

Phase diagram of a pure substance ?

Jamil A. Nasser^a

Laboratoire d'Ingénierie des Systèmes de Versailles (LISV),
EA 4048, CNRS, Université de Versailles Saint Quentin,
45 avenue des Etats-Unis, 78035 Versailles, France

^a e-mail: jamil.nasser@uvsq.fr

April 7, 2020

Abstract

We discuss a two-dimensional model that leads to a phase diagram which reproduces at least qualitatively that of a pure substance. It is known that a spring between two atoms is due to a bond created by the interaction between the electrons of both atoms. Consequently a variation of the quantum state of the electrons involved in the bond can modify the elastic force constant of the spring. That is a kind of atom-phonon coupling.

We consider a square lattice of N identical atoms linked by springs between atoms first and second nearest neighbors. We assume that the elastic force constants of all the springs can vary. The system is studied by using a variational method. First order phase transitions are obtained. The phase diagram of the system displays the features observed in the phase diagram of a pure substance: three thermodynamic phases, three coexistence curves, one triple point and one critical point. Applied pressure can be introduced in the model.

key words: phase transition

1 Introduction

In this study we can reproduce at least qualitatively the features of the phase diagram of a pure substance, that is : three thermodynamic phases, three coexistence curves, one triple point and one critical point. This study is inspired by that of molecules with two electronic energy levels [1].

When there is an electronic bond between two atoms the potential energy of interaction of both atoms $V(r)$ displays a minimum at r_0 , r being the distance between both atoms. The molecule vibrates around this minimum. For

small displacements the vibrations are harmonic. Then, we can say that there is an harmonic spring between both atoms. The force constant of this spring k is the second derivative of $V(r)$ and the vibrational energy varies as \sqrt{k} . In the adiabatic approximation [2, 3], the potential energy $V(r)$ is the sum of the electrostatic repulsion of the nuclei of both atoms and of $E(r)$, one eigenvalue of the electronic Hamiltonian. This electronic Hamiltonian is obtained by neglecting the kinetic energy and the electrostatic repulsion of both nuclei. We neglect the possible variation of r_0 with the eigenvalue. So, for the fundamental level $E_1(r)$, $V(r)$ can be written

$$V(r) = E_1 + \frac{1}{2}k_1(r - r_0)^2$$

and for the first excited level, $V(r)$ can be written

$$V(r) = E_2 + \frac{1}{2}k_2(r - r_0)^2$$

At low temperature the electronic system is in the fundamental energy level E_1 and the force constant is k_1 . Heating the molecule it can pass in an excited level E_2 and the force constant becomes k_2 . If $k_2 < k_1$ the vibrational energy is lower in the excited level than in the fundamental one. Consequently, when the electrons are in the fundamental level the electronic energy is small but the vibrational energy is large while when they are in the excited level the electronic energy is large but the vibrational energy is small. So there is a competition between the electronic interactions which favour the fundamental level and the vibrational interaction which favours the excited one. In solid state this competition can lead to a first order phase transition between the phase where all the molecules are in the fundamental level and that where they are all (or nearly all) in the excited one [4]. The previous discussion made with energy can be made with the free energy.

Let us consider a square lattice of N identical atoms where each atom is linked by springs with its first nearest neighbors and with its second nearest neighbors. Up to now the only case studied is that where the force constant of springs which link two atoms first nearest neighbors can have two values k_1 or k_2 [5, 6]. In this study we are concerned with the case where the force constant of all the springs can have two values.

In Section 2, we present the crystal Hamiltonian and the variational method used to study it. In Section 3, we give the results obtained by numerical calculations and the last Section is devoted to discussion and conclusion.

2 Theoretical study

2.1 Lattice Hamiltonian

Let us consider a square lattice of N identical atoms. Each atom l moves around a lattice point l . The position vector of the lattice point l is

$$\vec{R}_l = l_1 \vec{a}_1 + l_2 \vec{a}_2 \quad (1)$$

where \vec{a}_1 and \vec{a}_2 , the basis vectors of the lattice, are orthogonal and have the same length a_0 , and where $l_1 = 0, 1, 2, \dots, N_1 - 1$ and $l_2 = 0, 1, 2, \dots, N_2 - 1$. So the lattice point l is defined by the set (l_1, l_2) , and we can write $l = (l_1, l_2)$. It is clear that $N = N_1 N_2$.

For studying the atoms movements, we introduce the orthogonal axes \vec{Ox} and \vec{Oy} which are parallel to \vec{a}_1 and \vec{a}_2 , respectively, the origin, O , being at the lattice point $(0, 0)$. We assume that each atom is linked to its first nearest neighbors and to its second nearest neighbors by harmonic springs.

The four first nearest neighbors of the atom $l = (l_1, l_2)$, are the atoms : $l^{(1)} = (l_1 + 1, l_2)$, $l^{(2)} = (l_1, l_2 + 1)$, $l^{(3)} = (l_1 - 1, l_2)$ and $l^{(4)} = (l_1, l_2 - 1)$. We call $e_{ll^{(\alpha)}}$, the elastic force constant of the spring linking the atoms l and $l^{(\alpha)}$, with $\alpha = 1, 2, 3, 4$. The potential energy of the elastic interaction between the atom l and its four first nearest neighbors is $E_{p1}(l)$ given by

$$E_{p1}(l) = \frac{1}{2} (e_{ll^{(1)}} (u_l - u_{l^{(1)}})^2 + e_{ll^{(3)}} (u_l - u_{l^{(3)}})^2 + e_{ll^{(2)}} (v_l - v_{l^{(2)}})^2 + e_{ll^{(4)}} (v_l - v_{l^{(4)}})^2) \quad (2)$$

where u_l and v_l are the components, on the respective axes \vec{Ox} and \vec{Oy} , of the displacement of the atom l around the lattice point l . So, the total elastic interaction between pairs of atoms first nearest neighbors is

$$E_{p1tot} = \frac{1}{2} \sum_{(l)} E_{p1}(l) \quad (3)$$

$\sum_{(l)}$ is the sum over the N lattice points. Periodic boundary conditions are assumed.

The four second nearest neighbors of the atom $l = (l_1, l_2)$ are the atoms: $L^{(1)} = (l_1 + 1, l_2 + 1)$, $L^{(2)} = (l_1 - 1, l_2 + 1)$, $L^{(3)} = (l_1 - 1, l_2 - 1)$ and $L^{(4)} = (l_1 + 1, l_2 - 1)$. We call $\tilde{e}_{l,L^{(\alpha)}}$, the elastic force constant of the spring which links the atoms l and $L^{(\alpha)}$, with $\alpha = 1, 2, 3, 4$. The potential energy of the elastic interaction between the atom l and its four second nearest neighbors is then

$$E_{p2}(l) = \frac{1}{2} (\tilde{e}_{lL(1)} b_{lL(1)} + \tilde{e}_{lL(2)} b_{lL(2)} + \tilde{e}_{lL(3)} b_{lL(3)} + \tilde{e}_{lL(4)} b_{lL(4)}) \quad (4)$$

with

$$b_{lL(1)} = \frac{1}{2} (u_{L(1)} - u_l + v_{L(1)} - v_l)^2 \quad (5)$$

$$b_{lL(2)} = \frac{1}{2} (u_l - u_{L(2)} + v_{L(2)} - v_l)^2 \quad (6)$$

$$b_{lL(3)} = \frac{1}{2} (u_{L(3)} - u_l + v_{L(3)} - v_l)^2 \quad (7)$$

$$b_{lL(4)} = \frac{1}{2} (u_l - u_{L(4)} + v_{L(4)} - v_l)^2 \quad (8)$$

So, the total elastic interaction between pairs of atoms second nearest neighbors is

$$E_{p2tot} = \frac{1}{2} \sum_{(l)} E_{p2}(l) \quad (9)$$

The Hamiltonian of the crystal vibrations is

$$H_{ph} = E_c + E_{p1tot} + E_{p2tot} \quad (10)$$

where E_c is the kinetic energy of the atoms.

Now we introduce the following assumptions :

i) Each atom l contains two electronic subsystems (1) and (2). The electronic subsystem (1) contains the electrons which are involved in the bond between the atom l and its four first nearest neighbors and the electronic subsystem (2) contains the electrons which are involved in the bond between the atom l and its four second nearest neighbors. The electronic subsystem (i) ($i = 1, 2$) has two energy levels separated by Δ_i : the fundamental level, called (a_i) is not degenerated while the excited one, called (b_i) has the degeneracy r_i . To the subsystem (i) is associated the fictitious spin $\hat{\sigma}_{il}$ which has two eigenvalues $\sigma_{il} = \pm 1$. In others words, each subsystem (i) has its own space of quantum states and its physical observable $\hat{\sigma}_{il}$. And we work in the tensorial (or direct) product of both spaces.

The electronic Hamiltonian of the atom l can be written

$$H_e(l) = \frac{\Delta_1}{2} \hat{\sigma}_{1l} + \frac{\Delta_2}{2} \hat{\sigma}_{2l} \quad (11)$$

and the electronic Hamiltonian of the crystal is

$$H_e = \sum_{(l)} \left(\frac{\Delta_1}{2} \hat{\sigma}_{1l} + \frac{\Delta_2}{2} \hat{\sigma}_{2l} \right) \quad (12)$$

ii) The value of the spring constant $e_{ll(\alpha)}$, with $\alpha = 1, \dots, 4$, depends only on the quantum states of the electronic subsystems (1). This spring constant takes three different values λ , μ or ν , following the relation

$$e_{ll(\alpha)} = \frac{\lambda + 2\mu + \nu}{4} + \frac{\nu - \lambda}{4} (\sigma_{1l} + \sigma_{1l(\alpha)}) + \frac{\lambda - 2\mu + \nu}{4} \sigma_{1l} \sigma_{1l(\alpha)} \quad (13)$$

We can verify that the above formula gives $e_{ll(\alpha)} = \lambda$ when $\sigma_{1l} = \sigma_{1l(\alpha)} = -1$, $e_{ll(\alpha)} = \nu$ when $\sigma_{1l} = \sigma_{1l(\alpha)} = +1$ and $e_{ll(\alpha)} = \mu$ when $\sigma_{1l} \neq \sigma_{1l(\alpha)}$. Moreover, we assume that

$$\lambda \geq \mu \geq \nu \quad (14)$$

iii) The value of the spring constant $\tilde{e}_{lL(\alpha)}$, with $\alpha = 1, \dots, 4$, depends only on the quantum states of the electronic subsystems (2). This spring constant takes three different values $\tilde{\lambda}$, $\tilde{\mu}$ or $\tilde{\nu}$, following the relation

$$\tilde{e}_{lL(\alpha)} = \frac{\tilde{\lambda} + 2\tilde{\mu} + \tilde{\nu}}{4} + \frac{\tilde{\nu} - \tilde{\lambda}}{4} (\sigma_{2l} + \sigma_{2L(\alpha)}) + \frac{\tilde{\lambda} - 2\tilde{\mu} + \tilde{\nu}}{4} \sigma_{2l} \sigma_{2L(\alpha)} \quad (15)$$

We can verify that the above formula gives $\tilde{e}_{lL(\alpha)} = \tilde{\lambda}$ when $\sigma_{2l} = \sigma_{2L(\alpha)} = -1$, $\tilde{e}_{lL(\alpha)} = \tilde{\nu}$ when $\sigma_{2l} = \sigma_{2L(\alpha)} = +1$ and $\tilde{e}_{lL(\alpha)} = \tilde{\mu}$ when $\sigma_{2l} \neq \sigma_{2L(\alpha)}$. Moreover, we assume that

$$\tilde{\lambda} \geq \tilde{\mu} \geq \tilde{\nu} \quad (16)$$

Ultimately, H , the Hamiltonian of the crystal is

$$H = E_c + E_{p1tot} + E_{p2tot} + \sum_{(l)} \left(\frac{\Delta_1}{2} \hat{\sigma}_{1l} + \frac{\Delta_2}{2} \hat{\sigma}_{2l} \right) \quad (17)$$

2.2 Reduced parameters

It is interesting to take λ as the unit of elastic force constant and to introduce the sets of reduced parameters (x, y) and (\tilde{x}, \tilde{y}) defined by

$$x = \frac{\nu}{\lambda} \quad (18)$$

$$\tilde{x} = \frac{\tilde{\nu}}{\tilde{\lambda}} \quad (19)$$

$$2\mu = (\lambda + \nu) + y(\lambda - \nu) \quad (20)$$

$$2\tilde{\mu} = (\tilde{\lambda} + \tilde{\nu}) + \tilde{y}(\tilde{\lambda} - \tilde{\nu}) \quad (21)$$

From the relations (14) and (16), the parameters x and \tilde{x} are comprised between 0 and 1, and the parameters y and \tilde{y} must be comprised between -1 and $+1$.

With these new parameters, $e_{l(\alpha)}$ and $\tilde{e}_{lL(\alpha)}$ can be written

$$e_{l(\alpha)} = \lambda (a + b (\sigma_{1l} + \sigma_{1l(\alpha)}) + c \sigma_{1l} \sigma_{1l(\alpha)}) \quad (22)$$

and

$$\tilde{e}_{lL(\alpha)} = \tilde{\lambda} (\tilde{a} + \tilde{b} (\sigma_{2l} + \sigma_{2L(\alpha)}) + \tilde{c} \sigma_{2l} \sigma_{2L(\alpha)}) \quad (23)$$

with

$$a = \frac{1+x}{2} - c \quad (24)$$

$$b = \frac{x-1}{4} \quad (25)$$

$$c = yb \quad (26)$$

and

$$\tilde{a} = \frac{1+\tilde{x}}{2} - \tilde{c} \quad (27)$$

$$\tilde{b} = \frac{\tilde{x}-1}{4} \quad (28)$$

$$\tilde{c} = \tilde{y}\tilde{b} \quad (29)$$

It is worth to notice that the parameters b and \tilde{b} are negative or equal to zero.

2.3 Phonon - atom interaction

By inserting relation (22) in the expression of $E_{p1}(l)$, equation (2), the potential energy E_{p1tot} can be written

$$E_{p1tot} = \frac{1}{4} \lambda a \sum_{(l)} A_l + V_Z + V_{Ex} \quad (30)$$

with

$$A_l = (u_l - u_{l(1)})^2 + (u_l - u_{l(3)})^2 + (v_l - v_{l(2)})^2 + (v_l - v_{l(4)})^2 \quad (31)$$

$$V_Z = \frac{1}{2} \lambda b \sum_{(l)} A_l \sigma_{1l} \quad (32)$$

and

$$\begin{aligned} V_{Ex} = & \frac{\lambda c}{2} \sum_{(l)} ((u_l - u_{l(1)})^2 \sigma_{1l} \sigma_{1l(1)} + (u_l - u_{l(3)})^2 \sigma_{1l} \sigma_{1l(3)} \\ & + (v_l - v_{l(2)})^2 \sigma_{1l} \sigma_{1l(2)} + (v_l - v_{l(4)})^2 \sigma_{1l} \sigma_{1l(4)}) \end{aligned} \quad (33)$$

The energy term V_Z is a Zeeman-like interaction which can be written

$$V_Z = \sum_{(l)} -h_l \hat{\sigma}_{1l} \quad (34)$$

with

$$h_l = -\frac{1}{2} \lambda b A_l \quad (35)$$

As the parameter b is negative, the field-like h_l which acts on the fictitious spins $\hat{\sigma}_{1l}$ favours the eigen value $\sigma_{1l} = +1$. The energy term V_{Ex} is an exchange-like interaction between the fictitious spin $\hat{\sigma}_{1l}$ and its first nearest neighbors $\hat{\sigma}_{1l(\alpha)}$ ($\alpha = 1, \dots, 4$). When the parameter c is positive, this interaction favours the case $\sigma_{1l} = -\sigma_{1l(\alpha)}$ when this parameter is negative this interaction favours the case $\sigma_{1l} = \sigma_{1l(\alpha)}$ and when it is equal to zero, the exchange-like interaction is equal to zero.

For the following we assume

$$y = 0 \quad (36)$$

which implies that the exchange-like interaction V_{Ex} is equal to zero.

By inserting relation (23) in the expression of $E_{p2}(l)$, equation (4), the potential energy E_{p2tot} can be written

$$E_{p2tot} = \frac{1}{4} \tilde{\lambda} \tilde{a} \sum_{(l)} B_l + \tilde{V}_Z + \tilde{V}_{Ex} \quad (37)$$

with

$$B_l = b_{lL(1)} + b_{lL(2)} + b_{lL(3)} + b_{lL(4)} \quad (38)$$

$$\tilde{V}_Z = \frac{1}{2} \tilde{\lambda} \tilde{b} \sum_{(l)} B_l \hat{\sigma}_{2l} \quad (39)$$

and

$$\tilde{V}_{Ex} = \frac{\tilde{\lambda} \tilde{c}}{2} \sum_{(l)} (b_{lL(1)} \sigma_{2l} \sigma_{2L(1)} + b_{lL(2)} \sigma_{2l} \sigma_{2L(2)} + b_{lL(3)} \sigma_{2l} \sigma_{2L(3)} + b_{lL(4)} \sigma_{2l} \sigma_{2L(4)}) \quad (40)$$

As previously, the energy term \tilde{V}_Z is a Zeeman-like interaction. As the parameter \tilde{b} is negative, the field-like which acts on the fictitious spin $\hat{\sigma}_{2l}$ favours the eigenvalue $\sigma_{2l} = +1$. The energy term \tilde{V}_{Ex} is an exchange-like interaction between the fictitious spin $\hat{\sigma}_{2l}$ and its second nearest neighbors $\hat{\sigma}_{2L(\alpha)}$ ($\alpha = 1, \dots, 4$).

When the parameter \tilde{c} is positive, this interaction favours the case $\sigma_{2l} = -\sigma_{2L(\alpha)}$ when this parameter is negative this interaction favours the case $\sigma_{2l} = \sigma_{1L(\alpha)}$ and when it is equal to zero, the exchange-like interaction is equal to zero.

For the following we assume that

$$\tilde{y} = 0 \quad (41)$$

which implies that the exchange-like interaction \tilde{V}_{Ex} is equal to zero.

2.4 Variational method: effective parameters

For the variational Hamiltonian H_0 [7, 8], we take the sum of a phonon Hamiltonian H_{0ph} and of a spin Hamiltonian H_{0sp}

$$H_0 = H_{0ph} + H_{0sp} \quad (42)$$

2.4.1 Variational phonon Hamiltonian H_{0ph}

We introduce two parameters E and \tilde{E} . The first one, E , is an effective spring constant that replaces the spring constants $e_{ll(\alpha)}$, and the second one is an effective spring constant that replaces the spring constants $\tilde{e}_{lL(\alpha)}$. Those E and \tilde{E} do not depend on the electronic states of the subsystems (1) and (2). The phonon Hamiltonian $H_{0ph}(E, \tilde{E})$ is then

$$H_{0ph}(E, \tilde{E}) = E_c + E_{p10}(E) + E_{p20}(\tilde{E}) \quad (43)$$

with

$$E_{p10}(E) = \frac{1}{2} \sum_{(l)} \frac{1}{2} E A_l \quad (44)$$

$$E_{p20}(\tilde{E}) = \frac{1}{2} \sum_{(l)} \frac{1}{2} \tilde{E} B_l \quad (45)$$

The Hamiltonian $H_{0ph}(E, \tilde{E})$ is the Hamiltonian of vibrations of a square lattice of atoms linked by springs between atoms first and second nearest neighbors, the spring constants being E and \tilde{E} , respectively. It is known that there are two dispersion relations

$$\omega = \omega_1(\vec{k})$$

and

$$\omega = \omega_2(\vec{k})$$

which correspond to two acoustic branches of the crystal. In the previous relations the vector \vec{k} is the phonons wave vector. The previous dispersion relations are given in the Appendix.

The free energy associated to the Hamiltonian $H_{0ph}(E, \tilde{E})$ is

$$F_{0ph} = k_B T \sum'_{(\vec{k})} \ln \left(2 \sinh \left(\beta \frac{\hbar \omega(\vec{k})}{2} \right) \right) \quad (46)$$

where k_B is the Boltzmann constant, $\beta = \frac{1}{k_B T}$ and $\sum'_{(\vec{k})}$ is the sum over the

two phonons branches. Using the matrix density of $H_{0ph}(E, \tilde{E})$ the thermal mean values of the parameters A_l and B_l are $\langle A_l \rangle_0$ and $\langle B_l \rangle_0$, respectively. We have

$$\langle A_l \rangle_0 = \frac{4}{N} \sum'_{(\vec{k})} \coth \left(\beta \frac{\hbar \omega(\vec{k})}{2} \right) \frac{\hbar}{2} \frac{\partial \omega}{\partial E} \quad (47)$$

and

$$\langle B_l \rangle_0 = \frac{4}{N} \sum'_{(\vec{k})} \coth \left(\beta \frac{\hbar \omega(\vec{k})}{2} \right) \frac{\hbar}{2} \frac{\partial \omega}{\partial \tilde{E}} \quad (48)$$

where $\frac{\partial \omega}{\partial E}$ and $\frac{\partial \omega}{\partial \tilde{E}}$ are the partial derivatives of the dispersion relations. The expressions of $\frac{\partial \omega}{\partial E}$ and $\frac{\partial \omega}{\partial \tilde{E}}$ are given in the Appendix.

2.4.2 Variational spin Hamiltonian H_{0sp}

We consider the case where the exchange-like interactions V_{Ex} and \tilde{V}_{Ex} are equal to zero. We introduce two fields-like h_1 and h_2 which act over the fictitious spin $\hat{\sigma}_{1l}$ and $\hat{\sigma}_{2l}$, respectively. Those fields-like are uniform.

The spin Hamiltonian H_{0sp} is

$$H_{0sp} = H_{0sp1} + H_{0sp2} \quad (49)$$

with

$$H_{0sp1} = \sum_{(l)} -h_1 \hat{\sigma}_{1l} \quad (50)$$

and

$$H_{0sp2} = \sum_{(l)} -h_2 \hat{\sigma}_{2l} \quad (51)$$

With this spin Hamiltonians, all the fictitious spins of the electronic subsystem i , ($i = 1, 2$), have the same thermal mean value m_i given by

$$m_i = \frac{-\exp(-\beta h_i) + r_i \exp(\beta h_i)}{\exp(-\beta h_i) + r_i \exp(\beta h_i)} \quad (52)$$

Equations (52) are called self-consistent equations.

The free energy related to H_{0sp} is

$$F_{0sp} = -Nk_B T (\ln z_{0sp1} + \ln z_{0sp2}) \quad (53)$$

where the partition function z_{0spi} is given by

$$z_{0spi} = \exp(-\beta h_i) + r_i \exp(\beta h_i) \quad (54)$$

Ultimately the variational Hamiltonian is given by

$$H_0 = E_c + E_{p10}(E) + E_{p20}(\tilde{E}) + \sum_{(l)} -h_1 \hat{\sigma}_{1l} + \sum_{(l)} -h_2 \hat{\sigma}_{2l} \quad (55)$$

The free energy associated with H_0 is given by

$$F_0 = F_{0ph} + F_{0sp} \quad (56)$$

that is

$$F_0 = k_B T \sum_{(\vec{k})}' \ln \left(2 \sinh \left(\beta \frac{\hbar \omega(\vec{k})}{2} \right) \right) - Nk_B T \ln z_{0sp1} - Nk_B T \ln z_{0sp2} \quad (57)$$

At the first order of a perturbation calculation we obtain

$$E = \lambda (a + 2bm_1 + cm_1^2) \quad (58)$$

$$\tilde{E} = \tilde{\lambda} (\tilde{a} + 2\tilde{b}m_2 + \tilde{c} m_2^2) \quad (59)$$

$$h_1 = -\frac{\Delta_1}{2} - \frac{1}{2} \langle A_l \rangle_0 \lambda (b + cm_1) \quad (60)$$

$$h_2 = -\frac{\Delta_2}{2} - \frac{1}{2} \langle B_l \rangle_0 \tilde{\lambda} (\tilde{b} + \tilde{c}m_2) \quad (61)$$

In the present study the parameters c and \tilde{c} are equal to zero.

2.5 Thermodynamic Parameters

The crystal free energy, at the thermodynamic equilibrium, is

$$F = F_0 + N \left(\frac{\Delta_1}{2} + h_1 \right) m_1 + N \left(\frac{\Delta_2}{2} + h_2 \right) m_2 \quad (62)$$

The fraction of atoms in the excited level (b_1) is

$$n_1 = \frac{1 + m_1}{2} \quad (63)$$

and the fraction of atoms in the excited level (b_2) is

$$n_2 = \frac{1 + m_2}{2} \quad (64)$$

When the parameter m_i is equal to -1 , the fraction n_i is equal to zero and the electronic subsystems (i) are in the fundamental level (a_i) and when $m_i = +1$, they are in the excited level (b_i).

By taking the infinitesimal variation of F (eq. 62) we obtain

$$dF = -SdT + Nm_1d\frac{\Delta_1}{2} + Nm_2d\frac{\Delta_2}{2}$$

We can calculate the crystal entropy by using the relation

$$S = -\frac{\partial F}{\partial T} \quad (65)$$

So we obtain

$$S = S_{ph} + S_{sp} \quad (66)$$

with

$$S_{ph} = \frac{1}{T} \sum'_{(\vec{k})} \coth \left(\beta \frac{\hbar\omega(\vec{k})}{2} \right) \frac{\hbar\omega(\vec{k})}{2} - k_B \sum'_{(\vec{k})} \ln \left(2 \sinh \left(\beta \frac{\hbar\omega(\vec{k})}{2} \right) \right) \quad (67)$$

and

$$S_{sp} = Nk_B (\ln z_{0sp1} + \ln z_{0sp2}) - N \frac{1}{T} (m_1 h_1 + m_2 h_2) \quad (68)$$

From the relation

$$F = U - TS \quad (69)$$

we deduce

$$U = \sum'_{(\vec{k})} \coth \left(\beta \frac{\hbar\omega(\vec{k})}{2} \right) \frac{\hbar\omega(\vec{k})}{2} + N \frac{\Delta_1}{2} m_1 + N \frac{\Delta_2}{2} m_2 \quad (70)$$

3 Numerical study

The numerical study consists essentially in solving the self-consistent equations (52) by taking into account the relations (58) to (61). For that, it is interesting to use the reduced parameters previously introduced. Moreover, we take $\hbar\omega_M(\lambda)$ as the unit of energy with

$$\omega_M(\lambda) = 2\sqrt{\frac{\lambda}{m_a}} \quad (71)$$

where m_a is the mass of the atoms. The value of $\hbar\omega_M(\lambda)$ is roughly estimated to $1000K$ or 695 cm^{-1} . With this unit of energy, we introduce the following reduced parameters:

- the reduced temperature t

$$t = \frac{kT}{\hbar\omega_M(\lambda)} \quad (72)$$

- the reduced energy gaps

$$\delta_1 = \frac{\Delta_1}{\hbar\omega_M(\lambda)} \quad (73)$$

and

$$\delta_2 = \frac{\Delta_2}{\hbar\omega_M(\lambda)} \quad (74)$$

- the reduced free energy per atom

$$f = \frac{F}{N \hbar\omega_M(\lambda)} \quad (75)$$

The crystal entropy can then be written

$$s_{mol} = -R \frac{\partial f}{\partial t} \quad (76)$$

for one mole, where R is the gas constant.

3.1 Study of the self-consistent equations

We fix the values of the temperature and that of all the model parameters and we look for the values of m_1 and m_2 which satisfy the self-consistent equations (52). A solution is a set (m_1, m_2) . For each solution we can calculate the values of the crystal free energy f and that of the parameters n_1 and n_2 .

If there is only one solution, this solution is the thermodynamic state of the crystal. If there are several solutions, the free energy values of those solutions must be compared. The solution which has the lowest free energy value is the thermodynamic state of the crystal. When the free energy value of two solutions (m_1, m_2) and (m'_1, m'_2) are equal and are the lowest, both solutions are thermodynamic states of the crystal which then displays a first order phase transition between both thermodynamic states.

At the transition there is an entropy discontinuity, that means that the value of the crystal entropy is not the same for both solutions. The entropy discontinuity is defined by $\Delta S = S' - S$, where S' and S are the values of the entropy for the solutions (m'_1, m'_2) and (m_1, m_2) , respectively. Similarly, the parameters n_1 and n_2 can be discontinuous. The discontinuity in n_i ($i = 1, 2$) is defined by $\Delta n_i = n'_i - n_i$. When the transition temperature increases the magnitudes of those discontinuities decrease. At the critical temperature T_C (or t_C) the magnitudes of those discontinuities are equal to zero. We have used this property for finding the critical temperature value.

3.2 Results

In this study $N_1 = 40$, $N_2 = 50$, $r_1 = r_2 = 4$, $y = \tilde{y} = 0$, $x = 10^{-5}$ and $z = \frac{\tilde{\lambda}}{\lambda} = 0.2$. So, the results depend on the temperature t and on the three parameters δ_1 , δ_2 and \tilde{x} . One can expect that the stable state at very low temperature is $(0, 0)$, that is $(m_1 = -1, m_2 = -1)$ and $(1, 1)$, that is $(m_1 = 1, m_2 = 1)$, at high temperature. Between the brackets, the first number corresponds to the value of n_1 and the second one to that of n_2 .

We have particularly studied the cases where δ_1 is equal to 0.5, 0.7, 0.9 and 1.3.

3.2.1 Thermodynamic phases and discontinuities

When we fix the values of \tilde{x} , δ_1 and δ_2 , the thermal variation of the solutions shows the presence of one or two first order phase transitions depending on whether δ_2 is small or large. When δ_2 is large there are two first order phase transitions at the thermodynamic states A_1 and A_2 . When δ_2 is small there is

one first order phase transition at the thermodynamic states A_3 . Let us call t_1 , t_2 and t_3 the temperature of the states A_1 , A_2 and A_3 , respectively, we have

$$t_2 \geq t_1 \geq t_3 \quad (77)$$

For each thermodynamic state A_1 , A_2 and A_3 there are two stable solutions with the same free energy value (or two thermodynamic states). The thermodynamic states A_1 , A_2 and A_3 are shown in Fig.1. This Figure is obtained with $\delta_1 = 0.5$, $\tilde{x} = 10^{-3}$ and $\delta_2 = 0.6$ and 0.45 . In this Figure the slope of the curves $f(t)$ displays a discontinuity at t_1 , t_2 and t_3 .

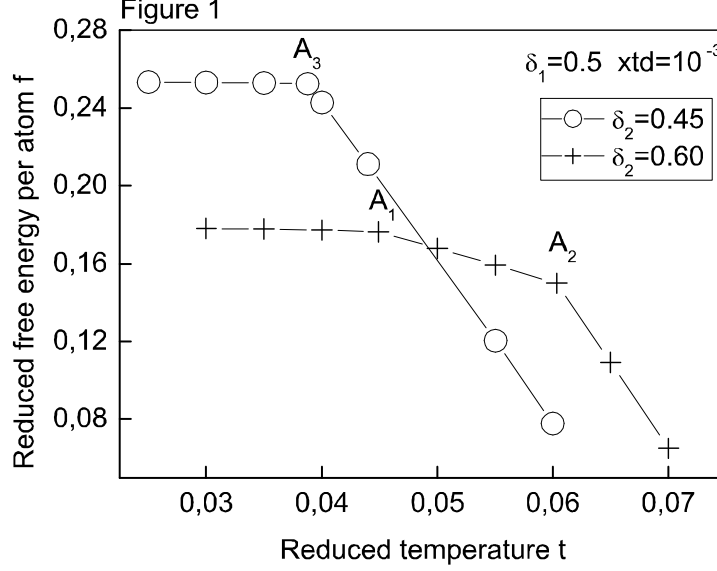
At the thermodynamic state A_1 (or at the temperature t_1) of Fig.1 the two stable solutions are $(0.039, 0.000)$ and $(1, 0.000)$. In the state $(0.039, 0.000)$, the majority of the electronic subsystems (1) and (2) are in their fundamental level (a_1) and (a_2) , respectively. We say that this state belongs to the thermodynamic phase (a, a) . In the state $(1, 0.000)$, all the electronic subsystems (1) are in the excited level (b_1) and all the electronic subsystems (2) are in the fundamental level (a_2) . We say that this state belongs to the thermodynamic phase (b, a) . So, at A_1 there is a first order phase transition between the phases (a, a) and (b, a) . The discontinuity in n_1 is $\Delta n_1 = 0.961$ and that in n_2 is $\Delta n_2 = 0.000$.

At the thermodynamic state A_2 (or at the temperature t_2) of Fig.1 the two stable solutions are $(1, 0.002)$ and $(1, 1)$. The state $(1, 0.002)$ belongs to the phase (b, a) . In the state $(1, 1)$, all the electronic subsystems (1) and (2) are in their excited level (b_1) and (b_2) , respectively. We say that this state belongs to the thermodynamic phase (b, b) . At A_2 there is a first order phase transition between the phases (b, a) and (b, b) . The discontinuity in n_1 is $\Delta n_1 = 0.000$ and that in n_2 is $\Delta n_2 = 0.998$.

For other values of the parameters δ_1 , \tilde{x} and δ_2 , the states which belong to the phase (a, a) are of the form (n_1, n_2) , with n_1 and n_2 lower than 0.5; those which belong to the phase (b, a) are of the form $(1, n'_2)$ and those which belong to the phase (b, b) are of the form $(1, 1)$ or $(1, n''_2)$, with n''_2 near the unit. As for the discontinuities they are $\Delta n_1 > 0.6$ and $\Delta n_2 < 0.2$ at A_1 and $\Delta n_1 = 0$ at A_2 . The value of the discontinuity Δn_2 at A_2 varies but must be equal to zero at the critical point. We have used this property for finding the critical point.

We have verified that the states of the (a, a) phase are stable below t_1 , those of the (b, a) phase are stable between t_1 and t_2 and those of the (b, b) phase are stable above t_2 .

At the thermodynamic state A_3 (or at the temperature t_3) of Fig.1, the two stable solutions are $(0.018, 0.000)$ and $(1, 1)$. So, at A_3 there is a first order phase transition between the phases (a, a) and (b, b) . The discontinuities are



$\Delta n_1 = 0.982$ and $\Delta n_2 = 1$. For other values of the parameters δ_1 , \tilde{x} and δ_2 those discontinuities are always near the unit.

At the states A_1 , A_2 and A_3 of Fig.1, the slope of the curves $f(t)$ displays a discontinuity which corresponds to the discontinuity in the entropy. The approximative values of the slope of the curves are: -0.1901 and -1.6683 at A_1 ; -1.7638 and -8.7084 at A_2 and $-1.0358 \cdot 10^{-4}$ and -7.7855 at A_3 .

To sum up there are three thermodynamic phases (a, a) , (b, a) and (b, b) and three first order phase transitions $(a, a) - (b, a)$, $(b, a) - (b, b)$ and $(a, a) - (b, b)$.

Figure 1. Thermal variation of the reduced free energy per atom. In the Figure, xtd stands for \tilde{x} . The reduced temperatures of the thermodynamic states A_1 , A_2 and A_3 are t_1 , t_2 and t_3 , respectively. The slope of the curves is discontinuous at A_1 , A_2 and A_3 . Consequently the entropy of the crystal is discontinuous at t_1 , t_2 and t_3 .

3.2.2 Triple point

The values of t_1 , t_2 and t_3 vary with the change of δ_2 at fixed values for δ_1 and \tilde{x} . The plot of those values in a diagram (δ_2, t) allows to obtain the phase

diagram of the crystal for δ_1 and \tilde{x} fixed.

The phase diagram for $\tilde{x} = 10^{-3}$ and $\delta_1 = 0.50$ is shown in Fig. 2. In this Figure, the value of t_2 minus that of t_1 , $t_2 - t_1$, is equal to 0.029680 for $\delta_2 = 0.7$ and decreases when the value of δ_2 decreases. There is a value of δ_2 such as t_2 is equal to t_1 . Let us call δ_{2T} this value. Similarly let us call t_T the value of t_1 when t_1 and t_2 are equal. The set (δ_{2T}, t_T) are the coordinates of the triple point T in the diagram (δ_2, t) . The triple point T is a thermodynamic state where the free energy values of three states are equal, one state belonging to the (a, a) phase, another to the (b, a) phase and the last one to the (b, b) phase.

For a given value to δ_1 and \tilde{x} , the crystal displays one first order phase transition for δ_2 lower than δ_{2T} and two first order phases transition for δ_2 larger than δ_{2T} .

In the case of Fig. 2, the coordinates of the triple point are (0.499, 0.044876). In fact, it is difficult to obtain the condition $t_1 = t_2$. We consider that this condition is reached when $t_2 - t_1 \leq 3 \cdot 10^{-4}$. We then take for t_T the value of t_1 and for δ_{2T} the corresponding value of δ_2 .

We have calculated the values of the triple point coordinates δ_{2T} and t_T for different values of δ_1 and \tilde{x} . The results are shown in Fig.3 and Fig.4. The variation of t_T with \tilde{x} is very small, less than one per cent, when \tilde{x} varies from 10^{-3} to 10^{-2} .

Figure 2. The values of t_1 , t_2 and t_3 as functions of the energy gap δ_2 . In the Figure, xtd stands for \tilde{x} . The value of t_2 minus that of t_1 , $t_2 - t_1$, decreases when δ_2 decreases. It is equal to zero at the triple point T . In the Figure the values of δ_1 and \tilde{x} are constant.

Figure 3. Value of the triple point coordinate δ_{2T} as a function of the parameters δ_1 and \tilde{x} . In the Figure xtd stands for \tilde{x} . As shown in the Figure, δ_{2T} decreases when \tilde{x} increases.

Figure 4. Value of the triple point coordinate t_T as a function of the parameters δ_1 and \tilde{x} . In the Figure xtd stands for \tilde{x} . As shown in the Figure, t_T does not depend on \tilde{x} .

Figure 2

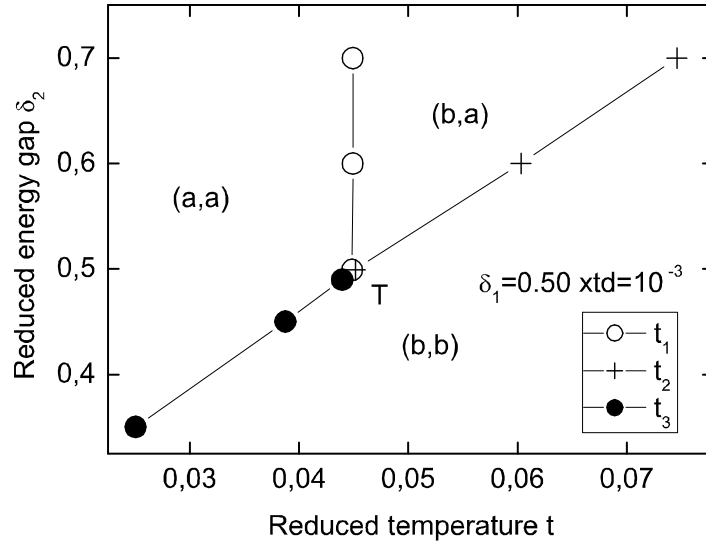
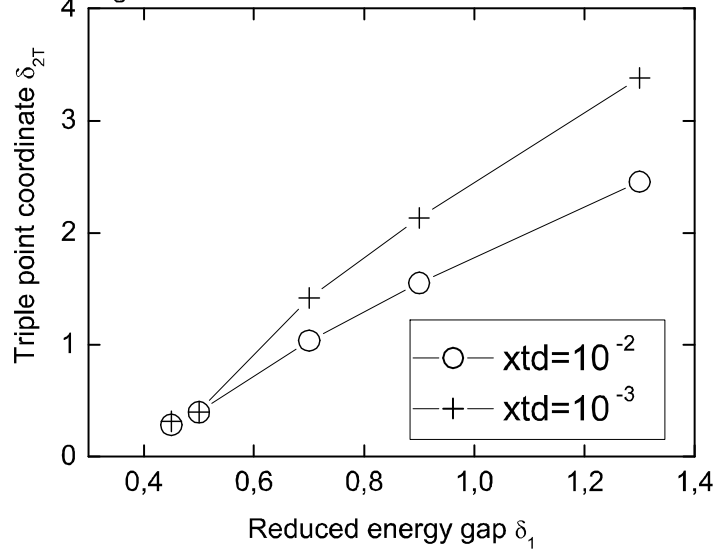
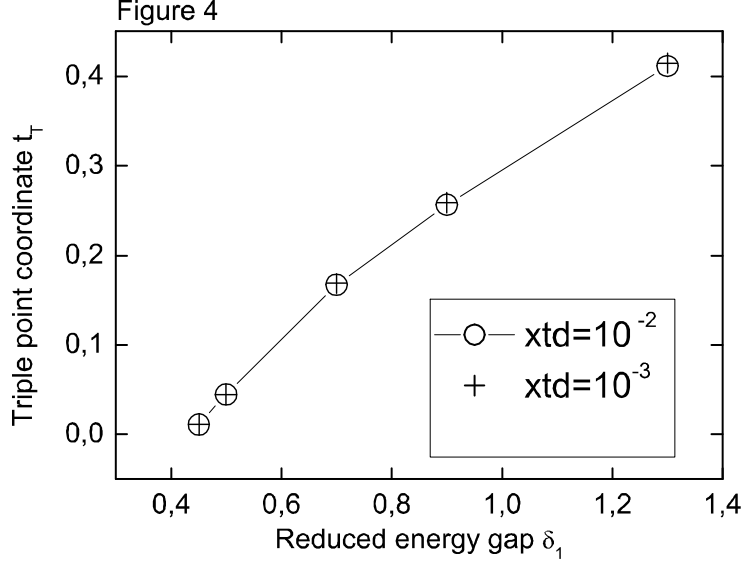


Figure 3



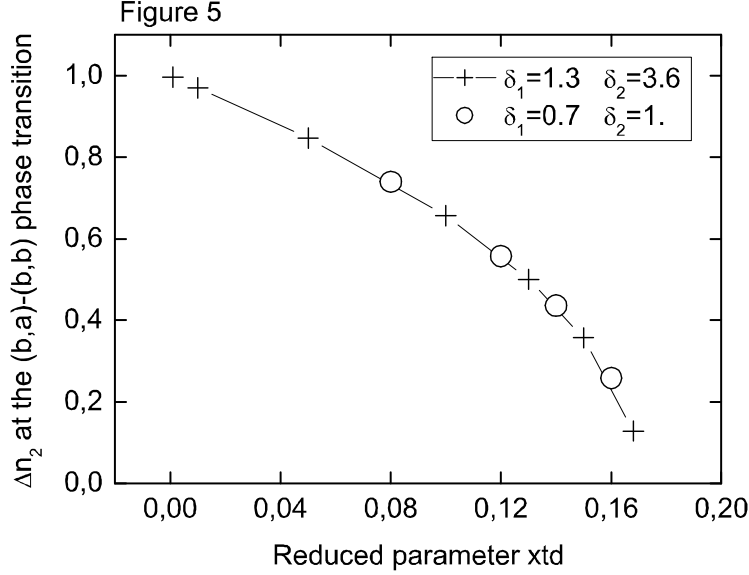


3.2.3 Critical point

In the phase diagram shown in Fig.2, the discontinuity in n_2 along the $(b, a) - (b, b)$ coexistence curve is constant and equal to 0.998 when δ_2 (or t_2) increases. So this phase diagram has not a critical point or this critical point is at infinite.

We have verifies that the discontinuity Δn_2 at A_2 , that is along the $(b, a) - (b, b)$ coexistence curve, does not depend on the values of the parameters δ_1 and δ_2 and depends only on the values of the parameter \tilde{x} . The variations of Δn_2 with the values of \tilde{x} for the sets $(\delta_1 = 0.7, \delta_2 = 1.)$ and $(\delta_1 = 1.3, \delta_2 = 3.6)$ are shown in Fig.5. From this Figure, it is clear that the value of Δn_2 does not depend of the values of the set (δ_1, δ_2) . Moreover, it is clear that there is a value of \tilde{x} for which the discontinuity Δn_2 is equal to zero. This value that we call \tilde{x}_C is, from Fig.5, lower than 0.18. So, for \tilde{x} higher than \tilde{x}_C the first order phase transition $(b, a) - (b, b)$ does not exist for any value of the set (δ_1, δ_2) . That means that for \tilde{x} higher than \tilde{x}_C the temperature t_2 and the state A_2 do not exist, the crystal passes from the phase (b, a) to the phase (b, b) continuously. The value of t_2 for $\tilde{x} = \tilde{x}_C$ is the critical temperature t_C of the crystal. This temperature varies with the values of the set (δ_1, δ_2) .

We can obtain the value of \tilde{x}_C by increasing slowly or continuously the value of \tilde{x} from the value 0.166. This procedure makes difficult to obtain \tilde{x}_C . In Fig.5,



for \tilde{x} equal to 0.166 and 0.169 the discontinuity Δn_2 is equal to 0.170 and 0.102, respectively. Taking into account the difficulty for finding \tilde{x}_C and t_C , we take in this study $\tilde{x}_C = 0.166$. We then can calculate the value of t_C which depends on those of (δ_1, δ_2) . So, for $(\delta_1 = 1.3, \delta_2 = 3.6)$ and $(\delta_1 = 0.7, \delta_2 = 1.)$ t_C is equal to 1.437067 and 0.39268, respectively.

Figure 5. Value of the discontinuity Δn_2 as a function of \tilde{x} . In the Figure xtd stands for \tilde{x} . The discontinuity does not depend on the values of the set (δ_1, δ_2) .

3.2.4 Phase diagram

In order to obtain a phase diagram which presents a critical point we have to take into account different values of the parameter \tilde{x} . The phase diagram of the crystal in the (\tilde{x}, t) diagram for $\delta_1 = 0.8$ and $\delta_2 = 0.7$ is shown in Fig.6. The numbers in the brackets are the values of the discontinuity Δn_2 along the $(b, a) - (b, b)$ coexistence curve.

We call \tilde{x}_T the value of the parameter \tilde{x} for the triple point T . In Fig.6, $\tilde{x}_T = 0.096$ and $t_T = 0.194896$. We know that $\tilde{x}_C = 0.166$. In Fig.6, $t_C = 0.269601$ and t_{1C} , that is the value of t_1 for $\tilde{x} = \tilde{x}_C$ is $t_{1C} = 0.197445$. For $\tilde{x} = 0.18$ we are sure that the temperature t_2 does not exist.

The ratio t_{1C}/t_T is 1.01. That shows that the variation of the temperature of the transition $(a, a) - (b, a)$ between the triple point and the critical point is small. The ratio t_C/t_T is equal to 1.38.

If we want to obtain a phase diagram in the diagram (P, t) , where P is the applied pressure, we must assume that the parameter \tilde{x} varies with the pressure. Assuming a linear relation between P and \tilde{x} , we can write

$$\tilde{x} = \tilde{x}_T + c_{\tilde{x}}(P - P_T) \quad (78)$$

In the above relation P_T is the value of the applied pressure at the triple point and $c_{\tilde{x}}$ is a parameter that we consider as constant.

From Fig.6, we see that if we know Δn_2 we can obtain the correspondent value of \tilde{x} . Consequently, if, by experimental studies, we can obtain the relation between Δn_2 and P , then we can deduce that between \tilde{x} and P . Then we can calculate the values \tilde{x}_T , $c_{\tilde{x}}$ and P_T of relation (78).

Here we introduce an arbitrary unit of Pressure by the relation

$$\text{for } (P - P_T) = 1 \quad \tilde{x} = 0.12 \quad (79)$$

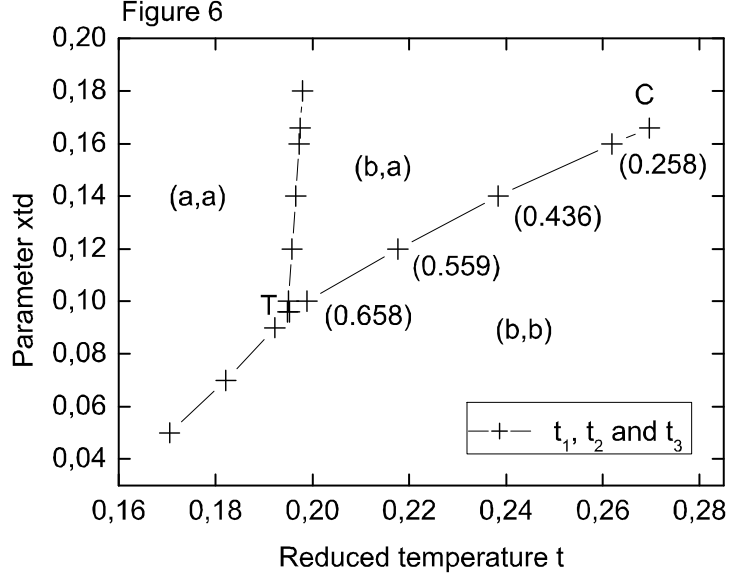
From this relation we deduce $c_{\tilde{x}} = 0.024$. We then can obtain in the (P, t) diagram a phase diagram which looks like that of Figure 6.

Figure 6. Phase diagram of the crystal in the (\tilde{x}, t) diagram for $\delta_1 = 0.8$ and $\delta_2 = 0.7$. In the Figure, xtd stands for \tilde{x} . The number between the brackets is the discontinuity Δn_2 along the $(b, a) - (b, b)$ coexistence curve. This discontinuity is equal to zero at the critical point C .

4 Conclusion

The assumption that in an atom there are two subsystems of electrons with their own space of quantum states leads to very interesting results. This assumption is very often used in physics and in quantum chemistry. As for the results, they have been obtained by using only three parameters of the model δ_1 , δ_2 and \tilde{x} .

In this study we have found that the value of \tilde{x}_C does not depend on that of the set (δ_1, δ_2) . We have given to the parameter z the value 0.2 following the



study of Blackman [9]. It could be interesting to see if the value of \tilde{x}_C depends on that of z .

We have given to the parameter x the value 10^{-5} in order to prevent the presence of a critical point on the $(a, a) - (b, a)$ coexistence curve. This small value of x means that in the (b, a) phase the bonds between an atom and its first nearest neighbors are broken. Indeed, we consider that the electronic bond disappears when the elastic force constant disappears.

In the phase diagram of Fig.6 the parameters δ_1 and δ_2 are constant. We can try to obtain a phase diagram where the three parameters δ_1 , δ_2 and \tilde{x} vary. For that, we can assume that the variations of those parameters are linked to the applied pressure P by the linear relations

$$\delta_1 = \delta_{10} + c_1 P \quad (80)$$

$$\delta_2 = \delta_{20} + c_2 P \quad (81)$$

and

$$\tilde{x} = \tilde{x}_0 + c_{\tilde{x}} P \quad (82)$$

where c_1 , c_2 and $c_{\tilde{x}}$ are constant.

In the Fig.6, the ratio t_C/t_T is equal to 1.38. In the case of the carbon dioxide CO_2 this ratio is near 1.41. Moreover by changing the values of the parameters δ_1 and δ_2 it is possible to obtain very different values for t_C and t_T . In the case of pure substances the values of t_C and t_T are very varied. From those reasons we think that this model can describe the phase diagram of a pure substance. In that case, the phases (a, a) , (b, a) and (b, b) are the solid, liquid and gas phases, respectively. From our results, in the liquid and gas phases all the electronic bond between an atom and its first nearest neighbors are broken while the bonds between an atom and its second nearest neighbors are still present. Concerning the gas phase, this last result is contained in the van der Waals equation.

Acknowledgements

The author would like to thank Antoine-Alexis Nasser for his precious help for improving the quality of the figures.

Author contribution statement

The author has done alone this study and has written alone this manuscript.

APPENDIX

4.1 Phonon dispersion relations for the square lattice

The dispersion relations for the two acoustics branches are

$$\omega_1 = \left(\frac{1}{2} \left(c_1 + c_2 + \sqrt{(c_1 - c_2)^2 + 4c_3^2} \right) \right)^{1/2}$$

$$\omega_2 = \left(\frac{1}{2} \left(c_1 + c_2 - \sqrt{(c_1 - c_2)^2 + 4c_3^2} \right) \right)^{1/2}$$

with

$$c_1 = \frac{2E}{m_a}(1 - \cos k_x a) + \frac{2\tilde{E}}{m_a}(1 - \cos k_x a \cos k_y a)$$

$$c_2 = \frac{2E}{m_a}(1 - \cos k_y a) + \frac{2\tilde{E}}{m_a}(1 - \cos k_x a \cos k_y a)$$

$$c_3 = \frac{2\tilde{E}}{m_a} \sin k_x a \sin k_y a$$

In the above relations, m_a is the atoms mass, a is the distance of the equilibrium positions of the atoms, E and \tilde{E} are the elastic force constants for atoms pairs first neighbors and second neighbors, respectively.

With the boundary periodic conditions, the components k_x and k_y of the wave vectors \vec{k} are

$$k_x = \alpha_x \frac{2\pi}{N_1 a} \quad \text{and} \quad k_y = \alpha_y \frac{2\pi}{N_2 a}$$

with $\alpha_x = 0, \pm 1, \pm 2, \dots, \pm \left(\frac{N_1}{2} - 1\right)$, $\frac{N_1}{2}$ and $\alpha_y = 0, \pm 1, \pm 2, \dots, \pm \left(\frac{N_2}{2} - 1\right)$, $\frac{N_2}{2}$.

The wave vector $\vec{k} (0, 0)$ corresponds to a translation mode. So, there are $N_1 N_2 - 1$ different wave vectors which correspond to phonon frequency values.

The parameters N_1, N_2 and a are defined in the text.

4.2 Calculation of the partial derivatives $\frac{\partial \omega}{\partial E}$ and $\frac{\partial \omega}{\partial \tilde{E}}$

We introduce r by

$$\omega = \sqrt{r}$$

with

$$r = \frac{1}{2} \left((c_1 + c_2) \pm \sqrt{(c_1 - c_2)^2 + 4c_3^2} \right)$$

We can write

$$r = \frac{1}{2} \left(\frac{2E}{m_a} d_1 + \frac{4\tilde{E}}{m_a} d_2 \pm \sqrt{\left(\frac{2E}{m_a}\right)^2 d_3^2 + 4 \left(\frac{2\tilde{E}}{m_a}\right)^2 d_4^2} \right)$$

or

$$r = \frac{E}{m_a} d_1 + \frac{2\tilde{E}}{m_a} d_2 \pm \sqrt{\frac{E^2}{m_a^2} d_3^2 + \frac{4\tilde{E}^2}{m_a^2} d_4^2}$$

where

$$d_1 = 2 - \cos k_x a - \cos k_y a$$

$$d_2 = 1 - \cos k_x a \cos k_y a$$

$$d_3 = \cos k_y a - \cos k_x a$$

$$d_4 = \sin k_x a \sin k_y a$$

So we have

$$\frac{\partial \omega}{\partial E} = \frac{1}{2\omega} \frac{\partial r}{\partial E}$$

with

$$\frac{\partial r}{\partial E} = \frac{1}{m_a} \left(d_1 \pm \frac{E}{m_a} \frac{d_3^2}{\sqrt{\frac{E^2}{m_a^2} d_3^2 + \frac{4\tilde{E}^2}{m_a^2} d_4^2}} \right)$$

and

$$\frac{\partial \omega}{\partial \tilde{E}} = \frac{1}{2\omega} \frac{\partial r}{\partial \tilde{E}}$$

with

$$\frac{\partial r}{\partial \tilde{E}} = \frac{1}{m_a} \left(2d_2 \pm \frac{4\tilde{E}}{m_a} \frac{d_4^2}{\sqrt{\frac{E^2}{m_a^2} d_3^2 + \frac{4\tilde{E}^2}{m_a^2} d_4^2}} \right)$$

For some values of wave vector components (k_x, k_y) the parameter d_4 is equal to zero. In that case the above relations are modified. So, r becomes

$$r = \frac{E}{m_a} d_1 + \frac{2\tilde{E}}{m_a} d_2 \pm \frac{E}{m_a} |d_3|$$

the parameters $\frac{\partial r}{\partial \tilde{E}}$ and $\frac{\partial r}{\partial E}$ become

$$\frac{\partial r}{\partial \tilde{E}} = \frac{d_1}{m_a} \pm \frac{|d_3|}{m_a}$$

and

$$\frac{\partial r}{\partial E} = \frac{2d_2}{m_a}$$

where $|d_3|$ is the absolute value of d_3

References

- [1] J. A. Nasser, Eur. Phys. J. B **91**, 277 (2018)
- [2] A. Messiah, *Mécanique Quantique*, tome 2 (Paris, Dunod, 1960)
- [3] C. Cohen-Tannoudji, B. Diu, Franck Laloë, *Mécanique Quantique*, tome 1 (Paris, Hermann, 1992)
- [4] J. A. Nasser Eur. Phys. J. B **21**, 3 (2001)
- [5] J. A. Nasser, S. Topçu, L. Chassagne, M. Wakim, B. Bennali, J. Linares and Y. Alayli, Eur. Phys. J. B **83**, 115-132 (2011)
- [6] J. A. Nasser, L. Chassagne, Y. Alayli, S. E. Allal, Francisco de Zela, J. Linares, Eur. J. Inorg. Chem., 493 (2018)
- [7] R. Balian, *Microphysics to Macrophysics. Methods and Applications of Statistical Physics* , Vol. 1(Berlin Heidelberg New York, Springer-Verlag, 1991)
- [8] N. Boccara, *Symétries Brisées - Théorie des Transitions avec Paramètre d'Ordre* (Paris, Hermann, 2003)
- [9] M. Blackman, Proc. Roy. Soc. Lond. A **148**, 384 (1935)