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July 13, 2023

Abstract

A spin-conversion molecule is organised around an iron ion Fe^{+2}. This ion has two quantum energy levels : a low spin (LS) ground level, $S = 0$, and a high spin (HS) excited level, $S = 2$, where S is the total spin of the $3d$ electrons. We call Δ the distance in energy of the two levels. This result is described by introducing a fictitious spin $\widehat{\sigma}$ which has two eigenvalues ± 1. For a set of two molecules we introduce the sum $\widehat{\sigma}_1 + \widehat{\sigma}_2$ of two fictitious spins which has the eigen values ± 2 and 0. The vibrations inside each molecule and the vibrations between the two molecules are taken into account. These vibrations are independent of each other but their frequency depends on the electronic states of the two molecules. For the following, each molecule is designated by atom and the set of two molecules is designated by molecule.

From the statistical study, its appears at equilibrium, for fixed T and $\Delta/2$, three thermodynamic states (-2), (0) and (2) with occupation probabilities $P(-2)$, $P(0)$ and $P(2)$, respectively. For each state we can calculate its Gibbs potential, its entropy and its enthalpy.

For an ensemble of N identical molecules, there are at the (Boltzmann) equilibrium $NP(-2)$ molecules in the state (-2), $NP(0)$ in the state (0) and $NP(2)$ in the state (2). But, as the Gibbs potentials of the three states are not equal, this canonical distribution is not stable. Then, due to random exchanges of heat between the thermostat and the molecules, the molecules will all go to the the state with the lowest Gibbs potential. The consequences are described.

1 Introduction

A spin-conversion molecule is organised around an iron ion Fe^{+2}. This ion has two quantum energy levels : a low spin (LS) ground level, $S = 0$, and a high spin (HS) excited level, $S = 2$, where S is the total spin of the $3d$ electrons$[1-3]$. Let us call Δ the difference between the energies of the two levels and r the degeneracy of the excited level. This degeneracy is given by $r = 2S + 1$.

In 1974, M. Sorai and S. Seki [4] measured the heat capacities of $[Fe\,(phen)_2\,(NCS)_2]$ and $[Fe\,(phen)_2\,(NCSe)_2]$ crystals. These molecules are spin-conversion molecules. They concluded that "there is significant coupling between electronic state and phonon system" and that excitation of phonons is much easier in the high temperature phase. In order to take into account these results, J. A. Nasser [5] assumed that the elastic force constant of the spring linking two molecules first neighbours in a crystal of spin conversion molecules depends on the electronic states of both molecules.

In 2006, Kate L. Ronayme et al. [6] determined by DFT calculations and from different experimental results the values of the intramolecular vibration frequencies of the molecule $[Fe\,(phen)_2\,(NCS)_2]$ when this molecule is in the (LS) and (HS) levels. They found that these values are generally smaller when the molecule is in the (HS) level. Taking into account the results of Ronayme et al. J. A. Nasser et al. [7] studied the influence of intramolecular vibrations on this two electronic energy levels system.

Now, we study the thermal behavior of two identical spin-conversion molecules linked by a chemical bond. We assume that i) the elastic force constant of the spring which exists between the two molecules depends on the electronic state of both molecules and that ii) there are in each molecule p independent linear harmonic oscillators.

For the following, each molecule is designated by atom and the set of two molecules is designated by molecule.

In Section 2, we present the theoretical study. In Section 3 we give the results obtained for a set of values given to system parameters. The last section is devoted to discussion and conclusion.

2 Theoretical Study

2.1 Hamiltonian and Partition function

Consider a system of N identical molecules in contact with a heat reservoir at the absolute temperature T. We do not take into account the degrees of freedom of translation and of rotation of the molecules. And we consider the interaction between the molecules to be negligible.

Each molecule is made up of two identical atoms (1) and (2) linked by a chemical bond. Let us call k_{12} the elastic force constant of the spring that acts between both atoms. The atoms oscillate around their equilibrium position with the frequency ω_{12} given by

$$\omega_{12} = \sqrt{\frac{2k_{12}}{m_a}} \tag{1}$$

where m_a is the mass of an atome and $m_a/2$ is the reduced mass of the two atoms. The relation (1) can be established by means of classical mechanics [8].

The eigen values of the Haliltonian of vibrations $\widehat{H}_{vib12}$ are $\hbar\omega_{12}\left(n_{12}+\frac{1}{2}\right)$ with $n_{12} = 0, 1, 2, ...\infty$ and where $\hbar$ is the Planck's constant divided by 2π. So, the partition function associated to the Hamiltonian $\widehat{H}_{vib12}$ is

$$z_{12vib} = \frac{1}{2\sinh\left(\beta\frac{\hbar\omega_{12}}{2}\right)} \tag{2}$$

We recall that

$$\sum_{n=0.1.2...} e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} = \frac{1}{2\sinh\left(\beta\frac{\hbar\omega}{2}\right)} \tag{3}$$

with $\beta = \frac{1}{k_B T}$ and where k_B is the Boltzmann constant.

We assume that each atom has two energy levels separated by Δ. The fundamental level is not degenerated while the excited one has the degeneracy r. We associate the fictitious spin $\widehat{\sigma}_i$ to the atom (i) $(i = 1, 2)$ and we assume that $\widehat{\sigma}_i$ has two eigenvalues $\sigma_i = \pm 1$ [9]. The degeneracy r comes from an other space of states.

The spin Hamiltonian of the atom (i) can be written

$$\widehat{H}_{sp}(i) = \frac{\Delta}{2}\widehat{\sigma}_i \tag{4}$$

and the spin Hamiltonian of the molecule is

$$\widehat{H}_{sp} = \frac{\Delta}{2}\left(\widehat{\sigma}_1 + \widehat{\sigma}_2\right) \tag{5}$$

The eigen values of the operator $\widehat{m} = \widehat{\sigma}_1 + \widehat{\sigma}_2$ are $m = -2, 0, 2$. The corresponding eigen kets are $|-2\rangle = |-1,-1\rangle$, $\left|0^{(1)}\right\rangle = |-1,1\rangle$, $\left|0^{(2)}\right\rangle = |1,-1\rangle$ and $|2\rangle = |1,1\rangle$. In the brackets the first number is the value of σ_1 and the second

that of σ_2. The two kets $\left|0^{(1)}\right\rangle$ and $\left|0^{(2)}\right\rangle$ are the eigen states of the eigen value $m = 0$. The eigen values of the Hamiltonian $\widehat{H}_{sp}$ are $-\Delta$, 0 and Δ and the corresponding eigen kets are those of $\widehat{m} = \widehat{\sigma}_1 + \widehat{\sigma}_2$.

The eigen values of the Hamiltonian $\widehat{H}_{sp} + \widehat{H}_{vib12}$ are :

$$\begin{aligned} -\Delta + \hbar\omega_{12}\left(n_{12} + \frac{1}{2}\right), \text{ with } n_{12} &= 0, 1, 2, ..\infty \\ \hbar\omega_{12}\left(n'_{12} + \frac{1}{2}\right), \text{ with } n'_{12} &= 0, 1, 2, ..\infty \\ \Delta + \hbar\omega_{12}\left(n''_{12} + \frac{1}{2}\right), \text{ with } n''_{12} &= 0, 1, 2, ..\infty \end{aligned} \tag{6}$$

Taking into account the degeneracy r and that of the eigen value $m = 0$, the partition function $z_{spvib12}$ associated to the Hamiltonian $\widehat{H}_{sp} + \widehat{H}_{vib12}$ is

$$z_{spvib12} = \left(e^{\beta\Delta} + 2r + r^2 e^{-\beta\Delta}\right) \frac{1}{2\sinh\left(\beta\frac{\hbar\omega_{12}}{2}\right)} \tag{7}$$

As the Hamiltonians $\widehat{H}_{sp}$ and $\widehat{H}_{vib12}$ are independent, the partition function $z_{spvib12}$ is the product of the partition functions associated with each of the two Hamiltonians.

Now we introduce the following assumptions :

i) We assume that the value of the elastic force constant k_{12} depends on the electronic states of the two atoms. This elastic force constant is equal to λ when both atoms are in their fundamental level (that corresponds to the state $|-2\rangle$), to ν when they are both in their excited level (that corresponds to the state $|2\rangle$) and to μ when the two atoms are not in the same level (that corresponds to the states $\left|0^{(1)}\right\rangle$ and $\left|0^{(2)}\right\rangle$). This assumption can be written as following [5] :

$$k_{12} = \frac{\lambda + 2\mu + \nu}{4} + \frac{\nu - \lambda}{4}(\sigma_1 + \sigma_2) + \frac{\lambda - 2\mu + \nu}{4}\sigma_1\sigma_2 \tag{8}$$

We assume

$$\lambda \geqslant \nu \tag{9}$$

and

$$\mu = \frac{\lambda + \nu}{2} \tag{10}$$

The relation (8) introduces a coupling between the fictious spins and the interatomic vibrations. Taking into account this coupling, the partition function becomes

$$\left(z_{spvib12}\right)_{coupl} = e^{\beta\Delta}\frac{1}{2\sinh(\beta\frac{\hbar\omega_{--}}{2})} + \frac{2r}{2\sinh(\beta\frac{\hbar\omega_{+-}}{2})} + r^2 e^{-\beta\Delta}\frac{1}{2\sinh(\beta\frac{\hbar\omega_{++}}{2})} \tag{11}$$

where

$$\omega_{--} = \sqrt{2\frac{\lambda}{m}} \tag{12}$$

$$\omega_{+-} = \omega_{-+} = \sqrt{2\frac{\mu}{m}} = \omega_{--}\sqrt{\frac{\mu}{\lambda}} \tag{13}$$

and

$$\omega_{++} = \sqrt{2\frac{\nu}{m}} = \omega_{--}\sqrt{\frac{\nu}{\lambda}} \tag{14}$$

ii) We also assume also that in each atom there are p identical and independent one-dimensional harmonic oscillators. The frequency value of one oscillator is ω_{int} when the atom is in its fundamental level and $\widetilde{\omega}_{int}$ when it is in its excited one. With this new assumptition the partition function of the molecule becomes

$$z_{mol} = \frac{e^{\beta\Delta}}{2\sinh(\beta\frac{\hbar\omega_{--}}{2})}\left(\frac{1}{2\sinh(\beta\frac{\hbar\omega_{int}}{2})}\right)^{2p} + \frac{2r}{2\sinh(\beta\frac{\hbar\omega_{-+}}{2})}\left(\frac{1}{2\sinh(\beta\frac{\hbar\omega_{int}}{2})}\right)^{p}\left(\frac{1}{2\sinh(\beta\frac{\hbar\widetilde{\omega}_{int}}{2})}\right)^{p} + \frac{r^2e^{-\beta\Delta}}{2\sinh(\beta\frac{\hbar\omega_{++}}{2})}\left(\frac{1}{2\sinh(\beta\frac{\hbar\widetilde{\omega}_{int}}{2})}\right)^{2p} \tag{15}$$

Factorizing $\left(\frac{1}{2\sinh(\beta\frac{\hbar\omega_{int}}{2})}\right)^{2p}$ in the relation (15), we obtain

$$z_{mol} = \left(\frac{1}{2\sinh(\beta\frac{\hbar\omega_{int}}{2})}\right)^{2p} z'_{mol} \tag{16}$$

with

$$z'_{mol} = \frac{e^{\beta\Delta}}{2\sinh(\beta\frac{\hbar\omega_{--}}{2})} + \frac{2rR_{vib}}{2\sinh(\beta\frac{\hbar\omega_{-+}}{2})} + \frac{r^2R_{vib}^2e^{-\beta\Delta}}{2\sinh(\beta\frac{\hbar\omega_{++}}{2})} \tag{17}$$

and

$$R_{vib} = \left(\frac{2\sinh(\beta\frac{\hbar\omega_{int}}{2})}{2\sinh(\beta\frac{\hbar\widetilde{\omega}_{int}}{2})}\right)^{p} \tag{18}$$

In the relation (16), the partition function z_{mol} appears as that of two independent systems : a system of $2p$ identical and independent harmonic oscillators which vibrate with the frequency ω_{int} and the system of the two fictitious spins $\widehat{\sigma}_1$ and $\widehat{\sigma}_2$ coupled to the vibrations of the molecule. We are concerned with z'_{mol} .

2.2 Probability and partial Gibbs-potential

As the partition function z'_{mol} depends on the intensive parameters T and $\Delta/2$, the thermodynamic potential associated to z'_{mol} is the free enthalpy, or the Gibbs potential, denoted g. We have

$$g = -k_B T \ln\left(z'_{mol}\right) \tag{19}$$

Let $\langle \widehat{m} \rangle$ be the thermal mean value of the operator $\widehat{\sigma}_1 + \widehat{\sigma}_2$,

$$\langle \widehat{m} \rangle = \langle \widehat{\sigma}_1 + \widehat{\sigma}_2 \rangle \tag{20}$$

For the following $\langle \widehat{m} \rangle$ is called magnetization per molecule. Accordind to the Hamiltonian $\widehat{H}_{sp}$, relation (5), $\langle m \rangle$ is the extensive parameter associated to $\frac{\Delta}{2}$. So we have

$$\langle \widehat{m} \rangle = \frac{\partial g}{\partial \frac{\Delta}{2}} \tag{21}$$

and then

$$\langle \widehat{m} \rangle = \frac{1}{z'_{mol}} \left(\frac{-2e^{\beta\Delta}}{2\sinh(\beta\frac{\hbar\omega_{--}}{2})} + \frac{2r^2 R_{vib}^2 e^{-\beta\Delta}}{2\sinh(\beta\frac{\hbar\omega_{++}}{2})} \right) \tag{22}$$

Let us introduce the parameters a_1, a_2 and a_3 defined by

$$a_1 = \frac{e^{\beta\Delta}}{2\sinh(\beta\frac{\hbar\omega_{--}}{2})} \tag{23}$$

$$a_2 = \frac{2rR_{vib}}{2\sinh(\beta\frac{\hbar\omega_{-+}}{2})} \tag{24}$$

and

$$a_3 = \frac{r^2 R_{vib}^2 e^{-\beta\Delta}}{2\sinh(\beta\frac{\hbar\omega_{++}}{2})} \tag{25}$$

The partition function z'_{mol} can be writen

$$z'_{mol} = a_1 + a_2 + a_3 \tag{26}$$

and the mean value $\langle \widehat{m} \rangle$ is given by

$$\langle \widehat{m} \rangle = \frac{1}{z'_{mol}} \left(-2a_1 + 2a_3\right) \tag{27}$$

From relation (27) we see that the thermal probability to find the system in the quantum state $|-2\rangle$ is

$$P\left(|-2\rangle\right) = P\left(-2\right) = \frac{a_1}{z'_{mol}} \tag{28}$$

Likewise

$$P\left(|2\rangle\right) = P\left(2\right) = \frac{a_3}{z'_{mol}} \tag{29}$$

and

$$P\left(\left|0^{(1)}\right\rangle \text{ and } \left|0^{(2)}\right\rangle\right) = P\left(0\right) = \frac{a_2}{z'_{mol}} \tag{30}$$

We introduce three thermodynamic states : The thermodynamic state (2) that takes into account all the vibration energy levels associated with the eigen value $m = 2$ and likewise the thermodynamic states (0) and (-2).

While z'_{mol} corresponds to the sum $\sum_{(l)} e^{-\beta E_l}$ over all the microscopic states (l) of the molecule, the parameter a_1 corresponds to the sum over all microscopic states for which the eigen value m is equal to -2, the sum is made over the energy levels of the oscillators. For this set of microscopic states one introduce the partial Gibbs potential $g\left(-2\right)$

$$g\left(-2\right) = -k_B T \ln\left(a_1\right) \tag{31}$$

In the same way we define the partial Gibbs potential $g\left(0\right)$ by

$$g\left(0\right) = -k_B T \ln\left(a_2\right) \tag{32}$$

and the partial Gibbs potential $g\left(2\right)$ by

$$g\left(2\right) = -k_B T \ln\left(a_3\right) \tag{33}$$

From the relations (31- 33), we have

$$a_1 = \exp\left(-\frac{g\left(-2\right)}{k_B T}\right) \tag{34}$$

$$a_2 = \exp\left(-\frac{g\left(0\right)}{k_B T}\right) \tag{35}$$

and

$$a_3 = \exp\left(-\frac{g\left(2\right)}{k_B T}\right) \tag{36}$$

We can verify that

$$\frac{\partial g\left(2\right)}{\partial \frac{\Delta}{2}} = 2 \tag{37}$$

$$\frac{\partial g\left(-2\right)}{\partial \frac{\Delta}{2}} = -2 \tag{38}$$

and

$$\frac{\partial g\left(0\right)}{\partial\frac{\Delta}{2}}=0 \tag{39}$$

So the magnetization per molecule in the states (2), (0) and (-2) is equal to 2, 0 and -2, respectively.

The parameters $\frac{\Delta}{2}$ corresponds to the pressure for gas and $\langle\widehat{m}\rangle$ to its volume per molecule.

2.3 Entropy

The entropy related to the Gibbs potential g is

$$s=-\frac{\partial}{\partial T}g \tag{40}$$

So,

$$s=k_B\ln\left(z'_{mol}\right)+k_BT\left(\frac{a_1}{z'_{mol}}\frac{\partial}{\partial\beta}\ln\left(a_1\right)+\frac{a_2}{z'_{mol}}\frac{\partial}{\partial\beta}\ln\left(a_2\right)+\frac{a_1}{z'_{mol}}\frac{\partial}{\partial\beta}\ln\left(a_3\right)\right)\frac{d\beta}{dT} \tag{41}$$

with

$$\frac{\partial}{\partial\beta}\ln\left(a_1\right)=\left(\Delta-\frac{\hbar\omega_{--}}{2}\coth\left(\beta\frac{\hbar\omega_{--}}{2}\right)\right) \tag{42}$$

$$\frac{\partial}{\partial\beta}\ln\left(a_2\right)=\frac{\partial}{\partial\beta}\ln\left(R_{vib}\right)-\frac{\hbar\omega_{+-}}{2}\coth\left(\beta\frac{\hbar\omega_{+-}}{2}\right) \tag{43}$$

$$\frac{\partial}{\partial\beta}\ln\left(a_3\right)=2\frac{\partial}{\partial\beta}\ln\left(R_{vib}\right)-\Delta-\frac{\hbar\omega_{++}}{2}\coth\left(\beta\frac{\hbar\omega_{++}}{2}\right) \tag{44}$$

$$\frac{\partial}{\partial\beta}\ln\left(R_{vib}\right)=p\left(\frac{\hbar\omega_{int}}{2}\coth\left(\beta\frac{\hbar\omega_{int}}{2}\right)-\frac{\hbar\widetilde{\omega}_{int}}{2}\coth\left(\beta\frac{\hbar\widetilde{\omega}_{int}}{2}\right)\right) \tag{45}$$

As

$$\frac{d}{dT}\beta=-\frac{1}{k_BT^2} \tag{46}$$

we obtain

$$s=k_B\ln\left(a_1+a_2+a_3\right)-\frac{k_B}{k_BT}\left(P\left(-2\right)\frac{\partial}{\partial\beta}\ln\left(a_1\right)+P\left(0\right)\frac{\partial}{\partial\beta}\ln\left(a_2\right)+P\left(2\right)\frac{\partial}{\partial\beta}\ln\left(a_3\right)\right) \tag{47}$$

For the state (-2) the entropy is

$$s\left(-2\right)=-\frac{\partial}{\partial T}g\left(-2\right) \tag{48}$$

So

$$s\left(-2\right)=k_{B}\ln\left(a_{1}\right)-\frac{k_{B}}{k_{B}T}\frac{\partial}{\partial\beta}\ln\left(a_{1}\right) \tag{49}$$

Likewise, we have for the state (0) and (2)

$$s\left(0\right)=k_{B}\ln\left(a_{2}\right)-\frac{k_{B}}{k_{B}T}\frac{\partial}{\partial\beta}\ln\left(a_{2}\right) \tag{50}$$

and

$$s\left(2\right)=k_{B}\ln\left(a_{3}\right)-\frac{k_{B}}{k_{B}T}\frac{\partial}{\partial\beta}\ln\left(a_{3}\right) \tag{51}$$

2.4 Enthalpy

The enthalpy related to the Gibbs potential g is given by

$$h=-\frac{\partial}{\partial\beta}\ln\left(z'_{mol}\right) \tag{52}$$

or by

$$g=h-Ts \tag{53}$$

So we obtain

$$h=-\left(P\left(-2\right)\frac{\partial}{\partial\beta}\ln\left(a_{1}\right)+P\left(0\right)\frac{\partial}{\partial\beta}\ln\left(a_{2}\right)+P\left(2\right)\frac{\partial}{\partial\beta}\ln\left(a_{3}\right)\right) \tag{54}$$

For the state (-2) the enthalpy is

$$h\left(-2\right)=-\frac{\partial}{\partial\beta}\ln\left(a_{1}\right) \tag{55}$$

Likewise, we have for the states (0) and (2)

$$h\left(0\right)=-\frac{\partial}{\partial\beta}\ln\left(a_{2}\right) \tag{56}$$

and

$$h\left(2\right)=-\frac{\partial}{\partial\beta}\ln\left(a_{3}\right) \tag{57}$$

2.5 Ensemble of N identical molecules

Let us consider the ensemble of N identical molecules. At equilibrium they are distributed between the three states according to the canonical distribution given by relations (28-30). So there are $N(-2)$ molecules in the state (-2), $N(0)$ in the state (0) and $N(2)$ in the state (-2) with

$$N(-2) = NP(-2) \tag{58}$$

$$N(0) = NP(0) \tag{59}$$

$$N(2) = NP(2) \tag{60}$$

We recall that T and $\Delta/2$ are fixed.

2.5.1 Extensive parameters

Let M be the total magnetization

$$M = N\langle \widehat{m} \rangle \tag{61}$$

From relation (27) we can verify that

$$M = -2N(-2) + 2N(2) \tag{62}$$

So M is the sum of the magnetizations of the three separate states.

Let H be the total enthalpy

$$H = Nh \tag{63}$$

Using equations (54-57) we obtain

$$H = N(-2)\,h(-2) + N(0)\,h(0) + N(2)\,h(2) \tag{64}$$

So H is the sum of the enthalpies of the three separate states.

Let S be the total entropy,

$$S = Ns \tag{65}$$

Using relation (47), we obtain

$$S = Nk_B \ln(a_1 + a_2 + a_3) - \frac{k_B}{k_B T}\left(N(-2)\frac{\partial}{\partial\beta}\ln(a_1) + N(0)\frac{\partial}{\partial\beta}\ln(a_2) + N(2)\frac{\partial}{\partial\beta}\ln(a_3)\right) \tag{66}$$

Let S' be the sum of the entropies of the three separate states. Using relations (49-51) we have

$$\begin{aligned} S' &= k_B \left(N(-2) \ln(a_1) + N(0) \ln(a_2) + N(2) \ln(a_3) \right) \\ &\quad - \frac{k_B}{k_B T} \left(N(-2) \frac{\partial}{\partial \beta} \ln(a_1) + N(0) \frac{\partial}{\partial \beta} \ln(a_2) + N(2) \frac{\partial}{\partial \beta} \ln(a_3) \right) \end{aligned} \quad (67)$$

So, S and S' are not equal and the quantity $S - S'$ is given by

$$S - S' = N k_B \ln(a_1 + a_2 + a_3) - k_B \left(N(-2) \ln(a_1) + N(0) \ln(a_2) + N(2) \ln(a_3) \right) \quad (68)$$

The quantity $S - S'$ corresponds to the entropy of mixing.

2.5.2 Random heat exchanges

At the triple point of a pure substance there are three phases having N_1, N_2 and N_3 molecules. As the Gibbs potentials of the three phases are equal the system is stable and these numbers remain constant. However they can be modified, given P and T, when the molecules receive, in algebraic sense, macroscopic heat and work. The work received is related to volume variation.

In the present study, there are three thermodynamiques states having $N(-2)$, $N(0)$ and $N(2)$ molecules at the same values for $\Delta/2$ and T. But, as the Gibbs potentials of the three states are not equal the system is not stable. These numbers of molecules can and must vary.

It is known that the thermostat randomly exchange heat with the molecules. Let us call δq the heat receive, in algebraic sense, by a molecule. As $\Delta/2$ is constant,

$$\delta q = \delta h \quad (69)$$

where δh is the variation of the enthalpy of the molecule. From relation (53), the variation of the Gibbs potential of the molecule is

$$\delta g = \delta h - T \delta s \quad (70)$$

So

$$\delta g = \delta q - T \delta s \quad (71)$$

We know that when the thermostat gives the quantity of heat δq its entropy varies according to the relation

$$\delta q = -T \ \delta S_{thermostat} \quad (72)$$

So

$$\delta g = -T\left(\delta S_{thermostat} + \delta s\right) \tag{73}$$

So the entropy variation of the total system (thermostat+molecules) verifies the relation

$$\delta S_{thermostat} + \delta s = -\frac{\delta g}{T} \tag{74}$$

From relation (74), this entropy variation is positive when δg is negative. So, if a molecule leaves a state (i) to go in a state (j) $(i, j = -2, 0, 2)$, this process is possible and is an irreversible process if $g\left(j\right)$ is lower than $g\left(i\right)$.

So, for T and $\Delta/2$ fixed, all the molecules are found in the state where the gibbs potential is the smallest. This state is the stable state.

3 Numerical study

3.1 Reduced parameters

We take λ as the unit of elastic force constant and $\hbar\omega_{-\ -}$ as the unit of energy. We then introduce the reduced energy gap

$$\delta = \frac{\Delta}{\hbar\omega_{-\ -}} \tag{75}$$

the reduced temperature

$$t = \frac{k_B T}{\hbar\omega_{-\ -}} \tag{76}$$

and the following reduced parameters

$$x = \frac{\nu}{\lambda} \tag{77}$$

$$zz = \frac{\omega_{int}}{\omega_{-\ -}} \tag{78}$$

$$\widetilde{x} = \frac{\widetilde{\omega}_{int}}{\omega_{int}} \tag{79}$$

3.2 Values of the system parameters

The numerical study is done with $r = 5$, $zz = 1.2$, $\widetilde{x} = 0.9$, $p = 2$, $x = 0.1$.

With the choice $\widetilde{x}$ and x smaller than the unit, the vibration frequencies values are lower when the spin conversion molecules are in the excited level than when they are in the fundamental one.

The value of ω_{--} depends on the mass of a spin conversion molecule, while the value of ω_{int} depends on the mass of a few atoms of a spin conversion molecule. For this reason we take ω_{int} larger than ω_{--} and then $zz > 1$.

The value of the parameter r is $2S + 1$ with $S = 2$.

As R_{vib} is higher than the unit and as ω_{++} is smaller than ω_{--}, the vibrations favour a_3, that is the state (2), while the parameter Δ favours a_1, that is the state (-2).

3.3 Case $\delta = 0.35$

The thermal variations of the probabilities $P(-2)$, $P(0)$ and $P(2)$ for $\delta = 0.35$ are shown in Figure 1. From this Figure, the probabilities $P(-2)$ and $P(2)$ are equal at the temperature value denoted t_3. From relations (28) and (29), the probabilities $P(-2)$ and $P(2)$ are equal when the parameters a_1 and a_3 are equal. So the parameters a_1 and a_3 are equal at t_3. In case $\delta = 0.35$, $t_3 = 0.0367$.

The thermal variations of the partial Gibbs potentials $g(-2)$, $g(0)$ and $g(2)$ for $\delta = 0.35$ are shown in Figure 2. The temperature at which $g(-2)$ and $g(2)$ are equal is t_3 because at this temperature a_1 and a_3 are equal. As shown in Figure 2, the lowest partial Gibbs potential is $g(-2)$ is below t_3 and $g(2)$ above t_3. So all the molecules are in the state (-2) below t_3 and in the state (2) above t_3.

In Figure 2, it should be noted that the partial Gibbs potential $g(0)$ is higher than the partial Gibbs potentials $g(2)$ and $g(-2)$ between t_1 and t_2. In case $\delta = 0.35$, $t_1 = 0.0188$ and $t_2 = 0.0438$.

Following the canonical distribution, $\langle m \rangle$, the magnetization per atom, is given by relation (27). But due to the irreversible process mentioned previously the magnetization per atom is equal to -2 below t_3 and to $+2$ above t_3. So there is a discontinuity in the magnetization per atom at t_3. These results are shown in Figure 3.

Figure 1

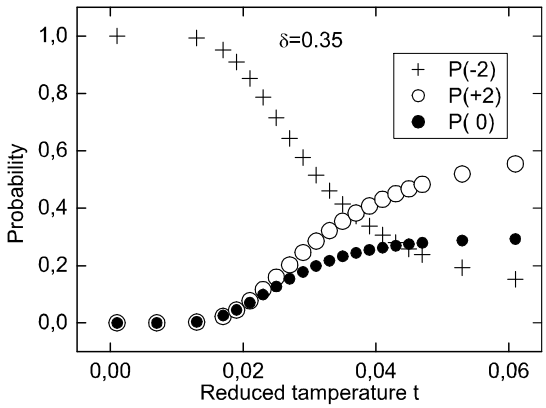

Figure 2

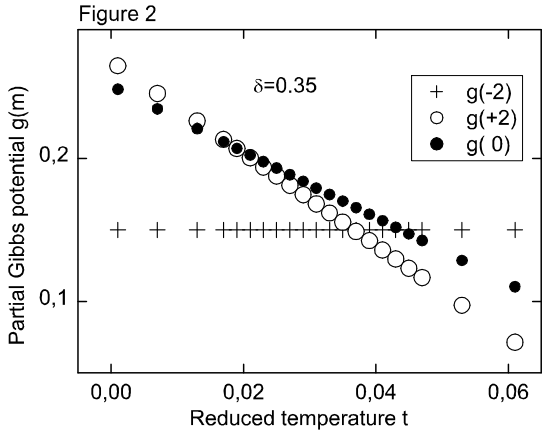

Figure 1. Thermal variations of the probabilities $P(-2)$, $P(0)$ and $P(2)$. The probabilities $P(-2)$ and $P(2)$ are equal at $t_3 = 0.0367$.

Figure 2. Thermal variations of the partial Gibbs potentials $g(-2)$, $g(0)$ and $g(2)$. The Gibbs potentials $g(-2)$ and $g(2)$ are equal at t_3. The Gibbs potential $g(0)$ is higher than $g(-2)$ and $g(2)$ between $t_1 = 0.0188$ and $t_2 = 0.0438$.

Figure 3. Thermal variations of the magnetization per atom. According to the canonical distribution this parameter varies continuously with temperature. But taking into account stable states, this parameter has only two values ± 2.

3.4 Other δ values

The variation with δ of the parameters t_1, t_2 and t_3 are shown in Figure 4. For $\delta = 0.28$, the value of t_3 does not exist. This means that state (2) is the stable state from $t = 0.001$. This result comes from the fact that the energy of vibrations at $0K$ (zero-point energy) is higher than Δ.

For δ values between 0.30 and 0.38 approximately the results are the same as in the case $\delta = 0.35$: the molecules are in the state (-2) below t_3 and in the state (2) above t_3. The t_3 value is between t_1 and t_2.

As shown in Figure 5, for δ values greater than 0.38 the stable state is (-2) at low temperature, (0) above t_4 and finally (2) above t_5. Thus the thermal variation of the magnetization per atom is discontinuous at t_4 and t_5.

Figure 4

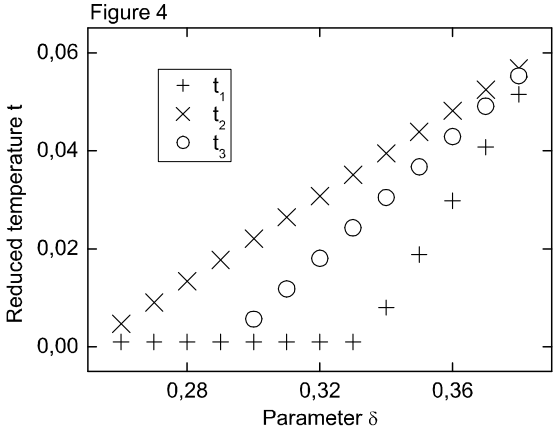

Figure 5

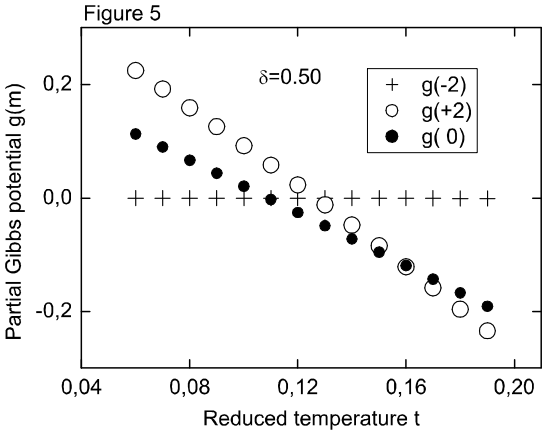

Figure 4. Variations with δ of the parameters t_1, t_2 and t_3. These parameters are defined in Figure 2. The state (2) is the stable state for $t > t_3$.

Figure 5. Thermal variations of the partial Gibbs potentials $g(-2)$, $g(0)$ and $g(2)$ for $\delta = 0.5$. The state (-2) is the stable state between 0.001 and $t_4 = 0.1089$. It is the state (0)between t_4 and $t_5 = 0.1587$ and the state (2) above t_5.

4 Discussion and Conclusion

4.1 Discussion : entropy of mixing

As the molecules are identical the additional entropy, $S - S'$, " does not make physical sense" (see Reif p. 244). If we remove this additional entropy, the Gibbs potential of the system is $N(-2)g(-2) + N(0)g(0) + N(2)g(2)$. It is clear that this Gibbs potential value is higher than the value $Ng(\min)$, where $g(\min)$ is the smallest of the three values $g(-2)$, $g(0)$ and $g(2)$.

4.2 Discussion : about discontinuity

In the case $\delta = 0.35$, the presence of a discontinuity at t_3 leads to the question: is there a first order phase transition at t_3 ? We do not know.

In the case of the van der Waals gas, the first order phase transition is related to the fact that the stability condition [10]

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T \geq 0 \tag{80}$$

is not satisfied. In the above relation, F and V are the free energy and the volume, respectively.

In the present study, we have verified that the stability conditions [11]

$$\left(\frac{\partial^2 g}{\partial T^2}\right)_{\Delta/2} \leq 0 \qquad \left(\frac{\partial^2 g}{\partial \Delta/2^2}\right)_{T} \leq 0 \tag{81}$$

are satisfied.

It is interesting to recall that, to our knowledge, there is no theorem, no theoretical result concerning the size of a system for a first order phase transition.

4.3 Discussion : study around t_3

At t_3, $g(-2)$ and $g(+2)$ are equal and the transition of a molecule between states (-2) and (2) is a reversible process. There is no reason for a molecule that is in state (-2) to go in state (2) and vice versa. Close to t_3 the absolute value $|g(-2) - g(2)|$ is small so the transition of a molecule between states (-2) and (2) is a weakly irreversible process. So, we assume that, around t_3, the time for the molecules to go into the stable state can be very long. This time can be a macroscopic time. Also in an experimental study the molecules could be observed in a state which is not the stable state.

Previously, we have studied the permanent states. Now we will see the transitional states for temperature values close to t_3, in the case $\delta = 0.35$. We use the master equation [10], [12].

4.3.1 Master equation

Let us denote $(1), (2), (3)$ the states $(-2), (0), (2)$, respectively and $P_i(\tau)$, $i = 1, 2, 3$, the probability that the studied molecule is found in state (i) at time τ. With $j = 1, 2, 3$, the master equation is

$$\frac{dP_i}{d\tau} = \sum_{j \neq i} (P_j W_{ji} - P_i W_{ij}) \tag{82}$$

where the parameter W_{ji} is the transition probability per unit time from the state (j) to the state (i). The parameters W_{ji} are positive and depend on the temperature T.

Relation (82) leads to the three differential equations

$$\frac{dP_1(\tau)}{d\tau} = P_2(\tau) W_{21} - P_1(\tau) W_{12} + P_3(\tau) W_{31} - P_1(\tau) W_{13} \tag{83}$$

$$\frac{dP_2(\tau)}{d\tau} = P_1(\tau) W_{12} - P_2(\tau) W_{21} + P_3(\tau) W_{32} - P_2(\tau) W_{23} \tag{84}$$

$$\frac{dP_3(\tau)}{d\tau} = P_1(\tau) W_{13} - P_3(\tau) W_{31} + P_2(\tau) W_{23} - P_3(\tau) W_{32} \tag{85}$$

which are not independent because

$$P_1(\tau) + P_2(\tau) + P_3(\tau) = 1 \tag{86}$$

We will study the functions $P_1(\tau)$, $P_2(\tau)$ and $P_3(\tau)$ for different temperature values between t_1 and t_2. We consider the case where the molecules are heated from a low temperature value . This precision plays a role in the choice of initial conditions, that is the values of the parameters $(P_1)_0$, $(P_2)_0$ and $(P_3)_0$ introduced below.

We assume that the parameter W_{ij}

i) is equal to zero if $g(j) - g(i)$ is positive (impossible process) or equal to zero

$$W_{ij} = 0 \text{ if } g(j) - g(i) \geq 0 \tag{87}$$

ii) is small when $g(j) - g(i)$ is equal to $-\epsilon$, where ϵ is positive and small

$$W_{ij} = \epsilon' \text{ if } g(j) - g(i) = -\epsilon, \ \epsilon \text{ and } \epsilon' \text{ positive and small} \tag{88}$$

4.3.2 General results

With these assumptions W_{12} and W_{32} are equal to zero for any temperature between t_1 and t_2 because $g(2)$ is higher than $g(1)$ and $g(3)$. So, equation (84) becomes

$$\frac{dP_2(\tau)}{d\tau} = -(W_{21} + W_{23}) P_2(\tau) \tag{89}$$

The solution of the equation (89) is

$$P_2(\tau) = (P_2)_0 \exp(-(W_{21} + W_{23})\tau) \tag{90}$$

where $(P_2)_0$ is the initial value of $P_2(\tau)$. The relaxation time of $P_2(\tau)$ is

$$\tau_2 = \frac{1}{W_{21} + W_{23}} \tag{91}$$

As the absolute values $|g(1) - g(2)|$ and $|g(3) - g(2)|$ are large (see Figure 2), we can consider τ_2 as a microscopic time. So the permanent solution $P_2(\tau) = 0$ is achieved quickly.

When $P_2(\tau)$ is equal to zero, the equations (83) and (85) become

$$\frac{dP_1(\tau)}{d\tau} = -P_1(\tau) W_{13} + P_3(\tau) W_{31} \tag{92}$$

$$\frac{dP_3(\tau)}{d\tau} = -P_3(\tau) W_{31} + P_1(\tau) W_{13} \tag{93}$$

with

$$P_1(\tau) + P_3(\tau) = 1 \tag{94}$$

Using (94), equation (92) becomes

$$\frac{dP_1(\tau)}{d\tau} = -(W_{13} + W_{31}) P_1(\tau) + W_{31} \tag{95}$$

and equation (93) becomes

$$\frac{dP_3(\tau)}{d\tau} = -(W_{13} + W_{31}) P_3(\tau) + W_{13} \tag{96}$$

To solve equation (95), we make a change of function [13]. We introduce $Y_1(\tau)$ by

$$Y_1(\tau) = P_1(\tau) - \frac{W_{31}}{W_{13} + W_{31}} \tag{97}$$

We then obtain the equation

$$\frac{dY_1(\tau)}{d\tau} = -(W_{13} + W_{31}) Y_1(\tau) \tag{98}$$

The solution of (98) is

$$Y_1(\tau) = (Y_1)_0 \exp(-(W_{13} + W_{31})\tau) \tag{99}$$

where $(Y_1)_0$ is the initial value of $Y_1(\tau)$. This initial value is related to $(P_1)_0$, the initial value of $P_1(\tau)$, by

$$(Y_1)_0 = (P_1)_0 - \frac{W_{31}}{W_{13} + W_{31}} \tag{100}$$

Finally, between t_1 and t_2, the expression of $P_1(\tau)$ is

$$P_1(\tau) = \left((P_1)_0 - \frac{W_{31}}{W_{13} + W_{31}}\right) \exp(-(W_{13} + W_{31})\tau) + \frac{W_{31}}{W_{13} + W_{31}} \tag{101}$$

and that of $P_3(\tau)$ is

$$P_3(\tau) = \left((P_3)_0 - \frac{W_{13}}{W_{13} + W_{31}}\right) \exp(-(W_{13} + W_{31})\tau) + \frac{W_{13}}{W_{13} + W_{31}} \tag{102}$$

4.3.3 Above and below t_3

For $t \leq t_3$, as $g(3)$ is higher than $g(1)$, W_{13} is equal to zero and relations (101) and (102) become

$$P_1(\tau) = ((P_1)_0 - 1)\exp(-W_{31}\tau) + 1 \tag{103}$$

and

$$P_3(\tau) = (P_3)_0 \exp(-W_{31}\tau) \tag{104}$$

The relaxation time of $P_1(\tau)$ and $P_3(\tau)$ is

$$\tau_{31} = \frac{1}{W_{31}} \tag{105}$$

For a temperature value far from t_3 the absolute value $|g(1) - g(3)|$ is large and this relaxation time is very short, it is a microscopic time. For a temperature value close to t_3 $|g(1) - g(3)|$ is small and this relaxation time is very long, it is a macroscopic time. At t_3 the value of τ_{31} is infinite.

For $t \geq t_3$, as $g(1)$ is higher than $g(3)$, W_{31} is equal to zero and relations (101) and (102) become

$$P_1(\tau) = (P_1)_0 \exp(-W_{13}\tau) \tag{106}$$

and

$$P_3(\tau) = ((P_3)_0 - 1)\exp(-W_{13}\tau) + 1 \tag{107}$$

The relaxation time of $P_1(\tau)$ and $P_3(\tau)$ is

$$\tau_{13} = \frac{1}{W_{13}} \tag{108}$$

For a temperature value far from t_3 the absolute value $|g(3) - g(1)|$ is large and the relaxation time τ_{13} is very short, it is a microscopic time. For a temperature value close to t_3 the absolute value $|g(3) - g(1)|$ is small and this relaxation time is very long, it is a macroscopic time. At t_3 the value of τ_{13} is infinite.

4.3.4 Description of an experimental study

We consider an experiment where the measurements are made at $t_3 - 2\delta t$, $t_3 - \delta t$, t_3, $t_3 + \delta t$ and $t_3 + 2\delta t$. The quantity δt is a small positive variation of the temperature.

We assume that τ_{31} is a microscopic time at the temperature values $t_3 - 2\delta t$ and a macroscopic time for $t_3 - \delta t$. Likewise, we assume that τ_{13} is a macroscopic

time at $t_3 + \delta t$ and a microscopic time at $t_3 + 2\delta$. At t_3 the relaxation times τ_{31} and τ_{13} are infinite.

At $t_3 - 2\delta t$, the value of the function $\exp(-W_{31}\tau)$ is quickly zero and, from relations (103) and (104), the result of the measurement is $P_1(\tau) = 1$ and $P_3(\tau) = 0$ which means that the molecules are in the state(1).

Raise the temperature.

At $t_3 - \delta t$, we assume that the initial values $(P_1)_0$ and $(P_3)_0$ that appear in relations (103) and (104) are the values obtained for $P_1(\tau)$ and $P_3(\tau)$ at $t_3 - 2\delta t$. Also we take $(P_1)_0 = 1$ and $(P_3)_0 = 0$ in relations (103) and (104). As τ_{31} is a macroscopic time the value of the function $\exp(-W_{31}\tau)$ remains close to the unit during the measurement. So the result of the measurement is $P_1(\tau) = 1$ and $P_3(\tau) = 0$ which means that the molecules are in the state(1). The same is true at t_3.

So heating the molecules from a small temperature value they remain in the state (1) until t_3.

Raise the temperature.

At $t_3 + \delta t$, we must use the equations (106) and (107). For the initial values $(P_1)_0$ and $(P_3)_0$ we take the values obtained at t_3, that is $(P_1)_0 = 1$ and $(P_3)_0 = 0$. As the relaxation time τ_{13} is a macroscopic time, the value of the function $\exp(-W_{13}\tau)$ remains close to the unit during the measurement. So the result of the measurement is $P_1(\tau) = 1$ and $P_3(\tau) = 0$. That means that the molecules are still in the state (1) which is no longer the stable state.

Raise the temperature.

At $t_3 + 2\delta t$ we take for the initial values $(P_1)_0$ and $(P_3)_0$ which appear in relations (106) and (107) the values obtained at $t_3 + \delta t$, that is $P_1(\tau) = 1$ and $P_3(\tau) = 0$. But now, as τ_{13} is a microscopic time, the value of the function $\exp(-W_{13}\tau)$ quickly goes to zero and the result of the measurement is $P_1(\tau) = 0$ and $P_3(\tau) = 1$.

Thus the molecules have passed into the stable state (3) not at t_3 but at $t_3 + \delta t$.

We would show in the same way that by cooling the molecules from the temperature $t_3 + 2\delta t$, where they are in the state (3), that they pass into the stable state (1) at $t_3 - \delta t$.

4.4 Conclusion

Thus, the molecules change state at $t_3 + \delta t$ or $t_3 - \delta t$ depending on whether they are heated or cooled. This result should be able to be verified by Monte Carlo

simulations.

It would be interesting to resume this study with three molecules linked by chemical bonds.

In this model the information on the electronic states of the two atoms is transmitted by vibrations. In magnetism the information concerning the quantum states of two spins is transmitted by the overlapping of orbitals.

We would like to thank H. T. Diep for our inspiring discussions and L. Chassagne for his support as director of LISV.

5 Data Availability Statement :

No Data associated in the manuscript

6 References

References

[1] C.N.R. Rao, International Reviews in Physical Chemistry **4** No 1, 19 (1985)

[2] E. König, *Struct. Bonding,* **76**, 51, (1991)

[3] J.-P. Martin, *Mécanisme des Transitions de Spin dans les Composés Moléculaires à l'Etat Solide. Effet de la Dilution de l'Ion Métallique*, Thèse, Université de Paris-Sud, Centre d'Orsay, (1994)

[4] M. Sorai and S. Seki, J. Chem. Solids,(1974), Vol. **35**, pp. 555-570 DOI : 10.1016/S0022-3697(74)80010-7

[5] J. A. Nasser Eur. Phys. J. B **21**, 3 (2001)

[6] Kate L. Ronayne, Hauke Paulsen, Andreas Höfer, Andrew C. Dennis, Juliusz A. Wolny, Aleksandr I. Chumakov, Volker Schünemann, Heiner Winkler, Harmut Spiering, Azzedine Bousseksou, Philipp Gütlich, Alfred X. Trautwein and John J. McGarvey, Phys. Chem. Chem. Phys., (2006), **8**, 4685-4693

[7] J. A. Nasser, S. Topçu, L. Chassagne, A. Bousseksou, T. Guillon, Y. Alayli, Chemical Physics Letters **446** (2007) 385-390

[8] L. Landau et E. Lifchitz, *Physique théorique, tome 1, Mécanique* (Edition Mir Moscou,1982)

[9] A. Bousseksou, J. Nasser, J. Linares, K. Boukheddaden et F. Varret, J. Phys. I, **2**, 1381-1403 (1992)

[10] B. Diu, C. Guthmann, D. Lederer, B. Roulet *Physique Statistique (*Hermann Paris 1989*)*

[11] Herbert B. Callen, *Thermodynamics and an introduction to Thermostatistics* (USA, John Wiley & Sons,1985)

[12] F. Reif, *Fundamentals of statistical and thermal physics (*McGraw-Hill 1965*)*

[13] Gabriel Soum, Raymond Jagut, Pierre Dubouix, *Techniques Mathématiques Pour La Physique-II (*Hachette Livre Paris 1995*)*