

Lecture notes
on
Wetting, Filling and Wedge Covariance

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Abstract

A large volume of work has been done in the past three decades on *wetting* transitions with considerable success. Nevertheless some problems remain unsolved, e.g., the discrepancy between theory and simulations of 3D critical wetting with short-range forces. The study of the related, but not similar, phenomena of *filling* on a wedge geometry has uncovered remarkable connections between the two transitions, named *wedge covariance*. In the framework of filling and exploiting wedge covariance it is possible to shed light on some unsolved problems on wetting. Most notably, the careful reevaluation of the method to construct an interfacial model, prompted by these studies, seems to lead, finally, to the solution of the 3D critical wetting problem.

We'll start with a short overview of bulk critical phenomena and proceed to the study of the Landau theory of interfaces (also referred to as square-gradient theory). The formulation of the interfacial model will show us that capillary waves cause the interface to be rough in $d \leq 3$ dimensions. We'll then move on to study the phenomenology of wetting and formulate a Landau theory of this phase transition. After this, we study the effects of fluctuations in 2D and look carefully at the unsolved problem of 3D critical wetting. Next we turn our attention to the phenomena of filling, showing that there is a hidden symmetry between this and wetting. Finally, we end with a short tour on the *non-local model*, that seems to hold the key to the solution of many problems in interfacial critical phenomena.

Contents

1	Introduction	2
2	Summary of Bulk Critical Phenomena	3
3	Landau Theory of Interfaces	6
4	Interfacial Model	8
5	Phenomenology of Wetting Transitions	11
6	Landau Theory of Wetting	13
7	2D Critical Wetting With Short-Range Forces	15
8	3D Critical Wetting With Short-Range Forces	18
9	Filling Transitions	21
10	2D Critical Filling	24
11	3D Critical Filling	26
12	The Non-Local Model	27
13	Future Work	28
A	Solution of the Functional Equation in the LGW Model	29
B	“Derivation” of the Interfacial Model	29

1 Introduction

The focus of our work is *wetting*, so a sensible point to start is the definition of what we mean by wetting. As often happens in science, a word taken from everyday experience is used to describe a phenomena and, with time, the meaning in a technical context is different, but related, to the meaning in common usage. Words like energy and force are clear illustrations.

When we think of wetting we think of water, or any other liquid, in contact with a solid (e.g. a dish or a piece of cloth). In our work this is one of the models we'll always keep in our minds: a solid, inert, substrate covered with a film of liquid in equilibrium with its vapour. The word, however, came to have a more general meaning, describing phenomena where there is no liquid present. For us wetting will occur whenever a phase, C, intrudes between phases A and B, with A, B, and C in coexistence.

As we see our definition encompasses a wide variety of phenomena, all described by the same formalism. As is so typical of theoretical statistical mechanics, we study wetting in the simplest possible model, either the Ising model or continuous models of ferromagnets. Our system will be a magnet in contact with a wall that favours, say, positive magnetisation and placed in an infinitesimally small field that favours negative magnetisation in the bulk. We expect that a film of positive magnetisation forms between the wall and the bulk phase. Simple as the model may be, we shall see that its behaviour is far from trivial and theory is still inadequate to describe simulations.

Looking at a glass of water it is clear that, away from the *interface* with air, water will behave as it does without the surface, or, in the bulk. Since the most interesting things happen in the surface of the water (like light refraction), where the properties of the medium change rapidly, it is natural to build a physical model that focus on this region. This is the *interfacial model*. We shall think of the system as composed of just a thin interface, that behaves like a stretched membrane, ignoring the bulk properties from the outset. This simplifies the analysis of wetting by orders of magnitude. However, as we'll see, a careful derivation of the interfacial model from the full model must be done as a naive approach leads to subtle errors in the description of the interface.

When we have a system as described before, the film of phase C can either be thin (microscopic) or thick (macroscopic). In fact, when we mention wetting in this work, most of the time, we are actually referring to the phase transition that may happen in some systems. If for some region of the phase space the film is thin, and in another the film is thick, we have surface phase transition - a wetting transition. A natural framework to describe wetting is as an *interfacial phase transition*. This fact, by itself, justifies its study because, as we'll see, the extension of statistical mechanics and Renormalization Group Theory to interfacial phenomena brings to light subtle, but important, physical effects and allows one to sharpen the theories themselves.

It is now clear what is the "scientific path" we must walk. In the next chapter we quickly skim over bulk critical phenomena, with a slight emphasis on some facts relevant for interfacial phase transitions. We refrain, however, from reviewing much of the background material, apart from pointing to some references. Descending in scope, we shall skip the Meaning of Life, the Universe and Everything (Adams, 1979), Thermodynamics (Callen, 1985), general Statistical Physics (Huang, 1987), Statistical Physics of Liquids (Hansen & McDonald, 1990) and much of Physics and Statistical Mechanics of Interfaces (Rowlinson & Widom, 1982; Evans, 1990). We shall also not go into the details of simulation methods (Landau & Binder, 2005).

2 Summary of Bulk Critical Phenomena

A good starting point for a (really) short review of *critical phenomena* (Yeomans, 1992; Stanley, 1987; Goldenfeld, 1992) is the phase diagram of a simple substance like the one depicted in figure 1. The lines in the PT diagram represent the locus of points where we have coexistence of phases, in this case lines of first-order phase transitions. The liquid-vapour line ends at a *critical point* beyond which there is no distinction between these two phases. A similar phenomenon occurs in the Ising model of ferromagnetism with short range (SR) forces for $d \geq 2$ (figure 2). For external magnetic field $H = 0$ and $T < T_C$ the model displays *spontaneous* magnetisation, whereas for $T > T_C$ it behaves like a paramagnet. In both these systems there is a parameter, the *order parameter*, that is zero on one side of the critical point and non-zero on the other side. For the liquid-vapour system the order parameter is the difference of density between the two phases. For the Ising model the order parameter is the magnetisation.

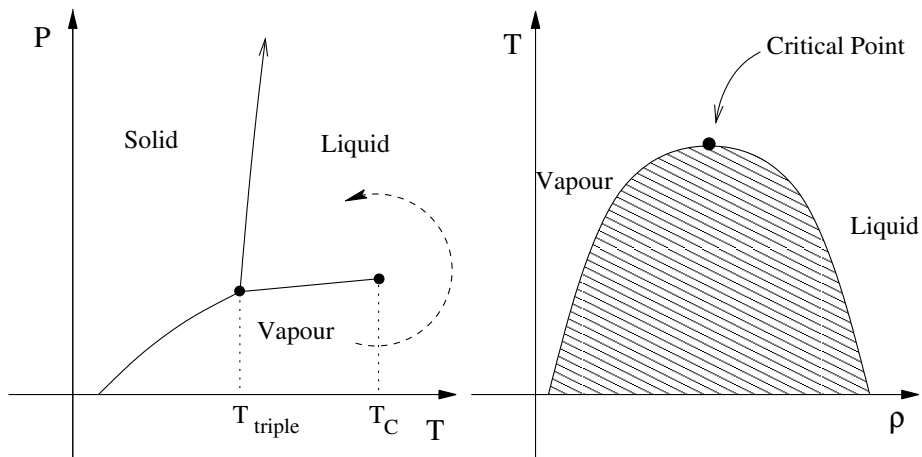


Figure 1: Generic phase diagram of a simple substance. We see the *triple* point where we have three phase coexistence and the *critical* point where the densities of the liquid and vapour become equal and thus there is only a unique fluid phase for $T > T_C$. We can trace a thermodynamic path between vapour and liquid without going through a phase transition.

The physics near the critical point is characterised by a set of *critical exponents* which quantify the singularities of the free-energy. To settle the notation we shall use magnetic systems language and define the reduced temperature

$$t \equiv \frac{T_C - T}{T_C} \quad (1)$$

We suppose that close to the critical point any thermodynamic quantity can be decomposed into a regular part (which can be discontinuous) and a singular part (which may diverge or have divergent derivatives). We define the critical exponents by the asymp-

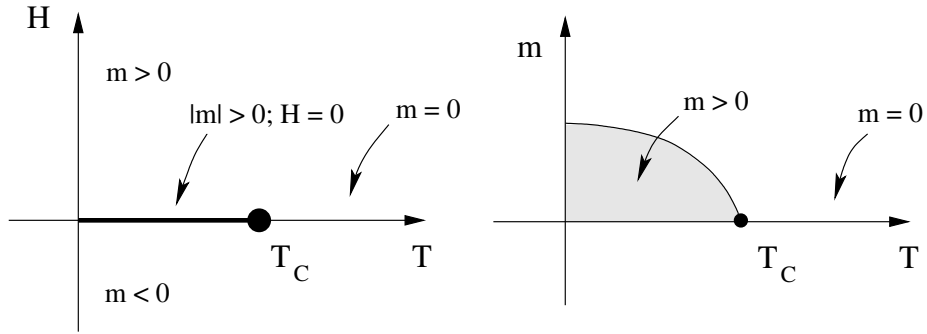


Figure 2: Phase diagram of the Ising model with SR forces. For $d \geq 2$ the model displays spontaneous magnetisation if $T < T_C$.

otic behaviour of the singular part::

$$\text{Specific Heat: } C_N \equiv -\frac{T}{N} \frac{\partial^2 F}{\partial T^2} \sim |t|^{-\alpha} \quad (2)$$

$$\text{Magnetisation: } m \sim t^\beta \quad (3)$$

$$\text{Magnetisation } (t = 0): m \sim |H|^{1/\delta} \quad (4)$$

$$\text{Susceptibility: } \chi \equiv k_B T \frac{\partial m}{\partial H} \sim |t|^{-\gamma} \quad (5)$$

$$\text{Correlation Length: } \xi \sim |t|^{-\nu} \quad (6)$$

$$\text{Correlation Function: } G(r) \sim \frac{1}{r^{d-2+\eta}} \quad (7)$$

Here \sim means “has a singular part proportional to”. All the definitions, except δ and η , are for $t \rightarrow 0$. The definition of δ implies $t = 0$ and $H \rightarrow 0$, and that of η implies $t = 0$. Finally the definition of η and ν comes from the behaviour of the correlation function:

$$G(r) \equiv \langle m(0)m(r) \rangle \sim r^{-(d-2+\eta)} e^{-r/\xi} \quad (8)$$

The Van der Waals theory of gases and the Weiss theory of ferromagnets were the first theories with a critical point. Both resulted in the same set of (wrong) critical exponents. Landau’s theory of critical phenomena provided a more general view on the subject and allowed the inclusion of small fluctuations, an extension known as Ornstein-Zernike (OZ) theory, but the exponents are the same as in previous theories. This is due to the fact that all these are mean-field (MF) theories which ignore or underestimate the fluctuations that turn out to dominate the behaviour near the critical point. Table 1 lists the values of the critical exponents for the Ising model. They are also the same for a wide variety of fluids and ferromagnets.

Dimension	β	α	γ	δ	ν	η
2	1/8	0 (ln)	7/4	15	1	1/4
3	0.315...	0.11...	1.24...	4.81...	0.63...	0.04...
≥ 4 (MF)	1/2	0 (disc)	1	3	1/2	0

Table 1: Values of some critical exponents.

Further insight into critical behaviour was provided by studies of the Ising model. In $d = 1$ *transfer matrix* techniques can be used to solve the model exactly and there is no critical point at finite temperature. The behaviour of the model for $T \rightarrow 0$ has some peculiarities, though. In 2D, Lars Onsager famously solved the Ising model with $H = 0$ and found non-classical exponents. Yet other valuable techniques are high and low temperature series expansions of the partition function and computer simulations which provide approximate, but reliable, values of the exponents, again showing non-classical values .

Only with Wilson's *Renormalization Group* (RG) theory was a true understanding of what happens near the critical point achieved. A first important result of RG is the fact that the exponents are the same irrespective of the side from which we approach the critical point (we anticipated this in the definitions of the critical exponents). Another important result is the fact that the critical exponents are largely insensitive to the details of the models and depend only on the dimensionality of the system, the nature of the order parameter (scalar, vector, etc) and the range of the interactions. When some systems share these proprieties we expect them to exhibit the same critical behaviour, i.e. same critical exponents, and say that they are on the same *universality class*. From the table of critical exponents we see that for $d \geq 4$ the MF exponents are correct. This is a general feature and we call *upper critical dimension*, d^* , to the lowest dimension at which MF behaviour is correct.

Only two of the critical exponents are independent as they obey a set of relations, known as *scaling relations*:

$$\text{Fisher:} \quad \gamma = \nu(2 - \eta) \quad (9)$$

$$\text{Rushbrooke:} \quad \alpha + 2\beta + \gamma = 2 \quad (10)$$

$$\text{Widom:} \quad \gamma = \beta(\delta - 1) \quad (11)$$

$$\text{Josephson or Hyperscaling} \quad 2 - \alpha = d\nu \quad (12)$$

Hyperscaling is only valid for $d < d^*$. A common strategy to find d^* is to do MF theory, calculate the critical exponents and replace their values in the hyperscaling relation to determine d^* . For SR forces we expect MF critical exponents to be correct above d^* but that the fluctuations dominate the behaviour for $d < d^*$. For $d = d^*$ the behaviour is more subtle and not known a priori as expressed in figure 3. A common scenario is the existence of logarithmic corrections to the behaviour of the singularities.

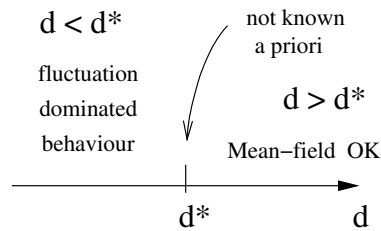


Figure 3: The dependence of the values of the critical exponents with the dimension of the system. Valid for systems with SR forces.

It is often stated that in 1D there is no phase transition. With long-range (LR) forces this picture is changed. As an example, for the Ising model in $d = 1$ and LR forces ($\sim \frac{1}{r^p}$), we have:

- $p > 2$ - Qualifies as SR. No phase transitions.
- $p = 2$ - We have a phase transition. *Non-universality*: critical exponents depend on temperature.

- $1 < p < 2$ - There is a phase transition. Some exponents have MF values, others don't.
- $p < 1$ - MF theory is correct. Qualifies as infinite range force model.

Other common statement is that MF theories are correct far from the critical point. This is true for most situations but not always. As an example, OZ theory gives for the decay of the correlation function

$$G(r) \sim \frac{e^{-r/\xi}}{r^{(d-1)/2}} \quad (13)$$

But for the Ising model in $d = 2$, $H = 0$, $T < T_C$ we have

$$G(r) \sim \frac{e^{-r/\xi}}{r^2} \quad (14)$$

This phenomena is known as the Kadanoff-Wu anomaly and turns out to be related to interfacial phenomena. Later we'll formulate a MF description of an interface and see that, here too, fluctuations play a fundamental role, even far from the critical point.

3 Landau Theory of Interfaces

As stated in the introduction, the full 3D LGW model is too complex to yield to analytical methods so we resort to a mesoscopic description of the system by focusing on the properties of the interface using the so called "*interfacial model*". Before we turn our attention to wetting transitions using the interfacial model, we first study what is the shape of an interface in LGW theory.

Let us, then, build a mean-field theory for a free interface. We study a 3D magnetic system with $m = \pm m_0$ at $z = \mp \infty$ described by a Landau-Ginzburg-Wilson (LGW) functional

$$H_{\text{LGW}}[m] = \int d\mathbf{r} \left[\frac{1}{2} (\nabla m)^2 + \phi(m) \right] \quad (15)$$

the gradient term accounts for SR forces that tend to homogenise the system and $\phi(m)$ describes how the Hamiltonian depends on the local value of the magnetisation. We'll not always write the \mathbf{r} dependence of m but keep it in mind. The partition function is given by

$$Z = \int D_m e^{-H_{\text{LGW}}/k_B T} \quad (16)$$

where D_m is the measure of the integral and stands for integration over all profiles consistent with the boundary conditions. In MF theory we neglect fluctuations and consider just the most likely profile, given by the minimum of the Hamiltonian. Thus

$$Z \simeq e^{-\min H/k_B T} \Rightarrow F^{\text{MF}} = \min H[m] \quad (17)$$

Since by symmetry the solution is translationally invariant in x and y we can integrate immediately on these coordinates (obtaining the area A) and write the equation with m now dependent only on z

$$\frac{H}{A} = \int_{-\infty}^{+\infty} dz \left[\frac{1}{2} m'(z)^2 + \phi(m) \right] \quad (18)$$

In figure 4 we see a sketch of the shape of $m(z)$ as well as the typical double-well shape of $\phi(m)$. We assume that we can expand ϕ and conserve only the lowest terms in the expansion consistent with the symmetry of the Hamiltonian:

$$\phi(m) = -\frac{t}{2}m^2 + \frac{u}{4}m^4 \quad t \propto T_C^{\text{MF}} - T ; u > 0 \quad (19)$$

Recall from the Landau theory of bulk critical phenomena that we have

$$\phi'(\pm m_0) = 0 \Rightarrow m_0 = \sqrt{\frac{t}{u}} \quad ; \quad \xi = \frac{1}{\sqrt{\phi''(m_0)}} = \frac{1}{\sqrt{2t}}$$

and define

$$\Delta\phi = \phi - \phi(m_0) = \frac{k^2}{8m_0^2} (m^2 - m_0^2)^2 \quad ; \quad k = \frac{1}{\xi}$$

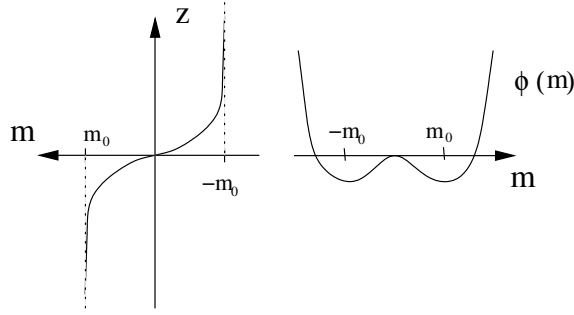


Figure 4: Magnetisation profile with z and shape of $\phi(m)$

Using the definition of functional derivative and with some manipulation (see appendix A) we reduce the functional equations 17 and 18 to a differential equation

$$m'' = \phi'(m) \quad (20)$$

which we can solve

$$m'm'' = m'\phi'(m) \quad (21)$$

$$\Leftrightarrow \frac{1}{2} \frac{d}{dz} m'^2 = \frac{d}{dz} \phi(m) \quad (22)$$

Integrating once

$$\Leftrightarrow \frac{1}{2} m'(z)^2 = \phi(m) + C \quad (23)$$

and with the boundary conditions at $z \rightarrow \infty$ we have $C = -\phi(m_0)$, thus

$$\frac{1}{2} m'(z)^2 = \Delta\phi(m) \quad (24)$$

$$m'(z) = \pm \frac{k}{2m_0} (m^2 - m_0^2) \quad (25)$$

and, integrating one last time

$$m = m_0 \tanh \frac{k}{2} (l - z) \quad (26)$$

with l arbitrary. This is the famous *hyperbolic tangent* profile. We can see that most of the change from $-m_0$ to m_0 occurs in a region of width 2ξ around l and that the profile decays exponentially.

Replacing this result back into $H[m]$ we get

$$\frac{F^{\text{MF}}}{A} = H[m(z)] = \int_{-\infty}^{+\infty} dz \left[\frac{1}{2}m'^2 + \phi(m) \right] \quad (27)$$

$$= \int_{-\infty}^{+\infty} dz \phi(m_0) + \int_{-\infty}^{+\infty} dz \left[\frac{1}{2}m'^2 + \Delta\phi(m) \right] \quad (28)$$

or, with an obvious rearrangement

$$F = \underbrace{V\phi(m_0)}_{\text{bulk free-energy}} + A \underbrace{\int_{-\infty}^{+\infty} dz \left[\frac{1}{2}m'^2 + \Delta\phi(m) \right]}_{\text{surface tension } \sigma \text{ (by definition)}} \quad (29)$$

From equation 24

$$\sigma = \int_{-\infty}^{+\infty} dz m'(z)^2 \quad (30)$$

$$= \left| \int_{-m_0}^{m_0} dm \frac{dm}{dz} \right| \quad (31)$$

$$= \int_{-m_0}^{m_0} dm \sqrt{2\Delta\phi(m)} \quad (32)$$

$$= 2 \int_0^{m_0} dm \frac{k}{2m_0} (m_0^2 - m^2) \quad (33)$$

$$= \frac{2}{3} km_0^2 \quad (34)$$

$$\propto (T_C^{\text{MF}} - T)^{3/2} \quad (35)$$

Thus we have

$$\sigma \sim t^{\tilde{\mu}} \quad \text{with} \quad \tilde{\mu}_{\text{MF}} = 2\beta + \nu = \frac{3}{2} \quad (36)$$

From dimensional analysis we expect

$$\sigma \sim \frac{F}{V} \xi \quad (37)$$

and so

$$\tilde{\mu} = 2 - \alpha - \nu \quad (38)$$

The calculation of the surface tension is OK except, unsurprisingly, near T_C where $\sigma \sim t^{1.26}$, however the square gradient theory resulting in the hyperbolic tangent profile for the interface is flawed. This is so because, as we'll see later, long-wavelength (capillary-wave-like) fluctuations cause the interface to be rough in $d \leq 3$.

4 Interfacial Model

As stated before we base our analysis of wetting on a mesoscopic model of an interface. The full LGW model has more detail than what we can or need to account for. Since

the wetting transition occurs (if it happens at all) for a temperature below the critical point, the bulk fluctuations are finite and important only up to a length of ξ . If we integrate out these bulk fluctuations we get two uniform phases separated by a smooth interface. We carry out this scheme in detail later in sections 8 and 12. In the present section we just assume that the interface is smooth enough, without wild fluctuations or overhangs. Even if at a microscopic scale this is not true, we can imagine we “zoom out” up to a point where all the bulk fluctuations are so small, as to be invisible, and that the interface looks like a smooth membrane whose position at $\mathbf{x} = (x, y)$ is given by $l(\mathbf{x})$. Further assuming that we can describe the shape of the interface at each point as an hyperbolic tangent:

$$m(z, \mathbf{x}) = m_0 \tanh \frac{k(z - l(\mathbf{x}))}{2} \quad \text{with} \quad |\nabla l| \ll 1 \quad (39)$$

substituting this into the LGW model and using the above assumptions we get, after some algebra (see appendix B)

$$H_{\text{LGW}}[l(\mathbf{x})] = \phi(m_0)V + L^{d-1}\sigma + \frac{\sigma}{2} \int (\nabla l)^2 d\mathbf{x} + \dots \quad (40)$$

We could have easily anticipated this result if we think of an interface as a stretched membrane with a tension σ . If the membrane is distorted from $A \rightarrow A + \delta A$, this distortion has an energy of $\sigma\delta A$. By the definition of area we have

$$A = \int d\mathbf{x} \sqrt{1 + (\nabla l)^2} \quad (41)$$

$$= \int d\mathbf{x} + \frac{1}{2} \int d\mathbf{x} (\nabla l)^2 + \dots \quad (42)$$

$$= L^{d-1} + \frac{1}{2} \int d\mathbf{x} (\nabla l)^2 + \dots \quad (43)$$

Thus the energy cost of an undulation, ignoring higher order terms, is $\frac{\sigma}{2} \int d\mathbf{x} (\nabla l)^2$, as we have in equation 40.

The partition function is given by

$$Z = \int D_m e^{-H_{\text{LGW}}[m]} \simeq \underbrace{e^{-V\phi - \sigma L^{d-1}}}_{\text{constant}} \int D_l e^{-H_I[l]} \quad (44)$$

and now this is a straightforward calculation because

$$H_I = \frac{1}{2} \int (\nabla l)^2 d\mathbf{x} \quad (45)$$

is gaussian.

To calculate the height correlations between two points on the interface define as usual

$$S(\mathbf{x}, \mathbf{x}') \equiv \langle l(\mathbf{x})l(\mathbf{x}') \rangle - \langle l(\mathbf{x}) \rangle \langle l(\mathbf{x}') \rangle \sim \frac{1}{|\mathbf{x} - \mathbf{x}'|^{d-3}} g(|\mathbf{x} - \mathbf{x}'|/\xi_{\parallel}) \quad (46)$$

with $g(x)$ a scaling function. We also define the roughness exponent

$$\xi_{\perp}^2 = \langle l(\mathbf{x})^2 \rangle - \langle l(\mathbf{x}) \rangle^2 \quad (47)$$

we can set $\langle l(\mathbf{x}) \rangle = 0$ without loss of generality. Going to Fourier space

$$H_I = \frac{\sigma}{2} \sum_{\mathbf{k}} |\tilde{l}(\mathbf{k})|^2 k^2 \quad \frac{2\pi}{L} \leq |\mathbf{k}| \leq \frac{2\pi}{\Lambda} \quad (48)$$

where Λ stands for a short wavelength cut-off, like the lattice spacing, the atomic separation or in the case of the interfacial model ξ . Using the equipartition theorem

$$\langle |\tilde{l}(\mathbf{k})|^2 \rangle = \frac{k_B T}{\sigma k^2} \quad (49)$$

We see that a $k = 0$ mode costs no energy, i.e. it is a Goldstone mode. From this observation we expect that long wavelength capillary waves to have an important contribution to the physics of the interfacial model. Now

$$\xi_{\perp}^2 \propto \int \frac{d\mathbf{k}}{\sigma k^2} \propto \int_{\frac{2\pi}{L}}^{\frac{2\pi}{\xi_b}} dk \frac{k^{d-2}}{k^2} \quad (50)$$

and integrating we have

$$\xi_{\perp} = \begin{cases} L^{(3-d)/2} & d < 3 \\ \left(\frac{k_B T}{2\pi\sigma} \ln \frac{L}{\xi_b} \right)^{1/2} & d = 3 \\ \text{finite as } L \rightarrow \infty & d > 3 \end{cases} \quad (51)$$

Notice that ξ_{\perp} diverges for $d \leq 3$ and so the interface is rough for the relevant physical systems. We define a wandering exponent

$$\xi_{\perp} \sim \xi_{\parallel}^{\zeta} \quad (52)$$

and for fluctuations dominated by thermal disorder $\zeta = (3-d)/2$ for $d < 3$. In figure 5 we see the relevant length scales of the interface. ζ depends on the presence (or not) of impurity induced disorder. As an example with random bonds $\zeta(d=2) = 2/3$ and $\zeta(d=3) \simeq 0.43$. With random fields $\zeta(d) = (5-d)/3$. We'll see later that ζ also depends on the geometry.

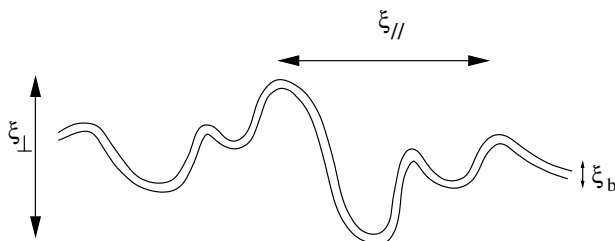


Figure 5: Interface with the definition of the relevant length scales.

The above considerations are for continuum fluid-like interfaces. For a system defined on a lattice the surface tension is angle-dependent. In $d = 3$ we have a roughening transition in the simple cubic Ising model at $T_R \simeq 0.54T_C$. For $T < T_R$ the interface is pinned between lattice spacings, as $T \rightarrow T_R^-$ the interface develops spikes and “skyscrapers”, depins from the lattice and behaves like a liquid. In $d = 2$ $T_R = 0$ so the interface is always rough. Duality tells us that roughening at T_R belongs to the universality class of the Kosterlitz-Thouless phase transition. For $T > T_R$ on a lattice

$$H_I = \frac{\Sigma}{2} \int (\nabla l)^2 d\mathbf{x} \quad (53)$$

where Σ is the stiffness defined as

$$\Sigma \equiv \sigma(0) + \sigma''(0) \quad (54)$$

we'll use Σ from now on as this is a more general definition than σ .

5 Phenomenology of Wetting Transitions

Think of a volume V of liquid at a temperature T and pressure P (or chemical potential μ) placed on a wall and in equilibrium with its vapour. Two things can happen, as described in figure 6. If the contact angle $\theta > 0$ we have a hemispherical cap and equating the forces acting on the point of contact of wall-liquid-gas, we get Young's equation

$$\sigma_{wg} = \sigma_{wl} + \sigma_{lg} \cos \theta \quad (55)$$

describing a partially wet surface. If the forces between the wall and liquid molecules are strong enough compared to the ones between liquid molecules we can have a completely wet surface, that is $\theta = 0$ and Antonow's equation is valid

$$\sigma_{wg} = \sigma_{wl} + \sigma_{lg} \quad (56)$$

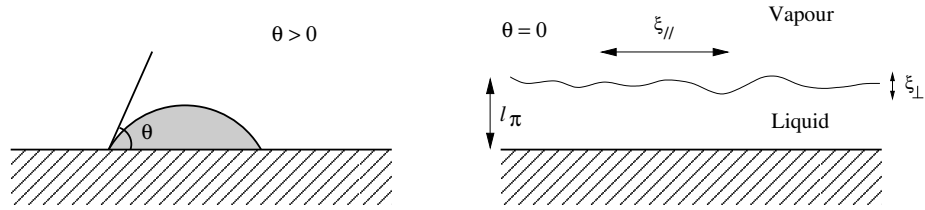


Figure 6: The possible situations when a liquid in equilibrium with its vapour is in contact with a surface. If $\theta > 0$ we have an hemispherical cap (surface partially wet). If $\theta = 0$ a macroscopic film of liquid forms and the liquid is said to wet the surface

We can have a phase transition at a temperature $T_w < T_C$ if θ vanishes as $T \rightarrow T_w$. Alternatively we can think of a film of liquid that forms between the wall and the vapour. If at a given T and P the film is microscopic then the wall is partially wet, if the film is macroscopic the wall is completely wet. The wetting transition was first explored theoretically by Cahn (1977) and by Ebner & Saam (1977). Much more detail than we give here is available in review articles by Schick (1990), Sullivan & Telo da Gama (1986), Dietrich (1988), and Forgacs *et al.* (1991).

If we approach the coexistence line from the vapour side and $T > T_w$ the amount of liquid adsorbed on the surface (Γ) will diverge as $\Delta\mu \equiv \mu - \mu_0 \rightarrow 0$ (μ_0 is the chemical potential at coexistence) and we call this phase transition *complete wetting*. If we approach T_w along the coexistence line from $T < T_w$ we can either have *first-order wetting* (figure 7) or *critical (continuous) wetting* (figure 8). The discontinuity in the free-energy at first order wetting is prolonged off-coexistence in a *pre-wetting* line and terminates at a $(d - 1)$ Ising universality class critical point.

As is usual we characterise the phase transition by a set of critical exponents. Define

$$t \equiv \frac{T_w - T}{T_w} \quad (57)$$

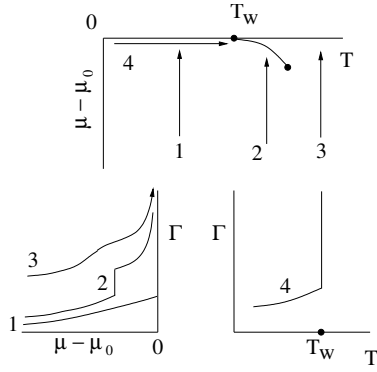


Figure 7: Phase diagram of a first-order wetting transition. Four thermodynamic paths are drawn and the film thickness of each one is depicted below. We can also see the pre-wetting line

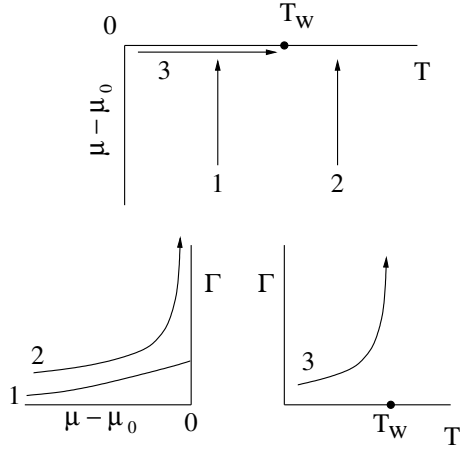


Figure 8: Phase diagram of a continuous wetting transition. Three thermodynamic paths are drawn and the corresponding film thickness is shown in the diagrams below.

for critical wetting

$$l_\pi \sim t^{-\beta_s} \quad (58)$$

$$\xi_\perp \sim t^{-\nu_\perp} \quad (59)$$

$$\xi_\parallel \sim t^{-\nu_\parallel} \quad (60)$$

and the excess surface free-energy

$$f_{\text{singular}} \equiv \sigma_{\text{wg}} - (\sigma_{\text{wl}} + \sigma_{\text{lg}}) \quad (61)$$

$$= \sigma_{\text{lg}} (\cos \theta - 1) \quad (62)$$

$$\simeq -\sigma_{\text{lg}} \frac{\theta^2}{2} \quad (63)$$

$$\sim t^{2-\alpha_s} \quad (64)$$

We can also define an exponent related to the singularity of the 3-phase line contact free-energy

$$\tau_{\text{singular}} \sim t^{2-\alpha_l} \quad (65)$$

We define also critical exponents for complete wetting

$$h \equiv \mu_0 - \mu \quad (66)$$

$$l_\pi \sim h^{-\beta_s^{\text{co}}} \quad (67)$$

$$\xi_\perp \sim h^{-\nu_\perp^{\text{co}}} \quad (68)$$

$$\xi_\parallel \sim h^{-\nu_\parallel^{\text{co}}} \quad (69)$$

$$f_{\text{singular}} \sim \sigma_{\text{wg}} - (\sigma_{\text{wl}} + \sigma_{\text{lg}}) = h^{2-\alpha_s^{\text{co}}} \quad (70)$$

As we have two scaling fields for critical wetting (one for complete wetting) we expect that only two critical exponents are independent (one for complete wetting), the others being obtained by scaling relations. In fact in critical wetting only one exponent is independent (zero for complete wetting) since the equivalent to η is zero. We have the following scaling relations

$$2 - \alpha_s = 2\nu_\parallel - 2\beta_s \quad (71)$$

$$2 - \alpha_s^{\text{co}} = 2\nu_\parallel^{\text{co}} - 2\beta_s^{\text{co}} \quad (72)$$

also valid for $d < d^*$ are the hyper-scaling relations

$$2 - \alpha_s = (d - 1)\nu_\parallel \quad (73)$$

$$2 - \alpha_s^{\text{co}} = (d - 1)\nu_\parallel^{\text{co}} \quad (74)$$

and conjectured, based on MF, by Indekeu & Robledo (1993)

$$\alpha_1 = \alpha_s + \nu_\parallel \quad (75)$$

6 Landau Theory of Wetting

We now focus on wetting with short-range forces. We study a magnetic system with a wall which favours up spins and $h = 0^-$ such that spins point down far from the substrate. We anticipate a profile qualitatively similar to the one in figure 4 but with the position of the interface determined by the boundary conditions. Our starting point (Nakanishi & Fisher, 1982; Sullivan & Telo da Gama, 1986) is the LGW Hamiltonian but with a surface term added

$$H_{\text{LGW}}[m] = \int d\mathbf{r} \left[\frac{1}{2}(\nabla m)^2 + \phi(m) \right] + \int d\mathbf{x} \phi_1(m_1) \quad (76)$$

where

$$m_1 \equiv m(z = 0, \mathbf{x}) \quad (77)$$

$$\phi_1 \equiv \frac{cm_1^2}{2} - m_1 h_1 \quad (78)$$

Assuming translational invariance along the \mathbf{x} direction

$$\frac{H}{A} = \int dz \left[\frac{1}{2}m'^2 + \phi(m) \right] + \phi_1(m_1) \quad (79)$$

we must now get the magnetisation profile that minimises the Hamiltonian:

$$\frac{\delta H/A}{\delta m} = 0 \quad (80)$$

Following a procedure similar to the one in appendix A and using the boundary conditions

$$m'' = \phi'(m) \quad (81)$$

$$m(\infty) = -m_0 \quad (82)$$

$$\left. \frac{dm}{dz} \right|_0 = \phi'_1(m_1) = cm_1 - h_1 \quad (83)$$

From 81 and 82

$$\frac{1}{2}m'^2 = \Delta\phi(m) = \phi(m) - \phi(m_0) \quad (84)$$

and so our solution satisfies

$$m'(z) = -\sqrt{2\Delta\phi(m)} \quad (85)$$

$$m'(0) = cm(0) - h_1 \quad (86)$$

which can be solved by graphical construction. The intercept of 85 with $Y = cm - h_1$ determines m_1 . The nature of the transition is determined by c and k . If $c < k$ the transition is first-order, if $c > k$ the transition is continuous. It is now clear that the solution is a section of a hyperbolic tangent profile

$$m(z) = m_0 \tanh \frac{k}{2}(l_\pi - z) \quad (87)$$

with l_π determined by boundary conditions. As we saw, critical wetting occurs for $Y = 0 \Rightarrow m_1 = h_1/c$, i.e.

$$cm_0(T_w) = h_1 \quad (88)$$

Expanding $m(z)$

$$m(z) = m_0 \frac{e^{\frac{k}{2}(l_\pi - z)} - e^{-\frac{k}{2}(l_\pi - z)}}{e^{\frac{k}{2}(l_\pi - z)} + e^{-\frac{k}{2}(l_\pi - z)}} \quad (89)$$

$$= m_0 \frac{1 - e^{-k(l_\pi - z)}}{1 + e^{-k(l_\pi - z)}} \quad (90)$$

$$= m_0 \left[1 - 2e^{-k(l_\pi - z)} + O(e^{-2k(l_\pi - z)}) \right] \quad (91)$$

so

$$m'(0) = -2km_0 e^{-kl_\pi} + \dots \quad (92)$$

$$= c \left(m_0 - 2m_0 e^{-kl_\pi} \right) - h_1 + \dots \quad (93)$$

and

$$2e^{-kl_\pi} m_0 (c - k) = cm_0(T) - h_1 \quad (94)$$

finally

$$kl_\pi \sim -\ln(cm_0(T) - h_1) \quad (95)$$

thus

$$\beta_s = 0 \quad (96)$$

Substitution of the solution for the shape of the interface into H/A allows us to calculate the excess free-energy defined by

$$\sigma_{w\downarrow} = \sigma_{w\uparrow} + \sigma_{\uparrow\downarrow} + f_{\text{sing}} \quad (97)$$

and

$$f_{\text{sing}} \propto (T_w - T)^2 \Rightarrow \alpha_s = 0 \quad (98)$$

with some more work we can calculate

$$\xi_{\parallel} \sim (T_w - T)^{-1} \Rightarrow v_{\parallel} = 1 \quad (99)$$

Notice that $2 - \alpha_s = 2(v_{\parallel} - \beta_s)$. Substitution of the previous result into

$$2 - \alpha_s = (d - 1)v_{\parallel} \quad (100)$$

gives us the upper critical dimension

$$d^* = \frac{2 - \alpha_s^{\text{MF}}}{v_{\parallel}^{\text{MF}}} + 1 = 3 \quad (101)$$

7 2D Critical Wetting With Short-Range Forces

The problem of 2D critical wetting with short range forces is well understood. Abraham (1980) solved the Ising model exactly and Fisher (1984, 1986, 2004) provided some heuristic arguments based on random-walks. Here we solve the interfacial model using transfer matrices. We begin with the interfacial Hamiltonian

$$H_{\pi}[l] = \int dx \left[\frac{\Sigma}{2} (\nabla l)^2 + W(l) \right] \quad (102)$$

Since $d = 2 < d^*$, the structure of $W(l)$ doesn't really matter (for SR forces) as we expect fluctuations to dominate the critical behaviour, so we use a square-well

$$W(l) = \begin{cases} \infty & l < 0 \\ -\mu & 0 < l < R \\ 0 & l > R \end{cases} \quad (103)$$

We start by discretising the system and using the Restricted Solid On Solid model

$$H = \sum_{i=1}^{\infty} k |l_{i+1} - l_i| \quad (104)$$

with $|l_{i+1} - l_i| = 0$ or 1 . So

$$Z = \sum_{l_1} \sum_{l_2} \sum_{l_3} \dots e^{-k|l_2 - l_1| - k|l_3 - l_2| - k|l_4 - l_3| - \dots} \quad (105)$$

$$= \sum_{l_1} \sum_{l_2} \sum_{l_3} \dots T(l_1, l_2) T(l_2, l_3) \dots \quad (106)$$

$$= \text{Tr } T^N \quad (107)$$

$$= \sum_{i=1} \lambda_i^N \quad (108)$$

$$(109)$$

where we have used periodic boundary conditions and

$$T(l, l') = e^{-k|l - l'|} \quad (110)$$

$$T = \begin{pmatrix} 1 & e^{-k} & 0 & \dots \\ e^{-k} & 1 & e^{-k} & \dots \\ 0 & e^{-k} & 1 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (111)$$

also λ_i are the eigenvalues of T and obey

$$\sum_{l'} T(l, l') \Psi_i(l') = \lambda_i \Psi_i(l) \quad (112)$$

with $\Psi_i(l)$ the eigenvectors. We can write this as

$$e^{-k} \Psi_i(l-1) + \Psi_i(l) + e^{-k} \Psi_i(l+1) = \lambda_i \Psi_i(l) \quad (113)$$

This is a second-order difference equation and so in the continuum limit we'll have a second-order differential equation, that is a Schrödinger equation

$$-\frac{(k_B T)^2}{2\Sigma} \Psi_i'' + W \Psi_i = E_i \Psi_i \quad (114)$$

and

$$Z_\pi(l_1, l_2; X) = \sum_i \Psi_i^*(l_1) \Psi_i(l_2) e^{-E_i X / k_B T} \quad (115)$$

In the limit $X \rightarrow \infty$

$$f_{\text{sing}} = \lim_{X \rightarrow \infty} \frac{-k_B T \ln Z}{X} = E_0 \quad (116)$$

$$P_\pi(l) = |\Psi_0(l)|^2 \quad (117)$$

Now consider a square well potential and suppose that the ground state is bounded $E_0 < 0$ and set $k_B T = 1$. If $l < R$

$$-\frac{1}{2\Sigma} \Psi_0'' - U \Psi_0 = E_0 \Psi_0 \quad (118)$$

$$\Rightarrow \Psi = A \sin(\sqrt{2\Sigma(U + E_0)}l) + B \cos(\sqrt{2\Sigma(U + E_0)}l) \quad (119)$$

since $\Psi_0(0) = 0$ we have $B = 0$. If $l > R$

$$-\frac{1}{2\Sigma} \Psi_0'' = E_0 \Psi_0 \Rightarrow \Psi_0 = C e^{-\sqrt{2\Sigma|E_0}|l} + D e^{\sqrt{2\Sigma|E_0}|l} \quad (120)$$

and since $\Psi(\infty) = 0$ we have $D = 0$. Since Ψ'/Ψ must be continuous at R thus we have

$$-\sqrt{\frac{|E_0|}{U + E_0}} = \cot\left(\sqrt{2\Sigma(U + E_0)}R\right) \quad (121)$$

In the transition to the unbound state $E_0 = 0$ when $U = U^*$ with

$$\sqrt{2\Sigma U^*} R = \frac{\pi}{2} \quad (122)$$

If $U > U^*$, $E_0 \sim -(U^* - U)^2 \Rightarrow \alpha_s = 0$ ($\theta > 0$); if $U < U^*$, $E_0 = 0$ ($\theta > 0$). Far from the wall the probability distribution function (PDF) goes as

$$P_\pi(l) = N e^{-2l\sqrt{2|E_0|\Sigma}} \quad ; \quad N = 2\sqrt{2\Sigma|E_0|} \quad ; \quad l > R \quad (123)$$

from which we can easily calculate the average height of the interface

$$l_\pi \equiv \langle l \rangle = \frac{1}{\sqrt{2|E_0|\Sigma}} \sim \frac{1}{U^* - U} \Rightarrow \beta_s = 1 \quad (124)$$

Since for the exponential PDF the standard deviation is the same as the average we have

$$l \sim \xi_\perp \sim (U^* - U)^{-1} \Rightarrow \nu_\perp = 1 \quad (125)$$

and (from a standard transfer matrix result)

$$\xi_\parallel = \frac{1}{E_1 - E_0} \sim (U^* - U)^{-2} \Rightarrow \nu_\parallel = 2 \quad (126)$$

Let us make a few remarks on these results. From the previous equations we see that $\nu_\perp/\nu_\parallel = 1/2$ so $\xi_\perp \sim \xi_\parallel^{1/2}$, thus the wandering exponent $\zeta = 1/2$, which makes the results for β_s consistent with heuristic random-walk arguments: $\beta_s = \frac{\zeta}{1-\zeta}$. In preparation for covariance we cast the results in a different form using $E_0 = -\frac{\Sigma\theta^2}{2}$ the PDF can be written as

$$P_\pi(l, \theta) = 2\Sigma\theta e^{-2\Sigma\theta l} \quad (127)$$

and

$$\langle l \rangle = \frac{1}{2\Sigma\theta} \quad (128)$$

This result for the PDF can be easily interpreted using physical arguments, noting that $P_\pi(l) \propto e^{-\Delta F(l)}$ and calculating the free-energy cost of a triangular interfacial fluctuation with height l :

$$\frac{\Delta F}{2} = -\Sigma \left(\frac{l}{\tan\theta} - \frac{l}{\sin\theta} \right) + \frac{l}{\tan\theta} \Sigma(1 - \cos\theta) \simeq \Sigma\theta l \quad (129)$$

The calculation can be done with random-bond disorder yielding the results for the critical exponents: $\beta_s = 2$, $\nu_\parallel = 3$, $\alpha_s = 0$ and, from $\beta_s = \frac{\zeta}{1-\zeta}$, $\zeta = 2/3$.

The focus of our attention is short-range (SR) critical wetting but we shall make a digression into long-range (LR) forces. In general critical wetting falls into 3 fluctuations regimes. One regime is the strong fluctuation regime (SFL) where critical behaviour is fluctuation dominated and the critical exponents are on the same universality class as SR forces. On the other extreme is the MF regime where fluctuations are negligible and the exponents are given by Landau theory. For LR forces an intermediate regime of weak fluctuations (WFL) is present. In the WFL some of the exponents are MF and others are renormalised by fluctuations. These results are backed up by RG and transfer matrix calculation but we can reason heuristically to grasp the physical origin of these different regimes.

A fluctuation of height l decays in a distance of ξ_\parallel so, by the definition of derivative, the term $\frac{\Sigma(\nabla l)^2}{2} \sim \frac{l^2}{\xi_\parallel^2}$. When $l \sim \xi_\perp$ the fluctuations are important and, as $\xi_\perp \sim \xi_\parallel^\zeta$, we have $\frac{l^2}{\xi_\parallel^2} \sim l^{-\tau}$ where

$$\tau = 2 \left(\frac{1}{\zeta} - 1 \right) \quad (130)$$

As an example $\tau = 2$ for thermal fluctuations in $d = 2$.

If this result is now inserted in the Hamiltonian with long range forces we have the heuristic potential:

$$W_{\text{eff}} = -\frac{a}{l^p} + \frac{b}{l^a} + \frac{c}{l^\tau} \quad (131)$$

and this allows us to clearly see the origin of the different regimes. If $\tau > q$ the fluctuation term doesn't matter and we have MF exponents, $\beta_s = \frac{1}{q-p}$. If $p < \tau < q$ then $W_{\text{eff}} \sim -\frac{a}{l^p} + \frac{c}{l^\tau}$ and MF breaks down, $\beta_s = \frac{1}{\tau-p}$. Finally, if $\tau < p$ the fluctuations dominate and the full calculations must be done, e.g. $\beta_s = \frac{\zeta}{1-\zeta}$ in $d = 2$.

As a final remark we estimate the upper critical dimension for critical wetting. As we saw MF breaks down when $\tau = q$. Using definition 130 and $\zeta = \frac{3-d}{2}$ we get $d^* = 3 - \frac{4}{q+2}$. For Van der Waals forces ($p = 2, q = 3$) we have $d^* = \frac{11}{5}$ and in limit of $q \rightarrow \infty$ (SR forces) we get $d^* = 3$.

8 3D Critical Wetting With Short-Range Forces

Analytical studies of SR critical wetting are based on the semi-phenomenological interfacial model. As we have seen the upper critical dimension for SR forces is three, thus we expect non-universal behaviour and also that the detailed structure of the potential in the interfacial model is absolutely crucial. Brézin *et al.* (1983b,a) (BHL) constructed $W(l)$ so that the MF results are reproduced when fluctuations are ignored:

$$W(l) = -ae^{-kl} + be^{-2kl} \quad (132)$$

where as usual $a \propto T_C^{\text{MF}} - T$, $b > 0$ and $k = 1/\xi$. We can check that we recover the MF results. The MF equilibrium interface length is given by the minimum of the potential, the correlation length by the second derivative at the minimum and the free-energy by the value at the minimum:

$$e^{-kl_\pi^{\text{MF}}} = \frac{a}{2b} \Rightarrow kl_\pi^{\text{MF}} = -\ln(T_W^{\text{MF}} - T) \Rightarrow \beta_s = 0 \quad (133)$$

$$W''(l_\pi^{\text{MF}}) = \frac{a^2 k^2}{2b} \Rightarrow \xi_{\parallel} \propto (T_W^{\text{MF}} - T)^{-1} \quad ; \quad \nu_{\parallel} = 1 \quad (134)$$

$$W(l_\pi^{\text{MF}}) = -\frac{a^2}{4b} \propto (T_W^{\text{MF}} - T)^2 \quad ; \quad \alpha_s = 0 \quad (135)$$

thus recovering the MF results. As an aside, we write l_π in terms of θ , a result which will be useful later when we study covariance:

$$-\frac{a^2}{4b} = -\frac{\Sigma\theta^2}{2} \Rightarrow a = \sqrt{2\Sigma b\theta} \quad (136)$$

$$kl_\pi^{\text{MF}} = -\ln \sqrt{\frac{\Sigma}{2b}} \theta \quad (137)$$

BHL used a linearised RG theory to study the interfacial Hamiltonian and their results show non-universal behaviour, with 3 different regimes depending on a ‘‘wetting parameter’’, with similar results obtained by Fisher & Huse (1985); Kroll *et al.* (1985); Lipowsky *et al.* (1983):

$$w = \frac{k_B T k^2}{4\pi\Sigma} \quad (138)$$

- $0 \leq w < 1/2$; T_w is not renormalised; $v_{\parallel} = \frac{1}{1-w}$; $kl_{\pi} = (1+2w) \ln \xi_{\parallel}$
- $1/2 < w < 2$; T_w is not renormalised; $v_{\parallel} = \frac{1}{(\sqrt{2}-\sqrt{w})^2}$; $kl_{\pi} \sim \sqrt{8w} \ln \xi_{\parallel}$
- $w > 2$; $T_w < T_w^{\text{MF}}$; $\xi_{\parallel} \sim e^{\frac{1}{(T_w-T)}}$; $l_{\pi} \sim \frac{1}{T_w-T}$

Notice that the MF results are recovered in the $w \rightarrow 0$ limit.

In a series of simulations Kurt Binder and coworkers ((Binder & Landau, 1985; Binder *et al.*, 1986; Binder & Landau, 1988; Binder *et al.*, 1989, 1995a,b, 1996) studied an Ising system in a simple cubic lattice with opposite boundary fields. The simulations were made at $w \simeq 0.8$, for which theory predicts $v_{\parallel} \simeq 3.8$, but the results show no deviation from MF predictions. Halpin-Healy & Brézin (1987) suggested that the asymptotic critical regime had not been reached in the simulations. This explanation is doubtful, though, as simulations using the capillary model observed strong non-universal behaviour (Gomper & Kroll, 1988), suggesting that the problem is in the construction of the interfacial model from the full Hamiltonian.

The problem was then tackled by Fisher and Jin (FJ) (Fisher & Jin, 1991, 1992; Jin & Fisher, 1993a,b; Fisher *et al.*, 1994) who precised the methodology to construct the interfacial Hamiltonian from the full LGW model. The interface is defined as the surface of iso-magnetisation $m^{\times} = 0$ (crossing criteria)¹. The partition function is constructed by performing a partial integration of the configurations with given $\{l(\mathbf{x})\}$:

$$Z = \int \mathcal{D}_m e^{-H_{\text{LGW}}[m]} = \int \mathcal{D}_l \int' \mathcal{D}_m e^{-H_{\text{LGW}}[m]} \quad (139)$$

defining

$$e^{-H[l]} = \int' \mathcal{D}_m e^{-H_{\text{LGW}}[m]} \quad (140)$$

For fixed interfacial configuration, $\{l(\mathbf{x})\}$, the CW fluctuations are frozen, the only fluctuations are bulk-like and given by ξ . Since we are far from the critical point a MF treatment, using saddle-point, will suffice:

$$e^{-H[l]} = e^{-\min H[m]} \quad (141)$$

$$H[l] = H_{\text{LGW}}[m_z(\mathbf{r}; [l])] \quad (142)$$

where m_z is a constrained profile that minimises H_{LGW} subject to constraints and boundary conditions.

Functional minimisation of H_{LGW} gives:

$$\nabla^2 m_z = \phi'(m_z) \quad (143)$$

with the boundary conditions

$$m_z(\mathbf{r} = (\mathbf{x}, l(\mathbf{x}))) = 0 \quad (144)$$

at the interface and

$$\left. \frac{\partial}{\partial z} m_z \right|_{z=0} = c m_z \Big|_{z=0} - h_1 \quad (145)$$

at the wall. In ϕ^4 theory the profile is an hyperbolic tangent but we approximate the potential by a double parabola (DP approximation) giving an exponential tail to the

¹ In FJ other alternative definitions for the interface are used, however they don't change the main results.

magnetisation profile. FJ constructed $m_z(\mathbf{r}; [l])$ perturbatively in terms of planar constrained profiles $m_\pi(z; l)$. If the profile is constrained to be planar the PDE reduces to an ODE which is easily solved:

$$\frac{d^2 m_\pi}{dz^2} = \begin{cases} k^2(m_\pi - m_0) & m > 0 \quad (z < l) \\ k^2(m_\pi + m_0) & m < 0 \quad (z > l) \end{cases} \quad (146)$$

The solution of this ODE is easy:

$$m_\pi(z) = \begin{cases} Ae^{-k(z-l)} + Be^{k(z-l)} + m_0 & z < l \\ -m_0 + Ce^{-k(z-l)} & z > l \end{cases} \quad (147)$$

with A, B, C determined by the boundary conditions. Replacing back in the Hamiltonian we get the potential for when the interface is flat

$$H_{\text{LGW}}[m_\pi(z, l)] = H[l] = A \left(-ae^{-kl} + (b + ca^2)e^{-2kl} + \dots \right) \equiv W(l) \quad (148)$$

Perturbatively (to order $(\nabla l)^2$)

$$m_\equiv(\mathbf{r}; [l]) \simeq m_\pi(z; l(\mathbf{x})) \quad ; \quad \mathbf{r} = (\mathbf{x}, z) \quad (149)$$

Then

$$H_{\text{FJ}}[l] = H_{\text{LGW}}[m_\pi(z; l(\mathbf{x}))] \quad (150)$$

$$= \int d\mathbf{x} \left[\frac{\Sigma_\infty + \Delta\Sigma(l)}{2} (\nabla l)^2 + W(l) \right] \quad (151)$$

with a position dependent stiffness

$$\Sigma(l) = \Sigma_\infty + \Delta\Sigma = \int_0^\infty dz \left(\frac{\partial}{\partial l} m_\pi(z; l) \right)^2 \quad (152)$$

$$\Delta\Sigma(l) = -ae^{-kl} - 2bkle^{-2kl} + \dots \quad (153)$$

An RG analysis of this potential shows that under renormalisation the flows of $W(l)$ and $\Delta\Sigma(l)$ mix and the second term in the potential drives the transition first order transition. These results were further reinforced by an analysis of Boulter (1997).

However nice these results are, there are some questions that they raise:

- There is no hint of a first order phase transition in the simulations;
- Don't explain quantitatively why MF behaviour is observed in the simulations;
- If this analysis is correct then the global phase diagram of wetting in Nakanishi & Fisher (1982) would be reversed. This seems unlikely as the results of NF are based on general considerations of phase transition phenomenology, RG, scaling, etc;
- No physical explanation of why there is a position dependent stiffness;
- There is no explanation of why there is a -2 factor in the second term of the potential;

For a review of the situation in 3D wetting until recently see Parry (1996) and Binder *et al.* (2003) for a thorough review of the simulation results. We'll see later that all these issues are settled by a non-local model that is constructed following the FJ methodology but using a non-perturbative method to derive $m_\equiv(\mathbf{r}; [l])$.

9 Filling Transitions

So far we've been concerned with wetting on a planar substrate. If the substrate is not planar we anticipate interesting effects due to the geometry. One such geometry of interest is a wedge. Thermodynamic arguments (Concus & Finn, 1969; Pomeau, 1986; Hauge, 1992) show that the amount of liquid adsorbed in the apex of the wedge diverges when the contact angle θ equals the opening angle of the wedge α :

$$\theta(T_F) = \alpha \quad (154)$$

We then have a phase transition, at a temperature T_F , which anticipates wetting (see the work by Rejmer *et al.* (1999) and all the Parry and coworkers papers). This *filling transition* is clearly related to wetting but it is a different phenomena. We'll see that the values of the critical exponents will be different for these phase transitions. Remarkably, even though these are distinct phenomena, there is a hidden symmetry between these phase transitions, named *wedge covariance*.

We start by a thermodynamic analysis of filling. Suppose we have a wedge of longitudinal length M and height $L/\cos\alpha$, with α the opening angle. If the wedge is filled to height l the grand potential is

$$\Omega = -pV + \text{Area} \times \text{Surface Tension} \quad (155)$$

Since the bulk contribution, pV , doesn't depend on the height of liquid the relevant contribution is from the surface terms:

$$\text{Area} \times \text{Surface Tension} = \left\{ \frac{l}{\sin\alpha} \sigma_{wl} + \left(L - \frac{l}{\sin\alpha} \right) \sigma_{wg} + \frac{\sigma_{lg} l}{\tan\alpha} \right\} \quad (156)$$

$$= A \sigma_{wg} + \frac{2Ml}{\sin\alpha} (\sigma_{wl} - \sigma_{wg} + \sigma_{lg} \cos\alpha) \quad (157)$$

but using Young's equation (equation 55) we get

$$A \sigma_{wg} + \frac{2M}{\sin\alpha} \sigma_{lg} (\cos\alpha - \cos\theta) l \quad (158)$$

for a shallow wedge the second term:

$$\approx \frac{M}{\alpha} \sigma_{lg} (\theta^2 - \alpha^2) l \quad (159)$$

We see that if $\cos\theta > \cos\alpha$, i.e. $\theta < \alpha$ the system lowers its free-energy arbitrarily by making l macroscopic.

Before we proceed to a MF analysis of the filling transition we start by a definition of the critical exponents. The relevant length-scales are indicated in figures 9 and 10.

$$l_w \sim (\theta - \alpha)^{-\beta_w} \sim (T_F - T)^{-\beta_w} \quad (160)$$

$$\xi_x = 2l_w \cot\alpha \quad (161)$$

$$\xi_{\perp} = \sqrt{\langle l(0)^2 \rangle - \langle l(0) \rangle^2} \sim (\theta - \alpha)^{-\nu_{\perp}} \quad (162)$$

$$\xi_y \sim (\theta - \alpha)^{\nu_y} \quad (163)$$

we also anticipate a wedge wandering exponent in $d = 3$

$$\xi_{\perp} \sim \xi_y^{\zeta_y^w} \quad (164)$$

for the wedge free-energy

$$\Omega = -pV + \sigma_{wg}A + f_w M \quad (165)$$

$$f_w \sim (\theta - \alpha)^{2-\alpha_w} \quad (166)$$

We also have the critical exponents relations

$$1 - \alpha_w = -\beta_w \quad (167)$$

from $\frac{\partial f_w}{\partial \alpha} \propto l_w$ and also hyperscaling

$$2 - \alpha_w = (d-2)\nu_y \quad (168)$$

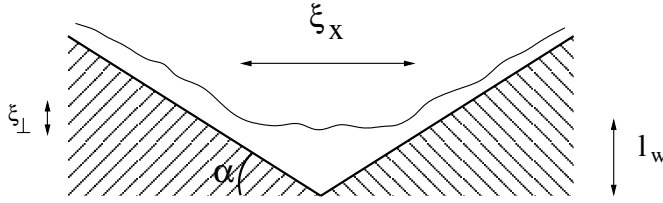


Figure 9: Filling transition in $d = 2$ with the relevant length scales indicated

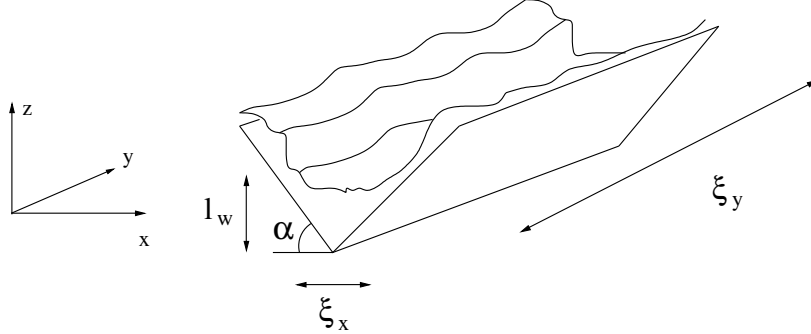


Figure 10: Filling transition and relevant length scales in $d = 3$

We are now ready to a MF analysis of filling. We start with the interfacial Hamiltonian, with the potential being the same as in wetting

$$H = \int dy \int dx \left\{ \frac{\Sigma}{2} (\nabla l)^2 + W(l - \psi(x)) \right\} \quad (169)$$

where $\psi(x) = \tan \alpha |x| \approx \alpha |x|$ and the vertical interaction, implicit in the potential, is expected to be valid for shallow wedges.

If we have translational invariance along the wedge and do functional minimisation of the Hamiltonian we have:

$$\Sigma \frac{d^2 l}{dx^2} = W'(l - \psi(x)) \quad (170)$$

noting that

$$\left. \frac{dl}{dx} \right|_{x=0} = 0 \quad (171)$$

With a change of variable

$$\eta = l - \psi(x) \quad (172)$$

$$\Sigma \frac{d^2 \eta}{dx^2} = W'(\eta) \quad (173)$$

integrating this equation once

$$\frac{\Sigma}{2} \left(\frac{d\eta}{dx} \right)^2 = W(\eta) + C \quad (174)$$

and using the fact that

$$\lim_{|x| \rightarrow \infty} \eta(x) = l_\pi \quad (175)$$

we get

$$\frac{\Sigma}{2} \left(\frac{d\eta}{dx} \right)^2 = W(\eta) - W(l_\pi) = \Delta W(\eta) \quad (176)$$

and

$$\frac{d\eta}{dx} = \pm \alpha \quad (177)$$

so

$$\frac{\Sigma \alpha^2}{2} = W(l_w) + \frac{\Sigma \theta^2}{2} \quad (178)$$

and

$$W(l) = \frac{\Sigma}{2} (\alpha^2 - \theta^2) \quad (179)$$

For LR forces:

$$-\frac{a}{l_w^p} + \frac{b}{l_w^q} = \frac{\Sigma}{2} (\alpha^2 - \theta^2) \quad (180)$$

$$\frac{a}{l_w^p} \simeq \Sigma (\alpha + \theta)(\theta - \alpha) \quad (181)$$

and finally

$$l_w \sim (\theta - \alpha)^{-1/p} \quad (182)$$

so $\beta_w = 1/p$. For SR forces:

$$-ae^{-kl_w} + be^{-2kl_w} = \frac{\Sigma}{2} (\alpha^2 - \theta^2) \quad (183)$$

$$\frac{\Sigma \theta^2}{2} - \sqrt{2\Sigma b \theta} e^{-kl_w} + be^{-2kl_w} = \frac{\Sigma \alpha^2}{2} \quad (184)$$

$$\sqrt{\frac{\Sigma}{2}} \theta - \sqrt{b} e^{-kl_w} = \sqrt{\frac{\Sigma}{2}} \alpha \quad (185)$$

$$kl_w = -\ln \sqrt{\frac{W}{2b}} (\theta - \alpha) \quad (186)$$

from where we can see both that $\beta_w = 0$ and that

$$l_w(\theta, \alpha) = l_\pi(\theta - \alpha) \quad (187)$$

this last relation is what we called *wedge covariance* before. For completeness we also include the values of other exponents without deriving them here:

$$f_w \sim -(\theta - \alpha) \ln(\theta - \alpha) \Rightarrow \alpha_w = 1 \quad (188)$$

$$\xi_y \sim \sqrt{-\ln(\theta - \alpha)} (\theta - \alpha)^{-1/2} \Rightarrow \nu_y = 1/2 \quad (189)$$

and from the hyperscaling relation

$$2 - \alpha_w = (d - 2)\nu_y \Rightarrow d_{\text{fill}}^* = 4 \quad (190)$$

For LR forces at MF level in $d = 3$:

$$l_w \sim (\theta - \alpha)^{-1/p} \quad (191)$$

$$\xi_y \sim (\theta - \alpha)^{-\nu_y} \quad \text{with} \quad \nu_y = 1/2 + 1/p \quad (192)$$

$$\xi_{\perp} \sim (\theta - \alpha)^{-1/4} \quad (193)$$

MF results are OK if $p < 4$ but breakdown if $p > 4$ in which case the critical behaviour is in the universality class of SR forces.

To finalise this section we remark that the filling transition temperature can be controlled by changing the opening angle of the wedge. Also we recall that for first order wetting there is spinodal temperature above which the potential develops an activation barrier responsible for first order wetting. If $T_{\text{fill}} < T_{\text{spinodal}}$ then even in a system with first-order wetting the filling transition will be critical.

10 2D Critical Filling

We now focus our attention on 2D filling, adapting the transfer matrix technique we used for 2D wetting (Parry *et al.*, 1999, 2000b, 2002; Abraham *et al.*, 2002; Romero-Enrique *et al.*, 2004). We work with the approximations made before for a shallow wedge. For a wedge of width $2X$ the Hamiltonian is

$$H = \int_{-X}^X dx \left[\frac{\Sigma}{2} \left(\frac{dl}{dx} \right)^2 + W(l - \alpha|x|) \right] \quad (194)$$

we now do the same change of variable we made before

$$\eta = l - \alpha|x| \quad (195)$$

$$\frac{d\eta}{dx} = \begin{cases} \frac{dl}{dx} + \alpha & x < 0 \\ \frac{dl}{dx} - \alpha & x > 0 \end{cases} \quad (196)$$

thus

$$\left(\frac{dl}{dx} \right)^2 = \left(\frac{d\eta}{dx} \right)^2 \pm 2\alpha \frac{d\eta}{dx} - \alpha^2 \quad (197)$$

$$H = -2X \frac{\Sigma\alpha^2}{2} + H_{\pi}[\eta]_{-X}^0 - 2\Sigma\alpha l(0) + H_{\pi}[\eta]_0^X + \alpha\Sigma(l_{<} + l_{>}) \quad (198)$$

where the first and last terms are constants and thus irrelevant and

$$H_{\pi} = \int dx \left[\frac{\Sigma}{2} \left(\frac{d\eta}{dx} \right)^2 + W(\eta) \right] \quad (199)$$

By definition

$$P_w(l_0) = \lim_{X \rightarrow \infty} \frac{e^{-\Sigma \alpha^2 X} Z_\pi(\eta_{<}, l_0; X) e^{2\Sigma \alpha l_0} Z_\pi(l_0, \eta_{>}; X)}{\int dl_0 [e^{-\Sigma \alpha^2 X} Z_\pi(\eta_{<}, l_0; X) e^{2\Sigma \alpha l_0} Z_\pi(l_0, \eta_{>}; X)]} \quad (200)$$

if we now use

$$Z_\pi(l_1, l_2; X) = \sum \Psi_n(l_1) \Psi_n^*(l_2) e^{-E_0 X} \quad (201)$$

we have

$$P_w(l) = N |\Psi_0(l)|^2 e^{2\Sigma \alpha l} \quad (202)$$

with

$$-\frac{1}{2\Sigma} \frac{d^2 \Psi_0}{dl^2} + W(l) \Psi_0 = E_0 \Psi_0 \quad (203)$$

recalling the result for a square well potential, equation 120, we get

$$P_w(l; \theta, \alpha) = 2\Sigma(\theta - \alpha) e^{-2\Sigma(\theta - \alpha)l} \quad (204)$$

$$\langle l \rangle = l_w = \frac{1}{2\Sigma(\theta - \alpha)} \Rightarrow \beta_w = 1 \quad (205)$$

As in the case of wetting due to the fact that the PDF is exponential the transition is fluctuation dominated as $\xi_\perp \sim l$. Comparing these results with results 127 and 128 we see that we have covariance:

$$P_w(l; \theta, \alpha) = P_\pi(l; \theta - \alpha) \Rightarrow l_{w(\theta, \alpha)} = l_\pi(\theta - \alpha) \quad (206)$$

Before we close this section a number of remarks are in order. If we do the calculations with LR forces we get

$$\Psi_0 \sim e^{-\Sigma \theta l} + Cl^{1-p} + \dots \Rightarrow \langle l \rangle \equiv l_w \sim \begin{cases} (\theta - \alpha)^{-1} & p > 1 \quad \text{Universal} \\ (\theta - \alpha)^{-1/p} & p \leq 1 \quad \text{MF True} \end{cases} \quad (207)$$

If we do calculations with random bonds we again get covariance.

In $d = 2$ and SR forces, if we relate the wedge free-energy with the line tension, $f_w(\theta, \alpha) = \tau(\theta) - \tau(\theta - \alpha)$ and do the derivative in relation to the angle we get

$$\frac{\partial f_w}{\partial \alpha} = 2\Sigma l_w = \frac{\partial \tau}{\partial \alpha} = -\frac{\partial \tau(\theta - \alpha)}{\partial \theta} \quad (208)$$

and taking the limit as $\alpha \rightarrow 0$

$$l_\pi(\theta) = -\frac{1}{2\Sigma} \frac{\partial \tau}{\partial \theta} \quad (209)$$

and a with simple power count

$$\alpha_l = \alpha_s + v_\parallel \quad (210)$$

a result conjectured by Indekeu & Robledo (1993). Covariance immediately implies that $\beta_w = \beta_s = \frac{\zeta}{1-\zeta}$ for SR forces. Finally we derived covariance for a shallow wedge but, from the exact solution for the Ising model in a corner, $\theta = \frac{\pi}{4}$ (Abraham & Maciulek, 2002) and computer simulations, we now that it remains exact for acute wedges as well.

11 3D Critical Filling

The problem of filling on a 3D wedge for SR forces can be tackled by reducing it to an effective 1D problem (Parry *et al.*, 2000a, 2001; Greenall *et al.*, 2004; Rascón & Parry, 2005; Romero-Enrique & Parry, 2005; Rascón & Parry, 2000). Recalling that $\xi_x \sim l_w \sim -\ln(\theta - \alpha)$ and $\xi_y \sim \sqrt{|\ln(\theta - \alpha)|}(\theta - \alpha)^{1/2}$ we see that the fluctuations are strongly anisotropic and that $\frac{\xi_x}{\xi_y} \rightarrow 0$ as $\theta \rightarrow \alpha$. So starting with the full CW Hamiltonian we integrate out all degrees of freedom (“a la” FJ) except the 1D “breather mode” excitations described by a local midpoint height $l_0 \equiv l(x=0, y)$. So

$$e^{-H_F[l_0]} \equiv \int' D l e^{-H_w[l]} \quad (211)$$

which we calculate in MF with $l_0(y)$ fixed

$$H_F[l_0] = \min H_{LGW}[l] \quad (212)$$

If we further assume a local cross-section described by a thin wetting layer of width $l_\pi(\theta)$ and a near planar interface near the bottom of the wedge of height $l_0(y)$ we get

$$H_F[l_0] = \int dy \left[\frac{\Sigma l_0}{\alpha} \left(\frac{dl_0}{dy} \right)^2 + V_w(l_0) \right] \quad (213)$$

with

$$V_w(l_0) = \frac{\Sigma}{\alpha} (\theta^2 - \alpha^2) l_0 + \begin{cases} A l_0^{-p+1} + \dots & \text{LR forces} \\ A e^{-k l_0} + \dots & \text{SR forces} \end{cases} \quad (214)$$

A first check on this treatment is to recover MF results. By calculation the minimum of the potential we see that $l_0 \sim (\theta - \alpha)^{-1/p}$ for LR forces and that $l_0 \sim \ln(\theta - \alpha)$ for SR forces. We also get $\xi_y = \sqrt{\frac{l_0}{v''(l_0)}} \Rightarrow v_y = \frac{1}{2} + \frac{1}{p}$ and $\xi_\perp^2 = \int \frac{dQ}{v'' + \frac{\Sigma}{2} Q^2} \Rightarrow \xi_\perp = (\theta - \alpha)^{-1/4}$. MF is OK if $\frac{\xi_\perp}{l_0} \ll 1 \Rightarrow p = 4$ is marginal.

Heuristically we anticipate that for $p > 4$ the l^{-p+1} term is irrelevant (in the RG sense). Start with the Hamiltonian

$$H = \int dy \left[l \left(\frac{dl}{dy} \right)^2 + (\theta - \alpha) l + A l^{-p+1} \right] \quad (215)$$

now let $l \rightarrow l' = \frac{l}{b^{1/3}}$ and $y \rightarrow y' = \frac{y}{b}$

$$H[l'] = \int dy' \left[l' b^{1/3} \left(\frac{dl' b^{1/3}}{db y'} \right)^2 + t b^{1/3} l' + A l'^{-p+1} b^{1/3(1-p)} \right] \quad (216)$$

with $t = (\theta - \alpha)$, finally

$$H[l'] = \int dy' \left[\frac{\Sigma l'}{2} \left(\frac{dl'}{dy} \right)^2 + t' l' + A' l'^{-p+1} \right] \quad (217)$$

from where we can see that $t' = b^4/3t$, thus relevant, and $A' = A b^{\frac{4-p}{3}}$, thus irrelevant if $p > 4$. As $t' = b^{y_t} t$ where $y_t = 1/v$ so $v_y = 3/4$ for $p > 4$. Alternatively consider a pure SR system

$$H_F = \int dy \left[\frac{\Sigma l}{2} \left(\frac{dl}{dy} \right)^2 + (\theta + \alpha) l \right] \quad (218)$$

defining

$$\lambda = (\theta - \alpha)^{1/4} l \quad (219)$$

$$Y = (\theta - \alpha)^{3/4} y \quad (220)$$

$$H_F[\lambda] = \int dY \left[\frac{\Sigma}{2} \lambda \left(\frac{d\lambda}{dY} \right)^2 + 2\Sigma\lambda \right] \quad (221)$$

and without further calculations $\langle \lambda \rangle = \text{constant} \Rightarrow \langle l \rangle \sim (\theta - \alpha)^{-1/4}$ and has the correlations, $\langle \lambda(y)\lambda(y') \rangle$, have a finite length $\Rightarrow \xi_y \sim (\theta - \alpha)^{-3/4}$. Alternatively think of an effective potential

$$V_{\text{eff}} = \frac{\Sigma}{2} (\theta^2 - \alpha^2) l_0 + A l_0^{-p+1} + \frac{l_0^3}{\xi_y^2} \quad (222)$$

where the last term comes from the $l(\nabla l)^2$ term in the Hamiltonian. But as $l_0 \sim \xi_y^{1/3}$

$$V_{\text{eff}} = (\theta - \alpha) l_0 + l_0^{-p+1} + l_0^{-3} \quad (223)$$

with the last term representing a fluctuation induced contribution to the potential. By comparing the previous results we have:

- $p < 4$, MF regime, $l_0(\theta - \alpha)^{-1/p}$, $\xi_{\perp} \sim (\theta - \alpha)^{1/4}$, $\xi_y \sim (\theta - \alpha)^{-1/2-1/p}$.
- $p > 4$, Fluctuations regime, $l \sim (\theta - \alpha)^{-1/4}$, $\xi_y \sim (\theta - \alpha)^{-3/4}$.

If we make a full transfer matrix calculation with

$$Z = \int D l_0 e^{-\int dy \left[\frac{\Sigma l_0}{2} \left(\frac{d l_0}{d y} \right)^2 + V(l_0) \right]} \quad (224)$$

we get an equation that is same formally the same as the one that describes a quantum mechanics problem with a position dependence mass. For SR forces an exact solution for $P_w(l)$ in terms of Hermite polynomial is known and the results are very different from 3D critical wetting, e.g. $\xi_{\perp}^F \sim (\theta - \alpha)^{-1/4}$ but $\xi_{\perp}^w \sim \sqrt{|\ln \theta|}$. So the wandering exponent is changed.

We end this section by remarking that unlike the situation for 3D wetting the results from both computer simulations (Albano *et al.*, 2003; Milchev *et al.*, 2003a,b, 2005a; De Virgiliis *et al.*, 2005; Milchev *et al.*, 2005b) and experiments (Bruschi *et al.*, 2003a, 2002, 2001, 2003b) are in very good agreement with the theory.

12 The Non-Local Model

Numerical analysis shows that wedge covariance is satisfied for both shallow and acute wedges (Greenall *et al.*, 2004), however, if a local potential (normal distance to the wall) is used to study wedge filling the *incorrect* result $l_w(\theta, \alpha) = \sec \alpha l_{\pi}(\theta - \alpha)$ is obtained (Rejmer *et al.*, 1999). In other geometries the deficiencies of the local model are even more pronounced and produce nonsensical results (Parry & Rascón, 2006; Binder, 2006).

In this section we describe briefly a non-local model that results from a careful construction of the potential from the full LGW theory (for details see Parry *et al.* (2006a)). This model seems to hold the key to the study of wetting in non-planar

substrates and, simultaneously, to explain the longstanding discrepancy between theory and simulations in 3D critical wetting.

The derivation of the interfacial model in (Parry *et al.*, 2006a) is essentially an improved version of the methodology of Fisher and Jin (Fisher & Jin, 1991, 1992; Jin & Fisher, 1993a,b; Fisher *et al.*, 1994) described in section 8. With the Fisher and Jin method, the problem boils down to solve a Helmholtz equation in the region between the wall and the interface. Fisher and Jin solved the equation for the planar wall, planar interface case, and constructed the solutions for a non-planar profile perturbatively. Parry *et al.* (2006a) use a Green's function method to obtain the interfacial potential, which can be expressed in an elegant diagrammatic expansion. In this diagrammatic expansion the diagrams can be interpreted as contribution to the correlation function between a point in the interface and a point in the wall due to tubes of reversed spins that connect the two points (Abraham, 1983; Abraham *et al.*, 1984). The method is based on a multiple-reflection expansion used in other problems (Balian & Bloch, 1970), including Kac's famous question: "Can one hear the shape of a drum?" (Kac, 1966). In a sense we ask "Can one see the shape of the free-energy?"

The new form for the potential not only identifies the interfacial Hamiltonian to exponentially accurate order in the radii of curvature, but retains a non-local character that turns out to contain important physics in it. In Parry *et al.* (2004) the non-local model is used both to recover wedge covariance and to explain the discrepancy between theory and simulations of the 3D critical wetting transition. In Parry *et al.* (2006b) the potential for a spherical wall with a spherical interface is obtained exactly and compared to the results of the non-local model. As stated before, the results of the non-local model capture all the important contribution, including some polynomial pre-factors on the terms of the potential not suspected before, up to exponential order in the radii of curvature.

13 Future Work

The non-local model provides a powerful tool for the analysis of interfacial phenomena. Many questions can now be tackled. An obvious point to start is the application of the non-local model to non-planar geometries, where local models are known to produce nonsensical results, for example for a parabola (Parry & Rascón, 2006) or a double pyramid (Binder, 2006). Unlike the sphere, where the non-local model only produces minor corrections to local behaviour, in these geometries the improvement should be dramatic.

As a more formal, but necessary, check we must do an RG analysis of the new diagrams that appear in perturbation theory to see how they influence (or not) critical behaviour. From previous experience with the double parabola approximation we anticipate that the new diagrams will not have a strong influence on the results obtained with the simplest theory except, probably, close to the tricritical point.

The forces in real fluids are known to be of LR character, Van der Waals like. Can we construct the LR equivalent of the non-local model to study interfacial phenomena in these systems? If so, we have opened the way for a systematic and unified study of interfacial phenomena in all sorts of substrate geometries. It is not difficult to anticipate the value of such a theory for the study of the behaviour of fluids in sculpted geometries.

A Solution of the Functional Equation in the LGW Model

Let us derive equation 20 from equations 17 and 18. Without being concerned with mathematical rigour we introduce the notion of functional derivative by replacing $m(z)$ with $m(z) + \delta m(z)$ in the Hamiltonian (with $A = 1$), where $\delta m(z)$ a small perturbation beginning and terminating in the same points as $m(z)$:

$$H[m + \delta m] = \int dz \left[\frac{1}{2} (m' + \delta m')^2 + \phi(m + \delta m) \right] \quad (225)$$

expanding the functions inside the integral around $\delta m = 0$

$$H[m + \delta m] = \underbrace{\int dz \left[\frac{1}{2} m'^2 + \phi(m) \right]}_{=H[m]} + \int dz [m' \delta m' + \phi'(m) \delta m] + O(\delta m^2) \quad (226)$$

so

$$\delta H[m] \equiv H[m + \delta m] - H[m] = \int dz [m' \delta m' + \phi'(m) \delta m] \quad (227)$$

integrating by parts and writing explicitly the z dependence of m again

$$\delta H[m(z)] = \underbrace{[m'(z) \delta m(z)]_{-\infty}^{+\infty}}_{=0} + \int dz [(-m''(z) + \phi'(m(z))) \delta m(z)] \quad (228)$$

and thus for $\frac{\delta H}{\delta m} = 0$ it is sufficient to have

$$m''(z) = \phi'(m(z)) \quad (229)$$

B “Derivation” of the Interfacial Model

The derivation of the interfacial Hamiltonian from the more microscopic LGW model is easy if a few assumptions and approximations are made. As stated before we assume that the interface is smooth and doesn't fluctuate wildly so overhangs and bubbles are ignored. Then the interface is like a membrane with thickness given by the bulk correlation length and described by a coordinate $l(\mathbf{x})$ and $\mathbf{x} = (x, y)$. We also assume that the fluctuations of $l(\mathbf{x})$ are small (i.e. $|\nabla l| \ll 1$). So

$$H_{\text{LGW}} = \iint d\mathbf{x} dz \left[\frac{(\nabla m)^2}{2} + \phi(m) \right] \quad (230)$$

$$= \iint d\mathbf{x} dz \left[\frac{1}{2} \left(\frac{\partial m}{\partial z} \right)^2 + \phi(m) \right] + \iint d\mathbf{x} dz \left[\frac{1}{2} \left(\frac{\partial m}{\partial l} \right)^2 \left(\left(\frac{\partial l}{\partial x} \right)^2 + \left(\frac{\partial l}{\partial y} \right)^2 \right) \right] \quad (231)$$

Considering l as constant, $l \simeq \langle l \rangle$, due to the fact that fluctuations are small, the first integral is now independent of \mathbf{x} . Performing the integration as we did in MF theory (derivation of equation 29) we see that the first part of the Hamiltonian is

$$H_1[l(\mathbf{x})] = \phi(m_0) V + L^{d-1} \sigma \quad (232)$$

Finally, to obtain the third term in equation 40, we write explicitly $\partial m/\partial l$ (equation 26) and, using again the approximation that $l \simeq \text{constant}$, perform the integration over z to obtain the interfacial Hamiltonian. So

$$\left(\frac{\partial m}{\partial l}\right)^2 = \frac{m_0^2 k^2}{4} \text{sech}^4 \frac{k(z-l)}{2} \quad (233)$$

and the integration over z is elementary since

$$\int_{-\infty}^{+\infty} dz \frac{k}{2} \text{sech}^4 \frac{k(z-l)}{2} = \frac{4}{3}$$

finally recalling the expression for the surface tension (equation 34) we obtain for this last term

$$\frac{\sigma}{2} \int d\mathbf{x} (\nabla l)^2 \quad (234)$$

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