Interfacial Structural Changes and Singularities in Non-Planar Geometries

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Abstract

We consider phase coexistence and criticality in a thin-film Ising magnet with opposing surface fields and non-planar (corrugated) walls. We show that the loss of translational invariance has a strong and unexpected non-linear influence on the interface structure and phase diagram. We identify 4 non-thermodynamic singularities where there is a qualitative change in the interface shape. In addition, we establish that at the finite-size critical point, the singularity in the interface shape is characterized by two distinct critical exponents in contrast to the planar case (which is characterised by one).

Similar effects should be observed for prewetting at a corrugated substrate. Analogy is made with the behaviour of a non-linear forced oscillator showing chaotic dynamics.

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There are a number of well studied examples of fluid interfacial phenomena for planar systems in which surface phases with distinct adsorptions co-exist along a line of first-order phase transitions which terminates at a surface critical point. Examples include the pre-wetting transition associated with first-order wetting and also interfacial localization in thin-film magnets (with opposite surface fields) associated with confinement effects at critical wetting. In both cases, the difference in adsorption between the two phases vanishes continuously as the critical point, signifying the end of two-phase coexistence, is approached. This second order phase transition is characterized by the critical exponents belonging to the two dimensional Ising universality class (for three dimensional bulk systems) since the adsorption difference acts as a scalar order parameter. In this letter, we describe a wealth of new interfacial structural changes and singularities which emerge when the analogous phenomena are considered in slightly non-planar geometries and which are intimately associated with non-linear behaviour. In addition to a shift in the finite-size (FS) critical point (compared to the planar confined system), the shape of the non-planar interface undergoes a number of structural changes as we move along and beyond the line of coexistence. This behaviour has no counterpart in the planar geometry, and has not been reported previously. Moreover, as the shifted surface critical point is approached, the function describing the shape of the non-planar interface shows non-analyticities which are characterised by two critical exponents. Whilst one of these appears to be identical with the usual critical exponent describing the singularity in the total (or average) adsorption, the general identification of the second is a more difficult problem, although scaling arguments (consistent with our explicit results) suggest that its value is related to the energy density. Our predictions are based on a detailed numerical analysis of a simple mean-field (MF) model of interfacial behaviour which we believe is qualitatively correct beyond MF approximation (in three dimensions). These are rather dramatic effects emanating from the introduction of a slight non-planar perturbation to the interface can be viewed profitably by making analogy with the classical mechanics of an extremely sensitive non-linear dynamical system exhibiting chaotic behaviour. As we will see, the interface behaviour may be elegantly
portrayed as the temperature evolution of a phase plane plot, similar to that employed in
dynamical systems, allowing us to distinguish different qualitative types of interface shape
separated by non-thermodynamic singularities.

To begin, we recall the relevant properties and phase diagram of the planar system prior
to a discussion of the non-planar generalization. The transition that we concentrate on
occurs in a thin-film magnet with opposing surface fields but the phenomena are generic
to other situations such as prewetting at a planar wall. Consider then an Ising-like thin
film magnet of width \( L_z \) and infinite transverse area in zero bulk field and below the bulk
critical temperature \( T_{c}^{BULK} \) with surface fields \( h_1 \) and \( h_2 = -h_1 \) acting on the spins in the
\( z = 0 \) and \( z = L_z \) planes respectively. We further suppose (through a judicial choice of
surface enhancement \([4]\)) that in the semi-infinite limit \( L_z \to \infty \) each surface undergoes a
critical wetting transition at temperature \( T_w \). For such a system, MF \([2]\) and simulation
studies \([3]\) show that the finite size phase diagram is dominated by wetting effects which
are able to suppress bulk-like coexistence over a large temperature regime. At sufficiently
low temperatures \( T < T_c(L_z) \), with the finite-size critical temperature satisfying \( T_c(L_z) < T_w \),
phase coexistence is possible between phases corresponding to an interface being bound
to either wall. As the temperature increases, the interface position moves continuously to
the middle of the system and for \( T > T_c(L_z) \) only one phase is possible. Thus, in the
temperature window \( T_{c}^{BULK} > T > T_w \), the FS effects suppress bulk-like phase coexistence
for all \( L_z \). This temperature range is also characterised by a near soft-mode phase since
the transverse correlation length \( \xi_\parallel \) is extremely large due to capillary-wave like excitations.
These features can be most easily understood using a simple effective interfacial Hamiltonian
model \([2]\):

\[
H[\ell] = \int d\mathbf{r} \left[ \frac{\Sigma}{2} (\nabla \ell)^2 + W(\ell; L_z) \right]
\]

where \( \ell(\mathbf{r}) \) is the collective co-ordinate describing the interface position at vector displace-
ment \( \mathbf{r} = (x, y) \) along the wall and \( \Sigma \) is the stiffness coefficient of the up-spin-down-spin
interface. The total finite-size binding potential \( W(\ell; L_z) \) acting on the interface (whose
minima determine the MF location/s of the interface) is the sum of the two contributions from each wall:

\[ W(\ell; L_z) = W_\infty(\ell) + W_\infty(L_z - \ell) \]  

(2)

where \( W_\infty(\ell) \) is the appropriate semi-infinite binding potential for the ranges of forces in the model. For systems with short ranged forces this is usually specified as

\[ W(\ell) = a_o(T - T_w) e^{-\kappa\ell} + b_o e^{-2\kappa\ell} ; \quad \ell > 0 \]  

(3)

with \( a_o, b_o \) positive constants and \( \kappa \) being the inverse bulk correlation length. For \( T < T_c(L_z) \), with \( T_c(L_z) = T_w - 4(b_o/a_o)e^{-\kappa L_z/2} \) in MF approximation, the total potential \( W(\ell; L_z) \) has a double well structure with two equal minima at \( \ell_\pi < L_z/2 \) and \( \ell^*_\pi = L_z - \ell_\pi \). As \( T \to T_c(L_z)^- \), the adsorption difference \( \Delta \Gamma = 4m_o(L_z/2 - \ell_\pi) \) (with \( m_o \) the bulk magnetization) vanishes like \( \Delta \Gamma \sim (T_c(L_z) - T)^{1/2} \), corresponding to a standard order-disorder transition. For \( T > T_c(L_z) \), the potential \( W(\ell; L_z) \) has only one minimum at \( \ell_\pi = L_z/2 \) and the correlation length \( \xi_\parallel \sim e^{\kappa L_z/4} \). Interestingly, most of these quantitative MF predictions are confirmed by extensive Monte Carlo simulation studies which established that the true asymptotic critical regime where we can expect Onsager-like behaviour \( \Delta \Gamma \sim (T_c(L_z) - T_c)^{1/8} \) is extremely small [3]. All these facts support MF theory as an excellent quantitative description of the thin film system.

We now wish to consider the MF phase diagram for the analogous phase transition in a slightly non-planar geometry. We will take as our starting point the simplest possible phenomenological model of this system which generalises [1] and suppose that the configuration energy is specified by

\[ H[\ell; z^{(1)}_w, z^{(2)}_w] = \int d\mathbf{r} \left[ \frac{\Sigma}{2} (\nabla \ell)^2 + W(\ell; L_z, z^{(1)}_w, z^{(2)}_w) \right] , \]  

(4)

where \( z^{(1)}_w(\mathbf{r}) \) and \( z^{(2)}_w(\mathbf{r}) \) describe the (small) deviations of the walls near the \( z = 0 \) and \( z = L_z \) respectively and \( W(\ell; L_z, z^{(1)}_w, z^{(2)}_w) = W_\infty(\ell - z^{(1)}_w) + W_\infty(L_z + z^{(2)}_w - \ell) \). Whilst the model could certainly be improved by including further coupling terms involving \( \nabla \ell \cdot \nabla z_w \)
with associated position dependent (stiffness) coefficients, we do not expect these to make any significant difference to the interfacial behaviour described here [3]. In any case, even with the further assumption of corrugated walls such that \( z_w^{(1)} \) and \( z_w^{(2)} \) only depend on a single-coordinate \((x\text{ say})\), the interfacial behaviour generated is sufficiently complex to warrant attention within the simple model above. Writing \( z_w^{(1)}(x) = a\sqrt{2}\sin(qx) \), we have considered the geometry for which \( z_w^{(1)} = z_w^{(2)} \) although, of course, many other choices are possible [6]. The r.m.s. width \( a \) and wavelength \( L_x = 2\pi/q \) of the wall corrugation are assumed to be small and large respectively in comparison with the bulk correlation length. With these assumptions, the wetting transition remains second order and located at \( T_w \) in the semi-infinite limit [7].

The equilibrium non-planar interfacial profile/s \( \ell_\nu(x) \) satisfies the Euler-Lagrange equation

\[
\Sigma \ddot{\ell}_\nu(x) = W'_\infty(\ell_\nu - z_w^{(1)}) - W'_\infty(L_z + z_w^{(2)} - \ell_\nu)
\]

where dot and prime signify differentiation w.r.t. \( x \) and argument respectively. Periodic boundary conditions are imposed after a large multiple of wavelengths \( L_x \). Two preliminary remarks are as follows: firstly, the Euler-Lagrange equation is inversion symmetric so that if \( \ell_\nu(x) \) is a solution, \( \ell_\nu^*(x) = L_z - \ell_\nu(x + \pi/q) \) is also a solution with the same free energy and is distinct from \( \ell_\nu(x) \) in the two-phase regime. Secondly, we have established numerically that the stable phases all have the same wavelength as the wall corrugation \( L_x \). However, this is not the case for the metastable states [8]. Finally, we note that an elegant description of the interfacial shape is afforded by a reduce phase plane plot \( \ell/\sqrt{2}a \text{ vs. } \ell/\sqrt{2}a \) and helps distinguish different types of structural regimes. A section of the equilibrium phase diagram, with suitable reduced units [8], is shown in Fig. 1 and shows a critical line (corresponding to an order-disorder transition) and four non-thermodynamic singularities where there is a qualitative change of interfacial structure. In this way, we are able to distinguish five different interfacial types (see Fig. 2).

Phase coexistence and order is most easily revealed through the mean interfacial height
\[ \ell_o \equiv \frac{1}{L_x} \int_{0}^{L_x} dx \, \ell_{\nu}(x) \]  

which is single valued (\( \ell_o = L_z/2 \)) in the disordered regime above the critical temperature \( T_c(L_z, a, q) \), but is double valued (with \( \ell^*_o = L_z - \ell_o \)) in the order regime, analogous to \( \ell_\pi \) and \( \ell^*_\pi \) for the planar system. Our numerics indicate that the singularity in \( \ell_o \) is of the expected type:

\[
\frac{L_z}{2} - \ell_o \simeq \begin{cases} 
 t^2 & \text{if } t > 0 \\
 0 & \text{if } t < 0
\end{cases}
\]  

where we have introduced the scaled temperature variable \( t \equiv (T_c(L_z, a, q) - T)/T \). In addition to the mean interface height, however, the shape function shows a number of qualitative changes with temperature. At very low temperatures, the interface is closely bound to one of the walls and follows the corrugation (See Fig. 2(A)). Over one period \( L_x \), the graph \( \ell_{\nu}(x) \) has one maximum and one minimum which are in phase with the wall function \( z_w^{(1)}(x) \). For this case, the phase plane plot is a simple loop. Nevertheless, notice that its form is not precisely circular, indicating that non-linear effects are important even when the interface is close to the wall. On increasing the temperature, the interface smoothly deforms and shows a number of non-thermodynamic singularities where the minima and maxima of the graph undergo a series of bifurcations. These reveal themselves as the appearance/disappearance of loops in the phase plane portrait as illustrated in Fig. 2(B) which also shows the locus of the maxima/minima with temperature (Fig. 2(C)). Corresponding profiles are shown in Fig. 2(A). Two counter intuitive features are worth emphasising here. Firstly, there are two regimes, II and IV, where the interface shape has two and three maxima per wavelength of the wall corrugation. Secondly, in the vicinity of the order-disorder transition, regime III, the interface shape is similar to the wall (i.e. there is only one max/min pair per period) but is out of phase with it. Finally, at high temperatures above the two super critical non-thermodynamic singularities, the interface shape returns to that of a simple sinusoidal-like function in phase with the wall and the phase portrait is basically a circle of radius
(1 + q^2ξ_0^2)^{-1} centred at $L_z/2$.

Next, we focus on the singularity in the shape profile at the order-disorder transition. We have established that the stable phase/s can be represented by a Fourier series

$$\ell_\nu(x) = \ell_o + \sigma_1 \sin(qx) +$$

$$\sum_{k=1}^{\infty} \{\sigma_{2k+1} \sin((2k + 1)qx) + \gamma_{2k} \cos(2kqx)\}$$

throughout the phase diagram. In this expression $\ell_o$ is the mean interface position (given by Eq. (6)), whilst the second term is the harmonic response to the wall corrugation. The final term represents the higher order harmonic excitations arising from the non-linearity of the Euler-Lagrange equation and are responsible for the complicated evolution of the interface structure with temperature. We stress that, without this term (i.e. just considering linear response), the phase plane portrait would be simply circular. Note that there are not even sine terms and no odd cosine terms. The temperature dependence of the two sets of coefficients $\{\sigma_{2k-1}\}$ and $\{\gamma_{2k}\}$ is extremely involved but near $T_c(L_z, a, q)$ only two types of singularity are observed in our numerical analysis (See Fig. 3). The coefficients $\{\gamma_{2k}\}$ all vanish above $T_c(L_z, a, q)$ and behave precisely as the mean order-parameter $L_z^2 - \ell_o$, i.e. they are characterised by the usual MF order-parameter critical exponent $\beta = 1/2$. In contrast, the terms $\{\sigma_{2k-1}\}$ all have a cusp-like singularity

$$\sigma_{2k-1} - \sigma_{2k-1}^c \simeq |t|^{\theta} ; \quad t \rightarrow 0^\pm$$

where $\sigma_{2k-1}^c$ is the value at criticality and the critical exponent $\theta = 1$. There is no analogy of this singularity in the planar system. Furthermore, whilst it is natural to identify the cosine term singularities with the order-parameter exponent $\beta$ of the $d-1$ dimensional bulk universality class ($\beta = 1/2$ in MF, $\beta = 1/8$ beyond MF for three dimensional thin films), a similar identification for $\theta$ is not so obvious. Nevertheless, we have constructed scaling arguments which suggest that $\theta = 1 - \alpha$, where $\alpha$ is the specific heat critical exponent, consistent with our numerical results [6]. Similarly, we have also established that, for fixed $L_z$, the critical line is consistent with the scaling law
\[ T_c(L_z, a, q) - T_c(L_z, 0, 0) \simeq a^2 \Lambda \left( \frac{a}{q} \right) \] (10)

where \( \Lambda \) is an appropriate scaling function. This behaviour can be understood using finite-size scaling ideas with MF critical exponents and indicates that the effective width of the system is reduced by corrugation \[6\].

To finish our article, we make some pertinent remarks. Firstly, the interfacial structural changes reported here are not peculiar to short-ranged forces with the exponential binding potential Eq. (3), and also emerge if long-ranged forces are considered instead \[6\]. Also, we emphasise that in previous studies of the effect of roughness on wetting transitions most authors have considered binding potentials with a single minimum which do not exhibit the same subtle non-linear behaviour discussed here \[7,9\]. Next, we note that on making a change of variable \( \eta(x) \equiv \ell(x) - L_z - z^{(1)}_w \) and expanding to appropriate (cubic) order, the Euler-Lagrange equation can be written

\[ \Sigma \ddot{\eta} = -\tilde{t}\eta + \tilde{u}\eta^3 + aq^2 \sin(qx) \] (11)

where \( \tilde{t} \propto (T_c(L_z) - T) \) and \( \tilde{u} \) is positive in the region of interest. This is essentially equivalent to the Duffing equation of a soft-polynomial oscillator (without a damping term) which is known to yield extremely rich (including chaotic) dynamics \[5\]. In this context, the non-thermodynamic singularities described above are analogous to the harmonic excitations of the non-linear oscillator (however, this analogy does not shed any light on the nature of the singularities near the order-disorder transition and their identification beyond MF).

In summary, we have shown from a simple MF model of interfacial behaviour in a slightly non-planar geometry that new types of structural phase changes and additional critical singularities can emerge which are intimately related to non-linear phenomena. Similar behaviour is also expected for pre-wetting at a non-planar substrate \[6\]. Also of interest is the structure of metastable states in this system which we do not discuss here \[6\]. We believe that future studies of improved models which include thermal fluctuations and different type of non-planarity will also uncover new structural and fluctuation related behaviour.
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FIG. 1. Phase diagram for $L_z = 10$ and $q = 2\pi/10$ in reduced units \[8\]. The solid line separates the ordered and the disordered phases. The dashed lines show the location of the non-thermodynamic singularities and divide the phase diagram into 5 regions.

FIG. 2. Behaviour of the system for $L_z = 10$, $a = 1.5$ and $q = 2\pi/10$ showing the shape of the interface in the different regimes (A) and their corresponding phase portraits $\ell$ vs. $\ell$ (B). The circle represents the point $x=0$. For clarity, scales related to $\ell$ are omitted but can be checked in Fig. 3. The loci of the interface minima and maxima are represented as a function of the temperature (C). The FS critical temperature $T_c(L_z, a, q) \approx 0.845$ is represented by a thin line and is within regime $III$.

FIG. 3. Behaviour of the coefficients $L_z/2 - \ell_o$, $\sigma_1$, $\gamma_2$ and $\sigma_3$ of Eq. \[8\] near $T_c(L_z, a, q)$ for $L_z = 10$, $a = 1.5$ $q = 2\pi/10$. They are multiplied by $1$, $10L_x$, $10^2L_x$ and $10^3L_x$, respectively.
