Dynamics of a Nonlinear Diatomic Chain. II* Thermodynamic Properties

B. I. Henry^{A,B} and J. Oitmaa^A

^A School of Physics, University of New South Wales,
P.O. Box 1, Kensington, N.S.W. 2033.
^B Present address: Department of Physics,
University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

Abstract

We compute the free energy density of a nonlinear diatomic model for a solid which may undergo a displacive structural phase transition using (i) a two-component transfer integral operator equation and (ii) an ideal gas phenomenology incorporating the stable solutions of the coupled Euler-Lagrange equations as elementary excitations. The agreement between the two calculations formally establishes that the low temperature excitation spectrum is dominated by both the familiar linearized phonon solutions and by nonlinear domain wall or kink soliton solutions. The ideal gas phenomenology is then used to compute the kink density, order parameter correlation functions, and the kink contribution to the dynamical structure factor. The dynamical structure factor is found to exhibit a central peak.

1. Introduction

In a previous paper (Henry and Oitmaa 1983, hereafter referred to as Part I) we set up the Hamiltonian and the coupled field equations describing a nonlinear diatomic model for a solid which may undergo a displacive structural phase transition (DSPT). The model consists of a diatomic chain of harmonically coupled nearest neighbour atoms including a nonlinear on-site potential on one species. The model differs from previously studied models in that it has two species per unit cell. This is an important extension because many of the solids which undergo a DSPT have a diatomic structure along a certain crystallographic direction. There have been other studies of nonlinear diatomic models in this regard. However, most of these models include the nonlinear term in the nearest neighbour interactions (Buttner and Bilz 1978; Yajima and Satsuma 1979; Dash and Patnaik 1981; Mokross and Buttner 1981; Pnevmatikos et al. 1983). Our model differs from nonlinear diatomic shell models (Bilz et al. 1980; Buttner and Bilz 1981) in that in the shell models the nonlinear potential is an internal translationally invariant interaction arising from electron-ion coupling, whereas in the present model the nonlinear potential is a fixed external potential thought of as arising from the inactive sublattices of the crystal.

In Part I we set up the Hamiltonian and derived the continuum limit equations of motion. A number of physically distinct solutions were identified including linearized phonons, large amplitude equal-displacement-field kink and pulse type solitary waves, and nonlinear periodic waves.

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In this paper we derive topological kink solitary waves for an expanded parameter space. These kinks are shown to participate in the statistical mechanics in a crucial way. A fundamental result of this paper is that the realistic extension of including an additional sublattice as part of the vibrating complex does not preclude nonlinear domain walls from the excitation spectrum at low temperatures.

The plan of this paper is as follows: In Section 2 we present the model Hamiltonian [the same as equation (5) in Part I], the equations of motion, and the finite energy solutions of these equations. In addition to the solutions reported in Part I a new class of kink solitary waves is derived for an expanded parameter space. In Section 3 we use the transfer integral technique to examine the statistical mechanics for the diatomic ϕ^4 chain. Some order parameter correlation functions are also derived using the transfer integral formalism. In Section 4 we calculate thermodynamic functions for our model using an ideal gas phenomenology which incorporates the finite energy density calculated in this way is found to agree with the exact calculation in the low temperature limit. Finally, in Section 4 we use the phenomenology to compute the kink contribution to the dynamical structure factor. In Section 5 we present our conclusions.

In a third paper (Henry and Oitmaa 1985; Part III, present issue p. 191) we will examine the dynamics and the statistical mechanics of the diatomic chain using the molecular dynamics technique.

2. Hamiltonian and Finite Energy Excitations

The Hamiltonian for the discrete lattice is taken to be

$$H = \sum_{i=1}^{N} \frac{1}{2} M_i \dot{u}_i^2 + \frac{1}{2} M_2 \dot{v}_i^2 + \frac{1}{2} \gamma (u_i - v_{i-1})^2 + \frac{1}{2} \gamma (u_i - v_i)^2 + V(u_i), \qquad (1)$$

where M_1 and M_2 are the masses of the two types of atom. Nearest neighbour atoms are coupled by linear forces with force constant γ . The M_1 atom also moves under the influence of a nonlinear on-site potential V(u). The analysis in this paper may be readily extended to include any on-site potential which has at least two degenerate minima (cf. Currie *et al.* 1980). However, for computational purposes, we consider the ϕ^4 potential

$$V(u) = -\frac{1}{2}Au^2 + \frac{1}{4}Bu^4.$$
 (2)

The discrete lattice equations of motion are

$$M_1 \ddot{u}_n + \gamma (2u_n - v_{n-1} - v_n) - Au_n + Bu_n^3 = 0, \qquad (3a)$$

$$M_2 \ddot{v}_n + \gamma (2v_n - u_n - u_{n+1}) = 0.$$
 (3b)

Three physically distinct solutions of these equations are:

(i) The ground state solution

$$u_n = v_n = \pm u_0; \qquad u_0 = (A/B)^{\frac{1}{2}}.$$
 (4)

This is the minimum energy configuration for the chain.

(ii) Small amplitude phonons,

$$u_n = u_0 + u_L \sin(qan - \omega t), \qquad v_n = v_0 + v_L \sin(qa(n + \frac{1}{2}) - \omega t), \qquad (5a, b)$$

with dispersion

$$\omega_{\rm L}^2(\pm) = \frac{\gamma(M_1 + M_2) + AM_2}{M_1 M_2} \Big\{ 1 \pm \Big(1 - \frac{4M_1 M_2 (A\gamma^{-1} + \sin^2 \frac{1}{2}qa)}{\{(M_1 + M_2) + M_2 A\gamma^{-1}\}^2} \Big)^{\frac{1}{2}} \Big\}.$$
(6)

These solutions describe small oscillations about the ground state. The lower branch $\omega_{\rm L}(-)$ is a quasi-acoustic mode and the upper branch $\omega_{\rm L}(+)$ is a quasi-optic mode.

(iii) Nonlinear periodic solutions

$$u_n = F_0 \sin(\omega t - qan), \tag{7a}$$

$$v_n = G_0 \sin(\omega t - qa(n+\frac{1}{2})) + G\sin(3\{\omega t - qa(n+\frac{1}{2})\}),$$
(7b)

with amplitudes given explicitly in Part I and with frequency

$$\omega = (2\gamma/9M_2)^{\frac{1}{2}}.$$
 (7c)

Similar nonlinear periodic solutions (called 'periodons') have been reported by Buttner and Bilz (1981) in a nonlinear diatomic shell model for a ferroelectric which may undergo a DSPT.

In the displacive regime,

$$\gamma u_0^2 \gg |V(u_0)|, \tag{8}$$

a Taylor series expansion can be used to connect displacement fields of like atoms in neighbouring unit cells. The continuum Hamiltonian

$$H = \int \frac{\mathrm{d}x}{a} \left(\frac{1}{2} M_1 \dot{u}^2 + \frac{1}{2} M_2 \dot{v}^2 + \gamma (u - v)^2 + \frac{1}{4} \gamma a^2 \frac{\partial u}{\partial x} \frac{\partial v}{\partial x} + V(u) \right) \tag{9}$$

now involves the displacement fields u(x, t) and v(x, t). The coupled Euler-Lagrange equations of motion which follow from equation (9) are

$$M_1 \ddot{u} + 2\gamma(u-v) - \frac{1}{4}\gamma a^2 v'' + \frac{\partial V}{\partial u} = 0, \qquad (10a)$$

$$M_2 \ddot{v} + 2\gamma (v - u) - \frac{1}{4} \gamma a^2 u'' = 0.$$
 (10b)

These equations reduce to the equation of motion for the monatomic ϕ^4 chain [see Krumhansl and Schrieffer (KS) (1975)] in the limit $M_2 \rightarrow 0$. In the absence of the nonlinear on-site potential the equations reduce to the continuum equations of motion for a harmonic diatomic chain. The excitation energy for a solution to the field equations is found from

$$E = \int_{-\infty}^{\infty} \frac{\mathrm{d}x}{a} \left\{ \frac{1}{2} M_1 \dot{u}^2 + \frac{1}{2} M_2 \dot{v}^2 + \gamma (u - v)^2 + \frac{1}{4} \gamma a^2 u' v' - \frac{1}{2} A (u^2 - u_0^2) + \frac{1}{4} B (u^4 - u_0^4) \right\}.$$
 (11)

Continuum limit descriptions of the ground state solution (equation 4), the low amplitude phonons (equations 5), and the nonlinear periodic waves (equations 7) can also be obtained from the field equations (Henry and Oitmaa 1983).

A more interesting class of solutions consists of the localized travelling waves (solitary waves) u(x, t) = f(s) and v(x, t) = g(s) with s = x - ct, where c is the speed of the travelling waves in the lattice. In previous work (Henry *et al.* 1982) we derived equal-displacement-field kink and pulse type solitary waves which propagate at the characteristic velocity

$$c_0 = (\gamma a^2 / 4M_2)^{\frac{1}{2}}.$$
 (12)

Explicitly these solutions are:

(i) Equal-displacement-field kink, for $M_1 < M_2$,

$$v(x,t) = u(x,t) = \pm u_0 \tanh(s/\xi_{\rm K}); \qquad \xi_{\rm K} = \{(2c_0^2/A)(M_2 - M_1)\}^{\frac{1}{2}}.$$
(13)

(ii) Equal-displacement-field pulse, for $M_2 < M_1$,

$$v(x,t) = u(x,t) = \pm \sqrt{2} u_0 \operatorname{sech}(s/\xi_{\rm P}); \qquad \xi_{\rm P} = \{(c_0^2/A)(M_1 - M_2)\}^{\frac{1}{2}}.$$
(14)

The pulse solution is an infinite energy solution. The kink however is topologically stable and has a finite energy of excitation. The kink excitation energy, derived by inserting the kink profile (equation 13) into the energy equation (11) is

$$E_{\rm K} = 2a\gamma u_0^2/3\xi_{\rm K}\,.\tag{15}$$

At velocities other than the characteristic velocity c_0 the g field may be separated out of the coupled equations resulting in a quartic equation for the f field:

$$\begin{split} \{c^{4}M_{1}M_{2} - (\frac{1}{4}\gamma a^{2})^{2}\}\frac{\mathrm{d}^{4}f}{\mathrm{d}s^{4}} + \{2\gamma c^{2}(M_{1} + M_{2}) - \gamma^{2}a^{2}\}\frac{\mathrm{d}^{2}f}{\mathrm{d}s^{2}} \\ &+ c^{2}M_{2}\frac{\mathrm{d}^{2}}{\mathrm{d}s^{2}}\frac{\partial V}{\partial f} + 2\gamma\frac{\partial V}{\partial f} = 0, \end{split}$$
(16a)
$$g = \left(\{c^{4}M_{1}M_{2} - (\frac{1}{4}\gamma a^{2})^{2}\}\frac{\mathrm{d}^{2}f}{\mathrm{d}s^{2}} + \{2\gamma (c^{2}M_{2} - \frac{1}{4}\gamma a^{2})\}f \\ &+ c^{2}M_{2}\frac{\partial V}{\partial f}\right) \Big/ 2\gamma (c^{2}M_{2} - \frac{1}{4}\gamma a^{2}). \end{aligned}$$
(16b)

For velocities $c < c_A$, where

$$c_{\rm A} = \{\gamma a^2 / 2(M_1 + M_2)\}^{\frac{1}{2}}$$
(17)

is the speed of sound in the lattice, the fourth order term in equation (16a) may be neglected to a reasonable approximation (Henry 1984), in which case equation (16a) reduces to a second order nonlinear differential equation which can be written in the form

$$(M_1 + M_2)(c^2 - c_A^2)\frac{\mathrm{d}^2 f}{\mathrm{d}s^2} + \frac{\partial V}{\partial f} = -\frac{c^2 M_2}{2\gamma}\frac{\mathrm{d}^2}{\mathrm{d}s^2}\frac{\partial V}{\partial}.$$
 (18)

Note that this equation is exact for the particular velocity

$$c = \{\gamma a^2 / 4(M_1 M_2)^{\frac{1}{2}}\}^{\frac{1}{2}}.$$
(19)

Equation (18) can be solved exactly (Henry and Oitmaa 1983). In the case of the ϕ^4 potential the solution is given by

$$s = \int_{f(0)}^{f(s)} \frac{(3Bc^2M_2f^2 - \alpha_0 - c^2M_2A) df}{\pm \{C - (2\gamma c^2M_2A^2 + 2\gamma\alpha_0A)f^2 + (\gamma\alpha_0B + 4AB\gamma c^2M_2)f^4 + 2\gamma c^2M_2B^2f^6\}},$$
(20)

where

$$\alpha_0 = 2\gamma (M_1 + M_2)(c_A^2 - c^2), \qquad (21)$$

and C is an integration constant which is determined by the boundary conditions for the solution. In Part I we derived nonlinear periodic solutions from equation (20) which are the continuum analogue of the discrete lattice periodic waves (equations 7). The quadrature (20) also however permits kink solutions. Employing the kink boundary conditions

$$df_{\rm K}/ds|_{s=\pm\infty} = 0, \qquad f_{\rm K}|_{s=\pm\infty} = \pm u_0$$
 (22)

in equation (20) yields the kink integration constant

$$C_{\rm K} = \gamma \alpha_0 A^2 / B, \qquad (23)$$

with the restriction that

$$\alpha_0 \neq 2c^2 M_2 A \,. \tag{24}$$

The kink quadrature is now found by inserting equation (23) into (20). After a bit of algebra we derive

$$\pm s = \int_{f_{\mathbf{K}}(0)}^{f_{\mathbf{K}}(s)} \frac{(\alpha_0 + c^2 M_2 A - 3Bc^2 M_2 f^2) \, \mathrm{d}f}{\{1 - (B/A)f^2\}\{\gamma \alpha_0 (A^2/B)(1 - 2Bc^2 M_2 f^2/\alpha_0)\}^{\frac{1}{2}}}.$$
 (25)

The following special cases may be immediately derived:

(i) c = 0; static limit,

$$\pm x = \int_{f_{\mathbf{K}}(0)}^{f_{\mathbf{K}}(x), \underline{v}} \frac{(\gamma a^2/B)^{\frac{1}{2}} \, \mathrm{d}f}{(A/B)f^2},$$

then

$$f_{\rm K}(x) = \pm u_0 \tanh(x/\xi_0); \qquad \xi_0 = (\frac{1}{4}\gamma a^2)^{\frac{1}{2}}.$$
 (26a, b)

The g field for this case follows from equations (16b) and (26) with c = 0:

$$g_{\rm K}(x) = u_0(1 - a^2/4\xi_0^2) \tanh(x/\xi_0) + u_0(a^2/4\xi_0^2) \tanh^3(x/\xi_0).$$
⁽²⁷⁾

(ii) $M_2 = 0$; monatomic limit,

$$\pm s = \int_{f_{K}(0)}^{f_{K}(s)} \frac{\{(\gamma a^{2} - 2M_{1}c^{2})/B\}^{\frac{1}{2}} df}{(A/B) - f^{2}},$$

then

$$f_{\mathbf{K}}(s) = \pm u_0 \tanh(s/\xi); \qquad \xi = \{2A^{-1}(\frac{1}{2}\gamma a^2 - M_1 c^2)\}^{\frac{1}{2}}.$$
 (28a, b)

This is precisely the KS kink solitary wave with the coupling reduced by a factor of two.

The kink quadrature also permits kink solutions for more general values of the parameters. If we introduce the dimensionless quantities

$$\bar{f} = f/u_0, \quad \bar{g} = g/u_0, \quad \bar{\gamma} = \gamma/A,$$

 $\bar{m} = M_2/M_1, \quad \bar{c} = a^{-1}(M_1/A)^{\frac{1}{2}}c, \quad \bar{s} = s/a,$ (29)

the kink quadrature can be written in the form

$$\bar{s} = \left(\frac{2\bar{c}^2\bar{m}}{\bar{\gamma}}\right)^{\frac{1}{2}} \int_{\bar{f}_{\mathbf{K}}(0)}^{\bar{f}_{\mathbf{K}}(\bar{s})} \frac{(a_0-1)\,\mathrm{d}\bar{f}}{(1-\bar{f}^2)(a_0-\bar{f}^2)^{\frac{1}{2}}} + \left(\frac{9\bar{c}^2\bar{m}}{2\bar{\gamma}}\right)^{\frac{1}{2}} \int_{\bar{f}_{\mathbf{K}}(0)}^{\bar{f}_{\mathbf{K}}(\bar{s})} \frac{\mathrm{d}\bar{f}}{(a_0-\bar{f}^2)^{\frac{1}{2}}},\tag{30}$$

with

$$a_0 = \bar{\gamma}^2 / 2\bar{c}^2 \overline{m} - \bar{\gamma}(\overline{m}^{-1} + 1).$$
(31)

Imposing the physical conditions that \bar{s} is purely real and that $\bar{f}_{K}(\bar{s})$ is bounded for all \bar{s} , we arrive at the solution

$$\pm \bar{s} = (9\bar{c}^2 \bar{m}/2\bar{\gamma})^{\frac{1}{2}} \sin^{-1}(\bar{f}_{\rm K}/a_0) + (2\bar{c}^2 \bar{m}/\bar{\gamma})^{\frac{1}{2}} (a_0 - 1)^{\frac{1}{2}} \tanh^{-1}\{\bar{f}_{\rm K}(a_0 - 1)^{\frac{1}{2}}/(a_0 - \bar{f}_{\rm K}^2)^{\frac{1}{2}}\},$$
(32)

with $a_0 > 1$ and $0 \le |\bar{f}_K(\bar{s})| \le 1$. The dimensionless g field in this case is given by

$$\bar{g}_{\mathrm{K}} = \frac{\bar{c}^4 \overline{m} - \frac{1}{16} \bar{\gamma}^2}{2 \bar{\gamma} (\bar{c}^2 \overline{m} - \frac{1}{4} \bar{\gamma})} \frac{\mathrm{d}^2 \bar{f}_{\mathrm{K}}}{\mathrm{d}\bar{s}^2} + \bar{f}_{\mathrm{K}} + \frac{\bar{c}^2 \overline{m}}{2 \bar{\gamma} (\bar{c}^2 \overline{m} - \frac{1}{4} \bar{\gamma})} (\bar{f}_{\mathrm{K}}^{\ 3} - \bar{f}_{\mathrm{K}}), \qquad (33a)$$

with

$$\frac{\mathrm{d}^{2}\bar{f}_{\mathrm{K}}}{\mathrm{d}\bar{s}^{2}} = \frac{2\bar{\gamma}}{\bar{c}^{2}\bar{m}} \frac{(3\bar{c}^{2}\bar{m}/\bar{\gamma})\bar{f}_{\mathrm{K}}(\mathrm{d}\bar{f}_{\mathrm{K}}/\mathrm{d}\bar{s})^{2} - \bar{f}_{\mathrm{K}} + \bar{f}_{\mathrm{K}}^{3}}{1 + 2a_{0} - 3\bar{f}_{\mathrm{K}}^{2}},$$
(33b)

$$\frac{\mathrm{d}\bar{f}_{\mathrm{K}}}{\mathrm{d}\bar{s}} = \left(\frac{2\bar{\gamma}}{\bar{c}^2\bar{m}}\right)^{\frac{1}{2}} \frac{(1-\bar{f}_{\mathrm{K}}^2)(a_0-\bar{f}_{\mathrm{K}}^2)^{\frac{1}{2}}}{1+2a_0-3\bar{f}_{\mathrm{K}}^2}.$$
(33c)

The condition $a_0 > 1$ restricts the velocity as follows:

$$\bar{c} < \bar{\gamma} / [2\{\overline{m} + \bar{\gamma}(1+\overline{m})\}]^{\frac{1}{2}}.$$

Note that this condition is satisfied for all velocities less than the acoustic velocity c_A .

The excitation energy for these kinks is found using equations (11), (29) and (33c). Explicitly, we have

$$\begin{split} \bar{E}_{\mathrm{K}} &= \left(\frac{\bar{c}^2 \overline{m}}{2 \bar{\gamma}}\right)^{\frac{1}{2}} \int_{-1}^{+1} \mathrm{d}\bar{f}_{\mathrm{K}} \left[(1 + 2a_0 - 3\bar{f}_{\mathrm{K}}^2) \left(\frac{1}{2} \bar{c}^2 \left(\frac{\mathrm{d}\bar{f}_{\mathrm{K}}}{\mathrm{d}\bar{s}}\right)^2 \right. \\ &\left. + \frac{1}{2} \overline{m} \bar{c}^2 \left(\frac{\mathrm{d}\bar{g}_{\mathrm{K}}}{\mathrm{d}\bar{s}}\right)^2 + \bar{\gamma} (\bar{f}_{\mathrm{K}} - \bar{g}_{\mathrm{K}}) + \frac{1}{4} \bar{\gamma} \frac{\mathrm{d}\bar{f}_{\mathrm{K}}}{\mathrm{d}\bar{s}} \frac{\mathrm{d}\bar{g}_{\mathrm{K}}}{\mathrm{d}\bar{s}} - \end{split}$$

$$-\frac{1}{2}(\bar{f}_{K}^{2}-1)+\frac{1}{4}(\bar{f}_{K}^{4}-1)\bigg\}\Big/(1-\bar{f}_{K}^{2})(a_{0}-\bar{f}_{K}^{2})^{\frac{1}{2}}\bigg],$$
(34)

where $\overline{E}_{K} = E_{K}B/A^{2}$. The integrand in equation (34) can be written as an explicit function of \overline{f}_{K} by making use of equations (33), together with the following expressions:

$$\frac{d\bar{g}_{K}}{d\bar{s}} = \frac{\bar{c}^{4}\bar{m} - \frac{1}{16}\bar{\gamma}^{2}}{2\bar{\gamma}(\bar{c}^{2}\bar{m} - \frac{1}{4}\bar{\gamma})} \frac{d^{3}\bar{f}_{K}}{d\bar{s}^{3}} + \frac{d\bar{f}_{K}}{d\bar{s}} + \frac{\bar{c}^{2}\bar{m}}{2\bar{\gamma}(\bar{c}^{2}\bar{m} - \frac{1}{4}\bar{\gamma})} (3\bar{f}_{K}^{2} - 1) \frac{d\bar{f}_{K}}{d\bar{s}}, \quad (35a)$$

$$\frac{d^{3}\bar{f}_{K}}{d\bar{s}^{3}} = \frac{2\bar{\gamma}}{\bar{c}^{2}\bar{m}} \Big\{ (1 + 2a_{0} + 3\bar{f}_{K}^{2}) \frac{3\bar{c}^{2}\bar{m}}{\bar{\gamma}} \Big(\frac{d\bar{f}_{K}}{d\bar{s}} \Big)^{3} + (1 + 2a_{0} - 3\bar{f}_{K}^{2}) \frac{6\bar{c}^{2}\bar{m}}{\bar{\gamma}} \bar{f}_{K} \frac{d\bar{f}_{K}}{d\bar{s}} \frac{d^{2}\bar{f}_{K}}{d\bar{s}^{2}} - (1 + 2a_{0} - 6a_{0}\bar{f}_{K}^{2} + 3\bar{f}_{K}^{4}) \frac{d\bar{f}_{K}}{d\bar{s}} \Big\} \Big/ (1 + 2a_{0} - 3\bar{f}_{K}^{2})^{2}. \quad (35b)$$

The kink solutions described by equations (32) and (33) occur for all three mass ratios: $\overline{m} < 1$, $\overline{m} = 1$ and $\overline{m} > 1$. The excitation energy and the domain wall width $\overline{\Delta}$ [where $\overline{f}(\frac{1}{2}\overline{\Delta}) = \tanh 1$] vary as the square root of the coupling. This feature is also exhibited by the equal-displacement-field kinks; however, the excitation energy of the equal-displacement kinks is greater than the excitation energy of the above kinks for similar values of \overline{m} and $\overline{\gamma}$ (Henry 1984).

3. Exact Statistical Mechanics

The classical canonical partition function for the nonlinear diatomic chain is given by

$$Z = \prod_{i=1}^{N} \left(\int \frac{\mathrm{d}\dot{u}_{i}}{h} \frac{\mathrm{d}\dot{v}_{i}}{h} \mathrm{d}u_{i} \mathrm{d}v_{i} \exp\{-\beta H(\dot{u}_{i}, \dot{v}_{i}, u_{i}, v_{i}, u_{i+1})\} \right),$$
(36)

where the Hamiltonian H is given by equation (1). Planck's constant h is included in the integral in the usual way to represent the 'volume' that each state occupies in phase space. Integrating over the velocity coordinates we can write the partition function in the factored form

$$Z = Z_u Z_v Z_{u,v}, \tag{37}$$

where

$$Z_{u}^{\cdot} = (2\pi M_{1} k_{\rm B} T/h^{2})^{\frac{1}{2}N}, \qquad Z_{v}^{\cdot} = (2\pi M_{2} k_{\rm B} T/h^{2})^{\frac{1}{2}N}.$$
 (38a, b)

The configurational contribution $Z_{u,v}$ is now a two component path integral:

$$Z_{u,v} = \int_{-\infty}^{+\infty} du_N \int_{-\infty}^{+\infty} dv_N \dots \int_{-\infty}^{+\infty} du_1 \int_{-\infty}^{+\infty} dv_1$$

 $\times \prod_{i=1}^{N} \exp\left[-\beta \{\frac{1}{2}\gamma(u_{i+1} - v_i)^2 + \frac{1}{2}\gamma(u_i - v_i)^2 + \frac{1}{2}V(u_i) + \frac{1}{2}V(u_{i+1})\}\right].$ (39)

This can be reduced to a one-component path integral by first performing the integrations over all the 'v' field coordinates. The result is given by

$$Z_{u,v} = (\pi/\beta\gamma)^{\frac{1}{2}N} Z_u, \qquad (40)$$

where the *u*-field configurational factor

$$Z_{u} = \int_{-\infty}^{+\infty} du_{N} \dots \int_{-\infty}^{+\infty} du_{1} \prod_{i=1}^{N} f(u_{i}, u_{i+1}), \qquad (41a)$$

with

$$f(u_i, u_{i+1}) = \exp[-\beta\{\frac{1}{4}\gamma(u_i - u_{i+1})^2 + \frac{1}{2}V(u_i) + \frac{1}{2}V(u_{i+1})\}],$$
(41b)

is equivalent to the configurational contribution to the canonical partition function for the monatomic ϕ^4 chain, with the harmonic coupling reduced by a factor of two.

The *u*-field configurational contribution is evaluated most easily using the transfer integral technique [Scalapino *et al.* (1972); Krumhansl and Schrieffer (1975); see also Henry and Oitmaa (1984) for an illustrative application]. We outline the approach here using the bra-ket notation. This notation is convenient for calculating correlation functions. Following Kogut (1979) we begin by introducing the operator \hat{T} such that

$$\langle u' | \hat{T} | u \rangle = f(u, u'), \qquad (42)$$

where the state $|u\rangle$ corresponds to a particle having a displacement u. The path integral (equations 41) can now be expanded in the following way:

$$Z_{u} = \int \dots \int \langle u_{N+1} | \hat{T} | u_{N} \rangle \, \mathrm{d}u_{N} \langle u_{N} | \hat{T} | u_{N-1} \rangle \, \mathrm{d}u_{N-1} \dots \langle u_{2} | \hat{T} | u_{1} \rangle \, \mathrm{d}u_{1} \,. \tag{43}$$

Using the completeness relation for the $|u\rangle$ basis,

$$\int \mathrm{d}u \,|\, u \rangle \langle u \,|\, = \, 1 \,, \tag{44}$$

we arrive at

$$Z_{u} = \int \langle u_{N+1} | \, \widehat{T}^{N} | \, u_{1} \rangle \, \mathrm{d}u_{1} \,. \tag{45}$$

For periodic systems where $u_1 = u_{N+1}$ this simplifies to

$$Z_{\mu} = \operatorname{Tr}\{\hat{T}^{N}\}.$$
(46)

In order to find a suitable transfer operator \hat{T} we introduce the transfer integral operator equation (TIOE)

$$\int_{-\infty}^{+\infty} \mathrm{d}u \ f(u,u')\psi_n(u) = \lambda_n\psi_n(u'), \qquad (47)$$

in which the form of the kernel ensures that the eigenfunctions $\{\psi_n\}$ form a complete set on the interval $u \in (-\infty, +\infty)$. Inserting equation (42) into (47) yields

$$\int_{-\infty}^{+\infty} \mathrm{d}u \,\langle u' \,|\, \hat{T} \,|\, u \rangle \langle u \,|\, \psi_n \rangle = \lambda_n \langle u' \,|\, \psi_n \rangle, \tag{48}$$

where $|\psi_n\rangle$ is a state vector corresponding to the eigenfunction $\psi_n(u)$. Now using the completeness relation (44), we get

$$\langle u' | \hat{T} | \psi_n \rangle = \lambda_n \langle u' | \psi_n \rangle.$$
⁽⁴⁹⁾

Multiplying each side of equation (49) by $\int du' |u'\rangle$ and using the completeness relation (44) again yields

$$\hat{T} | \psi_n \rangle = \lambda_n | \psi_n \rangle. \tag{50}$$

Finally, using the completeness for the $|\psi_n\rangle$ basis,

$$\sum_{n} |\psi_n\rangle \langle \psi_n| = 1, \qquad (51)$$

we derive

$$\widehat{T} = \sum_{n} \lambda_{n} | \psi_{n} \rangle \langle \psi_{n} |.$$
(52)

The *u*-field configurational contribution to the canonical partition function is now obtained by combining equations (41) and (52). The result is

$$Z_u = \sum_n \lambda_n^N, \tag{53}$$

where λ_n are the eigenvalues of the transfer integral equation (47). In the thermodynamic limit $N \to \infty$ the configurational contribution can be expressed as

$$Z_{\mu} \approx \lambda_0^N, \tag{54}$$

where λ_0 is the largest eigenvalue of the TIOE. In the displacive limit $\gamma/A \ge 1$, the TIOE may be replaced by the differential eigenvalue equation (see e.g. Henry and Oitmaa 1984)

$$d^{2}\Phi_{s}/du^{2} + \beta^{2}\gamma\{\varepsilon - V_{0} - V(u)\}\Phi_{s} = 0,$$
(55)

with

$$V_0 = \ln(\beta \gamma / 4\pi) / 2\beta.$$
⁽⁵⁶⁾

The eigenvalues ε_s and eigenfunctions Φ_s of the differential eigenvalue equation are related to the eigenvalues λ_s and the eigenfunctions ψ_s of the TIOE according to

$$\varepsilon_{\rm s} = -k_{\rm B} T \ln \lambda_{\rm s},\tag{57}$$

$$\Phi_s = \exp\{-\frac{1}{2}\beta V(u)\}\psi_s.$$
(58)

The maximum eigenvalue of the TIOE

$$\lambda_0 = \exp(-\beta\varepsilon_0) \tag{59}$$

therefore corresponds to the minimum eigenvalue of the Schrödinger-like equation (55). The eigenvalue ε_0 may be obtained from a standard WKB tunneling result. At low temperature the result is given by (see e.g. Henry 1984)

$$\varepsilon_0^{(1)} \approx \left(\frac{A}{\beta^2 \gamma}\right)^{\frac{1}{2}} \pm \frac{1}{\pi} \left(\frac{A}{\beta^2 \gamma}\right)^{\frac{1}{2}} \exp\{-\frac{2}{3}u_0^2(\beta^2 \gamma A)^{\frac{1}{2}}\} + V(u_0) + V_0.$$
(60)

The free energy density for the diatomic ϕ^4 chain is defined by

$$f = \lim_{L \to \infty} -k_{\rm B} T \ln Z_u Z_v Z_{u,v} / L.$$
⁽⁶¹⁾





Now using equation (49) we get

$$\langle fg \rangle = \sum_{n} \lambda_{n}^{N-m} \int \langle \psi_{n} | u_{j+m} \rangle g(u_{j+m}) \, \mathrm{d}u_{j+m} \langle u_{j+m} | \hat{T}^{m} | u_{j} \rangle$$
$$\times f(u_{j}) \, \mathrm{d}u_{j} \langle u_{j} | \psi_{n} \rangle / Z_{u}.$$
(70)

Thus in the thermodynamic limit $N \to \infty$, we have

$$\langle fg \rangle = \lambda_0^{-m} \int \psi_0^*(u_{j+m}) g(u_{j+m}) \, \mathrm{d}u_{j+m} \langle u_{j+m} | \, \widehat{T}^m | \, u_j \rangle f(u_j)$$
$$\times \psi_0(u_j) \, \mathrm{d}u_j \,.$$

Using the completeness of the $\{\psi_n\}$ it is possible to expand the above equation as follows:

$$\langle fg \rangle = \sum_{n} \lambda_{0}^{-m} \int \psi_{0}^{*}(u_{j+m}) g(u_{j+m}) \, \mathrm{d}u_{j+m} \langle u_{j+m} | \psi_{n} \rangle$$
$$\times \langle \psi_{n} | \hat{T}^{m} | \psi_{n} \rangle \langle \psi_{n} | u_{j} \rangle f(u_{j}) \psi_{0}(u_{j}) \, \mathrm{d}u_{j}.$$

Dropping the subscripts and using equation (50) together with the orthonormality of the $\{\psi_n\}$, we finally derive

$$\langle f(u_0)g(u_m)\rangle = \sum_n \left(\frac{\lambda_n}{\lambda_0}\right)^m \int \psi_0^*(u)\psi_n(u)g(u)\,\mathrm{d} u \int \psi_n^*(u)\psi_0(u)f(u)\,\mathrm{d} u\,. \tag{71}$$

An example is the displacement-displacement static correlation

$$\langle u(0) \, u(x) \rangle = \sum_{n} \left(\frac{\lambda_{n}}{\lambda_{0}} \right)^{x/a} \left| \langle \psi_{0} \, | \, u \, | \, \psi_{n} \rangle \right|^{2}.$$
(72)

In the strong coupling and low temperature regime the sum in equation (72) will be dominated by the lowest pair of tunneling states of the differential eigenvalue equation (55). Explicitly, using equation (59), we have

$$\langle u(0)u(x)\rangle \approx \exp\{-\beta(\varepsilon_1-\varepsilon_0)x/a\} \left| \int_{-\infty}^{+\infty} \Phi_0^*(u) u \Phi_1(u) du \right|^2,$$
 (73)

with the lowest tunnel split eigenfunctions

$$\Phi_0(u) = \sqrt{\frac{1}{2}} \{ \psi_0(u-u_0) + \psi_0(u+u_0) \}, \qquad \Phi_1(u) = \sqrt{\frac{1}{2}} \{ \psi_0(u-u_0) - \psi_0(u+u_0) \},$$
(74a, b)

where $\psi_0(u)$ is the n = 0 single-well state. Using the eigenvalues of the two lowest levels, equation (60) in (73) yields

$$\langle u(0) u(x) \rangle \approx u_0^2 \exp(-|x|/\lambda_c),$$
 (75a)

with the correlation length

$$\lambda_{\rm c} = \frac{1}{2}\pi (\gamma a^2/A)^{\frac{1}{2}} \exp\{\frac{2}{3}\beta u_0^2(\gamma A)^{\frac{1}{2}}\}.$$
 (75b)

4. Kink/Phonon Ideal Gas Phenomenology

The classical partition function for the nonlinear diatomic chain may also be written in the functional integral form

$$Z(\dot{u}, \dot{v}, u, v) = \int \delta(\dot{u}) \,\delta(\dot{v}) \,\delta(u) \,\delta(v) \exp\left(-\beta \int \frac{\mathrm{d}x}{a} H\right),\tag{76}$$

where the Hamiltonian density H is defined by equation (9). The dominant contribution to the above path integral will come from the steepest descent trajectories minimizing $\int (dx/a)H$, i.e. from all solutions of the Euler-Lagrange equations of motion. These dominant contributions acquire gaussian corrections from trajectories nearby to the extremal ones corresponding to interactions between the different sectors of the solution space. These ideas are the primary motivation (Bishop *et al.* 1980) for an attempt to construct a phenomenological ideal gas type model which will include all sectors of solution space as quasi-particles. The success of such an ideal gas phenomenology for nonlinear monatomic chains has been well documented (Krumhansl and Schrieffer 1975; Currie *et al.* 1980; De Leonardis 1980).

At sufficiently low temperatures $\beta E_{K}^{0} \ll 1$ (with E_{K}^{0} the rest energy of the kinks in the chain), where the kink density is also very low, interactions may be neglected in a first approximation.

We now derive the free energy density for an ideal gas of noninteracting kinks, anti-kinks and phonons on a chain of length L. In this section we closely follow the derivation of Currie *et al.* (1980). The number of kinks in the system is variable, and thus it is convenient to commence with the grand canonical partition function

$$Z_{\rm G} = \sum_{N=0}^{\infty} \sum_{r=1}^{\infty} \exp\{\beta(\mu N - E_{N_r})\},$$
(77)

where E_{N_r} is the energy of the *r*th state of N particles of the system and μ is the chemical potential. In the absence of interactions the grand partition function factors into

$$Z_{\rm G} = \exp(-\beta L F_0) Z_{\rm G}^{\rm K,\overline{\rm K}},\tag{78}$$

where F_0 is the phonon free energy density and

$$Z_{\mathbf{G}}^{\mathbf{K},\overline{\mathbf{K}}} = \sum_{N=0}^{\infty} Z^{\mathbf{K},\overline{\mathbf{K}}}(T,V,N) \exp(\beta \mu N)$$
(79)

is a weighted sum of partition functions for systems with fixed numbers N = 0, 1, 2, ... of particles. The kink and anti-kink have the same chemical potential μ .

The classical free energy density for phonons in the diatomic ϕ^4 chain is given by

$$F_0 \approx \frac{k_{\rm B}T}{2\pi} \int_{-\pi/a}^{+\pi/a} \ln\left(\frac{\omega(+)\hbar}{k_{\rm B}T} \frac{\omega(-)\hbar}{k_{\rm B}T}\right) \,\mathrm{d}k\,,\tag{80}$$

where the two dispersion branches $\omega(\pm)$ are defined by equation (6). The integral can be evaluated analytically yielding

$$F_{0} = \frac{k_{\rm B}T}{a} \ln\left(\frac{\hbar^{2}\gamma}{k_{\rm B}^{2}T^{2}(M_{1}M_{2})^{\frac{1}{2}}}\right) + \frac{k_{\rm B}T}{2a} \ln\left[\frac{2A}{\gamma} + 1 + \left\{\left(\frac{2A}{\gamma} + 1\right)^{2} - 1\right\}^{\frac{1}{2}}\right].$$
 (81)

The first term in this equation is equivalent to the classical phonon free energy density for a diatomic chain including only harmonic interactions. The other term represents the anharmonic contribution to the phonon gas resulting from the nonlinear on-site potential. In the strong coupling regime the anharmonic contribution reduces to $(A/\gamma)^{\frac{1}{2}}/a$. The resulting expression for the phonon gas free energy density

$$F_{0} \approx \frac{k_{\rm B}T}{a} \ln\left(\frac{h^{2}\gamma}{k_{\rm B}^{2}T^{2}(M_{1}M_{2})^{\frac{1}{2}}}\right) + \frac{k_{\rm B}T}{a}\left(\frac{A}{\gamma}\right)^{\frac{1}{2}}$$
(82)

is equivalent to the oscillating contribution to the exact free energy density (equation 62b) for the diatomic chain.

The grand partition function for a gas of $N_{\rm K}$ kinks, and $N_{\rm \overline{K}}$ anti-kinks which are topologically ordered so that kinks are followed by anti-kinks (and vice versa) is given by equation (79) with (Currie *et al.* 1980)

$$Z^{K,\overline{K}}(T,V,N) = \frac{2L^N}{h^N N!} \left(\int_{-\infty}^{+\infty} d\rho_K \exp(-\beta E_K) \right)^N,$$
(83)

where $N = N_{\rm K} + N_{\rm \bar{K}} = 2N_{\rm K}$. At low velocities we approximate the kink energy by

$$E_{\rm K} \approx E_{\rm K}^0 + \rho^2 / 2M_{\rm K}, \qquad (84)$$

where $E_{\rm K}^{0}$ is the rest energy of the kink, and $M_{\rm K}$ is the kink 'mass'. Inserting equations (83) and (84) into (79) yields

$$Z_{\rm G}^{\rm K,\vec{K}} = 2 \exp\left\{\exp(\beta\mu)\frac{L}{h}\left(\frac{2\pi M_{\rm K}}{\beta}\right)^{\frac{1}{2}}\exp(-\beta E_{\rm K}^{0})\right\}.$$
(85)

Thermodynamic quantities for the phenomenological ideal gas are now derived from the grand canonical partition function, equations (78), (82) and (85): The grand canonical potential density is given by

$$\Omega \equiv -\frac{k_{\rm B}T}{L}\ln Z_{\rm G} = F_0 - \frac{k_{\rm B}T}{h} \left(\frac{2\pi M_{\rm K}}{\beta}\right)^{\frac{1}{2}} \exp(\beta\mu) \exp(-\beta E_{\rm K}^0).$$
(86)

The average total kink number density is

$$n_{\rm K}^{\rm tot} \equiv (N_{\rm K} + N_{\rm \overline{K}})/L = -(\partial \Omega/\partial \mu)_{\mu = 0}$$
$$= h^{-1} (2\pi M_{\rm K} \beta)^{\frac{1}{2}} \exp(-\beta E_{\rm K}^{0}).$$
(87)

The free energy density is given by Ω with $\mu = 0$:

$$F = F_0 - k_{\rm B} \, T n_{\rm K}^{\rm tot} \,. \tag{88}$$

The chemical potential is set to zero in the above thermodynamic functions as the kink-anti-kink density is assumed to be controlled by temperature alone.

The kink rest energy is now calculated explicitly by substituting the static kink solution given by equations (26) and (27) into the excitation energy (11). The result is

$$E_{\rm K}^{0} = \frac{2}{3} u_0^2 (\gamma A)^{\frac{1}{2}}.$$
 (89)

The same result may be obtained by taking the static limit $(M_2 \ge M_1)$ in the dynamic equal-displacement-field kink energy (15). The kink mass may be approximated as the number of unit cells in a domain wall times the mass of a unit cell. Using the domain wall width $2\xi_0$ from equation (26b), we derive

$$M_{\rm K} \approx 2(\gamma/A)^{\frac{1}{2}}(M_1 + M_2).$$
 (90)

The free energy density for the ideal kink-phonon gas is finally obtained by inserting equations (89) and (90) with (87) into (88). The result is

$$F = F_0 - 2\left(\frac{k_{\rm B}T}{\pi}\right)^{\frac{1}{2}} \left(\frac{1}{\gamma A}\right)^{\frac{1}{2}} \frac{\pi}{h} \{\gamma(M_1 + M_2)\}^{\frac{1}{2}} \exp\{-\frac{2}{3}u_0^2(\beta^2 \gamma A)^{\frac{1}{2}}\}.$$
 (91)

The kink-anti-kink term in the ideal gas free energy density corresponds to the tunneling contribution (63) in the free energy density for the nonlinear diatomic chain. The precise equivalence of these two terms would depend upon the inclusion of kink/phonon interactions in the phenomenology. Kink/phonon interactions have been successfully incorporated in the ideal gas phenomenology for nonlinear monatomic chains (Currie *et al.* 1980). The kink/phonon interaction leads to a change in the phonon free energy density. This can be incorporated into the phenomenology as a kink self-energy correction term leading to the appropriate renormalization of the kink-anti-kink free energy density. We have not developed this extension in the diatomic ϕ^4 chain as we have been unable to find an analytic form for the phase shift of phonons in the presence of kinks. However, in Part III we report on molecular dynamics experiments which show that the interaction between a single kink and a phonon wave packet in the diatomic ϕ^4 chain.

The correspondence between the exact free energy density calculation for the nonlinear diatomic chain and the phenomenological calculation based on an ideal gas which incorporates kinks and phonons as elementary excitations constitutes a 'proof' that the low temperature excitation spectrum for the nonlinear diatomic chain is dominated by low velocity kinks and by phonons. The low temperature phonon solutions (5) and the static kink solutions (26) and (27) are therefore nonlinear vibrational excitations in our diatomic model.

The low temperature thermodynamic functions calculated above are dominated by phonon contributions since the kink density is exponentially small at low temperatures. An important quantity which bears a strong kink signature is the dynamic structure factor for the displacement fields:

$$S(q,\omega) = \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \mathrm{d}t \,\mathrm{d}x \exp(-\mathrm{i}\,\omega t) \exp(+\mathrm{i}\,qx) \langle u(0,0)\,u(x,t) \rangle \,. \tag{92}$$

Here the wave vector q is in units of π/a in the chain direction. The dynamical structure factor is proportional to the coherent neutron scattering cross section, which is directly measured in inelastic neutron scattering experiments. In the harmonic approximation (e.g. the self-consistent phonon approximation), when the frequency dependence of $S(q, \omega)$ exhibits sharp peaks, the frequency of these peaks as a function of wave number q defines a dispersion curve (e.g. the self-consistent phonon dispersion law) for elementary excitations in the system (Bottger 1983). An interesting question concerns the contribution of the anharmonic kinks (also elementary excitations) to the dynamical structure factor for nonlinear displacement fields.

At present there have been no exact calculations of the dynamical structure factor for nonlinear ϕ^4 systems. The most reliable calculations are obtained from molecular dynamics simulations (Schneider and Stoll 1976, 1978, 1981; see also Part III); however, these calculations still require interpretation in order to isolate contributions from the elementary modes.

An approximate expression for the kink contribution to the dynamical structure factor for the *u*-field displacements in the diatomic ϕ^4 chain can be derived from a kink/phonon ideal gas phenomenology [cf. the derivation given by Sahni and Mazenko (1979) for the monatomic ϕ^4 chain]. Following Sahni and Mazenko we begin by introducing the grand partition function Ξ for a set of particles with positions $\{X_i\}$ and momenta $\{P_i\}$ and governed by a spatial distribution function $F(X_i)$ and a momentum distribution function $G(P_i)$ in the following way:

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^{N} \frac{\mathrm{d}X_i}{a} \frac{\mathrm{d}P_i}{\overline{P}} F(X_i) G(P_i), \qquad (93)$$

where \overline{P} denotes the thermal momentum of these particles and is related to their mass M and the temperature $k_{\rm B}T$ as follows:

$$\bar{P} = (2\pi k_{\rm B} T M)^{\frac{1}{2}}.$$
(94)

By assuming a grand ensemble of N indistinguishable kinks with energies given by equation (89), the kink contribution to the time dependent u-field correlation function can be estimated by

$$\left\langle u_{\mathbf{K}}(0,0)\,u_{\mathbf{K}}(x,t)\right\rangle = \sum_{N=0}^{\infty} \frac{1}{N!} \int u_{\mathbf{K}}(0,0)\,u_{\mathbf{K}}(x,t)\,\prod_{i=1}^{N} \left(\frac{\mathrm{d}X_{i}}{a}\,\frac{\mathrm{d}P_{i}}{\bar{P}}\exp(-\beta E_{\mathbf{K},i})\right) \Big/\Xi\,.\tag{95}$$

In order to account for the topological constraint of kinks followed by anti-kinks, we introduce the product *ansatz* (see Mazenko and Sahni 1978)

$$u_{\rm K}(x,t) = u_0 \prod_{i=1}^N \tanh\{(x - X_i - P_i t/M_{\rm K})/\xi_0\}.$$
 (96)

Substituting equation (96) into (95) we obtain

$$\langle u_{\rm K}(0,0) \, u_{\rm K}(x,t) \rangle = u_0^2 \exp[n_0 \{ I(0,0;x,t) - L \}], \tag{97}$$

with

$$I(0,0;x,t) = \int_{-\frac{1}{2}L}^{+\frac{1}{2}L} dX \int_{-\infty}^{+\infty} \frac{dP}{\overline{P}} \exp(-\beta P^2/2M_K) \\ \times \tanh(-X/\xi_0) \tanh\{(x-X-Pt/M_K)/\xi_0\},$$
(98)

and the free kink density

$$n_0 = \exp(-\beta E_{\rm K}^0)/a. \tag{99}$$

The integral over the position coordinate in equation (98) may be evaluated exactly yielding

$$I(0,0;x,t) = \int_{-\infty}^{+\infty} \frac{dP}{P} \exp(-\beta P^2 / 2M_{\rm K}) \Big\{ L - 2\xi_0 \coth\{(x - Pt/M_{\rm K})/\xi_0\} \\ \times \tanh^{-1} \Big(\frac{\tanh\{(x - Pt/M_{\rm K})/\xi_0\} \tanh(L/\xi_0)}{1 + \tanh\{(x - Pt/M_{\rm K})/\xi_0\} \cosh(L/\xi_0)} \Big) \Big\}.$$
 (100)

For large L this simplifies to

$$I(0,0;x,t) = \int_{-\infty}^{+\infty} \frac{\mathrm{d}P}{\overline{P}} \exp(-\beta P^2/2M_{\rm K}) \{L-2 \mid x-Pt/M_{\rm K} \mid \coth\{(x-Pt/M_{\rm K})/\xi_0\}.$$
(101)

In the special static case t = 0, equation (101) reduces to

$$I(0; x) = L - 2 |x| \coth(|x|/\xi_0).$$
(102)

If we now use the interpolating formula $x \coth x \approx 1 + x$ (which is valid for large and small x), then the kink contribution to the static *u*-field correlation function at long and short ranges is from equations (97) and (102)

$$\langle u_{\mathbf{K}}(0) \, u_{\mathbf{K}}(x) \rangle \approx u_0^2 \exp(-2n_0 \xi_0 - 2n_0 |x|).$$
 (103)

In the low temperature regime $\beta E_{\rm K}^0 \ge 1$, we have from equations (99) and (103)

$$\langle u_{\rm K}(0) u_{\rm K}(x) \rangle \approx u_0^2 \exp(-|x|/\lambda_{\rm c}),$$
 (104a)

where

$$\lambda_{\rm c} = \frac{1}{2}a \exp(\beta E_{\rm K}^{0}). \tag{104b}$$

The phenomenological calculation of the kink contribution to the static *u*-field correlation function given by equations (104) is thus in good agreement with the exact calculation described by equations (75) at low temperatures. This important result, which was first derived by Krumhansl and Schrieffer (1975) for the monatomic ϕ^4 chain, demonstrates that at low temperatures (well below the kink excitation energy) the correlation length begins to increase exponentially with decreasing temperature. Phonon based theories cannot account for this feature.

The time dependent correlation function obtained by inserting equation (100) into (97),

$$\langle u_{\rm K}(0,0) \, u_{\rm K}(x,t) \rangle = u_0^2 \exp\left(-\frac{2n_0}{\bar{P}} \int_{-\infty}^{+\infty} dP \, \exp(-\beta P^2/2M_{\rm K}) \, | \, x - Pt/M_{\rm K} \, | \, \coth\{(x - Pt/M_{\rm K})/\xi_0\}\right), \quad (105)$$

is much more cumbersome to evaluate analytically. An approximate expression which reduces to the correct form for the static kink correlation function in the limit $T \rightarrow 0$ is given by (Sahni and Mazenko 1979)

$$\langle u_{\mathbf{K}}(0,0) u_{\mathbf{K}}(x,t) \rangle = u_0^2 \exp(-2n_0 \xi_0) \exp(-|t|/\tau_0 \sqrt{\pi}) \exp(-2n_0 |x|), \quad (106a)$$

where

$$\tau_0 = (m_{\rm K} \beta)^{\frac{1}{2}} / 2n_0 \tag{106b}$$

is a relaxation time which is inversely proportional to the free kink density. The kink contribution to the dynamic structure factor is finally approximated by inserting equations (106) into (92). The result is

$$S_{\mathbf{K}}^{0}(q,\omega) \approx (1/2\pi)^{2} \exp(-2n_{0}\,\xi_{0}) \frac{2/\tau_{0}\,\sqrt{\pi}}{\omega^{2} + (1/\tau_{0}\,\sqrt{\pi})^{2}} S_{\mathbf{K}}^{0}(q), \qquad (107)$$

where the static structure factor $S_{\mathbf{K}}^{0}(q)$ is given by

$$S_{\rm K}^{0}(q) = 4n_0/(q^2 + 4n_0^2). \tag{108}$$

Equation (107) predicts a central peak [i.e. a peak in $S(q, \omega)$ at $\omega = 0$], with height proportional to τ_0 , which grows exponentially as the temperature is lowered towards $T \to 0$. The width of the central peak is proportional to τ_0^{-1} and becomes very small as the temperature is lowered. Sahni and Mazenko (1979) have extended the above calculation to include kink/phonon interactions. In a first approximation the bare kink density is replaced with an interacting kink density. In the presence of the interaction the central peak broadens and decreases in intensity.

5. Conclusions

In this paper we have examined the thermodynamical properties of a nonlinear diatomic model for a solid which may undergo a DSPT. This model (the diatomic ϕ^4 chain) differs from the conventional model (the monatomic ϕ^4 chain) in that it includes two species per unit cell. The nonlinear on-site potential influences only one of the species.

The equations of motion describing the diatomic ϕ^4 chain yield linearized phonon solutions, nonlinear kink-type solitary waves, and nonlinear periodic waves. Similar types of solution have been reported in the equations of motion for the monatomic ϕ^4 chain, however some important additional features are obtained for the diatomic solutions. The dispersion relation for the linearized phonon solutions in the diatomic lattice exhibits two branches corresponding to a quasi-acoustic and a quasi-optical mode. The Lorentz invariance of kinks in the diatomic lattice is destroyed. The anharmonic phonon solutions in the diatomic lattice are exact solutions of both the discrete lattice equations and the continuum field equations. The anharmonic phonons appear in the diatomic lattice as nonlinear periodic waves.

Despite differences in detail the diatomic ϕ^4 chain shares many of the physical features exhibited by the monatomic ϕ^4 chain. This fundamental correspondence is due to the existence of nonlinear vibrational excitations in both lattices which are an essential part of the framework for calculating the formal properties. The main results may be summarized as follows:

- (1) The low temperature excitation spectrum for the lattice is dominated by both linearized phonons and by nonlinear kink-type solitary waves.
- (2) The kink density increases exponentially with increasing temperature.

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- (3) The correlation length for the static displacement-displacement correlation function begins to increase exponentially with decreasing temperature at low temperatures.
- (4) The kinks are responsible for a central peak in the dynamical structure factor. The height of this peak increases exponentially with decreasing temperature.

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