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The shear viscosity of fluids exhibits an anomalous enhancement in the close vicinity of the critical point. A detailed experimental study of the viscosity of steam in the critical region has been reported by Rivkin and collaborators. A reanalysis of the experimental data indicates that the behavior of the viscosity of steam near the critical point is similar to that observed for other fluids near the critical point. An interpolating equation for the viscosity of water and steam is presented that incorporates the critical viscosity enhancement.

KEY WORDS: critical region; critical viscosity enhancement; steam; viscosity; water; water vapor.

1. INTRODUCTION

It has been known since the beginning of the century that the viscosity of partially miscible liquid mixtures shows an abnormal increase when the critical point of mixing is approached. For a survey of the history of the subject the reader is referred to earlier reviews [1, 2]. During the past fifteen years it has become evident that the viscosity of one-component fluids shows an anomalous increase in the viscosity of the gas-liquid critical point as well. Experimental evidence for this effect has been reported by Kestin et al. for carbon dioxide [3], by Strumpf et al. for xenon and ethane [4], by Zozulya and Blagoi for nitrogen [5], and by Iwasaki and Takahashi for ethylene, carbon dioxide, and ethane [6]. An experimental study of the viscosity of steam indicating an anomalous behavior in the critical region was reported by

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Rivkin and coworkers [7, 8]. Additional evidence for the existence of a critical viscosity enhancement in steam was provided subsequently by Oltermann [9].

The International Association for the Properties of Steam (IAPS) issued a new representation for the viscosity of water substance in 1975. A description of this representation can be found in a number of publications [10-16]. At the time the new agreement was reached, the data of Rivkin and coworkers [7, 8] for the viscosity of steam in the critical region had just become available, but it was not clear how the critical viscosity enhancement could be incorporated into a comprehensive equation for the viscosity. The situation was aggravated by the fact that the critical behavior as reported by Rivkin and colleagues seemed to differ somewhat from the critical behavior of the viscosity observed for other fluids such as nitrogen [5]. As a consequence, the Special Committee on Transport Properties of IAPS preparing the new international formulations decided that an analysis of the critical anomaly in the viscosity of steam had better be left for the future. An account of the deliberations has been given by Nagashima [12]. From the concluding remarks in Nagashima's article we quote: "One of the most interesting topics left for future study is the behavior of the viscosity in the critical region. Neither the actual magnitude nor the functional form of the anomaly are now known satisfactorily." It is the purpose of the present paper to address this question.

2. THEORETICAL REMARKS

The state of a system near a critical point is characterized by the presence of large-scale fluctuations in the order parameter associated with the phase transition. For a fluid near the gas-liquid critical point, this implies the presence of large-scale density fluctuations causing the compressibility and the specific heat to diverge at the critical point. Because of the slow decay of these fluctuations, they also lead to an anomalous enhancement of the thermal conductivity and the viscosity near the critical point.

In order to represent the viscosity of a fluid near the critical point, one attempts to separate the viscosity η into a normal viscosity $\bar{\eta}$ in the absence of critical fluctuations and a critical enhancement $\Delta \eta$ due to the critical fluctuations:

$$\eta = \bar{\eta} + \Delta \eta \tag{1}$$

This separation is analogous to the decomposition of the thermal conductivity λ into a normal or background thermal conductivity $\overline{\lambda}$ and an anomalous thermal conductivity $\Delta\lambda$ discussed elsewhere [2, 17]:

$$\lambda = \bar{\lambda} + \Delta \lambda \tag{2}$$

Furthermore, theoretical and experimental evidence indicates that the critical viscosity enhancement $\Delta \eta$ of fluids near the gas-liquid critical point, as well as that of binary liquids near the consolute point, is proportional to the (normal) viscosity $\bar{\eta}$ [2, 18–24]. Hence rather than considering the absolute critical viscosity enhancement $\Delta \eta$, it is more appropriate to consider the relative critical viscosity enhancement $\Delta \eta/\bar{\eta}$ or the viscosity ratio $\eta/\bar{\eta}$.

It is possible to consider the anomalous behavior of the transport properties as arising from a coupling between hydrodynamic modes [21, 25]. Assuming the Ornstein-Zernike form for the order-parameter correlation function and neglecting a variety of higher-order effects, Kawasaki [18] and Perl and Ferrell [19] showed that in the first approximation,

$$\frac{\Delta\eta}{\bar{\eta}} \simeq \frac{8}{15\pi^2} \ln(q\xi) \tag{3}$$

where ξ is the range of the order-parameter correlation function and q is a system-dependent wave number. Generalizing an argument presented by Oxtoby and Gelbart [26], one finds [27]

$$q \simeq \frac{ck_B T \rho (c_p - c_v)}{8\pi \bar{\eta} \bar{\lambda} \xi^2} = \frac{ck_B T^2}{8\pi \bar{\eta} \bar{\lambda} \rho^2} \left(\frac{\partial P}{\partial T}\right)_{\rho}^2 \frac{\chi_T}{\xi^2}$$
(4)

where c is a function to be calculated numerically, approaching 0.9 at the critical point.³

Refinements of the theoretical treatment of the viscosity anomaly based on the mode coupling theory have been considered by several investigators [28-36]. Furthermore, the renormalization-group theory of critical phenomena has been extended to include dynamical critical phenomena [37-42]. The relationship between the two approaches has recently been further elucidated by Gunton [43]. These theories indicate a power-law divergence for the viscosity such that $\eta \propto \xi^{\phi}$, where ϕ is a universal exponent independent of the nature of the fluid. The simplified theoretical expression (3) may be written in the form of a power law by noting that

$$\frac{\eta}{\bar{\eta}} = 1 + \ln(q\xi)^{\phi} \simeq (q\xi)^{\phi} \tag{5}$$

where $\phi = 8/15\pi^2 \simeq 0.054$. Various attempts have been made to calculate the exponent value ϕ theoretically as summarized in Table I. For the approximations made in calculating these values, the reader is referred to the original publications [30, 34, 35, 37, 40, 43].

³For an explanation of symbols, see nomenclature at end of article.

Exponent value	Authors	
$\phi = 0.054$	Ohta [30], Ohta and Kawasaki [35]	
$\phi = 0.065$	Siggia et al. [37], Gunton [43]	
$\phi = 0.070$	Garisto and Kapral [34]	

Table I. Theoretical Values for the Critical Viscosity Exponent

3. OBSERVED CRITICAL VISCOSITY ENHANCEMENT

A detailed experimental study of the viscosity of steam in the critical region was made by Rivkin and coworkers [7, 8]. In Fig. 1 we reproduce the values reported for the dynamic viscosity as a function of density along five isotherms. Before interpreting these data, it should be noted that the experiments actually yielded the kinematic viscosity η/ρ as a function of pressure and temperature. In deducing values for the dynamic viscosity η , an uncertainty is introduced due to the fact that the densities have to be calculated from the given pressures and temperatures. In the original publications of Rivkin and coworkers, the 1968 IFC Formulation for Scientific and General Use [44, 45] was used for this purpose. However, there are problems with the accuracy of this equation of state in the critical region.

The thermodynamic behavior of fluids, including steam, in the vicinity of the critical point can be characterized in terms of scaling laws [46, 47]. We



Fig. 1. Dynamic viscosity of steam near the critical point deduced from the experiments of Rivkin and coworkers when the densities are calculated from the 1968 IFC Formulation for Scientific and General Use.

have reevaluated the experimental data of Rivkin et al. by calculating the densities from a scaled equation of state. For this purpose we used a parametric equation of state formulated by Murphy and coworkers [48], which is based on the so-called restricted linear model, first proposed by Schofield et al. [49]. In this approach one replaces the physical variables $\Delta \tilde{T}$ and $\Delta \tilde{\rho}$ by parametric variables r and θ such that

$$\Delta \tilde{T} = (T - T_c)/T_c = r(1 - b^2 \theta^2)$$
(6a)

$$\Delta \tilde{\rho} = (\rho - \rho_c) / \rho_c = r^\beta k \theta \tag{6b}$$

In terms of the new parametric variables, the pressure is represented as

$$\Delta \tilde{P} = (P - P_c) / P_c = a r^{\beta \delta} \theta (1 - \theta^2) + a k r^{\beta(\delta+1)} \{ \theta^2 (1 - \theta^2) - f_0 - f_2 \theta^2 - f_4 \theta^2 \} + \sum_{i=1}^3 \tilde{P}_i (\Delta \tilde{T})^i$$
⁽⁷⁾

with

$$f_{0} = -\frac{\beta(\delta - 3) - b^{2}\alpha\gamma}{2b^{4}(2 - \alpha)(1 - \alpha)\alpha}$$

$$f_{2} = +\frac{\beta(\delta - 3) - b^{2}\alpha(1 - 2\beta)}{2b^{2}\alpha(1 - \alpha)}$$

$$f_{4} = -\frac{1 - 2\beta}{\alpha}$$
(8)

Here α , β , γ , δ are critical exponents for the specific heat, coexistence curve, compressibility, and chemical potential, respectively, while the constants a, b^2 , and k are related to the amplitudes of the critical power laws. Further details can be found in a recent review [47].

Upon approaching the critical point, a fluid is expected to satisfy scaling laws with universal critical exponent values that are the same for all so-called Ising-like systems [50, 54]. However, it turns out that the asymptotic range of the validity of the theoretical equation is small and restricted to approximately $|\Delta \tilde{T}| \leq 10^{-4}$ [51, 55]. When covering a larger range, the theory predicts the presence of additional revised and extended scaling terms [51, 56]. However, in this paper we follow a practical approach by retaining the simple equation of state defined by (6) and (7), but using effective critical exponent values [46, 47]. In Table II we have listed the critical-region parameters thus deduced by Murphy et al. [48] from the equation of state

Critical parameters	$ ho_c = 324.383 \text{ kg/m}^3$ $P_c = 22.0477 \text{ MPa}$ $T_c = (\text{sec text})$
Critical exponents	$ \begin{array}{l} \alpha = 0.08712 \\ \beta = 0.3505 \\ \gamma = 1.2119 \\ \delta = 4.45757 \\ \nu = 0.6367 \end{array} $
Linear model parameters	a = 24.0999 k = 1.6837 $b^2 = 1.40991$
Coefficients \tilde{P}_i	$\tilde{P}_1 = 7.87425$ $\tilde{P}_2 = -25.8448$ $\tilde{P}_3 = 3.96522$
Correlation length amplitude	$\xi_0 = 1.31 \times 10^{-10} \mathrm{m}$

Table II. Parameters in Critical Region Equations for Steam

Note: $2 - \alpha = \beta (\delta + 1), \gamma = \beta (\delta - 1), \nu = \beta (\delta + 1)/3, b^2 = (\delta - 3)/(\delta - 1) (1 - 2\beta).$

data of Rivkin and coworkers [57, 58]. These parameters satisfy the exponent relations

$$2 - \alpha = \beta(\delta + 1), \qquad \gamma = \beta(\delta - 1) \tag{9}$$

and the condition for the restricted linear model [47, 49]

$$b^{2} = \frac{\delta - 3}{(\delta - 1)(1 - 2\beta)}$$
(10)

This equation of state has been generalized by Levelt Sengers to a fundamental equation for the critical regions of steam [59]. The equation may be used in a range of temperatures and densities bounded by

$$|\Delta \tilde{T}| \le 0.05, \qquad |\Delta \tilde{\rho}| \le 0.25 \tag{11}$$

which encompasses the region where the viscosity becomes anomalous. Outside the range bounded by (11) we have continued to use the 1968 IFC formulation [44].

The viscosity values thus deduced from the experimental data using $T_c = 646.996$ K [48] are plotted as a function of density in Fig. 2. Since the temperatures of Rivkin's data, as well as the temperatures used in formulat-



Fig. 2. Dynamic viscosity of steam near the critical point deduced from the experiments of Rivkin and coworkers when in the critical region the densities are calculated from a scaled equation of state with $T_c = 646.996$ K.

ing the international viscosity equation recommended by IAPS, refer to the international practical temperature scale of 1948, we have continued to express the temperatures in terms of IPTS-48 in this paper. Recommendations for the use of the resulting equations in terms of IPTS-68 are discussed elsewhere [60].

Since the point of singularity is the critical point, we expect that at a given temperature sufficiently close to T_c the anomalous viscosity $\Delta \eta/\bar{\eta}$ will reach a maximum at the critical density. This expectation is confirmed by measurements for fluids such as nitrogen [5], and ethylene and carbon dioxide [6], where the density was measured directly. On the other hand, from Figs. 1 and 2 we see that this condition is not satisfied for the dynamic viscosities deduced from Rivkin's data. In our experience this behavior is an indication that we did not attribute the correct densities to the data points. The analysis is sensitive to the value adopted for the critical temperature T_c . In the procedure discussed above we have used the same value for T_c as that deduced by Murphy and coworkers by fitting the linear model equation of state to Rivkin's PVT data [48]. However, because of the possibility of temperature gradient and other systematic errors, a careful analysis of experimental data near the critical point should preferably be conducted with a value for T_c determined in the same experiment. In the absence of such a



Fig. 3. Dynamic viscosity of steam near the critical point deduced from the experiments of Rivkin and coworkers when the densities in the critical region are calculated from a scaled equation of state with $T_c - 646.956$ K. The curves indicate the values calculated from the representative equation proposed in this paper.

determination we have reanalyzed the experimental viscosity data using T_c as an adjustable parameter. As the most probable value of T_c corresponding to the experimental viscosity data, we adopted $T_c = 646.956$ K. This value differs by 0.04 K from the value deduced by Murphy and coworkers from the equation of state data. This difference is to be compared with a claimed accuracy of 0.02 K in the measured temperature and 0.01 MPa in the measured pressure which, dP/dT being 0.27 MPa/K at the critical point, yields an overall accuracy of 0.06 K in temperature. Thus the difference between the two critical temperatures is well within the claimed experimental accuracy.

In Fig. 3 we present the dynamic viscosity deduced from the original data of Rivkin and coworkers [7, 8], adopting $T_c = 646.956$ K. A tabulation of the reevaluated data will be published elsewhere [60]. These reevaluated data have been used in the subsequent analysis.

Additional experimental viscosity data for steam in the critical region obtained using an oscillating disk viscometer have been reported by Oltermann [9]. Among the many data reported, only a few data points fall in the range where an anomalous critical viscosity enhancement is observed. However, these data yield important supplementary information to determine the normal viscosity $\bar{\eta}$ in the critical region.

4. PROPOSED EQUATION FOR CRITICAL VISCOSITY ENHANCEMENT

The theoretical equation (5) for the viscosity ratio $\eta/\bar{\eta}$ represents the asymptotic behavior when $q\xi \gg 1$, i.e. when the system is sufficiently close to the critical temperature and density. The question arises as to how close to the critical point will this equation become rigorously valid. As mentioned earlier, in the case of the thermodynamic properties, the asymptotic scaling behavior with theoretically calculated critical exponents is restricted to a range of about 10^{-4} in $|\Delta \tilde{T}|$, which for steam corresponds to $|T - T_c| < 0.1$ K. Since in deriving (5), use is made of the theoretical results for the equilibrium correlation function, the strict range of validity of (5) will be at least as small. However, the situation may be worse. In deriving a theoretical value for the critical viscosity exponent ϕ [34], it is also asumed that $\Delta \eta \gg \bar{\eta}$ (i.e., $\eta/\bar{\eta} \gg 1$), a condition that is not satisfied for steam unless the critical temperature is approached even more closely. Therefore, just as in the case of the equation of state, where we used a scaled equation with effective exponent values, we take a practical approach by adopting (5) for all values of $q\xi > 1$, but treating q and ϕ as adjustable parameters to be deduced from the experimental data. Furthermore, to connect the behavior of the anomalous viscosity with that of the normal viscosity, we neglect the viscosity enhancement for $q\xi \le 1$, so that

$$\eta = \overline{\eta}(q\xi)^{\phi} \quad \text{for} \quad q\xi > 1$$

$$\eta = \overline{\eta} \qquad \text{for} \quad q\xi \le 1$$
(12)

The same equation was previously shown to represent the critical viscosity enhancement observed for nitrogen [27]. It may be possible to consider a refined analysis including correction terms in the future. However, because of uncertainties in the present experimental data, as discussed in the preceding section, such an analysis does not appear warranted at this time. Since such correction terms are now effectively hidden in (12), the effective exponent ϕ may be slightly smaller than the value predicted theoretically and may vary somewhat from fluid to fluid.

From (4) we note that the parameter q may in fact be a slowly varying function of temperature and density. In our approach q is treated as an effective constant. In the absence of direct experimental information for the correlation length of steam, we calculate ξ from an approximate equation [47],

$$\xi = \xi_0 (\tilde{\chi}_T / \Gamma)^{\nu / \gamma} \tag{13}$$

where ξ_0 and $\Gamma = k/a$ are the amplitudes of the critical power laws for ξ and

 $\tilde{\chi}_{T}$, and where the exponent v is related to β and γ by

$$\nu = (2\beta + \gamma)/3 \tag{14}$$

The values adopted for the correlation length parameters [47] are included in Table II. Using the restricted linear model, (13) becomes

$$\xi = \xi_0 r^{-\nu} \left[1 + \left(\frac{2\beta \delta - 3}{1 - 2\beta} \right) \theta^2 \right]^{-\nu/\gamma}$$
(15)

We have used Eq. (12) to determine an effective critical viscosity exponent ϕ for a variety of fluids, namely, nitrogen, xenon, ethane, ethylene, and carbon dioxide, and found the exponent ϕ to lie between 0.045 and 0.06 [27], in agreement with values quoted by other authors for fluids near the gas-liquid critical point [61]. An exception is a somewhat smaller effective value of ϕ implied by the viscosity data of Iwasaki and Takahashi for carbon dioxide.

We conclude this section by indicating the relationship proposed here and those proposed by other investigators. D'Arrigo and coworkers have used (3) to represent the anomalous behavior of the viscosity of the binary liquid aniline-cyclohexane near the critical mixing point as a function of temperature and concentration, again treating q as an effective constant [62].

Upon substituting (13) into (12), we conclude that in our approach the viscosity ratio $\eta/\bar{\eta}$ will scale as $\tilde{\chi}_T^{\nu\phi/\gamma}$ in the critical region. Using different theoretical arguments, the same scaling function was recently proposed by Peliti and Calmettes [63].

5. RESULTS OF ANALYSIS

In accordance with (12) we represent the dynamic viscosity of water and steam by

$$\eta(\rho, T) = \overline{\eta}(\rho, T)(q\xi)^{\phi} \quad \text{for} \quad q\xi > 1$$

= $\overline{\eta}(\rho, T) \qquad \text{for} \quad q\xi \le 1$ (16)

In order to represent the normal viscosity $\bar{\eta}(\rho,T)$ as a function of density and temperature, we adopt a form similar to the one recommended by IAPS [10–15]:

$$\overline{\eta}(\rho, T) = \eta_0(T) \exp\left[\rho^* \left\{ \sum_{i=0}^{j} \sum_{j=0}^{j} a_{ij} (T^{*-1} - 1)^i (\rho^* - 1)^j \right\} \right]$$
(17)

Table III. Coefficients a_k in Eq. (19) for $\eta_0(T)$

		$a_0 = 0.018 \ 158 \ 3$ $a_1 = 0.017 \ 762 \ 4$ $a_2 = 0.010 \ 528 \ 7$ $a_3 = -0.003 \ 674 \ 4$	
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where $T^* = T/T_r$ and $\rho^* = \rho/\rho_r$ are dimensionless temperatures and densities in terms of the reference values

$$T_r = 647.27 \text{ K}, \qquad \rho_r = 317.763 \text{ kg/m}^3$$
 (18)

For the function $\eta_0(T)$, which represents the viscosity in the low density limit as a function of temperature, we continued to use an equation proposed by Aleksandrov et al. [64] and incorporated in the current international equation:

$$\frac{\eta_0(T)}{10^{-6} \mathrm{Pa} \cdot \mathrm{s}} = T^{*1/2} \left[\sum_{k=0}^3 \left(\frac{a_k}{T^{*k}} \right) \right]^{-1}$$
(19)

The coefficients a_k in this equation are reproduced in Table III.

However, using the values of the coefficients a_{ii} in (17) recommended by IAPS [10-15], we noticed that Eq. (17) does not represent the normal viscosity in the critical region with sufficient accuracy to analyze the critical viscosity enhancement. Furthermore, it appears that in developing the current international equation, many more terms with nonvanishing coefficients a_{ii} were retained than necessary. Hence it became desirable to redetermine optimum values for the coefficients a_{ii} in (17). For this purpose, Eqs. (16) and (17) were fitted to all available critically evaluated viscosity data of water and steam. It was found that in the same range of temperatures and pressures covered by the current international equation, the experimental viscosity data could be represented using only 19 nonvanishing coefficients listed in Table IV. This number of 19 nonzero coefficients a_{ij} is substantially smaller than the 30 nonzero coefficients a_{ii} in the international equation. The details of the fitting procedure, as well as a comprehensive comparison of Eq. (17) with the available experimental data outside the critical region, will be published elsewhere [60]. Here we restrict ourselves to a discussion of the behavior of the viscosity in the critical region.

In Fig. 4 we have plotted $\ln(\eta/\bar{\eta})$ in the region of the critical anomaly as deduced from the experiments of Rivkin and coworkers as a function of $\ln\xi$ with $\bar{\eta}$ evaluated from (17) and (19) with the coefficients listed in Tables III and IV. The slope of the line approximating the experimental behavior yields

i	j	a _{ij}
0 1	0 0	$a_{00} = 0.513\ 204\ 7$ $a_{10} = 0.320\ 565\ 6$
4 5	0 0	$a_{40} = -0.778\ 256\ 7$ $a_{50} = 0.188\ 544\ 7$
0 1 2 3	1 1 1	$a_{01} = 0.215 177 8$ $a_{11} = 0.731 788 3$ $a_{21} = 1.241 044$ $a_{22} = 1 476 783$
0 1 2	2 2 2	$a_{02} = -0.281 810 7$ $a_{12} = -1.070 786$ $a_{22} = -1.263 184$
0 1 2 3	3 3 3 3	$a_{03} = 0.177\ 806\ 4$ $a_{13} = 0.460\ 504\ 0$ $a_{23} = 0.234\ 037\ 9$ $a_{33} = -0.492\ 417\ 9$
0 3	4	$a_{04} = -0.041\ 766\ 10$ $a_{34} = -0.160\ 043\ 5$
1 3	5 6	$a_{15} = -0.015\ 783\ 86$ $a_{36} = -0.003\ 629\ 481$

Table IV. Coefficients a_{ij} in Eq. (17) for $\overline{\eta}(\rho, T)$



Fig. 4. The logarithm of $\eta/\overline{\eta}$ near the critical point as a function of the logarithm of ξ .

the exponent ϕ , and the intercept with the abscissa at $\ln(\eta/\bar{\eta}) = 0$ yields the constant q^{-1} . In analyzing the experimental data in the critical region, we estimated the error σ in the viscosity from

$$\sigma^{2} = \sigma_{\eta}^{2} + \left(\frac{\partial\eta}{\partial P}\right)_{T}^{2} \sigma_{P}^{2} + \left(\frac{\partial\eta}{\partial T}\right)_{T}^{2} \sigma_{T}^{2}$$
(20a)

with

$$\sigma_{\eta} = 0.01\eta, \qquad \sigma_{\rho} = 0.01 \text{ MPa}, \qquad \sigma_{T} = 0.02 \text{ K}$$
(20b)

as given by Rivkin and coworkers [7, 8]. We varied q and ϕ (and also T_c as discussed earlier) and concluded

$$\phi = 0.05 \pm 0.01$$

$$q^{-1} = (26.6 \pm 6) \times 10^{-10} \text{ m}$$

$$T_c = (646.956 \pm 0.04) \text{ K}$$
(21)

The value $\phi = 0.05 \pm 0.01$ may be compared with the theoretical values quoted in Table I. The value $q^{-1} = (26.6 \pm 6) \times 10^{-10}$ m may be compared with the value $q^{-1} = (26 \pm 3) \times 10^{-10}$ m deduced from (4) in the range of densities and temperatures under consideration.

The values of the viscosity in the critical region calculated from (16), with

$$\phi = 0.05, \qquad q^{-1} = 26.6 \times 10^{-10} \,\mathrm{m}$$
 (22)

are represented by the solid curves in Fig. 3. The percentage difference between the experimental and calculated viscosity data in the critical region are shown in Fig. 5. The equation reproduces the (reevaluated) data with only 5 of the 50 critical region points exceeding the estimated accuracy.

In Fig. 6 we show the deviations of the same data points in the critical region when compared with the values calculated from the current international formulation for viscosity [10–15]. All deviations are positive since the critical viscosity enhancement was neglected in the international formulation.

In our representation the range of the critical viscosity enhancement is determined by $q\xi > 1$, which is located within a region of temperature and densities bounded by [60]

645.30 K < T < 652.55 K, 240 kg/m³ <
$$ho$$
 < 410 kg/m³ (23)



Fig. 5. Comparison of the viscosity data in the critical region with the values calculated from the interpolating equation proposed in this paper.



Fig. 6. Comparison of the viscosity data in the critical region with the values calculated from the current international formulation.

Adopting the parameter values quoted in (22) and using (13), we conclude that Eq. (16) for the critical viscosity enhancement can be written in the form

$$\frac{\eta}{\overline{\eta}} = 0.922 \,\chi_T^{*0.0263} \quad \text{for} \quad \chi_T^* > \chi_0$$

$$\frac{\eta}{\overline{\eta}} = 1 \qquad \qquad \text{for} \quad \chi_T^* \le \chi_0$$
(24)

where the constant χ_0 is chosen such that

$$0.922 \,\chi_0^{\ 0.0263} = 1 \tag{25}$$

6. CONCLUSIONS

Upon reevaluating the experiments of Rivkin et al., it is found that the critical viscosity enhancement observed for steam is in reasonable agreement with current theoretical predictions. An effective representation of the viscosity in the critical region can be incorporated into an equation of the normal viscosity $\bar{\eta}$ outside the critical region by the simple approximation

$$\eta = \tilde{\eta}(q\xi)^{\phi} \quad \text{for } q\xi > 1 \tag{26}$$

with the values of q and ϕ given in (22).

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NOMENCLATURE

- *a* critical region equation of state parameter
- a_k coefficients in equation for η_0

- coefficients in equation for $\bar{\eta}$ a_{ii}
- critical region equation of state parameter b
- specific heat at constant pressure C_p
- specific heat at constant volume C_{v}
- k critical region equation of state parameter
- Boltzmann constant k_R
- Р pressure
- 22.115 MPa Ρ,
- P* P/P_r
- critical pressure
- P_c \tilde{P}_i coefficients in critical region equation of state

 $\Delta \tilde{P}$ $(P-P_c)/P_c$

- parameter in equation for critical viscosity enhancement q
- parametric variable in critical region equation of state r
- temperature in K (IPTS-48) Т
- Τ, 647.27 K
- T^* T/T_r
- T_{c} critical temperature

$$\Delta \tilde{T} (T - T_c)/T_c$$

V volume

- critical exponent of specific heat α
- β critical exponent of coexistence curve
- critical exponent of compressibility γ
- critical exponent of chemical potential at $T = T_c$ δ
- dynamic viscosity η
- $\lim_{n\to 0} \eta$ η_0
- normal viscosity $\bar{\eta}$
- critical viscosity enhancement $\Delta \eta$
- thermal conductivity λ
- λ normal thermal conductivity
- $\Delta\lambda$ critical thermal conductivity enhancement
- parametric variable in critical region equation of state θ
- correlation length ξ
- correlation length amplitude above T_c at $\rho = \rho_c$ ξ0
- critical exponent of correlation length v
- density ρ
- 317.763 kg/m³ ρ_r
- ρ^* ρ/ρ_r
- critical density ρ_c

 $\Delta \tilde{
ho}$ $(\rho - \rho_c)/\rho_c$

- estimated error of pressure σ_p
- estimated error of temperature σ_T

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- σ_{η} estimated error of viscosity
- ϕ exponent of critical viscosity enhancement
- $\chi_T = \rho (\partial \rho / \partial P)_T =$ "symmetrized" compressibility
- $\chi_T^* = \chi_T P_r / \rho_r^2$
- $\tilde{\chi}_T = \chi_T P_c / \rho_c^2$

REFERENCES

- J. V. Sengers, in Critical Phenomena, NBS Misc. Publ. 273, M. S. Green and J. V. Sengers, eds. (U.S. Gov't. Printing Office, Washington, D.C., 1966), pp. 165–178.
- J. V. Sengers, in Critical Phenomena, Proc. Int. School "Enrico Fermi," Course LI, M. S. Green, ed. (Academic, New York, 1971), pp. 445-507.
- 3. J. Kestin, J. H. Whitelaw, and T. F. Zien, Physica 30: 161 (1964).
- 4. H. J. Strumpf, A. F. Collings, and C. J. Pings, J. Chem. Phys. 60: 3109 (1974).
- 5. V. N. Zozulya and Yu. P. Blagoi, Sov. Phys.-JETP 39: 99 (1974).
- 6. H. Iwasaki and M. Takahashi, in *Proc. 4th Int. Conf. High Pressure* (Kyoto, 1974), pp. 523–529; and to be published.
- S. L. Rivkin, A. Ya. Levin, L. B. Izrailevsky, and K. G. Kharitonov, in *Proc. 8th Int. Conf.* Properties of Water and Steam, P. Bury, H. Perdon, and B. Vodar, eds. (Editions Europeénnes Thermiques et Industries, Paris, 1975), pp. 153-162.
- 8. S. L. Rivkin, A. Ya. Levin, and L. B. Izrailevsky, *Teplofiz. Svoistva Veshchestv i* Materialov 10: 232 (1976).
- 9. G. Oltermann, Messung der Viskosität von Wasserdampf in der Nähe des Kritischen Zustandes (Dissertation, Technische Universität, Hannover, 1977).
- R. C. Hendricks, R. B. McClintock, and G. J. Silvestri, J. Eng. Power, Trans. ASME 99: 664 (1977).
- 11. C. A. Meyer, R. B. McClintock, G. J. Silvestri, and R. C. Spencer, *ASME Steam Tables*, 3rd edn. (American Society of Mechanical Engineers, New York, 1977).
- 12. A. Nagashima, J. Phys. Chem. Ref. Data 6: 1133 (1977); 7: 1755 (1978).
- 13. A. A. Aleksandrov, Teploenergetika 24(4): 87 (1977).
- 14. K. Scheffler, N. Rosner, J. Straub, and U. Grigull, Brennst-Wärme-Kraft 30: 73 (1978).
- 15. E. Schmidt, Properties of Water and Steam in SI-Units, 2nd edn., U. Grigull, ed. (Springer-Verlag, New York, 1979).
- 16. J. Kestin, in Proc. 9th Int. Conf. Properties of Steam (Pergamon, in press).
- 17. R. S. Basu and J. V. Sengers, in *Proc. 8th Symp. Thermophys. Properties*, A. Cezairliyan, ed. (American Society of Mechanical Engineers, New York, 1977), pp. 822-830.
- K. Kawasaki, in Critical Phenomena, Proc. Int. School "Enrico Fermi," Course LI, M. S. Green, ed. (Academic, New York, 1971), pp. 342-379.
- 19. R. Perl and R. A. Ferrell, Phys. Rev. A6: 2358 (1972).
- J. V. Sengers, in *Transport Phenomena-1973, AIP Conf. Proc. no. 11*, J. Kestin, ed. (American Institute of Physics, New York, 1973), pp. 229–277.
- 21. K. Kawasaki, in *Phase Transitions and Critical Phenomena*, Vol. 5A, C. Domb and M. S. Green, eds. (Academic, New York, 1976), pp. 165-403.
- 22. T. Ohta, J. Phys. C10: 791 (1977).
- 23. P. Calmettes, Phys. Rev. Lett. 39: 1151 (1977).
- 24. D. Beysens, S. H. Chen, J. P. Chabrat, L. Letamendia, J. Rouch, and C. Voucamps, J. Physi. Lett. 38: L203 (1977).
- 25. L. P. Kadanoff and J. Swift, Phys. Rev. 166: 89 (1968).
- 26. D. W. Oxtoby and W. M. Gelbart, J. Chem. Phys. 61: 2957 (1974).
- 27. R. S. Basu and J. V. Sengers, J. Heat Transfer, Trans. ASME 101: 3 (1979); 101: 575 (1979).
- 28. K. Kawasaki and S. M. Lo, Phys. Rev. Lett. 29: 48 (1972).
- 29. S. M. Lo and K. Kawasaki, Phys. Rev. A5: 421 (1972); A8: 2176 (1973).

- 30. T. Ohta, Progr. Theor. Phys. 54: 1566 (1975).
- 31. D. W. Oxtoby, J. Chem. Phys. 62: 1463 (1975).
- 32. K. Kawasaki and J. D. Gunton, Phys. Lett. 53A: 119 (1975).
- 33. F. Garisto and R. Kapral, J. Chem. Phys. 63: 3560 (1975); 64: 3826 (1976).
- 34. F. Garisto and R. Kapral, Phys. Rev. A14: 884 (1976).
- 35. T. Ohta and K. Kawasaki, Progr. Theor. Phys. 55: 1384 (1976).
- 36. J. K. Bhattacharjee and R. A. Ferrell, Phys. Lett. 76A: 290 (1980).
- 37. E. D. Siggia, B. I. Halperin, and P. C. Hohenberg, Phys. Rev. B13: 2110 (1976).
- 38. K. Kawasaki and J. D. Gunton, Phys. Rev. B13: 4658 (1976).
- 39. J. D. Gunton and K. Kawasaki, Progr. Theor. Phys. 56: 61 (1976).
- 40. P. C. Hohenberg and B. I. Halperin, Revs. Mod. Phys. 49: 435 (1977).
- 41. C. De Dominicis and L. Peliti, Phys. Rev. B18: 353 (1978).
- M. H. Ernst, in *Fundamental Problems in Statistical Mechanics IV*, E. G. D. Cohen and W. Fiszdon, eds. (Zaklad Narodowy im. Ossolinskich-Wydawnictwo, Wroclaw, Poland, 1978), pp. 161-197.
- 43. J. D. Gunton, in *Dynamical Critical Phenomena and Related Topics*, C. P. Enz, ed. (Springer-Verlag, New York, 1979), pp. 1–24.
- 44. The 1968 IFC Formulation for Scientific and General Use (American Society of Mechanical Engineers, New York, 1968).
- 45. S. L. Rivkin, A. A. Aleksandrov, and E. A. Kremenevskaya, *Thermodynamic Derivatives* for Water and Steam (Halsted Press, Wiley, New York, 1978).
- 46. J. M. H. Levelt Sengers, W. L. Greer, and J. V. Sengers, J. Phys. Chem. Ref. Data 5: 1 (1976).
- J. V. Sengers and J. M. H. Levelt Sengers, in *Progress in Liquid Physics*, C. A. Croxton, ed. (Wiley, New York, 1978), pp. 103-174.
- 48. T. A. Murphy, J. V. Sengers, and J. M. H. Levelt Sengers, in *Proc. 8th Int. Conf. Properties of Water and Steam*, P. Bury, H. Perdon, and B. Vodar, eds. (Editions Européennes Thermiques et Industries, Paris, 1975), pp. 603-613.
- 49. P. Schofield, J. D. Litster, and J. T. Ho, Phys. Rev. Lett. 23: 1098 (1969).
- 50. J. Hubbard and P. Schofield, Phys. Lett. 40A: 111 (1972).
- 51. M. Ley-Koo and M. S. Green, Phys. Rev. A16: 2483 (1977).
- 52. J. M. H. Levelt Sengers, in *Proc. 7th Symp. Thermophys. Properties*, A. Cezairliyan, ed. (American Society of Mechanical Engineers, New York, 1977), pp. 766–773.
- 53. M. R. Moldover, J. V. Sengers, R. W. Gammon, and R. J. Hocken, *Revs. Mod. Phys.* 51: 79 (1979).
- 54. J. F. Nicoll, Phys. Lett. 76A: 112 (1980).
- 55. J. M. H. Levelt Sengers, R. Hocken, and J. V. Sengers, *Physics Today* 30(12): 42 (1977).
- F. W. Balfour, J. V. Sengers, M. R. Moldover, and J. M. H. Levelt Sengers, Phys. Lett. 65A: 223 (1978).
- 57. S. L. Rivkin and T. S. Akhundov, Teploenergetika 9(1): 57 (1962); 10(9): 66 (1963).
- 58. S. L. Rivkin, T. S. Akhundov, E. A. Kremenevskaya, and N. N. Asadullaeva, *Thermal Eng.* 13(4): 77 (1966).
- J. M. H. Levelt Sengers, in Proc. 7th Symp. Thermophys. Properties, A. Cezairliyan, ed. (American Society of Mechanical Engineers, New York, 1977), pp. 774–785.
- 60. J. T. R. Watson, R. S. Basu, and J. V. Sengers, J. Phys. Chem. Ref. Data, in press.
- 61. S. P. Lee, Chem. Phys. Lett. 57: 611 (1978).
- G. D'Arrigo, L. Mistura, and P. Tartaglia, J. Chem. Phys. 66: 80 (1977); in Proc. 7th Symp. Thermophys. Properties, A. Cezairliyan, ed. (American Society of Mechanical Engineers, New York, 1977), pp. 831-835.
- 63. P. Calmettes, J. Physi. Lett., 40: L535 (1979).
- 64. A. A. Aleksandrov, A. I. Ivanov, and A. B. Matveev, Thermal Eng. 22 (4): 77 (1975).