

A THERMODYNAMIC APPROACH OF STRUCTURAL SECOND-ORDER PHASE TRANSITION AND THE DISCONTINUITY OF THE SPECIFIC HEAT IN SOLIDS

MELO, Michael¹

PULICI, Angelo Rober²

ABSTRACT

The purpose of this work is simply to present the thermodynamic theory of the structural phase transition in solids. Second-order phase transition will be described in detail as well as the evaluation of entropy and the specific heat of a physical system when undergoing a structural transition. It was found that lowering the temperature from higher temperature (above Curie temperature) the entropy decreases continuously, indicating a decreasing of number of accessible states in this specific thermal condition and structure rearrangement. The specific heat C_p has showed to be discontinuously in T_c and increase linearly with temperature.

Keywords: Structural phase transition. Entropy. Discontinuity of specific heat.

INTRODUCTION

The classical thermodynamic deals mainly with the macroscopic behaviour of the materials. There are relations among physical properties that are established by some thermodynamic laws. In order to understand better the phase transition phenomena and the related effects, it is necessary to employ the concept of free energy, such as thermodynamics functions and potentials, e.g., Gibbs and Helmholtz free energy (LANDAU; LIFSHITZ, 1980). The basic principle is, considering a given specific system with determined number of possible accessible states, the system will tend to occupy the states whose energies are minimum if the internal energy U is as low as possible and the entropy is as high as possible. In the next topic will be

¹ Michael Melo is Bachelor in Physics for USP, with master in Civil Engineering for UNESP and PhD candidate for UNESP at Applied Physics. Currently is professor at Centro Educacional de Votuporanga-Unifev. E-mail: michaeldemelo@hotmail.com

² Angelo Rober Pulici is Bachelor in Physics by Makenzie and is master in Molecular Biophysics for UNESP. Also is professor at Centro Educacional de Votuporanga – Unifev.

presented some relevant physical concepts that are fundamental to describe the phenomenological theory of structural and its consequence ferroelectric phase transitions.

1 ENTROPY AND ENERGY DISTRIBUTION BETWEEN NON-STOCHASTIC SYSTEMS

Consider an isolated system A , whose number of accessible states is Ω_i and these states are related to some constrain. Suppose in moment t' , the constrain associated to the system is removed so the system may access or may not access non accessible states up to the time of restriction removal. In this way, the number of accessible states for $t > t'$ is greater or equal than the number of possible states for $t < t'$. This means that $\Omega_f > \Omega_i$, in which Ω_f is the number of possible states after the constrain removal of the system A , and the probability of occurrence of initial states is given by $P(\Omega_i) = \Omega_i / \Omega_f$. In a structural phase transition of solids, the system undergoes to a changing of its structural arrangement and energy that can be associated to the changing of possible states of the system in a phase transition.

Suppose there are two systems, A and A' , and the number of possible states of the system A is given by $\Omega(E)$, where the energy of the system A is between E and $E + \delta E$. Similarly, for the system A' , we have the number of possible states $\Omega'(E')$ with energy between E' and $E' + \delta E'$. Suppose that both systems are not isolated between them, being able to exchange energy each other. However, the combined system given by $A^0 = A + A'$ is hermetic and isolated, maintaining constant the total energy, i.e., $E^0 = E + E'$. Though the total energy is constant, the energies E and E' are not fixed. Somehow, because the systems are interacting each other, the Hamiltonian of the combined system must have terms of the both isolated systems and one interaction term. Therefore, the total Hamiltonian of the system A^0 is $H^0 = H + H' + H^{\text{int}}$. Worthy to notice that H^{int} can not be null, since this term is responsible for explaining the interaction between the two systems. Thus, we have to consider that the interaction term is much smaller than the sum of the Hamiltonian of the two systems, i.e., $H^{\text{int}} \ll H + H'$ and H^{int} is associated as a perturbation of the combined system A^0 .

The probability of finding the combined system in a state that has energy E for the system A is proportional to the number of possible states with energy between E

and $E + \delta E$ and is also proportional to the number of possible states of the system A' with energy $E^0 - E$, since the system A^0 is a restricted system. As the states are independent, we can infer that the number of possible states of the combined system is given by $\Omega^0(E) = \Omega(E) \cdot \Omega'(E')$ and, consequently, the probability $P(E)$ is given by $P(E) = C \cdot \Omega^0(E) = C \cdot \Omega(E) \cdot \Omega'(E')$ where C is a constant of normalization.

To find the position of maximum probability, or equivalently the position of maximum of its logarithm, we also need to find the value of most probable energy. Therefore, differentiating the logarithm of $P(E)$ with respect to E and equating to zero, we have Equation (1) given by

$$\frac{d \ln P(E)}{dE} = \frac{d}{dE} \ln[C \cdot \Omega(E) \cdot \Omega'(E')] = \frac{d \ln C}{dE} + \frac{d \ln \Omega(E)}{dE} - \frac{d \ln \Omega'(E')}{dE} = 0 \quad (1)$$

where we used the fact that as the derivative is with respect to E , it follows that $dE = -dE'$, from $E = E^0 - E'$. Denoting $\beta(\tilde{E}) = \frac{d \ln \Omega(E)}{dE}$, follows that $\beta(\tilde{E}) = \beta(\tilde{E}')$ where \tilde{E} and \tilde{E}' are the energies of the system A and A' in the maximum of probability. By definition, we have that β has units reciprocal to that of energy. It is convenient introduce the quantity $kT = \beta^{-1}$, in which k is a constant (Boltzmann constant) with units of energy per units of temperature in absolute scale (Kelvin). Thus, follows that and calling $S = -k \ln \Omega(E)$, where S here is defined as entropy, in a differential form we have that $TdS/dE = -1$. Somehow, the condition of maximum probability $P(\tilde{E})$ is expressed as a condition in which the total entropy of the combined system is maximum. This can be expressed by Equation (2)

$$\frac{dS}{dE} - \frac{dS'}{dE'} = 0 \rightarrow \frac{d}{dE} [S + S'] = 0 \quad (2)$$

Summarily, we observed that in a combined system composed by two systems that interact thermally with each other will reach the equilibrium when the total entropy of the system is maximum. This result is rather important to investigate the phase transition in systems due to the fact that systems with symmetric structures pass through a critical point and undergoes structural distortions, changing the accessible states of the perturbed system and altering the entropy of the material (LANDAU; LIFSHITZ, 1980).

2. STRUCTURAL PHASE TRANSITION OF SECOND ORDER AND CRITICAL PHENOMENA

Structural phase transitions (SPT) in crystals between high-symmetry, disordered and low-symmetry or ordered phases have been of much interest of both experimentalist and theoreticians for a time long (SCOTT, 1974). The transition between different modifications of solids is generally affected through a phase transition in which there is a sudden ordering of the crystalline lattice and the material state changes discontinuously. Another type of phase transition in which there is no sudden changing of the lattice, but involving just a change of symmetry, called second-order phase transition (PROYKOVA, et al., 1999). Second order phase transitions occur when a new state of reduced symmetry develops discontinuously from disordered phase at high temperature to ordered phase at low temperature (HOHENBERG; KREKHOV, 2015).

Barium titanate (BaTiO_3) (LETTERS, 1945; HARWOOD; POPPER; RUSHMAN, 1947) is a ferroelectric material that undergoes a phase transition from a symmetric cubic structure at high temperature to a non-symmetric structure as the temperature is lowering, giving the appearance of the ferroelectric state near Curie temperature (MEYERHOFER, 1958). This structural changing undergone by the crystal is performed in a continuously way, from a cubic symmetry to a less-symmetric tetragonal structure, resulting in a continuous structural modification previously denoted as a second-order phase transition.

The breaking symmetry changes abruptly, i.e., discontinuously in the transition point. In any time, it is possible to conclude about the phase that material is found if the structural transition is of first-order. However, while at transition point in first-order transition a material is found in different equilibrium phase states, in a second-order transition the states of both phases are the same (LANDAU; LIFSHITZ, 1980).

Changing in symmetry of a material occurs by atom displacements and, in the transition point, symmetry changings lead to rearrangements in crystal lattice. In order to describe in a quantitatively way the structural transformation in solids when submitted to a second-order phase transition, it is convenient to use an order parameter η . The order parameter η can assume positive and negative values for asymmetric phases and null value for symmetric ones. In a specific symmetric

condition of a crystalline lattice, a changing from the atom positions leads to a breaking symmetry that is represented by η . The dependence of the order parameter with temperature can be seen in Figure 1(a) for second-order transition, 1(b) for second-order transition near first transition and 1(c) for first-order transition.

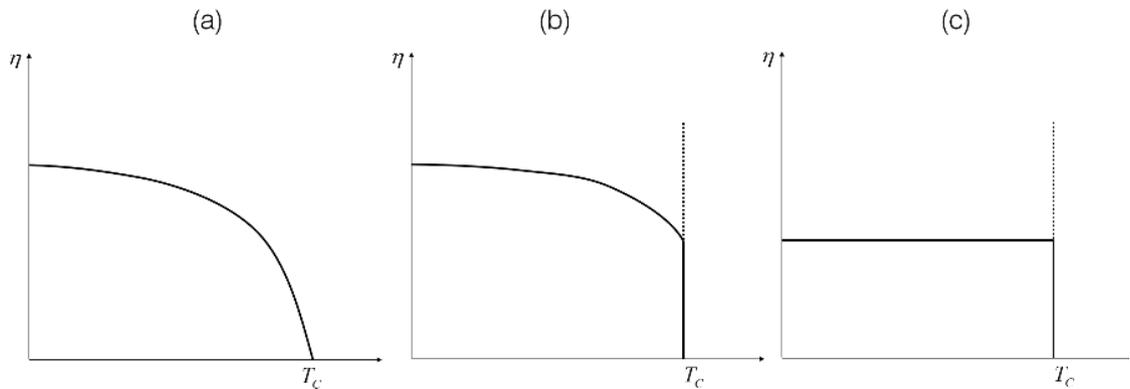


Figure 1: Dependence of order parameter on temperature near phase transition. (a) Second-order transition, (b) second-order transition near a first-order transition and (c) first-order transition.

It is appropriate to bring an example of a breaking symmetry using a bi-dimensional model of a diatomic rhombic crystalline lattice in a symmetric phase. In this lattice, an atom A is fixed in the corners while other atom B is centred between four atoms A. The group of points of the symmetric structure includes the following symmetry operations: $1, \bar{1}, m_1$ and m_2 where 1 and $\bar{1}$ are the identity operator and the inversion center, and m_1 and m_2 are the reflection symmetry operations with respect the axis of the bi-dimensional coordinates (MANDULA; ZWEIG; GOVAERTS, 1983). The relative atom displacement that leads a breaking symmetry can be thought as a changing of the B atom in the direction a_1 , arising a non-null η and remaining only the 1 and m_2 symmetry operations.

The order parameter η can show different sort of dependence on temperature in the transition regions. In a second-order transition, η presents a continuous dependence on temperature, while in the first-order an abruptly behavior is observed (Fig.1). It is rather important to notice that the continuous features of a second-order phase transition results in a continuous characteristic of the thermodynamic functions, such as entropy, energy, volume, pressure, etc. Fig. 1b shows the sudden behavior of η with T_c , presenting a dependence on temperature in the non-symmetric phase with

$\eta \neq 0$. This transition could be a second-order transition if physical parameters as pressure or external field were variable. The main characteristic of this second-order transition is that in the transition point the atoms shift from the original position resulting in a changing of symmetry, being generally called of phase transition of displacement type.

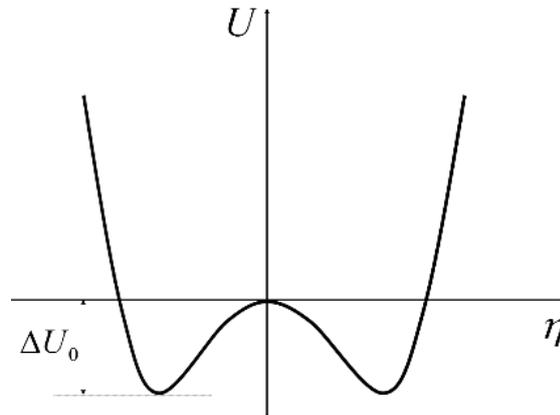


Figure 2: Potential barrier of a solid with respect to the order parameter.

On the other hand, the breaking symmetry can be thought as local probability redistribution of finding atoms in different equilibrium positions in the unit cell. Obviously, when the crystal is in a symmetric phase $\eta = 0$ and consequently, the probability of finding an atom in its original position is maximum. Undergoing a transition from non-symmetric to symmetric phase, the atomic displacements lead to probability redistribution of finding the atoms in a specific position in the crystalline lattice. To energies $\Delta U_0 \ll kT$, the atoms have energy to surpass the potential barrier of the non-symmetric phase (See Figure 2). Here, both $\eta = \eta_0$ and $\eta = -\eta_0$ are equally probable. With decreasing the temperature and when the system has $\Delta U_0 \approx kT$, the phase transition manifests itself as the appearance of probability redistribution of finding the atoms in a specific position in which $\eta = \eta_0$ and $\eta = -\eta_0$. In the transition point, this difference is given by $\eta = \frac{\rho_1 - \rho_2}{\rho_1 + \rho_2}$ in which ρ_1 and ρ_2 are the probability density of finding the atoms of different types in any point of the crystalline lattice. This transition is denoted as order-disorder type and there is no relevant difference between this type of transition and the displacement type. In a symmetrical point of view, there is no distinction between them.

In STP there is not absorption neither emission of heat, i.e., there is no latent heat of phase transformation. However, there are physical quantities that are not changed continuously, being derived from thermodynamic functions, such as specific heat, calorific capacity, coefficient of thermal expansion, compressibility, etc., being discontinuous in the phase transition point (LANDAU; LIFSHITZ, 1980).

3. THE SPECIFIC HEAT DISCONTINUITY

A second-order phase transition is manifest by a discontinuity of the second derivative of the free energy at the transition temperature T_c (Curie temperature) and one of the most important features is also the specific heat discontinuity (LANDAU; LIFSHITZ, 1980; KRASNYTSKA, et al., 2015). A quantitative theory of the second-order phase transition is based on thermodynamic quantities associated to the specific values of η . We can represent any solid by the thermodynamic potential as a function of carried on pressure p , temperature T , and the order parameter η , i.e., $\Phi(p, T, \eta)$. Only p and T can be arbitrarily specified while the order parameter η will depend on the equilibrium thermal conditions in which the thermodynamic potential $\Phi(p, T, \eta)$ is minimum.

In the vicinity of $T \sim T_c$ is expected that η is so closed to the symmetric phase as the non-symmetric one and because there is no abruptly change in the symmetry in a second-order transition, we can infer that $\eta \approx 0$. It is convenient to expand the thermodynamic potential $\Phi(p, T, \eta)$ around $\eta \approx 0$, is given by the Equation (3),

$$\Phi(p, T, \eta) = \Phi_0(p, T) + \alpha\eta + A\eta^2 + B\eta^3 + C\eta^4 + \mathcal{G}(\eta) \quad (3)$$

where the coefficients α , A , B , and C are functions of p and T and $\mathcal{G}(\eta)$ is the term representing higher orders. Taking into account that $\eta = 0$ and $\eta \neq 0$ are related to different phase symmetries the Hamiltonian of the system can not be changed by a simple symmetry operation. As a result, not all terms of the expansion in Eq. (3) are maintained and the potential shall satisfy the condition $\Phi(p, T, \eta) = \Phi(p, T, \eta^*)$ where η^* is an operation symmetries, causing the odd terms to be null.

The coefficient A is easily seen to vanish to zero since at the transition point $\Phi(\eta = 0) = \Phi_0$. For $\eta \neq 0$ at the transition point, we shall have $\Phi(\eta = 0) = \Phi(\eta \neq 0)$, with

$A(p_c, T_c) = 0$. The minimum of $\Phi(p, T, \eta)$ for $\eta \neq 0$ can be obtained by differentiating Eq. 3 with respect to η , that results in Equation (4)

$$\frac{\partial \Phi(p, T, \eta)}{\partial \eta} = \frac{\partial \Phi_0(p, T, \eta)}{\partial \eta} + 2A\eta + 4B\eta^3 = 0 \rightarrow \begin{cases} \eta = 0 \\ \eta^2 = \frac{-A}{2B} \end{cases} \quad (4)$$

For $\eta = 0$ it is also a solution of minimum of the thermodynamic potential in the symmetric phase. However, only in case of $A < 0$, η will have two real possible solutions in which $\Phi(p, T, \eta)$ is minimum. The form of the thermodynamic potential relative to the A signal is presented in Fig. 3.

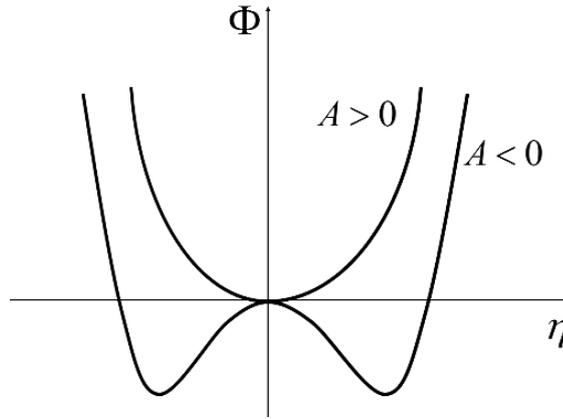


Figure 3: Dependence of $\Phi(p, T, \eta)$ on signal of A .

Rearranging Eq. 3 accordingly to the considerations, the potential has the following form $\Phi(p, T, \eta) = \Phi_0(p, T) + A\eta^2 + C\eta^4$ where $C > 0$. As we can observe in Figure 3, the transitions points are determined by $A(p, T) = 0$. As $A(p, T)$ changes its signal when go through a phase transition, we notice that $A(p, T)$ is continuous and we can expand it as a function of temperature, i.e., $A(p, T) = a(p)(T - T_c)$. Replacing the latter term in Eq. 3, we have that

$$\Phi(p, T, \eta) = \Phi_0(p, T) + a(p)(T - T_c)\eta^2 + C\eta^4 \quad (5)$$

with $C(p) > 0$. Taking advantage of Eq. (4) with the respective replacement of A , we can find the dependence of the order parameter on temperature near transition ($T \approx T_c$) in non-symmetric phase. Then, we have in Equation (6)

$$\frac{\partial \Phi(p, T, \eta)}{\partial \eta} = 2a(p)(T - T_c)\eta_0 + 4C\eta_0^3 = 0. \quad (6)$$

where $a(p) < 0$ for $\eta \neq 0$. The solutions of Equation (6) including $\eta_0 = 0$ are given by Equation (7),

$$\eta_0 = \pm \left(\frac{-a(p)(T - T_C)}{2C} \right)^{1/2}. \quad (7)^*$$

In order to study the specific heat discontinuity, it is necessary to present its relation with thermodynamic potential of a system and the macroscopic thermodynamic variables that represents a specific physical state. It has been shown previously that in a quasi-static infinitesimal process a system is found to increase its total entropy accordingly to relation $dS/dE = 1/T$ where E is the total energy of a system. The total energy dE can be split in internal energy dU and the infinitesimal work done by the system at constant pressure p , given by pdV . In this way, we have that $dU = TdS - pdV$.

In a real experiment with solids that present structural phase transitions generally the thermodynamic variables that are more easily controlled are the temperature and pressure. Therefore, it is convenient to express the internal energy dU as a function of controlled-variables. As and we have that in Equation (8)

$$\begin{aligned} d(ST) &= SdT + TdS \rightarrow TdS = d(ST) - SdT \\ d(pV) &= pdV + Vdp \rightarrow pdV = d(pV) - Vdp. \end{aligned} \quad (8)$$

Replacing the results of Equation (8) in $dU = TdS - pdV$, it is quite appropriate recognize the thermodynamic potential, known as Gibbs free energy, that is given by Equation (9)

$$dU + d(ST) + d(pV) = -SdT + Vdp = d\Phi(p, T). \quad (9)$$

To find the entropy of the system simply differentiate the Gibbs free energy with respect to temperature, maintaining the pressure constant, i.e., $(\partial\Phi/\partial T)_p = -S$. Consequently, we have that

$$\partial_{T,p}\Phi = \partial_{T,p}\Phi_0 + 2a\partial_{T,p}\eta^2(T - T_C) \rightarrow S = S_0 - 2a[(T - T_C)\partial_{T,p}\eta^2 + \eta^2] \quad (10)$$

where $\partial_{T,p}\Phi$ and $\partial_{T,p}\Phi_0$ are $-S$ and $-S_0$, respectively. As $\partial_{T,p}\eta^2 = 2\eta\partial_{T,p}\eta$, finally we have that $S = S_0 - 2a[(T - T_C)2\eta\partial_{T,p}\eta + \eta^2]$. Worthy to notice as the system is in equilibrium the derivate of the Gibbs free energy with respect to order parameter

* It is Worthy to mention that the value of $\eta_0 = 0$ in the symmetric phase is not a value of minimum of the thermodynamic potential, but a value of maximum.

has to be zero, i.e., $\partial_\eta \Phi = 0$ and this implicates that the term containing the temperature derivative of η is zero, because $\partial_\eta \Phi = \partial_T \Phi \cdot \partial_{\eta,p} T = 0$ and necessarily $\partial_T \Phi \neq 0 \propto S$. Finally, the total entropy of the system is given by $S = S_0 - 2a\eta^2$. In the symmetrical phase, $S = S_0$; in the unsymmetrical phase, the entropy is given by Equation (11),

$$S = S_0 - 2a\eta^2 = S_0 + a^2 \frac{(T - T_C)}{C}. \quad (11)$$

At the transition point itself, this expression becomes $S = S_0$ and the entropy is therefore continuous, as it should be (LANDAU; LIFSHITZ, 1980).

Finally, the specific heat discontinuity can be verified, at pressure maintained constant, using that $C_p = T(\partial S / \partial T)_p = T(\partial_{T,p} S)$. Differentiating Eq. 11 with respect to T , we have $C_p = C_{p0} + a^2 T / C$. Consequently, we can observe a discontinuity in the specific heat when the temperature is near T_C , because $C_p(T_C) = C_{p0} + a^2 T_C / C$. Since the value of C is positive, the specific heat is increased at the transition point, and for the symmetrical phase, $S = S_0$ and $C_p = C_{p0}$. Other physical quantities are also discontinuous at the phase transition point, such as specific heat at a constant volume.

CONCLUSION

The main purpose of this work was to describe theoretically the structural phase transition in solids using the thermodynamic approach. It was shown that a phase transition is accompanied by a symmetry breaking when the temperature decreases from above the Curie temperature. It was presented the order parameter can assume two values in which the Gibbs free energy is minimum, indicating a position of unsymmetrical phase is also an equilibrium condition when the system undergoes a phase transition. Moreover, it was found that in a particular system under a quasi-static process, the entropy is always as maximum as possible, and consequently, the entropy in a structural second-order transition is always continuously growing with temperature while the specific heat has a discontinuity near the Curie temperature.

REFERENCES

Harwood, M. G., P. Popper, and D. F. Rushman. "Curie Point of Barium titanate." *Nature*, 1947: 58-59.

Hohenberg, P. C., and A. P. Krekhov. "An introduction to the Ginzburg–Landau theory of phase transitions and nonequilibrium patterns." *Physics Reports*, Apr 2015: 1-42.

Krasnytska, M., B. Berche, Yu. Holovatch, and R. Kenna. "On the discontinuity of the specific heat of the Ising model on a scale-free network." *Condensed Matter Physics*, 2015: 440601:1-4.

Landau, L. D., and E. M. Lifshitz. *Statistical Physics*. 3^a. Vol. 5. 9 vols. Pergamon Press Ltd., 1980.

Letters , Editor. "Crystal Structure of Barium Titanate." *Nature*, 1945: 484-485.

Mandula, Jeffrey E., George Zweig, and Jan Govaerts. "Representations of the rotations reflection symmetru group of the fous-dimensional cubic lattice." *Nuclear Physics*, 1983: 91-108.

Meyerhofer, D. "Transition to the ferroelectric state in Barium Titanate." *Phys. Rev.*, 1958: 1-14.

Proykova, Ana, Rossen Radev, Feng-Yin Li, and Stephen Berry. "Structural transitions in small molecular clusters." *J. Chem. Phys.*, 1999: 1-11.

Scott, J. F. "Soft-mode spectroscopy: Experimental studies of structural phase transitions." *Reviews of Modern Physics*, 1974: 83-125.