

# Local-Functional Theory of Critical Adsorption

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(April 5, 2001)

Local-functional methods are applied to critical adsorption in 3-dimensional Ising-like systems. The universal order-parameter-profile scaling functions,  $P_{\pm}(x)$ , along the critical isochore (+) and phase boundary (-), are calculated along with their associated universal amplitudes. Good agreement is found with the results of Monte Carlo simulations. General properties of  $P_{\pm}(x)$  for small and large scaled distance,  $x$ , are elucidated. A new order-parameter scaling function,  $P_c(x)$ , for critical adsorption along the *critical isotherm* is introduced and calculated.

68.35.Rh, 64.60.Fr, 82.65.Dp

There has been much recent interest in the effects of delimiting boundaries on systems near their bulk critical points of which the phenomenon of *critical adsorption* is an important example. Consider, for instance, a uniaxial (Ising) ferromagnet (or a system in the equivalent universality class such as a binary fluid etc.) against a wall containing a symmetry-breaking field  $h_1 > 0$ . Such a boundary tends to cause the order parameter (e.g., magnetisation,  $m$ , or fluid density,  $\rho$ ) to increase over a distance of about the bulk correlation length,  $\xi$ , from the wall. In a seminal paper, Fisher and de Gennes [1] predicted that on approaching the bulk critical point, where  $\xi \rightarrow \infty$ , the order-parameter profile at large distances from the wall attains a characteristic scaling form involving bulk critical exponents which can be described by a *universal* scaling function — a situation referred to as critical adsorption. This prediction has stimulated much experimental work [2] and theoretical (including Monte Carlo) analysis [3–8].

We start by describing, in magnetic language, the main quantities of interest in critical adsorption. Let  $m(z)$  be the magnetization profile in the semi-infinite sample at a perpendicular distance of  $z$  from the wall with the bulk magnetization,  $m_b(t, h)$ , given by  $m_b(t, h) := \lim_{z \rightarrow \infty} m(z)$  where  $t := (T - T_c)/T_c$ ,  $T$  is the temperature,  $T_c$  is its critical value, and  $h$  is the applied bulk magnetic field. Near the critical point (both  $|t|$  and  $|h|$  small),  $m_b(t, 0) \approx B|t|^\beta$  for  $t \rightarrow 0^-$  (phase boundary);  $m_b(t, 0) = 0$  for all  $t > 0$  (critical isochore); and  $m_b(0, h) \approx (|h|/D)^{1/\delta} \text{sgn } h$  for  $h \rightarrow 0$  (critical isotherm). This then defines in standard notation the critical exponents  $\beta$  and  $\delta$ , and amplitudes  $B$  and  $D$ . Along the phase boundary/critical isochore, Fisher and de Gennes [1] proposed the following scaling law

$$m(z; t, h = 0) \approx B|t|^\beta P_{\pm}(z/\xi) \text{ as } z \rightarrow \infty, t \rightarrow 0^{\pm}, \quad (1)$$

where, throughout,  $\xi = \xi(t, h)$  is the *true* correlation length, with  $\xi(t, 0) \approx \xi_0^{\pm}|t|^{-\nu}$  as  $t \rightarrow 0^{\pm}$ , and, with this choice of normalization,  $P_{\pm}(x)$  are *universal* scaling functions. Also of interest is the Gibbs adsorption,  $\Gamma(t, h)$ , defined by

$$\Gamma(t, h) := \int_0^{\infty} [m(z; t, h) - m_b(t, h)] dz. \quad (2)$$

For dimension  $d < 4$ , where  $\nu > \beta$ , the adsorption diverges on approach to the critical point like  $\Gamma(t, 0) \approx \Gamma_{\pm}|t|^{\beta-\nu}$  as  $t \rightarrow 0^{\pm}$  and for  $d \geq 4$  (mean field theory), where  $\nu = \beta$ , one finds  $\Gamma(t, 0) \sim \ln|t|^{-1}$  as  $t \rightarrow 0$ .

Since  $P_{\pm}(x)$  are universal, various amplitudes extracted from  $P_{\pm}(x)$  at large and small  $x$  are also universal as well as integrals involving  $P_{\pm}(x)$ . Thus, with  $P_{\pm}(x) \approx c_{\pm} x^{-\beta/\nu}$  as  $x \rightarrow 0$  and  $P_{\pm}(x) - P_{\pm}(\infty) \approx P_{\pm,1}^{\infty} e^{-x}$  as  $x \rightarrow \infty$  (where clearly  $P_+(\infty) = 0$  and  $P_-(\infty) = 1$ ) we find universal numbers  $c_{\pm}$  and  $P_{\pm,1}^{\infty}$ . In addition, the integrals [6]

$$g_{\pm} := (\nu - \beta) \int_0^{\infty} [P_{\pm}(x) - P_{\pm}(\infty)] dx \quad (3)$$

are also universal and related to the adsorption amplitudes  $\Gamma_{\pm}$  via  $g_{\pm} = (\nu - \beta)\Gamma_{\pm}/B\xi_0^{\pm}$ . Finally, we have the universal adsorption amplitude ratio  $R_{\Phi} := \Gamma_+/\Gamma_-$ .

One can similarly define universal quantities along the *critical isotherm*. Thus we have  $m(z; t = 0, h) \approx m_b(0, h)P_c(z/\xi)$  as  $z \rightarrow \infty$ ,  $h \searrow 0^+$ , where  $\xi(0, h) \approx \xi_c|h|^{-\nu/\beta\delta}$  [9] and the properties of the universal scaling function,  $P_c(x)$ , for large and small  $x$ , i.e.,  $P_c(x) \approx c_c x^{-\beta/\nu}$  as  $x \rightarrow 0$  and  $P_c(x) - 1 \approx P_{c,1}^{\infty} e^{-x}$  as  $x \rightarrow \infty$ , defines the universal amplitudes  $c_c$  and  $P_{c,1}^{\infty}$ . Furthermore, one can define a universal number,  $g_c$ , through an expression identical to (3) except that the integrand is replaced by  $P_c(x) - 1$ . Along the critical isotherm, the Gibbs adsorption diverges like  $\Gamma(0, h) \approx \Gamma_c|h|^{(\beta-\nu)/\beta\delta}$  as  $h \searrow 0^+$  for  $d < 4$  and  $\Gamma(0, h) \sim \ln|h|^{-1}$  for  $d \geq 4$ . The *nonuniversal* amplitude  $\Gamma_c$  is related to  $g_c$  via  $g_c = (\nu - \beta)D^{1/\delta}\Gamma_c/\xi_c$ .

Thus, for critical adsorption we have a number of universal quantities amenable to experimental and theoretical investigation. It is well established that mean field theory ( $d \geq 4$ ) predicts [3,6] that  $P_+(x) = \sqrt{2} \text{cosech } x$ ,  $P_-(x) = \text{coth}(x/2)$ , with  $c_+ = \sqrt{2}$ ,  $c_- = 2$ ,  $P_{+,1}^{\infty} = 2\sqrt{2}$ , and  $P_{-,1}^{\infty} = 2$ , and for the adsorption quantities we have  $g_+ = 1/\sqrt{2}$ ,  $g_- = 1$ , and  $R_{\Phi} = 1$  (strictly speaking  $g_{\pm}$  are only defined at  $d = 4$  in the sense of the limit  $d \rightarrow 4^-$ ).

Along the *critical isotherm* the results of mean field theory appear not to have been presented before but these are given as

$$P_c(x) - 1 = \frac{3\sqrt{2}}{\sinh[x + \sinh^{-1}(\sqrt{2})] - \sqrt{2}} \quad (4)$$

with  $c_c = \sqrt{6}$ ,  $P_{c_1}^\infty = 6\sqrt{2}(\sqrt{3} - \sqrt{2})$ , and  $g_c = \sqrt{3/2}$ .

The purpose of this paper is to go beyond mean field theory and present the results of extensive calculations which provide a complete description of critical adsorption at the experimentally important dimension of  $d = 3$ . The pioneering analysis of experimental data by Liu and Fisher [3], based on approximants, was followed by further analysis [6–8] of other experiments. Renormalization group (RG) studies of a semi-infinite  $\phi^4$  field theory [4,5], carried out to linear order in  $\epsilon := 4 - d$  (i.e., 1 loop) and extrapolated to  $\epsilon = 1$ , provide the only *purely theoretical* predictions of  $P_\pm(x)$  (and associated amplitudes) at  $d = 3$  apart from Monte Carlo (MC) simulations of the  $d = 3$  Ising model [5].

In this paper we use a method based on local free-energy functionals of the type introduced by Fisher and Upton [10]. These are functionals of  $m(z)$ , so constructed to incorporate *nonclassical* criticality as appropriate for dimensions  $d < 4$ . The method is *nonperturbative* and can be applied directly to  $d = 3$  without extrapolating — an important advantage over field-theoretical  $\epsilon$  expansions. However, one can also use these functionals to generate expansions in  $\epsilon$ , thus providing a useful cross-check with field theory. Indeed, results of previous applications were found to compare very well with field-theoretical  $\epsilon$  expansions [11,12] (usually within about 1% for the coefficient of the order- $\epsilon$  term). Also, for Casimir-type problems, local-functional calculations applied directly to  $d = 2$  gave results in excellent agreement with those obtained from conformal invariance [12,13]. The method is relatively easy to implement making it applicable to situations which appear intractable when using other theoretical techniques.

The local-functional method [10] starts from the assertion that  $m(z)$  minimizes the following (approximate) functional

$$\mathcal{F}[m] = \int_0^\infty \mathcal{A}(m, \dot{m}; t, h) dz + f_1(m_1; h_1, \dots) \quad (5)$$

where  $\dot{m} := dm/dz$  and  $m_1 := m(z = 0)$ . The surface contribution incorporates the symmetry-breaking surface field  $h_1$  via  $f_1(m_1; h_1, \dots) = -h_1 m_1 + \dots$  as required for critical adsorption. The integrand  $\mathcal{A}(\cdot)$  contains only *bulk* quantities and we use the choice considered in Ref. [10]

$$\mathcal{A}(m, \dot{m}; t, h) = \{\mathcal{G}[\Lambda(m; t, h)\dot{m}] + 1\}W(m; t, h) \quad (6)$$

with

$$W(m; t, h) := \Phi(m; t) - \Phi(m_b; t) - h(m - m_b) \quad (7)$$

where  $\Phi(m; t)$  is the bulk Helmholtz free energy density. Note that the equation  $\partial W/\partial m|_{m_b} = 0$  gives the bulk equation of state. It is required that the combination  $\dot{m}\Lambda(m)$  be *scale free* which is satisfied if  $\Lambda(m)$  takes the form

$$\Lambda(m; t, h) := \xi(m; t)/\sqrt{2\chi(m; t)W(m; t, h)} \quad (8)$$

where  $\xi(m; t)$  and  $\chi(m; t)$  are, respectively, the bulk correlation length and susceptibility of the homogeneous system at  $(m, t)$ . The function  $\mathcal{G}(x)$  must be *even* in  $x$  with  $\mathcal{G}(0) = 0$  and is required to satisfy several desiderata as set out in Refs. [10,12]. What is quite remarkable though, is that for *semi-infinite* problems the specific functional form of  $\mathcal{G}(x)$  does not enter into any expressions obtained from minimizing (5) [10].

Mean field theory ( $d > 4$ ) follows when  $\Phi(m; t)$  takes Landau form with  $(\xi^2/2\chi)(m; t)$  being *constant* in  $m$  and  $t$ . For more general  $d > 1$ , the bulk functions have the following scaling forms

$$W(m; t, 0) \approx |m|^{\delta+1}Y_\pm(m/B|t|^\beta), \quad (9)$$

$$(\xi^2/2\chi)(m; t) \approx |m|^{-\eta\nu/\beta}Z_\pm(m/B|t|^\beta), \quad (10)$$

in the simultaneous scaling limit  $t \rightarrow 0^\pm$  with  $m \rightarrow 0$ , where  $\eta$  is the critical bulk correlation function exponent in standard notation.

Specific choices for the bulk scaling functions,  $Y_\pm(y)$  and  $Z_\pm(y)$ , appropriate to  $d = 3$ , will be addressed later. First we note that analyticity of  $\Phi(m; t)$  and  $\xi(m; t)$  in  $m$  and  $t$  throughout the one-phase region of the phase diagram (excluding the critical point) implies that  $Y_\pm(y)$  and  $Z_\pm(y)$  have the following expansion properties [10]. Analyticity of  $\Phi(m; t)$  across  $t = 0$  for nonzero  $m$  (critical isotherm) gives

$$Y_\pm(y) = \frac{A_\pm|By|^{-(\delta+1)}}{(2-\alpha)(1-\alpha)} + \sum_{n=0}^\infty Y_{\infty,n}(\pm 1)^n|y|^{-n/\beta}, \quad (11)$$

as  $|y| \rightarrow \infty$  where  $\alpha$  and  $A_\pm$  are the *specific-heat* critical exponent and amplitudes in standard notation. Similar expansions hold for  $Z_\pm(y)$  except that the term containing  $A_\pm$  is *absent*. Analyticity across  $m = 0$  for  $t > 0$  (critical isochore) implies

$$Y_+(y) = |y|^{-(\delta+1)} \sum_{n=1}^\infty Y_{0,2n} y^{2n}, \quad \text{as } y \rightarrow 0. \quad (12)$$

A similar expansion holds for  $Z_+(y)$  except that the  $|y|^{-(\delta+1)}$  prefactor is replaced by  $|y|^{\eta\nu/\beta}$  and the sum starts at  $n = 0$ . Note that  $Y_+(y)$  and  $Z_+(y)$  contain only *even* powers of  $y$  as a consequence of the assumed symmetry,  $W(-m) = W(m)$  and  $\xi(-m) = \xi(m)$ . Finally, we assume the existence of *asymptotic* expansions about the phase boundary which leads to

$$Y_{\pm}(y) \approx (y \mp 1)^2 \sum_{n=0}^{\infty} Y_{1,n} (\pm 1)^n (y \mp 1)^n, \quad (13)$$

as  $y \rightarrow \pm 1^{\pm}$ . Similar expansions hold for  $Z_{\pm}(y)$  as  $y \rightarrow \pm 1^{\pm}$  but *without* the factor of  $(y \mp 1)^2$  in front of the sums.

Minimizing the functional given by Eqs. (5) to (8), such that  $m(z) \rightarrow m_b$  as  $z \rightarrow \infty$ , leads to the first integral  $\dot{m}\Lambda(m; t, h) = -1$  subject to a boundary condition at  $z = 0$ . Then taking the scaling limit,  $z \rightarrow \infty$  and  $\xi \rightarrow \infty$  with  $x = z/\xi$  finite, gives the scaling functions,  $P_{\pm}(x)$ , through

$$x = \frac{B^{-\nu/\beta}}{\xi_0^{\pm}} \int_{P_{\pm}(x)}^{\infty} dy y^{-(1+\nu/\beta)} [Z_{\pm}(y)/Y_{\pm}(y)]^{1/2}, \quad (14)$$

and the critical-isotherm scaling function,  $P_c(x)$ , is determined by

$$x = \int_{P_c(x)}^{\infty} \frac{[\delta(\delta+1)/2]^{1/2} dy y^{-(1+\nu/\beta)}}{[1 - (1+\delta)y^{-\delta} + \delta y^{-(1+\delta)}]^{1/2}}. \quad (15)$$

Note that, within local-functional theory,  $P_c(x)$  depends only on bulk critical exponents — bulk critical amplitudes and scaling functions do not enter at all. Before presenting quantitative  $d = 3$  results obtained from these formulae, we first describe some *general* properties of  $P_{\pm}(x)$  which follow from local-functional theory *whenever*  $Y_{\pm}(y)$  and  $Z_{\pm}(y)$  satisfy the necessary analyticity requirements.

*Short-Distance Behaviour* The expansions of  $Y_{\pm}(y)$  and  $Z_{\pm}(y)$  for large  $y$ , (11), substituted into (14) implies that

$$P_{\pm}(x) = x^{-\beta/\nu} [c_{\pm} + a_{\pm} x^{1/\nu} + b_{\pm} x^{d^*} + a'_{\pm} x^{2/\nu} + o(x^{2/\nu})] \quad (16)$$

as  $x \rightarrow 0$  where  $d^* = (2 - \alpha)/\nu = \min(d, 4)$ . From (15), a similar expansion follows for  $P_c(x)$  but with the terms in  $x^{1/\nu}$ ,  $x^{2/\nu}$  replaced by  $x^{\beta\delta/\nu}$ ,  $x^{2\beta\delta/\nu}$ . Also, on defining the universal number  $U_{\xi} := \xi_0^+/\xi_0^-$ , we find that  $c_+/c_- = U_{\xi}^{-\beta/\nu}$ ,  $a_+/a_- = -U_{\xi}^{(1-\beta)/\nu}$ ,  $a'_+/a'_- = U_{\xi}^{(2-\beta)/\nu}$ , and  $b_+/b_- = U_{\xi}^{d^*-\beta/\nu} A_+/A_-$  (this last ratio, involving bulk-specific-heat amplitudes, being universal for  $d \leq 4$ ). The expansion (16) is fully consistent with field-theoretic expectations [4], the term in  $x^{d^*}$  being a consequence of the *short-distance expansion* [14], and corresponds to the following expansion of the boundary magnetization,  $m_1(t) := m(z = 0; t, 0)$ , for  $t \rightarrow 0^{\pm}$ ,

$$m_1(t) = m_1(0) + At + B_{\pm}|t|^{2-\alpha} + A't^2 + \dots \quad (17)$$

(which also follows directly from local-functional theory) with  $B_+/B_- = A_+/A_-$  and the terms in  $A$  and  $A'$  are part of the analytic background. The leading singular term,  $|t|^{2-\alpha}$ , was first conjectured by Bray and Moore [15] but is now well established using near-exact arguments [14,16].

*Large-Distance Behaviour* Substituting (12) [resp. (13)] into (14) for  $P_+(x)$  [resp.  $P_-(x)$ ], and the equivalents for  $Z_{\pm}(y)$ , gives

$$P_{\pm}(x) - P_{\pm}(\infty) = \sum_{n=1}^{\infty} P_{\pm,n}^{\infty} e^{-nx}, \quad \text{as } x \rightarrow \infty. \quad (18)$$

Although, in general,  $P_{\pm,n}^{\infty}$  are nonzero for *both* odd and even  $n$ , it is important to note that  $P_{+,n}^{\infty} = 0$  for *all even*  $n$ . That  $P_+(x)$  contains only *odd* powers of  $e^{-x}$  in its expansion for large  $x$  appears not to have been noted before and follows directly from bulk *up-down symmetry* along the critical isochore. This observation has important implications in the analysis of experimental data, placing additional constraints on the approximants used for  $P_+(x)$ . The expansion property of  $P_+(x)$ , which clearly holds within mean-field theory, can also be understood from a diagrammatic high-temperature approach to the  $d = 3$  Ising model [17]. Also, it has been shown that  $P_{+,2}^{\infty} = 0$  to linear order in  $\epsilon$  [5]. From (15) it follows that  $P_c(x)$  has a similar expansion to that of  $P_-(x)$  for large  $x$  (containing both odd and even powers of  $e^{-x}$ ).

To obtain *quantitative* predictions at  $d = 3$  for  $P_{\pm}(x)$ ,  $P_c(x)$ , and associated amplitudes, we need to substitute into (14) and (15) specific values for the bulk critical exponents along with suitable choices for  $Y_{\pm}(y)$  and  $Z_{\pm}(y)$ . We represent the bulk scaling functions using the parametric models introduced by Schofield [18]. These have recently been developed further [10,19] and are believed to give the best available fits to bulk data and, by their very construction, give scaling functions satisfying the required analyticity properties (11), (12), and (13). For our purposes the original “linear” parametric model [18] was found to suffice. At  $d = 3$  we take  $\beta = 0.328$  and  $\nu = 0.632$  and a satisfactory fit to the bulk amplitude relations, being properties of the bulk scaling functions, is provided by taking  $b^2 = 1.30$  and  $a_2 = 0.28$ , in the notation of [19], in the linear model. The resulting  $P_{\pm}(x)$  are shown in Figure 1 and are plotted in comparison to MC [5,7] and extrapolated 1-loop RG results [4,7]. Strikingly, we find that the local-functional predictions lie very close to the curves obtained from a splined-least-square fit to the MC data [almost indistinguishable in the case of  $P_+(x)$ ]. Modifying the linear-model parameters,  $b^2$  and  $a_2$ , in a way consistent with bulk data, hardly changes the resulting plots for  $P_{\pm}(x)$ .

Numerical results for the associated surface amplitudes are displayed in Table I and compared to the results of other theories [4–7] and experiment [8]. Again, we find close agreement between the results of local-functional theory and MC simulations. For all these amplitudes, local-functional theory can also be used to generate expansions in  $\epsilon$ . In almost all cases, the coefficients of the order- $\epsilon$  terms were found to agree with those calculated using the RG [4–6] to within 1% [17]; e.g., for  $c_+$ , local-functional theory predicts  $c_+ = \sqrt{2} - 0.96115\epsilon + O(\epsilon^2)$  whereas from the RG one has  $c_+ = \sqrt{2} - 0.96054\epsilon + O(\epsilon^2)$ .

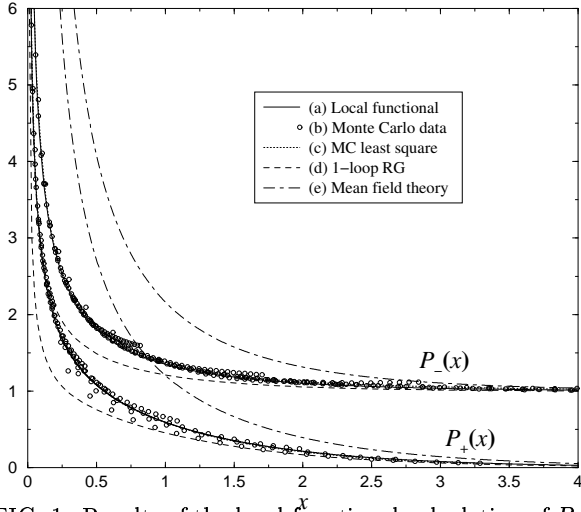


FIG. 1. Results of the local-functional calculation of  $P_{\pm}(x)$  at  $d = 3$  are plotted as (a) and compared to: (b) Monte Carlo data; (c) splined-least-square fit of MC data; (d) 1-loop RG calculation extrapolated to  $d = 3$ ; and (e) mean field theory.

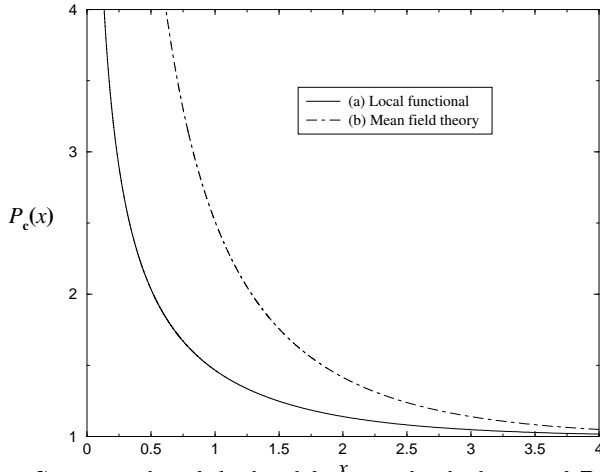


FIG. 2. Results of the local-functional calculation of  $P_c(x)$  at  $d = 3$  plotted as (a) and compared to (b) mean field theory.

The local-functional curve for  $P_c(x)$ , (15), is plotted in Figure 2 along with the mean-field result, (4). At  $d = 3$ , local-functional theory predicts that  $c_c^{\nu/\beta} = 1.93$  [20],  $P_{c,1}^{\infty} = 0.95$  and  $g_c = 0.71$ .

To conclude, using local free-energy functionals we have developed a comprehensive theory of critical adsorption applicable to general  $d$  but particularly to the experimentally important case of  $d = 3$ . Not only are our results largely consistent with MC simulations but also, to first order in  $\epsilon$ , with RG calculations giving credence to our nonperturbative  $d = 3$  predictions.

We thank M. Smock for sending us data files of his results, R. Evans for critical reading of the manuscript, and H.W. Diehl for hospitality at the Universität-GH Essen. Z.B. is grateful for a University of Bristol Scholarship and P.J.U. acknowledges financial support from the EPSRC (UK) under Grant No. AF/100607.

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TABLE I. Universal critical-adsorption amplitudes at  $d = 3$  determined using local-functional theory (LFT) and compared to the results of Monte Carlo simulations (MC); 1-loop RG calculations extrapolated to  $\epsilon = 1$  (RG); interpolated results of Flöter and Dietrich (FD); and some experimental results (Expt.). Also, for comparison, are displayed the results of mean field theory (MFT).

	$c_+$	$c_-$	$g_+$	$g_-$	$R_{\Phi}$	$P_{+,1}^{\infty}$	$P_{-,1}^{\infty}$	$c_+/P_{+,1}^{\infty}$
LFT	0.857	1.214	0.679	0.574	2.3	1.601	0.679	0.54
MC	0.866	1.22	0.663	0.599	2.17	1.5	1.0	0.577
RG	0.717	1.113	0.581	0.438	2.60	1.621		0.442
FD	0.94	1.24	0.69	0.56	2.28			
Expt.	0.79	1.12	0.599	0.502	2.34	0.96	0.57	0.75
MFT	1.414	2.0	0.707	1.0	1.0	2.828	2.0	0.50