Statistical Mechanics of the Collective Jahn-Teller Phase Transition

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An exact treatment of a cooperative Jahn-Teller transition is presented. The results are expressed in terms of the thermodynamic properties of the Ising model. The dynamic behavior of fluctuations is discussed in terms of irreversible thermodynamics.

I. INTRODUCTION

Models describing cooperative Jahn-Teller transitions have for the most part been treated in the random-phase approximation (RPA).[1-4] In RPA, the static thermal averages are determined in the mean-field approximation, while the dynamic behavior is described by equations of motion linearized about the mean-field values. A somewhat improved approximation, which has been considered by Halperin, is applicable under certain conditions for the case of two nondegenerate electronic levels.[5] In the present paper an exact statistical mechanical treatment is given for a model containing all the essential features of the cooperative Jahn-Teller transition. The results are expressed in terms of the statistical mechanical properties of the Ising model. The model describes the interaction of a doubly degenerate electronic level at each lattice site with nondegenerate elastic strain and optic phonons of a given symmetry (at $q = 0$). Only a linear coupling between the phonons and the electronic system will be considered.

The Hamiltonian then takes the form[1-4]

$$\mathcal{H} = \sum_{nq}\left[\tfrac{1}{2}P_n(q)P_n(-q) + \tfrac{1}{2}\omega_n^2(q)Q_n(q)Q_n(-q)\right] + \sum_{nq} \xi_n(q)Q_n(q)\sigma_3(-q)\,. \qquad (1)$$

The first two terms describe noninteracting phonons, while the last term describes the coupling of these with the doubly degenerate electronic level where $\sigma_3(q)$ is the lattice Fourier transform of the Pauli operator $\sigma_3(l)$ associated with lattice site l. The sum runs over all phonon modes of a given symmetry. This symmetry is different for acoustic and optic modes. The coupling coefficient for optic phonons, $\xi_n(q=0)$, is nonzero, whereas for acoustic modes $\xi_n(q)$ is linear in q in the small-q limit, and its value is direction dependent. The symmetry of the strain field to which the electronic levels couple determines the way the limit is to be taken. The special features associated with the $q \to 0$ limit for acoustic modes have been discussed elsewhere.[4]

II. FREE ENERGY

The free energy in a state described by the density matrix ρ is

$$F = \mathrm{Tr}[\rho H + (1/\beta)\rho \ln\rho]\,, \qquad (2)$$

where $\beta = 1/kT$. The density matrix satisfies the relation

$$1 = \mathrm{Tr}\rho\,. \qquad (3)$$

The density matrix ρ_0 and hence the free energy F_0 of the equilibrium state can be obtained by minimizing the expression, Eq. (2), for F with respect to variations in the density matrix under the constraint given by Eq. (3). The result for ρ_0 is the Gibbs distribution. However, in order to discuss the dynamics of the fluctuations in the system we also need the free energy for nonequilibrium states.

A nonequilibrium state may be described by specifying the expectation values of the phonon and pseudospin operators

$$\phi_n(q) = \mathrm{Tr}\rho Q_n(q)\,, \qquad (4)$$

$$\dot{\phi}_n(q) = \mathrm{Tr}\rho P_n(q)\,, \qquad (5)$$

$$m(q) = \mathrm{Tr}\rho\sigma_3(q)\,. \qquad (6)$$

The density matrix describing this nonequilibrium state and hence the free energy, $F(T, \phi_n(q), \dot{\phi}_n(q), m(q))$, is obtained by minimizing the expression Eq. (2) for F under the constraints (3)–(6). The equilibrium free energy is obtained by minimizing $F(T, \phi_n(q), \dot{\phi}_n(q), m(q))$ with respect to $\phi_n(q)$, $\dot{\phi}_n(q)$, and $m(q)$.

Minimization of Eq. (2) under the constraints (3)–(6) is achieved by introducing Lagrange parameters. We obtain

$$\rho = (1/Z_e)\,e^{-\beta H_e}\,, \qquad (7)$$

where

$$Z_e = \mathrm{Tr}\,e^{-\beta H_e} \qquad (8)$$

and

$$H_e = H - \sum_{nq}[A_n(-q)Q_n(q) + B_n(-q)P_n(q)] - \sum_q h(-q)\,\sigma_3(q)\,. \qquad (9)$$

The Lagrange parameters $A_n(q)$, $B_n(q)$, and $h(q)$, are to be determined by Eqs. (4)–(6). In terms of the introduced variables these conditions may be written

$$\phi_n(q) = -\frac{\partial}{\partial A_n(-q)}[-(1/\beta)\ln Z_e],$$

$$\dot{\phi}_n(q) = -\frac{\partial}{\partial B_n(-q)}[-(1/\beta)\ln Z_e], \quad (10)$$

$$m(q) = -\frac{\partial}{\partial h(-q)}[-(1/\beta)\ln Z_e].$$

In order to calculate Z_e it is convenient first to introduce a canonical transformation

$$\hat{Q}_n(q) = Q_n(q) + [\xi_n(-q)\sigma_3(q) - A_n(q)]/\omega_n^2(q),$$
$$\hat{P}_n(q) = P_n(q) - B_n(q). \quad (11)$$

In terms of the new coordinates the Hamiltonian H_e takes the form

$$H_e = \frac{1}{2}\sum_{nq}[\hat{P}_n(q)\hat{P}_n(-q) + \omega_n^2(q)\hat{Q}_n(q)\hat{Q}_n(-q)] - \frac{1}{2}\sum_{nq}\{B_n(q)B_n(-q) + [1/\omega_n^2(q)]A_n(q)A_n(-q)\}$$
$$-\frac{1}{2}\sum_q J(q)\sigma_3(q)\sigma_3(-q) - \sum_q b(-q)\sigma_3(q), \quad (12)$$

where we have introduced the definitions,

$$J(q) = \sum_n \frac{\xi_n(q)\xi_n(-q)}{\omega_n^2(q)}, \quad (13)$$

$$b(q) = h(q) - \sum_n \frac{\xi_n(q)A_n(q)}{\omega_n^2(q)}. \quad (14)$$

The first two terms of Eq. (12) describe displaced harmonic oscillators of the same frequencies as before. The last two terms describe an Ising model in an external field b, while the middle two terms result from the introduction of Lagrange parameters. The free energy corresponding to the Hamiltonian in Eq. (12) may be written

$$F_e = -kT\ln Z_e = F_L + F_I + F'. \quad (15)$$

F_L is the free energy for noninteracting phonons of frequencies $\omega_n(q)$[6]:

$$F_L = -\frac{1}{\beta}\sum_{nq}[\tfrac{1}{2}\beta\omega_n(q) + \ln N_n(q)], \quad (16)$$

where $N_n(q)$ is the Bose occupation number factor. $F_I(b)$ is the free energy of the Ising-model Hamiltonian,

$$H_I = -\frac{1}{2}\sum_q J(q)\sigma_3(q)\sigma_3(-q) - \sum_q b(-q)\sigma_3(q). \quad (17)$$

Although exact expressions for $F_I(b)$ are known only for special cases, large amounts of information are available for the Ising model also where exact solutions do not exist.[7]

Finally F' is given by

$$F' = -\frac{1}{2}\sum_{nq}\{B_n(q)B_n(-q) + [1/\omega_n^2(q)]A_n(q)A_n(-q)\}. \quad (18)$$

The Lagrange parameters may now be determined using Eq. (10) and Eqs. (15)–(18) with the result

$$A_n(q) = \omega_n^2(q)\phi_n(q) + \xi_n(-q)\,m(q), \quad (19)$$

$$B_n(q) = \dot{\phi}_n(q), \quad (20)$$

$$m(q) = m_I(b(-q)). \quad (21)$$

The function $m_I(b(-q))$ is the magnetization of the Ising model in the presence of the field b defined by

$$m_I(b(-q)) = \left.\frac{\partial F_I(b)}{\partial b(-q)}\right|_T. \quad (22)$$

Equation (21) determines $b(q)$ implicitly as function of temperature and $m(q)$ which may be used with Eq. (19) to determine $h(q)$ from Eq. (14),

$$h(q) = b(q) + J(q)m(q) + \sum_n \xi_n(q)\phi_n(q). \quad (23)$$

The set of Eqs. (19)–(23) completely determines the Lagrange multipliers. Using these, the free energy for the nonequilibrium state may finally be written

$$F = F_L + F_I(b) + \frac{1}{2}\sum_{nq}\dot{\phi}_n(q)\dot{\phi}_n(-q) + \frac{1}{2}\sum_{nq}\omega_n^2(q)\phi_n(q)\phi_n(-q) + \sum_{nq}\xi_n(-q)m(q)\phi_n(-q)$$
$$+\frac{1}{2}\sum_q J(q)m(q)m(-q) + \sum_q b(-q)m(q). \quad (24)$$

The equilibrium values of $\phi_n(q)$, $\dot{\phi}_n(q)$, and $m(q)$ are obtained by minimizing F. From

$$\frac{\partial F}{\partial \phi_n(q)} = \frac{\partial F}{\partial \dot{\phi}_n(q)} = \frac{\partial F}{\partial m(q)} = 0 \tag{25}$$

we obtain

$$\phi_n^0(q) = -[\xi_n(-q)/\omega_n^2(q)]\, m^0(q) , \tag{26}$$

$$\dot{\phi}_n^0(q) = 0 , \tag{27}$$

$$b^0(q) = 0 . \tag{28}$$

To obtain the last equation we have made use of Eq. (26). From Eq. (21) it follows that

$$m^0(q) = \langle \sigma_3(q) \rangle = m_I(b=0,\ q) . \tag{29}$$

Further, in the absence of external space-varying fields the magnetization of the Ising model is spatially uniform,

$$m_I(b=0,\ q) = m_I \delta_{q,0} . \tag{30}$$

The optic-phonon normal-mode coordinate is then given by

$$\phi_n^0(q) = \langle Q_n(q) \rangle = -[\xi_n(0)/\omega_n^2(0)]\, m_I\, \delta_{q,0} . \tag{31}$$

The corresponding result for elastic strain is

$$\langle e \rangle = -(\eta/cv)\, m_I ; \tag{32}$$

c is the elastic constant defined by

$$\omega_a^2(q) = c q^2 , \tag{33}$$

where a denotes the acoustic mode, v is the volume of the unit cell, and η is the coupling constant to the strain determined by the limiting procedure,[4]

$$\lim_{q\to 0} \frac{\xi_a(q)\,\langle Q_a(q) \rangle}{\omega_a^2(q)} = \frac{\eta \langle e \rangle}{cv} . \tag{34}$$

Thus the temperature dependence of the order parameters $\langle \sigma_3 \rangle$, $\langle Q_n \rangle$, and $\langle e \rangle$ are all determined by the magnetization $m_I(T)$ of the pure Ising model with no external field.

The equilibrium free energy is given by

$$F_0 = F_L + F_I(b=0) .$$

III. TIME DEPENDENCE OF FLUCTUATIONS

In order to construct equations of motion describing the fluctuations about the equilibrium values we shall use the phenomenological equations of irreversible thermodynamics. These equations have the general form[7,8]

$$\sum_{ij} R_{ij}(q)\, \dot{x}_j(q) = -X_i(q) , \tag{35}$$

where the x_j's are the coordinates describing the state of the system, chosen such that their equilibrium values vanish. X_i is the thermodynamic force conjugate to x_i and is given in terms of the free energy by

$$X_i(q) = -\frac{1}{T}\left(\frac{\partial F}{\partial x_i(-q)} + \frac{d}{dt}\, \frac{\partial F}{\partial \dot{x}_i(-q)} \right) . \tag{36}$$

The kinetic coefficients $R_{ij}(q)$ satisfy the Onsager relations,

$$R_{ij} = R_{ji} . \tag{37}$$

Applying these equations to the variables $\phi_n(q)$ and $m(q)$ we obtain from the free energy, Eq. (24),

$$\left(\frac{d^2}{dt^2} + \omega_n^2(q) + \frac{d}{dt}\, \Gamma_n(q) \right) \Delta\phi_n(q) + \xi_n(-q)\Delta m(q) = 0 ,$$

$$\sum_n \xi_n(q)\, \Delta\phi_n(q) + \left(\chi_I^{-1}(q) + J(q) - \gamma \frac{d}{dt} \right) \Delta m(q) = 0 , \tag{38}$$

where

$$\Delta\phi_n(q) = \phi_n(q) - \phi_n^0(q)$$

and (39)

$$\Delta m(q) = m(q) - m^0(q)$$

describe the deviations of $\phi_n(q)$ and $m(q)$ from their equilibrium values; $\Gamma_n(q) = TR_{nn}(q)$ is a kinetic coefficient describing the damping of the phonons, and $\gamma(q) = TR_{mm}(q)$ measures the relaxation rate of the electronic levels. Other off-diagonal kinetic coefficients such as R_{nm} or $R_{nn'}$ which lead to a coupling of the equations through the damping terms have been neglected. In Eqs. (38) we have also introduced the susceptibility of the Ising model defined by

$$\chi_I(q) = \frac{\partial m_I(q)}{\partial b(q)} \bigg|_T^0 . \tag{40}$$

When Fourier transformed, Eqs. (38) become

$$[\omega_n^2(q) - \omega^2 - i\omega\Gamma_n(q)]\, \Delta\phi_n(q) + \xi_n(-q)\Delta m(q) = 0 ,$$

$$\sum_n \xi_n(q)\Delta\phi_n(q) + [\chi_I^{-1}(q) + J(q) - i\omega\gamma(q)]\, \Delta m(q) = 0 . \tag{41}$$

Introducing the vector $\underline{x}(q) = (\Delta\phi_1(q), \ldots, \Delta\phi_n(q), \Delta m(q))$ these equations may be written in the matrix form

$$\underline{\chi}^{-1}(q\omega) \cdot \underline{x}(q) = 0 , \tag{42}$$

where $\underline{\chi}^{-1}(q\omega)$ is the inverse of the linear response function of the system.

Equations (41) are identical to those derived elsewhere[4] in RPA except that the $\chi_{I,\mathrm{RPA}}$ is here replaced by the exact susceptibility of the Ising model. Requiring that the determinant of $\chi^{-1}(q\omega)$ vanishes we obtain the coupled mode dispersion relation,[4]

$$G^{-1}(q\omega) - \sum_n |\xi_n(q)|^2 D_n(q\omega) = 0 , \tag{43}$$

where we have introduced the definitions

$$G^{-1}(q\omega)=\chi_I^{-1}(q)+J(q)-i\omega\gamma(q),$$
$$D_n^{-1}(q\omega)=\omega_n^2(q)-\omega^2-i\omega\Gamma_n(q). \quad (44)$$

Of particular interest is the acoustic-phonon susceptibility $\chi_{aa}(q\omega)$. From Eqs. (41) and (42),

$$\chi_{aa}^{-1}(q\omega)=\omega_a^2(q)-\omega^2-i\omega\Gamma_a(q)-\frac{\delta^2\tilde{\gamma}(q\omega)}{-i\omega+\tilde{\gamma}(q\omega)}, \quad (45)$$

where

$$\tilde{\gamma}(q\omega)=\frac{1}{\gamma}\Big(\chi_I^{-1}(q)+|\xi_a(q)|^2D_a(q,0)+\sum_{n\neq a}|\xi_n(q)|^2[D_n(q,0)-D_n(q\omega)]\Big), \quad (46)$$

and

$$\delta^2=|\xi_a(q)|^2/\gamma\tilde{\gamma}. \quad (47)$$

For frequencies low compared to the optic-phonon frequencies, $\omega_n^2(q)\gg\omega^2+i\omega\Gamma_n(q)$, the last term in Eq. (46) may be neglected, and $\tilde{\gamma}(q)$ becomes frequency independent. The dynamic structure factor $S(q\omega)$ which may be derived from Eq. (45) by the use of the fluctuation dissipation theorem then exhibits a central peak[9–11] in addition to the acoustic-phonon sidebands. The half-width of the central peak is given by

$$\Gamma_c(q)=\chi_I^{-1}(q)/\gamma \quad (48)$$

and the low-frequency isothermal elastic constant $\tilde{c}$ by[12]

$$\tilde{c}=c\chi_I^{-1}(0)/[\chi_I^{-1}(0)+J_a(0)], \quad (49)$$

where

$$J_a(0)=\lim_{q\to 0}\frac{|\xi_a(q)|^2}{\omega_a^2(q)}=\frac{\eta^2}{cv}. \quad (50)$$

Both $\Gamma_c(0)$ and $\tilde{c}$ depend on χ_I and vanish at the transition point T_c of the Ising model.

Thus the relevant thermodynamic variables of the Jahn-Teller phase transition may be expressed in terms of the properties of the Ising model. The temperature dependence of the relative elastic constant is determined entirely by the susceptibility. The order parameters $\langle\sigma_3\rangle$, $\langle e\rangle$, and $\langle Q_n\rangle$ are all proportional to the magnetization of the Ising model. Of these, $\langle\sigma_3\rangle$ measures the splitting of the electronic levels, the strain $\langle e\rangle$ measures the change in the shape of the unit cell, and the optic-phonon normal-mode coordinates $\langle Q_n\rangle$ determine the internal displacements.

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