Comments and Addenda

The section Comments and Addenda is for short communications which are not appropriate for regular articles. It includes only the following types of communications: (1) Comments on papers previously published in **The Physical Review** *or* **Physical Review Letters**. *(2) Addenda to papers previously published in* **The Physical Review** *or* **Physical Review Letters**, *in which the additional information can be presented without the need for writing a complete article. Manuscripts intended for this section must be accompanied by a brief abstract for information-retrieval purposes. Accepted manuscripts follow the same publication schedule as articles in this journal, and page proofs are sent to authors.*

X-ray critical multiple scattering from fluids

William A. Holm
Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia 30332
(Received 10 November 1976)

A multiple scattering theory, using the Ornstein-Zernike approximate for the correlation functions, previously obtained for thermal-neutron critical scattering from ferromagnets and fluids, is applied to x-ray critical scattering from fluids. These results are compared to the single-scattering theory using Fisher's approximate for the correlation function in order to obtain a multiple-scattering-induced η for critical x-ray scattering. Comparison is made with experiment.

No exact calculation for a physically realizable system has ever been done for the correlation functions that appear in critical scattering theory. Many approximations for these correlation functions have been proposed, the original and classic one being the Ornstein-Zernike (OZ) approximate.[1] In recent years, other approximates, e.g., the Fisher approximate,[2] the Fisher-Burford approximate,[3] etc., for these correlation functions have been introduced. These later modifications of the OZ approximate introduced the critical exponent η, which is essentially a measure of the deviation from the Lorentzian line shape predicted by the single (first Born) scattering theory utilizing the OZ ($\eta = 0$) approximate.

In the past, experimentally observed deviations from a Lorentzian line shape, i.e., an experimentally measured nonzero η, have been interpreted as verification of the superiority of these later approximates for the correlation functions over the OZ approximate. However, these experiments are usually interpreted under the assumption that multiple scattering is negligible. As shown by Oxtoby and Gelbart[4] for the case of critical light scattering from fluids, a similar qualitative deviation from the usual Lorentzian line shape is produced in the theory utilizing the OZ approximate if double scattering is present and taken into account. So even the presence of even a small amount of double scattering in an experiment, when interpreted within the framework of a single-scattering theory, can appear to require a modified OZ theory. Oxtoby and Gelbart concluded that these deviations in line shape could arise from at least three different sources: double scattering, a genuine deviation from OZ theory, and density gradients (an ever-present problem when dealing with fluids in Earth's gravitational field).

In previous work,[5,6] we presented a general quantum-mechanical formulation for multiple scattering of thermal neutrons from macroscopic targets, and applied that theory to neutron critical multiple scattering from both ferromagnets and fluids. In that application to critical scattering, the OZ approximate was used for both the spin-spin correlation function (for magnetic scattering) and the density-density correlation function (for nuclear scattering) in order to estimate the deviation from the usual Lorentzian line shape produced by the presence of multiple scattering. Comparing our results with the single scattering (first Born) theory utilizing Fisher's approximate for the correlation functions, we displayed, in terms of relevant experimental parameters, a multiple-scattering-induced η for neutron scattering from both ferromagnets and fluids. Comparing this multiple-scattering-induced η with the values of η measured in various experiments, we concluded that multiple scattering induced deviations in line shape can compete with similar line-shape deviations predicted by Fisher's modification of the correlation functions from their OZ form used in a single scattering theory.

In this note, our previously obtained multiple-scattering theory utilizing the OZ approximate is now applied to x-ray critical scattering from fluids in order to obtain the appropriate multiple-scattering-induced η for x-ray scattering, and to compare this with an η measured in a recent experiment.

It was shown[6] that for the typically small angles involved in neutron critical scattering, the Glauber high-energy approximation is applicable, and when sufficiently close to the critical point yields the following closed-form expression for the coherent differential cross section of unpolarized neutrons scattered from a target with slab geometry:

$$\frac{d\sigma}{d\Omega}=\frac{2\beta A k_i^2}{\pi\mu^2}\, e^{-\rho\sigma_B l}\left(\frac{1}{k\mu^{-1}}\right)^{2-4\beta}, \quad (k\gg\mu), \tag{1}$$

where[7]

$$\beta=\pi l\rho \mathfrak{A}^2/2k_i^2 r_1^2. \tag{2}$$

The cross section given by Eq. (1) includes all orders of scattering. A is the cross-sectional area of the target, k_i is the wave number of the incoming neutron, μ^{-1} is the correlation length, ρ is the particle (atom) number density of the target, σ_B is the total cross section per target atom as given by the first Born approximation, l is the length of the target parallel to the incoming neutron beam, k is the magnitude of the wave-vector transfer to the target, r_1 is the OZ direct correlation length and $\mathfrak{A}$, the scattering amplitude, for nuclear scattering from fluids is given by $\mathfrak{A}=b$, where b is the nuclear S-wave scattering length. For magnetic scattering from ferromagnets,

$$\mathfrak{A}^2=\tfrac{2}{3}S(S+1)(ge^2/mc^2)^2, \tag{3}$$

where S is the Heisenberg spin quantum number, $g=1.91$, e is the magnitude of the electron's charge, and m is the electron's mass.

The Glauber approximation yields for the single-scattering differential cross section

$$\frac{d\sigma^{(1)}}{d\Omega}=\frac{2\beta A k_i^2}{\pi\mu^2}\, e^{-\rho\sigma_B l}\left(\frac{1}{k\mu^{-1}}\right)^{2}, \quad (k\gg\mu), \tag{4}$$

which, neglecting the extinction factor, $\exp(-\rho\sigma_B l)$, is identical to the first Born approximation to the differential cross section,

$$\frac{d\sigma^{(\mathrm{Born})}}{d\Omega}=\frac{2\beta A k_i^2}{\pi\mu^2}\left(\frac{1}{k\mu^{-1}}\right)^{2}, \quad (k\gg\mu). \tag{5}$$

The cross section given by Eq. (1) has the same form as Fisher's modified form for the differential cross section[2] and gives a multiple-scattering-induced η of

$$\eta=4\beta. \tag{6}$$

The cross sections given by Eqs. (1), (4), and (5) also hold for small-angle, critical scattering of unpolarized x rays from fluids, once the appropriate form for β is determined. Neglecting the forward scattering term, the first Born approximation for the coherent differential cross section of x-ray scattering from a fluid is given by[8]

$$\frac{d\sigma^{(\mathrm{Born})}}{d\Omega}=\frac{I(k)}{I_0}r^2 = N\left(\frac{e^2}{mc^2}\right)^2\frac{1+\cos^2\theta}{2}f^2(k)\rho\int d^3r\, e^{-i\vec{k}\cdot\vec{r}}g(r), \tag{7}$$

where N is the number of atoms in the fluid, θ is the scattering angle, $f(k)$ is the atomic form factor, and $g(r)$ is the pair correlation function of the fluid. When the fluid is near its critical point, $g(r)$, as given by Ornstein and Zernike, is

$$g(r)=\frac{1}{4\pi\rho r_1^2}\frac{e^{-\mu r}}{r}. \tag{8}$$

For small-angle scattering, the atomic form factor is well approximated by

$$f(k)\cong Z, \tag{9}$$

where Z is the number of electrons per atom. Thus, for small-angle x-ray scattering sufficiently close to the critical point, the differential cross section given by Eq. (7) becomes

$$\frac{d\sigma^{(\mathrm{Born})}}{d\Omega}=N\left(\frac{e^2Z}{mc^2}\right)^2\frac{1}{r_1^2\mu^2}\left(\frac{1}{k\mu^{-1}}\right)^2, \quad (k\gg\mu). \tag{10}$$

Comparing Eq. (10) with Eq. (5), the multiple-scattering parameter β for small-angle critical x-ray scattering is given by

$$\beta=\frac{\pi l\rho}{2k_i^2r_1^2}\left(\frac{e^2Z}{mc^2}\right)^2 \tag{11}$$

The relevant experimental parameters necessary in calculating β taken from a recent experiment on x-ray critical scattering from argon ($Z=18$) by Lin and Schmidt[9] are

$$l=0.025\text{ cm},\quad r_1=3.45\text{ Å},\quad k_i=4.09\text{ Å}^{-1}.$$

The critical particle number density for argon is

$$\rho=8.0\times10^{21}\ \text{atoms/cm}^3.$$

This gives a value for the multiple-scattering parameter β, Eq. (11), of $\beta=4.1\times10^{-5}$ for that experiment, and, from Eq. (6), gives rise to a multiple-scattering-induced η of $\eta=1.6\times10^{-4}$, which is negligible compared to the experimentally measured η ($\eta=0.10\pm0.05$).

Because of the smallness of the multiple-scattering-induced η as compared to the experimentally measured η, one might conclude that this is evidence of the failure of the OZ theory. However, Tracy and McCoy[10] in analyzing this experiment have concluded that since the scaling relation $(2-\eta)\ \nu=\gamma$ was assumed in analyzing the data, an independent measurement of η was not provided. In fact, at the time of their writing (1975), Tracy and McCoy concluded that "no experiment to date unambiguously and directly establishes that the critical exponent η is greater than zero."

In critical scattering, an experimentally measured deviation in Lorentzian line shape, i.e., an experimentally measured nonzero η, can arise from many sources, e.g., multiple scattering, genuine deviations in OZ theory, inelasticity, experimental errors, etc. Certainly, no determination was, or is, made by us that this deviation has its origins solely in one source, i.e., multiple scattering. However, it is clear, that better, more careful experiments, in which all of these possible sources, including multiple scattering, are correctly taken into account, are needed if the existence of an η greater than zero is to be unambiguously experimentally verified.

The author wishes to thank Professor H. A. Gersch for his helpful comments and suggestions regarding this work.

[1]L. S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam 17, 793 (1914); Phys. Z. 19, 134 (1918).
[2]M. E. Fisher, J. Math. Phys. 5, 944 (1964).
[3]M. E. Fisher and R. J. Burford, Phys. Rev. 156, 583 (1967).
[4]D. W. Oxtoby and W. M. Gelbart, Phys. Rev. A 10, 738 (1974).
[5]W. A. Holm and H. A. Gersch, Phys. Rev. B 13, 4984 (1976).
[6]H. A. Gersch and W. A. Holm, Phys. Rev. B 14, 1307 (1976).
[7]The multiple-scattering parameter β used in this note is not to be confused with the critical exponent β.
[8]L. V. Azánoff, *Elements of X-Ray Crystallography* (McGraw-Hill, New York, 1968), Chap. 8.
[9]J. S. Lin and P. W. Schmidt, Phys. Rev. A 10, 2290 (1974).
[10]C. A. Tracy and B. M. McCoy, Phys. Rev. B 12, 368 (1975).