

Thermal stability of extended nonlinear structures related to the Davydov soliton

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A Gibbs approach to the much studied problem of the thermal stability of nonlinear structures such as Davydov solitons is used with focus on spatially extended systems. The systems studied consist of a quantum-mechanical quasiparticle such as an electron or an excitation, interacting strongly with classical vibrations of the lattice, the entire assembly being in thermal equilibrium with a heat bath. The technique used for the study of thermal stability consists of the diagonalization of an $N \times N$ matrix where N is the number of sites among which the quasiparticle moves, followed by M thermal integrations where M is the number of vibrational coordinates with which the quasiparticle interacts. A basic duality emerges regarding the effect of temperature on the stability of nonlinear structures: temperature is found to help the nonlinearity in certain parameter and temperature regimes by inducing disorder and to destroy the nonlinearity in other regimes, e.g., always at large temperatures as a consequence of Boltzmann equalization. Particularly interesting features are found at low temperatures. A magnetic analogy reported earlier for smaller systems is reinforced by the present analysis for extended systems.

I. INTRODUCTION

The purpose of the present paper is to investigate the thermal stability of nonlinear structures such as the Davydov soliton¹⁻³ which arise in condensed-matter systems in which a moving quasiparticle such as an electron, or an electronic or vibrational excitation, interacts strongly with a boson field such as the phonons of the lattice. The method to be employed is a study of the equilibrium partition function following the procedure set out in a recent paper⁴ which will be referred to as KC. The system studied in KC was the simplest possible one, viz., a dimer, i.e., a two-state system. In this paper, we analyze larger systems. In Sec. II, we introduce the basic models and explain the method of attack. In Sec. III, we comment on the magnetic analogy which is at the heart of our method. In Sec. IV, we consider systems of arbitrary size (arbitrary number of sites N among which the quasiparticle can move) but restrict the analysis to coupling to a single frequency of vibration. Particular cases explored in detail are $N=2$, which makes contact with KC, as well as $N=4$ and $N \rightarrow \infty$. We also study in Sec. IV, the $N=4$ system with coupling to a higher wavelength mode, and a system we term the hypermer in which the quasiparticle intersite interactions are independent of site. In Sec. V, we investigate a different kind of extension of KC, by allowing interactions with any number of vibrational modes but restricting the quasiparticle to move between two sites only. Interesting features which arise in the low-temperature regime of all systems studied are the content of Sec. VI. Concluding remarks form Sec. VII. The rest of this section provides the background for our study.

A well-known example of nonlinear structures that have been suggested in biology and condensed matter is

the Davydov soliton.¹⁻³ It has been used to address transport, along proteins, of the free energy released by the hydrolysis of adenosine triphosphate. That the question of the thermal stability of these solitons at temperatures of relevance is *wide* open is clear from the juxtaposition of the following two extreme comments in the recent literature: (a) “. . . the original soliton proposal does not work at biological temperature. The ‘‘crisis in bioenergetics’’ is still with us!”⁵ (b) “. . . thermal vibrations not only do not prevent the soliton transport of energy but . . . become its necessary condition.”⁶

The surprising fact that such diametrically opposite views are held in this field may be attributed to two separate sources. One is the uncertainty in the values of the physical parameters involved. The other is the considerable variety in the nature of the theoretical approaches used so far to investigate the problem, along with an almost complete absence of an understanding of the interrelations among the diverse methods of attack. It is very difficult (indeed, impossible, at the moment) to understand why the approaches disagree (or agree) when they do. The approaches have been basically five: (i) calculations directly from the Hamiltonian of the interacting system via perturbation methods,⁷ variational principles and other procedures,⁸⁻¹⁰ (ii) quantum Monte Carlo calculations taking the full Hamiltonian as the point of departure,¹¹ (iii) Monte Carlo methods starting from the *semiclassical* Hamiltonian in which the interacting boson field is represented classically and the moving quasiparticle quantum mechanically,¹² (iv) numerical simulations of the semiclassical model with stochastic interactions with a thermal reservoir appended explicitly,^{5,13,14} and (v) analytic calculations, via a Fokker-Planck treatment, of the semiclassical model in thermal interaction with a reservoir.^{15,16}

One of the reasons for this diversity in the literature stems from the fact that a thermal reservoir has two different kinds of effect on a system: phase-space effects and fluctuation effects. The former are associated with the (Boltzmann) statistical weights for states of varying energies, and arise from a consideration of equilibrium statistical mechanics. The latter are associated with the dynamics of fluctuations, and arise from a study of non-equilibrium statistical mechanics. The treatment of nonzero temperature by the introduction of a canonical density matrix involving Boltzmann thermal weights, typified by (i)–(iii), addresses the first of these effects but not the second. Langevin or Fokker-Planck (generally *stochastic*) methods, characterized by (iv) and (v), address the second effect and also, as a byproduct, the first. These latter, stochastic, methods are also able, in contrast to the former, to address the *approach* to equilibrium and not merely the nature of the equilibrium state. However, they are considerably more difficult to implement, except through numerical techniques. Surely, whenever properly interpreted, both approaches should yield the same answers about the equilibrium state—in the present context, about the stability of the soliton. However, the inevitable approximations and assumptions necessary to carry out the investigations lead to divergence in the results.

The important issue of the relations among the various theories of thermal stability is being studied actively at the moment and will be the subject of a future publication. As stated above, the present paper employs a Gibbs analysis based on a study of the partition function of the system, addressing thus the phase-space effects and the equilibrium state directly from the Hamiltonian. We find that the opposing effects of thermal interactions, enhancement of nonlinear structures, and their destruction, both emerge as natural consequences of the underlying physics, and manifest themselves in different temperature regimes. The conclusions drawn in the present paper lend support to the approach to thermal stability suggested in KC on the basis of a simple two-site system.⁴

II. BASIC MODEL AND METHOD OF INVESTIGATION

Our study is limited to systems in which the *semiclassical* approximation is valid, the system we analyze being a composite of a quantum-mechanical carrier of charge, or excitation, or mass, moving in a lattice and interacting strongly with its classical vibrations. Even after repeated suggestions that the Davydov soliton and related nonlinear structures can explain a number of interesting observations, the challenging question^{2,3,17} of whether these structures are really consequences of the fully quantum-mechanical Hamiltonian of the system as stated, or the artifact of an ansatz, is unanswered *even at zero temperature*. What is now evident is that the ansatz, which yields the soliton, need no longer be couched in obscure terms. One can state clearly that the Davydov soliton and related evolution equations such as the discrete nonlinear Schrödinger equation are zero-temperature consequences of the semiclassical approximation, whereby the moving

quasiparticle is treated quantum mechanically but the interacting boson field (the vibrations) is taken to be classical. While this conclusion is clear to many,^{18,19} it is made particularly obvious in a recent demonstration.¹⁸ From that analysis, or even from very early arguments such as those of Holstein,²⁰ it is clear that the semiclassical model does have the nonlinear structures as an exact consequence. Knowing that they do *occur* in the semiclassical environment, we would like to ask whether, and how well, they *last* at nonzero temperatures in that environment. That is the question we address in KC and in the present paper. In further stages of our investigation into thermal stability, we will return to the question of the range of validity of the semiclassical approximation in the thermal context.

Consider the Hamiltonian

$$\hat{H} = \sum_m \epsilon_m a_m^\dagger a_m + \sum_{m,n} V_{m,n} a_m^\dagger a_n + \sum_q \hbar \omega_q (b_q^\dagger b_q + \frac{1}{2}) + N^{-1/2} \sum_q \hbar \omega_q g_q \exp(iq \cdot m) (b_q + b_{-q}^\dagger) a_m^\dagger a_m. \quad (2.1)$$

It appears in a great variety of contexts and describes a quasiparticle whose annihilation operator at site m is a_m , interacting with vibrations of modes q whose annihilation operator is b_q , the ϵ 's and V 's being site energies and intersite matrix elements of the quasiparticle, respectively, the ω 's being the frequencies of the vibrational modes, and the g 's the quasiparticle-vibration coupling constants. The quantities m and q are generally dimensionless vectors, and N is the total number of sites in the system. Henceforth, we put $\hbar=1$. The semiclassical assumption replaces the vibration operators and their conjugate momenta, viz.,

$$\hat{y}_q = \frac{b_q + b_{-q}^\dagger}{\sqrt{2}}, \quad \hat{\pi}_q = \frac{b_{-q} - b_q^\dagger}{i\sqrt{2}} \quad (2.2)$$

by c numbers y_q and π_q , respectively. The Hamiltonian of our system is then

$$\hat{H} = \sum_m \epsilon_m a_m^\dagger a_m + \sum_{m,n} V_{m,n} a_m^\dagger a_n + \sum_q \frac{\omega_q}{2} (y_q y_{-q} + \pi_q \pi_{-q}) + (N/2)^{-1/2} \sum_{q,m} \omega_q g_q e^{iq \cdot m} y_q a_m^\dagger a_m. \quad (2.3)$$

Our approach to the study of thermal stability is to decide on an appropriate feature of our system, such as localization, select an appropriate observable \hat{O} capable of describing the feature, and calculate from the Gibbs statistical-mechanics prescription the equilibrium average value of \hat{O} at any temperature T of interest:

$$\langle\langle \hat{O} \rangle\rangle = \frac{\int \int dy d\pi \text{Tr}(\hat{O} e^{-\hat{H}/k_B T})}{\int \int dy d\pi \text{Tr}(e^{-\hat{H}/k_B T})}, \quad (2.4)$$

where k_B is the Boltzmann constant, the integrations are over all the vibrational coordinates and momenta, and the trace is over the quasiparticle states.

Equation (2.4) is the starting point of our semiclassical investigation of the thermal stability of nonlinear structures. Our procedure consists of the diagonalization of

an $N \times N$ Hamiltonian matrix and the evaluation of the matrix elements of the operator \hat{O} , followed by N thermal integrations over the vibrational coordinates. The first part of the procedure is quantum mechanical, and is easy to do when N is small or the system is simple in some other way. The second is simple or complex depending on the outcome of the first. Even within our semiclassical approach, the full problem can be quite complicated for arbitrary N . We are in the process of studying it by treating the diagonalization exactly (not numerically) and the integrations via Monte Carlo methods.²¹ However, in the present paper, we restrict ourselves to two cases in which the complexity of the problem can be reduced significantly by simplifying each of its two parts in turn, while keeping the other part fully general. In the first case, the quasiparticle moves in a translationally periodic lattice (crystal) of arbitrary size (N arbitrary), but in interaction with vibrational modes of a single frequency and coupling constant. For instance,

$$\hat{H} = \sum_m \epsilon a_m^\dagger a_m + \sum_{m,n} V_{m-n} a_m^\dagger a_n + \sum_q \frac{\omega_q}{2} (y_q y_{-q} + \pi_q \pi_{-q}) + \sum_m \sqrt{2/N} \omega_k g_k (e^{ikm} y_k + e^{-ikm} y_{-k}) a_m^\dagger a_m, \quad (2.5)$$

where the interacting modes are two: k and $-k$. In the second case we allow interactions with an arbitrary number of vibrational modes but restrict the quasiparticle to move between two sites only:

$$\hat{H} = \epsilon (a_1^\dagger a_1 + a_2^\dagger a_2) + V (a_1^\dagger a_2 + a_2^\dagger a_1) + \sum_q \frac{\omega_q}{2} (y_q y_{-q} + \pi_q \pi_{-q}) + \sum_q \omega_q g_q y_q (a_1^\dagger a_1 - a_2^\dagger a_2). \quad (2.6)$$

Both are generalizations of the simple dimer interacting with a single vibration treated in KC and, as we will see below, are amenable to analytic study.

III. CHOICE OF OBSERVABLE AND MAGNETIC ANALOGY

The success of our approach in describing temperature effects in our system is crucially dependent on the choice of the observable \hat{O} in (2.3). This choice should be guided by the necessity to focus on the correlation between the carrier and the vibrational field as the essential signature of the nonlinear structures under investigation. A complete explanation for the reasons for our choice, along with a magnetic analogy on which it is based, are given in KC. Here we mention the essential details, and restrict the discussion to the extended systems we study in this paper.

Consider (2.5), assume N to be even (for simplicity), let the interacting mode be the π mode so that $y_k = y_{-k} = y$, and, although the methods and results are easily generalized to arbitrary dimensions, take the crystal to be a one-dimensional chain. It is straightforward to calculate the eigenvalues and eigenvectors of the Hamiltonian. The method²² consists of treating every two neighboring sites

as a cell, carrying out a Fourier transformation of the cell index to wave vectors q , and diagonalizing the 2×2 matrix for each q . The results for the eigenvalues E_q^\pm is

$$E_q^\pm = \sum_r \frac{\omega_r}{2} (y_r^2 + \pi_r^2) \pm \sqrt{(g\omega y)^2 + V_q^2}, \quad (3.1)$$

$$g = g_k \sqrt{8/N} = g_{-k} \sqrt{8/N},$$

$$\omega = \omega_k = \omega_{-k}, \quad (3.2)$$

$$V_q = 2V \cos(q/2).$$

The partition function Z of our system is obtained by substituting the Hamiltonian (2.5) in the denominator on the right-hand side of (2.4), and using (3.1):

$$Z = \left[(2\pi k_B T)^{N/2} \prod_q (1/\omega_q) \right] \left[\sum_q \int_{-\infty}^{+\infty} dy F_q(y, T) \right], \quad (3.3)$$

$$F_q(y, t) = e^{-(g\omega y)^2/4k_B T} \cosh\left\{ \sqrt{(g\omega y)^2 + V_q^2}/k_B T \right\}. \quad (3.4)$$

The ground state of the Hamiltonian (2.5) can be studied by taking the zero-temperature limit of the second factor in Z . As expected, the ground state undergoes symmetry breaking if the intersite interaction is sufficiently small. In order to see this from (3.3), we write $F_q(y, T)$ as an exponential and find its peak by differentiation with respect to y . We do not display the details of the calculation. They are similar to their simpler counterparts given explicitly in KC. The position y_m at which $F_q(y, T)$ peaks is the value of the π -mode vibrational amplitude at $T=0$. It is given by

$$y_m^2 = g^2 [1 - (2V/g^2\omega)^2]. \quad (3.5)$$

We thus see that the ground state of our system is "dimerized," i.e., the chain at $T=0$ consists of pairs of sites in a state of contraction or expansion, the extent being given by y_m . This dimerization only occurs if $2V < g^2\omega$. A plot of the distortion versus V would thus show a decrease with increasing V and an abrupt disappearance of the distortion at $2V = g^2\omega$. As elaborated upon in KC, this suggests a magnetic analogy, the vibrational amplitude y playing the role of the magnetic field. In the dimer studied in KC, the probability difference between the two sites plays the role of the magnetization. In the present extended system, that role is clearly played by the appropriate Fourier component of the probability of the quasiparticle. Generally, the observable we choose as \hat{O} in (2.4) is thus simply the variable conjugate to y in the Hamiltonian (2.5),

$$p = (2/N) \sum_m P_m \cos(km), \quad (3.6)$$

where P_m is the probability for the quasiparticle to be on site m , and k is the wave vector of the vibrational mode(s) which interacts with the quasiparticle. For the N -site chain interacting with the π mode, (3.6) gives

$$p = -(2/N)(P_1 - P_2 + P_3 - P_4 + \cdots - P_N). \quad (3.7) \quad (1, C_q^\pm) \text{ at each value of } q \text{ are given by}$$

For the dimer ($N=2$), the correlation observable p becomes the probability difference between the sites whose analogy to magnetization can be seen clearly.⁴ The explicit analysis given in Sec. IV below concerning a tetramer ($N=4$) will also show clearly that the variable p as defined in (3.6) does indeed correspond to a quantity akin to magnetization, with different dipole strengths and energy differences arising from different eigenstates of the quasiparticle.

IV. ARBITRARY SIZE OF CRYSTAL, INTERACTION WITH A SINGLE VIBRATIONAL MODE

Our study of the thermal stability consists, as explained, of an examination of the temperature dependence of (2.5). We have identified \hat{O} in (2.5) to be given by (3.6) for the system of arbitrary size interacting with modes of a single frequency and coupling constant. In order to evaluate (2.5), we require the eigenvectors of the Hamiltonian as well as the eigenvalues given by (3.1). The eigenvectors are also obtained from the method²² of Fourier transforming the cell index and diagonalizing the 2×2 matrix for each q mentioned in Sec. III. The quantities C_q^\pm appearing in the unnormalized eigenvectors

$$C_q^\pm = \frac{-g\omega y \pm \sqrt{(g\omega y)^2 + V_q^2}}{V(1 + e^{iq})}. \quad (4.1)$$

The factor $(1 + e^{iq})$ appearing in (4.1) is not present for the special case of the dimer, the reason being essentially the same as the one for the dimer bandwidth being $2V$ rather than $4V$: the latter result applies for nearest-neighbor rings with $N > 2$. The correlation observable as given by (3.6) is found to be

$$p = \frac{1 - |C_q^\pm|^2}{1 + |C_q^\pm|^2} = \pm \frac{z}{\sqrt{z^2 + 4v^2 \cos^2(q/2)}}, \quad (4.2)$$

$$z = \frac{y}{g}, \quad v = \frac{2V}{\chi}, \quad \chi = 2g^2\omega. \quad (4.3)$$

Equation (4.2), when combined with (3.6) and (2.5), yields an expression for the primary quantity in our analysis. In terms of the dimensionless reciprocal temperature

$$\beta = \frac{\chi}{2k_B T} = \frac{g^2\omega}{k_B T}, \quad (4.4)$$

the localization parameter $\langle\langle p \rangle\rangle$ is given by

$$\langle\langle p \rangle\rangle = \frac{\sum_q \int_0^{+\infty} dz \exp(-\beta z^2/2) [z/\sqrt{z^2 + 4v^2 \cos^2(q/2)}] \sinh[\beta \sqrt{z^2 + 4v^2 \cos^2(q/2)}]}{\sum_q \int_0^{+\infty} dz \exp(-\beta z^2/2) \cosh[\beta \sqrt{z^2 + 4v^2 \cos^2(q/2)}]}. \quad (4.5)$$

The q summation is over $N/2$ integral multiples of $4\pi/N$, and refers not to the vibrational mode but to the quasiparticle wave vectors (Fourier modes). Needless to say, one must ensure that a trivial cancellation does not occur in the thermal average in (4.5) because of the inherent symmetry of the available phase space. Following standard magnetic treatments, we average only over half the phase space.

Equation (4.5) is one of our central results in this paper. Whether an increase of temperature enhances or destroys the nonlinear structure can be studied by merely inspecting whether (4.5) results in an increase or decrease of the localization parameter $\langle\langle p \rangle\rangle$. The integral in the numerator of (4.5) can be evaluated exactly in terms of error functions but the one in the denominator requires numerical or approximate analytical evaluation. One of the approximate formulas we have developed for (4.5) is

$$\langle\langle p \rangle\rangle = \frac{\sum_q e^{(\beta/2)(v_q^2+1)} \{ \operatorname{erf}[\sqrt{\beta/2}(v_q+1)] - \operatorname{erf}[\sqrt{\beta/2}(v_q-1)] \}}{\sum_q \{ 2 \cosh(\beta v_q) \operatorname{erf}[(v_q/c)\sqrt{\beta/2}] \} + e^{\beta/2} \{ 2 - \operatorname{erf}(c v_q \sqrt{\beta/2} + \frac{1}{2}\sqrt{2\beta}) - \operatorname{erf}(c v_q \sqrt{\beta/2} - \frac{1}{2}\sqrt{2\beta}) \} + \mathcal{M}(\beta)}, \quad (4.6)$$

where $v_q = |2v \cos(q/2)|$, c is a number which can be adjusted to increase the accuracy of the approximation, and $\mathcal{M}(\beta)$ is given by

$$\mathcal{M}(\beta) = \frac{4}{\sqrt{\pi}} \int_{(v_q/c)\sqrt{\beta/2}}^{v_q c \sqrt{\beta/2}} dx e^{-x^2} \cosh \left[2\beta \left[x^2 + \frac{\beta v_q^2}{2} \right]^{1/2} \right]. \quad (4.7)$$

The larger the value of c with respect to 1, the better the approximation. The term $\mathcal{M}(\beta)$ tends to 0 as c approaches 1, and is generally given at large temperatures by

$$\mathcal{M}(\beta) = \frac{4}{\sqrt{\pi}} v_q \sqrt{\beta/2} e^{-v_q^2(c+1/c)^2(\beta/8)} \left[c - \frac{1}{c} \right]. \quad (4.8)$$

For the figures we present, we carry out the integrations numerically rather than through the above approximation, in order to ensure accuracy in all regimes. We now study various particular cases of (4.5).

(1) $N=2$: *Dimer*. This is the case treated in KC. It is recovered from (4.5) by putting $N=2$ and making the familiar change $2V \rightarrow V$ necessary to go from $N > 2$ to

$N=2$. The localization parameter is given by

$$\langle\langle p \rangle\rangle = \frac{\int_0^{+\infty} dz e^{-(1/2)\beta z^2} \sinh(\beta\sqrt{z^2+v^2})(z/\sqrt{z^2+v^2})}{\int_0^{+\infty} dz e^{-(1/2)\beta z^2} \cosh(\beta\sqrt{z^2+v^2})} \quad (4.9)$$

and has been discussed in KC.

(2) $N=4$: *Tetramer*. It might be instructive in this case to observe that \hat{H}_{int} , the interaction part of the Hamiltonian, may be written explicitly as

$$\hat{H}_{\text{int}} = \begin{pmatrix} g\omega y & V & 0 & V \\ V & -g\omega y & V & 0 \\ 0 & V & g\omega y & V \\ V & 0 & V & -g\omega y \end{pmatrix} \quad (4.10)$$

with the eigenvectors

$$\frac{1}{\sqrt{2}}(1, 0, -1, 0),$$

$$\frac{1}{\sqrt{2}}(0, 1, 0, -1),$$

$$\frac{1}{\sqrt{2(1+\eta^2)}}(1, \eta, 1, \eta),$$

$$\frac{1}{\sqrt{2(1+\eta^2)}}(-\eta, 1, -\eta, 1),$$

and the respective eigenvalues

$$g\omega y, -g\omega y, \sqrt{4V^2+(g\omega y)^2}, -\sqrt{4V^2+(g\omega y)^2}, \quad (4.12)$$

where

$$\eta = \left[1 + \left[\frac{g\omega y}{2V} \right]^2 \right]^{1/2} - \frac{g\omega y}{2V}. \quad (4.13)$$

We plot in Fig. 1 the localization parameter $\langle\langle p \rangle\rangle$ given by the $N=4$ case of (4.5):

$$\langle\langle p \rangle\rangle = \frac{\int_0^{+\infty} dz e^{-\beta(z^2/2)} [\sinh(\beta z) + (z/\sqrt{z^2+4v^2})\sinh(\beta\sqrt{z^2+4v^2})]}{\int_0^{+\infty} dz e^{-\beta(z^2/2)} [\cosh(\beta z) + \cosh(\beta\sqrt{z^2+4v^2})]}. \quad (4.14)$$

A major conclusion from KC was the existence of a *dual tendency* in the effect of temperature on the nonlinear structures: an enhancement with an increase in temperature at low temperatures, followed by a destruction at high temperatures. Figure 2(a), obtained from the three-dimensional plot of Fig. 1 by constraining the system parameter v to the value 1.5, shows that the dual effect is present in extended systems as well. Figure 2(b) shows the v dependence of the localization parameter for several values of the temperature.

(3) $N \rightarrow \infty$: *Infinite chain or ring*. Equation (4.5) yields

$$\langle\langle p \rangle\rangle = \frac{\int_{-\pi}^{\pi} \int_0^{+\infty} dq dz e^{-\beta(z^2/2)} [z/\sqrt{z^2+4v^2\cos^2(q/2)}] \sinh[\beta\sqrt{z^2+4v^2\cos^2(q/2)}]}{\int_{-\pi}^{\pi} \int_0^{+\infty} dq dz e^{-\beta(z^2/2)} \cosh[\beta\sqrt{z^2+4v^2\cos^2(q/2)}]}. \quad (4.15)$$

in the limit that the number of sites in the ring becomes infinitely large, as the q summations in (4.5) become integrations over a continuous variable. In Fig. 3, we show the dependence on size of the localization parameter and observe no catastrophic occurrence as N is varied.

(4) *Hypermer*. We have given the above expressions for arbitrary N for the simple case of nearest-neighbor interactions only for specificity. In the general case of arbitrary-ranged interactions, the simple cosine factors in (4.5) and (4.15) are merely replaced by the appropriate Fourier transforms of the intersite interaction. There is an interesting case which, while not physical for truly large systems, is of relevance in small systems: the hypermer.²³ It is characterized by equal intersite interactions among all the sites. We obtain

$$\langle\langle p \rangle\rangle = \frac{\int_0^{+\infty} dz e^{-\beta_h(z^2/2)} (z/\sqrt{z^2+v_h^2}) \sinh(\beta_h\sqrt{z^2+v_h^2})}{\int_0^{+\infty} dz e^{-\beta_h(z^2/2)} [\cosh(\beta_h\sqrt{z^2+v_h^2}) + (N/2-1)e^{\beta_h v_h} \cosh\beta_h z]}. \quad (4.16)$$

Equation (4.16) is very similar to that for the dimer in Eq. (4.9). One of the differences is that $\beta_h = 2g^2\omega/(Nk_B T)$ and $v_h = Nv/2$ appear in (4.16) rather than β and v . The other difference is an additional term proportional to $N/2-1$ which appears in the denominator. For $N=2$, the additional term vanishes and β_h and v_h become identical to β and v , respectively. Equation (4.16) then reduces to (4.9) since a dimer is indeed a hypermer with

two sites.

(5) $\pi/2$ *mode in the tetramer*. In all the above cases we have considered the interacting vibrational mode to be the one with the shortest wavelength, viz., the π mode. The analysis of single-mode interactions increases in complexity as the wavelength increases. We consider here the case of the $\pi/2$ mode in the tetramer. This is not a particular case of (4.5). The interaction Hamiltonian

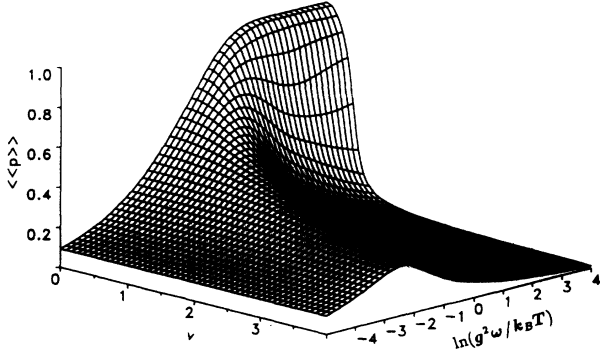


FIG. 1. Three-dimensional representation of the dependence of the localization parameter $\langle\langle p \rangle\rangle$ on the dimensionless intersite interaction v (linear scale), and on the reciprocal of the temperature T in units of $k_B/g^2\omega$ (logarithmic scale). The system considered is a tetramer interacting with the π mode. See (4.14) in the text.

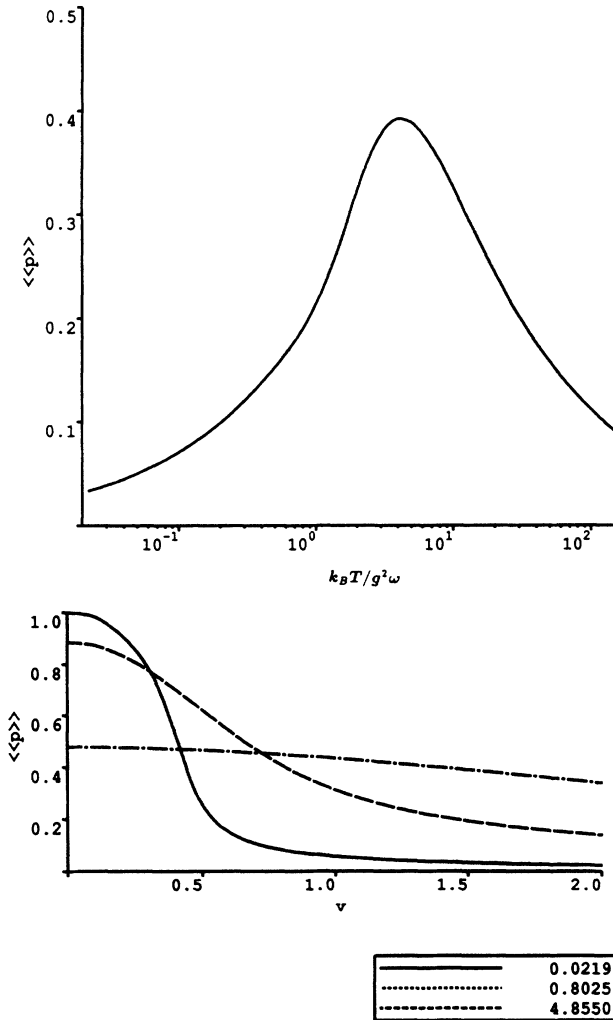


FIG. 2. Localization parameter $\langle\langle p \rangle\rangle$ for a tetramer interacting with the π mode plotted (a) as a function of temperature T (in units of $\chi/2k_B = g^2\omega/k_B$) for the dimensionless intersite interaction $v = 2V/\chi = V/g^2\omega = 1.5$, showing the dual tendency of $\langle\langle p \rangle\rangle$, and (b) as a function of v for $k_B T/g^2\omega$ equal to 0.022 (solid line), 0.8 (dashed line), and 4.9 (dot-dashed line).

an for this mode can be written as

$$\hat{H}_{\text{int}} = \sum_m \frac{g_{\pi/2}\omega_{\pi/2}}{\sqrt{2}} a_m^\dagger a_m (e^{im\pi/2} y_{\pi/2} + e^{-im\pi/2} y_{\pi/2}^*), \quad (4.17)$$

from the $N=4$ case of (2.5). In terms of the magnitude y_M and phase ϕ of $y_{\pi/2}$, the interaction part of the Hamiltonian (4.17) is

$$\hat{H}_{\text{int}} = \sum_m g_{\pi/2}\omega_{\pi/2} \sqrt{2} a_m^\dagger a_m y_M \cos(m\pi/2 + \phi). \quad (4.18)$$

The eigenvalues can be calculated in a straightforward way:

$$E = \pm 2V \left[\frac{\xi^2 + 1 \pm \sqrt{(\xi^2 + 1)^2 - \xi^4 \sin^2(2\phi)}}{2} \right]^{1/2}, \quad (4.19)$$

where

$$\xi = \frac{g_{\pi/2}\omega_{\pi/2} y_M}{\sqrt{2}V}. \quad (4.20)$$

We shall now investigate four specific cases of (4.18): $\phi = 0, \pi/2, \pi/4, -\pi/4$.

The case $\phi = 0$ shows from (4.19) that the eigenvalues are

$$0, 0, 2V\sqrt{1+\xi^2}, -2V\sqrt{1+\xi^2}. \quad (4.21)$$

The eigenvectors are found to be

$$\frac{1}{\sqrt{2}}(0, 1, 0, -1),$$

$$\frac{1}{\sqrt{2(1+\xi^2)}}(-1, \xi, 1, \xi), \quad (4.22)$$

$$\frac{1}{2\sqrt{1+\xi^2}}(1/\eta, 1, \eta, 1),$$

$$\frac{1}{2\sqrt{1+\xi^2}}(\eta, -1, 1/\eta, -1),$$

$$\eta = \sqrt{1+\xi^2} - \xi. \quad (4.23)$$

The expression for the localization parameter is

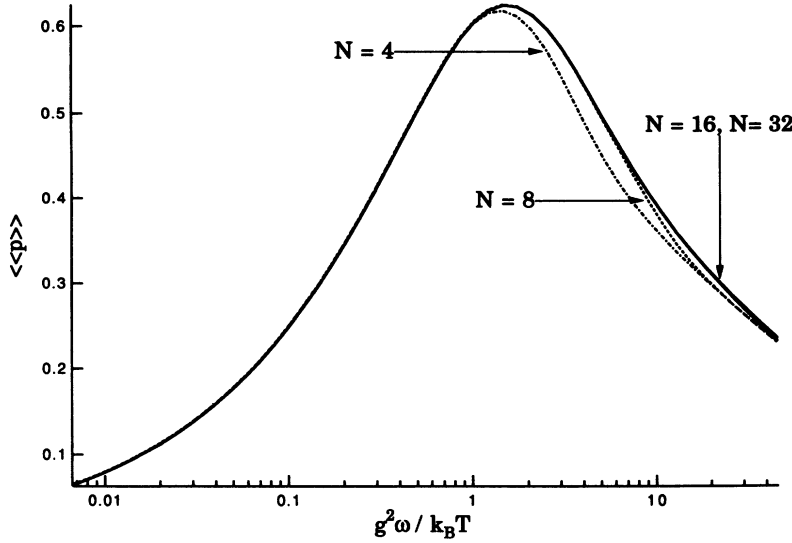


FIG. 3. Effect of lattice size N on the localization parameter: $\langle\langle p \rangle\rangle$ plotted as a function of T for the dimensionless intersite interaction $v=0.561$ for various values of N as shown. The case $N \rightarrow \infty$ is indistinguishable from the case $N=32$.

$$\langle\langle p \rangle\rangle = \frac{\int_0^{+\infty} dz e^{-\beta(z^2/2)} (z/\sqrt{2v^2+z^2}) \sinh[\beta\sqrt{2}\sqrt{2v^2+z^2}]}{\int_0^{+\infty} dz e^{-\beta(z^2/2)} \{1 + \cosh[\beta\sqrt{2}\sqrt{2v^2+z^2}]\}}. \quad (4.24)$$

If, in (4.18), $\phi = \pi/2$, results identical to (4.21) and (4.22) are obtained except that the eigenvectors are all shifted by one site:

$$\frac{1}{\sqrt{2}}(1, 0, -1, 0), \quad \frac{1}{\sqrt{2(1+\xi^2)}}(\xi, 1, \xi, -1), \quad \frac{1}{2\sqrt{1+\xi^2}}(1, \eta, 1, 1/\eta), \quad \frac{1}{2\sqrt{1+\xi^2}}(1, -1/\eta, 1, -\eta). \quad (4.25)$$

The expression for the localization parameter $\langle\langle p \rangle\rangle$ is the same as in the previous case, viz., (4.24).

If $\phi = \pi/4$ in (4.18), the following eigenvectors are obtained:

$$\begin{aligned} & \frac{1}{\sqrt{2(1+\eta_1^2)}}(1, \eta_1, \eta_1, 1), \\ & \frac{1}{\sqrt{2(1+\eta_1^2)}}(-\eta_1, 1, \eta_1), \\ & \frac{1}{\sqrt{2(1+\eta_1^2)}}(1, \eta_1, -\eta_1, -1), \\ & \frac{1}{\sqrt{2(1+\eta_1^2)}}(\eta_1, -1, -1, \eta_1), \end{aligned} \quad (4.26)$$

$$\eta_1 = \sqrt{1+\xi_1^2} - \xi_1, \quad \xi_1 = \xi\sqrt{2}, \quad (4.27)$$

the respective eigenvalues being

$$V(\eta_1 + \xi_1 + 1), \quad -V(\eta_1 + \xi_1 + 1), \quad V(\eta_1 + \xi_1 - 1), \quad -V(\eta_1 + \xi_1 - 1). \quad (4.28)$$

For the case $\phi = -\pi/4$, the eigenvalues are the same as in (4.28) and the eigenvectors are found by interchanging the second and the fourth elements of the eigenvectors in (4.26). For both these cases, one obtains, for the localization parameter

$$\langle\langle p \rangle\rangle = \frac{\int_0^{+\infty} e^{-\beta z^2} \left[\frac{z}{\sqrt{(v/\sqrt{2})^2 + z^2}} (\sinh\{(\beta/\sqrt{2})[\sqrt{(v/\sqrt{2})^2 + z^2} + v/\sqrt{2}]\} + \sinh\{(\beta/\sqrt{2})[\sqrt{(v/\sqrt{2})^2 + z^2} - v/\sqrt{2}]\}) \right]}{\int_0^{+\infty} e^{-\beta z^2} (\cosh\{(\beta/\sqrt{2})[\sqrt{(v/\sqrt{2})^2 + z^2} + v/\sqrt{2}]\} + \cosh\{(\beta/\sqrt{2})[\sqrt{(v/\sqrt{2})^2 + z^2} - v/\sqrt{2}]\})} dz. \quad (4.29)$$

We do not show the corresponding plots for the localization parameter because they are similar in appearance and characteristics to those shown in Figs. 1 and 2. The conclusion to be drawn from the results in this section is that the insights gained in the thermal stability problem from the simple two-site analysis in KC are reinforced by a study of the spatial extensions treated here.

V. ARBITRARY NUMBER OF VIBRATIONAL MODES, TWO QUASIPARTICLE SITES

In this section, we study an extension of the simple dimer of KC which is different in spirit from that in Sec. IV. The size of the crystal is restricted to two sites but the quasiparticle is taken to interact with an arbitrary number of vibrational modes with coupling constants which are different for the two sites. The Hamiltonian is

given by (2.6), and is a simpler version of

$$\begin{aligned} \hat{H} = & \epsilon(a_1^\dagger a_1 + a_2^\dagger a_2) + V(\hat{a}_1^\dagger \hat{a}_2 + \hat{a}_2^\dagger \hat{a}_1) \\ & + \sum_q \frac{\omega_q}{2} (y_q y_{-q} + \pi_q \pi_{-q}) \\ & + \sum_q \omega_q y_q (g_{1q} \hat{a}_1^\dagger \hat{a}_1 + g_{2q} \hat{a}_2^\dagger \hat{a}_2) \end{aligned} \quad (5.1)$$

obtained by taking the coupling constants g_{1q} and g_{2q} to be of the same magnitude g_q but to differ in phase by π . The dynamics of such dimers has been studied in the past in a variety of ways, including via the calculation of memory functions,²⁴ dressing transformations,²⁵ and stochastic methods.²⁶ While the dynamics possesses considerable complexity, we will see that the Gibbs analysis of the localization parameter is extremely simple.

The interaction part of the Hamiltonian in (5.1) can be written as

$$\hat{H}_{\text{int}} = \begin{pmatrix} \sum_q \omega_q (g_{Rq} y_{Rq} - g_{Iq} y_{Iq}) & V \\ V & -\sum_q \omega_q (g_{Rq} y_{Rq} - g_{Iq} y_{Iq}) \end{pmatrix}, \quad (5.2)$$

where we have displayed explicitly the real and imaginary parts of the displacement y_q (denoted, respectively, by R and I) and have also taken the coupling constant g_q to be generally complex. The eigenvalues and eigenvectors are found as in Sec. IV. The eigenvalues are

$$E^\pm = \sum_q \frac{\omega_q}{2} [y_{Rq}^2 + y_{Iq}^2 + \pi_q \pi_{-q}] \pm \left[V^2 + \left(\sum_q \omega_q (g_{Rq} y_{Rq} - g_{Iq} y_{Iq}) \right)^2 \right]^{1/2}. \quad (5.3)$$

The correlation observable is

$$p = \pm \frac{\sum_q \omega_q (g_{Rq} y_{Rq} - g_{Iq} y_{Iq})}{\sqrt{\left(\sum_q \omega_q (g_{Rq} y_{Rq} - g_{Iq} y_{Iq}) \right)^2 + V^2}}. \quad (5.4)$$

The definitions

$$\omega = \left(\sum_q \omega_q^2 \right)^{1/2}, \quad g = \left[\sum_q (g_{Rq}^2 + g_{Iq}^2) \left(\frac{\omega_q}{\omega} \right) \right]^{1/2}, \quad f_q = \frac{g_q}{g} \sqrt{\omega_q / \omega}, \quad z_q = \frac{y_q}{g} \sqrt{\omega_q / \omega}, \quad (5.5)$$

and

$$\chi = 2g^2 \omega, \quad \beta = \frac{\chi}{2k_B T} = \frac{g^2 \omega}{k_B T}, \quad v = \frac{2V}{\chi} \quad (5.6)$$

lead to the following expression for the localization parameter:

$$\langle\langle p \rangle\rangle = \frac{\int \prod_q dz_{Rq} dz_{Iq} \exp \left[-\frac{\beta}{2} \left(\sum_q z_{Rq}^2 + z_{Iq}^2 \right) \right] \frac{\left| \sum_q f_{Rq} z_{Rq} - f_{Iq} z_{Iq} \right|}{\left[v^2 + \left(\sum_q f_{Rq} z_{Rq} - f_{Iq} z_{Iq} \right)^2 \right]^{1/2}} \sinh \left\{ \beta \left[v^2 + \left(\sum_q f_{Rq} z_{Rq} - f_{Iq} z_{Iq} \right)^2 \right]^{1/2} \right\}}{\int \prod_q dz_{Rq} dz_{Iq} \exp \left[-\frac{\beta}{2} \left(\sum_q z_{Rq}^2 + z_{Iq}^2 \right) \right] \cosh \left\{ \beta \left[v^2 + \left(\sum_q f_{Rq} z_{Rq} - f_{Iq} z_{Iq} \right)^2 \right]^{1/2} \right\}}. \quad (5.7)$$

Equation (5.7) appears to be quite complicated and to require multiple numerical integrations. However, a major simplification occurs if we introduce a transformation from z_q to new variables \bar{z}_γ . The transformation is linear and corresponds to a formal rotation of the z_q 's into the \bar{z}_γ 's, the quantity $\sum_q (z_{Rq}^2 + z_{Iq}^2)$ being the invariant length of the ro-

tated vector. We choose one of the quantities \bar{z}_γ to equal $\sum_q f_{Rq} z_{Rq} - f_{Iq} z_{Iq}$:

$$\bar{z}_1 = \sum_q f_{Rq} z_{Rq} - f_{Iq} z_{Iq} . \quad (5.8)$$

Equation (5.7) is then transformed into

$$\langle\langle p \rangle\rangle = \frac{\int \prod_\gamma d\bar{z}_\gamma \exp \left[-\frac{1}{2} \beta \sum_\gamma \bar{z}_\gamma^2 \right] \sinh(\beta \sqrt{\bar{z}_1^2 + v^2}) (|\bar{z}_1| / \sqrt{\bar{z}_1^2 + v^2})}{\int \prod_\gamma d\bar{z}_\gamma \exp \left[-\frac{1}{2} \beta \sum_\gamma \bar{z}_\gamma^2 \right] \cosh(\beta \sqrt{\bar{z}_1^2 + v^2})} . \quad (5.9)$$

The convenient feature of (5.9), viz., the appearance of a single \bar{z}_γ in all expressions except the exponential, allows the simplification of (5.9) to

$$\langle\langle p \rangle\rangle = \frac{\int_0^{+\infty} d\bar{z}_1 e^{-(1/2)\beta\bar{z}_1^2} \sinh(\beta \sqrt{\bar{z}_1^2 + v^2}) (\bar{z}_1 / \sqrt{\bar{z}_1^2 + v^2})}{\int_0^{+\infty} d\bar{z}_1 e^{-(1/2)\beta\bar{z}_1^2} \cosh(\beta \sqrt{\bar{z}_1^2 + v^2})} . \quad (5.10)$$

Expression (5.10) is identical to the expression for the localization parameter for the dimer, (4.9). The seemingly complex problem presented by the infinite number of modes in (2.6) is thus solved exactly. The thermal behavior of the nonlinear structures is identical to that discussed in Sec. IV. It is interesting to note here that, although the coupling constants g_q have been taken to be differing in sign only between the two sites, the result (5.10) obtains for a more general case wherein g_{1q} and g_{2q} differ from each other by an arbitrary phase.

The KC analysis is thus reinforced in that it is unchanged in essentials or in detail when the vibrations which interact with it are spread over a realistic band rather than being concentrated in a single model.

VI. NOVEL FEATURES AT LOW TEMPERATURES

The primary question addressed in this paper has been about whether increasing temperature aids or hampers the nonlinear structures. Plots such as those in Figs. 1–3 show clearly that the effect is to help the nonlinearity at low temperatures and to destroy it at larger temperatures, the demarcation temperature being T_p at which the localization parameter $\langle\langle p \rangle\rangle$ has a maximum. We will now show that curious new effects can occur at low temperatures. Although the effects appear in all the systems studied, we will illustrate them only for the case of the two-site system.

In Fig. 4, we display the localization parameter $\langle\langle p \rangle\rangle$, given by (4.9), as a function of the system quantity $v = 2V/g^2\omega$ for $T=0$. The dashed lines separate the v axis into three regions. In the rightmost region $v > 1$, shown in Fig. 4 as region III, the localization parameter $\langle\langle p \rangle\rangle$ starts off with a 0 value for $T=0$. The temperature effect is to make it increase from the 0 value for small temperatures. In the leftmost region, shown in Fig. 4 as region I, $v < 0.52$ and the localization parameter starts off with a nonzero value. A study of (4.9) shows that the temperature effect in this case is to make $\langle\langle p \rangle\rangle$ decrease from its $T=0$ value throughout the temperature

range. Of the dual tendency of $\langle\langle p \rangle\rangle$ that we have mentioned in Secs. IV and V, only the second aspect, that of the destruction of the nonlinearity is seen in this case. The zero-temperature localization is already so large that only the Boltzmann equalization effect as temperature increases is visible. Figure 5(a) makes this clear.

Interesting features surface from an investigation of $\langle\langle p \rangle\rangle$ in the middle region II in Fig. 4. For $v_0 < v < 1$, where $v_0 = 0.52$, $\langle\langle p \rangle\rangle$ decreases from its $T=0$ value at low temperatures as in Fig. 5(a) but hits a minimum at a temperature we call T_t . It then *increases*, reaches a peak, and then decreases at large temperatures. A three-sided curve as in Fig. 5(b) results. The dependence of the trough temperature T_t and the peak temperature T_p on the system parameter v clearly contains important information about the thermal stability of the nonlinear structure. Figure 6 displays this information. We see that,

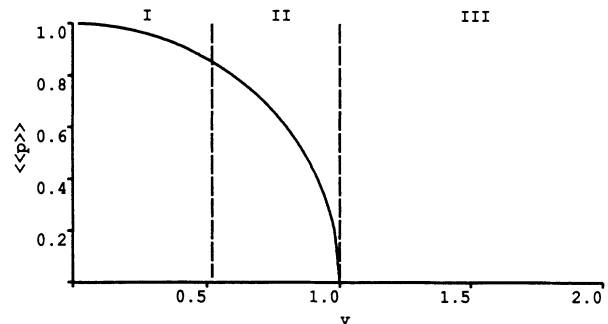


FIG. 4. The three v regions which correspond to different T variations of the localization parameter $\langle\langle p \rangle\rangle$ at low temperatures. The system described is the dimer as given by (4.9). The T dependence of $\langle\langle p \rangle\rangle$ in v region III, i.e., for $v > 1$, exhibits the dual tendency shown in Fig. 2. However, the temperature dependence differs in the other two regions, as is clear from Figs. 5 below.

below $v = v_0$, there is no T_t or T_p since the $\langle\langle p \rangle\rangle$ curve decreases monotonically as in Fig. 5(a). At $v = v_0$, T_t and T_p make their appearance. As v increases beyond v_0 , T_t decreases while T_p increases. As the middle region ends, i.e., when $v \geq 1$, T_t tends to 0 and disappears, while T_p continues its upwards march. The disappearance of T_t corresponds to the ground state of the system being delocalized rather than selftrapped, i.e., to $\langle\langle p \rangle\rangle$ at $T=0$ being 0.

At $v = v_0$, the trough temperature T_t has its maximum value, the peak temperature T_p has its minimum value,

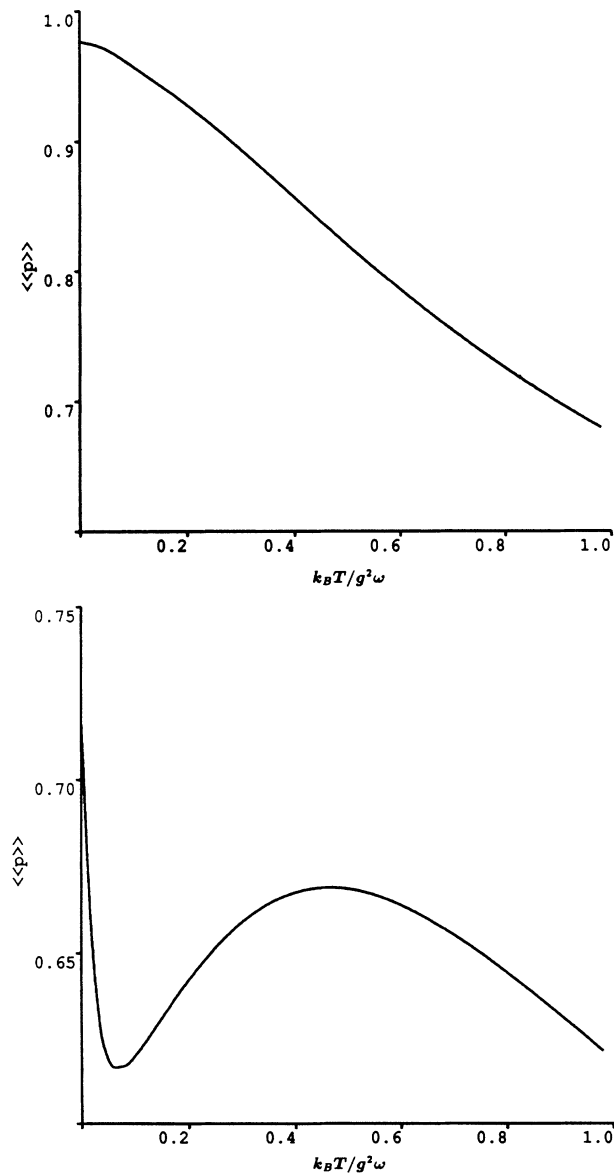


FIG. 5. Temperature dependence of the localization parameter $\langle\langle p \rangle\rangle$ in the v regions II and III: (a) $v=0.216$, the system lies in region I, and one sees a single tendency, viz., a decrease of $\langle\langle p \rangle\rangle$ with an increase in T ; (b) 0.696 , the system lies in region II, and one sees a decrease in localization followed first by an increase, and then by an eventual decrease.

and $T_t = T_p \equiv T_0$. It is interesting to observe that this characteristic temperature T_0 is below 1 K for parameters believed to be representative of the α -helix³ and in the range 30–100 K for parameters deduced for photoinjected carriers in naphthalene.²⁷ The significance of these estimated values is that the novel features of the temperature dependence discussed in this section can be unimportant if T_0 is very small since the additional aspect, the trough, appears only for temperatures below T_0 . For systems in which T_0 is well below temperatures of experiment, the dual tendency consisting of the rise of the nonlinearity at low temperatures followed by its destruction at high temperatures is all that would be discernible in observations.

VII. CONCLUSIONS

The broad aim of the investigation whose results we have reported in this paper is to help decide whether nonlinear structures such as the Davydov soliton, which have often been postulated to explain observations in biological and condensed-matter systems, are merely the result of an academic exercise, of little use to experiment, or whether they are bonafide constructs from an observational point of view, particularly at the temperatures of experiment. The specific aim of the work presented in this paper has been to extend the thermal stability study initiated in a previous paper (KC) to systems more realistic than the dimer.

Our starting point is the semiclassical Hamiltonian (2.3) which is obtained from (2.1) via the assumption that, for the systems we consider, the vibrations of the lattice may be considered to be classical. The moving quasiparticle is treated fully quantum mechanically. Our focus is on two kinds of extension of the dimer studied in KC: systems in which the quasiparticle moves among a crystal of arbitrary number of sites but interacts only with a finite (small) number of vibrational modes, and systems in which the number of interacting modes can be arbitrary but the crystal size is small, i.e., $N=2$. Equations (2.5) and (2.6) describe these systems, respectively, and Secs. IV and V contain the respective treatments. Our general finding is that the present study of these soluble extensions of the dimer bears out the conclusions drawn in KC from a study of the simple dimer interacting with a single vibrational mode.

Our approach to thermal stability consists of a careful definition of a correlation observable which measures the extent of nonlinearity, followed by an evaluation of its thermal average (which we call the localization parameter $\langle\langle p \rangle\rangle$) and an examination of its temperature dependence. Section III explains the reasoning behind our choice of the correlation observable along with the magnetic analogy which it entails, and equations such as (4.5) and (5.9) give explicit expressions for the localization parameter. We have studied the temperature dependence of the localization parameter for a variety of systems described in Secs. IV and V, and have found that it consists generally of a characteristic rise followed by a drop as the temperature is increased. The rise represents temperature-induced disorder and the eventual drop,

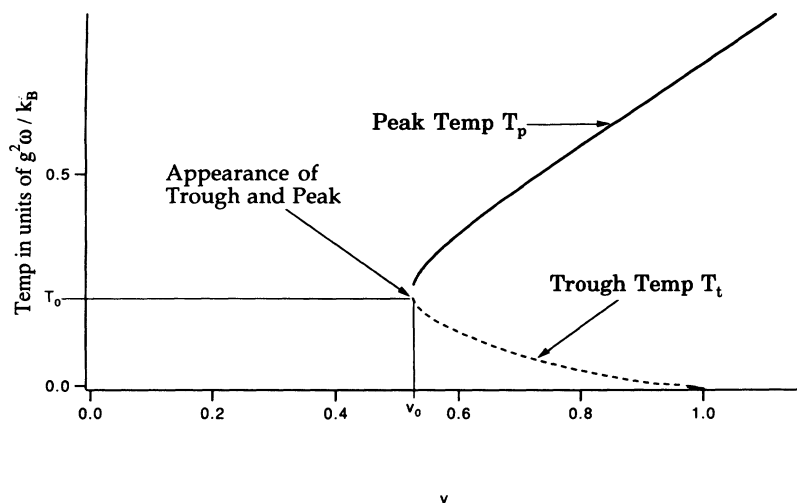


FIG. 6. The v dependence of the trough temperature T_t (dashed line), and the peak temperature T_p (solid line), at the local minimum and maximum of $\langle\langle p \rangle\rangle$, respectively. Neither T_t nor T_p exists for $v < v_0$. Beyond $v = 1$, T_t disappears while T_p increases in an approximately linear relation to v .

which is always present at sufficiently high temperatures, represents Boltzmann weight equalization. At low temperatures, further subtleties can occur for the appropriate system parameters. If the system is strongly localized already at $T = 0$, the localization parameter shows only the single tendency of a drop, as T increases, rather than the Janus-like two faces.²⁸ If the system is localized at $T = 0$, but not too strongly, it is possible to see a decrease of localization, followed by an increase, followed by the inescapable decrease. The dependence of the trough and peak temperatures corresponding to this behavior on system parameters is seen in Fig. 6.

The crucial role played by the selection of an appropriate correlation observable can be appreciated from an analysis of an alternate observable, viz., py , given in KC. That analysis, which we will not repeat here, shows clearly that such alternate observables do not exhibit the dual nature of the temperature effect. It appears that such a situation arising from a different choice of observable has occurred in some earlier investigations reported in the literature.

At the heart of our approach to thermal stability is the magnetic analogy which has been mentioned in Sec. III and explained in greater detail in KC. The quantities in our problem which correspond to the magnetization and the magnetic field are, respectively, the localization parameter $\langle\langle p \rangle\rangle$ and the vibrational amplitude y . The analogy, however, is not straightforward. One of the important differences is that the effective value of y is itself decided by the temperature in our problem whereas, in the magnetic case, the applied field is imposed externally, and is *not* dependent on the temperature. Another difference has to do with the fact that it is convenient to compare

the zero-temperature v dependence of $\langle\langle p \rangle\rangle$ of our system to the zero-field *temperature dependence* of the magnetization of the respective magnetic systems. Among the similarities is the relation which exists between the correlation observable (the magnetization) and the vibrational amplitude (the magnetic field). This relation is precisely the content of the mean-field assumption in a mean-field theory of ferromagnetism. In our problem the relation is exact, is a consequence of the Hamiltonian, and is typified by (4.2). Unlike in the magnetic problem, the relation is not linear except for very high values of the vibrational amplitude.

The analysis in this paper has treated extensions of the dimer model presented in KC. As we have seen, it fully supports the findings of KC. However, one should not overestimate the significance of this support: the extensions we have considered here all possess a certain kinship to the dimer. Even in the case of the spatial extensions considered in Sec. IV, we see dimerlike expressions such as (4.5). A number of further extensions which we have analyzed but not discussed in the present paper also result in dimerlike expressions. The fact that only one or two modes with a single frequency of vibration interact with the quasiparticle is responsible for this result. Analytic ease is lost as soon as we drop this restriction. We are then forced to adopt Monte Carlo procedures, which we hope to report in a future publication.

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