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BEHAVIOUR OF THE PAIR CORRELATION FUNCTION IN THE CRITICAL REGION

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ABSTRACT: The pair correlation function is obtained from general scaling laws and, independently, from an equation of state, which has been proposed recently to describe the behaviour of some fluids in the critical region. The consistency condition between the two results is used to establish lower and upper bounds for the critical exponents. We find that these results are also valid for other systems, e.g. magnetic systems and three-dimensional Ising models, and do not depend on the internal structure of the system, but only on their dimensionality. Therefore, the idea of universal behaviour of different systems, in the vicinity of critical points, looks a promising one.

I. INTRODUCTION

In a recent paper[1] it has been shown that the experimental PVT data for He^4, CO_2 and Xe in the critical region, can be accounted for through a

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scaling-law equation of state which can be expressed in an analytical form. Following the ideas set forth by Widom[2] and Griffiths[3] one can write the chemical potential $\Delta\mu$ as

$$\Delta\mu = \Delta\rho^{\delta} h(x) \tag{1}$$

where

$$\Delta\mu = \mu(\rho, T) - \mu(\rho_c, T) \text{ and } \Delta\rho = (\rho - \rho_c)/\rho_c$$

The proposed form for $h(x)$ is given by[1],

$$h(x) = E_1 \left(\frac{x + x_0}{x_0}\right) \left[1 + E_2 \left(\frac{x + x_0}{x_0}\right)^{2\beta}\right]^{(\gamma - 1)/2\beta} \tag{2}$$

where $x = t\left|\Delta\rho\right|^{-1/\beta}$, $t = (T - T_c)/T_c$; E_1 and E_2 are adjustable parameters and $x = -x_0$ represents the values of t and $\Delta\rho$ along the coexistence curve. As usual, the critical indices δ, β and γ have the conventional meaning[4]. For fixed values of E_1, E_2, β, x_0 and ρ_c the data for the above mentioned gases was analyzed using several values for T_c and δ. It has been found that the estimated values for γ and α agree with experiment and also that Eq. (2) describes the data for the three gases to within their estimated precision. Furthermore, it is shown that of the parameters selected to perform the scaling, β, δ, E_1 and E_2 are quite steady, the only one varying from substance to substance being x_0.

The purpose of the present paper is to extend these calculations to analyze the behaviour of the pair correlation function in the critical region[5]. Indeed, since we have an analytical expression for the equation of state we can calculate the isothermal compressibility κ_T and then use the fluctuation theorem[4] to find $G(r)$. Furthermore, Cooper[6] has recently shown how to generalize Kadanoff's scaling arguments[7] by using the asymptotic behaviour of a strongly coupled many body system. Applying this method to a fluid, taking $\Delta\rho$ as the order parameter and $\Delta\mu$ as its thermodynamic conjugate variable one can also find the behaviour of the pair correlation in the critical region. Thus we are led to two expressions for $G(r)$, which should be identical, consistently with the scaling assumption. The main results of this procedure are that we are led to a series of inequalities which must be satisfied by some of the critical indices [c.f. Eqs. (33, a-e)] and to obtain estimates for the critical indices η and ν. The predicted values for these two indices are found to agree with the experimental data quoted by Heller[8] and furthermore, they are also in agreement with the calculations quoted for three-dimensional spin systems by Fisher and Burford[9]. Section II of this paper contains a short discussion of Cooper's method and its extension to the pair correlation function. The usual relationship between the critical indices ν and η is therefrom obtained. In Section III we shall give the calculation of the pair correlation function via the fluctuation theorem using the equation of state given by Eq. (1). Comparing the results of sections II and III we obtain the set of inequalities given by Eqs. (33 a-e) which are then compared with experimental results, not only for fluids but for other systems also. This is done in section IV where also an estimate of the indices ν and η is given, together with some concluding remarks about the nature of the results obtained.

II. GENERALIZATION OF SCALING-LAWS

The purpose of this section is to extend the arguments given by Cooper[6] to the study of the pair correlation function in the critical region. For a system consisting of a large number of particles, in the thermodynamic limit, we fix our attention in the Gibbs function G which depends on two variables, the reduced temperature $t = (T - T_c)/T_c$ and the order parameter $p(t,h)$. Here, h is the thermodynamic conjugate variable of p defined through $h(t,p) = \partial G(t,h)/\partial p$. The idea is to assume that both t and h are related to the structure of the system through the following relations, namely,

$$t = \tilde{t}\; T(L) \quad \text{and} \quad h = \tilde{h}\, H(L)\,, \tag{3}$$

where both T and H are nonsingular, differentiable unspecified functions of the positive variable L. This variable is the "cell parameter" in Kadanoff's description of the physical system which for the particular case of a rectangular lattice of dimensionality d, yields for T and H the expressions[7],

$$T(L) = L^{-(2-\eta)/\gamma}\,; \qquad H(L) = L^{-\frac{1}{2}(d+2-\eta)}\,.$$

The functions H and T appearing in Eq. (3) are thus the generalization of the scaling equations introduced by Kadanoff, and in some way relate the site variables with the cell variables. If we now assume that the Helmholtz's free energy of the system is the same whether it is calculated through sites or cells, we get Cooper's essential equation, namely, that

$$p(t,h) = \frac{L^{-d}}{H(L)}\, p(\tilde{t}, \tilde{h}) , \qquad (4)$$

which is a functional equation for the order parameter p. Its most general solution, is given by[10]

$$p(t,h) = \begin{cases} h^{A} f(x) & h \neq 0 \qquad (5a) \\ t^{B} & h = 0 , \qquad (5b) \end{cases}$$

where $x = t/h^{A/B}$, A and B are arbitrary constants and $f(x)$ is an arbitrary function of x. Substitution of Eqs. (5a) and (5b) back into Eq. (4) leads to the following consistency conditions,

$$L^{-d} H^{-(A+1)}(L) = 1 \qquad (6a)$$

$$L^{-d} H^{-1}(L)\, T^{-B}(L) = 1 \qquad (6b)$$

$$H^{A/B}(L)\, T^{-1}(L) = 1 . \qquad (6c)$$

The relationship between the indices A and B, and the critical exponents is now obtained through the study of the equation of state $p(t,h)$ in the critical region. Indeed, the equation for the critical isotherm is given by

$$p(0,h) = h^{A} f(0) \qquad (7)$$

and that of the coexistence curve by

$$p(t,0) = t^{B} . \qquad (8)$$

Comparing Eqs. (7) and (8) with the definition of β and δ[4] we find that $A = \delta^{-1}$ and $B = \beta$. Thus,

$$p(t,h) = h^{1/\delta} f(x) \qquad h \neq 0 \tag{9a}$$

$$= t^{\beta} \qquad h = 0, \tag{9b}$$

where $x = t/h^{1/\beta\delta}$. Notice here that the parameter L which is of a mathematical nature has dissapeared. Also, Eqs. (9) shows Widom's[2] conjecture, namely, that the equation of state is a homogeneous function of the variable x. Furthermore, from Eq. (9a),

$$h = p^{\delta} f^{-\delta}(t/h^{1/\beta\delta})$$

or, in general, we can write that

$$h = p^{a} g(x') \tag{10}$$

where $x' = t/p^{b}$. The calculation of a and b follows the same lines as that of A and B yielding $a = \delta$ and $b = \beta^{-1}$, so that

$$h(t,p) = p^{\delta} g(t/p^{1/\beta}), \tag{11}$$

which gives the dependence of h with p. The functions g and f are not independent but are related through the expression,

$$g(t/p^{1/\beta}) = f^{-\delta}(t/h^{1/\beta\delta})$$

The functions f or g are arbitrary but must obey the conditions set up by Griffiths[3] namely, those of convexity and analiticity in the region $-x_0 < x' < \infty$ where $-x_0$ represents the values of t and p on the coexistence curve, so that $g(-x_0) = 0$. These conditions are met if $g(x)$ possesses a series expansion of the type

$$g(x) = \sum_{n=1}^{\infty} \eta_n x^{\beta(\delta+1-2n)} \tag{12}$$

near $x = \infty$ where η_n is a constant and $x = t/p^{1/\beta}$. Applying Eq. (11) to a fluid we have that

$$\Delta\mu = \Delta\rho^{\delta} g(x), \tag{13}$$

all quantities being defined as in the introduction. Using the definitions for the isothermal compressibility κ_T and the specific heat c_v, we can now use (13) to study the behaviour of the fluid in the critical region. In fact, from

$$\kappa_T = \frac{1}{\rho^2} \left[\left(\frac{\partial \mu}{\partial \rho}\right)\right]^{-1} \tag{14}$$

we find that

$$\kappa_T = \frac{1}{\rho^2} \left[\delta \Delta\rho^{\delta - 1} g(x) - \frac{\Delta\rho^{\delta} t}{\beta \Delta\rho^{1/\beta + 1}} \frac{dg(x)}{dg} \right]^{-1} =$$

$$= \frac{1}{\rho^2} \left(\frac{t}{x}\right)^{-\beta(\delta - 1)} \frac{1}{g(x)} \left[\delta - \frac{x}{\beta} \frac{d \ln g(x)}{dx} \right]^{-1},$$

which compared with the definition of γ, yields

$$\gamma = \beta(\delta - 1), \tag{15}$$

showing symmetry between γ and γ' since Eq. (14) holds for temperatures both above and below T_c.

Furthermore, since

$$c_v = -T \frac{\partial^2}{\partial t^2} \int \Delta\mu d\rho \tag{16}$$

we have that

$$c_v = T\beta \int x^{-\beta(\delta+1)} g(x)\, dx \frac{\partial^2}{\partial t^2} t^{\beta(\delta+1)} =$$

$$= T\beta A \left[\beta(\delta+1)\right]\left[\beta(\delta+1) - 1\right] t^{\beta(\delta+1) - 2}$$

where A is just the value of the integral. Comparing with the definition of

α we get that

$$\beta(\delta + 1) = 2 - \alpha , \tag{17}$$

showing symmetry between α and α' because Eq. (16) is valid for temperature above and below T_c. Eq. (17) represents, in the form of an equality, the inequality first obtained by Griffiths[11] and if combined with Eq. (15) yields, in the form of an equality, Rushbrooke's inequality[12].

Let us now apply the previous arguments to the study of the pair correlation function $g(R) \equiv \langle p(r)\, p(r') \rangle$. Using Eq. (4) we have that

$$g(t,h,R) = \left\langle \frac{L^{-d}}{H(L)}\, \tilde{p}(r)\, \frac{L^{-d}}{H(L)}\, \tilde{p}(r') \right\rangle = \frac{L^{-2d}}{H^2(L)}\, g(\tilde{t}, \tilde{h}, \tilde{R}) \tag{18}$$

where $R = |\mathbf{r} - \mathbf{r}'|$ is the interparticle separation and $\tilde{R} = R/L$. Eq. (18) is a functional equation for g whose most general solution is found to be given by[10]

$$G(R) \equiv g(t,h,R) = h^{a}\, W(x,z) \qquad h \neq 0 \tag{19a}$$

$$= t^{b} F(z) \qquad t \neq 0 \tag{19b}$$

$$= AR^{-c} \qquad t = h = 0 , \tag{19c}$$

where $x = t/h^{a/b}$, $z = Rt^{b/c}$ and the constants A, a, b and c, together with the functions W and F, are arbitrary. Substitution of Eqs. (19) back into Eq. (18) yields a set of consistency conditions, namely,

$$L^{-2d} H^{-(2+a)}(L) = 1 \tag{20a}$$

$$L^{-2d} H^{-2}(L)\, T^{-b}(L) = 1 \tag{20b}$$

$$L^{-2d} H^{-2}(L)\, L^{c} = 1 \tag{20c}$$

$$H^{a/b}(L)\, T^{-1}(L) = 1 \tag{20d}$$

$$T^{b/c}(L)\, L = 1 , \tag{20e}$$

which must be satisfied by the indices a, b and c. These indices are related to the critical exponents through the trivial requirement of consistency between Eqs. (6) and Eqs. (20). This immediately yields the following equalities:

$$a = 2A = 2/\delta$$

$$b = 2B = 2\beta$$

$$c = \frac{2ad}{a+1} = \frac{2Ad}{A+1} = \frac{2d}{\delta+1}$$

and, with their aid, Eqs. (19) for $G(R)$ can be cast into the expressions,

$$G(R) = h^{2/\delta}\, W(x,z) \qquad h \neq 0 \qquad (21a)$$

$$= t^{2\beta} F(z) \qquad t \neq 0 \qquad (21b)$$

$$= AR^{-2d/\delta+1} \qquad t = h = 0\,, \qquad (21c)$$

where $x = t/h^{1/\beta\delta}$, $z = R\, t^{\beta(\delta+1)/d}$. The arbitrariness of the functions W and F is restricted, since they are related to $f(x)$ or $g(x')$ through the fluctuation theorem.

Using Eqs. (21a-c) and the definition of the critical exponents ν and η we immediately arrive to the following equations,

$$\nu = \beta(\delta+1)/d \qquad (22a)$$

$$2 - \eta = d\,\frac{\delta-1}{\delta+1}\,. \qquad (22b)$$

Combining Eqs. (22a,b) with Eq. (15) we find that

$$\nu(2-\eta) = \gamma\,, \qquad (23)$$

thus recovering the same expressions as those predicted by Kadanoff[7]. It is interesting to notice that the indices characterizing the pair correlation function $G(R)$ obey, in the form of equalities, the inequalities obtained by Fisher[12] for a d-dimensional ferromagnet near its critical point. These inequalities can also be found by substitution of the expressions obtained for η and ν into the Griffiths-Rushbrooke's inequalities for α, β, δ and γ. It is also worth pointing out that we shall obtain some inequalities which must hold for the critical indices of a fluid, from the behaviour of $G(R)$ near the critical point. These expressions although different in their mathematical structure as the ordinary ones are nevertheless consistent both with scaling-laws predictments as well as with experimental results.

III. CALCULATION OF THE PAIR CORRELATION FUNCTION.

The subject of this section is devoted to the calculation of $G(R)$ using the well known fluctuation theorem, which relates this function to the isothermal compressibility of the system. For this latter quantity we shall use the expression obtained in the previous section which itself arises from the equation of state proposed by M. Vicentini-Missoni et al[1]. The resulting form for $G(R)$ which is rather complicated, will be studied in the vicinity of the critical region ($t \simeq 0$) and the asymptotic form thus obtained will be compared with the one derived from scaling arguments, i.e. Eq.(21c). From the comparison of these results we find that the critical indices obey certain inequalities which are themselves consistent with experimental results. This matter will be dealt within the following section.

Maintaining the idea that our main task is to study the form of $G(R)$ in the vicinity of the critical region we shall make some approximations from the very beginning of this calculation. Thus, the compressibility obtained in the previous section may be written as:

$$\kappa_T = \frac{1}{\rho^2} \frac{t^{-\gamma} x_0^{\gamma}}{E_1 \delta} \sum_{n=0}^{\infty} \frac{x^{n+\gamma}}{\beta^n \delta' (x+x_0)^{n+1}} \frac{[x_0^{2\beta} + \gamma E_2 (x+x_0)^{2\beta}]^n}{[x_0^{2\beta} + E_2 (x+x_0)^{2\beta}]^{\frac{\gamma-1}{2\beta}+n}},$$

where we have expanded $(g(x))^{-1}$ in a power series of x and we have taken into account that for values of x close to zero,

$$\delta >> \frac{x}{\beta} \frac{d \ln g(x)}{dx}.$$

Using $z = R t^{\beta(\delta+1)/d}$ as the independent variable and recalling that the most general form of the pair correlation function will be a function of x and z we find, from the fluctuation theorem, that the integral equation which must be satisfied by $G(R)$ is:

$$1 + \rho t^{-\beta(\delta+1)/d} \int_0^x G(x,z)\, dz = \frac{kT}{\rho} \frac{t^{-\gamma} x_0^{\gamma}}{\delta E_1} \times$$

$$\times \sum_{n=0}^{\infty} \frac{x^{n+\gamma}}{(\beta\delta)^n (x+x_0)^{n+1}} \frac{[x_0^{2\beta} + \gamma E_2 (x+x_0)^{2\beta}]^n}{[x_0^{2\beta} + E_2 (x+x_0)^{2\beta}]^{\frac{\gamma-1}{2\beta}+n}}, \tag{24}$$

where the integration limits have been chosen so that we can study the correlation function in the critical region, namely from the critical isotherm towards the coexistence curve or the critical isochore, if $x \to \infty$.

To find the solution of Eq. (24) we use the following property of Laplace transforms,

$$F(x,z) = \mathcal{L}^{-1} \left\{ s\, \mathcal{L} \int_0^x F(x,z)\, dz \right\}$$

where $\mathcal{L}$ and $\mathcal{L}^{-1}$ are the direct and inverse transforms, respectively and s the parameter characterizing such transformation. Setting $y = z + x_0$ the Laplace transform of Eq. (24) is given by:

$$\mathcal{L} \left\{ \int_0^x G(x,z)\, dz \right\} = \frac{kT}{\rho^2} \frac{t^{\beta(\delta+1)/d - \gamma} x_0^{\gamma}}{E_1 \delta} \times$$

$$\times \sum_{n=0}^{\infty} \frac{1}{(\beta\delta)^n} \int_{x_0}^{\infty} \frac{(y-x_0)^{n+\gamma}}{y^{n+1}} \frac{[x_0^{2\beta} + \gamma E_2 y^{2\beta}]^n}{[x_0^{2\beta} + E_2 y^{2\beta}]^{\frac{\gamma-1}{2\beta}+n}} \times$$

$$\times e^{-s(y-x_0)}\, dy - \frac{t^{\beta(\delta+1)/d}}{s\rho}. \tag{25}$$

Expanding all the binomials, we have that

$$(y - x_0)^{n+\gamma} = \sum_{a=0}^{n+\gamma} \binom{n+\gamma}{a} y^{n+\gamma-a} (-1)^a x_0^a$$

$$[x_0^{2\beta} + \gamma E_2 y^{2\beta}]^n = \sum_{b=0}^{n} \binom{n}{b} x_0^{2\beta(n-b)} (E_2 \gamma y^{2\beta})^b$$

$$[x_0^{2\beta} + E_2 y^{2\beta}]^{-\left(\frac{\gamma-1}{2\beta}+n\right)} \simeq x_0^{-2\beta\left(\frac{\gamma-1}{2\beta}+n\right)} \times$$

$$\times \sum_{c=0}^{\frac{\gamma-1}{2\beta}+n} \binom{\frac{\gamma-1}{2\beta}+n}{c} (-1)^c E_2^c \left(\frac{y}{x_0}\right)^{2\beta c} .$$

where in this last expression, we have assumed that

$$y < \frac{x_0}{E_2^{1/2\beta}} \qquad \text{or} \qquad R < \frac{x_0(1 - E_2^{1/2\beta})}{E_2^{1/2\beta}} \, t^{-\beta(\delta+1)/d} ,$$

which is not inconsistent with Eq. (24) since for $\Delta\rho$ fixed, $x \to 0$ implies $t \to 0$, which means that R will always be less than the coherence lenght R_0 in order to guarantee the existence of correlations. Substituting these results back into Eq. (25) and using the definition of the incomplete gamma function, we find that

$$\mathcal{L} \int_0^x G(x,z)\, dz = \frac{kT}{\rho^2} \frac{x_0^\gamma}{E_1 \delta} \, t^{\beta(\delta+1)/d - \gamma} I \, \frac{\Gamma(\lambda, s x_0)}{s^\lambda} \, e^{s x_0} - \frac{t^{\beta(\delta+1)/d}}{s\rho} , \tag{26}$$

$\Gamma(\lambda, sx_0)$ being the incomplete gamma function, λ a positive parameter defined as $\lambda = \gamma + 2\beta(b+c) - a$ ($\lambda > 0$) and I a constant defined by the following expression,

$$I = \sum_{n=0}^{\infty} \frac{1}{(\beta\delta)^n} \sum_{a,b,c} \binom{n+\gamma}{a} \binom{n}{b} \binom{n + \frac{\gamma - 1}{2\beta}}{c}$$

$$\times \; (-1)^{a+c} E_2^{b+c} \gamma^b x_0^{a+1-2\beta(b+c)-\gamma} .$$

Taking the inverse Laplace transform of Eq. (26), the correlation function reads

$$G(x,z) = \frac{kT}{\rho^2} \frac{x_0^{\gamma}}{E_1 \delta} t^{\beta(\delta+1)/d - \gamma} I \mathcal{L}^{-1} \left[e^{s x_0} \frac{\Gamma(\lambda, s x_0)}{s^{\lambda - 1}} \right] - \mathcal{L}^{-1} \left[\frac{t^{\beta(\delta+1)/d}}{\rho} \right] \tag{27}$$

Furthermore, if k_{ν} is the third class modified Bessel function of order ν, then[14]

$$\mathcal{L} \left\{ 2a^{\nu/2} t^{-\nu/2} K_{\nu} (2 (at)^{\frac{1}{2}}) \right\} = \Gamma(1-\nu) \frac{1}{s^{\nu-1}} e^{as} \Gamma(\nu, as), \tag{28}$$

so that taking the inverse Laplace transform of Eq. (28) and substituting the result back into Eq. (26), identifying ν with λ and a with x_0 we find that

$$G(x,z) = \frac{kT}{\rho^2} \frac{x_0^{\gamma} I}{E_1 \delta} t^{\beta(\delta+1)/d - \gamma} \frac{2x_0^{\lambda/2} z^{-\lambda/2} K_{\lambda}(2\sqrt{x_0 z})}{\Gamma(1-\lambda)} - \frac{t^{\beta(\delta+1)/d}}{z\rho} , \tag{29}$$

with $\lambda < 1$. But since we have already found that $\lambda > 0$ we have that this parameter has to satisfy the condition that $0 < \lambda < 1$. Hence, for a given system this will impose severe restrictions on the binomial terms which appear in the constant I. Writing Eq. (29) in terms of R we finally arrive to the result that

$$G(R) = \frac{kT}{\rho^2} J t^{-\gamma - \lambda\beta(\delta+1)/2d} R^{-(1+\lambda/2)} z K_{\lambda}(2\sqrt{x_0 z}) - \frac{1}{R\rho} , \tag{30}$$

where $J = \dfrac{2x_0^{\lambda/2} I}{\Gamma(1-\lambda) E_1 \delta}$ is a numerical constant.

We can now use Eq. (30) to compare it with the result predicted by the scaling laws, namely Eq. (21c) giving the behaviour of $G(R)$ in the neighbourhood of the critical point. Since $x = t/h^{1/\beta}$ and $z = Rt^{\beta(\delta+1)/d}$ we examine the asymptotic part of Eq. (30) when $t \simeq 0$, that is T very close to T_c and fixed R. Then the dominant term in Eq. (30), noticing that $z\, K_\lambda(2\sqrt{x_0 z})$ also goes to zero for small values of t, is

$$G(R) \sim CR^{-(1+\lambda/2)} \tag{31}$$

C being a constant. Thus, comparing Eqs. (31) and (21c) we find that λ is related to the critical exponents δ through the expression,

$$1 + \frac{\lambda}{2} = \frac{2d}{\delta+1}\ , \tag{32}$$

and since λ is bounded, we shall have a natural bound imposed on δ. Indeed, since $0 < \lambda < 1$, we get that

$$\frac{4}{3}\, d - 1 < \delta < 2d - 1\ , \tag{33a}$$

d being the dimensionality of the system.

Using the Eqs. (15) and (17) relating δ to the critical exponents α, β and γ and Eqs. (22a,b) relating δ to ν and η we find from (33a) the following inequalities, namely

$$2\beta \left(\frac{2d}{3} - 1\right) < \gamma < 2\beta(d-1) \tag{33b}$$

$$2(1 - d\beta) < \alpha < 2\left(1 - \frac{2\beta d}{3}\right) \tag{33c}$$

$$\frac{4}{3}\beta < \nu < 2\beta \tag{33d}$$

$$3 - d < \eta < \frac{7}{2} - d\ , \tag{33e}$$

which amounts to the fact that given one critical exponent, say β in this case, the remaining ones are bounded, the bounds depending only on one more parameter, the dimensionality of the system.

On the other hand for systems such that $d \geqslant 3$, the Ornstein-Zernike's theory gives an expression for $G(R)$[4] which, if compared with Eq. (31), yields for λ the value

$$\lambda_{O.Z.} = 2(d-3)$$

and hence,

$$\frac{1}{2}(\lambda - \lambda_{O.Z.}) = \left(2 - d\,\frac{\delta - 1}{\delta + 1}\right) = \eta \qquad (34)$$

λ being the value given by Eq. (32). Thus one half of the difference between the values of the parameter λ will give a measure of the deviation between the behaviour of $G(R)$ in the critical region as obtained from classical theories and from experiment. In the case $d = 3$, $\lambda_{O.Z.} = 0$ so that $1/2\,\lambda = \eta$ is precisely the measure of such deviation, consistently with the definition of η. Also, Eq. (30) cannot reproduce the classical behaviour of $G(R)$ because it would require a value of $\lambda = 0$, in disagreement with the bound found for this parameter. In short, the scaling-law equation of state proposed by M. Vicentini-Missoni et al[1] predicts a correlation function $G(R)$ which, consistently with the scaling laws, has a non-classical behaviour near the critical point.

IV. COMPARISON WITH EXPERIMENT

Using the values of β and δ for He^4, CO_2 and Xe given in Ref. 1, those for CrO_2 and Ni quoted by Kouvel and Rodbell[15] and for other magnetic systems which are summarized in a recent paper by Cooper et al[16], we have used Eqs. (22a, b) to calculate the values of ν and η, the results being shown in Table I.*

*Different values for the same substance correspond to reports given by different authors[16].

TABLE I.

Critical Exponents

Substance	β	δ	ν	η
CO_2	0.35	4.6	0.653	0.071
Xe	0.35	4.6	0.653	0.071
He^4	0.359	4.5	0.652	0.101
CrO_2	0.34	5.7	0.759	- 0.103
$CrBr_3$	0.368	4.28	0.647	0.137
$CrBr_3$	0.364	4.32	0.642	0.128
Ni	0.41	4.22	0.713	0.149
Ni	0.373	4.44	0.676	0.104
Ni	0.375	4.48	0.681	0.105
Ga	0.370	4.39	0.664	0.113

From these results we notice that, except for CrO_2, all values of δ lie within the range specified by Eq. (33a), namely, $3 < \delta < 5$. It is also easy to check that ν and η are also consistent with Eqs. (33d,e). Thus, we conclude that the data for CrO_2 is inconsistent with scaling. A similar statement is also applied to a two dimensional Ising system for which $\delta = 15$.

It is also interesting to point out that for the majority of the systems analized in the wide literature on this subject, one finds that $\beta \sim 1/3$ and $\delta \sim 23/5$ which predict $\nu \sim 0.62$ and $\eta \sim 0.07$, all of these estimates lying within the specified bounds given by Eqs. (33) and also in agreement with the recent calculations reported by Fisher and Burford[9] for three dimensional spin systems. However, the numerical estimates for ν and η cannot be yet compared with accurate experimental results due to the difficulties involved in their measurement[8].

Some concluding remarks are pertinent in view of the results derived here. First, it is important to emphasize the fact that from the scaling-law equation of state proposed for three gases, in their critical region, it is possible to derive on equation for the pair correlation function $G(R)$ which, if required to be consistent with its own scaling-law form, imposes some bounds on the critical exponents, except for the one chosen to be independent. Furthermore, these results hold true not only for these fluids but also for some magnetic systems, thus suggesting that indeed the idea of seeking for a universal behaviour of physical systems in their critical regions is promising.

Secondly, it is interesting to notice that once a critical exponent is chosen to be fixed by experiment, the bounds imposed on the remaining ones depend only on the dimensionality of the systems and not on their intrinsic structure. This fact, once more suggests that the interactions between the particles will be similar for all systems near critical points, which is of course consistent with the generalization of the scaling-laws. In fact, since we have an analytical expression for $G(R)$, (so far too complicated), we could in principle derive from it the form of such interactions.

Finally, the bounds for the critical exponents η and ν found here have some bearing on the remarks made by Fisher in a recent paper[13]. In fact Eq. (30) indeed shows that the pair correlation function for a fluid, and optimistically for other systems also, will show an oscillatory behaviour for small values of $\boldsymbol{R}$, through the appearance of the Bessel function $K_\lambda(2\sqrt{x_0}z)$, and a monotonic decaying tail with a dependence on R given by Eq. (31). Due to the complexity of the expression obtained here for $G(R)$ it is premature to make stronger statements; however, qualitatively, we can expect the desired behaviour.

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RESUMEN

La función de correlación de dos partículas es obtenida a partir de las leyes generales del escalamiento e, independientemente, a partir de una ecuación de estado propuesta recientemente para describir el comportamiento de algunos fluídos simples en la región crítica. La condición de consistencia a que deben obedecer ambos resultados se traduce en establecer cotas inferior y superior para los exponentes críticos. Se encuentra además que estos resultados son válidos para otros sistemas, e.g. sistemas magnéticos y modelos de Ising tridimensionales y no dependen de la estructura interna del sistema, sino solamente de su dimensionalidad. Así pues, la idea de que los fenómenos que se observan en diversos sistemas físicos, en la vecindad de puntos críticos, obedecen a un comportamiento universal, parece ser más prometedora.