Simple Two-Dimensional Model for the Elastic Origin of Cooperativity among Spin States of Spin-Crossover Complexes

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We study the origin of the cooperative nature of spin crossover (SC) between low spin (LS) and high spin (HS) states from the point of view of elastic interactions among molecules. As the size of each molecule changes depending on its spin state, the elastic interaction among the lattice distortions provides the cooperative interaction of the spin states. We develop a simple model of SC with intra- and intermolecular potentials which accounts for the elastic interaction including the effect of the inhomogeneity of the spin states, and apply constant temperature molecular dynamics based on the Nosé-Hoover formalism. We demonstrate that, with increase of the strength of the intermolecular interactions, the temperature dependence of the HS component changes from a gradual crossover to a first-order transition.

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The discovery of LIESST (light-induced excited spin state trapping)\textsuperscript{5,6} phenomena has accelerated studies of functional spin-crossover (SC) molecular solids. SC compounds have been studied intensively not only because of their potential applicability to novel optical devices, e.g., optical data storage and optical sensors, etc., but also because of the fundamental scientific interest in the mechanism of the phase transition and the accompanied non-linear relaxation processes\textsuperscript{7-9,10,11,12,13,14,15,16,17,18,19,20,21,22}.

To control electronic and magnetic states of SC compounds, it is important to understand the bistable nature of these compounds. The SC transition between the low-spin (LS) and high-spin (HS) states can be induced by change of temperature, pressure, magnetic field, light-irradiation, etc. It has been clarified that the interaction between spin states causes various types of cooperative phenomena between the LS and HS phases\textsuperscript{3,4}.

In order to take into account the cooperativity in the SC transition, Wajnflasz and Pick (WP) proposed an Ising model\textsuperscript{20}, in which the spin state is described by a fictitious spin \(\sigma = -1\) (1) for the LS (HS) state) and the short-range interactions \(J\) between the spin states are introduced in the form \(\mathcal{H} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j + \sum_i (\Delta - \frac{1}{2} k_B T \ln(g)) \sigma_i\), where \(g\) is the degeneracy ratio between the HS and LS states. Using this model, the change between a gradual crossover and a first-order transition has been well explained as a function of the parameters \(J, \Delta\) and \(g\).

We perform molecular dynamics (MD) simulations on a 2D system with a simple square lattice. The intramolecular potential energy depending on the molecular size is given by a double-well adiabatic potential \(V_{\text{intr}}(r_i)\), which is a function of the radius \(r_i\) of the \(i\)th molecule. Let \(p_i\) be the corresponding relative momentum and let \(m\) be the reduced mass.

We set an intermolecular binding interaction between SC molecules (the \(i\)th and \(j\)th molecules) as \(V_{\text{inter}}(X_i, X_j, r_i, r_j)\), where \(X_i = (X_{iX}, X_{iY})\) is the coordinate of the center of the \(i\)th molecule (Fig. 2 (a)). The corresponding momentum is \(P_i = (P_{iX}, P_{iY})\) and the mass of the molecule is \(M\).

To model this scenario we apply the following Hamil-
and that for the HS state ($A$ with coefficient $\text{the radius of the molecule is } r$)

Setting $\text{has minima at } x = 0$ (ideal LS) and $x = 1$ (ideal HS). Setting $r_{LS} = 9$ and $r_{HS} = 10$ for the ideal radius of the LS molecule and that of the HS molecule, respectively, the radius of the molecule is $r = r_{LS} + x$.

When a parabolic potential for the LS state ($y = ax^2$) and that for the HS state ($y = b(x - c)^2 + d$) are mixed by off-diagonal element $J$, the lowest potential function with coefficient $A$ is given by

$$V(x) = \frac{A}{2} \left( d + b(c - x)^2 + ax^2 - \sqrt{4J^2 + (d + b(c - x)^2 - ax^2)^2} \right).$$

Because the entropy of the harmonic oscillator ($\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}Kx^2$) is $S = NK_B \left( 1 - \ln \frac{p}{K_B T} \sqrt{\frac{K_B}{m}} \right)$, the entropy difference between the LS and HS states is given by

$$\Delta S = S_{HS} - S_{LS} = NK_B \ln \sqrt{\frac{K_{LS}}{K_{HS}}}.$$
details of the potential form, and thus we adopt one of the simplest forms
\[
f(u) = D \left( e^{a(u-u_0)} + e^{-b(u-u_0)} \right), \tag{6}
\]
where \(a' = 0.5\) and \(b' = 1.0\). \(u_0\) is a constant such that 
\(f(u)\) has the minimum at \(u = 0\). When molecules (circles in Fig. 2 (a))  
\(i\) and \(j\) contact each other (\(d_{ij} = 0\)), the function has a minimum value.

In order to maintain the crystal structure (the coordination number), we introduce a potential between the next-nearest neighbors (\(i\) and \(k\), see Fig. 2 (a))
\[
V_{\text{inter}}(X_i, X_k, r_i, r_k) = f(d_{ik} - \Delta r) \tag{7}
\]
with \(a' = 0.1\) and \(b' = 0.2\), which is much smaller than that of the nearest neighbors. Next-nearest neighbors do not contact each other as depicted in Fig. 2 (a), and there is a spatial gap between them. For simplicity, we assume here that next-nearest neighbors are most stabilized when the gap is \(\Delta r = 2(\sqrt{2} - 1)\tilde{r}\), where we take \(\tilde{r} = (r_{\text{LS}} + r_{\text{HS}})/2\) although \(\Delta r\) can be temperature dependent. We focus on the dependence of the spin state on the strength of the intermolecular interaction, and thus we study the dependence on \(D\). Common \(D\) is used for both Eqs. (5) and (7).

To study the temperature dependence, we adopt the Nosé-Hoover method\textsuperscript{24,25} to generate the canonical ensemble for a given temperature \(T\). The Hamiltonian of the thermal reservoir is given by
\[
\mathcal{H}_{\text{therm}} = \frac{P_s^2}{2M} + 3Nk_BT\ln s, \tag{8}
\]
where \(s\) is a scaling factor, \(P_s\) is the conjugated momentum of \(s\) and \(Q\) is an effective mass associated with \(s\). Therefore, the total Hamiltonian including the effect of thermal reservoir is given by \(\mathcal{H}_{\text{total}} = \mathcal{H}_{\text{system}} + \mathcal{H}_{\text{therm}}\).

Applying the Nosé-Hoover formalism to the present system, the time evolution of the system is realized according to the following equations of motion.
\[
\frac{dr_i}{dt} = \frac{p_i}{m}, \tag{9}
\]
\[
\frac{dp_i}{dt} = -\frac{\partial V_{\text{intra}}}{\partial r_i} - \frac{\partial V_{\text{inter}}}{\partial r_i} - \xi p_i, \tag{10}
\]
\[
\frac{dX_i}{dt} = \frac{P_i}{M}, \tag{11}
\]
\[
\frac{dP_i}{dt} = -\frac{\partial V_{\text{inter}}}{\partial X_i} - \xi P_i, \tag{12}
\]
\[
\frac{ds}{dt} = s\xi, \tag{13}
\]
\[
\frac{d\xi}{dt} = \frac{1}{Q} \left[ \sum_i \frac{p_i^2}{m} + \sum_i \frac{P_i^2}{M} - 3Nk_BT \right], \tag{14}
\]
where \(V_{\text{inter}}\) stands for the summation of the intermolecular potentials for the nearest and next-nearest pairs, and \(\xi \equiv \frac{P_s}{M}\).

We adopt \(x\) as a parameter to characterize the spin state. We study the open-boundary system of \(L^2 = 26 \times 26\) molecules. We warm up the system from \(T = 0.1\) to \(2.0\) in steps of increment 0.1, and cool it down to \(T = 0.1\). At each temperature, 40000 MD steps are discarded as transient time and subsequent 20000 MD steps are used to measure \(x\) with the time step \(\Delta t = 0.01\). We employ an operator decomposition method in which the numerical error is of the order \(O(\Delta t^3)\). We set \(m = 1.0\), \(M = 1.0\), and \(Q = 1.0\). \langle x \rangle does not depend on \(m\), \(M\), and \(Q\) in the equilibrium state.)

In Figs. 3 (a), (b), (c) and (d), the temperature dependence of \langle x \rangle are shown. When \(D = 10\) (Fig. 3 (a)), \langle x \rangle in the warming process and that in the cooling process overlap, indicating that a smooth (gradual) SC crossover is realized. When the interaction parameter becomes larger: \(D = 20\) (Fig. 3 (b)), variation of \langle x \rangle becomes sharper, which implies that the SC transition becomes more cooperative.

When \(D = 28\) (Fig. 3 (c)), a clear hysteresis loop of \langle x \rangle is found. As the interaction parameter increases further: \(D = 42\) (Fig. 3 (d)), the hysteresis width becomes larger. Here, we found that when the interaction between molecules becomes large, the SC transition changes from a gradual crossover to a first order transition. The critical value of \(D\) is \(D_{\text{critical}} \approx 20\).

In Figs. 4 (a) and (b), snapshots of the complete LS state and the complete HS state are shown, in which the system length changes by 11 %.
FIG. 4: Snapshots of configurations. HS molecules (red circles) are allocated when $r$ is larger than $r = r_{LS} + x_{c}$. LS molecules are drawn by blue circles. (a) Complete LS phase. (b) Complete HS phase. (c) A snapshot of configuration at $T = 0.6$ in the system of $D = 10\ (L^2 = 16^2)$, where 80 molecules are in the HS state. (d) A snapshot of configuration at $T = 1.0$ in the system of $D = 42\ (L^2 = 16^2)$, where 79 molecules are in the HS state.

a snapshot of configuration at $T = 0.6$ for the parameter $D = 10$ and that at $T = 1.0$ for $D = 42$ are given, where the concentration of HS molecules is about 30% in both configurations. Although the number of HS molecules is almost the same, the average cluster size of HS in (d) is bigger than in (c). This indicates that there is higher correlation between spin states of molecules in the case of strong intermolecular interaction (case (d)), which promotes first-order transition.

In this study, we investigated the cooperativity of spin-crossover phenomena induced by the elastic interaction among lattice distortions which are triggered by the difference of molecular sizes caused by the different spin states. This effect is inherent to the high dimensionality (2D and 3D). The present 2D model can be applied straightforwardly to the 3D case. Although the lattice relaxation through a change of molecular sizes has been studied phenomenologically by a mean-field treatment\textsuperscript{12}, as far as we know, this is the first attempt to investigate the cooperativity attributed to the effect of local distortions (fluctuation) and that of the propagation to the overall lattice.

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