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ULTRASONIC RELAXATION IN MOLECULAR CRYSTALS

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Abstract. - One of the main mechanisms of ultrasonic attenuation in molecular gases and liquids is due to a slow transfer of energy between external and internal degrees of freedom of molecules. In 1959 Liebermann propounded the extension of this relaxation to the solid state and used the approach soon derived in gaseous and liquid phases. A Boltzmann-equation approach is suggested here which makes it possible to consider this ultrasonic relaxation as an anomaly of the Akhieser loss. Moreover it is shown that anisotropy of the solid state does not act on the frequency dependence of the relaxational term but mainly on its magnitude whose expression used up to now is proving incorrect; a new expression is given.

1. Introduction. - It is well established that a relaxation process may occur in molecular gases and liquids due to a slow transfer of energy between the internal and external degrees of freedom of molecules perturbed by an ultrasonic wave. In 1959 Liebermann suggested that this phenomenon might also occur in the solid state; moreover he proposed the use of the phenomenological approach soon derived by Richards in the gaseous and liquid phases to relate the ultrasonic absorption coefficient $\alpha$ and the relaxation time $\tau$. This relation may be expressed in the following way:

$$\alpha = \frac{1}{2s} \frac{C_p - C_v}{C_p} \frac{C_I}{C_v - C_I} \frac{\Omega^2 \tau}{1 + \Omega^2 \tau^2}$$

(1)

where:

. $\Omega$ and $s$ are respectively the angular frequency and the velocity of the ultrasonic wave.

. $C_p$ and $C_v$ are the specific heats at constant pressure and constant volume respectively and $C_I$ the specific heat associated with the internal degrees of freedom of molecules.

This pioneering work of Liebermann has entailed a certain number of ultrasonic studies on molecular crystals and at the present time an ultrasonic relaxational behaviour has soon been identified in several compounds.

In this work, in contrast to Liebermann's approach, we suggest a solid state viewpoint to analyse this relaxation phenomenon. Molecular crystals may indeed be first of all considered such as dielectric crystals for which the ultrasonic

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attenuation is well described in the hydrodynamical regime of propagation of sound by the classical theory suggested by Akhieser. So we propose to follow the Boltzmann-equation approach of Woodruff and Ehrenreich (which is an improved version of Akhieser's theory) to describe this ultrasonic relaxation.

2. Boltzmann-equation approach. - In Akhieser's theory the ultrasonic wave is considered as an external field which modulates in space and time the population of thermal phonons. More precisely the lattice deformation associated with the ultrasonic wave induce a shift of the frequency $\omega_\lambda$ of phonons $\lambda^k$ describable by the Grüneisen tensors $\gamma_{\lambda,ij}$; these Grüneisen parameters depending on the mode $\lambda$, the phonon gas is not in equilibrium and the phonon distributions depart from Boltzmann distributions (we noted $n_\lambda$). Nevertheless the evolution of phonons can be described by Boltzmann equations which enable us to determine the actual phonon distributions.

The standard ultrasonic experiments lead to strains which are typically about $10^{-7}$ to $10^{-5}$ and thus Boltzmann equations may be linearized; under this approximation the collision terms of these equations may be described by the phonon collision operator $M$.

Now it can be shown in a very general way that the ultrasonic absorption coefficient may be expressed in terms of the eigenvectors $X_i$ and eigenvalues $-1/\tau_i$ ($i = 1,p$) of the collision operator $M$ in the following way:

$$\alpha = \frac{1}{2ps^3} \frac{1}{k_BT} \frac{p}{\sum_{i=1}^{p} \frac{\omega_i^2 \tau_i}{1+\omega_i^2 \tau_i^2}} (\sum_{\lambda} \gamma_{\lambda} \hbar \omega_\lambda X_{i,\lambda})^2$$

(2)

here:

- the eigenvectors $X_i$ are such that the eigenvectors $\tilde{X}_i$ defined by:

$$\tilde{X}_{i,\lambda} = [n_\lambda (n_\lambda + 1)]^{-1/2} X_{i,\lambda}$$

(3)

are normalized vectors.

- $\rho$ is the density and $\gamma_{\lambda}$ is defined as follows:

$$\gamma_{\lambda} = \gamma_{\lambda,ij} \hat{e}_i \hat{K}_j$$

(4)

where $\hat{e}$ and $\hat{K}$ are respectively the directions of polarization and of propagation of the ultrasonic wave.

Eq. (2) has been obtained by neglecting the group velocity of phonons which would lead to the classical thermoelastic loss due to the thermal conduction between the compressed and rarefied regions.

Further informations about $\tau_i$ and $X_i$ are necessary to get an available expression of $\alpha$.

* The index "$\lambda$" means that the phonon $\lambda$ belongs to a mode of wave vector $\vec{k}$ and polarization $\sigma$. 
3. "Hard" dielectric crystals. - The term "hard" suggested by Victor et al.\textsuperscript{6} will be used in this paper to distinguish two classes of dielectric crystals:

- Hard dielectric crystals would be those in which the strengths of the various bonds have the same order of magnitude.

- Molecular crystals would be those in which strong bonds forming discernible units which may be termed "molecules" (in a broad sense) coexist which weak bonds which link these molecules.

Now, we may assume that in hard dielectric crystals the homogeneity of the strengths of the various bonds leads, on the anharmonic level, to the homogeneity of the interactions between the modes or between the phonons. This assumption makes it possible to use the collision time approximation which is generally written in the following way:

\[
M_{\lambda\lambda'} = -\frac{1}{\Theta} \delta_{\lambda\lambda'}
\]

(5)

In fact this formulation is slightly incorrect because it can be shown\textsuperscript{7} that \( M \) must possess a zero eigenvalue. The corresponding eigenvector is given by:

\[
X_{1,\lambda} = (k_B T^2 C_v)^{1/2} \frac{C_{\lambda}}{\Theta C_v} C_{\lambda}
\]

(6)

where \( C_{\lambda} \) is the specific heat associated with the mode \( \lambda \). This property of \( M \) comes from a conservation law of the deformation energy (to the first order in strain) which \( M \) obeys.

Thus it is more consistent to formulate the collision time approximation by saying that the collision operator has the zero eigenvalue eigenvector \( X_1 \) and a second eigenvalue \((-1/\Theta)\) whose eigensubspace has a degeneracy equal to \((N-1)\); \( N \) is the number of modes and \( \Theta \) is the mean lifetime of thermal phonons. With these assumptions, Eq. 2 gives:

\[
\alpha = \frac{C_v T}{2 \Theta s^3} \left[ \langle \gamma^2 \rangle - \langle \gamma \rangle^2 \right] \Omega^2 \Theta
\]

(7)

which is the well-known expression of the Akhieser loss. We have put:

\[
\begin{align*}
\langle \gamma^2 \rangle &= \sum \frac{C_{\lambda}}{C_v} \gamma_{\lambda}^2 \\
\langle \gamma \rangle &= \sum \frac{C_{\lambda}}{C_v} \gamma_{\lambda}
\end{align*}
\]

(8)
4. Molecular crystals. - It is clear that the collision time approximation fails in molecular crystals for which the homogeneity of the strength of the various phonon interactions no longer holds. Nevertheless it is possible to obtain interesting informations about the behaviour of ultrasonic attenuation in molecular crystals under light and realistic approximations: we may define a "collision time approximation" restricted to the modes which are efficiently coupled with long wavelength acoustic modes. These modes $\lambda$ would be termed "external" modes and define a subspace $E$ while the other modes would be termed "internal" modes and define a subspace $I$.

Thus we may assume that the collision operator has a zero eigenvalue ($-1/\tau_1=0$), a main eigenvalue ($-1/\tau_2=-1/0$) and that the other eigenvalues ($-1/\tau_i;i>2$) correspond to slow relaxation times and are much lower than ($-1/0$). Two consequences may be deduced from the assumptions above:

i) Phonons belonging to the external modes are thermalized in fast times ($\approx\delta$) after a lattice deformation. Thus we may write:

$$X_{1,\lambda} = \nu_i \left( k_B T^2 C_v \right)^{1/2} \frac{1}{\pi \omega_\lambda} \frac{C_{\lambda}}{C_v}$$

where $\nu_i$ are normalizing factors which now contain all the hindered informations about the collisions between phonons. (We recall that we normalize the vectors $\overline{X}_1$).

ii) Grüneisen parameters of the internal modes may be neglected.

Thus Eq. (2) may be written in the following way:

$$\alpha = \alpha_A + \alpha_R$$

where $\alpha_A$ is the loss due to the fast relaxation time $\theta$ and $\alpha_R$ is a relaxational term given by:

$$\alpha_R = \frac{C_v T}{2 ps^3} \left< \gamma \right>^2 \sum_{i>2} \nu_i^2 \frac{\Omega^2 \tau_i}{1+\Omega^2 \tau_i^2}$$

Though normalizing factors $\nu_i^2$ are not explicit, we know that they only depend on intrinsic properties of the collision operator and thus we may deduce an interesting information about the relaxation with the expression above: whatever would be the relaxation spectrum, the frequency dependence of $\alpha_R$ must stay invariant under any change of the direction of propagation of the ultrasonic wave. Thus the anisotropy of the solid state can only affect the magnitude of the relaxation.

Now it would be interesting to compare the expression of the magnitude given by Eq. (11) with that proposed by Liebermann (Eq. (1)) which has been used in mostly previous papers on this field.

5. Comparison with Liebermann's approach. - Liebermann's relation is implicitly built on the assumption of a single relaxation time which leads in our approach
to only three eigenvalues 0, -1/\theta and -1/\tau for M. Moreover to bring our expression of \( \alpha_R \) as close as possible to Liebermann's one we will also assume that \( \tau \) corresponds to the rate of transfer of energy between external modes (carrying the energy \( U_E \)) and internal modes (carrying the energy \( U_I \)); thus:

\[
\frac{\partial}{\partial t} \left( \frac{U_E}{C_E} - \frac{U_I}{C_I} \right)_{\text{coll.}} = -\frac{1}{\tau} \left( \frac{U_E}{C_E} - \frac{U_I}{C_I} \right)
\]

(12)

where:

\[
C_E = C_V - C_I
\]

(13)

Now it has been discussed in Ref. (5) how the following expression of \( X_3 \) can be derived from Eq. (12):

\[
X_{3,\lambda} = \varepsilon_\lambda (k_B T^2 C_V)^{1/2} \frac{1}{\beta_{\lambda}} \frac{C_\lambda}{C_V}
\]

(14)

with:

\[
\varepsilon_\lambda = \left( \frac{C_E C_I}{C_E} \right)^{1/2}, \quad \lambda \in E
\]

and:

\[
\varepsilon_\lambda = -\left( \frac{(C_E C_I)^{1/2}}{C_I} \right), \quad \lambda \in I
\]

(15)

which leads to:

\[
u_3^2 = \varepsilon_\lambda^2 = \frac{C_I}{C_E}
\]

(16)

To get an expression of \( \alpha_R \) in terms of thermoelastic quantities available in the experimental field we can express the generalized Gr"uneisen tensor \( \langle \gamma_{ij} \rangle \) in terms of the specific heat at constant volume \( C_V \), the elastic constants \( C_{ijkl} \) and the thermal expansion tensor \( \beta_{kl} \) using the following relation valid in the quasi-harmonic approximation:\n
\[
\langle \gamma \rangle = \langle \gamma_{ij} \rangle e_i K_j = \frac{1}{C_V} C_{ijkl} \beta_{kl} e_i K_j
\]

(17)

Then with the help of Eqs. (11), (16) and (17) we obtain:

\[
\alpha_R = \frac{1}{2s} \left( \frac{C_{ijkl} \beta_{kl} e_i K_j}{C_V C_E 1 + \Omega^2 \tau^2} \right)
\]

(18)

It is impossible to introduce in a natural way the quantity \( \left( \frac{C_p - C_V}{C_V} \right) \) in the equation above except for the isotropic and cubic symmetries where we may write:

\[
\alpha_R = \frac{1}{2s} \left( \frac{C_{p,-C_V}}{C_V} \left( \frac{C_{11} + 2C_{12}}{3ps^2} \right) \right) \left( \varepsilon, R \right) \frac{C_I}{C_V - C_I} \frac{\Omega^2 \tau}{1 + \Omega^2 \tau^2}
\]

(19)

The main difference with relation (1) used by Liebermann is the existence in Eq. (19) of the structure factor \( \left( \frac{C_{11} + 2C_{12}}{3ps^2} \right) \) which results from the actual
nature of the solid state. An analysis of experimental results obtained on cubic
crystals has been made with both relations (1) and (19) and the results plead in
favour of Eq. (19).

Now it is possible to use the following thermodynamic relation:
\[ C^S_{ijkl} - C^T_{ijkl} = \frac{T}{C_v} \sum_{mnrs} C^T_{ijmn} C^T_{klrs} \beta_{mn} \beta_{rs} \]
which leads to this expression of \( \alpha_R \):
\[ \alpha_R = \frac{\beta}{5} \frac{C^S_{ijkl} - C^I_{ijkl}}{C^E_{ijkl}} \frac{\Omega_T}{s} \frac{\Omega_T}{1 + \Omega_T^2} \]
(21)
(the indexes "S" and "T" mean respectively adiabatic and isothermal). This attenua-
tion is related to a dispersion on the ultrasonic velocity given by:
\[ \frac{s - s_0}{s} = \frac{C^I_{ijkl}}{C^E_{ijkl}} \frac{s^S - s^T}{s} \frac{\alpha_T^2}{1 + \Omega_T^2} \]
(22)

We think that Eqs. (21) and (22) which are valid for any symmetry could
be obtained straight by a purely phenomenological approach built on the assumptions
discussed in this work.

6. Conclusion. - We have shown in this work that ultrasonic relaxation in molecular
crystals may be described in the same way as Akhieser loss in dielectric crystals
by a Boltzmann-equation approach; in fact these two mechanisms of sound absorption
seem to have quite the same status in the hydrodynamical regime of propagation of
sound. The two main products of this approach are:
- Firstly, for any relaxation spectrum it has been shown that the anisotropy
  of the solid state mainly acts on the magnitude of the relaxation but not on its
  frequency dependence.
- Secondly, for the special case of a single relaxation time it has been pro-
  ved that the relation used previously in this field is incorrect and a new relation
  which takes into account the actual nature of the solid state has been given.

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