Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Ultrasonic Absorption and Dispersion at Phase Transitions in Liquid Crystalline Compounds

Peter D. Edmonds [a] & Donald A. Orr [a]

[a] Department of Biomedical Engineering, The Moore School of Electrical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, 19104

To cite this article: Peter D. Edmonds & Donald A. Orr (1966): Ultrasonic Absorption and Dispersion at Phase Transitions in Liquid Crystalline Compounds, Molecular Crystals, 2:1-2, 135-166

To link to this article: http://dx.doi.org/10.1080/15421406608083066

Molecular Crystals. 1966. Vol. 2, pp. 135–166

Printed in Great Britain

Ultrasonic Absorption and Dispersion at Phase Transitions in Liquid Crystalline Compounds

PETER D. EDMONDS and DONALD A. ORR
Department of Biomedical Engineering, The Moore School of Electrical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Received December 3, 1965

Abstract—Previously published data concerning ultrasonic absorption and dispersion at phase transitions in liquid crystals are reviewed. Extensions of the quantitative interpretation of such data are proposed. The similarities between the ultrasonic behavior of liquid crystalline compounds near the isotropic–nematic transition and that of simpler compounds in the critical region leads to the application of Fixman's (1965) expressions to the data for *p*-azoxyanisole. Fixman's theory provides as satisfactory a fit to experimental data at temperatures just above the transition point, T_c, as Frenkel's heterogeneous fluctuation theory (1955). Furthermore, it has the advantage of treating a specific mechanism of absorption, namely, the temperature-dependent oscillation of the spatial decay constant, κ, in the approximation of Ornstein and Zernicke to the radial distribution function. A value of Debye's short range ordering parameter, l, equal to 11.2 Å is found for *p*-azoxyanisole and $T > T_c$. In the nematic state ($T < T_c$) Maier and Saupe's (1960) theory appears to be inadequate to account for the measured ultrasonic absorption. This conclusion is tentative. A combination of Maier and Saupe's expressions and Fixman's expressions with $l = 8.1$ Å can bring about agreement with the experimental data of Hoyer and Nolle (1956) just below the transition point. In this case Fixman's expressions are considered to be applicable to transition regions between adjacent domains having different orientations of the local optic axis.

Introduction

This article will first review previously published data concerning ultrasonic absorption and dispersion at phase transitions in liquid crystals. Also, by use of an analogy with the behavior of normal liquids in the vicinity of critical points, it will seek to extend the quantitative interpretation of such ultrasonic data. Phenomenological analogies are drawn (a) between the isotropic–nematic transition region of thermotropic liquid crystalline compounds and the critical region of the vapor–liquid transition of pure compounds and (b) between the isotropic–nematic transition region of lyotropic liquid crystalline compounds and the critical solution region of binary liquid mixtures:

(a) In the case of the isotropic–nematic transition of a thermotropic material it is necessary for an individual molecule to orient itself by a process of rotary diffusion to achieve a state of alignment with neighboring molecules. The necessity of considering cooperative movement of a number of neighboring molecules can be avoided by considering the rotation of spherical units comprising a few molecules which are already aligned locally.[1] When all such spherically symmetrical groups within a domain are in a state of approximate alignment with one another the transition to the nematic state has occurred. Such orientational ordering is in addition to the ordering of the centers of mass of the spherical entities. The latter should be similar to that of a normal isotropic liquid.

A normal liquid which does not display liquid crystalline properties is in a partially ordered state in the isotropic phase. The order is associated only with the radial distribution of the positions of nearest-neighbor molecules and it is acquired when the vapor condenses to form the isotropic liquid. Fluctuations in the state of ordering occur by a process of translational diffusion. The state of ordering of isotropic liquids is most susceptible to investigation in the critical region of the vapor–liquid transition. The ultrasonic behavior of pure normal liquids in the critical region and that of thermotropic liquid crystalline compounds in the isotropic–nematic transition region show distinct similarities. It appears reasonable to enquire to what extent similarities may exist in the possible interpretations at the molecular level which can be advanced to explain these phenomena. Ornstein[2] has already used such an analogy as the basis for the Swarm Theory of the nematic mesophase.

(b) A corresponding analogy may be seen to apply to the isotropic–nematic transition in a lyotropic liquid crystalline system. When the solute molecules associate to form locally ordered regions, it is necessary for individual molecules which are considered to be initially in the isotropic phase to undergo translational diffusion followed by rotational diffusion in order to achieve a state of association and alignment. On the other hand, the separation of a mixture of normal liquids into isotropic phases requires only the translational diffusion process to achieve aggregation, which is followed by gross separation in a gravitational field. Ultrasonic investigations of the behavior of binary liquid mixtures in the vicinity of critical solution temperatures have been carried out[10, 17] and the behavior is clearly comparable with that of pure compounds in the critical region. However, no results of ultrasonic absorption or dispersion measurements in the vicinity of a lyotropic liquid crystalline transition have been reported to the authors' knowledge.

Fixman[3, 4] has recently enlarged the possibilities of quantitative interpretation of ultrasonic data applicable to the critical regions of pure compounds and solutions. The theory of Fixman and co-workers relies upon the approximations to the radial distribution functions proposed by Ornstein and Zernicke[15] and their validity has been questioned. However, the interest of critics is usually concentrated on the regions extremely close to the critical point. At temperatures equal to or greater than 1° C above the transition temperature the approximations of Ornstein and Zernicke are acceptable, provided that the isothermal compressibility is still large in that region.[18]

In the nematic region below the transition temperature the theory of Maier and Saupe[5, 1] is applicable. Their results can be extended to the point of predicting the magnitude of the ultrasonic absorption coefficient. The conclusion will be reached that a combination of the models of Maier and Saupe and of Fixman could account for the magnitude and temperature dependence of the measured ultrasonic absorption coefficient in the nematic region and that either the theory of Fixman[4] or that of Frenkel[6] would be suitable for the same purpose in the isotropic region at temperatures in the vicinity of the transition temperature.

These conclusions apply to a sample of liquid crystalline material which is remote from the walls of a containing vessel (and therefore is uninfluenced by boundary conditions) and which is not situated in an orienting electric or magnetic field. The ultrasonic measurement technique gives information on the bulk properties of a sample under infinitesimal perturbation of the local pressure and temperature. The simultaneous use of an orienting field is optional. In the experiments to be discussed, no field was applied.

Ultrasonic Measurements

The propagation of a low amplitude, plane, longitudinal ultrasonic wave in a homogeneous, isotropic, visco-elastic medium can be represented by a solution of the wave equation and an adiabatic equation of state.

$$p(x,t) = p_0 e^{-\alpha x} e^{j\omega(t-x/c_\omega)} \tag{1}$$

$$\Theta(x,t) = (\gamma-1)(\beta_S/\theta)\, p(x,t) \tag{2}$$

p is the amplitude of the sound pressure at any point in the sound field, p_0 is the initial amplitude of the sound pressure at the source, x and t are the spatial and time coordinates, α is the amplitude absorption coefficient, measured in Neper cm^{-1}, ω is the angular frequency of the ultrasonic wave, c_ω is the phase velocity at frequency ω, Θ is the amplitude of the temperature oscillation accompanying the sound wave, γ is the ratio of specific heats, β_S is the adiabatic compressibility, θ is the isobaric volumetric thermal expansion coefficient. The oscillations of pressure, p, and temperature, Θ, occur in phase. This fact is of great importance in the interpretation of ultrasonic absorption data. At a frequency of 1 Mc and a power level of 1 mW cm^{-2} the magnitudes of p and Θ are approximately 0.03 atmosphere and 2×10^{-3} °C respectively in common liquids, other than water. Oscillations of these magnitudes are therefore imposed upon the existing internal conditions in the liquid, typically an internal pressure of 1000 atmospheres and an absolute temperature of 300 to 400°K; they are therefore infinitesimal. The phase velocity, c_ω, is typically 1000 m/sec, so that the wavelength of ultrasound at 1 Mc is of the order of 1 mm. Since the wavelength is very much greater than the mean dimension of an ordered region in the nematic phase in the absence of an external

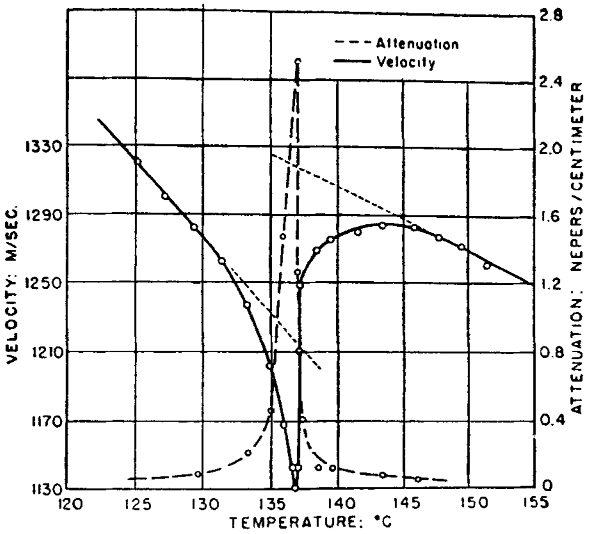

Figure 1. Absorption coefficient and velocity as a function of temperature for p-azoxyanisole, at $f = 2$ Mc/s (after Hoyer and Nolle).

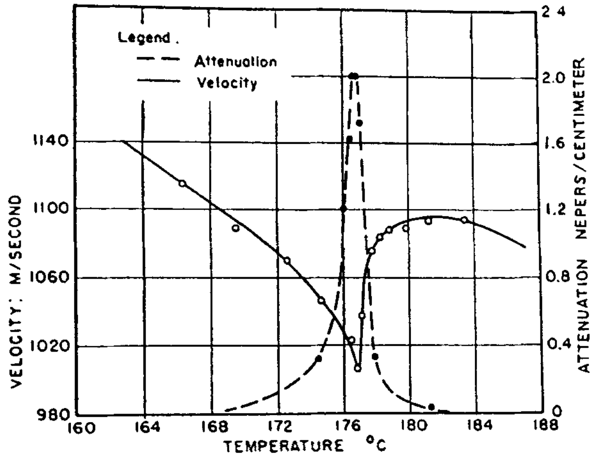

Figure 2. Absorption coefficient and velocity as a function of temperature for cholesteryl benzoate, at $f = 0.5$ Mc/s (after Hoyer and Nolle).

orienting field the assumption of an isotropic medium may be retained under these conditions.

The absorption coefficient, α, may be measured by pulse techniques with an accuracy of 2–5% depending upon the magnitude of the absorption concerned.[7, 8] The phase velocity, c_ω, may be measured by an interferometric technique with an accuracy of 0·1%.[8] The results of such measurements by others are reproduced in the following figures.

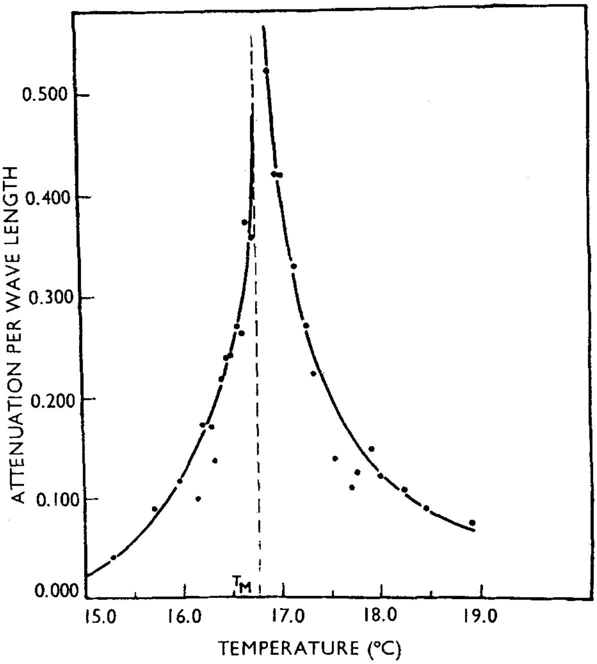

Figure 3. Absorption per wavelength as a function of temperature for xenon near the vapor–liquid critical point, at $f = 0.25$ Mc/s (after Chynoweth and Schneider).

Figure 1 shows the results of Hoyer and Nolle[7] for the temperature dependence of the absorption coefficient and the phase velocity in the vicinity of the isotropic–nematic transition temperature of pure *p*-azoxyanisole. Figure 2 shows their data for cholesteryl benzoate in the vicinity of the isotropic–cholesteric transition temperature. Figures 3 and 4 show the results of Chynoweth and Schneider[9] for xenon in the vicinity of the critical point for transition from vapor to liquid at the critical density. Figures 5 and 6 show results of the same authors[10] which were obtained in the vicinity of the critical solution temperature of the mixture, aniline-n-hexane. The similarity in behavior of the systems under ultrasonic exitation is obvious in these cases, which may be regarded as typical of first-order phase transitions. In Figs. 7 and 8 the results of Zvereva and Kapustin[11] for cholesteryl caprate are reproduced; these data extend throughout the entire cholesteric region, and into the smectic region at temperatures below 77° C. The behavior at the isotropic–cholesteric transition is similar to the previous examples; the behavior at the cholesteric–smectic transition temperature is clearly different since there is no peak in the absorption coefficient and no minimum in the velocity of propagation.†

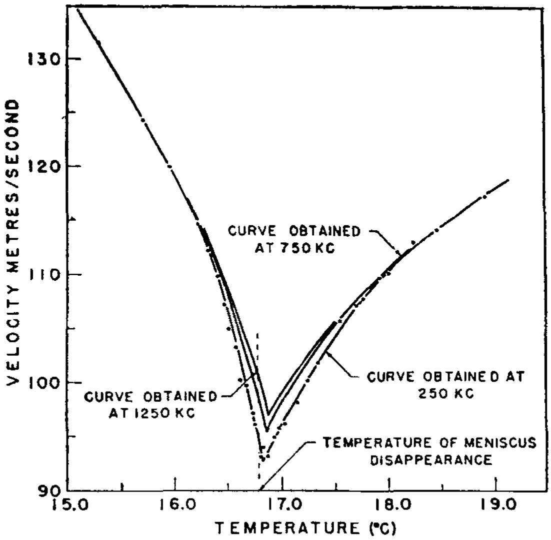

Figure 4. Velocity as a function of temperature for xenon near the critical point, at three frequencies (after Chynoweth and Schneider).

---

† Subsequently Zvereva reported similar data for cholesteryl caprinate.[22] (Note added in proof.)

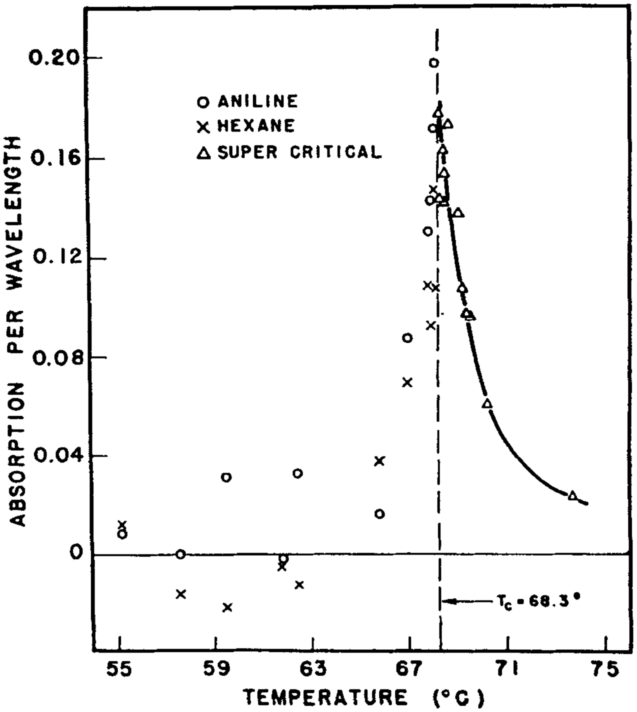

Figure 5. Absorption per wavelength as a function of temperature near the critical solution point of the binary mixture, aniline and n-hexane, at 0.60 Mc/s (after Chynoweth and Schneider).

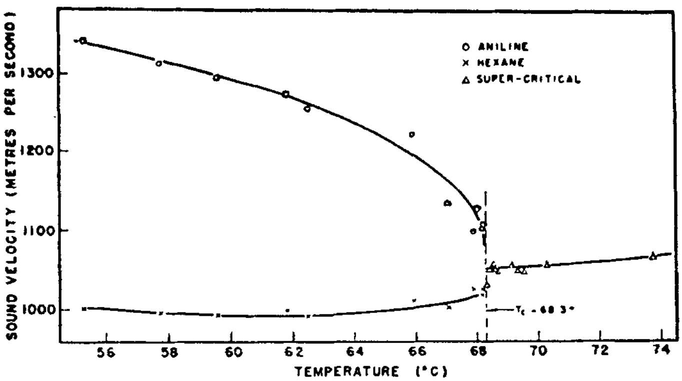

Figure 6. Velocity as a function of temperature near the critical solution point of aniline and n-hexane, at 0.60 Mc/s (after Chynoweth and Schneider).

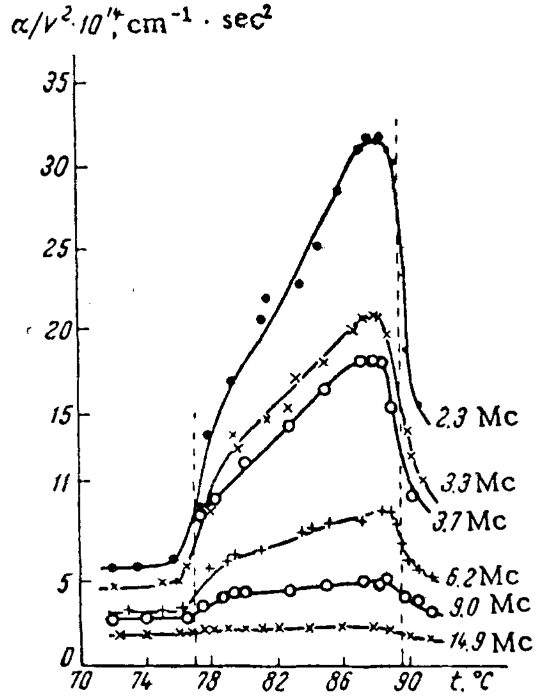

Figure 7. Absorption parameter α/f^2 as a function of temperature and frequency for cholesteryl caprate. Dashed lines indicate the isotropic–cholesteric and cholesteric–smectic transition temperatures (after Zvereva and Kapustin).

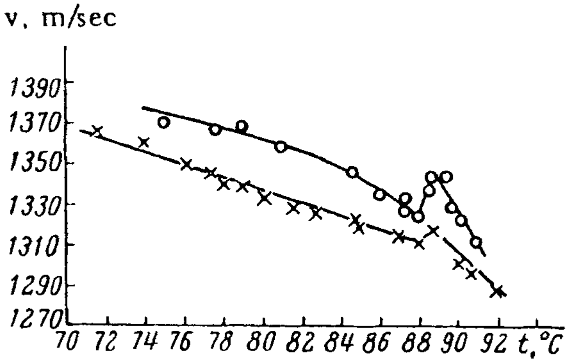

Figure 8. Velocity as a function of temperature for cholesteryl caprate at 14.7 Mc/s (○) and 3.1 Mc/s (×) (after Zvereva and Kapustin).

Measurements on *p*-azoxyanisole have also been made by Gabrielli and Verdini[12] and by Busch and Maier.†‡ The results of Gabrielli and Verdini for cholesteryl benzoate are probably unreliable, due to possible oxidation of their material.[7]

The velocity of propagation of sonic waves is related to the adiabatic compressibility by Eq. (3) and, since the compressibility passes through a maximum at the transition temperature, the velocity exhibits a minimum. The velocity shows only slight dependence upon frequency, i.e., dispersion, in Figs. 4 and 8.

$$c^2 = 1/\rho\beta_S \tag{3}$$

In all the foregoing cases the magnitude of the absorption coefficient which has been measured is very much greater than that which would represent the absorption of sound energy by the process of viscous resistance to displacement of elemental volumes of liquid. Thus viscous absorption is negligible in all cases. Additional mechanisms of the relaxation or hysteresis classes must be invoked to account for the results. Absorption mechanisms based upon hysteresis are excluded from present consideration because the energy absorbed per cycle of the ultrasonic wave is not constant. Relaxational mechanisms are appropriate to describe systems which respond to a perturbation by achieving a new equilibrium state after a certain time delay. Such mechanisms are appropriate in the present instances because the response of the liquid systems is controlled by diffusion processes.

In practice Hoyer and Nolle find that the variation of α/f^2 with frequency at constant temperature resembles Fig. 9 in the case of *p*-azoxyanisole. This figure shows the necessary variation with frequency of the quantities α/f^2 and absorption per wavelength $\alpha\lambda$, when a single relaxation mechanism is involved, controlled by a single time constant, τ. In all the instances for which results have been cited above, the variation of these quantities with frequency,

---

† Personal communication by Dr. A. Saupe, relating to the dissertation by G. Busch, Freiburg i. Br., 1956.

‡ Relative absorption and acoustic birefringence data are reported by Tsvetkov and Krozer.[23] (Note added in proof.)

is more gradual than that shown in Fig. 9. This is the behavior observed when more than one relaxation time is required to describe the phenomena. In general a distribution of relaxation times will be anticipated. The accuracy and range of measurement in any given case does not yet permit the determination of such a distribution of relaxation times. Attention will therefore be confined to the approximate single relaxation time which best describes the observations.

Equations (4) and (5) show the relationships between the parameters indicated on Fig. 9. f is the frequency of the sound wave, $f = \omega/2\pi$. f_r is the relaxation frequency, $f_r = 1/2\pi\tau$.

$$\alpha/f^2 = A[1+(\omega\tau)^2]^{-1}+B \tag{4}$$

$$(\alpha\lambda)_{\max} = \tfrac{1}{2}Af_r c = \frac{Ac}{4\pi\tau} \tag{5}$$

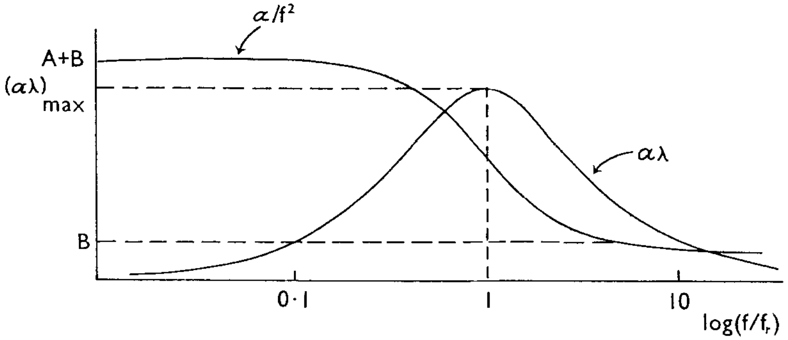

Figure 9. Absorption parameter α/f^2 and absorption per wavelength $(\alpha\lambda)$ as a function of frequency for a single relaxation process (schematic.)

The existence of a time delay in the response of a system to an applied perturbation will result in a phase lag in the response when the applied perturbation is sinusoidal. In the case of an ultrasonic wave the perturbations are the sinusoidal variation of local pressure and temperature. Consequently, energy will be absorbed from the sound wave whenever one or more of the conditions shown in Eq. (6) is satisfied. The integration is performed over one sonic cycle.

$$\oint pdV \neq 0; \quad \oint C_V dT \neq 0; \quad \oint TdS \neq 0 \tag{6}$$

Any molecular mechanism which involves either a change of volume, entropy or internal energy of the system is suitable for consideration as a source of ultrasonic energy absorption. Such mechanisms have been classified into two types: *structural*, for which a finite volume change and a zero internal energy change are assumed, and *thermal*, for which a finite internal energy change and a zero volume change are assumed. In either case a change of entropy may occur. The so-called structural mechanisms are those which respond to the imposed oscillation in pressure and the so-called thermal mechanisms are those which respond to the imposed oscillation in temperature. The foregoing classification scheme is inappropriate to phenomena occurring in the critical region and at phase transitions. The work of Fixman has shown that changes in structure which are significant for ultrasonic experiments can result directly from the oscillations of temperature. Consequently, the above classification into two types of relaxation mechanisms will not be used.

Interpretations of Ultrasonic Measurements

In Section A we first give the essential features of the interpretation proposed by Hoyer and Nolle[7] to account for their measurements.

A. FRENKEL'S HETEROGENEOUS FLUCTUATION THEORY ($T > T_c$)

Frenkel[6] shows that groups of molecules which are associated so that they exhibit anisotropic properties can exist in equilibrium in the presence of molecules of the isotropic phase when the temperature of the system is slightly greater than the transition temperature, T_c. If **A** and **B** denote the isotropic phase and the anisotropic phase respectively, then the equilibrium number of groups of phase **B**, each containing g molecules, is

$$N_g = F(N_{\mathrm{A}}/F)^g \exp\left[-\Phi(g)/kT\right] \tag{7}$$

where

$$\Phi(g) \equiv \frac{\delta H_c(T-T_c)}{T_c} g + \delta V_c(p-p_c)\, g + \mu g^{2/3} \tag{8}$$

F is the total number of entities (groups + phase A molecules), N_A is the total number of molecules in phase A, k is Boltzmann's constant, T is the absolute temperature, δH_c is the energy change per molecule at the transition temperature, $\delta V_c = V_B - V_A$ is the volume difference per molecule at transition and μ is a coefficient related to the surface energy for the formation of a group of g molecules.

$$\mu = (36\pi)^{1/3}\sigma V_B^{2/3} \tag{9}$$

where σ is the interfacial tension between the pure phases.

If an ultrasonic wave traverses a sample to which this model applies the distribution of molecules between the isotropic phase and the groups responds to the oscillations of pressure and temperature. Since diffusional processes are concerned, the response cannot be instantaneous and there will be an appropriate time constant or distribution of time constants. The phase lag in the response of the system to the applied sinusoidal perturbation will be recognized as absorption of sound energy. The magnitude of the sound absorption will be determined by the ratio of the measurement frequency to the relaxation frequency and by the magnitudes δH_c and δV_c. The latter quantities are related to the sound absorption through their derivatives, the incremental specific heat δC_p, and the incremental compressibility $\delta\beta_T$. Furthermore, the incremental isobaric thermal expansion coefficient $\delta\theta$ is related to the sound velocity through the density and Eq. (3). Hoyer and Nolle obtained the following expressions for the incremental thermodynamic quantities.

$$\delta\beta_T = \frac{(\delta V_c)^2}{VRT}\cdot D \tag{10}$$

$$\delta\theta = \frac{\delta H_c}{RT_c^2}\cdot\frac{\delta V_c}{V}\cdot D \tag{11}$$

$$\delta C_p = R\left(\frac{\delta H_c}{RT_c}\right)^2\cdot D \tag{12}$$

where $D \equiv S_2/(1+S_1)^2$ and S_1 and S_2 are given by:

$$S_j = \sum_{g_0}^{\infty} g^j \exp[-\Phi(g)] \simeq \int_{g_0}^{\infty} g^j \exp[-\Phi(g)]\,dg \tag{13}$$

g_0 represents the minimum viable size of a group forming phase **B** and its magnitude is to be inferred from experimental data.

If ψ represents any one of the quantities β_T, θ, C_p then the total measurable magnitude of ψ at any temperature is given by the sum of contributions representing simple mixing and the heterophase fluctuations or incremental values $\delta\psi$.

$$\psi = \frac{\psi_{\mathrm{A}}}{1+S_1} + \frac{\psi_{\mathrm{B}} S_1}{1+S_1} + \delta\psi \qquad (14)$$

ψ_{A} and ψ_{B} are the values appropriate to the pure phases and it was assumed that ψ_{B} is also applicable to a Frenkel group.

Hoyer and Nolle[7] were able to make a satisfactory fit between the preceding theory and the data at temperatures between 0.5° and 2.0° C above the transition temperature. They assumed the heat of transition of *p*-azoxyanisole to be 410 cal/mole, following Kreutzer and Kast,[13] and deduced an interfacial energy of 0.30 erg/cm^2 and a minimum effective group size $g_0 = 840$. They suggested that the large value of g_0 might have been necessary to compensate for the effects neglected in the original free energy expressions, in particular the temperature dependence of the surface energy.

The measurements of sound absorption were used to estimate the order of magnitude of the relaxation time for response of the system to applied perturbations. The magnitude of the sound absorption used by Hoyer and Nolle was

$$\alpha\lambda = \pi\left(\frac{c}{c_0}\right)^2 \frac{\Delta\beta_S}{\beta_{S_0}} \cdot \frac{\omega\tau}{1+(\omega\tau)^2} \qquad (15)$$

Here subscript 0 means the value at very low frequencies and Δ indicates the *molar* change in the succeeding quantity. Pairs of values of τ can be calculated to achieve agreement between this expression and the measured absorption at any chosen temperature. One value of τ from each pair was rejected with the experimental information that the relaxation frequency is greater than the frequency of measurement of 2 Mc. The incremental adiabatic compressibility $\Delta\beta_S$ was obtained from Eqs. (10) through (12) and the standard thermodynamic relations

$$\Delta\beta_S = \Delta\beta_T/\gamma \quad \text{and} \quad \gamma = 1+TV\theta^2/C_p\beta_S \tag{16}$$

The use of Eq. (15) involves the simplification of assuming that the behavior of the system can be described by a single relaxation time, τ. However, in the absence of sufficiently extensive data in the frequency domain, no better assumption can be made at the present time. Hoyer and Nolle obtained single relaxation times for *p*-azoxyanisole in the range 0.5 to 3.5×10^{-8} sec, applicable within the region 4° C above the transition temperature (Fig. 11, curve 1).

Equation (15) may be reformulated[14] to show more explicitly one of the difficulties in the interpretation of ultrasonic absorption data.

$$\alpha\lambda = \pi(c_\infty/c_0)\{[\Delta\beta_T/\beta_{S_0}]^{1/2} - [(\gamma_0-1)\,\Delta C_p/C_{p_0}]^{1/2}\}^2\,\frac{\omega\tau}{1+(\omega\tau)^2} \tag{17}$$

In Eq. (17) the responses of the system to the perturbations of pressure of temperature have been separated. This separation results from recognition of the fact that $\Delta\beta_S$ contains incremental contributions from both the isothermal compressibility and the ratio of specific heats γ. The response of the system by changing its volume will be induced by the applied oscillation of pressure and will result in the fluctuation contribution $\Delta\beta_T$. The response of the system by changing its internal energy will be induced by the temperature oscillation and will result in the fluctuation contribution ΔC_p. However, states of the system corresponding to higher internal energy will also normally correspond to larger volumes. It will be recalled that the pressure and temperature oscillations occur in phase. Hence, the applied oscillations of pressure and temperature act in opposition in inducing responses of the system, the one tending to displace the system towards a state of smaller volume and the other towards a state of larger volume. Consequently the measured sound absorption is proportional to the difference of the two terms appearing in the bracket of Eq. (17).

Sound absorption measurements thus provide a very critical test of any theory based on a molecular model of a system in equilibrium. Not only does $(\alpha\lambda)$ depend upon $\Delta\beta_T$ and ΔC_p, which are increments in the second derivative of free energy, but it also depends upon the difference between these quantities. Hence, even qualitative agreement between theory and experiment may be cause for satisfaction.

Relaxation times for *p*-azoxyanisole have been recalculated from Hoyer and Nolle's data and Eq. (17) leading to curve 2 on Fig. 11. Frenkel's model is probably not valid at temperatures very close to the transition temperature nor for temperatures less than T_c, since it assumes that groups of associated molecules are dispersed in a large volume of the isotropic phase. Curve 2 therefore does not extend into the region $T < T_c$. The increase of the relaxation time at the transition temperature is reproduced but in a less pronounced form than in curve 1. The modification is due to the appearance of different ratios of sound velocities, c, in Eqs. (15) and (17). The agreement between curves 1 and 2 regarding magnitudes is evidence that the method of evaluating $\Delta\beta_T$ and ΔC_p separately, which requires approximation and extrapolation, was satisfactorily performed. We shall use the same method in Section B to interpret data for the nematic phase.

B. MAIER AND SAUPE'S LONG RANGE ORDERING THEORY ($T < T_c$)

Maier and Saupe's theory[1, 5] describes the state of parallel alignment of molecules in a nematic mesophase by means of an ordering parameter, s:

$$s = 1 - \tfrac{3}{2}\overline{\sin^2\theta} \tag{18}$$

where θ is the mean angle between the length axis of the extended molecule and the optic axis of a homogeneously oriented layer of nematic liquid. In the sound absorption experiments presently being discussed the material is not subjected to an external orienting field. Therefore the appropriate optic axis will be that of the domain in the immediate vicinity of the molecule under consideration. This domain will be considered to have the approximate dimensions of a "swarm", described by Ornstein[2] as comprising approximately 10^6 molecules.

Maier and Saupe calculate the interaction energy of an arbitrary molecule situated in the interior of a nematic liquid. The interaction responsible for the formation of the nematic phase is that described by dispersion forces. One of their results is an expression for the increment in entropy of molecules in the nematic phase relative to the entropy at the same temperature of a distribution of molecules which is isotropic with respect to orientation:

$$\Delta S = \frac{N_{\mathrm{L}} k}{m}[-\tfrac{1}{2}Qs(2s+1)+\ln I(Qs)] \qquad (19)$$

where N_{L} is Avogadro's number, m is the number of molecules in the spherical entity (referred to in the Introduction), $Q = A/kTV_n^2$, A is a number which is specific for a given chemical substance, having the dimensions of energy × $(\text{volume})^2$, V_n is the molar volume in the nematic phase and

$$I(Qs) \equiv \int_0^{\pi/2} \exp[\tfrac{3}{2}Qs(1-\sin^2\theta_l)]\sin\theta_l \cdot d\theta_l \qquad (20)$$

θ_l is the angle of orientation of a representative molecule, l.

In addition the internal energy is available in terms of the ordering parameters[5]:

$$\Delta U = -\tfrac{1}{2}\frac{N_{\mathrm{L}}}{m}\cdot\frac{A}{V_n^2}\cdot s^2 \qquad (21)$$

The use of Eq. (19) in the following interpretation of ultrasonic absorption data will provide a partial description of the response of a comparatively large volume of nematic material to an applied ultrasonic perturbation. The description is partial because it relates only to those molecules situated in the interior of a nematic domain. Contributions from a number of adjacent domains with different orientations of their local optic axis are summed. Any specific features of the responses of molecules situated on the boundaries of the domains and in locations between domains have not been included.

The theoretical values of the sound absorption per wavelength at temperatures below the transition temperature for *p*-azoxyanisole were calculated by the following procedure. In this paragraph the symbol Δ indicates a temperature-dependent incremental parameter. It is the difference per mole between the values of the parameter in the nematic state of aggregation and as obtained by linear extrapolation to the same temperature from the isotropic region. The incremental specific heat required in Eq. (17) is obtained by differentiating the incremental entropy:

$$\begin{aligned}\Delta C_p &= T\left(\frac{\partial \Delta S}{\partial T}\right)_p \\ &= (T_c N_L k^2/mA)\left(V_n^2 + 2TV_n\frac{\partial V_n}{\partial T}\right) \\ &\qquad \left\{\left[-\frac{Q}{2}(4s+1)\,Q_c\frac{\partial s}{\partial q} + \frac{Q^2}{2}(2s+1)\,s\right]\right. \\ &\qquad \left. +\left[Q_c Q\frac{\partial s}{\partial q} - Q^2 s\right] I'(a)\right\} \qquad (22)\end{aligned}$$

where subscript c denotes the value at the transition point, $T = T_c$, and $q = Q_c/Q = TV_n^2/T_cV_{nc}^2$. The symbol $I'(a)$ represents

$$\tfrac{3}{2}\int_0^1 x^2 e^{ax^2}\,dx \bigg/ \int_0^1 e^{ax^2}\,dx \quad \text{where} \quad a = 3Qs/2.$$

The total specific heat is the extrapolated value from the isotropic region plus this increment.

$$C_p = C^i_{p(T>T_c)} + \Delta C_p \qquad (23)$$

Differentiation of Eq. (21) and extrapolation yields the incremental value of the specific heat at constant volume.

$$\Delta C_V = \left(\frac{\partial \Delta U}{\partial T}\right)_V = -(N_L k Q_c s/m)\frac{\partial s}{\partial q} \qquad (24)$$

The total specific heat at constant volume is obtained similarly by addition of the increment to the extrapolated value.

$$C_V = C^i_{V(T>T_c)} + \Delta C_V \qquad (25)$$

The ratio of specific heats, γ, may therefore be calculated:

$$\gamma = \frac{C_p}{C_V} \qquad (26)$$

The adiabatic compressibility was obtained through Eq. (3) from the measurements of sound velocity and the known temperature dependence of the density.

The incremental isothermal compressibility can now be calculated by a similar process of extrapolation from the isotropic state and by use of the value of γ calculated previously.

$$\Delta\beta_T = \gamma[\beta_S - \beta^i_{S(T>T_c)}] \tag{27}$$

The process of extrapolation makes the resultant values of the incremental parameters subject to uncertainty. However it is possible to use them to calculate a theoretical value of the maximum sound absorption per wavelength, given by Eq. (17) with $\omega\tau = 1$.

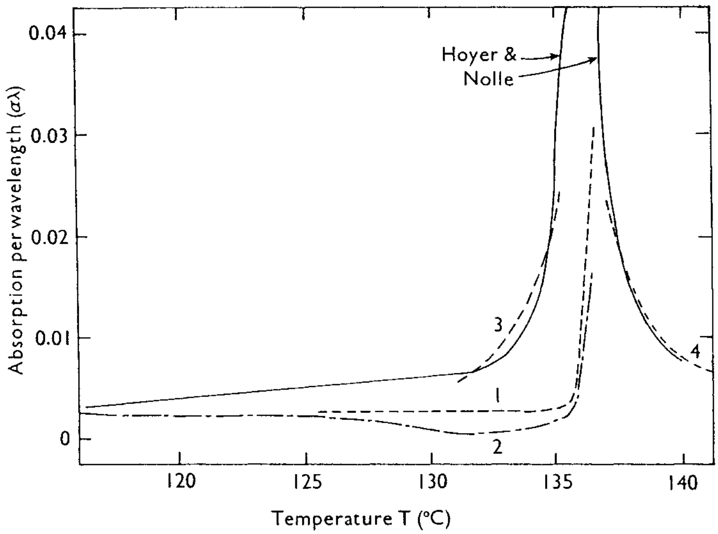

Figure 10. Absorption per wavelength as a function of temperature for *p*-azoxyanisole. Comparison of Hoyer and Nolle's experimental data with predictions from theories: 1, $(\alpha\lambda)_{\max}$ based on Maier and Saupe's theory; 2, $(\alpha\lambda)$ obtained from curve 1 by use of Hoyer and Nolle's estimates of relaxation times (see Fig. 11); 3, curve $1+(\alpha\lambda)$ from Fixman's theory; 4, $(\alpha\lambda)$ from Fixman's theory.

All values of the maximum sound absorption per wavelength that are calculated are smaller than the measured absorption per wavelength reported by Hoyer and Nolle. Consequently, no possible value of the relaxation time can be chosen to bring theory and experiment into agreement. Figure 10 shows a plot of the theoretical and experimental results.

This quantitative disagreement between theory and experiment should not be taken as implying any substantial criticism of the theory of Maier and Saupe. As previously stated, the qualitative agreement which has indeed been achieved can be considered quite satisfactory at the present time. It is also apparent that as the temperature is lowered, departing further from the transition temperature, the theoretical and experimental curves approach one another. Such lowering of temperature causes an increase in the stability of the nematic phase with respect to the isotropic phase with a resultant increase in the numbers of molecules which are situated in the interior of a nematic domain and decrease in the

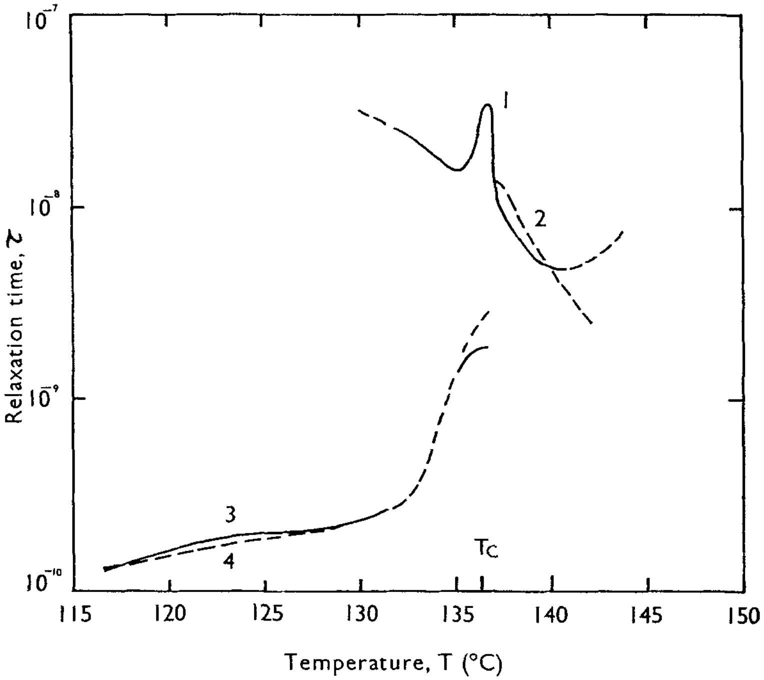

Figure 11. Relaxation times as a function of temperature for *p*-azoxyanisole: 1, Hoyer and Nolle's data; 2, curve 1 recalculated using Eq. (17); 3, for a hypothetical "thermal" process; 4, for a hypothetical "structural" process.

number situated at boundaries or intermediate regions. Consequently, a larger proportion of the sample will be assuming a state of aggregation which the theory seeks to describe. The model therefore appears more applicable as the temperature is lowered.

It may be noted that if either the pressure-dependent or the temperature-dependent contribution to the total calculated absorption is ignored, then the maximum value of the sound absorption per wavelength becomes greater than the experimental value and it is possible to select relaxation times τ_p or τ_T which are compatible with the experimental results (Fig. 11, curves 3 and 4). Such a procedure may be adopted with ample justification in other investigations. For example, in the case of rotational isomerism,[14] there is clear justification for assuming that the volume change ΔV is negligible. However, in the present case there is no justification for making such an assumption nor the corresponding assumption for the "structural" relaxation mechanism, $\Delta U = 0$.

In Section D, we shall argue that the sound absorption contribution which is unaccounted for in the nematic state, could be due to the response of molecules situated on the boundaries of domains and in intermediate locations, in a manner which has not yet been taken into consideration. We shall first return to the temperature range above the critical temperature and adapt the theoretical description which has been advanced by Fixman to explain the absorption of ultrasonic waves in the vicinity of a critical point.

C. FIXMAN'S CRITICAL STATE THEORY ($T > T_c$)

Botch and Fixman[4] have explained the sound absorption in the case of a one-component system of small molecules by considering the thermal perturbation of the radial distribution function, $g(r)$:

$$g(r) = n^{(2)}(r)/n^2 \tag{28}$$

where $n^{(2)}$ is the pair distribution function, and n is the number density of molecules. The function $g(r)$ describes the probability of finding the center of mass of a neighboring molecule at a distance r from any similar molecule situated at the origin of co-ordinates. Ornstein and Zernicke[15] obtained an approximate expression for the radial distribution function in a one-component system, which is valid for values of r greater than two or three intermolecular distances and for temperatures more than 1 °C above the critical point. This long range approximation is

$$g(r)-1 = \Gamma(r) \simeq \frac{a}{r}e^{-\kappa r} \tag{29}$$

where a is a constant and κ has been represented by Debye in the case of simple fluids at the critical density as

$$\kappa^2 = \frac{6}{l^2}\frac{|T-T_c|}{T_c} \tag{30}$$

l is a short-range spatial correlation parameter. A numerical value for l will be sought by fitting theory and experimental data.

These expressions describe with some considerable degree of approximation the state of aggregation of molecules of a simple vapor which is about to undergo a phase transition to the liquid state at the critical density. Fluctuations in density occur which are associated with comparatively long lifetimes and similarities with the heterogeneous fluctuation theory[6] are apparent. The analogy with the phase transition from an isotropic liquid to a nematic liquid was first apparent to Ornstein,[2] who gave a similar approximate form for an orientational distribution function, describing the relative orientation of molecules forming an incipient nematic phase:

$$\Gamma_\theta(r) \simeq \frac{a'}{r}e^{-\kappa r} \tag{31}$$

This function still describes a radial distribution of orientations and is applicable above the transition temperature where significant changes in the distances between the centers of masses of molecules may still occur.

In the theory proposed by Botch and Fixman[4] the interaction of the sound wave with the model is more specifically described than is the case in Frenkel's theory.[6] Since κ is strongly temperature dependent in the vicinity of the critical point the temperature oscillation in the sound wave will produce oscillation of κ, which must therefore be replaced by an equilibrium value plus a sinusoidal increment.

$$\kappa^2 \rightarrow \kappa_0^2 + \delta\kappa^2 e^{j\omega t} \tag{32}$$

Hence the state of local order of a simple fluid in the vicinity of its critical point is considered to be capable of interaction with an ultrasonic wave by means of an oscillation of the scale of the exponential decay of the radial distribution function. Molecules that are most loosely associated with any given molecule at the origin are most easily influenced by the sound wave and the interaction phenomenon is supposed to occur at the extreme edge of an aggregate where it merges into the isotropic phase. Thus, the theory is applicable to the local boundary phenomena between phases.

The expression obtained by Botch and Fixman for the sound absorption per wavelength for a single component fluid is

$$\alpha\lambda = \frac{9k}{\pi\rho_c C_V^0}\left(\frac{\zeta}{\omega}\right)^{1/4}\frac{1}{l^4}\cdot J(\epsilon) \tag{33}$$

where $\epsilon \equiv \kappa^2(\zeta/\omega)^{1/2}$, ρ_c is the critical density, k is Boltzmann's constant, C_V^0 is the specific heat at constant volume and zero frequency, $J(\epsilon)$ is a function which has been evaluated numerically and plotted[4] as a function of ϵ, ζ is an adjustable parameter. This result is subject to the restriction that it cannot be expected to apply at temperatures less than 1° C above the critical temperature. The restriction results from the procedure of truncating the Fourier transform of the radial distribution function, so that only those terms containing the factors, e^{jkr}, where $k \leqslant k_{\max}$, are retained.† The theory becomes intractable if this truncation is omitted.

We have applied Eq. (33) to the case of the transition of *p*-azoxyanisole from the isotropic to the nematic state and have fitted it to the absorption data of Hoyer and Nolle above the critical temperature. The values of parameters necessary for the very satisfactory fit shown by curve 4 on Fig. 10 are $l = 11.2$ Å and $\zeta = 4 \times 10^{-15}$.

---

† In this sentence k represents the propagation constant of the Fourier component.

These figures may be compared with the corresponding values obtained by Botch and Fixman[4] in applying their theory to simple fluids, i.e. $l = 6.14$ Å, $\zeta = 8.2 \times 10^{-18}$ for xenon and $l = 19.6$ Å, $\zeta = 3.6 \times 10^{-17}$ for hydrogen chloride.

In the case of *p*-azoxyanisole, this result for l leads to the values of the spatial decay constant κ shown in Table 1 as a function of temperature. These figures for $1/\kappa$ should be a measure of the radius of an aggregate of oriented molecules and they are comparable with the radius of a spherical region (about 35 Å) which would be required to enclose the 840 molecules constituting the minimum viable aggregate deduced by Hoyer and Nolle from Frenkel's theory.

TABLE 1

$T - T_c$ (°C)	$1/\kappa$ (Å)
1.0	95
2.0	67
5.0	42

Since Eq. (33) was developed with normal fluids in mind, it takes no account of the rotational diffusion process which is needed to bring molecules of liquid crystalline compounds into alignment. Further development along these lines can be envisaged. In lieu of this we take the liberty of using Eq. (33) at temperatures below T_c.

D. COMBINATION OF MAIER AND SAUPE'S AND BOTCH AND FIXMAN'S THEORIES ($T < T_c$)

The foregoing demonstration that Fixman's result, Eq. (33), may be used in the range $T > T_c$ to account for the measured values of $(\alpha\lambda)$ with a reasonable value of l leads to consideration that it may also be useful in the range $T < T_c$. In the experiments of Hoyer and Nolle, no orienting field was applied and therefore no correlation of the direction of the optic axes of domains throughout the nematic material would be anticipated. If the directions of the optic axes of domains are randomly oriented throughout a nematic material, then a certain fraction of molecules will be situated at boundaries between domains. Such intermediate locations may be layers with local properties resembling the isotropic state rather than the nematic state, i.e., transition regions where the state of aggregation would be particularly susceptible to perturbations of temperature, as considered by Fixman.

It may be argued that there is no evidence from n.m.r. measurements[19] to support the existence of such transition layers in the nematic state. However n.m.r. techniques require the sample to be situated in a magnetic field which would cause parallel orientation of optic axes. The state of the nematic specimen would thus be altered in such a way that the occurrence of the transition regions of interest would not be favored or would even be excluded. Hence, ultrasonic techniques should be more sensitive for the detection of phenomena at transition layers between randomly oriented domains.

An attempt has therefore been made to use Eq. (33) to account for the difference $(\alpha\lambda)_d$ between Hoyer and Nolle's results (Figs. 1 and 10) and the maximum absorption per wavelength calculated in Section B from Eq. (17) and shown as curve 1 on Fig. 10.

$$(\alpha\lambda)_d = (\alpha\lambda)_{\text{meas}} - (\alpha\lambda)_{\text{max}}.$$

The major discrepancy occurs over the range 5° C below the transition temperature. This is the range over which the ordering parameter, s, departs most markedly from unity.[5] The magnitude of $(\alpha\lambda)$ to be allocated to the process considered in Section B should be somewhat less than $(\alpha\lambda)_{\text{max}}$ by a factor depending on $\omega\tau_n$, where τ_n is the unknown equivalent single relaxation time for molecules in the interior of nematic domains. For example, if Hoyer and Nolle's estimates of τ_n are used (Fig. 11, curve 1, $T < T_c$) then curve 2 on Fig. 10 is obtained. These values of τ_n were deduced, however, by applying Frenkel's theory to the region $T < T_c$, where it is no more applicable than Fixman's. One could certainly proceed with equal justification to consider a combination of the values of $(\alpha\lambda)$ predicted by Maier and Saupe's and by Frenkel's theories in the region $T < T_c$. The reason for preferring to use Fixman's rather than

Frenkel's theory in the present instance is that the mechanism of absorption postulated by Fixman is more explicit.

The use of the parameters $l = 8.1$ Å and $\zeta = 10^{-18}$ in Eq. (33), together with the specific heat for the *isotropic* state, results in a contribution $(\alpha\lambda)_d$ which raises curve 1 on Fig. 10 to the position of curve 3. This is the minimum contribution $(\alpha\lambda)_d$ that can be required since curve 1 is a plot of $(\alpha\lambda)_{\max}$ deduced from Maier and Saupe's theory. No attempt should be made to achieve a fit at $|T - T_c| < 1°$ C as stated previously.

The result of this exercise is a value of l which is less than that obtained in the range $T > T_c$, consistent with the expectation of a smaller scaling parameter for the transition layer when the nematic state is dominant.

Two-Component Systems

A. Lyotropic Liquid Crystalline Systems

The author is not aware of any ultrasonic absorption or velocity data which has been obtained on lyotropic liquid crystalline systems, either in the vicinity of a phase transition or elsewhere. The nearest approach to such a system is that studied by McKellar and Andreae[16] who observed a departure from normal behavior in the ultrasonic absorption coefficient of n-octylamine in water as a function of concentration. This departure from normal behavior occurred in the region of critical micelle formation of the amine.†

Any model seeking to explain future ultrasonic absorption data in a lyotropic system must incorporate a translational diffusion mechanism as well as rotational diffusion to achieve ultimate alignment of the molecules constituting the nematic phase. The slowest and therefore the controlling mechanism in the response of a system to an ultrasonic perturbation is likely to be translational diffusion. An indication of expected behavior may be obtained by considering the ultrasonic behavior of binary mixtures of simple liquids. Several binary systems have been studied by ultrasonic

† Similar behavior had been observed previously in gelatin solutions by Mikhailov and Tarutina.[21] (Note added in proof.)

techniques.[10, 20] The recent measurements of Anantaraman, Walters, Edmonds, and Pings will be summarized here.[12]

B. Binary Liquid Mixtures

Anantaraman *et al.*,[12] carried out measurements of ultrasonic absorption on the system nitrobenzene–iso-octane over the full composition range at temperatures of 30.5° C, 34.8° C, and 44.8° C for five frequencies between 4.5 and 16.5 Mc. The critical temperature for this system is 30.2° C. Measurements were made by the pulse technique.[8]

At the lowest frequency and at 0.3° C above the critical temperature the absorption is anomalously large by a factor of 47; 14.6° C above the critical temperature, the absorption is still in excess of predictions of that due to viscosity by a factor of 11. The data cannot be represented by a model involving only a single relaxation frequency. Fixman's theory[3] for binary liquid mixtures is in reasonable but not exact agreement with the data with regard to functional conformity in temperature and frequency; in particular the predicted frequency dependence, $\alpha/f^2 \propto f^{-5/4}$ at the critical state is verified within experimental error.

The theoretical expression for the sound absorption per wavelength in this case[3] is

$$\alpha\lambda = (\gamma_0 - 1)\frac{R}{C_p^0}\left[T_c\frac{\partial\kappa^2}{\partial T}\right]^2 \frac{1}{4\pi(n_1+n_2)}\left(\frac{h}{\omega}\right)^{1/4} \mathrm{Im}(F) \qquad (34)$$

$$F \equiv F(\kappa^2\sqrt{h/\omega})$$

κ^2 is given by Eq. (30), (h/ω) is an effective translational diffusion coefficient, n_1 and n_2 are the number densities of components 1 and 2, respectively.

Figures 12 and 13 show the concentration and temperature dependences of the absorption coefficient for the system nitrobenzene–iso-octane with the frequency as a parameter in each case. In Fig. 13 the solid lines are experimental and the dashed lines are theoretical. In fitting the theory to obtain numerical values for adjustable parameters use has been made of the points measured at 16.5 Mc and the points at 4.5 Mc measured at the highest and lowest

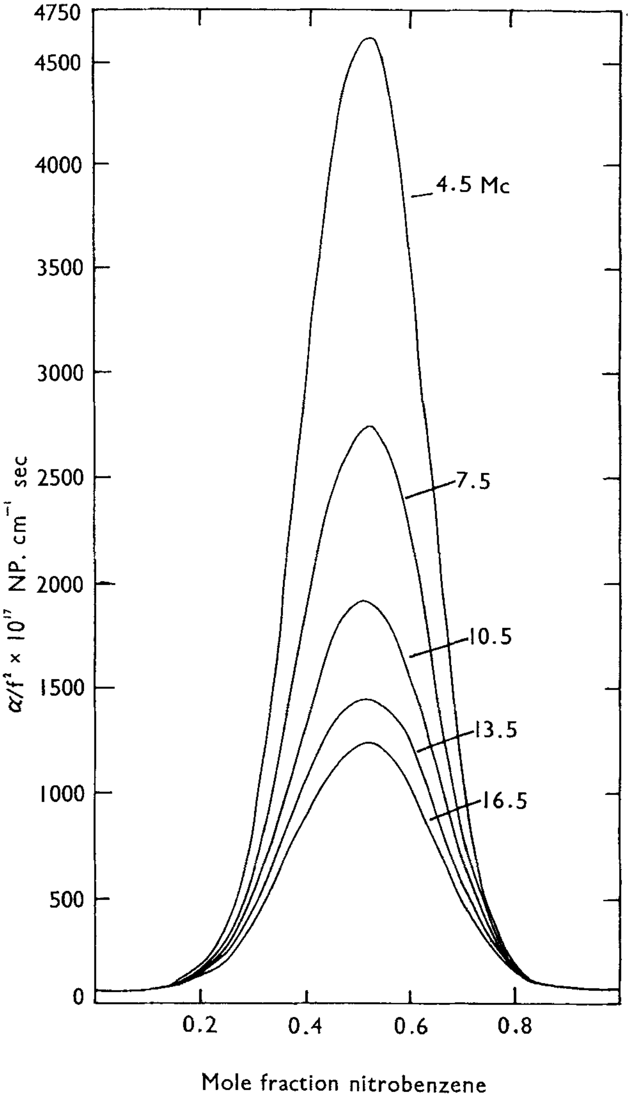

Figure 12. Absorption parameter α/f^2 as a function of concentration and frequency for the binary mixture, nitrobenzene and iso-octane (after Anantaraman, Walters, Edmonds and Pings).

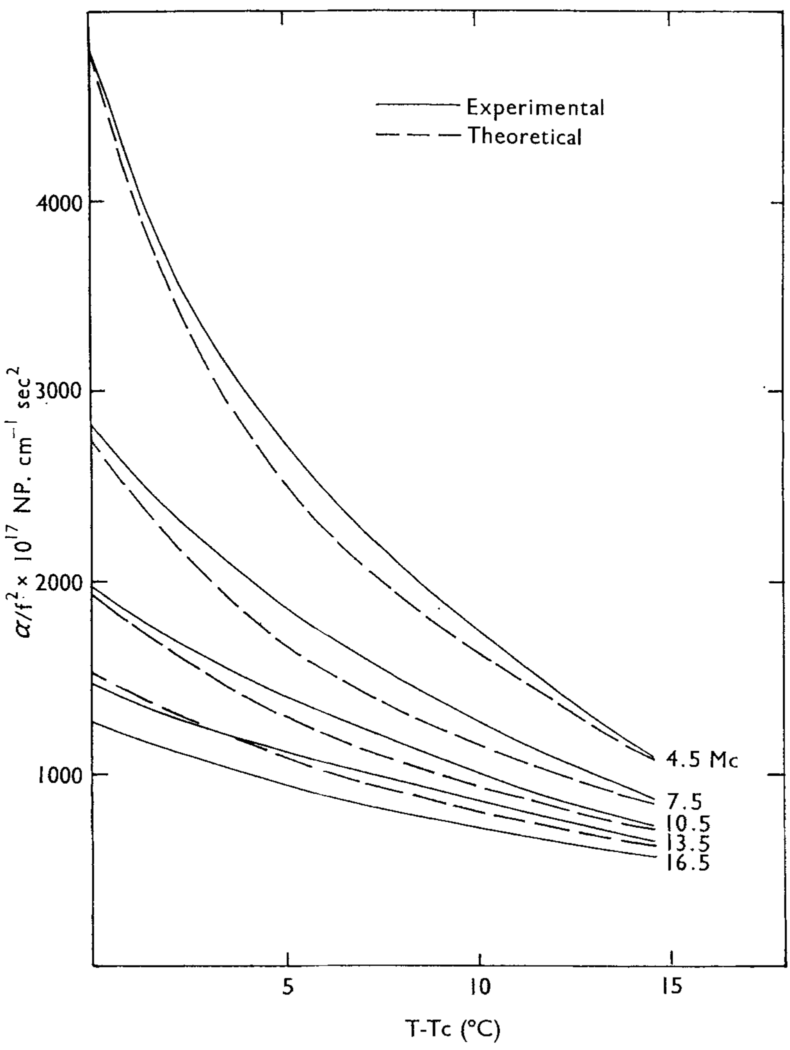

Figure 13. Absorption parameter α/f^2 as a function of temperature and frequency for nitrobenzene and iso-octane, showing a comparison with Fixman's theory (after Anantaraman, Walters, Edmonds and Pings).

temperatures. Consequently, the agreement between theory and experiment is deduced from the shapes of the curves at intermediate temperatures and from the intercepts on the vertical axis.

This agreement is considered to be remarkably satisfactory considering that the theory has distinct limitations imposed by the approximations used in its development. Two of these limitations have already been noted, namely, the use of the highly approximate Ornstein and Zernicke relation for the radial distribution function and the inapplicability of the theory to temperature closer than approximately 1° C above the critical temperature. A third limitation is imposed by the necessity of using Eq. (30). A more general form of this equation allows the exponent of the temperature to differ from unity:

$$\kappa^2 = \frac{6}{l^2}\frac{|T-T_c|^\nu}{T_c} \tag{35}$$

If Eq. (35) is used in Fixman's theory with any value of ν other than unity then the absorption does not remain finite at $T = T_c$. However the theory is not valid at this point in any case. An appropriate value of ν may therefore be sought. At temperatures T greater than T_c a better fit with the experimental data is obtained by using $\nu = 1.08$. A variety of other experiments and theoretical deductions have been reviewed by Fisher[13] and lead to the expectation that $1.1 \leqslant \nu \leqslant 1.25$.

Conclusions

It appears that ultrasonic techniques of absorption measurements are at present most useful in the range $T > T_c$ where incipient aggregation is taking place. Relaxation times may be directly determined experimentally if a large enough range of frequency is covered or if an equivalent single relaxation time suffices. A spectrum of relaxation times is likely to be encountered in association with phase transition phenomena; therefore a sufficiently wide frequency range must be investigated experimentally. Frenkel's theory for the interpretation of ultrasonic data yields a minimum size of aggregates and an interfacial energy. Fixman's theory when applied to the pre-transitional region yields a short range correlation length, l, and the probable temperature dependence of the scale factor $1/\kappa$.

In the nematic region below the transition temperature, no adequate model exists to explain ultrasonic absorption data with any degree of certainty. Maier and Saupe's theory is the best available model to describe the state of orientation of molecules within a nematic domain. In combination with Fixman's theory, which has been applied to a postulated transition region between domains, a means is available of constructing sufficiently great values of ultrasonic absorption coefficients from present theoretical work. However no great confidence can be placed at present in the numerical values obtained for the adjustable parameters because of the highly approximate methods which are needed to perform the comparison and neglect of orientational diffusion in the region between domains.

Ultrasonic absorption and velocity data provide a very stringent test of present and future theoretical models of the nematic liquid crystalline phase. There is evidence[11] that they will also provide a critical means of testing theories of the cholesteric phase. As the measurements of Zvereva and Kapustin also show, the absorption in the smectic state appears to be lower. It is not yet known if this is a result of general validity.

Acknowledgments

We wish to thank Dr. Alfred Saupe for helpful discussion and criticism. We are also obliged to former colleagues, Dr. C. J. Pings and Dr. A. V. Anantaraman, for kindly making available data on binary mixtures in advance of main publication.

This work was supported by the National Science Foundation under grant number GK-440 from the Division of Engineering.

REFERENCES

1. Maier, W. and Saupe, A., *Z. Naturf.* **15a**, 287 (1960).
2. Ornstein, L. S., *Z. Kristallogr.* **79**, 90 (1931).
3. Fixman, M., *J. Chem. Phys.* **36**, 1957 and 1961 (1962).

4. Botch, W. and Fixman, M., *J. Chem. Phys.* **42,** 196 and 199 (1965).
5. Maier, W. and Saupe, A., *Z. Naturf.* **14a,** 882 (1959) and **13a,** 564 (1958).
6. Frenkel, J., *Kinetic Theory of Liquids* (Dover, New York, 1955), p. 382.
7. Hoyer, W. A. and Nolle, A. W., *J. Chem. Phys.* **24,** 803 (1956).
8. McSkimin, H. J., in *Physical Acoustics* by W. P. Mason (ed.) (Academic Press, New York, 1964), Vol. IA, Chap. 4.
9. Chynoweth, A. G. and Schneider, W. G., *J. Chem. Phys.* **20,** 1777 (1952).
10. Chynoweth, A. G. and Schneider, W. G., *J. Chem. Phys.* **19,** 1566 (1951) and **20,** 760 (1952).
11. Zvereva, G. E. and Kapustin, A. P., *Soviet Physics* (*Acoustics*) **10,** 97 (1964).
12. Gabrielli, I. and Verdini, L., *Nuovo Cim.* (series 10) **2,** 426 (1955).
13. Kreutzer, K. and Kast, K., *Naturwissenschaften* **25,** 233 (1937).
14. Lamb, J., in *Physical Acoustics* by W. P. Mason (ed.) (Academic Press, New York, 1965), Vol. IIA, Chap. 4.
15. Zernicke, F., *Proc. Acad. Sci. Amsterdam* **18,** 1520 (1916).
16. McKellar, J. F. and Andreae, J. H., *Nature* **195,** 865 (1962).
17. Anantaraman, A. V., Walters, A. B., Edmonds, P. D., and Pings, C. J. *J. Chem. Phys.*, **44,** 2651 (1966).
18. Fisher, M. E., *J. Math. Phys.* **5,** 944 (1964).
19. Englert, G. and Saupe, A., *Z. Naturf.* **19a,** 172 (1964).
20. Sette, D., *Nuovo Cim.* **1,** 800 (1955).
21. Mikhailov, I. G. and Tarutina, L. I., *Doklady Akad. Nauk. S.S.S.R.* **74,** 41 (1950), *Chem Abs.* **45**: 416 (1951).
22. Zvereva, G. E., *Soviet Physics* (*Acoustics*) **11,** 212 (1965).
23. Tsvetkov, V. N. and Krozer, S. P., *Soviet Physics* (*Technical Physics*) **3,** 1340 (1958).