

Supporting Information for

**Role of Surface Effects in the Vibrational Density of States
and the Vibrational Entropy in Spin Crossover
Nanomaterials: A Molecular Dynamics Investigation**

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S1 Low-Spin vibrational density of states

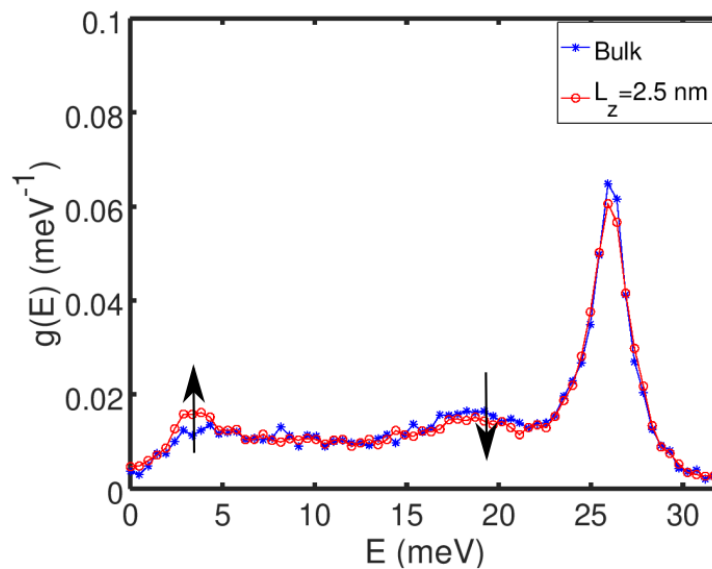


Figure S1: Partial vDOS in the LS state for a film of thickness $L_z = 2.5 \text{ nm}$ (red open circles). The vDOS corresponding to the simulated bulk material is shown for comparison (blue stars). The arrows indicate the shift of bulk modes between 15-25 meV towards the low-frequency range and the emergence of surface modes at $\approx 5 \text{ meV}$ due to the presence of free surfaces.

S2 Internal energy and mean force constant

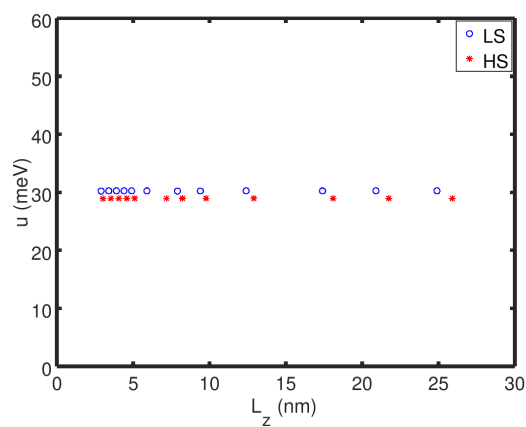


Figure S2: Size evolution of the vibrational internal energy u in the two spin states.

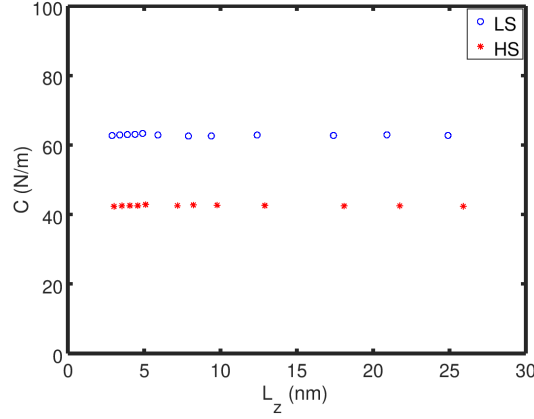


Figure S3: Size evolution of the mean force constant C in the two spin states.

S3 Estimation of Me-L elastic force constant using the diatomic chain problem

Based on the Newton's equation of motion, the dynamical matrix provides the elastic force constant k_{MeL} using the experimental Raman frequency data ω_R . For the infinite diatomic chain illustrated in Figure S4, we calculate k_{MeL} by resolving the eigenvalue problem of the dynamical matrix as follows:

$$Det(D(\vec{q}, k_{MeL}) - \nu_R^2 I) = 0 ; \quad (S1)$$

The obtained solution for optical Me-L modes can be written as a function of ω_R^2 :

$$k_{MeL} = 4\pi^2\alpha \frac{\omega_R^2}{\frac{1}{M_{Me}} + \frac{1}{2M_L} + \sqrt{(\frac{1}{M_{Me}} + \frac{1}{2M_L})^2 - \frac{2}{M_{Me}M_L}}} ; \quad (S2)$$

where $\alpha = 2.148 * 10^{-6}$ is the pre-factor for converting from $(\text{cm}^{-1})^2 \cdot \text{g/mol}$ to $\text{kcal/mol} \cdot \text{\AA}^2$. Herein, we can estimate k_{MeL} by injecting the Raman frequencies ω_R for LS state between 200-400 cm^{-1} (see reference 30), the obtained k_{MeL} is between 36-145 $\text{kcal/mol} \cdot \text{\AA}^2$, in good agreement with DFT calculations (see reference 41). We chose the median value $k_{MeL} = 90 \text{ kcal/mol} \cdot \text{\AA}^2$, which corresponds to $\omega_R \approx 270 \text{ cm}^{-1}$. According to the experimental measurements, we consider a decrease of k_{MeL} when the LS \rightarrow HS transition takes place ($k_{MeL}^{LS} = 1.5k_{MeL}^{HS}$), and a decrease of $k_{LL-intra}$ ($k_{MeL} = 1.5k_{LL-intra}$). We fix the intermolecular cohesion energy in the LS(HS) state at $\epsilon_{LS} = 5.73(\epsilon_{HS} = 5.55) \text{ kcal/mol}$, which is high enough in order to simulate the mean energy of the interactions connecting the molecules.

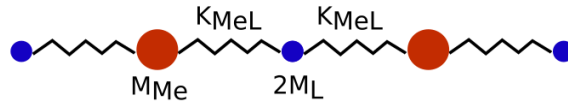


Figure S4: Schematic representation of the infinite diatomic chain with harmonic interaction between the metal and the coarse grained ligand adapted for the simulated structure.

S4 Calculation of $\gamma(\tau)$, $g(E)$ and the thermodynamic quantities

We calculate the velocity auto-correlation function $\gamma(\tau)$ using the following relation:

$$\gamma(\tau) = \frac{\left\langle \sum_i^N v_i(t)v_i(t+\tau) \right\rangle}{\left\langle \sum_i^N v_i^2(t) \right\rangle} \quad (\text{S3})$$

where $v_i(t)$ is the velocity at time t of the atom i and \sum_i^N is the sum over the N considered atoms. The normalized (vDOS) is the real part of the Fourier's transformation of $\gamma(\tau)$ divided by the integral of $g(\omega)d\omega$:

$$\tilde{g}(\omega) = \frac{\int_0^{\tau_{max}} \gamma(\tau) \cos(\omega\tau) d\tau}{\int_0^{\omega_{max}} g(\omega) d\omega} \quad (\text{S4})$$

The calculation of (vDOS) using the previous equation opens the possibility to extract the thermodynamical properties, such as the vibrational entropy s per atom, the vibrational internal energy per atom u , the mean force constant C and the Debye sound velocity v_D using the following equations:

$$u_{vib} = \frac{3}{2} \int_0^{E_{max}} \tilde{g}(E) E \frac{e^{\beta E} + 1}{e^{\beta E} - 1} dE ; \quad (\text{S5})$$

$$s_{vib} = 3k_B \int_0^{E_{max}} \tilde{g}(E) \left[\frac{\beta E}{2} \frac{e^{\beta E} + 1}{e^{\beta E} - 1} - \ln(e^{\frac{\beta E}{2}} - e^{-\frac{\beta E}{2}}) \right] dE ; \quad (\text{S6})$$

$$\langle C \rangle = \frac{\tilde{m}}{\hbar^2} \int_0^{E_{max}} \tilde{g}(E) E^2 dE ; \quad (\text{S7})$$

$$v_D = \lim_{E \rightarrow 0} \left(\frac{\tilde{m}}{2\pi^2 \rho \hbar} \frac{E^2}{\tilde{g}_D(E)} \right)^{\frac{1}{3}} ; \quad (\text{S8})$$

where k_B is the Boltzmann constant, T the temperature, $\beta = \frac{1}{k_B T}$, \hbar is the Planck constant, and \tilde{m} corresponds to the resonant mass, which is the mass of ^{57}Fe , and $\rho = \frac{N \langle m \rangle}{V}$ is the material density.

S5 Estimation of the error due to numerical artifacts

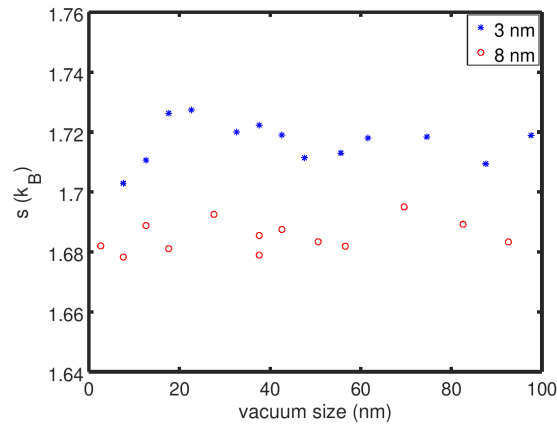


Figure S5: The entropy versus the vacuum size of LS thin films of thickness 3 nm (in blue stars) and 8 nm (in red circles).

One of the numerical artifacts that can disturb the results is the vacuum size fixed by the simulation box size. It is important therefore to quantify the error caused by this artifact. In Figure S5, we have calculated the entropy variation with the vacuum size for two thin-films. We estimate this error by calculating first the maximal absolute error of each thin film as follows:

$$\epsilon_N = \max(|s_N - \langle s \rangle|), \quad (\text{S9})$$

where $\langle s \rangle$ is the mean value of entropy data. After that, we take the maximum error of the two thin films:

$$\epsilon = \max(\epsilon_{3nm}, \epsilon_{8nm}) \approx 0.01 k_B, \quad (\text{S10})$$

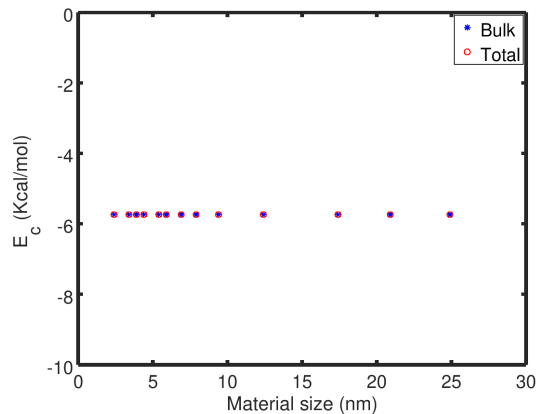


Figure S6: Size evolution of the cohesion energy E_c in the "Bulk" and the system with free surface "Total".

This error bar is imputed to entropy results of the system with free surface, which still faraway from the bulk entropy, rejecting the idea that the entropy increment is a vacuum effect. In any case, we fix the simulation box at $L_{vacuum} \approx 10L_z$, which is big enough to ensure that the numerical uncertainties by vacuum creation remain negligible.

We have also checked the cohesion energy of the bulk system and the system with free surfaces, which is still constant with the variation of the material size (see Figure S6), and matches perfectly the cohesion energy that we have chosen for the Lennard-Jones potential in the LS state. We demonstrate again that there is no numerical artifact at T=0K.