parameters obtained from the first four points of the log-log and log-linear plots for the nondimerized system. The values in the Even and Odd columns refer to c_1, c_2, c_3 in Eq. (11). The subscript indicates whether the calculation included spin force or if it was run using pure Einstein dispersion without the spin force.

Variable	Exponent	Regime	Even	Odd
g	$\kappa_{\text{harmonic and spin force}}$	Classical	2.34(10)	2.35(8)
g	$\kappa_{\text{harmonic force only}}$	Classical	1.80(4)	1.87(5)
g	$\kappa_{\text{harmonic and spin force}}$	Quantum	2.01(6)	2.04(4)
g	$\kappa_{\text{harmonic force only}}$	Quantum	1.63(9)	1.72(8)
k	$\kappa_{\text{harmonic and spin force}}$	Classical	-1.44(9)	-1.40(9)
k	$\kappa_{\text{harmonic force only}}$	Classical	-0.89(6)	-0.92(5)
m	$\kappa_{\text{harmonic and spin force}}$	Quantum	-1.05(9)	-1.05(7)
m	$\kappa_{\text{harmonic force only}}$	Quantum	-0.79(6)	-0.83(5)
ω^2	$\kappa_{\text{harmonic and spin force}}$	Quantum	-1.03(10)	-0.94(8)
ω^2	$\kappa_{\text{harmonic force only}}$	Quantum	-0.74(5)	-0.70(4)

form is again unimportant. At zero temperature, the classical system would be motionless and perfectly dimerized at $\pm q_{\text{eq}}$ for any finite coupling, which would lead to short-range spin correlation. The quantum system, by contrast, would be in constant motion and g would need to be sufficiently large to lead to dimerization.

The numerical results for c_1, c_2, c_3 are collected in Tables I and II, which show subtle deviations from the analysis given above. Including the spin force in the nondimerized regime increases the nonrelative values of the decay exponent parameters, with the power of g increasing from 1.8 to 2.3 in the classical and from 1.6 to 2.0 in the quantum regime, while the power of $m\omega^2$ changes from -0.9 to -1.4 in the classical and from -0.8 to -1.0 in the quantum regime. There are many cases where the scaling is different for even and odd site distances. In the classical dimerized regime there is no difference in scaling from that obtained for the fixed geometry. In the quantum regime there is barely any deviation, with the power of ω^2 being slightly more negative than that of m , which is still half that of g . It is interesting that the quantum effects which influence the bond length distribution so noticeably have little effect on the spin-spin correlation in the dimerized regime.

TABLE II. Fitted parameters obtained from the first four points of the log-log and log-linear plots for the dimerized system. The values in the Even and Odd columns refer to c_1, c_2, c_3 in Eq. (11). The subscript indicates whether the calculation included spin force or if it was run using pure Einstein dispersion without the spin force and static minimum means the calculation was run for the dimerized system with atoms at constant positions at the energy minimum.

Variable	Exponent	Regime	Even	Odd
g	$\epsilon_{\text{harmonic and spin force}}$	Classical	1.70(5)	1.84(3)
g	$\epsilon_{\text{static minimum}}$	Classical	1.69(5)	1.82(3)
g	$\epsilon_{\text{harmonic and spin force}}$	Quantum	1.83(12)	2.03(11)
k	$\epsilon_{\text{harmonic and spin force}}$	Classical	-0.86(9)	-0.92(7)
k	$\epsilon_{\text{static minimum}}$	Classical	-0.86(9)	-0.93(8)
m	$\epsilon_{\text{harmonic and spin force}}$	Quantum	-0.94(6)	-1.03(7)
ω^2	$\epsilon_{\text{harmonic and spin force}}$	Quantum	-1.03(7)	-1.13(8)

The spin-spin correlation results also shed light on why the subsystem partitioning works so well for force calculation and where its limitations lie. For large spin-phonon coupling g and large displacements of the $k = \pi$ phonon the correlation drops exponentially quickly and all of the correlation is fully contained in the few bonds in the vicinity of the central atom, so the subsystem spin force is accurate. On the other hand, for small spin-phonon coupling the spin-spin correlation is longer ranged and so the subsystem spin force is less accurate. However, the magnitude of the spin force decreases in this limit so the relative error is not so significant. The largest absolute errors can be expected in the intermediate regime where the spin force becomes relevant, but correlation is still moderately long ranged. However, this error is still reasonably small, as shown in the Supplemental Material. These longer-ranged interactions provide additional stabilization per atom along the $k = \pi$ phonon, which explains why the subsystem spin force along the Peierls mode is underestimated and needs to be corrected with the scaling $C(Q_\pi)$ as discussed in the Appendixes. Finally, at higher temperatures, the correlations become shorter ranged [39] and the subsystem naturally captures all of the relevant information to calculate the spin forces and no correction is needed. The practical limit on the system size will depend on the exact calculation being done, desired accuracy, temperature, etc., but given that the underlying problem is sign problem free, the methods will scale in a subexponential manner.

IV. CONCLUSION

In conclusion, we have presented and analyzed bond length and spin-spin correlation results from a path integral molecular dynamics method for treating the 1D spin-phonon problem, with a focus on the spin-Peierls transition. More details on the method will be included in a longer paper which is in preparation. This method can be applied just as well to other static properties, e.g., magnetic susceptibility, heat capacity, free energy landscapes, etc., and to other lattice models such as the Hubbard model and SSH model, as well as the anisotropic Heisenberg model. Using RPED is currently the fastest and most reliable way of calculating the spin force, which is particularly well suited to 1D lattices. Preliminary work suggests that machine learning might provide an efficient alternative for higher dimensional lattices. It remains to be seen how well this method would work for time-dependent properties such as the dynamic structure factor and transport properties, i.e., by interpreting the ring-polymer dynamics as a short-time approximation to the real-time dynamics, as in the RPMD method [23]. While we focused on solids in this paper, the method also applies to molecular systems, for which exact diagonalization is potentially easier. The methods generally apply when the underlying electronic structure problem (ground and relevant excited states) can be efficiently solved for any realistic nuclear geometry.

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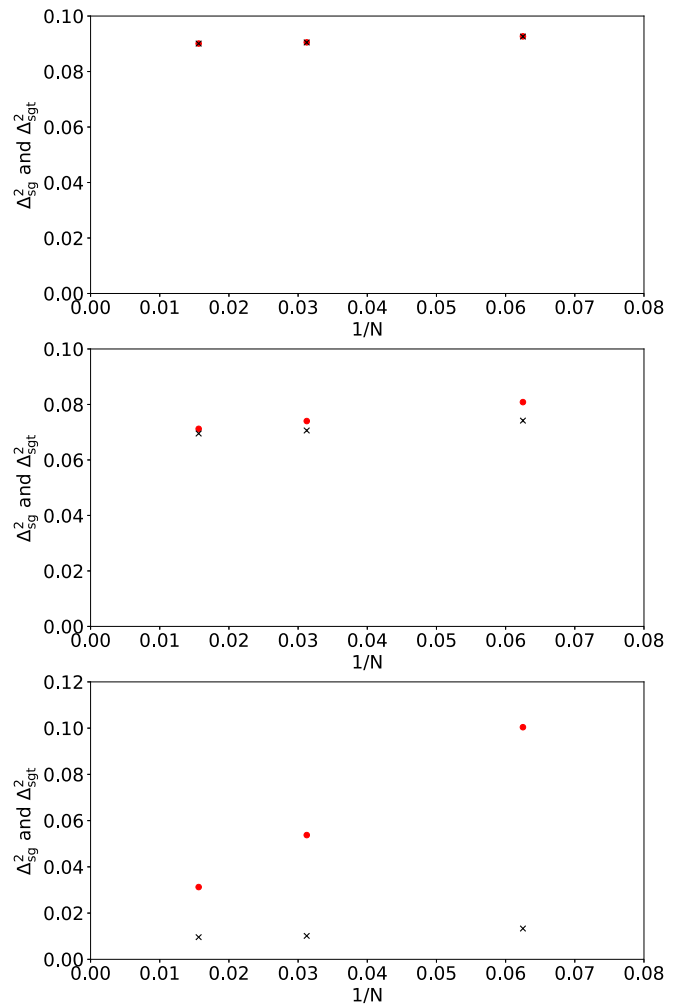


FIG. 4. Plots of Δ_{sg}^2 (red circles) and Δ_{sgt}^2 (black crosses) against $1/N$ for $m = 10000$ (top), $m = 100$ (middle), and $m = 1$ (bottom) for the purpose of comparison with Fig. 5 from [41].

DATA AVAILABILITY

The data that support the findings of this article are openly available [40].

APPENDIX A: SCALING THE SPIN FORCE

To speed up the evaluation of RPED we are using an approximation we will call subsystem partitioning, where we assume that the relevant information for the spin force is relatively short ranged and can be estimated well by cutting smaller subsystems of length M from the full chain and calculating the force of the central atoms of the subsystem. This approach can be very efficient for $M \leq 8$ and is more accurate the larger the M .

Due to the finite size effects which decrease the stabilization of short dimerized chains there is a softening of the Peierls mode. This is the main phonon of interest when describing the dimerization and the spin force along it will be accurately captured even for short chains at large displacements, but at smaller displacements the forces are underestimated if the chain length is not converged to include all interactions. To improve the accuracy along this normal mode,

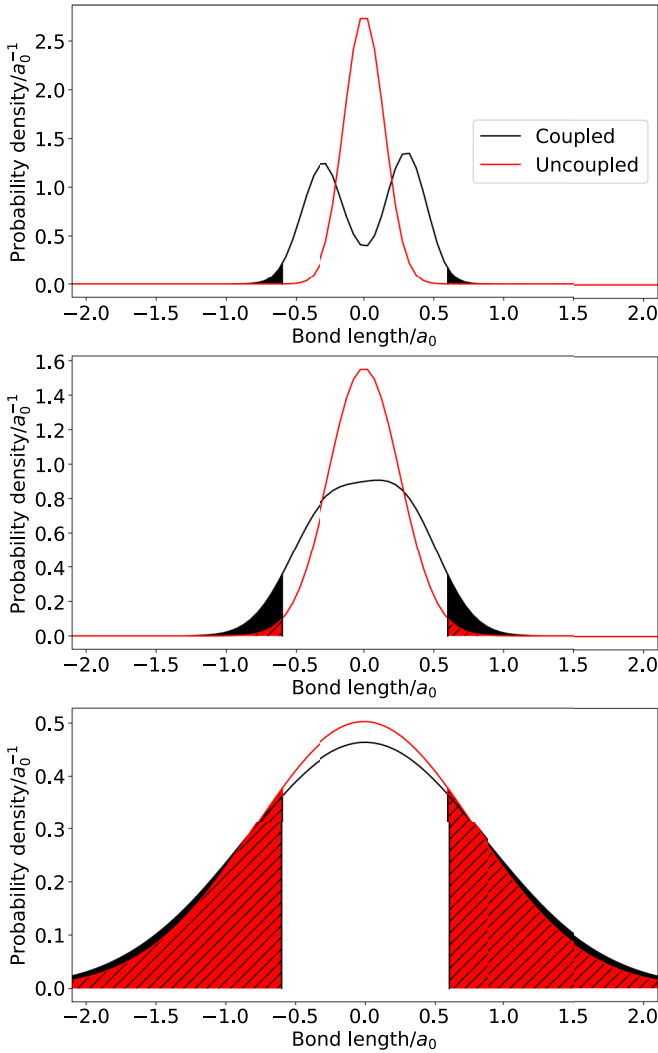


FIG. 5. Plots of bond length distributions for calculations featured in Fig. 4 for $N = 64$ for the system with and without spin-phonon coupling. The shaded areas indicate the bonds outside the cutoff set by the authors.

the force along it can be scaled by a predetermined function to minimize this source of error. The exact values of the force components are dependent on all phonons of the system, so there will always be some error from this partitioning, but through the comparison with the exact RPSSE forces, the average inaccuracy is small (see the Supplemental Material), so in all calculations we used $M = 8$.

The scaling $C(Q_\pi)$ as a function of the Peierls mode Q_π is determined using the force on the Peierls mode with all other modes fixed at zero. For M sites this is

$$F_M(Q_\pi) = - \left. \frac{\partial \mathcal{F}_M}{\partial Q_\pi} \right|_{Q_{k \neq \pi} = 0}. \quad (\text{A1})$$

The scaling $C(Q)$ is then

$$C(Q_\pi) = \frac{F_\infty(Q_\pi)}{F_M(Q_\pi)}, \quad (\text{A2})$$

so that scaling $F_M(Q_\pi)$ by $C(Q_\pi)$ gives the force on the Peierls mode in the thermodynamic limit. To interpolate we fit $C(Q_\pi)$

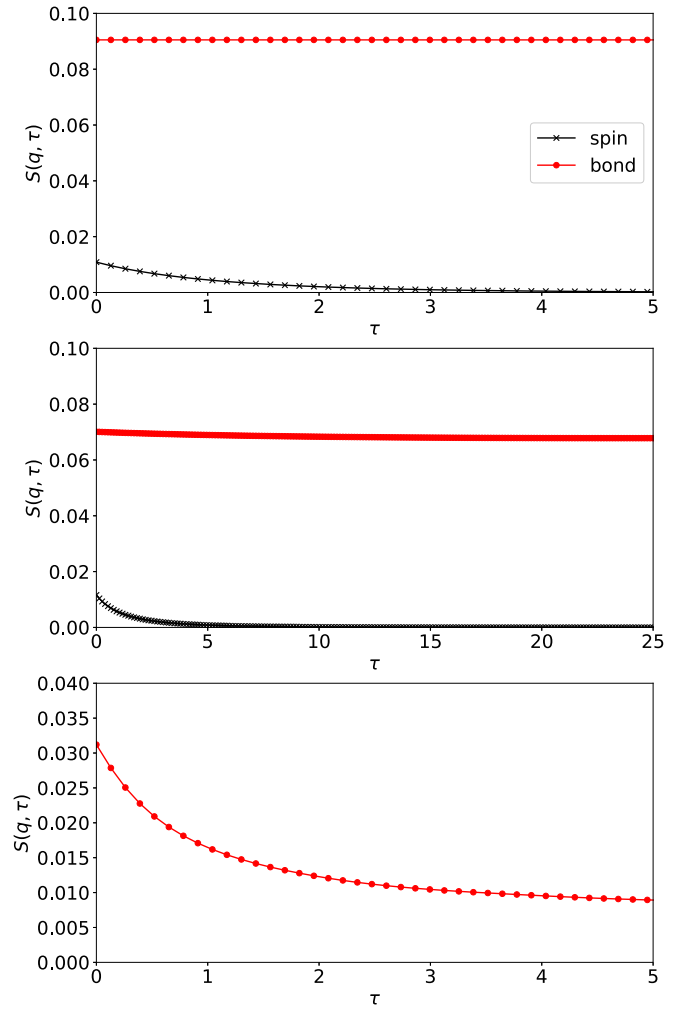


FIG. 6. Plots of $S_{\text{bond}}(\pi)$ (red circles) and $S_{\text{spin}}(\pi)$ (black crosses) against imaginary time for $m = 10\,000$ (top), $m = 100$ (middle), and $m = 1$ (bottom) for the purpose of comparison with Fig. 8 from [41].

to the following functional form,

$$C(Q_\pi) = 1 + a e^{\frac{b|Q_\pi|}{\sqrt{NP}}}, \quad (\text{A3})$$

using linear regression of $\ln(C(Q_\pi) - 1)$. a is typically close to 1 and b is negative. Note that $\sqrt{NP}$ is a normalization factor. As the spin-phonon coupling increases, b becomes more negative and at a sufficiently strong coupling in the dimerized system we have just $C(Q_\pi) = 1$, i.e., no further correction is needed. As shown in the Supplemental Material, the fit is excellent for $M = 8$ and the other parameters as in the article.

APPENDIX B: COMPARISON WITH ONISHI AND MIYASHITA

As a comparison with previous work, we repeated the calculations from the paper by Onishi and Miyashita [41] with our method. The authors used cosine dispersion potential and a sampling method based on Trotter splitting to sample the quantum nuclear motion via individual discrete changes of positions, together with a Monte Carlo algorithm for sampling the spins. The authors decided to implement a hard wall

cutoff, which made their simulations very stable, especially the ones with small mass, but also affected the results to an unknown degree. As a result, a direct comparison of values is not possible in all cases. Our method cannot simply be restricted in the same way, so we will sample the whole phase space as determined by the potential. Despite this, it is still a useful test case and provides a good control calculation to observe the effect the hard wall confinement makes. The authors mention that their value of $S_{\text{bond}}(\pi)$ in absence of spin-phonon coupling is roughly eight times smaller than the analytical value. We therefore expect significantly larger values of $S_{\text{bond}}(\pi)$ once the system is pushed to displacements beyond the value set at the hard wall boundary. The comparison with Fig. 5 from [41] is given in Fig. 4. In Fig. 5 we have plotted the bond length distributions and the locations of the cutoff. The $m = 10\,000$ case is in agreement with [41] since the system is dimerized and localized within the cutoff; only 2.4% of bonds lie outside the cutoff range. Already in the $m = 100$ case we see quantitative disagreements with [41], but the qualitative trends stay the same. The origin of this disagreement is 11% of bond lengths outside of the cutoff

range. In the $m = 1$ case we have the same observations as in the previous case, with 48% of bond lengths outside of the cutoff range.

The comparison with Fig. 8 from [41] is given in Fig. 6. As before, $m = 10\,000$ in case we are in a similar numerical range with their results, whereas $m = 100$ and $m = 1$ show similar trends, but significantly different values. The effect of quantum narrowing is not as pronounced for us as it is in [41], where it appears to be enhanced by confining the system to a narrow part of phase space. In the $m = 1$ case we only feature $S_{\text{bond}}(\pi)$ and not $S_{\text{spin}}(\pi)$, as RPSSE experiences a strong sign problem in this regime, due to strong fluctuations of the sign of the exchange coupling. Confining the system, as done by the authors in [41], avoids this problem as all coupling constants remain positive. It is important to note that while this can be a problem for a model system with very weak bonds, small mass, and a small coupling constant, most real systems are based on metal atoms with strong bonds and strong coupling constants which make a sign problem of any magnitude unlikely to occur.

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