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Ultrasonic Investigation of the Order-Disorder Transition in Ammonium Chloride

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Introduction

The lambda transition in solid ammonium chloride was discovered by Simon [1] from heat-capacity measurements. An x-ray analysis by Simon and von Simson [2] showed that ammonium chloride has a CsCl-type cubic structure both above and below the critical temperature; thus the transition could not be due to a change in lattice type. Hettich [3] found that ammonium chloride is weakly piezoelectric in the low-temperature modification, whereas it is not piezoelectric above the critical temperature. From this he concluded that the tetrahedral ammonium ions are oriented parallel in the low-temperature modification. Menzies and Mills [4] came to the same conclusion on the basis of the Raman effect. Pauling [5] suggested that the transition was related to the onset of free rotation of the ammonium ions, and quantitative refinements of this idea were carried through by Fowler [6] and by Kirkwood [7]. In opposition to this, Frenkel [8] interpreted the transition as being

202

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- [10] The deviations from a 1/3-power law observed by Edwards and Woodbury appear to be much too large to ascribe to experimental error. If these deviations are real, they might be attributed to quantum corrections to the law of corresponding states (J. de Boer, Physica **14**, 139, 149 (1948); J. de Boer and R. J. Lunbeck, Physica **14**, 509 (1948)), and similar behavior ought to be observed in He³. Such appears to be the case (see paper by R. H. Sherman in this conference).
- [11] The line in the figure actually has a finite intercept of +4.6 millidegrees on the abscissa. This may indicate flattening of the coexistence curve close to the critical point, or may be the result of errors in the measured temperatures in reference 7 or the assignment of T_c .
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- [13] Note that if the velocity minima did not fall exactly on the line $\rho = \rho_c$, the agreement would be worse, for a smaller value of u is required to fit the theoretical curve.

of the order-disorder type, involving the relative orientations of the tetrahedral ammonium ions; it was assumed that in both the ordered and the disordered states the ammonium ions liberate about an equilibrium position. This idea has been confirmed by many subsequent experiments.

In particular, Levy and Peterson [9] have carried out a neutron-diffraction determination of the hydrogen positions in both the low- and high-temperature modification, and Purcell [10] has analyzed the nmr data to obtain the relaxation time for an NH₄⁺ ion to move from one orientation in its cubic cell to the other orientation. Both these investigations show that free rotation does not occur.

Indeed, in many respects NH₄Cl is an ideal crystal for studying cooperative order-disorder phenomena. The ordering is completely analogous to that for a simple-cubic ferromagnet in a zero external field. The change in interaction energy between parallel and antiparallel NH₄⁺ ions is almost completely due to octopole-octopole terms between nearest and next-nearest NH₄⁺ neighbors

[11], and thus NH₄Cl is quite a good example of an Ising lattice. Furthermore, the ordering process should have little effect on the dynamics of such an ionic lattice.

We wish to discuss here a variety of ultrasonic measurements which have been made on single-crystal ammonium chloride. Longitudinal and transverse (shear) acoustic velocities have been measured [12, 13] over a wide range of frequencies (5 to 60 Mc/s), temperatures (150 to 320 °K) and pressures (0 to 12 kbar). The attenuation of longitudinal ultrasonic waves has been measured [14] at 1 atm for frequencies between 5 and 55 Mc/s and temperatures from 200 to 270 °K. In all these investigations, special emphasis was given to the "anomalous" behavior near the lambda transition. As shown in figure 1, the transition temperature is a fairly strong function of pressure, increasing from ~242 °K at 1 atm to ~308 °K at 10 kbar. (Note the pronounced curvature of the lambda line and the hysteresis observed at low pressures.) At a constant pressure of 1 atm, the ultrasonic velocities were originally measured by a pulse-echo method as a function of frequency and temperature, and no dispersion was observed [12]. Recently, the McSkimin pulse-superposition method has been used at a fixed frequency of 20 Mc/s. The temperature dependence at 1 atm has been restudied, and the pressure dependence of the velocities were

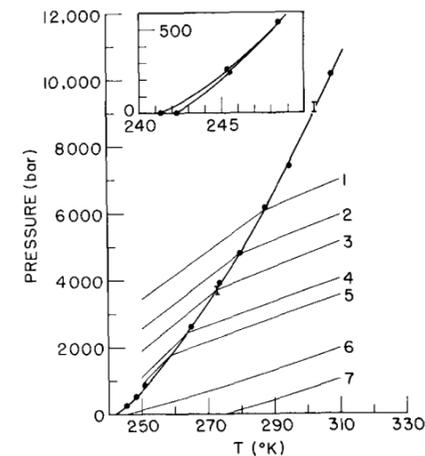


FIGURE 1. Phase diagram for NH₄Cl (the high-pressure, low-temperature field corresponds to the ordered phase).

The solid data points were obtained from the abrupt "break" in the ultrasonic shear velocities at the lambda transition point (see figs. 2 and 3). The vertical bars indicate static measurements of Bridgeman [15]. The light lines numbered 1 through 7 represent various isochores.

measured at five fixed temperatures spaced between 250 and 308 °K. Thus, we have very precise velocity data ($\pm 0.005\%$) on both the ordered and disordered phases. This experimental data will be described elsewhere [13] in detail, but is presented here in a graphical form.

All the results given below are in terms of the variation of one of the three elastic constants c_{11} , c_{44} , and $C' = (c_{11} - c_{12})/2$. Third-order elastic constants are not used, and at high pressures the quantities c_{11} , c_{44} , and C' are in a sense "effective" elastic constants. The constants c_{11} and c_{44} were calculated from the experimental longitudinal and transverse velocities (U) in the [100] direction with the relations $\rho U_l^2 = c_{11}$ and $\rho U_t^2 = c_{44}$; the constant C' was calculated from $\rho U_p^2 = C'$, where U_p is the velocity in the [110] direction of a shear wave polarized perpendicular to the [001] axis.

Experimental Results

The variations of the shear constants c_{44} and C' and of the compressional constant c_{11} with pressure at five different temperatures are given in figures

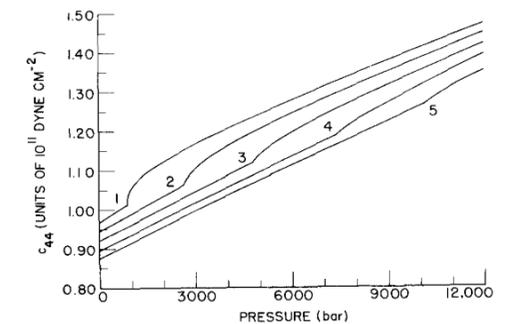


FIGURE 2. Dependence of c_{44} on pressure at $T_1=250$, $T_2=265$, $T_3=280$, $T_4=295$, and $T_5=308$ °K.

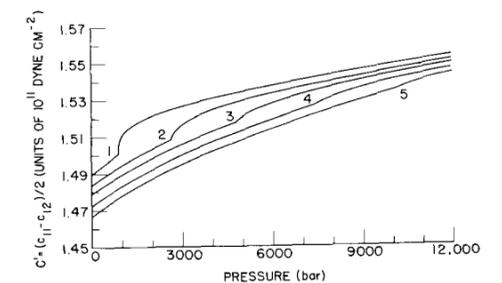


FIGURE 3. Dependence of C' on pressure at various temperatures (see fig. 2 legend).

203

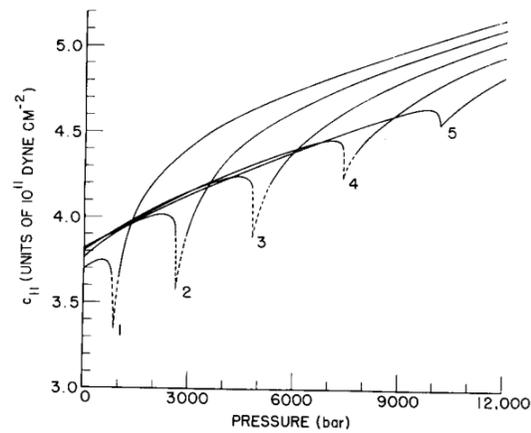


FIGURE 4. Dependence of c_{11} on pressure at various temperatures (see fig. 2 legend). Dashed portions of the curves indicate regions where data are less accurate or are missing due to high attenuation.

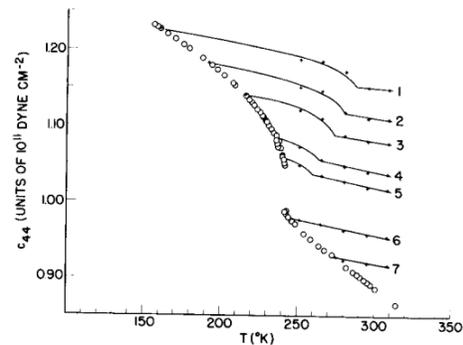


FIGURE 5. Variation of c_{44} with temperature at 1 atm (open circles) and at $V_1 = 34.00$, $V_2 = 34.15$, $V_3 = 34.27$, $V_4 = 34.43$, $V_5 = 34.51$, $V_6 = 34.77$, $V_7 = 34.93$ $\text{cm}^3 \text{mole}^{-1}$ (crosses). The transition temperature is known for each of these volumes, and thus the location of the change in slope for each of the constant-volume lines is fixed.

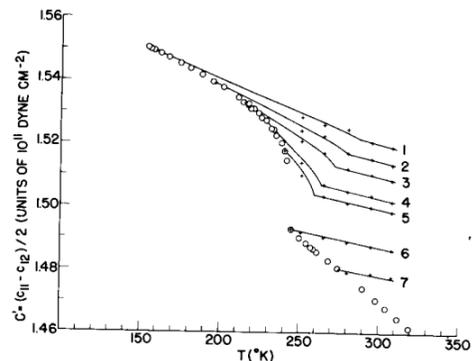


FIGURE 6. Variation of C' with temperature at 1 atm (open circles) and at various constant volumes (see fig. 5 legend).

204

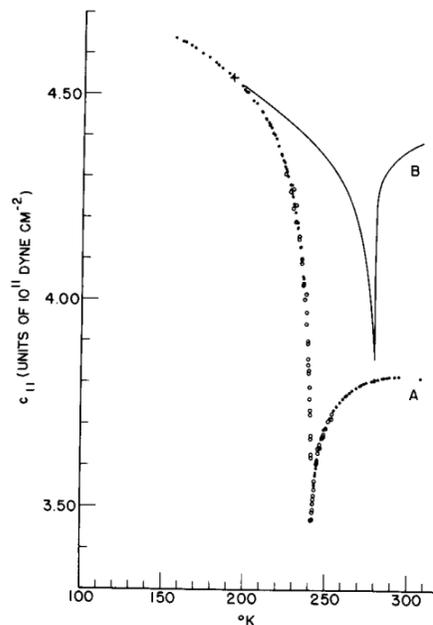
FIGURE 7. Variation of c_{11} with temperature. Curve A: data at 1 atm (solid circles = pulse superposition method [13], open circles = corrected pulse-echo data [12]). Curve B: calculated curve at constant volume $V_2 = 34.15$ $\text{cm}^3 \text{mole}^{-1}$; V_2 corresponds to V_λ at 280 °K and to the volume at 1 atm and 191.25 °K (marked by cross).

2, 3, and 4. Data points are not shown on these figures since a variety of corrections must be applied to the data, which requires some smoothing. Each isotherm is based on at least 30 experimental points which show very little scatter. Note that c_{44} is much more sensitive to pressure than C' but that the character of the anomalous variation near the lambda line is very similar for both these shear constants. Indeed, there is a marked reduction in the rapid variation just above the transition as the lambda line is crossed at higher pressures. This same reduction in anomalous behavior is also seen in the c_{11} data. The adiabatic compressibility β^S can be calculated from

$$1/\beta^S = \frac{1}{3}(c_{11} + 2c_{12}) = c_{11} - \frac{4}{3}C' \quad (1)$$

and it is clear that β^S goes through a sharp maximum at a lambda point.

Experimental data points are shown in figures 5, 6, and 7 for the constants c_{44} , C' , and c_{11} as functions of temperature at 1 atm. In addition, the variation of c_{44} and C' with temperature is given for seven different constant volumes, and the behavior of c_{11} at a single constant volume is also shown.



These constant-volume curves were obtained by determining the pressure required at a given temperature to give the desired volume (Bridgeman's data [15] and our own were used) and then reading the appropriate elastic constant values from figures 2 to 4.

For the shear constants, one can immediately see that most of the temperature change near T_λ at 1 atm is due to the rapid change in volume in the transition region. Our data permit us to completely analyze the effects of volume changes and temperature changes so that one can see the effect of ordering at a constant volume and temperature. For longitudinal waves, volume changes do have a significant effect on the velocity, but the anomalous dip in c_{11} is essentially due to ordering effects. In figure 7, the shift in the minimum between curves A and B is merely a result of the value chosen for the constant volume; the important difference between these curves is their shape near the minimum.

For shear waves there is no indication of excess ultrasonic attenuation near the lambda line, but for longitudinal waves there is a very sharp maximum in the attenuation coefficient α at the transition point. Quantitative measurements of α for longitudinal waves along [100] have been made at 1 atm as a function of frequency and temperature [14]. The results are shown in figure 8 for 15, 25, 45, and 55 Mc/s. Data have also been taken at 5 Mc/s, where a rather large (0.5 dB cm^{-1}), temperature-independent background attenuation is present (presumably due to beam-spread losses).

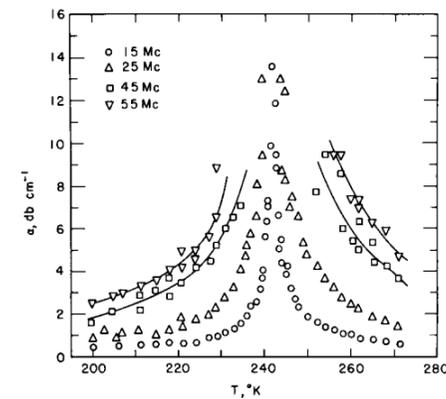


FIGURE 8. Attenuation coefficient α at various ultrasonic frequencies.

Data obtained on two samples with different path lengths were in excellent agreement at 15 and 25 Mc/s. Scatter in the 45 and 55 Mc/s data is caused by high α values and weak initial pulses (9th and 11th harmonics of 5 Mc/s transducer).

Further experimental work on attenuation is currently in progress.

Since there is no excess attenuation near the lambda point for shear waves, it is possible to follow the behavior of the shear velocities through the transition region. Both c_{44} and C' showed a small hysteresis, the magnitude of which is indicated in the insert on figure 1. We have not shown data points in this region on figures 5 and 6 since equilibrium was very difficult to achieve (slow changes in the shear velocities occurred even after 45 min). The presence of this hysteresis and the very abrupt change in shear velocities near T_λ are significant properties of our measurements at 1 atm. (Similar indications of hysteresis and abrupt changes near T_λ are seen from volume measurements and cooling curves.)

Discussion

Equilibrium data. Because of the formal analogy between the ordering of NH_4Cl and of a ferromagnet in the absence of an external field, it is appropriate to consider the mechanical behavior of an Ising lattice. If the coupling between the lattice system and the "spin" system is sufficiently weak, an Ising lattice will become unstable in the immediate vicinity of its critical point and a first-order transition will occur. Furthermore, hysteresis will be expected in the critical region. This instability has been demonstrated for a two-dimensional square lattice [16,17], where there is an analytic solution to the Ising problem. The important conditions for this instability are (1) weak lattice-spin coupling, (2) a finite compressibility for the disordered lattice, and (3) an infinite C_r for the "spin" system at the critical temperature. The effect will be large only when (a) the lattice is soft, (b) the critical temperature is large, and (c) dJ/dV is large (where J is the usual Ising interaction energy). Such an instability has been proposed previously for other models [18,19] and discussed in general thermodynamic terms by Rice [20], but little attention seems to have been paid to this problem. It would appear that NH_4Cl is a much more appropriate system for observing these effects than most ferromagnetic solids would be.

To illustrate the instability and the possible hysteresis in order-disorder transitions, let us look at the two-dimensional case [16]. Figure 9 shows a plot of p_l and $-p_d$ against the area σ at several temperatures $T_1 < T_2 \dots T_6 < T_7$. The pressure

205

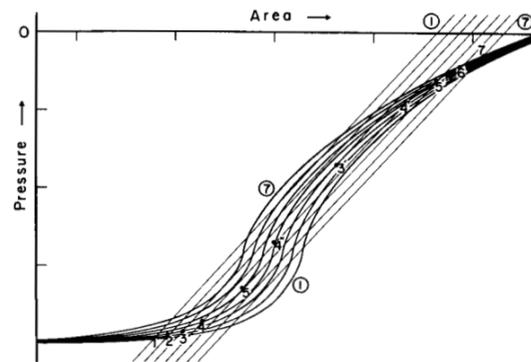


FIGURE 9. Plot of p_l and $-p_{dl}$ versus the area σ for a two-dimensional Ising lattice. The family of curves p_l were calculated at seven evenly spaced temperatures from T_1 up to T_7 . The family of lines $-p_{dl}$ were drawn to represent a disordered lattice with typical compressibility and thermal expansion coefficients. The encircled numbers 1 and 7 indicate the spin and lattice isotherms at T_1 and T_7 .

p_{dl} is that of the completely disordered lattice, and p_l represents the attractive (negative) pressure due to the ordering of an Ising spin system. An intersection of the two appropriate isotherms (p_l and $-p_{dl}$) will correspond to $p = p_l + p_{dl} = 0$ and will give an equilibrium area σ if the stability condition ($\partial^2 A / \partial \sigma^2 > 0$) is satisfied. The stability condition requires that the slope of $-p_{dl}$ be greater than that of p_l ; e.g., the system is unstable at a point such as 4'. Now consider the change in area with T for a system under zero external stress ($p = 0$). As the temperature increases from T_1 to T_5 , σ can increase continuously from σ_1 to σ_5 (points 1 to 5 on fig. 9) but as $T \rightarrow T_5$ from below the system becomes unstable ($\partial^2 A / \partial \sigma^2 = 0$) at point 5 and there must be a first-order change in area from σ_5 to σ_5' . On further heating, σ increases continuously from σ_5' to σ_7 . However, on cooling from T_7 to T_3 the area can decrease smoothly from σ_7 to σ_3 . As $T \rightarrow T_3$ from above the instability occurs at point 3' and there is a first-order change from σ_3' to σ_3 . Below T_3 , σ decreases smoothly on cooling. Thus, there can be a hysteresis loop near the critical point with a first-order jump in σ at T_5 on heating and a first-order drop in σ at T_3 on cooling. The values T_3 and T_5 determine the maximum width of this loop since the system becomes mechanically unstable at points 5 and 3'. Naturally, there is a temperature T_4 for which the free energy at point 4 equals that at point 4'; thermodynamic equilibrium would give a first-order transition at T_4 and no hysteresis. The region

between 4 and 5 on heating or 4' and 3' on cooling is only metastable. Although the shape of the p_l curves will be different for a three-dimensional Ising lattice, the instability will still occur if C_r (and thus $\partial p_l / \partial V$) $\rightarrow \infty$ at the critical point. Thus the hysteresis described above can still occur.

As seen in figures 2, 3, 5, and 6, the shear constants of NH_4Cl are sensitive functions of volume. Thus the experimental hysteresis in c_{11} and C' can indicate the presence of the proposed hysteresis in V . Note that experimentally the hysteresis decreases for a transition higher up along the lambda line (i.e., at some finite external pressure). This would be expected from our analysis of the Ising lattice since the only difference between working at zero pressure and at some large constant pressure is in the lattice stiffness. For high external pressures, the slope of $-p_{dl}$ will be greater and the maximum width ΔT of the hysteresis will be less. Moreover, a semiquantitative estimate of the magnitude of ΔT at 1 atm is in reasonable agreement with experiment. Completely analogous considerations can be developed for an instability and hysteresis on compressing an Ising lattice at constant temperature. An elaboration of the effects of hysteresis and instability on measurements at either constant pressure or constant volume will be given in detail elsewhere [16]. In addition, our shear data strongly suggest a sluggish first-order transition in the critical region. For points taken at temperatures more than 1 °K away from T_λ and at pressures more than 100 bar away from p_λ , equilibrium was achieved within about 15 min after the temperature or pressure was adjusted. In the immediate vicinity of a critical point, very slow changes in velocity were still observed 45 min after the temperature or pressure was adjusted, as would be expected in a metastable region. Also the changes in c_{44} and C' in this narrow hysteresis region are extremely abrupt, even when compared with the very rapid variations observed in the ordered phase near the transition line.

Leaving aside the important but relatively narrow range where instability may occur, it is possible to discuss the effect of ordering at constant volume on the elastic constants in terms of an Ising model. We have carried out a general stress-strain analysis of the two-dimensional Ising lattice (using Onsager's analytic solution for the case $J \neq J'$) and have obtained explicit formulae for the isothermal stiffnesses c_{11} , c_{44} , and $C' = (c_{11} - c_{12})/2$. The details will be reported elsewhere [21], but the essential

features can be seen from the simpler formula for the isothermal volume compressibility β^T :

$$\frac{1}{V\beta^T} = \left(\frac{\partial^2 A}{\partial V^2} \right)_T = \left(\frac{1}{V\beta^T} \right)_{dl} - \frac{T}{J^2} C_l(0, H) \left(\frac{dJ}{dV} \right)^2 + \frac{U_l(0, H)}{J} \left(\frac{d^2 J}{dV^2} \right) \quad (2)$$

where $C_l(0, H)$ and $U_l(0, H)$ are the Ising heat capacity and internal energy at zero field as a function of $H \equiv J/kT$. The subscript dl denotes the appropriate quantity for a completely disordered lattice (for which C_l and U_l equal zero). The elastic constants c_{ij} are given by $(\partial^2 A / \partial x_i \partial x_j)_T$ where the x 's are the appropriate strains. Thus the expression for c_{11} will have a form similar to eq (2), and the dominant term in determining the shape of c_{11} near T_λ will involve C_l . For $C' = (c_{11} - c_{12})/2$ one requires a difference between two such expressions, and the singular part involving C_l will cancel out. The final expression for C' is complicated in its dependence on V and T , but it does predict a smooth variation through the transition region. For c_{44} the term containing C_l disappears identically since $dJ/d\gamma = 0$ (γ is the change in angle during a c_{44} shear), but $d^2 J / d\gamma^2 \neq 0$ and the shape of c_{44} near T_λ is determined by U_l . In general terms these predictions are all fulfilled by our NH_4Cl data as functions of temperature at constant volume. In the case of c_{11} one must take account of the significant difference between the adiabatic and the isothermal constants near T_λ , but even so the shape of c_{11} is strikingly related to the shape of the heat capacity curve. In addition, the shape of c_{44} is what one would expect from an internal energy curve. No detailed discussion of C' will be given here, but in crude terms the effect of ordering is very small for this shear mode and this indicates that the "anomalous" variations in c_{11} and c_{12} almost completely compensate each other.

A final remark about the equilibrium properties of NH_4Cl can be made in connection with the Pippard equations. It is known that these phenomenological relations are fairly well obeyed [12] in NH_4Cl , but a generalization of them in terms of stress-strain variables [22] shows that there are some unexplained difficulties. We have recently discussed the Pippard equations [23] on the basis of a three-dimensional Ising model and can now give a better insight into the reasons for their behavior.

Dynamical data. In the past few years there has been increasing interest in the theory of the dynamical properties of substances near a lambda point. Landau and Khalatnikov [24] were the first to treat this problem by combining the thermodynamics of irreversible processes with an approximate equilibrium solution to the Ising problem. This approach has been extended and improved by others [25, 26] and a somewhat simplified result for the relaxation time τ for long-range ordering can be given in the form

$$\tau^{\pm} = A^{\pm} / |T - T_c| \quad (3)$$

where $+$ and $-$ denote temperatures above and below T_c . The phenomenological constants A^+ and A^- depend on the substance involved but have a fixed ratio of $A^+ / A^- = 2$. A more general statistical-mechanical treatment of this problem has been given by Kikuchi [27]. For a temperature range close to the lambda point one can show that Kikuchi's results for the long-range relaxation times are still of the form given in eq (3). However, the constants A^+ and A^- now depend on microscopic transition probabilities and the ratio A^+ / A^- near T_c is ~ 1.6 rather than 2.

An essential feature of our ammonium chloride data which requires explanation is the fact that the attenuation α has its maximum at T_λ . One would expect α to vanish at T_λ if τ becomes infinite there. However, the theories mentioned above deal with τ_{TV} , the relaxation time for ordering at constant temperature and volume. The experimental conditions for measuring attenuation are adiabatic rather than isothermal, and although the process is irreversible one can consider it to be essentially isentropic for small sound amplitudes. In this case the appropriate relaxation time is τ_{SV} , which can be related to τ_{TV} by

$$\frac{1}{\tau_{SV}} = \frac{1}{\tau_{TV}} + \frac{\bar{k}T}{\bar{C}_r} \left(\frac{\partial S}{\partial \xi} \right)_{T,V}^2 \quad (4)$$

where \bar{k} is a rate constant, \bar{C}_r is the specific heat at infinite frequency ("frozen" specific heat), and ξ is a progress variable characterizing the internal (non-equilibrium) state of the system at a given V and T .

The detailed behavior of $(\partial S / \partial \xi)^2$ is not known, but it seems likely that this quantity varies only slowly with temperature near T_λ . We shall assume below that the quantity $\bar{k}T(\partial S / \partial \xi)^2 / \bar{C}_r$ has a constant value (call it B) over the temperature range of

interest. With this assumption and eqs (3) and (4), we find that

$$\frac{1}{\tau_{SV}} = \frac{\Delta T}{A} + B \quad (5)$$

for the relaxation time associated with long-range ordering, where $\Delta T = |T - T_\lambda|$ and the constant A has different values above and below T_λ . According to eq (5), τ_{SV} will have a finite maximum value at T_λ and if this value is reasonably small (i.e., $\omega^2\tau^2 < 1$) the attenuation will have its maximum at T_λ .

For a mechanism involving a single relaxation time, we have the usual expression

$$\alpha = \left[\frac{c_{f1} - c_{l1}}{2Uc_{11}} \right] \frac{\omega^2\tau_{SV}}{1 + \omega^2\tau_{SV}^2} \quad (6)$$

Unfortunately the variation of $(c_{f1} - c_{l1})/2Uc_{11}$ with temperature is not known, but it is unlikely that this could be an important factor in determining the temperature dependence of α . One would probably expect only a small and slowly varying dependence of $c_{f1} - c_{l1}$ on temperature. We shall assume (as did Chase in his analysis of helium [28]) that $(c_{f1} - c_{l1})/2Uc_{11}$ has a constant value throughout the transition region. We shall also assume (and can subsequently justify) that $\omega^2\tau_{SV}^2 \ll 1$ for all temperatures near T_λ . With these assumptions and eq (5), we can rewrite eq (6) in the form

$$\frac{\omega^2}{\alpha} = \frac{2Uc_{11}}{c_{f1} - c_{l1}} \frac{1}{\tau_{SV}} = \frac{2Uc_{11}}{c_{f1} - c_{l1}} \left(\frac{\Delta T}{A} + B \right) \quad (7)$$

If all our assumptions are valid, then ω^2/α should be independent of frequency and should vary linearly with the temperature on both sides of T_λ .

Figure 10 shows a plot of ω^2/α , in units of $\text{cps}^2 \text{ N}^{-1} \text{ cm}$, versus temperature for all of our data close to T_λ . Various details concerning the correction for background attenuation and the justification of $\omega^2\tau^2 < 1$ are given elsewhere [14], but in a general way the data shown in figure 10 seem to agree with eq (7). The value of ω^2/α at its minimum (at $\sim 242.0 \text{ }^\circ\text{K}$) is 0.52×10^{16} ; the slope above T_λ is 0.46×10^{16} and the slope below T_λ is 0.66×10^{16} . These slopes give a ratio $A^+/A^- = 1.43$, as compared to ~ 1.6 expected on the basis of Kikuchi's model.

When the analysis is extended to data obtained at higher frequencies and at temperatures further away from T_λ , the deviations from eq (7) are not

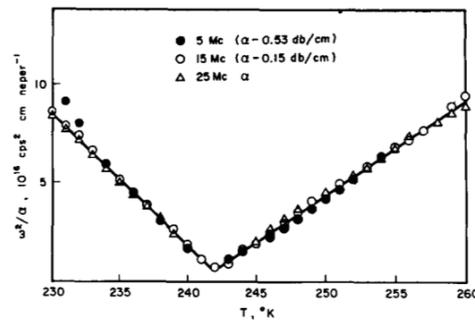


FIGURE 10. Plot of ω^2/α versus temperature, close to the lambda point at $p = 1 \text{ atm}$.

Data at 45 and 55 Mc/s were not available over this temperature range. Note that the α values for 5 and 15 Mc/s have been corrected for a temperature-independent background attenuation (beam-spread losses).

quite what one would expect [14] and new experimental work along these lines is currently in progress. Also if NH_4Cl undergoes a first-order transition very close to the "lambda point," then one would expect τ to undergo a discontinuous change between two finite values. This may supersede the explanation given above for the behavior of α [29].

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Discussion

E. H. W. Schmidt presented some experimental observations on convective heat transfer near the critical point of CO_2 [1] emphasizing the difficulties which arise in measuring the thermal conductivity in the critical region.

J. J. M. Beenakker: I have a problem concerning the dimensions of the apparatus in which one tries to measure the transport properties near the critical point. As soon as one expects that any anomaly in viscosity or thermal conductivity is related to the long range correlations or fluctuations, care has to be taken that the dimensions are large compared to the magnitude of the correlation length.

M. E. Fisher: It seems to me there is no need to worry about the dimensions relative to the correlation length because all the light scattering and neutron scattering experiments show that even when you have what you call long range correlations, they are still of the order of 1000 Å when you come very close to the critical point. And that is for the pair correlation function. Most of these transport coefficients involve higher order correlation functions which one would expect to die out more rapidly. Thus although in principle one could get difficulties very close to the critical point, I don't think one has to worry about this in practice.

J. J. M. Beenakker: In the case of an oscillating disk viscometer one has to consider a penetration depth between oscillating plates and the gas layer. As in the critical region the density is changing rapidly with height, I wonder whether you can make a statement of the absence of an anomaly in the viscosity close to the critical point.

J. V. Sengers: That was one of the reasons why I made the statement that any anomaly in the viscosity is absent at temperatures more than 1 percent away from the critical temperature. At present I would rather leave open the question of the behavior of the viscosity closer to the critical point.

J. S. Rowlinson: I would like to raise the question whether the C_r of a binary mixture has an anomaly near the critical mixing point. There is certainly an anomaly in C_p , but as far as I know there is no anomaly in C_r in this case.

J. V. Sengers: I don't know. I looked for experimental data for C_r near the critical mixing point of binary mixtures in the literature, but I did not find any.

C. J. Pings: Dr. Sengers, did you not also run your experiments with two different distances between the plates? You seem to get the same results which proves the absence of an effect from convection.

J. V. Sengers: At the isotherms close to the critical temperature (31.2, 32.1, 34.8 °C) measurements were taken using only one plate distance, because it is difficult to do those measurements with a larger plate distance. However, the anomalous behavior is already present at higher temperatures where measurements with two different plate distances were indeed carried out, which give an additional proof of the reality of the anomaly.

M. S. Green: I want to point out that the difference in behavior between viscosity and thermal conductivity is theoretically very surprising. Both the viscosity and the thermal conductivity can be expressed as the time average correlation of relevant fluxes. As the flux for the thermal conductivity and the flux for the viscosity have a similar form, it is hard to imagine why there would be any difference in behavior.

R. Zwanzig: If you analyze these correlation function formulas for fluids which have internal degrees of freedom interacting weakly with the translational degrees, it turns out that the shear viscosity does not show any particular effect from the internal degrees of freedom. On the other hand the thermal conductivity shows some effect and the bulk viscosity even a bigger effect [2]. Thus there exists a counter example to Dr. Green's suggestion that the correlation function formulas should show roughly the same behavior.

E. Helfand: I think the anomaly in the thermal conductivity arises from the thermodynamic force involved. Any molecular model would speak in terms of energy transport. However, the thermal conductivity is related to a temperature gradient. Therefore to go from the energy gradient to the temperature gradient one has to introduce the specific heat. This is similar to the case of the diffusion coefficient where one has to transform a gradient of the chemical potential into a concentration gradient. For this reason a connection between the anomaly in the thermal conductivity and in the C_r is not surprising.

R. Zwanzig: I would suggest to the experimentalists to study the dependence of the friction on the frequency with the oscillating disk viscometer as well as observing slow oscillations. If there were nonlocal effects involving a penetration length and a correlation length, one would perhaps be able to see from the frequency dependence of the friction whether any peculiar behavior would occur.

J. Kestin: One can regard all these experiments as having been performed at zero frequency. When one wants to go to higher frequencies, one must consider the possibility that hydrodynamic instabilities will be encountered.

As Dr. Sengers pointed out, I think one should measure the two quantities: density and viscosity or density and thermal conductivity, simultaneously. This does not seem to be impossible.

N. J. Trappeniers presented experimental data for the spin-lattice relaxation time of deuterated methanes [3].

N. J. Trappeniers: We have also made diffusion measurements in the critical region, but I did not present those, because one has to be extremely careful to find the density. I think that one cannot say much, if one does not have accurate density measurements. In the critical region the density varies extremely rapidly. Therefore I would like to ask Dr. Bloom the following: You make your measurements of the diffusion coefficients with an accuracy of about 5 percent in the critical region. If you would make an error in density of 5 percent or even 10 percent, which is easily made if one does not have accurate P - V - T data, would it not be possible to accumulate the errors by plotting the product $D\rho$ so that the scattering in your points thus obtained would explain the anomaly which you think to detect in the critical region?

M. Bloom: I agree with you that it is dangerous. We have made density measurements in three different samples (these were the impure samples) and I showed the ratio ρ_l/ρ_v of the liquid and gas densities. These were obtained by making measurements at the top end of the tube and at the bottom end of the tube, while the density gradient was in the middle of the tube. We measured the ratio ρ_l/ρ_v to within 2 percent. The diffusion coefficient was measured within approximately 2 percent. An error of 5 percent has been assigned to D to take into account systematic errors and that is a conservative estimate. The anomalous decrease in $D\rho$ which we observed is about 20 percent. But I agree with you that it is dangerous. I think one should do measurements with a flat horizontal sample to eliminate gravitational effects.

C. J. Pings presented experimental data for the sound absorption in the nitrobenzene-iso-octane system [4].