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A simple extension of the Ornstein-Zernike theory of critical scattering gives rise to correlation functions which do not scale. The critical-point exponents have values $\eta = 0$ and $2\nu \geq \gamma$.

I. INTRODUCTION

The classical Ornstein-Zernike theory[1] of critical scattering relates critical opalescence to the slow decay of correlations with distance and hence to the divergence at the critical point of the isothermal compressibility.[2] It also leads to the relation $2\nu = \gamma$ between the critical exponents[3] ν and γ. If, in addition, the thermodynamic functions are assumed analytic in the temperature, then the classical values $\gamma = 1$ and $\nu = \frac{1}{2}$ may be obtained. Unfortunately, these results for the critical exponents do not agree with those found for different fluids.[4]

The Ornstein-Zernike theory is usually carried out to its lowest approximation. One wonders what values can be obtained for the critical exponents from a general theory based on the Ornstein-Zernike idea. In particular, can an Ornstein-Zernike theory give rise to a result other than $2\nu = \gamma$?

If the scattering intensity is not analytic in the square of the wave vector near the origin—if it is, say, a multivalued function with a branch point at the origin—and the scaling hypothesis[5] is valid, then[6] $(2 - \eta)\nu = \gamma$. Hence deviations from the classical result of Ornstein and Zernike, $2\nu = \gamma$, are connected with nonanalyticity of the scattering intensity. Experimental evidence on the scattering of neutrons from liquid neon[7] suggests $\eta > 0$, that is, $2\nu > \gamma$. This would represent a breakdown of the Ornstein-Zernike theory, which entails $\eta = 0$.

The analysis of light scattering by a simple fluid near its critical point is made difficult by double-scattering[8] and gravity-induced[9] effects. The experimental data are consistent with both of the aforementioned effects and with $\eta = 0$. At the same time, experimental values for the critical exponent[10] ν and the exponent[4] γ for fluids definitely suggest $2\nu > \gamma$.

Thus the present experimental situation gives rise to serious theoretical questions by the possibility $\eta = 0$ and $2\nu > \gamma$. Therefore it seems appropriate to consider higher-order corrections to the classical Ornstein-Zernike theory and study their possible implications for the values of the critical-point exponents.

In this work it is shown that a realization of the Ornstein-Zernike program can be carried out to higher orders by assuming $\eta = 0$, and that it leads to $2\nu \geq \gamma$.

II. GENERALIZATION OF THE CLASSICAL ORNSTEIN-ZERNIKE THEORY

The Ornstein-Zernike theory of critical scattering is concerned with the calculation of the pair-correlation function in order to explain critical opalescence. This is accomplished by defining a direct correlation function $C(\vec{r})$ by the integral equation[11]

$$G(\vec{r}_1 - \vec{r}_2) = C(\vec{r}_1 - \vec{r}_2) + \rho \int C(\vec{r}_1 - \vec{r}_3) G(\vec{r}_3 - \vec{r}_2)\, d\vec{r}_3 \qquad (1)$$

for the net correlation function $G(\vec{r})$.

We shall consider only the case of a liquid or gas in three spatial dimensions. The (net) correlation function $G(r)$ is related to the two-particle distribution function $n_2(\vec{r}_1, \vec{r}_2)$ by

$$G(r) = n_2(\vec{r}_1, \vec{r}_2)/\rho^2 - 1, \qquad (2)$$

with $r = |\vec{r}_1 - \vec{r}_2|$. The isothermal compressibility is given by

$$k_B T \rho K_T = 1 + 4\pi\rho \int_0^\infty G(r) r^2\, dr, \qquad (3)$$

the Fourier transform by

$$\hat{G}(k) = 4\pi \int_0^\infty \frac{\sin kr}{kr} G(r) r^2\, dr, \qquad (4)$$

and hence $[\hat{G}(k)]^* = \hat{G}(k^*)$. (The complex conjugate of z is denoted by z^*.)

The fundamental assumption of the Ornstein-Zernike theory is that $C(r)$ should be short ranged even at the critical point—reflecting the short-ranged nature of the pair potential. Hence its Fourier transform $\hat{C}(k)$, even at the critical point, is analytic in k^2 in a domain containing the origin.

It is clear that $\hat{C}(k)$ cannot be an entire function of k^2. As $|k| \to \infty$ $\hat{C}(k)$ must vanish—so its Fourier transform exists—hence, by Liouville's theorem, $\hat{C}(k)$ must vanish identically.[12] Therefore $\hat{C}(k)$ must have at least one singular point. We shall assume $\hat{C}(k)$ has isolated singular points only. Consequently, $\hat{C}(k)$ is meromorphic in k^2 with no pole at $k^2=0$—short-ranged assumption of $C(r)$—and vanishes as $|k| \to \infty$.

From (1) we have for the Fourier transforms

$$1+\rho\hat{G}(k)=1/[1-\rho\hat{C}(k)]. \qquad (5)$$

Therefore $\hat{G}(k)$ is also meromorphic. The assumed absence of a pole in $\hat{C}(k)$ at $k^2=0$ implies, from (3) and (5), $K_T>0$. Of course, the converse is not necessarily true. Therefore a necessary condition for the validity of any Ornstein-Zernike-type description is the nonvanishing of the isothermal compressibility.

III. CRITICAL-POINT EXPONENTS

The Mittag-Leffler partial-fractions theorem allows us to write the most general form of a meromorphic function.[12] We consider first the case when $\hat{G}(k)$ has only simple poles. Then

$$\hat{G}(k)=\tfrac{1}{2}\sum_{j=1}^{\infty}\left(\frac{L_j}{k^2+A_j}+\frac{L_j^*}{k^2+A_j^*}\right). \qquad (6)$$

We may assume $|A_j| \leq |A_{j+1}|$ for all j. From (3),

$$k_B T\rho K_T=1+\rho\sum_{j=1}^{\infty}\frac{\mathrm{Re}(L_j^*A_j)}{|A_j|^2}. \qquad (7)$$

Also, from (6) we have, when $a_j>0$,

$$G(r)=\frac{1}{8\pi r}\sum_{j=1}^{\infty}(L_j e^{-r\sqrt{A_j}}+L_j^* e^{-r\sqrt{A_j^*}})$$
$$=\frac{1}{4\pi r}\sum_{j=1}^{\infty}e^{-ra_j}(C_j\cos rb_j+D_j\sin rb_j), \qquad (8)$$

with $\sqrt{A_j}=a_j+ib_j$, $C_j=\mathrm{Re}L_j$, and $D_j=\mathrm{Im}L_j$.

As the critical point is approached, a finite number of poles of $\hat{G}(k)$, say $j=1,\ldots,l$, approach the origin. (Recall that a meromorphic function may have an infinite number of poles but with no finite limit point.)

Let $|A_j| \to t^{2\nu_j}$ as $t\to 0$, where $\nu_j>0$, $j=1,\ldots,l$, with $t\equiv(T-T_c)/T_c$ and let $\nu\equiv\max(\nu_1,\ldots,\nu_l)$. The correlation length for each term in (8) is defined by $\xi_j\equiv 1/\sqrt{|A_j|}$. If $\xi\equiv\max(\xi_1,\ldots,\xi_l)$, then $\xi\sim t^{-\nu}$. {It should be noted that our definition of the correlation length is a simple generalization from that when the exponential factor $1/\sqrt{A_j}$ is real. Also, in general, ξ will have no direct connection to $[\int r^2G(r)d\vec{r}/\int G(r)d\vec{r}]^{1/2}$.} Now, from $|A_j|\to t^{2\nu_j}$ as $t\to 0$ it follows that $\mathrm{Re}(L_j^*A_j)\sim t^{2\omega_j}$ as $t\to 0$ with $\omega_j \geq \nu_j$. Therefore, from (7),

$$K_T\approx\sum_{j=1}^{l}\frac{B_j}{t^{2(2\nu_j-\omega_j)}}, \qquad (9)$$

where B_j is constant and $2\nu_j-\omega_j\leq\nu_j\leq\nu$. Since $K_T\sim 1/t^{\gamma}$, we have

$$\gamma\leq 2\nu. \qquad (10)$$

The strict inequality in (10) is satisfied, in the simplest case, for $G(r)\sim(1/r)e^{-ar}\cos br$ with $a\to 0$, $b\to 0$, and $a/b\to 1$. In this case

$$2\nu-\gamma=\lim_{t\to 0}\frac{\ln[(a-b)/a]}{\ln t}>0.$$

Note that b, as well as the correlation length $\xi\sim a^{-1}$, represents another length in the fluid that is characteristic of the approach to the critical point. Thus scaling is violated.

What happens when higher order poles—even essential singularities—are included? The Mittag-Leffler theorem gives us the appropriate construction as sums of the principal parts of the meromorphic function at its poles.[12] The principal part at a given pole of order $n+1$, $n\geq 1$, would contribute to $\hat{G}(k)$,

$$\hat{G}^{(n)}(k)=\tfrac{1}{2}\sum_{l=0}^{n}\left(\frac{L^{(l)}}{(k^2+A)^{l+1}}+\frac{L^{(l)*}}{(k^2+A^*)^{l+1}}\right). \qquad (11)$$

Let $\sqrt{A}=a+ib$ and for[13] $a>0$

$$G^{(n)}(r)=\sum_{l=0}^{n}\frac{1}{4\pi 2^{2l}l!}\left(\frac{e^{-r(a+ib)}L^{(l)}}{(a+ib)^{2l-1}}\sum_{k=0}^{l-1}\frac{(2l-k-2)!}{k!(l-k-1)!}\times[2r(a+ib)]^k+\text{c.c.}\right). \qquad (12)$$

Hence this term would give rise for $t=0$, $|A|=0$, to a correlation function $G(r)$ which would not vanish as $r\to\infty$. [Note that for simple poles such terms—given by the sine term in (8)—vanish for $t=0$.] Although for $t=0$ $G(r)\to$ const. as $r\to\infty$ cannot be ruled out in general,[14] this behavior would seem to be rather unphysical. Therefore arbitrary sums of terms like (12) do appear in the general expression for $G(r)$. However, the poles associated with them cannot approach the origin as $t\to 0$.

It is interesting to investigate what effect terms like (11) would have on the critical-point exponents. If $|A|\to t^{2\nu}$ as $t\to 0$, then $\mathrm{Re}(L^*A^{n+1})\sim t^{2\bar{\omega}(n+1)}$ as $t\to 0$ with $\bar{\omega}\geq\nu$. Hence

$$K_T\sim\mathrm{Re}(L^*A^{n+1})/|A|^{2(n+1)}\sim 1/t^{2(n+1)(2\nu-\bar{\omega})}, \qquad (13)$$

and so $\gamma=2(n+1)(2\nu-\bar{\omega})\leq 2\nu(n+1)$. Therefore γ could exceed 2ν. Consequently, for $\hat{G}(k)$ meromorphic, the requirement that for $t=0$ $G(r)$ decrease with distance implies $2\nu\geq\gamma$.

IV. SUMMARY AND DISCUSSION

The assumption that for $t=0$ $\hat{C}(k)$ is analytic in a neighborhood of $k^2=0$ and that $\hat{C}(k)$ may be continued analytically, lead to the existence of its singularities. We have shown that if $\hat{G}(k)$ is meromorphic in k^2 and if for $t=0$ $G(r)$ vanishes as $r\to\infty$, then $2\nu \geq \gamma$.

The scattering intensity $I(k)$ for single light scattering by a simple uniform fluid is related to $\hat{G}(k)$ by

$$I(k)/I_0(k) = 1 + \rho\hat{G}(k) \geq 0\,, \tag{14}$$

where $I_0(k)$ is the scattering intensity in the absence of correlation. Hence our assumed form for $\hat{G}(k)$ gives plots of the inverse scattered irradiance $[I(k)/I_0(k)]^{-1}$ versus k^2 which are linear—for k^2 sufficiently close to the origin.

On the other hand, scaling—exact in the two-dimensional Ising (lattice-gas) model—implies Fisher's relation $\nu(2-\eta)=\gamma$. It requires $2\nu=\gamma$ if plots of the inverse scattering intensity are linear—a distinct experimental possibility. Hence, nonanalyticity of $\hat{G}(k)$ is directly linked to $2\nu\neq\gamma$. Our extension of the classical Ornstein-Zernike theory clearly allows for nonscaling of the correlation function and hence to linear plots and $2\nu>\gamma$.

The assumption that $\hat{G}(k)$ is meromorphic in the entire plane may be relaxed without altering our main result—$\eta=0$ and $2\nu\geq\gamma$. The weaker assumption would require that only $\hat{G}(k)$ be meromorphic in a neighborhood of the origin. In this case, results (8) and (12) hold asymptotically ($r\to\infty$) and our main result follows just as before.

The general form for $\hat{G}(k)$ due to (6) and terms like (11) is rather complicated. However, near the critical point and for k^2 small we have

$$\hat{G}(k) \approx \tfrac{1}{2}\sum_{j=1}^{l}\left(\frac{L_j}{k^2+A_j}+\frac{L_j^*}{k^2+A_j^*}\right). \tag{15}$$

Expression (15) can give rise to interesting features in the inverse scattered irradiance. Since $\hat{G}(k)$ is large near the critical point and for k^2 small, one has from (14) that $[I(k)/I_0(k)]^{-1} \approx 1/\rho\hat{G}(k)$. Therefore the actual intercept of $[I(k)/I_0(k)]^{-1}$ with the line $k^2=0$ is

$$[I(k)/I_0(k)]^{-1}\big|_{k^2=0} = 1\Big/\rho\sum_{j=1}^{l}\mathrm{Re}\frac{L_j}{A_j}$$

with

$$\sum_{j=1}^{l}\mathrm{Re}\frac{L_j}{A_j}>0\,.$$

For k^2 "large" one has from (15) that

$$\left[\frac{I(k)}{I_0(k)}\right]^{-1} \approx k^2\Big/\rho\sum_{j=1}^{l}\mathrm{Re}L_j + \sum_{j=1}^{l}\mathrm{Re}(L_jA_j)\Big/\rho\left(\sum_{j=1}^{l}\mathrm{Re}L_j\right)^2. \tag{16}$$

Therefore the large-k^2 curve gives the apparent intercept

$$\sum_{j=1}^{l}\mathrm{Re}(L_jA_j)\Big/\rho\left(\sum_{j=1}^{l}\mathrm{Re}L_j\right)^2.$$

It is interesting that the actual intercept may be greater or less than the apparent intercept. Hence for single light scattering by a simple uniform fluid a downward or upward turn of the experimental data may be fitted with (15).

A simple example with an upward turn—actual intercept greater than apparent intercept—is given by (15) with a single term with $L>0$, $\mathrm{Re}A>0$, and $\mathrm{Im}A\neq 0$. The apparent intercept is $(\mathrm{Re}A)/\rho L$, and the actual intercept is $[\rho L\mathrm{Re}(1/A)]^{-1}$. Hence $[\rho L\mathrm{Re}(1/A)]^{-1}>(\mathrm{Re}A)/\rho L$. An example of (15) with a downward turn—apparent intercept greater than actual intercept—is given by (15) with A_1, A_2, L_1, and L_2 real and positive with $A_1\neq A_2$. The apparent intercept is $(L_1A_1+L_2A_2)/\rho(L_1+L_2)^2$, and the actual intercept is $[\rho(L_1/A_1+L_2/A_2)]^{-1}$. Hence

$$\frac{L_1A_1+L_2A_2}{\rho(L_1+L_2)^2} > \frac{1}{\rho(L_1/A_1+L_2/A_2)}\,,$$

which gives $A_2/A_1+A_1/A_2>2$.

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