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X-ray investigation of the critical exponent η in argon*

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Measurements were made of the small-angle x-ray scattering intensity from argon near the critical point. After the scattering curves are corrected for all known effects except those resulting from irrelevant variables, a value of the critical exponent $\eta = 0.09 \pm 0.02$ is obtained, while if a correction for the estimated effect of irrelevant variables is also made, $\eta = 0.03 \pm 0.03$. The scattering data for argon therefore show that if irrelevant variables can be neglected, the critical exponent η for argon is in good agreement with the value obtained by Warkulwiz, Mozer, and Green from small-angle neutron scattering data for neon. These values of η, however, are clearly greater than those obtained by calculations using high-temperature expansions and renormalization-group techniques. On the other hand, if the effects of irrelevant variables are given by the estimate used in correcting the scattering data, the η value computed from the scattering curves agrees with the theoretical results.

I. INTRODUCTION

Knowledge of the value of the critical exponent η,[6] which determines the rate of decay of the pair correlation function at large distances at the critical point, is important for understanding many properties of a system near its critical point.

One important reason for evaluating η for several simple fluids is to learn whether the result $\eta = 0.11^{+0.03}_{-0.02}$ obtained by Warkulwiz, Mozer, and Green,[1] is typical for simple fluids. This value of η is appreciably higher than the exponent calculated by series-expansion[2,3] and renormalization-group[4] techniques.

Recent results obtained by Hocken and Moldover[5] have shown that the limiting behavior characteristic of the critical point is observed only in a region which is considerably smaller than was believed previously. It therefore is important to determine whether the high value of η found by Warkulwiz *et al.* may have been due to the fact that the measurements were made under conditions not close enough to the critical point.

Usually η has been evaluated by use of scaling equations relating it to other critical exponents. For example, Hocken and Moldover[5] have estimated η for some simple fluids by applying these scaling relations to the critical exponents calculated from their refractive index data. Since η is a small positive number, the value of η obtained in this way can be quite sensitive to uncertainties in the other exponents employed in the calculation.

Warkulwiz, Mozer, and Green[1] used a more direct method to find η. When a one-component fluid is near its liquid-vapor critical point, there is a large increase in the x-ray and neutron scattering at scattering angles of a few degrees or less. (This small-angle x-ray and neutron scattering corresponds to the critical opalescence observed with visible light.)

When a fluid is close enough to its critical point to satisfy the condition

$$q\xi \gg 1 , \tag{1}$$

where ξ is the long-range correlation length, $q = 4\pi\lambda^{-1}\sin\frac{1}{2}\alpha$, λ is the x-ray wavelength, and α is the scattering angle, and if the inequality

$$qa \ll 1 \tag{2}$$

also is satisfied, where a is the nearest-neighbor distance, the scattered intensity will be proportional[6] to $q^{\eta-2}$. Thus, if the small-angle scattering can be measured under conditions for which (1) and (2) are satisfied, a direct determination of η is possible.

While this technique in principle is simple, a number of precautions are necessary if a reliable value of η is to be obtained. First, the measurements must be made under conditions for which (1) and (2) are fulfilled. Tracy has recently pointed out[7] some of the difficulties which may occur when (1) is not satisfied. Moreover, the conditions for which (1) and (2) hold are just the conditions for which experimental measurements are quite difficult.

Thus, if a reliable value of η is to be expected, the measured scattering curves must be carefully corrected both for any distortions produced by the apparatus and the measuring techniques and also for the fact that the data were not obtained at conditions for which (1) and (2) are strictly satisfied.

Below, we describe a recent determination of η from small-angle x-ray scattering data for argon. We have applied corrections to our results for instrumental effects and also have made calcu-

lations to estimate the effect of the fact that our data may not have been obtained under the limiting conditions specified by (1) and (2).

When we have corrected for all known experimental effects and made allowance for the fact that (1) was not perfectly satisfied, we found that $\eta = 0.09 \pm 0.02$. This result is in essential agreement with the work of Warkulwiz *et al.*

The exponent η obtained from the scattering data for neon and argon thus indicates that for these fluids, η either is considerably larger than predicted by theoretical calculations or that the experimental results are influenced by the fact that inequality (2) is not fulfilled. As we explain below, we have estimated how our results will be affected if qa is small but not negligible. These estimates show that (2) may not be satisfied because of the effects of irrelevant variables,[8,9] which, while restricting the extent of the region near the critical point in which the limiting behavior is observed, do not affect the value of the critical exponents. Our calculations have shown that even though the precision of our data does not permit a really quantitative determination of the correction for irrelevant variables, use of correction factors based on reasonable estimates[9] of the effect of irrelevant variables can lower η sufficiently to bring it into agreement with the calculated value.

II. EXPERIMENTAL TECHNIQUES

In our scattering measurements, we used the same copper-target x-ray tube ($\lambda = 1.54$ Å), scattering system, sample cell, and cryostat as in our previous investigation[10,11] of argon.

As before, we used special slits[10] to reduce the beam length in some of the measurements. These collimation conditions will be referred to as the "short slits," while the normal collimation conditions will be called the "long slits."

Our temperature regulator held the sample temperature constant within ±0.002 °C.

From measurements of the temperature dependence of the level of the meniscus, as determined by methods outlined in Ref. 10, and by use of x-ray absorption measurements[10] to determine the vapor and liquid densities and the density in the one-phase region above the critical temperature, we estimate that the average sample density was between the critical density ρ_c and $0.98\rho_c$.

From our absorption data, with the technique described in Ref. 10 we determined the coexistence curve and used these results to calculate the critical temperature T_c, which, as measured by the thermometer in our sample cell, was within 0.01° of the result determined previously.[10]

The scattering curves were corrected for the background scattering, which was determined by measuring the scattering from the empty cell, and for the photoelectric absorption of the x rays in the sample. Allowance was also made for the "room background"—that is, for the counts registered by the detector when the x-ray beam was blocked by inserting a piece of lead into the beam path. The room background was quite small and had an appreciable effect on the value of η only when measurements were made with the short slits, for which the scattered intensity was only about 30% of the scattering obtained with the long slits.

Corrections were made[12,13] for the effects of the length and width of the collimating slits. Normally,[14] collimation corrections are not especially sensitive to small changes in the slit-length weighting function[15] employed in the collimation corrections. However, when the scattering curve must be obtained with as much precision as possible, as in our determination of η, greater care must be given to finding the proper form of the weighting function.

As in all of our other work with the four-slit collimation system, we used a Gaussian approximation[16] to the exact weighting function. To find the width of the Gaussian, instead of assuming, as we normally have done, that the slit nearest the x-ray tube is uniformally illuminated, we used the special slits, set at a length of 0.25 mm, to find the intensity distribution at the slit next to the x-ray tube. The exact weighting function was then calculated[17] for these conditions, and the Gaussian approximation was then found for the exact weighting.

To verify our determination of the width of the weighting function, we measured the scattering from a polyethylene sample with the long slits and also with the short slits, for which our tests showed that the assumption of uniform illumination of the slit next to the tube was valid. The scattering curve for the long slits was corrected with the Gaussian approximation to the exact weighting function and also with Gaussians with widths equal to 111% and 89% of the correct approximation. The curve for the long slits, when corrected with the Gaussian approximation to the exact weighting function, was in better agreement with the corrected curve for the short slits than were the long-slit curves corrected with the other two Gaussian weighting functions.

Further evidence in support of our choice of a weighting function for the long slits is provided by the fact that when we compared the values of η computed from the scattering curves for the short and long slits, the best agreement of results from

the data for the long and short slits was obtained when we used the Gaussian approximation to the exact weighting function.

Our tests of collimation correction techniques show the importance of proper collimation corrections in determinations of η from scattering curves for fluids in the critical region, since changing the effective width of the Gaussian function by about 10% caused the calculated value of η to change by 0.03 or 0.04. We found, in fact, that uncertainty in the collimation corrections is one of the largest sources of uncertainty of the result for η obtained from the scattering measurements.

Since the logarithm of the scattered intensity $I(q)$ is a linear function of the logarithm of q when the intensity is proportional to $q^{\eta-2}$, we calculated η by making a linear least-squares fit of $\log I(q)$ as a function of $\log q$. In the least-squares fit, the weights were inversely proportional to the inverse squares of the estimated errors in $I(q)$.

Least-squares fits were made for scattering angles from 0.005 or 0.006 rad through 0.045 rad and also from 0.015 through 0.045 rad.

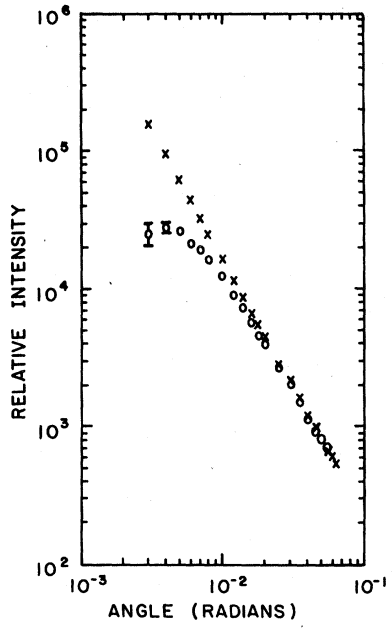

FIG. 1. Scattering curves, corrected for collimation effects and background scattering, for the one-phase region at temperatures 0.01 °C (upper curve) and 1.02 °C (lower curve) above the critical temperature.

III. RESULTS AND DISCUSSION

Two sets of scattering curves were recorded with the same argon sample, the second several months after the first. The two sets of curves were equivalent.

Figure 1 shows a typical scattering curve for the one-phase region within 0.01° of T_c and also a curve recorded when the sample was 1.02° above T_c.

The long-range correlation length ξ computed from the latter curve is in good agreement with the value for this temperature given in Ref. 10. The long-range correlation length can be found from the scattering curve only when data are available at scattering angles small enough that the intensity is not proportional to $q^{-2+\eta}$. Our collimation system did not permit measurements to be made at small enough q values to give precise values of ξ at temperatures within a few hundredths of a degree of the critical temperature. Therefore, near T_c we estimated ξ from Fig. 4 of Ref. 10. This plot shows that for $0 \leq T - T_c \leq 0.03$ °C, $\xi > 350$ Å.

To obtain an idea of whether our values of q were large enough to satisfy (1), we made a series of calculations in which we used theoretical scattering curves as intensities in the least-squares-fitting program with which we computed η from the experimental curves. On the critical isochore above T_c we used the Fisher-Aharony equation[18] in which the specific-heat exponent α was set equal to 0.1. After assuming a value for η, we calculated the intensity from the theoretical curves and then used these theoretical intensities with our least-squares program for an interval of $q\xi$ beginning at $(q\xi)_0$ and ending at $10(q\xi)_0$. (The length of this interval of angles corresponded approximately to extent of our experimental data.) The values of η obtained from the calculation are shown in Figs. 2 and 3 for $\eta = 0.10$ and $\eta = 0.05$, respectively. As can be seen from Figs. 2 and 3, for $(q\xi)_0 \geq 8$, the exponent η calculated from the least-squares fit is within 0.01 or 0.02 of the value used in the calculation of the theoretical scattering curves.

For samples not on the critical isochore, there is evidence[19] that $q\xi$ may have to be larger to satisfy (1) than is necessary at the critical density. Therefore, to estimate the effects of deviations of the average sample density from the critical density, we used theoretical scattering curves computed from the Tarko-Fisher scattering equation[19] with our least-squares program for the same interval of $q\xi$ that we employed for the critical isochore. We calculated theoretical intensity curves from the Tarko-Fisher equation for $\eta = 0.05$ and $\eta = 0.10$ and used the values from Ref. 19 for all other parameters in the theoretical scattering equation. As the curves in Figs. 2 and 3 show, for $(q\xi)_0 > 8$ and $0 \leq \theta \leq 0.4$, the value of η

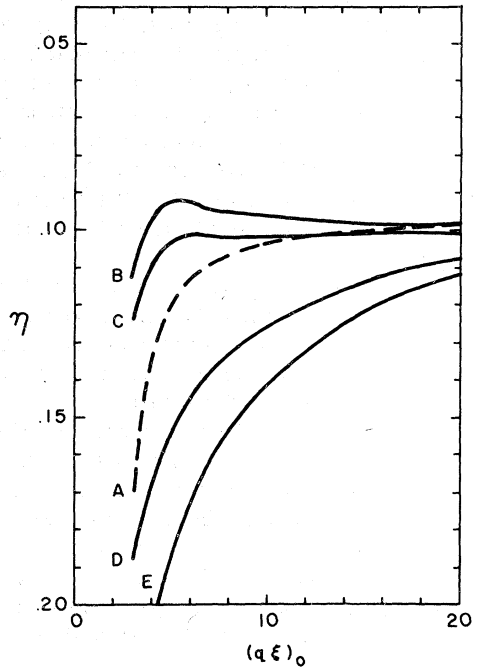

FIG. 2. Exponents η obtained by a least-squares fit for scattering angles from $(q\xi)_0$ to $10(q\xi)_0$ with intensities calculated for $\eta = 0.10$ with the Fisher-Aharony equation on the critical isochore (curve A) and with the Tarko-Fisher equation on the critical isochore (curve B), for $\theta = 0.2$ (curve C), for the critical isotherm (curve D), and for the coexistence curve (curve E). The curve for $\theta = 0.4$ lies between curves B and C.

calculated from the least-squares program is within 0.01 or 0.02 of the value assumed in the calculation of the theoretical scattering curve. (The "angular" coordinate θ in the parametric equation of state should not be confused with the scattering angle α.)

From the linear-model parametric equation of state[20] we estimate that for our measurements $0 < \theta < 0.4$. Our test calculations therefore suggest that in our scattering studies, inequality (1) was satisfied well enough that the exponent η calculated from the scattering curves should be within 0.01 or 0.02 of the correct result.

Further evidence for this conclusion is provided by the fact that in the calculations of η from our scattering curves for $0 \leq T - T_c \leq 0.03$ °C, we could detect no consistent trend in the variation of η with $T - T_c$. We therefore conclude that within the uncertainty of our results, our calculations from the scattering curves give results which represent the limit for infinite $q\xi$.

The average value $\eta = 0.10 \pm 0.02$ was obtained from 10 scattering curves recorded with the long slits for $0 \leq T - T_c \leq 0.03$ °C.

The individual values of η computed from different scattering curves in a group usually differed 0.01 or 0.02 from the average. We believe that one of the principal sources of this variation was the change of the incident x-ray intensity from day to day. The background scattering from the empty cell was measured before the sample was filled. The actual background scattering that had to be subtracted from a given scattering curve thus had to be adjusted for variations in the incident intensity. Uncertainty in this adjustment can cause the calculated η values to vary by 0.01 or 0.02.

We also computed η for seven scattering curves obtained with the short slits for $0 \leq T - T_c \leq 0.03$ °C. A calculation analogous to the procedure described above gave the average $\eta = 0.09 \pm 0.02$. As we have mentioned previously, because of the necessary corrections that must be made, our values of η should always be considered to have an uncertainty ± 0.02.

We also used the short slits to obtain scattering data in the vapor phase at temperatures 0.01, 0.03, and 0.05 deg below T_c. At these tempera-

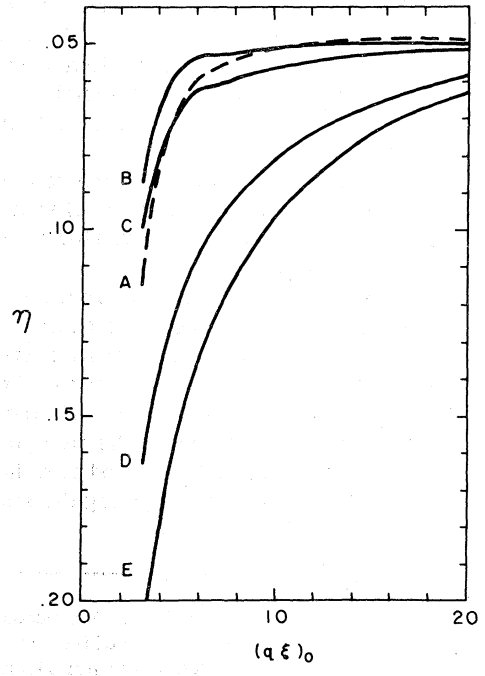

FIG. 3. Exponents η obtained by a least-squares fit for scattering angles from $(q\xi)_0$ to $10(q\xi)_0$ with intensities calculated for $\eta = 0.05$ with the Fisher-Aharony equation on the critical isochore (curve A) and with the Tarko-Fisher equation on the critical isochore (curve B), for $\theta = 0.2$ (curve C), for the critical isotherm (curve D), and for the coexistence curve (curve E). The curve for $\theta = 0.4$ lies between curves B and C.

tures our least-squares fit gave η values of 0.11, 0.15, and 0.20, respectively. These results are in reasonable agreement with exponents estimated from Figs. 2 and 3 for the coexistence curve.

As argon and neon are fluids which have many similar properties, the critical exponent η should be expected to be very nearly the same or identical for the two fluids. The fact that our x-ray scattering curves and the neutron scattering data[1] give essentially equivalent results for η therefore strongly suggests that large systematic errors are unlikely to be present in either investigation.

The above calculations do not allow for the fact that (2) may not be satisfied. We therefore made series of tests to estimate the magnitude of the effects resulting from the fact that qa was not negligible.

To allow for these effects, before analyzing scattering data by the least-squares-fitting process used previously, we divided all the corrected intensities by the additional correction factor

$$Q(qa) = 1 + b(qa)^{3/4} + \tfrac{1}{20}(qa)^2 . \qquad (3)$$

The quadratic term in (3) is the first lattice-structure correction in the Fisher-Burford scattering equation.[21] (The same correction term is obtained for the simple cubic, body-centered cubic, and face-centered cubic lattices.) The term $b(qa)^{3/4}$ was inserted[9] to allow for the effects of irrelevant variables. In our calculations with (3) we set a equal to 3.8 Å, the nearest-neighbor distance obtained from large-angle x-ray scattering studies[22] of argon.

To test the effect of the lattice structure alone, we first used the correction factor $Q(qa)$ with $b = 0$. These corrections reduced the calculated value of η only be about 0.01.

We then made a set of calculations in which we used a series of b values in the interval from 0.05 through 0.7 for each of the 10 scattering curves obtained with the long slits. As a criterion for the choice of b, we evaluated χ^2, the weighted sum[23] of the squares of the deviations of the data points from the fitting function, and assumed that the "best" choice of b was the value giving the smallest χ^2.

The best fit was obtained for $b = 0$ for two of the 10 curves. With two other curves, $b = 0.7$ gave the best fit. But since the exponent η calculated for these latter curves was negative, we did not consider these results to be meaningful. Instead, we interpreted the calculations to mean that $\eta = 0$ and that for these curves the best value of b corresponded to the condition that $\eta = 0$. For the other six curves, we obtained a best fit for b within the interval $0.05 \leq b \leq 0.7$.

The relatively large variations in the b values giving the best fits for the different curves indicates that our data are not reliable enough to give precise results for this kind of analysis. Moreover, our interpretation of the results which gave negative values of η is not really justified. Still, we do not feel that a more refined interpretation of the data would be worthwhile until we can improve our x-ray techniques by more precise background corrections, by better monitoring of the incident intensity, and by doing what else may be necessary to obtain scattering data in which different runs give more nearly identical results for η.

Nevertheless, our least-squares fits definitely provide evidence that reasonable choices of the parameters correcting for the effect of irrelevant variables can bring the value of η from the scattering measurements into agreement with the exponent calculated from theory. Averaging the results from the 10 curves suggests that after corrections are made for irrelevant variables, $\eta = 0.3 \pm 0.03$ and $b = 0.3 \pm 0.1$.

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