Behavior of Viscosity and Thermal Conductivity of Fluids Near the Critical Point

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1. Introduction

This paper reviews the experimental information on the behavior of the viscosity and thermal conductivity of fluids near the critical point. Section 2 presents some general remarks on experimental complications associated with the measurement of these properties in the critical region. Experimental work on the viscosity of one component fluids near the liquid-vapor critical point is reviewed in section 3. The thermal conductivity of one component fluids is considered in section 4. The behavior of the viscosity and thermal conductivity in binary liquid mixtures near the critical mixing point is discussed in sections 5 and 6, respectively. Section 7 is a summary of conclusions based on these experimental results.

2. Some General Remarks

In addition to the usual difficulties associated with experiments in the critical region, measurements of the transport coefficients are hampered by the fact that they are nonequilibrium quantities. Most accurate measurements have been carried out by introducing macroscopic gradients into the system. In order to obtain the transport coefficients, the hydrodynamic equations must be solved under certain imposed boundary conditions. Exact solutions of these equations are known only for fluids with constant properties in idealized geometrical situations. However, in the critical region a number of physical properties like local density and specific heat vary appreciably with position as a result of the gradients. This complicates the analysis considerably. Close to the critical point even the validity of the Navier-Stokes equations [41] and of the linear laws has been questioned [38, 42, 59].

If in a fluid near the liquid-vapor critical point the temperature is not uniform, gravity can easily generate convection currents and convective heat flow which must be distinguished from the irreversible fluxes associated with the thermodynamic forces by the linear laws. This is the most serious difficulty encountered in measuring the thermal conductivity and will be further discussed in section 4. As is well known, equilibrium or a steady state is approached very slowly by a physical system near a critical point. Consequently, some authors have observed hysteresis effects in their experimental observations of the viscosity [2, 6, 50].

A prerequisite for the study of the behavior of any physical property in the critical region is a knowledge of the values of the appropriate thermodynamic variables at which the property is measured. Near the liquid-vapor critical point the temperature and density and near the critical mixing point of a binary liquid mixture the temperature and concentration should be known. If a P-V-T relationship is known, one can calculate the density from the measured pressure and temperature. Close to the critical point, where the isotherms become very flat, this procedure becomes inaccurate. This inaccuracy is greatly increased by uncertainties in the absolute value of the temperatures at which either the transport coefficients or the isotherm data were measured. Uncertainties in the temperature also hamper a comparison with other properties near the critical point. Such a comparison for a binary liquid mixture is complicated by the fact that the critical parameters are very sensitive to impurities.

If one measures the transport coefficients as a function of pressure and temperature, care should be taken to work at small enough pressure and temperature intervals as otherwise the whole critical region is easily overlooked. In experimental work on transport coefficients this has led to considerable confusion, which will be discussed further in section 4 in connection with thermal conductivity measurements. It is equally important for the study of any other property near the liquid-vapor critical point.

Another procedure consists in following an isochoric method where the temperature is varied...
while the total amount of gas is kept constant. However, this method also has its pitfalls. First, if one lowers the temperature at constant density, phase transition occurs at a certain temperature which is equal to the critical temperature at the critical density. Below this transition temperature one measures either in the vapor or in the liquid, depending on the experimental arrangement. As a consequence the density, at which the properties under consideration actually are measured, does change rapidly as a function of temperature, although the density averaged over vapor and liquid phase is kept constant. The temperature at which this transition occurs should be determined accurately. Moreover, even above this temperature a large density gradient is developed close to the critical temperature so that the local density at a certain position in the vessel is still not independent of the temperature. Ultimately, close to the liquid-vapor critical point a knowledge of the local value of the density is required.

The influence of critical phenomena is not restricted to the immediate vicinity of the critical point. For instance, an anomaly in the specific heat can be detected at temperatures considerably higher than the critical temperature. In this paper the qualitative properties of viscosity and thermal conductivity regarding the existence of similar anomalies in the critical region will be discussed. However, the precise mathematical character of such anomalies can only be obtained from measurements very close to the critical point. In view of the difficulties mentioned above an analysis of the latter kind is not yet possible for the transport coefficients.

3. The Viscosity of a One Component Fluid Near the Liquid-Vapor Critical Point

Accurate measurements of the viscosity of compressed gases have been mainly carried out either by a transpiration method or by the oscillating disk method. In the first method the gas is caused to flow through a capillary and the viscosity is obtained from the flow rate. In the latter method the damping of an oscillating disk due to the viscosity of the surrounding medium is determined. Both methods have been used to measure the viscosity at the critical region. Close to the critical point the oscillating disk method has the advantage that it allows the measurement of the viscosity at a certain horizontal level in the fluid and consequently, in principle, at a certain local density. In the capillary flow method the density varies along the capillary.

An example of the "normal" behavior of the viscosity outside the critical region is shown in figure 1; the viscosity coefficient of argon [3, 7] at three temperatures, high relative to the critical temperature \( T_c = 122.3^\circ C \), as a function of density. One amagat unit of density is the density at 0 °C and 1 atm. At a given temperature the viscosity coefficient increases monotonically with the density; \( \eta (\rho) \) and \( \eta (\rho) \) are both positive. The temperature-derivative \( \eta (\rho) / \eta (\rho) T \) is positive up to a density well beyond the critical. At very high densities \( \eta (\rho)/\eta (\rho) \) becomes negative [3, 8]. But this is not relevant for our present discussion. Sometimes the excess viscosity \( \eta - \eta_0 \), where \( \eta_0 \) is the viscosity coefficient in the dilute state at the given temperature, is considered to be only a function of the density. This is, however, not true in general. Most measurements of the viscosity and thermal conductivity in the critical region have been carried out for carbon dioxide because of its easily accessible critical temperature. The discussion will therefore be mainly based on the phenomena observed for CO₂.

The experimental investigation of the viscosity of CO₂ in the supercritical region started with the work of WARBURG and von BABO in 1902 using a capillary flow method [15]. Even that early these authors were aware that knowledge of the density is essential and were careful to determine the density as well as pressure and temperature. They realized that the pressure difference along the capillary should be kept small and applied corrections for the variation of the density along the capillary. In an illuminating discussion of this experimental work M. BRILLOUIN [1] remarked that these corrections are practically canceled by the variation of the viscosity associated with the variation of the density.

The data of Warburg and von Babo at 32.6 °C are shown in figure 2. They also measured viscosities isotherms at 35.0 and 40 °C which have not been included in figure 2 since the temperature effect turned out to be small. Since the viscosity isotherms at 35 and 40 °C are nearly parallel to the one at 32.6 °C, the authors conclude that any anomalous increase of the same order of magnitude as that observed at critical point is not justified.

A pronounced anomalous increase in a wider temperature range and with the viscosity increased by a factor 2 at 31.1 °C was reported by MICHELS, BOTZEN, and SCHERMAN [8]. Their data were obtained with a capillary flow method which was known to be accurate outside the critical region. As pointed out by the authors, the method is not reliable in the critical region due to the large density gradient in the capillary resulting from the use of a pressure difference of about 0.5 atm. Nevertheless, they conjectured that the anomalous behavior observed was essentially real [8, 9].

In order to resolve the discrepancy between these results, new measurements of the viscosity of CO₂ were carried out by KESTIN, WHITEAL, and ZIEN using an oscillating disk method [9]. They approached the critical region using different isochores as did Naldrett and Maass. Their results show convincingly that any anomalous increase is much smaller than that reported by Michels et al. Close to the critical point they find an anomalous increase of the same order of magnitude as that

\[ \eta (\rho) \text{amagat} = \frac{\eta_0}{\left(1 + \frac{a T_c}{T - T_c} \right)^3} \]

where \( \eta_0 \) is the viscosity coefficient in the dilute state at the given temperature, \( T_c \) is the critical temperature, and \( a \) is a constant.

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reported by Naldrett and Maass. The data obtained by Kestin et al., at 31.1 °C and at 34.1 °C are shown in figure 3a, b as a function of density. For comparison the behavior of the viscosity iso-
temperature 33,000 K is indicated and data obtained by
Naldrett and Maass and a few data of Michels et al., outside the critical region are included in the figure.
Recently the viscosity of CO₂ with the oscillating disk method [6, 10] has been measured by BARUA and ROSS with a capillary flow method [12]. By using a horizontal capillary and extrapolating to zero flow rate [4], they were able to avoid the difficulties inherent in the viscometer of Michels et al. The analysis of their experimental data has not yet been completed, yet it seems that their results are in agreement with those of Kestin et al.

Close to the critical temperature they find an increase of 1 to 2 percent on one isotherm, which is of the order of the measuring accuracy in this difficult region. As shown in the experimental work described, we can draw the following two conclusions.

1. Measurements of the viscosity of CO₂ with the oscillating disk method [12, 15] have shown that the viscosity coefficient does not show any anomalous behavior at supercritical temperatures down to a temperature (T - Tc) / Tc = -1 percent from the critical.

2. The significance for the small anomalous increase at temperatures close to the critical is not clear at present. A correction should be subtracted from the data of Naldrett and Maass in this region, which is in the opposite direction to that to be applied to the data of Naldrett and Maass and therefore tends to enlarge the anomalous effect. The authors point out that the difference in the behavior of density obtained by the different apparatus is less reliable in this difficult region, because their oscillating disk is located at a position somewhat higher than the center, the variation of density leads to a correction in the opposite direction to that to be applied to the data of Naldrett and Maass.

Two methods for the measurement of the thermal conductivity of compressed gases have had widespread acceptance, the concentric cylinder and the parallel plate method. In the former the fluid is enclosed between two coaxial cylinders, either in horizontal or in vertical position, and the heat flowing through the gas layer is determined as a function of the temperature difference between the cylinders. In the latter method the fluid is contained between two horizontal plates and the heat flowing from the upper plate to the lower plate is determined as a function of the temperature difference. A special case of the concentric cylinder method is the hot-wire method. This method is not suitable for the critical region because the convective flow analysis is complicated, too large temperature differences are usually involved and, most importantly, corrections cannot be avoided.

Another procedure sometimes used to obtain a thermal conductivity value associated with the critical point is based on the assumption that the excess thermal conductivity is a function of the temperature difference. Indeed, the data on this isotherm do not show any appreciable anomaly near the critical density. However, the conclusion is based only on a few experimental points for which calculations of the density from the P-V-T data are difficult. An analysis of the viscosity data on adjacent isotherms shows that the precision is only a few percent. Therefore, no decisive conclusion can be drawn from this work regarding the existence of a small anomaly.

4. The Thermal Conductivity of a One Component Fluid Near the Liquid-Vapor Critical Point

Outside the critical region the behavior of the thermal conductivity is very similar to that of the viscosity described in the previous section. However, there exists a serious controversy in the literature whether the thermal conductivity exhibits a pronounced anomaly in the critical region. An introductory survey has already been presented by Zirkland [17].

The thermal conductivity is sometimes studied either as a function of pressure at constant temperature or as a function of temperature at constant pressure, without considering the dependence on the density. The region around the critical density is restricted to very narrow pressure and temperature intervals in this procedure, because both the viscosity and the density are determined simultaneously and the effect of a variable density on the interpretation of the viscosity measurements is carefully analyzed.

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Additional data on the thermal conductivity of a one-component fluid near the liquid-vapor critical point are required, because the critical region is complicated, too large temperature differences are usually involved and, most importantly, corrections cannot be avoided.
Papers reporting an anomalous increase of the thermal conductivity in the critical region are generally considered with much skepticism due to the high probability of convection. An exact theoretical analysis of convection is very complicated and has been carried out only in very special cases. We do not go into the details here, but remark that the presence of convection can be detected by varying the thickness of the gas layer or the temperature difference across this layer. The heat transfer coefficient or so-called apparent thermal conductivity coefficient, which includes a contribution from convection, depends on the geometry of the apparatus and of the boundary conditions involved.

Heat transferred by convection is usually related to the Rayleigh number \( R \) defined as

\[
R = \frac{g \mu \rho \Delta T \Delta \rho}{\kappa \eta d}
\]

where \( g \) is the gravitation constant, \( \mu \) the expansion coefficient, \( \rho \) the density, \( \kappa \) the specific heat at constant pressure, \( d \) the thickness of the gas layer, \( \Delta T \) the temperature difference, \( \Delta \rho \) the thermal conductivity and \( \eta \) the viscosity coefficient. In the critical region the Rayleigh number becomes extremely large [26, 30]. By the use of many approximations and assuming that the convection is small, the error introduced by convection can be derived explicitly:

\[
\lambda' - \lambda = CR \frac{d}{\sin \epsilon}
\]

where \( \lambda' \) is the apparent thermal conductivity coefficient as measured, \( \lambda \) the length of the gas layer, \( \epsilon \) the angle between the temperature gradient and the vertical, and \( C \) a proportionality constant. In order to obtain (2) one neglects the variation with temperature of the fluid properties other than the density, linearizes the hydrodynamic equations, assumes a spatially uniform temperature gradient and considers the limiting solution for \( d/T \rightarrow 1 \).

Without these approximations the error may well depend on \( d \) and \( \Delta T \) in a more complicated way. The absence of convection is verified, nevertheless, if the measured thermal conductivity coefficient at a given density and temperature does not change under sufficient variation of \( \Delta T \) or \( d \).

If convection is present, one sometimes tries to obtain the correct value of \( \lambda \) by extrapolating to \( \Delta T = 0 \) from the experimental data obtained for \( \Delta T \) using various values of \( \Delta T \). In the critical region the contribution of convection becomes very large and such an extrapolation can diminish the accuracy considerably even when care is taken that only values for \( \lambda' \) corresponding to the same average density and average temperature are used. In some cases, such as a horizontal fluid layer heated from below, convection only seems to start if the Rayleigh number becomes larger than a certain critical value [64]. This has also been reported for a concentric cylindrical layer in horizontal position [23, 58]. When this instability occurs, extrapolation to \( \Delta T = 0 \) is not legitimate and can lead to overcorrections.

The controversy over the existence of a thermal conductivity anomaly started in 1934. KARDOŠ attempted to measure the thermal conductivity of \( CO_2 \) using a hot wire method [21]. He found a tremendous increase of heat transfer in the critical region, which was later recognized as an effect of convection [28]. SELLSCHOPP measured the thermal conductivity of \( CO_2 \) with two concentric cylinders in horizontal position [29]. He observed an increase in the apparent thermal conductivity near the critical density at supercritical temperatures, but his measurements were also influenced by convection. The whole effect was attributed to convection and it was assumed, without experimental justification however, that in the critical region the thermal conductivity was only dependent on the density and not on the temperature [18, 29].

TIMROD and OSKOLKOV [33] reported that the thermal conductivity of \( CO_2 \) did not show any anomaly in the supercritical region, but their measurements obtained with a hot wire method were actually carried out too far away from the critical point.

COMINGS et al., measured the thermal conductivity of several gases using two concentric cylinders in horizontal position. Anomalies in the supercritical region were reported for ethane, propane, and butane [22] but the reality of the effect could not be established again due to the possibility of convection. An anomalous increase of the thermal conductivity of argon at 0 °C, originally reported by the present author among others, later turned out to be entirely caused by convection [24].

The first critical study of the existence of a thermal conductivity anomaly was carried out by GUILDNER [19]. He measured the thermal conductivity of \( CO_2 \) using a vertical cylindrical gas layer with a thickness of 0.68 mm. Convection could not be avoided in this apparatus so that \( \lambda \) was determined from measurements at various temperature differences by extrapolation to \( \Delta T = 0 \) at constant average temperature. He concluded that the thermal conductivity itself exhibits a pronounced anomaly. This anomaly increase is already 30 percent at 40 °C at the critical density. He approached the critical temperature to within 1 °C. Although at 75 and 40 °C the influence of convection was small, closer to the critical temperature the influence of convection became large diminishing the accuracy of the data.

On the other hand, VARGAFTIK stated that the thermal conductivity did not exhibit an anomaly in the critical region [34]. This assertion was based on experimental work of SHINGAREV, which unfortunately, has not been made available and therefore cannot be critically examined. According to the discussion given by Vargaftik, these conclusions were drawn after applying corrections for convection by extrapolation to zero temperature difference. It is clear that measurements in the critical region free of convection are highly desirable. For this purpose a detailed study of the thermal conductivity of \( CO_2 \) was carried out by MICHELS, SENGERS, and VAN DER GULIK using a parallel plate method [25, 26, 30]. Contrary to the concentric cylinder method the horizontal flat layer method has the advantage that the angle between temperature gradient and the vertical can be made very small to suppress convection. The experimental results obtained for the thermal conductivity as a function of density are presented in figure 4. The thermal conductivity shows indeed a pronounced anomaly at the critical point. An anomalous increase can be detected as much as 20 °C above the critical temperature which becomes 250 percent at 1 °C above the critical temperature. Convection was avoided by the use of a small distance between the plates (\( d=0.4 \) mm) and small temperature differences \( \Delta T \) varied from 0.03 to 0.25 °C. The absence of convection was verified experimentally; in the whole critical region the thermal conductivity values measured were independent of the temperature difference used. Of course, one should compare measurements with different \( \Delta T \), but at the same average density and temperature. For the details we refer to the previous publication. The reality of the anomaly was independently confirmed by a few measurements with a larger plate distance. An attempt was made to include a measurement of the thermal conductivity isotherm at 31.2 °C using even smaller temperature differences. These results are shown in figure 5. Obviously the values at this temperature are less...
accurate than those of figure 4, since the experimental verification of the density becomes more difficult due to the inaccuracy in the density.

Due to the variation of temperature, the density variation in the pressure vessel is very complicated. It is therefore difficult to approach the critical region by the isochoric method. The densities must be calculated from the experimentally measured pressure and temperature, which may introduce systematic errors at each isotherm. Thus the detailed behavior along the critical isochore particularly the character of the divergence of the thermal conductivity, cannot accurately be deduced from the data. It is notable that at 75 and 40 °C, where the amount of convection in the apparatus of Guildner was reasonably small, there is a satisfactory agreement with the data of Guildner, confirming the anomaly of 30 percent at 40 °C. It turned out, however, that closer to the critical temperature the anomalous increase is considerably smaller than that reported by Guildner.

The fact that the thermal conductivity measured in the temperature difference used not only guarantees the absence of convection, but also verifies the validity of the law of Fourier in the temperature range considered. The validity of the law of Fourier in the critical region was questioned by Simon and Eckert [32]. From interferometric studies of laminar free convection near a vertical wall a quantity k was derived, which they identified with the thermal conductivity. Consequently, the measurements were not carried out near the critical densities. The interpretation of Abas-Zade that he followed the coexistence line up to the critical temperature is erroneous.

Very careful thermal conductivity measurements were carried out by Amirkhanov and Adamos using both a horizontal parallel plate method and a vertical concentric cylinder method [17]. Using the parallel plate apparatus, a series of measurements was carried out with plate distances of 0.5 mm and 0.07 mm, and the temperature difference was varied from 0.07 to 1 °C. With the smaller plate distance the data turned out to be independent of ΔT, which guarantees absence of convection. Data obtained with the larger plate distance and also those obtained using the concentric cylinder apparatus were dependent on ΔT showing the presence of convection. The results obtained with the smallest value of ΔT agreed for all 3 series of measurements. The values obtained for the thermal conductivity therefore seem to be very reliable. As has been pointed out repeatedly before, it is equally important to verify whether the measurements were carried out sufficiently close to the critical density. Unfortunately, the authors do not describe their experimental procedure. They do not report whether or how either pressure or density was determined. In addition, although they measure the temperature difference ΔT carefully, no device was presented for measuring the absolute average temperature of the gas layer, which obviously differs from the temperature of the surrounding thermostat. It is not clear at which temperatures and densities the thermal conductivity actually was determined. If the measurements were carried out at the coexistence line, one would expect a large variation of the density when the temperature difference was varied from 0.1 to 1.0 °C, at the liquid side even leading to evaporation of the liquid. On the contrary, their results indicate that even up to a few hundredths of a degree below the critical temperature the density did not change when ΔT was varied from 0.1 to 1 °C. Thus it seems that the measurements were not carried out near the critical density.

From the data given in figure 4 it is evident that the first indication of the existence of the thermal conductivity anomaly can be noticed from the occurrence of intersections of the thermal conductivities as a function of density at temperatures considerably higher than the critical temperature. It is interesting therefore to study as a function of density data given in the literature somewhat remote from the critical point. As an example, we considered the experimental data obtained by Ziebland and Burton [35] for the λ of nitrogen. These data were obtained using an apparatus consisting of two concentric cylinders with a gap of 0.2 mm. The results obtained at two supercritical temperatures are shown as a function of density in figure 7. An anomalous increase can be noticed near the critical density even at 157.1 °C. The absence of convection was verified by measurements with different values of ΔT. At 138.8 °C the thermal conductivity goes through a maximum. The densities were estimated by Needham and Ziebland from P-V-T data published in the literature. However, at 138.8 °C these P-V-T data are virtually unknown, so that the densities cannot be calculated with sufficient accuracy to conclude that the maximum does not occur at the critical density.

We conclude that the existence of a pronounced anomaly in the thermal conductivity has been verified by convection free measurements obtained both with a parallel plate method and with a concentric cylinder method.
An interesting question is whether the anomaly in the thermal conductivity is related to that in the specific heat. For this reason the variation of $\lambda$ of CO$_2$ as a function of temperature at the critical isochore is compared with the variation of $c_p$ and $c_v$ in Table 1. For $c_p$ the experimental data [62] are supplemented with values calculated from the $P-T$ data at temperatures where no experimental data for $c_v$ are available [63]. The values for $c_v$ are obtained by adding the calculated difference $c_p-c_v$ to the values for $c_v$ obtained as mentioned above. It is evident that $c_v$ increases much faster in the critical region than $\lambda$, so that the ratio $\lambda/c_v$ decreases by two orders of magnitude when the temperature is varied from 75 to 31.2°C. On the other hand the variation of $\lambda/c_v$ is an order of magnitude smaller than that of $\lambda$ itself. Very close to the critical point $c_v$ as well as $\lambda$ is not accurately known. A relationship between the anomaly in $\lambda$ and $c_v$ is well possible. In view of the recent work on the $c_v$ anomaly, it is natural to ask whether $\lambda$ diverges logarithmically. Such questions about the detailed behavior cannot be decided at present and further experimental research is required.

According to the classical theory the line width of the central component of the spectrum of the scattered light is determined by the thermal diffusivity $\lambda/c_v$. The line width to be expected for CO$_2$ from the static measurements of $\lambda$ is presented in Figure 8 for $k=10^9$ cm$^{-1}$, which corresponds to light from a He-Ne laser scattered through an angle of 60°. Because $c_v$ diverges much faster than $\lambda$, the thermal diffusivity [31] and consequently the line width of the central component decreases rapidly in the critical region.

### Table 1. Comparison of the thermal conductivity with the specific heat along the critical isochore of CO$_2$ ($\rho = 236$ amagat)

<table>
<thead>
<tr>
<th>$t$ (°C)</th>
<th>$\lambda/c_v$ (10$^{-7}$ cm$^2$/s)</th>
<th>$\lambda/c_p$ (10$^{-7}$ cm$^2$/s)</th>
<th>$\lambda/c_p$ (10$^{-7}$ cm$^2$/s)</th>
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<td>1.0</td>
<td>1.0</td>
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<td>1.1</td>
<td>1.0</td>
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<td>1.3</td>
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<td>2.5</td>
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<tr>
<td>31.2</td>
<td>6.1</td>
<td>1.6</td>
<td>0.02</td>
</tr>
</tbody>
</table>

### 5. The Viscosity of a Binary Liquid Mixture Near the Critical Mixing Point

Many binary liquid mixtures exhibit a critical mixing point near room temperature. The viscosity of a number of different mixtures of this type has been studied. There are not enough data obtained by different authors for the same substance. Moreover, the critical parameters are very sensitive to the purity of the components. Although some attention has been given to the influence of a third component on the viscosity in the critical mixing region [43, 47, 50, 51, 53], the influence of any impurity on this anomaly is not clear. It seems that the effect depends on the binary system as well as on the character of the impurity.

Most viscosity measurements for binary liquid mixtures have been carried out with some version of the capillary flow method. We have not made a critical analysis of the experimental procedures used by the various authors. However, there is sufficient agreement to establish the existence of an anomaly in the viscosity near the critical mixing point for systems with either an upper or lower critical solution point [39, 40, 43–53].

In the beginning of the century, an anomalous increase of the viscosity near the critical mixing point was reported by various authors, among others by FRIEDLANDER [43] for the systems isobutyl alcohol-water; by SCARPA [48] for phenoxy alcohol-water, by DRAPIER [40] for nitrobenzene-ethylene; and by TSAKALOTOS [52] for isophoronic acid-water, trimethylene-tetramine-water, and nicotine-water.

For simple binary liquid mixtures the anomalous increase of the viscosity is of the order of 15 to 25 percent at the critical mixing point. REED and TAYLOR observed an anomalous increase in the viscosity of the systems isooctane-perfluorocyclohexane, n-hexane-perfluorocyclohexane, isooctane-perfluorohexane [46]. The effect was most pronounced in the mixture isooctane-perfluorooctane; their results for this system are shown in Figure 9. The viscosity exhibits an anomalous increase up to 25 percent. According to these data the anomalous behavior can be detected as far away as 10°C from the critical temperature. However, other authors found that for some systems the anomaly occurs only at temperatures much closer to the critical.

Figure 9. The viscosity of the mixture isooctane-perfluorocyclohexane as a function of concentration according to Reed and Taylor [46].

SEMEMOCHenko and ZORINA investigated the viscosity of the systems triethylamine-water and nitrobenzene-hexane [49]. The first mixture has a lower critical mixing temperature. For both systems an anomalous increase of the viscosity up to 20 percent was found. The anomalous phenomenon only occurred at temperatures within 1.0 or 1.5°C from the critical and in a concentration range of 10 mole percent.

Recent measurements of the viscosity of the nitrobenzene-isooctane mixture obtained by PINGS et al., confirmed that for this system also a viscosity anomaly occurs in a very small temperature range [45]. No anomaly could be detected at 4.5°C above the critical temperature, but an anomalous increase of 3 to 7 percent was noticed at 0.45°C above the critical temperature.

We conclude that the viscosity does show an anomalous increase near the critical mixing point, but for a number of simple mixtures the anomalous behavior occurs only at temperatures within 2°C of the critical temperature.

### 6. Thermal Conductivity of a Binary Liquid Mixture Near the Critical Mixing Point

Experimental investigations of the thermal conductivity of binary liquid mixtures near the critical
The most extensive study was carried out by GERTS and FILIPPOV, who measured the thermal conductivityApparatus [54]. Measurements of the thermal conductivity of the system nitrobenzene-n-hexane near the hot wire apparatus [54]. Measurements of the thermal conductivity of the system nitrobenzene-n-heptane, methanol-n-hexane and triethylamine-water were investigated. The results obtained by Gerts and Filippos for the nitrobenzene-n-hexane mixture are shown in figure 10 and those for the nitrobenzene-n-heptane system in figure 11. It is evident that, contrary to the behavior near the liquid-vapor critical point, the thermal conductivity of these binary liquid mixtures shows an anomaly near the critical mixing point. Similar results were obtained for the other two systems mentioned. An anomaly even as small as that found for the viscosity of binary mixtures seems to be absent. The data were not obtained at enough different concentrations to study the behavior in detail and the results cannot be plotted as a function of concentration as was done for the viscosity in figure 9. The absence of a pronounced anomaly near the critical mixing point seems to be established. This difference between the behavior of the thermal conductivity near the liquid-vapor critical point and that near the critical mixing point was noticed before by SKIRPOV [56]. Additional experimental data are highly desirable to verify this conclusion and to study smaller details.

On the other hand an anomalous increase of the thermal conductivity near the liquid-vapor critical point if the temperature is not within 

1.01, 0.01,

1.11. It is found to be independent of this temperature difference. In addition the systems nitrobenzene-n-heptane, methanol-n-hexane and triethylamine-water were investigated. The results obtained by Gerts and Filippos (ammonia shown in figure 7. The author also acknowledges the stimulating interest of several colleagues at the National Bureau of Standards and in particular that of Dr. M. S. Green.

7. Summary

The experimental information on the viscosity and thermal conductivity in the critical region can be summarized as follows:

1. Measurements of the viscosity with the oscillating disk method as well as with the capillary flow method have shown that the viscosity does not show any anomaly near the liquid-vapor critical point if the temperature is not within 

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1.11. It is found to be independent of this temperature difference. Additional experimental information on the systems nitrobenzene-n-heptane, methanol-n-hexane and triethylamine-water were investigated. The results obtained by Gerts and Filippos (ammonia shown in figure 7. The author also acknowledges the stimulating interest of several colleagues at the National Bureau of Standards and in particular that of Dr. M. S. Green.

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1. Measurements of the viscosity with the oscillating disk method as well as with the capillary flow method have shown that the viscosity does not show any anomaly near the liquid-vapor critical point if the temperature is not within 

1.01, 0.01,

1.11. It is found to be independent of this temperature difference. Additional experimental information on the systems nitrobenzene-n-heptane, methanol-n-hexane and triethylamine-water were investigated. The results obtained by Gerts and Filippos (ammonia shown in figure 7. The author also acknowledges the stimulating interest of several colleagues at the National Bureau of Standards and in particular that of Dr. M. S. Green.
Viscosity of Binary Liquid Mixtures


Miscellaneous


over the entire volume of the sample. i and k are unit vectors in the x- and z-directions respectively.

The spin system is assumed to be in equilibrium before the first of the two r-f pulses applied at times $t = 0$ and $t = T$, respectively. Assume that the r-f pulses are sufficiently intense and that their frequency is sufficiently close to the Larmor frequency $\omega_0 = \gamma B_0$, where $\gamma$ is the nuclear gyromagnetic ratio, that the lengths of the pulses can be chosen such that the z-component of magnetization is rotated by an angle $\frac{\pi}{2}$ by each of the pulses. Then, if the z-component of the nuclear magnetization relaxes towards its equilibrium value exponentially with a time constant $T_1$, the maximum amplitudes of the detected nuclear induction signals $A(0)$ and $A(\tau)$ following the pulses are related by [1]

$$A(0) - A(\tau) = \exp\left[-\frac{\tau}{T_1}\right].$$

If the $x$ and $y$ components of the nuclear magnetization relax towards their equilibrium value zero exponentially with a common time constant $T_2$ and if the spatial motion of the spins in the sample is adequately described by the solution to the diffusion equation, the maximum amplitude of the "spin-echo" at time $2\tau$ is given by [2]

$$A(2\tau) = \exp\left[-\frac{2\tau}{T_2} - \frac{9}{8}\gamma^3 QD\tau^2\right].$$

(5)

(6)

Note that the typical values of $Q$ are of the order of $10^{-3}$ which is an extremely low frequency insofar as the dynamical motions of fluids are concerned. The other important point to notice about eq. (6) is that $I(\omega)$ gets its major contribution from pairs of molecules which are very close together, because of the $r^{-6}$ dependence of the dipole-dipole interaction.

Physically, one can say that $I(\omega)$ gives a measure of a specific type of inelastic scattering cross section corresponding to collisions between pairs of molecules in which the total nuclear Zeeman energy is changed. The low frequency $\omega_0$ corresponds to the fact that the energy exchanged between the spin system and the translational degrees of freedom is very small ($<10^{-1}eV$).

There are no detailed molecular theories for $I(\omega)$ in dense liquids except for liquid $H_2$ [9], and this has inhibited the interpretation of the many $T_1$ measurements already performed on liquids.