PERGAMON

Solid State Communications 118 (2001) 215–219

solid state communications

www.elsevier.com/locate/ssc

Exact, numerical, and mean field behavior of a dimerizing lattice in one dimension

Vasili Perebeinos[a,1], Philip B. Allen[a,*], J. Napolitano[b]

[a]Department of Physics and Astronomy, State University of New York, Stony Brook, NY 11794-3800, USA
[b]Commack High School, 10 Radburn Drive, Commack, NY 11725, USA

Received 2 January 2001; accepted 9 January 2001 by E.E. Mendez; received in final form by the Publisher 8 February 2001

Abstract

The thermodynamics and dynamics of a one-dimensional dimer-forming anharmonic model is studied in the classical limit. This model mimics the behavior of materials with a Peierls instability. Specific heat $C(T)$, correlation length $l_c(T)$, and order parameter are calculated in three ways: (a) by mean-field (MF) approximation, (b) by numerical molecular dynamics (MD) simulation, and (c) by an exact transfer matrix method. The neighbor distribution function $F(x)$ and vibrational density-of-states $D(\omega)$ (Fourier transform of velocity–velocity correlation function) are found numerically. MF theory fails completely to describe the destruction of long-range order by fluctuations, but nevertheless, the MF answers for $C(T)$, $l_c(T)$, $F(x)$, and $D(\omega)$ give helpful interpretations of the exact behavior. © 2001 Published by Elsevier Science Ltd.

PACS: 63.70.+h; 71.45.Lr

Keywords: D. Electron–phonon interactions; D. Phonons; D. Anharmonicity

1. Introduction

Polyacetylene [1,2] and blue bronze [3,4] are examples of quasi-one-dimensional (1D) materials with Peierls-type broken-symmetry ground states [5,6], driven by electron–phonon interactions. In strictly 1D models, phonon fluctuations destroy long-range order at temperature $T > 0$. Mean field (MF) theories that ignore these fluctuations are therefore unrealistic. Numerical studies of the Peierls problem in 1D have produced results which converge towards exact answers [7–11]. In 3D, the opposite situation holds. Numerical studies are so far prohibitive, but fluctuations are not very important except to renormalize the transition temperature T_c downwards a little and to introduce a narrow critical regime where MF exponent rules are violated. The 'universality' properties of the fluctuation-dominated region attract a lot of attention but are quite unimportant from a materials science point of view in 3D. MF theory provides a reasonably accurate and very helpful physical understanding of actual 3D behavior.

MF studies of the Peierls problem have generally omitted lattice dynamical aspects, focussing on electronic excitations. The lattice is kept frozen at the position, which minimizes electronic free energy. When too many electrons are thermally excited above the Peierls gap, the gap collapses and dimerization ends. Various authors [12–15] have pointed out that both electronic and lattice (zero-point and thermal) fluctuations should be taken into account. Even with no electronic excitations, lattice kinetic energy at higher T will excite atoms out of their dimer-forming Peierls potential wells, ending the dimerized phase. Lattice fluctuations also work as an effective disorder on the electronic system, becoming stronger as T increases [16].

A full MF treatment of both lattice and electronic fluctuations has not been presented to our knowledge, perhaps because higher-dimensional models are difficult to address. As a first step, the present paper analyses a classical 1D model with only lattice-dynamical fluctuations. Exact answers are found both by a transfer matrix (TM) method and by classical molecular dynamics (MD). MF and exact answers are carefully compared. It should be possible to generalize our MD treatment to 3D classical systems with

* Corresponding author. Present address: Rensselaer Polytechnic Institute, Troy, NY 12180, USA.

[1] Current address: Physics Department, Brookhaven National Laboratory, Upton, NY 11973, USA.

0038-1098/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0038-1098(01)00045-X

only lattice dynamics, and also to generalize the MF treatment to 3D and to quantum systems with both lattice and electron dynamics.

We take the following Hamiltonian

$$H = \sum_{\ell}\left(-\frac{\kappa_1}{2}x_\ell^2 + \frac{\kappa_2}{4}x_\ell^4 + \frac{\kappa_3}{2}(x_\ell + x_{\ell+1})^2 + \frac{p_\ell^2}{2M}\right). \tag{1}$$

The first two terms are a single-site (Einstein oscillator) double-well potential with minima at $\pm u_0$,where $u_0 = \sqrt{\kappa_1/\kappa_2}$. The next term is a first neighbor spring which prefers displacements to alternate, $x_\ell = (-1)^\ell u_0$. After introducing dimensionless atom displacements $\tilde{x}_n = x_n/u_0$, time $\tilde{t} = t(\kappa_1/M)^{1/2}$, and energy $\tilde{E} = E/\kappa_1 u_0^2$, only one free parameter $\xi = \kappa_3/\kappa_1$ is left in the problem. This model was frequently studied in the past [17–23]. These studies have been reviewed by Dieterich [24]. McKenzie [25] considered a continuous version of the model.

Here we solve this problem numerically by MD simulation and compare with a MF approximation as well as an exact TM method. The MD simulation enables us to evaluate such properties as position distribution functions and frequency spectra not available by the TM method; we compare them with the MF results.

2. Mean-field solution

Using the Gibbs–Bogoliubov inequality [26,17,18], MF theory can be formulated in a variational approach. It can be implemented in all dimensions, using either classical or quantum mechanics. A function Φ is defined which bounds the exact free energy function $F(T)$ from above

$$F(T) \le \Phi(\alpha_i, T) = F_0 + \langle H - H_0\rangle_0. \tag{2}$$

Here H_0 is a trial Hamiltonian which depends on a set of adjustable parameters $\{\alpha_i\}$ used to minimize the right hand side of the expression (2). F_0 is the free energy of the trial Hamiltonian. The average $\langle\ \rangle_0$ is taken with respect to H_0. If H_0 is harmonic, then minimization leads to temperature-dependent frequencies of H_0. This procedure is also known as the 'self-consistent phonon method.' We choose the trial Hamiltonian

$$H_0 = \sum_{\ell}\left(\frac{\omega_0^2 y_\ell^2}{2} + \frac{\omega_0^2\delta^2}{2}(y_\ell + y_{\ell+1})^2 + \frac{v_\ell^2}{2}\right). \tag{3}$$

The values of $\{\alpha_i\} = \{\omega_0, \delta, u\}$ which minimize Eq. (2) depend on $\xi = \kappa_3/\kappa_1$ and on the inverse temperature β. All quantities are dimensionless; y_ℓ is a displaced position variable $\tilde{x}_\ell + (-1)^\ell u$, and v_ℓ is the corresponding velocity. If one raises T, the dimerization amplitude u goes to zero at a transition temperature T_c. The harmonic Hamiltonian H_0 (Eq. (3)) describes traveling waves with frequency $\omega_k^2 = \omega_0^2(1 + 4\delta^2\cos^2(ka/2))$. We study here only the classical limit for comparison with the MD simulation and the TM solution. Let Φ_{MF} denote the minimum value of the trial free energy Φ. From this we can compute the specific heat $C_{\mathrm{MF}} = -T\partial^2\Phi_{\mathrm{MF}}/\partial T^2$.

We define a displacement correlation function G as

$$G(m) = \frac{1}{N}\sum_{\ell}\langle(-1)^\ell x_\ell(-1)^{\ell+m}x_{\ell+m}\rangle. \tag{4}$$

The square of the order parameter is the correlation function at large distance $G(m\to\infty)$. In MF approximation, this order parameter is the variational parameter u. The correlation length l_c, defined as decay rate of the correlation function at large m, is given by

$$l_{\mathrm{MF}}^{-1} = 1\mathrm{n}\left(\frac{1 + 2\delta^2 + \sqrt{1 + 4\delta^2}}{2\delta^2}\right). \tag{5}$$

Using the phonon dispersion law of the trial Hamiltonian (3) we define a density of phonon states $D_{\mathrm{MF}}(\omega) = (a/2\pi)\,\mathrm{d}k/\mathrm{d}\omega$, which is a function of temperature-dependent parameters ω_0 and δ.

Another quantity of interest is the function

$$F(x) = \frac{1}{N}\left\langle\sum_{\ell}\delta(x - x_\ell + x_{\ell+1})\right\rangle, \tag{6}$$

which gives the distribution of the separation between nearest atoms. At zero temperature, $x_\ell = u(-1)^\ell$, and the distribution consists of a pair of delta functions $F(x) = (\delta(x - 2u) + \delta(x + 2u))/2$. At non-zero temperature it can be evaluated in MF approximation

$$F_{\mathrm{MF}}(x) = \frac{(8\pi)^{-1/2}}{\sqrt{\langle(y_{\ell+1} - y_\ell)^2\rangle}}\sum_{\pm}\exp\left(\frac{-(x \pm 2u)^2}{2\langle(y_{\ell+1} - y_\ell)^2\rangle}\right). \tag{7}$$

3. Transfer matrix method

The TM method has been applied to 1D anharmonic systems [19,22,23]. To evaluate the classical partition function, one first writes it as

$$Z = \prod_{i=1}^{N}\int \mathrm{d}z_i\,\exp(-\beta f(z_{i+1}, z_i)), \tag{8}$$

Where $f(z,z')$ contains the part of the potential energy associated with atom at z', $f(z,z') = -z'^2/2 + z'^4/4 + \xi(z - z')^2/2$, and z_i is $(-1)^i\tilde{x}_i$ and obeys periodic boundary conditions $z_{N+1} = z_1$. We follow the standard procedure and construct a complete orthonormal set of functions $\Psi_n(z)$ which satisfy the integral equation

$$\int \mathrm{d}z'\,\exp(-\beta f(z,z'))\Psi_n(z') = \exp(-\beta\epsilon_n)\Psi_n(z). \tag{9}$$

Then the answer for the partition function in the thermodynamic limit $N\to\infty$ is $Z = \exp(-N\beta\epsilon_t)$, where ϵ_ϵ is the 'ground state' ($\exp(-\beta\epsilon_t)$ is the largest eigenvalue) of the integral Eq. (9). The exact free energy is thus $F(T) = N\epsilon_t$. The leading term of the displacement correlation

function is [19]

$$G(m) = |\langle \Psi_t' | y | \Psi_t \rangle|^2 \exp(-ml_c), \tag{10}$$

where the correlation length is, $l_c = 1/\beta(\epsilon_t' - \epsilon_t)$. Here Ψ_t'(and ϵ_t') are the first excited state of the integral Eq. (9). By a variational method we found the two lowest 'eigenenergies' and the corresponding eigenfunctions to accuracy 10^{-10} and 10^{-5}, respectively. The specific heat is found from the second derivative of the free energy ϵ_t with respect to temperature. The first derivative is given to high accuracy using the Feynman–Hellman theorem, and the second derivative is found by finite differences.

4. Numerical simulation

We solved Newton's equations for a ring of 250 atoms governed by the Hamiltonian (1). A small time step $dt = 0.014$ was used. Each simulation lasted for a time 70,000 (5×10^6 dt). The position and velocity of each atom were updated using the Verlet algorithm [27] with error proportional to dt^4. To control the temperature, the atoms suffered random collisions with 'gas molecules' of equal mass. A collision was modeled by exchanging an atom's velocity with a gas molecule's velocity, which was randomly generated according to the Maxwell–Boltzmann distribution. Collisions occurred randomly, but on average, once every 10 dt. The atom that suffered the collision was also chosen randomly. Atoms were initially in the positions ($x_\ell = (-1)^\ell u_0$), with random initial velocities chosen from a Boltzmann distribution. The specific heat was calculated using

$$C = \frac{\langle E^2 \rangle - \langle E \rangle^2}{T^2}. \tag{11}$$

Each simulation was divided into four intervals of 17,500 time units (1,250,000 dt). Over each of these four intervals, the total energy E in the system was measured at 100,000 randomly chosen times. The specific heat was calculated for each of the four intervals. The standard deviation of the four calculations served as an error bar. The correlation function $G(m)$, for $m = 0$ to 30, was calculated at 400,000 randomly chosen time intervals and then averaged. The value of $-\ln(G(m))$ was graphed versus m. The range of m values appropriate for linear fitting was chosen by eye. The slope of the linear fit was taken as the reciprocal correlation length.

The frequency spectrum was similarly calculated from the velocity correlation function

$$\chi(t) = \frac{1}{N} \sum_{i=l}^{N} \langle v_i(T+t) v_i(T) \rangle. \tag{12}$$

It was necessary to calculate $\chi(t)$ from $t = 0$ up to 3000 in order for $\chi(t)$ to approach zero. Each value of $\chi(t)$ was calculated 1249 times and then averaged. At the end of the simulation, the frequency spectrum was calculated by Fourier transform

$$D(\omega) = \int_0^\infty \chi(t) \cos(\omega t)\, \mathrm{d}t. \tag{13}$$

The nearest neighbor distribution function (6) was found by averaging histograms for the displacement distribution over 1000 randomly chosen times.

5. Results and discussion

The exact solution has no ordered state at any $T > 0$. MF theory gives a critical temperature T_c at which the trial free energies evaluated at $u \neq 0$ and $u = 0$ coincide, indicating a first order transition. The resulting order parameter u^2 versus temperature is shown on the top graph of Fig. 1. The qualitative behavior is similar for all ξ, so we show results only for $\xi = 0.5$.

The specific heat in MFA is shown on the bottom graph of Fig. 1 along with TM and MD solutions. The numerical MD and TM specific heats agree well. The uncertainty in the MD specific heat arises from statistical error, which should diminish as $N^{-1/2}$, when we take an average over a large number N of time slices.

There is a big difference between exact and MF solutions for the specific heat, except in the high and low T limits, where they coincide. To understand why MF approximation is accurate in the extreme T limits, consider the nearest neighbor distribution function in the MF and MD cases plotted on Fig. 2 for different values of T. At low T atoms are close to the bottom of the well $x_\ell = (-1)^\ell u_0$. In this situation, approximating the actual Hamiltonian (1) by the harmonic version (3) works well. In the opposite

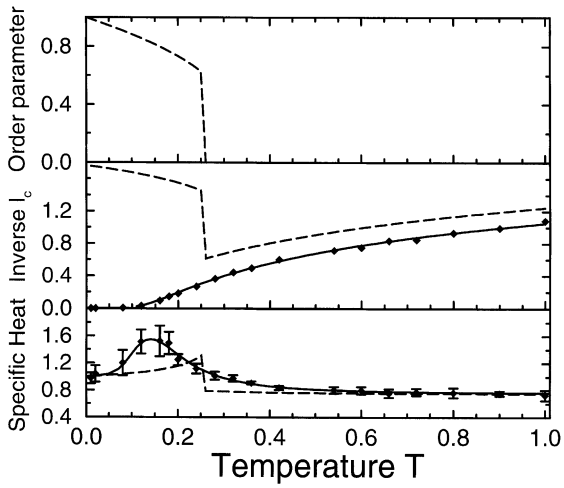

Fig. 1. Specific heat, inverse correlation length and order parameter versus temperature for the case $\xi = \kappa_3/\kappa_1 = 0.5$. The solid lines are exact solutions by the TM method; the long-dashed line is MF approximation; diamonds are the MD results. The TM and MD results agree.

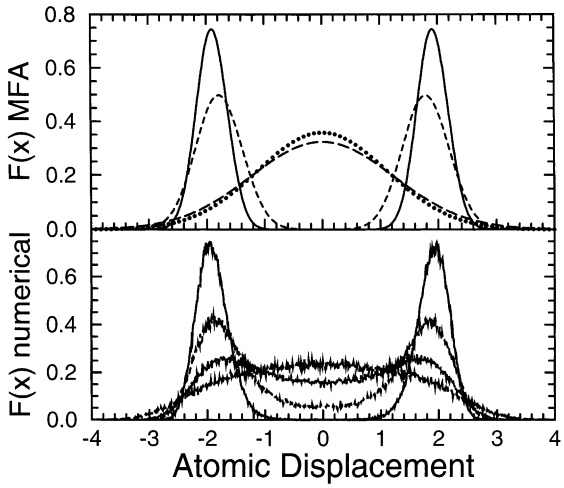

Fig. 2. Nearest neighbor distribution function from MF and MD solutions for $T = 0.08$ (solid line), $T = 0.16$ (dashed line), $T = 0.28$ (dotted line), $T = 0.8$ (long-dashed line). The atomic displacement is measured in units of $(\kappa_1/\kappa_2)^{1/2}$.

limit of high T, the harmonic approximation also works well because the nearest-neighbor coupling term dominates the total energy. Averages of the first and the second terms of the MF Hamiltonian (3), namely $\omega_0^2\langle y_\ell\rangle^2/2$ and $\omega_0^2\delta^2\langle y_\ell + y_{\ell+1}\rangle^2/2$, coincide at $\delta^2 = 3/4$, which happens at $T = 0.74$. At $T = 0.8$, exact and MF results agree well for both the specific heat and the nearest neighbor distribution function. Fig. 2 shows that the maximum deviation in $F(x)$ happens at $T = 0.28$, just above $T_c = 0.26$. The numerical result tells us that particles are mostly in the potential wells, while the MF result has maximum probability when particles are in undisplaced central sites.

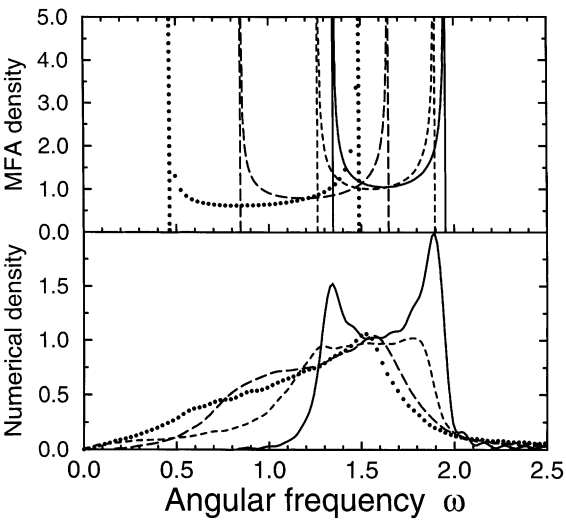

Fig. 3. Vibrational density of states versus frequency (in units of $(\kappa_1/M)^{1/2}$) from MF and MD calculations for $T = 0.08$ (solid line), $T = 0.16$ (dashed line), $T = 0.28$ (dotted line), and $T = 0.8$ (long-dashed line).

Results for the MF, TM, and MD correlation lengths are plotted on Fig. 1. The latter two coincide. The error bars of the MD solution come from the least square fit of the numerical correlation function. These error bars are smaller than the size of the points and not shown on Fig. 1. The correlation length diverges at $T = 0$ and fits the 1D Ising solution $A\exp(B/T)$, where the coefficients (A,B) depend on ξ, and approximately equal (0.18, 0.6) for $\xi = 0.5$. MF approximation gives l_c smaller than the exact value at all T and gives wrong behavior at $T < T_c$. Above the MF T_c, the predicted dl_c/dT is consistent with the exact solution.

In MF approximation, the specific heat peaks at T_c. The temperature T_{max} of the specific heat maximum in the exact solution is $\approx 50\%$ smaller than the MF value of T_c, but tracks the MF transition point as the parameter ξ is varied.

The vibrational density of states of the MD and MF calculations are shown on Fig. 3. In the low T limit the MFA and MD solutions agree. When T is raised, the MF density of states becomes broader and moves to lower frequency. Since the trial Hamiltonian (3) does not have translational symmetry, no acoustic modes occur; below a lower bound, the spectrum has no states. According to MD, a non-zero density of states appears at low frequency when T is comparable to the double well barrier $T_B = 0.25$. Particles with kinetic energy slightly greater than T_B take a very long time to overcome the barrier, and contribute to the density of states at arbitrarily low frequencies. When we raise T well above $T = 0.25$, this low frequency contribution diminishes, and the spectrum becomes more similar to the MF result.

6. Conclusions

An accurate description of the 1D chain obviously requires improvements on MF theory. Topological defects (phase slips) in the order parameter destroy long-range order and perturb thermodynamic properties [22,23]. In 3D, the topological defects are high-energy planar twin boundaries that are less likely to play a major role. MF theories are needed to understand materials properties, and are likely to be quite accurate. The present study of dynamical properties shows that, even in 1D, the MF picture gives sensible insights into the position distributions and the spectral properties even though oversimplifying the fluctuations of the exact system.

Acknowledgements

We thank N. Stojic for help with MD calculations, and S. Brazovskii for help with the TM method. This

work was supported in part by NSF grant no. DMR-9725037.

References

[1] W.P. Su, J.R. Schrieffer, A.J. Heeger, Phys. Rev. Lett. 42 (1979) 1698.
[2] A.J. Heeger, S. Kivelson, J.R. Schrieffer, Rev. Mod. Phys. 60 (1988) 781.
[3] L. Degiorgi, G. Grüner, K. Kim, R.H. McKenzie, P. Wachter, Phys. Rev. B 49 (1994) 14754.
[4] L. Degiorgi, St. Thieme, B. Alavi, G. Grüner, R.H. McKenzie, K. Kim, F. Levy, Phys. Rev. B 52 (1995) 5603.
[5] G. Grüner, Rev. Mod. Phys. 60 (1988) 1129.
[6] G. Grüner, Density Waves in Solids, Addison-Wesley, Redwood City, 1994.
[7] E. Fradkin, J.E. Hirsch, Phys. Rev. B 27 (1983) 1680.
[8] R.J. Bursill, R.H. McKenzie, C.J. Hamer, Phys. Rev. Lett. 80 (1998) 5607.
[9] R.J. Bursill, R.H. McKenzie, C.J. Hamer, Phys. Rev. Lett. 83 (1999) 408.
[10] A.W. Sandvik, D.K. Campbell, Phys. Rev. Lett. 83 (1999) 195.
[11] R. Werner, C. Gros, Phys. Rev. B 57 (1998) 2897.
[12] R.N. Bhatt, W.L. McMillan, Phys. Rev. B 6 (1975) 2042.
[13] M.J. Rice, S. Strassler, Solid State Commun. 13 (1973) 1389.
[14] M. Nakahara, K. Maki, Phys. Rev. B 25 (1982) 7789.
[15] R.H. McKenzie, Phys. Rev. B 52 (1995) 16428.
[16] R.H. McKenzie, J.W. Wilkins, Phys. Rev. Lett. 69 (1992) 1085.
[17] N.S. Gillis, Phys. Rev. B 11 (1975) 309.
[18] M. Cohen, T.L. Einstein, Phys. Rev. B 7 (1973) 1932.
[19] D.J. Scalapino, M. Sears, R.A. Ferrell, Phys. Rev. B 6 (1972) 3409.
[20] T.R. Koehler, A.R. Bishop, J.A. Krumhansl, J.R. Schrieffer, Solid State Commun. 17 (1975) 1515.
[21] T.R. Koehler, N.S. Gillis, Phys. Rev. B 13 (1976) 4183.
[22] J.A. Krumhansl, J.R. Schrieffer, Phys. Rev. B 11 (1975) 3535.
[23] S. Aubry, J. Chem. Phys. 62 (1975) 3217.
[24] W. Dieterich, Adv. Phys. 25 (1976) 615.
[25] R.H. McKenzie, Phys. Rev. B 51 (1995) 6249.
[26] H. Falk, Am. J. Phys. 38 (1970) 858.
[27] L. Verlet, Phys. Rev. 159 (1967) 98.