Universal order-parameter profiles for critical adsorption and the extraordinary transition: a comparison of $\epsilon$ expansion and Monte Carlo results

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Abstract

The universal, scaled order parameter profiles $P_{\pm}(z/\xi)$ for critical adsorption of a fluid or fluid mixture onto a wall or interface, and for the extraordinary transition of the semi-infinite Ising model, are discussed theoretically, where $z$ is the distance from the interface, $\xi(T)$ is the bulk correlation length, and the subscript $+(-)$ refers to the approach from above (below) $T_c$. Recent results to first order in the $\epsilon = 4 - d$ expansion are extrapolated to $d = 3$ space dimensions and compared with new Monte Carlo results. In order to obtain meaningful extrapolations it is crucial that both the exponential decay at large $\zeta$ as well as the known algebraic behavior $P_{\pm}(\zeta) \sim \zeta^{-\beta/\nu}$ at small $\zeta$ be correctly reproduced. To this end a recently developed novel RG scheme involving a $z$ dependent amplitude renormalization is used. Reason-

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able agreement of our extrapolations with the Monte Carlo results and some experimental results is obtained.

1. INTRODUCTION

The phenomenon of critical adsorption of fluids or binary mixed fluids onto walls or interfaces has attracted considerable attention, both theoretically and experimentally, in recent years [1–4,16]. It was originally predicted by Fisher and de Gennes [2]. Considering a semi-infinite fluid bounded by a planar wall at $z = 0$ and invoking scaling ideas, these authors concluded that the phenomenon has two important signatures:

(i) Between a microscopic scale $a$ and the macroscopic bulk correlation length $\xi$ there exists a regime $a < z < \sim \xi$ of distances $z$ from the interface in which the order parameter $m(z) \equiv \langle \phi(x) \rangle$ at position $x = (x_\parallel, z)$ decays only algebraically $\sim z^{-\beta/\nu}$.

(ii) The excess order parameter

\[ m_s = \int_0^\infty [m(z) - m(\infty)] dz , \]

i.e., the total amount of adsorbed fluid, behaves as $m_s \sim \tau^{-(\nu - \beta)}$ as $\tau \equiv (T - T_c)/T_c \to 0$, where $T_c$ is the bulk critical temperature. Since $\nu - \beta \simeq 0.3$ in three dimensions, $m_s$ diverges.

On a qualitative level both signatures (i) and (ii) have been verified experimentally. However, with regard to detailed quantitative investigation of the phenomenon and its quantitative comparison with theoretical predictions, much remains to be done. A detailed theoretical analysis of optical data for critical adsorption has been made by Liu and Fisher [4], who found evidence both for (i) as well as for crossover of $m(z, \tau \geq 0)$ from a power-law regime at small $\zeta \equiv z/\xi$ to exponential behavior, $m(z) \sim e^{-\zeta}$, at large $\zeta$. Although they were able to extract also some quantitative information about the nature of the order parameter profile from the data, the precision and reliability of their estimates was somewhat limited, partly because of the limited accuracy of the available experimental data, but partly also because of the lack of quantitatively reliable theoretical results needed as input for the
analysis of the experiments. In particular, it became clear that detailed quantitative results for the scaling functions $P_{\pm}(\zeta)$ governing the asymptotic form

$$m(z) \approx M_\pm |\tau|^{\beta} P_{\pm}(z/\xi)$$

for $\tau \to 0^\pm$ would be highly desirable. Here $M_\pm$ is a nonuniversal constant, which we fix such that $P_{\pm}(\infty) = 1$. The functions $P_{\pm}$ also depend on the precise definition of the correlation length $\xi$, i.e., on the choice of the nonuniversal coefficients $\xi_0^\pm$ in the asymptotic expression $\xi(\tau \to 0^\pm) \approx \xi_0^\pm |\tau|^{-\nu}$. We fix these by taking $\xi$ to be the true correlation length, defined through the requirement that the bulk two-point cumulant function decays $\propto e^{-|x-x'|/\xi}$ as $|x-x'| \to \infty$.

Recently two of us [6,7] succeeded in computing the first two terms in the $\epsilon = 4 - d$ expansion of $P_{\pm}(z/\xi)$. Upon extrapolation to $d = 3$ space dimensions explicit results for $P_{\pm}(\zeta)$ were obtained, which had the correct physical features, displaying, in particular, a smooth and monotonous crossover from the behavior $P_{\pm}(\zeta) \sim \zeta^{-\beta/\nu}$ as $\zeta \to 0$ to the exponential decay at large $\zeta$. In the present paper we elaborate on these results, extending them and checking them versus Monte Carlo results. We begin with a brief summary of the $\epsilon$-expansion results of Ref. [6], recalling that their naive extrapolation to $d = 3$ would yield profiles $P_{\pm}(\zeta)$ with a totally unacceptable, incorrect short-distance behavior. We show that this problem can be overcome in a systematic manner by means of a recently developed novel renormalization group (RG) scheme [8], which ensures the proper, exponentiated form of the leading short-distance singularity. We then compare the so-obtained extrapolations $P_{\pm}(\zeta, d = 3)$ with the results of Monte Carlo calculations. Finally, we present the $\epsilon$ expansion of a number of universal amplitude ratios, estimate their values for $d = 3$, and compare them with experimental estimates, if possible.

2. RESULTS OF THE $\epsilon$ EXPANSION AND BEYOND

The analytic results of Ref. [6] were obtained by means of RG improved perturbation theory applied to the semi-infinite $\phi^4$ model [8]. Since this model and its physics is reviewed
in a separate contribution by Diehl \cite{7} in these proceedings, we will focus on the explanation of the results. Critical adsorption (or the so-called normal transition) is described by a fixed point $P_{ca}^*$; the extraordinary transition by a fixed point $P_{ex}^*$. Although being located in different regions of parameter space of the model, these fixed points are equivalent in the sense that they yield identical results for the scaling functions $P_\pm$ and other quantities to arbitrary order of the $\epsilon$ expansion. In Ref. \cite{6} the first two terms in the expansion

$$P_\pm(\zeta; \epsilon) = P_\pm(\zeta; \epsilon = 0) + \epsilon \partial_\epsilon P_\pm(\zeta; \epsilon = 0) + O(\epsilon^2)$$  \hspace{1cm} (3)$$

were obtained. Note that in contrast to our convention here the second-moment definition of $\xi$ was used in Ref. \cite{6}. We denote this latter correlation length as $\hat{\xi}$, reserving the symbol $\xi$ exclusively for the true correlation length. The difference between $\xi$ and $\hat{\xi}$ is fairly small near criticality since the associated amplitudes $\xi^{\pm}_0$ and $\hat{\xi}^{\pm}_0$ differ by less than a few per cent \cite{10}. The scaling functions $P_\pm$ and $\hat{P}_\pm$ corresponding to these two conventions can be easily transformed into each other using

$$\hat{P}_\pm(\zeta) = P_\pm(\zeta \xi^{\pm}_0 / \hat{\xi}^{\pm}_0) .$$  \hspace{1cm} (4)$$

Since $\xi^+_0 / \hat{\xi}^+_0 = 1 + O(\epsilon^2)$ and $\xi^-_0 / \hat{\xi}^-_0 = 1 + (\epsilon/12)(11/2 - \pi\sqrt{3}) + O(\epsilon^2)$ \cite{14}, the $\epsilon$ expansions of $P_+$ and $\hat{P}_+$ agree to order $\epsilon$, but those of $P_-$ and $\hat{P}_-$ differ already at order $\epsilon$.

As $\zeta \to 0$, the two terms in (3) behave as $P_\pm(\zeta; \epsilon = 0) \approx c_\pm \zeta^{-1}$ and $\partial_\epsilon P_\pm(\zeta; \epsilon = 0) \approx (c_\pm / 6\zeta) \ln \zeta$. If one extrapolated this result naively to $d = 3$ by setting $\epsilon = 1$, one would obtain a totally unacceptable short-distance behavior of the form $P_\pm(\zeta) \sim [1 + (\epsilon/6) \ln \zeta] / \zeta$. As discussed in Refs. \cite{6} and \cite{7}, the correct limiting form is

$$P_\pm(\zeta \to 0) \approx \zeta^{-\beta/\nu}(c_\pm + a_\pm \zeta^{1/\nu} + a'_\pm \zeta^{2/\nu} + b_\pm \zeta^d + \ldots) .$$  \hspace{1cm} (5)$$

Equation (3) is consistent with (5) in that the $\epsilon$ expansion of the latter agrees with the limiting form of (3) for small $\zeta$. The coefficients have the expansions

$$a_+ = \sqrt{2} \left( -\frac{1}{6} + \frac{1}{216} (1 - 6 C_E - 6 \ln 2) \right) + O(\epsilon^2) ,$$  \hspace{1cm} (6)$$
\[ a_\pm = \frac{1}{6} + \frac{\varepsilon}{216} \left( 6C_E + 8 - \pi 3\sqrt{3} \right) + O(\varepsilon^2), \]  
\[ a'_\pm = \frac{\sqrt{2}}{36} + O(\varepsilon), \quad a'_\mp = -\frac{1}{72} + O(\varepsilon), \]  
\[ b_\pm = -\frac{\sqrt{2}}{120} + O(\varepsilon), \quad b_\mp = -\frac{1}{60} + O(\varepsilon), \]  
\[ c_\pm = \sqrt{2} \left[ 1 + \frac{\varepsilon}{12} \left( 6 C_E + 2 \ln 2 - 13 \right) \right] + O(\varepsilon^2), \]  
\[ c_\mp = 2 + \frac{\varepsilon}{6} \left( 6 C_E - 16 + \pi \sqrt{3} \right) + O(\varepsilon^2), \]

where \( C_E = 0.5772\ldots \) is Euler’s constant. Due to the difference between \( \xi \) and \( \hat{\xi} \), the \( O(\varepsilon) \) terms of \( a_- \) and \( c_- \) differ from those of \( \hat{a}_- \) and \( \hat{c}_- \) given in Ref. [6].

For large arguments the scaling functions have the expected exponentially decaying forms

\[ P_+(\zeta \to \infty) \approx 2\sqrt{2} \left\{ 1 + \varepsilon \left[ \frac{1}{4} + \frac{1}{6} \ln 2 - \frac{2}{3}\pi \left( 1 - 2\sqrt{3} \right) + \frac{4\sqrt{3}}{3} \ln \frac{2\sqrt{3}+3}{2\sqrt{3}-3} \right] + O(\varepsilon^2) \right\} e^{-\zeta}, \]  
and

\[ P_-(\zeta \to \infty) \approx 1 + \left[ 2 - \varepsilon \frac{\pi}{6} \left( 4 - 1/\sqrt{3} \right) \right] + O(\varepsilon^2) e^{-\zeta}, \]

where it should be noted that \( e^{-\zeta} \) would get replaced by \( e^{-\text{const} \zeta} \) for any choice of the correlation length other than the true one.

In light of the discussion given in Ref. [4] we also determined the next-to-leading terms in the asymptotic expansion

\[ P_+(\zeta) = P_{+,1}^{(\infty)} e^{-\zeta} + P_{+,2}^{(\infty)} e^{-2\zeta} + P_{+,3}^{(\infty)} e^{-3\zeta} + \ldots. \]  

The value of \( P_{+,1}^{(\infty)} \) can be read off of (12). For the remaining coefficients one has

\[ P_{+,2}^{(\infty)} = O(\varepsilon^2) \]  
and

\[ P_{+,3}^{(\infty)} = 1 + \varepsilon \left[ \frac{1}{4} + \frac{1}{6} \ln 2 - 2\pi \left( 1 - 2\sqrt{3} \right) - 4\sqrt{3} \ln \frac{2\sqrt{3}+3}{2\sqrt{3}-3} \right] + O(\varepsilon^2). \]
The above results provide valuable quantitative information about the nature of the scaling functions beyond what is known from scaling considerations. The limiting forms of $P_{\pm}(\zeta)$ at large and small $\zeta$ can be extrapolated to $d = 3$ in a straightforward manner either by simply setting $\epsilon = 1$ in the corresponding coefficients or, preferably, by using improved extrapolation techniques (e.g., Padé analyses, into which the exact results for $d = 2$ have been incorporated [12]). To obtain extrapolations $P_{\pm}(\zeta, d = 3)$ giving a proper description of the $\zeta$ dependence for all values of $\zeta$ is a more challenging problem. A prime requirement is that both the leading asymptotic terms at small and large $\zeta$ be correctly reproduced. As we have seen above, the most naive extrapolation procedure — setting $\epsilon = 1$ in (3) — grossly fails in this regard. A number of alternative extrapolation schemes have been suggested [13,6], but all of these contain some degree of arbitrariness. Only recently a more systematic way of handling this problem was developed [8].

The crux of this method is a specially adapted, novel RG scheme. Its details are beyond the scope of the present paper, so we restrict ourselves to a few remarks. In renormalized field theory the amplitude of the order parameter $\phi(x)$ usually is reparametrized in a $z$ independent fashion to define the renormalized density $\phi_R = Z_\phi^{-1/2} \phi$. Here the amplitude renormalization factor $Z_\phi(u)$ depends on $u$, the dimensionless renormalized coupling constant, but not on $z$. The basic new element of the approach of Ref. [8] is that in place of $Z_\phi$ a $z$ dependent amplitude renormalization factor $\tilde{Z}(u, z\mu)$ is used, where $\mu$ is an arbitrary reference momentum. This generalized renormalization factor $\tilde{Z}$ is required to absorb in addition to the usual ultraviolet singularities (corresponding to poles in $\epsilon$ in the dimensionally regularized theory) also the short-distance singularities $\sim z^{-1} \ln(\mu z)$. That is, we require that the renormalized profile $m_R(z, u, \tau; \mu) = \tilde{Z}^{-1/2} m(z)$ have a finite limit

$$\lim_{z \to 0} z m_R(z, u, \tau; \mu).$$

At one-loop order a convenient choice is

$$\tilde{Z} = 1 + \frac{3}{2} u \ln\left(1 + \frac{1}{\mu z}\right) + O(u^2).$$
The advantage of this scheme becomes clear when the resulting RG equations are exploited. Due to the \( z \) dependence of \( \tilde{Z} \), these are somewhat more complicated than usual, albeit solvable by standard methods. The resulting RG-improved perturbation theory yields scaling functions \( P_{\pm}(\zeta, \epsilon) \) which exhibit for all \( \epsilon > 0 \) a smooth crossover from the correct short-distance form \( \sim \zeta^{-\beta/\nu} \) to the exponential decay at large \( \zeta \). Accordingly, meaningful extrapolations are obtained upon setting \( \epsilon = 1 \) (see Figs. 1 and 2).

3. MONTE CARLO RESULTS

Monte Carlo calculations have proved to be a very powerful alternative tool for studying critical phenomena in confined geometries. To get independent information on the scaling functions \( P_{\pm} \) we analyzed data of a Monte Carlo simulation of an \( L \times L \times D \) \((L = 128, D = 80)\) simple-cubic Ising film with periodic boundary conditions in the \( L \)-directions and free boundaries in the \( D \)-direction. The spins were assumed to interact via ferromagnetic nearest-neighbor exchange couplings that take the values \( J_1 \) and \( J \) for all bonds lying entirely within the two boundary layers and all other bonds, respectively. All bulk and surface magnetic fields were set to zero. To observe the universality class of the extraordinary transition, the surface coupling \( J_1 \) was chosen to be supercritical, i.e., larger than the critical value for the occurrence of a special transition in the thermodynamic limit \( L, D \to \infty \) (cf. Refs. [14,7,9]).

To model critical adsorption of fluids it would seem more realistic to take \( J_1 \) subcritical and to add a surface magnetic field \( h_1 > 0 \) (accounting for the wall-fluid interaction), i.e., to consider the so-called normal surface transition [7] of the model. However, as discussed in Ref. [7] and demonstrated exactly in Ref. [15], the surface critical behavior at critical adsorption and the normal transition is representative of the same universality class as the extraordinary transition.

The Monte Carlo data show that the behavior of the order parameter \( m(z) \) for \( z \ll \xi \) is well described by \( m(z) \propto (z + z_e)^{-\beta/\nu} \), where the exponent is in conformity with the value \( \beta/\nu = 0.519 \pm 0.007 \) quoted in Ref. [4]. The quantity \( z_e \) is a microscopic (‘extrapolation’)

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length depending on $J_1/J$, which ensures that $m_1 = m(0)$ is finite. It drops out in the scaling regime $z \gg z_e$. In accordance with our expectations we found it to have the same value for $T > T_c$ and $T < T_c$. For large distances $z$, which are still sufficiently small so that finite size effects are negligible, the profiles $m_{\pm}(z)$ decay exponentially on the scale of $\xi$, where the value of $\xi$ is in conformity with the results of Ref. [10]. At even larger values of $z$ finite size effects are clearly visible.

In order to check whether scaling holds we analyzed the data for $m(z)$ in the first twenty layers closest to the surface, using the scaling ansatz

$$m(z) \simeq M_\pm |\tau|^{\beta} P_{\pm}(z^{+z_e}/\xi)$$

(19)

for reduced temperatures $\tau$ in the ranges given in Figs. 1 and 2. As is borne out by these figures, the data collapsing on a single curve $P_{\pm}$ works reasonably well both for $\tau > 0$ and $\tau < 0$, within the limitations caused by statistical error and finite size effects. The resulting Monte Carlo profiles $P_{\pm}(\zeta)$ agree qualitatively quite well with our extrapolated $\epsilon$ expansion results. Quantitatively, the agreement is not very satisfactory. To appreciate these results, one should note, however, that our extrapolated RG results are free of any adjustable parameter. Likewise, no adjustable parameter remains in the Monte Carlo results for $P_{\pm}$, since the scales and amplitudes are fixed by the required large-distance forms (12) and (13). (One probably could get improved agreement at intermediate values of $\zeta$ by exploiting the freedom to make $O(\epsilon^2)$ errors at order $\epsilon$, but in contrast to our procedure, this would be unsystematic.)

The results for $P_{\pm}$ may be used to estimate various universal ratios. The ratio

$$R_{MA} \equiv \int_0^\infty d\zeta P_{+}(\zeta)/\int_0^\infty d\zeta [P_{-}(\zeta) - 1],$$

(20)

which is proportional to the ratio of the amplitudes of the excess order parameter $m_s$ above and below $T_c$, has been investigated experimentally by Law and Smith [16] recently. Integration of our Monte Carlo results yields $R_{MA} \simeq 1.14$ in good agreement with their experimental estimate $1.18 \pm 0.13$. Integration of our extrapolated RG results yields a somewhat higher
value $\simeq 1.3$. Of considerable interest are also the universal ratios $c_{\pm}$. From our Monte Carlo results we find the estimates $c_+ = 0.866 \pm 0.07$ and $c_- = 1.22 \pm 0.08$. Flöter and Dietrich [12] estimated $c_+$ theoretically by means of Padé approximants into which both the $\epsilon$ expansion results of Ref. [6] and the exact results for $d = 2$ were incorporated. They also extracted values of $c_+$ from a number of experiments. These experimental estimates were found to scatter around their theoretical estimate $c_+ \simeq 0.95$, which is in accordance with our Monte Carlo estimate. Finally, we mention that the universal ratio $P_{+1}^\infty/c_+$ was considered first by Liu and Fisher [4]. From their analysis of critical adsorption data they obtained the estimate $\simeq 0.85$. Our Monte Carlo data yield a considerably larger value of $\simeq 1.85$. This discrepancy might be due to the limited accuracy of the experimental data available at that time. A problem could also be that the approximate forms of $P_+(\zeta)$ used in the analysis of the experimental data were not accurate enough. (As discussed by Liu and Fisher [4] the estimate is rather sensitive to the chosen form of $P_+$.)

4. CONCLUDING REMARKS

In summary, we presented results for the universal scaled order parameter profiles $P_{\pm}(\zeta)$ at critical adsorption and the extraordinary transition. These were obtained by two distinct methods, namely, by RG-improved perturbation theory in $4 - \epsilon$ dimensions and by Monte Carlo simulations. To obtain meaningful extrapolations of the RG results to the physically interesting dimension $d = 3$, a novel renormalization scheme was used that guarantees the correct exponentiation of the leading short-distance singularity. Both the latter method and the Monte Carlo simulations yield profiles for $d = 3$, which exhibit the expected smooth and monotonous crossover from the power-law behavior [12] at small $\zeta$ to the large-distance form [12]. The results of both methods are in fair agreement with each other. The knowledge of the profiles can be utilized to estimate various universal amplitude ratios, which can also be determined by experiments. The agreement of our theoretical estimates with the few available experimental estimates [16,12] of the universal numbers $c_+$ and $R_{MA}$ is
encouraging. Yet, much more detailed experimental checks of the theoretical predictions are clearly needed.

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FIGURES

Fig. 1: Scaling function $P_+(\zeta)$. The dashed curve shows the mean-field approximation. The full curve is the extrapolation to $d = 3$ of the one-loop RG result obtained with the help of our specially adapted renormalization scheme. The symbols show Monte Carlo results for different reduced temperatures.

Fig. 2: Scaling function $P_-(\zeta)$. The dashed and full curves are the $\tau < 0$ analogs of the curves in Fig. 1. The symbols represent Monte Carlo results for different reduced temperatures.
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