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Attenuation and Dispersion of Acoustic Waves in Reacting Nematic Liquid Crystal Mixtures

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The Ericksen-Leslie theory of nematic liquid crystals is extended to non-diffusive reacting binary mixtures. This mixture theory allows for the reaction rate to depend on both the rate-of-deformation tensor and the anisotropic axis. Thermodynamic arguments result in reactive terms appearing in the expression for the stress tensor. The theory is applied to the propagation of acoustic waves. The equations are linearized assuming a forced infinitesimal harmonic plane wave, and a biquadratic polynomial is obtained for the complex wave number. In a low frequency expansion the attenuation is the sum of three parts: (1) the classical reaction contribution, (2) the thermoviscous contribution, and (3) the viscoreactive contribution arising from the dependence of the reaction rate on the alignment of the anisotropic axis and rate-of-deformation tensor. Additionally, the sound speed is a function of orientation of the anisotropic axis and frequency. The observed velocity anisotropy of acoustic waves in *N*-*p*-methoxybenzylidine-*p'*-*n*-butylaniline (MBBA) is consistent with the predicted anisotropy and is thus attributed to conformational changes where the rate of conformational change is a function of the rate-of-deformation tensor and the anisotropic axis.

Keywords: acoustics, internal relaxation, nematics, reacting mixtures

1. INTRODUCTION

Ultrasonic experiments in the megahertz range on nematic liquid crystals far below the isotropic transition temperature indicate the occurrence of internal relaxation. For example, in the nematic MBBA acoustic waves show a small velocity anisotropy that is frequency dependent and an attenuation anisotropy that varies approximately linearly with frequency in the range 2–6 MHz.[1,2] Such results are not predicted by a purely hydrodynamic theory of liquid crystals, which at low frequencies gives an attenuation proportional to the square of the frequency and a velocity effectively independent of orientation of the anisotropic axis and frequency.[3] Neither are they due to critical fluctuations associated with a phase change.[2] The frequency dependence of the attenuation and velocity at a fixed orientation is however characteristic of that in isotropic fluids with internal relaxation.

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For MBBA the source of the acoustic relaxation is generally thought to be due to the occurrence of restricted internal rotations of the molecules.[4,5] Many nematics such as MBBA consist of molecules having a relatively central rigid backbone with flexible extremities, so that the possible conformations differ by rotations of the endgroups, with the physical and chemical properties of each conformer generally different. Because of the low energy barriers between the conformational isomers these substances can exist as a mixture in equilibrium. Any disturbance from equilibrium, such as that produced by an acoustic wave, changes the relative concentration of conformers. Part of the energy of the wave is irreversibly transformed as it is exchanged between translational energy and conformational energy of the molecules.

With the possibility of conformational changes occurring during the propagation of the waves, nematics must be treated as chemically reacting mixtures. Acoustic waves in *isotropic* reacting mixtures have been extensively studied theoretically and experimentally, the propagation of acoustic waves depending on the thermoviscous properties as well as the chemical properties of the medium.[6-8] For an infinitesimal plane harmonic wave and a single unimolecular reaction, one obtains at low frequencies the classical formulas

$$\frac{\alpha}{f^2} = \frac{A}{1 + \omega^2\tau_{\eta\rho}^2} + B, \qquad c^2 = c_\infty^2 + \frac{(c_0^2 - c_\infty^2)}{1 + \omega^2\tau_{\eta\rho}^2}, \tag{1.1}$$

where α is the attenuation coefficient, ω is the angular frequency $(=2\pi f)$, $\tau_{\eta\rho}$ denotes the chemical relaxation time at constant entropy and density, A and B are material constants with A representing the reaction contribution and B the thermoviscous contribution, c is the sound speed, c_0 is the equilibrium sound speed, and c_∞ is the frozen sound speed. By fitting experimental data with (1.1), one can determine various material parameters characterizing the reaction. These formulas have also been used to interpret results from experiments on liquid crystals where B is now a known function of the orientation of the anisotropic axis with respect to the direction of propagation of the waves.[4,9-11] Obviously, this procedure fails to account for the observed velocity anisotropy in MBBA, leading some to suggest the possibility of viscoelasticity as the source of the velocity anisotropy.[1,12,13] By allowing for an arbitrary frequency-dependence in the viscous and elastic terms, the coefficients are adjusted at each frequency until they fit experimental data. Generally with such a procedure, one can fit just about any data. Here we prefer to determine what the theory for reacting mixtures predicts *without* any complications of viscoelasticity. The reaction contribution (1.1) is derived by assuming an *isotropic* fluid. We will show that (1.1) does not fully take into account the *anisotropy* of liquid crystals, i.e., the possibility of anisotropic reactions.

In this paper we present a continuum theory of the propagation of acoustic waves in a non-diffusive reacting binary mixture of nematic liquid crystals. Our objective is twofold: to theoretically develop a consistent model for reactions in nematics fully taking into account their anisotropy and to determine the effect of the reactions on the propagation of acoustic waves. First we generalize the Ericksen-Leslie theory of liquid crystals to include binary reactions, the simplest extension of the theory.

We have the homogeneous, non-diffusive unimolecular reaction

$$C_1 \rightleftharpoons C_2, \tag{1.2}$$

C_1 and C_2 being the two coexisting chemical constituents, or in the case of MBBA, two possible conformers. The theory can be easily extended to more complex processes by including additional variables. We give the appropriate balance laws, constitutive relations, and thermodynamic restrictions. In this theory the material symmetry allows for a partial mass supply that depends on the anisotropic axis and the rate-of-deformation tensor. This dependence implies additional terms in the stress tensor due to the reaction. Our presentation emphasizes these additional terms, called viscoreactive, because traditionally they are neglected, but their presence will be shown to be important to account for some experimental observations. Physically it is easy to motivate these additional terms since velocity gradients may affect the orientation, structure, and collisions of the molecules and, consequently, the reaction rate. Next we linearize the equations about the equilibrium state of uniform alignment assuming a forced infinitesimal harmonic plane wave. A necessary and sufficient condition for the existence of solutions to these linearized equations yields a polynomial equation for the complex wave number, whose solutions yield measures for the attenuation and dispersion. To obtain explicit formulas for the interpretation of experimental measurements, we give a low-frequency expansion of the wave number. The resulting expression for the attenuation is a sum of three parts: (1) the classical reaction contribution, (2) the thermoviscous contribution, and (3) the viscoreactive contribution arising from the dependence of the reaction rate on the anisotropic axis and rate of deformation. Additionally the sound speed is a function of frequency and orientation. These results are compared to the experimental data on MBBA by Mullen *et al.*,[1] Lord and Labes,[2] and Bacri,[11] where it is shown that the orientation dependence of the observed velocity anisotropy agrees well at low frequencies with that of the predicted velocity anisotropy. Consequently, we attribute the velocity anisotropy in MBBA to conformational changes where the rate of conformational change is a function of the anisotropic axis and the rate of deformation. Assumptions of viscoelasticity do not appear to be needed to account for the experimental observations of MBBA as generally asserted.[1,12,13]

We point out that the exact nature of an observed acoustic relaxation is generally unknown. Acoustic data tend to be ambiguous about the details and source of the relaxation. In this case the common procedure[7,8] is to treat the material as having additional, unspecified structure that allows the material to coexist in several different but interchangeable states, for example, excited energy levels. Consequently, the relaxational processes become equivalent to chemical reactions with unknown mechanisms. Each state can be thought of as a different chemical constituent and the corresponding extents of reactions thus regarded as internal variables. With this multi-state point of view of internal relaxation, the mixture theory presented here can also be interpreted as applying to these more general relaxational processes. Thus our theory shows that the possibility exists in liquid crystals of *anisotropic* internal relaxation.

This work is the sequel to a previous paper[3] in which we discussed the purely thermoviscous theory of acoustics in nematic liquid crystals. For details on our notation and on our procedure, we refer the reader to this paper. Phase transitions, radiation, electric field effects, and gravitation are neglected in the present paper.

2. BALANCE LAWS AND CONSTITUTIVE RELATIONS

In this section we present the balance laws, constitutive relations, and thermodynamic restrictions for the Ericksen-Leslie theory of non-diffusive reacting binary mixtures of compressible nematic liquid crystals. The previously considered[3] balance laws for mass, linear momentum, moment of momentum, director momentum, and energy are used here with the interpretation that the variables represent mixture quantities. In addition, a partial mass balance for each constituent is needed:

$$\frac{d\omega_\alpha}{dt} = \omega_\alpha^+, \tag{2.1}$$

where ω_α is the molar concentration of the α-constituent and ω_α^+ represents the molar production of the α-constituent due to chemical reactions. For a non-diffusive mixture, an extent of reaction ζ_γ can be introduced for each independent reaction, γ, so that

$$\omega_\alpha = \omega_\alpha^0 + S_{\alpha\gamma}\zeta_\gamma, \tag{2.2}$$

where ω_α^0 is the reference molar density, $S_{\alpha\gamma}$ is the signed stoichiometric coefficient of the independent reactions, and the repeated index indicates a sum over the independent reactions. The partial mass balance (2.1) takes the form

$$S_{\alpha\gamma}\dot{\zeta}_\gamma = \omega_\alpha^+ \equiv S_{\alpha\gamma}\zeta_\gamma^+, \tag{2.3}$$

or equivalently

$$\dot{\zeta}_\gamma = \zeta_\gamma^+, \tag{2.4}$$

where $\dot{\zeta}_\gamma$ is the reaction rate of the γ-independent reaction and ζ_γ^+ is the supply term that must be specified by a constitutive relation. This reaction equation supplements the balance laws.

We assume that the flexibility in the molecules associated with the conformational changes is small enough that the concept of a director is still applicable. Also for an arbitrary reaction, the magnitude of the director is in general variable. Here we will ignore this complication and assume that the director has unit magnitude. Additionally we assume that the inertial coefficient for the director is constant. This approximation seems to be reasonable for conformational changes such as those thought to occur in MBBA. Thus for our binary mixture with the single

reaction (1.2), the balance laws become

$$\dot{\zeta} = \zeta^+,$$

$$\dot{\rho} + \rho v_{i,i} = 0,$$

$$\rho \dot{v}_i = T_{ji,j} + \rho b_i,$$

$$\rho\sigma \ddot{d}_i = S_{ji,j} + \rho(G_i + g_i),$$

$$\epsilon_{ijk}\rho d_j g_k = \epsilon_{ijk}(T_{jk} + S_{mk}d_{j,m}),$$

$$\rho\dot{\epsilon} = \rho r - q_{i,i} + T_{ji}D_{ij} + S_{ji}N_{ij} - \rho g_i N_i. \tag{2.5}$$

In the above, ρ is the density, v_i the velocity, T_{ij} the total stress tensor, D_{ij} the symmetric part of the velocity gradient, d_i the director, N_i and N_{ij} are objective quantities given by

$$N_i = \dot{d}_i + W_{ki}d_k, \qquad N_{ij} = (\dot{d}_i)_{,j} + W_{ki}d_{k,j}, \tag{2.6}$$

W_{ij} the antisymmetric part of the velocity gradient, σ the inertial coefficient, S_{ij} the director stress tensor, G_i the external director body force per unit mass, g_i the intrinsic director body force per unit mass, ϵ the specific internal energy, q_i the outward heat flux vector, r the external radiation per unit mass, ϵ_{ijk} the permutation tensor, the comma the derivative with respect to the spatial variable, and the superposed dot the material time derivative. We use the notation that the Latin subscripts i–m refer to Cartesian components and the subscript α refers to the constituents occurring in the reaction.

To complete the balance laws, constitutive relations must be postulated for

$$\mathbf{T}, \mathbf{S}, \mathbf{g}, \mathbf{q}, \psi, \quad \text{and} \quad \zeta^+ \tag{2.7}$$

in terms of a set of independent variables. In addition to the commonly chosen independent variables for single constituent nematics, further information such as the concentration of each constituent is needed to specify the state with the occurrence of chemical reactions. Consequently, we take as the independent variables the set

$$\{\zeta, \rho, \theta, \nabla\theta, \mathbf{D}, \mathbf{d}, \mathbf{N}, \nabla\mathbf{d}\}. \tag{2.8}$$

This choice of independent variables is the simplest possible for a reacting nematic mixture. The six variables in (2.7) are assumed to be functions of all the independent variables (2.8).

We now determine the thermodynamic restrictions on (2.7) imposed by the requirement of non-negative entropy production. We use the entropy inequality

in the form

$$\rho\dot{\eta} + \operatorname{div}\left(\frac{\mathbf{q}}{\theta}\right) - \frac{\rho r}{\theta} \geq 0. \tag{2.9}$$

Eliminating the radiation term through the energy equation and introducing the specific Helmholtz free energy $\psi = \epsilon - \theta\eta$, where θ is the temperature and η the specific entropy, the inequality (2.9) becomes

$$T_{ji}D_{ij} + S_{ji}N_{ij} - \rho g_i N_i - \rho(\dot{\psi} + \dot{\theta}\eta) - \frac{q_i\theta_{,i}}{\theta} \geq 0. \tag{2.10}$$

The equilibrium state is taken here to be that when ζ^+, $\nabla\theta$, $\mathbf{D}$, and $\mathbf{N}$ vanish, minimizing the entropy production. For (2.10) to be a minimum in equilibrium, the first variation must vanish, which implies

$$\psi = \psi(\zeta, \rho, \theta, \mathbf{d}, \nabla\mathbf{d}), \qquad \eta = -\frac{\partial\psi}{\partial\theta},$$

$$T_{ij} = -p\delta_{ij} - \rho A\frac{\partial\zeta^+}{\partial D_{ji}} - \rho\frac{\partial\psi}{\partial d_{k,i}}d_{k,j} + T^d_{ij},$$

$$S_{ij} = \rho\frac{\partial\psi}{\partial d_{j,i}} + \tau_i d_j,$$

$$\rho g_i = -\rho\frac{\partial\psi}{\partial d_i} + \rho A\frac{\partial\zeta^+}{\partial N_i} + \nu d_i - (d_i\tau_j)_{,j} + \rho g^d_i,$$

$$\epsilon_{ijk}\left(\frac{\partial\psi}{\partial d_i}d_j + \frac{\partial\psi}{\partial d_{i,m}}d_{j,m} + \frac{\partial\psi}{\partial d_{m,i}}d_{m,j}\right) = 0, \tag{2.11}$$

where the superscript d means the dynamic terms due to the motion of the material. The coefficients τ_i and ν are lagrangean multipliers that appear because of the constraint of a rigid director. The affinity of the reaction A and thermostatic pressure p have been introduced above and are defined by

$$A \equiv -\frac{\partial\psi}{\partial\zeta} \qquad p \equiv \rho^2\frac{\partial\psi}{\partial\rho}. \tag{2.12}$$

Note that as a consequence of the entropy inequality there are reaction terms in the stress tensor $\mathbf{T}$ and the intrinsic body force $\mathbf{g}$. Here we consider only the case of strong equilibrium, i.e., $\zeta^+ = 0$ implies $A = 0$. Consequently, the pressure p is the isotropic stress in strong equilibrium and uniform alignment of the director.

The residual entropy inequality becomes

$$\left(T_{ji}^{d} - \rho A \frac{\partial \zeta^{+}}{\partial D_{ji}}\right) D_{ij} - \rho\left(g_i^d + A \frac{\partial \zeta^{+}}{\partial N_i}\right) N_i - \frac{q_i \theta_{,i}}{\theta} + \rho A \zeta^{+} \geq 0. \tag{2.13}$$

For the dynamic terms we make the standard assumption: they are linear in $\mathbf{N}$, $\mathbf{D}$, and $\nabla\theta$, and independent of $\nabla\mathbf{d}$. Isotropic representation theorems consistent with the material symmetry and objectivity yield the following relations:

$$\begin{aligned}
\zeta^{+} &= \zeta_0^{+} + \zeta_1^{+} D_{kk} + \zeta_2^{+} D_{kj} d_k d_j, \\
T_{ij}^{d} &= (\mu_3 D_{kk} + \mu_4 D_{kl} d_k d_l)\delta_{ij} + (\mu_5 + \mu_7 D_{kk} + \mu_8 D_{kl} d_k d_l) d_i d_j \\
&\quad + \mu_9 d_i N_j + \mu_{10} d_j N_i + \mu_{11} D_{ij} + \mu_{12} d_k d_i D_{jk} + \mu_{13} d_j d_k D_{ki}, \\
\rho g_i^{d} &= \lambda_5 N_i + \lambda_6 D_{ji} d_j, \\
q_i &= -\kappa_a d_j \theta_{,j} d_i - \kappa_{\perp} \theta_{,i},
\end{aligned} \tag{2.14}$$

with

$$\lambda_5 \equiv \mu_9 - \mu_{10}, \qquad \lambda_6 \equiv \mu_{12} - \mu_{13}, \qquad \kappa_a \equiv \kappa_{\perp} - \kappa_{\parallel},$$

and the coefficients being functions of ζ, ρ, and θ.

The term ζ_0^{+} is given by the mass-action expression

$$\zeta_0^{+} = k^F(p,\theta,\mathbf{d},\nabla\mathbf{d}) \prod a_\alpha^{S_\alpha^-} - k^R(p,\theta,\mathbf{d},\nabla\mathbf{d}) \prod a_\alpha^{S_\alpha^+}, \tag{2.15}$$

where k^F and k^R are the reaction rate functions in the forward and reverse directions, $a_\alpha = \gamma_\alpha(p,\theta,\zeta,\mathbf{d},\nabla\mathbf{d})x_\alpha$ is the activity of the α-constituent, γ_α the activity coefficient, x_α the mole fraction of the α-constituent, and S_α^+, S_α^- are the positive signed stoichiometric coefficients ($S_\alpha = S_\alpha^- - S_\alpha^+$). Since

$$\prod a_\alpha^{S_\alpha} = K(p,\theta,\mathbf{d},\nabla\mathbf{d}) \exp\left(-\frac{A}{R\theta}\right), \tag{2.16}$$

where K is the equilibrium constant, (2.15) can be written as

$$\zeta_0^{+} = \left[1 - \exp\left(-\frac{A}{R\theta}\right)\right] k^F \prod a_\alpha^{S_\alpha^-}. \tag{2.17}$$

It is traditional to use the pressure, defined by (2.12), instead of the density as an independent variable in ζ_0^{+}. We follow this practice. All functions here are assumed

to be invertible so that it makes no difference which independent variables are used. Note that in order for this to be true we must allow for a dependence on **d** and $\nabla\mathbf{d}$ in the coefficients.

In addition to ζ_0^+, two other terms appear in the expression for ζ^+. The term with ζ_1^+ also appears in Newtonian fluids,[8,14] though it is usually neglected. For incompressible materials it vanishes identically because $D_{kk} = 0$. The term with ζ_2^+, however, is unique to anisotropic fluids. It is this term that applies anisotropy in the reaction rate. From (2.11) these two coefficients also appear in the stress tensor **T**,

$$T_{ij} = p\delta_{ij} - \rho A(\zeta_1^+\delta_{ij} + \zeta_2^+ d_i d_j) - \rho \frac{\partial \psi}{\partial d_{k,i}} d_{k,j} + T_{ij}^d. \tag{2.18}$$

Note that reciprocity relations, used in theories of linear irreversible thermodynamics,[7,8] are *not* needed to obtain this result, which follows directly from the entropy inequality. Also, when the material is at rest the rate of deformation tensor is zero, so that the expression for ζ^+ reduces to (2.17). Because of the constraint of constant director magnitude, ζ^+ is independent of **N**, thus no reaction terms appear in the director equation. Similar relations for stress tensor **T** and chemical supply term ζ^+ were obtained independently by Rubin.[15] In conformity with the literature on isotropic fluids, we call ζ_1^+ and ζ_2^+ *viscoreactive* coefficients.

The constitutive relations (2.14) must also satisfy the residual entropy inequality (2.13). Substitution into (2.13) along with the requirement of positive-definiteness leads to the results

$$\begin{gathered}
\kappa_\parallel > 0, \qquad \kappa_\perp > 0, \qquad A\zeta_0^+ \geq 0, \\
\mu_5 = 0, \quad \mu_{11} > 0, \quad \mu_3 + \mu_{11} > 0, \quad \lambda_5 < 0, \\
2\mu_{11} + \mu_{12} + \mu_{13} > 0, \quad 2\mu_8 + 3\mu_{11} + 2\mu_{12} + 2\mu_{13} > 0, \\
\mu_3 + \mu_4 + \mu_7 + \mu_8 + \mu_{11} + \mu_{12} + \mu_{13} > 0, \\
9\mu_3 + 3\mu_4 + 3\mu_7 + \mu_8 + 3\mu_{11} + \mu_{12} + \mu_{13} > 0, \\
-4\lambda_5(2\mu_{11} + \mu_{12} + \mu_{13}) > (\mu_9 + \mu_{10} - \lambda_6)^2, \\
-4\lambda_5(9\mu_3 + 3\mu_4 + 3\mu_7 + \mu_8 + 3\mu_{11} + \mu_{12} + \mu_{13}) > (\mu_9 + \mu_{10} - \lambda_6)^2.
\end{gathered} \tag{2.19}$$

No restrictions are placed on ζ_1^+ or ζ_2^+ since they do not affect the dissipation.

The free energy ψ is expanded to second order in $\nabla\mathbf{d}$, allowing for the coefficients K_n to be functions of ζ, ρ, and θ:

$$2\psi = K_0 + K_1(\text{div } \mathbf{d})^2 + K_2(\mathbf{d} \cdot \text{curl } \mathbf{d})^2 + K_3(\mathbf{d} \cdot \nabla)\mathbf{d} \cdot (\mathbf{d} \cdot \nabla)\mathbf{d}. \tag{2.20}$$

Surface energy terms have been neglected in (2.20). Finally, we assume that the external body forces are given by the usual expressions of the external magnetic field **H** and magnetization **M**,

$$\rho \mathbf{b} = (\mathbf{M} \cdot \nabla)\mathbf{H}, \qquad \rho G = \chi_a (\mathbf{d} \cdot \mathbf{H})\mathbf{H}, \tag{2.21}$$

where the magnetic susceptibility anisotropy is positive and defined by

$$\chi_a \equiv \chi_{\parallel} - \chi_{\perp}. \tag{2.22}$$

3. LINEARIZED EQUATIONS

In this section we linearize the balance laws and constitutive relations to obtain the equations for the propagation of forced infinitesimal compressional plane waves in uniformly aligned reacting binary mixtures of nematic liquid crystals.

Given a semi-infinite homogeneous uniformly aligned material at rest, the $y-z$ plane is oscillated harmonically in time in the x-direction with angular frequency ω. The displacement of the wall and resulting motion of the fluid is assumed to be infinitesimal so that the acoustic wave creates a small disturbance to the equilibrium value any variable I,

$$I = I^0 + I^a, \tag{3.1}$$

where I^0 is the equilibrium contribution with uniform alignment of the director and I^a is the acoustic contribution. We write the acoustic variables as the propagation of a damped harmonic oscillation:

$$I^a = \hat{I}^a \exp i(\omega t - kx), \qquad k \equiv \frac{\omega}{c} - i\alpha. \tag{3.2}$$

Second-order terms in the acoustic variables will be ignored.

In the rest state, the director is uniformly aligned by a sufficiently strong external magnetic field **H**:

$$\mathbf{H} = H\mathbf{d}^0, \qquad \nabla \mathbf{d}^0 = 0, \qquad \mathbf{d}^0 = \begin{pmatrix} \cos\Theta \\ \sin\Theta \\ 0 \end{pmatrix}, \tag{3.3}$$

where the director lies in the $x-y$ plane, making an angle Θ with the x-axis. In the perturbed state the transverse and longitudinal components of the velocity field are generally coupled. Consequently the simplest assumptions for the velocity and director perturbations, taking into account the constraint of constant director magnitude, have the form

$$\hat{\mathbf{v}}^a = \begin{pmatrix} \hat{v}_x^a \\ \hat{v}_y^a \\ 0 \end{pmatrix} \qquad \hat{\mathbf{d}}^a = \hat{d}^a \begin{pmatrix} -\sin\Theta \\ \cos\Theta \\ 0 \end{pmatrix} \tag{3.4}$$

Several thermodynamic relations exist between variables. We record here those that will be used in this paper. In equilibrium, ζ_0^+ vanishes so that the two terms on the right in (2.15) equal each other. Denote their common value by ζ_e^+. The linear form of (2.17) near strong equilibrium becomes

$$\frac{\hat{\zeta}_0^{+a}}{\zeta_e^+} = \left(\frac{\partial A/R\theta}{\partial\theta}\right)_{p\zeta}^0 \hat{\theta}^a + \left(\frac{\partial A/R\theta}{\partial p}\right)_{\zeta\theta}^0 \hat{p}^a + \left(\frac{\partial A/R\theta}{\partial\zeta}\right)_{\theta p}^0 \hat{\zeta}^a, \tag{3.5}$$

where

$$\left(\frac{\partial A/R\theta}{\partial\theta}\right)_{p\zeta}^0 = \frac{h}{R(\theta^0)^2}, \quad \left(\frac{\partial A/R\theta}{\partial p}\right)_{\zeta\theta}^0 = -\frac{v}{R\theta^0}, \quad \left(\frac{\partial A/R\theta}{\partial\zeta}\right)_{\theta p}^0 = -\frac{1}{\tau_{\theta p}\zeta_e^+}. \tag{3.6}$$

Here v is the molar volumetric change at constant temperature and pressure, h the molar heat of reaction at constant temperature and pressure, $\tau_{\theta p}$ the relaxation time at constant temperature and pressure and zero velocity, and R the gas constant. Similar linear relations for the density, internal energy, and entropy can be written,

$$\begin{aligned} \hat{\rho}^a &= \left(\frac{\partial\rho}{\partial\theta}\right)_{p\zeta}^0 \hat{\theta}^a + \left(\frac{\partial\rho}{\partial p}\right)_{\theta\zeta}^0 \hat{p}^a + \left(\frac{\partial\rho}{\partial\zeta}\right)_{\theta p}^0 \hat{\zeta}^a, \\ &= -\rho^0\beta_\theta^\infty\hat{\theta}^a + \rho^0\beta_p^\infty\hat{p}^a - (\rho^0)^2 v\hat{\zeta}^a, \end{aligned} \tag{3.7}$$

$$\begin{aligned} \rho^0\hat{\epsilon}^a &= \rho^0\left(\frac{\partial\epsilon}{\partial\theta}\right)_{p\zeta}^0 \hat{\theta}^a + \rho^0\left(\frac{\partial\epsilon}{\partial p}\right)_{\theta\zeta}^0 \hat{p}^a + \rho^0\left(\frac{\partial\epsilon}{\partial\zeta}\right)_{\theta p}^0 \hat{\zeta}^a;, \\ &= \rho^0 c_p^\infty\hat{\theta}^a - \theta^0\beta_\theta^\infty\hat{p}^a + \rho^0 h\hat{\zeta}^a, \end{aligned} \tag{3.8}$$

$$\begin{aligned} \rho^0\hat{\eta}^a &= \rho^0\left(\frac{\partial\eta}{\partial\theta}\right)_{p\zeta}^0 \hat{\theta}^a + \rho^0\left(\frac{\partial\eta}{\partial p}\right)_{\theta\zeta}^0 \hat{p}^a + \rho^0\left(\frac{\partial\eta}{\partial\zeta}\right)_{p\theta}^0 \hat{\zeta}^a, \\ &= \frac{\rho^0 c_p^\infty}{\theta^0}\hat{\theta}^a - \beta_\theta^\infty\hat{p}^a + \frac{\rho^0 h}{\theta^0}\hat{\zeta}^a, \end{aligned} \tag{3.9}$$

where β_θ^∞, β_p^∞, and β_η^∞ are the frozen isobaric expansion coefficient, isothermal coefficient of compressibility, and isentropic coefficient of compressibility, and c_p^∞ is the frozen specific heat at constant pressure. For simplicity of notation we do not write the superscript zero for the material parameters.

Quantities measured at constant extent of reaction are called frozen and are designated here with the superscript ∞. Changes of the system occur so rapidly that the composition cannot equilibrate. Experiments sometimes are done at constant affinity rather than at constant extent of reaction. In this case changes of the system occur slowly enough that the concentrations of the components are in equilibrium. Quantities measured at constant affinity are called equilibrium and are designated here by the same symbol but without a superscript. Using (3.5–9) the correspondence between the frozen and equilibrium parameters is

$$\beta_\theta = \beta_\theta^\infty + \frac{\rho^0 \nu h \tau_{\theta p} \zeta_e^+}{R(\theta^0)^2}, \quad \beta_p = \beta_p^\infty + \frac{\rho^0 \nu^2 \tau_{\theta p} \zeta_e^+}{R\theta^0},$$
$$c_p = c_p^\infty + \frac{h^2 \tau_{\theta p} \zeta_e^+}{R(\theta^0)^2}, \quad \beta_\eta = \beta_\eta^\infty + \frac{\tau_{\theta p} \zeta_e^+ \rho^0}{R\theta^0} \frac{\left(\nu - \dfrac{\beta_\theta^\infty h}{\rho^0 c_p^\infty}\right)^2}{\left(1 + \dfrac{h^2 \tau_{\theta p} \zeta_e^+}{R(\theta^0)^2 c_p^\infty}\right)}. \tag{3.10}$$

Other thermodynamic relations that we will make use of are

$$\frac{\gamma^\infty - 1}{\gamma^\infty} = \frac{\theta^0 (\beta_\theta^\infty)^2}{\rho^0 c_p^\infty \beta_p^\infty}, \quad \beta_\eta^\infty = \frac{\beta_p^\infty}{\gamma^\infty}. \tag{3.11}$$

An equivalent set of relations holds for the equilibrium counterpart of (3.11). Also, different relaxation times can be introduced depending on the choice of independent variables. We write

$$\begin{aligned}
\tau_{\eta p}^{-1} &= -\zeta_e^+ \left(\frac{\partial A/R\theta}{\partial \zeta}\right)_{\eta p}^0 = \tau_{\theta p}^{-1} + \frac{\zeta_e^+ h^2}{c_p^\infty R(\theta^0)^2}, \\
\tau_{\eta\theta}^{-1} &= -\zeta_e^+ \left(\frac{\partial A/R\theta}{\partial \zeta}\right)_{\eta\theta}^0 = \tau_{\theta p}^{-1} + \frac{\zeta_e^+ \rho^0 \nu h}{\beta_\theta^\infty R(\theta^0)^2}, \\
\tau_{\eta\rho}^{-1} &= -\zeta_e^+ \left(\frac{\partial A/R\theta}{\partial \zeta}\right)_{\eta\rho}^0 = \tau_{\eta p}^{-1} + \frac{\zeta_e^+ \rho^0}{R\theta^0} \left(\nu - \frac{\beta_\theta^\infty h}{\rho^0 c_p^\infty}\right)^2, \\
\tau_{\theta\rho}^{-1} &= -\zeta_e^+ \left(\frac{\partial A/R\theta}{\partial \zeta}\right)_{\theta\rho}^0 = \tau_{\theta p}^{-1} + \frac{\zeta_e^+ \rho^0 \nu^2}{\beta_p^\infty R\theta}.
\end{aligned} \tag{3.12}$$

To obtain the first-order acoustic equations, the balance laws and constitutive relations are systematically linearized by decomposing the variables into the sum of the equilibrium part and the acoustic part, then neglecting second-order terms in the acoustic variables. For infinitesimal waves propagating into a uniformly

aligned material at rest, the linearized equations become:

$$
\begin{aligned}
(i\omega + \tau_{\theta p}^{-1})\hat{\zeta}^a &= \frac{\zeta_e^+ h}{R(\theta^0)^2}\hat{\theta}^a - \frac{\zeta_e^+ v}{R\theta^0}\hat{p}^a \\
&\quad - ik\frac{\zeta_e^+}{R\theta^0}(\bar{\zeta}_1 + \bar{\zeta}_2\cos^2\Theta)\hat{v}_x^a - \frac{1}{2}ik\frac{\zeta_e^+\bar{\zeta}_2}{R\theta^0}\hat{v}_y^a \sin 2\Theta, \\
ik\hat{v}_x^a &= -i\omega\beta_\theta^\varkappa\hat{\theta}^a + i\omega\beta_p^\varkappa\hat{p}^a - i\omega\rho^0 v\hat{\zeta}^a, \\
i\omega\rho^0\hat{v}_x^a &= ik\hat{p}^a - k\omega\rho^0(\bar{\zeta}_1 + \bar{\zeta}_2\cos^2\Theta)\hat{\zeta}^a \\
&\quad - k^2 f^*(\Theta)\hat{v}_x^a - k^2 g^*(\Theta)\hat{v}_y^a, \\
i\omega\rho^0\hat{v}_y^a &= -\frac{1}{2}k\omega\rho^0\bar{\zeta}_2\hat{\zeta}^a \sin 2\Theta - k^2 h^*(\Theta)\hat{v}_x^a - k^2\ell^*(\Theta)\hat{v}_y^a, \\
-k^2\hat{\theta}^a\kappa(\Theta) &= i\omega\rho^0 c_p^\varkappa\hat{\theta}^a - i\omega\theta^0\beta_\theta^\varkappa\hat{p}^a + i\omega\rho^0 h\hat{\zeta}^a.
\end{aligned}
\tag{3.13}
$$

Above, we have introduced the following functions

$$
\begin{aligned}
\bar{\zeta}_i &\equiv \frac{\zeta_i^+ R\theta^0}{\zeta_e^+}, \\
f^* &\equiv f_1 + f_2 + f_3, \\
g^* &\equiv g_1 + g_2 + g_3, \\
h^* &\equiv h_1 + h_2 + h_3, \\
\ell^* &\equiv \ell_1 + \ell_2 + \ell_3, \\
\kappa &\equiv \kappa_a\cos^2\Theta + \kappa_\perp,
\end{aligned}
\tag{3.14}
$$

where

$$
\begin{aligned}
f_1 &\equiv \mu_3 + \mu_{11} + (\mu_4 + \mu_7 + \mu_{12} + \mu_{13})\cos^2\Theta + \mu_8\cos^4\Theta, \\
g_1 &\equiv \frac{1}{2}\left(\mu_4 + \frac{1}{2}\mu_{12} + \frac{1}{2}\mu_{13} + \mu_8\cos^2\Theta\right)\sin 2\Theta, \\
h_1 &\equiv \frac{1}{2}(\mu_7 + \mu_{13} + \mu_8\cos^2\Theta)\sin 2\Theta, \\
\ell_1 &\equiv \frac{1}{2}\mu_{11} + \frac{1}{2}\mu_{12}\cos^2\Theta + \frac{1}{2}\mu_{13}\sin^2\Theta + \mu_8\cos^2\Theta\sin^2\Theta,
\end{aligned}
\tag{3.15}
$$

$$f_2 \equiv \frac{i(\mu_9 + \mu_{10})\omega\lambda_6 \sin^2 2\Theta}{4[H^2\chi_a - i\omega\lambda_5 + k^2\rho^0(K_1 \sin^2\Theta + K_3\cos^2\Theta) - \rho^0\sigma\omega^2]},$$

$$g_2 \equiv -\frac{i(\mu_9 + \mu_{10})\omega\lambda_6 \sin 4\Theta}{8[H^2\chi_a - i\omega\lambda_5 + k^2\rho^0(K_1 \sin^2\theta + K_3\cos^2\Theta) - \rho^0\sigma\omega^2]},$$

$$h_2 \equiv \frac{i(\mu_{10}\sin^2\theta - \mu_9\cos^2\Theta)\omega\lambda_6 \sin 2\Theta}{2[H^2\chi_a - i\omega\lambda_5 + k^2\rho^0(K_1 \sin^2\theta + K_3\cos^2\Theta) - \rho^0\sigma\omega^2]}, \tag{3.16}$$

$$\ell_2 \equiv -\frac{i(\mu_{10}\sin^2\Theta - \mu_9\cos^2\Theta)\omega\lambda_6 \cos 2\Theta}{2[H^2\chi_a - i\omega\lambda_5 + k^2\rho^0(K_1 \sin^2\theta + K_3\cos^2\Theta) - \rho^0\sigma\omega^2]},$$

$$f_3 \equiv \frac{\rho^0\zeta_e^+}{R\theta^0}(\bar{\zeta}_1 + \bar{\zeta}_2\cos^2\Theta)^2,$$

$$g_3 = h_3 \equiv \frac{1}{2}\frac{\rho^0\zeta_e^+}{R\theta^0}(\bar{\zeta}_1 + \bar{\zeta}_2\cos^2\Theta)\bar{\zeta}_2 \sin 2\Theta, \tag{3.17}$$

$$\ell_3 \equiv \frac{1}{4}\frac{\rho^0\zeta_e^+}{R\theta^0}(\bar{\zeta}_2 \sin 2\Theta)^2.$$

Here the subscript 1 indicates the contribution arising from the dynamic stress tensor, the subscript 2 indicates the contribution arising from the director equation, and the subscript 3 indicates the contribution arising from the affinity of the reaction. The coefficients $\bar{\zeta}_i$ are introduced to simplify some of the expressions.

4. ATTENUATION AND DISPERSION

A necessary and sufficient condition for the existence of solutions to (3.13) is the vanishing of the determinant of the coefficients, which yields a polynomial equation in the wave number. This procedure is straightforward, though tedious and algebraically complicated due to the large number of terms. In order to get simple and explicit results we make several simplifying approximations. First, in (3.16) we neglect the terms involving the director inertia and the elastic constants K_1, K_2, and K_3. Second, we assume that the wave is purely longitudinal so that we neglect the terms containing g^*, $\hat{v}_y^a$ in (3.13) and the y-component (3.13c). In a single constituent material, the coupling of the velocity components has been shown[3] to be a second-order effect in terms of a dimensionless frequency number in the attenuation and dispersion.

With these assumptions the determinant now yields a quadratic polynomial equation in square of the wave number. It is most conveniently written in terms of

dimensionless quantities. We introduce the following dimensionless groups:

- Dimensionless wave number ..... $K^\infty \equiv \dfrac{k}{\omega(\rho^0\beta_\eta^\infty)^{1/2}}$
- Thermoviscous number ..... $T^\infty \equiv \dfrac{\kappa}{f^* c_p^\infty}$
- Frequency number ..... $F^\infty \equiv \omega f \beta_\eta^\infty$
- Viscoreactive number .... $Z \equiv \dfrac{\rho^0 \nu \zeta_e^+}{R\theta^0}(\bar{\zeta}_1 + \bar{\zeta}_2 \cos^2 \Theta)$
- Viscosity number ..... $V \equiv \dfrac{f_3}{f^*}$
- Dimensionless heat capacity..... $\Delta C_p \equiv \dfrac{h^2 \tau_{\theta p} \zeta_e^+}{c_p^\infty R\theta^0}$
- Dimensionless isobaric expansion coefficient..... $\Delta B_\theta \equiv \dfrac{\rho^0 h \nu \tau_{\theta p} \zeta_e^+}{\beta_\theta^\infty R(\theta^0)^2}$
- Dimensionless isothermal expansion coefficient ..... $\Delta B_p \equiv \dfrac{\rho^0 \nu^2 \tau_{\theta p} \zeta_e^+}{\beta_p^\infty R\theta^0}$
- Dimensionless isentropic compressibility..... $\Delta B_\nu \equiv \dfrac{\rho^0 \tau_{\eta p} \zeta_e^+}{\beta_\eta^\infty R\theta^0}\left(\nu - \dfrac{\beta_\theta^\infty h}{\rho^0 c_p^\infty}\right)^2$ (4.1)

For low frequencies, the following groups will also prove useful:

$$K^2 \equiv \frac{k^2}{\rho^0 \beta_\eta \omega^2}, \quad T \equiv \frac{\kappa}{f^* c_p}, \quad F \equiv \omega f^* \beta \eta. \tag{4.2}$$

These quantities are not all independent. From (3.10–12) we have

$$\gamma^\infty \Delta B_p \Delta C_p = (\gamma^\infty - 1)(\Delta B_\theta)^2, \quad \omega \tau_{\theta p} Z^2 = \gamma^\infty \Delta B_p V F^\infty,$$
$$(1 + \Delta C_p)\Delta B_\eta = \gamma^\infty \Delta B_p + (\gamma^\infty - 1)(\Delta C_p - 2\Delta B_\theta), \tag{4.3}$$
$$(K^\infty)^2 = K^2(1 + \Delta B_\eta), \quad T^\infty = T(1 + \Delta C_p), \quad F = F^\infty(1 + \Delta B_\eta).$$

Thus with the above dimensionless groups we obtain the biquadratic

$$(K^\infty)^4\left[iF^\infty T^\infty\left(1 - \frac{2i\omega\tau_{\theta p} Z}{1 + i\omega\tau_{\theta p}} + i\gamma^\infty F^\infty\left(1 + \frac{\Delta B_p - i\omega\tau_{\theta p} V}{1 + i\omega\tau_{\theta p}}\right)\right)\right]$$
$$- (K^\infty)^2\left[1 + \frac{\Delta C_p}{1 + i\omega\tau_{\theta p}} - \frac{2i\omega\tau_{\theta p} Z}{1 + i\omega\tau_{\theta p}}\left(1 - \frac{(\gamma^\infty - 1)}{\gamma^\infty}\frac{\Delta B_\theta}{\Delta B_p}\right)\right.$$

$$+ iF^{\infty}\left(1 + \frac{1}{1 + i\omega\tau_{\theta p}}(\gamma^{\infty}\Delta C_p + \gamma^{\infty}\Delta B_p - 2(\gamma^{\infty} - 1)\Delta B_{\theta} - i\omega\tau_{\theta p}V) + \gamma^{\infty}T^{\infty}\left(1 + \frac{\Delta B_p}{1 + i\omega\tau_{\theta p}}\right)\right)\Bigg] \tag{4.4}$$

$$+ \left[1 + \frac{1}{1 + i\omega\tau_{\theta p}}(\gamma^{\infty}\Delta C_p + \gamma^{\infty}\Delta B_p - 2(\gamma^{\infty} - 1)\Delta B_{\theta})\right] = 0.$$

To obtain explicit formulas we make a low-frequency approximation. If we temporarily neglect the viscous and viscoreactive effects, (4.4) reduces to

$$(K^{\infty})^2 = \frac{1 + i\omega\tau_{\eta p} + \Delta B_{\eta}}{1 + i\omega\tau_{\eta p}}, \tag{4.5}$$

or equivalently,

$$K^2 = \frac{1 + i\omega\tau_{\eta\rho}}{1 + i\omega\tau_{\eta p}}. \tag{4.6}$$

Now if

$$|F| \ll 1 \quad \text{and} \quad \omega\tau_{\theta p}|Z| \ll 1, \tag{4.7}$$

the viscous and viscoreactive effects will produce a small change in the wave number so that

$$K^2 = \frac{1 + i\omega\tau_{\eta\rho}}{1 + i\omega\tau_{\eta p}} + \epsilon, \tag{4.8}$$

where ϵ is a small perturbation such its order of magnitude is given by

$$\epsilon = O(|F|, \omega\tau_{\theta p}Z). \tag{4.9}$$

Substitution in (4.4) yields

$$\epsilon = \left(\frac{1 + i\omega\tau_{\eta\rho}}{1 + i\omega\tau_{\eta p}}\right)\left[\frac{2i\omega\tau_{\eta p}Z}{(1 + i\omega\tau_{\eta p})}\left(1 - \frac{(\gamma^{\infty} - 1)}{\gamma^{\infty}}\frac{\Delta B_{\theta}}{\Delta B_p}\right) - iF\left(\frac{1 + i\omega\tau_{\eta\rho}(1 - V)}{1 + i\omega\tau_{\eta p}} + \gamma T\left(\frac{1 + i\omega\tau_{\theta\rho}}{1 + i\omega\tau_{\eta p}}\right) - T\frac{(1 + i\omega\tau_{\theta p})(1 + i\omega\tau_{\eta\rho})}{(1 + i\omega\tau_{\eta p})^2}\right)\right]. \tag{4.10}$$

In this low-frequency approximation, (4.8) and (4.10) show that the wave number is composed of three parts: (1) the classical reaction contribution given by (4.6), which is independent of orientation and thus the same as that of isotropic fluids, (2) the thermoviscous contribution, which is proportional to F and depends on frequency and orientation, and (3) the viscoreactive contribution, which is proportional to Z and depends also on frequency and orientation. Here we concentrate on the effect of the reaction, so that we temporarily neglect the thermoviscous contribution. If we also make the standard assumption

$$K_2 \ll K_1, \tag{4.11}$$

where

$$K = K_1 - iK_2, \tag{4.12}$$

then

$$K^{-2} \approx \left(\frac{c}{c_0}\right)^2\left[1 + 2i\left(\frac{\alpha c}{\omega}\right)\right], \tag{4.13}$$

or equivalently,

$$(K^\infty)^{-2} \approx \left(\frac{c}{c_\infty}\right)^2\left[1 + 2i\left(\frac{\alpha c}{\omega}\right)\right], \tag{4.14}$$

where we introduce the equilibrium and frozen sound speeds

$$c_0^2 = \frac{1}{\rho^0\beta_\eta}, \quad c_\infty^2 = \frac{1}{\rho^0\beta_\eta^\infty}. \tag{4.15}$$

Separating real and imaginary parts yields

$$c^2 = c_\infty^2 + \frac{c_0^2 - c_\infty^2}{1 + \omega^2\tau_{\eta\rho}^2} + 2\left(\frac{\omega\tau_{\eta\rho}(c_\infty^2 - c_0^2) - \omega\tau_{\eta p}(c_0^2 + c_\infty^2\omega^2\tau_{\eta\rho}^2)}{(1 + \omega^2\tau_{\eta\rho}^2)(1 + \omega^2\tau_{\eta p}^2)}\right)\left(\nu - \frac{\beta_\theta^\infty h}{\rho^0 c_p^\infty}\right) \times \left(\frac{\omega\tau_{\eta p}\rho^0\zeta_e^+}{R\theta^0}\right)(\bar{\zeta}_1 + \bar{\zeta}_2\cos^2\Theta), \tag{4.16}$$

$$\alpha = \frac{(c_\infty^2 - c_0^2)\omega^2\tau_{\eta\rho}}{2c^3(1 + \omega^2\tau_{\eta\rho}^2)} - \frac{c_0^2 + c_\infty^2\omega\tau_{\eta\rho} + \omega^2\tau_{\eta\rho}\tau_{\eta p}(c_\infty^2 - c_0^2)}{c^3(1 + \omega^2\tau_{\eta\rho}^2)(1 + \omega^2\tau_{\eta p}^2)} \times \left(\nu - \frac{\beta_\theta^\infty h}{\rho^0 c_p^\infty}\right)\left(\frac{\omega^2\tau_{\eta p}\rho^0\zeta_e^+}{R\theta^0}\right)(\bar{\zeta}_1 + \bar{\zeta}_2\cos^2\Theta).$$

Thus if viscosity and heat conduction are neglected, the sound speed and attenuation are in general functions of orientation and frequency.

There are two interesting subcases of (4.10). First, if in addition to (4.9) we have $\omega\tau << 1$, where τ is a generic relaxation time, then (4.8) and (4.10) reduce to

$$K^2 \approx 1 + i\omega(\tau_{\eta\rho} - \tau_{\eta p}) + 2i\omega\tau_{\eta p} Z\left(1 - \frac{(\gamma^\infty - 1)}{\gamma^\infty}\frac{\Delta B_\theta}{\Delta B_p}\right) - iF(1 + (\gamma - 1)T), \tag{4.17}$$

and using (4.13) we find that

$$c = c_0$$

$$\frac{2\alpha\rho^0 c_0^3}{\omega^2} = \rho^0(c_\infty^2 - c_0^2)\tau_{\eta\rho} - 2c_0^2\tau_{\eta p}\left(\nu - \frac{\beta_\theta^\infty h}{c_p^\infty \rho^0}\right)\frac{\rho^0\zeta_e^+}{R\theta^0}(\bar{\zeta}_1 + \bar{\zeta}_2\cos^2\Theta)$$

$$+ \frac{\rho^0\zeta_e^+}{R\theta^0}(\bar{\zeta}_1 + \bar{\zeta}_2\cos^2\Theta)^2$$

$$+ \mu_3 + \mu_{11} + (\mu_4 + \mu_7 + \mu_{12} + \mu_{13})\cos^2\Theta + \mu_8\cos^4\Theta$$

$$- \frac{1}{4}\left(\frac{\lambda_6}{\lambda_5}\right)\frac{(\mu_9 + \mu_{10})}{\left[\left(\frac{H^2\chi_a}{\omega\lambda_5}\right)^2 + 1\right]}\sin^2\Theta + (\kappa_a\cos^2\Theta + \kappa_\perp)\frac{(\gamma - 1)}{c_p}. \tag{4.18}$$

Second, if in addition to (4.9), $\omega\tau >> 1$,

$$(K^\infty)^2 \approx 1 + 2Z\left(1 - \frac{(\gamma^\infty - 1)}{\gamma^\infty}\frac{\Delta B_\theta}{\Delta B_p}\right) - iF^\infty(1 - V + (\gamma^\infty - 1)T^\infty), \tag{4.19}$$

and using (4.14) we find,

$$c^2 = c_\infty^2\left[1 - 2\left(\nu - \frac{\beta_\theta^\infty h}{c_p^\infty\rho^0}\right)\frac{\rho^0\zeta_e^+}{R\theta^0}(\bar{\zeta}_1 + \bar{\zeta}_2\cos^2\Theta)\right]$$

$$\frac{2\alpha\rho^0 c^3}{\omega^2} = \mu_3 + \mu_{11} + (\mu_4 + \mu_7 + \mu_{12} + \mu_{13}\cos^2\Theta + \mu_8\cos^4\Theta$$

$$- \frac{1}{4}\left(\frac{\lambda_6}{\lambda_5}\right)\frac{(\mu_9 + \mu_{10})}{\left[\left(\frac{H^2\chi_a}{\omega\lambda_5}\right)^2 + 1\right]}\sin^2\Theta + (\kappa_a\cos^2\Theta + \kappa_\perp)\frac{(\gamma^\infty - 1)}{c_p^\infty}. \tag{4.20}$$

The two results, (4.18) and (4.20), show that for frequencies well below the relaxation frequency the product αc^3 always contains terms due to the reaction, but that for frequencies well above the relaxation frequency these terms do not explicitly appear. Since $\bar{\zeta}_1$ also appears in isotropic fluids, this conclusion also applies to isotropic fluids. Low-frequency acoustic experiments are sometimes used to determine viscosity coefficients. The result (4.16) demonstrates, however, that any measured attenuation generally contains a reaction contribution that can be interpreted as an effective change in the viscosity coefficients, complicating the determination of the viscosity coefficients if the viscoreactive coefficients are unknown. From the above we see that to separate out the reaction contribution from the viscous contribution, one must use frequencies such that $\omega\tau \gg 1$. This result tends to support Bacri's experiments at 200 MHz on MBBA (relaxation frequency below 15 MHz) to determine the viscosity coefficients. Additional complications in his work, however, are discussed by Sellers *et al.*[3] Additionally (4.16) shows that the reaction induces an anisotropy in the sound speed, the anisotropy disappearing at low frequencies. Thus c_∞ is *not* necessarily the high-frequency sound speed when neglecting viscosity and heat conduction.

5. DISCUSSION

Various theoretical approaches to wave propagation in mixtures have been proposed. For isotropic reacting binary mixtures, Mazo[16] followed a similar procedure to ours in which he obtained a biquadratic for the wave number, but neglected the viscoreactive term Z. For this special case our result (4.4) reduces closely to his (19), the difference appearing to be due to a misprint. García-Colín and De la Selva[14] used linear irreversible thermodynamics for low-frequency wave propagation in isotropic binary mixtures in which they included the viscoreactive term and obtained a quadratic for the wave number. Their results agree with ours when reduced to this special case and when quadratic terms in the viscoreactive coefficients are neglected. Margulies and Schwarz[17] extended Mazo's method to acoustic waves in isotropic fluids with several reactions, but did not include the viscoreactive coefficients in the stress tensor. Rubin[15] proposed a theory of internal relaxation in liquid crystals that included the viscoreactive terms and obtained a sound speed depending on orientation, but his results do not agree with ours. Due to his lack of detail, we have been unable to determine the source of disagreement. Our presentation appears to be the first to consistently include the viscoreactive terms in the determination of the attenuation and sound speed.

In an experimental study of acoustic waves in MBBA, Lord and Labes[2] found an attenuation anisotropy and a small velocity anisotropy in the range 2–6 MHz. In particular, the attenuation was roughly proportional to the frequency. In an effort to determine the dependence of the sound speed on orientation in MBBA, Mullen *et al.*[1] used a phase comparison technique with an accuracy of approximately 3 parts in 10^6 for relative changes in velocity. Between 2 and 10 MHz, they found the sound speed at a given frequency to behave as

$$c^2(\Theta) = c^2(\pi/2) + [c^2(0) - c^2(\pi/2)] \cos^2 \Theta. \tag{5.1}$$

Additionally, the magnitude of the total anisotropy increased as a function of frequency, being of the order of magnitude of .1% of the velocity at 10 MHz. Additional work on the temperature dependence of the attenuation as well as with other materials with similar molecular structures have indicated the source of the frequency dependence of the attenuation to be due to conformational changes.[9] At a given orientation of the anisotropic axis, the attenuation was found to roughly obey (1.1), where the relaxation frequency is somewhat below 15 MHz. The orientation dependence in the sound speed, however, led Mullen *et al.*[1] to conclude that at the frequencies used the material behaves in some respects as an anisotropic solid. Consequently they introduced frequency-dependent free energy terms containing elastic strains, which gave a result equivalent to (5.1). Subsequently, Jähnig[12] proposed a theory of viscoelasticity for liquid crystals, which with additional assumptions on certain elastic parameters also yielded a velocity anisotropy of the form of (5.1).

If in (4.16) we set $\omega\tau = 1$, we find that the attenuation is linear in frequency and is a function of orientation as was found by Lord and Labes.[2] Additionally, the sound speed anisotropy is proportional to $\cos^2 \Theta$ and vanishes at low frequencies, in agreement with Mullen *et al.* and Lord and Labes. By treating the material as a binary mixture where the reaction rate is a function of the anisotropic axis and the rate-of-deformation tensor, our theory predicts results consistent with experimental observations. No additional assumptions on the free energy and viscous or elastic coefficients appear to be needed to obtain the velocity anisotropy.

Bacri[11] also measured the velocity anisotropy in MBBA at 200 MHz in which he found deviations from the $\cos^2 \Theta$ orientation dependence. At this higher frequency the low frequency approximation (4.9) may no longer be valid, so that the orientation dependence is more complicated than indicated by (4.20). Additionally, the discrepancies may also be due to the coupling of the transverse and longitudinal velocity components, which can become important at high frequencies.

The experiments of Mullen *et al.*[1] appear to be strong evidence that velocity gradients can affect the reaction rate. From the agreement of our results with the data of Mullen *et al.*, we propose that the velocity anisotropy in MBBA is due to conformational changes where the rate of conformational change is a function of the anisotropic axis and the rate-of-deformation tensor. A similar idea was suggested by Miyano and Ketterson[18] based on purely physical arguments. They suggested that the velocity anisotropy comes from conformational relaxation of alkyl chains, where the relaxation is stronger when a sample is squeezed along the chains (parallel to the director) rather than in the normal direction. Our work provides a theoretical foundation for the physical arguments.

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