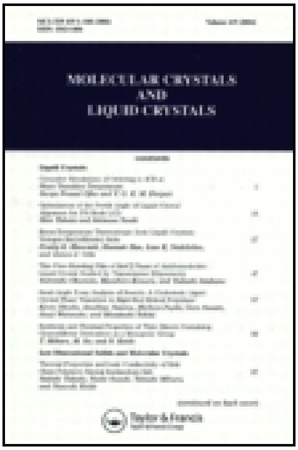

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: A. A. Tabidze (1983): Rheological Model and Acoustic Properties of Molecular Crystals in the Melting Region, Molecular Crystals and Liquid Crystals, 100:1-2, 41-48

To link to this article: http://dx.doi.org/10.1080/00268948308073717

Mol. Cryst. Liq. Cryst., 1983, Vol. 100, pp. 41–48
0026-8941/83/1002-0041/$18.50/0

Printed in the United States of America

Rheological Model and Acoustic Properties of Molecular Crystals in the Melting Region

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(Received December 9, 1982)

A rheological model of the medium has been constructed which makes it possible to interpret the frequency dependences of ultrasonic velocity and absorption in molecular crystals in the melting region. This model is based on the model of a standard linear viscoelastic body and incorporates, parallel to a viscosity element, an additional element characterizing the internal inertia of the material. A crystallite in a polycrystal is assumed to act as an oscillator (the carrier of internal inertia of the medium). Relationship between the crystallite mass and size and the parameters of the suggested model has been established. Where the ultrasonic wave length is much greater than crystallite dimensions, there is satisfactory coincidence between crystallite sizes measured visually (by means of a microscope) and those calculated on the basis of ultrasonic velocity and absorption coefficient determinations.

The frequency dependences of ultrasonic velocity $C(\omega)$ and absorption coefficient $\alpha(\omega)$ in homogeneous viscoelastic media can be successfully interpreted on the basis of the relaxation theory involving one or several relaxation times.[1] In the past few years, however, a significant discrepancy has been found between the values calculated in accordance with this theory and the experimental dependences $C(\omega)$ and $\alpha(\omega)$ for molecular crystals in the polycrystalline state.[2–5] Discrepancy also manifests itself in that the position of the absorption maximum times the wave length $\alpha\lambda(\omega)$ remains constant despite varying the thermodynamic conditions, *e.g.* temperature, while the relaxation theory envisages that temperature variations cause shifting of the $\alpha\lambda(\omega)$ maximum.

The authors of the cited papers ascribe this behavior of ultrasound characteristics to the onset of resonance properties of the medium due to the effects of internal inertia which, in certain frequency ranges, exceed those of elasticity and viscosity. To describe the resonance properties of molecular crystals, various approaches have been used. For example, in Adhamov's paper[6] an attempt was made to modify the relaxation theory of the Mandelstam Leontovich nonequilibrium thermodynamics by introducing into the theory of the internal parameter ξ, in addition to internal parameter relaxation an inertia term. Then the equation of internal parameter motion will be

$$m_1 \ddot{\xi} + \beta_1 \cdot \dot{\xi} + \frac{\partial \phi}{\partial \xi} = 0$$

wherein m_1 is the constant which characterizes the measure of internal parameter inertia, β_1 is the kinetic coefficient characterizing internal parameter relaxation, and ϕ is the thermodynamic potential.

In contrast to the relaxation theory, in which $m_1 = 0$ in the cited paper the internal parameter is assumed to strive to equilibrium by performing damped oscillations. The parameter m_1 characterizes the internal inertia of the medium. The dependence of ultrasonic velocity C and absorption coefficient α on frequency ω in the medium in question is expressed as follows:[6]

$$C(\omega) = C_0 \left[1 + \frac{\Delta}{2} \cdot f_1(\omega) \right], \qquad \alpha(\omega) = \frac{\omega \cdot \Delta}{2 \cdot C_0} \cdot f_2(\omega)$$

$$f_1(\omega) = \frac{\omega^2 \tau^2 - \dfrac{\omega^2}{\omega_0^2} + \dfrac{\omega^4}{\omega_0^4}}{\left(1 - \dfrac{\omega^2}{\omega_0^2}\right)^2 + \omega^2 \tau^2}$$

$$f_2(\omega) = \frac{\omega \tau}{\left(1 - \dfrac{\omega^2}{\omega_0^2}\right)^2 + \omega^2 \tau^2} \tag{1}$$

wherein $f_1(\omega)$, $f_2(\omega)$ are the frequency functions of velocity and absorption coefficient, $\Delta = (C_\infty^2 - C_0^2)/C_0^2$ and C_0 and C_∞ stand for the ultrasonic velocity at $\omega \rightarrow 0$ and $\omega \rightarrow \infty$, respectively.

Equation 1 was obtained under the assumption that the dispersion of ultrasonic velocity is low ($\Delta \ll 1$). The parameters ω_0 and τ which define the dispersion characteristics of ultrasound are expressed in terms of the parameters m_1 and β_1 introduced into the theory:

$$\omega_0 = \sqrt{\frac{\phi}{m_1}}, \qquad \tau = \frac{\beta_1}{\phi} \tag{2}$$

Equation 1 is in good agreement with the result of measuring the velocity and absorption of ultrasound in molecular crystals in the melting region.

Another approach to the interpretation of the observed resonance properties of molecular crystals in the case of ultrasound propagation therein was evolved within the framework of the dislocation theory of Granato and Lucke[7] which assumes the resonance properties of a medium to be associated with the forced oscillations of dislocations possessing some inertia. In this model, the frequency dependences of velocity and absorption coefficient very closely coincide with Eq. 1, except for the fact that the parameters ω_0 and τ are expressed in terms of the effective mass of dislocation unit length, m_2, and the coefficient of friction, β_2:

$$\omega_0 = \frac{\pi}{l}\sqrt{\frac{A}{m_2}}, \qquad \tau = \frac{\beta_2}{m_2} \tag{3}$$

wherein l stands for the dislocation loop length, and A is the coefficient characterizing the dislocation loop tension.

Despite good agreement between the frequency dependencies of ultrasonic velocity and absorption coefficient described by Eq. 1 and the experimental data, the aforementioned theories fail to clarify the physical meaning of the introduced parameters, *viz.*, the internal parameter effective mass, m_1, and, in the case of molecular crystals in the polycrystalline state, the effective mass of dislocation unit length, m_2.

In the investigation of acoustic properties of viscoelastic media, a further method relies on a phenomenological approach, wherein use is made of pictorial electromechanical circuits to construct rheological models, the models in question being generally constructed on the basis of experimental data analysis and thereafter employed both for the examination of macroscopic behavior of the medium and the analysis of its structure. The available rheological models of viscoelastic media agree well with the relaxation theories and, in particular, adequately describe the characteristics of ultrasonic wave propagation in homogeneous media.[8] These models, however, fail to describe the acoustic properties of media defined by Eq. 1.

The object of the present investigation comprises constructing a rheological model of the medium displaying internal resonance *properties, viz.*, the medium, the frequency characteristics of which are described by Eq. 1.

To solve the problem at hand, we suggest a circuit (Figure 1) comprising a modified mechanical model of the standard linear viscoelastic body (Zener's model) incorporating an element η parallel to the element M. In Figure 1, E_0, E_1 are the elastic moduli, η is the friction coefficient, and M denotes the additional parameter characterizing the internal inertia of the material. The physical meaning of the above parameters will be described hereinbelow. For the given model, the complex elastic modulus E^* can be expressed as follows:

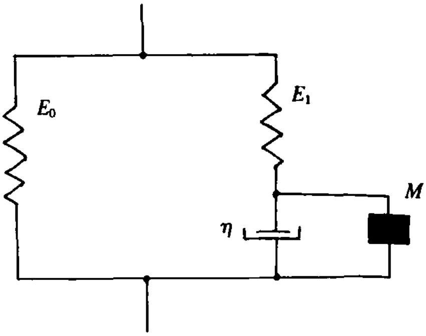

FIGURE 1 Rheological model representing ultrasound propagation in polycrystalline specimens of molecular crystals in melting region.

$$E^* = E_0 + E_1 \frac{j\omega\tau - \dfrac{\omega^2}{\omega_0^2}}{1 + j\omega\tau - \dfrac{\omega^2}{\omega_0^2}} \tag{5}$$

In Eq. 5, ω_0 and τ are expressed in terms of the model parameters (see Figure):

$$\omega_0^2 = \frac{E_1}{M}, \qquad \tau = \frac{\eta}{E_1} \tag{6}$$

Next, Eq. 5 should be separated into the real and the imaginary part of the complex elastic modulus $E^* = E' + jE''$:

$$E' = E_0 + E_1 \cdot f_1(\omega), \qquad E'' = E_1 \cdot f_2(\omega). \tag{7}$$

It will be noted that the thus-obtained frequency functions $f_1(\omega)$ and $f_2(\omega)$ in Eq. 7 coincide with the frequency functions defined in Eq. 1.

Let us find the ultrasonic velocity C and absorption coefficient α in the medium described by the suggested model. Expressing the complex wave number K^* in terms of the complex elastic modulus E^*, one obtains:

$$K^* = \frac{\omega}{C} - j\alpha = \omega\sqrt{\frac{\rho}{E' + jE''}}$$

Equating the imaginary and the real part of the above expression yields

$$\frac{\omega^2}{C^2} - \alpha^2 = \frac{\omega^2 \cdot \rho \cdot E'}{|E^*|^2}, \qquad \frac{2\alpha}{C} = \frac{\omega \cdot \rho \cdot E''}{|E^*|^2} \tag{8}$$

Substituting the values of E' and E'' from Eq. 7 into Eq. 8 and assuming the absorption to be low $\omega/C \gg \alpha$ and $E_0 \gg E_1$ the following expressions for $C(\omega)$ and $\alpha(\omega)$ will be obtained:

$$C(\omega) = \sqrt{\frac{E_0}{\rho} + \frac{E_1}{\rho}\cdot f_1(\omega)} \simeq C_0\left[1 + \frac{1}{2}\cdot\frac{E_1}{E_0}\cdot f_1(\omega)\right]$$

$$\alpha(\omega) = \frac{1}{2}\cdot\frac{\omega}{C_0}\cdot\frac{E_1}{E_0}\cdot f_2(\omega) \tag{9}$$

The relationship between the constants of the medium E_0 and E_1 and the limiting values of ultrasonic velocity C_0 and C_∞ are found as follows. Insofar as for $\omega \rightarrow 0\, f_1$ also approaches zero, and accordingly $C_0^2 = E_0/\rho$. If $\omega \rightarrow \infty$ then $f_1 \rightarrow 1$ and, hence, $C_\infty^2 = C_0^2 + E_1/\rho$. As can be seen from the foregoing

$$\frac{E_1}{E_0} = \frac{C_\infty^2 - C_0^2}{C_0^2} = \Delta \tag{10}$$

Substituting the expression (10) into (9), one readily notes that Eq. 9 is precisely coincident with the frequency dependences of ultrasonic velocity and absorption coefficient in Eq. 1. This coincidence is indicative of the adequacy of description of the properties of a medium having internal inertia by the suggested rheological model.

Let us consider the parameters involved in the model in question. Where the medium, under varying thermodynamic conditions, retains unchanged its resonance frequency characteristics, then the macroscopic mechanical properties of the material are affected by the mechanical structure to a greater extent than by thermodynamic processes. Hence, the common feature of the media characterized by internal inertia comprises the internal inhomogeneity of the structure, such as crystallites in molecular crystals. It is reasonable to assume that a crystallite in a polycrystal acts as an oscillator (the carrier of internal inertia of the medium) excited by an ultrasonic wave. In the melting region, intercrystallite bonds become weaker and the resonance effect of crystallite oscillations in an ultrasonic wave is predominant.

When a crystallite travels in the field of an acoustic wave with the wave length greater than the crystallite dimensions D, the forces acting on the crystallite will be elastic forces F_1 elast with the rigidity factor æ and friction forces F_2 with the effective loss coefficient η which characterizes the friction on intergranular boundaries:

$$F_1 = -æ\eta, \qquad F_2 = -D\cdot\eta\cdot\frac{du}{dt}$$

where u denotes the displacement of a crystallite. The crystallite having the mass m, under the effect of these two forces, performs damped oscillations with the fundamental frequency ω_0 equal to

$$\omega_0 = \sqrt{\frac{æ}{m}} \tag{11}$$

The relaxation time τ, which characterizes the attenuation of crystallite oscillations, is given by the equation

$$\tau = \frac{D \cdot \eta}{æ} \tag{12}$$

Assuming that the coefficient η in Eq. 6 defining characterizes losses due to friction on intergranular boundaries, a comparison of Eqs. 6 and 11 would yield

$$æ = E_1 \cdot D$$

Equating expressions (6) and (12) for the resonance frequency makes it possible to define the parameter M introduced into the suggested model:

$$M = \frac{m}{D} = \rho \cdot D^2 \tag{13}$$

The parameter M characterizing the internal inertia of the material is equal to the ratio of the crystallite mass m and the crystallite dimensions D. As can be suggested from the analysis of the model, the elastic modulus E_1 defines the elasticity of intergranular bonds in a polycrystal. In Eq. 13 the density of crystallite was assumed to equal the density ρ of the material under examination.

A comparison of the parameters ω_0 and τ (Eqs. 11 and 12) for our model with the analogous parameters defined by formulae (2) in the case of nonequilibrium thermodynamics involving internal inertia enables one to express the effective mass m_1 and the attenuation coefficient β_1 in terms of the crystallite parameters m and D.

Correlating Eqs. 11 and 12 with formulae (3) provides the possibility of expressing the effective mass of dislocation unit length m_2 and the damping coefficient β_2 employed in Ref. 7 in terms of the crystallite parameters m and D.

The thus-obtained relationship between the magnitudes ω_0 and τ which characterize the dispersion of ultrasound in molecular crystals, and the parameters of the rheological model makes for determining the crystallite size by measuring $C(\omega)$ and $\alpha(\omega)$. Eqs. 6, 10 and 13 upon correlation yield the following formula:

$$D = \frac{C_0}{\omega_0} \cdot \sqrt{\Delta} \tag{14}$$

Listed in the table which follows are the results of using formula (14) to calculate the dimensions of crystallites of various molecular crystals in the melting region on the basis of data reported in Ref. 9. By way of comparison, the table also includes the dimensions of crystallites $\bar{D}$ measured visually by means of a microscope. In the table, $t°, C$ denotes the temperature at which measurements were carried out, t_f is the fusion point of the substance, and λ is the ultrasonic wave length. It should be noted that the frequency dependences of ultrasonic velocity and absorption coefficient were obtained for an infinite medium on the assumption that the wave length λ is much greater than the inhomogeneity dimensions $\bar{D}$, this condition being satisfied in the case of cyclohexane, for which $\lambda/\bar{D} \simeq 30$. As can be seen from the table, here the polycrystallite size D calculated using formula (14) coincides with the observed size $\bar{D}$. When the ratio $\lambda/\bar{D}$ decreases, the calculated results according to formula (14) start deviating from the visual observation data. For example, in the case of benzene $\lambda/\bar{D} = 10$ and $D/\bar{D} \simeq 0.4$. Where the crystallites are large (diphenyl, naphthalene), the ultrasonic wave length will be smaller than the size of crystallites and there appears a significant discrepancy between the value of D calculated using formula (14) and the experimental value $\bar{D}$. This disagreement is associated with the fact that formula (14) deduced under the assumption that $\lambda \gg \bar{D}$ becomes invalid in the case under consideration.

The coincidence of the sizes of crystallites calculated on the basis of measuring the frequency dependence of ultrasonic velocity and absorption

TABLE

Compound	$t°, C$	Δ, %	C_0, m/c	ω_0, 10^7 c^{-1}	$\bar{D}$, mm	D, mm	λ, mm
Benzene (t_f = 5.5°C)	5.4	6.5	2196	1.4	0.1–0.2	0.04	0.95
p-Xylene (t_f = 13.3°C)	13.0	14.0	2560	4.9	0.5–1.0	0.02	0.30
Cyclohexane (t_f = 6.6°C)	4.5	4.0	1495	3.0	0.01–0.02	0.01	0.30
Diphenyl (t_f = 69.2°C)	65.0	21.5	2838	2.0	1.0	0.07	0.90
Naphthalene (t_f = 79.6°C)	79.0	22.0	2759	4.3	1.0	0.03	0.39

coefficient in molecular crystals and the visually observed crystallite sizes is indicative of the validity of the internal inertia and relaxation mechanism described by the suggested rheological model and discussed in the present paper. The model in question makes it possible to determine the size of crystallites by measuring the values of Δ, C_0 and ω_0 which define the dispersion characteristics of ultrasound propagation in the polycrystalline specimens of molecular crystals in the melting range.

Acknowledgments

The author expresses his gratitude to N. I. Koshkin and V. M. Sorokin for fruitful discussion of the results and valuable comments.

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