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Effect of gravity on the Rayleigh linewidth near the critical point

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The influence of Earth's gravity on measurements of the Rayleigh linewidth Γ of a simple fluid near its critical point is investigated in detail. Special attention is given to the scaled linewidth Γ^*. From a number of different viewpoints it is found that gravity significantly affects linewidth measurements in the critical region. Small errors in beam centering render available experimental data useless for the purposes of distinguishing between modern theories, as variations in beam height split the universal curve of the scaled linewidth into a single-parameter family. The mode-mode coupling and decoupled-mode theories, which in the gravity-free case predict slightly different results for Γ and Γ^*, predict qualitatively different behavior in the dependence of Γ on height and scattering angle when gravity is taken into account. When the relative deviation of Γ^* from its gravity-free uniform fluid value is plotted versus the reduced correlation length, it exhibits distinct patterns characterizing the different theories used to compute it. By comparing these patterns with the results of carefully controlled experiments, gravity should prove to be a useful tool for eventually selecting a correct theory.

I. INTRODUCTION

When a simple fluid is near its gas-liquid critical point the spontaneous density fluctuations become so large that illuminating light is scattered strongly in all directions. This phenomena was discovered over 100 years ago and is called critical opalescence. Besides great intensity, the scattered light exhibits another anomaly: The width of the Rayleigh (central) line of its spectrum narrows, approaching a small nonzero value, as the critical point is approached. This is related to the fact that near the critical point the lifetime of density fluctuations becomes very long, which is commonly referred to as "critical slowing down."

Studies of the Rayleigh linewidth Γ reveal valuable information about the dynamic properties of a fluid in the critical region. During the last ten years direct measurements of Γ became possible with the development of high-resolution light beating spectroscopy.[1,2] Theories were proposed and modifications were introduced so that now we are able to explain the observations fairly well. One of the most dramatic results is that for most cases the scaled linewidth Γ^* of simple fluids as well as liquid mixtures falls at least approximately on a single universal curve. It should be noted that, on occasion, considerable deviations from the universal curve have been observed.[3]

Recent theories of the linewidth differ from one another only slightly in the nonhydrodynamic region, which is located so close to the critical point that the usual assumption that long-wavelength fluctuations obey linear hydrodynamics breaks down. Not surprisingly, this is the same region where the gravity-induced density gradient, which results from the singular behavior of the compressibility in the critical region, is known to have a strong influence on critical phenomena.

In two previous investigations we found that in the critical region of a fluid the effect of gravity on measurements of the angular distribution[4] and the turbidity[5] of the scattered intensity is significant. Recently, Kim, Henry, and Kobayashi examined the effect of gravity on the Rayleigh linewidth and found that it is important here as well.[6] They use a partial moment approximation to determine approximate deviations from the Lorentzian line shape due to the finite beam diameter of the incident light. This method is applicable when the influence of gravity is relatively weak, so that deviations from the Lorentzian line shape are small.

The purpose of this paper is to describe some alternative approaches for using gravity effects to distinguish between different theories of the Rayleigh linewidth. To facilitate comparison and in the interest of brevity, we consider the same theories of the linewidth as Kim *et al.*, with the deletion of a minor inconsistency. Thus this work complements theirs.

A number of geometrical considerations are carefully taken into account. We find that the influence of gravity on linewidth is sufficiently great that the practical experimental uncertainty in locating the height where the critical density occurs, as well as the finite beam diameter, make it impossible to distinguish which theory, if any, best represents the available experimental data. Because of gravity we also find that deviations from the so-called universal curve of Γ^* are inevitable, regardless of the theory used to describe Γ^*. Of major significance is the *deviation* from the gravity-free case of the scaled linewidth associated with each theory. Our studies indicate that each theory is characterized by a deviation that has a distinct pattern, independent of the scattering geometry, beam diameter, or sample. By distinguishing between these patterns, gravity may play an important role in eventually selecting a correct theory. We conclude that a scattering geometry where the incident beam is directed vertically, parallel to the density gradient, is most practical for examining these deviations. The vertical beam geometry minimizes the effects of multiple scattering and eliminates beam bending (due to refraction). It is insensitive to small variations in the average sample density and location of the height where the critical density occurs. Finally, in the vertical beam geometry, knowledge of the intensity profile or beam diameter of the incident beam is unnecessary.

II. FORMULATION

For a uniform fluid the scattered intensity per unit solid angle and per unit frequency is given in the Lorentzian form as

$$\mathcal{I}(\Omega,\omega)=(1/\pi)I(\Omega)\Gamma/[(\omega-\omega_0)^2+\Gamma^2], \tag{1}$$

where ω_0 is the frequency of the incident laser light. Γ is the half width of the intense central peak of the scattered light and the diffusive decay rate of the local density fluctuations. $I(\Omega)$ is the angular distribution of the scattered intensity and is given by the Ornstein-Zernike (OZ) theory as[7]

$$I(\Omega)=CK_T\sin^2\psi/(1+q^2\xi^2), \tag{2}$$

where K_T is the isothermal compressibility, ξ is the correlation length, ψ is the angle between the directions of observation and polarization of the incident light, and C is proportional to the volume of the fluid. The scattered wave number is related to the refractive index at the critical point n_c, the vacuum wavelength of the incident light λ and the scattering angle θ by

$$q=(4\pi/\lambda)n_c\sin\tfrac{1}{2}\theta. \tag{3}$$

Two modern theories of the decay rate, or Rayleigh linewidth, have been reviewed in much detail by Swinney and Henry.[1] Here we adopt the same notation and the same numerical values for all physical quantities. The total linewidth can be decomposed into the sum of a background contribution and a critical part which arises from the pathological fluctuation dynamics in the critical region. Following Swinney and Henry, we also assume that the background contribution to the total linewidth can be written in the OZ theory as

$$\Gamma^B=(\lambda_B/\rho c_P)q^2(1+x^2), \tag{4}$$

where $x=q\xi$, λ_B is the background contribution to the thermal conductivity, c_P is the specific heat at constant pressure, and ρ is the density of the fluid.

When the OZ correlation function is assumed, Kawasaki's mode-mode coupling[8] (MMC) theory predicts for the critical part of the linewidth

$$\Gamma^c=(k_BT/6\pi\eta_s)q^3[K_0(x)/x^3]H(x), \tag{5}$$

where η_s is the shear viscosity and

$$K_0(x)=\tfrac{3}{4}[1+x^2+(x^3-x^{-1})\tan^{-1}x]. \tag{6}$$

The monotonically increasing function $H(x)$ here represents the modifications which result from considering the dependence of the shear viscosity on q and ω.[9]

In Ferrell's decoupled-mode[10] (DM) theory the critical contribution is

$$\Gamma^c=(k_BT/6\pi\eta_s^{\text{eff}})q^3[K_0(x)/x^3], \tag{7}$$

where

$$\eta_s^{\text{eff}}=\eta_s^B\left[1+\frac{8\overline{\eta}}{15\pi^2\eta_s^B}\ln\left(\frac{q_D}{q}\frac{x}{(1+x^2)^{1/2}}\right)+\tau(x)\right]. \tag{8}$$

In the above η_s^{eff} is the effective shear viscosity, η_s^B is its background contribution, $\overline{\eta}$ and q_D are parameters characterizing the fluid, and $\tau(x)$ increases monotonically with x.

Note that we do not include the relatively small vertex correction[11] to the MMC theory. In neither the MMC nor the DM theories do we include corrections due to a modified OZ theory of the pair correlation function. This omission is based not merely on the fact that this correction itself is comparatively small, but also on the fact that it involves a reasonable choice of the critical exponent η, as well as a choice of one of several possible functional forms of the modified correlation function, each of which gives both a quantitatively and qualitatively different modification factor to Γ^c.[12,13] Furthermore, such a correction to Γ^c is only meaningful when it is consistently applied to the calculation of K_T (in terms of ξ), $I(\Omega)$ in Eq. (2), and Γ^B in Eq. (4). Although Kim *et al.* have included such a correction, they have not done so consistently.[6]

The study of the effect of gravity on the linewidth is carried out along the same lines as our earlier work on the angular distribution and turbidity.[5,14] Again we use the simple equation of state[15] for a fluid in the critical region

$$\frac{\partial P}{\partial \rho}=A\epsilon^\gamma+\delta B\,|\rho_r|^{\delta-1}, \tag{9}$$

where A and B are constants for a given fluid, γ

and δ are the usual critical exponents, and the reduced temperature ϵ and density ρ_r are defined by

$$\epsilon = (T - T_c)/T_c, \quad \rho_r = (\rho_c - \rho)/\rho_c. \tag{10}$$

The subscript c always indicates evaluation at the critical point. Using optical measurements, Wilcox and Balzarini have shown that this equation generates good density profiles for xenon in the laboratory.[15] This is an essential requirement for any candidate employed for the study of gravity effects. The profiles generated by Eq. (9) are quantitatively as well as qualitatively similar to those of the linearized equation of state.[16]

The effect of gravity on the scattered spectrum is computed by assuming that the Lorentzian line shape is locally valid for small, relatively homogeneous volume elements. The contribution of a horizontal fluid layer to the spectrum is thus found by evaluating the density in the layer from Eq. (9) and the barometric equation, and using this value of the density to evaluate the thermodynamic quantities in Eq. (1). Details of this procedure are to be found in our previous papers.[4,5]

Because of gravity, the shape of the composite spectrum that arises from integrating the local scattered intensity over a finite height in a fluid is no longer Lorentzian. Rather, it is a continuous weighted sum of Lorentzians having a continuously varying linewidth. Thus, when the influence of gravity is appreciable, the composite spectrum cannot be closely approximated by a single Lorentzian line. Here we make no attempt to study the detailed shape of the spectrum. Rather, we examine the behavior of the linewidth, defined as half the frequency spread at which the intensity is half maximum, in the critical region. In all cases the integration over height is carried out numerically.

Only the Rayleigh peak of the scattered light is taken into consideration; the contribution of the two inelastic Brillouin peaks to the total intensity is negligible within the temperature range where the gravity effect is significant. For example, Ford *et al.* have observed that near the critical point of carbon dioxide

$$I_R/2I_B \simeq 0.542\epsilon^{-1.02},$$

where I_R and I_B are the intensities of the Rayleigh and Brillouin lines, respectively.[17]

III. RAYLEIGH LINEWIDTH

To date linewidth data have been compared with the MMC and DM theories, Eqs. (5)–(7), possibly with some other minor modifications. The experimental fluid samples are assumed to be uniform so that all thermodynamics quantities are calculated at the critical density ρ_c. In practice this procedure is valid only when the light scattering occurs at the precise height in the fluid (say $z = z_c$) where the critical density occurs ($\rho = \rho_c$).

For temperatures close to T_c a strong density gradient will develop throughout the fluid due to the coupling of the Earth's gravity with the large isothermal compressibility in the critical region. Only within a small layer of the sample will the density be close to ρ_c. As T_c is approached from above, the density gradient diverges at z_c and the layer becomes vanishingly thin. Regarding a finite sample of the fluid as a whole, the effect of approaching the critical point by lowering T towards T_c is offset by the tendency of the density in most of the sample to drift away from its value at the critical point. The net result is twofold: First, local thermodynamic quantities vary strongly with height z; second, and more significantly, the singular nature of the critical point is mitigated by gravity.

The dependence of the linewidth on height $\Gamma(z)$ occurs through its dependence on local thermodynamic quantities and has been studied carefully by Kim *et al.*[6] With them we find that, because of slight differences in curvature in the variation of linewidth with x, $\Gamma(x)$, the MMC and DM theories predict different patterns of $\Gamma(z)$ (see Fig. 1). By using smaller modification factors for both theories, we obtain corresponding smaller curvatures in $\Gamma(x)$, and hence slightly different results for $\Gamma(z)$. In contrast to their work, we find that the single minimum of $\Gamma(z)$ generated by the DM theory occurs exactly at $z = z_c$, and that the double minima generated by the MMC theory are positioned closer to $z = z_c$. It should be mentioned that, in the absence of the shear viscosity dispersion correction, the MMC theory also yields simply a

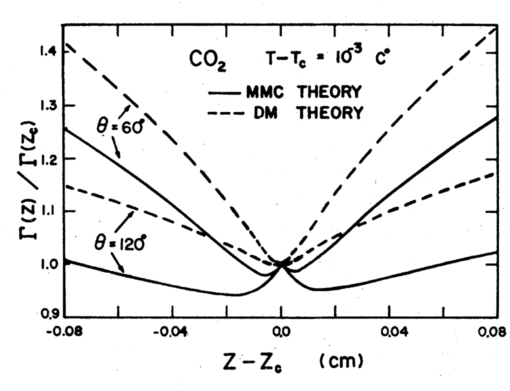

FIG. 1. Reduced linewidth $\Gamma(z)/\Gamma(z_c)$ vs $z - z_c$ for CO_2 at $T - T_c = 0.001$ C°. The MMC theory predicts that the minimum of $\Gamma(t)$ does not occur at $z = z_c$. The DM theory predicts that the minimum always occurs at z_c.

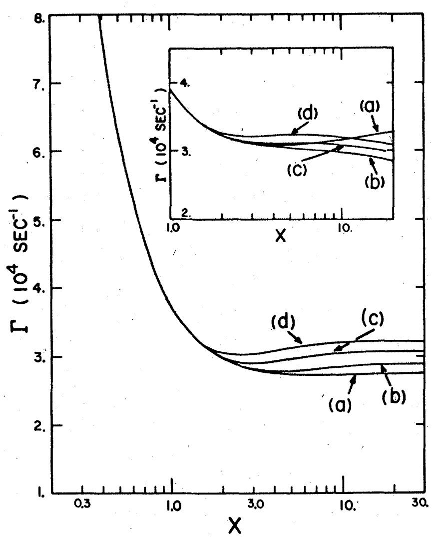

FIG. 2. Linewidth of CO_2 at $\theta=90°$ vs $x=q\,\xi$, from the DM theory for four values of $z-z_c$ (in cm): (a) 0.0; (b) 0.01; (c) 0.03; and (d) 0.05. The corresponding results for the MMC theory are given in the insert.

single minimum.

Because $\Gamma(z)$ is a rapidly varying function of height, a small experimental error in the location of z_c will produce a considerable alteration of the curve $\Gamma(x)$. This is shown in Fig. 2 for carbon dioxide with scattering angle $\theta=90°$. For xenon the effect of gravity on $\Gamma(x)$ will be larger, and, as a rule, for smaller θ the effect is larger. Examining Fig. 2 leads us to conclude that the influence of gravity coupled with possible errors in locating z_c makes it extremely difficult to compare the MMC and DM theories simply by inspecting the curvature of experimental $\Gamma(x)$ plots in the critical region. A slight error in z_c can make an MMC plot look like a DM plot, or vice versa.

Uncertainty in the experimental determination of z_c is not the only complicating feature. Another practical consideration is the finite diameter of the incident laser light. The observed spectrum is the result of scattering throughout the entire cross section of the incident beam which simultaneously illuminates layers of varying density gradient, and hence varying $\Gamma(z)$. For an incident laser beam with diameter D the intensity profile may be expressed in a Gaussian form,

$$I(r)=I_0(\tfrac{1}{2}\pi^{1/2}D)^{-2}\exp[-(r/\tfrac{1}{2}D)^2], \qquad (11)$$

where r is the distance from the beam axis and I_0 is the incident power. $I(r)$ is employed as a weighting function for the scattered intensity $\mathcal{I}(\Omega,\omega)$ in performing the integration over height. This provides us with a spectrum and a linewidth that depend both on the height of the beam axis and on the beam diameter as well.

For the special case of a laser beam of diameter D centered exactly at z_c we can determine quantitatively how much gravity will affect the measurement of Γ at a scattering angle θ by computing

$$R_D(\theta)=[\Gamma(\theta,D)-\Gamma(\theta,D=0)]/\Gamma(\theta,D=0) \qquad (12)$$

in an obvious notation. Plots of R_D vs θ are shown in Fig. 3 for xenon when $D=0.01$ cm. The influence of gravity on Γ is found to be appreciable for scattering angles $\theta<40°$ when T is close to T_c. In carbon dioxide the gravity effect is smaller and we get similar curves of $R_D(\theta)$; but with smaller values of $|R_D-1|$ at all temperatures and angles. Figure 3 also provides a comparison of the two theories: R_D is monotone decreasing with θ in each theory; the DM theory yields a positive definite R_D in conformity with its single minimum for $\Gamma(z)$ at z_c.

For larger values of D the light beam encounters a greater range of the density gradient so that more of the illuminated sample is further from the critical point, yielding larger values of R_D. In a more realistic situation neither D nor $z-z_c$ vanish, and the effect of a beam axis displaced from z_c must also be considered. When $z\neq z_c$ the linewidth is less sensitive to variations in beam diameter than z_c since the density gradient is greatest at z_c.

IV. SCALED LINEWIDTH Γ^*

The scaled linewidth, defined as

$$\Gamma^*=(6\pi\eta_S/k_BTq^3)\Gamma^c, \qquad (13)$$

is regarded as a better tool than Γ itself for comparing different theories of Γ. When Γ^* is plotted as function of x, the MMC theory predicts a single universal curve for all fluid systems independent

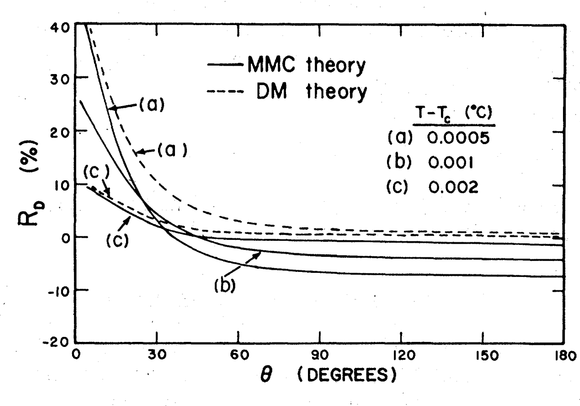

FIG. 3. Relative change of the linewidth R_D vs the scattering angle θ for a beam of diameter $D=0.01$ cm centered at $z=z_c$.

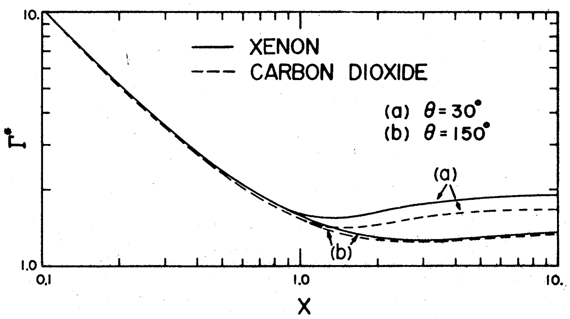

FIG. 4. Scaled linewidth $\Gamma^*(x)$ from the DM theory when $z-z_c=0.01$ cm.

of the particular thermodynamic path or scattering angles. For the DM theory it is evident from the expression for η_S^{eff}, Eq. (8), that Γ^* is not simply a function of the combined variable $x=q\xi$, but also exhibits a slight dependence on $\overline{\eta}$ and q_D, a parameter characterizing the sample.

In practice, $\Gamma^*(x)$ is derived from the linewidth data with background contribution subtracted. In a similar way, we simulate the gravity-affected Γ^* by first calculating the corresponding Γ_G as the experimental linewidth and then subtracting from this the gravity-free background Γ^B associated with a uniform fluid of density ρ_c:

$$\Gamma_G^*(x)=\frac{6\pi\eta_S(\rho=\rho_c)}{k_BT_cq^3}[\Gamma_G(x)-\Gamma^B(z=z_c)], \tag{14}$$

where η_S and x are assumed to be taken at $z=z_c$.

The effect of gravity on the $\Gamma^*(x)$ curve so obtained is evident from the fact that only the correlation length ξ of the combined variable $x=q\xi$ is subjected to change along the density gradient, while another factor,

$$q=(4\pi/\lambda)n_c\sin\tfrac{1}{2}\theta\,,$$

depends on scattering angle, wavelength, and the refractive index, which may vary from fluid to fluid. Thus it is not surprising that an error in locating z_c by a small amount, say, $z-z_c=0.01$ cm, will produce considerable change in the universal $\Gamma^*(x)$ curve. Figure 4 illustrates this situation. Results from the DM theory are shown for carbon dioxide and xenon, and for both cases two angles are used. The scatter of $\Gamma^*(x)$ curves is quite large.

The comparison of the two theories of Γ^* under the influence of gravity is shown in Fig. 5, where the relative deviation

$$R_z^*=[\Gamma^*(z)-\Gamma^*(z_c)]/\Gamma^*(z_c) \tag{15}$$

is introduced. As in the case of $\Gamma(x)$ shown in Fig. 3, the MMC theory predicts smaller deviations from the gravity free $\Gamma^*(x)$ curve, and yields negative values of $R_z^*(x)$ for some cases. In general, a large modification factor $H(x)$ generates a large upward curvature for $\Gamma(\chi)$ and an increasingly negative $R_z^*(x)$ for selected regions of x.

Actual experimental results do show deviations from the so-called universal $\Gamma^*(x)$ curve. In the hydrodynamic region ($x\ll 1$), these might be attributed to the errors in the background contribution which becomes predominant for temperatures far from T_c. Gülari and Pings find that by slightly adjusting the thermodynamic quantities involved in Γ^B of ethane, the agreement between theory and Γ^* data is improved considerably in the region $x\ll 1$, but not in the critical region.[18] The systematic and reproducible deviations in the nonlocal hydrodynamic region ($0.1<x<1.0$) observed by Schmidt and Harker[3] might suggest that either Γ^B, Γ^c, or both, must be modified to produce the observed q dependence. The weak q dependence of Γ^c in the DM theory is too small to explain these deviations. The effect of gravity is not expected to enhance the deviations until the critical region ($x>1$) is reached. Schmidt also finds that systematic deviations become more pronounced in the critical region.[3] Gravity may play an important role here.

The MMC and DM theories may be compared effectively only in the region where $x>10$. Reports on Γ (or Γ^*) in or near this region are sparse and subjected to considerable uncertainty. Both absolute values and relative curvatures of $\Gamma(x)$ or $\Gamma^*(x)$ in both theories have been compared with experimental results. Observations[19,20] seem to

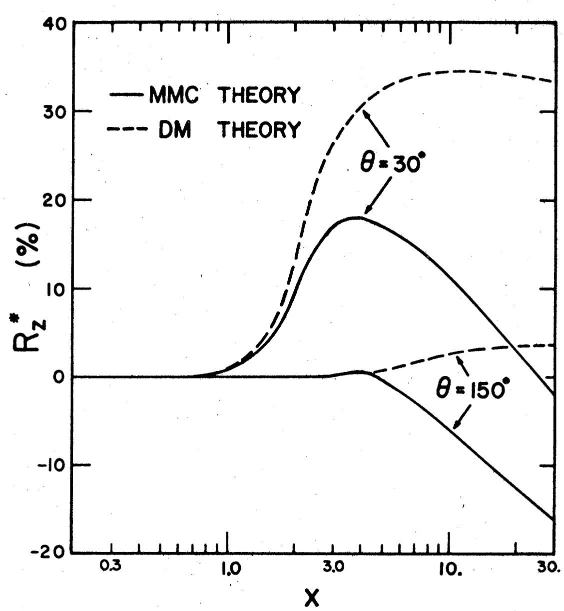

FIG. 5. Relative deviation of Γ^*, $R^*_z(x)$, for CO_2 with $z-z_c=0.01$ cm.

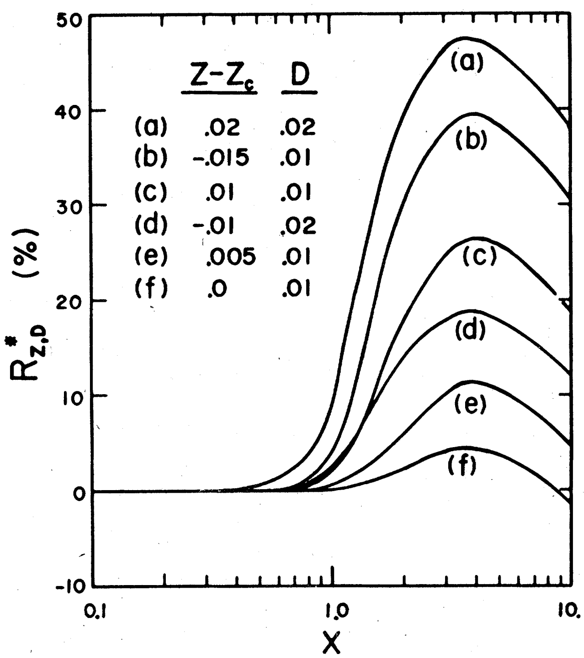

FIG. 6. Relative deviation of Γ^* from the MMC theory for xenon at $\theta = 30°$. Plots for six combinations of $z - z_c$ and D are shown (all in cm).

imply that the MMC theory with modifications is better than the unmodified original theory of Kawasaki,[8] i.e., the data shows upward curvature of $\Gamma(x)$ or $\Gamma^*(x)$ in the critical region. Swinney and Henry suggest that the DM theory might be better than the MMC theory in their analysis of $\Gamma^*(x)$ curves.[1] The results are not conclusive. More data is needed in the critical region, especially for $x > 10$. Furthermore, accurate data of $\eta_s(\epsilon)$ is needed in this region for better reliability.

From Fig. 5, it is found that $R_z^*(x)$ plots exhibit different patterns for the two theories, as is the case for $\Gamma(z)$. Instead of examining the absolute values or the relative curvature of Γ (or Γ^*), which may be affected to an uncertain extent by gravity as well as other ambiguities, it is more practical to test theories by observing the shapes of $R_z^*(x)$ curves with gravity taken into consideration.

Figure 6 shows the percentage deviations for more realistic situations. The results of several combinations of $z - z_c$ and beam diameter D are presented for a sample of xenon with $\theta = 30°$ in the MMC theory. Although the effect of assuming $D \neq 0$ is to introduce deviations for the case of $z = z_c$, conversely it reduces deviations from the case of a point light source when $z \neq z_c$. The general features of $R_{z,D}^*(x)$ are almost the same for various combinations of z and D. Furthermore, the same pattern is obtained for a sample of carbon dioxide when the same theory is used. The only change is the peak value of R^* which is related to the "sensitivity" of a fluid to the gravity effect. For example, the peak value of R_z^* in the MMC theory, with $\theta = 30°$, is 30% for xenon and 18% for carbon dioxide.

Difficulty arises in using $\Gamma(z)$ and $R_{z,D}^*$ to test the theory due to the uncertainties in z, z_c, and D. This difficulty may be avoided if we choose a different experimental geometry where the light is incident from below and traverses the fluid of sample height h vertically, parallel to the density gradient. The characteristic pattern of $R_h^*(x)$, the percentage change of $\Gamma^*(x)$, is the same as that of $R_{z,D}^*(x)$ with the exception of larger peak values. Figure 7 illustrates some of the results.

It is a consequence of the fact that only a small layer near z_c contributes most to the scattered intensity $\mathcal{I}(\Omega, \omega)$, as well as the fact that the height (z) asymmetry of the density gradient $\rho(z)$ is insignificant, that the error in determining h and locating z_c will have negligible effect on R_h^*. We have carefully examined the case of xenon and determined that for $h = 0.1$, 0.5, and 1.0 cm, variations of z_c by $\pm 0.1h$ produce almost unnoticeable changes in R_h^* for all angles.

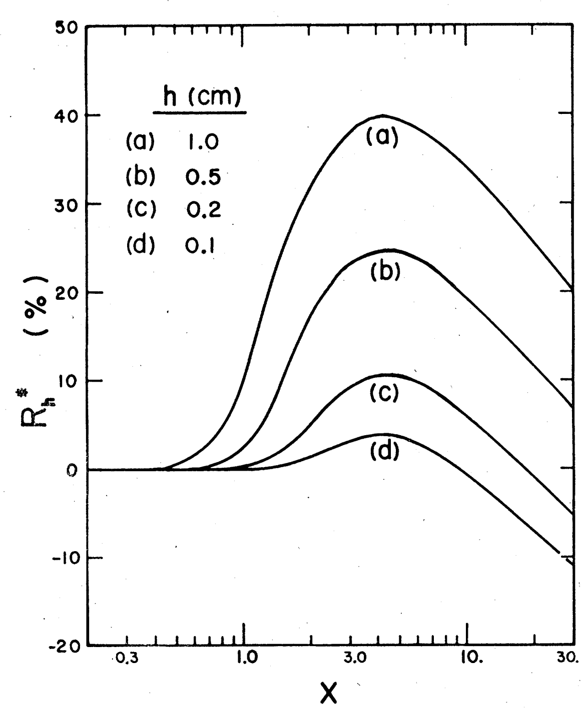

FIG. 7. Relative deviation of Γ^* from the MMC theory for xenon at $\theta = 90°$. Plots for four values of sample height h are shown.

In the general case, both theories predict a small, weak, θ-dependent R^* for large angles, say $75° \lesssim \theta \lesssim 180°$ when gravity is considered. This can be roughly seen in Fig. 3 which applies only to the limited case where the beam is centered at z_c. Furthermore, R^* at large angles is comparatively less sensitive to changes in z, D, and h. Thus, for the purpose of reducing gravity effects on Γ, large-angle measurements are suggested. Alternatively, if plots of R^* vs x are used to distinguish between different theories, measurements at smaller angles are considerably more useful.

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