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Calculation of the non-linear relaxational acoustic attenuation in glasses

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Résumé. — L’atténuation acoustique non linéaire de relaxation dans les matériaux amorphes est calculée par une méthode de perturbation. Pour les verres isolants, une saturation de l’atténuation est trouvée. Au contraire, pour les métaux amorphes idéaux, où la relaxation est due aux seuls électrons, une augmentation de l’atténuation est obtenue. Finalement, pour les métaux amorphes réels, où les électrons et les phonons sont simultanément actifs dans le processus de relaxation, les deux comportements précédents peuvent être obtenus, selon la température. La comparaison de ces prédictions avec les résultats expérimentaux montre qu’un processus d’atténuation purement relaxational n’est pas suffisant pour expliquer les faits observés. Un effet plus complexe mettant en jeu à la fois un processus relaxational et un processus résonnant doit être considéré.

Abstract. — The non-linear relaxational acoustic attenuation in amorphous materials is calculated by a perturbation method. A saturation of the attenuation is found for insulating glasses. On the contrary an increase of attenuation is obtained in ideal glassy metals where relaxation is due to electrons only. In the case of real amorphous metals, where both electrons and phonons are active in the relaxation process, the previous two behaviours are obtained, depending on the temperature range. The comparison with experimental results indicates that a purely relaxational attenuation process is not sufficient to explain the observed features. A more complicated mechanism (where both resonant and relaxational processes are present) has to be considered.

1. Introduction.

Glasses exhibit at low temperatures very peculiar thermal and acoustic properties which are quite well explained by assuming the presence in any amorphous material of specific entities, the famous two-level-systems (TLS), whose nature is still unknown. The strong coupling of the TLS with an elastic strain makes acoustic waves a tool very well fitted to the study of these materials. An acoustic wave can interact with the TLS through two different processes: i) in the resonant process, the wave induces transitions between the two levels of the TLS; ii) in the relaxation process, the wave modulates the energy splitting between the two levels. These two processes are actually independent only in the framework of the linear response theory. In all other cases, things are much more complicated. However, surprisingly, the first non-linear effects measured in glasses were very well explained by saturation of resonant attenuation only. Indeed the observation of this effect was one of the most striking arguments in favour of the TLS theory.

Recently an unexpected non-linear effect was observed on the sound attenuation of several metallic glasses [1-6]. This new effect is a challenge since it was shown not to be a saturation of the resonant attenuation (the frequency dependence is not correct) and since the relaxation attenuation was not believed to be saturable. Two possibilities were then offered to explain this phenomenon: i) first by a cross effect between resonant and relaxation processes; this way was explored by Arnold et al. [7]; ii) secondly by a more careful examination of the non-linearities due to the relaxation process only. In a series of articles Galperin et al. [8-10] were the first to consider the latter point of view, a particular case of which has been rigorously solved in our previous paper [11].

This very short review shows that the problem of non-linear acoustic attenuation in glasses is far from being solved. The present article is a further step in the understanding of this complicated question.

In our article we calculate through a perturbation calculation the attenuation coefficient $\alpha$ of an acoustic wave in a glass. This calculation is achieved to the
lowest order (in the acoustic strain $\varepsilon$) necessary to obtain a non-linear effect. We limit ourselves to the purely relaxational process but otherwise we take fully into account the specific properties of glasses.

The organization of the article is as follows. First we recall the necessary basis of the TLS theory and we examine, more carefully than was done above, the articles previously quoted. Then we give our formalism and the main results we have deduced in the case of the relaxational process. Thereafter we present and discuss our numerical data for the cases of metallic and insulating glasses. Finally we discuss our results from the physical and mathematical points of view, and we conclude.

2. Prelude.

The two levels of these mysterious entities characteristic of the amorphous state are taken as the two eigenstates of fictitious spins $S = \frac{1}{2}$ in a biasing magnetic field. Ipso facto, the formalism of the paramagnetic resonance (more exactly the acoustic paramagnetic resonance) can be used.

2.1 STARTING EQUATION. — The Hamiltonian of an isolated TLS interacting with an elastic strain $\varepsilon$ is:

$$\mathcal{H} = \hbar \omega_0 S_z + G \cdot S \cdot \varepsilon + \frac{1}{2!} H \cdot S \varepsilon^2 + \ldots$$

(1)

The first term (the « Zeeman » term) is the Hamiltonian of the TLS when no strain is applied. The other terms are the beginning of an expansion in increasing powers of $\varepsilon$. The vectorial coefficients $G, H, \ldots$ are constants. By a convenient choice of the quantization axes (the rotation around the Z axis is free) the $Y$-component of one of these vectors can be put equal to zero without loss of generality. The usual choice is $G_Y = 0$.

We note that the quantization axes $X, Y, Z$, do not depend on the strain $\varepsilon$ and consequently even if $\varepsilon$ depends on time they are time-independent.

We also note that the tensorial character of the strain is omitted here ; it will be taken into account by simply adding a polarization index $\tau$ (if $\tau = l$ or $t$ for compressional or shear waves respectively).

In what follows we use the same symbol $S$ for both the vectorial operator and its mean value. Using Ehrenfest’s equation, the evolution equation of $S$ is deduced:

$$\frac{dS}{dt} = i [\mathcal{H}, S]$$

(2)

where $\mathcal{L} = \mathcal{L}_{\varepsilon} (\varepsilon)$ is an antisymmetric $(3 \times 3)$ operator which gives the Larmor precession of $S$. In order to have a more realistic description of the spin evolution the relaxation phenomenon must be included. When this is done the Bloch equation is obtained

$$\frac{dS}{dt} = i [\mathcal{H}, S] - T (S - S_{eq})$$

(3)

where $S_{eq} = S_{eq} (\varepsilon)$ is the equilibrium value of $S$ when the strain $\varepsilon$ is applied. $T = T (\varepsilon)$ is a symmetric $(3 \times 3)$ operator with three positive eigenvalues, $T_2$ (twice) and $T_1$. In the usual language of the Bloch equation, $T_2$ is the transverse relaxation rate while $T_1$ is the longitudinal relaxation rate (the inverse of the spin-lattice relaxation time $T_1$). We neglect $T_2$ which is not necessary for our purpose.

On the contrary, the exact form of the relaxation rate $T_1$ is of central interest. It is given in the following section.

2.2 A MODEL FOR THE TLS. — A TLS is often seen as a particle tunneling between the two minima of a double well potential. We briefly recall the main lines of this model. More details can be found in many papers [12-15]. If we call $\Delta$ the asymmetry of the potential and $\Delta_0$ the tunnelling energy, the energy splitting of the TLS is

$$\hbar \omega_0 = 2 E = 2 \sqrt{\Delta^2 + \Delta_0^2}$$

(4)

The parameters $\Delta$ and $\Delta_0$ both depend, in principle, on the strain $\varepsilon$. However the variation of $\Delta_0$ is practically negligible compared to that of $\Delta$. Let $\Delta_1$ be the value of $\Delta$ when a strain is applied. (The index $s$ stands for strained).

We are now able to calculate the Hamiltonian of the strained TLS as defined in equation (1). For the sake of simplicity we only keep in (1) the term linear in $\varepsilon$. We set this as rule. This rule indeed, eliminates a cause of non-linearities, but we must keep in mind that the same hypothesis is currently used when the saturation of resonant attenuation is calculated [16, 17]. Under these conditions the two coefficients $G_X$ and $G_Z$ are equal to

$$G_X = 2 \frac{\Delta_0}{E}, \quad G_Z = \frac{2 \Delta}{E} \quad \text{with} \quad \gamma = \frac{\partial \Delta}{\partial \varepsilon} \bigg|_{\varepsilon = 0}$$

(5)

It is important to notice that the values of $\Delta$ and $E$ in equation (5) are the unstrained values. With the linearized Hamiltonian the half-energy splitting of the strained TLS is equal to

$$E_s = \sqrt{\left( E + \frac{G_{x}\varepsilon}{2} \right)^2 + \left( \frac{G_{x}\varepsilon}{2} \right)^2}$$

Every unstrained TLS is characterized by a couple of parameters : either $\Delta$ and $\Delta_0$, or $E = \sqrt{\Delta^2 + \Delta_0^2}$ and $r = \left( \frac{\Delta_0}{E} \right)^2$. The last two are easier to handle.

The values of these parameters are distributed. A distribution function $P(E, r)$ takes this feature into account

$$P(E, r) = \frac{A}{2 r \sqrt{1 - r}}$$

(6)
where \( A \) is the normalization constant. The total number of TLS per unit volume (all energies included) is \( N \). Even strained, every TLS is labelled by the pair of unstrained parameters \( E \) and \( r \).

When the TLS population is driven out of its thermal equilibrium it can relax if it is in contact with a thermostat. In an insulating glass the phonon bath is the thermostat. The relevant coupling Hamiltonian is

\[
\mathcal{H} = \sum_{q, \tau} G_{X, \tau} S_X \epsilon_{q, \tau}^{th}, \tag{7}
\]

where \( \epsilon_{q, \tau}^{th} \) is the thermal strain produced by the phonon mode \( q, \tau \); \( q \) is the wavevector and \( \tau \) is an index giving the phonon polarization \( (\tau = l \text{ or } t) \).

The resulting relaxation rate is:

\[
\Gamma_{li}^{ph} = \frac{k^3}{\pi \hbar} \rho \sum_{\tau} V_r^3 F_3(\beta E_s), \tag{8a}
\]

or

\[
\Gamma_{li}^{th} = r K_3 T^3 F_3(\beta E_s), \tag{8b}
\]

with

\[
F_3(x) = x^3 \coth x, \tag{8c}
\]

\( \rho \) is the mass density; \( V_r \) is the sound velocity for polarization \( \tau \) and

\[
K_3 = \frac{4}{\pi \hbar^4} \sum_{\tau} \frac{\gamma_r^2}{\rho V_r^3}. \tag{9}
\]

It may be useful to recall that in equation (8a) the coupling coefficients \( G_{X, \tau} \) are functions of the unstrained parameters (see Eq. (5)) while in function \( F_3(\beta E_s) \) it is the strained half-energy \( E_s \) which appears. In metals, electrons constitute a supplementary thermostat. The coupling Hamiltonian is

\[
\mathcal{H}'' = \frac{1}{N} \sum_{q, \sigma, q'} V_X S_X a_{q, \sigma}^+ a_{q', \sigma}, \tag{9}
\]

where \( N \) is the number of electrons and \( a_{q, \sigma}^+ \) (resp. \( a_{q, \sigma} \)) is the annihilation (resp. creation) operator for an electron of wavevector \( q \) (resp. \( q' \)) and spin component \( \sigma \). This elementary process is the scattering of an electron from the state \( q, \sigma \) to the state \( q', \sigma \) without changing its spin component. The resulting relaxation rate is:

\[
\Gamma_{li}^{el} = \frac{\pi k}{2 \hbar} \left( \frac{\rho}{V_X} \right)^2 T F_1(\beta E_s), \tag{10a}
\]

or

\[
\Gamma_{li}^{el} = r K_1 T F_1(\beta E_s), \tag{10b}
\]

with

\[
F_1(x) = x \coth x, \tag{10c}
\]

where \( \rho \) is the electronic density of states at the Fermi level and

\[
K_1 = \frac{2 \pi k}{\hbar} \left( \frac{\rho}{E} \right)^2. \tag{11}
\]

Similarly to the coefficient \( G_X \) of equation (5), the coupling coefficient \( V_X \) has been written:

\[
V_X = 2 \omega \frac{A_0}{E}, \tag{11}
\]

\( n = 3 \) for phonons and \( n = 1 \) for electrons. In the framework of the linear response theory, \( E_s = E \) and it is licit to write

\[
\Gamma_1 = \frac{K_n}{k^n} \Delta_0^2 E_s^{n-2} \coth(\beta E). \tag{12}
\]

On the contrary in the non-linear case this is forbidden. Of course, in a real metal the two relaxation rates \( \Gamma_{li}^{ph} \) and \( \Gamma_{li}^{el} \) must be added. Other processes (Raman process, etc) are not considered here as they imply higher order mechanisms.

2.3 ON THE NON-LINEARITIES OF THE BLOCH EQUATION. — There are many reasons for equation (3) to be non-linear.

First the Hamiltonian (1) is generally non-linear in \( \epsilon \) and so is the Larmor operator \( L \). However, as seen above, we limit our calculation to the case of a linear coupling.

Second, another non-linearity originates in the \( \epsilon \)-dependence of the equilibrium value \( S^{eq}(\epsilon) \). In particular, the energy splitting \( 2E \), which varies with \( \epsilon \) occurs through a \( \tanh \) function.

Third, the energy dependence of the relaxation rate \( \Gamma_1 \) is also a cause of non-linearity through the functions \( F_1(\beta E_s) \) and \( F_3(\beta E_s) \). We take these two non-linearities into account.

2.4 REVIEW OF PREVIOUS WORKS. — We have established more precisely than we have done in the introduction all the equations necessary for discussing the methods and the approximations used by the authors who have already studied the question of non-linear acoustic relaxational attenuation in glasses [7-10]. This discussion is done now.

The Hamiltonian which describes our problem is:

\[
\mathcal{H} = \hbar \omega_0 S_Z + \left( G_X S_X + G_Z S_Z \right) \epsilon. \tag{14}
\]
In the language of paramagnetic resonance we are dealing with a field with both a longitudinal component (index Z) and a transverse component (index X). We recall that in the non-linear regime, the effects of the two components cannot be simply added.

In their article [7] Arnold et al. have adopted a method which is not fully satisfactory. They treated the longitudinal field linearly but assuming that the population has been saturated (a non-linear effect) by the transverse field. Finally they implicitly added the resonant and the relaxation attenuations. However, the merit of this article is to have tried to take into account both fields simultaneously.

Galperin et al. [8-10] limited their purpose to the case of a purely longitudinal field. We also take this as our rule. They found a saturation of the acoustic attenuation in metallic glasses but they used the simplification written in equation (13) which is, in our opinion, forbidden. Consequently their « protraction » of the relaxation time cannot exist.

Finally, in reference [11] we also treated the purely longitudinal case \( G_x = 0 \) with the additional assumption of a constant relaxation rate \( \Gamma_1 \). This restrictive hypothesis allows the attenuation to be exactly calculated. We find that there is no saturation at all! This result is a remarkable consequence of the broad width of the TLS spectrum. Indeed some TLS give a positive contribution to the non-linear attenuation while others produce a negative contribution. What is surprising (but fully explained) is their perfect cancellation. What happens when \( \Gamma_1 \) depends on the energy splitting?

3. Formalism and general results.

In this section we establish the formalism used to solve the Bloch equation by a perturbation calculation. We begin with the general case of the longitudinal and transverse fields applied simultaneously. However, we achieve the calculation in the longitudinal case only.

3.1 Fictitious spin evolution.

— Evolution equation (3) can be written

\[
\frac{dS}{dt} = \overline{P} S + Q \quad \text{with} \quad \overline{P} = \overline{L} - \overline{I} \quad \text{and} \quad Q = \overline{I} S^{eq}.
\]

The operator \( \overline{P} \) and the vector \( Q \) depend on the strain \( \varepsilon \) which is: \( \varepsilon (t) = \varepsilon_0 \cos \omega t \). The solution \( S(\varepsilon_0, t) \) of equation (15) is expanded in a series of \( \varepsilon_0 \):

\[
S(\varepsilon_0, t) = \sum_{p=0}^{\infty} S_p(t) \varepsilon_0^p.
\]

Similarly the operator \( \overline{P} \) and the vector \( Q \), which depend on time only through \( \varepsilon (t) \), are expanded in series of \( 2 \varepsilon (t) \):

\[
\overline{P}(\varepsilon_0, t) = \sum_{q=0}^{\infty} \overline{P}_q \varepsilon_0^q (e^{i\omega t} + e^{-i\omega t})^q
\]

\[
Q(\varepsilon_0, t) = \sum_{r=0}^{\infty} Q_r \varepsilon_0^r (e^{i\omega t} + e^{-i\omega t})^r.
\]

Substituting equations (16), (17), (18) into equation (15) and equalizing the coefficients of \( \varepsilon_0^p \) we obtain:

\[
\frac{dS_p}{dt} = \sum_{q=0}^{p} \overline{P}_q S_{p-q} (e^{i\omega t} + e^{-i\omega t})^q + Q_p (e^{i\omega t} + e^{-i\omega t})^p.
\]

To solve this equation for \( S_p \) we need to know all the \( S_{p-q} (1 \leq q \leq p) \). Therefore an iterative method must be used. The differential equations we have to solve have the following form

\[
\frac{dS_n}{dt} - \overline{P}_0 S_n = \sum_{m=-n}^{n} K_m e^{-im\omega t}.
\]

In the c.w. regime where the vectors \( K_m \) do not depend on time the solution is:

\[
S_n = - \sum_{m=-n}^{n} \overline{P}_{n-m}^{-1} K_m e^{-im\omega t}
\]
with
\[ \overline{\Pi}_m = \overline{P}_0 + im\omega \overline{I}. \]

Using this result we find for the successive orders:

- **Zeroth order**
  \[ S_0 = \sigma_{0,0} \quad \text{with} \quad \sigma_{0,0} = -\overline{\Pi}_0^{-1}Q_0 \] (22)

- **First order**
  \[ S_1 = \sigma_{1,1} e^{-i\omega t} + \sigma_{1,-1} e^{i\omega t} \] (23)
  with
  \[ \sigma_{1,1} = -\overline{\Pi}_1^{-1}\left(\overline{P}_1 \sigma_{0,0} + Q_1\right) \quad \text{and} \quad \sigma_{1,-1} = \sigma_{1,1}^* \]

- **Second order**
  \[ S_2 = \sigma_{2,2} e^{-i2\omega t} + \sigma_{2,0} + \sigma_{2,-2} e^{i2\omega t} \] (24)
  with
  \[ \sigma_{2,2} = -\overline{\Pi}_2^{-1}\left(\overline{P}_1 \sigma_{1,1} + \overline{P}_2 \sigma_{0,0} + Q_2\right) \]
  \[ \sigma_{2,0} = -\overline{\Pi}_0^{-1}\left(\overline{P}_1 \sigma_{1,1} + \overline{P}_1 \sigma_{1,-1} + 2\overline{P}_2 \sigma_{0,0} + 2Q_2\right) \]
  and \[ \sigma_{2,-2} = \sigma_{2,2}^* \]

- **Third order**
  \[ S_3 = \sigma_{3,3} e^{-i3\omega t} + \sigma_{3,1} e^{-i\omega t} + \sigma_{3,-1} e^{i\omega t} + \sigma_{3,-3} e^{i3\omega t} \] (25)
  with
  \[ \sigma_{3,3} = -\overline{\Pi}_3^{-1}\left(\overline{P}_1 \sigma_{2,2} + \overline{P}_2 \sigma_{0,0} + \overline{P}_3 \sigma_{0,0} + Q_3\right) \]
  \[ \sigma_{3,1} = -\overline{\Pi}_1^{-1}\left(\overline{P}_1 \sigma_{2,2} + \overline{P}_1 \sigma_{2,0} + \overline{P}_2 \sigma_{0,0} + 2\overline{P}_2 \sigma_{0,0} + 3\overline{P}_3 \sigma_{0,0} + 3Q\right) \]
  and \[ \sigma_{3,-1} = \sigma_{3,1}^*, \quad \sigma_{3,-3} = \sigma_{3,3}^* \]

It is easy to show that \( S_n \) has the general form:
\[ S_n = \sum_{m=0}^{n} \sigma_{n,n-2m} e^{-i \left(n-2m\right) \omega t} \] (27)

The explicit calculation of the vectors \( \sigma_{n,n-2m} \) for \( n > 3 \) is straightforward but tedious.

### 3.2 Ultrasonic Attenuation

- The ultrasonic power absorbed by a (fictitious) spin is:
  \[ q = -\langle \mathbf{S} \cdot \mathbf{G} \rangle \] (28)
  where the vector \( \mathbf{G} \) is defined in equation (1) and \( \dot{\varepsilon} \) is the time derivative of the strain. The symbol \( \langle \rangle \) means an average over a period. By substituting equations (16) and (27) into (28) we obtain:
  \[ \dot{q} = -\omega \varepsilon_0^2 \sum_{i=0}^{\infty} e_0^{2i} \Im \left( \mathbf{G} \cdot \mathbf{a}_{2i+1,1} \right) \] (29)
  where \( s = 0 \) correspond to the linear regime. \( s = 1 \) gives the first non-linear effects; we have carried out our calculation up to this order.

  For the total population of TLS the absorbed ultrasonic power is:
  \[ \dot{Q} = N \int \int \mathrm{d}E \, \mathrm{d}r \, P(E, r) \, q(E, r). \] (30)

Consequently, the ultrasonic attenuation coefficient is defined by:
\[ \alpha_\tau = \frac{\dot{Q}}{\Phi_\tau} \] (31)
where \( \Phi_\tau = \frac{1}{2} \rho V_\tau^3 \varepsilon_0^2 \) is the acoustic flux. The index \( \tau \) recalls the polarization of the acoustic wave which may be a compressional or a shear wave.
The previous calculation allows us to write down the expansion
\[ \alpha_r = \sum_{i=0}^{\infty} \alpha_{r2i+1} e_{0}^{2i} \] (32)
The even terms \( \alpha_{r2i} \) are missing because they automatically vanish in the time average \( \langle \rangle \) over a period.

4. Particular case of longitudinal field.
When the field is purely longitudinal the problem has a high symmetry: the spin \( S \) is collinear to the \( Z \) axis. Moreover all the involved \( (3 \times 3) \) operators have the \( Z \)-direction as eigenspace. Therefore, this case is one-dimensional. The only relaxation rate we have to consider is \( \Gamma_1 \), that we shall simply note \( \Gamma \) in the following sections. Let \( \bar{n} \) be the difference of the populations between the two levels of the TLS. \( \bar{n} \) is defined as a positive quantity when no strain is applied. The \( Z \)-component of the equilibrium (dimensionless) vector \( S^e \) is then
\[ S_Z = -\frac{1}{2} \bar{n} . \] (33)
We designate by \( \Gamma_1', \Gamma_1'', \ldots \) and \( \bar{n}', \bar{n}'', \ldots \), the successive derivatives of \( \Gamma \) and \( \bar{n} \) with respect to the reduced half-energy splitting \( x = \beta E \). Using (29) for that particular case we find the following results:

i) At first order we obtain the well-known linear relaxation attenuation:
\[ \alpha_{r1} = \frac{C_r \omega}{V_r} \int_{0}^{\infty} dx \text{sech}^2 x \int_{0}^{1} dr \sqrt{1 - \frac{r}{r^2 + v^2}} \] (34)
where
\[ C_r = \frac{\mathcal{N} A \gamma^2_r}{2 \rho V_r^2} \quad \text{and} \quad v = v(x) = \frac{\omega}{\Gamma_M} . \]
\( \Gamma_M \) is the maximum value of \( \Gamma \) (obtained for \( r = 1 \)) for a given energy. We can give an analytical expression of \( \alpha_{r1} \) only for two limiting cases:

- in the high-temperature regime \( (v \ll 1 \text{ for most of the TLS}) \):
  \[ \alpha_{r1} = \frac{\pi C_r \omega}{2 V_r} \] (35)
independently of the relaxation process;

- in the low-temperature regime \( (v \gg 1 \text{ for all the TLS}) \):

\[ \alpha_{r1} = \pi^2 C_r K_1 \frac{T}{V_r} \] (36)
in an insulating glass

\[ \alpha_{r1} = \frac{\pi^2 C_r K_1 T}{12 V_r} \] in a metallic glass

(At low temperatures the relaxation by electrons is dominant.)

ii) At third order we get
\[ \alpha_{r3} = -C_r \omega \frac{\gamma^2_0}{8} \int_{0}^{\infty} dx \int_{0}^{1} dr (1 - r)^{3/2} \times \]
\[ \left( \frac{F_1(x)}{r^2 \Gamma_M^2 + \omega^2} + \frac{F_2(x)}{r^2 \Gamma_M^2 + 4 \omega^2} + \frac{r^2 \Gamma_M^2 F_3(x)}{(r^2 \Gamma_M^2 + \omega^2)^2} \right) \] (37a)
where
\[ F_1(x) = -\left[ \bar{n}'' \Gamma_M + 2 \bar{n}' \Gamma_M' + 3 \bar{n} \left( \Gamma_M' - 2 \frac{\Gamma_M^2}{\Gamma_M} \right) \right] \]
\[ F_2(x) = 4 \left( \bar{n}' \Gamma_M' - 2 \bar{n} \frac{\Gamma_M^2}{\Gamma_M} \right) \]
\[ F_3(x) = 4 \bar{n} \Gamma_M' \] (37b)
When the integration over \( r \) is achieved, it comes:
\[ \alpha_{r3} = -\frac{C_r \gamma^2_0}{8 V_r (kT)^2} \int_{0}^{\infty} dx v^2 \left( I_1(v) F_1(x) + I_1(2v) F_2(x) + I_2(v) F_3(x) \right) \] (38)
As for the linear case, the calculation of $\alpha_{r3}$ can be performed only with a computer. However, in the two limiting cases (low and high temperatures), an analytical expression of $\alpha_{r3}$ can be derived. This will be done in the comments of the next section.

5. Numerical results and comments.

We present our numerical data obtained by computation of equation (38) with the following realistic values: $C_\tau = 10^{-4}$, $\nu = 5 \times 10^5$ cm/s, $\omega / 2\pi = 10^8$ Hz, $\gamma_\nu = 1$ eV. (For $K_1$ and $K_3$, see below). Three cases were considered:

- Ideal amorphous metal (relaxation by the electrons only: $K_1 = 10^{10}$ s$^{-1}$ K$^{-1}$ and $K_3 = 0$).
- Amorphous insulator (relaxation by the phonons only: $K_1 = 0$ and $K_3 = 10^9$ s$^{-1}$ K$^{-3}$).
- Real amorphous metal (both electron and phonon relaxation processes: $K_1 = 10^{10}$ s$^{-1}$ K$^{-1}$ and $K_3 = 10^9$ s$^{-1}$ K$^{-3}$).

5.1 IDEAL AMORPHOUS METAL. — The coefficient $\alpha_{r3}$ is plotted as a function of temperature in figure 1 on a log-log scale. The explored temperature domain is perhaps not realistic but it provides a clear evidence of the two limiting regimes.

Our first comment concerns the sign of the effect: it is positive in the whole temperature range. In other words the attenuation is enhanced when the acoustic power is increased. In contradiction with previous articles [8, 9, 10], our result shows that $\alpha_{r3}$ decreases as $T^{-2}$. As in the previous case, expansions of $I_1(v)$ and $I_2(v)$ (but for small values of $v$) give:

$$\alpha_{r3} = \frac{\pi C_\tau \omega \gamma_\nu^2}{8 V_\nu k^2 T^2} \int_0^\infty dx \phi_{\nu}^{el}(x) \sech^2 x \quad (40a)$$

The result of the integral is 0.506. On the other side, at high temperatures, $\alpha_{r3}$ decreases as $T^{-2}$. The slopes of the limiting regimes are respectively $-1$ at low temperatures and $-2$ at high temperatures.

$$I_1(v) = \frac{i}{v} \Im \left( w^3 \ln \left( \frac{w + 1}{w - 1} \right) - 2w^2 \right)$$

$$I_2(v) = 1 + \frac{1}{4} \Re \left( \frac{2w^2}{w^2 - 1} - 3 \ln \left( \frac{w + 1}{w - 1} \right) \right) + \frac{1}{2} I_1(v)$$

with

$$w = \sqrt{1 + iv}$$

$$\phi_{\nu}^{el}(x) = x \coth x - 2 + \coth^2 x + x \coth^3 x - 2 \coth x \frac{\coth x}{x} \quad (39b)$$
The value of the integral is 0.133.

In any case the ratio \( \alpha_{36} / \alpha_{31} \) is of the order of \( (\gamma_e e_0 / kT)^2 \). For \( T = 1 \) K and \( \gamma_e = 1 \) eV = 10^6 K a notable effect needs \( e_0 \) of the order of \( 10^{-4} \) which is hardly obtained in experiments.

5.2. AMORPHOUS INSULATORS. — The coefficient \( -\alpha_{3} \) (note the minus sign) is plotted as a function of temperature in figure 2 on a log-log scale.

\[
\varphi_{HT} (x) = \frac{\cosh x}{x} - \frac{\tanh x}{x} - \frac{1}{x^2} + 1 - \tanh^2 x \quad (40b)
\]

The value of the integral is 7.11. At high temperatures, \( -\alpha_{3} \) decreases as \( T^{-1/2} \), a behaviour which is not simple to guess. In this case an expansion of \( I_1 (v) \) and \( I_2 (v) \) for small \( v \) is not correct: even for high temperatures, the relaxation time of TLS of vanishing energy becomes infinite; therefore, for these TLS \( v \) is very large in contradiction with the hypothesis of the expansion. An approximation consists in truncating the integration domain at a lower limit corresponding to \( v = 1 \). This limit varies as \( T^{-3/2} \), finally leading to the previously mentioned \( T^{-1/2} \) law with a coefficient which has the right order magnitude.

In this case also, a notable effect for \( T = 1 \) K needs \( e_0 \) of the order of \( 10^{-4} \).

5.3 REAL METAL. — In figure 3 \( |\alpha_{3}| \) is plotted on a log-log scale. It is not surprising that the sign of the effect is positive at low temperatures (the relaxation by electrons is dominant) while it is negative at high temperatures (the relaxation by phonons is dominant). This is obvious in the insert which is drawn on linear scales. But things are indeed not so simple as shown by the limiting cases.

Although the low-temperature behaviour is exactly the same as in the ideal metal (see Eq. (38)) the high-temperature behaviour is not identical to that of the insulating glass \( (T^{-1} \) instead of \( T^{-1/2} \). However the difference is easily explained. In the present case, the relaxation rate is the sum of the phonon relaxation rate and of the electron relaxation rate: \( \Gamma = \Gamma^{el} + \Gamma^{ph} \). Therefore the term \( \Gamma^{el} \) which stays finite for the TLS of vanishing energy, prevents divergence of the relaxation time for these TLS. Consequently, expansions of \( I_1 (v) \) and \( I_2 (v) \) for small \( v \) are perfectly licit here. They lead to the following analytical form, valid at high temperatures:

\[
\alpha_{3} = -\frac{\pi^2 C_e \omega \gamma_e^2}{16 V_t k^2} \frac{K_3}{K_1} 1/2 \frac{1}{T}. \quad (42)
\]

Finally we note that the temperature \( T_0 \) where \( \alpha_{3} \) changes sign is roughly given by the condition \( T_0 = (K_1/K_3)^{1/2} \). With the realistic values used here we find \( T_0 \approx 3 \) K. Therefore, the experimental conditions of references [1-6] correspond to what we call the low-temperature behaviour.

As a conclusion of this section we recall that we have found a non-linear contribution to the acoustic attenuation which is positive for a relaxation due to

Fig. 2. — Variation of the opposite of the non-linear acoustic attenuation divided by \( e_0^2 \) as a function of the temperature \( T \) on a log-log scale. The slopes are respectively equal to +1 and \(-1/2\) in the low temperature and in the high temperature regimes.

Here too, our first comment concerns the sign of the effect: it is negative in the whole temperature range. This means that the higher the acoustic power, the smaller the attenuation: this is a true saturation effect.

The two limiting regimes deserve some comments.
Fig. 3. — Variation of the modulus of the non-linear acoustic attenuation divided by $\epsilon_0^2$ as a function of the temperature $T$ on a log-log scale for a real metallic glass. At low temperatures the slope is $-1$ and $\alpha_{r3}$ is positive while at high temperatures the slope is also $-1$ but $\alpha_{r3}$ is negative. The insert shows on linear scales the variation of $\alpha_{r3}$ versus $T$.

6. Discussion.

In order to have a better understanding of the physical origin of the non-linear attenuation, we focus our attention on the contribution of the TLS which have the same reduced energy splitting $2\chi$ (this implies that the integration over the coupling parameter $\tau$ has been performed).

We first remark that the non-linear effect does not exist if the equilibrium population difference $\bar{n}$ is not modulated since the actual population difference obviously remains constant at its Boltzmann equilibrium value. This can be seen (for the particular case of the third order) in equation (37b). On the contrary if the relaxation rate $\Gamma_M$ is not modulated, a third order contribution still remains (see Eq. (37b)) proportional to the third derivative

$$\bar{n}'' = 2 \text{sech}^2 \chi (2 - 3 \text{sech}^2 \chi) \quad (43)$$

the sign of which changes for $\chi = \cosh^{-1} (\sqrt{3}/2)$.

However it is easy to show that, after integration over $\chi$, the total effect equals zero. This particular case was studied in a previous article [11], where it was shown that such a property holds for any order of perturbation.

Now, generally speaking, the sign of the total effect does not necessarily imply that all the TLS behave in the same manner. For instance in the high temperature regime of the ideal metal, the contribution of the TLS of a given reduced energy $2\chi$ is proportional to the function $\varphi_{HT}^{el}(\chi) \text{sech}^2 \chi$ of equation (40b) the sign of which changes (see Fig. 4). This change of sign, already found in the

Fig. 4. — Variation of the function $F(\chi) = \varphi_{HT}^{el}(\chi) \text{sech}^2 \chi$ versus the reduced (unstrained) half-energy $\chi = \beta E$ on linear scales for an ideal metallic glass. The sign of the function changes for $\chi = 0.92$. However the integral over $\chi$ is positive.

case of the constant relaxation rate, is observed in most of the limiting cases considered above. The case of the low temperature regime of the ideal metal makes an exception to that rule : the relevant function $\varphi_{LT}^{el}(\chi) \text{sech}^2 \chi$ of equation (39b) is everywhere positive (see Fig. 5). Concerning this last example we should like to emphasize an important point : the contribution of the TLS of small $\chi$ (where $\Gamma_M$ is nearly constant) is positive while it is negative (see Eq. (43)) for the case quoted above where
\( \Gamma_M \) is rigorously constant. This shows the fundamental role of the derivatives of \( \Gamma_M \). In order to back up this argument we have used some (unphysical) analytical forms of \( \Gamma_M (x) \) for which the curvature could be controlled. Our results demonstrate the extreme sensitivity of \( \alpha_{13} \) to this curvature.

Finally, it appears that the problem we have attempted to treat is a very complicated one: even for TLS of a given energy it is difficult to have a simple physical insight on the roles of the modulations of \( \Gamma \) and of \( \bar{n} \) respectively.

6. Conclusion.

We have performed a perturbation calculation of non-linear acoustic attenuation in glasses, using only the term \( G_z S_z \varepsilon \) as coupling interaction between the ultrasonic wave and the TLS. Our main result is that the calculated effect is weak and leads to an enhancement of the acoustic attenuation with increasing power in glassy metals at low temperatures. This is in contradiction both with the experimental data [1-6] and with previous theoretical works [8-10].

We consider these features as strong arguments in favour of a crossed non-linear effect (taking into account both the \( G_z S_z \varepsilon \) and \( G_x S_x \varepsilon \) coupling terms) as the true explanation of the experimental data. This effect has been phenomenologically studied in [7] but an exact calculation, using for example a perturbation approach, is still to be made.

References