International Journal of Thermophysics, Vol. 6, No. 3, 1985

Transport Properties of Fluids Near Critical Points[1]

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Received February 20, 1985

The paper reviews the theoretical and experimental results for the asymptotic behavior of the dynamics of critical fluctuations in fluids and fluid mixtures near a critical point. The implications of these results for the development of accurate representative equations for the viscosity and thermal conductivity of gases in the critical region are discussed.

KEY WORDS: critical fluctuations; critical phenomena; diffusion; light scattering; mode-coupling theory; thermal conductivity; viscosity.

1. INTRODUCTION

Near a critical point a fluid exhibits large fluctuations of the order parameter associated with the critical-point phase transition. For gases near the vapor–liquid critical point the order parameter is the density ρ, and for liquid mixtures near the critical mixing point the order parameter is the concentration c. The range of the fluctuations can be characterized by a correlation length ξ. When the critical temperature T_c is approached in the one-phase region at the critical density or at the critical concentration, this correlation length diverges as [1]

$$\xi = \xi_0 |\Delta T^*|^{-\nu} \tag{1}$$

where $\Delta T^* = (T - T_c)/T_c$, ξ_0 is a system-dependent amplitude, and $\nu = 0.63$ is a universal exponent.

The fundamental dynamic phenomenon near the critical point is that the order-parameter fluctuations decay slowly in time. Specifically, the dif-

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[1] Invited lecture presented at the 10th International Conference on the Properties of Steam, Moscow, USSR, September 2–7, 1984.

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fusion coefficient associated with the decay of these fluctuations tends to zero at the critical point in the hydrodynamic limit, i.e., in the limit of zero wave number q and zero frequency ω. The classical methods of measuring the response of a system as a result of an imposed gradient become inaccurate near the critical point, since the state of the system becomes very sensitive to an imposed field. However, the time dependence of the order-parameter fluctuations in a system in equilibrium can be investigated accurately with light-scattering techniques [2]. Such measurements probe these fluctuations at a wave number $q = 2q_0 \sin(\theta/2)$, where q_0 is the wave number of the incident light and θ is the scattering angle. Measurements of the intensity of the scattered light as a function of the scattering angle yield the correlation length ξ, and from measurements of the time dependence of the scattered light one can deduce the diffusion coefficient associated with the critical fluctuations [3–5].

Some of the most accurate results have been obtained for binary liquids near the critical point. The primary limitation of light-scattering measurements is the appearance of multiple scattering close to the critical point. In our laboratory we have made extensive experimental studies for the mixture 3-methylpentane + nitroethane, since in this system multiple scattering appears to be negligibly small up to about a tenth of a millidegree from the critical temperature. The basic phenomenon is illustrated in Fig. 1, where the diffusion coefficient, obtained at three different wave numbers q, is plotted as a function of the temperature [6, 7].

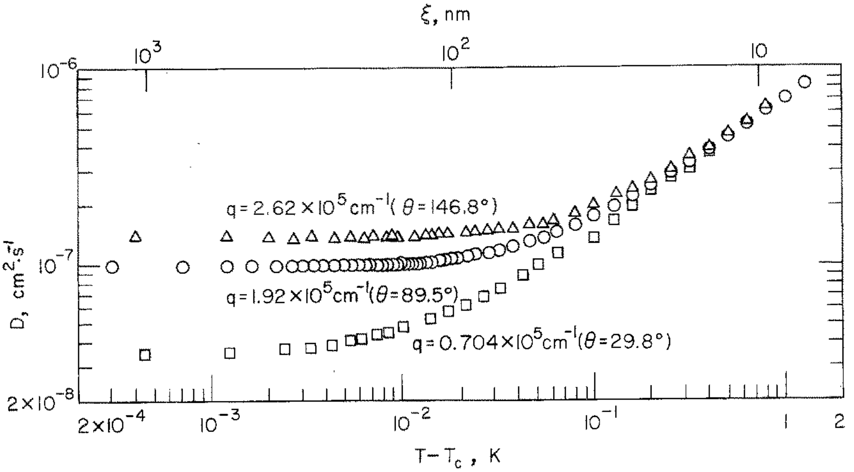

Fig. 1. Diffusion coefficient of a mixture of 3-methylpentane + nitroethane at the critical concentration as a function of $T - T_c$, deduced from light-scattering measurements at three different scattering angles θ [6, 7].

At temperatures away from T_c the correlation length ξ is sufficiently small so that $q\xi \ll 1$ and the diffusion coefficient D at wave number q may be identified with the diffusion coefficient in the hydrodynamic limit $q \to 0$. This hydrodynamic diffusion coefficient decreases upon approach of the critical temperature, indicating the critical slowing down of the fluctuations. At the same time the correlation length ξ increases in accordance with the power law given by Eq. (1), and at temperatures $T - T_c < 0.1°\mathrm{C}$ one reaches a nonlocal critical regime where $q\xi > 1$ and the diffusion coefficient D becomes explicitly dependent on the wave number q.

It is now possible to characterize this behavior quantitatively with considerable accuracy. Near the critical point the diffusion appears to be inversely proportional to the correlation length ξ and the shear viscosity η. Thus in order to assess the status of the subject we shall review the results obtained for both the diffusion coefficient and the viscosity.

2. REVIEW OF THEORETICAL PREDICTIONS

In the theory of critical phenomena systems are classified in terms of universality classes. Systems within the same static universality class have the same critical exponents and the same scaling functions that characterize the asymptotic behavior of the equilibrium properties near the critical point. These universality classes depend on the dimensionality d of the system, the number of components n of the order parameter, and whether the forces between the constituent particles are short-range or long-range. Specifically, gases near the vapor–liquid critical point and fluid mixtures near the critical mixing point all belong to the same static universality class as the three-dimensional Ising model ($d = 3$, $n = 1$). The specification of dynamic universality classes depends on the number of relevant hydrodynamic modes. Since in fluids and fluid mixtures there are two relevant coupled modes, namely, the diffusive decay of the order-parameter fluctuations and that of the transverse momentum fluctuations, all gases near the vapor–liquid critical point and fluid mixtures near the critical mixing point are expected to belong to the same dynamic universality class. As we shall see, there is evidence that fluid mixtures near a tricritical point belong to this same dynamic universality class also.

The decay rate of the order-parameter fluctuations in gases near the vapor–liquid critical point is proportional to the thermal diffusivity $D_T = \lambda/\rho c_p$, where λ is the thermal conductivity and c_p the isobaric specific heat [3, 5]. Universality of critical dynamics implies that the behavior of the thermal diffusivity D_T of gases near the vapor–liquid critical point will be completely analogous to the behavior of the binary diffusion coefficient D of fluid mixtures near the critical mixing point discussed in the previous section. The decay rate of the transverse part of the momentum fluctuations is related to the viscosity, which is predicted to exhibit the same divergent behavior for all these systems.

Two approaches have been developed for the theoretical treatment of dynamic critical phenomena. The first is the mode-coupling theory of critical dynamics; the second is the dynamic renormalization-group theory. The relationship between these theories has been discussed by Hohenberg and Halperin [8] and by Gunton [9]. The predictions of these theories are quite similar. The dynamic renormalization-group theory is suitable for an analysis of the universal aspects of the divergent behavior of the transport properties. The mode-coupling theory yields two coupled integral equations for the diffusion D and the viscosity η which yield a relation between these transport coefficients and other properties of the system.

The diffusion coefficient D can be related to a conductivity L and a response function χ as $D = L/\chi$ [10]. For the binary diffusion coefficient, L is the mass conductivity and $\chi = (\partial c/\partial \mu)_T$ in the limit $q \to 0$; for the thermal diffusivity, L is the thermal conductivity λ and $\chi = \rho c_\mathrm{p}$ in the limit $q \to 0$. In the treatment of dynamic critical phenomena it is customary to separate the transport coefficients L, λ, and η into background contributions $\bar{L}$, $\bar{\lambda}$, and $\bar{\eta}$ and singular contributions ΔL or $\Delta\lambda$ and $\Delta\eta$ [11].

$$L = \Delta L + \bar{L}, \qquad \lambda = \Delta\lambda + \bar{\lambda}, \qquad \eta = \Delta\eta + \bar{\eta} \tag{2}$$

This procedure was originally suggested from an analysis of the experimental data [12] and corresponds to the separation of the transport coefficients into a bare part and a singular part in the mode-coupling theory [13]. The idea is that the bare coefficients are the transport coefficients in the absence of the long-range critical fluctuations. Unfortunately, there does not exist a rigorous procedure for making this separation. In our approach we have identified the background contributions with the values obtained when experimental data outside the critical region are extrapolated into the critical region [14]. This procedure is suitable only if the background contributions are weak functions of temperature, and the question of how to deal with background contributions is still subject to some controversy. In the dynamic-renormalization group theory consideration of background contributions does not appear explicitly, since the theory is designed to isolate the asymptotic behavior only. However, the temperature range where the singular viscosity $\Delta\eta$ is larger than the background viscosity $\bar{\eta}$ is completely inaccessible [15], and in practice one cannot avoid consideration of background contributions in the interpretation of the experimental data.

The dynamic renormalization-group theory predicts that the viscosity η will diverge as [8]

$$\eta \propto \xi^z \tag{3}$$

where z is a universal critical exponent which has the same value for all systems belonging to the same dynamic universality class. This prediction applies to the asymptotic behavior, presumably when $\Delta\eta \gg \bar{\eta}$. On the other hand, the mode-coupling theory enables one to estimate the singular viscosity when $\Delta\eta$ is small, and in first approximation one finds [13, 16]

$$\bar{\eta} + \Delta\eta = \bar{\eta}\left[1 + \frac{8}{15\pi^2}\ln(Q\xi)\right] \tag{4}$$

The two predictions can be reconciled if one considers Eq. (4) as the first approximation of a power law of the form

$$\eta = \bar{\eta}(Q\xi)^z \tag{5}$$

with $z = 8/15\pi^2 = 0.054$ a first-order estimate for the critical exponent. This is the origin of the postulate that the viscosity exhibits a multiplicative anomaly, that is, the exponent z is the exponent of a power law for the viscosity ratio $\eta/\bar{\eta}$ rather than for the singular viscosity itself [17]. The system-dependent amplitude Q is related to the background contribution $\bar{L}$ in the conductivity L as noted by Oxtoby and Gelbart [18]. However, as pointed out by Bhattacharjee et al. [19], Q also depends on a Debye cutoff wave number q_D in the mode-coupling equations. In practice, the amplitude Q is treated as an adjustable parameter.

The theoretical estimates available for the exponent z are presented in Table I. In the renormalization-group theory the universal quantities are often evaluated from a perturbation expansion in terms of the parameter

Table I. Theoretical Values for the Viscosity Exponent z

Theory[a]	Exponent z	Reference
RG, order ε	0.053	Halperin et al. [20]
RG, order ε^2	0.065	Siggia et al. [21]
RG, order ε^3	0.050	Bhattacharjee and Ferrell [22]
MC	0.054	Ohta and Kawasaki [23]
MC	0.051	Bhattacharjee and Ferrell [22]

[a] RG, renormalization-group theory; MC, mode-coupling theory.

$\varepsilon = 4 - d$. The predictions from the renormalization-group theory and from the mode-coupling theory are in reasonable agreement. The first-order estimate $z = 8/15\pi^2$, mentioned above, appears to yield a surprisingly good estimate of what is likely to be the theoretical value [22]. In preparing Table I, as well as all the other tables in this paper, I have made some personal judgments in omitting information which I consider less reliable. For instance, a theoretical estimate for z as high as 0.07 has been reported by Garisto and Kapral [24] and by Paladin and Peliti [25]. The estimate of Garisto and Kapral is based on the numerical evaluation of an integral which in retrospect appears to be logarithmically divergent [22]. The estimate of Paladin and Peliti is based on a first-order evaluation and Paladin et al. do not quote this estimate in a subsequent comparison with experimental data [26].

It should be emphasized that the power law given by Eq. (5) refers to the viscosity η in the hydrodynamic limit $q \to 0$ and $\omega \to 0$. Dependence of the viscosity on the wave number q [27] and on the frequency ω [28] becomes important in the critical region, and the experimental data should be corrected for such effects in order to extract a value for the exponent z from the experimental data.

The separation of the conductivity L into a singular contribution ΔL and a background contribution $\bar{L}$ implies a similar separation for the diffusion D:

$$D = \Delta D + \bar{D} \tag{6}$$

where $\bar{D} = \bar{L}/\chi$. In principle, the diffusion coefficient also depends on both the wave number q and the frequency ω. The frequency dependence has been detected experimentally in our laboratory [29, 30]; the effect is small, in agreement with the theory, and can be neglected here. However, as discussed in Section I, it is important to consider the dependence of the diffusion coefficient on the wave number q in the interpretation of light-scattering data.

The theory predicts that the singular diffusion coefficient ΔD should asymptotically satisfy an equation of the form [8]

$$D - \bar{D} = \Delta D(q) = \frac{k_B T}{6\pi\eta\xi}\,\Omega(q\xi) \tag{7}$$

where k_B is Boltzmann's constant, η is the viscosity in the hydrodynamic limit $q \to 0$ as given by Eq. (5), and $\Omega(x)$ is a universal dynamical scaling function. The function $\Omega(x)$ satisfies the boundary conditions

$$\lim_{x \to 0} \Omega(x) = R, \qquad \lim_{x \to \infty} \Omega(x) \propto x^{y} \tag{8}$$

where R is a universal constant and where y satisfies the exponent relation

$$y = 1 + z \tag{9}$$

Equation (7) implies that in the hydrodynamic limit $q\xi \ll 1$, $\Delta D(0)$ will vary in accordance with the Stokes-Einstein diffusion law $\Delta D(0) = Rk_B T/6\pi\eta\xi$ independent of q and, hence, will go to zero as ξ^{-y}. On the other hand, at the critical point ($q\xi \to \infty$), $\Delta D(q)$ is no longer independent of q but will vary as q^y.

Burstyn et al. [7] have derived for $\Omega(x)$ a closed-form approximant of the form

$$\Omega(x) = R\Omega_K(x)\left[1 + \left(\frac{x}{2}\right)^2\right]^{z/2} \tag{10}$$

where $\Omega_K = (3/4x^2)[1 + x^2 + (x^3 - x^{-1}) \arctan x]$ is the so-called Kawasaki function. This Kawasaki function is a first-order approximant for the dynamic scaling function obtained when one neglects the singular viscosity $\Delta\eta$ in the evaluation of the mode-coupling integral for $\Delta D(q)$ [13]. A slightly different approximant for $\Omega(x)$ has been proposed by Paladin and Peliti [25].

The theoretical estimates reported for the universal dynamic amplitude ratio R are presented in Table II. From the mode-coupling theory one has deduced the estimate $R = 1.03$. Calculations on the basis of the renormalization-group theory have yielded values which vary from 0.79 to 1.20.

3. VISCOSITY OF LIQUID MIXTURES NEAR A CRITICAL POINT

In the interpretation of experimental viscosity data one may need to consider corrections for a nonlinear dependence of the viscosity on the shear gradient [27, 32] or, when appropriate, for a possible dependence on

Table II. Theoretical Values for the Dynamic Amplitude Ratio R

Theory[a]	Amplitude ratio R	Reference
RG, order ε^2	0.79	Siggia et al. [21]
RG, order ε^2 + MC	1.20	Siggia et al. [21]
RG	1.07	Paladin and Peliti [25]
MC	1.03	Kawasaki and Lo [31]
MC	1.03	Burstyn et al. [7]

[a] RG, renormalization-group theory; MC, mode-coupling theory.

frequency [28]. Moreover, the critical temperature T_c itself is also affected by a shear gradient [33, 34]. Furthermore, to compare the experimental data with the predicted power law given by Eq. (5), one needs an estimate for the background viscosity $\bar{\eta}$ as a function of temperature. This is a problem in binary liquid mixtures where the measurements have all been made at constant pressure, so that the density and, hence, the background viscosity $\bar{\eta}$ change appreciably as a function of the temperature. Sufficient independent information to determine $\bar{\eta}$ as a function of temperature is usually not available. Instead, one adopts an empirical equation for $\bar{\eta}$ as a function of temperature, such as an Arrhenius-type equation, and then tries to determine the parameters in the equation for $\bar{\eta}$ and the exponent z simultaneously from the experimental viscosity data. This procedure has two disadvantages. First, one does not know a priori whether the postulated equation for $\bar{\eta}$ is really correct, and the values deduced for the exponent z may be biased by the choice for this equation. Second, the procedure does not yield a determination of the amplitude Q, which is also of physical interest.

The viscosity of the liquid mixture 3-methylpentane + nitroethane near the critical mixing point has been measured by a number of investigators [35–39]. For this mixture attempts have been made to obtain an independent estimate of $\bar{\eta}$. Figure 2 shows a log–log plot of the ratios $\eta/\bar{\eta}$ thus

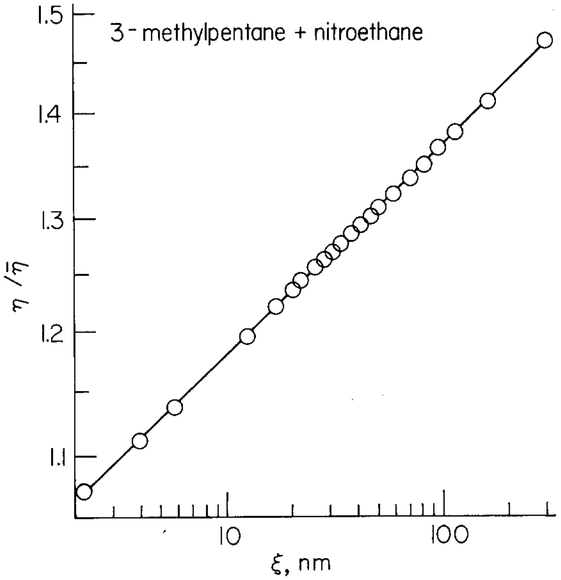

Fig. 2. Log–log plot of the viscosity ratio $\eta/\bar{\eta}$ as a function of the correlation length ξ for 3-methylpentane + nitroethane at the critical concentration [7].

deduced from the experimental data of Tsai and McIntyre [36] as a function of ξ. The data satisfy the power law given by Eq. (5) with parameters [7]

$$Q = 1.4\ \mathrm{nm}^{-1}, \qquad z = 0.063 \tag{11}$$

It is difficult to assess the accuracy of the exponent value determined experimentally. From an analysis of data of several investigators for 3-methylpentane + nitroethane, Burstyn et al. [7] concluded that $z = 0.062 \pm 0.005$, a value slightly larger than the theoretical estimate $z \simeq 0.054$.

Table III gives a list of experimental values that have been obtained for the universal dynamic exponent z. In all cases I have assigned a minimum error of ± 0.005 to the reported exponent value. The experimental values cover a range from a minimum value of 0.046 to a maximum value of 0.066. Beysens et al. [26] have attributed the differences in exponent values to the presence of nonanalytic corrections to the asymptotic power law. While this is indeed possible in principle, I think it more likely that the differences are a result of errors either in the

Table III. Experimental Values for the Viscosity Exponent z

System	Exponent z	Reference
Isobutyric acid + water	0.061 ± 0.005	Izumi and Miyake [40]
Isobutyric acid + water	0.063 ± 0.005	Calmettes [41]
2,6-Lutidine + water	0.062 ± 0.005	Calmetter [41]
Butyl Cellosolve + water	0.060 ± 0.005	Izumi et al. [42]
Polydimethylsiloxane + diethylcarbonate	0.052 ± 0.005	Hamano et al. [43]
3-Methylpentane + nitroethane	0.062 ± 0.005	Burstyn et al. [7]
3-Methylpentane + nitroethane	0.056 ± 0.005	Pegg and McLure [39]
2-Butoxyethanol + water	0.065 ± 0.005	Pegg and McLure [39]
Hexadecane + acetone	0.063 ± 0.005	Pegg and McLure [39]
Polystyrene + cyclohexane	0.046 ± 0.005	Izumi et al. [44]
n-Hexane + nitrobenzene	0.063 ± 0.005	Beysens et al. [26]
n-Dodecane + chlorez	0.066 ± 0.005	Beysens et al. [26]
Triethylamine + water	0.051 ± 0.005	Beysens et al. [26]
Ethanol + water + benzene + ammonium sulfate	0.054 ± 0.005	Izumi and Miyake [45]
Nitrogen	0.057 ± 0.007	Basu and Sengers [46]
Carbon dioxide	0.055 ± 0.005	Iwasaki and Takahashi [47]
Carbon dioxide	0.056 ± 0.005	Bruschi and Torzo [48]

experimental data themselves or due to various assumptions in the analysis, such as the estimated behavior of $\bar{\eta}$. For instance, while we found $z = 0.062 \pm 0.005$ for 3-methylpentane + nitroethane [7], a recent experimental study by Pegg and McLure [39] has yielded $z = 0.056 \pm 0.005$ for the same system. In view of these uncertainties, I think that the agreement between theory and experiment is reasonable. It would be of interest, of course, if the exponent z could be determined with a higher accuracy.

It is interesting to note that Izumi and Miyake [45] have also studied the behavior of the viscosity in the quaterny mixture ethanol + water + benzene + ammonium sulfate near its tricritical point. They found $z = 0.054 \pm 0.005$, which strongly indicates that liquid mixtures near a tricritical point belong to the same dynamic universality class. Experimental evidence that fluid mixtures near a plait point belong to the same dynamic universality class as well has been presented by D'Arrigo et al. [49] and Lee [32].

It is possible to determine the exponent z independently from measurements of the diffusion coefficient D. The theory predicts that at the critical point, D will vary as $q^y = q^{1+z}$ in accordance with Eqs. (8) and (9). If one therefore determines an effective exponent $y_{\text{eff}}(T)$ such that $D \propto q^{y_{\text{eff}}(T)}$ at temperatures close to T_c, one can determine $1 + z$ as the limiting value of $y_{\text{eff}}(T)$ at $T = T_c$. In Fig. 3 we show the exponent y_{eff} as a function of the temperature obtained by us for 3-methylpentane + nitroethane. Extrapolating these values to T_c we find $y = 1.05 \pm 0.02$, in

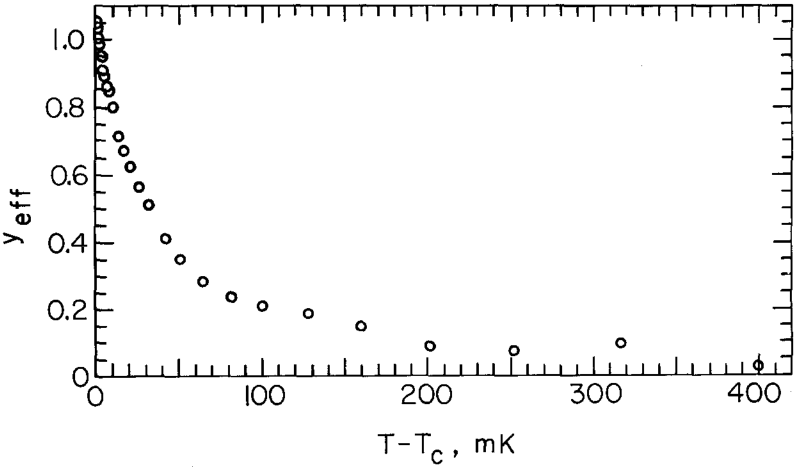

Fig. 3. The effective exponent y_{eff} as a function of $T - T_c$ for 3-methylpentane + nitroethane at the critical concentration [6, 7].

excellent agreement with the exponent values determined for z from the viscosity data [7]. However, we cannot discriminate between $z=0.05$ and $z=0.06$ on the basis of the light-scattering measurements.

4. VISCOSITY OF GASES NEAR THE CRITICAL POINT

It is somewhat more difficult to determine the exponent z for the viscosity of gases near the vapor–liquid critical point. First, the data have to be taken at elevated pressures. Second, the attainable experimental accuracy is complicated by the divergent behavior of the compressibility. The presence of gravitationally induced density gradients needs also to be considered [50]. Furthermore, as we shall see, the magnitude of the anomalous behavior of the viscosity of gases near the vapor–liquid critical point appears to be smaller than that of the viscosity of liquid mixtures near the critical mixing point. On the other hand, at a given density, the background viscosity $\bar{\eta}$ is only a very weak function of temperature.

The viscosity near the vapor–liquid critical point has been investigated for various gases such as xenon [51], nitrogen [2], ethylene [53], ethane [47], sulfur hexafluoride [54], and carbon dioxide [47, 48]. The available information for steam is discussed later in this paper.

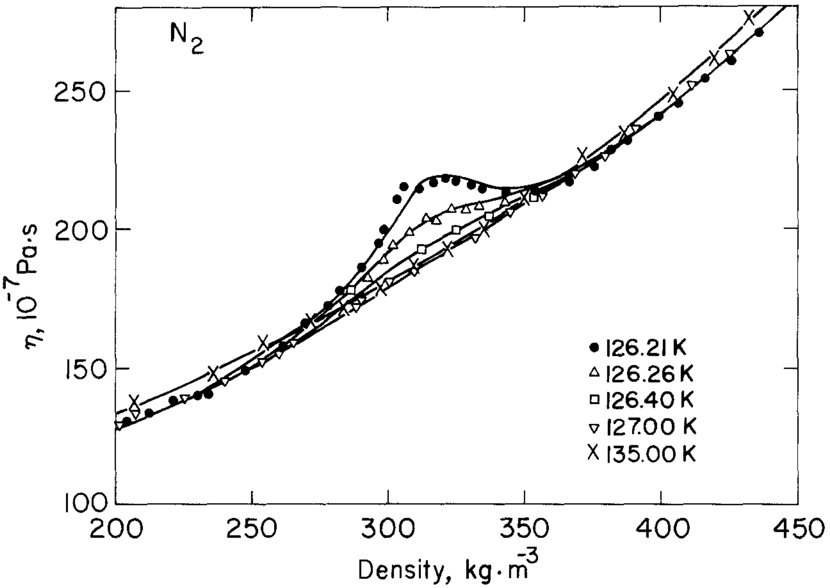

Fig. 4. Viscosity of nitrogen as a function of density at various temperatures near $T_c = 126.20$ K. The data were obtained by Zozulya and Blagoi [52] and the curves are calculated from Eq. (15).

The data of Strumpf et al. [51] have limited accuracy and may be affected by frequency dependence. The early viscosity data obtained by Zozulya and Blagoi [52] are shown in Fig. 4. These data have been analyzed by Basu and Sengers [46]. The viscosity ratio $\eta/\bar{\eta}$ is shown in Fig. 5 as a function of the correlation length ξ, and the data are consistent with the asymptotic power- law given by Eq. (5) with parameter values [46]

$$Q = 0.45\ \text{nm}^{-1}, \qquad z = 0.057 \tag{12}$$

On comparing Eq. (12) with Eq. (11) we note that the amplitude Q for gases is smaller than the corresponding amplitude Q for binary liquids. As a consequence, the temperature range of the anomalous behavior is also smaller is gases. For instance, from the data in Fig. 2 we note that the asymptotic power law is already satisfied at ξ as small as about 10 Å, which corresponds to $T - T_c \simeq 20°\text{C}$ so that $\Delta T^* < 9 \times 10^{-2}$. On the other hand, from Fig. 5 we note that the asymptotic power law is not reached until ξ is well beyond 100 Å, which corresponds to $T - T_c \leqslant 0.2°\text{C}$ or $\Delta T^* < 2 \times 10^{-3}$. This result indicates that the mode-coupling effects disappear in gases at smaller wave numbers than in liquids [19].

Because of the small temperature range of this asymptotic behavior, we do not have sufficient data in the asymptotic range to deduce a reliable

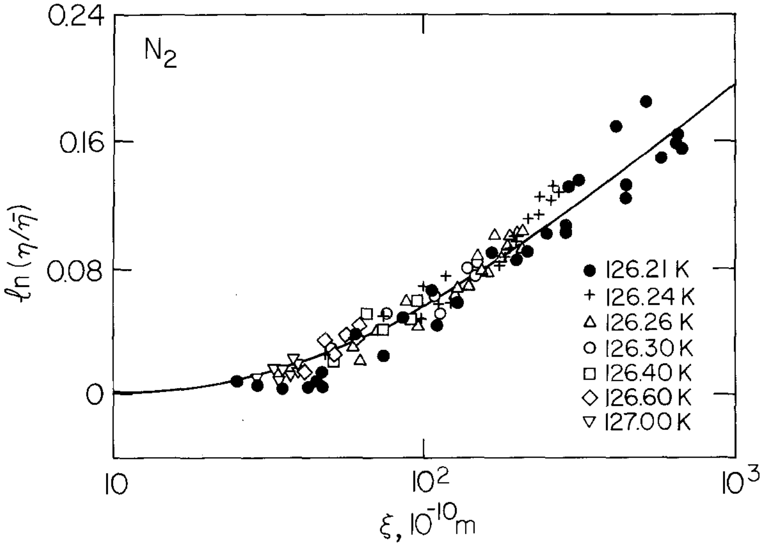

Fig. 5. Log–log plot of the viscosity ratio $\eta/\bar{\eta}$ of nitrogen as a function of the correlation length ξ [55].

exponent z for most gases [55]. Taking into account correction terms to the asymptotic behavior described below, we estimate that the data of Iwasaki and Takahashi [47] for carbon dioxide are consistent with $z = 0.055 \pm 0.005$ [56]. Recently, Bruschi and Torzo [48] reported some new viscosity data for carbon dioxide which supersede their earlier frequency-dependent data for the same gas [57]. From these data they deduce $z = 0.056$ with high apparent precision.

5. DIFFUSION OF LIQUID MIXTURES NEAR A CRITICAL POINT

In order to compare experimental data for the diffusion coefficient D with the theoretical prediction (7), one needs to consider possible corrections for a background contribution $\bar{D} = \bar{L}/\chi$. For liquid mixtures near the critical mixing point, estimating this background contribution is complicated by the fact that no independent measurements for the mass conductivity L are available. Background contributions have often been neglected in analyzing experimental light-scattering data near the critical mixing point [58, 59]. However, it has been demonstrated that corrections due to background contributions are important in the interpretation of experimental data for gases [12] as well as for binary liquids [60, 61].

A procedure has been developed to estimate $\bar{D}$ from the amplitude Q of the power law given by Eq. (5) for the viscosity ratio $\eta/\bar{\eta}$ [7, 18, 19]. We do not discuss the problem here except to note that for the experimental data shown in Fig. 1, the correction is smaller than 1% when $T - T_c \leqslant 0.1\,^{\circ}\mathrm{C}$.

From Eq. (7) it follows that it is convenient to define a scaled diffusion coefficient as

$$D^* = \frac{6\pi\eta\xi}{k_B T} \Delta D(q) \tag{13}$$

The experimental values deduced for D^* are shown in Fig. 6. The data, obtained as a function of both q and ξ, indeed collapse onto a single curve $\Omega(q\xi)$. The solid curve in Fig. 6 represents the theoretical dynamic scaling function (10); it reproduces the data within experimental accuracy [7].

There has been some controversy concerning the experimental value of the dynamic amplitude ratio R. Currently available experimental values are presented in Table IV. When Siggia et al. [1] estimated $R \simeq 1.20$, it was speculated that the diffusion coefficient would satisfy a Stokes-Einstein diffusion law with prefactor $1.2/6\pi \simeq 1/5\pi$ in accordance with Stokes's law for a spherical droplet with radius ξ moving in a medium with the same

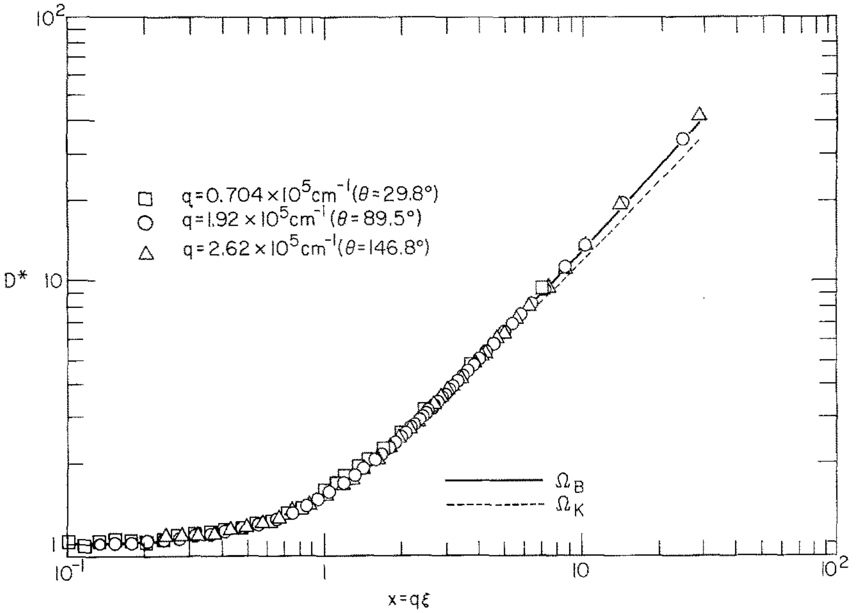

Fig. 6. Scaled diffusion coefficient $D^* = 6\pi\eta\xi(D-\bar{D})/k_BT$ as a function of $q\xi$ for 3-methylpentane + nitroethane. The dashed curve represents the Kawasaki function $\Omega_K(q\xi)$, and the solid curve the approximant (10) for $\Omega(q\xi)$ [7].

Table IV. Experimental Values for the Dynamic Amplitude Ratio R

System	Amplitude ratio R	Reference
3-Methylpentane + nitroethane	1.02 ± 0.06	Burstyn et al. [37]
3-Methylpentane + nitroethane	1.01 ± 0.04	Burstyn et al. [7]
Polydimethylsiloxane + diethylcarbonate	1.03 ± 0.06	Hamano et al. [43]
n-Hexane + nitrobenzene	0.99 ± 0.05	Zalczer et al. [66]
n-Hexane + nitrobenzene	1.06 ± 0.07	Beysens et al. [26]
n-Dodecane + chlorex	1.06 ± 0.06	Beysens et al. [26]
Triethylamine + water	1.06 ± 0.06	Beysens et al. [26]
Ethanol + water + benzene + ammonium sulfate	1.0 ± 0.1	Kim et al. [67]
Xenon	1.01 ± 0.06	Güttinger and Cannell [68]
Ethane	1.01 ± 0.10	Chang and Doiron [69]

viscosity as that of the liquid droplet [62]. This result appeared to be confirmed by several investigators [63–65]. As we see below a value of $R \simeq 1.2$ appeared also to be supported by the thermal conductivity for gases in the critical region. However, we were unable to reproduce this result from the light-scattering measurements obtained at that time in our laboratory and we were forced to study this amplitude ratio R more carefully [37].

From Eqs. (7), (10), and (13) we note that R can be deduced from the experimental data as

$$R = D^*/\Omega_K(q\xi)\left[1+\left(\frac{q\xi}{2}\right)^2\right]^{z/2} \tag{14}$$

The values, thus obtained for R from our light-scattering data at 90°C, which have the higher accuracy [7], are shown in Fig. 7 as a function of ξ. For small ξ the values deduced do depend on the background correction, but for large ξ they do not. The dynamic amplitude ratio thus obtained is

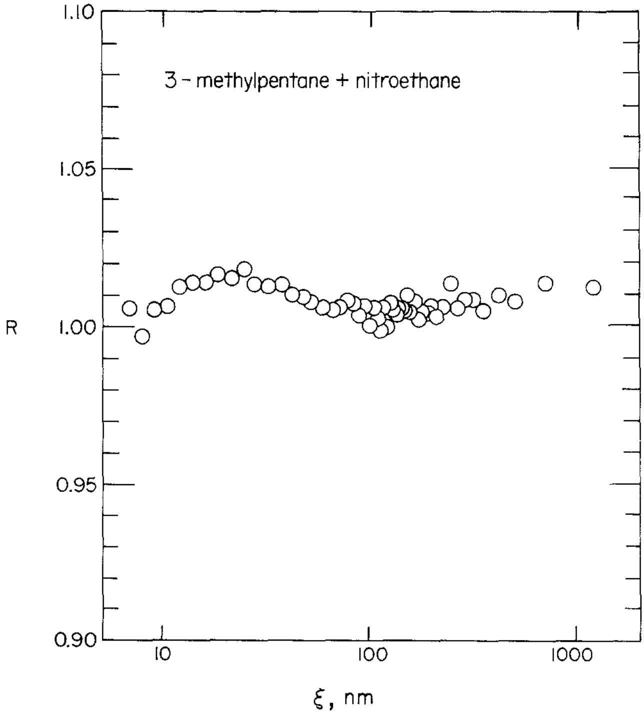

Fig. 7. Dynamic amplitude ratio R for 3-methylpentane + nitroethane as a function of ξ.

indeed independent of ξ, and we find $R = 1.01$ with a precision of ± 0.04 [7]. This result is in good agreement with the value $R = 1.03$ predicted from the mode-coupling theory but differs from the most recent theoretical estimate $R = 1.075$ from the renormalization-group theory (see Table II). In Table IV we list experimental values for R reported by several investigators. Good agreement with the predicted value $R = 1.03$ has also been found by Hamano et al. [43] for polydimethylsiloxane + diethylcarbonate and by Chen et al. [61] for *n*-hexane + nitrobenzene.

An accurate determination of R requires reliable information for D, ξ, and η for the same system. Also, the value obtained for R may be too large if one neglects background contributions to D [59]. As in the other tables, I have omitted in Table IV reported values that I consider less reliable. For instance, Beysens et al. [26] recently reported light-scattering data for 3-methylpentane + nitroethane earlier obtained by Calmettes, from which they deduce that $R = 1.14 \pm 0.07$, in disagreement with the value $R = 1.01 \pm 0.04$ obtained by us. Since they use the same data for ξ and η, the difference can be traced to a difference between our decay-rate data and those of Calmettes. The decay rates have been remeasured by Jefferson et al. for this system and they find agreement with our data within 2% at all temperatures [70].

It is also of interest to consider an earlier investigation by Kim et al. [67], who measured the decay rate together with ξ and η for the quaterny mixture ethanol + water + benzene + ammoniumsulfate near the tricritical point. They found that their data were consistent with $R = 1.0$ to within 10%, a result which again indicates that fluid mixtures near a tricritical point belong to the same dynamic universality class.

6. THERMAL DIFFUSIVITY OF GASES NEAR THE CRITICAL POINT

Several investigators have measured the Rayleigh linewidth of light scattered through gases near the critical point which yield the thermal diffusivity D_T. It turns out that the effect of background contributions is quite important for gases, but in this case they can be estimated from independent thermal conductivity data [12, 14, 58]. The early experimental work was reviewed by Swinney and Henry [58]. Most experimental light-scattering data reported in the literature for gases are not sufficiently accurate to yield the dynamic amplitude ratio R within an accuracy of 10% or better. An exception is the work of Güttinger and Cannell [68], who made a careful study of R for xenon at about the same time we were determining this quantity for 3-methylpentane + nitroethane. They found $R = 1.01 \pm 0.04$, in excellent agreement with the value found by us for 3-

methylpentane + nitroethane near the critical mixing point. Light-scattering measurements of Chang and Doiron [69] for ethane have yielded $R = 1.01 \pm 0.10$, consistent with the above results.

It should be noted that the data shown in Fig. 7 for the amplitude ratio R of the binary liquid 3-methylpentane + nitroethane corresponds to a temperature range for which $\xi \geqslant 80$ Å. Hence, the validity of Eq. (14) with $R = 1.01 \pm 0.04$ has been verified for this binary liquid mixture for $\Delta T^* \leqslant 3 \times 10^{-3}$. On the other hand, to obtain $R = 1.01 \pm 0.04$ for xenon, Güttinger and Cannell [68] had to restrict the data to temperatures for which $\Delta T^* \leqslant 2 \times 10^{-4}$. Just as for the viscosity, the range of validity of the asymptotic behavior for the diffusion of the order-parameter fluctuations could be smaller for gases than for binary liquids.

7. CROSSOVER FUNCTIONS FOR THE VISCOSITY OF GASES IN THE CRITICAL REGION

As discussed earlier, the viscosity ratio $\eta/\bar{\eta}$ of gases does not reach its asymptotic power law given by Eq. (5) unless the temperature is very close to T_c. Hence, in order to represent the actual experimental viscosity data in the critical region, one needs a crossover function that reproduces both the asymptotic power law given by Eq. (5) close to T_c and the normal behavior of the viscosity away from the critical point. A similar problem is encountered in the theory of equilibrium properties, where one needs a crossover function that connects the scaling-law behavior of the thermodynamic properties near the critical point with the regular analytic behavior of these properties sufficiently away from the critical point [71–73].

For the viscosity we define a crossover function as

$$\frac{\eta}{\bar{\eta}} = F_\eta(\xi) \tag{15}$$

such that

$$\lim_{\xi \to \infty} F_\eta(\xi) = (Q\xi)^z, \qquad \lim_{\xi \to 0} F_\eta(\xi) = 1$$

The simplest approximation is a step function

$$\begin{aligned} F_\eta(\xi) &= (Q\xi)^z \qquad \text{for} \quad Q\xi > 1 \\ F_\eta(\xi) &= 1 \qquad\quad\;\; \text{for} \quad Q\xi \leqslant 1 \end{aligned} \tag{16}$$

Such a step function was originally used by Basu and Sengers [46] for nitrogen and is represented by the curves in Fig. 3. The disadvantages of this step function are twofold. First, the transition between the asymptotic power law given by Eq. (5) and the regular behavior does not occur sharply at $Q\xi = 1$. Second, this representation uses the power law given by Eq. (5) in a temperature range where the asymptotic behavior is not fully reached and, hence, tends to yield an effective exponent value z which may be smaller than the asymptotic value.

In principle, a crossover function can be derived from the mode-coupling theory, since the validity of the mode-coupling equations is not limited to the asymptotic behavior only. In order to obtain a crossover function in a mathematically closed form, one is forced to consider approximate solutions of the mode-coupling equations. Using this procedure we have proposed a crossover function of the form [19]

$$F_\eta(\xi) = \exp(zH) \tag{17}$$

where

$$H = q_C \xi \int_0^{\Psi} \frac{\sin^4\psi \, d\psi}{1 + q_C \xi \cos\psi} \tag{18}$$

with $\Psi = \arccos(1 + q_D{}^2\xi^2)^{-1/2}$. Here q_C is a wave number related to the background values $\bar{\eta}$ and $\bar{\lambda}$ at the critical point and q_D is a Debye cuttoff wave number where the mode-coupling contributions disappear. The function H reproduces the power law $(Q\xi)^z$ in the limit $\xi \to 0$ with

$$Q^{-1} = \frac{1}{2}(q_C^{-1} + q_D^{-1})\, e^{4/3} \tag{19}$$

The integral in Eq. (18) can be evaluated by elementary techniques and the explicit form of the crossover function H is given elsewhere [19]. This function has been used by Basu and Sengers [55] to represent the experimental viscosity of a variety of gases in the critical region with q_D as an adjustable parameter and with an exponent value $z = 0.065$, which in retrospect may be slightly too large. The values thus obtained for the viscosity ratio $\eta/\bar{\eta}$ for nitrogen in the critical region are represented by the solid curve in Fig. 5.

Improved versions of this crossover function for the viscosity of gases in the critical region are presently being developed by our research group. Such more refined crossover functions depend on the temperature and density not only via the correlation length ξ but also through other thermodynamic properties such as compressibility and specific heat.

8. CROSSOVER FUNCTIONS FOR THE THERMAL CONDUCTIVITY OF GASES IN THE CRITICAL REGION

From Eq. (7) it follows that the thermal conductivity of a gas in the hydrodynamic limit will asymptotically near the critical point behave as

$$\Delta\lambda = R\frac{k_B T}{6\pi\eta\xi}\rho c_p \tag{20}$$

Since c_p diverges as $\xi^{2-\tilde{\eta}}$, where $\tilde{\eta} \simeq 0.03$ is a small exponent that characterizes deviations of the static order-parameter correlation function from the classical Ornstein-Zernike form [1], it follows from Eqs. (5) and (20) that the singular thermal conductivity $\Delta\lambda$ will diverge as

$$\Delta\lambda \propto \xi^{\phi} \propto |\Delta T^*|^{-\phi\nu} \tag{21}$$

with

$$\phi = 1 - \tilde{\eta} - z \tag{22}$$

Attempts have been made to determine the exponent ϕ from experimental thermal conductivity data [11, 12, 14, 74], the most successful being that of Pittman et al. [75] for ^{3}He. In all these attempts the data deduced for $\Delta\lambda$ were fitted either to the simple power law given by Eq. (21) at $\rho = \rho_c$ or to a simple scaling law when data off the critical isochore were included, which in fact extended to values of ΔT^* as large as 0.1. However, in Section 4 we noted that the corresponding power law given by Eq. (5) for the viscosity η of gases was restricted to $\Delta T^* < 2 \times 10^{-3}$. Moreover, as discussed in Section 6, the corresponding power law for the thermal diffusivity $\Delta D_T = \Delta\lambda/\rho c_p$ has thus far been verified only for $\Delta T^* < 2 \times 10^{-4}$. Hence, it is questionable whether this procedure reveals the truly asymptotic behavior of the thermal conductivity. In order to interpret the available experimental thermal conductivity data for gases in the critical region, it is desirable to formulate a crossover function for $\Delta\lambda$ which approaches Eq. (20) asymptotically at the critical point and approaches zero far away from the critical point.

In the case of the viscosity almost any crossover function works in practice since the anomaly is weak and restricted to a small temperature range. In the case of the thermal conductivity the singular contribution $\Delta\lambda$ is significant in a large range of temperatures and densities around the critical point. As a consequence the requirements for a suitable crossover function for the thermal conductivity are more demanding if one wants to obtain a representative equation that reproduces the thermal conductivity contribution $\Delta\lambda$ at all temperatures and densities within experimental accuracy.

To date empirical crossover functions have been employed to represent the thermal conductivity of gases in the critical region. In our earlier work we have proposed an equation of the form [76, 77]

$$\Delta\lambda = R\frac{k_B T}{6\pi\eta\xi}\rho(c_p - c_v)\,F_\lambda(\Delta T^*, \Delta\rho^*) \tag{23}$$

where c_v is the specific heat at constant volume, $\Delta T^* = (T - T_c)/T_c$, $\Delta\rho^* = (\rho - \rho_c)/\rho_c$, and $F_\lambda(\Delta T^*, \Delta\rho^*)$ is an exponential damping function

$$F_\lambda(\Delta T^*, \Delta\rho^*) = \left(\frac{\rho}{\rho_c}\right)^n \exp\{-[A(\Delta T^*)^2 + B(\Delta\rho^*)^4]\} \tag{24}$$

The coefficients A and B are treated as adjustable constants, while $n = 0$ or $n = 1/2$ is a simple exponent. In the absence of light-scattering data the correlation length ξ can be estimated from an approximate relationship with the isothermal compressibility [78]. This empirical function has been used by several investigators [79–84]. Other types of empirical functions have also been proposed [85–87].

In Fig. 8 we show the values predicted by Eq. (23) for the thermal conductivity of carbon dioxide in the critical region with parameters

$$n = 0, \qquad R = 1.0, \qquad A = 39.8, \qquad B = 5.45 \tag{25}$$

The equation is compared with the thermal conductivity data of Michels et al. [89] and with the values deduced from the thermal diffusivity data obtained by Becker and Grigull [90] for CO_2 from holographic interferometry. In applying Eq. (23) we imposed the value $R = 1.02$ as originally determined by Burstyn et al. [37] for the asymptotic behavior of the diffusivity from light-scattering data and treated A and B as adjustable constants. The equation yields a reasonable representation of the thermal conductivity in the critical region. There are some discrepancies, but it should be kept in mind that close to the critical point, the analysis becomes extremely sensitive to uncertainties in T_c, which affect the value calculated for c_p that enters into the comparison between the thermal conductivity data and the equation as well as in the comparison between the thermal conductivity data and the experimental thermal diffusivity data. For instance, it makes a difference in the analysis whether one attributes to the data of Becker and Grigull the best value for T_c of CO_2 quoted in the literature, as done in constructing Fig. 8 [88], or the different value for T_c quoted by Becker and Grigull themselves.

Nevertheless, there exist some unsolved problems. First, there is evidence from our work as well as that of others [83, 85] that Eq. (23)

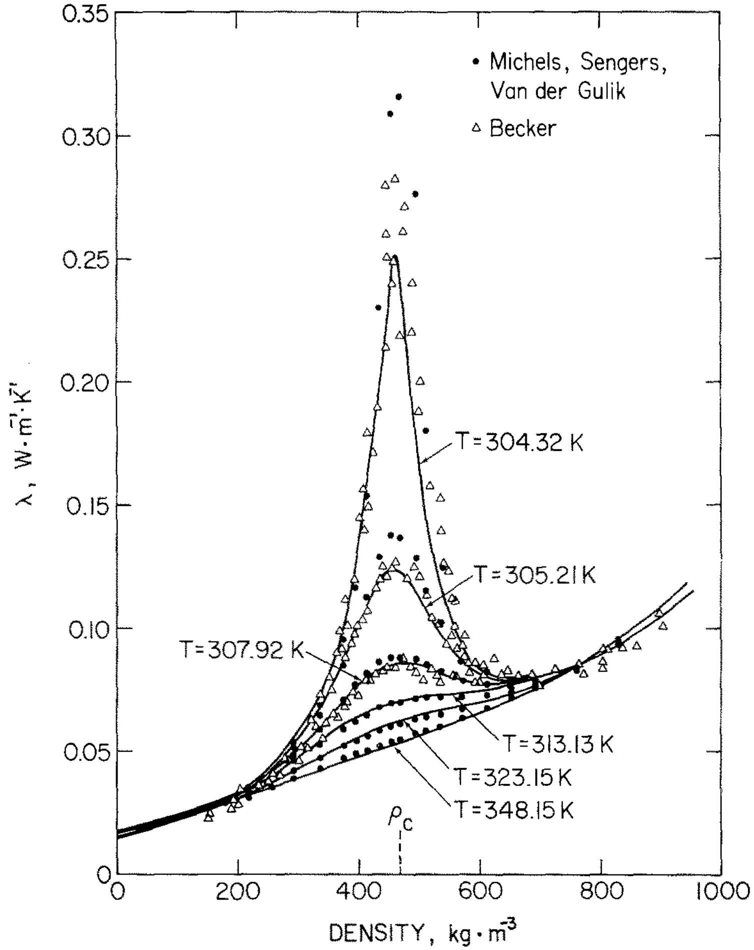

Fig. 8. Thermal conductivity data for CO_2 in the critical region as a functions of density along isotherms. The curves represent the values calculated from Eqs. (23) and (24) with the parameter values given in Eq. (25) [88].

does not always reproduce the thermal conductivity at all temperatures and densities where a critical enhancement is observed. Second, when Eq. (23) or a similar equation is used to fit the experimental thermal conductivity data with R as adjustable parameters, one often finds a value $R \cong 1.2$, in disagreement with the value $R = 1.01 \pm 0.04$ established for the asymptotic behavior of the diffusion of the critical fluctuations in fluids from light-scattering experiments. Our own thermal conductivity measurements seemed to indicate that $R = 1.15 \pm 0.05$ [14, 76]. A value

$R = 1.2$ has been reported by Le Neindre and co-workers [87] for the thermal conductivity of ammonia and propane and by Trappeniers [74] and co-workers for the thermal conductivity of argon. Weber also needed $R = 1.2$ to represent his thermal diffusivity data for oxygen obtained from light-scattering measurements [83]. I am puzzled by these results. The most probable explanation is that the thermal conductivity data are not in the asymptotic range and that Eq. (23) is not accurate enough to yield the correct asymptotic behavior from experimental data outside the asymptotic regime. This possibility is illustrated by the work of Tufeu et al. [84, 91], who measured for ammonia the thermal conductivity directly as well as the thermal diffusivity from light scattering. The light-scattering data are consistent with $R = 1.0$, but the thermal conductivity data require $R = 1.2$. Nevertheless, the two data sets are not inconsistent, but the light-scattering data probe a temperature range closer to T_c then the thermal conductivity data. In those cases where the light-scattering data and the thermal conductivity data overlap near T_c, the combined accuracy is usually not much better than 20% [75, 87, 92].

Hence, it becomes imperative to develop crossover functions for the singular thermal conductivity $\Delta\lambda$ that have better foundations in theory. Such a crossover function can be derived in principle from the mode-coupling equations in a manner similar to the formulation of a crossover function for the viscosity discussed earlier. Such research is currently in progress.

9. VISCOSITY OF STEAM IN THE CRITICAL REGION

In conclusion we consider the behavior of the transport properties of steam in the critical region. The primary source of information for the viscosity of steam in the critical region is a set of experimental data obtained by Rivkin and co-workers [83]. These data do indicate an anomalous behavior of the viscosity near the critical point. The phenomenon has been confirmed for steam by Oltermann [94]. Unfortunately, Rivkin et al. have measured the kinematic viscosity η/ρ as a function of temperature and pressure. To convert these data to values for the shear viscosity η as a function of temperature and density, one needs to calculate the densities from the equation of state. As discussed elsewhere the results are very sensitive to the choice of $T - T_c$ to be assigned to the data [95]. In Fig. 9 we show the viscosity η as a function of density at temperatures close to the critical temperature T_c; this figure is based on the data of Rivkin and co-workers as reinterpreted by Watson et al. [96].

In order to represent the critical behavior of the viscosity, we need an equation for the background viscosity of steam. In 1975 the International

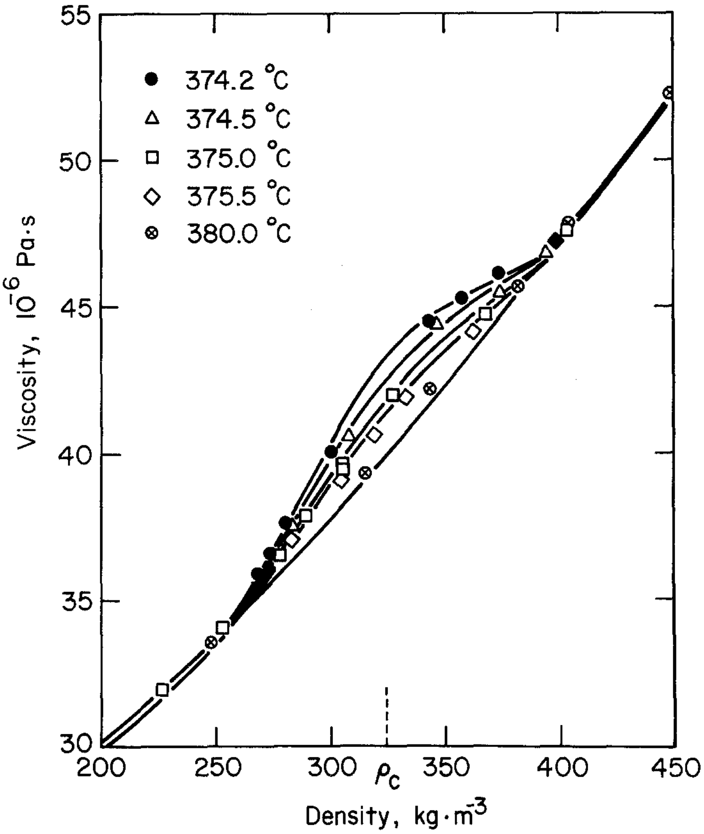

Fig. 9. The viscosity η of steam as a function of density at temperatures close to the critical temperature. The data points are deduced from the measurements reported by Rivkin et al. [93] and the curves represent values calculated from the equation of Watson et al. [96].

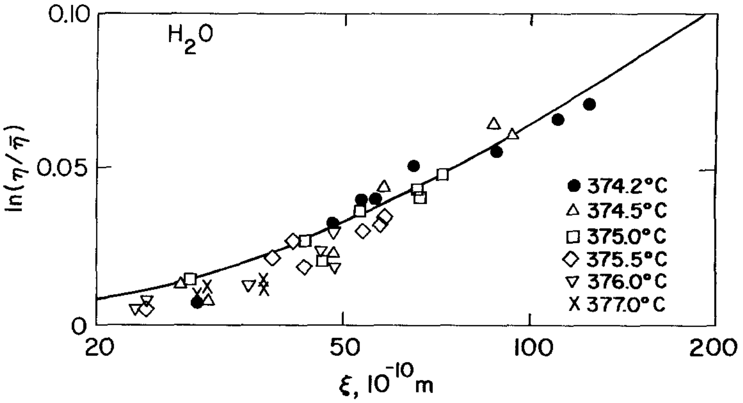

Fig. 10. Log–log plot of the viscosity ratio $\eta/\bar{\eta}$ of steam as a function of the correlation length ξ [55].

Association for the Properties of Steam (IAPS) adopted an equation for the viscosity of water substance of the form

$$\bar{\eta}=\eta_0\left(\frac{T}{T_\mathrm{r}}\right)\times\eta_1\left(\frac{T}{T_\mathrm{r}},\frac{\rho}{\rho_\mathrm{r}}\right) \tag{26}$$

where $T_\mathrm{r}=647.27\ \mathrm{K}$ and $\rho_\mathrm{r}=317.763\ \mathrm{kg\cdot m^{-3}}$ are reference constants close, but not identical, to the critical parameters T_c and ρ_c. The functions $\eta_0(\bar{T})$ and $\eta_1(\bar{T},\bar{\rho})$ are defined by

$$\eta_0(\bar{T})=\sqrt{\bar{T}}\left[\sum_{k=0}^{3}a_k^\eta/\bar{T}^k\right]^{-1} \tag{27}$$

$$\eta_1(\bar{T},\bar{\rho})=\exp\left[\bar{\rho}\sum_i\sum_j b_{ij}^\eta\left(\frac{1}{\bar{T}}-1\right)^i(\bar{\rho}-1)^j\right] \tag{28}$$

with coefficients a_k^η and b_{ij}^η given elsewhere [97]. The IAPS equation (26) does not account for any critical enhancement of the viscosity and, in principle, must therefore be considered an equation for the background viscosity $\bar{\eta}$. In practice, the IAPS equation does not yield sufficiently reliable values for the background viscosity $\bar{\eta}$ in the critical region. For this purpose Watson and co-workers [96] developed an improved version of the IAPS equation by redetermining the coefficients b_{ij}^η in Eq. (28). With this improved equation for the background viscosity, the critical viscosity enhancement can be represented in terms of the crossover function (15) with parameter values

$$Q=0.38\ \mathrm{nm}^{-1},\qquad z=0.05 \tag{29}$$

The values thus calculated are represented by the curves in Fig. 9 [96, 98].

In Fig. 10 we show a log–log plot of the viscosity ratio $\eta/\bar{\eta}$ of steam as a function of the correlation length ξ. Again it appears that we have not yet reached the fully asymptotic regime where the viscosity ratio $\eta/\bar{\eta}$ has reached the simple power law $(Q\xi)^z$ and the actual exponent z may be slightly larger than 0.05. As shown by Bhattacharjee et al. [19], it is possible to represent the viscosity data for steam with a slightly larger value of the exponent z, if one introduces the more complete crossover function given by Eq. (17).

I conclude that the behavior of the viscosity of steam in the critical region is fully consistent with the behavior found for the viscosity of other gases near the critical point.

10. THERMAL CONDUCTIVITY OF STEAM IN THE CRITICAL REGION

That the thermal conductivity of steam exhibits a pronounced enhancement in the critical region was first demonstrated by Le Neindre and coworkers [99]. The thermal conductivity of steam in the critical region has been investigated subsequently by Sirota and co-workers [100, 101] in great detail and with considerable accuracy. In 1977 the IAPS adopted a

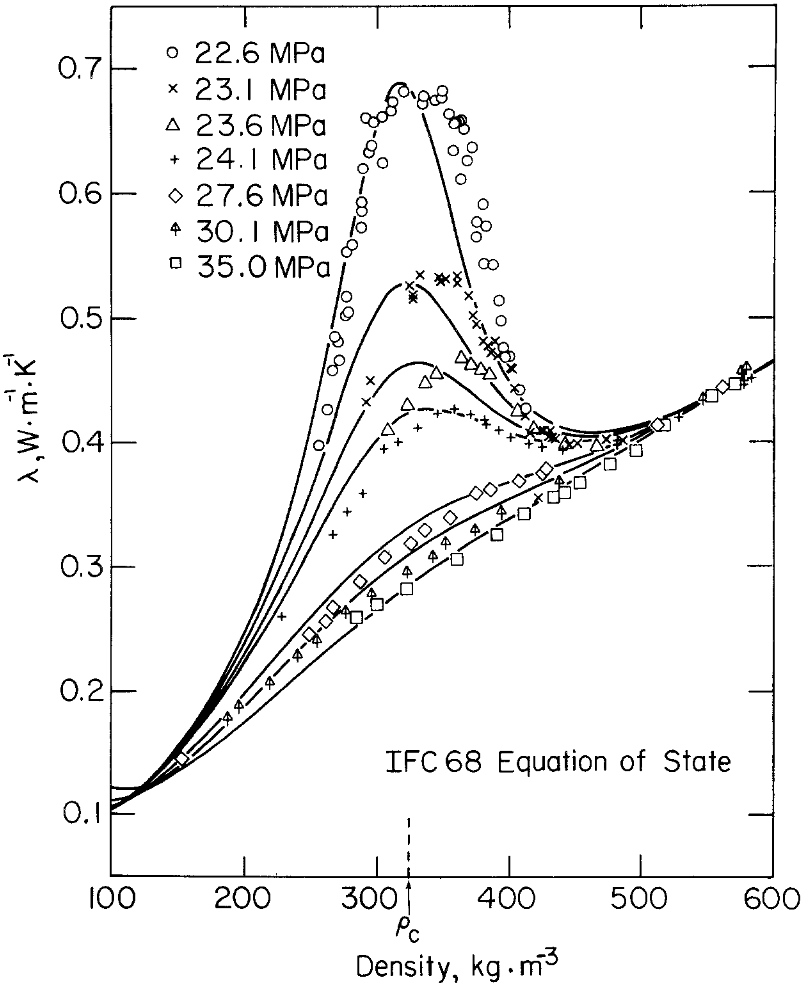

Fig. 11. The thermal conductivity of steam in the critical region as a function of density at constant pressures. The data are those of Sirota et al. [101] and the curves represent the values calculated from the IAPS equation adopted in 1977 [102].

representative equation for the thermal conductivity of water and steam that takes into account the enhancement of the thermal conductivity in the critical region [102]. The equation for the background thermal conductivity $\bar{\lambda}$ adopted by the IAPS has the same mathematical form as the equation (26) for the viscosity.

$$\bar{\lambda}=\lambda_0\left(\frac{T}{T_r}\right)\times\lambda_1\left(\frac{T}{T_r},\frac{\rho}{\rho_r}\right) \tag{30}$$

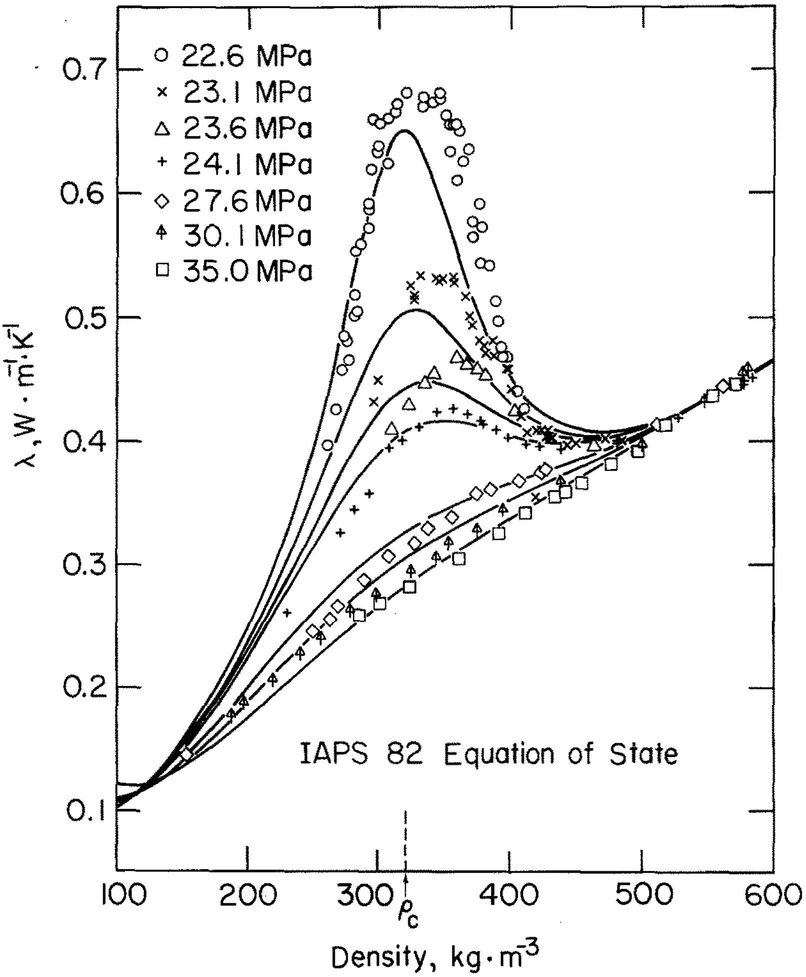

Fig. 12. The thermal conductivity of steam in the critical region as a function of density at constant pressures. The data are those of Sirota et al. [101] and the curves represent the values calculated from the IAPS equation as amended in 1982 [102].

with

$$\lambda_0(\bar{T}) = \sqrt{\bar{T}}\left[\sum_{k=0}^{3} a_k^\lambda/\bar{T}^k\right]^{-1} \tag{31}$$

$$\lambda_1(\bar{T}, \bar{\rho}) = \exp\left[\bar{\rho}\sum_i\sum_j b_{ij}^\lambda\left(\frac{1}{\bar{T}} - 1\right)^i (\bar{\rho} - 1)^j\right] \tag{32}$$

The singular contribution $\Delta\lambda$ for steam is represented by the crossover function given by Eq. (23) with parameter values [81, 102]

$$n = 1/2, \qquad R = 1.2, \qquad A = 18.66, \qquad B = 1 \tag{33}$$

In Figs. 11 and 12 we show a comparison between the values thus calculated for the thermal conductivity of steam in the critical region and the experimental data of Sirota et al. The thermal conductivity equation adopted by the IAPS was originally developed with the aid of the 1968 IFC formulation for the thermodynamic properties; the values thus calculated are shown in Fig. 11. In 1982 the IAPS adopted a new formulation for the thermodynamic properties of water substance which was developed by Haar et al. [103, 104] and the IAPS release on thermal conductivity was amended so as to be used with this new formulation for the thermodynamic properties; the values obtained by the latter procedure are shown in Fig. 12. For further details the reader is referred to a separate publication [102].

In developing a representative equation for the thermal conductivity of steam, we encountered the same problem mentioned earlier for other gases. To obtain satisfactory agreement with the experimental data we had again to select $R = 1.2$, in disagreement with the expected limiting value of $R = 1.01 \pm 0.04$. The behavior of the thermal conductivity of steam in the critical region appears to be quite similar to that observed for other gases. However, as of yet we do not have a representative equation fully consistent with the expected value for the amplitude R.

ACKNOWLEDGMENTS

The author is indebted to H. C. Burstyn for the experimental light-scattering measurements, to J. K. Bhattacharjee for his assistance in developing crossover functions for the transport properties, and to R. S. Basu and G. A. Olchowy for their assistance in the interpretation of some of the experimental data for gases. The author also acknowledges some stimulating discussions with H. Meyer.

The research was supported by National Science Foundation Grant DMR 82-05356 and by the U.S. Office of Standard Reference Data.

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