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LATTICE SYMMETRIES AND THERMAL EXPANSION

by

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LATTICE SYMMETRIES AND THERMAL EXPANSION

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ABSTRACT

It is well known that many of the thermomechanical properties of crystals are due to anharmonic effects in the motion of the atoms. The anharmonic terms in the potential energy which lead to this behavior depend, in part, on the symmetry of the crystal lattice. Thus the thermomechanical properties of the crystal, including the coefficient of thermal expansion, depend on the point group of the lattice. In order to study this symmetry dependence the path integral representation of the density matrix in the adiabatic approximation is used here to evaluate the thermal expectation value of the atomic positions. From this result the approximate scaling behavior of the atomic displacement with temperature, mass, bond strength (harmonic coupling), and anharmonic coupling is determined. The path integral calculation is fully quantum mechanical and can be used, in principle, to derive all the thermomechanical properties of the crystal within the adiabatic approximation.

1. INTRODUCTION

The standard approach for deriving many of the properties of crystals is the harmonic approximation which in quantum language becomes the phonon representation of lattice vibrations [1]. Unfortunately, this approximation does not include many of the known thermomechanical properties of crystals [1]. For example, the size of a rigorously harmonic crystal is independent of the temperature and thus in this approximation the coefficient of thermal expansion of all crystals is zero. There have been many studies of the effects of anharmonicity on crystal properties [1][2]. They usually proceed by using the phonon (harmonic) representation of lattice vibrations as a basis for the perturbative calculation of phonon-phonon (anharmonic) interaction effects. Here we use the path integral approach developed by Feynman for calculating the quantum density matrix [3]. It provides a compact and useful representation of quantum mechanical systems at finite temperature. Using the density matrix we can calculate, in principle, all the thermomechanical properties of the crystal. Note that since the path integral uses the entire normal mode spectrum of the lattice, it includes both the distortion of unit cells as well as the motion of the unit cells with respect to each other.

2. PATH INTEGRAL FOR THE ANHARMONIC OSCILLATOR

In this section we present the path integral result for a single anharmonic oscillator. This will be generalized below to cover the coupled oscillators (atoms) which describe a crystal lattice.

As shown in [3] the quantum mechanical density matrix for a single particle of mass M interacting with a potential $V(x, s)$ at temperature T is given by

$$\rho(x_2, x_1) = \int \delta x \exp\left[-\frac{1}{\hbar} \int_0^{\beta\hbar} ds \left(\frac{M}{2} (\partial_s x)^2 + V(x(s), s) \right) \right] \tag{1}$$

The notation is as follows: $\beta = 1/k_B T$ where k_B is the Boltzmann constant, $\hbar$ is Plancks constant, s is a dummy integration variable which parametrizes the "path" $x(s)$ and acts as a "time" variable, and δx indicates integration over all possible paths $x(s)$ that satisfy $x(0) = x_1$ and $x(\beta\hbar) = x_2$.

All thermodynamic quantities can be calculated from the density matrix. For example, the partition function, Z, is given by the trace of the density matrix

$$Z = tr[\rho] = \int dx\, \rho(x, x) \tag{2}$$

The potential $V(x, s)$ can be expanded in a power series

$$V(x, s) = f(s)x + \frac{1}{2}kx^2 + C_3 x^3 + C_4 x^4 + \ldots \equiv f(s)x + \frac{1}{2}kx^2 + U(x) \tag{3}$$

where $f(s)$ represents an external driving force, k is the harmonic oscillator force constant and the coefficients $C_3, C_4, \ldots$ are the cubic, quartic and higher order anharmonic coupling constants, respectively. $U(x)$ is called the anharmonic potential.

Using a standard trick [3] we can write

$$\rho(x_2, x_1) = \exp\left[-\frac{1}{\hbar}\int ds\, U(-\hbar\delta/\delta f(s))\right]\int \delta x \exp\left[-\frac{1}{\hbar}\int ds \left(\frac{M}{2}(\partial_s x)^2 + \frac{k}{2}x^2 + f(s)x\right)\right]$$

$$\equiv \exp\left[-\frac{1}{\hbar}\int U\right]\rho_0[f] \tag{4}$$

in an obvious notation. Note that ρ_0 is a functional of the external force $f(s)$. Expanding the first exponential in a power series yields the perturbation expansion of the density matrix. The functional derivatives $\delta/\delta f(s)$ can be performed once U is written as the anharmonic series in (3). In many cases $f(s) = 0$. Thus after performing the functional derivatives to obtain the perturbation to a given order, $f(s)$ should be set to zero. Clearly, in any case where the external force is not zero we set $f(s)$ equal to the given external force after taking the functional derivatives.

ρ_0 can be evaluated exactly using the technique of stationary phase [3]. The result is

$$\rho_0[f] = \left[\frac{M\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{1/2} \exp(-S_0[f]) \tag{5}$$

where $S_0[f]$ is the "action" for the "classical" trajectory with $\omega = \sqrt{k/M}$. The reader is referred to Ref. [3] where S_0 is given explicitly.

Since we wish to study the thermal expectation values of position, $< x^n >$ with $n = 1, 2, \ldots$ we compute the generating function for these expectation values

$$< \exp(-\eta x) > = \frac{tr[\exp(-\eta x)\,\rho]}{tr[\rho]} = \frac{\int dx \exp(-\eta x)\,\rho(x, x)}{\int dx\,\rho(x, x)} \equiv \frac{Z(\eta)}{Z(0)} \tag{6}$$

From the definition of $Z(\eta)$ we have

$$< x^n > = \frac{\left[(-\partial_\eta)^n Z(\eta)\right]_{\eta=0}}{Z(0)} \tag{7}$$

Performing the traces in (6) yields

$$Z(\eta) = \exp\left[-\frac{1}{\hbar}\int U\right] \exp\left[\frac{b\eta}{2a} + \frac{\eta^2}{4a} + \frac{1}{2}\int_0^{\beta\hbar} ds\, ds'\, f(s)\, G(s, s')\, f(s')\right] \tag{8}$$

where

$$a = \frac{M\omega}{\hbar}\,\frac{\cosh(\beta\hbar\omega) - 1}{\sinh(\beta\hbar\omega)} \tag{9}$$

$$b = \frac{M\omega}{\hbar}\,\frac{(I + J)\,(\exp(\beta\hbar\omega) - 1)}{\sinh(\beta\hbar\omega)}$$

$$I = \frac{\hbar}{2M\omega}\int_0^{\beta} ds \exp(-\hbar\omega s)\, f(s)$$

$$J = \frac{\hbar}{2M\omega}\int_0^{\beta} ds \exp(-\hbar\omega(\beta - s))f(s)$$

$$G(s, s') = -\frac{\hbar}{2M\omega}\exp(-\hbar\omega|s - s'|)$$

Using the above results we can evaluate $< x >$ to lowest order

$$< x > \approx -C_3\frac{3\hbar}{2M^2\omega^3}\coth(\beta\hbar\omega/2) \tag{10}$$

This is the standard result [2][3] and shows how the average position of the particle (to lowest order) depends on the temperature. Note that $< x >$ does not go to zero at $T = 0$ due to the quantum zero point fluctuations of the particle position.

3. THE ANHARMONIC CRYSTAL

The atoms in a crystal can be treated as coupled anharmonic oscillators. In the adiabatic approximation [1] the electron degrees of freedom are replaced by an effective potential energy V which depends on the positions of the atoms. The classical zero temperature equilibrium position of each atom is determined by

$$\vec{\partial} V = 0 \tag{11}$$

For a crystal the equilibrium positions form a lattice of points that can be labelled by a unit cell index, $m = m_1, m_2, m_3$ and a basis index μ [1][2]. For a primitive lattice with only one atom per unit cell, $\mu = 1$, whereas for a non-primitive lattice with S atoms per unit cell $\mu = 1,\ldots, S$. At any finite temperature the atoms vibrate around their equilibrium positions. Generally these vibrations are not too large and we can expand V around the equilibrium positions, $R^m{}_{\mu a}$, where a labels the xyz components of the position vectors. For ease of notation we can collectively denote the indices $m\ \mu\ a$ by the index A. Letting $x_A = R_A + q_A$, the expansion of V about the equilibrium positions, R_A takes the form

$$V = \sum_A f_A(s)\, q_A + \frac{1}{2} \sum_{AB} C_{AB}\, q_A q_B + \sum_{ABC} C_{ABC}\, q_A q_B q_C + \ldots \tag{12}$$

As before the anharmonic terms in the above expansion will be denoted by the anharmonic potential U, the expansion coefficients, C, are the harmonic and anharmonic coupling constants and the functions $f_A(s)$ are external forces.

For the crystal in the adiabatic approximation the argument of the exponential in the path integral for ρ_0 is $-1/\hbar$ times the integral with respect to s of

$$\frac{1}{2} \sum_A M_A (\partial_s q_A)^2 + \frac{1}{2} \sum_{AB} C_{AB}\, q_A q_B + \sum_A f_A(s)\, q_A \tag{13}$$

where $M_A = M_\mu$ is the mass of the μ *th* type of atom in the basis. (13) can be written as the sum of uncoupled normal mode harmonic oscillators using the transformation [1]

$$q^m{}_{\mu a}(s) = \sum_{k\alpha} \Gamma^m{}_{\mu a \alpha}(\vec{k})\, \xi_\alpha(\vec{k}, s) \tag{14}$$

with

$$\Gamma^m{}_{\mu a \alpha}(\vec{k}) = \frac{\hbar}{\sqrt{N M_\mu}}\, \varepsilon^{\mu\alpha}{}_a(\vec{k}) \exp\left(i\vec{k}\cdot\vec{R}^m{}_\mu\right) \tag{15}$$

where ε is the polarization vector of the normal modes labelled by α, N the number of atoms in the crystal, and $\vec{k}$ the spatial frequency. In obtaining (15) we have used the standard Born-von Karman (periodic) boundary conditions [1].

Substituting (14) into (13) gives

$$\sum_{\vec{k}\alpha}\left[\frac{1}{2}\left|\partial_s\xi_\alpha(\vec{k},s)\right|^2+\frac{1}{2}\,\omega^2{}_\alpha(\vec{k})\left|\xi_\alpha(\vec{k},s)\right|^2+g_\alpha(\vec{k},s)\xi_\alpha(\vec{k},s)\right] \tag{16}$$

where $\omega_\alpha(\vec{k})$ is the fundamental frequency of the $\vec{k}\,\alpha$ normal mode and $g_\alpha(\vec{k},s)=\sum_A \Gamma_{A\alpha}(\vec{k})f_A(s)$.

With this factorization ρ and $Z(\eta_\alpha(\vec{k}))$ take the same form as in (4) and (8) but with a sum in the exponent over all the $\vec{k}\,\alpha$ values. As in the single particle case the expectation value of the position, q_A, can be evaluated order by order in the anharmonic potential by taking the appropriate derivatives. The lowest order contribution from the cubic coupling term takes the form

$$< q_A > \approx \sum_\alpha \frac{1}{8(\omega_\alpha(0))^2}\,\Gamma_{A\alpha}(0)\sum_{\vec{k}\mu}\frac{\overline{C}_{\alpha\mu}(\vec{k})}{\omega_\mu(\vec{k})}\coth\left[\frac{\beta\hbar\omega_\mu(\vec{k})}{2}\right] \tag{17}$$

where $\overline{C}$ is given by

$$\delta_{\vec{k},0}\,\overline{C}_{\alpha\mu}(\vec{k}')=\sum_{ABC}C_{ABC}\,\Gamma_{A\alpha}(\vec{k})\left[\,\Gamma^*_{B\mu}(\vec{k}')\Gamma_{C\mu}(\vec{k}')+c.c.\,\right] \tag{18}$$

with *c.c.* being the complex conjugate of the preceeding term.

In the above result only optical phonons ($\omega_\alpha(0)\neq 0$) contribute. Therefore this term is non-zero only for non-primitive lattices. For primitive lattices, higher order terms in the expansion must be evaluated. This can be done straightforwardly by computing the higher order functional derivatives in the perturbation expansion of Z. Note that (17) has the same form as (10) as would be expected. Again due to the quantum zero point fluctuations $< q_A >$ does not vanish at $T = 0$.

Detailed predictions from (17) and higher order terms require the input of lattice symmetries and specific coupling constant strengths as discussed in the next section. But, we can use (17) to determine the approximate scaling dependence of $< q_A >$ with temperature, mass, bond strength (harmonic coupling) and anharmonic coupling. Since we want an approximate scaling law we will ignore the $\vec{k}\,\alpha$ dependence of ω and M. Note that with this assumption we are losing the distinction between the mass of single atoms and the reduced mass. For high temperatures, i.e., temperatures with $k_BT >> \hbar\omega_{max}$ where ω_{max} is the maximum optical phonon frequency, $\coth(\beta\hbar\omega/2) \sim 1/\beta\hbar\omega$. Taking $\omega \sim \sqrt{K/M}$ where K is the harmonic force constant or bond strength and including the M dependence of Γ, we find

$$< q_A > \sim \frac{\overline{C}T}{K^2M} \tag{19}$$

This result is very similar to other scaling laws and shows a dependence on mass, coupling and temperature which is in accord with expectation, and matches that predicted by equation (10).

4. LATTICE SYMMETRIES

Uniform translation and rotation of the crystal as well as the symmetry of the lattice will impose restrictions on the coupling constants. These requirements have been worked out in detail for many simple crystals. Here we present only a few of these results. For more details, see Refs. [1][2].

Since the coupling constant are given by derivatives of V evaluated at the classical zero temperature equilibrium positions and derivatives commute, the coefficients must be invariant under interchange of their indices, i.e.,

$$C_{ABC\ldots} = C_{BAC\ldots} = C_{CBA\ldots} = \ldots \tag{20}$$

Uniform translation of the crystal, which is equivalent to the conservation total linear momentum, yields the constraint

$$\sum_{n\nu} C^{lm\ldots n}_{\lambda\alpha\mu b\ldots\nu c} = 0 \tag{21}$$

Uniform rotation of the crystal, which is equivalent to the conservation of total angular momentum, yields constraints which relate the n and n + 1 order constants. The relation between the quadratic and cubic coupling constants is

$$\sum_{l\lambda} C^{mnl}_{\mu a\nu b\lambda c'} q^{l}_{\lambda c} + C^{mn}_{\mu c'\nu b}\,\delta_{ac} + C^{mn}_{\mu a\nu c'}\,\delta_{bc} \tag{22}$$

is symmetric under the interchange of c and c'.

The symmetries that depend specifically on the lattice yield constraints that take the form

$$C^{\overline{m}\ldots\overline{n}}_{\overline{\mu}a\ldots\overline{\nu}b} = \sum_{cd} \Omega_{ac} \ldots \Omega_{bd}\, C^{m\ldots n}_{\mu c\ldots\nu d} \tag{23}$$

where the matrix Ω is an element of the lattice point group. Thus Ω maps the positions labelled by $m\mu\ldots n\nu$ to those labelled by $\overline{m}\overline{\mu}\ldots\overline{n}\overline{\nu}$.

These symmetry constraints determine which elements of the coupling constants are zero and what the relationship is between the remaining non-zero elements. The absolute value of the non-zero elements is determined, of course, by the strength of the interatomic bonds which are in many cases only approximately known. But, even in the absence of accurate values for these bond strengths, a range of possible expansion behaviors can be determined by using the symmetry constraints and varying the absolute values over reasonable ranges. Further, the effective potentials developed, for example, in Refs [4][5], can be used to directly calculate the coupling constants and thus evaluate the thermal position dependence of the atoms.

5. SUMMARY

The path integral technique for evaluating the quantum density matrix has been used to determine the form of the thermal expectation value of the position of an atom in a crystal lattice. From this result we have predicted the lowest order scaling behavior of the atomic position with mass, temperature, bond strength and anharmonic coupling. This scaling law is in accord with expectation. Further, the result explicitly contains the anharmonic coupling constants which depend on the symmetry of the lattice. Thus, using this formalism it is possible to directly calculate the effects of lattice symmetry on the thermal position dependence of the atoms in the lattice. From these results it is possible to determine a range of thermal expansion behaviors for each type of lattice. The results of other theoretical analyses, such as those in [4] and [5] can be substituted into the above formulation to obtain predictions of all the thermomechanical properties of each type of lattice.

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