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Statistical mechanics of the double-quadratic chain: Exact results and ideal-gas phenomenology for nonreflectionless solitary waves

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The ideal-gas phenomenology of Currie and co-workers is extended to systems which bear solitary-wave excitations that are nontransparent to small oscillations. This extension enlarges the class of nonlinear systems which may be viewed at low temperatures as ideal gases of kinks and phonons. The authors treat the double-quadratic chain in detail, finding that the analysis can be carried quite far for this simple example system.

I. INTRODUCTION

The subject of solitary-wave (soliton) phenomena in condensed matter[1] is now enjoying a remarkable boom period. A great deal is known about the properties of solitary waves in a variety of physical situations, and the ease with which these properties can be studied is surely one of the primary ingredients of the soliton success story. In a seemingly endless string of investigations, workers in the area have been able to carry their studies quite far analytically. Moreover, the principal themes[2] regarding solitons can be stated simply and understood quite easily by the novice.

Leaving aside philosophical arguments concerning the esthetic requirement that *correct* physics should be *simple*, one nevertheless can be quite amazed by the beauty and simplicity of two example systems which bear solitary-wave excitations, namely, those governed by the sine-Gordon[3] (SG) and the so-called "ϕ^4" nonlinear wave equations.[4] These two equations have a great deal in common, and many discussions of their solitary-wave or "kink" solutions can be, and have been,[5-7] based on fundamental features which they share. For example, analytic solutions[3-7] are known in both cases for the kinks (and their antikinks); perturbation theories for both types of kinks have a very similar structure,[8,9] relying heavily on the existence of a kink "translation mode"; both types of kink solutions can be quantized using the same procedure.[6]

One of the fascinating features shared by SG and ϕ^4 kinks is their transparency to linear extended-waves solutions. The presence of a kink in the system provides a localized "potential" seen by the linear solutions ("phonons") in the sense that small deviations from the kink waveform must satisfy a Schrödinger-like equation[5-8,10,11] in which the potential well is due to the presence of the kink. Remarkably, the SG and ϕ^4 kink potentials appearing in this one-dimensional Schrödinger problem are completely reflectionless[10,11] since the reflection coefficient[12] for the scattering (or "continuum") states *vanishes* for *all* k values.

The fact that the SG and ϕ^4 kinks are reflectionless or transparent to small oscillations has enabled Currie *et al.*[7] to carry out an analytic investigation of the statistical mechanics of these systems at low temperatures. By comparing with exact results obtained via the transfer-operator technique, these workers were able to justify the use of a phenomenological approach which treats the system as an "ideal gas" of kinks and "phonons" at low temperatures, based on the work of Krumhansl and Schrieffer.[4] One of the key points in Ref. 7 is that care must be exercised in treating the effect of kinks on the phonon density of states, since phonon degrees of freedom are taken up by the kinks and this provides the mechanism for free-energy sharing among the modes of these *nonlinear* systems. The reflectionless property of SG and ϕ^4 kinks allows one to easily examine the effect of kinks on the phonon density of states in an analytic fashion and obtain closed-form expressions for various thermodynamic functions via the phenomenological approach.

The purpose of the present paper is to extend the ideal-gas phenomenology to systems bearing kinks which are *nonreflectionless*. Such systems are very likely to be the rule rather than the exception, since it is unlikely that a physical condensed system will be *exactly* described by either of the special cases having reflectionless kinks. Since the general approach is discussed in Ref. 7, we limit ourselves here to an illustration of the methodology by considering a simple example which can be examined analytically, namely, the double-quadratic (DQ) chain. This is a linear chain of harmonically coupled point masses each of which moves in a double-well potential similar to the ϕ^4 potential but different in analytic form.

In Sec. II we describe this example system in detail and discuss the kink solutions to the equation

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of motion as well as small oscillations (phonons) in the presence of a kink. The exact statistical mechanics of the DQ chain is discussed in Sec. III via the transfer-operator technique, and an explicit expression is given for the free energy at low temperatures. In Sec. IV we construct the ideal-gas phenomenology at low temperatures by making use of the results of Sec. II to explicitly account for the nonreflectionless nature of the DQ kink. By comparing the phenomenological free energy with that obtained in Sec. II we conclude that the ideal-gas concept of Krumhansl and Schrieffer is valid for these more general systems as well. Finally, in Sec. V we give a brief summary.

II. EQUATION OF MOTION AND SOLITARY-WAVE SOLUTIONS

In this section we describe a simple example of a solitary-wave-bearing system in which the solitary waves (kinks) present a nonreflectionless potential for scattering the linearized excitations (phonons). The analysis can be carried quite far in closed form, and we present explicit expressions for the kink solutions, phonon solutions in the presence of a kink, and the modification of the phonon density of states by a kink. The results in this section provide the basis for the phenomenological statistical mechanics discussed in Sec. IV.

The system under consideration consists of a one-dimensional chain of N harmonically coupled oscillators governed by the Hamiltonian

$$H=\sum_{i=1}^{N} lA\left(\tfrac{1}{2}\dot{\phi}_i^2+\frac{1}{2}\,\frac{c_0^2}{l^2}\,(\phi_{i+1}-\phi_i)^2+\omega_0^2\,V(\phi_i)\right), \tag{2.1}$$

where ϕ_i is the "displacement" coordinate of the ith oscillator, l the equilibrium spacing between nearest neighbors, and $V(\phi)$ is an "on-site" potential having the form of a double-quadratic (DQ) well[13] (as shown in Fig. 1):

$$V(\phi)=\tfrac{1}{2}(|\phi|-1)^2. \tag{2.2}$$

The first term in Eq. (2.1) represents the kinetic energy carried by the displacement field (a dot denotes a time derivative) and the second term represents harmonic coupling ("strain" energy) between field values at neighboring lattice sites. The constant c_0 is the characteristic velocity in the system and represents the limiting velocity of the kink (see below). The constant ω_0 is the characteristic frequency of oscillation and represents the limiting frequency of long-wavelength phonons. The overall constant A sets the energy scale and has dimensions of energy $\times$ (length)$^{-1}$ $\times$ (time)^2.

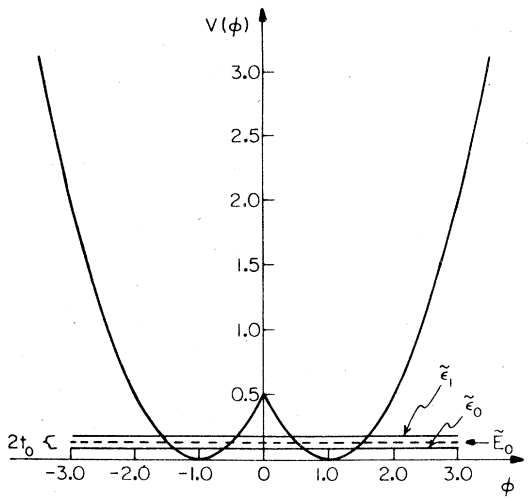

FIG. 1. Double-quadratic (DQ) potential. The lowest two eigenvalues, $\tilde{\epsilon}_0=\epsilon_0-V_0$ and $\tilde{\epsilon}_1=\epsilon_1-V_0$, of Eq. (3.9) are represented schematically by the horizontal solid lines. These two eigenvalues are symmetrically tunnel split (total splitting $=2t_0$) from the lowest level $\tilde{E}_0=E_0-V_0$ of an isolated harmonic well. The height of $\tilde{E}_0$ above zero and the magnitude of the splitting are grossly exaggerated for clarity.

We restrict ourselves to the so-called displacive limit when the coupling between sites is strong enough to ensure that variations of ϕ from site to site are quite small, at least at low temperatures. In this limit we may replace the site index i by a continuous position variable x so that ϕ becomes a continuous function of x and t, $\phi(x,t)$. The relevant length scale then becomes $d\equiv c_0/\omega_0$ $(d\gg l)$, and it is in this limit that nonlinear kinks become well-defined[14] elementary excitations with long lifetimes, and as such behave[8] very much like particles.

In the continuum (displacive) limit the Hamiltonian (2.1) is replaced by

$$H=A\int dx\,\{\tfrac{1}{2}[\dot{\phi}(x,t)]^2+\tfrac{1}{2}c_0^2[\phi_x(x,t)]^2+\omega_0^2\,V(\phi)\}, \tag{2.3}$$

where

$$\phi_x(x,t)=\frac{\partial}{\partial x}\,\phi(x,t)$$

replaces the finite difference $(\phi_{i+1}-\phi_i)/l$. We shall have occasion to employ both forms [(2.1) and (2.3)] of the Hamiltonian for the system. The discrete form (2.1) is used in obtaining exact statistical-mechanical results via the transfer-operator formalism (Sec. III), whereupon the process

of taking the continuum limit afterwards becomes explicit. The continuum form (2.3) is used to study the nature of the solitary-wave (kink) and linear (phonon) excitations of the system; these excitations are then introduced into the statistical mechanics through an ideal-gas phenomenology (Sec. IV).

The excitations we are concerned with arise as solutions of the Euler-Lagrange equation of motion following from Eq. (2.3):

$$\ddot{\phi} - c_0^2 \phi_{xx} + \omega_0^2(|\phi| - 1)\,\mathrm{sgn}\phi = 0 . \tag{2.4}$$

The linear "phonon" solutions of Eq. (2.4) have the form

$$\phi \pm 1 = \phi_0 \cos(kx - \omega_k t) , \tag{2.5}$$

where the magnitude of ϕ_0 must be less than 1, ($|\phi_0|<1$), but is *not* required to be infinitesimally small, since the individual potential wells are *perfectly* harmonic for $|\phi_0|<1$. The dispersion relation for these solutions is given by

$$\omega_k^2 = \omega_0^2 + c_0^2 k^2 , \tag{2.6}$$

which is the continuum limit of the discrete-lattice dispersion relation,

$$\omega_k^2 = \omega_0^2 + 4(c_0/l)^2 \sin^2(lk/2) . \tag{2.7}$$

The solitary-wave (kink) solutions of Eq. (2.4) evolve the field from one minimum of the DQ well to the other minimum. Because of the covariance of Eq. (2.4), we may solve first for the static-kink waveform and then "boost" the solution to any frame moving with velocity v ($|v|<c_0$). The static-kink solution can be obtained quite easily by considering the regions $x>0$ and $x<0$ separately. For the kink solution we impose the boundary conditions $\phi(+\infty)=1$, $\phi(0)=0$, and $\phi(-\infty)=-1$, while for the antikink solution the sign of ϕ is reversed. For the kink we have $\phi>0$ for $x>0$, and Eq. (2.4) in this region becomes

$$-c_0^2 \phi_{xx} + \omega_0^2(\phi - 1) = 0 \quad (x>0) , \tag{2.8}$$

with the solution

$$\phi(x) = 1 - \exp(-x/d) \quad (x>0) . \tag{2.9}$$

For $x<0$, we have $\phi<0$, and

$$-c_0^2 \phi_{xx} - \omega_0^2(\phi + 1) = 0 \quad (x<0) , \tag{2.10}$$

with the solution

$$\phi(x) = -[1 - \exp(x/d)] \quad (x<0) . \tag{2.11}$$

Combining Eqs. (2.9) and (2.11), we have the full static solution:

$$\phi_K^{(0)} = \pm(\mathrm{sgn}x)[1 - \exp(-|x|/d)] , \tag{2.12}$$

where we have included the antikink case (−sign) as well. The traveling-kink solutions are obtained by boosting to velocity v:

$$\phi_K^{(v)}(x,t) = \pm\,\mathrm{sgn}\left(\frac{x-vt}{(1-v^2/c_0^2)^{1/2}}\right)\left[1 - \exp\left(-\frac{|x-vt|}{d(1-v^2/c_0^2)^{1/2}}\right)\right] \tag{2.13}$$

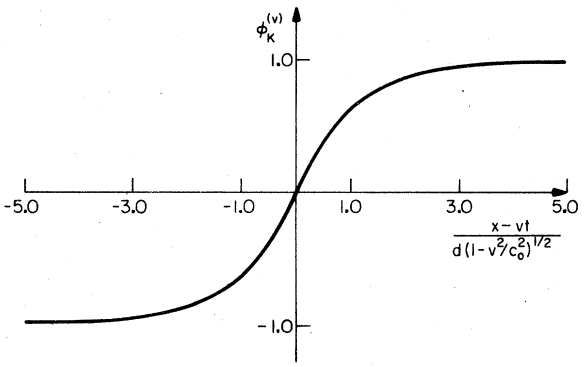

FIG. 2. Waveform $\phi_K^{(v)}$ of the traveling kink, viewed in its rest frame. The antikink waveform is obtained by reflection through the horizontal axis.

In Fig. 2 we have plotted the waveform of the kink in its rest frame.

The energy required to create a kink (or antikink) can be obtained by substituting the static-kink solution (2.12) into Eq. (2.3) and performing the integration over x. The kink rest energy is thus found to be

$$E_K^{(0)} = A\omega_0 c_0 = M_k c_0^2 , \tag{2.14}$$

and the energy of a kink moving with velocity v is simply

$$E_K^{(v)} = A\omega_0 c_0 (1 - v^2/c_0^2)^{-1/2} . \tag{2.15}$$

The "rest mass" M_K of the kink is

$$M_K = A/d . \tag{2.16}$$

We now turn our attention to an examination of small oscillations in the presence of a kink. We suppose that a kink is at rest at the origin ($x=0$). The subsequent analysis can be made applicable to a moving kink as well by simply transforming to the kink rest frame. We write

$$\phi(x,t) = \phi_K^{(0)}(x) + \psi(x,t) , \tag{2.17}$$

where $\phi_K^{(0)}(x)$ is the static-kink waveform (2.12) and $\psi(x,t)$ is assumed to be a small deviation. Using the fact that $\phi_K^{(0)}$ satisfies Eq. (2.4), we find that $\psi(x,t)$ is governed by

$$\ddot{\psi}(x,t) - c_0^2 \psi_{xx}(x,t) + \omega_0^2 V''[\phi_K^{(0)}(x)]\,\psi(x,t) = 0 . \tag{2.18}$$

By writing

$$\psi(x,t)=f(x)e^{-i\omega t} \tag{2.19}$$

and making use of the relation

$$V''(\phi_K(x))=1-2d\delta(x)\,, \tag{2.20}$$

where $\delta(x)$ is the Dirac δ function, Eq. (2.18) reduces to

$$-c_0^2 f_{xx}(x)-2d\omega_0^2\delta(x)f(x)=(\omega^2-\omega_0^2)f(x)\,. \tag{2.21}$$

This equation has the form of Schrödinger's equation for a particle in the presence of a δ-function potential well. There exists exactly one "bound state" with eigenvalue

$$\omega_b^2=0 \tag{2.22}$$

and corresponding normalized eigenfunction

$$f_b(x)=d^{1/2}\exp(-|x|/d)\,. \tag{2.23}$$

We note that this bound-state solution for small oscillations about the kink simply corresponds to the "translation mode"[5-10] of the kink and its presence is required by Goldstone's theorem.

We now turn our attention to the scattering or continuum-state solutions of Eq. (2.21). First we note that the δ-function potential is *not* reflectionless, in contrast to the potentials which arise in the ϕ^4 and SG cases.[6] This is easily seen by supposing that a "particle" is incident from the left so that the assumed solution of Eq. (2.21) takes the form

$$f_k^<(x)=e^{ikx}+re^{-ikx}\,, \tag{2.24a}$$

$$f_k^>(x)=\tau e^{ikx}\,, \tag{2.24b}$$

with

$$\omega_k^2=\omega_0^2+c_0^2k^2\,. \tag{2.25}$$

The $<(>)$ signs refer to $x<0(>0)$. The coefficients r and τ are determined by the continuity condition

$$f_k^<(0)=f_k^>(0)\equiv f_k(0)\,, \tag{2.26}$$

and by the relation

$$[(f_k^<(x))_x-(f_k^>(x))_x]_{x=0}=(2/d)f_k(0)\,, \tag{2.27}$$

which is obtained by integrating Eq. (2.21) over an infinitesimal neighborhood of $x=0$. After simple algebra, one finds

$$r=-1/(1+idk) \tag{2.28a}$$

and

$$\tau=idk/(1+idk)\,, \tag{2.28b}$$

so that the reflection and transmission coefficients, R and T, are given by

$$R=|r|^2=1/(1+d^2k^2) \tag{2.29a}$$

and

$$T=|\tau|^2=d^2k^2/(1+d^2k^2)\,, \tag{2.29b}$$

with the condition $R+T=1$ being obviously satisfied.

In contrast to the usual quantum-mechanical situation just described (e.g., a particle incident from one side), the physical situation we have in mind is rather that we have a kink placed at $x=0$ and want to determine the allowed "extended" states of small oscillation about the kink. Thus, there is no *a priori* reason to assume an asymmetric solution of the form (2.24). Indeed, it is more convenient to consider continuum-state solutions having definite parity. In the statistical-mechanical calculations described below, we impose (for convenience) periodic boundary conditions on the field configurations of the chain of length L (L is taken to infinity only *after* the calculation of partition functions, etc.). One way to view the system is as a ring of large circumference L. Imagine for the moment that there is only one kink present on the ring. This violates the periodic boundary condition (the ring becomes a Möbius strip), but at low temperatures ($k_BT \ll E_K^{(0)}$) the actual equilibrium kink density will be very low and we may add the effects of an equal number of essentially isolated kinks and antikinks on the continuum density of states. By imposing periodic boundary conditions on the small oscillations, we ensure the satisfaction of periodic boundary conditions when *equal* numbers of kinks and antikinks are present.

The continuum states of odd parity are unaffected by the presence of the δ-function potential since $f(x)$ vanishes at $x=0$ if $f(x)$ is odd. Thus

$$f_{k,-}(x)=S_k\sin(kx)\,, \tag{2.30}$$

where the minus sign $(-)$ denotes odd parity and S_k is a normalization constant. The states of even parity may be written in the form

$$f_{k,+}^<(x)=C_k\cos[kx-\tfrac{1}{2}\Delta_+(k)] \tag{2.31a}$$

and

$$f_{k,+}^>(x)=C_k\cos[kx+\tfrac{1}{2}\Delta_+(k)]\,, \tag{2.31b}$$

where C_k is a normalization constant and the function $\Delta_+(k)$ allows for the discontinuity in slope at $x=0$. Conditions (2.26) and (2.27) determine the form of $\Delta_+(k)$:

$$\Delta_+(k)=2\cot^{-1}(dk)\,, \tag{2.32a}$$

or, equivalently,

$$\Delta_+(k)=\pi k/|k|-2\tan^{-1}(dk)\,. \tag{2.32b}$$

The function $\Delta_+(k)$ may be interpreted as a k-dependent phase shift of the cosine function (2.31). For more general kink-bearing systems, the states of odd parity may also be "phase shifted", so that a function $\Delta_-(k)$ may be needed as well.

However, $\Delta_-(k)=0$ for the DQ case treated here. We note that because of the pointlike nature of the δ function, the phase shift $\Delta_+(k)$ occurs entirely at the kink center, rather than developing gradually as in the case[10,11] of the ϕ^4 and SG kinks.

The allowed k values for the continuum states are determined by the periodicity conditions

$$f_{k,-}(x+L)=f_{k,-}(x) \tag{2.33a}$$

and

$$f^{>}_{k,+}(x+L)=f^{<}_{k,+}(x)\,. \tag{2.33b}$$

For the odd states, the allowed k values are $k=2n\pi/L$ $(n=\pm1,\pm2,\ldots)$. However, the states at $+k$ and $-k$ are not physically distinct, as can be seen from Eq. (2.30). We may choose either the states with $n<0$ or the states with $n>0$ as the physical states. For convenience we choose $k=2n\pi/L$ $(n=-1,-2,-3,\ldots)$ for the odd states. For the even states, k and $-k$ also represent the same state, and we choose the *positive* k states with k values determined by

$$kL+\Delta_+(k)=2n\pi \quad (n=1,2,\ldots)\,, \tag{2.34}$$

which follows from substitution of (2.31) into (2.33b). We see that the allowed k values for the even states are shifted *due to the presence of a kink*. Indeed, the $k=0$ even state is "lost" altogether, becoming "trapped" by the kink to become the kink's translation mode.

The reason for our seemingly arbitrary choice of labeling odd states by negative k values and even states by positive k values is that we may now define a density of states $\rho(k)$ for all k values running from $-\infty$ to $+\infty$. To this end, we note that the positive k values are shifted [due to $\Delta_+(k)$] while the negative k values are unshifted. We thus find it convenient to define a generalized phase-shift function

$$\begin{aligned}\tilde{\Delta}(k)&\equiv\Theta(k)\Delta_+(k)\\&=\Theta(k)[\pi-2\tan^{-1}(dk)]\,,\end{aligned} \tag{2.35}$$

where $\Theta(k)$ is the Heaviside step function defined by $\Theta(k)=0$ for $k<0$ and $\Theta(k)=1$ for $k\geq0$. Thus $\tilde{\Delta}(k)=0$ for $k<0$ and $\tilde{\Delta}(k)=\Delta_+(k)$ for $k>0$. The density of states in the presence of a kink is then given by

$$\rho(k)=\frac{dn}{dk}=\frac{L}{2\pi}+\frac{1}{2\pi}\,\frac{d\tilde{\Delta}(k)}{dk}-\delta(k)\,, \tag{2.36}$$

where the subtraction of the δ function incorporates the loss of the $k=0$ state. Substitution of Eq. (2.35) into Eq. (2.36) yields

$$\rho(k)=L/2\pi-\tfrac{1}{2}\,\delta(k)-\Theta(k)d/\pi(1+d^2k^2)\,. \tag{2.37}$$

The density of states in the *absence* of a kink has the uniform value $\rho_0(k)=L/2\pi$, since in this case $k=2\pi n/L$ $(n=-1,-2,\ldots)$ for the odd states and $k=2\pi n/L$ $(n=0,1,2,\ldots)$ for the even states. The *change* in the density of states due to the presence of a kink is thus

$$\Delta\rho(k)=\rho(k)-\rho_0(k)=-\tfrac{1}{2}\,\delta(k)-\Theta(k)d/\pi(1+d^2k^2)\,. \tag{2.38}$$

The total change in the *number* of states is then

$$\Delta N=\int_{-\infty}^{+\infty}dk\,\Delta\rho(k)=-1\,, \tag{2.39}$$

i.e., the total number of continuum states is decreased by one. Note that this is consistent with Levinson's theorem[15]: $\tilde{\Delta}(0^+)=\pi$ times the number of bound states. This trapping of a continuum state by the kink is the mechanism by which degrees of freedom are shared among the nonlinear "normal modes" of the system. This feature plays a central role in the phenomenological statistical mechanics discussed in Sec. IV, but first we turn to an exact calculation of the statistical mechanics in Sec. III.

III. EXACT STATISTICAL MECHANICS

In this section we discuss an exact calculation of the classical partition function for the discrete DQ system governed by the Hamiltonian given in Eq. (2.1) above. We shall be particularly interested in the low-temperature free-energy correlation functions, etc., in the continuum limit (as $l/d\to0$). It is in these limits that we expect to be able to identify kink and "phonon" contributions separately.

The exact statistical mechanics can be investigated using a transfer-integral operator technique which has been well documented.[4,16-18] The classical partition function factors as

$$Z=Z_\phi Z_\phi\,, \tag{3.1}$$

with

$$Z_\phi=(2\pi Al/\beta h^2)^{N/2} \tag{3.2}$$

and

$$Z_\phi=\sum_n\exp(-\beta A\omega_0^2L\epsilon_n)\,, \tag{3.3}$$

where $\beta\equiv(k_BT)^{-1}$, h is Planck's constant, and $L=Nl$ is the total length of the system of N particles with periodic boundary conditions: $\phi_{N+1}=\phi_1$. The quantities ϵ_n appearing in Eq. (3.3) for the "configurational" partition function Z_ϕ are the eigenvalues of the transfer-integral operator defined[18] by

$$\begin{aligned}\int_{-\infty}^{+\infty}d\phi_i\exp[-\beta lA\omega_0^2f(\phi_{i+1},\phi_i)]\Phi_n(\phi_i)\\=\exp[-\beta lA\omega_0^2\epsilon_n]\Phi_n(\phi_{i+1})\,,\end{aligned} \tag{3.4}$$

where

$$f(\phi_{i+1},\phi_i)\equiv\tfrac{1}{2}(d^2/l^2)(\phi_{i+1}-\phi_i)^2+\tfrac{1}{2}[V(\phi_i)+V(\phi_{i+1})]. \tag{3.5}$$

The eigenfunctions $\{\Phi_n\}$ constitute a complete orthonormal set on the interval $(-\infty,+\infty)$.

In the thermodynamic limit ($N\to\infty, L\to\infty, L/N=l$ = constant), Z_ϕ is dominated by the lowest eigenvalue ϵ_0 so that the configurational (i.e., potential energy) contribution to the free-energy density becomes

$$F_\phi/L=-(k_BT/L)\ln Z_\phi \xrightarrow[L\to\infty]{} A\omega_0^2\epsilon_0. \tag{3.6}$$

Other equilibrium properties can be calculated[4,16] with the same technique. For instance, the static-correlation functions for the field and the squared field are given by[16]

$$C_1(x)\equiv\langle\delta\phi(x)\delta\phi(0)\rangle = \sum_n |\langle n|\delta\phi|0\rangle|^2\exp[-\beta A\omega_0^2(\epsilon_n-\epsilon_0)x] \tag{3.7}$$

and

$$C_2(x)\equiv\langle\delta\phi^2(x)\delta\phi^2(0)\rangle = \sum_n |\langle n|\delta\phi^2|0\rangle|^2\exp[-\beta A\omega_0^2(\epsilon_n-\epsilon_0)x], \tag{3.8}$$

respectively, where $\delta\phi(x)\equiv\phi(x)-\langle\phi\rangle$ and $\delta\phi^2(x)=\phi^2(x)-\langle\phi^2\rangle$. At large distances $C_1(x)$ and $C_2(x)$ are dominated by the state with the smallest eigenvalue for which the corresponding matrix elements (between $\Phi_n=|n\rangle$ states) are nonvanishing (excluding the $n=0$ terms).

In the displacive limit ($l/d\ll 1$) the Fredholm integral equation (3.4) for $\Phi(\phi)$ can be replaced[18] by the following differential eigenvalue equation [valid to $O(l/d)$] for a related eigenfunction

$\psi(\phi)=\exp[-\frac{1}{2}\beta lA\omega_0^2V(\phi)]\Phi(\phi)$:

$$-\frac{1}{2m^*}\frac{d^2\psi}{d\phi^2}+\tfrac{1}{2}(|\phi|-1)^2\psi=(\epsilon-V_0)\psi, \tag{3.9}$$

where

$$m^*=A^2\omega_0^2c_0^2\beta^2=(E_K^{(0)}/k_BT)^2 \tag{3.10}$$

and

$$V_0=(2\beta\omega_0^2lA)^{-1}\ln(Ac_0^2\beta/2\pi l). \tag{3.11}$$

We are thus faced with a pseudo-Schrödinger equation for a single particle of dimensionless mass m^* in one dimension, moving in the double-quadratic potential well [Eq. (2.2)]. We note that V_0 acts as a temperature-dependent "energy" zero which is important for free energy, entropy, etc., but not for correlation functions. No real quantum mechanics is involved in Eq. (3.9) ($\hbar$ is replaced essentially by temperature) but intuition from the familiar quantum problem is very helpful.

Physical interpretations of thermodynamic functions following from Z are possible at both high[19] and low temperatures. Here we shall concentrate on the low-temperature region, specifically $\beta E_K^{(0)}\gg 1$, where kink excitations are well defined and play a prominent role even though their density is low. In this regime $m^*\gg 1$ and the eigenspectrum of Eq. (3.9) will be "tunnel split" to remove degeneracy from the eigenstates of the individual wells in the DQ potential. Referring to Fig. 1, if E_0 is the lowest level in a single isolated harmonic well, then

$$\epsilon_0=E_0-t_0, \tag{3.12}$$

where t_0 is the tunneling component. At low T ($m^*\gg 1$), E_0 is given by the lowest harmonic-oscillator level:

$$E_0=\tfrac{1}{2}m^{*-1/2}+V_0. \tag{3.13}$$

The tunneling component t_0 can be obtained approximately by the WKB method or by a more accurate technqiue based on Goldstein's method.[20,21] The eigensolutions of Eq. (3.9) may be obtained by recognizing[22] that on either side of $\phi=0$, Eq. (3.9) is the parabolic-cylinder equation.[23] The eigenvalues $\tilde{\epsilon}=\epsilon_n-V_0$ are determined by the transcendental equations[22]

$$D'_{\tilde{\epsilon}-1/2}(-2^{1/2}m^{*1/4})=0 \tag{3.14a}$$

for the even states, and

$$D_{\tilde{\epsilon}-1/2}(-2^{1/2}m^{*1/4})=0 \tag{3.14b}$$

for the odd states, where $D_\nu(z)$ is the parabolic-cylinder function.[23] When $m^*\gg 1$, the asymptotic expansions[23] of $D_\nu(z)$ may be used to obtain the splitting between the two lowest levels, with the result[22] that t_0 is given by

$$t_0=\pi^{-1/2}m^{*-1/4}\exp(-m^{*1/2}), \tag{3.15}$$

or, using Eq. (3.10), we have

$$t_0=\pi^{-1/2}(k_BT/E_K^{(0)})^{1/2}\exp(-E_K^{(0)}/k_BT). \tag{3.16}$$

The tunneling part of the free-energy density is thus given by

$$F_t/L=-\pi^{-1/2}A\omega_0^2(\beta E_K^{(0)})^{-1/2}\exp(-\beta E_K^{(0)}). \tag{3.17}$$

The appearance of the kink rest energy in the tunneling free energy leads us naturally to the question of whether the kink and phonon excitations

appear as elementary excitations in the formal statistical mechanics, and in particular, to what extent the excitations may be treated as a composition of "noninteracting gases". Following the qualitative suggestions of Krumhansl and Schrieffer[4] (KS) in the ϕ^4 example, it is not difficult to demonstrate that the component E_0 of ϵ_0, taken together with *all* of $L^{-1}F_{\dot\phi}$ [from Eq. (3.2)], corresponds *exactly* to the free-energy density $L^{-1}F_0$ of a set of one-dimensional classical harmonic phonons—calculated to $O(l/d)$ to be consistent with Eq. (3.9). It is essential that the discrete dispersion relation (2.7) be used in order to be consistent with the transfer-operator technique. We find

$$L^{-1}F_0 = \frac{k_BT}{2\pi}\int_{-\pi/l}^{\pi/l} dk\,\ln(\beta\hbar\omega_K)$$
$$= l^{-1}k_BT\left(\ln(\hbar\omega_0\beta) + \ln\left\{\tfrac{1}{2}\left[1+(1+4d^2/l^2)^{1/2}\right]\right\}\right) \tag{3.18}$$

$$\xrightarrow[l\to 0]{} k_BT[l^{-1}\ln(\hbar\omega_0\beta d/l) + (2d)^{-1}]$$
$$= A\omega_0^2 E_0 - k_BTL^{-1}\ln Z_{\dot\phi}\,. \tag{3.19}$$

This appealing identification of E_0 leads us to speculate that t_0 corresponds to the free energy of a gas of independent kinks. However, we see from Eq. (3.19) that *all* of the "dynamical" free energy ($F_{\dot\phi}$) is apparently taken up by the phonon modes. We shall see in Sec. IV. that this is remedied by the subtle sharing of degrees of freedom hinted at in Sec. II.

IV. IDEAL-GAS PHENOMENOLOGY

In this section we describe a phenomenological approach to the statistical mechanics of the double-quadratic chain in which kinks and phonons serve as elementary excitations which share degrees of freedom. The key to understanding the role of kink-phonon interactions lies in recognizing that at low temperatures, $k_BT \ll E_K^{(0)}$, the kink density will be very low, and as a consequence, the behavior of small oscillations (phonons) of the field in regions *between* the kinks will be very similar to the behavior of such oscillations in the kink-free system as a whole. This observation prompted KS to neglect[4] kink-phonon interactions altogether. However, we shall see that it is possible to include these interactions explicitly in the phenomenological statistical mechanics, and by so doing, extend the results of Currie *et al.*[7] to reflecting kinks (e.g., DQ kinks) as well as reflectionless kinks (e.g., ϕ^4 and SG kinks).

The presence of kinks in the system leads to a modification in the phonon density of states as discussed in Sec. II. At sufficiently low temperatures we may add the change due to each kink independently, since the kink density will be low. We shall find it convenient to regard the kink modification of the phonon free energy as a kink "self-energy" as explained below. In Sec. II we saw that a kink traps a phonon mode and this is *precisely* the mechanism by which the kink can divert two degrees of freedom from the phonons to provide for its *creation* and *translational motion* (recall the $k=0$ state becomes the translation mode of the kink).

We are now in a position to calculate the *change* $L^{-1}\Delta F$ in the phonon free-energy density due to the presence of a kink moving at very low velocity $v \ll c_0$ (there will be very few kinks traveling with high velocity when $k_BT \ll E_K^{(0)}$). The velocity of the kink may then be neglected to zeroth order. We then have

$$L^{-1}\Delta F = \frac{k_BT}{L}\int_{-\pi/l}^{\pi/l} dk\,\Delta\rho(k)\ln(\beta\hbar\omega_k)\,, \tag{4.1}$$

or, using Eq. (2.37),

$$L^{-1}\Delta F = \frac{k_BT}{L}\ln(\beta\hbar\omega_0)\int_{-\pi/l}^{\pi/l} dk\,\Delta\rho(k) + \frac{k_BT}{2L}\int_{-\pi/l}^{\pi/l} dk\,\Delta\rho(k)\ln\left[1+4\left(\frac{d}{l}\right)^2\sin^2\left(\frac{lk}{2}\right)\right]. \tag{4.2}$$

In the limit as $l\to 0$, this becomes [using Eq. (2.38)]

$$L^{-1}\Delta F = -\frac{k_BT}{L}\ln(\beta\hbar\omega_0) + \frac{k_BT}{2L}\int_{-\infty}^{\infty} dk\,\Delta\rho(k)\ln(1+d^2k^2)$$
$$= -\frac{k_BT}{L}\ln(\sqrt{2}\,\beta\hbar\omega_0)\,. \tag{4.3}$$

We see that at low temperatures ΔF will be negative, i.e., the phonon free energy is *reduced* by the presence of a kink, as expected from the reduction in the number of allowed phonon states. We shall interpret this change in the phonon free energy as a kink "self-energy". This viewpoint is similar in spirit to that adopted by Dashen, Hasslacher, and Neveu[24] in their calculations of the quantum renormalization of the kink mass due to its effect on the zero-point energy of the vacuum. Thus we define

$$\Sigma_K(T) = -k_BT\ln(\sqrt{2}\,\beta\hbar\omega_0) \tag{4.4}$$

as a kink self-energy.

At low temperatures the kink density will be small and we associate $\Sigma_K(T)$ with each of the (slowly moving) kinks and antikinks. The large average separation of kinks also allows us to neglect kink-kink interactions to an excellent ap-

proximation. Such interactions will only appear at higher order in a virial expansion involving the kink density. We note that for periodic boundary conditions on $\phi(x)$, the number of kinks will equal the number of antikinks so that

$$N_K = N_{\bar{K}} = \tfrac{1}{2} N_K^{\mathrm{tot}}, \tag{4.5}$$

where $\bar{K}$ denotes an antikink, and N_K^{tot} is the total number of kinks *plus* antikinks.

We are now ready to construct the phenomenological free-energy density based on the above considerations. Our approach involves the grand partition function Ξ for the system. Since the phonon excitations are perturbed by the presence of kinks, Ξ cannot be rigorously factored into phonon and kink pieces. However, note that the *change* in the phonon free-energy density is proportional to the *number* of kinks (for low kink densities). This prompts us to write Ξ as

$$\Xi = \Xi_P^{(0)} \Xi_K \Xi_{\bar{K}}, \tag{4.6}$$

where $\Xi_P^{(0)}$ is the *free* phonon grand-canonical partition function,

$$\Xi_P^{(0)} = e^{-\beta F_0}, \tag{4.7}$$

with F_0 given by Eq. (3.19), and $\Xi_K = \Xi_{\bar{K}}$ is the kink (antikink) partition function,

$$\Xi_K = \sum_{N_K=0}^{\infty} e^{\beta \mu_K N_K} Z_K(N_K). \tag{4.8}$$

In Eq. (4.8), $Z_K(N_K)$ is the classical partition function for an ideal gas of N_K indistinguishable relativistic particles (kinks) with self-energy Σ_K [Eq. (4.4)]:

$$Z_K(N_K) = \frac{1}{B^{N_K} h^{N_K} N_K!} \left(\int_0^L dq_K \int_{-\infty}^{+\infty} dp_K \exp\{-\beta[(p_K^2 c_0^2 + E_K^{(0)2})^{1/2} + \Sigma_K]\} \right)^{N_K}. \tag{4.9}$$

In Eq. (4.9), the dimensionless constant B is a temperature-independent phase-space reduction factor which can only be determined at a later stage by comparing the phenomenological results with those obtained using the transfer-operator approach. As we shall see, the constant B possibly has a very interesting interpretation.

Since we have already explicitly accounted for the kink self-energy, Σ_K in Eq. (4.9), we shall eventually set the kink "chemical potential" μ_K equal to zero, since there is no external constraint on the kink number; the average kink density is determined solely by the temperature! It is convenient, however, to retain μ_K until we have obtained an explicit formula for the average kink density.

The integration over p_K in Eq. (4.9) can be performed exactly with the result being expressible in terms of the modified Bessel function $K_1(\beta E_K^{(0)})$. The asymptotic form of $K_1(x)$ for large x then yields

$$Z_K = \frac{1}{N_K!} \left[\frac{L}{Bh} \frac{E_K^{(0)}}{c_0} \left(\frac{2\pi}{\beta E_K^{(0)}} \right)^{1/2} \exp[-\beta(E_K^{(0)} + \Sigma_K)] \right]^{N_K} \qquad (\beta E_K^{(0)} \gg 1). \tag{4.10}$$

The summation over N_K in Eq. (4.9) may now be performed exactly to give

$$\Xi_K = \Xi_{\bar{K}} = \exp\left[e^{\beta \mu_K} \frac{L}{Bh} \frac{E_K^{(0)}}{c_0} \left(\frac{2\pi}{\beta E_K^{(0)}} \right)^{1/2} \exp[-\beta(E_K^{(0)} + \Sigma_K)] \right]. \tag{4.11}$$

The grand-canonical potential density Ω is given by

$$\Omega = -(k_B T/L) \ln \Xi, \tag{4.12}$$

or, using Eqs. (4.6) and (4.11),

$$\Omega = L^{-1} F_0 - k_B T \frac{2E_K^{(0)}}{Bhc_0} \left(\frac{2\pi}{\beta E_K^{(0)}} \right)^{1/2} \times e^{\beta \mu_K} \exp[-\beta(E_K^{(0)} + \Sigma_K)]. \tag{4.13}$$

The average total kink number density

$$n_K^{\mathrm{tot}} = (N_K + N_{\bar{K}})/L = N_K^{\mathrm{tot}}/L,$$

is then given by

$$n_K^{\mathrm{tot}} = -\left[\frac{\partial \Omega}{\partial \mu_K} \right]_{T,L}. \tag{4.14}$$

We set $\mu_K = 0$ after performing the derivative in Eq. (4.14) to obtain

$$n_K^{\mathrm{tot}} = \frac{2E_K^{(0)}}{Bhc_0} \left(\frac{2\pi}{\beta E_K^{(0)}} \right)^{1/2} \exp[-\beta(E_K^{(0)} + \Sigma_K)]. \tag{4.15}$$

By substituting Eq. (4.4) into Eq. (4.15), the kink density may be rewritten

$$n_K^{\mathrm{tot}} = (2/\sqrt{\pi})(1/Bd)(\beta E_K^{(0)})^{1/2} e^{-\beta E_K^{(0)}}. \tag{4.16}$$

The free-energy density is given by $L^{-1}F = \Omega$ (with $\mu_K = 0$), or,

$$L^{-1} F = L^{-1} F_0 - k_B T n_K^{\mathrm{tot}}. \tag{4.17}$$

The phase-space reduction factor B is now determined by equating the phenomenological ex-

pression (4.17) for $L^{-1}F$ with the exact transfer-operator result from Sec. III:

$$L^{-1}F = L^{-1}F_0 + L^{-1}F_t , \tag{4.18}$$

where

$$L^{-1}F_t = -A\omega_0^2 t_0 . \tag{4.19}$$

Comparing Eq. (4.18) with Eq. (4.17), we obtain

$$k_B T n_K^{\rm tot} = A\omega_0^2 t_0 . \tag{4.20}$$

Substitution of Eq. (4.16) into Eq. (4.20) and the use of Eqs. (2.14) and (3.16) then yields

$$B = 2 , \tag{4.21}$$

and $n_K^{\rm tot}$ then becomes

$$n_K^{\rm tot} = (1/\sqrt{\pi}d)(\beta E_K^{(0)})^{1/2} e^{-\beta E_K^{(0)}} . \tag{4.22}$$

We emphasize that the *only* temperature dependence appearing in $n_K^{\rm tot}$ occurs through the ratio $E_K^{(0)}/k_B T = \beta E_K^{(0)}$. This temperature dependence is the same as that which appears in the ϕ^4 and SG cases[7]; the only differences are in the numerical prefactors. It is intriguing that the phase-space reduction factor B should turn out to be such a simple number as 2 [Eq. (4.21)] in the DQ case, particularly in view of the fact that $B=1$ for the SG case[7] and $B=4$ for the ϕ^4 case.[7] The fact that $B=1$ for the SG system means that no phase-space reduction for the kinks is necessary in this case. One possible interpretation of why no reduction is necessary is that the SG kinks are *not* forced to be sandwiched by antikinks; a kink can be followed by another kink. The DQ kink, however, *is* forced by the topology of the potential to be preceded and followed by an antikink along the chain. It is interesting to note that if one replaces the DQ potential by a periodic array of truncated parabolas (multiquadratic potential), the tunnel-splitting t_0 is reduced by a factor of 2,[25] leading to $B=1$. For such a potential, a kink can be followed by another kink, just as in SG.

Now that we have determined the free-energy density given by Eqs. (4.17), (4.22), and (3.19), the other thermodynamic functions can be readily obtained. For example, the internal-energy density

$$u = \frac{U}{L} = \frac{1}{L}\frac{\partial(\beta F)}{\partial\beta} \tag{4.23}$$

becomes

$$u = l^{-1}k_B T + (E_K^{(0)} - \tfrac{1}{2}k_B T)n_K^{\rm tot} . \tag{4.24}$$

This can be rewritten in the more suggestive form

$$u = (l^{-1} - n_K^{\rm tot})k_B T + n_K^{\rm tot}(E_K^{(0)} + \tfrac{1}{2}k_B T) , \tag{4.25}$$

or

$$U = Lu = (L/l - N_K^{\rm tot})k_B T + N_K^{\rm tot}(E_K^{(0)} + \tfrac{1}{2}k_B T) . \tag{4.26}$$

This is simply the internal energy of a system with $(L/l - N_K^{\rm tot})$ classical phonon modes and $N_K^{\rm tot}$ "nonrelativistic particles" of rest energy $E_K^{(0)}$, each having $\frac{1}{2}k_B T$ translational energy. Thus the kinks obtain their necessary degrees of freedom at the expense of precisely the correct number of degrees of freedom in the phonon modes.

The entropy S is easily found to have the form

$$\frac{S}{k_B} = \frac{L}{l}\left[1 - \frac{l}{2d} - \ln(\beta\hbar\omega_0 d/l)\right] + N_K^{\rm tot}\left(\frac{E_K^{(0)}}{k_B T} + \frac{1}{2}\right) , \tag{4.27}$$

and the specific heat $c_L = (\partial u/\partial T)_L$ has the form

$$c_L = k_B l^{-1} + k_B\left[\left(\frac{E_K^{(0)}}{k_B T} - \frac{1}{2}\right)^2 - \frac{1}{2}\right] n_K^{\rm tot} . \tag{4.28}$$

All of the thermodynamic functions (F, U, S, C_L) are, of course, dominated by phonon contributions, since the kink density is exponentially small at low temperatures $(\beta E_K^{(0)} \gg 1)$. However, the density of kinks is quite important information for several features which are insensitive to phonons; for example, the DC conductivity[26] in charge-density-wave condensates. Another place where the kinks dominate is in the low-temperature correlation length for the field ϕ. From Eq. (3.7) we see that the behavior of the correlation function $C_1(x)$ at large x is given by

$$C_1(x) \sim \exp[-\beta A\omega_0^2(\epsilon_1 - \epsilon_0)x] , \tag{4.29}$$

where ϵ_0 and ϵ_1 are the two lowest eigenvalues of Eq. (3.9). Equation (4.29) can be rewritten as

$$C_1(x) \sim \exp(-x/\xi) \tag{4.30}$$

where the correlation length ξ is given by

$$\xi = [\beta A\omega_0^2(\epsilon_1 - \epsilon_0)]^{-1} . \tag{4.31}$$

At low temperatures ϵ_1 and ϵ_0 are separated by the exponentially small tunnel splitting $2t_0$. From Eq. (4.20) $2t_0$ is simply

$$2t_0 = 2(A\omega_0^2)^{-1}k_B T n_K^{\rm tot} , \tag{4.32}$$

so that

$$\xi = (2n_K^{\rm tot})^{-1} \tag{4.33}$$

or, using Eq. (4.22),

$$\xi = \tfrac{1}{2}\sqrt{\pi}d(\beta E_K^{(0)})^{-1/2} e^{\beta E_K^{(0)}} . \tag{4.34}$$

Thus the correlation length is proportional to the average *separation* between neighboring kinks, which is the distance over which the field remains correlated. Note that ξ grows exponentially with decreasing temperature, becoming infinite at $T=0$ when no kinks remain in the system.

V. SUMMARY AND DISCUSSION

In this paper we have extended the phenomenological method of Currie *et al.*[7] for treating the statistical mechanics of systems bearing reflectionless kinks (e.g., ϕ^4 and SG) to those systems of a more general nature in which the kinks are *not* transparent to the small oscillations. In particular, we have examined the double-quadratic chain system in detail and developed an ideal-gas phenomenology which explicitly incorporates the effect of kinks on the phonons, thereby accounting for the sharing of degrees of freedom among these nonlinear normal modes of the system. We have found that the reflectionless property of the ϕ^4 and SG kinks is *not* a requirement for the existence of a straightforward phenomenology. Indeed, by carefully considering the nature of small oscillations in the presence of nontransparent kinks (such as DQ), one can develop a phenomenology in these cases with equal ease, and we find that the thermodynamic functions have the same functional dependence on $E_K^{(0)}/k_BT$ as was found[7] for the ϕ^4 and SG cases.

The double-quadratic chain in particular affords us an opportunity to extend the above results to higher temperatures, since the small oscillations are linear up to large amplitudes, and this should help in isolating higher-order temperature corrections. We hope to deal with this extension in a future paper.

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