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# Anharmonic Model for Phonon-Induced First-Order Transition in 1-D Spin-Crossover Solids

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We propose a new hamiltonian intended to mimic low-spin to high-spin transition in spin-crossover solids, that displays a vibrational-entropy-driven first order phase transition. The present model is based on the existence of anharmonic intersite coupling (dependent on the electronic state of the sites) which alters the stiffness of the vibrations in the high temperature phase (high spin). The present exactly solvable model, studied at one dimension, clearly demonstrates the existence of a first-order transition accompanied with hetero-phase fluctuations around the transition temperature at higher dimensions.

### §1. Introduction

The thermally induced spin crossover (SC) transition between the low spin (LS) and the high spin (HS) states of Fe(II) complexes with suitable ligands, which are examples of molecular bistable solids, have been studied<sup>1)-4)</sup> for many years. Their bistability, originating from intra-molecular vibronic coupling, can be enhanced by inter-molecular interactions. At the solid state, the elastic interactions constitute the basic mechanism from which the richness of the behavior of these systems is originated. They lead to rather abrupt thermal spin transitions, and in many cases even to hysteresis behavior denoting a first-order phase transition or two-step transition,<sup>5)-7)</sup> instead of a gradual transition corresponding to the simple Boltzmann distribution between two states, which are generally obtained in highly diluted crystals (i.e. non cooperative systems).

From the experimental point of view, extensive research efforts have been directed these last decades toward linear polymeric Fe(II) SC chains.<sup>8)–11)</sup> Different behavior has been observed on this class of low dimensional materials: first-order transition, two-step transition and specific response of the high spin (HS) fraction under pressure.<sup>10)</sup> The relaxation of the photoexcited HS fraction in 1-D systems was also studied;<sup>11)</sup> it shows a non-linear relaxation due to cooperative effects.

From the theoretical point of view, many works have been devoted to clarify the nature of the interaction. As a part of these works, the SC transitions were microscopically modeled using Ising-like models<sup>7),12)-14)</sup> or domain models based on cooperative regular solutions.<sup>15),16)</sup> Recently, we have studied<sup>17)</sup> the relation between these two classes of models and derived the analytical expressions between their parameters, proving that they are isomorphic. In the Ising-like model, the

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SC phenomenon is described by the hamiltonian of interacting two-level units, the energy levels of which have different energies and degeneracies. The low-spin (LS) and HS states are then respectively associated with the degenerated eigenvalues of a fictitious Ising spin  $\sigma = -1, +1$ . Accounting for the isomorphism<sup>13),18</sup> between the Ising-like model and the Ising model under temperature-dependent field, the hamiltonian which describes the SC phenomena involves two terms: (i) interaction energy  $-J \sum_{\langle i,j \rangle} \sigma_i \sigma_j$  and (ii) the temperature-dependent energy  $\sum_i (\Delta - kT \ln g) \sigma_i$ . The parameter  $\Delta$  is the ligand field energy between the two-levels, and g is their degeneracy ratio. It is related to the molar entropy change upon  $\Delta S = R \ln g$ . In the case of iron II, the LS state has a spin S = 0 and the HS state S = 2, leading to a degeneracy ratio of  $(2S + 1) \times 3 = 15$ , where 3 is the orbital contribution. This degeneracy ratio, combined with the interaction, acts as a motor of the first-order transition. The HS fraction  $n_{HS}$ , measured experimentally, is expressed in the Ising-like model as a simple function of the average value of the 'fictitious magnetization':  $n_{HS} = (1 + \langle \sigma \rangle)/2$ .

In this model, the interaction is introduced as in magnetism. However, we know from the experiments that there is no magnetic order in SC solids. Therefore, J is essentially a phenomenological parameter which does not help directly to understand the elastic nature of the transition in SC solids, even if it is able to produce it. In addition, the two-level scheme represents a drastic simplification of the complete vibronic level scheme of the molecule. It is worth noting, that all the tentative to go beyond the Ising-like model have used either the phenomelogical interaction form<sup>19</sup> or the spin formulation as in 20).

In the present study we prospect, for the first time in the field of SC, a onedimensional model including explicitly the on-site potentials of the spin-crossover molecules, coupled by an elastic interaction. Thus, the model accounts for the intramolecular information coming from the molecules, which interact via phonon field. This elastic interaction incorporates two terms coming from harmonic and anharmonic contributions of the lattice. The latter leads, as a consequence, the change in the vibrational entropy which drives the first order transition. Indeed, the elastic strength coupling two atoms is taken as dependent on their vibrational states. Such problem is exactly solvable at one dimension in the classical limit.

The present manuscript is organized as follows. Section 2 is devoted to the presentation of the hamiltonian of the molecule and the local interaction potential energy between the sites. In §3, we solve exactly the statistical problem using the transfer integral technique<sup>21)</sup> and we study the equilibrium properties of the present model. We conclude in §4.

# §2. The model

Consider the following hamiltonian for 1D SC lattice with sites labelled by index i:

$$H = \sum_{i} \left[ \frac{p_i^2}{2m} + V_{\text{intra}}(u_i) \right] + \sum_{\langle i,j \rangle} V_{\text{inter}}(u_i, u_j), \qquad (1)$$

where  $V_{intra}(u_i)$  is the on-site potential of the spin-crossover unit;  $\frac{p_i^2}{2m}$  is its kinetic energy and  $V_{inter}(u_i, u_j)$  is the potential energy accounting for the elastic interaction between the sites *i* and *j*.

The symbol  $\langle i, j \rangle$  denotes neighbor pairs. The constant  $u_i$  can be viewed as the lattice distortion at site *i*. It can be related to the metal-ligand distortion of the molecule located at site *i*.

#### 2.1. The on-site potential

The potential energy of one particle results from the following on-site hamiltonian  $H_i$ :

$$H_{i} = \frac{p_{i}^{2}}{2m} + \frac{1}{2}k(u_{i} - u_{0})^{2} + \begin{bmatrix} -\delta_{\text{eff}} + \ell(u_{i} - u_{0}) & J\\ J & \delta_{\text{eff}} - \ell(u_{i} - u_{0}) \end{bmatrix}, \quad (2)$$

where the matrix hamiltonian is written in the basis of the electronic LS and HS states.  $\delta_{\text{eff}} = \delta - 1/2k_{\text{B}}T \ln g$  is the well known effective ligand field energy accounting for the energy gap  $\delta$  and the effective electronic degeneracy ratio g.<sup>13),14)</sup> The parameter  $\ell$  represents the vibronic interaction responsible for the two different equilibrium positions of the HS and LS states. J is an off-diagonal element resulting from high order spin-orbit coupling<sup>22),23)</sup> which mixes the HS and LS states.

Solving the one particle hamiltonian in the Born-Oppenheimer approach, we deduce that the potential energy  $V_{os}(u_i)$  of the fundamental state, is given by

$$V_{\text{intra}}(u_i) = \frac{1}{2}k(u_i - u_0)^2 - \sqrt{\left(\delta_{\text{eff}} - \ell(u_i - u_0)\right)^2 + J^2}.$$
(3)



Fig. 1. The true on-site potential  $V_{os}$  energy as function of the deformation  $u_i$  on site *i* resulting from Eq. 3. The parameter values are: k = 1,  $\delta = 0.1$ , g = 1,  $\ell = 1$ , J = 0.1,  $u_0 = 1/2$ .

 $V_{\text{intra}}(u_i)$  has two minima, the lowest one corresponds to the LS state and the highest to the HS state, as represented in Fig. 1. We have chosen the parameters of the model (i.e.  $\delta, g, J, k, \ell, u_0$ ) so as to have the two minima of the potential energy at u = 0(resp. u = 1) for the LS state (resp. the HS state), as shown in Fig. 1. Moreover, we set k = 1 and the electronic degeneracy ratio g = 1 for all the calculation performed in this work. Using the following values for the reduced parameters  $\delta = 0.1, \ell = 1$ , and  $J = 0.1, u_0 = 1/2$ , we found the reduced energy barrier height to  $\approx 0.271$ , which fixes the energy scale and the transition temperature. All the previous parameter values are kept as constant in all the calculations presented in this work. At low temperatures, the system is localized on u = 0 corresponding to the LS state; at high temperature it will oscillate around u = 1. The thermodynamic properties of these non-interacting double wells lead to trivial results: a simple Bolzmann population of the HS spin state and a Schottky anomaly on the specific heat. These types of behavior are similar to the well known results on two levels system.

#### 2.2. The interaction energy

The interaction energy between the SC units is mapped here through an elastic force,  $^{20),24}$  it is written under the following general form:

$$V_{\text{inter}}(u_i, u_{i+1}) = V_{\text{har}}(u_i, u_{i+1}) + V_{\text{anh}}(u_i, u_{i+1}) = \frac{1}{2}C_{i,i+1}(u_{i+1} - u_i)^2.$$
(4)

It accounts for the intersite coupling (or intermolecular interactions) and contains harmonic and anharmonic contributions. Here  $C_{i,i+1}$  is the local elastic constant between the sites i and i + 1. Due to the fact that the atoms or the molecules located on the sites i and i + 1 may have different electronic states, namely HS or LS, it becomes clear that, from a general point of view, the elastic strength  $C_{i,i+1}$  may depend on the electronic states of the atoms on these sites and on their vibrational states as well.

Therefore, the interaction energy of Eq. (4) must incorporate (i) the usual harmonic interaction between degrees of freedom

$$V_{\text{har}}(u_i, u_{i+1}) = \frac{1}{2} K (u_{i+1} - u_i)^2$$
(5)

and (ii) an anharmonic contribution,  $V_{\text{anh}}(u_i, u_{i+1})$ , accounting for the change in effective restoring forces between molecules at the transition. The latter cannot be here reasonably treated as a perturbation, in the case of SC systems, as it is frequently found in the literature.<sup>25)</sup>

Indeed, for the SC phenomenon, it is well known from the experimental literature<sup>1),23),26)</sup> that the lattice is more rigid in the low temperature phase (LS) than that at high temperature (HS). This behaviour is essentially due to the size change of the SC molecule during the transition, which is included in our two-wells potential of Fig. 1. Consequently, since the lattice is expanding during the thermal transition, it becomes natural to consider that the elastic force constants depend on the deformations of the molecules. Quite recently, Nasser<sup>20)</sup> has suggested the same idea of phonon coupling one-dimensional SC units, in which the elastic force depends on the electronic states of the neighbours. However, in this treatment, each spin-crossover molecule is represented by an Ising fictitious spin leading to neglect the intramolecular properties of the molecules. In addition, the treatment has been performed in mean-field approximation, in spite of the one-dimensional character of the model, leading to show the existence of a first-order transition between the LS and HS states. An extension of this treatment including short-range correlations, and respecting its one-dimensional character is in press.<sup>27</sup>

So, let us denote by  $C_{HH}$ ,  $C_{HL}$  (or  $C_{LH}$ ) and  $C_{LL}$  the elastic constants respectively associated with the electronic configurations HS-HS, HS-LS (or LS-HS) and LS-LS of our model. Then it follows immediately that  $C_{HH} < C_{LL}$ . We are now concerned by the analytical form of the non-harmonic contribution of the elastic force, i.e.  $C_{i,i+1}$  as a function of the deformations  $u_i$  and  $u_{i+1}$  of the connected molecules. In the following, we suggest to write the deformation dependence of the local anharmonic elastic constants  $C_{i,i+1}^{Anh}$  under the simplest form

$$C_{i,i+1}^{\text{Anh}} = \frac{\alpha}{2} \left[ (u_i - 1)^2 + (u_{i+1} - 1)^2 \right].$$
(6)

Thus, the total interaction energy can be written

$$V_{\text{inter}}(u_i, u_{i+1}) = \frac{1}{2} \left( u_{i+1} - u_i \right)^2 \left[ K + \frac{\alpha}{2} \left( (u_i - 1)^2 + (u_{i+1} - 1)^2 \right) \right].$$
(7)

In Eq. (7), the parameter  $\alpha$  is the coupling strength related to the anharmonic part



Fig. 2. The total potential energy of two interacting molecules (i, j) as a function of their respective deformations  $u_i$ ,  $u_j$ . The four minima correspond to the four equilibrium states HS-HS (HH), HS-LS (HL), LS-HS (LH) and LS-LS (LL). Parameter values are: K = 200,  $\alpha = K$ , k = 1,  $\delta = 0.1$ , g = 1,  $\ell = 1$ , J = 0.1,  $u_0 = 1/2$ .

of the lattice. In the present case, the anharmonic coupling is introduced through a quartic contribution in the potential energy. Then the total potential energy  $V_{\text{tot}}(u_i, u_{i+1})$  of two interacting molecules located at sites *i* and *i* + 1 writes:

$$V_{\text{tot}}(u_i, u_{i+1}) = V_{\text{intra}}(u_i) + V_{\text{intra}}(u_{i+1}) + V_{\text{inter}}(u_i, u_{i+1}).$$
(8)

 $V_{\text{tot}}(u_i, u_{i+1})$  which includes harmonic and anharmonic contributions, is represented for K = 200 and  $\alpha = K$  in Fig. 2. It has four minima, corresponding to the four states HS-HS ( $u_i = 1, u_{i+1} = 1$ ), HS-LS, LS-HS (two-degenerated states) and LS-LS ( $u_i = 0, u_{i+1} = 0$ ).

The coupling for the special case  $\alpha = 0$ , which corresponds to consider that  $C_{HH} = C_{LL} = C_{HL}$ , is purely harmonic. It is worth noting that most standard models for SC systems only include harmonic coupling.<sup>25)</sup> The coupling strength is identical in both low- and high-temperature phases and thus the dispersion of these modes is identical. To show the influence of the anharmonic term on the effective coupling, note that at high temperatures (i.e. HS state) we have  $\langle u \rangle \approx 1$ , which gives an effective coupling  $C = C_{HH} \approx K$ . At low temperatures (i.e. LS state) we obtain  $\langle u \rangle \approx 0$ , therefore the effective coupling is  $C = C_{LL} \approx K + \alpha$  with  $C_{HH} < C_{LL}$ . Thus, the low temperature phase has stiffer vibrations than the high temperature phase by a factor of  $\sqrt{(K+\alpha)/K}$ . This entropy difference plays an important role in "driving" the transition. In the absence of anharmonic contribution (i.e.  $\alpha = 0$ ), there is a change of the system behavior as the temperature is varied when the thermal energy is of the same order as the energy difference between the stable and metastable wells. The temperature range over which the change occurs is broad (see Figs. 3(a) and (b)). Considering the anharmonic contribution  $(C_{LL} \neq C_{HH})$ , the vibrational entropy of the low temperature phase is lowered, and thus this enhanced difference in the free energies as a function of temperature sharpens the transition. The present exact calculations clearly demonstrate that this new contribution provides a modification to the harmonically coupled Hamiltonian that displays these effects.

At one dimension, the classical partition function may be solved exactly using transfer integral (TI) technique.<sup>21),28)–30)</sup> It is straightforward that there is no true transition in one dimension, due to the domain wall entropy; however the exact calculations demonstrate the effect of the effective coupling on the thermodynamic quantities. The partition function may be written  $Z = Z_p Z_u$ , where  $Z_p$  is the one dimension free-particle partition function

$$Z_p = \left[ \int e^{-p^2/2mk_B T} dp \right]^N = (2\pi m k_B T)^{N/2} \,. \tag{9}$$

This term gives the usual contribution to the specific heat of  $\frac{1}{2}k_BT$  and has no interesting behavior. In contrast, the configuration partition function  $Z_u$  related with the potential energy leads to nontrivial behavior.  $Z_u$  can be written

$$Z_u = \int \prod_{i=1}^{N} \exp\{-\beta [V_{\text{intra}}(u_i) + V_{\text{inter}}(u_i, u_{i+1})]\} du_i.$$
(10)



Fig. 3. Thermal dependence of the mean deformation  $\langle u \rangle$  for the same harmonic coupling K = 200and different anharmonic elastic strengths. From right to left (curves (a) to (d)):  $\alpha/K = 0, 0.4, 0.7, 1$ . Note that the increase of the anharmonic contribution lowers the transition temperature and drives the "first-order" transition (see text). The parameter values are: k = 1,  $\delta = 0.1, g = 1, \ell = 1, J = 0.1, u_0 = 1/2$ .

In this work, and as a first attempt, we determine exactly the thermodynamical properties of our atomic chain in the frame of the classical statistical mechanics. At this end we must calculate exactly the partition function  $Z_u$ .

# §3. Transfer-integral method

The transfer integral (TI) formalism<sup>21),28),29)</sup> provides an elegant technique for calculating thermodynamic quantities exactly for our linear chain of non-linear coupled oscillators. We consider here a closed linear chain of N atoms with boundary conditions, i.e.  $u_{N+1} = u_1$ . For such a system the configurational partition function is written

$$Z_{u} = \int du_{N+1} \int du_{N} T(u_{N}, u_{N+1}) \cdots \int du_{1} T(u_{1}, u_{2}) \,\delta(u_{1}, u_{N+1}), \qquad (11)$$

where the matrix  $T(u_i, u_j)$  is given by

$$T(u_i, u_j) = \exp\left\{-\beta \left[\frac{1}{2}V_{\text{intra}}(u_i) + \frac{1}{2}V_{\text{intra}}(u_j) + V_{\text{inter}}(u_i, u_j)\right]\right\}$$
$$= \exp(-\beta U(u_i, u_j)), \tag{12}$$

where the effective potential energy  $U(u_i, u_j)$  has a similar shape to that of Fig. 2. The  $\delta$  function enforces periodic boundary conditions. The transfer matrix  $T(u_i, u_j)$  is symmetric, real and positive, with eigenfunctions  $\Phi_n$  satisfying

$$\int du_j T(u_i, u_j) \Phi_n(u_j) = \lambda_n \Phi_n(u_i), \quad n = 0, 1, 2, \cdots$$
$$= \exp(-\beta \varepsilon_n) \Phi_n(u_i), \quad (13)$$

where  $\lambda_n = \exp(-\beta \varepsilon_n)$  is the eigenvalue associated with the eigenfunction  $\Phi_n$ . Since  $T(u_i, u_j)$  is a positive matrix, then following Frobenius theorem  $T(u_i, u_j)$  has a positive eigenvalue  $\lambda_0$  so that

$$\lambda_0 > |\lambda_1| > \dots > |\lambda_i|, \qquad (14)$$

where  $|\lambda_i|$  is the modulus of the eigenvalue  $\lambda_i$  which can be a complex variable in the general case where the matrix  $T(u_i, u_j)$  is nonsymmetric. Further, the eigenvalues are chosen to satisfy the orthogonality relation

$$\delta(u_i, u_j) = \sum_n \Phi_n^{\star}(u_i) \Phi_n(u_j).$$
(15)

Using this identity and the relations (11) - (13), the partition function can be written as

$$Z_u = \sum_{n=0}^{\infty} \lambda_n^N.$$
(16)

It is worth noting that in the thermodynamical limit, i.e. with  $N \to \infty$ , only the dominant eigenvalue remains, leading to

$$\lim_{N \to \infty} Z_u = \lambda_0^N = \exp\left(-N\beta\varepsilon_0\right) \tag{17}$$

which gives for the free energy per atom

$$F/N = -\frac{k_B T}{N} \ln Z_u Z_p = \varepsilon_0 - \frac{1}{2\beta} \ln 2m\pi/\beta \text{ with } \beta = \frac{1}{k_B T}.$$
 (18)

In a similar way, using now Dirac notation, we may write the statistical average value of any function  $f(u_i)$  through the following formula:

$$\langle f(u_i) \rangle = \frac{1}{Z} \sum_{n} \left\langle \Phi_n^{\star} \left| T^N f \right| \Phi_n \right\rangle.$$
(19)

In the thermodynamic limit, Eq. (19) becomes

$$\lim_{N \to \infty} \left\langle f(u_i) \right\rangle = \left\langle \Phi_0^* \left| T^N f \right| \Phi_0 \right\rangle = \int du_i \left| \Phi_0(u_i) \right|^2 f(u_i).$$
(20)

In practice, to find the transfer matrix eigenvalues and corresponding eigenvectors, we first discretize the states. It follows that the intra- and inter-molecular potentials must be discretized, which transforms the equation (13) to the following:

$$\sum_{i=1}^{M} \sum_{j=1}^{M} \Delta u_i \Delta u_j T\left(u_i, u_j\right) \Phi_n(u_j) \Phi_n(u_i) = \lambda_n = \exp(-\beta \varepsilon_n) \,. \tag{21}$$

The problem is now reduced into a calculation of eigenvalues and eigenvectors of a real and symmetric matrix, which can be solved numerically.

#### §4. Results

We have solved numerically the eigenvalues problem of Eq. (21). For that reason, we typically discretized the potential  $U(u_i, u_j)$  into 1000 states; increasing the number of states up to 2000 did not appreciably alter the results.

Following the experimental data of X-rays measurements,<sup>31)-33)</sup> showing that the HS fraction is proportional to the thermal mean-value of the metal-ligand distance, it becomes reasonable to consider here that the HS spin fraction,  $n_{HS}$ , as proportional to the average value  $\langle u \rangle$  of the deformation.

In the general case where the electronic degeneracy g is taken as different from 1, the two minima of the intramolecular potential of Fig. 1 become temperature dependent. Therefore, the HS fraction can be defined as

$$n_{\rm HS} = \frac{\langle u \rangle - u_{\rm LS}}{u_{\rm HS} - u_{\rm LS}},\tag{22}$$

where  $u_{\rm LS}$  (resp.  $u_{\rm HS}$ ) is the average value of the deformation u at low temperature (resp. high temperature) in the low spin (resp. high spin) state.

For the present calculations, we have considered g = 1 and  $u_0 = 1/2$ , so as to have  $u_{\rm LS} = 0$  and  $u_{\rm HS} = 1$  at all temperatures. Using the spectrum of eigenvalues and eigenvectors, we derive easily the expression of  $n_{HS}$  in the thermodynamical limit, i.e.  $N \to \infty$ , as given by

$$n_{\rm HS} \propto \langle u \rangle = \int du u \left| \Phi_0(u) \right|^2,$$
 (23)

where  $\Phi_0(u)$  is the eigenfunction of the fundamental state. In Fig. 4, we show the thermal behaviour of the mean value of the deformation  $\langle u \rangle$  for the following cases: non-interacting case (a)  $K = 200, \alpha/K = 0$ ;

quasi-harmonic cases: (b)  $K = 200, \alpha/K = 0.4$ ; and (c)  $K = 200, \alpha/K = 0.7$ ; anharmonic case (d) K = 200 with  $\alpha/K = 1$ .

In the harmonic limit  $(K = 200, \alpha = 0)$ , for which the lattice has a uniform elastic force constant, the thermal transition occurs smoothly over a large interval of temperature (see Figs. 3(a) and (b)), due to Boltzmann population. It appears from our results that the transition temperature is sizeably lowered when we increase the anharmonic coupling. In addition, the anharmonic intersite coupling causes a sharp change in the deformation over a very small temperature range (Figs. 3(c) and (d)), indicative of a first-order phase transition driven by phonons. To confirm the previous results, we have calculated the heat capacity per particle at constant volume (length), given by

$$C_{\rm v} = -T \frac{\partial^2 (F/N)}{\partial T^2}.$$
(24)

The heat capacity for two cases is shown in Fig. 4. With a small anharmonic contribution ( $\alpha/K = 0.4$ ), a small and broad peak (dashed curve) in the heat capacity is seen. This peak is related to the Shotky anomaly. In the strong anharmonic case where  $\alpha/K = 1$ , represented by the solid curve, the peak becomes very narrow, with a very high value of  $C_v$  at the transition. This indicates the *existence* 



Fig. 4. The specific heat vs temperature of quasi-harmonic  $\alpha/K = 0.4$  (dashed curve) and the anharmonic  $\alpha/K = 1$  (solid curve) cases. The heat capacity of the harmonic weakly coupled system shows a Shottky anomaly, while that of the strong anharmonic coupled system shows a very narrow peak, with a large maximum around the transition temperature  $T_{1/2} = 0.69$ . The other parameter values are k = 1,  $\delta = 0.1$ , g = 1,  $\ell = 1$ , J = 0.1,  $u_0 = 1/2$ .

of a true first-order transition at higher dimensions, where the heat capacity would have a divergence ( $\delta$ -function) at the transition. Also, we note that the peak occurs at lower temperature; this clearly demonstrates that phonons increase the stability of the HT phase. We also found that the anharmonic coupling drastically changes the entropy over a small temperature range around the transition temperature. In addition, the change in entropy ( $\Delta S$ ) for the anharmonic ( $\alpha/K = 1$ ) case is clearly increased relative to the harmonic ( $\alpha = 0$ ) limit. This also demonstrates that the anharmonic contribution does stabilize the high temperature phase by lowering the low-temperature phase vibrational entropy.

The above equilibrium properties show that the spin-crossover transition can be reasonably described as a vibrational-entropy-driven first-order transition. It is also possible to use TI calculations to show the existence of heterophase fluctuations at temperatures around the transition temperature  $T_{eq}$ . From Eq. (20), we deduce that at the thermodynamical limit, the probability of finding a particle in the range u to u + du is given by

$$P(u)du = |\Phi_0(u)|^2 \, du.$$
(25)

Figure 5 shows the probability distribution P(u) for temperatures T = 0.695 (in full line) and T = 0.685 (in dashed line) just above and below the transition temperature; the peak of the specific heat occurs at  $T = T_{1/2} = 0.69$ . Figure 5 clearly shows that near the transition, when non-linear excitations are important, there are long-lived



Fig. 5. The probability distribution function P(u) for the anharmonic case  $\alpha/K = 1$  around the transition temperature at T = 0.685 K in dashed line, and at T = 0.695 K in full line. Note the existence of heterophase fluctuations below and above the transition temperature. The other parameter values are k = 1,  $\delta = 0.1$ , g = 1,  $\ell = 1$ , J = 0.1,  $u_0 = 1/2$ .

heterophase fluctuations.<sup>30),34)</sup> Indeed, the probability distribution P(u) shows two distinct peaks with opposite contributions: above the transition temperature, for T = 0.695, the probability density peaks near u = 1; however there is a distinct peak near u = 0. These peaks demonstrate the existence of dynamical fluctuations. For a temperature T = 0.685 slightly below the transition temperature, the situation is reversed: the maximum contribution in P(u) occurs near u = 0 and a second peak survives near u = 1.

# §5. Conclusion

We have presented an exact examination of the thermodynamics of a simple one-dimensional model which mimics the change in phonon frequency of molecular SC solids. Such a model may be also extended to describe other systems in which the transition is driven by phonons, even with more complicated intra-molecular potential energy form.

The present model clearly shows that it reproduces the "first-order phase transition", observed in many SC systems, when adequate anharmonic contributions are included. Therefore, the SC transition is described here as a vibrational-entropydriven first-order transition. The main difference when we compare this model with the usual Ising-like models,<sup>12),35)</sup> lies in the fact that here the intermolecular coupling is temperature dependent, through the change of the energy of the phonon spectrum. Consequently, the interaction energies are different in the HS and LS states, whereas they are the same in the Ising models.

An important equilibrium property, exactly obtained within the transfer integral technique, is the probability distribution function P(u). In an extremely narrow regime around the transition temperature, we found evidence of an anharmonic behaviour, i.e. heterophase fluctuations corresponding to excitations connecting the LS and the HS phases. As a first attempt to understand these excitations, we have planned to perform molecular dynamics simulations and to extract the dynamic structure factor for this system. The extension of the model in order to produce double step transitions,<sup>5),6),12),36)</sup> which needs long range-order, is also in progress.

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