Effective interfacial Hamiltonian theories of correlation functions at wetting transitions

1993 J. Phys. A: Math. Gen. 26 L667

(http://iopscience.iop.org/0305-4470/26/15/009)

J. Phys. A: Math. Gen. 26 (1993) L667–L672. Printed in the UK

LETTER TO THE EDITOR

Effective interfacial Hamiltonian theories of correlation functions at wetting transitions

A O Parry

Department of Mathematics, Imperial College, London SW7 2BZ, UK

Received 6 April 1993

Abstract. The recent Fisher–Jin crossing criterion derivation of the effective interfacial Hamiltonian for wetting transitions is generalized to consider surfaces of fixed magnetization that may remain bound to the wall in the limit of infinite adsorption. It is shown that an infinite set of such effective Hamiltonians is required to construct the mean-field order-parameter correlation function $G(r_1, r_2)$. Surfaces that remain bound to the wall in the limit of complete wetting are shown to exhibit fluctuations which have a coherent quality. We emphasize that the construction of G from an infinite set of effective Hamiltonians is required for full thermodynamic consistency.

In this letter we consider the relationship between effective interfacial Hamiltonian models and the connected spin–spin correlation function $G(r_1, r_2)$ at wetting transitions [1]. In a series of important recent communications Fisher and Jin (FJ) [2–5] have systematically derived an effective interfacial Hamiltonian $H_I[\ell(y)]$, with $\ell(y)$ the collective co-ordinate representing the position of the surface of fixed magnetization m^x, from a Landau–Ginzburg–Wilson (LGW) Hamiltonian $H_{LGW}[m(r)]$ which is a functional of the microscopic local spin density $m(r)$. The systematically derived interfacial Hamiltonian properly accounts for the influence of the wall-α phase interface on the depinning $\alpha\beta$ interface. This has extremely important consequences for the 'critical' wetting transition in $d \geqslant 3$ which generically becomes fluctuation-induced first-order provided $d < \infty$. Recent work by the author [6] has also emphasised that a proper treatment of the influence of the wall-α and $\alpha\beta$ interfaces on order-parameter fluctuations is again crucial in order that the theory correctly indentifies all the singular behaviour manifest in G at critical and complete wetting [6]. In the present leter we shall calculate the exact mean-field correlation function (corresponding to $d = \infty$) from the effective Hamiltonian theory. We shall show that it is essential to consider the fluctuations of all generalized surfaces of fixed magnetization m^x, described by the corresponding infinite set of effective Hamiltonians $\{H_I[\ell(y); m^x]\}$ with

$$H_I[\ell(y); m^x] = \int \mathrm{d}y \left\{ \frac{\tilde{\Sigma}\,(\ell(y); m^x)}{2} (\nabla\, \ell(y))^2 + W(\ell(y); m^x) \right\}. \tag{1}$$

Here $\tilde{\Sigma}\,(\ell(y); m^x)$ and $W(\ell(y); m^x)$ are the (position dependent) stiffness and binding potential functions for the surface of fixed magnetization m^x. It transpires that it is insufficient to use one effective Hamiltonian with collective co-ordinate $\ell(y)$ to exactly

0305-4470/93/150667+07$07.50

construct G. Moreover such a single Hamiltonian *does not even reproduce the required singular behaviour* manifest in the transverse moments of G at critical *and* complete wetting [6]—one also needs to consider generalized surfaces that remain bound to the wall in the limit of infinite adsorption. Our analysis explicitly highlights the subtle modification of capillary-wave-like fluctuations that occur near the wall. For example, at the complete wetting transition we show that surfaces that remain bound to the wall in the limit of infinite adsorption have stiffness coefficients containing non-vanishing contributions from both wall-α and $\alpha\beta$ interfaces. The fluctuations of such surfaces thus have a demonstrably coherent quality which clarifies earlier speculations [7].

To begin we recall the important features of the FJ derivation of $H_\mathrm{I}[\ell(y); m^x]$. FJ start from the standard LGW Hamiltonian pertinent to describing semi-infinite systems ($z>0$) with short ranged forces

$$H_{\mathrm{LGW}}[m(r)] = \int \mathrm{d}y \int_0^\infty \mathrm{d}z \left\{ \frac{K}{2}(\nabla m)^2 + \phi(m(r)) + \delta(z)\phi_1(m(r)) \right\} \tag{2}$$

where $\phi(m)$ and $\phi_1(m)$ are bulk and surface free-energy densities respectively. $\phi(m)$ has (for sub-critical temperatures $T<T_c$) a standard double well form showing bulk two phase coexistence between phases α (with $m_\alpha>0$) and β (with $m_\beta<0$) in zero bulk field $h=0$. We shall assume that ϕ_1 takes the standard expression $\phi_1(m) = -(h_1 m_1 + g m_1^2/2)$ with h_1 the surface field. The mean-field phase diagram of (2) is well understood [8] and exhibits first-order, tricritical, critical and complete wetting transitions. Later we shall concentrate on the case where the wall-β phase interface is completely wet by the α phase above a critical wetting temperature T_w.

FJ define $\ell(y)$ as being the surface of fixed magnetization

$$m(r=(\ell(y), y)) = m^x \tag{3}$$

and define $H_\mathrm{I}[\ell(y); m^x]$ via

$$H_\mathrm{I}[\ell(y); m^x] = H_{\mathrm{LGW}}[m_\Xi(r; \ell(y))] \tag{4}$$

where $m_\Xi(r; \ell(y))$ is the profile that minimizes (2) subject to the crossing condition (3). The identification (4) corresponds to a saddle-point approximation to the partial trace used to formally define H_I [2]. By first considering planar profiles $m_\pi(z; \ell_\pi)$ FJ derive the binding potential

$$W(\ell; m^x) = \int_0^\infty \left[\frac{K}{2}\left(\frac{\partial m_\pi}{\partial z}\right)^2 + \phi(m_\pi(z;\ell)) - \phi(m_\beta) \right] \mathrm{d}z + \phi_1(m_\pi(0;\ell))$$
$$+ \ell \text{ independent terms} \tag{5}$$

which accounts for the translations of the planar profile with the specified crossing constraint (3). For convenience we have dropped the implicit field dependence in (5) but have included the m^x dependence explicitly to emphasize that (5) defines a family of binding potentials. The ℓ independent terms in (5) are usually defined such that $W(\infty; m^x) = 0$ in the absence of a bulk field h. These terms are related to the surface free-energy per unit area Σ. Recall that in the limit of large adsorption we write [1]

$$\Sigma_{w\beta} = \Sigma_{w\alpha} + \Sigma_{\alpha\beta} + \Sigma^{\mathrm{sing}}. \tag{6}$$

The first two terms correspond to the (zero-field) wall-α and $\alpha\beta$ interfacial tensions respectively. Σ^{sing} is the singular contribution to the excess free-energy. For critical wetting ($h=0^-$, $T \to T_w^-$) we write $\Sigma^{\mathrm{sing}} \sim (T_w - T)^{2-\alpha_s}$ whilst for complete wetting

($h \to 0^-$; $T_c > T > T_w$) $\Sigma^{\text{sing}} \sim |h|^{2-\alpha_s^{co}}$. At mean-field level where fluctuations are negligible recall that $\Sigma^{\text{sing}} \sim (T_w - T)^2$ for critical wetting whilst $\Sigma^{\text{sing}} \sim h \ln|h|$ for complete wetting [8].

To calculate $\Sigma(\ell(y); m^x)$ FJ consider small fluctuations $\delta\ell(y) \equiv \ell(y) - \ell_\pi$ from the planar case. The crossing criterion (3) specifies that the corresponding magnetization fluctuation $\delta m(r) \equiv m_\Xi(r; \ell(y)) - m_\pi(z; \ell)$ satisfies

$$\delta m(r)\bigg|_{r=(\ell(y),y)} = -\frac{\partial m_\pi}{\partial z}(\ell_\pi, \ell_\pi)\delta\ell(y) + 0(\delta\ell(y)^2). \tag{7}$$

From (2), (3) and (7) FJ derive the expression

$$\delta m(r) = \frac{\partial m_\pi}{\partial \ell}(z; \ell_\pi)\delta\ell(y) + 0(\delta\ell(y)^2). \tag{8}$$

Rather than follow FJ we choose to specify $\delta m(r)$ in terms of derivatives with respect to z only. It is possible to show [9] that an equivalent expression for $\delta m(r)$ is

$$\delta m(r) = -\frac{\partial m_\pi}{\partial z}(z; \ell_\pi)\left\{\alpha + (1-\alpha)\frac{\int_0^{\min(z;\ell_\pi)} dz' \left(\frac{\partial m_\pi(z;\ell_\pi)}{\partial z'}\right)^{-2}}{\int_0^{\ell_\pi} dz'' \left(\frac{\partial m_\pi(z;\ell_\pi)}{\partial z''}\right)^{-2}}\right\}\delta\ell(y) \tag{9}$$

where α is determined by a boundary condition that follows from analysis of (4). From (9) we derive an alternative expression for $\Sigma(\ell; m^x)$

$$\tilde{\Sigma}(\ell; m^x) = K\int_0^\infty \left(\frac{\partial m_\pi(z;\ell)}{\partial z}\right)^2 \left\{\alpha + (1-\alpha)\frac{\int_0^{\min(z;\ell)} dz' \left(\frac{\partial m_\pi}{\partial z'}\right)^{-2}}{\int_0^{\ell} dz'' \left(\frac{\partial m_\pi}{\partial z''}\right)^{-2}}\right\}^2 dz \tag{10}$$

Whilst being somewhat less elegant than the FJ expression it will prove easier to interpret. To see this consider the function

$$\tilde{\Sigma}_0(z) \equiv \tilde{\Sigma}(z; m_0(z)) \tag{11}$$

where $m_0(z)$ is the planar equilibrium mean-field profile. The behaviour of the function defined in (11) depends on the value of $m_0(z)$ which in turn is related to the qualitative behaviour of the corresponding generalized surface. We distinguish between two cases:

(i) If $m_\alpha > m_0(z) > m_\beta$, then, in the limit of infinite adsorption Γ (with $\Gamma - \int_0^\infty dz(\langle m(r)\rangle - m_\beta)$) we find the simple result

$$\tilde{\Sigma}_0(z) \to \Sigma_{\alpha\beta}^{\text{MF}} \qquad \Gamma \to \infty \tag{12}$$

where $\Sigma_{\alpha\beta}^{\text{MF}}$ is the mean-field result for the $\alpha\beta$ stiffness. Note that in the limit $\Gamma \to \infty$ the position z where $m_0(z) = m^x$ diverges; z corresponds to a measure of the thickness of the wetting layer.

(ii) If $\exists m_0(z) > m_\alpha$ then in the limit of infinite adsorption

$$\tilde{\Sigma}_0(z) > \Sigma_{\alpha\beta}^{\text{MF}} \qquad \Gamma \to \infty. \tag{13}$$

This inequality reflects a non-vanishing contribution from the wall-α phase. The distance z remains finite in this limit. The precise value of $\tilde{\Sigma}_0(z)$ is dependent on z. In the limit of $z \to 0$ it is straightforward to see that

$$\tilde{\Sigma}_0(0) = \Sigma_{w\beta}^{MF} - \phi_1(m_0(0)) \tag{14}$$

valid for any Γ. Here $\Sigma_{w\beta}^{MF}$ is the *mean-field* expression for the total surface free-energy of the wall β interface. As the value $m^x = m_0(z)$ is decreased to m_α, z increases and the difference $\tilde{\Sigma}_0(z) - \Sigma_{\alpha\beta}^{MF}$ vanishes providing the limit $\Gamma \to \infty$ is taken first. From (14) it follows that even surfaces that remain bound to the wall in the approach to complete wetting reflect singularities defined in thermodynamic functions (recall (6)).

The above considerations have important implications for theories of correlation functions. Here we shall restrict our attention to the mean-field regime where the set $\{H_I[\ell(y); m^x]\}$ may be well approximated by the set of local Gaussion (LG) Hamiltonians $\{H_I^{LG}[\ell(y); m_0(z)]\}$ with

$$H_I^{LG}[\ell(y); m_0(\ell_0)] = \int \mathrm{d}y \left\{ \frac{\tilde{\Sigma}_0(\ell_0)}{2} (\nabla \ell)^2 + \frac{W''(\ell; m_0(\ell_0))(\ell - \ell_0)^2}{2} \right\} \tag{15}$$

which models the fluctuations of surfaces of fixed magnetization $m^x (= m_0(\ell_0))$ about their respective equilibrium positions ℓ_0. In deriving (15) we have simply expanded about the equilibrium position and used the result

$$W'(\ell_0; m_0(\ell_0)) \equiv \frac{\mathrm{d}}{\mathrm{d}\ell} W(\ell; m^x) \Big|_{\substack{\ell = \ell_0 \\ m^x = m_0(\ell_0)}} = 0.$$

Each Hamiltonian of the set $\{H_I[\ell(y); m^x]\}$ may be used to calculate the corresponding expectation values $\langle \cdot \rangle_{m^x}$. Moreover by virtue of (7), (8) and (9), each Hamiltonian provides a prescription for calculating a correlation function $G_I^{LG}(r_1, r_2; m^x)$. Here we shall concentrate on calculating the transverse Fourier transform

$$\begin{aligned} \tilde{G}(z_1; z_2; Q) &= \int \mathrm{d}y_{12} G(r_1, r_2)\, \mathrm{e}^{\mathrm{i}Q \cdot y_{12}} \\ &= \tilde{G}_0(z_1 z_2) + Q^2 \tilde{G}_2(z_1, z_2) + \cdots \end{aligned}$$

where the small wavevector expansion defines the zeroth and second moments. The set of Hamiltonians $\{H_I[\ell(y), m^x]\}$ therefore define a corresponding set of correlation functions $\{\tilde{G}_I^{LG}(z_1; z_2; Q; m^x)\}$ where

$$\tilde{G}_I^{LG}(z_1, z_2; Q; m^x) = \frac{k_B T \dfrac{\partial m}{\partial \ell}(z_1; \ell_0) \dfrac{\partial m_\pi}{\partial \ell}(z_2; \ell_0)}{W''(\ell_0; m^x) + Q^2 \tilde{\Sigma}_0(\ell_0)}. \tag{16}$$

Note that each allowed value of m^x satisifies $m^x = m_0(\ell_0)$ and $m_\pi(z; \ell_0) = m_0(z)$. The set $\{\tilde{G}_I^{LG}(z_1, z_2 Q; m^x)\}$ may be viewed as a set of local approximations to the full G_I. It is straightforward to show [9] that no single choice of m^x will reproduce all the required thermodynamic related singularities in G. For example, the local approximation for G based on the crossing criterion used by FJ [2–5] would correspond to $\tilde{G}_I^{LG}(z_1, z_2; Q; 0)$. Whilst this is an excellent description for $z_1 \sim z_2 \sim \ell_0$ it does not correctly identify the singular contribution to $G_2(O^+, O^+)$ [9] for critical *and* complete wetting (see equation (19) below). This difficulty may be overcome if we define the mean-field effective Hamiltonian expression for $\tilde{G}_{\mathrm{I}}(z_1, z_2; Q)$ for different values of z_1, z_2 using the associated local expression from the set $\{\tilde{G}_{\mathrm{I}}^{\mathrm{LG}}(z_1, z_2; Q; m^x)\}$. For the case $z_1 = z_2$ there is no ambiguity over the choice of $H_{\mathrm{I}}[\ell(y); m^x]$. We define

$$\tilde{G}_{\mathrm{I}}^{\mathrm{MF}}(z, z; Q) = \tilde{G}_{\mathrm{I}}^{\mathrm{LG}}(z, z; Q; m_0(z)) \tag{17}$$

which from (7) gives

$$\tilde{G}_{\mathrm{I}}^{\mathrm{MF}}(z, z; Q) = \frac{k_B T m_0'(z)^2}{W''(z; m_0(z)) + \tilde{\Sigma}_0(z) Q^2}. \tag{18}$$

Setting $z = 0^+$ and eliminating $W''(0; m_0(0))$ yields

$$\frac{\tilde{G}_{\mathrm{I}(2)}^{\mathrm{MF}}(0^+, 0^+)}{\tilde{G}_{\mathrm{I}(0)}^{\mathrm{MF}}(0^+, 0^+)^2} = \frac{\Sigma_{w\beta}^{\mathrm{MF}} - \phi_1(m_0(0))}{m_0'(0)^2} \tag{19}$$

where we have used (14). Equation (19) is infact the exact Landau theory result for same quantity defined on the left-hand side [10]. Importantly equation (19) correctly relates the singular behaviour in $\tilde{G}(0, 0; Q)$ to $\Sigma_{w\beta}^{\mathrm{MF}}$ which was emphasised in equation (6). To proceed, we note that a necessary condition for (19) to be satisfied is $\tilde{G}_{\mathrm{I}(0)}^{\mathrm{MF}}(0, z)$ α $m_0'(z)$ [6, 9]. From (18) it then follows that

$$\tilde{G}_{\mathrm{I}(0)}^{\mathrm{MF}}(z_1, z_2) = \frac{k_B T m_0'(z_1) m_0'(z_2)}{W''(z_1; m_0(z_1))} \tag{20}$$

for $z_2 \geqslant z_1$. Equation (20) is an explicit expression for $\tilde{G}_0$ $\forall z_1$, z_2. Using standard formuli we can use (20) to calculate $\tilde{G}_2(z_1, z_2)$. By seeking thermodynamic consistency with the expression for $\tilde{G}_2(z, z)$ implied in (18) we arrive at the identification

$$W''(z; m_0(z)) = \left[a + b \int_0^z \mathrm{d}z' \, m_0'(z')^{-2} \right]^{-1} \tag{21}$$

where a and b are determined by suitable boundary conditions. Equation (21) may also be derived by direct differentiation of (5) [9]. However, the identification (21) together with the formula (20) constitute the *exact* Zernike–Landau theory expression for $\tilde{G}_0(z_1, z_2)$ [10, 11] found by solving the Ornstein–Zenike equation. It follows that our method for constructing $\tilde{G}(z_1, z_2; Q)$ is exact (at mean-field level) in the limit of small Q. In contrast to the rather cumbersome Landau theory expressions for $\tilde{G}_0(z_1, z_2)$ and $\tilde{G}_2(z_1, z_2)$ our present study yields a compact expression for $\tilde{G}(z, z; Q)$ in terms of functions defined in the set of effective Hamiltonians. This makes the interpretation of the results considerably easier. Here we point out some implications for complete wetting. Near a complete wetting transition the equilibrium mean-field profile $m_0(z)$ is monotonic with $m_0(0) > m_\alpha$. Consequently there exist surfaces of type (ii) considered above. Surfaces of fixed magnetization $m_\alpha > m^x > m_\beta$ (type (i)) are located near the $\alpha\beta$ interface. These have fluctuations controlled by a surface stiffness coefficient $\tilde{\Sigma}(\ell_0) \approx \Sigma_{\alpha\beta} + 0(\mathrm{e}^{-\ell_0/\xi_b})$ [4, 5] where ξ_b is the (α phase) bulk correlation length. Clearly these surfaces unbind from the wall in the limit of complete wetting ($h \to 0^-$; $T_c > T > T_w$). Their fluctuations have a standard capillary-wave-like interpretation. If we look at surfaces of type (ii) which model the behaviour of $\tilde{G}(z, z; Q)$ when $m_0(z) > m_\alpha$ we find (recall (13) and (14)) that the fluctuations have a coherent quality, i.e. the stiffness coefficients have contributions from both wall-α and $\alpha\beta$ interfaces. This clarifies the picture of coherent fluctuations that had been speculated earlier [7]. Finally we note that in the approach to critical wetting ($h=0^-$; $T\to T_w^-$) we have $m_a > m_0(z)$ so that all surfaces of fixed magnetization unbind from the wall—there is no coherent manifestation of the capillary-wave-like modes.

In summary we have shown that it is possible to construct the exact mean-field order-parameter correlation function from a set of interfacial Hamiltonians. The analysis highlights the subtle modification of capillary-wave-like modes that occur near the wall and shows that even surfaces that remain bound to the wall in the limit of complete wetting have fluctuations which are related to thermodynamic singularities. Further work is required to understand the nature of G away from the mean-field regime when fluctuations are no longer negligible.

The author has benefitted from detailed correspondence with Professor M E Fisher and Dr A J Jin to whom he is also grateful for sending copies of references [4] and [5] prior to publication. The comments of Professor R Evans, Dr J R Henderson, Dr D B Abraham, Dr P J Upton and C J Boulter are also gratefully acknowledged. This research was supported by SERC.

References

[1] For a review see, e.g. Fisher M E 1988 '*Statistical Mechanics of Membranes and Surfaces* eds D R Nelson, T Piran and S Weinberg, (World Scientific) p 19
[2] Fisher M E and Jin A J 1991 *Phys. Rev.* **B44** 1430
[3] Jin A J and Fisher M E 1993 *Phys. Rev.* **B47** 7365
[4] Fisher M E and Jin A J 1992 *Phys. Rev. Lett.* **69** 792
[5] Jin A J and Fisher M E *Phys. Rev. B* to appear
[6] Parry A O and Evans R 1993 *Mol. Phys.* **78** 1527
[7] Parry A O and Evans R 1988 *Mol. Phys.* **65**, 455
[8] Nakanishi H and Fisher M E 1982 *Phys. Rev. Lett.* **49**, 1565
[9] Parry A O and Boulter C J to appear
[10] Parry A O 1989 PhD Thesis (University of Bristol) unpublished
[11] Lipowsky R and Speth W 1983 *Phys. Rev.* **B28** 3983