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

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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, correlation length, and order parameter are calculated three ways: (a) by mean field approximation, (b) by numerical molecular dynamics simulation, and (c) by an exact transfer matrix method. The single-particle spectrum (velocity-velocity correlation function) is found numerically and in mean field theory.

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I. INTRODUCTION

Polyacetylene and blue bronze are examples of quasi-one-dimensional materials with broken-symmetry ground states, driven by electron-phonon interaction, while CuGeO is driven by a spin-phonon interaction. In strictly one-dimensional (1D) models, phonon fluctuations destroy long range order at temperature $T > 0$. The electron-phonon problem has been extensively studied and numerical studies converging towards exact answers have been made. Most studies of the electron-phonon problem, especially studies of higher dimensional models, omit lattice dynamical fluctuations and focus on electronic fluctuations, keeping the lattice frozen. The present paper analyses a model with only lattice-dynamical fluctuations. Various authors pointed out that both electronic and lattice (zero-point and thermal) fluctuations should be taken into account to describe the thermodynamics of these materials. Lattice fluctuations work as an effective disorder on the electronic system, becoming stronger as the $T$ increases.

We take the following Hamiltonian:

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

(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 second-neighbor spring which prefers displacements to alternate, $u_{\ell} = (-1)^{\ell} u_0$. After introducing dimensionless atom displacements $\tilde{x}_\ell = x_{\ell}/u_0$, 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. These studies have been reviewed by Dieterich and McKenzie. considered a continuous version of the model.

Here we solve this problem numerically by molecular dynamics (MD) simulation and compare with a mean field approximation (MFA) as well as an exact transfer matrix (TM) method. The MD simulation enables us to evaluate a dynamical correlation function not available by the TM method; we compare it with the MFA.

II. MEAN FIELD SOLUTION.

Exact thermodynamic calculations of Hamiltonians like are possible only for a 1D lattice, and often only in the classical limit. A variational approach employing the Gibbs-Bogoliubov inequality can approximate the thermodynamics in all dimensions, either quantum or classical. Define a function $\Phi$ which bounds the exact free energy function $F(T)$ from above:

$$ F(T) \leq \Phi (\alpha_i, T) = F_0 + \langle H - H_0 \rangle_0, $$

(2)

where $H_0$ is a trial Hamiltonian which depends on adjustable parameters $\alpha_i$ used to minimize the right hand side of the expression. $F_0$ is the free energy of the trial Hamiltonian. The average $<\alpha_i>$ 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

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

(3)

All quantities are dimensionless; $y_{\ell}$ is a displaced position variable $x_{\ell} + (-1)^{\ell} u$. If one raises $T$, the dimerization amplitude $u$ goes to zero at a transition temperature $T_c$; $H_0$ (Eq. 3) describes uncoupled oscillators with frequency $\omega_0^2 = \omega_0^2 (1 + 4\delta^2 \cos^2 (\kappa a/2))$. We study here only the classical limit for comparison with the MD simulation and the TM solution. The values of $\omega_0$, $\delta$ and $u$ which
minimize \( \xi = \kappa_3/\kappa_1 \) and on the inverse temperature \( \beta \). Let \( \Phi_{MF} \) denote the minimum value of the trial free energy \( \Phi \). From this we can compute the specific heat in MFA, \( C_{MF} = -T\partial^2 \Phi_{MF}/\partial T^2 \). We define a displacement correlation function \( G \) as

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

The square of the order parameter is the correlation function at large distance \( G(m \to \infty) \). In MFA it is the variational parameter \( u^2 \). The correlation length, defined as decay rate of the correlation function at large \( m \), is given in MFA by

\[
\ell_{MF}^{-1} = \ln \left( \frac{1 + 2\delta^2 + \sqrt{1 + 4\delta^2}}{2\delta^2} \right)
\]

Using the phonon dispersion law of the trial Hamiltonian \( \mathcal{H} \) we define a density of phonon states \( \mathcal{D}_{MF}(\omega) = (a/2\pi)dk/d\omega \), which is a function of temperature-dependent parameters \( \omega_0 \) and \( \delta \).

Another quantity of the interest is the function

\[
F(x) = \frac{1}{N} \left( \sum_{\ell} \delta(x - x_\ell + x_{\ell+1}) \right)
\]

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

\[
F_{MF}(x) = \frac{(8\pi)^{-1/2}}{\sqrt{\langle (y_{\ell+1} - y_\ell)^2 \rangle}} \exp \left( \frac{-(x + 2u)^2}{2 \langle (y_{\ell+1} - y_\ell)^2 \rangle} \right).
\]

III. TRANSFER MATRIX METHOD.

The TM method has been applied to one dimensional anharmonic systems \([12, 14]\). To evaluate the classical partition function, one first writes it as

\[
Z = \prod_{i=1}^N \int dz_i \exp (-\beta f(z_{i+1}, z_i))
\]

\[
f(z_{i+1}, z_i) = -\frac{1}{2} z_{i+1}^2 + \frac{1}{4} z_{i+1}^4 + \frac{\xi}{2} (z_{i+1} - z_i)^2
\]

where \( z_i = (-1)^i z_i \) and obeys periodic boundary conditions \( z_{N+1} = z_1 \). Integration of \( Z \times \delta (z' - z_1) \) over the variable \( z' \) simplifies the process when the delta function is expanded in a complete set of functions

\[
\delta (z' - z_1) = \sum_n \Psi_n^* (z') \Psi_n (z_1)
\]

where the functions \( \Psi_n(z) \) satisfy the integral equation

\[
\int dz' \exp (-\beta f(z, z')) \Psi_n (z') = \exp (-\beta \varepsilon_n) \Psi_n (z)
\]

Then the answer for the partition function in the thermodynamic limit \( N \to \infty \) is \( Z = \exp (-N \beta \varepsilon_1) \), where \( \varepsilon_1 \) is the “ground state” \( \exp (-\beta \varepsilon_1) \) is the largest eigenvalue) of the integral equation \([11]\). The leading term of the displacement correlation function is \([12]\)

\[
G(m) = \langle |\Psi'_i|y|\Psi'_i| \rangle^2 \exp (-m l_c)
\]

\[
l_c = \frac{1}{\beta (\varepsilon'_1 - \varepsilon_1)}
\]

where \( \varepsilon'_1 \) and \( \varepsilon'_i \) are the first excited state of the integral equation \([11]\). Then \( l_c \) is the correlation length.

We make the kernel of the integral equation symmetric by transforming the wavefunction:

\[
\Upsilon(z) = \Psi(z) \exp \left( \frac{\beta}{2} \left( -\frac{1}{2} z^2 + \frac{1}{4} z^4 \right) \right)
\]

To find the smallest \( \varepsilon_n \) we use a variational trial function:

\[
\Upsilon_{tr}(z) = \exp \left( -\frac{b_1}{4} z^4 + \frac{b_2}{2} z^2 \right) \sum_{j=0}^m (\alpha_j z^j).
\]

Here we have introduced a set of adjustable parameters \( b_1, b_2, \{\alpha_j\} \) used to minimize \( \varepsilon_{tr} \left( b_1, b_2, \{\alpha_j\} \right) \) defined as:

\[
\exp (-\beta \varepsilon_{tr}) = \int \int dz dz' \Upsilon_{tr}(z) K(z, z') \Upsilon_{tr}(z') \int dz \Upsilon_{tr}^*(z)
\]

\[
K(z, z') = \exp \left( -\frac{\beta}{2} \left( f(z, z') + f(z', z) \right) \right)
\]

In the decoupled case \( \xi = 0 \) the trial wave function \([15]\) is exact with \( b_1 = b_2 = \beta/2 \) and \( m = 0 \). To find the first excited state we use an orthogonal function \( \Upsilon'_{tr} = x \Upsilon_{tr} \). Then we minimize \( \varepsilon'_1 \) which is defined similarly to \( \varepsilon_{tr} \) in expression \([16]\), but with \( \Upsilon_{tr} \) replaced by \( \Upsilon'_{tr} \). First we do minimization of \([16]\) only with respect to the parameters \( b_1 \) and \( b_2 \) setting all \( \alpha_j \) to zero except \( \alpha_0 = 1 \). Then we fix the values of \( b_1, b_2 \) and minimize equation \([16]\) with respect to the set of \( \{\alpha_j\}, j = 1 \ldots m \). By increasing the number of adjustable parameters \( m \) we find the convered value of \( \varepsilon_{tr} = \min \{\varepsilon_{tr}\} \). Usually \( m = 10 \) is sufficient to get an accurate answer with a relative difference less than \( 10^{-10} \) between subsequent steps.

Knowing the free energy \( \varepsilon_{tr} \) we can deduce the specific heat by taking its second derivative with respect to temperature. Using the fact that \( \varepsilon_{tr} \) is an extremum with respect to the adjustable parameters, we can evaluate its first derivative by computing the partial derivative with respect to temperature of the right hand side of Eq. \([16]\). Then a second derivative is found from finite differences of the computed first derivatives.
IV. NUMERICAL SIMULATION.

We solved Newton’s equations for the chain of atoms governed by Hamiltonian (1). The system was a chain of 250 atoms with periodic boundary conditions. A small time step $dt = 0.014$ was used. Each simulation lasted for time $70,000$ ($5 \times 10^6 dt$). The position and velocity of each atom were updated using the Verlet algorithm (2) 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 an average of once every 10 $dt$; the atom that suffered the collision was also chosen randomly. Atoms were initialized to be in the positions $(x_i = (-1)^i u_0)$, with random initial velocities. The specific heat was calculated using

$$ C = \frac{< E^2 > - < E >^2}{T^2} \quad (17) $$

Each simulation was divided into 4 periods of 17,500 time units ($1,250,000 \, dt$). Over each of these 4 periods, the total energy $E$ in the system was measured at 100,000 randomly chosen time intervals. The specific heat was calculated for each of the 4 periods. The standard deviation of the 4 calculations served as an error bar. 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

$$ \chi(t) = \frac{1}{N} \sum_{i=1}^{N} \langle v(T+t)v(T) \rangle \quad (18) $$

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

$$ \mathcal{D}(\omega) = \int_0^{\infty} \chi(t) \cos(\omega t) dt \quad (19) $$

The nearest neighbor distribution function (3) was found by averaging histograms for the displacement distribution over 1000 randomly chosen times.

V. RESULTS AND DISCUSSION.

The exact solution has no ordered state at any $T > 0$. In MFA there is 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 $\xi$, 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.

![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; long-dashed line is MFA; diamonds are MD results. TM and MD results agree.](image-url)

There is a big discrepancy in the exact and MF solutions for specific heat, except in high and low $T$ limits, where they coincide. To understand why MFA is accurate in the extreme $T$ limits, consider the nearest neighbor distribution function in MFA and MD cases plotted on Fig. 2 for different $T$. At low $T$ atoms are not far from the bottom of the well $x_i = (-1)^i u_0$. In this situation approximation of the actual Hamiltonian (1) by the harmonic version (4) works well. In the opposite limit of high $T$ harmonic approximation also works well, because the coupling term dominates the total energy. Averages of the first and the second terms of the MF Hamiltonian (4), namely $\omega_0^2 < y_t > /2$ and $\omega_0^2 \delta^2 < y_t + y_{t+1} > /2$, coincide at $\delta = 0.74$, which happens at $T = 0.74$. At $T = 0.8$, exact and MFA results agree well for both specific heat and 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 MFA has maximum probability when particles are in undisplaced central sites.

Results for the MF, TM, and MD correlation lengths are plotted on Fig. 3. 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 coefficients $(A, B)$ depend on $\xi$, and approximately equal $(0.18, 0.6)$ for $\xi = 0.5$. The MFA gives a correlation length smaller than the exact one at all $T$ and gives wrong behavior at $T < T_c$. Above the MF $T_c$ the predicted $d\xi_c/dT$ is consistent with the exact solution.

The maximum specific heat, which depends on $\xi$, occurs in MFA at $T_c$. The temperature $T_{\text{max}}$ of the specific heat maximum in the exact solution is $\approx 50\%$ smaller than the $T_c$ of MFA, but tracks the MF transition point.

The density of phonon states found by MD and by MFA are shown on Fig. 3. In the low $T$ limit again we see agreement between the MFA and MD solutions. When $T$ is raised, the phonon density in MFA becomes broader and moves to lower frequency. Since the trial Hamiltonian does not have translational symmetry, no acoustic modes occur; beyond 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 energy $\geq T_B$ take a very long time to overcome the barrier, which results in a contribution to the density of states at low frequencies. When we raise $T$ well above $T = 0.25$, this low frequency contribution disappears, and the spectrum becomes more similar to the MFA result.

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**FIG. 2.** Nearest neighbor distribution function in MFA and MD solution for $T=0.08$ (solid line), $T=0.16$ (dashed line), $T=0.28$ (dotted line), $T=0.8$ (long-dashed line). Atomic displacement is measured in units of $(\kappa_1/\kappa_2)^{1/2}$.

**FIG. 3.** Density of the phonon states versus frequency (in units of $(\kappa_1/M)^{1/2}$) in MFA and MD for $T=0.08$ (solid line), $T=0.16$ (dashed line), $T=0.28$ (dotted line), and $T=0.8$ (long-dashed line).