VI. COOPERATIVE PHENOMENA IN SOLIDS AND FLUIDS*

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RESEARCH OBJECTIVES AND SUMMARY OF RESEARCH

The general goal of our work is to obtain information about bulk systems near cooperative phase transitions or critical points. Primary emphasis is on ultrasonic investigations. In particular, ultrasonic velocities give direct information about the equilibrium thermodynamic properties and ultrasonic attenuation provides data about the dynamical behavior. The majority of the work has been concerned with order-disorder lambda transitions in solids, but critical points in fluids are also being studied. During the past year progress was made on a variety of ultrasonic problems. Interesting data have been obtained as a function of temperature for NH_4Br at 1 atm and for NH_4Cl at high pressures. In the case of NH_4Br, where an "antiparallel" ordering occurs, the behavior is quite different from that of NH_4Cl, where a "parallel" ordering takes place. In the case of NH_4Cl, the velocity and attenuation undergo a distinct change as the pressure is increased. This work is still being actively pursued. Our major ultrasonic results during 1971, however, involved investigations of fluids: xenon and the liquid crystal MBBA. The highlights of that work are described below.

A novel phase-sensitive detection technique with signal averaging has made possible the measurement of velocity and attenuation in a critical region where acoustic attenuation is very large. The critical attenuation per wavelength and the reduced velocity dispersion along the critical isochore in xenon were found to depend on temperature and frequency through a single, dimensionless variable ω/ω_D, where ω_D is the characteristic frequency for thermal diffusion. Overall agreement with recent theoretical predictions of Kawasaki[1] is good but not perfect. The data seem to suggest the presence of other relaxation processes very near the critical point. The same ultrasonic method was also used to measure the ultrasonic velocity and attenuation over a wide range of temperature and frequency in the region of the nematic-isotropic phase transition in MBBA. In the nematic phase, the relaxation time becomes very long as the clearing temperature is approached: $\tau = 4.1 \times 10^{-7} |\Delta T|^{-0.40}$ s. In the isotropic phase, there is a less pronounced variation in the relaxation time: $\tau = 9.0 \times 10^{-8} (T-T_o)$ s, where T_o is 2.4 deg below the clearing temperature. The data nearest the phase transition exhibit a relaxation spectrum which is definitely broader than that of a single relaxation time. This work represents the first detailed ultrasonic study of the phase transition in a liquid crystal.

In addition to ultrasonic investigations, work has also been carried out on dynamical calorimetry and high-pressure compressibility. The latter work, which is now complete, involved the measurement of anomalous variations in the length L of an

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NH_4Cl single crystal in the vicinity of its order-disorder transition line. At low pressures, there is a small first-order discontinuity ΔL superimposed on the expected lambda-like variation in L. At a "critical" point (255.95°K and 1491.8 bar), L varies continuously but κ_T and α appear to diverge. At higher pressures, the variation in L at the transition becomes progressively more gradual as the pressure increases. The compressibility along the critical isotherm varies like $(\Delta p)^{-y}$ in the immediate vicinity of the transition and the coefficient of thermal expansion along the critical isobar is fairly well represented by $(\Delta T)^{-x}$. The exponents x and y, which range from 0.4 to 0.9, are much larger than those associated with an ideal Ising lattice. This investigation shows the important role of stress-strain variables in determining the behavior near cooperative phase transitions in compressible solids.

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