Specific heat of the solids to low temperature*

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ABSTRACT. The calculation of the linear term of specific heat of metals is done in the framework where the conduction electrons are bound to their atom, have a trajectory and where only a small zeta fraction are involved in the current flow. The study shows equally that there is a T^3 term attached to the zeta electrons as a result of the disorder of their atoms.

1 Introduction

The study of the specific heat of solids to low temperature dates from the beginning of the twentieth century. The fact that it tends towards zero with the absolute temperature was a serious difficulty in particular for the theory of the free electron, which results in supposing the existence of a constant term. The discovery by Planck of the quantum state to explain the radiation of the black body let believe that the difficulties of interpretation of the specific heat were also related to quantum problems. In fact, as we showed recently, it is the model of the free electron, which is in question. The study of conductivity at low temperature shows that only a weak fraction dzêta of conduction electrons, about 10^{-4}, is temporarily free and from this fact can take part in the current flow [1]. Apart from this weak fraction the conduction electrons must be regarded as localised. The capacity of the electrons zeta to take part in the current flow comes to them from a disordered position, which makes the barrier of potential, i.e. the gap which retains them to their atom, sufficiently weak. These results lead to revisit the study of the specific heat to

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low temperature associated with conduction electrons. Moreover as the electrons of conduction are localised this suggests a similar origin between the term of specific heat of conduction electrons and the lattice term. It is what will show this study.

2 The cohesion.

Let us consider the specific heat of a metal at low temperature. The experiment is well expressed with the relation:

$$C = \gamma T + \alpha T^3 \tag{2.1}$$

The linear term γT is that allotted to the electrons of conduction, the αT^3 term is allotted to the crystal lattice [2,3]. Because of the model of the free electron these two terms are supposed to have quite distinct origins. On the other hand with localised electrons of conduction, which are the outermost of the atom, it is necessary to suppose that thermal energy must be stored by these electrons in the same way as by the electrons which are on the surface of the remainder of the atom i.e. the ion. Indeed the bonds of the electrons with their neighbourhood are the result of interactions between charges of opposed sign, it is not necessary thus to seek two distinct mechanisms of storage of energy according to whether the ion or the electron of conduction is considered. Consequently the calculation of the specific heat of each term α and γ must derive from the same approach.

For better understanding it it is useful to return on the mechanism of bond between the atoms. The atom must be regarded as a whole of inhomogenous directions, the screening constant of the core being variable with the direction considered and time. This property is obvious if we admit the concept of electronic trajectory. It is one of the properties which leads to the assumption of the traditional electronic trajectories if we want to understand the cohesion of the atoms [1,4]. There are thus, for the considered atom, directions with weak screening constant, directions in the vicinity of which the electrons of the neighbouring atoms are subjected to a positive attractive potential. For this reason we will call them the positive directions. There are also directions with strong screening constants, directions in the vicinity of which the electrons of the neighbouring atoms are subjected to a negative potential. This situation occurs when an electron of the considered atom passes in this vicinity. For this reason we will call them the negative directions. Thus in traditional terms the positive directions of an ion attract the greatest number of neighbouring atoms in their negative directions.

On an interval of time very short compared to the periods of the electronic motions this approach makes to play a dissymmetrical role to identical ions and atoms. But the movement of the electrons makes that the screening constants vary in time and transforms a positive direction into negative direction when electrons of the considered atom come to revolve in the vicinity of this direction. We admit that thus identical ions and atoms play identical roles on average in time. The term of cohesion which results from it is developed in the three directions of space. For the compounds of the metal type one can distinguish the ion and the outermost electrons. The ion for these bodies gives birth to the term in T^3 of the specific heat, the outermost electrons give birth at the term in T of the electronic specific heat.

Now for better understanding of the transfers of energy it is interesting to go further in the comprehension of attraction. With the study of the doublets, we introduced the assumption that the electric potential is matter and that there is a continual exchange between the electron and the electric potential considered as the proton itself [5-7]. The density of this matter characteristic of the electric potential is by assumption supposed inversely proportional to the distance which separates the zone from space considered of the center of charge of the proton. A given quantum state corresponds to a number n of quanta of action h to the mechanical meaning of the term. If E is the energy of the state and p the momentum, the quanta of action are the sum, over one period, of the elementary actions Edt or pdl. If the density of matter increases as a result of an external cause to the atom, the energy and the momentum exchanged on the interval {dt, dl} increases. Consequently, to respect the number of quanta of action exchanged over the period, this one and the length of the trajectory decreases. If the majority of the electrons of an atom, as a result of the presence of the neighbouring atoms, have the length of their trajectories which decreases the volume of the atom decreases. It is this phenomenon which is at the origin of attraction between the atoms of a solid. We suppose that it is by this type of mechanism that the energy of translation of the gas, which is the thermal energy of perfect gas, is transmitted to the solid with possibly a transmitting liquid such helium or another liquid gas.

If there are several protons we suppose that the electric potential is the sum of those created by the various protons. We will call center of the atom the barycentre of the positive charges of the atom. Let us suppose then the zone of space considered sufficiently far away from the core of the atom. For an isolated atom the density of matter which is characteristic of the electric potential, can be considered as inversely proportional to the distance which

separates it from the center of the atom. In addition, we suppose that it is possible to consider that its extension is infinite the electric potential tending towards zero with the infinity. When there are several atoms there is between the atoms a minimum of intensity of the electric potential that is of the density of matter which characterizes it. This minimum defines between a given atom and its neighbors a surface of minimum of density of matter or potential. The volume of the atom is consequently contained inside this surface. At the interior of this volume the electric potential is related to the presence of the protons and the electrons of the atom but also with that of the protons and the electrons of the neighbouring atoms. As a result in the positive directions of the neighbouring atoms but inside volume of an atom the electric potential and thus the corresponding density of matter are higher than in the absence of the neighbours.

3 The thermal energy of the solids.

The calculation of the heat capacity of a system consists in determining the thermal energy stored at the temperature considered, then to differentiate this energy with the temperature. Then let us consider a solid which bathes in a gas, it exchanges thermal energy with it (figure 1). If we are with balance, the heat flows entering and outgoing are equal. With each shock the gas atom running up against the surface of the solid stops then goes back. During the interaction with surface it loses or receives thermal energy. This energy is then transmitted gradually to the neighbour atoms. It is distributed thus on the whole of the atoms of the solid. It is useful to stress that the solid loses or receives only energy of translation. Indeed the interactions with the neighbour atoms do not make it possible the solid to store energy of rotation. Thus even if the solid bathes in a liquid or an unspecified gas all occurs as if it bathed in a perfect gas. Indeed the law of perfect gas PV = RT translates the fact that for these atoms the only energy which they have is energy of translation and which there is practically no interaction between them. Thus the only source of thermal energy to consider with respect to the solid is the perfect gas.

At low temperature the atoms of the solid form a whole. The absorbed energy is proportional to its volume. With high temperature the atoms of the solid tend to vibrate independently from each other, the absorbed energy is still proportional to the volume of the solid, but it tends to being proportional to the number of the atoms of the solid: that is 3kT by atom as shows it Dulong and Petit law. As long as the average energy stored by atom is weak in comparison to kT the cohesion of the solid is only little disturbed and the

solid can be regarded as a whole. It is the situation of the solid at low temperature which we suppose respected in this study.

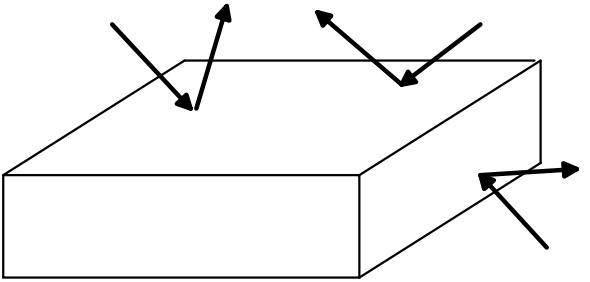

Figure 1. The energy exchanges between the gas and the solid. The arrows symbolize the gas atoms which come to run up against the surface of the solid then go back while having lost or acquired energy.

To calculate the energy of thermal origin of the solid at the temperature T let us consider the time and its role in the exchanges between the solid and perfect gas. It is a significant aspect of the problem which up to now does not seem to have been taken into account. When thermal balance is reached the solid receives from the gas, thermal energy as much than it gives back. As a result the only term to calculate is the received energy U_s. It is du to the fact that between the absorption and the return there is a given time. *It is the time need for the absorbed energy to be returned*, *which is characteristic of the heat capacity of the solid*. Indeed thermal energy continuously moves from one atom to another. There is thus a temporal factor $F(\tau)$ of transfer of this energy of one atom to the other. Compared to gas U_s energy stored by the solid is proportional to the energy of translation transported by each gas atom at the time of the shock, that is to say E. Moreover U_s is also proportional for each energy E to the probability of having atoms of gas with an energy close to E on the segment dE. This probability is proportional to the density of energy of the atoms of gas: either D(E, U) per unit of energy, the average energy being U. In addition the thermal energy absorbed by the solid is proportional to the number of the atoms of the solid. For simplicity we consider only the solids having only one atomic species. One thus has for a molecule gram if N is Avogadro number :

$$U_s = \int_0^{\infty} NEF(\tau)\ D(E,U)dE \tag{3.1}$$

The upper limit of integration is taken equal to infinity because energies likely to limit the field of integration are supposed very large in comparison to the thermal energy E. To calculate U_s it is thus necessary to determine the temporal factor $F(\tau)$.

4 The storage of the energy.

The temporal factor $F(\tau)$ is closely related to the synchronization of the movement of the electrons of bond. To characterize synchronization let us consider in a crystal a chain of atoms of the same chemical species and the same crystallographic site and on each one of them an electron in the same quantum state. To simplify we suppose closed and periodic its movement. For each one of these electrons the period of the associated movement is thus the same one. Maybe in this chain A and B two close atoms and on each one of them e_A and e_B the electron considered (figure 2).

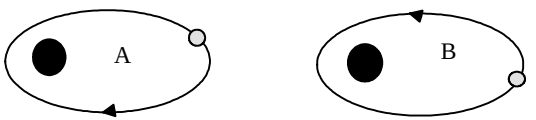

Figure 2. The synchronous motion.

Without disorder at zero degree Kelvin there is correlation between the motions of the conduction electrons in such a way to have the maximum cohesive energy. For example the electron e_A comes between A and B when e_B is as far as possible from e_A. The interaction of the electron e_A with the atom B is thus maximum. The kernel of the atom B thus attracts the electron e_A but the presence of e_B prevents him to leave its atom. In a similar way for e_B with its other neighbour in the same chain and so on. Thus each binding electron is attracted more by the kernel of its own atom than by that of a neighbour. It is the same for all the directions where there are identical chains. There is synchronisation of the motion of the electrons in the same quantum state on an atom of the same chemical species located in the same crystallographic site.

Let us then consider the solid at sufficiently low temperature so that absorbed energy preserves synchronization between the greatest number of homologous electron. Synchronization has a role in the transfer of the energy. Indeed, at the time of the interaction of a gas atom with the wall of the solid,

part of energy of translation of the atom of gas is transferred on one or more electrons from one or more atoms of the solid. Let us consider an electron e_A which absorbed this energy. The binding energy E_ℓ to its atom varies. Synchronization with its neighbors is not respected any more. The electron e_A tends after a certain number of revolutions to pass between the atoms A and B at the same time as e_B. This tendency causes to modify the period of the electron e_B by transfer of energy. Gradually all the electrons homologous with a same site tend to preserve synchronization. So that the tendency to preserve synchronization takes place, it is necessary however that transferred average energy ½kT for a direction remains weak compared to E_ℓ energy.

Thus absorbed energy is propagated. The period of the movement of the electron which transports absorbed energy is inversely proportional to E_ℓ. Consequently the transfer is all the more fast since binding energy E_ℓ is higher, $F(\tau)$ is inversely proportional to E_ℓ. To determine the temporal factor $F(\tau)$ more completely consider a gas atom which runs up against the surface of the solid. Absorbed energy is proportional to the energy E carried by the gas atom. The transfer of this energy on the neighbour atoms is all the more long since this one is significant. The corresponding temporal factor is in consequence of as much longer, we suppose it proportional to E carried energy. Thus we suppose that for each direction of bond, the temporal factor is proportional to carried energy E and inversely proportional to E_ℓ binding energy.

Let us suppose then to simplify that in the three directions of space the binding energies to be considered are the same ones. Like there are three independent directions of bond, the probability of absorption in volume is proportional to the product of the probabilities of absorption in the three directions. The expression (3.1) changes into:

$$U_s = \int_0^\infty N \frac{E^4}{E_\ell^3} D(E,U)dE \tag{4.1}$$

In this expression $D(E,U)$ is the density of probability for an atom of gas of having an energy E with mean energy U the which is equal to ½kT for one direction. This formula is valid only at low temperature when E carried energy by the atoms of gas can be regarded as weak in comparison to E_ℓ and

that consequently the upper limit of integration can be regarded as infinite. The expression of D(E,U) was determined elsewhere [8], we have:

$$\mathrm{D}(E,U) = \frac{\alpha}{A}\left[1+\exp\alpha\left(\frac{E}{U}-1\right)\right]^{-1} \quad \text{with} \quad \alpha = 1{,}5049 \text{ et } A = 1{,}7054 \qquad (4.2)$$

To calculate U_s let us introduce the change of variable $E = xU$. It comes :

$$U_s = N\frac{U^4}{E_\ell^3}\int_0^\infty x^4 D(x)dx \qquad (4.3)$$

with

$$D(x) = \frac{\alpha}{A}\left[1+\exp\alpha(x-1)\right]^{-1} \qquad (4.4)$$

Let us write :

$$J_4 = \int_0^\infty x^4 D(x)dx \qquad (4.5)$$

The calculation gives: $J_4 = 11{,}17$

Like U = ½kT, since it is mean energy in one independent direction, we find well the term in T^4 of the thermal energy of the solids at low temperature which corresponds at the term in T^3 of the specific heat. However it is necessary to associate this term with that γ of the electronic specific heat. Indeed the electrons of conduction correspond to a weak atomic disorder. We called the fraction of the disordered atoms zeta ζ [1]. For these atoms E_ℓ energy is weak compared to that of the ordered atoms. Consequently when the temperature increases the term in T^3 of the atoms zeta appears before that corresponding to the ordered atoms. For this term for an atom gram there are $N\zeta$ atoms which contribute.

Thus :

$$U_s = N\zeta\frac{k^4T^4}{16E_\ell^3}J_4 \qquad (4.6)$$

Let us differentiate with T to get the heat C and let α be the coefficient of the term in T^3. Writing $E_\ell = k\theta_\ell$ we have :

$$C = N\zeta \frac{kT^3}{4\theta_\ell^3} J_4 = \alpha T^3 \tag{4.7}$$

whence :

$$\theta_\ell = \left[\frac{\zeta R J_4}{4\alpha} \right]^{\frac{1}{3}} \tag{4.8}$$

For sodium α = 4,19 mJ/mol-degré^4 and ϕ = 3,1 10^{-4} [1], which gives θ_ℓ = 2,45K. It is a plausible value since the field of validity of term α [9] is for T < 4k. On the other hand if we have consider all the molecule gram taking $\zeta = 1$, like it does the model of Debye, we would have find θ_ℓ = 36,1K which is a too large value compared to field of validity of α. The value of θ_ℓ thus calculated is nothing else than the equivalent in this approach of the temperature θ_D of Debye. In the model of Debye α is given by the relation:

$$\alpha = \frac{234Nk}{\theta_D^3} \tag{4.9}$$

Whence the ratio between θ_D and θ_ℓ :

$$\theta_D = \left[\frac{936}{J_4} \right]^{\frac{1}{3}} \theta_\ell \tag{4.10}$$

or :

$$\theta_D = 4{,}38\ \theta_\ell \tag{4.11}$$

With θ_ℓ = 36,1K one can verify that θ_D (Na) = 158K as quoted in [9].

For metals we know that at low temperatures with the term of specific heat in T^3, it appears a term in T. This property comes from the metal atom in which one can distinguish two parts: electrons of conduction and the remain-

der of the atom which forms the ion, each one of these parts leading to a term of cohesion. It is the ion which gives rise to the term in T^3 we have now to determine the term in T.

5 The heat capacity of the conduction electrons

Let us consider the case of metals. Let us consider the sodium atom. Its electronic structure is $1s^2$, $2s^2$, $2p^6$, $3s^1$. The electron $3s^1$ is the conduction electron which is relatively far away from the electrons $1s^2$, $2s^2$, $2p^6$ which with the nucleus forms the ion. This last is bound in the three directions of space whereas the electron of conduction led to a state of bond with the neighbour atoms mainly in only one direction. It is this aspect of the phenomena which makes it possible to distinguish the specific heat of the conduction electrons to that of the ions.

Now let us consider the term of cohesion which results from the electrons of conduction. These electrons gravitate so as to be bound with the greatest possible number of positive directions of the neighbour ions. In addition they are bound to their atom by a barrier of energy or gap E_g. To some extent they belong to the atom on which they are bound. The gap depends on the considered direction. Indeed an electron all the more easily leaves its atom as its trajectory goes far from the center of the potential. As a result the gap presents a minimum in the direction of the semimajor axis, which is all the more small since the eccentricity of the trajectory is strong. Reciprocally the interaction during a shock or a transfer of energy between electrons will be all the more strong since the direction of the shock or the transfer is close to the semimajor axis. This analysis results in supposing that the conduction electrons primarily store thermal energy in only one direction of space. There we have a situation different from that of the ion which is bound to the solid in the three directions of space. As a result the temporal factor of the expression (3.1) is proportional to E/E_g instead of $(E/E_g)^3$ replacing E_ℓ by E_g.

It remains, as showed to us the study of metallic conductivity, that there are two types of electrons of conduction: those which take part in the the current flow with a very low number and others [1]. We called ζ the ratio of the first on the seconds. For sodium we found $\zeta = 3{,}1\ 10^{-4}$. Let us notice whereas the conduction electrons zeta which take part in the current flow have a gap weaker than their homologous. From this fact the absorbed energy on the surfaces when it is transferred to these atoms remains longer on their atom.

For one gram molecule we have :

$$N_i = \zeta N \tag{5.1}$$

Remplacing E_ℓ by E_g, then as we have seen $(E/E_g)^3$ by E/E_g the thermal energy U_{el} of the conduction electrons is then given by :

$$U_{el} = \int_0^\infty \zeta N \frac{E^2}{E_g} D(E,U)dE \tag{5.2}$$

With the same change of variable $E = xU$ as previously it comes :

$$U_{el} = \zeta N \frac{U^2}{E_g} \int_0^\infty x^2 D(x)dx \tag{5.3}$$

Where *D(x)* is define by the relation (4.4).

Let us write : $$J_{el} = \int_0^\infty x^2 D(x)dx \tag{5.4}$$

The calculation gives : $J_{el} = 1.688$

The energy U to consider is that of the perfect gas with $U = ½kT$. The relation (5.3) becomes :

$$U_{el} = J_{el} \zeta N \frac{k^2 T^2}{4E_g} \tag{5.5}$$

The term of specific heat $C_{el} = \gamma T$ is obtained differentiating U_{el} for T. It comes for the term γ :

$$\gamma = J_{el} \zeta N \frac{k^2}{2E_g} \tag{5.6}$$

That is introducing the temperature T_g with the relation $E_g = kT_g$:

$$\gamma = J_{el}\zeta N \frac{k}{2T_g} \tag{5.7}$$

Knowing γ = 1,38 mJ/mol-degré^2 and $\zeta = 3{,}1\ 10^{-4}$ for sodium we can compare the value of E_g thus calculated with its maximum of 2°K given by the study of the resistivity of sodium between 2°K and 20°K. The calculation gives Tg = 1,58K, that is a satisfactory agreement.

Let us note that the expression of the energy of the outermost electrons which are the conduction electrons in many solids is not specific of conducting state as shows by the experiment [10,11]. In the superconductors with a high critical temperature Tc the term γ exists what is surprising in the traditional approach [12,13]. This property is also observed on the insulating phases like Y_2BaCuO_5. For $BaCuO_2$, the term γ = 150mJ/K^2.mol-Cu.

6 Conclusion

Thus the γT term of the specific heat of the conduction electrons originates in two aspects. It comes on the one hand from that them thermal energy is proportional to that of the atoms of gas. On the other hand from a temporal factor of transfer from one atom to the other of the absorbed energy, which is itself proportional to the thermal energy of the atoms of gas. In addition the electrons zeta which take part in conduction being in small number and disordered, the corresponding ions are themselves disordered. This property implies a term αT^3 corresponding to the zeta electrons.

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