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Probability Distribution of Photocounts of the Light Scattered by Critical Fluctuations

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The probability distribution of photocounts $P(n, T)$ of the light scattered by concentration fluctuations in a binary system near the critical point has been measured. The results turn out to be consistent with the theoretical predictions for Gaussian–Lorentzian light.

KEY WORDS: Photonstatistics; critical fluctuation.

The technique of intensity correlation spectroscopy has been one of the most important tools to study time-dependent hydrodynamic fluctuations in fluids. In particular when close to a critical point this method allows to measure with a high precision the decay rate of the order parameter whose fluctuations decay very slowly in time. However, a crucial assumption for the applicability of the technique is that the scattered electric field $E_S(t)$ be a Gaussian random process. In this case$^{(1,2)}$ a factorization condition, known as the Siegert relation, is valid, i.e.,

$$g^{(2)}(t) = 1 + |g^{(1)}(t)|^2 \tag{1}$$

where $g^{(1)}(t)$ and $g^{(2)}(t)$ are given by

$$g^{(1)}(t) = \frac{\langle E_S(t) E_S^*(0)\rangle}{\langle |E_S(0)|^2\rangle}, \qquad g^{(2)}(t) = \frac{\langle |E_s(0)|^2 |E_S(t)|^2\rangle}{\langle |E_S(0)|^2\rangle^2} \tag{2}$$

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This Gaussian assumption is, however, only a sufficient condition for the validity of the factorization condition (1) which is fundamental to the photon correlation spectroscopy. We have previously shown$^{(3)}$ that (1) can result from a less restricted condition. We will consider here the case of scattering of laser light from a two-component liquid mixture near the consolute point. In this case the order parameter is the concentration of one of the components and $E_S(t)$ is proportional to its Fourier component of wave number q, the scattering vector, $c(q,t)$. $g^{(1)}(t)$ and $g^{(2)}(t)$ can then be written directly in terms of $c(q,t)$ as

$$g^{(2)}(t) = \frac{\langle |c(q,0)|^2 |c(q,t)|^2 \rangle}{\langle |c(q,0)|^2 \rangle^2} \tag{3}$$

$$g^{(1)}(t) = \frac{\langle c^*(q,0) c(q,t) \rangle}{\langle |c(q,0)|^2 \rangle} \tag{4}$$

regardless of the phase fluctuations of the laser beam. In fact Mandel$^{(4)}$ has shown that the scattered field $E_S(t)$ is necessarily non-Gaussian if one takes into account the phase fluctuations of laser light. However, we have shown that relation (1) still holds for $g^{(2)}(t)$ and $g^{(1)}(t)$ as given by (3) and (4) if the concentration fluctuations $c(q,t)$ obeys linearized hydrodynamics equations. This is the case for a dilute Brownian particle suspension and for binary liquid mixture away from the critical point. However, very near the critical point, $c(q,t)$ no longer obeys the linearized hydrodynamic equations and is expected to become a non-Gaussian process from Landau–Ginzburg–Wilson theory.$^{(5)}$ However, due to the fact that the scattering volume V is generally much larger than ξ^3, the correlation range of the fluctuations cubed, in a realistic experimental arrangement, it turns out that this non-Gaussian correction is too small to be observable.$^{(3)}$ For example in our experiment $V \simeq (10^{-3}\text{ cm})^3$ and $\xi^3 \simeq (5 \times 10^{-5}\text{ cm})^3$ at 3 mK from the critical point. Thus it is reasonably sure that (1) is always valid in practically any experimental condition and the non-Gaussian nature of $E_S(t)$ does not enter into discussion in a scattering experiment.

The situation, however, is different in a photon statistics measurement, since the photocount distribution depends not only on the two-time correlation functions such as (3) and (4) but also on all multitime correlation functions.$^{(3)}$ Thus, a statement of factorization condition for the two-time correlation function is not sufficient to characterize photon statistics. Measurements of photon statistics near the critical point therefore test a conjecture that one can effectively regard $c(q,t)$ as a Gaussian random process (through its implication of being a condition limiting all its multitime correlation functions) in a realizable experimental condition.

We constructed a sampling circuitry, working in connection with a multichannel analyzer operating in pulse height analysis mode to measure $P(n,T)$ the probability of counting n photoelectrons during a sampling time T, for $0 < n < 256$ and $10\ \mu\text{s} < T < 10$ ms.

As was shown by Mandel,(6) the probability density $P(n,T;t)$ of counting n photoelectrons in the time interval $t, t+T$ is given by

$$P(n,T;t) = \frac{1}{n!}\langle[\alpha u(T,t)]^n \exp[-\alpha u(T,t)]\rangle \tag{5}$$

where α is the quantum efficiency of the phototube and $u(T,t)$ is the integrated intensity of the light whose instantaneous intensity is $I(t)$:

$$u(T,t) = \int_t^{t+T} dt'\, I(t') \tag{6}$$

The angular bracket in Eq. (5) indicates an ensemble average to be taken with respect to u. In what follows we shall assume that the radiation field is stationary and ergodic and then $P(n,T;t)$ is independent of the time origin t.

Let us consider first the case of a stabilized single-mode laser operating well above threshold. It can be shown(7) that to a first approximation the instantaneous intensity $I(t)$ is a constant I for a sampling time of practical interest. Therefore $u(T) = IT$ and $P(n,T)$ is given by a Poisson distribution[5]

$$P(n,T) = \frac{1}{n!}\langle n\rangle^n \exp[-\langle n\rangle] \tag{7}$$

where $\langle n\rangle$ is the mean number of counts per sampling period T, i.e., $\langle n\rangle = \alpha IT$. Figure 1 shows the results obtained with the light emitted from single mode intensity stabilized He–Ne laser. The data obtained for various sampling time T agree very well with formula (7).

On the other hand we can consider a "white" source obtained from light whose spectral distribution is very broad. In this case the practical sampling time T is always by far greater than the coherence time of the source. All the fluctuations of intensity are then smoothed out in the duration of sampling and the integrated intensity is practically a constant $\langle u\rangle$. As in the previous case we also obtain a Poisson distribution for $P(n,T)$ although for a rather different reason. This is very well supported by our data plotted in Figure 2.

In the case of the light scattered by a dilute solution of polystyrene spheres we are dealing with a bandwidth-limited field. Indeed the coherence time of this source is the decay time t_c of Van Hove correlation function expressing the probability of finding a particle located at position

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[5] More sophisticated expressions have already been used by various authors; see Ref. 8.

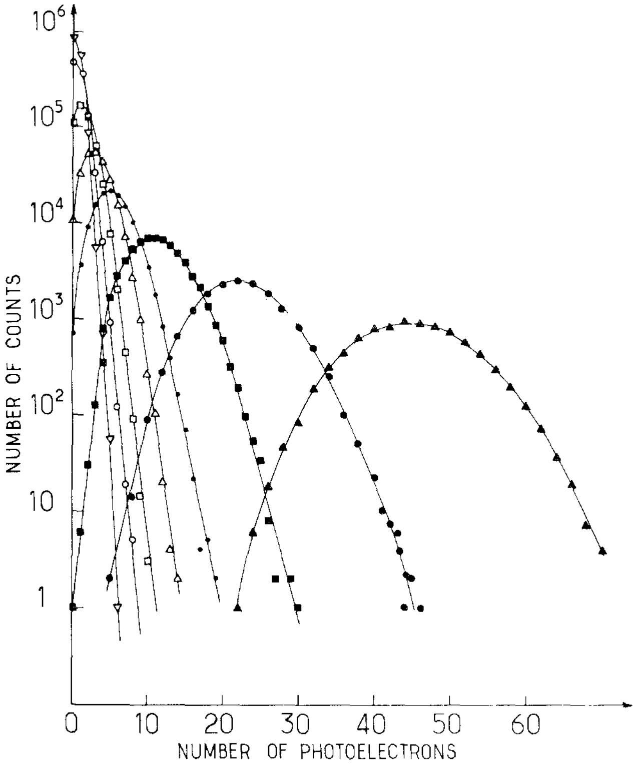

Fig. 1. Laser light: Probability distribution $P(n, T)$ (arbitrary units) vs n number of photoelectrons for different values of the sampling time T. ▽: $T = 40$ s; ○: $T = 100$ s; □: $T = 200$ s; △: $T = 400$ s; ●: $T = 800$ s; ■: $T = 1600$ s; •: $T = 3200$ s; ▲: $T = 6400$ s. The solid lines are calculated values according to Poisson distribution (counting rate: 7200 ± 300 c s^{-1}).

r at time t given that the particle was at the origin at $t = 0$. From classical hydrodynamics it can be shown (9) that for a particle undergoing Brownian motion this correlation function is an exponential whose decay time is $t_c = 1/Dq^2$, D being the Stokes–Einstein translational diffusion coefficient and q the transfer wave vector. Since the number of independent scatterers is usually large in the scattering volume the scattered field is Gaussian,(10) according to the central limit theorem. In this case (Gaussian light with Lorentzian spectral distribution) Bedard(11) has shown that the probability density $P(n, T)$ can be calculated for each value of T by a recurrence relation:

$$P(n,T) = \sum_{k=0}^{n-1} \frac{(-1)^{n+k+1}}{(n-k)!} \left[D_{n-k}(s)\right]_{s=1} P(n,T) \qquad (8)$$

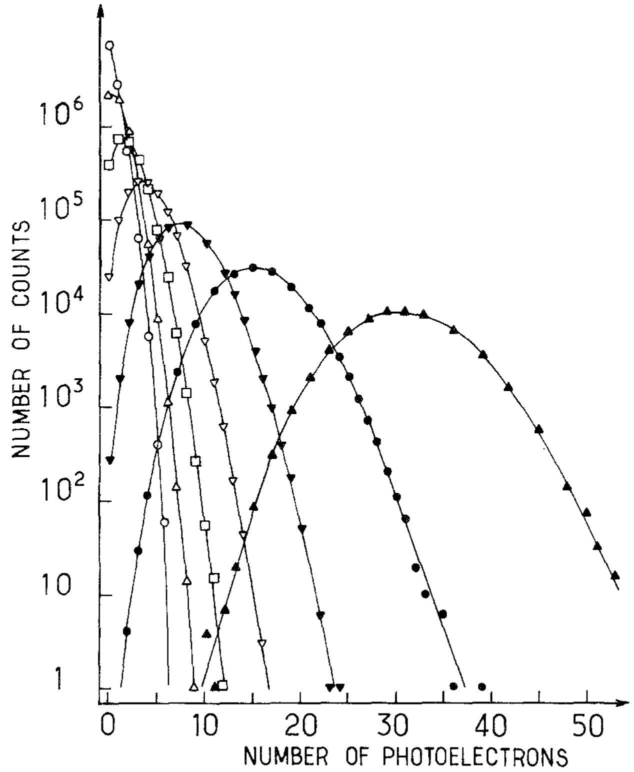

Fig. 2. White source: Probability distribution $P(n, T)$ (arbitrary units) vs n for different values of the sampling time T. ○: $T = 10$ s; △: $T = 20$ s; □: $T = 40$ s; ▽: $T = 80$ s; ▼: $T = 160$ s; ●: $T = 320$ s; ▲: $T = 640$ s. The solid lines are calculated values according to Poisson distribution (counting rate 4800 ± 100 c s^{-1}).

$D_s(x)$ being a complicated function involving modified spherical Bessel functions. The exact formula, (8), is rather difficult to handle but approximate expressions have been proposed.(6,12) Among these Glauber's(12) asymptotic formula is valid only for $T \gg t_c$. On the other hand Mandel(6) proposed a generalization of Bose–Einstein distribution describing the fluctuations of n Boson in s cells of phase space. The resultant expression for $P(n, T)$ is

$$P(n, T) \doteq \frac{\Gamma(n+s)}{n!\,\Gamma(s)} \frac{1}{(1 + \langle n\rangle/s)^s (1 + s/\langle n\rangle)^n} \tag{9}$$

where $\Gamma(x)$ is the Gamma function and

$$s = T^2/2\int_0^T dt\,(T - t)|g^{(1)}(t)|^2.$$

For the cases of Brownian particles and the critical mixture,

$$|g^{(1)}(g)|^2 = \exp\left[-\frac{2t}{t_c}\right]$$

where t_c is the correlation time and

$$s = \frac{u}{2}\left\{1 + \frac{1}{u}\left[\exp(-u) - 1\right]\right\}^{-1}$$

with $u = 2T/t_c$. The accuracy of the above formula (9) has been tested by Bedard *et al.*(13) and was found to be a very good approximation to $P(n, T)$. Equation (9) was used by Pearl and Troup(14) to interpret their experiments on scattering of laser light by a rotating ground glass disk. However, before we can test how well formula (9) fits our data we have to account for dead time corrections(15) and effects due to spatial coherence

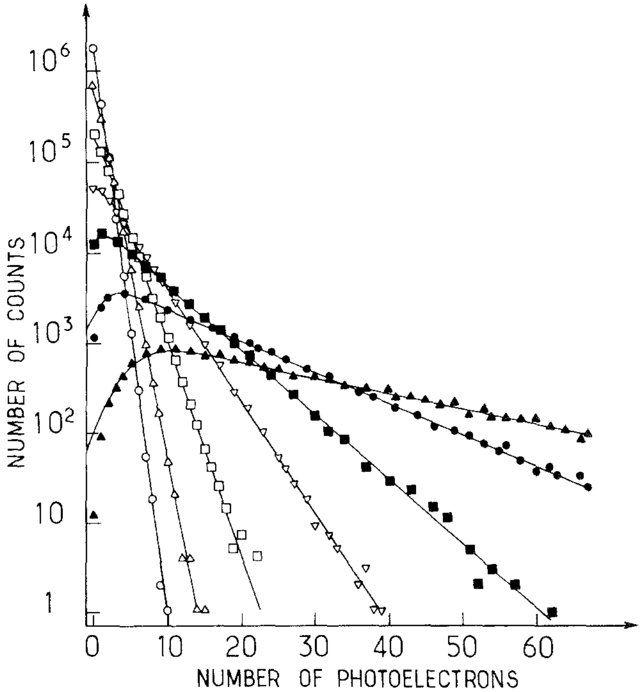

Fig. 3. Polystyrene latex in methanol. Probability distribution $P(n, T)$ vs n for various values of sampling time T. ○: $T = 40$ s; △: $T = 100$ s; □: $T = 200$ s; ▽: $T = 400$ s; ■: $T = 800$ s; ●: $T = 1600$ s; ▲: $T = 3200$ s. Solid lines: theoretical calculations according to Bedard formula [Eq. (23)]; counting rate 8000 + 200 c s^{-1}); correlation time $t_c = (3.30 + 0.05) \times 10^{-3}$ s.

of the field received on the phototube.(16) In order to minimize these distortions, the counting rate was set very low compared to the inverse of the dead time of the counter (100 MHz) and less than one coherence areas was subtended on the detector.

In Figs. 3 and 4 a quantity proportional to $P(n, T)$ is plotted as a function of n for various values of the sampling time T. The ratio T/t_c ranges from 1 to 10. Two systems have been studied, a dilute solution of

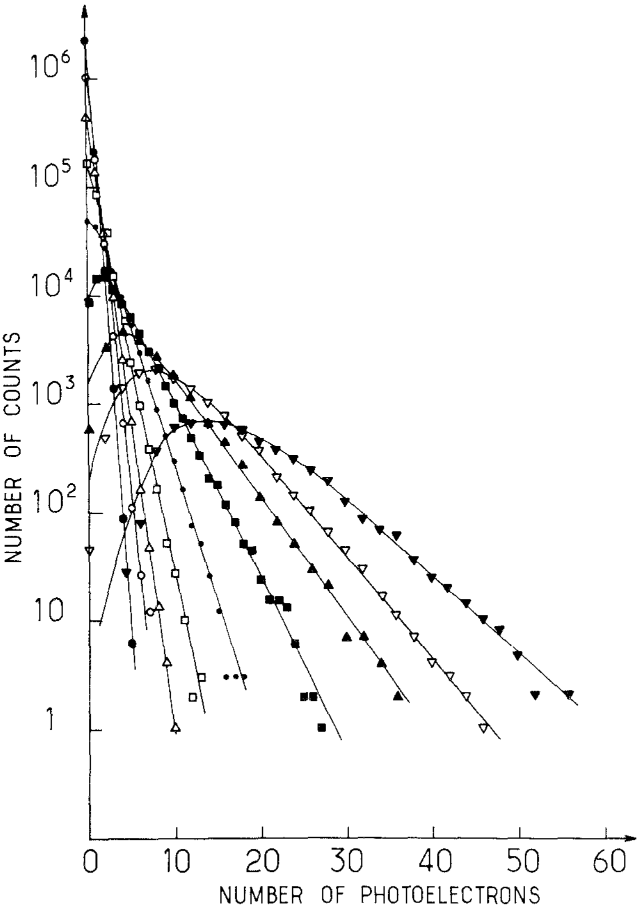

Fig. 4. Critical composition nitrobenzene n-hexane mixture a few millidegrees above T_c. Probability distribution $P(n, T)$ vs n for various values of the sampling time T. ●: $T = 40$ s; ○: $T = 80$ s; △: $T = 160$ s; □: $T = 340$ s; ·: $T = 640$ s; ■: $T = 1280$ s; ▲: $T = 2560$ s; ▽: $T = 4000$ s; ▼: $T = 8000$ s. Solid lines: Theoretical calculations according to Bedard formula [Eq. (23)]; counting rate 2500 ± 50 c s^{-1}; correlation time $t_c = (1.30 + 0.01) \times 10^{-3}$ s.

Brownian polystyrene spheres and a critical sample of nitrobenzene-*n*-hexane 3 millidegrees above the consolute temperature. The overall appearance of the two graphs is quite similar. For small values of T/t_c, $P(n, T)$ decays exponentially (note the semilog scale of Figs. 2 and 3) whereas for $T/t_c > 1$ $P(n, T)$ shows a maximum and then, for large values of n, decays almost exponentially.

Comparison between experiment and theory [Eq. (9)] needs only one adjustable parameter, the amplitude of $P(n, T)$ for a given value of n. For simplicity, the maximum value of $P(n, T)$ has been chosen to obtain the value of the parameter. Theoretical curves are plotted as solid lines on Figs. 3 and 4. Agreement between experiment and theory is very good for $T/t_c < 1$ whereas small discrepancies are observed for $T/t_c > 1$ for low values of n. However, the overall behavior of the theoretical curves is quite satisfactory.

For $T/t_c > 1$ a very good agreement between experiment and theory can be achieved if we assume s and n as free parameters. The values we obtain from the fits differ by about ±10% from those inferred from our experimental conditions.

Small deviations from Eq. (9) are to be expected since we know that it is only approximate and valid in the two limits $T/t_c \ll 1$ and $T/t_c \gg 1$. Furthermore, the Gaussian spatial distribution of the incoming laser beam has to be taken into account.(17) This might lead to corrections of the order of the observed differences. We may therefore conclude, in the light of the above results, that the field scattered by a critical mixture even very close to T_c [in our case $(T - T_c)/T_c < 10^{-5}$] behaves exactly like the one from a polystyrene sample. For both fields the probability distribution is very well accounted for by Mandel formula (9) for a Gaussian–Lorentzian source. This means that even at a few millidegrees above the critical temperature, the critical fluctuation can be regarded as a Gaussian random process.

We finally note that Beysens *et al.*(18) investigated the same critical mixture and measured the distribution of the integrated intensity which turns out to be exponential, in full agreement with our results.

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