Departures from Ornstein–Zernike Behavior in the Order-Parameter Dynamics of Fluids near the Critical Point*

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The effect of departures from Ornstein–Zernike correlations on the decay rate of order-parameter fluctuations in fluids near the critical point is considered here in the framework of the Kawasaki and Ferrell theories. For reasonable forms for the correlation function, the effect of departures from Ornstein–Zernike behavior varies from 1 to 11%, which is measurable using currently available light-scattering spectroscopic techniques.

The decay rate of order-parameter fluctuations in fluids near the critical point has been investigated theoretically by Kawasaki,[1] who obtained an integral expression for the leading singular term in the decay rate (Γ_{qs}) from a detailed mode-mode coupling analysis of order-parameter fluctuations, and by Ferrell,[2] who applied the fluctuation-dissipation theorem to obtain an integral form for Γ_{qs}. Kawasaki and Ferrell evaluated the integrals for Γ_{qs} using the Ornstein–Zernike form for the correlation function, in which case both theories yield for fluctuations of wave vector $\vec{q}$

$$\Gamma_{qs} = [k_B T / 6\pi\eta_s \xi^3]\, K_0(q\xi), \tag{1}$$

where ξ is the correlation range of the order-parameter fluctuations, η_s is the shear viscosity (called the "high-frequency" shear viscosity in the mode-mode coupling theory), and

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

The temperature dependence of the decay rate of order-parameter fluctuations has been extensively investigated in numerous light-scattering experiments[3] on pure fluids and binary mixtures near the critical point; in these experiments the decay rate Γ_q is equal to the linewidth of the central component in the spectrum of the scattered light. The singular part of the linewidth, obtained by subtracting from the measured linewidths the background terms which arise primarily from the nonsingular parts of the transport coefficients,[4] has been found to be described fairly accurately by Eq. (1), evaluated using independent data for η_s and ξ.[3,4] However, as the accuracy of the data has improved, it has become clear that there are systematic deviations from Eq. (1), especially very near the critical point.[3,4]

Recently Lo and Kawasaki[5] have refined the mode-mode coupling calculation of Γ_{qs}, obtaining the contribution of the simplest vertex corrections, all of which were ignored in Kawasaki's original derivation of Eq. (1); the vertex corrections reduce Eq. (1) by 2.44% for $q\xi \ll 1$ and increase it by 0.40% for $q\xi \gg 1$. Kawasaki and Lo[6] have also recently examined the viscosity which enters Eq. (1) in the mode-mode coupling theory and have obtained a relation between this "high-frequency" shear viscosity and the shear viscosity determined in macroscopic measurements. The result is that if η_s in Eq. (1) is taken as the macroscopic shear viscosity, then Eq. (1) must be increased by 5.5% in the hydrodynamic region ($q\xi \ll 1$), and the correction increases rapidly for increasing $q\xi$ above $q\xi = 1$, amounting to 23% at $q\xi = 10$. Perl and Ferrell[7] have also considered the effect of the q dependence of the viscosity in Eq. (1), using Ferrell's approach to the dynamics of a fluid near the critical point; however, in this calculation the nonlocal shear viscosity was obtained only in the limit $q\xi \gg 1$.

Kawasaki and Ferrell have both noted that the result for Γ_{qs} is sensitive to the form used for the correlation function. Thus it is of interest to evaluate the linewidth integrals for correlation functions other than the Ornstein–Zernike form which was used in all previous calculations. We report here the results of calculations of Γ_{qs} for three different forms for the correlation function which have been proposed to describe departures from Ornstein–Zernike behavior.[8]

Fisher and Burford[9] have shown that the Ornstein–Zernike form for the correlation function, which at the critical point decays asymptotically as $1/r$, is not valid for the three-dimensional Ising model and is probably incorrect for a real fluid as well. The correct asymptotic form for the correlation function at the critical point is expected to be $1/r^{1+\eta}$ with $\eta > 0$. The effect of a very small value for η would be difficult to detect experimentally; however, a lower bound for η significantly different from the Ornstein–Zernike value $\eta = 0$ is expected on the basis of the following inequality rigorously proved (for ferromagnets) by Fisher[10]: $\eta \geq 2 - 3(\delta - 1)/(\delta + 1)$, where δ is the exponent which describes the shape of the critical isotherm. A scaling-law analysis[11] of the data in the critical region of a number of ferromagnets and fluids yielded $\delta = 4.4 \pm 0.3$; hence the inequality implies $\eta \geq 0.11 \pm 0.06$.

Kawasaki's integral expression for the decay rate of order-parameter fluctuations, applicable for any correlation function, is[1]

$$\Gamma_{qs} = \frac{k_B T}{(2\pi)^3 \eta_s} \int d\vec{k} \left[\left(\frac{q}{k}\right)^2 - \left(\frac{\vec{q}\cdot\vec{k}}{k^2}\right)^2 \right] \frac{\hat{G}(\vec{q}-\vec{k})}{\hat{G}(\vec{q})}, \qquad (2)$$

where $\hat{G}(\vec{q}) = \int d\vec{k}\, G(\vec{r}) e^{i\vec{q}\cdot\vec{r}}$ and $G(\vec{r})$ is the density-density (or concentration-concentration) correlation function. Ferrell's expression corresponding to Eq. (2) is[2]

$$\Gamma_{qs} = \frac{k_B T q^2}{8\pi\eta_s \hat{G}(\vec{q})} \int d\vec{r} \left(\frac{1}{r} + \frac{(\vec{q}\cdot\vec{r})^2}{q^2 r^3} \right) G(\vec{r}) e^{i\vec{q}\cdot\vec{r}}. \qquad (3)$$

Equation (1) follows from either (2) or (3) when the Ornstein–Zernike form for the correlation function is used:

$$\hat{G}_{OZ}(\vec{q}-\vec{k}) \propto [\xi^{-2} + (\vec{q}-\vec{k})^2]^{-1}$$

in Eq. (2) or

$$G_{OZ}(\vec{r}) \propto (e^{-r/\xi})/r$$

in Eq. (3). [We omit proportionality factors independent of $\vec{q}$ or $\vec{r}$, since they cancel in both Eqs. (2) and (3).]

Before presenting the results of calculations of the linewidth for different correlation functions, we first point out that Kawasaki's result, Eq. (2), and Ferrell's result, Eq. (3), are equivalent for any form of the correlation function. This follows if $\hat{G}(\vec{q}-\vec{k}) = \int d\vec{r}\, G(\vec{r}) e^{i(\vec{q}-\vec{k})\cdot\vec{r}}$ is substituted into Eq. (2) and the integration is performed over $\vec{k}$, or $G(\vec{r})$ can be substituted into Eq. (3) and the integration performed over $\vec{r}$. Thus in evaluating the linewidth integrals for different correlation functions we can consider either Eq. (2) or Eq. (3), whichever is mathematically convenient.

We consider the following forms for the correlation function $\hat{G}(\vec{q})$:

$$\hat{G}_1 \propto \frac{\sin[(1-\eta)\tan^{-1} q\xi]}{q(\xi^{-2}+q^2)^{(1-\eta)/2}}, \qquad (4a)$$

$$\hat{G}_2 \propto [(\xi^{-2}+q^2)^{1-\eta/2}]^{-1}, \qquad (4b)$$

$$\hat{G}_3 \propto \frac{(\xi^{-2}+\phi^2 q^2)^{\eta/2}}{\xi^{-2}+(1+\frac{1}{2}\eta\phi^2)q^2}. \qquad (4c)$$

$\hat{G}_1$ is the q-space form [Ref. 9, Eq. (6.19)] of $G_1(\vec{r}) \propto (e^{-r/\xi})/r^{1+\eta}$, which is sometimes suggested as a form which may describe departures from Ornstein–Zernike behavior. $\hat{G}_2$ has frequently been used[12] in interpreting scattering experiments near the critical point, including neutron scattering in the antiferromagnets MnF_2[13] and $RbMnF_3$[14] and light scattering[15] in the binary mixture n-hexane and nitrobenzene; the values for the exponent η determined in these three experiments were 0.05 ± 0.02, 0.055 ± 0.010, and 0.06, respectively. If η is small, then $\hat{G}_1$ and $\hat{G}_2$ are related by[9]

$$\hat{G}_2 \propto (\hat{G}_1)\left(1 + \frac{\eta(2-\eta)q^2\xi^2}{6(1+q^2\xi^2)} + \cdots\right).$$

The function $\hat{G}_3$ was proposed by Fisher and Burford,[9] who found that this form accurately describes the Ising model of a ferromagnet in both two and three dimensions. For the three-dimensional Ising model, which also serves as a model for a lattice gas and a binary mixture, the parameters in $\hat{G}_3$ are $\eta = 0.056 \pm 0.008$ and $\phi = 0.15 \pm 0.01$, independent of the type of lattice.[9,16] Since both ϕ and η are small, the q dependence of $\hat{G}_3$ does not differ significantly from that of $\hat{G}_{OZ}$ unless $(q\xi)^2 \gg 1$. $\hat{G}_2$ and $\hat{G}_3$ behave in the same way in the limit $(\phi q\xi)^2 \gg 1$, where $\hat{G}_2 \propto \hat{G}_3 \propto q^{-2+\eta}$.

Careful experiments very near the critical point are required in order to observe definitely any departure from Ornstein–Zernike behavior. The correlation function $\hat{G}_3$ has seldom been used in the analysis of experimental data because the determination of the two small parameters (η and ϕ) which characterize the departure from Ornstein–Zernike behavior would be very difficult; however, this form is more satisfactory theoretically since, as explained in Ref. 9, it leads to the correct asymptotic behavior at large r both *at* the critical point and *away* from the critical point [where the Ornstein–Zernike form $G(r) \propto (e^{-r/\xi})/r$ should become valid].

We have evaluated[8] the Kawasaki–Ferrell linewidth integral for the correlation functions $\hat{G}_i$

TABLE I. Linewidth ratio $C_i(q\xi)$ for the correlation functions $\hat{G}_i$ ($i = 1, 2, 3$) in Eqs. (4).

	$C_1(q\xi)$		$C_2(q\xi)$		$C_3(q\xi)$	
$q\xi$	$\eta=0.05$	$\eta=0.1$	$\eta=0.05$	$\eta=0.1$	$\eta=0.05$	$\eta=0.1$
0	1.053	1.111	1.036	1.076	1.007	1.014
0.1	1.052	1.111	1.036	1.076	1.007	1.014
0.2	1.052	1.110	1.036	1.076	1.007	1.015
0.5	1.050	1.106	1.035	1.074	1.008	1.016
1	1.045	1.095	1.033	1.070	1.009	1.019
2	1.038	1.081	1.030	1.064	1.013	1.026
5	1.032	1.067	1.028	1.058	1.020	1.042
10	1.029	1.062	1.027	1.057	1.024	1.051
20	1.028	1.060	1.027	1.056	1.026	1.055
50	1.028	1.058	1.026	1.056	1.026	1.056
∞	1.027	1.058	1.026	1.056	1.026	1.056

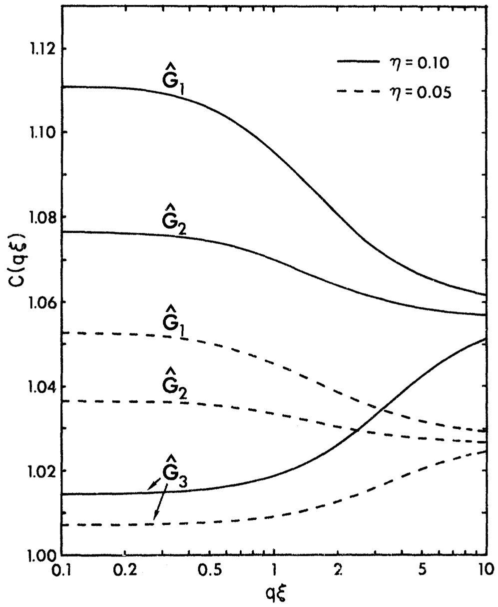

FIG. 1. The linewidth ratio $C(q\xi) \equiv \Gamma_{qs}(\hat{G}_i, \eta, q\xi)/\Gamma_{qs}(\hat{G}_{OZ}, 0, q\xi)$ calculated using different correlation functions $\hat{G}_i$ [Eqs. (4)] in the Kawasaki–Ferrell linewidth integral [with the parameter ϕ in $\hat{G}_3$ equal to 0.15 (Refs. 9 and 16)].

($i = 1, 2, 3,$) with $\eta = 0.05$ and $\eta = 0.1$, and the result for the linewidth ratio,

$$C(q\xi) \equiv \Gamma_{qs}(\hat{G}_i, \eta, q\xi)/\Gamma_{qs}(\hat{G}_{OZ}, 0, q\xi),$$

is shown in Fig. 1 and tabulated in Table I.[17] The linewidth integral involving $\hat{G}_1$ was obtained in closed form in terms of the hypergeometric function, but for $\hat{G}_2$ only the $|\vec{k}|$ and azimuthal-angle integrals were obtained in closed form, the polar-angle integral being evaluated numerically on a computer. For $\hat{G}_3$ both the $|\vec{k}|$ and polar-angle integrals were obtained numerically. The numerical integrations were performed for various meshes to check the accuracy of the results, and as a further check the integrals for all three correlation functions were evaluated using alternative techniques in the limits $q\xi \ll 1$ and $q\xi \gg 1$.

In each case most of the variation of the ratio $C(q\xi)$ is in the region $q\xi = 0.1$ to $q\xi = 10$, with $C(q\xi)$ approaching a constant in the limits of $q\xi \ll 1$ and $q\xi \gg 1$ (see Table I).[18]

The magnitude of the departure of the linewidth from the result previously calculated using the Ornstein–Zernike correlation function is typically several percent, comparable to the vertex correction calculated by Lo and Kawasaki[5] and the nonlocal shear viscosity corrections obtained by Kawasaki and Lo[6] and Perl and Ferrell.[7] With the recently developed precision pulse-correlation technique, light-scattering linewidth measurements can be performed with accuracies of 1% or better, so it is now possible to investigate these corrections. Indeed, Chu *et al.*,[19] who used the results of our calculation of $\Gamma_{qs}(\hat{G}_3, \eta, q\xi)$, have found that the inclusion of the vertex, viscosity, and correlation-function corrections significantly improves the fit of the theory to their linewidth data for the mixture isobutyric acid and water.

In scattering-intensity experiments the departures from Ornstein–Zernike behavior can be definitively detected only in measurements for $q\xi \gg 1$, a region where experiments are extremely difficult. On the other hand, the linewidth, which in the Kawasaki and Ferrell theories is given by an integral over *all* $q\xi$, reflects departures from Ornstein–Zernike behavior even for $q\xi \ll 1$. Furthermore, the ($q\xi$) dependence of the linewidth is quite different for the different correlation functions in the region $0.1 < q\xi < 10$, a region which is experimentally accessible. Therefore, insofar as the Kawasaki and Ferrell theories correctly describe the dynamics of fluids near the critical point, our calculations indicate that linewidth measurements on fluids near the critical point should yield new information on the form of the correlation function.

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[18]In the limit $q\xi \gg 1$ we find $\Gamma_{qs}(\hat{G}_3, \eta, q\xi) = \Gamma_{qs}(\hat{G}_2, \eta, q\xi)$, for any value of the parameter ϕ in $\hat{G}_3$.

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Exact Photocount Statistics: Lasers near Threshold

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A previously constructed laser model with quantum (noncommuting) noise sources was shown to lead near threshold to a quantum rotating-wave Van der Pol oscillator. A full dynamical correspondence between quantum and classical random processes allows one to compute the average of any time-ordered, normal-ordered operator function by averaging the associated function of classical random variables. Numerical calculations for the associated classical Van der Pol oscillator of the steady-state distribution, the total intensity fluctuations, and the linewidth versus operating point were amply confirmed experimentally. Measurements (and calculations) of higher than two-time correlations were sparse and contradictory. Photocount distributions, at times short compared to the intensity correlation time, confirm only the steady state of the laser. Photocount distributions at intermediate and longer times are difficult to compute because they involve multitime correlations of high (∞) order. By providing an exact solution for photocount distributions and their moments for all times, we expected to stimulate measurements near threshold which would provide an adequate test of the Van der Pol laser model. Comparison of the results reported here with recent photocount experiments of Meltzer, Davis, and Mandel and of Jakeman, Oliver, and Pike provides gratifying agreement and confirmation of our statistical understanding of laser fluctuations near threshold.

I. INTRODUCTION

The present paper provides an "exact" (i.e., with no stochastic approximations) solution of a long-standing problem in laser statistics: the probability $p(m, T)$ of observing m photocounts in a time T produced in a photodetector by a laser operating in the vicinity of threshold for all times T, short, comparable to, or long, compared to the laser-intensity correlation time T_c. Well above threshold, laser fluctuations are negligible, and the photocount distribution reduces to a Poisson distribution. Well below threshold, the statistics are Gaussian, and the problem reduces to a well-known but nontrivial problem on fluctuations of time-integrated intensities of a Gaussian variable for which exact numerical solutions have been given.[1–3] The region near threshold holds a special interest because the onset of lasing is a phase transition,[4,5] and the region near threshold is equivalent to the critical region near the transition temperature in a second-order phase transition.

Our solution is exact in that no quantum-mechanical or stochastic approximations are made in treating the rotating-wave Van der Pol (RWVP) model of a laser (described more fully in Sec. IV). Of course, many key approximations were made in arriving at this model: (i) The atom-field system was treated as a Markoffian system with noncommuting noise sources[6,7–13]; (ii) the atomic variables were adiabatically eliminated by assuming that they responded to the instantaneous field variables[14]; (iii) restoring forces higher than quadratic in the intensity were then neglected near threshold with a fractional error[15] of the order of $1/n^{\text{th}}$ where $n^{\text{th}} \sim 10^4$ is the number of photons at threshold. The Markoffian approximation assumes that the duration of a collision with a reservoir atom ($\sim 10^{-12}$ sec) is short compared to the mean time ($\Gamma^{-1} \sim 10^{-8}$ sec) between collisions—an excellent approximation used in the Boltzmann description of gases. The adiabatic approximation appears to assume that atomic decay rates ($\Gamma \sim 10^8$/sec) are fast compared to photon decay rates ($\gamma \sim 10^7$/sec), but actually involves the much weaker approximation that all of these rates are fast compared to the intensity relaxation rate near threshold,[16] $\sim \gamma/n^{\text{th}}$. These remarks support our gener-