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Microscopic theory of phase transitions in hydrogen-bonded phenol-amine adducts

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Second-order reversible ferroelastic phase transitions in a recently discovered class of hydrogen-bonded phenol-amine adducts has already been analyzed by Landau theory. The analysis is however phenomenological and does not directly indicate the microscopic origin of this phase transition. In this paper, a microscopic theory is presented. It is proposed that the main mechanism responsible for the phase transition is the interaction of hydrogen bonds with the lattice vibrations or phonons of the crystal. These interactions with the phonons induce long range cooperative interactions between the hydrogen bonds, which causes the phase transition behavior at the critical temperature. Critical exponents for unit cell parameters and heat capacity are derived with a variational meanfield approach, and shown to be consistent with the prediction of Landau's theory.

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I. INTRODUCTION

Crystalline solids containing phenol-amine adducts are widely used to study hydrogen bonds. Phenol-amine adducts are produced by the interaction of phenols, compounds having at least one hydroxyl group, and amines, compounds having at least one amino group. The phenols and amines in the solid state are generally linked by intermolecular $O-H\cdots O$, $O-H\cdots N$ or $N-H\cdots O$ types of hydrogen bonds which are among the most robust and versatile synthons in crystal engineering. Studies on the hydrogen bondings in these phenol-amine adducts can be used as a model for the more complicated hydrogen bonding in biological systems in which hydrogen bondings play a crucial and an important role. Owing to our interests in hydrogen bondings in such systems, we have investigated systematically in single crystal forms a class of phenol-amine adducts and their crystal structures were reported.[1–8] Some of these single crystals of phenol amine adducts undergo a reversible phase transition with variation in temperature. For these samples, a hydrogen atom is transferred from the phenol (which then becomes an anion) to the amine (which then becomes a cation). Hydrogen bonds are then established between the donor/amine/cation and the acceptor/phenol/anion. As a result, these crystals undergo a temperature-dependent structural phase transition, which is second-order ferroelastic in its nature. These are the first reported cases of structural phase transition induced by hydrogen bonding interactions.

The phase transition that has been observed are classified into two categories (1) orthorhombic-to-monoclinic transition, and (2) monoclinic-to-triclinic transition. In both these categories, the phase transitions are a result of the breaking of a mirror-plane symmetry when the temperature is lowered through the critical temperature, T_c; the lower symmetric phase being the low-temperature phase.

In this paper, a microscopic theory for the reversible ferroelastic-type structural phase transitions observed in a recently discovered class of hydrogen-bonded organic cystals is presented. It is proposed that the main mechanism responsible for the phase transition is the interaction of hydrogen bonds with the lattice vibrations or phonons of the crystal. The hydrogen bonds are modelled as two-level systems, and described by pseudo spin variables. (For a comprehensive overview of hydrogen bonding, see the book by Jeffrey[9] and references therein.) The spin-phonon coupling then induces long range cooperative interactions between pseudo spins, and results in a second-order phase transition at the critical temperature.

The steps involved in the calculation can be summarized as follows:

1 The hydrogen bonding interaction is modelled as a two-level system, and cast into the form of a spin-phonon Hamiltonian.

2 A variational principle involving a trial Hamiltonian is employed. The trial Hamiltonian is chosen such that spin and phonon are decoupled in a mean-field sense. The resulting variational free energy is thus a mean-field approximation.

3 Thermodynamics of the model is obtained from the mean-field free energy. A critical point is found, and various critical exponents calculated.

We believe this microscopic analysis of phase transitions caused by hydrogen bonds could have wide implications since hydrogen bonds occur in a large class of materials and the hydrogen bond plays an important and pivotal role in molecular biology and chemistry.

This is also the latest addition to the class of indirect cooperative phase transitions, which though being highly important, currently consist of relatively few cases. Well known examples of phonon mediated indirect cooperative transitions include superconductivity and Jahn-Teller transitions.

II. MODEL HAMILTONIAN

We assume that, if the additional hydrogen bond interactions can be "switched off," all the remaining inter- and intramolecular interactions can be approximated by a harmonic potential. This leads to harmonic phonon modes. The Hamiltonian of the crystal is then split into the sum of two parts:

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$$H = \sum_{\mathbf{k}j} \hbar \omega_{\mathbf{k}j}(a^{\dagger}_{\mathbf{k}j}a_{\mathbf{k}j}) + H_i, \tag{1}$$

where the first term on the RHS is the harmonic phonon Hamiltonian,[10] and H_i is the interaction energy of the "additional" hydrogen bonds.

A. Hydrogen bond interaction

A hydrogen bond is formed by the sharing of a hydrogen atom H between a donor σ and an acceptor κ. H is initially bonded to σ. As κ drawing nearer, it perturbs the σ-H system, and causes the hydrogenic energy level to split. In the simplest picture, the perturbed energy levels will be split into two: one has an energy lower than the original unperturbed orbital, and corresponds to the "bonding" configuration; the other is higher in energy than the original orbital, and corresponds to the "antibonding" configuration.[20]

The departure from the original energy level depends on the degree of overlapping of the hydrogenic orbitals. The more the overlap, the stronger the perturbation, and the energy level splitting grows larger. Other effects, such as electron-electron repulsion and nucleus-nucleus repulsion, at shorter distances play the role of maintaining equilibrium of the crystal.

Assume that a σ-κ pair is in the beginning held at a distance that is larger than their equilibrium separation, yet close enough for the hydrogen bond interaction to be significant. If the pair of molecules do not depart too far away from their initial positions, the energy levels of the bonding and antibonding orbitals may be approximated to the lowest order of their displacements as

$$E_{\text{bonding}} = -E_0 - 2\mu\Delta_{\kappa\sigma}; \tag{2}$$

$$E_{\text{antibonding}} = E_0 + 2\mu\Delta_{\kappa\sigma}, \tag{3}$$

where, for the initial configuration, the energy levels are split by $2E_0$. $\Delta_{\sigma\kappa}$ is the change in degree of overlapping due to the small displacements. μ is a suitable scalar coupling constant, with the factor of two purely for mathematical convenience. An order of magnitude estimation of μ is

$$\mu = \frac{\text{typical bond energy}}{\text{typical bond length}}.$$

A pseudo spin variable $s = \pm 1$ may be introduced to express (2) and (3) in a single equation. If $s = +1$ corresponds to the antibonding configuration, and $s = -1$ corresponds the bonding configuration, the hydrogen bond energy H_h is then given by

$$H_h = (E_0 + 2\mu\Delta_{\kappa\sigma})s. \tag{4}$$

As a simple argument, we now consider a system with two donors σ_1, σ_2 and one acceptor κ. A system with two acceptors and one donor can be described in a similar fashion.

We assume that there is a mirror plane in the crystal, that leaves κ invariant under its action, but maps σ_1 and σ_2 into each other. Since the two donors are related by the mirror symmetry, their interactions appear exactly identical to κ.

TABLE I. Summary of the states represented by four different *s*-*t* combinations.

s *t*	+1	−1
+1	antibonding to σ_1	bonding to σ_1
−1	antibonding to σ_2	bonding to σ_2

We further assume that, if bonded or antibonded to one of the donors, the acceptor κ is screened by the excess in hydrogen density, and unable to interact with the other donor. Therefore we can span the state space of σ_1-κ-σ_2 by the following four basis vectors: bonding to σ_1, antibonding to σ_1, bonding to σ_2, and antibonding to σ_2.

Another pseudo spin $t = \pm 1$ may be introduced alongside s to describe this four-state system completely. We assign $t = +1$ to the two states where κ is interacting with σ_1, and $t = -1$ to the two states where κ is interacting with σ_2. Tables I and II summarize how the four states are described by s and t.

Using s and t spins defined above, the bond energy of the σ_1-κ-σ_2 group can be written as,

$$H_b = s(1+t)\left(\frac{E_0}{2} + \mu\Delta_{\kappa\sigma_1}\right) + s(1-t)\left(\frac{E_0}{2} + \mu\Delta_{\kappa\sigma_2}\right). \tag{5}$$

Notice that spin t does not appear by itself. It is therefore more convenient to treat the product st as an independent spin variable instead. Let $w = st$ be a pseudo spin taking value of ±1, H_b can be rewritten as

$$H_b = s[E_0 + \mu(\Delta_{\kappa\sigma_1} + \Delta_{\kappa\sigma_2})] + w(\Delta_{\kappa\sigma_1} - \Delta_{\kappa\sigma_2}). \tag{6}$$

The states represented by each value of spin w are given in Table II.

B. The prototype model

Now we set up a prototype model in which these donor–acceptor–donor groups are based (see Fig. 1).

Let **a**, **b**, and **c** be the primitive translational lattice vectors which make up the Bravais lattice of the crystal. We assume that $\mathbf{c}\cdot\mathbf{a} = \mathbf{c}\cdot\mathbf{b} = 0$. That is, the lattice has monoclinic or higher symmetry, with **c** as the unique axis. Each unit cell of the lattice is labeled by a position vector **r**, the lattice vector enclosed in the unit cell.

An adduct consists of an acid part and a base part, held together by various interactions between them. For simplicity, we assume that in the crystal each unit cell contains exactly one acid unit and one base unit. We choose our unit

TABLE II. The states represented by each value of *w*.

w	+1	−1
	antibonding to σ_1 $(s=1, t=1)$ or bonding to σ_2 $(s=-1, t=-1)$	bonding to σ_1 $(s=-1, t=1)$ or antibonding to σ_2 $(s=1, t=-1)$

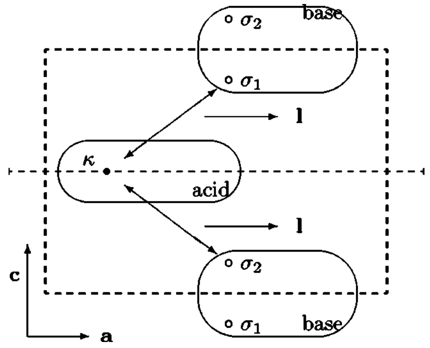

FIG. 1. The prototype phase of the crystal described in Sec. II B. The rectangular dashbox represents a unit cell, and the dashed line in the middle denotes the mirror plane. Acceptor κ interacts with donors σ_1 and σ_2 as shown in the figure.

cell in such a way that the acid unit sits in the middle, and two half base units are on the two sides.

We further assume that there is a set of mirror planes that leave the crystal invariant. The acid parts sit right on the mirror planes. The symmetry of the lattice requires that these mirror planes be perpendicular to **c**.

For our argument, there is one acceptor atom belonging to the acid part, and we shall label it κ. Without loss of generality κ can be placed at each lattice point. We assume that κ is invariant under the action of the mirror plane cutting through it.

(In the case where the acceptor unit consist of more than one atom, the whole group is considered approximately rigid, and therefore described by its center of mass position. The same applies to the donor group.)

Each unit cells contains two donors, labeled σ_1 and σ_2, respectively. We may take σ_1 to be within the upper half base unit, and σ_2 to be from the lower half base unit. They are mirror images of each other under the action of the mirror plane (see Fig. 1).

Let us write the degree of overlapping between κ and each σ_i as

$$\Delta_{\kappa\sigma_i} = [\mathbf{u}(\kappa,\mathbf{r}) - \mathbf{u}(\sigma_i,\mathbf{r})] \cdot \mathbf{l}. \tag{7}$$

Here $\mathbf{u}(\alpha,\mathbf{r})$ is the displacement vector from the equilibrium position of atom α belonging to unit cell $\mathbf{r}$. The vector $\mathbf{l}$ is a unit vector signifying the directionality of the interaction. $\mathbf{l}$ is chosen to be $\hat{\mathbf{a}} = \mathbf{a}/|\mathbf{a}|$ for simplicity, but it may point in any other directions, including those with a **c** component. The general critical behaviors shall not be affected by this simplification.

Note that this choice of $\mathbf{l}$ implies that the hydrogen bond interaction tends to rotate the donor-acceptor pair from their equilibrium position, without changing the separation. In fact (7), being linear in atomic displacements, should only be a valid approximation when the displacements are small.

The real space displacement vector can be written in terms of phonon operators using

$$\mathbf{u}(\alpha,\mathbf{r}) = \frac{2}{\sqrt{N}} \sum_{\mathbf{k}j} (a_{\mathbf{k}j} + a^{\dagger}_{-\mathbf{k}j}) e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}} \frac{\mathbf{e}(\alpha|\mathbf{k}j)}{\sqrt{m_\alpha}}, \tag{8}$$

all symbols have their usual meanings, as defined in Maradudin.[10] N is the total number of unit cells in the crystal.

There is one set of donor-acceptor-donor group per unit cell, so one set of s-w spins is needed per unit cell to fully describe the interaction. We denote $s_{\mathbf{r}}$ as the s spin in unit cell $\mathbf{r}$, and similarly $w_{\mathbf{r}}$ as the w spin in the same unit cell. The full interaction Hamiltonian is the sum of bond energy over the entire crystal.

Using (6), (7), and (8), the full interaction Hamiltonian may be written as

$$H_i = \mu \frac{2}{\sqrt{N}} \sum_{\mathbf{r}} \sum_{\mathbf{k}j} (a_{\mathbf{k}j} + a^{\dagger}_{-\mathbf{k}j}) e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}} (A_{\mathbf{k}j} s_{\mathbf{r}} + B_{\mathbf{k}j} w_{\mathbf{r}}) + E_0 \sum_{\mathbf{r}} s_{\mathbf{r}}, \tag{9}$$

where

$$A_{\mathbf{k}j} = \left(2\frac{\mathbf{e}(\kappa|\mathbf{k}j)}{\sqrt{m_\kappa}} - \frac{\mathbf{e}(\sigma_1|\mathbf{k}j)}{\sqrt{m_\sigma}} - \frac{\mathbf{e}(\sigma_2|\mathbf{k}j)}{\sqrt{m_\sigma}} \right) \cdot \mathbf{l}; \tag{10}$$

$$B_{\mathbf{k}j} = \left(\frac{\mathbf{e}(\sigma_2|\mathbf{k}j)}{\sqrt{m_\sigma}} - \frac{\mathbf{e}(\sigma_1|\mathbf{k}j)}{\sqrt{m_\sigma}} \right) \cdot \mathbf{l}. \tag{11}$$

Finally, the full Hamiltonian is

$$H = \sum_{\mathbf{k}j} \hbar\omega_{\mathbf{k}j} (a^{\dagger}_{\mathbf{k}j} a_{\mathbf{k}j}) + \sum_{\mathbf{r}} (E_0 s_{\mathbf{r}} + h w_{\mathbf{r}}) + \mu \frac{2}{\sqrt{N}} \sum_{\mathbf{r}} \sum_{\mathbf{k}j} (a_{\mathbf{k}j} + a^{\dagger}_{-\mathbf{k}j}) e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}} (A_{\mathbf{k}j} s_{\mathbf{r}} + B_{\mathbf{k}j} w_{\mathbf{r}}). \tag{12}$$

Here h is a fictitious "magnetic" field, coupled to w spin directly. In all physical situations it shall be set to zero.

C. Connection to real crystals

The model we propose above is in fact a simplification of the real situation in several ways and we summarize these simplifications here.

(a) In all experimental situations,[1] the crystal contains not only a set of mirror planes, but inversion centers as well. Since the proposed model interaction of a donor-acceptor-donor group contains a vector quantity $\mathbf{l}$, it cannot be invariant under space inversion. We justify neglecting this inversion symmetry in the following way. Since the two adduct molecules present in a unit cell are related to each other by inversion, they "see" effectively the same environment and can be treated as independent in a mean field theory. From the fact that this inversion symmetry remains unbroken across the phase transition, we know it should not play a vital role in the phase transition.

(b) We also treat the entire acid part as a rigid acceptor unit, and the entire base part as a rigid donor unit. This is justified by noting that atoms are bonded within each acid or base part by intramolecular bonds much stronger than hydrogen bonds, while the acid and base parts are linked to each other by interactions similar in nature and strength to the hydrogen bond interaction. It is also observed in the experiments that the internal structure within each part show very little distortion over the critical region, supporting our claim.

Note that σ_1 and σ_2 both refer to the whole base molecule and the 1 and 2 are used merely to distinguish between the two donors interacting with the acceptor in a unit cell. When there are more than one donor-acceptor-donor groups in a unit cell, more than one set of *s*-*w* spins must be used, making the self-consistent calculations intractable. See remarks preceding Eq. (64) for an estimate of the correction to the critical temperature when two molecules related by space inversion are taken into account.

III. CALCULATION OF FREE ENERGY

A. Variational calculation

We now proceed to calculate an upper bound to the free energy of the system using the Gibbs-Bogolyubov inequality. If $F=-k_BT \ln \mathrm{Tr}\, e^{-\beta H}$ is the exact free energy of the system, and H_t is a trial Hamiltonian depending on a set of variational parameters, then the inequality states that

$$F \leqslant F_v = F_t + \langle H - H_t\rangle_t, \tag{13}$$

where we define F_t and $\langle O\rangle_t$, the a priori average of any operator O with respect to H_t, to be

$$F_t = -k_BT \ln \mathrm{Tr}\, e^{-\beta H_t}, \tag{14}$$

$$\langle O\rangle_t = \frac{\mathrm{Tr}\, O e^{-\beta H_t}}{\mathrm{Tr}\, e^{-\beta H_t}}. \tag{15}$$

The equality of ((13)) is attained when H_t and H differs only by a *c*-number. Therefore the quality of this upper bound depends on how closely H_t resembles H.

The method of selecting the trial Hamiltonian and the formal calculation steps follow closely similar methods used by Lee[11–13] for other spin-phonon problems. We summarize the main results here.

The H_t introduced here is split into the phonon part H_{tp} and the spin part H_{ts}. Let us look at H_{tp} first.

In the original Hamiltonian H, the phonon operators $a_{\mathbf{k}j}$ and $a^\dagger_{\mathbf{k}j}$ appear not only in a quadratic term, but are also coupled linearly with the spins s and w in H_i. This coupling term can be treated as if $a_{\mathbf{k}j}$ and $a^\dagger_{\mathbf{k}j}$ are coupled to some mean fields of s and w, which are of course just scalar parameters. Therefore H_{tp} is chosen to be

$$H_{tp} = \sum_{\mathbf{k}j} g_{\mathbf{k}j}\left(a^\dagger_{\mathbf{k}j}a_{\mathbf{k}j} + \tfrac{1}{2}\right) + \sum_{\mathbf{k}j} f_{\mathbf{k}j}(a_{\mathbf{k}j} + a^\dagger_{-\mathbf{k}j}), \tag{16}$$

where $g_{\mathbf{k}j}$ and $f_{\mathbf{k}j}$ are variational parameters. A few constraints may be imposed on these two parameters. First, $g_{\mathbf{k}j}$, in the place of a phonon frequency, should be real and has the property that $g_{\mathbf{k}j}=g_{-\mathbf{k}j}$. It is also required that $f_{-\mathbf{k}j}=f^*_{\mathbf{k}j}$.

H_{ts} is chosen in the same way. s and w are thought to couple with some mean phonon field, to give an effective Hamiltonian

$$H_{ts} = \sum_{\mathbf{r}} (\nu_{\mathbf{r}} s_{\mathbf{r}} + \eta_{\mathbf{r}} w_{\mathbf{r}}), \tag{17}$$

where $\nu_{\mathbf{r}}$ and $\eta_{\mathbf{r}}$ are variational parameters. After diagonalizing H_{tp} in (16) with the substitutions $b_{\mathbf{k}j}=a_{\mathbf{k}j}+[(f_{-\mathbf{k}j})/g_{\mathbf{k}j}]$, $b^\dagger_{\mathbf{k}j}=a^\dagger_{\mathbf{k}j}+(f_{\mathbf{k}j}/g_{\mathbf{k}j})$, we can finally write down H_t as

$$H_t = \sum_{\mathbf{k}j} g_{\mathbf{k}j}\left(b^\dagger_{\mathbf{k}j}b_{\mathbf{k}j} + \frac{1}{2}\right) - \sum_{\mathbf{k}j} \frac{|f_{\mathbf{k}j}|^2}{g_{\mathbf{k}j}} + \sum_{\mathbf{r}} (\nu_{\mathbf{r}} s_{\mathbf{r}} + \eta_{\mathbf{r}} w_{\mathbf{r}}). \tag{18}$$

Finally, we obtain an upper bound of the free energy

$$\begin{aligned} F_v = {} & -k_BT \ln \mathrm{Tr}\, e^{-\beta\Sigma_{\mathbf{k}j} g_{\mathbf{k}j}(b^\dagger_{\mathbf{k}j}b_{\mathbf{k}j}+(1/2))} \\ & - k_BT \ln \mathrm{Tr}\, e^{-\beta\Sigma_{\mathbf{r}}(\nu_{\mathbf{r}}s_{\mathbf{r}}+\eta_{\mathbf{r}}w_{\mathbf{r}})} + \sum_{\mathbf{k}j} (\hbar\omega_{\mathbf{k}j} - g_{\mathbf{k}j}) \\ & \times\left(\langle b^\dagger_{\mathbf{k}j}b_{\mathbf{k}j}\rangle + \frac{1}{2}\right) + \sum_{\mathbf{k}j} \frac{\hbar\omega_{\mathbf{k}j}}{g^2_{\mathbf{k}j}}|f_{\mathbf{k}j}|^2 \\ & - \sum_{\mathbf{r}} \left[\nu_{\mathbf{r}} + \frac{4\mu}{\sqrt{N}}\left(\sum_{\mathbf{k}j} \frac{f_{-\mathbf{k}j}}{g_{\mathbf{k}j}} e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}} A_{\mathbf{k}j}\right) - E_0\right]\langle s_{\mathbf{r}}\rangle \\ & - \sum_{\mathbf{r}} \left[\eta_{\mathbf{r}} + \frac{4\mu}{\sqrt{N}}\left(\sum_{\mathbf{k}j} \frac{f_{-\mathbf{k}j}}{g_{\mathbf{k}j}} e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}} B_{\mathbf{k}j}\right) - h\right]\langle w_{\mathbf{r}}\rangle. \end{aligned} \tag{19}$$

Here,

$$\langle b^\dagger_{\mathbf{k}j}b_{\mathbf{k}j}\rangle = \frac{\mathrm{Tr}\, b^\dagger_{\mathbf{k}j}b_{\mathbf{k}j} e^{-\beta\Sigma_{\mathbf{k}j} g_{\mathbf{k}j}(b^\dagger_{\mathbf{k}j}b_{\mathbf{k}j}+(1/2))}}{\mathrm{Tr}\, e^{-\beta\Sigma_{\mathbf{k}j} g_{\mathbf{k}j}(b^\dagger_{\mathbf{k}j}b_{\mathbf{k}j}+(1/2))}}, \tag{20}$$

where

$$\langle s_{\mathbf{r}}\rangle = \frac{\mathrm{Tr}\, s_{\mathbf{r}} e^{-\beta\nu_{\mathbf{r}}s_{\mathbf{r}}}}{\mathrm{Tr}\, e^{-\beta\nu_{\mathbf{r}}s_{\mathbf{r}}}}; \tag{21}$$

$$\langle w_{\mathbf{r}}\rangle = \frac{\mathrm{Tr}\, w_{\mathbf{r}} e^{-\beta\eta_{\mathbf{r}}w_{\mathbf{r}}}}{\mathrm{Tr}\, e^{-\beta\Sigma_{\mathbf{r}}\eta_{\mathbf{r}}w_{\mathbf{r}}}}. \tag{22}$$

The free energy (19) must be minimized with respect to all four variational parameters, $f_{\mathbf{k}j}$, $g_{\mathbf{k}j}$, $\nu_{\mathbf{r}}$ and $\eta_{\mathbf{r}}$. The four minimization conditions are

$$\frac{\partial F_v}{\partial f_{\mathbf{k}j}} = 0; \tag{23}$$

$$\frac{\partial F_v}{\partial g_{\mathbf{k}j}} = 0; \tag{24}$$

$$\frac{\partial F_v}{\partial \nu_{\mathbf{r}}} = 0; \tag{25}$$

$$\frac{\partial F_v}{\partial \eta_{\mathbf{r}}} = 0. \tag{26}$$

Note that from (20), (21), and (22), $\langle b^\dagger_{\mathbf{k}j}b_{\mathbf{k}j}\rangle$, $\langle s_{\mathbf{r}}\rangle$, and $\langle w_{\mathbf{r}}\rangle$ depend on these parameters, too. These dependences must, of course, be taken into account when differentiating F_v.

The solutions for $f_{\mathbf{k}j}$ and $g_{\mathbf{k}j}$ are

$$f_{-\mathbf{k}j} = \frac{2\mu}{\sqrt{N}} \sum_{\mathbf{r}} \frac{g_{\mathbf{k}j}}{\hbar\omega_{\mathbf{k}j}} e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}} (A_{-\mathbf{k}j}\langle s_{\mathbf{r}}\rangle + B_{-\mathbf{k}j}\langle w_{\mathbf{r}}\rangle); \tag{27}$$

$$g_{\mathbf{k}j} = \hbar\omega_{\mathbf{k}j}. \tag{28}$$

The solutions for ν_r and η_r are

$$\nu_{\mathbf{r}} = -\frac{4\mu}{\sqrt{N}} \left(\sum_{\mathbf{k}j} \frac{f_{-\mathbf{k}j}}{g_{\mathbf{k}j}} e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}} A_{\mathbf{k}j} \right) + E_0; \tag{29}$$

$$\eta_{\mathbf{r}} = -\frac{4\mu}{\sqrt{N}} \left(\sum_{\mathbf{k}j} \frac{f_{-\mathbf{k}j}}{g_{\mathbf{k}j}} e^{i\mathbf{k}\cdot\mathbf{r}} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}} B_{\mathbf{k}j} \right) + h. \tag{30}$$

Using (19), (27), (28), (29), and (30), we arrive at an upper bound of the free energy,

$$F_v = -k_B T \ln \mathrm{Tr}\, e^{-\beta\Sigma_{\mathbf{k}j}\hbar\omega_{\mathbf{k}j}(b^{\dagger}_{\mathbf{k}j}b_{\mathbf{k}j}+(1/2))} + \sum_{\mathbf{k}j} \frac{|f_{\mathbf{k}j}|^2}{\hbar\omega_{\mathbf{k}j}} - k_B T \ln \mathrm{Tr}\, e^{-\beta\Sigma_{\mathbf{r}}(\nu_{\mathbf{r}}s_{\mathbf{r}}+\eta_{\mathbf{r}}w_{\mathbf{r}})}, \tag{31}$$

where

$$\nu_{\mathbf{r}} = -\frac{8\mu^2}{N} \sum_{\mathbf{q}} \sum_{\mathbf{k}j} \frac{e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{q})}}{2\omega^2_{\mathbf{k}j}} A_{\mathbf{k}j}(A_{-\mathbf{k}j}\langle s_{\mathbf{r}}\rangle + B_{-\mathbf{k}j}\langle w_{\mathbf{r}}\rangle) + E_0, \tag{32}$$

$$\eta_{\mathbf{r}} = -\frac{8\mu^2}{N} \sum_{\mathbf{q}} \sum_{\mathbf{k}j} \frac{e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{q})}}{2\omega^2_{\mathbf{k}j}} B_{\mathbf{k}j}(A_{-\mathbf{k}j}\langle s_{\mathbf{r}}\rangle + B_{-\mathbf{k}j}\langle w_{\mathbf{r}}\rangle) + h, \tag{33}$$

$$\sum_{\mathbf{k}j} \frac{|f_{\mathbf{k}j}|^2}{\hbar\omega_{\mathbf{k}j}} = \frac{4\mu^2}{N} \sum_{\mathbf{rq}} \sum_{\mathbf{k}j} \left[\frac{e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{q})}}{2\omega^2_{\mathbf{k}j}} (A_{-\mathbf{k}j}\langle s_{\mathbf{r}}\rangle \right. \tag{34}$$

$$\left. + B_{-\mathbf{k}j}\langle w_{\mathbf{r}}\rangle)(A_{\mathbf{k}j}\langle s_{\mathbf{q}}\rangle + B_{\mathbf{k}j}\langle w_{\mathbf{q}}\rangle) \right]. \tag{35}$$

The free energy is composed of a free phonon part and some nontrivial contribution from the spins.

If we assume the solution is uniform, i.e. $\langle s_{\mathbf{r}}\rangle = \langle s\rangle$ and $\langle w_{\mathbf{r}}\rangle = \langle w\rangle$ are quantities independent of position, we obtain

$$\nu_{\mathbf{r}} = -4\mu^2 \sum_{\mathbf{k}j} \left[\delta_{\mathbf{k},\mathbf{0}} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{2\omega^2_{\mathbf{k}j}} A_{\mathbf{k}j}(A_{-\mathbf{k}j}\langle s\rangle + B_{-\mathbf{k}j}\langle w\rangle) \right] + E_0; \tag{36}$$

$$\eta_{\mathbf{r}} = -4\mu^2 \sum_{\mathbf{k}j} \delta_{\mathbf{k},\mathbf{0}} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{2\omega^2_{\mathbf{k}j}} B_{\mathbf{k}j}(A_{-\mathbf{k}j}\langle s\rangle + B_{-\mathbf{k}j}\langle w\rangle) + h; \tag{37}$$

$$\sum_{\mathbf{k}j} \frac{|f_{\mathbf{k}j}|^2}{\hbar\omega_{\mathbf{k}j}} = 4\mu^2 N \sum_{\mathbf{k}j} \left[\delta_{\mathbf{k},\mathbf{0}} \frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{2\omega^2_{\mathbf{k}j}} (A_{-\mathbf{k}j}\langle s\rangle + B_{-\mathbf{k}j}\langle w\rangle) \times (A_{\mathbf{k}j}\langle s\rangle + B_{\mathbf{k}j}\langle w\rangle) \right]. \tag{38}$$

Here $\delta_{\mathbf{k},\mathbf{0}}$ is the usual Kronecker δ. It takes value of unity if $\mathbf{k}=\mathbf{0}$, and zero otherwise.

B. Thermodynamic limit

By introducing phonon modes into the Hamiltonian, the periodic boundary condition is implicitly assumed. Compared with a real crystal, where the boundaries are free, the periodic boundary condition is a mathematically convenient but unphysical device. This is especially so in the analysis of our present problem, since the periodic boundary condition forces the volume and shape of the crystal to stay unchanged, thereby forbids any macroscopic strain, and also possible structural phase transition.

Mathematically, the consequence of the periodic boundary condition is that the $\mathbf{k}=\mathbf{0}$ mode corresponds to a translation of the whole system, and should not give any contribution to the free energy. However (36), (37), and (38) can only pick up contribution from the $\mathbf{k}=\mathbf{0}$ mode because of the $\delta_{\mathbf{k}}$ factor. Therefore, for any crystal with a finite size, there is no nontrivial contribution to the free energy from the spins.

To remedy this situation, we must take the thermodynamic limit, in which the size of the crystal tends toward infinity. In this limit, we may expect the boundary effect to become irrelevant and drop off from the physics (Ledderman's theory, see for example, Chapt. 2 of Maradudin).[10]

If we consider our goal of describing a structural phase transition, it also makes sense that a uniform tilt in one of the principle axes should be related to a shear wave of infinite wavelength, which is only allowed when the size of crystal tends toward infinity.

This idea of using $\mathbf{k}\to 0$ modes to describe macroscopic deformation was first due to Born and Huang,[14] and has been employed in similar problems.[11,15]

Yet we are not dealing with an isotropic solid; the direction in which $\mathbf{k}$ tends towards zero does affect the result. In the physical picture, even when the shear pattern has an infinite period and zero frequency, it still retains a directionality, as demonstrated in Fig. 2.

At the thermodynamic limit, terms of order k or higher all tend to zero, and terms of order unity remain unaffected by the limit. We discuss the details of the limits in Appendix B. Finally we obtain

$$\nu_{\mathbf{r}} = -\mu^2 \mathcal{K}\langle s\rangle + E_0, \tag{39}$$

$$\eta_{\mathbf{r}} = -\mu^2 \mathcal{L}\langle w\rangle + h, \tag{40}$$

$$\sum_{\mathbf{k}j} \frac{|f_{\mathbf{k}j}|^2}{\hbar\omega_{\mathbf{k}j}} = \frac{N\mu^2}{2}(\mathcal{K}\langle s\rangle^2 + \mathcal{L}\langle w\rangle^2), \tag{41}$$

where $\mathcal{K}$ and $\mathcal{L}$ are both constants independent of $\mathbf{r}$. They do not depend on the value of μ, either.

The value of $\mathcal{K}$ cannot be calculated without a full solution to the lattice dynamical equation. But for our present purpose it is enough to note these few properties.

First, $\mathcal{K}$ is finite since it is a sum over the finite number of branches. It is positive, because the only contribution to it comes from $|A_{\mathbf{k}j}|^2/\omega^2_{\mathbf{k}j}$, which is always positive. Also note

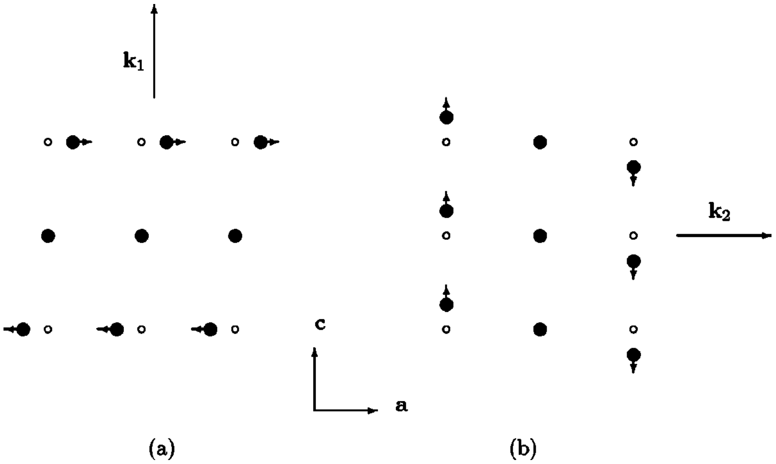

FIG. 2. A uniform shear of zero frequency and infinite wavelength is still directional. In both cases above the modulus of wave vector $|\mathbf{k_i}|=0$. But (a) $\mathbf{k}_1 \| \mathbf{c}$; (b) $\mathbf{k}_2 \| \mathbf{a}$.

that the acoustic $\mathbf{k}=(0,0,k_3)$ branches do not contribute.

Similarly, $\mathcal{L}$ is also finite and positive. It gets contribution from the acoustic $\mathbf{k}=(0,0,k_3)$ branches only. It may be evaluated with a few further assumptions, and we shall come back to it later. For future reference,

$$\mathcal{L} = \sum_{j=1}^{3} \lim_{k_3\to 0} \Bigg|_{k_1=k_2=0} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\omega_{\mathbf{k}j}^2} B_{\mathbf{k}j}B_{-\mathbf{k}j}. \tag{42}$$

Using (31) and (39)–(41), we finally arrive at the meanfield free energy

$$\begin{aligned} F_v = & -k_BT \ln \mathrm{Tr}\, e^{-\beta\Sigma_{\mathbf{k}j}\hbar\omega_{\mathbf{k}j}(b_{\mathbf{k}j}^{\dagger}b_{\mathbf{k}j}+(1/2))} + \frac{N\mu^2}{2}(\mathcal{K}\langle s\rangle^2 + \mathcal{L}\langle w\rangle^2) \\ & - k_BT \ln \mathrm{Tr}\, e^{-\beta(-\mu^2\mathcal{K}\langle s\rangle+E_0)\Sigma_{\mathbf{r}}s_{\mathbf{r}}} \\ & - k_BT \ln \mathrm{Tr}\, e^{-\beta(-\mu^2\mathcal{L}\langle w\rangle+h)\Sigma_{\mathbf{r}}w_{\mathbf{r}}}. \end{aligned} \tag{43}$$

The phonons and spins are completely decoupled from each other. The spins s and w, however, now see an effective coupling to their respective meanfields. This effective coupling is induced by the interaction with phonons, and can be thought of as the spins are interacting via exchanging virtual phonons.

The traces of spins may be performed to simplify the expression even further. Our final expression for the meanfield free energy is

$$\begin{aligned} F_v = & -k_BT \ln \mathrm{Tr}\, e^{-\beta\Sigma_{\mathbf{k}j}\hbar\omega_{\mathbf{k}j}(b_{\mathbf{k}j}^{\dagger}b_{\mathbf{k}j}+(1/2))} + \frac{N\mu^2}{2}(\mathcal{K}\langle s\rangle^2 + \mathcal{L}\langle w\rangle^2) \\ & - Nk_BT \ln \cosh[\beta(\mu^2\mathcal{K}\langle s\rangle - E_0)] \\ & - Nk_BT \ln \cosh[\beta(\mu^2\mathcal{L}\langle w\rangle - h)]. \end{aligned} \tag{44}$$

The fictitious magnetic field h is to be set to zero for all physical situations.

IV. CRITICAL BEHAVIOR

A. Two phases of hydrogen bonding

The spin part of meanfield free energy (44) is formally like the meanfield free energy of the Ising model of ferromagnet. Therefore we expect to see similar behavior, including a ferromagnetic transition at zero magnetic field.

The self-consistent meanfield equations for spin $\langle s\rangle$ and $\langle w\rangle$ are derived from thermodynamic relations

$$\frac{\partial f}{\partial E_0} = \langle s\rangle; \tag{45}$$

$$\frac{\partial f}{\partial h} = \langle w\rangle. \tag{46}$$

The free energy per unit cell f is approximated by the meanfield F_v/N. Let us look at $\langle s\rangle$ first,

$$\langle s\rangle = \tanh[\beta(\mu^2\mathcal{K}\langle s\rangle - E_0)]. \tag{47}$$

This coincides with the mean-field self-consistent equation for an Ising spin under a nonzero magnetic field. Here E_0 plays the role of the magnetic field equivalent, and is fixed at a positive value. The solution under this imposed condition of E_0 is well-known: $\langle s\rangle$ as a function of temperature T is continuous and increasing, with asymptotic values

$$\langle s\rangle = \begin{cases} -1 & T=0 \\ 0 & T\to\infty. \end{cases} \tag{48}$$

This result means the bonding states are always more favourable and predominate at a lower temperature. There are no multiple distinct phases for spin $\langle s\rangle$, though.

The spin $\langle w\rangle$ has a self-consistent equation

$$\langle w\rangle = \tanh(\beta\mu^2\mathcal{L}\langle w\rangle). \tag{49}$$

The field h is set to zero, since physically there is no such field coupled directly to w. The solutions to this equation is well-known:

$$\langle w\rangle \begin{cases} =0 & \text{when } T > T_c \\ = \pm\sqrt{\dfrac{3}{T_c}}\sqrt{T_c - T} & \text{when } 1 \gg \dfrac{(T_c-T)}{T_c} > 0. \end{cases} \tag{50}$$

The spin w shows two phases: a high temperature disordered phase with $\langle w\rangle=0$, and a low temperature ordered phase with $\langle w\rangle \neq 0$. Both signs of $\langle w\rangle$ are symmetrical and

TABLE III. Expansion properties used in this section. Here $\mathbf{U}(j)$ is a constant vector that does not depend on the atom type. θ_1, θ_2, and θ_3 are constant coefficients of expansion.

Expansion	Valid for
$[\mathbf{e}(\sigma_2\vert\mathbf{k}j)-\mathbf{e}(\sigma_1\vert\mathbf{k}j)]\cdot\mathbf{l}\sim O(k)$	All phonon branches
$\mathbf{e}(\epsilon\vert\mathbf{k}j)/\sqrt{m_\epsilon}=\mathbf{U}(j)$	Acoustic branches only; ϵ any atom type
$\mathbf{e}(\kappa\vert\mathbf{k}j)/\sqrt{m_\kappa}\cdot\mathbf{l}=\mathbf{U}(j)\cdot\mathbf{l}+O(k^2)$	Acoustic branches only
$\mathbf{e}(\sigma_1\vert\mathbf{k}j)/\sqrt{m_\kappa}\cdot\mathbf{l}=[1+i(k_1\theta_1+k_2\theta_2+k_3\theta_3)]\mathbf{U}(j)\cdot\mathbf{l}+O(k^2)$	Acoustic branches only
$\mathbf{e}(\sigma_2\vert\mathbf{k}j)\big/\sqrt{m_\kappa}\cdot\mathbf{l}=[1+i(k_1\theta_1+k_2\theta_2-k_3\theta_3)]\mathbf{U}(j)\cdot\mathbf{l}+O(k^2)$	Acoustic branches only

equally likely for the low temperature phase, but the crystal can only exhibit one sign. The critical temperature is given by

$$T_c = \frac{\mu^2\mathcal{L}}{k_B}. \tag{51}$$

Recall the states represented by each value of w summarized in Table II. Since the crystal always tends to be in a bonding state, the sign of $\langle w\rangle$ may be considered to indicate the predominant configuration of the hydrogen bonding. When $\langle w\rangle > 0$, all acceptors κ tend to form hydrogen bonds with donors σ_1, while they tend to bond with σ_2 when $\langle w\rangle < 0$.

There is a breaking of symmetry: the crystal is forced to settle on either one of two hydrogen bond configurations, which are originally symmetrical.

B. Structural phase transition

We now show that two phases in w spin correspond to two different crystal structures.

The phonon operators $b_{\mathbf{k}j}$ and $b^\dagger_{\mathbf{k}j}$ are displaced by the interactions with mean-field spins. Consequently the equilibrium position of atoms within the crystal can be expected to vary with $\langle s\rangle$ and $\langle w\rangle$.

In particular, the quantity $\mathbf{D}=\langle\mathbf{u}(\kappa,\mathbf{r})-\mathbf{u}(\kappa,\mathbf{r}-\mathbf{c})\rangle$ is of our interest. Here $\mathbf{r}$ is an arbitrary lattice point.

The displacement vectors are measured from the equilibrium positions in the high temperature phase, and the average should normally be zero. A nonzero average would imply a shift in equilibrium position. For instance, if $\mathbf{D}$ is a constant independent of position, it is obvious that from each atom one needs to translate by $\mathbf{c}+\mathbf{D}$ to hit the next equivalent atom. One of the primitive lattice vector is therefore changed from $\mathbf{c}$ to $\mathbf{c}+\mathbf{D}$.

First we write down $\mathbf{D}$ in terms of phonon modes, and using the fact that $\langle b_{\mathbf{k}j}\rangle=\langle b^\dagger_{\mathbf{k}j}\rangle=0$ to get

$$\begin{aligned}
\mathbf{D} &= \frac{2}{\sqrt{N}}\sum_{\mathbf{k}j}(\langle a_{\mathbf{k}j}\rangle+\langle a^\dagger_{-\mathbf{k}j}\rangle)e^{i\mathbf{k}\cdot\mathbf{r}}\sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}}(1-e^{-i\mathbf{k}\cdot\mathbf{c}})\frac{\mathbf{e}(\kappa|\mathbf{k}j)}{\sqrt{m_\kappa}} \\
&= \frac{4}{\sqrt{N}}\sum_{\mathbf{k}j}\frac{f_{-\mathbf{k}j}}{\hbar\omega_{\mathbf{k}j}}e^{i\mathbf{k}\cdot\mathbf{r}}\sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}}(1-e^{-i\mathbf{k}\cdot\mathbf{c}})\frac{\mathbf{e}(\kappa|\mathbf{k}j)}{\sqrt{m_\kappa}} \\
&= \frac{8\mu}{N}\sum_{\mathbf{k}j}\left(\sum_{\mathbf{q}}e^{i\mathbf{k}\cdot\mathbf{q}}\right)\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{2\omega^2_{\mathbf{k}j}}(1-e^{-i\mathbf{k}\cdot\mathbf{c}})(A_{-\mathbf{k}j}\langle s\rangle \\
&\quad + B_{-\mathbf{k}j}\langle w\rangle)\frac{\mathbf{e}(\kappa|\mathbf{k}j)}{\sqrt{m_\kappa}}.
\end{aligned} \tag{52}$$

The quantity $f_{\mathbf{k}j}$ is given by (27). Clearly, due to the factor of $\Sigma_{\mathbf{q}}e^{i\mathbf{k}\cdot\mathbf{q}}$, thermodynamic limit must be taken to produce a nontrivial result. Note that $1-e^{i\mathbf{k}\cdot\mathbf{c}}=0$ if $k_3=0$, we can write

$$\begin{aligned}
\lim_{\text{therm.}}\mathbf{D} &= 8\mu\sum_j\lim_{k_3\to0}\Bigg|_{k_1=k_2=0}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{2\omega^2_{\mathbf{k}j}}(1-e^{-i\mathbf{k}\cdot\mathbf{c}})(A_{-\mathbf{k}j}\langle s\rangle \\
&\quad + B_{-\mathbf{k}j}\langle w\rangle)\frac{\mathbf{e}(\kappa|\mathbf{k}j)}{\sqrt{m_\kappa}}.
\end{aligned} \tag{53}$$

Using (11), (12), and (13) and noting that $1-e^{i\mathbf{k}\cdot\mathbf{c}}=O(k_3)$, it is obvious that the above limit is convergent, and we may write

$$\lim_{\text{therm.}}\mathbf{D} = \sum_{j=1}^{3}c_j\langle w\rangle\mathbf{U}(j). \tag{54}$$

We denote the three acoustic branches by $j=1-3$. All optical branches contributions, and the term involving $A_{\mathbf{k}j}$ and $\langle s\rangle$ converge to zero. Coefficients c_j are constants independent of spins.

Since κ is invariant under the mirror reflection, the direction of its eigenvectors must be also invariant under the reflection. Therefore one of its three acoustic eigenvector must be parallel to $\mathbf{c}$, and the other two normal to $\mathbf{c}$. We may denote the branch with eigenvector parallel to $\mathbf{c}$ by $j=3$, and the other two by $j=1,2$.

Consequently, $\mathbf{U}(1)$ and $\mathbf{U}(2)$ are normal to $\mathbf{c}$ while $\mathbf{U}(3)$ is parallel to $\mathbf{c}$, since $\mathbf{e}(\kappa|\mathbf{k}j)=\sqrt{m_\kappa}\mathbf{U}(j)$. And we have $\mathbf{U}(3)\cdot\mathbf{l}=0$.

However, using the definition of $B_{\mathbf{k}j}$ from (11), and the acoustic eigenvector expansions from Table III, it is obvious that to the leading order $B_{\mathbf{k}j}\propto\mathbf{U}(j)\cdot\mathbf{l}$ for $j=1,2,3$. This implies that $c_3=0$.

$\mathbf{D}$ is then a linear combination of $\mathbf{U}(1)$ and $\mathbf{U}(2)$, and is normal to $\mathbf{c}$. When $|\mathbf{D}|$ is small, this correspond to a pure rotation, and the angle $\Delta\theta$ is directly proportional to $|\mathbf{D}|$. Therefore

$$\Delta\theta\propto\langle w\rangle\begin{cases}=0 & \text{if } T > T_c \\ \propto\ \pm\sqrt{T_c-T} & \text{if } 1 \gg \dfrac{T_c-T}{T_c} > 0.\end{cases} \tag{55}$$

The hydrogen bond interaction induces a second order structural phase transition in our simplified model. The angle of deviation of the unique axis from its high temperature orientation is identified as the main order parameter. The critical exponent for the transition is $1/2$, in agreement with the prediction made by a phenomenological Landau free energy expansion.[16] A broken symmetry is associated with this transition–as the axis tilted away, the mirror symmetry is necessarily broken.

We remark that the phonon modes contributing to the effective coupling of pseudo spins are the modes displaced by the hydrogen bond interaction. The w spin is responsible for the phase transition, which can be described by a shear wave of infinite wavelength along $[001]$ direction. In fact this is the only mode contributing to the effective coupling of w. Noting that some optical phonon modes contributes to the effective coupling of s, we suggest that other internal twisting and tilting of the structure are related to spin s only.

C. Estimation of T_c

We shall invoke the approximation discussed in Sec. II in order to estimate the critical temperature.

Now the acceptor κ is identified as the whole acid part of the adduct, and is a single rigid unit. The donors σ_1 and σ_2 are both contained in the base part, so they will be identified as the same unit σ. If we identify $\mathbf{e}(\sigma_1|\mathbf{k}j)=\mathbf{e}(\sigma|\mathbf{k}j)$, then it is necessary to identify $\mathbf{e}(\sigma_2|\mathbf{k}j)=e^{-i\mathbf{k}\cdot\mathbf{c}}\mathbf{e}(\sigma|\mathbf{k}j)$.

In this case $B_{\mathbf{k}j}=(1-e^{-i\mathbf{k}\cdot\mathbf{c}})\mathbf{e}(\sigma|\mathbf{k}j)$. Making use of (43), we can now write $\mathcal{L}$, the effective coupling for spin w, as

$$\mathcal{L} = 8\sum_{j=1}^{3} \lim_{k_3\to 0} \frac{k_3^2|\mathbf{c}|^2 + O(k_3^2)}{2\omega_{\mathbf{k}j}} |[\mathbf{U}(j) + O(k_3)]\cdot\mathbf{l}|^2. \quad (56)$$

Also, since the mirror symmetry now maps σ into itself, it is required that the directions of its eigenvectors to be invariant under the mirror reflection. Consequently for the three acoustic branches we have

$$\mathbf{e}(\sigma|\mathbf{k}3) \parallel \mathbf{c}; \quad (57)$$

$$\mathbf{e}(\sigma|\mathbf{k}1)\cdot\mathbf{c} = \mathbf{e}(\sigma|\mathbf{k}2)\cdot\mathbf{c} = 0. \quad (58)$$

In other words, we now have $\mathbf{U}(3)\cdot\mathbf{l}=0$. We make a further assumption that $\mathbf{U}(2)\cdot\mathbf{l}=0$, too, while $\mathbf{U}(1)\parallel\mathbf{l}$. Then the only contribution toward $\mathcal{L}$ comes from $\mathbf{k}=(0,0,k_3)$, $j=1$ branch:

$$\mathcal{L} = 8\lim_{k_3\to 0} \frac{k_3^2|\mathbf{c}|^2 + O(k_3^2)}{2\omega_{\mathbf{k}1}} |[\mathbf{U}(1) + O(k_3)]\cdot\mathbf{l}|^2. \quad (59)$$

For such an acoustic branch, the dispersion relation is of the form:

$$\omega_{\mathbf{k}1} = v^2 k_3^2 + O(k_3^4), \quad (60)$$

where v is the speed of wave propagation at the very long wavelength limit. This speed of sound wave may be written in terms the density ρ and shear modulus E_s of the macroscopic crystal:

$$v^2 = \frac{1}{E_s\rho}. \quad (61)$$

As discussed previously, this speed of sound is what it would be if the hydrogen bond interaction could be switched off, and is not physically observable. We should therefore use the shear modulus measured at a temperature significantly higher than the critical temperature as an approximated substitute of E_s.

Noting that $\mathbf{U}(1)\cdot\mathbf{l}=|\mathbf{U}(1)|$. By using the normalisation condition for eigenvectors[10] $\Sigma_{\epsilon,\alpha}e_\alpha(\epsilon|\mathbf{k}j)e_\alpha(\epsilon|\mathbf{k}j')=\delta_{jj'}$, it can be deduced that $M|\mathbf{U}(j)|^2=1$ for all j, where M is the molecular mass, in this case equal to the mass per unit cell.

We may now carry out the limit in (59):

$$\mathcal{L} = 4\frac{|c|^2\rho E_s}{M}. \quad (62)$$

Using (51), we arrive at an expression of critical temperature for our model,

$$T_c = \frac{4\mu^2|c|^2\rho E_s}{k_B M}. \quad (63)$$

Care must be taken when applying this formula to a real crystal, however. As mentioned before, in all observed situations there are at least two molecules per unit cell, related by space inversion. Because $|c|$ entered the above formula as the separation of two donors, to approximate the real situation, we should substitute it with the separation l between the centers of mass of the two neighboring base units. Also, since there are at least two molecules per unit cell now, M in the formula should be substituted by nM, where n the total number of molecules per unit cell.

For a real crystal with n molecules per unit cell related by space inversion, the modified expression for critical temperature is

$$T_c' = \frac{4\mu^2 l^2\rho E_s}{nk_B M}. \quad (64)$$

D. Heat capacity at zero pressure

Starting from the definition $F=-k_BT\ln\mathrm{Tr}\,e^{-\beta H}$, the internal energy can be recovered as

$$\frac{\partial F}{\partial T} = \frac{F}{T} - \frac{\langle H\rangle}{T}. \quad (65)$$

Therefore the heat capacity per molecule is[21]

$$C = \frac{1}{N}\frac{\partial\langle H\rangle}{\partial T} = -T\frac{\partial^2 f}{\partial T^2}. \quad (66)$$

Using the mean-field free energy (31), the heat capacity of our model may be calculated. Like all the previous results, this calculation is valid for zero external pressure, where there is no work associated with a reversible volume change.

The mean-field free energy F has two independent parts: the phonon parts involving only $b_{\mathbf{k}j}$ and $b_{\mathbf{k}j}^\dagger$, and the spin part involving only $\langle s\rangle$ and $\langle w\rangle$.

We concentrate our attention on the spin part.

The spin free energy per molecule is:

$$f_s = - k_B T \ln \cosh[\beta(\mu^2 \mathcal{K}\langle s\rangle - E_0)] - k_B T \ln \cosh(\beta\mu^2 \mathcal{L}\langle w\rangle) + \frac{\mu^2}{2}(\mathcal{K}\langle s\rangle^2 + \mathcal{L}\langle w\rangle^2). \tag{67}$$

The spin part of the heat capacity can be deduced by using (66):

$$C_s = - \mathcal{K}\langle s\rangle \frac{\partial\langle s\rangle}{\partial T} - \mathcal{L}\langle w\rangle \frac{\partial\langle w\rangle}{\partial T} + 2E_0 \frac{\partial\langle s\rangle}{\partial T}. \tag{68}$$

Both $\langle s\rangle$ and its derivative are analytic at $T = T_c$, while $\langle w\rangle$ is nondifferentiable, and its derivative discontinuous. We therefore look at the term involving w only. Using (50) and (51), we deduce that

$$- \mathcal{L}\langle w\rangle \frac{\partial\langle w\rangle}{\partial T} \begin{cases} = 0 & T > T_c; \\ = \dfrac{3}{2} k_B & 1 \gg \dfrac{(T_c - T)}{T_c} > 0. \end{cases} \tag{69}$$

Since both the s part and the phonon part are analytic in temperature, the total heat capacity of the system has a discontinuity at $T = T_c$ due to the hydrogen bond interaction. The magnitude of the jump is $\frac{3}{2}k_B$. This discontinuity in meanfield heat capacity is a common feature of all second order phase transitions, and is in agreement with the earlier Landau theory prediction.[16]

The specific heat jump in the bulk crystal is then given by

$$\Delta C_v = \frac{3}{2}\frac{k_B}{M}, \tag{70}$$

where M is the molecular mass.

E. Change in lattice parameters

In the harmonic phonon approximation, lattice thermal expansion is excluded as it involves aharmonic terms of third or higher orders in the potential. Nevertheless, through a minor modification of the free energy, and a few sensible assumptions, we may assess the effect of this structural phase transition on other lattice parameters. Note that the macroscopic shear strain is already handled by the microscopic theory in the $k \to 0$ limit.

To the right-hand side of free energy (44), an elastic energy term representing diagonal strain is added:

$$F_e = \tfrac{1}{2}(a_1 u_1^2 + a_2 u_2^2 + a_3 u_3^2), \tag{71}$$

where u_i is the ith component of elastic strain, and a_i is the corresponding modulus. For small strain, u_i is directly proportional to the change in the length of the ith primitive lattice vector. We denote this change by Δe_i.

We also assume that the coupling constant μ, and consequently T_c and the shear strain factor $\langle w\rangle$ too, depend on each u_i analytically. T_c and $\langle w\rangle$ can then be expanded as

$$T_c = T_c^{(0)} + O(u_i); \tag{72}$$

$$\langle w\rangle = \mathcal{K}\sqrt{T_c - T}[1 + O(u_i)] \quad \text{if } T < T_c. \tag{73}$$

Here $\mathcal{K}$ is a constant. Although $\sqrt{T_c - T}$ in fact depends on each u_i, we would like to keep this factor in the expansion of $\langle w\rangle$ nevertheless.

The phonon frequency $\omega_{\mathbf{k}j}$, however, is assumed not to be affected significantly by this change of lattice parameter. Consequently the phonon part of the free energy is decoupled from the spin and lattice expansion parts. The relevant part of the free energy to the macroscopic strain is then the following:

$$F_r = - Nk_B T \ln \cosh\left(\frac{T_c}{T}\langle w\rangle\right) - Nk_B T_c \langle w\rangle^2 + \frac{1}{2}(a_1 u_1^2 + a_2 u_2^2 + a_3 u_3^2). \tag{74}$$

This expression is expanded as a power series in each u_i and $(T_c - T)/T_c$. Note that whenever T is involved, it is expanded around the actual critical temperature T_c, disregarding any dependence of T_c on u_i. This approximated free energy around the critical point is:

$$F_r = - \gamma_1 \langle w\rangle^2 (\gamma_2 u_1 + \gamma_3 u_2 + \gamma_4 u_3) + \tfrac{1}{2}(a_1 u_1^2 + a_2 u_2^2 + a_3 u_3^2) + \mathcal{C} + \text{higher order terms}. \tag{75}$$

Note that the structure of the terms agree with the phenomenological Landau theory.[16]

Here each γ_i and $\mathcal{C}$ are constants independent from u_i and $(T - T_c)$. Minimizing this approximated free energy with respect to each u_i near the critical point, to leading order we get:

$$u_i \propto \langle w\rangle^2. \tag{76}$$

Since Δe_i is proportional to u_i for small strain, near the critical point it behaves like

$$\Delta e_i \begin{cases} = 0 & \text{if } T > T_c; \\ \propto \pm (T_c - T) & \text{if } 1 \gg \dfrac{T_c - T}{T_c} > 0. \end{cases} \tag{77}$$

This variation of lattice parameters induced by the hydrogen bond interaction should be considered as imposed on top of the "background" thermal expansion, induced by the anharmonic terms in the interatomic potential. This "background" variation should be analytic in temperature even at the critical point itself, and therefore can be described to the lowest order as linear in temperature.

We may then conclude that, around the critical point the lengths of the primitive lattice vectors vary continuously with temperature, although the first derivatives do not exist at the critical point. This is also consistent with the analysis of phenomenological Landau theory.[16]

V. VALIDITY OF THE THEORY

We have so far constructed a model of an adduct crystal with symmetrical hydrogen bond interactions, and derived its thermodynamics by invoking the meanfield approximation. In this section, we shall present arguments that the oversimplification made in the proposed model Hamiltonian and the meanfield nature of the derivation do not affect the accurate description of critical behaviors.

A. Model Hamiltonian

The crystal structure adopted in our model is a simplification to the real life situation. In particular, while all observed examples[1] have two or more adduct units per unit cell, ours has only one. The direct consequence of this is that the real crystals possess inversion centers, while our model does not.

In our proposed way of modeling hydrogen bonding, or in fact in the real life situations, a donor-acceptor-donor group involves a preferred direction, and consequently cannot be invariant under space inversion. The inversion symmetry therefore demands at least two such donor-acceptor-donor groups per unit cell, i.e., two molecules per unit cell, being the image of each other under space inversion.

But since the phase transition only involves the breaking of a reflection symmetry, we believe that the exclusion of the inversion symmetry should not cause any significant deviation from the real crystal.

It is possible to introduce a more sophisticated model respecting all symmetries observed, where in each unit cell there are two adduct molecules, being inversion images of each other. But due to the mean field nature of our derivation, the two symmetrically related parts shall behave identically, because they see the same environment. Therefore we believe that the meanfield behavior of this complete model should be identical to the simple model proposed in this paper.

Also it is difficult to relate the coupling constant μ to any physical observable quantities. In this paper only a order of magnitude estimation is given from the typical bond energy and bond length. Also, the two-state description of hydrogen bonding is a highly simplified and very crude model. As a consequence, the estimation of critical temperature is unlikely to be of great accuracy. However, the meanfield critical exponents should not be sensitive to these minor details.

In summary, although the model is overly simplified in many aspects, we believe that it gives a qualitatively correct picture.

B. Mean-field theory

Ising model has an upper-critical dimension of four. In three space dimension, we generally expect the meanfield critical exponents for an Ising-type model to be renormalized by the fluctuations.

However, it is also well-known that the mean-field results are indeed exact for an Ising model with an interactions of infinite range.[17] We claim that the effective spin-spin coupling induced by exchange of virtual phonons falls into this category. Since acoustic phonons are massless, the effective interaction is long-ranged, analogous to the electromagnetic interaction mediated by massless photons.

Comparison can be drawn with the Dicke model of atomic maser, which describes a system of two-level atoms coupled with photon field, a scenario very similar to our proposed model. The exact thermodynamics of the Dicke model was obtained by Hepp and Lieb.[18] For instance, the super-radiant phase transition exhibited by the Dicke model was shown to be identical to the behavior of a mean-field Ising model. Furthermore, Lee[19] has shown that the exact thermodynamics of this phase transition can be obtained from a mean-field theory. The variational scheme employed by Lee is essentially the same as the method we have used in this paper.

As a result, we feel confident that the predictions on critical behaviors made in this paper are qualitatively accurate, despite their mean-field nature.

VI. CONCLUSION

In this paper we have modelled the hydrogen bond interactions in certain amino-phenol adducts as pseudo spins coupled to lattice vibrations of the crystal.

A variational principle is deployed in finding a self-consistent mean field approximation of the free energy. The pseudo spins, though not explicitly coupled to each other, possess long-ranged interactions by exchanging phonons. When thermodynamic limit was taken, the spin part of the model possesses two phases separated by a critical point. This two-phase system is in the same universality class as the Ising model of ferromagnets. The two degenerate ground states below the critical temperature correspond to two symmetrical hydrogen bond configurations.

It is shown further that this phase transition corresponds to a structural phase transition in the crystal. The mirror symmetry of the high temperature phase was broken below the critical temperature, when the unique axis of the lattice tilts away from its original orientation. We identify the main order parameter of this phase transition as this angle of tilting $\Delta\theta$. The behavior is given in (55):

$$\Delta\theta \begin{cases} =0 & \text{when } T > T_c \\ \propto \pm\sqrt{T_c - T} & \text{when } 1 \gg \dfrac{T_c - T}{T_c} > 0. \end{cases}$$

An estimation of the critical temperature under zero pressure is also given in (64):

$$T_c' = \frac{4\mu^2 l \rho E_s}{n k_B M}.$$

The specific heat C is predicted to have a discontinuity at $T = T_c$ of magnitude $\Delta C_v = (3/2k_B/M)$.

Also, through the assumption that the coupling constant μ depends on macroscopic elastic strain, we are able to show that the lengths of primitive lattice vectors, Δe_i, in the region near the critical point behaves as in (77):

$$\Delta e_i \begin{cases} =0 & \text{if } T > T_c; \\ \propto \pm(T_c - T) & \text{if } 1 \gg \dfrac{T_c - T}{T_c} > 0. \end{cases}$$

The predicted critical exponents are all in agreement with previous predictions using a phenomenological Landau free energy expansion.[16]

The validity of the theory is discussed. Although the over-simplification in the model Hamiltonian would likely undermine the accuracy of the estimated critical temperature, we believe that the mean-field critical exponents should not be sensitive to minor details of our model. Also, due to the long-range nature of effective coupling via phonons, we believe that the meanfield results should be qualitatively accurate.

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APPENDIX A

In this appendix we derive some expansion properties of the eigenvectors.

First we expand $[\mathbf{e}(\sigma_2|\mathbf{k}j)-\mathbf{e}(\sigma_1|\mathbf{k}j)]\cdot\mathbf{l}$ for small $|\mathbf{k}|$ and any j.

Let S denote the mirror reflection which leaves the crystal structure invariant. S shall therefore bring σ_1 and σ_2 to each other. S acts on a vector $\mathbf{v}=(v_1,v_2,v_3)$ through a matrix S, defined by $\mathsf{S}\mathbf{v}=(v_1,v_2,-v_3)$. It is also obvious that $(\mathsf{S}\mathbf{v})\cdot\mathbf{u}=v\cdot(\mathsf{S}\mathbf{u})$.

The eigenvectors of σ_1 and σ_2 are related by (see, for example, Chap. 3 of Maradudin[10]):

$$\mathbf{e}(\sigma_2|\mathsf{S}\mathbf{k}j)=\mathsf{S}\mathbf{e}(\sigma_1|\mathbf{k}j). \tag{A1}$$

Since we have chosen $\mathbf{l}=(1,0,0)$, it is obvious that $\mathbf{v}\cdot\mathbf{l}=(\mathsf{S}\mathbf{v})\cdot\mathbf{l}$ for any vector $\mathbf{v}$. So

$$\mathbf{e}(\sigma_2|\mathsf{S}\mathbf{k}j)\cdot\mathbf{l}=\mathbf{e}(\sigma_1|\mathbf{k}j)\cdot\mathbf{l}. \tag{A2}$$

Note that when $\mathbf{k}=0$, the eigenvectors $\mathbf{e}(\sigma_2|\mathbf{0}j)\cdot\mathbf{l}=\mathbf{e}(\sigma_1|\mathbf{0}j)\cdot\mathbf{l}$. We may conclude that

$$[\mathbf{e}(\sigma_2|\mathbf{k}j)-\mathbf{e}(\sigma_1|\mathbf{k}j)]\cdot\mathbf{l}=[\mathbf{e}(\sigma_2|\mathbf{0}j)+O(k)]\cdot\mathbf{l}-[\mathbf{e}(\sigma_1|\mathbf{0}j)+O(k)]\cdot\mathbf{l}\sim O(k). \tag{A3}$$

Next we derive some other properties concerning only the acoustic phonon branches.

An eigenvector $\mathbf{e}(\epsilon|\mathbf{k}j)$ may always be written as a product of a real vector and a complex phase factor with unit modulus:

$$\mathbf{e}(\epsilon|\mathbf{k}j)=e^{i\theta(\epsilon|\mathbf{k}j)}\mathbf{v}(\epsilon|\mathbf{k}j)=[1+i\boldsymbol{\theta}^{(1)}(\epsilon j)\cdot\mathbf{k}+O(k^2)][\mathbf{v}^{(0)}(\epsilon j)+O(k)]. \tag{A4}$$

We use the fact that $\mathbf{e}(\epsilon|\mathbf{0}j)=\sqrt{m_\epsilon}\mathbf{U}j$, where $\mathbf{U}(j)$ is a real constant vector independent of atom type ϵ (see Chap. 2 of Maradudin[10]). Consequently we must have $\mathbf{v}^{(0)}(\epsilon j)=\sqrt{m_\epsilon}\mathbf{U}j$.

Also $\mathbf{e}^*(\epsilon|\mathbf{k}j)=\mathbf{e}(\epsilon|-\mathbf{k}j)$. This implies that the real part of $\mathbf{e}(\epsilon|\mathbf{k}j)$ must be even in $\mathbf{k}\rightarrow-\mathbf{k}$. There cannot be any odd order term in the expansion of $\mathbf{v}(\epsilon|\mathbf{k}j)$. We then have

$$\mathbf{e}(\epsilon|\mathbf{k}j)=[1+i\boldsymbol{\theta}(\epsilon j)\cdot\mathbf{k}]\mathbf{e}(\epsilon|\mathbf{0}j)+O(k_3^2). \tag{A5}$$

For an infinitesimal $\mathbf{k}$, we may identify $\boldsymbol{\theta}(\epsilon j)\cdot\mathbf{k}$ as a phase shift. An eigenvector does not change its length or direction, but merely acquires a phase when $|\mathbf{k}|$ is increased infinitesimally from zero.

The phase of a molecule ϵ in unit cell $\mathbf{r}$ can be separated into two parts. There shall be a phase factor of $e^{i\mathbf{k}\cdot\mathbf{r}}$, which is the exponential factor in the Fourier transform, corresponding to the phase variation from one unit cell to another. Also there will be a phase variation within each unit cell; this is attributed to phase of the eigenvector $\mathbf{e}(\epsilon|\mathbf{k}j)$.

Note that if we choose to measure all phases relative to the lattice points, κ should not have a phase and its eigenvector must be always real. This leads us to the expansions

$$\frac{\mathbf{e}(\kappa|\mathbf{k}j)}{\sqrt{m_\kappa}}\cdot\mathbf{l}=\mathbf{U}(j)\cdot\mathbf{l}+O(k^2); \tag{A6a}$$

$$\frac{\mathbf{e}(\sigma_1|\mathbf{k}j)}{\sqrt{m_\sigma}}\cdot\mathbf{l}=(1+i\mathbf{k}\cdot\boldsymbol{\theta}^{(1)})\mathbf{U}(j)\cdot\mathbf{l}+O(k^2); \tag{A6b}$$

$$\frac{\mathbf{e}(\sigma_2|\mathbf{k}j)}{\sqrt{m_\sigma}}\cdot\mathbf{l}=(1+i\mathbf{k}\cdot\boldsymbol{\theta}^{(2)})\mathbf{U}(j)\cdot\mathbf{l}+O(k^2). \tag{A6c}$$

Substituting (A6b) and (A6c) into (A2), which is always valid, it can be deduced that $\boldsymbol{\theta}^{(1)}=\mathsf{S}\boldsymbol{\theta}^{(2)}$. Or, in component form,

$$\theta_1^{(1)}=\theta_1^{(2)}=\theta_1; \tag{A7a}$$

$$\theta_2^{(1)}=\theta_2^{(2)}=\theta_2; \tag{A7b}$$

$$\theta_3^{(1)}=-\theta_3^{(2)}=\theta_3. \tag{A7c}$$

These results are summarized in Table III.

APPENDIX B

In this appendix, we consider the details of the limits contained in (36), (37), and (38).

We propose not to consider the thermodynamic limit of an expression $\Sigma_{\mathbf{k}}\delta_{\mathbf{k}}G(\mathbf{k})$, where $G(\mathbf{k})$ is a function of $\mathbf{k}$, as a single term $\lim_{\mathbf{k}\rightarrow 0}G(\mathbf{k})$. Not only is this interpretation physically not satisfying, but also mathematically ambiguous.

Instead, we write $G(\mathbf{k})$ as $G(k,\hat{\mathbf{k}})$, a function $k=|\mathbf{k}|$ and $\hat{\mathbf{k}}=\mathbf{k}/k$, and interpret the above thermodynamic limit as:

$$\lim_{\text{therm.}}\sum_{\mathbf{k}}\delta_{\mathbf{k}}G(\mathbf{k})=\sum_{\text{allowed }\hat{\mathbf{k}}}\lim_{k\rightarrow 0}G(k,\hat{\mathbf{k}}). \tag{B1}$$

Next we want to clarify what we mean by "allowed $\hat{\mathbf{k}}$."

Let us first return the δ back to a sum of exponentials. We are dealing with expressions of the form

$$\lim_{\text{therm.}}\frac{1}{N}\sum_{\mathbf{r}}\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}G(k,\hat{\mathbf{k}})\rightarrow\sum_{\hat{\mathbf{k}}}\lim_{k\rightarrow 0}G(k,\hat{\mathbf{k}}). \tag{B2}$$

Let each r_i run from $-Q$ to Q, then $N=(2Q+1)^3$. Also the quantity $\mathbf{k}\cdot\mathbf{r}$ may be written as $k_1r_1+k_2r_2+k_3r_3$.

A term with $\hat{\mathbf{k}}=(\alpha,\beta,\gamma)$ in the summation on the RHS of (B2) is effectively

$$\begin{aligned}\lim_{\text{therm.}}\frac{1}{N}\sum_{\mathbf{r}}\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}G(\mathbf{k}) &= \sum_i\left(\lim_{\text{therm.}}\frac{1}{2Q+1}\sum_{r_i,k_i}e^{ik_ir_i}\right)\\ &\quad\times\left(\sum_{k_j,j\neq i}\delta_{[k=k_i,\hat{\mathbf{k}}=(\alpha,\beta,\gamma)]}G(k,\hat{\mathbf{k}})\right)\\ &= \sum_i\lim_{k_i\to0}G(k_i,(\alpha,\beta,\gamma)).\end{aligned}\tag{B3}$$

By writing $\delta_{[k=k_i,\hat{\mathbf{k}}=(\alpha,\beta,\gamma)]}$, it is meant to be a product of two δ's which, upon the summation over all k_j's with $j\neq i$, shall force $\mathbf{k}=k_i(\alpha,\beta,\gamma)$.

We interpret the quantity

$$\lim_{\text{therm.}}\frac{1}{2Q+1}\sum_{r_i,k_i}e^{ik_ir_i}=\lim_{\text{therm.}}\delta_{k_3}\sim\lim_{k_3\to0}.\tag{B4}$$

First let us consider the case where $i=3$. The factor $\delta_{[k=k_3,\hat{\mathbf{k}}=(\alpha,\beta,\gamma)]}$ could be one of the following:

$$\delta_{[k=k_3,\hat{\mathbf{k}}=(\alpha,\beta,\gamma)]}=\begin{cases}\delta_{(\alpha k_2-\beta k_1),0}\,\delta_{(\gamma k_2-\beta k_3),0}, & \text{or}\\ \delta_{(\gamma k_1-\alpha k_3),0}\,\delta_{(\beta k_1-\alpha k_2),0};\end{cases}\tag{B5}$$

or other combinations with k_1 and k_2 interchanged.

Yet it is obvious that $\delta_{[k=k_3,\hat{\mathbf{k}}=(\alpha,\beta,\gamma)]}=1/(2Q+1)^2\Sigma_{r_1,r_2}e^{i(r_1k_1+r_2k_2)}$. Therefore we have a constraint:

$$\begin{aligned}&\frac{1}{(2Q+1)^2}\sum_{r_1,r_2}e^{i(r_1k_1+r_2k_2)}\\ &=\begin{cases}\dfrac{1}{(2Q+1)^2}\displaystyle\sum_{r_1}e^{i(\alpha k_2-\beta k_1)r_1}\sum_{r_2}e^{i(\gamma k_2-\beta k_3)r_2}, & \text{or}\\ \dfrac{1}{(2Q+1)^2}\displaystyle\sum_{r_1}e^{i(\gamma k_1-\alpha k_3)r_1}\sum_{r_2}e^{i(\beta k_1-\alpha k_2)r_2},\end{cases}\end{aligned}\tag{B6}$$

or other cases with 1 or 2 interchanged.

The first case cannot be satisfied consistently. The second case is possible only when $\alpha=\beta=0$ and $\gamma=1$.

Therefore, if $i=3$, the only possible direction for $\hat{\mathbf{k}}$ is (0,0,1).

Similarly, when $i=1$, the possible direction is $\hat{\mathbf{k}}=(1,0,0)$, while $j=2$ gives $\hat{\mathbf{k}}=(0,1,0)$.

Therefore we identify[22]

$$\lim_{\text{therm.}}\sum_{\mathbf{r},\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}G(\mathbf{k})=\sum_i\lim_{|\mathbf{k}|\to0}G(\mathbf{k})\Big|_{k_j=0,j\neq i}.\tag{B7}$$

Effective coupling: We now calculate $\nu_{\mathbf{r}}$, $\eta_{\mathbf{r}}$, and $\Sigma_{\mathbf{k}j}|f_{\mathbf{k}j}|^2/\hbar\omega_{\mathbf{k}j}$ in (36)–(38). Taking the thermodynamic limit as described previously, we have

$$\begin{aligned}\nu_{\mathbf{r}}=-\sum_i\left[\lim_{k_i=0}\Big|_{k_j=0,j\neq i}8\mu^2\sum_j\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{2\omega_{\mathbf{k}j}^2}A_{\mathbf{k}j}(A_{-\mathbf{k}j}\langle s\rangle+B_{-\mathbf{k}j}\langle w\rangle)\right]\\ +E_0;\end{aligned}\tag{B8}$$

$$\begin{aligned}\eta^{\mathbf{r}}=-\sum_i\left[\lim_{k_i=0}\Big|_{k_j=0,j\neq i}8\mu^2\sum_j\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{2\omega_{\mathbf{k}j}^2}B_{\mathbf{k}j}(A_{-\mathbf{k}j}\langle s\rangle+B_{-\mathbf{k}j}\langle w\rangle)\right]\\ +h;\end{aligned}\tag{B9}$$

$$\begin{aligned}\sum_{\mathbf{k}j}\frac{|f_{\mathbf{k}j}|^2}{\hbar\omega_{\mathbf{k}j}}=-\sum_i\Bigg[\lim_{k_i=0}\Big|_{k_j=0,j\neq i}4\mu^2\sum_j\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{2\omega_{\mathbf{k}j}^2}(A_{\mathbf{k}j}\langle s\rangle+B_{\mathbf{k}j}\langle w\rangle)\\ \times(A_{-\mathbf{k}j}\langle s\rangle+B_{-\mathbf{k}j}\langle w\rangle)\Bigg].\end{aligned}\tag{B10}$$

In order to calculate these, the small-k expansion of each quantity appearing in the above expressions must be known. We shall quote some of the expansion properties of the eigenvectors in Table III here. See appendix for derivations.

With these, the expansion of $A_{\mathbf{k}j}$ and $B_{\mathbf{k}j}$ may be calculated. Their exact formulas are given in (10) and (11),

$$A_{\mathbf{k}j}\sim\begin{cases}O(1) & \text{optical branches},\\ O(k) & \text{acoustic branches}, k_3=0,\\ O(k^2) & \text{acoustic branches}, k_3\neq0;\end{cases}\tag{B11}$$

$$B_{\mathbf{k}j}=\begin{cases}O(k) & \text{optical branches},\\ O(k^2) & \text{acoustic branches}, k_3=0,\\ ik_3\theta_3\mathbf{U}(j)\cdot\mathbf{l}+O(k^2) & \text{acoustic branches}, k_3\neq0.\end{cases}\tag{B12}$$

The frequency $\omega_{\mathbf{k}j}$ behaves like

$$\omega_{\mathbf{k}j}^2\sim\begin{cases}O(1) & \text{optical branches},\\ O(k^2) & \text{acoustic branches}.\end{cases}\tag{B13}$$

To the leading order in $\mathbf{k}$, the Fourier factor $e^{i\mathbf{k}\cdot\mathbf{r}}\sim1$. Using all the above results, we get

$$\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\omega_{\mathbf{k}j}^2}A_{\mathbf{k}j}A_{-\mathbf{k}j}\sim\begin{cases}O(k^2) & \text{acoustic branches}, k_3\neq0,\\ O(1) & \text{otherwise};\end{cases}\tag{B14}$$

$$\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\omega_{\mathbf{k}j}^2}A_{\mathbf{k}j}B_{-\mathbf{k}j}\sim O(k);\tag{B15}$$

$$\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\omega_{\mathbf{k}j}^2}B_{\mathbf{k}j}A_{-\mathbf{k}j}\sim O(k);\tag{B16}$$

$$\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\omega_{\mathbf{k}j}^2}B_{\mathbf{k}j}B_{-\mathbf{k}j}\sim\begin{cases}O(1) & \text{acoustic branches}, k_3\neq0,\\ O(k^2) & \text{otherwise}.\end{cases}\tag{B17}$$

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[20] In real life a hydrogen bond system is far more complicated. If we consider all the electrons and nuclei involved in the interaction, the exact solution of the Schrödinger equation should produce many more states than two. The two-level system is a more simplified model describing the essential physics.

[21] This expression is formally identical to the thermodynamic relation for heat capacity at constant volume $C_V = -T(\partial^2 f/\partial T^2)$. However, since we expect shape and volume changes across the critical point, this thermodynamic relation strictly does not apply. Therefore we rederive the expression in a different manner.

[22] Note that strictly speaking $\Sigma_{\mathbf{r}} \exp(i\mathbf{k}\cdot\mathbf{r}) = \delta_{k_1,0}\delta_{k_2,0}\delta_{k_3,0} = \delta_{(\alpha k_2-\beta k_1),0}\delta_{(\gamma k_2-\beta k_3),0}$, or in fact equals to any other such product of three δ's, which sets $\mathbf{k}=\mathbf{0}$ upon summing over all $\mathbf{k}$. What has been done in this section is that one of the three δ factors is singled out, and together with other operations identified as a limit. Its meaning is therefore different from the strict mathematical definition.