Observation of the Deviation from Ornstein-Zernike Theory in the Critical Scattering of Neutrons from Neon*†

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A deviation from the Ornstein-Zernike theory of critical scattering has been observed in a neutron-diffraction study of neon near its critical point. The critical exponent η was determined to have the value $0.11^{+0.03}_{-0.02}$.

Since the possibility of deviations from the Ornstein-Zernike (O-Z) theory of critical scattering in fluids was made by one of the authors[1] in 1960, there have been several attempts to verify this prediction and determine the exponent η which is a measure of this deviation.[2] A value of η different from zero has been found for a planar magnetic system K_2NiF_4 [3] and for three-dimensional magnetic systems MnF_2 [4] and $RbMnF_3$ [5] using neutron-scattering techniques. Determinations of η in fluids have been almost exclusively made using light-scattering techniques[6] except for a few x-ray measurements.[7] These measurements have been direct in attempting to measure the structure factor $S(\kappa)$ at small values of the momentum transfer $\kappa = (4\pi/\lambda)\sin\theta/2$, where λ is the wavelength of the radiation and θ the scattering angle. Indirect determinations of η have required the knowledge of the correlation length ξ and its exponent ν and the compressibility exponent γ. η is obtained through the static scaling relationship $\eta = 2 - \gamma/\nu$. In fluids, both of these approaches have been somewhat inconclusive. The direct method has the difficulty that the condition $\kappa\xi \gg 1$ imposed upon experiments in the critical region is very hard to attain since κ is quite small for optical wavelengths. Values of η determined by the indirect method suffer from the difficulty that both γ and 2ν are numerically very similar and experimental uncertainties in their determination yield large errors on η. Some of these uncertainties can be reduced by invoking additional relationships between critical exponents and using additional experimental data. The present Letter describes a direct measurement of η for liquid neon using neutron-scattering techniques. The primary advantage in this approach is the relative ease with which the condition $\kappa\xi \gg 1$ may be satisfied. In particular, κ can be chosen rather large (0.025 to 0.25 $Å^{-1}$) compared to optical experiments, and it is possible to achieve $\kappa\xi \gg 1$ by approaching the critical temperature T_c no closer than 8–10 mK.

A cylindrical neon sample container was made from 6061 aluminum alloy with sample height 1.75 cm and diameter 2.45 cm. A capacitor used to measure the density via the dielectric constant was placed in the bottom of the container out of the neutron beam and a fixture of thin cadmium disks was inserted in the container to reduce multiple scattering from the neon, the container, and the capacitor. The container was attached to a temperature-controlled copper block of a commercially available cryostat. Radiation shields were employed to reduce losses and help insure a uniform temperature over the length of the container. A combination resistance bridge and temperature controller permitted temperature control of the copper block to 1 or 2 mK near T_c. A thin-walled stainless-steel capillary was used to introduce neon into the container.

The critical temperature and density of neon were obtained from measurements of temperature and density along the coexistence curve and critical isochore. Temperatures were based upon the resistance of the platinum thermometer in the copper block. A more detailed description of these measurements can be found in the thesis of one of the authors (V.P.W.).

Conditions imposed upon the neutron-scattering part of the experiment are $\kappa a < 1$ and $\kappa\xi \gg 1$ where a is a characteristic short-range length of the system and is nominally a few angstroms. The first condition is necessary in order that O-Z theory is applicable. By satisfying the second condition we find that the more complicated expressions for the scattering intensity[8] reduce to

$$I(\kappa) \simeq (\xi\kappa)^{-2+\eta} \propto \kappa^{-2+\eta}, \qquad (1)$$

independent of the precise value of the correlation length and other parameters *in the determination of* η. Confining our sample temperature to 3–10 mK above the neon critical temperature will provide a correlation length large enough to satisfy the inequality and allow reasonable choices for neutron wavelength, wavelength spread, and scattering angles. Thus the experiment will only depend on precise measurements of the scattering angles.

A long-wavelength beam of neutrons with no fast-neutron contamination was extracted from the graphite thermal column at the National Bureau of Standards (NBS) reactor, filtered through 10 in. of refrigerated beryllium, and monochromated further with a velocity selector. To keep the scattering angles from being too small we chose a 5-Å-wavelength beam whose full width at half-maximum was 1.20 Å. The incoming beam was collimated via a number of cadmium masks on the beryllium filter, on the velocity selector, and a final mask on the inner radiation shield surrounding the sample. The collimation of the incoming beam was less than 20 min of arc in the horizontal and vertical directions. The scattered neutrons were detected by a shielded BF_3 counter mounted on the arm of a diffractometer whose angular position could be determined to within 1 min of arc. The scattered beam entering the detector was collimated to 10 min of arc by a vertical Soller-slit assembly. The total angular alignment of the system was done using a high-precision theodolite to a precision of 1 min of arc. The zero position of the diffractometer, as determined optically, was checked with the neutron beam in the forward direction. Vertical collimation was not restricted but amounted to 1.6° at the detector. The incoming beam of neutrons was monitored by a thin fission counter. Data were taken during seventeen cycles each of 48 h duration, after which liquid helium and nitrogen refrigerants were replenished. During each cycle data were taken over the whole of a predetermined angular range until a certain statistical precision was reached for a subset of angles; then the angular range was reduced until the required statistical precision was achieved for the next subset of angles, etc. This procedure provided a way of checking the data for consistency.

Figure 1 exhibits the raw diffraction data for neon in the critical region. Data were taken at

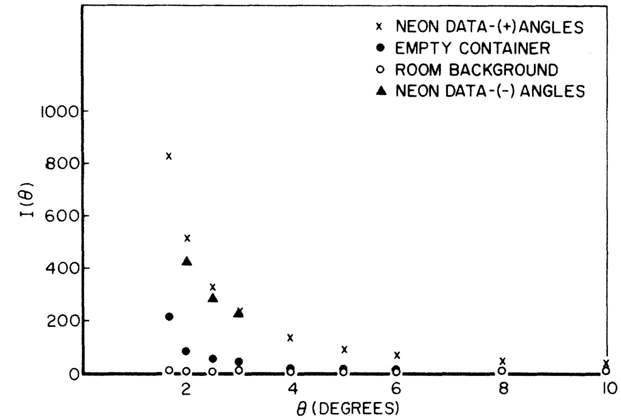

FIG. 1. Neutron-scattering intensity versus scattering angle in degrees. Counting statistics for all the runs are less than the size of the symbols.

nine positive angles between 1.5° and 10° and at four negative angles between −1.5° and −3°. Also shown in Fig. 1 are the background data from the empty container and room background. Statistical uncertainties for the positive-angle data are about 0.5% except for the two largest angles, and statistical uncertainties for the negative-angle data are about 1%. The positive- and negative-angle data do not coincide because of an asymmetry caused by an accidental shift during assembly of a cadmium mask used to define the sample. Overlap of the positive- and negative-angle data can be accomplished by a correction corresponding to a shift in the zero angle of 0.12°.

In addition to the zero-angle correction, other necessary corrections involved room background and empty-container-scattering contributions to the raw data, with the empty-container scattering being corrected for transmission through the neon; a small incoherent-scattering contribution to the total intensity; and a κ-independent contribution from multiple scattering. The incoherent- and multiple-scattering corrections were determined from the scattering in the asymptotic region of the structure factor measured in another diffraction experiment performed at large κ. These corrections amounted to a fraction of a percent except at the two largest angles. Resolution corrections were also required and were determined from the calculated effect of the collimation system on an assumed O-Z scattering $I(\kappa) \propto \kappa^{-2}$ in the asymptotic region. Corrections for inelastic scattering are negligible.

Exhibited in Fig. 2 are the corrected data proportional to the structure factor. The errors, the resultant of statistical and angular-correc-

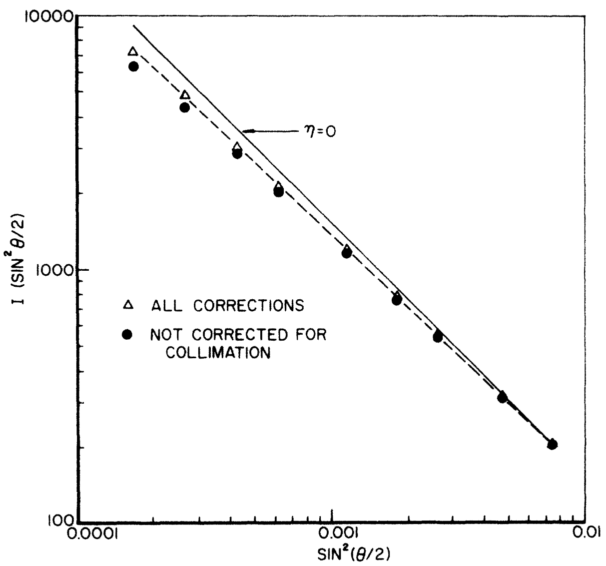

FIG. 2. Logarithms of the neon structure factor versus the logarithm of the square of the sine of half the scattering angle which is proportional to κ^2. Errors of 1 standard deviation which are the resultant of statistical errors and errors in our corrections are less than the size of the symbols.

tion uncertainties corresponding to 1 standard deviation, are less than the size of the symbols. The straight line was determined by a weighted linear least-squares fit of the logarithm of all the corrected data versus $\sin^2(\theta/2)$. A value for η of 0.105 ± 0.010 was obtained from the slope. If only the positive-angle data are used, a value for η of 0.103 ± 0.016 is obtained. Using positive-angle data and excluding the smallest angle yields a value for η of 0.110 ± 0.010. η changes from 0.110 to 0.180 in the analysis, depending on whether or not resolution corrections are taken into account. The other corrections do not influence the value of η to any significant extent.

An analysis of the positive-angle data using only the largest angles yields values of η from 0.090 to 0.140, depending upon inclusion of a combination of the resolution corrections or zero-angle corrections. The larger-angle data are not as sensitive to the zero-angle correction or the resolution correction.

In order to use Eq. (1) in our analysis and not more complicated expressions[8,9] necessary for temperatures further from the critical point, we estimated ξ as a function of sample height using the NBS equation of state of neon[10] for the thermodynamic parameters in our experiment. Our estimate for an effective ξ was greater than 300 Å, which satisfies $\kappa\xi \gg 1$, even for our smallest angle, and we can neglect higher-order terms in $\kappa\xi$ in our analysis. Support for this contention is to be noted by little curvature, if any, in our data.

The value of η obtained from this analysis of the neutron-diffraction data is $0.110^{+0.030}_{-0.020}$ upon consideration of the various corrections. Several points to be noted are that this value of η is more than twice the value obtained for magnetic systems.[4,5] The best series-expansion result for η for the Ising model[11] is 0.041, and the renormalization-group approach yields a value for η of 0.029 to $O(\epsilon^4)$ for the Ising model.[12] The lattice gas, often considered a model for fluids, is a reformulation of the Ising model where particles and holes are the physical variables replacing spins up and spins down. Thus, the values for η calculated using the lattice-gas model would be the same as for the Ising model. *Our experiment clearly demonstrates that the ordinary lattice-gas model cannot be used to calculate the critical exponent η for a fluid.* We find that using our value of η yields a value for δ (critical isotherm exponent) of 4.40 ± 0.13 upon application of the Buckingham-Gunton equality[13] $d(\delta-1)/(\delta+1) = 2-\eta$, where d is the dimension of the system. This value of δ agrees with values of δ of 4.45 ± 0.07 for CO_2, 4.46 ± 0.45 for Xe, and 4.34 ± 0.06 for ^{4}He obtained by recent scaling-theory analysis of equation-of-state data for CO_2, Xe, ^{4}He.[14] We may also use the Fisher equality to relate γ (exponent of isothermal compressibility), ν (correlation-length exponent), and η: $(2-\eta)\nu = \gamma$. We find a value of 0.64 for ν using $\gamma = 1.20$, as obtained for other gases.[14] These values are considered acceptable for the various exponents involved.[15] Thus our value for η can be used to give more credence to the idea of static scaling involving dimensionality but requires that a different theoretical treatment be used for liquid systems than for magnetic systems for estimates of the values of critical exponents.

Additional measurements in progress confirm these preliminary results, experimentally confirm the calculated collimation corrections, and show temperature effects which will provide a measure of other critical parameters.[16]

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[16]A detailed publication by one of the authors (B.M.) will follow.

Self-Consistent Screening Calculation of the Critical Exponent η

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A self-consistent version of the $1/n$ expansion is used to calculate the critical exponent $\eta(n,d)$ for an n-component Ginzburg-Landau field with spatial dimensionality d. The result is exact to first order in $1/n$ but also includes a partial summation of graphs to all orders in $1/n$. This leads to a bounding of η for small n, in contrast to the simple $1/n$ expansion. Results are $\eta(3,3) \simeq 0.079$, $\eta(2,3) \simeq 0.11$, and $\eta(1,3) \simeq 0.177$. For $d=2$ the theory leads to the conjecture that η vanishes for large values of n.

A recent approach[1-5] to the problem of second-order phase transitions consists of expanding the critical exponents as power series in $1/n$, where n is the number of components of the order parameter. This procedure (the "screening approximation") gives systematic corrections to the spherical model (Hartree approximation) which corresponds to the limit $n \to \infty$. At the present time exponents are known to order $1/n$ for all d in the range $2<d<4$. Unfortunately, it has thus far proved difficult to extend the expansion beyond the first order. (The exception is Abe's calculation,[2] to order n^{-2}, of η for the special case $d=3$.) It is possible, however, to include an infinite subset of such higher-order terms in a straightforward way by using self-consistently determined propagators in the graph-theoretic formulation to the problem.[6] The calculation of η within this "self-consistent screening approximation" (SCSA) is the purpose of this Letter.[7] In contrast to the simple $1/n$ expansion, the inclusion, within the SCSA, of terms of all orders in $1/n$ leads to a bounding of η for small n. In addition, the method is sufficiently powerful to deal with the case $d=2$, where the simple $1/n$ expansion breaks down (as far as the calculation of critical exponents is concerned[8]). For this case we find that η vanishes for $n \geqslant 2$. For $n<2$, a nontrivial solution appears with η increasing monotonically from zero at $n=2$ to unity at $n=0$. We conjecture that this result is qualitatively correct.