PHYSICAL REVIEW A VOLUME 24, NUMBER 3 SEPTEMBER 1981

Crossover function for the critical viscosity of a classical fluid

J. K. Bhattacharjee and R. A. Ferrell
Institute for Physical Science and Technology and Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

R. S. Basu* and J. V. Sengers
Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

(Received 13 April 1981)

A closed-form approximant is proposed for the crossover function which connects the asymptotic critical behavior of the viscosity of a fluid with the normal behavior of the viscosity away from the critical point. The expression is used to represent the critical viscosity enhancement near the gas-liquid critical point of fluids as a function of temperature and density.

I. INTRODUCTION

The shear viscosity of classical fluids diverges weakly at the critical point. In order to represent the behavior of the viscosity η in the critical region, it is decomposed into a critical viscosity enhancement $\Delta\eta$ induced by the critical fluctuations, and a normal or bare viscosity $\bar{\eta}$ in the absence of critical fluctuations

$$\eta=\Delta\eta+\bar{\eta}. \tag{1.1}$$

The normal viscosity $\bar{\eta}$ is obtained empirically by extrapolating the behavior of the viscosity outside the critical region into the critical region. Kawasaki[1] and Perl and Ferrell[2] derived an equation for the critical viscosity enhancement yielding a logarithmic divergence. Subsequent refined analyses of the theoretical equations governing critical dynamics have indicated that $\Delta\eta$, in fact, diverges as a power law with a small exponent[3]:

$$\Delta\eta\propto\xi^{x_\eta}, \tag{1.2}$$

where ξ is the correlation length. The critical exponent x_η is predicted to be universal, i.e., the same for fluids near the gas-liquid critical point and for fluid mixtures near the critical mixing point. The equations of Kawasaki and of Perl and Ferrell imply $x_\eta=8/15\pi^2\simeq 0.054$. Various authors have attempted to obtain a refined theoretical estimate for this exponent.[4-8] The theoretical value currently adopted is

$$x_\eta=0.065. \tag{1.3}$$

This value is obtained when the renormalization-group equations for critical dynamics, as well as the mode-coupling equations for critical dynamics, are expanded up to second order in $\epsilon=4-d$, where d is the dimensionality of the system.[7,8] The exponent x_η is related to the dynamic scaling exponent $z=3+x_\eta$ which characterizes the asymptotic behavior of the decay rate of the order-parameter fluctuations.[3] Recent light scattering experiments in a binary liquid very close to the critical point appear to yield excellent agreement with the theoretical prediction (1.3).[9]

Because small gradients in temperature and pressure induce large gradients in density, it is difficult to measure the viscosity very close to the critical point. This difficulty becomes particularly severe in gases near the gas-liquid critical point. Hence, the question arises whether the actual experimental viscosity data are close enough to the critical point for the predicted power-law behavior to be valid. An examination of the equations for critical dynamics[2,6] indicates that in the derivation of the power-law behavior (1.3) one assumes the critical point to be approached sufficiently close so that the viscosity is dominated by its critical part, i.e., $\Delta\eta\gg\bar{\eta}$. This condition is never satisfied for experimental viscosity data. To alleviate this difficulty it is commonly assumed that the viscosity anomaly is a multiplicative anomaly.[10,11] Thus rather than $\Delta\eta$, it is assumed that the viscosity ratio $\eta/\bar{\eta}$ diverges with the predicted power-law behavior

$$\eta/\bar{\eta}=(Q_0\xi)^{x_\eta}, \tag{1.4}$$

where Q_0 is an effective wave number which determines the amplitude of the power law. Indeed, when one fits experimental viscosity data of binary liquids near the critical mixing point to (1.4), good agreement with the theoretical exponent values $x_\eta\simeq 0.065$ is often found.[11-13]

The situation is more complicated when one wants to interpret experimental viscosity data of fluids near the gas-liquid critical point. Here, the experimentally observed critical viscosity enhancement is small and restricted to a small temperature range. When experimental viscosity data near the gas-liquid critical point are fitted to (1.4) with both Q_0 and x_η as adjustable parameters, it is our experience that the exponent x_η tends to be slightly smaller than the value $x_\eta \simeq 0.065$ found for binary-liquid mixtures. In retrospect, this tendency is also noted in the exponent values quoted by Lee[12] and indicates, in our opinion, that the asymptotic range is not fully approached by the experimental data. To obtain a satisfactory representation of the actual experimental data, one needs a crossover function that incorporates the predicted asymptotic power-law behavior at the critical point and that reduces to the normal viscosity behavior away from the critical point. For this purpose Basu and co-workers introduced the empirical equation[14,15]

$$\ln(\eta/\bar{\eta}) = x_\eta \ln(Q_0\xi)\Theta(Q_0\xi - 1), \tag{1.5}$$

where $\Theta(x)$ is the Heaviside step function such that $\Theta(x) = 1$ for $x > 1$ and $\Theta(x) = 0$ for $x < 1$. However, an empirical step function does not do justice to the smooth onset of the critical viscosity enhancement observed in reality.

A first attempt to solve this problem was made by Oxtoby and Gelbart who obtained a crossover function by integrating numerically the mode-coupling equation for the critical viscosity enhancement.[16] However, it turns out that the crossover implied by their solution is too slow and it does not yield a satisfactory representation of the experimental viscosity data as demonstrated in Sec. IV.

It is the purpose of this paper to present an improved crossover function for the critical viscosity. Moreover, it will be obtained in closed mathematical form so that it can be easily used in the analysis of experimental viscosity data. The critical viscosity enhancement can be expressed formally in terms of an integral over the wave-number-dependent decay rate of the order-parameter fluctuations. In evaluating this integral we treat the effect of the noncritical contribution to the decay rate as indicated by Oxtoby and Gelbart,[16] while retaining the Debye cutoff at large wave numbers introduced by Perl and Ferrell.[2] Using an approximate expression for the critical part of the decay rate, we derive in Sec. II a scaling function for the critical viscosity enhancement. Modifying this solution slightly, so as to ensure consistency with the theoretically predicted asymptotic power-law behavior, we propose an explicit crossover function for the critical viscosity in Sec. III. In Sec. IV we show how the crossover function can be used to obtain a satisfactory representation of the experimental critical viscosity enhancement of a fluid near the gas-liquid critical point as a function of temperature and density.

II. CRITICAL VISCOSITY ENHANCEMENT AND ORDER-PARAMETER FLUCTUATIONS

According to the mode-coupling theory of critical dynamics, the dominant contribution to the critical viscosity enhancement is given by an integral of the form[16]

$$\Delta\eta = \lim_{k\to 0} \frac{k_B T}{2k^2} \frac{1}{(2\pi)^3} \int d\vec{q}\, q^2 \sin^2\theta \sin^2\phi\, \chi(q)\chi(|\vec{k}-\vec{q}|)\left(\frac{1}{\chi(q)} - \frac{1}{\chi(|\vec{k}-\vec{q}|)}\right)^2 \frac{1}{\Gamma(q)+\Gamma(|\vec{k}-\vec{q}|)}\,. \tag{2.1}$$

Here k_B is the Boltzmann constant, T the absolute temperature, θ and ϕ the polar and azimuthal angle of the wave vector $\vec{q}$ in a coordinate system with the polar axis in the direction of $\vec{k}$, $\chi(q)$ the wave-number-dependent susceptibility which is the Fourier transform of the order-parameter correlation function, and $\Gamma(q)$ the decay rate of the order-parameter fluctuations with wave number q. Introducing the Ornstein-Zernike approximation

$$\chi(q) \propto \frac{\xi^2}{1+q^2\xi^2}\,, \tag{2.2}$$

and taking the hydrodynamic limit $k \to 0$, we obtain from (2.1)

$$\Delta\eta = \frac{k_B T}{(2\pi)^3} \int d\vec{q} \sin^2\theta \cos^2\theta \sin^2\phi \left(\frac{q^2\xi^2}{1+q^2\xi^2}\right)^2 \frac{1}{\Gamma(q)}\,, \tag{2.3}$$

which is precisely the decoupled-mode formula derived earlier by Perl and Ferrell for the critical viscosity enhancement.[2]

For binary liquids near the critical mixing point, $\Gamma = Dq^2/\chi$, where D is the binary-diffusion coefficient; for fluids near the gas-liquid critical point, $\Gamma = \lambda q^2/C_p$, where λ is the thermal conductivity and C_p the isobaric heat capacity per unit volume. In view of the intended applications, we adopt in this paper the thermodynamic variables appropriate for the gas-liquid critical region. In analogy to (1.1), the thermal conductivity λ is also decomposed into a critical thermal conductivity enhancement $\Delta\lambda$ and a normal thermal conductivity $\bar{\lambda}$,[17]

$$\lambda = \Delta\lambda + \bar{\lambda}. \tag{2.4}$$

As a consequence, one can distinguish in the decay rate Γ, a critical contribution $\Delta\Gamma$ and a normal contribution $\bar{\Gamma}$:

$$\Gamma = \Delta\Gamma + \bar{\Gamma} \tag{2.5}$$

with

$$\bar{\Gamma} = \frac{\bar{\lambda} q^2}{C_p(q)} \simeq \frac{\bar{\lambda}}{C_p(0)} (1 + q^2\xi^2), \tag{2.6}$$

where $C_p(0)$ is the isobaric heat capacity per unit volume in the thermodynamic limit $q \rightarrow 0$. The term $\bar{\Gamma}$ represents the normal critical slowing down of the fluctuations as predicted by Van Hove in the absence of a critical thermal conductivity enhancement.[18]

The critical decay rate $\Delta\Gamma$ in turn is given by a mode-coupling integral[1] or a decoupled-mode integral[19] over the wave-number-dependent viscosity $\eta(q)$. Hence, to deduce $\Delta\eta$ the two integrals have to be solved simultaneously which requires a cumbersome numerical procedure. In the first approximation one commonly neglects the effect of the critical viscosity enhancement on the decay rate Γ in (2.3). In this approximation[16,19,20]

$$\Delta\Gamma = \frac{k_B T}{6\pi\bar{\eta}\xi} q^2 K_0(q\xi), \tag{2.7}$$

where

$$K_0(x) = \tfrac{3}{4}[1 + x^2 + (x^3 - x^{-1})\arctan x], \tag{2.8}$$

is commonly referred to as the Kawasaki function. With (2.5), (2.6), and (2.7) the integral (2.3) for the critical viscosity enhancement can then be calculated numerically. For our purpose we prefer to rewrite the critical decay rate in the form

$$\Delta\Gamma = \frac{k_B T}{6\pi\bar{\eta}\xi} q^2 (1 + q^2\xi^2)^{1/2} \sigma(q\xi). \tag{2.9}$$

Here $\sigma(x)$ is a dynamical scaling function introduced by Ferrell[20]; it is a function of order unity which varies from $\sigma(0) = 1$ in the hydrodynamic regime to $\sigma(\infty) = 3\pi/8$ in the critical regime. As noted by Perl and Ferrell, the dominant contributions from $\Delta\Gamma$ to $\Delta\eta$ correspond to $q\xi > 1$. Thus to obtain a closed-form expression for $\Delta\eta$, we replace $\sigma(q\xi)$ in (2.9) by its asymptotic value $3\pi/8$ for all $q\xi$. In this approximation the decay rate Γ can be written in the form

$$\Gamma = \frac{k_B T q^2}{16\bar{\eta}\xi} \left((1 + q^2\xi^2)^{1/2} + \frac{1 + q^2\xi^2}{q_C \xi} \right) \tag{2.10}$$

with

$$q_C = \frac{k_B T}{16\bar{\eta}\bar{\lambda}} \frac{C_p(0)}{\xi^2} . \tag{2.11}$$

The wave number q_C measures the importance of the bare thermal conductivity coefficient, relative to that of the critical thermal conductivity, on the decay rate of the order-parameter fluctuations. It is a slowly varying function of temperature and density and related to the parameter a_0 of Oxtoby and Gelbart[16] by $q_C\xi = \pi/2a_0$. To determine the limiting value of q_C at the critical point, we note that $C_p(0)$ diverges as $T\rho^{-2}(\partial P/\partial T)^2_\rho \chi(0)$, where ρ is the density, P the pressure, and $\chi(0) = \rho(\partial\rho/\partial P)_T$. At the critical isochore $\chi(0)P_c/\rho_c^2 = \Gamma^+ |(T - T_c)/T_c|^{-\gamma}$ and $\xi = \xi_0 |(T - T_c)/T_c|^{-\nu}$, where $\gamma = 2\nu$ in the Ornstein-Zernike approximation considered here. Thus

$$\lim_{\substack{T \rightarrow T_c \\ \rho \rightarrow \rho_c}} q_C = \frac{k_B T_c^2}{16\bar{\eta}_c \bar{\lambda}_c P_c^2} \frac{\Gamma^+}{\xi_0^2} \left(\frac{\partial P}{\partial T}\right)^2_{\rho = \rho_c} , \tag{2.12}$$

where T_c, ρ_c, P_c, $\bar{\eta}_c$, and $\bar{\lambda}_c$ refer to the values of T, ρ, P, $\bar{\eta}$, and $\bar{\lambda}$ at the critical point.

To obtain an explicit expression for $\Delta\eta$, we substitute (2.10) into (2.3), integrate over the polar and azimuthal angles and obtain

$$\frac{\Delta\eta}{\bar{\eta}} = \frac{8}{15\pi^2} q_C \xi \int_0^{q_D} dq \left(\frac{q^2\xi^2}{1 + q^2\xi^2}\right)^2 \times \frac{\xi}{1 + q^2\xi^2 + q_C\xi(1 + q^2\xi^2)^{1/2}} , \tag{2.13}$$

where q_D is a final cutoff introduced by Perl and Ferrell.[2] Its presence reflects the physical fact that the critical viscosity enhancement is induced by the long-range fluctuations and is only correctly described by (2.13) for wave numbers substantially larger than those corresponding to the microscopic structure of the fluid.

To evaluate (2.13), we introduce an integration variable ψ defined as

$$\sec\psi = (1 + q^2\xi^2)^{1/2}, \tag{2.14}$$

so that

$$\frac{\Delta\eta}{\bar{\eta}} = \frac{8}{15\pi^2} H, \tag{2.15}$$

where

$$H = q_C \xi \int_0^{\psi_D} \frac{\sin^4\psi \, d\psi}{1 + q_C\xi \cos\psi} \tag{2.16}$$

with

$$\psi_D = \arccos(1 + q_D^2\xi^2)^{-1/2}. \tag{2.17}$$

The integral in (2.16) can be evaluated by elementary techniques and we obtain

$$H = \tfrac{1}{12} \sin 3\psi_D - \frac{1}{4q_C\xi} \sin 2\psi_D + \frac{1}{(q_C\xi)^2} [1 - \tfrac{5}{4}(q_C\xi)^2] \sin\psi_D - \frac{1}{(q_C\xi)^3} \{[1 - \tfrac{3}{2}(q_C\xi)^2]\psi_D - |(q_C\xi)^2 - 1|^{3/2} L(w)\} , \tag{2.18}$$

where the function $L(w)$ is given by

$$L(w)=\begin{cases}\ln\dfrac{1+w}{1-w}\,, & \text{for } q_C\xi>1\\[4pt] 2\arctan|w|\,, & \text{for } q_C\xi<1\end{cases} \tag{2.19}$$

with

$$w=\left|\frac{q_C\xi-1}{q_C\xi+1}\right|^{1/2}\tan\frac{\psi_D}{2}\,. \tag{2.20}$$

We find it convenient to introduce a dimensionless correlation length $q_0\xi$, where q_0 is an effective wave number defined as

$$q_0^{-1}=q_C^{-1}+q_D^{-1}, \tag{2.21}$$

and prefer to consider the function $H=H(q_0\xi, q_D/q_C)$ as a function of $q_0\xi$ and of the ratio q_D/q_C. In the extreme critical region $q_0\xi\gg 1$ and the function H has the asymptotic behavior

$$\lim_{q_0\xi\to\infty} H=\ln(2q_0\xi)-\tfrac{4}{3}, \tag{2.22}$$

indicated by the dashed line in Fig. 1. The limit considered by Oxtoby and Gelbart[16] corresponds to $q_D/q_C\to\infty$. In this limit $q_0\xi=q_C\xi$ and (2.18) reduces to

$$H(q_0\xi,\infty)=-\frac{4}{3}+\frac{1}{(q_0\xi)^2}\left(1+\frac{3\pi}{4}q_0\xi\right) -\frac{1}{(q_0\xi)^3}\left(\frac{\pi}{2}-|(q_0\xi)^2-1|^{3/2}L(w)\right) \tag{2.23}$$

with

$$w=\left|\frac{q_0\xi-1}{q_0\xi+1}\right|^{1/2}. \tag{2.24}$$

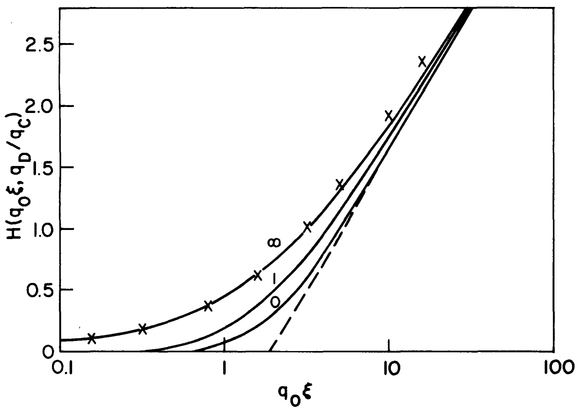

FIG. 1. Plot of the function $H(q_0\xi, q_D/q_C)$ as a function of $q_0\xi$ for various values of q_D/q_C, namely, $q_D/q_C=0, 1, \infty$. The dashed curve represents the limiting behavior $\ln(Q_0\xi)$ with $Q_0=2q_0e^{-4/3}$. The crosses represent values obtained numerically in the limit $q_D/q_C=\infty$ as discussed in the text.

This function is represented by the curve marked ∞ in Fig. 1. In this limit our function is an approximant to the crossover function proposed in numerical form by Oxtoby and Gelbart; the crosses in Fig. 1 indicate the values that are obtained numerically from (2.3) in the limit $q_D\to\infty$ when one uses (2.7) instead of (2.9) in the expression for $\Delta\Gamma$. Our crossover function has the advantage of having a closed mathematical form and is, therefore, more convenient in the representation of experimental viscosity data.

The limit $q_D/q_C\to 0$ corresponds to the case in which the effect of the background decay rate on the viscosity is neglected, as was done by Perl and Ferrell.[2] In this limit $q_0\xi=q_D\xi$ and we obtain

$$H(q_0\xi,0)=\ln\left(\frac{(1+q_0^2\xi^2)^{1/2}+q_0\xi+1}{(1+q_0^2\xi^2)^{1/2}-q_0\xi+1}\right) -\frac{q_0\xi}{(1+q_0^2\xi^2)^{1/2}}-\frac{q_0^3\xi^3}{3(1+q_0^2\xi^2)^{3/2}}\,. \tag{2.25}$$

This function is indicated in Fig. 1 by the curve marked 0. The curves marked ∞ and 0 form the limiting cases of a family of curves obtained by varying the ratio q_D/q_C. For arbitrary q_D/q_C one has to use (2.17) and (2.18) to calculate H as a function of $q_0\xi$. For $q_D/q_C=1$ the result is represented in Fig. 1 by the curve marked 1. Physically one must expect q_D/q_C to be finite. This is the reason why the Oxtoby-Gelbart limit $q_D/q_C\to\infty$ overestimates the range of the critical viscosity enhancement.

We also considered the effect of introducing a cutoff wave number q_D in the mode-coupling integral for the decay rate Γ. As a first estimate, such a cutoff yields a term of about $(k_BTq^2/16\bar{\eta}\xi)\times(1+q^2\xi^2)/2q_D$ to be subtracted from (2.7) or (2.9). In this approximation we can combine this term with the background contribution in (2.10) by reinterpreting q_C. Since in this paper q_C is not calculated theoretically, but deduced from the background data estimated experimentally, it does not modify the procedure presented here.

III. PROPOSED CROSSOVER FUNCTION

From (1.1) and (2.15) it follows that the viscosity in the critical region is given by

$$\frac{\eta}{\bar{\eta}}=1+\frac{8}{15\pi^2}H. \tag{3.1}$$

In the extreme critical region, (3.1) implies a logarithmic divergence originally derived by Kawasaki[1] and Perl and Ferrell.[2] However, as noted in the introduction, a more refined analysis[7,8] as well as experimental evidence[11-13] indicates that the viscosity η diverges asymptotically as a power law (1.3). To make our approximant consistent with the asymptotic power-law divergence, we treat the right-hand side of (3.1) as the first two terms of the expansion of an exponential function, so that

$$\frac{\eta}{\overline{\eta}} = \exp(x_\eta H). \tag{3.2}$$

Here we have identified $8/15\pi^2$ as the first approximation to the critical exponent x_η. Equation (3.2) is our proposed crossover function. From (2.22) it follows that (3.2) diverges in the limit $\xi \to \infty$ as $\eta/\overline{\eta} = (Q_0\xi)^{x_\eta}$, where the constant Q_0 in (1.4) is identified with

$$Q_0 = 2q_0 e^{-4/3} = 0.53q_0. \tag{3.3}$$

In the limit $\xi \to 0$, the function H vanishes as $\frac{1}{5}(q_C\xi)(q_D\xi)^5$ so that $\eta/\overline{\eta}$ approaches unity. In the Oxtoby-Gelbart limit $q_D \to \infty$, H vanishes as $3\pi q_C\xi/16$ which leads to a much slower decay of the critical viscosity enhancement.

The approximant (3.2) relates the critical viscosity ratio $\eta/\overline{\eta}$ to the correlation length with two system-dependent parameters, namely, q_D and q_C. These parameters are slowly varying functions of density and temperature which we treat as constants, q_C being identified with its critical value given by (2.12). Thus Eq. (3.2) with (2.12) and (2.18) allows us to represent the critical viscosity enhancement in terms of the correlation length, the equation of state, and the normal viscosity and thermal conductivity in the absence of critical fluctuations, leaving q_D as the only adjustable parameter.

IV. APPLICATION

As an application we reconsider the critical viscosity enhancement observed for nitrogen and steam which we previously analyzed in terms of the more primitive equation (1.5), using both Q_0 and x_η as adjustable parameters.[14,15] Instead, we now impose the value $x_\eta = 0.065$ as predicted theoretically[7,8] and confirmed by light scattering measurements for a binary liquid very close to the critical point.[9]

In order to analyze the experimental viscosity data in terms of (3.2), we need to know the correlation length as a function of both temperature and density. In principle, this correlation length can be determined experimentally from light scattering measurements. However, adequate sets of correlation length data covering the experimental range of temperatures and densities are currently not available. In the absence of such information, we estimate the correlation length from an approximate relationship with the compressibility

$$\xi = \xi_0(\chi_0 P_c/\rho_c^2 \Gamma^+)^{\nu/\gamma}, \tag{4.1}$$

while the amplitude ξ_0 can be estimated from the equation of state by applying the principle of two-scale-factor universality. For further details the reader is referred to a previous review.[21]

Critical region parameters, needed to calculate q_C from (2.10) are listed in Table I, together with the appropriate literature sources. Equations (3.2) and (4.1) enable us to relate the critical viscosity ratio $\eta/\overline{\eta}$ to the equation of state with q_D as the only adjustable parameter. Equations that reproduce the experimental compressibilities with adequate accuracy in a range of temperatures and densities approximately equal to the range where a critical viscosity enhancement is observed can be found elsewhere.[21]

As a first example, we consider the viscosity of nitrogen near the critical point, as measured by Zozulya and Blagoi.[23] The experimental data were obtained as a function of density at a large number of temperatures close to T_c. Data along some representative isotherms are shown in Fig. 2. The normal viscosity $\overline{\eta}$ can be deduced from the data at 135 K, where the critical viscosity enhancement has disappeared completely. For this purpose we use an empirical representation of the form

$$\overline{\eta} = \eta_0(T) + \eta_1\rho + \eta_2\rho^2 + \eta_3\rho^3 + \eta_4\rho^4, \tag{4.2}$$

where $\eta_0(T)$ is the viscosity in the low-density limit. The values of $\eta_0(T)$ for N_2 have been tabulated by Hanley and Ely,[28] while the coefficients

TABLE I. Critical region parameters for nitrogen and steam.

Nitrogen	Steam
$T_c = 126.20$ K[a,b]	$T_c = 647.03$ K[f]
$P_c = 3.398$ MPa[b]	$P_c = 22.03$ MPa[g]
$\left.\frac{\partial P}{\partial T}\right\|_{\rho=\rho_c} = 0.168$ MPa K^{-1}[b]	$\left.\frac{\partial P}{\partial T}\right\|_{\rho=\rho_c} = 0.268$ MPa K^{-1}[g]
$\Gamma^+ = 0.075$[c]	$\Gamma^+ = 0.075$[c]
$\xi_0 = 1.6$ Å[c]	$\xi_0 = 1.3$ Å[c]
$\overline{\eta} = 18.0 \times 10^{-6}$ Pa s[d]	$\overline{\eta}_c = 39.6 \times 10^{-6}$ Pa s[h]
$\overline{\lambda}_c = 0.0343$ W m^{-1} K^{-1}[e]	$\overline{\lambda}_c = 0.189$ W m^{-1} K^{-1}[i]
$q_C^{-1} = 19$ Å	$q_C^{-1} = 16$ Å
$q_D^{-1} = 12$ Å	$q_D^{-1} = 11$ Å

[a] Reference 14.
[b] Reference 22.
[c] Reference 21.
[d] Reference 23.
[e] Reference 24.
[f] Reference 15.
[g] Reference 25.
[h] Reference 26.
[i] Reference 27.

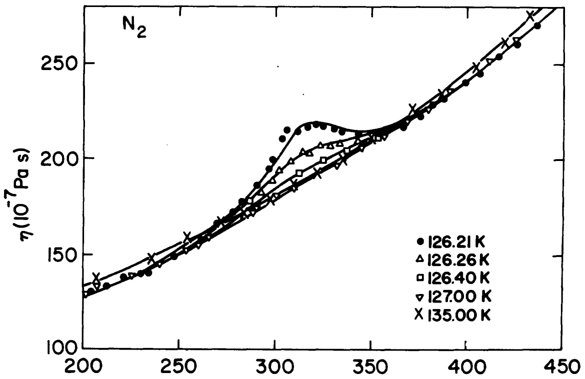

FIG. 2. Viscosity of nitrogen as a function of density at various temperatures close to T_c. The data points are those obtained by Zozulya and Blagoi (Ref. 23) and the curves represent the values calculated from the crossover function proposed in this paper.

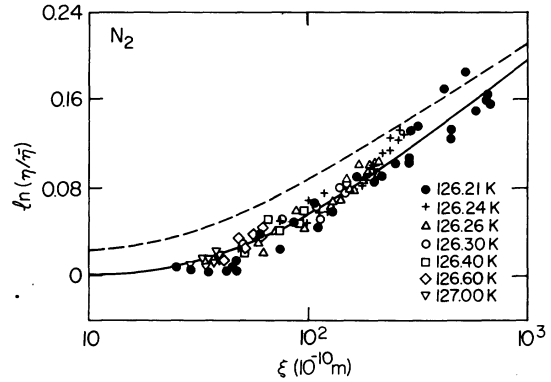

FIG. 3. Log-log plot of $\eta/\bar{\eta}$ as a function of ξ for nitrogen. The solid curve represents the crossover function with $q_D^{-1} = 12$ Å and the dashed curve represents the crossover function in the Oxtoby-Gelbart limit $q_D^{-1} = 0$.

η_1, η_2, η_3, η_4 can be determined from a fit to the data of Zozulya and Blagoi at 135 K. We thus obtain $\eta_1 = -0.0098 \times 10^{-6}$ Pa s m³/kg, $\eta_2 = +0.2430 \times 10^{-9}$ Pa s (m³/kg)², $\eta_3 = -0.5551 \times 10^{-12}$ Pa s (m³/kg)³, and $\eta_4 = +0.6336 \times 10^{-15}$ Pa s (m³/kg)⁴, valid in the range $200 \leqslant \rho \leqslant 450$ kg/m³ considered here. From the behavior of the viscosity outside the critical region, it is known that the temperature dependence of the coefficients η_1, η_2, η_3, η_4 can be neglected in the small temperature range considered here. For a few experimental temperatures, Zozulya and Blagoi tabulated $\Delta\eta$ rather than η; these values were reconverted into values of η with the use of (1.1) and (4.2).

In Fig. 3 we have plotted $\eta/\bar{\eta}$ as a function of ξ on a double logarithmic scale. The solid curve represents the crossover function (3.2) with $q_C^{-1} = 19$ Å as deduced from the information in Table I and with $q_D^{-1} = 12$ Å. For comparison we also indicate with the dashed curve the calculated behavior in the Oxtoby-Gelbart limit $q_D^{-1} = 0$. We conclude that introduction of a finite cutoff leads to a significant improvement in the representation of the experimental data.

As a second example, we consider the viscosity of steam near the critical point. The experimental data for the kinematic viscosity η/ρ, obtained by Rivkin and co-workers as a function of pressure and temperature,[29,30] were converted into values for η as a function of density and temperature by Basu *et al.*[15,26] Data obtained along five supercritical isotherms are shown in Fig. 4. In Fig. 5 we show the corresponding values of $\eta/\bar{\eta}$ as a function of ξ on a double logarithmic scale. For this purpose we used for $\bar{\eta}$ a global equation of the form

$$\bar{\eta} = \eta_0(T) \exp\left[\rho\left(\sum_{i=0}\sum_{j=0} a_{ij}(T^{-1}-1)^i(\rho-1)^j\right)\right], \quad (4.3)$$

with parameter values determined by Watson *et al.*[26] The solid curve in Fig. 5 represents the crossover function (3.2) with $q_C^{-1} = 16$ Å as deduced from the information in Table I and with $q_D^{-1} = 11$ Å. The corresponding function with $q_D^{-1} = 0$ is again indicated by the dashed curve.

V. CONCLUSION

We have formulated a crossover function for the critical viscosity which on the one hand reduces asymptotically to the power-law behavior

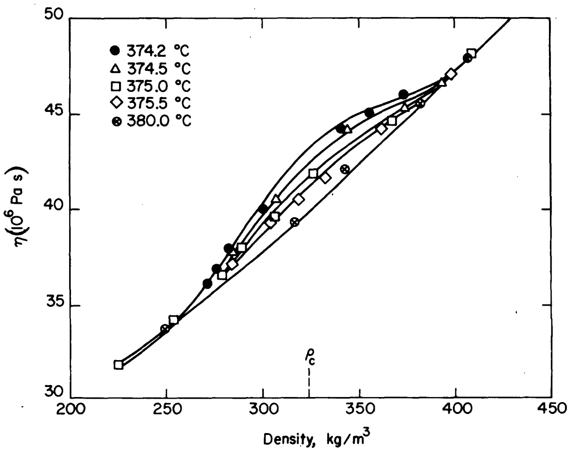

FIG. 4. Viscosity of steam as a function of density at various temperatures near T_c. The data points indicate the values deduced from the data of Rivkin and co-workers (Ref. 26) and the curves represent the values calculated from the crossover function proposed in this paper.

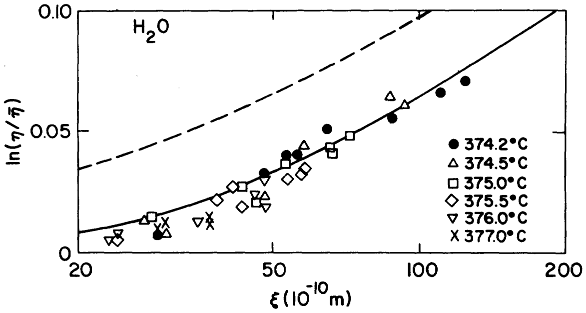

FIG. 5. Log-log plot of $\eta/\bar{\eta}$ as a function of ξ for steam. The solid curve represents the crossover function with $q_D^{-1} = 11$ Å and the dashed curve represents the crossover function in the Oxtoby-Gelbart limit $q_D^{-1} = 0$.

$\propto \xi^{x_\eta}$ with a universal exponent value, and on the other hand connects smoothly the viscosity in the critical region with the normal viscosity away from the critical point. The function is an approximant, in closed mathematical form, to the crossover function derived by Oxtoby-Gelbart in numerical form, but differs from it by the introduction of a finite Debye wave-number cutoff q_D. Introduction of this finite cutoff leads to a significant improvement in the representation of experimental viscosity data near the critical point. In principle, the method could be refined by allowing for possible variations of q_C and q_D with temperature and density. However, in the absence of further theoretical information concerning q_D, and in view of the still limited accuracy of the experimental data for the critical viscosity enhancement, such refinements do not seem warranted at this time.

ACKNOWLEDGMENTS

The authors acknowledge some valuable discussions with D. L. Henry in an early state of the analysis. The research was supported by NSF Grants Nos. DMR 79-10819 and DMR 79-01172 and by the Office of Standard Reference Data. Computer time for this project was provided by the Computer Science Center at the University of Maryland.

---

*Present address: Allied Chemical Corporation, Buffalo Research Laboratory, 20 Peabody Street, Buffalo, New York 14210.

[1] K. Kawasaki, in *Critical Phenomena*, Proceedings of the International School of Enrico Fermi, edited by M. S. Green (Academic, New York, 1971), p. 342.

[2] R. Perl and R. A. Ferrell, Phys. Rev. A 6, 2358 (1972).

[3] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. 49, 435 (1977).

[4] T. Ohta, Progr. Theor. Phys. 54, 1566 (1975).

[5] T. Ohta and K. Kawasaki, Progr. Theor. Phys. 55, 1384 (1976).

[6] F. Garisto and R. Kapral, Phys. Rev. A 14, 884 (1976).

[7] E. D. Siggia, B. I. Halperin, and P. C. Hohenberg, Phys. Rev. B 13, 2110 (1976).

[8] J. D. Gunton, in *Dynamical Critical Phenomena and Related Topics*, edited by C. P. Enz (Springer, Berlin, Heidelberg, and New York, 1979), p. 1.

[9] H. C. Burstyn and J. V. Sengers, Phys. Rev. Lett. 45, 259 (1980).

[10] T. Ohta, J. Phys. C 10, 791 (1977).

[11] P. Calmettes, Phys. Rev. Lett. 39, 1151 (1977).

[12] S. P. Lee, Chem. Phys. Lett. 57, 611 (1978).

[13] H. C. Burstyn, J. V. Sengers, and P. Esfandiari, Phys. Rev. A 22, 282 (1980).

[14] R. S. Basu and J. V. Sengers, J. Heat Transfer 101, 3 (1979); 101, 575 (1979).

[15] R. S. Basu, J. V. Sengers, and J. T. R. Watson, Int. J. Thermophys. 1, 33 (1980).

[16] D. W. Oxtoby and W. M. Gelbart, J. Chem. Phys. 61, 2957 (1974).

[17] J. V. Sengers and P. H. Keyes, Phys. Rev. Lett. 26, 70 (1971).

[18] L. Van Hove, Phys. Rev. 95, 1374 (1954).

[19] K. Kawasaki, Ann. Phys. (N. Y.) 61, 1 (1970).

[20] R. A. Ferrell, Phys. Rev. Lett. 24, 1169 (1970).

[21] J. V. Sengers and J. M. H. Levelt Sengers, in *Progress in Liquid Physics*, edited by C. A. Croxton (Wiley, New York, 1978), p. 103.

[22] R. T. Jacobsen and R. B. Stewart, J. Phys. Chem. Ref. Data 2, 757 (1973).

[23] V. N. Zozulya and Yu. P. Blagoi, Zh. Eksp. Teor. Fiz. 66, 212 (1974) [Sov. Phys.—JETP 39, 99 (1974)].

[24] H. J. M. Hanley, R. D. McCarty, and W. M. Haynes, J. Phys. Chem. Ref. Data 3, 979 (1974).

[25] F. W. Balfour, J. V. Sengers, and J. M. H. Levelt Sengers, in *Water and Steam: Their Properties and Current Industrial Applications*, edited by J. Straub and K. Scheffler (Pergamon, New York, 1980), p. 128.

[26] J. T. R. Watson, R. S. Basu, and J. V. Sengers, J. Phys. Chem. Ref. Data 9, 239 (1980).

[27] C. A. Meyer, R. B. McClintock, G. J. Silvestri, and and R. C. Spencer, *ASME Steam Tables*, 4th ed. (American Society of Mechanical Engineers, New York, 1979).

[28] H. J. M. Hanley and J. F. Ely, J. Phys. Chem. Ref. Data 2, 735 (1973).

[29] S. L. Rivkin, A. Ya. Levin, L. B. Izrailevsky, and K. G. Kharitonov, in *Proceedings of the 8th International Conference on the Properties of Water and Steam*, edited by P. Bury, H. Perdon, and B. Vodar (Editions Européennes Thermiques et Industries, Paris, 1975), p. 153.

[30] S. L. Rivkin, A. Ya. Levin, and L. B. Izrailevsky, Teplofiz. Svoistva Veshchestv Mater. 10, 232 (1976).