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REVIEW ARTICLE

Three-dimensional wetting revisited

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Abstract. We review progress made towards resolving long-standing problems associated with the theory of wetting transitions in three-dimensional systems with short-ranged forces (corresponding to the marginal dimension). We begin by emphasizing the importance of two seemingly unrelated problems faced by the standard (capillary-wave) effective interfacial Hamiltonian model:

(a) the discrepancy with the results of Monte Carlo simulation studies of the critical wetting transition in the Ising model which do not reveal any of the predicted non-universal behaviour;
(b) the failure of the interfacial model to describe the structure of correlation functions (at the wall) known from mean-field studies of the complete wetting transition.

Recent work suggests that these problems may be overcome by introducing new effective Hamiltonians which improve on the capillary-wave model and lead to novel fluctuation effects in $d = 3$. The new models follow directly from the development of much improved systematic techniques concerning their derivation and justification initiated by Fisher and Jin. These workers emphasized the importance of allowing for the position dependence of the stiffness coefficient and showed that it may drive a (bare) critical wetting transition first order. This has been further developed by Parry, Boulter and co-workers who argue that it is essential to model the coupling of order-parameter fluctuations at the wall and interface and show how this resolves problem (b). The coupled Hamiltonian also leads to new predictions for fluctuation effects in $d = 3$ which are in good agreement with more recent Ising model simulations by Binder and co-workers as well as providing a likely explanation for problem (a).

1. Introduction

Effective interfacial models are widely used in condensed-matter physics to describe the large-scale fluctuations that occur near the surface or interface separating different bulk regions. Such models have played a central role in developing equilibrium theories of roughening (see, e.g., [1]) and wetting phase transitions [2, 3] and also non-equilibrium phenomena involving driven interfaces [4]. Common to all these models is the use of a collective coordinate $l(\boldsymbol{y})$ to represent the position or height of the interface with respect to some plane. Of course the models are not truly microscopic but are usually considered valid for length scales larger than some appropriate cut-off (such as a lattice spacing or bulk correlation length). The prevailing belief is that interfacial models may be derived from more microscopic approaches if the degrees of freedom up to the cut-off are integrated out. Needless to say this is an extremely difficult task and all interfacial models retain a partly phenomenological status. In this article we review work aimed at resolving some long-standing problems associated with the effective interfacial Hamiltonian theory of wetting transitions in three-dimensional systems with short-ranged forces (corresponding to the marginal or upper critical dimension). In particular we wish to present a unified account

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of recent theoretical developments concerning the derivation and justification of interfacial models. These lead to a number of new predictions for observable fluctuation effects which may be favourably compared with recent Ising model simulation studies and which also provide a likely explanation of older problems.

To begin, we recall the basic phenomenology of continuous wetting transitions and end by stating two problems faced by the standard (capillary-wave (CW)) interfacial approach which have provided motivation for the continued development of theory. These will also serve as benchmarks by which we may gauge the success of improved models. Consider, then, a system showing bulk phase coexistence between fluid phases denoted α and β at subcritical temperatures $T < T_c$. In keeping with the rest of our article we shall adopt a magnetic notation and denote the local order parameter by $m(\boldsymbol{r})$. Thus in addition to the temperature we also specify a bulk ordering (magnetic) field h and suppose that the stable bulk phase corresponds to order parameter $m_\alpha > 0$ for $h \geqslant 0$ and $m_\beta < 0$ for $h \leqslant 0$. Now consider the system in contact with a planar wall situated in the $z = 0$ plane which provides an additional surface field h_1 acting on the local surface layer. If the surface field h_1 is strong enough, a thin film of α-phase may intrude between the wall and bulk β-phase (assuming that $h < 0$). However, in the limit $h \to 0^-$ (corresponding to two-phase coexistence) the thickness l of the adsorbed film may either remain finite or diverge depending on the temperature and surface field. A section of a surface phase diagram (for constant temperature T) showing two continuous wetting transitions is given in figure 1. The critical wetting transition refers to the divergence of l as $h_1 \to h_1^w$ and $h \to 0^-$. There are two relevant scaling fields corresponding to $t \equiv (h_1^w - h_1)/h_1^w$ and h. Equally we may consider the transition induced by temperature for a fixed surface field with a suitably defined scaling variable $t \equiv (T_w - T)/T_w$ (with T_w the wetting temperature). The complete wetting transition on the other hand refers to the divergence of l as $h \to 0^-$ for $h_1 > h_1^w$ or equivalently $T > T_w$, and there is only one scaling field. Associated with the divergence of l for each transition is the growth of large fluctuations characterized by perpendicular and transverse correlation lengths denoted $\xi_\perp$ and $\xi_\parallel$, respectively. This is shown schematically in figure 2. With each transition we may also define a singular contribution to the excess surface free energy per unit area or surface tension [5] of the wall–β interface as

$$\sigma_{w\beta} \equiv \sigma_{w\alpha} + \sigma_{\alpha\beta} + f_{sing} \tag{1.1}$$

where $\sigma_{w\alpha}$ is the corresponding wall–α-phase excess free energy (evaluated at $h = 0^+$) and $\sigma_{\alpha\beta}$ is the free α–β surface tension. The critical exponents for the critical wetting transition are defined as

$$l \sim t^{-\beta s} \qquad \xi_\parallel \sim t^{-\nu_\parallel} \qquad \xi_\perp \sim t^{-\nu_\perp} \qquad f_{sing} \sim t^{2-\alpha_s} \tag{1.2}$$

where for the time being we consider only $h = 0^-$. Similarly for the complete wetting transition we write

$$l \sim |h|^{-\beta_s^{co}} \qquad \xi_\parallel \sim |h|^{-\nu_\parallel^{co}} \qquad \xi_\perp \sim |h|^{-\nu_\perp^{co}} \qquad f_{sing} \sim |h|^{2-\alpha_s^{co}}. \tag{1.3}$$

The critical exponents (for each transition) are not independent but the existing exponent relations will not be quoted here [2, 3]. A suitable microscopic starting point for the calculation of the critical singularities modelling (surface) phase coexistence in systems with short-ranged (contact) forces is the Landau–Ginzburg–Wilson (LGW) Hamiltonian [6]

$$H_{LGW}[m(\boldsymbol{r})] = \int \mathrm{d}\boldsymbol{y} \int_0^\infty \mathrm{d}z \, [\tfrac{1}{2}(\nabla m)^2 + \phi(m(\boldsymbol{r})) + \delta(z)\phi_1(m(\boldsymbol{r}))] \tag{1.4}$$

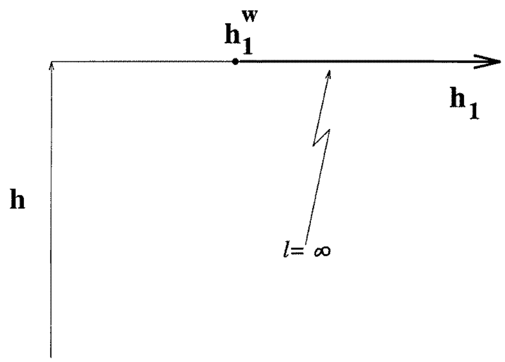

Figure 1. Section of the surface phase diagram at constant T. Along the cut in the $h = 0$ axis for $h_1 > h_1^w$ the wall–β interface is completely wetted by the α-phase. Critical and complete wetting transitions refer to the continuous divergence of l (and other length scales) as $h_1 \to h_1^w$, $h \to 0^-$ and $h \to 0^-$ for $h_1 > h_1^w$, respectively.

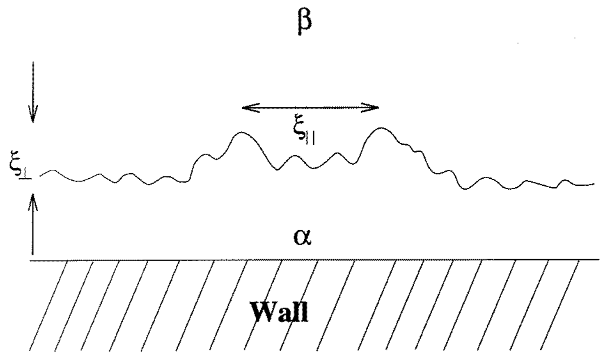

Figure 2. Schematic representation of interfacial fluctuations near a wall showing transverse and perpendicular correlation lengths.

where ϕ and ϕ_1 are the appropriate bulk and surface energy densities. The standard choice for ϕ_1 is

$$\phi_1(m) = \frac{cm^2}{2} - h_1 m \tag{1.5}$$

where c is the surface enhancement parameter. The bulk energy density ϕ has the usual double-well form for $T < T_c$ but will not be specified further. Unfortunately it is not possible to study (1.4) except in the mean-field (MF) approximation which ignores fluctuation effects. Minimizing (1.4) with respect to $m(\boldsymbol{r})$ yields the MF magnetization profile $m(z)$ and free-energy from which it is straightforward to calculate the surface phase diagram [6]. For our purposes we note only that for $c > \kappa$ sections of the phase diagram are of the form sketched in figure 1 with the wetting surface field (and temperature) determined by the relation

$$h_1^w = cm_\alpha \qquad h = 0. \tag{1.6}$$

Here κ is the inverse correlation length of the bulk α-phase. For $c < \kappa$ the wetting transition is first order so that l jumps discontinuously from a finite to infinite value at the phase boundary. We shall not discuss this possibility further. Using MF theory it is also straightforward to extract the critical exponents. For the critical wetting transition these are given by

$$\kappa l \sim \ln t^{-1} \qquad \xi_\parallel \sim t^{-1} \qquad f_{sing} \sim t^2. \tag{1.7}$$

For the complete wetting transition the critical singularities are

$$\kappa l \sim \ln |h|^{-1} \qquad \xi_\parallel \sim |h|^{-1/2} \qquad f_{sing} \sim h \ln |h| \tag{1.8}$$

where the form of f_{sing} will turn out to be of some significance. Note that, in order to determine the transverse correlation length $\xi_\parallel$, it is necessary to consider the connected correlation function

$$G(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv \langle m(\boldsymbol{r}_1)m(\boldsymbol{r}_2)\rangle - \langle m(\boldsymbol{r}_1)\rangle\langle m(\boldsymbol{r}_2)\rangle \tag{1.9}$$

and its transverse Fourier transform

$$G(z_1, z_2; Q) \equiv \int \mathrm{d}\boldsymbol{y}_{12} \exp(\mathrm{i}\boldsymbol{Q}\cdot\boldsymbol{y}_{12})G(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{1.10a}$$

$$\equiv \sum_{n=0}^{\infty} Q^{2n} G_{2n}(z_1, z_2) \qquad Q \to 0 \tag{1.10b}$$

where $\boldsymbol{y}_{12}$ is the parallel displacement of the points $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. Equation (1.10*b*) defines the moment expansion of the correlation function. Using standard techniques (see, e.g., [7, 8]) the form of G is easily found for positions z_1, z_2 near the α–β interface:

$$G(z_1, z_2; Q) \propto \frac{\xi_\parallel^2 m'(z_1)m'(z_2)}{1 + Q^2\xi_\parallel^2}. \tag{1.11}$$

The simple Lorentzian character of (1.11), which is equally applicable to critical and to complete wetting transitions, is of the expected form consistent with the interpretation that fluctuations about the MF profile are dominated by long-wavelength distortions in the position of the α–β interface (recall figure 2).

Substitution of the MF critical exponents into the hyperscaling relations [7, 9] $2 - \alpha_s = (d-1)\nu_\parallel$ and $2 - \alpha_s^{co} = (d-1)\nu_\parallel^{co}$ determines the marginal dimension for each transition, yielding $d^* = d^*_{co} = 3$. It is therefore possible that fluctuations alter the MF values of the critical exponents in $d = 3$. Note that, for systems with long-ranged forces, similar considerations show that MF treatments should suffice in three dimensions [2]. As a preliminary remark we recall that a well known defect of MF theory is its inability to describe the divergence of $\xi_\perp$ as $\xi_\parallel \to \infty$ in $d \leqslant 3$ (see, e.g., [10]). In particular in $d = 3$ we expect the width $\xi_\perp$ of the true equilibrium magnetization profile to satisfy (see, e.g., [10])

$$(\kappa\xi_\perp)^2 \approx \omega \ln(\kappa\xi_\parallel)^2 \tag{1.12}$$

where we have defined the wetting parameter ω as [11]

$$\omega \equiv k_B T\kappa^2/4\pi\Sigma_{\alpha\beta} \tag{1.13}$$

which will play a central role in our discussion. Here $\Sigma_{\alpha\beta}$ corresponds to the stiffness coefficient of the free α–β interface. For isotropic continuum models this can be identified with the tension $\sigma_{\alpha\beta}$ but for models defined on a lattice it also depends on the curvature of the surface tension with respect to angular orientation [12]. Of course for lattice models in $d = 3$ we need to specify that the temperature is greater than the roughening temperature so that the interface is fluid like. We shall assume that the temperature dependences of κ and $\Sigma_{\alpha\beta}$ can be found using other methods so that the value of ω for a given T is known [11, 13].

In the absence of any systematic technique for analysing three-dimensional models of wetting beyond the MF approximation (other than by simulation) we are forced to study effective Hamiltonian models to determine the non-classical behaviour. The standard CW model which has formed the basis for the general fluctuation theory of wetting is given by [2, 3]

$$H_{\mathrm{CW}}[l(\boldsymbol{y})] = \int \mathrm{d}\boldsymbol{y} \left(\frac{\Sigma_{\alpha\beta}}{2} (\nabla l)^2 + W(l(\boldsymbol{y})) \right) \tag{1.14}$$

where $W(l)$ is the binding potential. As is apparent the essential assumption of the CW model is that fluctuations in the position of the α–β interface (described by the collective coordinate $l(\boldsymbol{y})$) determine the extent to which the critical singularities of the wetting transition are MF like or not. These latter singularities are controlled by the binding potential which may be regarded as a direct or bare interaction between the α–β interface and wall. We shall not comment on the older arguments given for the model since a more systematic theory will be presented in section 2. The model is best regarded as a plausible phenomenological starting point for the investigation of long-wavelength interfacial fluctuations. Therefore, implicit in the model is a high-momentum cut-off which limits the fluctuations to length scales much greater than the bulk correlation length. Thus in $d = 3$ we specify the cut-off by $\Lambda \ll (\Sigma_{\alpha\beta}/k_B T)^{1/2}$. To proceed we need to specify the form of the binding potential. For systems with short-ranged forces the standard expression is [7, 14, 15]

$$W(l) = \bar{h} l - \tau \exp(-\kappa l) + b \exp(-2\kappa l) \tag{1.15}$$

together with a hard-wall contribution which limits the configurations to $l(\boldsymbol{y}) > 0$. Here $\tau \propto t$, $\bar{h} \propto |h|$ and b is necessarily positive near T_w and may be regarded as a constant. Again we postpone a discussion of the justification of (1.15) until section 2 where we develop a more general approach. For dimensions $d < 3$ the specific form of W is not essential because the critical singularities are controlled by the universal properties of a fixed-point Hamiltonian [16]. Thus in $d = 2$ approximating $W(l)$ by a square well potential (with a hard-wall for $l < 0$) generates the same universal critical exponents for the critical wetting transition as that found in the exact Ising model solution due to Abraham [17] (see, e.g., [3]) ($\beta_s = \nu_\perp = 1$, $\nu_\parallel = 2$ and $\alpha_s = 0$). However, for $d = 3$ the precise structure of $W(l)$ is essential because there is no non-trivial fixed-point Hamiltonian [16]. Before we quote the renormalization group (RG) results for $d = 3$ we note that, if we ignore fluctuations and simply minimize $W(l)$ with respect to l, we recover the MF expressions for l and f_{sing} quoted in equations (1.7) and (1.8). Similarly, if we consider Gaussian fluctuations about the MF position l_{MF}, we may calculate the structure factor

$$S(Q) \equiv \int \langle \delta l(\boldsymbol{y}_1) \delta l(\boldsymbol{y}_2) \rangle \mathrm{e}^{\mathrm{i}\boldsymbol{Q}\cdot\boldsymbol{y}_{12}}\, \mathrm{d}\boldsymbol{y}_{12} \tag{1.16}$$

where $\delta l(\boldsymbol{y}) \equiv l(\boldsymbol{y}) - l_{MF}$. Thus we find that

$$S(Q) = \frac{k_B T}{W''(l_{MF}) + \Sigma_{\alpha\beta} Q^2} \tag{1.17}$$

from which we may identify $\xi_\parallel^2 = \Sigma_{\alpha\beta}/W''$, recovering the MF results. $S(Q)$ has the simple Lorentzian form typical of order-parameter correlation near the α–β interface. Indeed, if we assume that small fluctuations in δl simply translate the MF profile, we are led to the prediction (see, e.g., [18])

$$G(z_1, z_2; Q) \approx m'(z_1) m'(z_2) S(Q) \tag{1.18}$$

for $z_1, z_2 \sim l_{MF}$ which is essentially identical with the explicit MF result. In section 2 we shall see that it is possible to make such identifications precisely correct for arbitrary z_1, z_2 using a generalized effective Hamiltonian approach.

In $d = 3$, RG calculations due to Brezin *et al* [14] and Lipowsky *et al* [15] (see also Fisher and Huse [19]) predict that the critical behaviour is non-universal depending on the value of the wetting parameter. For critical wetting the results are particularly dramatic. For example the correlation length critical exponent is given by

$$\nu_\parallel = \begin{cases} (1-\omega)^{-1} & 0 \leqslant \omega < 1/2 \\ (\sqrt{2} - \sqrt{\omega})^{-2} & 1/2 < \omega < 2 \\ \infty & \omega > 2 \end{cases} \tag{1.19}$$

where the last regime corresponds to $\xi_\parallel \sim \exp(\text{constant}\, t^{-1})$. The three regimes arise from the competition between the renormalized exponential terms in $W(l)$ and the renormalized hard-wall contribution. We also note that for the first two regimes the wetting film still grows logarithmically and the wetting temperature is unaltered. For the complete wetting transition the non-universality is less dramatic and the critical exponents remain MF like (i.e. $\nu_\parallel^{co} = \frac{1}{2}$). Nevertheless critical amplitudes are ω dependent. For example the mean interface position grows as

$$\kappa l \sim \theta_{\text{CW}} \ln |h|^{-1} \tag{1.20}$$

with $\theta_{\text{CW}} = 1 + \omega/2$ for $\omega < 2$. All these predictions recover the MF expressions if we set $\omega = 0$ (corresponding to infinite stiffness) which suppresses fluctuations. Whilst the RG analysis leading to these predictions is an approximate linear functional theory, the results are believed to be exact for this choice of binding potential (at least for the physically relevant regime $\omega < 2$ where the renormalization of the hard wall is not all important [20]).

The three-dimensional semi-infinite Ising model is the simplest available microscopic model which may be simulated to test these predictions. As mentioned above, the only proviso that we should stipulate is that the temperatures simulated should exceed the roughening temperature T_R (which is about $0.54T_c$ for the simple-cubic lattice). The values of the wetting parameter as a function of temperature are now known accurately from independent studies [11, 13]. In fact for all temperatures in the range $T_c > T \gtrsim 0.6T_c$ we expect $\omega \approx 0.8$, leading to the prediction $\nu_\parallel \approx 3.7$ for the critical wetting transition. We now meet our first problem.

Problem 1. Extensive Monte Carlo (MC) simulation studies by Binder, Landau and co-workers [21–23] appear to show that the critical exponents for the critical wetting transition are MF like. Specifically these workers study two wetting transitions occurring near $0.6T_c$ and $0.9T_c$ (corresponding to different choices of the surface field) and establish the divergence of the surface susceptibility $\chi_1 = \partial m_1/\partial h$, where m_1 is the surface layer magnetization. According to scaling expectations, χ_1 should behave as

$$\chi_1 \sim t^{-(1+\beta_s)} X(|h| t^{-\Delta}) \tag{1.21}$$

where $\beta_s = 0$ (assuming that $\omega < 2$) and the gap exponent $\Delta = 2\nu_\parallel$. Hence along the critical isotherm ($t = 0, h \to \bar{0}$) we anticipate that $\chi_1 \sim |h|^{-1/2\nu_\parallel}$. Contrary to the CW predictions the Ising model MC data are very well fitted by the MF result $\chi_1 \sim |h|^{-1/2}$.

Whilst the discrepancy between CW theory and Ising model simulations provoked much discussion [24–32], no substantial progress was made until Fisher and Jin (FJ) [33–37] reassessed the status of the CW model and proposed a novel explanation of the problem.

In retrospect, however, there is more to the problem of three-dimensional wetting than the above and the FJ analysis should be regarded as an important step towards a fuller description of fluctuation effects rather than an end in itself. We shall also emphasize the significance of a seemingly unrelated problem.

Problem 2. MF studies of correlation functions at the complete wetting transition [38–40] reveal intriguing features for particle positions near the wall which cannot be described using the CW model (or for that matter using the amended model proposed by FJ). For the LGW model the MF solution for $G(0, 0; Q)$ is [40]

$$G(0,0;Q) \approx \frac{k_B T m_1'^2}{(c+k)m_1'^2 + Q^2[\sigma_{w\alpha} - \phi_1(m_1) + (\sigma_{\alpha\beta} + f_{sing})/(1+Q^2\xi_\parallel^2)]} \tag{1.22}$$

where m_1' is the gradient of the magnetization profile at the wall. Near complete wetting, the local inhomogeneity in $m(z)$ near the wall is rather similar to that occurring at the wall–α interface and m_1' may be regarded as a constant in the above expression.

Interestingly the wavevector dependence shows strong crossover behaviour depending on the scaling variable $x \equiv Q\xi_\parallel$. For $x \to 0$ the effective coefficient of Q^2 in the denominator is the full excess free energy of the wall–β interface. Thus the second moment $G_2(0, 0)$ appearing in the wavevector expansion of G depends not only on surface tension of the $\sigma_{\alpha\beta}$ interface but also the singular contribution f_{sing}:

$$\begin{aligned} G_2(0,0) &\propto \sigma_{w\alpha} + \sigma_{\alpha\beta} + f_{sing} - \phi_1(m_1) \\ &= \sigma_{w\beta} - \phi_1(m_1). \end{aligned} \tag{1.23}$$

For obvious reasons we refer to $x \to 0$ as the coherent limit. On the other hand, in the limit $x \to \infty$, $G(0, 0; Q)$ reduces to the wall–α interface correlation function (which may be regarded as the intrinsic behaviour). The manifest non-Lorentzian form of (1.22) contrasts with that for particle positions near the α–β interface.

These remarks conclude our introduction concerning the problems of CW theory. In section 2 we present an account of recent developments in generalized effective Hamiltonian theory beginning with the theory of FJ and the derivation of a position-dependent stiffness coefficient. Then, following the work of Parry and Boulter (PB) [41–45] we show how a precise connection can be made with the MF correlation function $G(z_1, z_2; Q)$ if we further generalize the FJ analysis. This naturally leads to the introduction of a two-field Hamiltonian $H_2[l_1, l_2]$ which describes the coupling of order-parameter fluctuations at the wall and α–β interface. This theory elegantly solves problem 2 described above and also leads to a number of new relations, notably the stiffness-matrix–free-energy relation [45] and also a class of correlation function identities [46]. RG analysis of the FJ and two-field models leads to a number of new predictions for fluctuation effects in $d = 3$. In particular the FJ model suggests [34, 36] that the bare critical wetting transition is of a fluctuation-induced first-order nature for sufficiently small values of ω. In addition the two-field theory predicts that the effective value of the wetting parameter is renormalized at the complete wetting transition, implying that measurable critical amplitudes are different from those predicted by the CW and FJ theories [42, 44, 47, 48]. The model also suggests that the singularities characterizing local observables at the wall at a critical wetting transition are weaker than those of observables local to the α–β interface [49]. These ideas are made more quantitative in a slightly improved coupled model which is better suited to describing crossover effects for complete wetting near T_w. In particular a reanalysis of the Ginzburg criterion for the local susceptibility χ_1 at critical wetting [50] provides a quantitative explanation of the Ising model simulation results leading to problem 1.

In section 3 we review the results of Ising model simulation studies of phase coexistence and critically in a confined system with competing surface fields [51–54] recently reported by Binder *et al* [55–57]. This is a different geometry from the original simulation studies [21–23] and in many ways is better suited to analysing wetting properties. The new simulations provide independent confirmation of the wetting parameter renormalization effect predicted by the coupled theory and also allow a measurement of the wetting parameter ω in excellent agreement with theoretical expectations.

We conclude with a brief summary and make some final remarks.

2. Generalized effective Hamiltonian theory

2.1. The position-dependent stiffness

FJ begin their analysis by emphasizing the need to define carefully the collective coordinate $l(\boldsymbol{y})$. They propose two definitions: a crossing criterion (CC) in which $l(\boldsymbol{y})$ is defined as the position of the surface of fixed magnetization m^x and also integral criteria involving moments of the magnetization profile. Both approaches lead to similar conclusions although the CC is much easier to handle and will be the only one considered here. In their original calculation, FJ set $m^x = 0$ but following the subsequent analysis of PB we keep the value arbitrary. The generalized effective Hamiltonian for the surface of fixed magnetization is defined as

$$\exp\left(\frac{-H_{FJ}[l(\boldsymbol{y}); m^x]}{k_B T}\right) = \mathrm{Tr}'\left[\exp\left(\frac{-H_{LGW}[m(\boldsymbol{r})]}{k_B T}\right)\right] \tag{2.1}$$

where the prime denotes that the partial trace over configurations $m(\boldsymbol{r})$ respects the CC:

$$m(\boldsymbol{r} = (l(\boldsymbol{y}), \boldsymbol{y})) = m^x. \tag{2.2}$$

Next FJ suppose that for a given collective coordinate distribution all other fluctuations are small, leading to

$$H_{FJ}[l(\boldsymbol{y}); m^x] = H_{LGW}[m_\Xi(\boldsymbol{r}; l(\boldsymbol{y}))] \tag{2.3}$$

where m_Ξ is the magnetization distribution which minimizes H_{LGW} subject to the CC (2.2). In fact for most purposes it is enough to consider the properties of the planar constrained profile $m_\pi(z; l)$ satisfying a standard Euler–Lagrange equation together with an appropriate boundary condition including the CC (2.2). In this way, FJ derive

$$H_{FJ}[l(\boldsymbol{y}); m^x] = \int \mathrm{d}\boldsymbol{y} \left[\frac{\Sigma(l; m^x)}{2}(\boldsymbol{\nabla} l)^2 + W(l; m^x)\right] \tag{2.4}$$

where we have ignored curvature terms $\mathrm{O}(\nabla^2 l)$ which do not play any role with regard to determining critical properties [58]. The binding potential and position-dependent stiffness coefficient for the surface of fixed magnetization m^x are given by the formulae

$$W(l; m^x) = \int_0^\infty \mathrm{d}z \left(\frac{1}{2}\left(\frac{\partial m_\pi}{\partial z}\right)^2 + \phi(m_\pi(z; l))\right) + \phi_1(m_\pi(0; l)) \tag{2.5}$$

and

$$\Sigma(l; m^x) = \int_0^\infty \mathrm{d}z \left(\frac{\partial m_\pi}{\partial l}(z; l)\right)^2 \tag{2.6}$$

$$\equiv \Sigma_{\alpha\beta} + \Delta\Sigma(l; m^x) \tag{2.7}$$

where $\Sigma_{\alpha\beta}$ is the MF surface stiffness for the free α–β interface and $\Delta\Sigma \to 0$ as $l \to \infty$ (provided that $m_\alpha > m^x > m_\beta$). We now follow FJ and set $m^x = 0$ so that the surface of fixed magnetization is local to the α–β interface. The expansion of the binding potential is rather similar to the expression quoted earlier but the $\Delta\Sigma$ term is new. FJ derive

$$\Delta\Sigma(l;0) = -\tau\exp(-\kappa l) - q\kappa l\exp(-2\kappa l) + \cdots \tag{2.8}$$

where q is a positive constant near T_w.

The linear RG analysis of the FJ model is a little more complicated than the CW model because the RG flow equations for $\Delta\Sigma$ and W are coupled. Nevertheless FJ show that an appropriate effective binding potential $W^{(t)}_{eff}(l)$ given by

$$W^{(t)}_{eff}(l) \equiv W^{(t)}(l;0) + \frac{\omega\Lambda^2}{2\kappa^2}[1-\exp(-2t)]\Delta\Sigma^{(t)}(l;0) \tag{2.9}$$

satisfies the same diffusion-type equation familiar from the CW model analysis of Fisher and Huse [19] (where t is the infinitesimal rescaling parameter) and shows the mixing of the binding potential and stiffness under renormalization for $\omega > 0$. FJ point out that the next to leading-order term in (2.9) (for large t) is negative owing to the second term in (2.8). In this way, FJ argue that the bare (MF) critical transition is of a fluctuation-induced first-order nature for sufficiently small values of $\omega < \omega^*$, where ω^* is estimated to be in the range $\frac{1}{2} < \omega^* \lesssim 1$. For $\omega > \omega^*$ the transition is second order with the same critical exponents as the CW model. FJ suggest that the solution to problem 1 might be that the actual Ising model wetting transition observed by Binder *et al* [21–23] corresponds to a very weak first-order transition (although there appears to be no direct signature of this in the data). However, the FJ analysis is still not able to provide a quantitative explanation of why the susceptibility χ_1 measured in the simulations is MF like. For this reason and also problem 2 (which we turn to next) it is probably best to regard the FJ analysis as a first step towards a better theory.

2.2. Correlations and the stiffness matrix

The systematic structure of the FJ theory allows a precise connection to be made with the MF correlation functions of the LGW theory previously studied using standard (and somewhat cumbersome) techniques. Following PB, consider the continuous set of FJ Hamiltonians $\{H_{FJ}[l(\boldsymbol{y}); m^x]\}$ by allowing all possible choices of m^x belonging to the range of magnetizations $m_1 \geqslant m^x > m_\beta$ seen in the MF profile $m(z)$. For a given surface of fixed magnetization m^x the corresponding equilibrium value z of the collective coordinate satisfies $m^x = m(z)$. Similarly one may envisage a set of structure factors $\{S(Q;z)\}$ for all possible values $z \geqslant 0$ where $S(Q;z)$ has the standard definition (1.16) and is specific to the surface of fixed magnetization $m^x = m(z)$. Assuming that the fluctuations are small, we readily derive

$$S(Q;z) = \frac{k_BT}{W''(z;m(z)) + Q^2\Sigma(z;m(z))} \tag{2.10}$$

where W'' is the second derivative of W with respect to l evaluated at equilibrium. It transpires that there is a remarkable relation between the set $\{S(Q,z)\}$ and the MF correlation function $G(z,z;Q)$. To see this, first consider the set of zeroth moments $\{S(0;z)\}$. It can be shown that for fixed z the exact analytic MF expression for $G_0(z,z)$ can be recovered according to the rule

$$G_0(z,z) = \max\left(\frac{\partial m_\pi(z;l)}{\partial l}\right)^2_{l=z'} S(0;z') \tag{2.11}$$

$$= m'(z)^2 S(0; z). \tag{2.12}$$

The final identification turns out to be correct to order Q^2 (although we have to stop here for the model (2.4)), i.e.

$$G(z, z; Q) = m'(z)^2 S(Q; z). \tag{2.13}$$

Thus to recover the correlation function $G(z, z; Q)$ for a particular z we need to choose the appropriate Hamiltonian H_{FJ} with $m^x = m(z)$. These remarks make it clear why the FJ model with $m^x = 0$ (and hence the CW model) fail to describe the wall correlation function since the choice of m^x is entirely inappropriate.

PB next consider the properties of the set of two-field models $\{H_2[l_1, l_2; m_1^x, m_2^x]\}$ where each element denotes the effective Hamiltonian for two surfaces of fixed magnetizations m_1^x and m_2^x described by the pair of collective coordinates l_1 and l_2. Assuming that $l_2 > l_1$, it is straightforward to derive the coupled Hamiltonian

$$H_2[l_1, l_2] = \int \mathrm{d}\boldsymbol{y}[\tfrac{1}{2}\Sigma_{\mu\nu}(l_1, l_2)\boldsymbol{\nabla} l_\mu \cdot \boldsymbol{\nabla} l_\nu + W_2(l_1, l_2)] \tag{2.14}$$

where for simplicity we have dropped the explicit m_1^x, m_2^x dependence. Note that the $\Sigma_{\mu\nu}$ constitute the elements of a symmetric stiffness matrix $\boldsymbol{\Sigma}$. Explicit expressions for Σ and W_2 may be found in terms of the doubly constrained planar profile $m_\pi^{(2)}(z; l_1, l_2)$. Connection with MF correlations is made through a set of structure factor matrices $\{\mathbf{S}(Q; z_1, z_2)\}$ where z_1, z_2 denote the MF positions of the surfaces of fixed magnetizations m_1^x, m_2^x. Here

$$\mathbf{S}(Q; z_1, z_2) \equiv \begin{bmatrix} S_{11}(Q; z_1, z_2) & S_{12}(Q; z_1, z_2) \\ S_{12}(Q; z_1, z_2) & S_{22}(Q; z_1, z_2) \end{bmatrix} \tag{2.15}$$

where by analogy with (1.16) we have defined

$$S_{\mu\nu}(Q; z_1, z_2) \equiv \int \mathrm{d}\boldsymbol{y}_{12} \exp(\mathrm{i}\boldsymbol{Q} \cdot \boldsymbol{y}_{12})\langle \delta l_\mu(\boldsymbol{y}_1)\delta l_\nu(\boldsymbol{y}_2)\rangle. \tag{2.16}$$

These are easily calculated using the relation [44]

$$\mathbf{S}^{-1}(Q; z_1, z_2) = \begin{bmatrix} \partial_{11}^2 & \partial_{12}^2 \\ \partial_{12}^2 & \partial_{22}^2 \end{bmatrix} W_2 + Q^2\boldsymbol{\Sigma} \tag{2.17}$$

where $\partial_{\mu\nu}^2 \equiv \partial^2/(\partial l_\mu\, \partial l_\nu)$ and is evaluated at equilibrium. From the matrix elements, one can recover the MF expression for three different correlation functions using

$$G(z_\mu, z_\nu; Q) = m'(z_\mu)m'(z_\nu)S_{\mu\nu}(Q; z_1, z_2). \tag{2.18}$$

This turns out to be a rather useful formulation (at MF level and beyond). We now specialize to the complete wetting transition and choose $m_2^x = 0$ and $m_1^x \approx m_1$ so that l_2 and l_1 are representative of surfaces of fixed magnetization that unbind or remain bound to the wall as $h \to 0^-$. This allows us to address problem 2 mentioned in the introduction. Noting that the fluctuations of the lower surface are always small, the binding potential may be written

$$W_2(l_1, l_2; m_1, 0) \approx \frac{r l_1^2}{2} + W(l_{21}) \tag{2.19}$$

where $W(l_{21})$ (with $l_{21} \equiv l_2 - l_1$) is similar to the phenomenological result (1.15) and $r > 0$. Thus at the wall we derive

$$G(0, 0; Q) = \frac{k_B T m_1'^2}{r + Q^2[\Sigma_{11} + (\Sigma_{22} + 2\Sigma_{12})/(1 + Q^2\xi_\parallel^2)]}) \tag{2.20}$$

which is the desired form. Note that the $\Sigma_{\mu\nu}$ satisfy a stiffness-matrix–free-energy relation [44]

$$\sum_{\mu,\nu} \Sigma_{\mu\nu}(0, z_2) = \sigma_{w\beta} - \phi_1(m_1) \tag{2.21}$$

which ensures that the sum rule (1.23) is exactly obeyed. In fact this relation simplifies further because the leading-order decay of $\mathbf{\Sigma}$ is provided by the off-diagonal element $\Sigma_{12} \sim l_{21} \exp(-\kappa l_{21})$, leading to the remarkable relation

$$2\Sigma_{12}(0, z_2) \approx f_{sing} \tag{2.22}$$

and recall that the arguments 0 and z_2 refer to the mean positions of l_1 and l_2. Thus the coupling of fluctuations is essential in order to understand the singularity in $G_2(0, 0)$. Note that the decay of Σ_{12} is precisely of the form required to recover the free-energy singularity $h \ln(h)$ and is longer ranged than the FJ stiffness. Needless to say the formalism also recovers the simple Lorentzian structure of G near the α–β interface and in addition allows the calculation of $G(0, z_2; Q)$ which also shows strong crossover behaviour [44].

To conclude our discussion of MF correlations we mention that by considering the properties of the set of three-field Hamiltonians $\{H_3[\cdots]\}$ it is possible to derive two new identities for $G(z_1, z_2; Q)$. These are in fact applicable to the LGW model of fluid confinement between two planar walls with arbitrary surface fields and include the present semi-infinite system as a special case. We simply quote the results [46]

$$G(z_1, z_2; Q)G(z_2, z_3; Q) = G(z_1, z_3; Q)G(z_2, z_2; Q) \tag{2.23}$$

and

$$\frac{m'(z_2)G_0(z_1, z_1) - m'(z_1)G_0(z_1, z_2)}{m'(z_2)G_0(z_1, z_3) - m'(z_3)G_0(z_1, z_2)} = \frac{m'(z_2)G_0(z_1, z_3) - m'(z_1)G_0(z_2, z_3)}{m'(z_2)G_0(z_3, z_3) - m'(z_3)G_0(z_2, z_3)} \tag{2.24}$$

valid $\forall z_1 \leqslant z_2 \leqslant z_3$.

2.3. RG theory of coupling effects

We begin by discussing the complete wetting transition since the modelling of the coupling of fluctuation effects is easier for this case. To see the essential influence of coupling on the critical singularities it is sufficient to consider the Hamiltonian [42]

$$H_2[l_1, l_2] = \int \mathrm{d}\boldsymbol{y} \left[\frac{\Sigma_{11}}{2} (\nabla l_1)^2 + \frac{\Sigma_{\alpha\beta}}{2} (\nabla l_2)^2 + \frac{r l_1^2}{2} + \bar{h} l_{21} - \tau \exp(-\kappa l_{21}) \right] \tag{2.25}$$

where (for the moment) we have ignored the position dependence of $\Sigma_{\mu\nu}$ and have approximated $\Sigma_{11} = \sigma_{w\alpha} - \phi_1(m_1)$. This is the simplest model which accounts for order-parameter fluctuations near the wall and α–β interface. Recall that the CW theory predicts that the critical amplitude θ characterizing the divergence of the film thickness is $\theta_{\mathrm{CW}} = 1+\omega/2$. This result is unchanged in the FJ model. However, linear [44] and non-linear [48] functional RG analyses of the two-field model show that the effective value of ω is increased owing to the coupling of fluctuations. Consequently the critical amplitude θ is given by

$$\theta = 1 + \frac{1}{2} \left[\omega + \frac{k_B T \kappa^2}{4\pi \Sigma_{11}(1 + (\Lambda_1 \xi_{w\alpha})^{-2})} \right] \tag{2.26}$$

where $\xi_{w\alpha} = \sqrt{\Sigma_{11}/r}$ is the transverse correlation length of the intrinsic wall-α interface and Λ_1 is the momentum cut-off for the lower surface satisfying $\Lambda_1 \ll \sqrt{\Sigma_{11}/k_B T}$. Within the two-field theory described above, it is difficult to estimate precisely the increment to the CW expression θ_{CW} but PB argue that for $h_1 \gg h_1^w$ or equivalently $T \gg T_w$ the value appropriate to the Ising model (assuming that $\omega \approx 0.8$) should be $\theta \approx 1.8$ compared with $\theta_{\mathrm{CW}} \approx 1.4$. Subsequently Parry *et al* [47] have argued that, as the temperature is lowered towards T_w the incremental term in θ should vanish so that

$$\lim_{T \to T_w^+} \theta = 1 + \frac{\omega}{2}. \tag{2.27}$$

This may be viewed as resulting from the decoupling of modes at the wall and α–β interface associated with the vanishing of the local stiffness-matrix element $\Sigma_{11} \sim \tau^2$ as $\tau \to 0$.

It is possible to extend these ideas and to develop a more quantitative theory of the coupling effects near T_w. This involves modelling the order-parameter fluctuations near the wall in a slightly different way using an alternative collective coordinate which we denote as s (rather than l_1). We omit the details of the construction of the Hamiltonian [50] and simply quote its form for $T \gtrsim T_w$:

$$H[s, l_2] = \int \mathrm{d}\boldsymbol{y} \left[\frac{\overline{\Sigma}_{11}}{2} (\nabla s)^2 + \frac{\Sigma_{\alpha\beta}}{2} (\nabla l_2)^2 + \frac{\bar{r} s^2}{2} + \bar{h} l_2 - \tau \exp\{-\kappa [l_2 - \delta(\tau) s]\} + \cdots \right] \tag{2.28}$$

which may be regarded as a refinement of (2.25). The new stiffness coefficient $\overline{\Sigma}_{11}$ remains finite as $\tau \to 0$ (as does $\bar{r}$) and the extent of the coupling between the two fields is controlled by the variable $\delta(\tau) \propto \tau$. Using this model it is possible to show that the increment to the CW result θ_{CW} vanishes quadratically as $\tau \to 0$. If we consider sections of the wetting phase diagram at fixed T very close to T_c and induce wetting by varying h_1 (as shown in figure 1), then the critical amplitude θ is predicted [50] to have a universal expansion in $t \equiv (h_1^w - h_1)/h_1^w$ about the CW result which is itself universal (since ω tends to a universal value $\omega_c \approx 0.77$ [11]). Thus we write [50]

$$\theta \sim 1 + \frac{\omega_c}{2} + \frac{\Omega_c}{2} t^2 + \cdots \tag{2.29}$$

where Ω_c is further predicted to be related to standard bulk critical amplitude ratios (see, e.g., [59])

$$\Omega_c = \frac{1}{2\pi} \frac{R_c}{(R_\xi^+)^3} \left(\frac{\xi_0^+}{\xi_0^-} \right)^3 \frac{\Gamma^-}{\Gamma^+}. \tag{2.30}$$

Using the best available estimates [11, 59] we find that

$$\theta = 1.38 + 0.4 t^2 + \cdots. \tag{2.31}$$

These calculations implicitly assume that the wetting transition occurring at T_w (or h_1^w) is second order because they do not include the position dependence of the stiffness coefficients. Allowing for these does not significantly alter the predictions as regards the renormalization of the wetting parameter at complete wetting. However, application of the coupled model $H_2[l_1, l_2]$ to the critical wetting transition [49] does reveal a new effect in addition to the possibility that the transition is of a fluctuation-induced first-order nature (similar to the FJ theory). Specifically, calculation of the appropriate $\mathbf{S}$ matrix shows that S_{11} and S_{12} exhibit MF-like singularities even if S_{22} shows strong non-universality consistent with the CW prediction. A more quantitative assessment of the influence of coupling on the critical singularities is provided by the improved model $H[s, l_2]$. In particular Parry and Swain [50] have reassessed the Ginzburg criterion and find that the true asymptotic critical region for the local susceptibility χ_1 is much smaller than previously calculated using the CW model. In fact the transverse correlation length $\xi_\parallel$ has to be much greater than 40–60 lattice spacings (at the temperatures that the simulations were performed) compared with the CW estimate due to Halpin-Healey and Brezin [25]: $\xi_\parallel \gg 4$–8. Thus allowing for coupling between order-parameter fluctuations near the wall and α–β interface appears to solve our central problem 1 since the simulation studies fall well within the MF regime.

3. Ising model simulations

Binder, Landau and Ferrenberg (BLF) [54–56] have recently performed large-scale MC simulations of a finite-size Ising model with competing surface fields. This is a different system from the original simulation studies and in many ways is much better suited to analysing wetting properties since they play a dominant part in determining the phase coexistence and criticality in the finite-size geometry. In fact this was the original motivation of BLF who set out to test the MF prediction for the phase diagram first studied by Parry and Evans [51, 52]. To understand the relevance of the simulations to the fluctuation theory presented in the last section we briefly recall the MF analysis, emphasizing the role of interfacial fluctuations in the high-temperature phase.

Consider a parallel-plate geometry of infinite area and width D. We suppose that the spins in the planes $z = 0$ and $z = D$ are subject to surface fields h_1 and $-h_1$, respectively. The Landau theory expression for the free energy is taken to be

$$F[m(\boldsymbol{r})] = \int \mathrm{d}\boldsymbol{y} \int \mathrm{d}z \left[\frac{1}{2}(\boldsymbol{\nabla} m)^2 + \phi(m) + \left(\frac{cm^2}{2} - mh_1 \right) \delta(z) + \left(\frac{cm^2}{2} + mh_1 \right) \delta(z - D) \right] \tag{3.1}$$

and is minimized to find the equilibrium magnetization. We suppose that each semi-infinite surface is critically wetted by the appropriate bulk phase at a temperature T_w. We also impose an Ising symmetry so that $m_\beta = -m_\alpha$. Owing to the competitive nature of the surface fields the walls at $z = 0$ and $z = D$ preferentially adsorb a different phase leading to frustration effects in the finite-size geometry. A section of the phase diagram (in zero bulk field) is shown in figure 3. For temperatures less than a finite-size critical value, two distinct phases coexist in the system. These correspond to having thin wetting films of α-phase and β-phase at the left-hand side and right-hand side walls, respectively (see inset). As the temperature is increased, the difference between the total magnetization (per unit area) of the two phases diminishes (because the wetting films grow at each wall) and vanishes at $T_c(D)$. The MF analysis predicts that the critical temperature is shifted (owing to finite-size effects) below T_w:

$$T_w - T_c(D) \sim \exp(-\kappa D/2) \tag{3.2}$$

where scaling arguments suggest that the right-hand side is to be interpreted as $D^{-1/\beta s}$. The second-order phase transition occurring at $T_c(D)$ and $h = 0$ is predicted to belong to the $(d - 1)$-dimensional bulk Ising universality class. The intriguing feature here is that in the limit $D \to \infty$ the critical point of the finite-size system does not tend to bulk T_c. Whilst this scenario was initially queried [53], subsequent analyses [54] have confirmed this as the correct interpretation. Crucial to a full understanding of these rather dramatic finite-size effects is the nature of the fluctuations in the temperature window $T_c > T > T_w$. This is the regime where bulk phase coexistence has been completely suppressed and the magnetization profile resembles an α–β interface located at the centre of the system. Within MF theory, calculation of the midpoint susceptibility shows that the transverse correlation length is exponentially large [52], i.e.

$$\xi_\parallel \sim \exp(\kappa D/4) \tag{3.3}$$

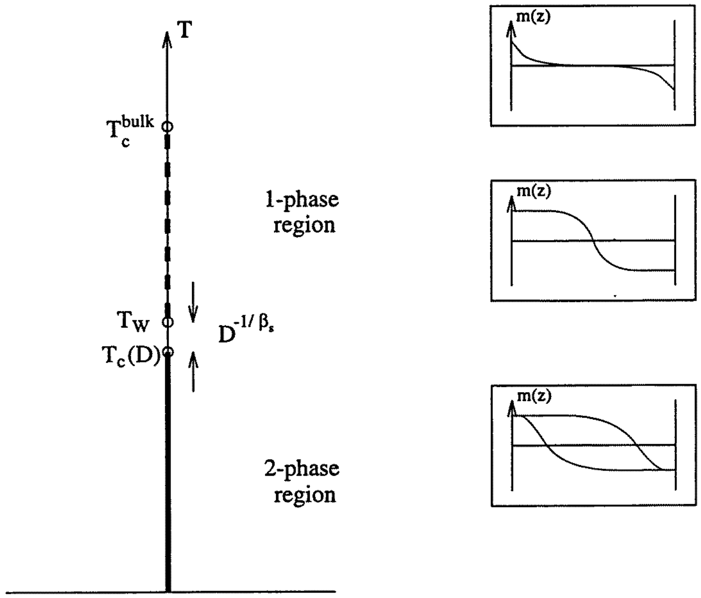

Figure 3. Schematic diagram showing typical phases in a parallel-plate geometry with competing surface fields as a function of temperature. Each semi-infinite surface shows a critical wetting transition at T_w.

and diverges as $D \to \infty$. One may understand the MF result using a simple binding potential $W(l; D)$ appropriate for an interface confined between two walls

$$W(l; D) = -\tau\{\exp(-\kappa\tau) + \exp[-\kappa(D-l)]\} + b\{\exp(-2\kappa l) + \exp[-2\kappa(D-l)]\} \qquad (3.4)$$

from which one can easily rederive (3.2) and (3.3).

With these MF ideas in mind, BLF studied thin Ising films of width D ranging from 6 to 28 (lattice spacings) and large transverse area L^2 where L may be as large as 256. The surface fields are chosen such that $T_w \approx 0.9T_c$ (much higher than T_R). BLF then seek answers to the following questions.

(a) Are the qualitative features of the MF phase diagram correct?
(b) Is there evidence of an exponentially large correlation length in the one-phase region?
(c) Is the transition at $T_c(D)$ in the two-dimensional bulk Ising universality class?

The answer to the first question is certainly yes and of significance is the observation that the values of $T_c(D)$ for the D studied all lie below T_w. If $T_c(D)$ was observed to be greater than T_w (for sufficiently large D), this would be indicative that the wetting transition was very weakly first order but there appears to be no indication of this in the new simulations.

From measurements of the local susceptibilities $\chi_n \equiv \partial m_n/\partial h$ and $\chi_{nn} \equiv \partial m_n/\partial h_n$ [60] (where n is the layer number), BLF show that there is clear evidence for an exponentially large correlation length for $T_c > T > T_w$. Indeed BLF are able to extract a length scale κ_{eff}^{-1} defined by

$$\kappa_{eff} = 2 \lim_{D\to\infty} \left(\frac{\ln(\max \chi_{nn})}{D} \right) \qquad (3.5)$$

which, according to the MF prediction, should be equal to the bulk correlation length κ^{-1}. Here $\max \chi_{nn}$ is the maximum value of χ_{nn} measured as a function of n. Note that the maximum occurs in the middle of the system (as expected) so that the data used are taken from measurements local to the α–β interface (in contrast with the earlier simulation studies). BLF observed that the measured values of κ_{eff}^{-1} are considerably larger than the Ising model bulk correlation length κ^{-1} and speculated that this has implications for theories of wetting. In fact, as pointed out by Boulter and Parry [42, 44] this observation is consistent with interfacial fluctuation effects described by the two-field model. They show that beyond MF the prediction (3.3) should be replaced by

$$\xi_{\parallel} \sim \exp(\kappa D/4\theta) \tag{3.6}$$

where θ is the complete wetting critical amplitude discussed earlier. This has been further developed by Parry *et al* [47] who plot the measured values of θ versus T obtained using the trivial relation $\theta = \kappa/\kappa_{eff}$ and is shown in figure 4. Recall that the CW prediction (assuming that $\omega \approx 0.8$) $\theta_{\rm CW} \approx 1.4$ and compares badly with the data. However, the predictions of the two-field theory appear to describe the measurements rather well. The value of θ is certainly greater than 1.4 for $T > T_w$ and is consistent with the rough estimate [42] $\theta \approx 1.8$ for $T \gg T_w$. Parry *et al* [47] pointed out that the extrapolated value of θ for $T \to T_w^+$ allows one to extract a value $\omega(T = T_w) \approx 0.84$. This is in very good agreement with the series expansion prediction [11] at this temperature.

Finally we comment on the final question concerning the nature of the phase transition occurring at $T_c(D)$ which BLF were not able to answer in their original study. The difficulty here is that the size of the true asymptotic critical regime is extremely small. However, in a subsequent reanalysis of their original data, Binder *et al* [57] show that both the susceptibility and the cumulant ratio exhibit crossover finite-size scaling behaviour at $T_c(D)$ which manifests the required universality. The scaling analysis is rather subtle since it has to account for the presence of several different length scales associated with the fusion of different critical singularities in the finite-size system. In particular the data collapse onto universal curves is achieved only if the value of the effective length scale κ_{eff} is chosen to coincide with the theoretical prediction incorporating the correct θ dependence. This is perhaps the most convincing evidence yet that the nature of interfacial fluctuations in the three-dimensional Ising model are understandable using effective Hamiltonian ideas.

4. Conclusions

In the introduction we stated two problems faced by the CW theory of wetting and have argued that they are both related to the inability of the CW model to account for coupling of order-parameter fluctuations at the α–β interface and wall. Problem 2 concerning the structure of MF correlation functions at the complete wetting transition is certainly understandable using the generalized effective Hamiltonian theory which provides an alternative method of calculating correlation functions complementing standard methods [7, 9]. This approach leads to some new relations and in particular the stiffness-matrix–free-energy relation which is central to the thermodynamic consistency of the method.

The FJ model and the coupled Hamiltonians lead to new predictions for fluctuation effects at wetting transitions for three-dimensional systems with short-ranged forces. The most important of these are as follows.

(a) The bare (MF) critical wetting transition may be driven first order for sufficiently small values of ω. Whilst this alone is not enough to explain problem 1, it may be that transition in the Ising model is very weakly first order. Further simulations have been suggested that might resolve this issue [61].

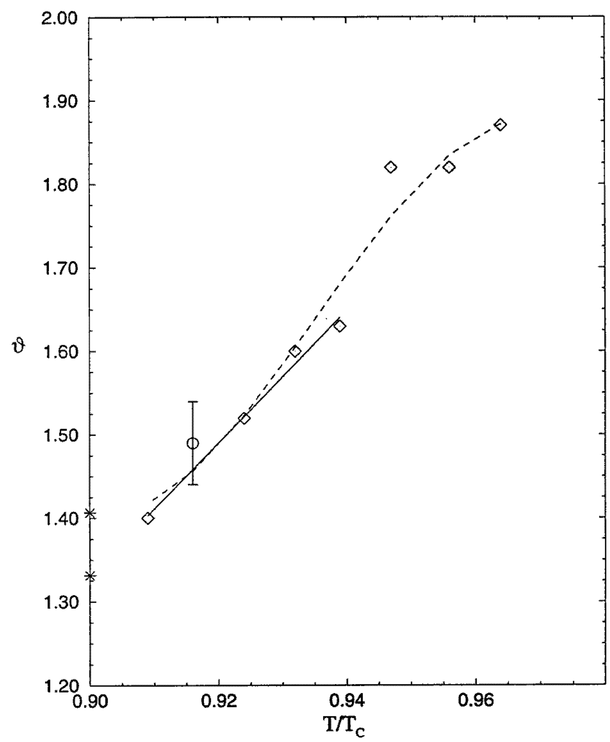

Figure 4. Plot of the critical amplitude ratio θ as extracted from the data of BLF. The value of θ is larger than the CW prediction $\theta_{\rm CW}$ but extrapolates to it as $T \to T_w^+$ consistent with the predictions of the coupled theory. Cubic and linear fits to the data are shown as broken and solid curves respectively together with their points of extrapolation. (Diagram taken from Parry *et al* [47].)

(b) The value of the critical amplitude θ at complete wetting is greater than the CW and FJ predictions. This appears to be in good agreement with the simulation studies of Binder *et al* [55, 56].

(c) The values of $\theta \to 1 + \omega/2$ as $T \to T_w^+$ yielding $\omega \approx 0.8$, in excellent agreement with long-standing expectations.

(d) Because of the coupling, the true critical region for the local susceptibility χ_1 at critical wetting is very small. This would seem to provide a quantitative explanation of problem 1.

(e) For critical and complete wetting transitions occurring close to the bulk critical temperature T_c the critical properties are predicted [50] to depend on two universal amplitude ratios ω_c and Ω_c. Thus whilst ω_c controls the correlation length critical exponent $\nu_\parallel$ for critical wetting, both ω_c and Ω_c determine the size of the critical region. Similarly ω_c and Ω_c enter into the expression for the renormalized wetting parameter $\overline{\omega}$ at complete wetting. The role of the second amplitude Ω_c does not emerge in the CW (and FJ) models and only appears in coupled theories if the fluctuations at the wall are treated in a careful manner beyond that of the two-field model $H_2[l_1, l_2]$.

Having said this, much of what has been achieved (with some effort) is still largely supportive of the CW picture. Thus the original critical wetting predictions of Brezin *et al* [13] and Lipowsky *et al* [14] concerning the dramatic renormalization of the correlation length exponent still stand for sufficiently large values of ω which may well be appropriate to the Ising model. In the light of the predictions of the coupled theory, however, any future simulation studies aimed at observing this criticality should make sure that their measurements of response functions, etc, are made as local to the α–β interface as possible if they are to avoid the problems of the earlier simulations.

The new effective Hamiltonian that have been put forward may all be regarded as small amendments to the CW theory which only lead to new critical properties at the upper critical dimension. Nevertheless, because the upper critical dimension for critical and complete wetting transitions in systems with short-ranged forces is the physical dimensionality of space, this is an important case. Moreover, despite the fact that at an experimental level it seems difficult to avoid the effect of long-ranged dispersion forces for traditional solid–liquid and liquid–liquid interfaces, the same is probably not true of wetting in metallic, superconducting [62] and polymer systems which may well have effective short-ranged forces. Indeed recent experiments involving adsorbed polymer blends have already made encouraging contact with some of the theoretical predictions of the last section [63]. Hopefully future simulation and experimental studies will be able to test them in more detail.

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