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Non-Ornstein–Zernike surface structure factor for complete wetting in three (and above) dimensions

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Abstract. We have derived a closed form expression for the transverse Fourier transform $\tilde{G}(0, 0; Q)$ (or surface structure factor) of the surface spin–spin correlation function near a complete wetting transition from Landau theory. Whilst $\tilde{G}(0, 0; Q)$ contains isolated singularities (poles) in the complex wavevector plane it does not have a simple Ornstein–Zernike (oz) form. Instead, the function exhibits two limiting oz-like behaviours characteristic of *intrinsic* and *coherent* capillary-wave-like fluctuations depending on the value of the scaling variable $Q|H|^{-\nu\phi}$. We also discuss the decay of surface correlations in real space and identify the appropriate singular (long-ranged) contribution. In contrast to the second-moment correlation length the true correlation length at the wall diverges as $|H|^{-\nu\phi}$ in the limit of complete wetting.

In developing the modern theory of critical phenomena much effort has been invested in understanding the asymptotic decay of order-parameter correlations. For isotropic homogeneous (bulk) systems with scalar order-parameter $m(r)$ (and short-ranged forces) it is believed that the truncated (connected) correlation function $G(r_1, r_2) \equiv \langle m(r_1)m(r_2) \rangle - \langle m(r_1) \rangle \langle m(r_2) \rangle$ generally decays like $G(r_1, r_2) \sim r_{12}^{-(d-1)/2} e^{-r_{12}/\xi}$ for distances $r_{12} \equiv |r_1 - r_2| \gg \xi$ corresponding to the true bulk correlation length [1]. This asymptotic decay is consistent with the classical Ornstein–Zernike (oz) theory of density fluctuations in simple fluids [2]. According to the oz theory the Fourier transform of $G(r_1, r_2)$ (or structure factor) $\tilde{G}(k)$ has the simple form $\tilde{G}(k) = \tilde{G}(0) (1 + \xi_b^2 k^2 + O(k^4))^{-1}$ where ξ_b is the oz or second-moment correlation length. Within the oz approximation the susceptibility diverges like $\tilde{G}(0) \sim \xi_b^2$. oz theory is known to break down for simple (Ising-like) bulk fluid systems in two cases: (a) In the vicinity of the critical point $\tilde{G}(k)$ has the scaling form $\tilde{G}(k) = k^{-(2-\eta)} \Lambda(kt^\nu, Ht^{-\Delta})$ where H and t are the ‘magnetic’ and ‘temperature’-like scaling fields and ν and Δ are the correlation length and gap exponents. Such deviations from oz theory are here related to non-zero values of Fisher’s correlation function exponent η for dimensions $d < 4$ [3]. (b) In two dimensions the correlation function decays according to the Kadanoff–Wu result $G(r_1, r_2) \sim r_{12}^{-2} e^{-r_{12}/\xi}$ [4] for $r_{12}/\xi \rightarrow \infty$, $H=0$ and subcritical temperatures. The poles in the corresponding structure factor are not isolated, which may be related to pronounced random-walk-like fluctuations of the contours describing the elementary ‘bubble-like’ excitations [5].

In the present paper we point out that the detailed form of the Fourier transform of the pair correlation function at a complete wetting phase transition does not exhibit simple oz behaviour when both particles are at the wall. Recall that nonlinear renormalization group (RG) studies of effective interfacial Hamiltonian models of wetting

transitions imply that the exponent analogous to η is zero in all dimensions [6]. However, this does not mean that the detailed wavevector dependence of the appropriate structure factor is described by a simple Lorentzian function characteristic of oz behaviour. For systems with short-ranged forces (on which we shall concentrate), $d=3$ corresponds to the marginal dimensionality. While RG studies indicate that the values of the critical exponents which characterize the transition are not altered from their mean-field (MF) values, the relationship between intrinsic and fluctuation-related effects is extremely subtle. We discuss the physical interpretation of the detailed form of the structure factor and show how the asymptotic decay of $G(r_1, r_2)$ at the wall is related to the locations of the poles and zeros of the structure factor in the complex wavevector plane.

The starting point for our analysis is the Landau-Ginzburg-Wilson (LGW) free-energy functional [7]

$$F[m(\mathbf{r})] = \int d\mathbf{r} \left\{ \frac{1}{2}(\nabla m(\mathbf{r}))^2 + \phi(m(\mathbf{r})) + \delta(z)\phi_1(m(\mathbf{r})) \right\} \quad (1)$$

appropriate for describing fluid adsorption (for systems with short-ranged forces) at a planar wall situated in the plane $z=0$. Here we shall adopt the familiar magnetic language [7] even though our analysis is appropriate to a continuum (fluid) system. The bulk free-energy density function $\phi(m)$ has a standard double-well form at subcritical temperatures but need not be specified further. The surface potential $\phi_1(m_1)$ acts on the surface layer magnetization $m_1 = m(\mathbf{r})|_{z=0}$ and is assumed to have the usual quadratic form $\phi_1(m_1) = cm_1^2/2 - h_1 m_1$. The surface phase diagram of (1) is well understood and shows first-order and second-order wetting transitions [7]. We shall focus on the case where in the limit of the bulk 'magnetic' field $H \rightarrow 0^-$ a layer of up-spins (with bulk magnetization $m_\alpha > 0$) completely wets the surface-down-spin (β) interface. In this limit, the (reduced) adsorption $\bar{\Gamma} \equiv \int_0^\infty (m(z) - m(\infty))/(m_\alpha - m_\beta)$ diverges like $\bar{\Gamma} \sim |H|^{-\beta_s^co}$ with $\beta_s^co = 0(\ln)$. Associated with this growth of a wetting layer is the divergence of a transverse correlation length $\xi_\parallel \sim |H|^{-\nu_\parallel^co}$ [8] with $\nu_\parallel^co = \frac{1}{2}$. In the approach to complete wetting the singular part of the excess grand potential per unit area $\Sigma^{sing} = \Sigma_{w\beta} - (\Sigma_{w\alpha} + \Sigma_{\alpha\beta})$ vanishes like $\Sigma^{sing} \sim H \ln|H|$ at the MF level. Here $\Sigma_{w\beta}$ refers to the wall- β phase excess grand potential per unit area, $\Sigma_{w\alpha}$ refers to the value of the potential for $H=0^+$ (referred to as the non-critical interface) and $\Sigma_{\alpha\beta}$ is the free interfacial tension of the (isotropic) continuum $\alpha\beta$ interface. As stated earlier the values of the critical exponents are not altered by fluctuations in $d=3$. Consequently the MF theory for the surface correlations is, we believe, a realistic model for the fluctuations. Let us write the truncated correlation function as $G(z_1, z_2; R_{12})$ with z_i the normal distance from the wall and R_{12} the parallel displacement. First let us follow earlier studies [9, 10] and define the moments of the correlation function by the expansion of the Fourier transform

$$\tilde{G}(z_1, z_2; Q) = \int dR_{12} e^{iQ \cdot R_{12}} G(z_1, z_2; R_{12}) \quad (2a)$$

$$= \sum_{n=0}^{\infty} Q^{2n} G_{2n}(z_1, z_2) \quad (2b)$$

where $Q \equiv |Q|$. Note that we expect the radius of convergence of this expansion to vanish in the limit of complete wetting.

For the LGW model functional the oz integral equation defining $G(r_1, r_2)$ reduces to the differential equation [11]

$$(-\nabla_r^2 + \phi''(m(r)))G(r_1, r_2) = \delta(r_1 - r_2). \tag{3}$$

From (2) and (3) it follows that the moment $G_{2n}(z_1, z_2)$ satisfies a linear differential equation of order $2n + 2$:

$$L_1^{n+1}G_{2n}(z_1, z_2) = -\delta(z_1 - z_2) \tag{4}$$

where $L_1 = \partial_{z_1}^2 - \phi''(m(r_1))$.

Here we seek to solve for the moments $G_{2n}(z_1, z_2)$ for an arbitrary bulk free-energy $\phi(m(r))$. Previous studies have concentrated only on the first two moments [9, 10]. The properties of the higher moments must be elucidated, however, in order that the expansion (2b) may be inverted to give $G(z_1, z_2; R_{12})$. First we recall [12] that $G_0(z_1, z_2)$ is given by

$$G_0(z_1, z_2) = m'(z_1)m'(z_2) \left\{ \frac{1}{m_1'(cm_1' - m_1'')} + \theta(z_1 - z_2) \int_0^{z_2} \frac{dz_3}{m'(z_3)^2} + \theta(z_2 - z_1) \int_0^{z_1} \frac{dz_3}{m'(z_3)^2} \right\} \tag{5}$$

where $\theta(x)$ is the Heaviside step function and $m'(z) \equiv dm(z)/dz$. The result (5) is consistent with the surface susceptibility sum rule

$$\left(\frac{\partial m_1}{\partial h} \right)_{T, h_1} = \int_0^\infty dz G_0(0, z) \tag{6a}$$

$$= \frac{-(m_1 - m(\infty))}{cm_1' - m_1''} \tag{6b}$$

The function $G_0(z_1, z_2)$ is the simplest of the expressions for the moments of G . The exact MF expressions for the higher moments $G_{2n}(z_1, z_2)$ rapidly become complicated as n increases. However, one might reasonably expect that the behaviour of $\tilde{G}(z_1, z_2; Q)$ exhibits characteristic wavevector scaling for (a) $z_1, z_2 \sim \bar{\Gamma}$, near the $\alpha\beta$ interface, and (b) $z_1 = z_2 = 0$, exactly at the wall.

The behaviour of $\tilde{G}(z_1, z_2; Q)$ near the $\alpha\beta$ interface is rather well understood from previous studies [10]. In this region the integrals in (5) dominate the expression for $G_0(z_1, z_2)$. In fact it is straightforward to show that for large $\bar{\Gamma}$ and $n \geq 0$

$$\frac{G_{2n+2}(z_1, z_2)}{G_{2n}(z_1, z_2)} \approx -\xi_\parallel^2; z_1, z_2 \sim \bar{\Gamma} \tag{7a}$$

where $\xi_\parallel^2 = \xi_\parallel^{(1)2} + \xi_\parallel^{(2)2}$ and

$$\xi_\parallel^{(1)2} = \frac{\Sigma_{\alpha\beta}}{m_1'(cm_1' - m_1'')} \quad \xi_\parallel^{(2)2} = \frac{\Sigma_{\alpha\beta} \xi_\beta}{(m_\alpha - m_\beta)|H|} \tag{7b}$$

Clearly, (7) implies that $\tilde{G}(z_1, z_2; Q) \approx \tilde{G}_0(z_1, z_2)/(1 + \xi_\parallel^2 Q^2)$ for $z_1, z_2 \sim \bar{\Gamma}$, consistent with simple oz theory. We now turn our attention to the behaviour of $\tilde{G}(0, 0; Q)$.

From (5)

$$G_0(0, 0) = \frac{m_1'}{(cm_1' - m_1'')^2} \quad (8)$$

and it follows that [13]

$$G_2(0, 0) = -\frac{(\Sigma_{\text{TOT}} - \phi_1(m_1))}{(cm_1' - m_1'')^2} \quad (9)$$

where Σ_{TOT} is the total excess grand potential per unit area. To solve for $G_4(0, 0)$, $G_6(0, 0)$ and higher moments we note that the solution to (4) may be written as

$$G_{2n}(0, z) = \frac{G_{2n}(0, 0)m'(z)}{m_1'} - m'(z) \int_0^z \frac{dz'}{m'(z')^2} \int_{z'}^\infty dz'' m'(z'') G_{2n-2}(0, z''). \quad (10)$$

When combined with the results (5) and (9) this allows the calculation of $G_4(0, 0)$ in terms of $G_2(0, z)$ and $G_0(0, z)$. By repeating this procedure we can generate $G_{2n}(0, 0)$ for arbitrary n . For example,

$$G_4(0, 0) = \frac{(\Sigma_{\text{TOT}} - \phi_1(m_1))^2}{m_1'(cm_1' - m_1'')^3} + \frac{1}{(cm_1' - m_1'')^2} \int_0^\infty dz m'(z)^2 \int_0^z \frac{dz_1}{m'(z_1)^2} \int_{z_1}^\infty dz_2 m'(z_2)^2 \quad (11)$$

$$G_6(0, 0) = \frac{-(\Sigma_{\text{TOT}} - \phi_1(m_1))^3}{m_1''(cm_1' - m_1'')^4} - \frac{2(\Sigma_{\text{TOT}} - \phi_1(m_1))}{m_1'(cm_1' - m_1'')^3} \int_0^\infty dz m'(z)^2 \int_0^z \frac{dz_1}{m'(z_1)^2} \int_{z_1}^\infty dz_2 m'(z_2)^2 - \frac{1}{(cm_1' - m_1'')^2} \int_0^\infty dz m'(z)^2 \int_0^z \frac{dz_1}{m'(z_1)^2} \int_{z_1}^\infty dz_2 m'(z_2)^2 \times \int_0^{z_2} \frac{dz_3}{m'(z_3)^2} \int_{z_3}^\infty dz_4 m'(z_4)^2. \quad (12)$$

Let us first consider the non-critical wall- α ($w\alpha$) interface in the limit $H \rightarrow 0^+$. The correlation function does not exhibit any singular behaviour and analysis shows that

$$\tilde{G}^{w\alpha}(0, 0; Q) = \frac{m_1'/(cm_1' - m_1'')}{1 + \xi_{w\alpha}^2 Q^2 + O(Q^4)} \quad (13)$$

where the (non-critical) wall- α phase surface second-moment correlation length satisfies $\xi_{w\alpha}^2 \approx \xi_b^2/2(1 + c\xi_b)$ away from the bulk critical temperature.

Now let us consider the approach to complete wetting $H \rightarrow 0^-$ corresponding to the wall- β ($w\beta$) interface. In this limit the surface magnetization m_1 (and its derivatives) approach the same value as from the $H \rightarrow 0^+$ side. Consequently the behaviour of $G_0(0, 0)$ is very similar for $H \rightarrow 0^\pm$. The behaviour of $G_2(0, 0)$ is more intriguing. As has been noted in earlier studies [9], in the limit of complete wetting $G_2(0, 0)$ retains knowledge of $\Sigma_{\alpha\beta}$ arising from the term Σ_{TOT} . No such term arises in the limit $H \rightarrow 0^+$ for the wall- α

interface. The higher moments diverge as $H \rightarrow 0^-$. The dominant singular behaviour of $G_4(0, 0)$ and $G_6(0, 0)$ is described by

$$G_4(0, 0) \approx \frac{(\Sigma_{TOT} - \phi_1(m_1))^2}{m_1^2(cm_1' - m_1^n)^3} + \frac{\xi_{||}^{(2)2} \Sigma_{\alpha\beta}}{(cm_1' - m_1^n)^2} \tag{14}$$

and

$$G_6(0, 0) \approx \frac{-(\Sigma_{TOT} - \phi_1(m_1))^3}{m_1^2(cm_1' - m_1^n)^4} - \frac{2(\Sigma_{TOT} - \phi_1) \Sigma_{\alpha\beta} \xi_{||}^{(2)2}}{m_1^2(cm_1' - m_1^n)^3} - \frac{\Sigma_{\alpha\beta} \xi_{||}^{(2)4}}{(cm_1' - m_1^n)^2} \tag{15}$$

In fact, it is possible to show that the power law divergence of $G_{2n+2}(0, 0)$ is related to that of $G_{2n}(0, 0)$, $G_{2n-2}(0, 0)$, etc, by

$$G_{2n+2}(0, 0) \approx \frac{-(\Sigma_{TOT} - \phi_1)G_{2n}(0, 0)}{m_1^2(cm_1' - m_1^n)} - \frac{\Sigma_{\alpha\beta}}{m_1^2(cm_1' - m_1^n)} \sum_{j=1}^n (\xi_{||}^{(2)})^{2j} (-1)^j G_{2n-2j}(0, 0). \tag{16}$$

The presence of terms related to $\xi_{||}^{(1)}$ and $\xi_{||}^{(2)}$ indicates that $\tilde{G}(0, 0; Q)$ is sensitive to the long-wavelength fluctuations at complete wetting. The recursion relation (16) is clearly much more complicated than (7), which, recall, is indicative of oz behaviour. After some patient inspection it is possible to show that the series (16) is generated by the following closed-form non-oz expression:

$$\tilde{G}^{w\beta}(0, 0; Q) \approx \frac{m_1^2(1 + Q^2 \xi_{||}^{(2)2}) / (cm_1' - m_1^n)}{(1 + Q^2 \xi_{||}^{(2)2}) \{1 + [Q^2(\Sigma_{TOT} - \phi_1(m_1)) / m_1^2(cm_1' - m_1^n)]\} - \xi_{||}^{(1)2} \xi_{||}^{(2)2} Q^4} \tag{17}$$

Equation (17) is the main result of this paper and we discuss some of its features. Firstly it can be seen that the function shows *two* different limiting oz behaviours. For finite Q and $\xi_{||}^{(2)} \rightarrow \infty$ the expression reduces to (13) (to order Q^4) pertinent to the wall- α interface. This is clearly the correct physical requirement—in the limit of complete wetting the properties of local expectation values near the wall must be the same as that of the wall- α interface. On the other hand, for $Q \xi_{||}^{(2)} \rightarrow 0$ we find

$$\tilde{G}^{w\beta}(0, 0; Q) \rightarrow \frac{m_1^2 / (cm_1' - m_1^n)}{1 + [Q^2 / m_1^2 (cm_1' - m_1^n)] (\Sigma_{TOT} - \phi_1(m_1)) + O(Q^4)} \tag{18}$$

so that extremely long-wavelength fluctuations are controlled by the total wall- β surface tension. This is indicative of the *coherent* manifestation of the capillary wave fluctuations in the extreme limit $Q \xi_{||}^{(2)} \rightarrow 0$ [13]. This may be understood as follows: consider a surface of fixed magnetization m^x whose value is very close to m_1 . The equilibrium position of this surface is $z = 0$. If this surface is constrained [14] to be non-planar close to $z = 0$ we may ask what profile $m(r)$ minimizes the free-energy functional (1). If the position $z(y)$ of the surface contains Fourier modes Q with wavelengths $|Q|^{-1} \gg \xi_{||}^{(2)}$ the profile which minimizes (1) subject to the constraint corresponds to a rigid shift of the equilibrium planar profile. The associated free-energy change clearly involves the total surface tension. If, on the other hand, $z(y)$ contains only modes with wavelengths $|Q|^{-1} \ll \xi_{||}^{(2)}$ the perturbation in $m(r)$ relative to the planar equilibrium profile is localized to the wall. Consequently the surface tension $\Sigma_{\alpha\beta}$ does not contribute.

To complete our analysis we discuss the decay of $G^{w\beta}(0, 0; R)$, which is sensitive to the behaviour of $\tilde{G}^{w\beta}(0, 0; Q)$ in the complex wavevector plane. The denominator

appearing in (17) may be factorized and shows that $\tilde{G}^{w\beta}(0, 0; Q)$ has conjugate poles at

$$Q = \pm \frac{i}{\xi_{w\alpha}} \left[1 + O\left(\frac{1}{\xi_{\parallel}^2}\right) \right] \quad Q = \pm i \xi_{\parallel}^{(2)-1} \left(1 - \frac{\xi_{\parallel}^{(1)2}}{\xi_{\parallel}^{(2)2}} + \dots \right).$$

From the isolated poles near $Q = \pm i \xi_{w\alpha}^{-1}$ it follows that $\tilde{G}^{w\beta}(0, 0; R)$ contains a 'non-singular' contribution which decays with a length scale characteristic of the wall- α interface. The poles near $Q = \pm i / \xi_{\parallel}^{(2)}$ are more interesting. Note that these singularities in \tilde{G} are asymptotically close to the zeros of \tilde{G} which occur at $Q = \pm i / \xi_{\parallel}^{(2)}$. The presence of the zeros are rather important for dimensionality $d-1=2$. Recall that the standard oz theory of correlations near bulk criticality breaks down in $d=2$ because it predicts an unbounded logarithmic growth of the function at the critical point. For the present problem we note that the presence of the zeros near the isolated singularities means that the amplitude of the resulting singular contributions to G vanishes as $\xi_{\parallel} \rightarrow \infty$. In fact, for general dimensionality $d \geq 3$ we find that G contains a singular contribution

$$G^{\text{sing}}(0, 0; R) \sim m_{\parallel}^2 \xi_{\parallel}^{(1)2} \xi_{\parallel}^{(2)-d} R^{-(d-3)} \tilde{\Lambda}(R/\xi_{\parallel}^{(2)}) \quad (19)$$

with $\tilde{\Lambda}(0)$ finite and $\tilde{\Lambda}(x) \rightarrow x^{-(4-d)/2} e^{-x}$ for $x \rightarrow \infty$. In two dimensions the relationship between 'intrinsic' and 'fluctuation-induced' effects in $\tilde{G}(0, 0; Q)$ may be different. For this dimensionality the nature of G at complete wetting is not known for any truly microscopic Hamiltonian although the results from standard capillary wave theory are known to exhibit scaling behaviour [15].

Comparing (17) and (19) clearly illustrates the non-oz character of the surface correlation function. From (17) we note that the second moment surface correlation length retains knowledge of the unbinding interface but is finite in the limit of complete wetting. This length scale is not the same as the corresponding wall- α phase quantity and diverges as the critical wetting temperature is approached from above. This is related to the behaviour of the surface susceptibility [16]. In contrast, the asymptotic decay of correlations does exhibit a pseudo-two-dimensional oz-like decay and the true surface correlation length diverges with critical exponent $\nu_{\parallel}^{\text{oz}}$.

In conclusion, we have derived a closed form expression for the structure factor $\tilde{G}(0, 0; Q)$ at complete wetting using an MF theory valid for $d \geq 3$. The structure factor shows the presence of both intrinsic and fluctuation-related coherent effects depending on the value of the scaling variable $Q|H|^{-\nu_{\parallel}^{\text{oz}}}$. The asymptotic real space decay of $G(0, 0; R)$ reflects the presence of the isolated singularity and (nearby) zeros of $\tilde{G}(0, 0; Q)$ in the complex wavevector plane. The singular contribution to $G(0, 0; R)$ (19) emerges despite the fact that the structure factor $\tilde{G}(0, 0; Q)$ does not contain a simple oz-like Lorentzian singularity (see (7)) as has been previously suggested [17].

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