Mean-field theory of the spin-Peierls transition

E. Orignac[1] and R. Chitra[2]

[1]*Laboratoire de Physique Théorique de l'École Normale Supérieure, CNRS UMR8549 24, Rue Lhomond 75231 Paris Cedex 05 France*
[2]*Laboratoire de Physique Théorique des Liquides CNRS UMR7600 2, Place Jussieu Tour 16 75252 Paris Cedex 05 France*

We revisit the problem of the spin-Peierls instability in a one-dimensional spin-$\frac{1}{2}$ chain coupled to phonons. The phonons are treated within the mean-field approximation. We use bosonization techniques to describe the gapped spin chain and then use the thermodynamic Bethe ansatz to obtain *quantitative* results for the thermodynamics of the spin-Peierls system in a whole range of temperature. This allows us to predict the behavior of the specific heat and the magnetic susceptibility in the entire dimerized phase. We study the effect of small magnetic fields on the transition. Moreover, we obtain the parameters of the Landau-Ginzburg theory describing this continuous phase transition near the critical point.

The spin-Peierls instability[1,2] is the magnetic analog of the Peierls instability of a one-dimensional metal.[3] In the spin-Peierls instability, an antiferromagnetic spin-1/2 chain coupled to optical phonons develops a spin gap via a static deformation (or dimerization) of the lattice at zero temperature. In this dimerized phase, the gain in magnetic energy resulting from the formation of the spin gap outweighs the loss of elastic energy due to the static deformation. For a system consisting of an array of spin chains coupled to two- or three-dimensional phonons, the dimerized phase can persist for temperatures $0 < T < T_{SP}$, where T_{SP} is the spin-Peierls transition temperature. For $T > T_{SP}$, the chains are undistorted and one recovers gapless spin excitations. The phase transition at $T = T_{SP}$ between the dimerized and the uniform state is a second-order phase transition and has been observed in a host of quasi-one-dimensional organic materials such as TTFCuS$_4$C$_4$(CF$_3$)$_4$ and TTFAuS$_4$C$_4$(CF$_3$)$_4$ (also known as TTFCuBDT and TTFAuBDT),[4] MEM-(TCNQ)$_2$,[5] (TMTTF)$_2$PF$_6$, (TMTTF)$_2$AsF$_6$,[6–8] and (BCPTTF)$_2$PF$_6$.[9] The discovery of the inorganic material[10] CuGeO$_3$ spurred further activity in this domain as this system is more convenient for neutron-scattering studies.

From the theory point of view, most of the treatments consider the phonons as static.[1,2,11] This mean-field treatment of the phonons is expected to work when the phonon frequency can be neglected (adiabatic limit) compared to the spin gap. Such an approach is thus better suited to the softer organic materials than to the inorganic compound CuGeO$_3$ where the frequency of the phonon driving the transition is not small compared to the spin gap.[12] However, a common feature of the spin-Peierls transition in all the spin-Peierls compounds is that some data indicate a BCS-type mean-field behavior of the thermodynamic quantities near the transition.[13] For instance, a BCS-type relationship,[14] $\Delta/k_B T_{SP} = 1.76$, between the zero-temperature spin gap and the spin-Peierls transition temperature T_{SP} has been observed in CuGeO$_3$, and this was used to argue that the transition in this material could also be described within mean-field theory. However, the exact nature of the transition in CuGeO$_3$ is still disputed.[15] In particular, no phonon softening was observed near the transition[16] in disagreement with the

mean-field scenario.[1,2,11] The absence of phonon softening could be attributed to the high frequency of the phonons coupled to the spin excitations.[17] Other discrepancies with the mean-field scenario are discussed in Ref. 13. Nevertheless, despite these deviations, phenomenological Landau-Ginzburg theories can be used to some extent to fit the critical behavior of CuGeO$_3$.[15] Therefore it is important to develop a more quantitative description of the mean-field theory of the spin-Peierls transition, particularly in the gapped phase in order to have a more reliable comparison of the predictions of the mean-field scenario with experimental data on the spin-Peierls materials.

In the first theoretical approaches to the spin-Peierls transitions,[1,2] the spin chain was mapped onto a model of interacting one-dimensional spinless fermions by the Jordan-Wigner transformation[18] and the interactions between the fermions were either neglected[1] or treated in the Hartree-Fock approximation.[2] Later, in Ref. 11, though the phonons were still treated at the mean-field level, the spin chain was described using bosonization which correctly describes the quantum critical behavior of the pure spin-$\frac{1}{2}$ chain.[19–22] A linear response treatment of the spin-phonon coupling resulted in a much improved estimation of dependence of the transition temperature on the spin-phonon interaction. Furthermore, a Landau-Ginzburg expansion was developed to study the vicinity of the transition.

However, in contrast to Refs. 1 and 2 no prediction could be made for the thermodynamics in the dimerized phase. There are two reasons for this. First, in Ref. 11, the dimerized phase is not described by a model of noninteracting fermions with a gap as in Ref. 1, but by a more complicated massive sine-Gordon model.[23] Second, in bosonization, although the expressions of the lattice operators in terms of sine-Gordon fields are known, the amplitudes in this expressions were unknown and have been determined quantitatively only recently.[24–26] Since the thermodynamics of the massive sine-Gordon model is now understood,[27–32] and the exact expression of the gap in the sine-Gordon theory is known,[33] it is now possible to study the thermodynamics of the dimerized spin-Peierls phase within the mean-field approximation, as well as study the zero-temperature properties.

In this paper, we will use the above developments to revisit the problem of the spin-Peierls transition in the adiabatic approximation for the phonons. Our methodology and results are also applicable to the chain mean-field theory of quasi-one-dimensional antiferromagnets since the latter presents a formal analogy to the theory of the spin-Peierls state.[34–39] The paper is organized as follows: In Sec. I, we present the model and its bosonized version. We obtain analytical results results for the spin-Peierls temperature T_{SP} and the total energy and gap at zero temperature. In Sec. II, the thermodynamic Bethe ansatz is used to study the thermodynamic properties of the dimerized chain at finite temperature. We obtain various results for the gap, the dimerization, the specific heat, and the static magnetic susceptibility for an entire range of temperatures smaller than the bandwidth. We use these results to derive the Ginzburg-Landau functional describing the mean-field transition and study the behavior of the correlation length near the transition.

I. MODEL

Within a mean-field treatment of the phonons, the full Hamiltonian describing the coupling of the lattice to the spin chain is given by

$$H = \sum_n \left[\frac{K}{2} \langle u \rangle^2 + J(1 + (-)^n \lambda \langle u \rangle) \mathbf{S}_n \cdot \mathbf{S}_{n+1} \right], \quad (1)$$

where $\langle u \rangle$ is the mean-field displacement along the chain and the $\mathbf{S}_i$ are spin-$\frac{1}{2}$ operators. K is the elastic constant for lattice deformations and λ is a parameter related to the amplitude of the spin-phonon coupling. For the sake of clarity, we introduce the dimensionless variable $\delta = \lambda \langle u \rangle$, and the reduced elastic constant $\bar{K} = K/\lambda^2$. To obtain the physics of the spin-Peierls transition, we need to evaluate the mean-field displacement $\langle u \rangle$, or equivalently, the parameter δ in a self-consistent manner, i.e., the value of δ which minimizes the free energy at any given temperature T. In the spin-Peierls phase $T \lesssim T_{SP}$, $\delta(T) \neq 0$, and $\delta(T) = 0$ for all temperatures $T > T_{SP}$. A self-consistent evaluation of $\delta(T)$ then permits a systematic calculation of various properties of the spin chain in a rather straightforward manner. Since we are mainly interested in the low-energy/long-wavelength physics of the spin-Peierls system, we study the Hamiltonian (1) in the continuum limit. In this limit, the continuum Hamiltonian reads

$$H = \int dx \frac{k}{2} \delta^2 + H_s, \quad (2)$$

where $k = \bar{K}/a$, a is the lattice spacing and H_s is the continuum approximation of the spin Hamiltonian. Using standard bosonization techniques,[19,21,22,40] the continuum spin Hamiltonian is found to be

$$H_s = u \int \frac{dx}{2\pi} [(\pi\Pi)^2 + (\partial_x \phi)^2] - \frac{2g\delta}{(2\pi a)^2} \int dx \cos \sqrt{2}\phi,$$

$$(3)$$

where the fields ϕ and Π are canonically conjugate to each other (i.e., $[\phi(x), \Pi(x')] = i\delta(x - x')$). The velocity of the bosonic excitations defined by the field ϕ is $u = (\pi/2)Ja$ and g is an amplitude proportional to the exchange interaction J. The Hamiltonian (3) is the well known sine-Gordon model with $\beta^2 = 2\pi$. In Eq. (3), we have omitted a marginally irrelevant term.[41] We will come back later to the effect of this term on the properties of the system. In the Hamiltonian (3), a nonzero dimerization δ induces the relevant operator, $\cos \sqrt{2}\phi$ of dimension $\frac{1}{2}$. This results in a gap $\Delta \sim \delta^{2/3}$, and a diminution of the ground-state energy[11,21] $E_s(\delta) - E_s(0) \sim -\delta^{4/3}$. For small δ, this reduction of magnetic energy compensates the loss of elastic energy in Eq. (1), resulting in a dimerized state at $T = 0$. Until recently, the proportionality constant between g and J was unknown, thus preventing a quantitative estimation of the magnetic energy $E(\delta)$ and hence the correct value of the spin gap Δ. Consequently, only exponents could be predicted from the above mean-field description, and no prediction could be made for the thermodynamics of the system below the spin-Peierls transition temperature. However, recent developments in integrable systems and bosonization, now permit a precise determination of the amplitudes in the continuum theory.[24–26] A correct mapping of the lattice spin model onto its bosonized version fixes the amplitude g in Eq. (3):

$$g = 6J \left(\frac{\pi}{2} \right)^{1/4} a. \quad (4)$$

Although the present paper focuses on the spin-Peierls system, we reiterate that the approach outlined below, is also applicable to the chain mean-field theory of quasi-one-dimensional antiferromagnets[34–38] as long as marginal operators are neglected. In the case of the antiferromagnet, the magnetization m and the inverse of the interchain exchange term $J_\perp^{-1}$ play the role of the dimerization and the elastic constant, respectively. We now analyze the full Hamiltonian (2) in certain limits.

A. Zero-temperature limit

At zero temperature, the dimerization δ is nonzero, resulting in a gap for spin excitations. As mentioned earlier, the precise mapping of the spin lattice model onto its continuum version, the sine-Gordon model, yields exact expressions for the gap and the total energy of the spin system.[33] In this model, the lowest energy excitation is a soliton[23] and using Eq. (4), its mass is given by

$$M = \frac{2}{\sqrt{\pi}} \frac{\Gamma(1/6)}{\Gamma(2/3)} \left[\frac{\Gamma(3/4)}{\Gamma(1/4)} \frac{3}{\pi^2} \left(\frac{\pi}{2} \right)^{1/4} \delta \right]^{2/3}. \quad (5)$$

Besides the soliton and the corresponding antisoliton excitations, the sine-Gordon model at $\beta_{SG}^2 = 2\pi$ possesses two other excitations, a light breather with a mass M and a heavy breather with a mass $M\sqrt{3}$. The soliton, the antisoliton and the light breather together form a SU(2) spin triplet while the heavy breather forms a SU(2) singlet.[42–44] The gap to the lowest energy excitation or equivalently, the singlet-triplet gap, is

$$\Delta = \frac{u}{a}M \simeq 1.723J\delta^{2/3}. \tag{6}$$

A comparison of this predicted value with the real gap of the spin-lattice system calculated numerically using the density-matrix renormalization group was done in Ref. 45 and a reasonably good accord was found. The knowledge of the soliton mass (5) also yields the ground-state energy per spin of the dimerized spin chain:[33]

$$E_s(\delta) = -\frac{\pi}{2}J\frac{M^2}{4}\tan\frac{\pi}{6} \simeq -0.2728J\delta^{4/3}, \tag{7}$$

which is in reasonable agreement with numerics.[45] To obtain the effective dimerization δ at zero temperature, we need to minimize the total ground-state energy per unit spin of the spin lattice system, $E = \bar{K}/2\delta^2 + E_s(\delta)$ which leads to the following results:

$$\Delta = \frac{2\sqrt{\pi}}{3\sqrt{3}}\left(\frac{\Gamma(1/6)}{\Gamma(2/3)}\right)^3\left[\frac{\Gamma(3/4)}{\Gamma(1/4)}\frac{3}{\pi^2}\left(\frac{\pi}{2}\right)^{1/4}\right]^2\frac{J^2}{\bar{K}} \simeq 0.627\frac{J^2}{\bar{K}},$$

$$\delta = \left(\frac{2}{3\sqrt{3}}\right)^{3/2}\left(\frac{\Gamma(1/6)}{\Gamma(2/3)}\right)^3\left[\frac{\Gamma(3/4)}{\Gamma(1/4)}\frac{3}{\pi^2}\left(\frac{\pi}{2}\right)^{1/4}\right]^2\left(\frac{J}{\bar{K}}\right)^{3/2}$$
$$\simeq 0.219\left(\frac{J}{\bar{K}}\right)^{3/2},$$

$$E = -\frac{1}{\pi^7\sqrt{3}}\left(\frac{\Gamma(1/6)}{\Gamma(2/3)}\right)^6\left(\frac{\Gamma(3/4)}{\Gamma(1/4)}\right)^4\frac{J^3}{\bar{K}^2} \simeq -0.012\frac{J^3}{\bar{K}^2}. \tag{8}$$

We note that the ratio $J^2/\bar{K}$ can be identified with the coupling constant λ_{CF} used in Ref. 11, and we indeed have the same exponents for the dependence of the gap on the coupling constant λ_{CF} as in Ref. 11. However, the prefactors in Eqs. (8) could not be obtained in Ref. 11.

The continuum approximation underlying our mean-field theory is valid when the zero-temperature correlation length is much larger than the lattice spacing, i.e., when $\Delta \ll J$. Clearly, this requires that $J \ll \bar{K}$, i.e., a sufficiently rigid lattice. This criterion leads to $\delta(T=0) \ll 1$. We note that relations similar to the ones in Eq. (8) have been previously obtained in the context of the chain mean-field theory of quasi-one-dimensional (quasi-1D) antiferromagnets.[39] In reality, the results of Eq. (8) are slightly modified by the presence of a marginally irrelevant term in the continuum Hamiltonian for the spin system.[41,46,47] When the marginal interaction is taken into account, it is found that in the spin-Peierls case $\Delta \sim \delta^{2/3}|\ln\delta|^{-1/2}$, whereas in the case of the antiferromagnet $\Delta \sim \delta^{2/3}|\ln\delta|^{1/6}$, i.e., the marginally irrelevant term frustrates the dimerization and favors antiferromagnetic ordering. The marginal interaction is eliminated in the $J_1 - J_2$ chain at its critical point[48,49] $J_2/J_1 \simeq 0.24$. With an additional dimerization of the nearest-neighbor exchange[49] in this critical chain, the gap $\Delta = 1.76\delta^{2/3}$. Moreover, in the absence of dimerization,[50] the spin velocity at the critical point is found to be $1.1936J_1a$. Generalizing the results obtained above, we find that the following amplitude $g = 0.806\pi^2J_1a$

should be used in the bosonized Hamiltonian (3) in order to describe the $J_1 - J_2$ chain with $J_2/J_1 = 0.2411$. The resulting energy gain from dimerization is then $E_s/J_1 = -0.3745\delta^{4/3}$ and one obtains the following zero-temperature results:

$$\Delta = 0.879\frac{J_1^2}{\bar{K}},$$

$$\delta = 0.353\left(\frac{J_1}{\bar{K}}\right)^{3/2},$$

$$E = -0.093\frac{J_1^3}{\bar{K}^2}. \tag{9}$$

Comparing Eqs. (9) and (8), we see that the introduction of J_2 results in a strong enhancement of the zero-temperature gap and of the dimerization, in agreement with a scenario proposed in Ref. 51 for the spin-Peierls transition in CuGeO$_3$.

B. Transition temperature

In this section, we redo the calculation of Ref. 11 yielding the spin-Peierls transition temperature. For any temperature, a self-consistent treatment of the problem requires a calculation of the free energy as a function of the dimerization δ taken as a variational parameter, followed by a minimization with respect to δ. Unlike the zero-temperature case, calculating the free energy for arbitrary temperatures requires the use of thermodynamic Bethe ansatz techniques,[27–29] and no closed analytic expressions can be obtained. However, to calculate the spin-Peierls transition temperature, this full treatment is not required.[11] Indeed, close to the spin-Peierls transition, the order parameter δ becomes small and a second-order perturbation theory in δ is sufficient to evaluate the leading behavior of the variational free energy. A straightforward perturbative development in δ of the Matsubara imaginary time path integral gives the following expression for the free energy of the sine-Gordon model:

$$F = -\frac{\pi}{6u}T^2 - \frac{1}{4}\frac{\pi a}{\beta u}\left(\frac{2g\delta}{(2\pi a)^2}\right)^2$$
$$\times \int_{-\infty}^{\infty}dx\int_0^{\beta}d\tau\frac{\sqrt{2}}{\sqrt{\cosh\frac{2\pi x}{\beta u} - \cos\frac{2\pi\tau}{\beta}}} + o(\delta^2). \tag{10}$$

Note that the first term in this expression is just the free energy of a noninteracting Bose gas in one dimension. Using Eq. (8.12.4) in Ref. 52 to integrate over the space variable x, we obtain

$$F_s(T,\delta) = -\frac{\pi}{6u}T^2 - \frac{a}{4}\left(\frac{2g\delta}{(2\pi a)^2}\right)^2\int_0^{\beta}\pi P_{-1/2}\left(-\cos\frac{2\pi\tau}{\beta}\right)d\tau, \tag{11}$$

where the function $P_{-1/2}$ is a Legendre function. A final integration over τ using Eq. (8.14.16) in Ref. 52 leads to

$$F_s(T,\delta) = -\frac{\pi}{6u}T^2 - \frac{a}{4}\left(\frac{2g\delta}{(2\pi a)^2}\right)^2 \frac{\pi^2}{\Gamma(3/4)^4 T}$$

$$= -\frac{\pi}{6u}T^2 - \frac{9J^2\delta^2}{4\pi^2\Gamma\left(\frac{3}{4}\right)^4 aT}\left(\frac{\pi}{2}\right)^{1/2}. \qquad (12)$$

The full mean-field variational free energy is $F_{MF}(T,\delta)$ $=(k/2)\delta^2+F_s(T,\delta)=C\delta^2+o(\delta^2)$. When $C>0$, which is obviously the case for high temperature, the mean-field free energy has a minimum for $\delta=0$ and for $C<0$, the energy is minimized by a state with nonzero dimerization. Therefore the spin-Peierls transition temperature is fixed by the condition $C=0$ and, using Eq. (12), we obtain

$$T_{SP} = \frac{9}{2\pi^2\Gamma(3/4)^4}\left(\frac{\pi}{2}\right)^{1/2}\frac{J^2}{\bar{K}} = 0.25342\frac{J^2}{\bar{K}}. \qquad (13)$$

Note that the validity of the continuum description requires that $T_{SP}\ll J$. In Ref. 11, the same dependence of T_{SP} on $J^2/\bar{K}$ (up to the prefactor) was derived using an equivalent response function formalism. Comparing the two expressions, we observe that in Ref. 11, the transition temperature T_{SP} $\simeq 1.01J^2/\bar{K}$ obtained there is a gross overestimate of T_{SP} highlighting the importance of having correct amplitudes in the bosonized theory. Comparing Eqs. (8) and (13), we note that the ratio

$$\frac{\Delta(T=0)}{T_{SP}} \simeq 2.47 \qquad (14)$$

is independent of the various coupling constants present in the theory. This ratio is in accord with values obtained in numerical studies of the spin-Peierls problem.[13] The existence of such a universal ratio is reminiscent of the BCS mean-field theory for superconductivity[53] where the ratio of the superconducting gap and transition temperature is approximately 1.76. In fact, one can use the Jordan-Wigner transformation[18] to map the Heisenberg spin chain onto a chain of interacting spinless fermions. Neglecting the interactions,[1] the resulting theory presents a formal similarity with the BCS theory,[53] which leads one to anticipate an universal ratio. We note, however, that the fact that the spinless fermions theory is strongly interacting renormalizes the BCS ratio away from the noninteracting value 1.76. In particular, as already discussed in Ref. 13, the observation of a ratio of 1.76 between the zero-temperature gap and the transition temperature in CuGeO$_3$ *cannot* be taken as an indication of adiabatic behavior in this compound. As discussed earlier, the results of Eq. (8) were obtained neglecting the logarithmic corrections induced by a marginally irrelevant interaction. These marginal interactions affect the dependence of the gap and the ground-state energy on the dimerization, particularly for $\delta\ll 1$ and at finite temperatures induce logarithmic corrections in response functions.[54] This inhibits a precise estimation of the BCS-like ratio especially in systems with a small dimerization at low temperatures.

For the next-nearest-neighbor chain with a critical coupling $J_{2c}=0.2411$, where logarithmic corrections vanish, Δ $=1.5386J_1^2/\bar{K}$ and $T_{SP}=0.623J_1^2/\bar{K}$. Note that these values respect the BCS relation (14). In the light of the preceding discussion, it is interesting to note that a small change in the velocity and the coefficient of the sine-Gordon term leads to a big change in the gap and the spin-Peierls temperature. This implies that the frustration engendered by J_2 enhances fluctuations towards spontaneous dimerization, hence favoring the formation of the spin-Peierls state.

C. Effect of logarithmic corrections

We now discuss the effect of the marginally irrelevant operator $\cos\sqrt{8}\phi$, neglected in the preceding sections. This operator is known to induce logarithmic corrections in the dimerization gap[41,46,48] as well as in response functions.[48,55–57] This results in a modification of Eqs. (8) and (13) and consequently deviations from the BCS-like ratio (14). Including these corrections, the gap at $T=0$ and the ground-state energy are

$$\Delta \sim J\frac{\delta^{2/3}}{|\ln\delta|^{1/2}}, \qquad (15)$$

$$E_0 \sim -J\frac{\delta^{4/3}}{|\ln\delta|} + \frac{\bar{K}}{2}\delta^2. \qquad (16)$$

Minimizing the ground-state energy with respect to δ, one finds

$$\delta^{2/3}|\ln\delta| \sim \frac{J}{\bar{K}}. \qquad (17)$$

For the transition temperature, it can be shown following Ref. 57 that the susceptibility associated with the dimerization operator is corrected by a logarithmic factor so that

$$\chi_d(T) \sim \frac{1}{T}\left(\ln\frac{J}{T}\right)^{-3/2}. \qquad (18)$$

With this result, Eq. (13) is modified into

$$T_{SP}\left(\ln\frac{J}{T_{SP}}\right)^{3/2} \sim \frac{J^2}{\bar{K}}. \qquad (19)$$

We see from Eqs. (17) and (19) that the effect of logarithmic corrections is to decrease the spin-Peierls transition temperature and the zero-temperature gap. In contrast, in the case of the Néel state, these logarithmic corrections enhance the transition temperature and the order parameter.[34,36–39]

Equation (17) leads to

$$\delta \sim \left(\frac{\dfrac{J}{\bar{K}}}{\dfrac{3}{2}\left|\ln\dfrac{J}{\bar{K}}\right|}\right)^{3/2}, \qquad (20)$$

resulting in a gap

$$\Delta \sim \frac{J^2}{\bar{K}} \frac{1}{\left| \ln \frac{J}{\bar{K}} \right|^{3/2}}. \tag{21}$$

Solving for T_{SP} in Eq. (19), and comparing with Eq. (21), we find that to lowest order a BCS-type relation holds. This relation, however, is obtained by retaining only the lowest-order logarithmic corrections.

II. THERMODYNAMIC BETHE-ANSATZ MEAN-FIELD THEORY

A. Mean-field equations

We now focus on the mean-field theory for the spin-lattice system at arbitrary temperatures. We use the thermodynamic Bethe ansatz (TBA) as a tool to evaluate the finite-temperature free energy of the sine-Gordon Hamiltonian (3). The TBA treatment of the generic sine-Gordon model with a relevant term $\cos \beta \phi$ has been formulated using the string hypothesis in Refs. 27–29. In general, this leads to an infinite number of coupled integral equations for the various pseudoenergies. However, at the so-called reflectionless points,[58] defined by $\beta^2 = 8\pi/n$, where n is an integer, the number of independent integral equations becomes finite.[29] Numerical methods can then be used to solve these integral equations and deduce the thermodynamics. The case of the dimerized spin chain with $\beta^2 = 2\pi$ falls into this category and the TBA equations of Refs. 27–29 can be used to calculate the free energy. For generic values of β away from the reflectionless points, the general formalism developed by Destri and de Vega[30–32] is more appropriate than the string approach. This latter method has been used successfully to obtain the thermodynamic properties of copper benzoate[59] in a magnetic field. This approach can be used to study the thermodynamics of the generalized spin-Peierls transition[60,61] or the antiferromagnetic transition[62] in systems of coupled spin ladders in a magnetic field. Before we embark on an application of the TBA method to the spin-Peierls system, we note that in Refs. 27–29 the free energy is taken to be zero at zero temperature. However, since our reference state is the undimerized chain, we must add the zero-temperature dimerization energy to the free energy calculated using the TBA of Refs. 27–29. Using the approach outlined in Refs. 27–29, we find that in our case, the sine-Gordon free energy reads

$$F_s(T, \delta) = -\frac{T}{2\pi u} \int_{-\infty}^{\infty} d\theta \Delta \cosh \theta [3 \ln(1 + e^{-\epsilon_1(\theta)/T})$$

$$+ \sqrt{3} \ln(1 + e^{-\epsilon_2(\theta)/T})] - \frac{u}{a^2} \tan \frac{\pi}{6} \frac{M^2}{4}, \tag{22}$$

where the pseudoenergies $\epsilon_1(\theta)$ and $\epsilon_2(\theta)$ are self-consistently determined by the following integral equations:

$$\epsilon_1(\theta) = \Delta \cosh \theta + \frac{3T}{2\pi} \int_{-\infty}^{\infty} d\theta' K_{11}(\theta - \theta') \ln(1 + e^{-\epsilon_1(\theta')/T})$$

$$+ \frac{T}{2\pi} \int_{-\infty}^{\infty} d\theta' K_{12}(\theta - \theta') \ln(1 + e^{-\epsilon_2(\theta')/T}),$$

$$\epsilon_2(\theta) = \Delta \sqrt{3} \cosh \theta + \frac{3T}{2\pi} \int_{-\infty}^{\infty} d\theta' K_{12}(\theta - \theta') \ln(1 + e^{-\epsilon_1(\theta')/T})$$

$$+ \frac{T}{2\pi} \int_{-\infty}^{\infty} d\theta' K_{22}(\theta - \theta') \ln(1 + e^{-\epsilon_2(\theta')/T}). \tag{23}$$

The integral kernels are given by

$$K_{11}(\theta) = \frac{2 \sin \frac{\pi}{3} \cosh \theta}{\sinh^2 \theta + \sin^2 \frac{\pi}{3}},$$

$$K_{12}(\theta) = \frac{2 \sin \frac{\pi}{6} \cosh \theta}{\sinh^2 \theta + \sin^2 \frac{\pi}{6}} + \frac{2 \cosh \theta \sin \frac{\pi}{2}}{\sin^2 \frac{\pi}{2} + \sinh^2 \theta},$$

$$K_{22}(\theta) = 3 K_{11}(\theta). \tag{24}$$

The pseudoenergies $\epsilon_{1,2}$ have a transparent physical interpretation:[63] $\epsilon_1(\theta)$ represents the dressed energy of the solitons and of the light breather (which have identical masses at the $\beta^2 = 2\pi$ point), whereas the pseudoenergy $\epsilon_2(\theta)$ represents the dressed energy of the heavy breather. In fact, because scattering is diagonal, Eqs. (22)–(24) can be easily re-derived using the approach outlined in Ref. 63. It is useful to recast the dimensionless free energy $f = aF/J$ in terms of the scaled energies $\bar{\epsilon}_i = \epsilon_i/J$ and the reduced temperature $\bar{T} = T/J$,

$$f = \frac{\bar{K}}{2J} \delta^2 - \frac{\bar{T}}{2\pi} \int d\theta M \cosh \theta [3 \ln(1 + e^{-\bar{\epsilon}_1(\theta)/\bar{T}})$$

$$+ \sqrt{3} \ln(1 + e^{-\bar{\epsilon}_2(\theta)/\bar{T}})] - \frac{\pi}{8\sqrt{3}} M^2, \tag{25}$$

$$\bar{\epsilon}_1(\theta) = \frac{\pi}{2} M \cosh \theta + \frac{3\bar{T}}{2\pi} \int_{-\infty}^{\infty} d\theta' K_{11}(\theta - \theta') \ln(1 + e^{-\bar{\epsilon}_1(\theta')/\bar{T}})$$

$$+ \frac{\bar{T}}{2\pi} \int_{-\infty}^{\infty} d\theta' K_{12}(\theta - \theta') \ln(1 + e^{-\bar{\epsilon}_2(\theta')/\bar{T}}), \tag{26}$$

$$\bar{\epsilon}_2(\theta) = \frac{\pi}{2} M \sqrt{3} \cosh \theta$$

$$+ \frac{3\bar{T}}{2\pi} \int_{-\infty}^{\infty} d\theta' K_{12}(\theta - \theta') \ln(1 + e^{-\bar{\epsilon}_1(\theta')/\bar{T}})$$

$$+ \frac{\bar{T}}{2\pi} \int_{-\infty}^{\infty} d\theta' K_{22}(\theta - \theta') \ln(1 + e^{-\bar{\epsilon}_2(\theta')/\bar{T}}). \tag{27}$$

To obtain the free energy for arbitrary temperatures we need to solve for a given soliton mass M, the pair of self-consistent equations (26) and (27) for the dispersions $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$. Here, we use numerical methods[28] to obtain the solutions
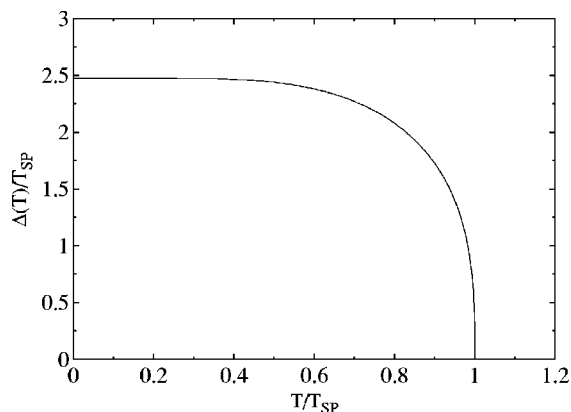
FIG. 1. The dimensionless scaling function $\bar{\Delta}$ describing the law of corresponding states followed by the spin-Peierls gap. The universal ratio 2.47 is reached for $T < 0.4 T_{SP}$. For $T \rightarrow T_{SP}$ the scaling function $\bar{\Delta} \sim (1 - T/T_{SP})^{1/3}$.

for any arbitrary temperature. We use a simple iterative procedure to solve Eqs. (26) and (27) numerically for various values of the dimerization δ at a fixed temperature T. This provides us with the variational free energy for an entire range of δ at fixed temperature. We then identify the value of δ for which the free energy is a minimum. Such a procedure is repeated for various values of the temperature T thereby permitting us to obtain $\delta(T)$. In particular, we find that the numerical estimate of T_{SP} coincides perfectly with the prediction of perturbation theory Eq. (13). This provides a first check of the validity of our TBA mean-field solution. In Fig. 2, we plot our results for the mean-field dimerization $\delta(T)$ as a function of the reduced temperature. These results for $\delta(T)$ are then used to obtain thermodynamic quantities. Figures 1 and 3 show a plot the gap and specific heat as as function of the temperature. In the vicinity of T_{SP}, the gap vanishes as $\Delta \propto (T_{SP} - T)^{1/3}$ and the specific heat jumps at T_{SP} as expected for a second-order transition. For low temperatures $T \ll T_{SP}$ the specific heat is exponentially suppressed by the spin gap and for $T \gtrsim T_{SP}$, the specific heat is simply that of the pure Heisenberg chain: $C_v = \pi/(3u)T = 2T/(3J)$ which is the same as that for a gas of free bosons.

B. Law of corresponding states

The mean-field theory leads to a law of corresponding states[64] or equivalently, scaling forms for the free energy and associated quantities. We use the $T = 0$ result $\delta \sim (J/\bar{K})^{3/2}$ [cf. Eq. (8)] to rewrite the finite temperature dimerization $\delta(T) = (J/\bar{K})^{3/2} \bar{\delta}(T)$. Inserting this in Eq. (5), and in Eqs. (26) and (27), and using Eq. (13), it is straightforward to see that the pseudoenergies satisfy the scaling form $\epsilon_i(\theta) = T_{SP} \bar{\epsilon}(T/T_{SP}, \theta)$. Consequently, this implies that the total free energy, gap, and dimerization can be re-expressed as

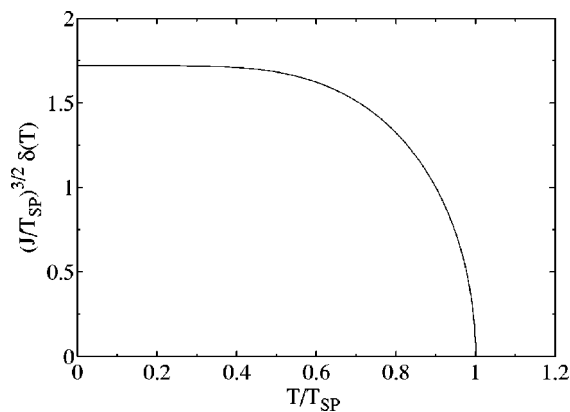$$F(T) = -\frac{T_{SP}^2}{J} f\left(\frac{T}{T_{SP}}\right), \qquad (28)$$

FIG. 2. The dimensionless scaling function $\bar{\delta}$ describing the law of corresponding states followed by the spin-Peierls dimerization. The zero-temperature value is reached for $T < 0.4 T_{SP}$. For $T \rightarrow T_{SP}$ the scaling function $\bar{\delta} \sim (1 - T/T_{SP})^{1/2}$.

$$\delta(T) = \left(\frac{T_{SP}}{J}\right)^{3/2} \bar{\delta}\left(\frac{T}{T_{SP}}\right), \qquad (29)$$

$$\Delta(T) = T_{SP} \bar{\Delta}\left(\frac{T}{T_{SP}}\right), \qquad (30)$$

where the functions $\bar{\Delta}, \bar{\delta}$, and f are universal functions of the scaled temperature. From Figs. 1 and 2, we see that the numerical solutions for $\bar{\Delta}$ and $\bar{\delta}$ do obey the above scaling form. From the expression for the free energy (28), one easily obtains the following result for the specific heat:

$$C_v = \frac{T_{SP}}{J} \frac{T}{T_{SP}} f''\left(\frac{T}{T_{SP}}\right). \qquad (31)$$

As expected in a mean-field theory, there is a jump in the specific heat at the transition whose magnitude is given by

$$\frac{J \Delta C_v}{T_{SP}} = f''(1^-) - \frac{2}{3} = \gamma_{SP}. \qquad (32)$$

The numerical solution of the mean-field equation yields $\gamma_{SP} = 1.39$. Our result for the specific heat is shown in Fig. 3.
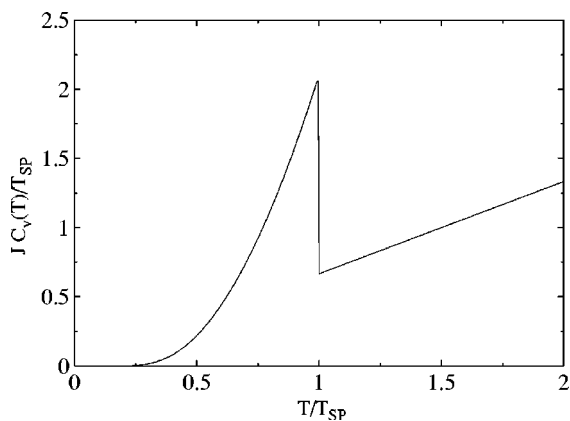

FIG. 3. The specific heat of the spin-Peierls problem in the mean-field approximation.

A universal ratio of the specific-heat jump to the specific heat above the critical temperature[53] exists in the BCS theory, where $\Delta C_v / C_v(T_{SP}^+) = 1.43$. Here again, the value of the ratio $\Delta C_v / C_v(T_{SP}^+) = 2.1$ in the spin-Peierls problem is different from the BCS ratio of 1.43 due to the strong interactions between the Jordan-Wigner pseudofermions. We note that in experiments on $CuGeO_3$, this ratio was found to be 1.5 or 1.6, which is close to the BCS prediction.[65] However, as in the case of the ratio of the gap to the transition temperature, this apparent agreement with the mean-field description proves to be spurious as we have seen that the ratio should be near 2.1 in a spin isotropic material.

C. Landau-Ginzburg expansion

In this section, we use the results of the preceding sections to obtain a simple Ginzburg Landau functional describing the vicinity of the spin-Peierls transition. In Ref. 11, it was shown that a soft Ising or ϕ^4 theory was enough to describe the vicinity of the transition. However, the coefficients, in particular, that of the quartic term, could not be entirely calculated. Our formalism permits us to obtain the leading terms in the functional with the correct prefactors. This will be useful for more sophisticated treatments of the transition taking into account the fluctuations of the lattice[66] or the role of solitons in the thermodynamics.[67] A Landau-Ginzburg expansion[64] of the variational free energy per unit length (22) in the vicinity of T_{SP} gives

$$F(T, \delta) = \frac{p}{2}(T - T_{SP})\delta^2 + \frac{q}{4}\delta^4. \tag{33}$$

The law of corresponding states (28) leads to some constraints on the form of the expansion. Minimization with respect to δ yields

$$\delta^2(T) = \frac{p}{q}(T_{SP} - T),$$

$$F(T) = -\frac{p^2}{4q}(T - T_{SP})^2. \tag{34}$$

The law of corresponding states (28) implies that $p/q \sim T_{SP}^2/J^3$ and that $p^2/q \sim 1/J$. Thus we have $p = c_1 J^2/T_{SP}^2$ and $q = c_2 J^5/T_{SP}^4$, where c_1, c_2 are dimensionless numbers. These predictions are in agreement with the ones obtained from the RG treatment in Ref. 68. The dependence of p can also be verified by the perturbation theory of Sec. I B. Although the precise value of q was not obtained in Ref. 11, it was shown using perturbation theory that the Landau-Ginzburg free energy had an expansion in powers of $(J/T_{SP})^{1/2}\Delta_0/T_{SP}$, where $\Delta_0 = J\delta$. Reporting this expansion in Eq. (5.5) of Ref. 11 leads precisely to the dependence of q on J and T_{SP}. Thus the perturbative expansion of the free energy is fully consistent with the law of corresponding states. In terms of the dimensionless constants,

$$\delta(T)^2 = \frac{c_1}{c_2}\left(\frac{T_{SP}}{J}\right)^3\left(1 - \frac{T}{T_{SP}}\right),$$

$$F(T) = -\frac{c_1^2}{4c_2}\frac{(T - T_{SP})^2}{J}. \tag{35}$$

This also implies from Eq. (5) that the spin-Peierls gap vanishes as $\sim(1 - T/T_{SP})^{1/3}$ near the transition. This behavior is entirely consistent with our numerical results. It now suffices to calculate the constants c_1 and c_2. A comparison with Eq. (12) fixes $c_1 = 0.2534$ and the value of $c_2 = 0.022\,76$ is obtained by fitting the TBA mean-field theory results for $\delta(T)$ to Eq. (34) in the range $0.9T_{SP} < T < T_{SP}$. Hence

$$p \simeq 0.2534\frac{J^2}{T_{SP}^2},$$

$$q \simeq 0.0228\frac{J^5}{T_{SP}^4}. \tag{36}$$

As a check of the correctness of the results of the Ginzburg-Landau expansion, we can compare the prediction for the specific-heat jump from Eq. (34), $\Delta C_v = c_1^2/(2c_2)(T/J) \simeq 1.4(1)(T/J)$ with the value given by the TBA mean-field theory in Eq. (32) $\Delta C_v \simeq 1.39(T/J)$. The 1% agreement between these two values provides a confirmation of the correctness of our Ginzburg-Landau expansion. From the behavior of the gap, we can obtain the behavior of the magnetic correlation length $\xi_{mag}(T)$. If the gap is Δ, the magnetic correlation length at $T = 0$ is u/Δ. Thus, neglecting thermal effects, we would obtain $\xi_{mag}(T) \sim J/T_{SP}(1 - T/T_{SP})^{-1/3}$. Near the transition, this correlation length becomes much larger than the thermal correlation length $\xi_{th} = u/(2\pi T)$. This means that the exponential decay of the magnetic correlation that would result from the gap $\Delta(T)$ is completely masked by the thermal fluctuations which leads to a much shorter correlation length. The above results are valid for the case of a uniform dimerization δ. In reality, near the transition, the dimerization can vary with the spatial location. To take into account the energy cost of these fluctuations, a $(\nabla\delta)^2$ term must be included in the Landau-Ginzburg effective theory. The bosonization approach allows us to calculate the coefficient of this gradient term as outlined in the Appendix. The full Landau-Ginzburg free energy is now given by

$$F_L = \int dx\left(\frac{c_0}{2}(\nabla\delta)^2 + \frac{p}{2}(T - T_{SP})\delta^2(x) + \frac{q}{4}\delta^4(x)\right), \tag{37}$$

where the constant c_0 measures the rigidity of the order parameter δ and is given (see the Appendix) by

$$c_0 = \frac{9}{8\pi^2}\left(\frac{\pi}{2}\right)^{1/2}\frac{\beta(2)}{\Gamma(3/4)^4}\frac{J^4 a}{T^3}, \tag{38}$$

where $\beta(2) \simeq 0.91596\cdots$ is Catalan's constant[52] and p, q are given by Eq. (36). It is interesting to note that the coefficient of the gradient term falls as T^3. We note that the Ginzburg-Landau coefficients calculated in Ref. 68 using a fermionic Renormalization Group treatment have the same dependence on T_{SP} as in the present mean-field calculation. However, we

do not expect an agreement of the numerical prefactors as the model studied in Ref. 68 is different from the one studied here. The structural correlation length close to the transition can be evaluated from Eq. (37) and is found be to be

$$\xi^2(T) = \frac{c_0}{p(T - T_{SP})} = \left(\frac{Ja}{2\pi T_{SP}}\right)^2 \beta(2) \frac{T_{SP}}{T - T_{SP}}$$
$$= \xi_{th}^2 \left(\frac{2}{\pi}\right)^2 \beta(2) \frac{T_{SP}}{T - T_{SP}}. \tag{39}$$

Near the transition, $\xi \gg \xi_{th}$. This justifies the Landau-Ginzburg approach where the magnetic fluctuations are integrated out and only structural fluctuations close to the transition are retained. As was done in Ref. 68, the contributions of these structural fluctuations to the specific heat can be analyzed by the techniques of Refs. 67 and 69.

D. Magnetic susceptibility

Here we consider the effect of a magnetic field on the spin-Peierls system. The field can close the spin triplet gap and induce incommensuration. Here, we restrict ourselves to fields much smaller than the gap and study their effect on the spin-Peierls transition temperature and the susceptibility. Using the perturbative approach[70] generalizing the one of Sec. I B we find that for small magnetic fields there is a reduction of the transition temperature T_{SP}, i.e., $T_{SP}(h) = T_{SP}(0) - \lambda h^2$, with $\lambda > 0$. Using bosonization (see the Appendix), we find

$$\lambda = \frac{\beta(2)}{\pi^2 T_{SP}} \simeq \frac{14.7}{16\pi^2 T_{SP}}. \tag{40}$$

This result is in accord with that of Ref. 70 where it was found that $\lambda \simeq 14.4/(16\pi^2 T_{SP})$. For large fields, a similar calculation can be done provided that the field is smaller than the soliton gap and the system does not exhibit a transition to the incommensurate phase.

On the other hand, to calculate the finite temperature susceptibility, we need to generalize the TBA equations to include the effect of a magnetic field. To recapitulate, in the absence of a field, we have two solitons of spin ± 1, a light breather of spin 0 forming a triplet and a heavy breather of spin 0. A field breaks the spin degeneracy and for small enough fields which do not induce any incommensuration we can use the TBA to calculate the magnetic susceptibility. Following Ref. 71, we obtain the following TBA equations:

$$\bar{\epsilon}_\sigma(\theta) = \frac{\pi}{2} M \cosh \theta - \bar{h}\sigma + \frac{\bar{T}}{2\pi} \sum_{\sigma=-1,0,1} \int d\theta' K_{11}(\theta - \theta')$$

$$\times \ln(1 + e^{-\bar{\epsilon}_\sigma(\theta')/\bar{T}}) + \frac{\bar{T}}{2\pi} \int d\theta' K_{12}(\theta - \theta')$$

$$\times \ln(1 + e^{-\bar{\epsilon}_2(\theta')/\bar{T}}),$$

$$\bar{\epsilon}_2(\theta) = \frac{\pi\sqrt{3}}{2} M \cosh \theta + \frac{\bar{T}}{2\pi} \sum_{\sigma=-1,0,1} \int d\theta' K_{12}(\theta - \theta')$$

$$\times \ln(1 + e^{-\bar{\epsilon}_\sigma(\theta')/\bar{T}}) + \frac{\bar{T}}{2\pi} \int d\theta' K_{22}(\theta - \theta')$$

$$\times \ln(1 + e^{-\bar{\epsilon}_2(\theta')/\bar{T}}),$$

$$f = \frac{\bar{K}}{2J} \delta^2 - \frac{\bar{T}}{2\pi} \int d\theta M \cosh \theta \left[\sum_{\sigma=1,0,-1} \ln(1 + e^{-\bar{\epsilon}_\sigma(\theta)/\bar{T}}) \right. $$
$$\left. + \sqrt{3} \ln(1 + e^{-\bar{\epsilon}_2(\theta)/\bar{T}}) \right] + \frac{M^2}{8\sqrt{3}}, \tag{41}$$

where the $\bar{\epsilon}_\sigma(\theta)$ denote the reduced pseudoenergies of the solitons ($\sigma = 1$), antisolitons ($\sigma = -1$), and light breathers ($\sigma = 0$) and $\bar{h} = h/J$. It is easy to see from the equations above that $\bar{\epsilon}_\sigma(\theta) = \bar{\epsilon}_0(\theta) - \bar{h}\sigma$. This allows us to reduce the set of TBA equations to 2:

$$\bar{\epsilon}_0(\theta) = \frac{\pi}{2} M \cosh \theta + \frac{3\bar{T}}{2\pi} \int d\theta' K_{11}(\theta - \theta') \ln(1 + e^{-\bar{\epsilon}_0(\theta')/\bar{T}})$$

$$+ \frac{\bar{T}}{2\pi} \int d\theta' K_{12}(\theta - \theta') \ln(1 + e^{-\bar{\epsilon}_2(\theta')/\bar{T}})$$

$$+ \frac{\bar{T}}{2\pi} \int d\theta' K_{11}(\theta - \theta') \ln \left[1 + \frac{\sinh^2\left(\frac{\bar{h}}{2\bar{T}}\right)}{\cosh^2\left(\frac{\bar{\epsilon}_0(\theta')}{2\bar{T}}\right)} \right],$$

$$\bar{\epsilon}_2(\theta) = \frac{\pi\sqrt{3}}{2} M \cosh \theta + \frac{3\bar{T}}{2\pi} \int d\theta' K_{12}(\theta - \theta') \ln(1$$

$$+ e^{-\bar{\epsilon}_0(\theta')/\bar{T}}) + \frac{\bar{T}}{2\pi} \int d\theta' K_{22}(\theta - \theta') \ln(1 + e^{-\bar{\epsilon}_2(\theta')/\bar{T}})$$

$$+ \frac{\bar{T}}{2\pi} \int d\theta' K_{12}(\theta - \theta') \ln \left[1 + \frac{\sinh^2\left(\frac{\bar{h}}{2\bar{T}}\right)}{\cosh^2\left(\frac{\bar{\epsilon}_0(\theta')}{2\bar{T}}\right)} \right]. \tag{42}$$

In the presence of a magnetic field, the law of corresponding states (28) now reads

$$F = -\frac{T_{SP}^2}{J} \mathcal{F}\left(\frac{T}{T_{SP}}, \frac{h}{T_{SP}}\right). \tag{43}$$

The magnetic susceptibility, $\chi(T) = -\lim_{h \to 0}(\partial^2 F/\partial h^2)$, satisfies the scaling relation

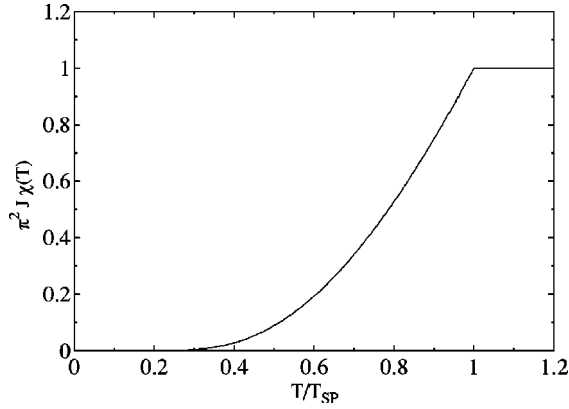FIG. 4. The magnetic susceptibility $\chi(T)$ versus the reduced temperature; for $T > T_{SP}$, $\chi(T) = 1/(\pi^2 J)$.

$$\chi(T) = \frac{1}{J} \mathcal{F}_y'' \left(\frac{T}{T_{SP}}, 0 \right), \tag{44}$$

where $\mathcal{F}_y'' = \partial_y^2 \mathcal{F}(x, y)$. For $T > T_{SP}$, the susceptibility is that of a free Bose gas: $\chi(T) = 1/(\pi^2 J)$. For temperatures $0 \leq T \leq T_{SP}$, the susceptibility can be obtained numerically from Eqs. (42) and (44). The results are plotted in Fig. 4.

As in the case of zero magnetic field, one has an effective-field-dependent Landau-Ginzburg functional which describes the physics in the vicinity of the transition. For $T \lesssim T_{SP}$ the behavior of the magnetic susceptibility is obtained from the following Landau-Ginzburg expansion:

$$F(T, h, \delta) = \frac{p}{2} [T - T_{SP}(h)] \delta^2 + \frac{q}{4} \delta^4 - \frac{\chi_0}{2} h^2, \tag{45}$$

where $\chi_0 = 1/(\pi^2 J)$ is the susceptibility of the undistorted chain. Minimizing F with respect to δ, one finds for $T < T_{SP}$:

$$F(T, h) = -\frac{p^2}{4q} [T - T_{SP}(0) + \lambda h^2]^2 - \frac{\chi_0}{2} h^2. \tag{46}$$

The definition of χ then gives

$$\chi(T < T_{SP}) = \chi_0 + \frac{p^2 \lambda}{q} [T - T_{SP}(0)]. \tag{47}$$

This behavior of the susceptibility is reminiscent of the one seen in a Néel antiferromagnet[72] which stems from the similarity of the mean-field equations for the spin-Peierls problem and the quasi-1D antiferromagnet. Using Eq. (40) and Eqs. (36) it is easily seen that the resulting susceptibility (47) satisfies to the law of corresponding states (44). Numerically, one finds that $p^2 \lambda / q = 0.257 / (J T_{SP})$ by fitting the susceptibility calculated near the transition to the Landau-Ginzburg form. If, on the other hand, we use the values of p and q obtained in Sec. II C combined with the value of λ in Eq. (40) we see that value $p^2 \lambda / q = 2.8 \times 14.7 / (16\pi^2 J T_{SP}) = 0.26 / (J T_{SP})$ differs from that obtained in the presence of a field by less than a percent. A Keesom-Ehrenfest relation[64] exists between the jump of the specific heat and the jump in the slope of the magnetic susceptibility as a function of temperature. This Keesom-Ehrenfest relation is given by the Landau-Ginzburg theory as

$$T_{SP}^2 \frac{\frac{d\chi}{dT}}{\Delta C_v} = \frac{\pi^2 - \psi^{(1)}(3/4)}{4\pi^2} = \frac{2\beta(2)}{\pi^2} \simeq 0.3724. \tag{48}$$

Such a proportionality has been observed in experiments on TTFAuBDT in magnetic fields.[73]

E. Low-temperature expansions

In the preceding sections, we have obtained analytical results for $T = 0$ and for $T \lesssim T_{SP}$. In fact, the TBA equations are amenable to analytical study for $T \gtrsim 0$ [more precisely $0 < T \ll \Delta(T=0)$]. In this regime, we expect that the mean-field gap $\Delta(T)$ remains very close to $\Delta(T=0)$, so that the thermodynamics does not differ from the one of the Heisenberg chain with dimerization. With this assumption, the TBA equations (for $h = 0$) to lowest order are

$$\epsilon_1(\theta) = \Delta(T=0) \cosh \theta + O(e^{-\Delta(T=0)/T}),$$

$$\epsilon_2(\theta) = \Delta(T=0) \sqrt{3} \cosh \theta + O(e^{-\Delta(T=0)/T}). \tag{49}$$

Substituting these in Eq. (22) for the free energy F, we see that the correction to F is indeed $O(e^{-\Delta(T=0)/T})$ which justifies our original assumption that $\Delta(T) \simeq \Delta(0)$. We now derive low-temperature expansions of the various physical quantities. It is convenient to use the the zero-temperature dimerization $\delta_0 = \delta(T=0)$, the zero-temperature gap $\Delta_0 = \Delta(T=0)$, and the zero-temperature ground-state energy E_0, the expressions of which are given in Eq. (8), to express the corresponding finite temperature quantities as a function of the dimensionless variable $\bar{\delta}$. We obviously have $\delta(T) = \delta_0 \bar{\delta}(T)$, and $\Delta(T) = \Delta_0 \bar{\delta}^{2/3}(T)$. The total energy at $T = 0$ reads

$$E(\bar{\delta}) = \frac{4}{\sqrt{3}} \left(\frac{\Gamma(1/6)}{\Gamma(2/3)} \right)^6 \left[\frac{\Gamma(3/4)}{\Gamma(1/4)\pi^2} \left(\frac{\pi}{2} \right)^{1/4} \right]^4 \frac{J^3}{k^2} \left[\bar{\delta}^2 - \frac{3}{2} \bar{\delta}^{4/3} \right] \tag{50}$$

and it is easy to see that $E(\bar{\delta})$ has a minimum for $\bar{\delta} = 1$. Expanding around this minimum we find

$$E(\bar{\delta}) - E_0 = \frac{2}{9\pi\sqrt{3}} \frac{\Delta_0^2}{J} (\bar{\delta} - 1)^2. \tag{51}$$

The expression (51) is not the full expression of the free energy for $T > 0$, as we have also to take into account the contributions of the solitons and the breathers that are thermally excited. Since the heavy breathers have mass $M\sqrt{3}$, as can be seen from Eq. (49), their contribution at low temperature is negligible with respect to the soliton contribution. Therefore, to lowest order, the thermal contribution to the free energy reads

$$F_{sol.} = -\frac{6T}{\pi^2} \frac{\Delta_0}{J} \bar{\delta}^{2/3} K_1 \left(\frac{\Delta_0}{T} \bar{\delta}^{2/3} \right), \tag{52}$$

where K_1 is a modified Bessel function[52] so that the full variational free energy is

$$F(T,\bar{\delta}) = E_0 + \frac{2}{9\pi\sqrt{3}}\frac{\Delta_0^2}{J}(\bar{\delta}-1)^2 - \frac{6T}{\pi^2}\frac{\Delta_0}{J}\bar{\delta}^{2/3}K_1\left(\frac{\Delta_0}{T}\bar{\delta}^{2/3}\right).$$

$$(53)$$

Minimizing Eq. (53) with respect to $\bar{\delta}$ we obtain

$$\bar{\delta} - 1 = \frac{9\sqrt{3}}{\pi}\left[K_1'\left(\frac{\Delta_0}{T}\bar{\delta}^{2/3}\right)\bar{\delta}^{1/3} + \frac{T\bar{\delta}^{-1/3}}{\Delta_0}K_1\left(\frac{\Delta_0}{T}\bar{\delta}^{2/3}\right)\right].$$

$$(54)$$

To lowest order, this gives

$$\bar{\delta} = 1 - 3^{7/2}\sqrt{\frac{2T}{\pi\Delta_0}}e^{-\Delta_0/T},$$

$$(55)$$

and

$$\Delta(T) = \Delta_0\left[1 - 6\sqrt{3}\sqrt{\frac{2T}{\pi\Delta_0}}e^{-\Delta_0/T}\right].$$

$$(56)$$

Substituting Eq. (55) in Eq. (53), we see that the correction to the elastic energy plus ground-state energy of the dimerized chain is of order $e^{-2\Delta_0/T}$ and is therefore negligible compared to the contribution of the solitons. In physical terms, this means that at sufficiently low temperature, the thermodynamics of the spin-Peierls chain is the same as the thermodynamics of a chain with a constant dimerization. Using this result, we find that

$$F(T) = -\frac{\Delta_0^2}{J}\left[\frac{6T}{\pi^2\Delta_0}K_1\left(\frac{\Delta_0}{T}\right)\right],$$

$$(57)$$

which leads to a low-temperature specific heat of the form

$$C_v(T) = \frac{3\sqrt{2}}{\pi^{3/2}}\frac{\Delta_0}{J}\left(\frac{\Delta_0}{T}\right)^{3/2}e^{-\Delta_0/T} + o(T^{-3/2}e^{-\Delta_0/T}).$$

$$(58)$$

In the presence of an infinitesimal applied magnetic field $h \ll T$, the lowest-order contribution to the low-temperature free energy is

$$F(T) = -\frac{\Delta_0^2}{J}\left[\frac{2T}{\pi^2\Delta_0}K_1\left(\frac{\Delta_0}{T}\right)\left(1 + 2\cosh\frac{h}{T}\right)\right],$$

$$(59)$$

and the magnetic susceptibility is readily obtained as

$$\chi(T) = \frac{1}{\pi^2 J}\sqrt{\frac{8\pi\Delta_0}{T}}e^{-\Delta_0/T} + o(T^{-1/2}e^{-\Delta_0/T}).$$

$$(60)$$

III. CONCLUSIONS

In this paper, we have studied the thermodynamics of the spin-Peierls system treated within a mean-field approximation. Using a combination of bosonization methods and the thermodynamic Bethe ansatz, we have been able to obtain quantitative results for the spin-Peierls transition temperature T_{SP}, the spin-Peierls gap to triplet excitations, the specific heat and magnetic susceptibility at arbitrary temperatures. Our calculations are a quantitative improvement of the results obtained by Cross and Fisher (who were restricted to

the vicinity of the spin-Peierls transition temperature) and consequently help us obtain the effective Landau-Ginzburg functional that describes the physics of dimerization close to the transition. It would be interesting to study this Landau-Ginzburg theory in one dimension, following Ref. 68 to understand more quantitatively how lattice fluctuations affect the thermodynamics. Similarly to Ref. 68, we should expect a regime of renormalized Gaussian fluctuations for $0.4T_{SP}^{MF} < T < T_{SP}^{MF}$, and a regime dominated by kinks for $0.3T_{SP} < T < 0.4T_{SP}$ as long as one-dimensional fluctuations dominate. Also, it should be possible to use the Landau-Ginzburg description to study the three-dimensional ordering of the dimerization along the lines of Refs. 67 and 69. The dependence of the transition temperature on interchain coupling will be similar to the one predicted in Ref. 74 since both models belong to the same universality class. A more direct extension of the present work would be to study the commensurate-incommensurate transition driven by an external magnetic field and then comparing the predicted results to various experiments on spin-Peierls systems. It would also be interesting to extend this study to the generalized spin-Peierls transition obtained in ladders under magnetic field[60] or to the antiferromagnetic phase transition obtained in the same system.[62] These questions are left for future work.

APPENDIX: CALCULATION OF THE RIGIDITY

Here, we present a derivation of the rigidity in our Landau-Ginzburg effective action. In the continuum limit, the space dependent dimerization leads to the modification of the sine Gordon term in Eq. (3),

$$H_{int} = -\frac{2g}{(2\pi a)^2}\int dx\,\delta(x)\cos\sqrt{2}\phi.$$

$$(A1)$$

Close to the transition, the second-order correction to the free energy of the spin chain induced by the spin-phonon coupling is given by

$$F_\delta = \frac{1}{4}\frac{\pi a}{\beta u}\left(\frac{g}{\pi a}\right)^2\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dx'\int_0^\beta \delta(x)\,\delta(x')\chi(x-x',\tau),$$

$$(A2)$$

and

$$\chi(x-x',\tau) = \sqrt{2}\left[\cosh\frac{2\pi x}{\beta u} - \cos\frac{2\pi\tau}{\beta}\right]^{-1/2}.$$

$$(A3)$$

In Fourier space, $F_\delta \propto \int dq/(2\pi)\delta(q)\delta(-q)\hat{\chi}(q,i\omega_n=0)$. To obtain the gradient term, it thus suffices to calculate the Fourier transform $\hat{\chi}$. In the limit $q\to 0$, $\hat{\chi}(q,i\omega_n=0) = \hat{\chi}(0,0) + q^2/2\hat{\chi}''(0,0)$. Plugging this form into Eq. (A2), it is straightforward to find the rigidity.

To find $\hat{\chi}(q)$ we generalize the calculation of the $q=0$ response function, and consider

$$\hat{\chi}(q) = \int dx\, d\tau\, \chi(x,\tau) e^{iqx}$$

$$= \int dx\, d\tau \frac{\sqrt{2}}{\sqrt{\left[\cosh\left(\frac{2\pi x}{\beta u}\right) - \cos\left(\frac{2\pi\tau}{\beta}\right)\right]}} e^{iqx}.$$

(A4)

Using Eq. (8.12.5) in Ref. 52, we can rewrite the integral:

$$\frac{a}{2}\int_{-\infty}^{\infty} dv \frac{e^{iq\beta u/(2\pi)v}}{\sqrt{\cosh v - \cos\frac{2\pi\tau}{\beta}}}$$

$$= \frac{\pi}{\sqrt{2}} a \frac{1}{\cosh\left(\frac{q\beta u}{2}\right)} P_{-1/2+i\beta uq/(2\pi)}\left(-\cos\frac{2\pi\tau}{\beta}\right).$$

(A5)

Consequently, to calculate Eq. (A4), we only need the integral:

$$\int_0^\beta P_{-1/2+i\beta uq/(2\pi)}\left(-\cos\frac{2\pi\tau}{\beta}\right) d\tau$$

$$= \frac{\pi\beta}{\left[\Gamma\left(\frac{3}{4} + \frac{iqu}{4\pi T}\right)\Gamma\left(\frac{3}{4} - \frac{iqu}{4\pi T}\right)\right]^2},$$

(A6)

which is easily obtained from Eq. (8.14.16) in Ref. 52. The final result is

$$\hat{\chi}(q) = \frac{\pi^2}{2\cosh\left(\frac{uq}{2T}\right)\Gamma\left(\frac{3}{4} + \frac{iqu}{4\pi T}\right)^2\Gamma\left(\frac{3}{4} - \frac{iqu}{4\pi T}\right)^2}.$$

(A7)

Expanding $\hat{\chi}(q)$ to second order in q, we find

$$F = F_0 - \frac{1}{16\pi^2 a^3 T\Gamma(3/4)^4}\int \frac{dq}{2\pi}|g(q)|^2\left[1 - \eta\left(\frac{uq}{2T}\right)^2\right],$$

(A8)

where

$$g(q) = \int g\,\delta(x) e^{iqx} dx,$$

(A9)

and $\eta = [\pi^2 - \psi^{(1)}(3/4)]/(2\pi^2)$ and $\psi^{(1)}(x)$ is the trigamma function (see Ref. 52, p. 260). The number $\psi^{(1)}(3/4)$ can be expressed as a function of Catalan's constant[52] $\beta(2)$ as $\psi^{(1)}(3/4) = \pi^2 - 8\beta(2) \simeq 2.5419$. Finally, using the expression of $g(x)$ as a function of $\delta(x)$ we obtain the rigidity c_0 as

$$c_0 = \frac{9}{64}\left(1 - \frac{\psi^{(1)}(3/4)}{\pi^2}\right)\left(\frac{\pi}{2}\right)^{1/2}\frac{1}{\Gamma(3/4)^4}\frac{J^4 a}{T^3}$$

$$= \frac{9}{8\pi^2}\left(\frac{\pi}{2}\right)^{1/2}\frac{\beta(2)}{\Gamma(3/4)^4}\frac{J^4 a}{T^3}.$$

(A10)

A similar calculation can be done to obtain the reduction of the critical temperature as a function of the magnetic field. When the system is magnetized, incommensuration in the staggered operator sets in as the wave vector shifts from $\pi/2$ to $\pi/2 \pm h/u$ and the equation giving the critical temperature reads

$$k = \frac{a}{2}\left(\frac{g}{2a\pi}\right)^2 \frac{\beta\,\text{sech}\left(\frac{\beta h}{2}\right)}{\Gamma\left(\frac{3}{4} - i\frac{\beta h}{4\pi}\right)^2\Gamma\left(\frac{3}{4} + i\frac{\beta h}{4\pi}\right)^2}. \quad (A11)$$

This implies that

$$T_{SP}(h)\cosh\left(\frac{h}{2T_{SP}(h)}\right)\left[\Gamma\left(\frac{3}{4} - i\frac{h}{4\pi T_{SP}(h)}\right)\right.$$

$$\left.\times\Gamma\left(\frac{3}{4} + i\frac{h}{4\pi T_{SP}(h)}\right)\right]^2 = T_{SP}(h=0)\Gamma(3/4)^4.$$

(A12)

Equation (A12) was obtained in Ref. 70 using a real time calculation of the response function. This can be seen explicitly by expressing the infinite products in Ref. 70 in terms of Gamma functions. Expanding Eq. (A12) around small h, one obtains for magnetic fields $h \ll T_{SP}(0)$

$$\frac{T_{SP}(h)}{T_{SP}(0)} \simeq 1 - 2[\pi^2 - \psi^{(1)}(3/4)]\left(\frac{h}{4\pi T_{SP}}\right)^2. \quad (A13)$$

In terms of Catalan's constant, the spin-Peierls transition temperature in the presence of a small field is given by

$$\frac{T_{SP}(h)}{T_{SP}(0)} = 1 - \beta(2)\left(\frac{h}{\pi T_{SP}}\right)^2 + o(h^2). \quad (A14)$$

[1] P. Pincus, Solid State Commun. **4**, 1971 (1971).

[2] E. Pytte, Phys. Rev. B **10**, 4637 (1974).

[3] R. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford, UK, 1955).

[4] I. S. Jacobs, J. W. Bray, H. R. Hart, Jr., L. V. Interrante, J. S. Kasper, G. D. Watkins, D. E. Prober, and J. C. Bonner, Phys. Rev. B **14**, 3036 (1976).

[5] S. Huizinga, J. Kommandeur, G. A. Sawatzky, B. T. Thole, K. Kopinga, W. J. M. de Jonge, and J. Roos, Phys. Rev. B **19**, 4723 (1979).

[6] A. Maaroufi, S. Flandrois, G. Fillion, and J. P. Morand, Mol. Cryst. Liq. Cryst. **119**, 311 (1985).

[7] J. P. Pouget, R. Moret, R. Comes, K. Bechgaard, J. M. Fabre, and L. Giral, Mol. Cryst. Liq. Cryst. **79**, 129 (1982).

[8] R. Laversanne, C. Coulon, B. Gallois, J. P. Pouget, and R. Moret, J. Phys. (France) Lett. **45**, L393 (1984).

[9] Q. Liu, S. Ravy, J. P. Pouget, C. Coulon, and C. Bourbonnais, Synth. Met. **56**, 1840 (1993).

[10] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).

[11] M. C. Cross and D. S. Fisher, Phys. Rev. B **19**, 402 (1979).

[12] J.-P. Pouget, S. Ravy, J. Schoeffel, G. Dhalenne, and A. Revcolevschi, Eur. Phys. J. B **38**, 581 (2004).

[13] J.-P. Pouget, Eur. Phys. J. B **20**, 321 (2001); **24**, 415(E) (2001).

[14] J. P. Boucher and L. P. Regnault, J. Phys. I **6**, 1939 (1996).

[15] R. J. Birgeneau, V. Kiryukhin, and Y. J. Wang, Phys. Rev. B **60**, 14 816 (1999).

[16] M. Braden, B. Hennion, W. Reichardt, G. Dhalenne, and A. Revcolevschi, Phys. Rev. Lett. **80**, 3634 (1998).

[17] C. Gros and R. Werner, Phys. Rev. B **58**, R14 677 (1998).

[18] P. Jordan and E. Wigner, Z. Phys. **47**, 631 (1928).

[19] A. Luther and I. Peschel, Phys. Rev. B **12**, 3908 (1975).

[20] F. D. M. Haldane, Phys. Rev. Lett. **45**, 1358 (1980).

[21] F. D. M. Haldane, Phys. Rev. B **25**, 4925 (1982); **26**, 5257(E) (1982).

[22] M. P. M. den Nijs, Phys. Rev. B **23**, 6111 (1981).

[23] R. Rajaraman, *Solitons and Instantons: An Introduction to Solitons and Instantons in Quantum Field Theory* (North Holland, Amsterdam, 1982).

[24] S. Lukyanov, Phys. Rev. B **59**, 11 163 (1999).

[25] I. Affleck, J. Phys. A **31**, 4573 (1998).

[26] S. Lukyanov and V. Terras, Nucl. Phys. B **654**, 323 (2003).

[27] M. Fowler and X. Zotos, Phys. Rev. B **24**, 2634 (1981).

[28] M. Fowler and X. Zotos, Phys. Rev. B **25**, 5806 (1982).

[29] M. D. Johnson, N.-N. Chen, and M. Fowler, Phys. Rev. B **34**, 7851 (1986).

[30] C. Destri and H. de Vega, Phys. Rev. Lett. **69**, 2313 (1992).

[31] C. Destri and H. de Vega, Nucl. Phys. B **438**, 413 (1995).

[32] C. Destri and H. de Vega, Nucl. Phys. B **504**, 621 (1997).

[33] A. B. Zamolodchikov, Int. J. Mod. Phys. A **10**, 1125 (1995).

[34] H. J. Schulz, Phys. Rev. Lett. **77**, 2790 (1996).

[35] Z. Wang, Phys. Rev. Lett. **78**, 126 (1997).

[36] F. H. L. Essler, A. M. Tsvelik, and G. Delfino, Phys. Rev. B **56**, 11 001 (1997).

[37] V. Y. Irkhin and A. A. Katanin, Phys. Rev. B **61**, 6757 (2000).

[38] M. Bocquet, Phys. Rev. B **65**, 184415 (2002).

[39] A. Zheludev, S. Raymond, L.-P. Regnault, F. H. L. Essler, K. Kakurai, T. Masuda, and K. Uchinokura, Phys. Rev. B **67**, 134406 (2003).

[40] H. J. Schulz, in *Mesoscopic Quantum Physics, Les Houches LXI*, edited by E. Akkermans, G. Montambaux, J. L. Pichard, and J. Zinn-Justin, (Elsevier, Amsterdam, 1995), p. 533.

[41] J. L. Black and V. J. Emery, Phys. Rev. B **23**, 429 (1981).

[42] I. Affleck, Nucl. Phys. B **265**, 448 (1986).

[43] A. M. Tsvelik, Phys. Rev. B **45**, 486 (1992).

[44] G. S. Uhrig and H. J. Schulz, Phys. Rev. B **54**, R9624 (1996).

[45] E. Orignac, Eur. Phys. J. B **39**, 335 (2004).

[46] L. P. Kadanoff, Phys. Rev. B **22**, 1405 (1980).

[47] M. Kohmoto, M. den Nijs, and L. P. Kadanoff, Phys. Rev. B **24**, 5229 (1981).

[48] I. Affleck, D. Gepner, T. Ziman, and H. J. Schulz, J. Phys. A **22**, 511 (1989).

[49] R. Chitra, S. Pati, H. R. Krishnamurthy, D. Sen, and S. Ramasesha, Phys. Rev. B **52**, 6581 (1995).

[50] K. Okamoto and K. Nomura, Phys. Lett. A **169**, 433 (1992).

[51] G. Castilla, S. Chakravarty, and V. J. Emery, Phys. Rev. Lett. **75**, 1823 (1995).

[52] M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).

[53] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).

[54] O. A. Starykh, R. R. P. Singh, and A. W. Sandvik, Phys. Rev. Lett. **78**, 539 (1997).

[55] T. Giamarchi and H. J. Schulz, Phys. Rev. B **39**, 4620 (1989).

[56] V. Barzykin and I. Affleck, J. Phys. A **32**, 867 (1999).

[57] V. Barzykin, J. Phys.: Condens. Matter **12**, 2053 (2000).

[58] P. Dorey, in *Conformal field theories and integrable models*, edited by Z. Horváth and L. Palla (Springer, Berlin, 1997), Lect. Notes Phys. **498**, 85 (1997).

[59] F. H. L. Essler, Phys. Rev. B **59**, 14 376 (1999).

[60] N. Nagaosa and S. Murakami, J. Phys. Soc. Jpn. **67**, 1876 (1997).

[61] R. Calemczuk, J. Riera, D. Poilblanc, J.-P. Boucher, G. Chaboussant, L. P. Lévy, and O. Piovesana, Eur. Phys. J. B **7**, 171 (1999).

[62] T. Giamarchi and A. M. Tsvelik, Phys. Rev. B **59**, 11 398 (1999).

[63] H. Saleur, in *Topological Aspects of Low Dimensional Systems*, edited by A. Comtet, T. Jolicoeur, S. Ouvry, and F. David, Les Houches Summer School No. 69 (Springer, Berlin, 1998), p. 475.

[64] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1960).

[65] J. C. Lasjaunias, P. Monceau, G. Remenyi, S. Sahling, G. Dhalenne, and A. Revcolevschi, Solid State Commun. **101**, 677 (1997).

[66] M. Le Bellac, *Quantum and Statistical Field Theory* (Oxford University Press, Oxford, UK, 1992).

[67] D. J. Scalapino, Y. Imry, and P. Pincus, Phys. Rev. B **11**, 2042 (1975).

[68] C. Bourbonnais and B. Dumoulin, J. Phys. I **6**, 1727 (1996).

[69] D. J. Scalapino and M. Sears, Phys. Rev. B **6**, 3409 (1972).

[70] M. C. Cross, Phys. Rev. B **20**, 4606 (1979).

[71] R. M. Konik and P. Fendley, Phys. Rev. B **66**, 144416 (2002).

[72] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continous Media* (Pergamon, New York, 1960).

[73] J. A. Northby, F. J. A. M. Greidanus, W. J. Huiskamp, L. J. de Jongh, I. S. Jacobs, and L. V. Interrante, J. Appl. Phys. **53**, 8032 (1982).

[74] M. Mostovoy and D. Khomskii, Z. Phys. B: Condens. Matter **103**, 209 (1997).