

²The interaction is more easily pictured, and the relation to the two-component model of Widom and Rowlinson more readily grasped, by stating the interaction as a hard-core repulsion between antibars and anti-molecules: If an antibar occupies any line segment,

no antimolecule can be present in the square on either side. The antibar-antimolecule model is of some interest in itself, and has been studied by B. Widom, *J. Chem. Phys.* **46**, 3324 (1967), who also exploited its equivalence to the lattice gas.

Dynamic Shear Properties of Some Smectic Liquid Crystals

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The real part of the shear mechanical impedance has been measured for three smectic liquid crystals using a shear-wave reflection technique. Results at 30 and 450 MHz are considerably lower than those expected for an isotropic, Newtonian fluid, suggesting the existence of viscoelastic relaxation.

A study has been made of the behavior in shear of three smectic liquid crystals, ethyl *p*-azoxybenzoate, heptyloxyazoxybenzene, and ethyl *p*-[(*p*-methoxybenzylidene) amino] cinnamate. The shear-wave properties of a liquid may be represented by the shear mechanical impedance, $Z_L = R_L + iX_L$, defined as the negative ratio of shear stress to the rate of change of shear displacement. For a Newtonian fluid, i.e., one exhibiting no viscoelastic relaxation, $R_L = X_L = (\pi\rho\eta f)^{1/2}$, where ρ is the density, η the steady-flow viscosity, and f the shear-wave frequency. For a viscoelastic fluid R_L and X_L diverge with increasing frequency. In the limit where the material behaves as an elastic solid, R_L attains a maximum value and X_L becomes zero.

The experimental technique involved determination of the reflection coefficient for shear waves at a solid-liquid interface.¹ Measurements were made at two frequencies, 30 and 450 MHz. At 30 MHz a pulse of shear waves was obtained by means of a thin *BC*-cut transducer bonded to one end of a fused quartz rod; at 450 MHz a rod of *BC*-cut crystal quartz was used and shear waves were generated directly by surface excitation. The free end of the rod was loaded by the sample, and the change in the reflection coefficient gave the real part R_L of the shear impedance. No particular efforts were made to achieve uniform orientation of the samples and the orientation in situ was not observable.

The liquid crystal samples were obtained from

Eastman Kodak Co., and were used as supplied. The results obtained did not differ significantly from those obtained using recrystallized material.

Ethyl *p*-azoxybenzoate has a single mesomorphic phase, smectic *A*, from 114 to 123°C. The viscosity has been reported by Vorländer² to be up to 9 cP for the isotropic liquid and from 30 to 160 P in the smectic phase. The variation of the shear resistance at 450 MHz is shown in Fig. 1. Although there is a large increase in steady-flow viscosity upon cooling through the isotropic liquid-to-smectic phase transition at 123°C, there is no appreciable change in R_L . At the freezing point (somewhat below the nominal transition temperature of 114°C) the shear reflection loss increases rapidly because of shear-wave transmission into the solid. The value of R_L below the freezing point indicates an elastic modulus approaching 10^{10} dyn/cm², a value typically obtained for simple organic glasses.³ Upon heating, R_L changes less abruptly, and a difference between the values for heating and cooling persists until the isotropic liquid state is reached. During the heating part of the cycle, pretransitional softening of the solid is evident. A Newtonian liquid of viscosity 100 P and unit density has a shear resistance of 0.96×10^5 dyn sec/cm³ at 30 MHz and 3.7×10^5 dyn sec/cm³ at 450 MHz. At 115°C the measured values of R_L were 3.6×10^3 and 1.3×10^4 dyn sec/cm³ at 30 and 450 MHz, respectively. Within the limits of experimental error,

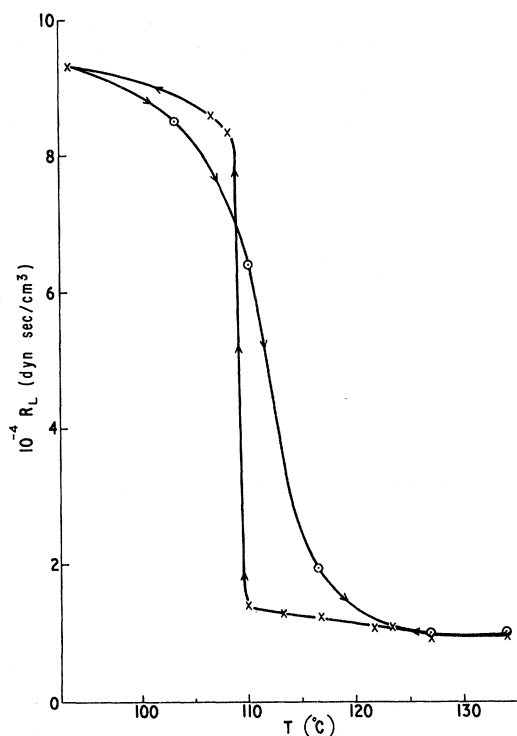


FIG. 1. Shear resistance of ethyl *p*-azoxybenzoate at 450 MHz. The transition from isotropic liquid to the nematic phase occurs at about 123°C.

about $\pm 5\%$, these figures correspond to the values expected for a Newtonian liquid of viscosity 0.13 P.

Heptyloxyazoxybenzene has two mesomorphic phases, nematic from 95 to 124°C and smectic C from 74 to 95°C. The shear viscosity of the smectic phase, as measured in this study, varies from 2 to 6 P. The behavior near the freezing point could not be determined because on contraction the solid became detached from the quartz rod. However, the values of shear resistance during heating and cooling cycles differ much less than those for ethyl *p*-azoxybenzoate shown in Fig. 1. Upon cooling, the curve showing the variation of R_L with temperature has only a slight change of slope at the nematic-smectic transition and there is no substantial change in R_L as might be expected from the change in steady-flow viscosity. The measured values of R_L in the smectic phase are 2×10^4 dyn sec/cm³ at 450 MHz and 4×10^3 dyn sec/cm³ at 30 MHz, and the equivalent Newtonian viscosity is about a tenth of the steady-flow viscosity.

Ethyl *p*-[(*p*-methoxybenzylidene) amino] cinnamate has three liquid crystalline phases. Measurements were made during cooling, which pro-

duces a nematic phase between 138 and 117°C, smectic A between 117 and 92°C, and smectic B below 92°C until freezing occurs.⁴ The viscosity as determined by Vorländer⁵ is about 8 cP in the nematic phase, increases from 20 cP to 37 P through the smectic A phase, and rises rapidly to 4800 P at 89.5°C in the smectic B phase. In the nematic phase, R_L was found to equal the Newtonian value to within experimental error, giving no indication of relaxation. At 100°C with $\eta = 5$ P and $(\pi\rho\eta f)^{1/2} = 8.5 \times 10^4$ dyn sec/cm³, R_L was found to be 2.3×10^4 dyn sec/cm³. Upon reducing the temperature to 89.5°C, R_L increased to only 3.7×10^4 dyn sec/cm³.

In each of the three liquids the measured shear resistance is considerably less than that which would be expected in an isotropic, Newtonian liquid. This could be due to two possible causes. First, isotropic liquids with such high viscosities would be expected to have non-Newtonian values due to the presence of viscoelastic relaxation. In most isotropic liquids a relaxation process causes the shear resistance to diverge from the Newtonian value below 10^4 dyn sec/cm³. In addition, the shear properties of smectic liquids are known to be highly anisotropic. The shearing of one smectic plane relative to another may be fairly easy while shearing across the planes is more difficult. Measured values of steady-flow shear viscosity are presumably some kind of average of these two processes. If the smectic planes in the present experiment are oriented parallel to the reflecting surface, the shear reflection coefficient is a measure of the dynamic behavior of the low-viscosity component only.

From the results reported here, we cannot be certain which of the causes is predominant. Ethyl *p*-azoxybenzoate, for example, when cooled from the isotropic liquid is known to have a tendency to have its smectic planes oriented parallel to a clean surface.⁶ On the other hand, the plot of $\log\eta$ vs $1/T$ for the isotropic liquid yields a straight line which has a value of about 0.13 P when extrapolated to 115°C. This would indicate that the viscosity characteristic of the smectic phase is completely relaxed at 30 and 450 MHz and that the observed results are due only to the residual viscosity characteristic of the isotropic liquid. In ethyl *p*-[(*p*-methoxybenzylidene) amino] cinnamate the changes of R_L at the phase transitions and the very large values of steady-flow shear viscosity lead us to believe that a viscoelastic relaxation is present. This conclusion is consistent with the recent report⁷ that the smec-

tic planes in the smectic *A* phase orient normal to a surface.

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Superfluidity in Quantum Crystals

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The speculations of Chester, Andreev and Lifshitz, and Leggett concerning the possibility of Bose-Einstein condensation and/or superfluidity in quantum crystals are examined. The existing body of experimental data on these systems places extremely strong constraints on the experimental realization of these speculations.

Recently Chester,¹ Andreev and Lifshitz,² and Leggett³ have speculated about the possibility of the occurrence of Bose-Einstein condensation and/or superfluidity in solids. Each of these speculations has contained the suggestion that the most likely candidates for the observation of this superfluidity is the quantum crystal, solid ⁴He. The purpose of this paper is (1) to describe what we believe to be the essential physical content of each of these speculations and (2) to scrutinize them in light of the large body of data on quantum crystals.

It is useful at the outset to introduce a model Hamiltonian which gives an adequate description of the important particle motions in quantum crystals and which provides a concrete framework on which to base our discussion. We take the particles in solid ⁴He to be described by

$$\mathcal{H}_{PM} = \sum_R \epsilon_0 b_R^\dagger b_R + \sum_{RR'} t(RR') b_R^\dagger b_{R'} + \varphi_0 \sum_R b_R^\dagger b_R^\dagger b_R b_R, \quad (1)$$

where b_R^\dagger creates a ⁴He atom in the ground state at lattice site R .^{4,5} The energies ϵ_0 , $t(RR')$, and φ_0 are ϵ_0 , the energy of a particle in the ground state at lattice site R ; $t(RR')$, the energy associated with tunneling from lattice site R to lattice site R' (approximately the off-diagonal kinetic energy); and φ_0 , the hard-core energy associated with double occupation of a lattice site.⁶ The particles may move through the solid because of

$t(RR')$, the tunneling term, but they are hindered in their motion by the strong repulsive interaction, the hard-core term. For the purposes of this model the numbers ϵ_0 , t , and φ_0 can be taken to be about 20, 0.1, and 10 K, respectively.

The particle motions that are necessary to have a superfluid component in the solid are difficult to achieve because of the hard-core repulsion between pairs of particles. We may partially avoid this difficulty by taking the $T=0$ ground state of the solid to contain a finite number of vacancies.

Case I. — At $T=0$ the ground state of the solid is N particles described by \mathcal{H}_{PM} on $N+n_v$ lattice sites. Here n_v is the number of vacancies in the ground state. These vacancies are called ground-state or "frozen-in" vacancies. The presence of n_v vacancies in the ground state does not mean that there are n_v vacant lattice sites. It means that there is a single-particle density in the vicinity of each lattice site which is less than 1, i.e., $N/(N+n_v)$. In his discussion of Bose-Einstein condensation in solids, Chester suggests that the usual proofs that this condensation cannot occur in solids are invalidated by the presence of "frozen-in" vacancies in the $T=0$ ground state.¹ The vacancies of Andreev and Lifshitz, which have a condensate and lead to the superfluid properties they discuss, are vacancies present in the $T=0$ ground state.⁷ Thus we take case I to represent the physical content of the speculations of Chester and of Andreev and Lifshitz.