# Double-scattering-induced deviations from Ornstein-Zernike behavior near the critical point*

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We consider double light scattering by a simple fluid near its critical point. It is shown that Ornstein-Zernike-Debye plots of inverse total (single plus double) scattering intensity are not linear, but show downward curvature at small scattering angles near the critical point. This effect has been observed experimentally and is usually attributed to a nonzero value for the critical exponent $\eta$. We compare our conclusions with those of Splittorff and Miller, who have found that such downward curvature can also be caused by density gradients near the critical point.

Splittorff and Miller[1] have recently discussed the effect of gravity on the light-scattering spectra of simple fluids near their critical points. Because of a gravity-induced density gradient which becomes large near the critical point, they find that Ornstein-Zernike-Debye (OZD) plots of inverse scattering intensity versus the square of the (momentum-transfer) wave vector are not linear, but show downward curvature for small scattering angles. Such curvature has been observed experimentally and attributed to deviations from Ornstein-Zernike behavior arising from a nonzero value of the critical exponent $\eta$.[2] Splittorff and Miller discuss the possibility that these effects may be due instead to density gradients.

We have investigated the effect of *double* light scattering on OZD plots, and have found that it also leads to downward curvature and nonzero values for the "apparent" exponent $\eta$. Whereas Splittorff and Miller have included only single scattering and have looked at density gradients, we have assumed uniform density and looked at multiple scattering effects; in this sense our work complements theirs.

We have previously considered[3] *de*polarized light scattering near the gas-liquid critical point. The only difference in studying double *polarized* scattering is that a different element of the dipole propagator tensor must be used. Since the calculations are so similar to our previous work,[3] we will only outline them here.

The total electric field at any point in the fluid satisfies the integral equation

$$\vec{E}(\vec{r})=\vec{E}_0e^{i\vec{k}_v\cdot\vec{r}}+\alpha\int_{V_s}d\vec{r}'\,\overleftrightarrow{T}_{k_v}(\vec{r}-\vec{r}')\cdot\rho(\vec{r}')\vec{E}(\vec{r}')\ , \tag{1}$$

where $\vec{E}_0e^{i\vec{k}_v\cdot\vec{r}}$ is the incident electric field (a plane wave with vacuum wave vector $\vec{k}_v$), and $\alpha$ is the atomic polarizability;

$$\rho(\vec{r}')=\sum_{i=1}^{N}\delta(\vec{r}'-\vec{R}_i)$$

is the instantaneous number density at the point $\vec{r}'$ and $\vec{R}_i$ denotes the vector position of the $i$th particle. $\overleftrightarrow{T}_{k_v}$, the dipole propagator, is given by

$$\overleftrightarrow{T}_{k_v}(\vec{r})=e^{ik_vr}(3/r^3-3ik_v/r^2-k_v^2/r)\hat{r}\hat{r}+e^{ik_vr}(k_v^2/r-ik_v/r^2-1/r^3)\overleftrightarrow{I} \tag{2}$$

and acts on an oscillating dipole to give the electric field at a distance $\vec{r}$ away. Now, we can write

$$\vec{E}(\vec{r})=\vec{E}^L(\vec{r})+\Delta\vec{E}(\vec{r})\ , \tag{3}$$

where $\vec{E}^L(\vec{r})$, the Lorentz local field, satisfies Eq. (1) with $\rho(\vec{r}')$ replaced by the average density $\rho$. $\Delta\vec{E}(\vec{r})$, the fluctuating field which gives rise to scattering, satisfies the integral equation

$$\Delta\vec{E}(\vec{r})=\alpha\int_{V_s}d\vec{r}'\,\overleftrightarrow{T}_{k_0}(\vec{r}-\vec{r}')\cdot\Delta\rho(\vec{r}')[\vec{E}^L(\vec{r}')+\Delta\vec{E}(\vec{r}')]\ , \tag{4}$$

where $\Delta\rho(\vec{r}')=\rho(\vec{r}')-\rho$ is the density fluctuation at $\vec{r}'$, and $\vec{k}_0$ is the wave vector in the medium (directly related to $\vec{k}_v$ through the Lorentz-Lorenz index of refraction). $\Delta\vec{E}(\vec{r})$ can be calculated to arbitrary order in $\alpha$ by iterating Eq. (4). If we take the incident light to be polarized in the $z$ direction, then polarized-scattering experiments correspond to measuring the $z$ component of the electric field at the detector: the $(zz)$ intensity there is given by

$$I_{\vec{R}}^{zz}=\langle[\Delta\vec{E}(\vec{R})]_z[\Delta\vec{E}(\vec{R})]_z^*\rangle\ , \tag{5}$$

where the angular brackets denote a canonical ensemble average over fluid configurations.

$I_{\vec{R}}^{zz}$ can then be written as a power series in $\alpha$. The leading term, proportional to $\alpha^2$, corresponds to single scattering and is the only term retained in most treatments. It is given by

$$I_{\vec{R}}^{zz}(\text{single})=(\alpha^2|\vec{E}^L|^2/R^2)k_0^4\rho V_I S(k)\ , \tag{6}$$

where $V_I$ is the part of the sample volume illuminated by the incident laser beam, and $S(k)$ is the usual static structure factor ($\vec{k}=\vec{k}'-\vec{k}_0$ is the momentum transfer—the change in propagation wave vector due to the scattering). Ornstein-Zernike theory corresponds to the result

$$S(k)=1+4\pi A\rho/[k^2+(1/\xi)^2] \ , \tag{7}$$

where $\xi$ is the correlation length, while deviations from Ornstein-Zernike behavior can be represented by such forms as[2]

$$S(k)=1+4\pi A'\rho/[k^2+(1/\xi)^2]^{(1-\eta/2)} \ . \tag{8}$$

The terms in $\alpha^3$ in the series for $I_{\mathrm{R}}^{zz}$ (arising from cross terms between single and double scattering) have only a small effect on the absolute scattering intensity and are found to have the same angular distribution as single-scattering terms, so they are not of interest here.

The double-scattering terms in $\alpha^4$ *do* affect the angular distribution. They can be calculated in a completely analogous fashion to the depolarized scattering contributions[3] [the only difference being that we look at the *zz* rather than the *xz* component of the tensor $\overline{\overline{\mathrm{T}}}$ in Eq. (2)]. We present only the final result of the calculation here: the dominant double-scattering contribution near the critical point is given by

$$I_{\mathrm{R}}^{zz}(\text{double})=(\alpha^4\rho^4V_Ik_0^4|\vec{\mathrm{E}}_L|^2/R^2)4\pi^2A^2R_s a^2\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\,\frac{\sin^5\theta}{(1+a\sin\theta\cos\phi)[1+a\sin\theta\cos(\phi+\phi_s)]} \ , \tag{9}$$

where

$$a=2k_0^2/[2k_0^2+(1/\xi)^2] \ ,$$

$R_s$ is a linear dimension characterizing the sample size[3] (the radius, for a spherical volume), and $\phi_s$ is the scattering angle. [Unfortunately, it is virtually impossible to treat theoretically more realistic (i.e., nonspherical) sample shapes, and so we are not able to obtain rigorous estimates of the geometry dependence of the predicted $I_{\mathrm{R}}^{zz}$(double)'s.]

The total (single-plus-double) scattering intensity can be calculated (numerically) for different correlation lengths and scattering angles from Eqs. (7) and (9). Its inverse can then be plotted in an OZD plot as a function of

$$k^2=4k_0^2\sin^2(\phi_s/2) \ .$$

In Fig. 1 we show such a plot, using parameters for xenon on the critical isochore, $k_0=10^5$ cm$^{-1}$, a sample radius $R_s=1$ cm, and a correlation length $\xi=600$ Å ($T-T_c=0.031$ °C). Even though we have assumed Ornstein-Zernike theory ($\eta=0$) throughout, the OZD plot shows downward curvature due to double-scattering effects. In fact, Fig. 1 can be fit quite accurately with a functional form such as Eq. (8): it can also be compared to Fig. 2 of Ref. 1, where downward curvature due to density gradients (a completely different cause) is found.

The value of $\eta$ which fits the points in Fig. 1 is near 0.7, a rather large value. Theoretically-predicted values of $\eta$ (near 0.1) would give, at least for $k_0\xi \lesssim 1$, barely observable downward curvature; thus double-scattering effects can be much larger than the effects of non-Ornstein-Zernike correlation functions. Of course, if the sample size is smaller, there will be less double scattering, and thus less downward curvature (for example, a sample radius of 1 mm would give an "apparent" $\eta$ near 0.1). Still closer to the critical point, triple and higher-order scattering effects become important and our expression for the total scattering intensity becomes invalid. Our work has assumed that there is a temperature region in which double scattering effects are visible (giving downward curvature in OZD plots), while higher-order scattering is still small.

Because the front-to-back asymmetry of the double-scattering contributions is so much smaller than that found for $I_{\mathrm{R}}^{zz}$(single), the angle dependence

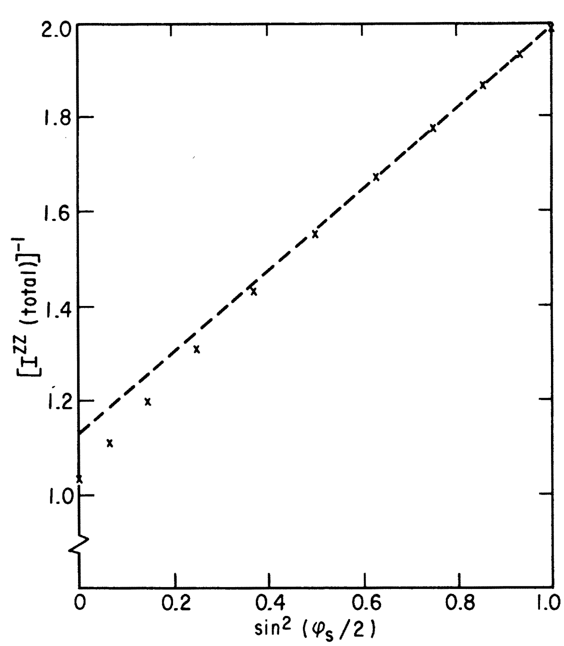


FIG. 1. OZD plot of predicted inverse scattering intensity (arbitrary units) vs. $\sin^2(\phi_s/2)$, for xenon at $T-T_c=0.031$ °C, with $R_s=1$ cm. Deviations from linear behavior are due to double-scattering effects.

of the total $zz$ intensity is weaker than what would be predicted by using (6) for small values of $\epsilon \equiv (T - T_c)/T_c$. This is consistent with recent $\xi(T)$ measurements of Lunacek and Cannell,[4] in which the temperature dependence of the correlation length $\xi$ is determined by looking at

$$R \equiv [I_{\text{R}}^{zz}(k_f) - I_{\text{R}}^{zz}(k_b)]/I_{\text{R}}^{zz}(k_f)$$

as a function of $\epsilon$: here $k_{f,b} = 2k_0 \sin(\phi_{f,b}/2)$, with $\phi_f \approx 15°$ and $\phi_b \approx 165°$. For $CO_2$, for example, and $\epsilon < 10^{-4}$, the asymmetry $R$ is smaller than one would predict from (6). This discrepancy arises from the onset of small $I_{\text{R}}^{zz}$(double) contributions (with weaker angle dependence), as is confirmed experimentally by monitoring the asymmetry and intensity of the light scattered by a volume immediately above the incident beam.

A complete theory should include both double-scattering and density-gradient effects simultaneously, but we do not think that this would significantly change either our conclusions or those of Ref. 1. It thus appears that downward curvature in OZD plots can arise from at least three different causes (density gradients, double scattering, and genuine deviations from Ornstein-Zernike theory) whose effects are extremely difficult to separate.

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[2]For a recent discussion, see H. L. Swinney and B. E. A. Saleh, Phys. Rev. A 7, 747 (1973).

[3]D. W. Oxtoby and W. M. Gelbart, J. Chem. Phys. 60, 3359 (1974).

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